

Rph 4-197 958

### 9th

# ONTARIO INDUSTRIAL WASTE CONFERENCE

## **Proceedings**

**JUNE 1962** 

SPONSORED BY

WATER AND POLLUTION ADVISORY COMMITTEE

TD 897.5 .057 1962 copy 2 MOE

A CARLER OF

TO THE

ONTARIO WATER RESOURCES COMMISSION

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact ServiceOntario Publications at <u>copyright@ontario.ca</u>

TD9th Ontario waste management897.5conference : proceedings /.057765731962copy 2

# ONTARIO INDUSTRIAL WASTE CONFERENCE

9th

JUNE 24 - 27, 1962

DELAWANA INN

HONEY HARBOUR

**ONTARIO** 

### CONTENTS

Page Preface Dr. A. E. Berry, (iii) Ontario Water Resources Commission, Toronto, Ontario. Applications of PVC as a Trickling Filter Media 1 J. T. Egan, The Mead Corporation. Ohio. and R. W. Brouillette, B. F. Goodrich Industrial Products Company, Ohio. Cannery Waste Treatment in Ontario 25 A. Townshend, Ontario Water Resources Commission, Toronto, Ontario. Ammonium Phosphate Plant Waste Disposal 49 O. J. Bolduc, The Austin Company, Chicago Heights, Illinois. A Realistic Approach to Waste Treatment 57 Richard W. Crain, Industrial Filter and Pump Mfg. Co., Cicero, Illinois. Pitfalls in Industrial Waste Treatment 65 L. F. Oeming, Michigan Water Resources Commission, Lansing, Michigan. Environmental Surveys for Nuclear Power Stations 71 Dr. W. E. Grummitt, Atomic Energy of Canada Ltd., Chalk River, Ontario. Plating Waste Treatment 87 E. W. Hettwer, Northern Electric Company, London, Ontario. Industrial Waste Control in Metropolitan Winnipeg 103 N. S. Bubbis, Metropolitan Corporation of Greater Winnipeg, Winnipeg, Manitoba.

The Effect of C - 14 and	Sr - 90 on Anaerobic Digestion Dr. Werner N. Grune, Georgia Institute of Technology, Atlanta, Georgia.	Page 125
Extreme Variations in Br their Effect on Treatme	ewery Waste Characteristics and nt J. T. O'Rourke, Ryckman, Edgerley, <sup>B</sup> urbank & Assoc.	179
and	H. D. Tomlinson, Washington University, St. Louis, Missouri.	
Industrial Waste Polluti	on of Streams in Quebec Jean-Paul Gourdeau, Surveyer, Nenniger & Chenevert, Consultants, Montreal, Quebec.	203
Procedures Regarding Con New York State	trol of Industrial Wastes in D. B. Stevens, New York State Water Pollution Control Board, Albany, New York.	223
Treatment of Chrome Tann Activated Sludge Plant	ing Wastes for Acceptance by an F. Wims, Collis Leather, Aurora, Ontario.	231
Hydraulic Tests of Sedime	entation Basins K. L. Murphy, McMaster University, Hamilton, Ontario.	271
The Search for Bio-degrad	dable Detergents Dr. H. Lomas, Ontario Research Foundation, Toronto, Ontario.	287
Water Conservation and Wa	aste Control R. Hobart Souther, Research Consultant, Chas. A. Dana Science Hall, Guilford College, Greensboro, North Carolina, U.S.A.	317
Registration List		325

2

.

#### PREFACE



Dr. A. E. Berry, General Manager, Ontario Water Resources Commission, Toronto

Conference Chairman

The papers contained in this brochure were presented at the Ninth Ontario Industrial Waste Conference held on June 24th, 25th, 26th and 27th, 1962 at Delawana Inn, Honey Harbour, Ontario. These papers are valuable discussions on industrial waste problems of current interest.

The Committee responsible for this Conference is desirous at all times of providing an opportunity for the exchange of information among the personnel in industry responsible for waste treatment and for protection of watercourses. The progress that has been made in Ontario in treatment of industrial wastes, as well as sewage, is most gratifying. There is much information needed on the complex problems involved in the treatment of industrial wastes. It is hoped that this publication will enable a wider dissemination of the material than would be possible otherwise. These papers will also serve as a ready reference for those who were in attendance or for those who are concerned in any way with these problems.

The thanks of the Water and Pollution Advisory Committee are extended to those who participated in the preparation of papers and in taking part in the discussions. This cooperation is most valuable in these programs. The water resources of the province remain a valuable asset, and it is imperative that there be the closest of cooperation in the efforts to protect these resources. The Committee feels that industry is continuing to cooperate in meeting its responsibilities in waste disposal, and through this mutual cooperation much progress can be expected.

A list of those who attended the Conference is enclosed along with the copy of the program and other relevant information.

For further information, write to the Water and Pollution Advisory Committee, Ontario Water Resources Commission, 801 Bay Street, Toronto 5, Ontario.

### APPLICATIONS OF PVC AS A TRICKLING FILTER MEDIA

.

.

.

by

R. W. Brouillette

ä



#### SESSION ONE

J. E. Buchan, Manager, Union Carbide Can Limited, Bakelite Division. Session Chairman.



R. W. BROUILLETTE

APPLICATIONS OF PVC AS A TRICKLING

FILTER MEDIA

BY

J. T. EGAN, The Mead Corporation, Ohio, U. S. A.

and

R. W. BROUILLETTE, Field Sales Engineer, B. F. Goodrich Indust.Prod. Co., Marietta, Ohio, U.S.A.

The seventy years that have elapsed since the introduction of the trickling filter have been marked innumerable times by the development of new media. Besides stone, such things as bundles of reeds, lath, tin cans and even corn cobs have been used in attempts to enhance the biological oxidation reaction rates.

In 1954, the first plastic media was developed for use in the treatment of phenolic wastes. Since then, many design and fabrication improvements have been made. One of the most recent of these was the introduction of a media fabricated from polyvinyl chloride.

The applicability of polyvinyl chloride for use in this type of media is dependent upon the basic properties of this thermoplastic. Since PVC, as it is often referred to, can be formulated to provide some rather divers combinations of properties, a simple characterization by properties is difficult. In general, rigid

#### page 2

PVC may be described as a hard horn-like material containing no plasticizers. It possesses exceptional chemical resistance, good weatherability, good dimensional stability, and good abrasion resistance. It can be formed into nearly any configuration prior to fabrication, thus eliminating any residual internal stresses when the components are electronically welded together. An infinite variety of textured surfaces can be provided, and colour coding for easy identification of material thickness is a simple procedure.

These material advantages have permitted the production of a PVC media\* having the design characteristics shown in this photograph. (Fig. 1)

The individual units are made of alternating flat and corrugated sheets dielectrically welded together to form a structurally self-supporting packing module measuring 2' x 2' x 4'. The void spaces measure 1.5" across and 3.69" long. Weight of the individual packs varies from 44 pounds to 66 pounds, and results from the variation in material thickness used in construction.

Selection of sheet thickness to compensate for structural, hydraulic, and biological load requirements, as well as temperature, permits the most efficient use of material while keeping installation costs to a minimum. Units fabricated from the heavier gauge material are placed in the bottom layers of the filter with succeeding layers being made of lighter material as the load bearing requirements are reduced.

The strict quality control procedures exercised during manufacturing give assurance that every unit falls within prescribed tolerances as to size, shape, and weight. Obviously, no re-screening or grading is necessary at the filter site, and the material may be handled by standard construction equipment.

You will note that during a packing operation that the workmen are able to walk on this plastic media without danger of breakage due to brittleness. This eliminates the need for an extensive system of scaffolding.

Some comparisons of the bulk properties of PVC media as compared with other filter media commonly used are shown in Tables 1 and 2.

The ratio of surface area to void space, combined with the pattern employed in packing this media eliminates the likelihood of channelling, plugging and ponding.

\* Manufactured and marketed exclusively by the B. F. Goodrich Industrial Products Company as Koroseal Vinyl Core. From the foregoing, it is apparent that polyvinyl chloride trickling filter media would be suitable for use in a wide variety of applications in the liquid waste treatment field. Actual operating experiences not only prove this to be true, but repeatedly demonstrate that filters packed with such media readily accommodate high-rate loadings, are stable to shock loadings, are simple and economical to operate, and their vertical construction permits great savings in land area. The applications reported here do not cover all of the full-scale installations using this material, but give a good representation of the variety of systems in which it may be used, as well as some of the treatment results which can be obtained.

#### FROZEN FOOD PROCESSING WASTE TREATMENT SYSTEM

A roughing filter employing PVC filter media is being used at the Morton Frozen Foods Company plant near Crozet, Va. Production at this plant is continuous rather than a seasonal nature, so there is only a brief annual shutdown period during the Christmas Holidays.

The effluent from the plant contains organic matter characteristic of that which is associated with the production of meat pies. The presence of fat in the effluent necessitates the operation of a grease flotation and recovery unit in the initial stages of treatment. The fat recovered is sold to a local rendering plant.

Following the degreasing process, the waste water enters the roughing filter through a series of fixed spray nozzles located at the top of the structure. (Fig. 2)

The filter tower is a rectangular structure measuring 19'10" wide by 26' long and contains a 21' depth of filter media. The major supporting members are of steel, with wooden wall studdings. The walls are composed of asbestos-cement (Transite) sheets 3/16" thick, which are bolted to the steel uprights.

The filter bed is composed of ten layers (each containing 65 packs) measuring the standard 2' x 2' x 4'. The top layer also contained 65 packs, but they had been sawed in half and measured 2' wide by 1' high by 4' long. In all, there were 682 packs weighing 35,625 pounds in the filter tower. A crew of 10 finished packing the media in  $10\frac{1}{2}$  hours.

PCV filter media can be easily and rapidly cut to odd sizes and shapes in a simple operation. This feature is particularly helpful in packing filters having round sections or other dimensions not conforming to the standard vinyl core pack.

The bed is supported at the bottom by a series of parallel rails or bars cast into the concrete floor. They measure approximately 4" wide by 10" high and are spaced about 12" apart. page 4

The effluent passing through the filter falls into the troughs between these rails and is channeled into a common discharge line leading into a settling tank. Provision has been made for recirculation of the filter effluent; however, at the time the data being presented here was gathered, none was recycled.

The initial seeding of the filter was accomplished by diverting the plant sanitary waste into the filter for a period of approximately four weeks. It does not enter the filter under normal operation, but is treated in pre-existing facilities. Nutrients in the form of nitrogen and phosphorous are not needed because of the proteinaceous nature of the waste.

This Table (3) shows the reduction across the roughing filter at various biological loadings. The hydraulic loading was 830 gallons per day per square foot (36 MGAD) with no recirculation. BOD removals averaged 296 lbs/day for the period being reported (approx. 4 mos.). The average percent BOD reduction was 53%.

The data reported in the month of January have not been included in either of these figures, because of the adverse effect of allowing the filter to dry out during the nine day Christmas shutdown. This without doubt has an adverse effect on the biota of the filter and a considerable reduction ir the number of viable organisms undoubtedly occurs. Therefore, it was felt that the results reported in January reflected startup conditions rather than those of normal operation. Re-establishment of the flora appears to have been accomplished in a relatively short period of time, since essentially normal removals were obtained after 11 days of operation.

The temperature of the waste water leaving the plant averages  $32^{\circ}$ C. and does not exceed  $38^{\circ}$ C. Although cooling occurs as it passes through the treatment process, the exact temperature drop has not been determined. The system was put into operation late in October so the conditions being reported on here reflect wintertime operating conditions for that section of the country. This may help to account for some of the BOD removal variations reported. It is interesting to note that the over-all filter efficiency remained satisfactory during this colder weather, and that BOD removals were not as low as might have been expected for that time of year.

#### APPLICATION IN PACKAGE PLANTS

The basic data which was developed on the applicability of plastic trickling filter media to industrial wastes were utilized to develop package units for the treatment of comparatively small volumes of industrial and domestic wastes. These plants have as their particular application those areas in which sewer systems are not available for such things as coin-operated laundries, small milk plants, schools, express highway restaurants and service stations, and other small sources of waste and where trained supervision of the operation of waste treatment is not available. In particular, of course, they are useful where filtration into the ground is not possible for one reason or another.

The particular installations which are to be discussed here were designed specially to handle intermittent flows of waste. It is the type of flow one gets from coin-operated laundries where the only flow to the sewer is during the discharge period of one or more washers. This results, of course, in surges of significant size reaching the sewer. In addition, in a coin operated laundry, the flow is primarily during the morning hours, tapering off during the afternoon, and dropping to practically nothing during the late evening and night hours. This particular waste flow pattern is also characteristic of the school, where the greatest flow of waste is during the periods of recess, lunch, and at the end of gymnasium periods in schools possessing such facilities.\*

Table 4 is the flow diagram for an installation of this type which is in operation on the effluent of a coin-operated. laundry at Churchill, Tenn. This unit consists of a lint trap, two 1500 gallon surge tanks, a 750 gallon final settling tank, and a chlorine contact chamber. The chlorine contact chamber is 150 gallons in capacity and provides an estimated 45 minutes retention time. Constructed on top of one of the 1500 gallon surge tanks, which are interconnected so as to provide continuous flow from one tank to the other, is a 2' x 4' x 10' trickling filter containing 80 cubic feet of PVC media. The flow in this unit is through the lint screen and then into the surge tanks. From the bottom of the surge tank, the waste is pumped to the top of the filter and allowed to flow through the filter and back to the surge tank. A portion of the flow to the filter is split off and sent back to the inlet of the surge tanks to provide recirculation considered necessary to keep the contents of the two tanks agitated. Waste then overflows from the surge tanks into the settling tank and from there through the baffled chlorination tank into the effluent line.

The major advantage of this design is that it produces a uniform effluent and a uniform load on the filter with an intermittent or slug-type influent. This is done by introducing the raw waste directly into the sump, and by continuous agitation and mixing of the sump contents, and by continuous circulation through the filter. The sump is sized to provide at least 24 hours theoretical detention.

When a surge enters the sump it is immediately mixed with the total content of the sump. The effluent is displaced from the sump into the settling tank consequently does not reflect the slug flow.

Unit developed and patent applied for by the Mead Corp.

\*

page 6

The results of sampling this unit are shown on Table 5. Because of the intermittent nature of the flow, it is impossible to collect the usual conventional type composite samples where collection is on a time basis. This was tried and resulted in samples of questionable representativeness. Consequently, in an attempt to gain a better insight into the loading of this unit, samples of wash water and rinse water from six different random selected washings were collected and the BOD, colour, alkalinity, ABS, and suspended solids were measured. These results were then composited mathematically to provide a loading for the unit. The effluent samples were collected on a conventional timed composite and each piece of data shown in this table is the result of an 8 hour composite. As can be seen, there is considerable variation in the makeup of the wash water. The alkalinity varied anywhere from 340 to 439 mg/l and the colour ranged from 25 to 115. This same wide variation can be seen in suspended solids 43-263 mg/l, and with ABS values ranging from 50 to 100 mg/l. The ABS was measured with the methylene blue test standardized against a sample of standard ABS supplied by the Soap and Glycerine Manufacturers Association. Perhaps the most significant variation, however, was in BOD which had a range from 104 to 645 mg/l. In the rinse water samples collected, these variations were not as significant. This is as would be expected since the rinse water is a more dilute waste.

Comparing the calculated influent characteristics with the effluent values obtained by direct sampling, the removals shown in this table (6) were obtained. As can be seen, removals in the order of 73% of the BOD and 40% of the ABS were obtained.

From the experience obtained in the operation of this unit, a modified unit was designed for installation in another coinoperated laundry, this time at Lynn Garden, Tenn. This unit is also handling the effluent of a septic tank which receives the domestic sewage from a beauty shop and a food market. For this installation, circular tanks rather than rectangular ones were used. (Table 7).

The sump under the filter is a 2500 gallon circular tank with a hopper shaped bottom. A filter 4' x 4' x 10' was installed which contains 160 cubic feet of PVC media, and the secondary settling and chlorination chambers were combined into one 800 gallon circular unit with a hopper bottom. Flow in this unit is again into the sump rather than the filter, from the bottom of the sump to the top of the filter and returned to the sump after passing through the filter. Again, a fraction is split off and returned to the sump to provide circulation and agitation. Both the inlet and recirculation flows are introduced tangentially to the tank to impart a rotating motion to the sump contents. Overflow from the sump is into another 800 gallon, circular hopper-bottomed chamber which discharges to the stream. Under study for this system is the use of an agitator in the tank rather than pumping for mixing. The economics of this will be the deciding factor. BOD removals across the filter are averaging 83%.

A third application of this unit has been constructed at the rural High School in Dungannon, Va. In this plant, the effluent from a septic tank receiving wastes from the school are taken to the sump below the filter.

In this case, as in the case at Lynn Garden laundry, circular tanks were used. One hundred and sixty cubic feet of PVC media were used in this installation, and, as you can see, the flow is similar. (Table 8).

The Virginia State Department of Health has observed the operation of this unit and has gathered data on it. Summer vacation has interrupted the operation of the system. The student population of this school is 650 students and the system was designed to handle 10,000 gallons of waste per day. The operating load during the period of operation was 5,000 gallons per day. Average efficiency for this secondary system was 89%. The selling price of the entire system was \$8500.00.

#### TREATMENT OF PAPER WASTES

Studies of the applicability of PVC media to the treatment of paper wastes were the subjects of papers by Egan and Sandlin (1) and Minch, et al (2). This work was primarily in connection with waste from the manufacture of unbleached kraft board.

In the design of the waste treatment system at the Rome mill, it was felt that the operating costs and maintenance problems associated with the activated sludge treatment method would not be justified when considered against the degree of treatment required. (Required treatment was on the order of a 50% reduction in total mill BOD). The high temperature of the waste (approx. 135°F. or 57.2°C. from the papermaking machines) and the wide fluctuation in BOD load of the mill effluent would have a deleterious effect upon an activated sludge system or at best, add to the operating problems and cost.

Sufficient information was available to determine that the land area required for spray irrigation or for oxidation ponds would be far in excess of that available at the Rome mill. These factors led to the consideration of the trickling filter principle. (Table 9).

The treatment plant was designed to handle 16 MGD of mill effluent having an average BOD of about 450 ppm or a daily load of 56,000 lbs. of BOD. Operating at a rated efficiency of 50%, the minimum BOD removal was expected to be about 28,000 lbs. of BOD per day. In addition, the design called for complete removal of settleable solids and at least 85% reduction in suspended solids. The influent to the treatment system consists primarily of mill white water which has been screened and black liquor from pulp mill washings and spills. The black liquor is first discharged to a strong waste lagoon from which it is metered to the surge tank. This pre-treatment of the mill effluents eliminated the need for primary clarification. The surge tank provides about 20 minutes detention and serves primarily as a mixing tank for the white water and black liquor.

Nitrogen and phosphorous are added to the effluent of the surge tank in the ratios of BOD:N:P of 100:20:1. Phosphoric acid and anhydrous ammonia are fed to the discharge side of the pumps conveying the liquor to the top of the filter.

The effluent of the filter is collected in a concrete basin beneath the filter and weirs are provided to permit recirculation of the filter effluent. Design of the system provided for a maximum recirculation ratio of 1:1, although it was planned to operate at 0.5:1 ratio. Hydraulic loadings during the past year of operation have not permitted any recirculation.

Flow of the filter effluent is by gravity to a circular clarifier having a retention time of two hours and an overflow rate of 800 gallons per day per square foot. Sludge scraping equipment is provided in the clarifier. Settled sludge from the clarifier is returned to the surge tank and ultimately to the filter for further oxidation.

From the clarifier, the effluent flows into a one million gallon "aeration" tank. This tank already existed at the plant, and it was decided to include it in the system for the purpose of reducing the high immediate oxygen demand of the waste prior to its introduction to the lagoons. Very little five day BOD reduction occurs across the aeration tank.

From the aeration tank, the waste enters a stabilization basin consisting of five lagoons operated in series. These lagoons cover an area of 31 acres with an effective surface area of 23 acres. The lagoons have an average depth of 4 feet and at the design load of 16 MGD, have a retention period of about 2 days.

The trickling filter tower is a concrete block, octagonal shaped unit containing about 370,000 lbs. of PVC media in 100,000 cu. ft. of volume. The tower is 80' in diameter and about 30' tall. The depth of the filter bed is 20' and contains ten layers of Koroseal vinyl cores. (Fig. 4).

There are 6,250 packs in the tower. The bed is supported at the bottom and in the middle by epoxy-coated steel grating. The grating in turn is supported on trapezoidal shaped beams which were designed to provide good distribution of the liquid over the underlying packs.

page 8

As previously stated, the treatment plant was designed for approximately 16 MGD at a recirculation ratio of 0.5:1 and a hydraulic load of 210 MGAD. Loadings to the system since startup have averaged 18 MGD. Table 10 gives a comparison between the design levels and actual operating levels, following one year of operation of the system.

#### ACKNOWLEDGEMENT

The authors wish to acknowledge that many other people played quite a significant part in the development of the material which was presented here. Mr. Richard W. Self and Mr. John K. Sullins of the Kingsport Division of the Mead Corporation are the co-developers of the package waste treatment plant. The authors wish to express their appreciation for the kindness of the Morton Food Company and in particular Mr. Robert Gibson, in making available the data on the operation of their waste treatment installation.

Certain portions of this paper were presented at the 34th Annual Meeting of the Water Pollution Control Federation and at the 11th Southern Municipal and Industrial Waste Conference.

#### REFERENCES

- 1. Egan, J. T., and Sandlin, McD., "The Evaluation of Plastic Trickling Filter Media." 15th Industrial Waste Conference, Purdue University, Lafayette, Indiana. (1960)
- Minch, V. A., Egan, J. T., and Sandlin, McD., "Plastic Trickling Filters - Design and Operation." Journal Water Pollution Control Federation (in print).
- 3. Modern Plastics Encyclopedia (1961).
- 4. Perry, J. H., "Stoneware Tower Packings." Chemical Engineers Handbook (1950).
- 5. McKinney, R. E., "Complete Mixing Activated Sludge." Water and Sewage Works, 107, 69-73 (1960).
- McKinney, R. E., Symons, J. M., Shifrin, W. G., and Vezina, M., "Design and Operation of a Complete Mixing Activated Sludge System." Sewage and Industrial Wastes, 30, 3, 287 (March, 1958).

## TABLE I

### Bulk Properties Of Koroseal Vinyl Core Compared With Other

3

### Trickling Filter Packing Material

Filter Media	Packing Unit Dimensions	Units/ Cu. Ft.	Unit Wt. Lbs/ Cu. Ft.	Surface Area Sq.Ft./Cu.Ft.	Void Space
Koroseal PVC	2' x 2' x 4'	1/16	2.75-4.13	37	97
Blast Furnace Slag	2월"to 3월"	50-60	67-70	21	45
Berl Saddles (4)	1출"	650	42	50	70
Raschig Rings (4)	2"	165	24	29	83

2

TABLE II

Physical Properties of Plastics Used for Trickling Filter Media

	Polyvinyl <u>Chloride</u>	Polystyrene (3)	Polyvinylidene Chloride <u>Copolymer</u>
		÷	
Tensile strength - psi	6,000 - 7,000	5,000 - 9,000	4,000 - 8,000
Elongation - %	10 - 15	1.0-2.5	15 - 25
Flexural Strength - psi	10,000 - 16,000	12,000 - 16,000	4,300 - 6,100
<pre>Impact strength - ft. lb/in.</pre>	1.0-5.0	0.25 - 0.4	0.3-1.0
Heat distortion temp <sup>O</sup> F @ 264 psi	155 - 160° F.	150 - 195 ° F.	130 - 150° F.
Max. Recommended service temperature - <sup>o</sup> F.	135° F.		
Burning rate	Self-exting.	. Slow.	Self-exting.
Specific gravity	1.50 - 1.60	1.04 - 1.06	1.65 - 1.72

### TABLE III

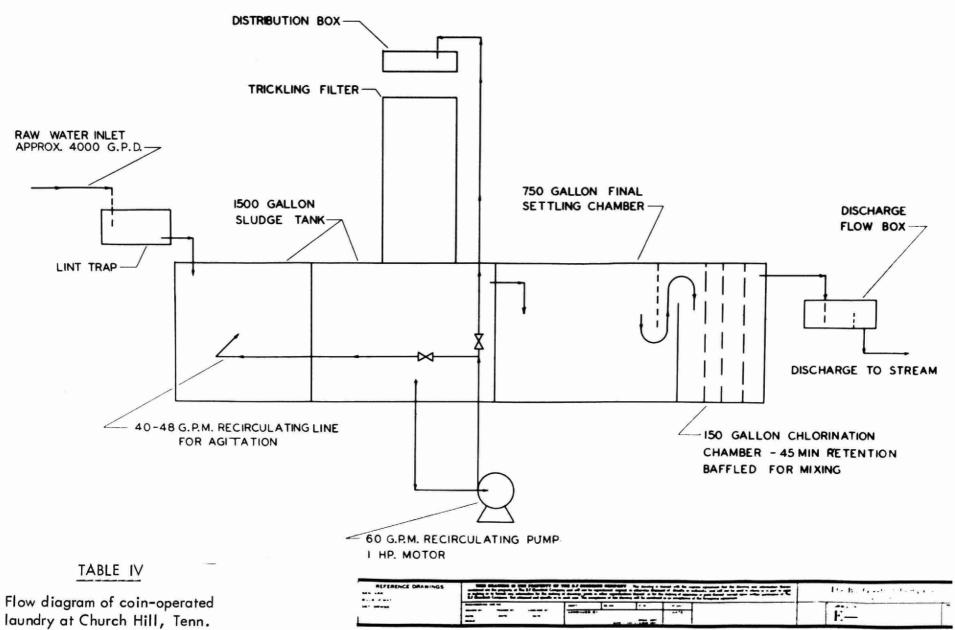
.

.

### FROZEN FOOD PROCESSING - ROUGHING FILTER

Hydraulic Load: 830 gal/day/sq. ft.

DATE	Applied BOD lbs/1000 ft/ 3day	Removed BOD lbs/1000 ft 3 day	% Reduction	pH Filter Feed	Filter Eff.	Susp.Solids ppm Filter Feed	Filter Eff.
							1
11/18/61	449	264	58			480	130
11/25/61	330	165	50	6.9	5.7	500	280
12/2/61	562	304	54	7.3	6.7	460 /	120
12/9/61	529	258	48	6.9	6.2	580	170
12/16/61	562	310	55	6.9	6.4	124	26
12/23/61	529	363	68	7.1	5.6	605	133
1/13/62	595	165	27	7.1	5.8	816	768
1/21/62	628	291	46			520	160
2/3/62	628	363	57	7.1	6.2	660	170
2/10/62	661	363	55	6.0	6.7	720	370
2/17/62	468	144	69	6.8	6.3	660	280
2/24/62	793	490	38	6.0	5.6	750	130
3/3/62							
3/17/62	793	338	57	5.9	5.7	740	330
3/24/62	648	266	58	4.6	5.9	660	208
3/25/62	826	360	56	5.0	5.7	660	350
AVERAGES	600	296	53	6.4	6.0	595	241



4

ω

### TABLE V

.

Ŧ

	Church Hill, Tenn. Wash Water Samples					
	Alkalinity (mg/l)	Colour	Susp. Solids (mg/l)	ABS (mg/l)	BOD (mg/l)	рН
	340	100	43	60	104	7.6
	325	115	. 58	60	181	7.8
	340	117	170	100	467	8.0
	380	95	263	100	645	8.4
	430	25	238	50	484	8.7
	300	160	163	80	632	8.4
AVG.	352	102	156	75	419	8.1
		Rinse Water Samples				
	170	10	18	30	10	6.9
	190	10	53	30	29	7.2
	195	10	33	15	10	7.3
	180	10	25	20	20	7.3
	200	10	58	30	28	7.2
	170	10	50	30	32	7.1
AVG.	184	10	40	26	22	7.2
			Combined Inf]	uent		
	268	56	98	51	221	

### TABLE VI

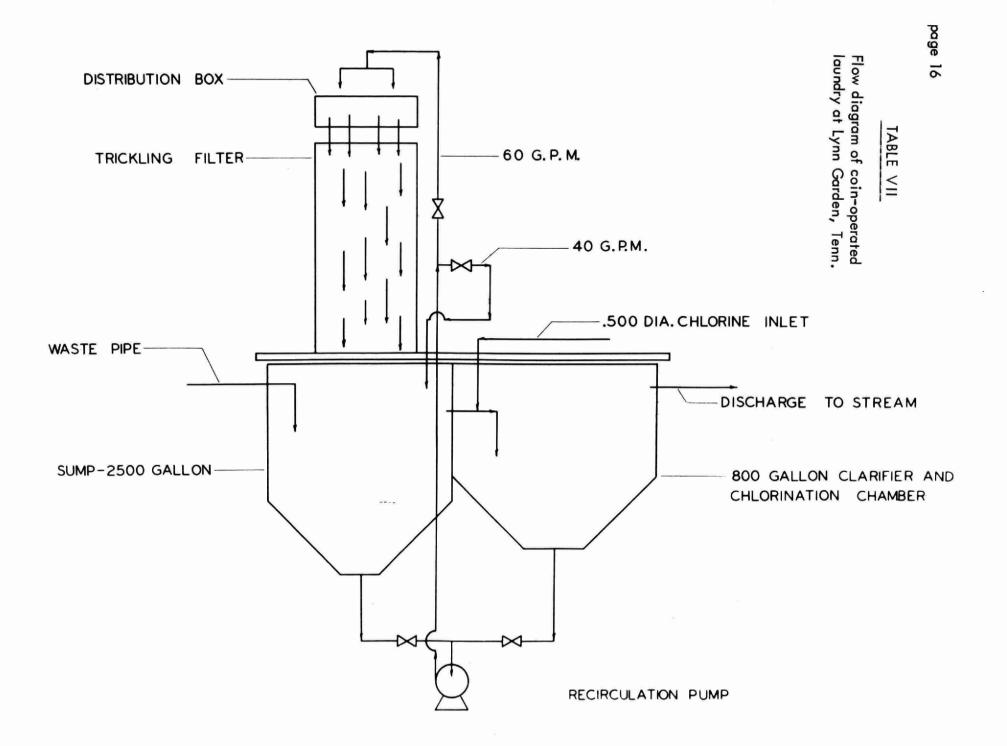
з. -

### Effluent Coin Operated Laundry Church Hill, Tenn.

¥.

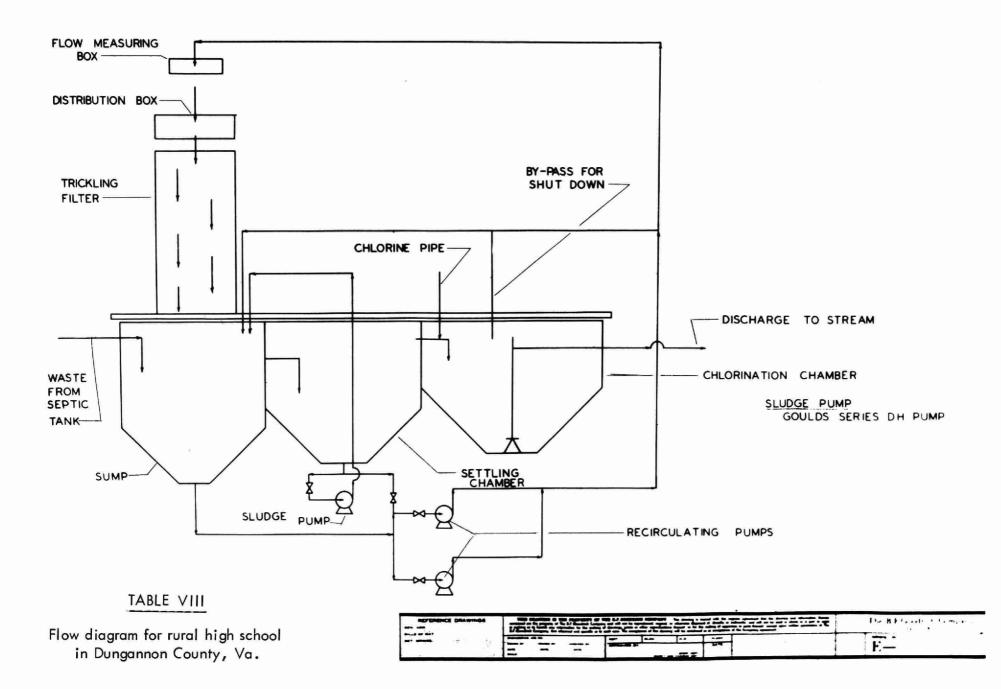
Alkalinity (mg/l.)	Colour	Susp. Solids (mg/l.)	ABS (mg/l)	BOD (mg/l)	РН	Temp (°C.)
330	53	28	30	64	76	24
275	17	50	30	61	76	11
300	65	27	30	44	78	12
300	70	10	30	63	77	18
340	50	25	30	74	78	20
AVG309	51	28	30	61		

Average	Percent	Removals
BOD		73
ABS		40
Suspende	ed Solids	s 72



.

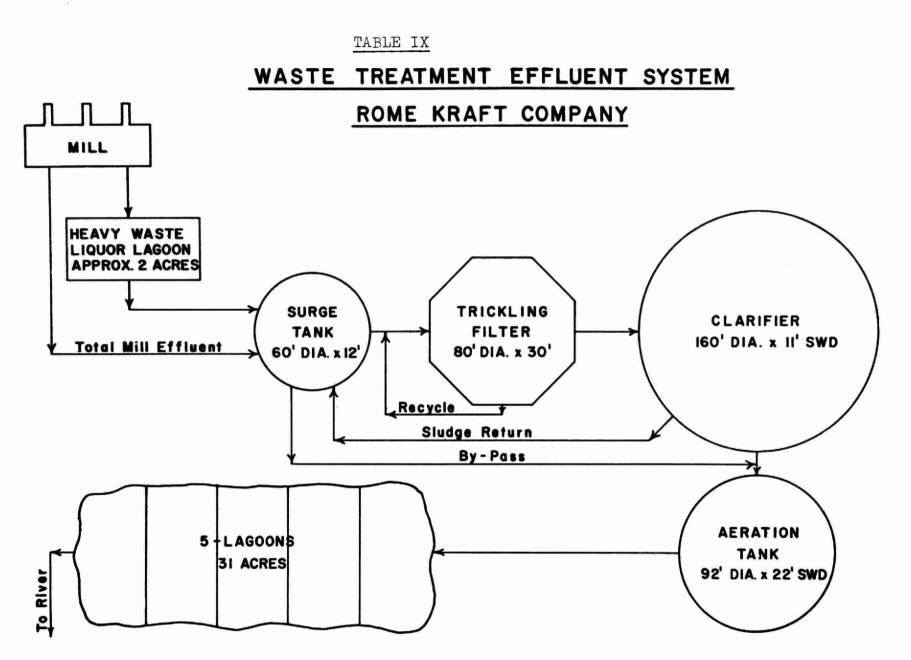
.



.

.

71



. .

.

.

page 18

.

.

### TABLE X

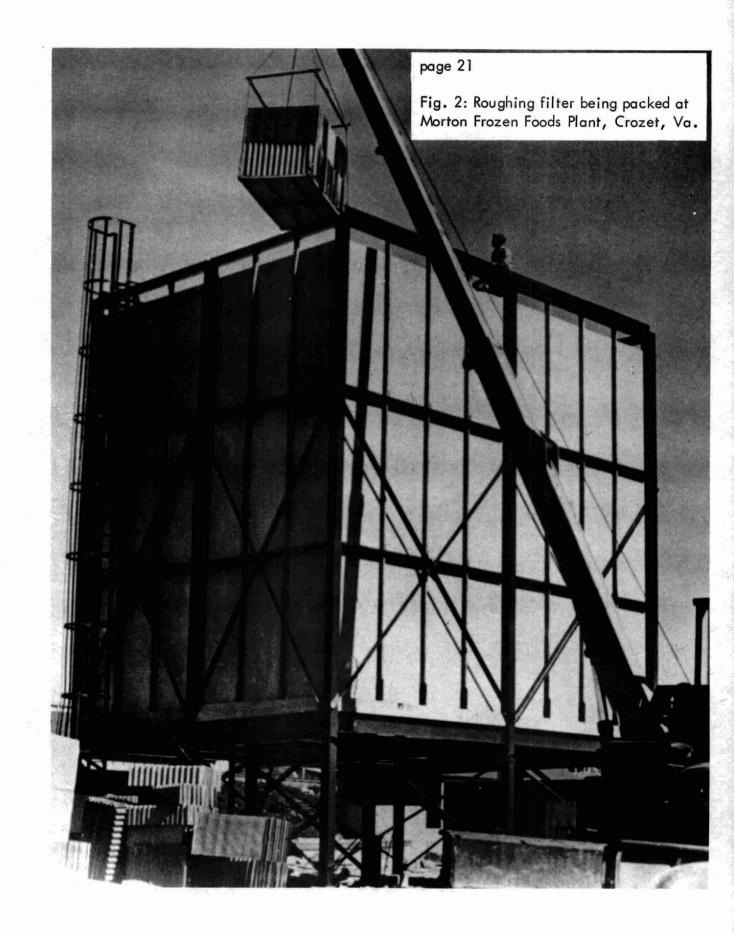
### A Comparison of Design Levels And Current Operating Levels

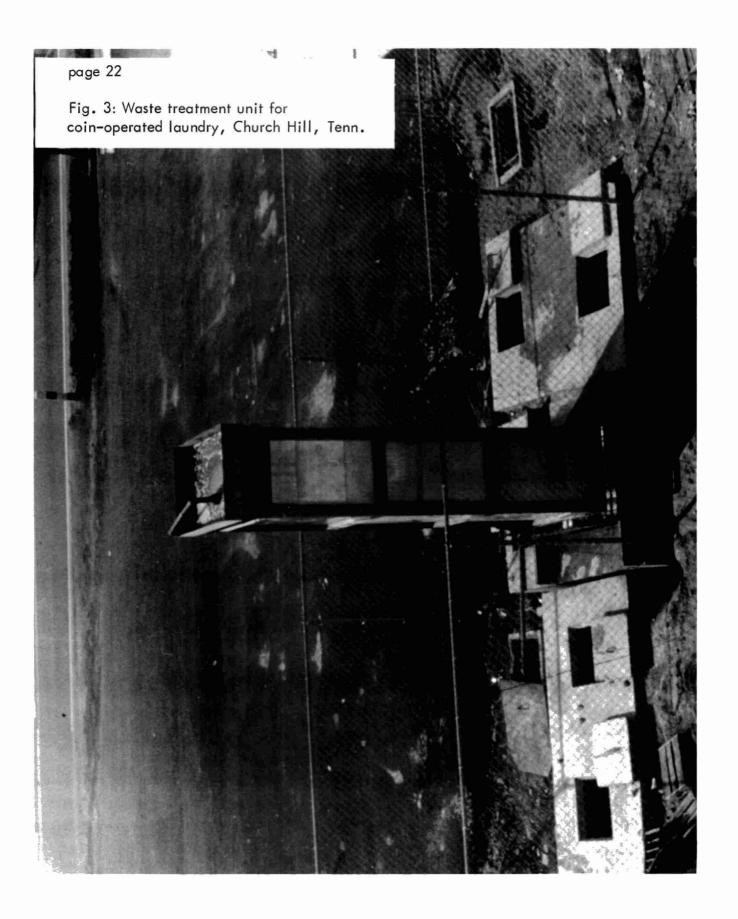
	Design	Actual
In	56,000 lbs. BOD/ day	90,000 lbs. BOD/day
Out	28,000 lbs. BOD/ day	42,500 lbs. BOD/day
Efficiency	50%	53%
Hydraulic Loading	16 MGD	18 MGD

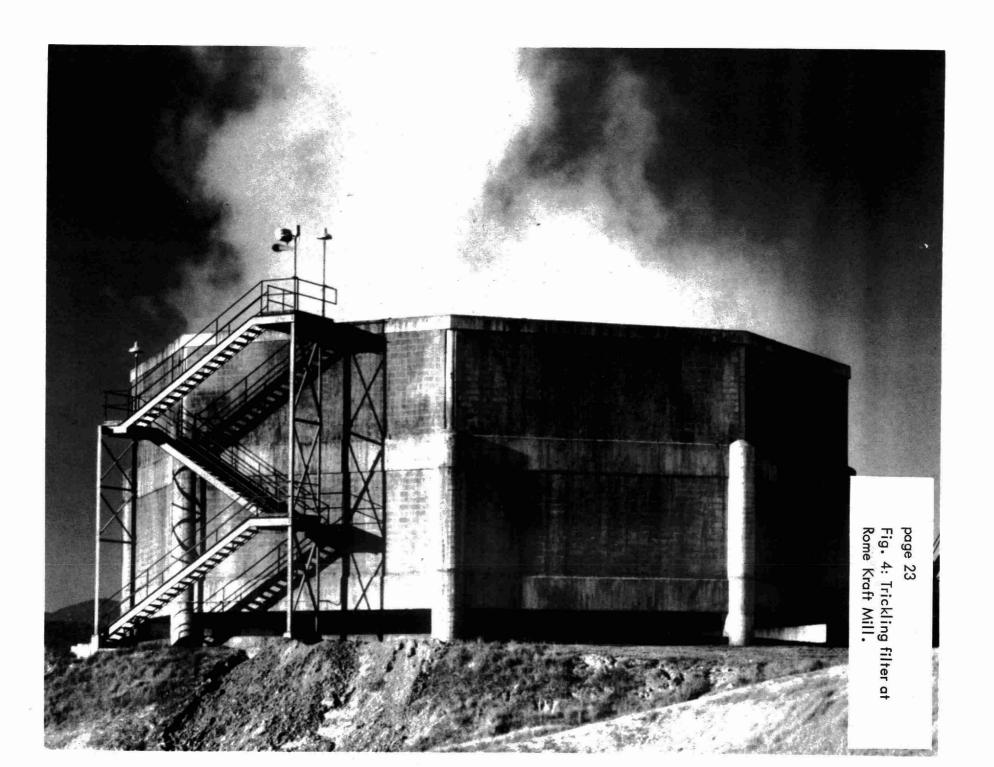


Fig. 1: Top view of individual Koroseal vinyl core, module looking in the direction of waste flow.







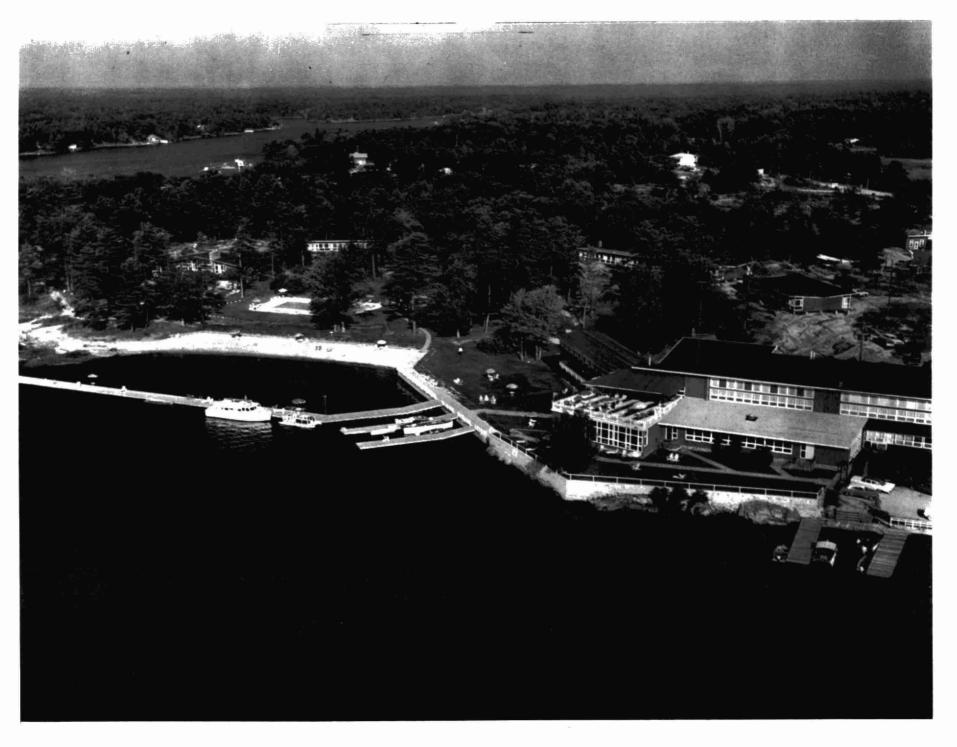


.

.

.

.



page 24

.

4

.

.

CANNERY WASTE TREATMENT IN ONTARIO

.

-

•

by

A. Townshend



CANNERY WASTE TREATMENT IN ONTARIO

by

A. R. TOWNSHEND, P. Eng.

and

R. G. BARRENS

Sanitary Engineering Division Ontario Water Resources Commission

#### INTRODUCTION

From a very modest beginning just before the turn of the century, the canning industry in Ontario now provides an annual outlet for enormous quantities of agricultural products and supplies an extensive and varied range of wholesome foods to Canadian and foreign markets.

The fruit and vegetable preparations industry in Ontario accounts for about 75% of Canadian production and up to 95% of the total production of soups and juices (Exhibit I).

It employs approximately 10,000 of the 16,000 average monthly salaried and production workers in the entire Canadian Industry.

Based on the Dominion Bureau of Statistics publication, "The Fruit and Vegetable Preparations Industry" total production in Ontario increased by approximately 65% during the ten-year period from 1949 to 1959. There was little increase in the production of canned vegetables and fruits (Exhibit II). Most of the increase was in tomato products, soups, apple products and baked beans. The production of corn was lower in 1959 than in 1949 (Exhibit III).

During this ten-year period the number of canners (85+) and the number of people employed (10,000+) remained about the same while the number of canning factories decreased from approximately 147 to 115.

Those canneries which specialize in the preparation of jams, jellies, marmalades, baby foods, macaroni, spaghetti, pickles, relishes, olives and frozen fruits and vegetables not page 26

used for reprocessing are excluded from the above statistics. Most of these canneries are located in larger centres. Their wastes are successfully treated without difficulty at municipal sewage treatment plants.

The location of those fruit and vegetable canneries which form the basis of this paper entitled "Cannerv Waste Treatment in Ontario" are shown in Exhibit IV.

The vegetable canneries are centered in Essex and Kent counties in the west; and Prince Edward, Northumberland, and Hastings counties in the east. The fruit canneries are concentrated in the Niagara Peninsula.

### PERIOD OF OPERATION

The fruit and vegetable canning season begins in May and continues until December. The Canning periods for various packs are shown in Table I.

Some canneries maintain a year-round operation by processing preparations during the off season.

The seasonal nature of the industry is illustrated in Exhibit V which shows the number of employees by month for the years 1949 and 1959. The peak production occurs in August and September.

### WATER REQUIREMENTS

The water use of a cannery depends upon its production volume, methods of handling, type of equipment employed, and the pack processed. Water requirements may vary widely for the same products from plant to plant because of differences in fluming and cooling water use; and re-use.

The requirements for various products based on a survey conducted by the Research Department, Continental Can Company, Inc. (Bulletin No. 22-1951) for U.S.A. Canneries are shown in Table II. Similar data prepared from information obtained at some Ontario canneries are also included for comparison purposes.

The water requirements range from a low of about 15 U.S. gallons per equivalent case of No. 2 cans to 230 depending upon the product. In Ontario, corn and peaches show the greatest range.

### WATER USE IN ONTARIO

Ontario canneries obtain water for processing, cooling and sanitary waste disposal from municipal systems; and private

1

wells, springs and surface supplies. Some of the municipal and most of the private supplies are not metered.

The total, seasonal, daily water use for 96 canneries based on a combination of metered consumption, period of operation, production, and product water requirement from Table II is estimated to be about 22 million gallons per day (Bottom of Table V).

This is equivalent to the water demand of an urban community having a population of about 220,000 persons or a city the size of London, Ontario.

Similarly, the estimated total yearly water use is 1,686 million gallons.

These estimates do not include the water use of approximately 19 smaller canneries which discharge sanitary and process wastes to municipal sewage systems.

Based on the total (1959) production of all 115 Ontario fruit and vegetable canneries (Bureau of Statistics) an average water use of 70 U.S. gallons per equivalent No. 2 case gives a total of 1,686 million gallons per year.

Although only 1959 production figures and the 1961 estimated water use from 96 of the 115 canneries are available, it may be concluded that the Ontario Canning Industry uses about 60 Imperial gallons for each case of canned goods produced.

In selecting a factory location the canner must give first consideration to an adequate, steady supply of potable water. Municipalities should not agree to furnish water without first determining whether adequate supplies and feeder mains are available to meet the cannery demand and still satisfy the needs of the community. As will be shown later, a cannery may require more water than all other users put together. The cannery should share in the capital cost of building any new municipal facilities that are needed to meet its water requirements.

#### SOLID AND LIQUID WASTES

The canner receives produce raw from the farm. The amount of solid waste varies greatly in quantity among peas and corn; pears and apples; and beans and plums. The canned net weight and the solid waste in per cent weight of raw product are given in Table III. The solid waste ranges from 85% for corn to 10% for plums.

It is interesting to note that for peaches and plums, the canned net weight exceeds the weight of raw product. In some packs the weight of syrup added may be as high as 40% of the canned net weight. This compensates for the loss of solid raw product. A large portion of these solid wastes are relatively easy to separate, collect, and dispose of in a satisfactory manner by return to the farm as feed or fertilizer.

This leaves a large volume of liquid process waste to be disposed of without causing stream pollution or public nuisance.

The volume of liquid process waste depends on the amount of water which is separated for cooling purposes and/or reused during the canning process.

Since there is a dearth of metering devices throughout the Ontario Canning Industry it is not possible to determine what per cent of the total water use is discharged as liquid process waste.

The strengths of raw cannery wastes for various products from U.S.A. and Ontario canneries are given in Table IV. The results of fifteen Ontario, screened, tomato product waste samples are also included. Average values are shown in brackets.

The waste strengths vary widely for almost every product. Canners who purchase metered water or have a limited private supply tend to use less water. This economy results in a smaller volume of stronger waste.

## SUMMARY OF CANNERY WASTE DISPOSAL AND TREATMENT METHODS

A summary of cannery waste disposal and treatment methods in Ontario as of January 1, 1962 is given in Table V. The total estimated daily and yearly water uses at the canneries are also shown to indicate the relative volumes of wastes handled by the various methods.

## SCREENING

Screens are provided at 68 of the 96 canneries. These are described by general types below:

Screen Type	Number
Manual Vibrating Rotary Sweco Hammer and Mill No details	14 28 9 3 2 12
Total	68

page 28

Of the twenty vibrating screen installations reporting mesh size, twelve at No. 20. The remainder range from No. 14 to No. 30. Of the twenty-eight canneries having no screens ten are followed by lagoons. The seven canneries which provide no treatment have an estimated annual water use of 84.8 million gallons or 5.0% of the total.

The majority of vegetable wastes can be successfully handled on a No. 40 mesh screen. For certain wastes, such as tomato, which tend to plug the smaller screen openings, No. 20 mesh is more frequently used. Where spray irrigation follows, coarser screens down to No. 14 mesh are satisfactory.

Screens should be installed on the processing waste lines of all canneries to remove gross insoluble solids and the larger suspended solids.

Except for the smallest of canning operations stationary screens alone are inadequate. Mechanical screens should be used. The installation of stationary screens following mechanical screens is highly recommended as a factor of safety.

To be effective it is essential that the screens be kept clean and that the facilities for removal of screenings be properly designed to prevent the screenings from falling back into the waste flow.

### COMBINED MUNICIPAL AND CANNERY WASTE TREATMENT

General

Approximately 45 Ontario canneries are now located in urban communities where isolation and land requirements limit the use of private spray irrigation and lagoon systems.

Since adequate private biological treatment plants mean high capital and operating costs, and the processes are not readily adapted to seasonal cannery operations, the most desirable solution to the waste disposal problem is discharge to the municipal sanitary sewer system with treatment at the municipal pollution control centre.

It is generally considered a good policy for a municipality to accept organic industrial wastes following such pretreatment at the industry as may be required to prevent undue burden on sewage treatment and to exclude wastes which injuriously affect sewers, pumping stations, and plant structures or the biological treatment processes themselves. Special attention is often required to see that these conditions are met.

Pretreatment Requirements

Usually screening constitutes adequate pretreatment for cannery wastes. Unscreened cannery process wastes should never page 30

be discharged to the municipal sewer system. The coarse solids interfere with the operation of comminutors, pumps and other mechanical equipment. Their removal means hours of additional manual labour for plant operators.

Often larger hydraulic shock loads are composed of relatively clean waters which should be separated and discharged to the storm sewers, or a receiving stream without pretreatment. It may, however, be necessary to provide an equalizing tank at the industry to level out the peak flows before discharge to the sanitary sewers.

Where existing municipal treatment plant sludge handling units are limited it may be considered more economical to provide settling tanks and sludge removal facilities at the industry rather than to enlarge the municipal plant.

### Cost Sharing

The peak cannery load comes at the season of the year when stream flow is low and air temperatures are high. This is the most critical period for the municipal plant whether or not it receives an additional cannery waste. The biological or secondary treatment units must be designed to handle the higher 5-day BOD and hydraulic loadings caused by the cannery. Some equitable method should be mutually agreed upon by the industry and the community to share the capital and operating costs of combined sewage treatment at the municipal plant.

#### Existing Combined Treatment

At the present time there are about 25 canneries which discharge their wastes into municipal sanitary sewers. Screening and cooling water separation are the only forms or pretreatment employed. Ten of the larger canneries of this group use approximately 15% of the total daily and 25% of the total yearly water requirements of the Ontario industry.

With the exception of Whitby and Collingwood the cannery waste volumes and strengths are small in proportion to the total municipal wastes loads and no detrimental effects results at the treatment plants.

The activated sludge plant at Whitby which has been in operation for one season was designed to handle a cannery flow of about 35% of the total flow or 54% of the municipal flow. The special features include step and dual aeration with optional aerated digester supernatent return for additional nutrients. Some particulars of the design are given on page two of Table VI.

The conventional, primary treatment plant at Collingwood has experienced difficulties from coarse solids because of lax screening procedures at the major cannerv. The 5-day BOD and suspended solids removals have been excellent in spite of interferences with mechanical equipment.

#### Proposed Projects

2

A total of 34 canneries now discharge wastes into municipal storm sewers or directly to water courses. These account for about 50% of the total water use of the industry in Ontario. Twenty are located within urban communities.

Fifteen of these twenty canneries are presently planning sewage works programmes in conjunction with nine municipalities. When these projects are completed the total water use of canneries discharging wastes to storm sewers and directly to water courses will be reduced to five million gallons daily and to two hundred and fifty million gallons annually. The remaining nineteen canneries will continue to account for about 20% of the total water use of the industry.

In addition, three other canneries which now have inadequate waste treatment facilities are planning projects involving municiplaities.

Adequate and economical treatment at these twelve municipalities is being proposed by the different consulting engineers in various ways depending on the relative magnitude of the cannery waste and the size of the receiving stream.

These proposed combined municipal and cannery waste treatment projects are summarized in Table VI. The basis of design for certain elements is also included.

At Leamington where the total cannery waste volume is about 315% of the municipal flow it is planned to provide complete primary treatment for the wastes from cannery A and to screen all wstes from cannery B before combined discharge through an outfall sewer into Lake Erie.

At Amherstburg, Port Dover and Trenton, where the cannery waste is 100%, 7% and 15% respectively of the municipal flow it is planned to give complete primary treatment before discharge through outfall sewers to the Detroit River, Lake Erie, and the Bay of Quinte respectively.

Preliminary OWRC approval has been given for a municipal lagoon in Waterford where the cannery waste is about 26% of the total municipal flow. A lagoon is also proposed at Brighton. Here the seasonal cannery flow is about 60% of the municipal flow and the cannery 5-day BOD loading is 71% of the total loading.

A private, aerated lagoon with settling pond followed by effluent discharge to the municipal lagoon is proposed at Tilbury.

At Simcoe it is planned to construct an activated sludge plant using the "INKA" aeration system. This system utilizes a grid of shallow air diffusion pipes; a central page 32

longitudinal baffle; and low pressure fans. If necessary, the increased air demand of the strong cannery waste can be easily met by operating both fans up to full capacity as required.

At Ridgetown, Wallaceburg and Essex, where the cannery waste volume exceeds the municipal waste flow, separate spray irrigation systems are planned.

At Chatham the total cannery flow is about 37% of the remaining municipal flow. Here the cost of providing complete secondary treatment for an additional 3.0 million gallons of seasonal, cannery waste would be prohibitive. Preliminary approval has therefore been given to the installation of a separate cannery irrigation system which will require up to 350 acres of spray area.

No special pretreatment facilities other than screening and cooling water separation are planned at these installations with the exception of the aerated lagoon system at Tilbury.

## SPRAY IRRIGATION

The first application of spray irrigation for the disposal of cannery wastes is credited to the Hanover Cannery Company at Hanover; Pa; U.S.A., which in 1947 used portable agricultural equipment to dispose of excess lagooned waste.

In Ontario this latest method of cannery waste disposal was first used by the Green Giant Company of Canada in 1956.

The system at this vegetable cannery at Tecumseh was described in a paper presented at the Fourth Ontario Industrial Waste Conference in 1957. The design and operation of cannery irrigation systems were also discussed in detail at the First Ontario Industrial Waste Conference in 1954 and the Sixth Conference in 1959.

Waste irrigation aims to use the minimum amount of land area with a maximum waste application without damaging the cover crop or causing surface run off.

Most canning waste is well suited to irrigation. While the organic content of BOD is usually high, this material is not detrimental to land or crops, except for a few of the concentrated wastes.

There are several reasons why spray irrigation is more attractive than the previous tried methods of cannery waste disposal. These are:

- 1. The seasonal nature of the canning industry corresponds in general to the growing season when land and crops utilize maximum amounts of water;
- 2. If properly designed and operated, irrigation satisfies the requirements of complete treatment;
- Odour problems are eliminated or are minimized;
- 4. No highly trained personnel are required;
- 5. The cost when compared to complete biological treatment is quite favourable;
- 6. Most of the equipment can be taken down and stored away during the winter months when not in use.

The basic requirements of a spray irrigation system

are:

1. A #10 to #20 mesh mechanical screen;

- 2. A gravity outfall sewer or pumping station and forcemain from the plant to the spray irrigation field;
- 3. A holding pond or pumping reservoir having from 30 minutes to 1 hour's storage to prevent the development of odours;
- Pumping equipment;
- 5. Adequate land area for the type of soil with a suitable cover crop;
- 6. A network of light metal or plastic mains and sub mains with commercial sprinklers.

In Ontario there are now 10 canneries using the spray irrigation system. The water use at these canneries ranges between 14,000 and 1 million gallons per day. Seven use in excess of 250,000 gallons per day. These canneries account for about 20% of the total daily water use and 12% of the total yearly water use of all canneries in Ontario (Table V).

A summary of cannery waste spray irrigation systems in Ontario is presented in Table VII. This table gives types of soil and cover, application rates, dosing periods, volumes sprayed and lengths of operating cycles.

It appears that application rates up to 0.08 inches per acre per hour for at least 4 hours are satisfactory on clay soils. Application rates of 0.35 and 0.17 have been used successfully for 3 and 2 hours respectively with clay loam soils. Satisfactory application rates for heavy clay soils have not been determined.

Higher application rates may be used on sandy soils. Two examples are given at the bottom of Table VII. It is noted however, that a long dosing period of 17 hours at Cannery 9 resulted in field run off. This indicates that the sprinklers should be moved more frequently.

The average volume sprayed successfully on clay soil is about 0.3 inches per acre per day. Cannery 4 has sprayed an average of 0.62 inches per acre per day on 7 acres of a clay loam soil without surface runoff. It follows that an average application of 1.3 inches per acre per day grossly overloads heavy clay soil.

Steps are being taken by Canneries 6 and 7 to obtain more land for spray irrigation before the 1962 season begins.

Average applications of 0.18 to 0.37 inches per acre per day, which are satisfactory for clay and clay loam soils, were used by the consulting engineers in designing the proposed combined municipal irrigation systems previously presented in Table VI.

It is hoped that more canneries will adopt this method of waste disposal.

### SEASONAL RETENTION LAGOONS

By the late 1940's the principles of cannery waste lagoon disposal were well established in the U.S.A. It was found in the Mid-West that the controlled day by day application of sodium nitrate in properly constructed storage lagoons permits the disposal of cannery wastes without stream pollution or atmospheric pollution beyond approximately 200 feet from the lagoon site.

The sodium nitrate furnishes oxygen for aerobic bacterial decomposition during the early stages before algae make their appearance, provides nutrients for the early growth of chlorophyllaceous protozoa and algae which in turn produce additional oxygen by photosynthesis; and helps to maintain a slightly alkaline pH. <u>Sufficient sodium nitrate should be</u> <u>added by weight to satisfy about 20% of the 5-day BOD when the</u> <u>waste is held in shallow (3-5 feet) lagoons.</u> This is equal to about 200 pounds of sodium nitrate per 1000, No. 2 cases of corn, peas or tomatoes.

During the winter months under ice cover sedimentation and stabilization of the waste takes place. It was found that sodium nitrate treated wastes are more stable at the time of spring thaw than untreated wastes. At one installation a treated lagoon resulted in a 5-day BOD of only 30 ppm while the BOD in the untreated lagoon was 350 ppm.

High BOD and low pH are characteristic of untreated cannery lagoons. These lagoons give rise to complaints of odour nuisance unless located in a completely isolated area.

The critical period for any lagoon is the first two or three weeks of loading at the beginning of the canning season.

The lagoon should be sized to hold at least 1.25 times the total seasonal waste volume. In the spring 25 + percent is retained to seed the waste from the coming year's production.

Presently in Ontario there are about 26 canneries utilizing the lagoon method of waste disposal (Table V). Their combined water requirement amounts to about 6% of the total fruit and vegetable canning industry water use. Eighteen of these canneries use less than 50,000 GPD. Only four use in excess of 125,000 GPD. One large water user (300,000 GPD) is presently planning to convert to spray irrigation.

The depth of these lagoons varies from 1.5 feet to 25 feet deep. Ten of these installations have no screens. This results in the formation of a surface scum which impedes the entry of sunlight into the lagoons. Generally speaking sodium nitrate has not been used. Few samples have been collected to determine the strength and effect of these untreated lagoon wastes when discharged to receiving streams during the spring runoff period.

Insufficient waste flow data are available to accurately calculate 5-day BOD surface loadings. By assuming that the process waste flow is one half of the total water use the 5-day BOD loading per acre per day ranges from 300 to 900 pounds. Only the lower loadings have not resulted in objectionable odours. The BOD loading should be considered as well as the retention requirements. It is not possible to develop an algae growth with high unit BOD loadings.

For this reason the lagoon system is not satisfactory for the high production, seasonal cannery. For optimum results any aerobic lagoon system requires the presence of bacteria, protozoa and algae which are capable of functioning in the environment to reduce the wastes to a satisfactory level before discharge. These micro-organisms do not survive when subjected to high volumes of strong wastes which may also be so opaque as to reduce transmission of sunlight.

The high cost of adding sufficient amounts of sodium nitrate to overcome the excessive 5-day BOD loading is often prohibitive. page 36

LAND DISPOSAL

The early methods of land waste disposal included broad irrigation, ridge and furrow irrigation, absorption or seepage beds and tilefields. These depend largely upon rapid soil absorption for a successful operation and may require chemical treatment (lime) for odour control.

These methods are still used by approximately fifteen smaller canneries in Ontario (Table V). They account for only 2% of the daily water use and 4% of the annual water use of the total canning industry in Ontario.

BIOLOGICAL OXIDATION

In the U.S.A. for large central canneries that process one vegetable after another as they ripen successively or store vegetables for later processing, high-rate trickling filters have proven entirely satisfactory. The seasonal nature of most canneries does not provide enough time for a trickling filter to come to full efficiency.

Most small canners cannot afford the high capital and operating cost of a complete, high-rate trickling filter plant. Unless two-stage filtration is practiced the effluent will not meet the present requirements of most state or provincial control agencies.

There are no longer any private trickling filter plants treating the main cannery process wastes in Ontario.

Also there are no private activated or modified activated sludge plants in Ontario. The canning industry has been slow to accept this method of treatment because of the relatively high capital cost and the elaborate degree of operational control required for efficient operation. This biological process is also not readily adaptable to the seasonal nature of the Ontario canning industry.

The results of experimental work conducted at the Canadian Canners Ltd., plants at Aylmer and Exeter during 1956-1957 were reported by Mr. Duncan, OWRC, at the Fifth Ontario Industrial Waste Conference (1948).

### OTHER METHODS

These are no chemical treatment plants serving canneries in Ontario. Fundamentally chemical precipitation is capable of removing only the suspended and colloidal solids. This treatment alone will not meet the present effluent requirements where there is a discharge to a receiving stream. The disposal of the sludge produced often limits the use of this method of treatment. In the early period of cannery waste treatment (1910-1925) sand filters were used to some extent. Except for very small canneries this method is now obsolete.

There is one cannery in Ontario that uses a sand filter after a sedimentation tank to treat its wastes. (Table V).

# TABLE 1

# APPROXIMATE PERIODS OF CANNING OPERATIONS

Pack	Period No. of Worki	ing days
Fruit		,
Strawberries	June 20th - July 2nd	10
Cherries (sweet	July 5th - July 15th	9
(sour	July 17th - July 30th	12
Peaches	Aug. 15th - Oct. 1st	33
Fruit Cocktail	Sept. 1st - Oct. 1st	22
Plums	Sept.10th - Oct. 1st.	16
Prunes	Sept.10th - Oct. 1st	23
Pears (Bartlett	Oct. 5th - Nov. 1st	20
(Kieffer	Nov. 1st - Nov. 20th	15
Apple Products	Sept.15th - Dec. 20th	66
Vegetables		
Asparagus	May 15th - June 30th	36
Potatoes	July 1st - Aug. 5th	28
Peas	July 5th - Aug. 10th	27
Beets	July 15th - Aug. 20th	28
Tomatoes	Aug. 28th - Oct. 5th	30
Corn	Sept. 5th - Oct. 8th	30
Pumpkin	Sept.25th - Oct. 6th	10
Pork and Beans	Oct. 25th - Dec. 1st	28
	· ·	

# TABLE 11

# CANNING WATER REQUIREMENTS

# (U.S. Gallons per Equivalent Case of No. 2 Cans)

PRODUCT	U.S.A. Canneries			Ontario Canneries		
	Range	Min.	Avg.	Max.	Remarks	
Tomato Products	35 - 45	12	33	60	ll canneries reporting	
Beans	55 - 70				Not available	
Apple Products	75 - 150	26	52	80	Excluding cooling Water 3 canneries reporting	
Corn	40 - 50	11	50	145	4 canneries reporting	
Peaches	20 - 230	15		116	2 canneries reporting	
Peas	31 - 135	11	44	96	6 canneries reporting	
Pears	17 - 125		116			
Beets	27 - 35				Not available	
Pumpkins & Squash	41 - 100				Not available	
Cherries	62 - 125		116			
Mushrooms			45		Excluding cooling water	

# TABLE 111

- 4

.

# SOLID WASTE FROM CANNING OPERATIONS

PRODUCT	CANNED NET WEIGHT (% wt. of raw product)	DRAINED WEIGHT (% net wt.)	SOLID WASTE (% wt. of raw product)	
Corn	-	-	86	
Peas	-	-	79	
Pears	85	58	42-50	
Peaches	106	57	40	
Apples	-	-	35	
Carrots	-	-	33	
Beets	-	-	25	
Tomatoes	66	60	25-36	
Cherries	-	-	20	
Beans	-	-	12	
Plums	164	55	10	

÷

# TABLE IV

٠

.

# STRENGTH OF RAW CANNERY WASTES - PPM

.

PRODUCT	U.S.A. CANNERIES		ONTARIO CAN	ONTARIO CANNERIES		
	5-Day BOD	Suspended Solids	5-Day BOD	Suspended Solids	Remarks	
Apple Products	(2400) 600-3800	250	1200-4200	158-306	2 canneries reporting	
Asparagus	100	30	30-120	34-76		
Beans	150-1500	60-430				
Beets	(3500) 1600–5500	75-3500	(1350) 640-3900	400-3450	( ) Average	
Carrots	(1750) 500-3000	1850	700	124	l Composite Sample	
Cherries	(2200) 600-4200	200-400	(3500) 1800–6700	(200) 42-564		
Corn	(3500) 620-6000	(400) 300-4000	(2800) 1480–4760	2814	2 Canneries reporting	
Peaches &	(2700) 1350-4700	600-6700	(3000) 1750-5400	(750) 182-1888		
Pears			2250	138	l Composite Sample	
Peas	(2540) 375-4700	375-400	(1400) 290-4000	(300) 156 <b>-</b> 506	4 Canneries Reporting	
Pea Stack Liquor	r		30,400-33,200	2336-30,556		
Pumpkin & Squas	h 4000-11,000	1480				
Strawberries			(124) 100-210	56-108		
Tomato Products	(2000) 575-4000	190-2000	(2670) 680-7900	(300) 106-806	Screened Waste	
			(1900) 261-4000	(475) 280-772	(15 Samples)	
Mushrooms			1100	200-924		

## TABLE V

.

• •

## SUMMARY OF CANNERY WASTE DISPOSAL AND TREATMENT METHODS IN ONTARIO (JANUARY 1. 1962)

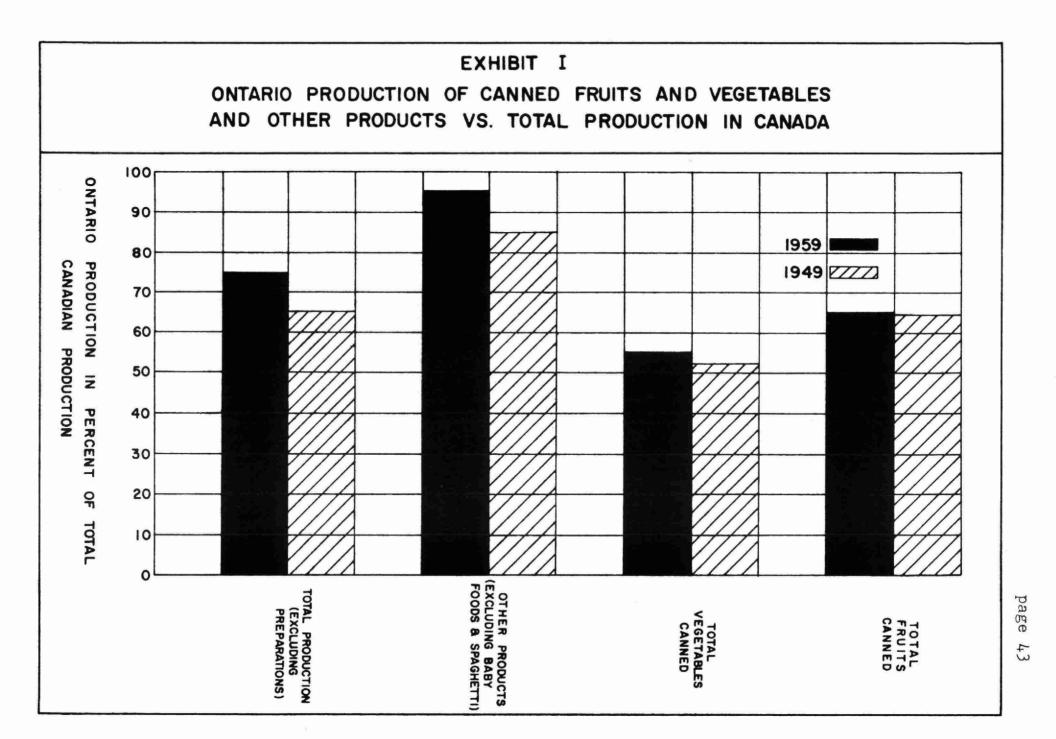
METHOD OF WASTE DISPOSAL OR TREATM	ESTIMATED TOTAL DAILY WATER USE		ESTIMATED TOTAL YEARLY WATER USE		
s. de	Number of Canneries	1000's of Gal.	% Total	Millions of	Gal. % Total
Screens (NO Screens) Municipal Sanitary Sewers Municipal Storm Sewers (No Screens) Direct to Water Courses (No Screens) Spray Irrigation Lagoons (No Screens) Broad Irrigation (No Screens) Tank Truck (No Screens) Retained on Own Property (No Screens) Ditch or Swamp (No Screens) Septic Tank & Tile Bed (No Screens) Septic Tank & Tile Bed (No Screens) Sedimentation and Sand Filter (No Screens)	$ \begin{array}{c} 68\\(28)\\10\\15\\(2)\\19\\(5)\\10\\26\\(10)\\2\\(1)\\3\\4\\(2)\\5\\(3)\\1\end{array} $	3,241 8,091 3,931 (1,345) 4,504 1,633 135 27 48 267 20 35	14.8 36.8 17.9 (6.1) 20.7 7.4 0.6 0.1 0.2 1.2 0.1 0.2	458.2 603.8 (3.0) 245.8 (81.8) 212.3 96.0 3.2 1.5 63.0 0.8 1.3	27.235.8(14.5(4.8)12.75.70.20.13.7-0.1
TOT	'AL 96	21,952	100.0	1,685.9	100.0
Storm Sewers and Direct to Water Courses	34	12,022	54.7	849.6	49.3

2

.

page 42

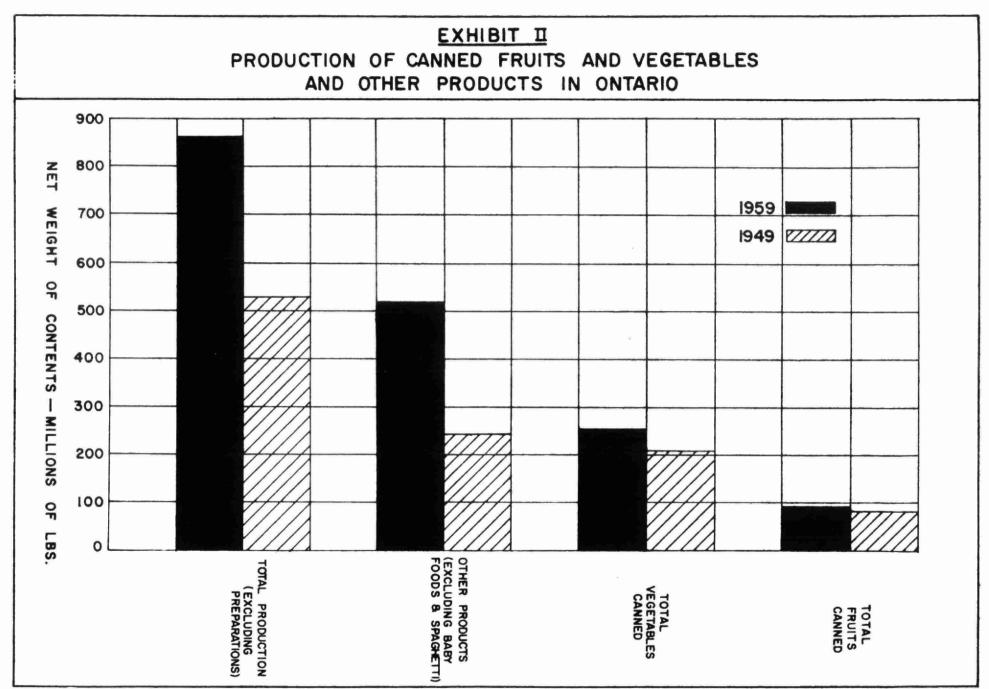
.



.

.

¢



.

.

.

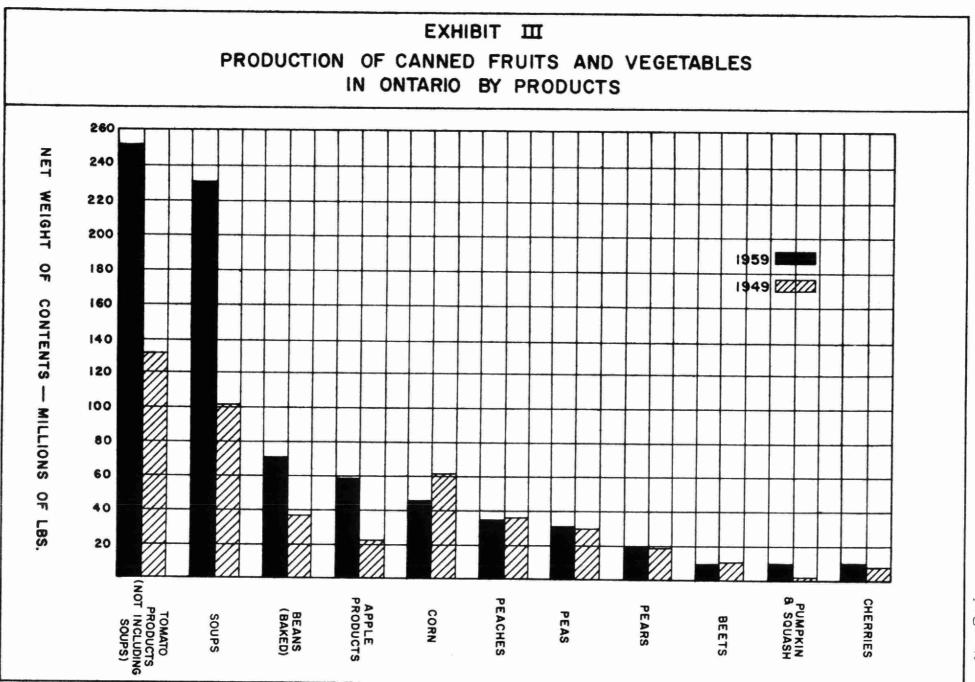
.

page 44

.

3

141



4

.

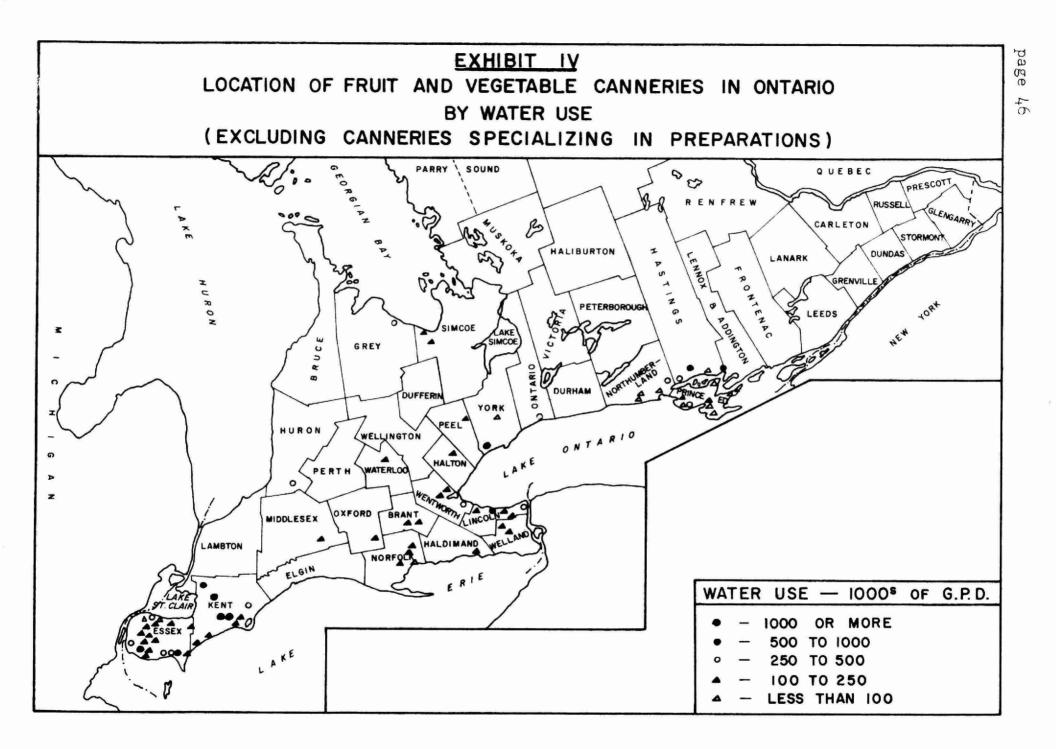
.

4

page 45

٠

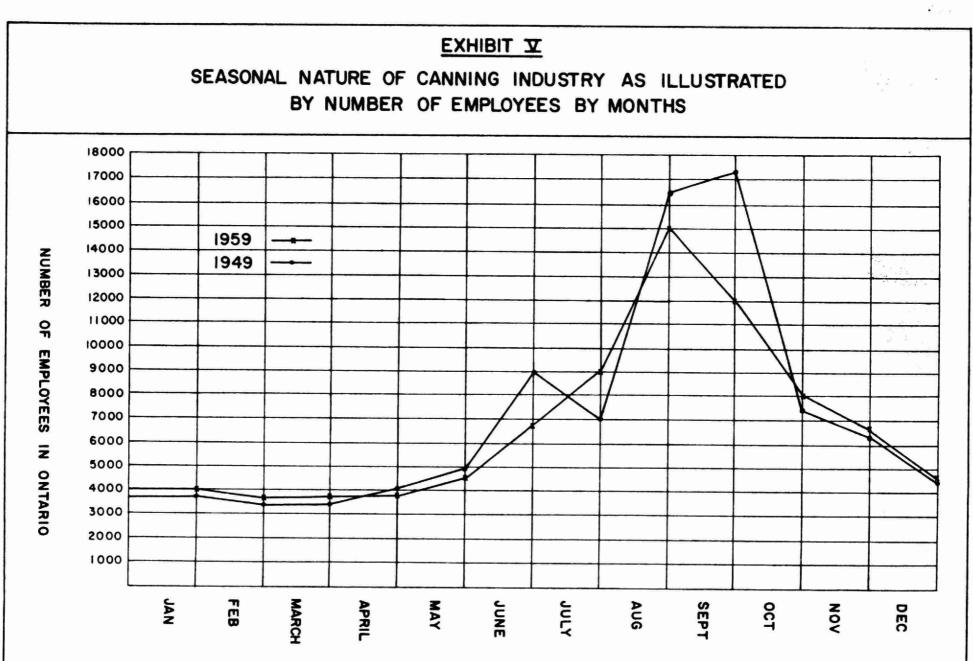
.



.

.

1 T



4 ł

. .

page 47

.

.

page 48







SOCIAL EVENING -- JUNE 26

AMMONIUM PHOSPHATE PLANT WASTE DISPOSAL

ê - 2

by

O. J. Bolduc



AMMONIUM PHOSPHATE PLANT

WASTE DISPOSAL

by

C. J. BOLDUC

The Austin Company Chicago Heights, Illinois

The paper which I am about to present is essentially the same as the paper which <sup>M</sup>r. William E. Jones of Northwest Cooperative Mills in St. Faul, Minnestoa prepared and presented at Furdue University on May 2nd of this year.

Mr. Jones and his people are quite busy at the present time making preparations for the dedication of their new multi-million dollar fertilizer plant which prevents his attendance here today.

You may wonder why a member of the Frocess Division of the Austin Company is appearing on your program as a substitute for Mr. Jones. My association with Mr. Jones stems from the fact that The Austin Process Division designed and built the new fertilizer plant for Northwest Mills. We worked long hours together on the problems which are described in the paper. Because of this association, Mr. Jones graciously suggested that I be invited to appear in his place to acquaint you with the solution of the waste disposal problems we encountered.

One of the major problems facing industry today is that of waste disposal; whether it be in relation to the atmosphere, such as smog, smoke and dust control or pollution. A related problem is conservation of water supplies.

The success or failure of governmental agencies charged with the responsibility of pollution and water conservation is dependent upon the degree of cooperation they receive from industry. Industry recognizes its obligation to provide its fullest cooperation; however it also recognizes the economics involved. If the controls imposed on industry impose financial burdens beyond which it is capable of supporting, the industry will be stifled and employment reduced.

The fertilizer industry is plagued with a serious problem in its public relations because of disposal of waste products and generation of dust inherent in the methods of production. This problem is further complicated by the fact that the fertilizer industry deals with large amounts of dusty material of a relatively low cost per unit. This low cost, high volume production makes it difficult for management to justify the investment funds necessary to install all of the abatement devices which might be desirable.

New processes, however, have been developed which are assisting industry and the farmer in maintaining better control of the dust problem. The bulk of the fertilizer manufactured and applied today is a granular material rather than a powder, making for easier control of dust from the producing plants. These new granular processes, on the other hand, have intensified the waste disposal of various liquid streams generated in the plant.

We believe that the approach taken during the design and operation of the fertilizer production unit erected by Northwest Cooperative Mills can serve as an example of close cooperation between government and the business community. In the development of the plant, Northwest Mills formed a philosophy of maximum utilization of water sources with the least possibility of contamination. The new plant posed a multiple problem of air pollution, stream pollution and waste disposal. Before describing the detailed approach taken to eliminate or, at least, minimize the problem, let us first briefly describe the new facility.

The new fertilizer plant is located on a 200 acre site in an union-corporated industrial area about 30 miles from St. Paul, Minnestoa, on the Mississippi River. The plant will produce 100,000 tons per year of water-soluble ammonium phosphate base fertilizer, incorporating the latest equipment and processing techniques.

Basically, ammonium phosphate is produced by the reaction of ammonia and phosphoric acid. Northwest Mills produces its own phosphoric acid by the reaction of sulfuric acid on phosphate rock. The produced phosphoric acid is then granulated, dried, cooled, screened, stored, bagged and shipped.

From the very beginning the process was developed in such a manner that there would be no process liquids effluent from the property except for natural run-off which occurs in periods of precipitation. The problem of sanitary disposal required that the problem be handled within the plant itself since no <u>municipal sewage disposal system</u> was available. It was, therefore, necessary in the development of the site to provide <u>two septic tank sanitary drain fields</u> for a concentration of approximately 50 people.

The first major processing step, the production of phosphoric acid, creates the largest problem of waste disposal both in size and complexity of solution. The problem divides itself into two broad catergories; the disposal of approximately 300 tons of gypsum produced daily; and the absorption and disposal of the fluorine liberated in the process. In order to discuss these problems, we must delve very briefly into the main chemistry involved in the process.

The raw materials for wet process phosphoric acid manufacture are phosphate rock and sulfuric acid. Phosphate and calcium fluoride, plus minor impurities. Phosphate rock is reacted with sulfuric acid to form calcium sulfate (gypsum) and phosphoric acid. Since there are many impurities in phosphate rock, several side reactions also occur. We shall discuss only those reactions which are concerned with the creation of disposal problems. The gypsum created by the reaction of sulfuric acid on the phosphate rock crystallizes as a solid and is separated from the phosphoric acid by filtration. This reaction is the most important in the system. Although the phosphoric acid is the desired product and the gypsum is discarded, it is the quality and character of the gypsum crystals produced which determines both the efficiency of the process and at the same time the magnitude of the disposal problem. The character of the gypsum crystal controls the degree of filterability and also the amount of inert and extraneous impurities which are carried to the disposal area with the gypsum crystals.

The second reaction with which we are concerned, in the consideration of waste disposal from this plant, is the hydrogen fluoride liberated from the phosphate rock when it comes in contact with the sulfuric acid. Fortunately, the phosphate rock used in the process contains an impurity of silicon in an amount sufficient to react with the hydrogen fluoride to produce fluo-silicic acid in the presence of water.

Another side reaction concerned is the decomposition of fluo-silicic acid to silicon tetrafluoride when heated under acid conditions. This is the characteristic odour which prevails in the fertilizer industry wherever phosphate rock acidulation operations are performed.

We shall now discuss the elimination of the disposal problems created by these reactions. The filtered gypsum cake is slurried with water to make an approximately 30% slurry which

#### page 52

is pumped to the disposal area. The disposal area is completely diked and is of sufficient area to allow the gypsum to settle completely. Clarified water from the gypsum pond is returned to the process and a portion, by means of a counter-current progression, becomes a part of the product acid while the remainder is used for cooling purposes. To provide a start-up area, approximately 2 acres of the disposal pond were black-topped to seal the surface against seepage. As the gypsum collected in this area accumulates, it will be worked outward to provide a seal for enlarging the settling pond area. The water balance over the plant is designed to allow recycle and utilization of all waters from the disposal pond for process uses. The digestion system, where rock and acid are reacted, the vacuum cooler, acid concentrator, and other areas where fluorine is evolved are connected to an absorption system. This system provides extremely high volumes of water in relation to the stream and is highly efficient. The effluent from this system forms a part of the water recycle and eventually is discharged as part of the product used for fertilizer manufacture.

Although this plant requires a constant recirculating water load in excess of 3,000 gallons per minute, multiple use and recycle reduces make-up requirements to less than 400 gallons per minute. It should be pointed out that this reuse and resultant product contamination could not be accomplished if a more highly purified product for use other than fertilizer manufacture were required. I should like to mention here that the reuse of the water from the gypsum pond involved an added expense in that special materials of construction had to be provided for pumps, piping and other process equipment because of the possible corrosive nature of the water. This use of 100% fresh water make-up would have eliminated this expense.

Another section of the disposal area, separated by dikes, is designated as a compositing basin for all drainage waters at the plant site. A system of culverts and ditches was constructed to direct the waters from roofs and other plant areas to this basin. From this basin these waters discharge through a sluiceway to public waters. A conductivity cell is installed in the sluiceway which sounds an alarm in the control room of the plant if these waters accidently become contaminated from any source. Should this occur, a means of treatment is provided in the sluiceway prior to discharge to make this <u>water suitable</u> for entrance into a public waterway.

The second major processing step, the manufacture of ammonium phosphate, yields two types of problems associated with the topic under discussion today. The first involves the problems encountered when ammonia and phosphate acid are combined and the subsequent problems during the granulation, drying, cooling and screening operations. The second, is from the handling of the finished product; primarily in the bagging of the product prior to shipping.

In the production of ammonium phosphate fertilizer, the reaction of ammonia with phosphoric acid is the heart of the process. This is accomplished in two steps. Phosphoric acid is introduced to the system through a venturi type scrubber which removes the dust and ammonia vapours from the exhaust air stream from the ammoniator, the unit in which the final stage of ammoniation is carried out. From the scrubber, the acid discharges to the preneutralizer where it is partially neutralized with ammonia. This partially ammoniated acid is sprayed on a rolling bed of solids in the ammoniator and further ammoniated. The degree of ammoniation controls the economics of the process and maximum neutralization must be accomplished. In order to achieve this, it is necessary to introduce more than the acid is capable of absorbing, creating a condition of high ammonia concentration in the exhaust air stream from the ammoniator. Because of this condition, it is neither economically sound nor, from a pollution point of view, feasible, to exhaust the air to the atmosphere. For these reasons an acid scrubber is employed to remove the ammonia from this air stream. This air stream is also nearly saturated with the steam generated by the heat of reaction in the ammoniator. Since the process will not tolerate a dilution of the input phosphoric acid, it is necessary to establish an accurately controlled operating temperature in the scrubber which will permit absorption of the ammonai but which will not cause the water vapour to condense. Despite the possible seriousness of this condition. little regulatory concern should be generated by this problem. The ammonia in this air stream is the objectionable pollutant and, although this control is delicate, the cost of the ammonia is such that a plant manufacturer cannot operate economically if ammonia is discharged to the atmosphere.

In the subsequent processing steps of drying, cooling and screening of the ammonium phosphate fertilizer, significant quantities of dust are generated. Drying and cooling are conventionally achieved in rotary drums which have been equipped with flights to shower the material through an air steam which is either heated (in the case of drying) or ambient ( in the case of cooling).

These dust-laden air streams from the dryer and cooler are exhausted to the atmosphere but the dust particles must first be recovered. The variety of materials handled in this plant complicates the recovery of dust particles because of the wide range of particle sizes. A high-efficiency dry recovery system has been installed which is efficient for recovering the larger particles. However, to absolutely minimize the discharge of dust to atmosphere, wet collectors are also provided. The value of the product recovered from the dry the

### page 54

collectors pays for the dry system, and the amount recovered minimizes the load disposal problem in the subsequent wet scrubbing, decreasing the cost of disposing of wet product and making this approach practical.

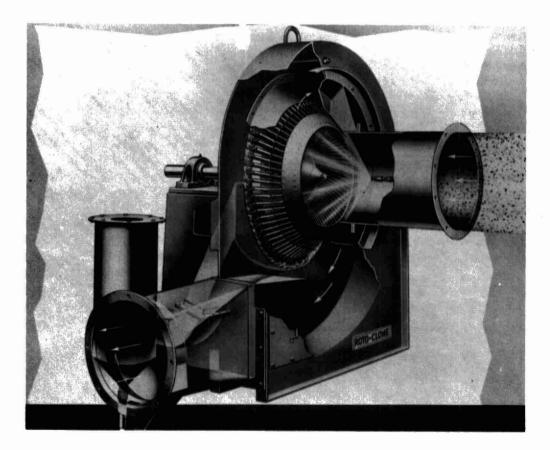
In this particular system, 36,000 cfm of air is required for the necessary drying application which enters the dust recovery system at 220°F. A dry cyclone was designed for this air volume which would remove more than 95% of the plus 20 micron material, with the recovered material recycled to the process. The exhaust air, which contains a minute quantity of dust, and a trace of ammonia vapour is washed with fresh phosphoric acid, before it is used in the process, in a type W Rotoclone which is capable of removing 99% of the plus 1 micron dust, and essentially all of the ammonia. The acid discharged from the Rotoclone is used further as a scrubbing liquid for the exhaust gases from the ammoniator. For the cooling operation, identical equipment is provided for dust removal; however, the air volume is only 25,000 cfm, and water is used for scrubbing in the Rotoclone since the exhaust vapour does not contain ammonia. The discharge from the cooler Rotoclone is sent to the disposal pond for settling no recovery being attempted because of the small quantity involved and the expense of recovery equipment. The Type W (Fig.1) Rotoclone was selected for this application because it combines the function of exhaust fan and dynamic precipitator in one piece of equipment. Also, a minimum volume of water is required for the scrubbing operation, although this was not significant in that all waters going to the gypsum disposal pond are recycled to the phosphoric acid plant for further use.

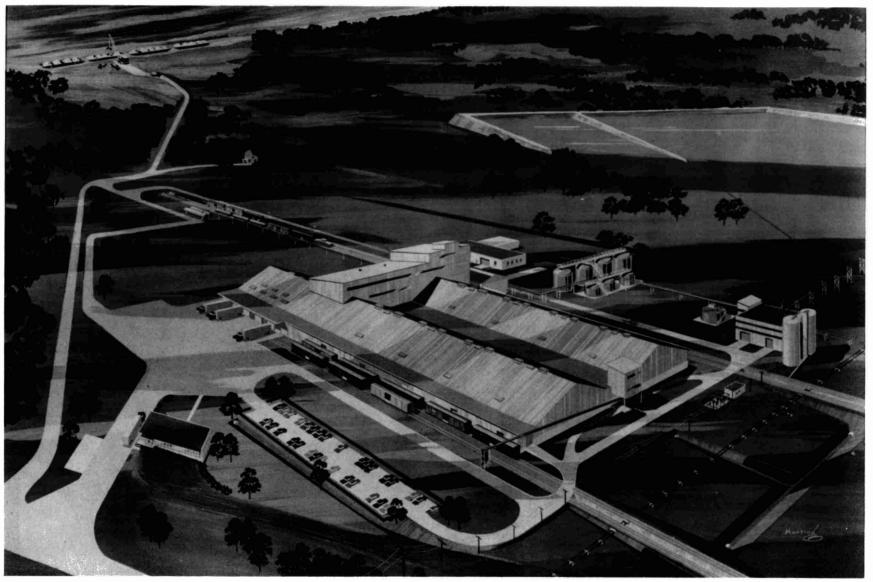
The remaining problem of dust from bagging and shipping operations is one that is often neglected in the fertilizer industry. This neglect in other installations has caused numerous complaints from neighbours resulting in strained relations. Bagging operations are normally located adjacent to shipping platforms making it easy for any dust that is generated to blow over to adjacent properties.

To eliminate this problem, an elaborate system was installed of suction pick-ups at each transfer point in the bagging and shipping system. This dust collection system has a high initial cost and maintenance expense, which is the reason why the industry has been reluctant to install such systems previously. The system will recover product sufficient only to cover the operation expenses. Initial capital investment has been justified on the basis of reduced complaints and improved public relations. In regard to public relations, I would like to quote a statement made by Mr. Jones in the original paper. He said "In the field of public relations, it is difficult to predict a return value. It has been daid that 50 cents of each dollar of public relations money is wasted. When I am able to ascertain which 50 cents, I will be able to reduce our public relations budget by 50%." considered many types of equipment to arrive at what we feel is an optimim design. Also, in the design of the plant we solicited and gratefully received the cooperation and assistance of the State Health Department in the solution of some of the problems presented here.

Many of you represent some of the various regulatory agencies charged with the preservation of what, if not now, will be in the near future, the limiting factor for both civil and industrial growth. The factor to which I refer is our water resources. This is a great challenge. I would like to suggest a mutual effort through understanding, rather than legislation, an effort which utilizes the facilities of governmental agencies to provide methods of solving waste disposal problems within the economic practicability of the industry involved. Remember that in the final analysis, economics is the overriding control for industrial operating practice. We hope that the design and operation of the Northwest Mills' new ammonium phosphate plant will serve as an example of good relationship between government and industry.

It has been a pleasure for me to be able to be with you this morning and share the problems we encountered, and their solutions, in the design of our new facilities.





.

.

Northwest Cooperative Mills - Pine Bend, Minnesota

.

Design and Construction by The Austin Company

.

# A REALISTIC APPROACH TO WASTE TREATMENT

.

.

÷

by

Richard W. Crain



### SESSION NUMBER TWO

D.B. Redfern Proctor & Redfern, 75 Eglinton E., Toronto, Ontario.

Session Chairman



"A REALISTIC APPROACH

TO WASTE TREATMENT"

by

R.W. CRAIN

INDUSTRIAL FILTER AND PUMP MANUFACTURING COMPANY CICERO, ILLINOIS

When Flexonics, (Fig. 1) a division of Calumet and Hecla, Inc., decided to consolidate its six existing plants into a large new manufacturing facility, it found that there were certain industrial waste disposal problems to be faced. The situation was unusually acute due to the fact that the new plant was to be located in the small Village of Bartlett, Illinois which had little industry and an inadequate municipal treatment plant to accommodate the increased flow. (Fig. 2)

The existing total municipal flow was reportedly 300 GPM and the estimated Flexonic's industrial waste flow was to be equal to this. Since the waste was to be comprised of rinses and concentrated dumps of Nitric-Hydrofluoric pickling baths, alkaline cleaners and sulfuric, citric, and chromic acids; it was decided that allowing such untreated wastes to enter the municipal works posed a real threat to the biological action of the treatment facilities. This decision was made by the Metropolitan Sanitary District of Greater Chicago, under whose jurisdiction the municipal sub-station fell. When flexonics was apprised of this situation, it willingly cooperated and consulted with several equipment manufacturers in order to determine what had to be done and which was the best approach to it. They found that the hexavalent chromium had to be reduced to the trivalent form; the acid-alkaline wastes had to be neutralized to between pH 5 and 9; the metallic ions, especially copper, had to be precipitated; and that the sludges resulting from the chemical reactions had to be removed. The biggest problem seemed to be this sludge removal because of the slow settling characteristics of the solids.

For this liquid-solids separation system a mechanized settling basin was first investigated, but the prospect of sending an effluent of at best 50 ppm of suspended solids to this small municipal plant, plus the large outside space requirement and outside maintenance problems during the winter months, made this approach unattractive. Lagooning was ruled out because of the space requirement, its inefficiency, and the fact that its unsightliness would certainly detract from Flexonic's esthetic approach to their manufacturing site.

Flexonics selected the Industrial Filter and Pump Mfg. Co. of Cicero, Illinois to provide the complete turnkey facility because of its ability to produce a sparkling clear effluent of such high quality that it need not pass through the sub-station; but rather could be discharged directly into the storm sewer and subsequently to a creek. There was also the added possibility of recycling this neutralized waste effluent back to process for reuse. This was accomplished by the use of pressure filters directly on the total neutralized waste without any preconditioning or thickening.

The total waste facility is housed in 1,200 ft.<sup>2</sup> and is comprised of:

- A. Chrome Reduction
- B. Acid-Alkali Neutralization
- C. Filtration
- D. Instrument and Motor Control Panel
- A. Chrome Reduction

The chrome reduction system continuously reduces 40 GPM of highly contaminated chrome rinses. Sulfur dioxide, fed automatically by a sulfonator, (Fig. 3) and sulfuric acid, pumped automatically, (Fig. 4) effect the reduction. A small chrome holding tank is provided for any necessary chromic dumps so that they may be held and slowly bled into the running rinses. When the hexavalent chrome has been converted to trivalent form, it flows continuously over a weir into the final neutralization basis (Fig. 5) where it is hydrated to be later removed with the other sludges by the filter.

B. <u>Acid-Alkali Neutralization</u>

The acid-alkaline neutralization system receives acid and alkaline rinses and dumps from three widely separated sources. (Fig. 6) They are pumped over from their respective areas, one of which is 500 feet away. The neutralization is

page 58

total approximately 260 GPM. An acid and alkaline holding tank is provided for the concentrated dumps so that they may be slowly bled into the system. The total waste, after being neutralized, then is approximately 300 GPM and flows continuously into a filter sump (Fig. 8).

### C. Filtration

The waste in the liquid-solid separation system is picked up from the 3,000 gallon filter sump and sent to one of the two 1,000 square foot pressure leaf filters (Fig. 10) where the liquid passes through the dacron cloth covered filter leaves and out to the storm sewer. Ordinarily these will run for four to five 16 hour days before the pressure differential builds up to such a point that the filtration is no longer effective. At that time the second filter is pre-coated with diatomaceous earth and the flow switched to that filter while the first chamber is evacuated with air and the cake on the filter leaves is blown dry to a crumbling state. The filter is then opened (Fig. 11) and the filter cake (Figs. 12, 13) removed with an air knife. The cake then drops down (Fig. 14) into carts (Fig. 15) which are designed to be picked up by a fork truck and periodically dumped. The sludge that is produced amounts to between 75 and 100 cubic feet per week. The effluent that is produced from the filter, after a number of analyses, in over one year's operation has never shown more than 1 ppm of suspended solids. It is crystal clear and even lower in dissolved salts than the well water source from which the water is originally taken. This is due to the lime softening effect which takes place in the filters. This water can be used again in the rinse tanks and Flexonics is currently considering a proposal for such a system.

There is no way for the industrial wastes to leave the plant site without passing through this treatment facility. It has received the complete approval of the Metropolitan Sanitary District of Greater Chicago.

D. Instrument and Motor Control Panel (Fig. 16)

The electrical panel contains the various motor starters, the pH and ORP instruments which are necessary for the automatic operation of this system.

One man is present part-time at this facility and has other duties throughout the plant.

In their discussions with the various equipment manufacturers, flexonics learned that the chrome reduction and acid and alkaline neutralization were basically the same by all waste treatment system suppliers. They were sold when they were page 60

shown that for the same amount of money needed for a mechanized settling basin and vacuum filter system, they could with pressure filters produce a high quality effluent possible of reuse, as well as, a sludge which is dry, crumbling, and easily handled.

After over one year's satisfactory operation, they are convinced that pressure filtration was the most realistic way to handle their biggest industrial waste problem.

In this age of increasing water demands and diminishing water supply, it becomes imperative that each industrial water user return the water to nature in as good or better condition than it is received. If the water can be used a number of times before returning it, so much the better.

## NOTE:

Other waste treatment installations of this type using pressure filters for liquid-solid separation may be seen at:

- 1. Northern Electric, London, Ontario, Canada (Currently under Construction.)
- 2. Robertshaw Fulton Controls, New Stanton, Pa.
- 3. Robertshaw Fulton Controls, Indiana, Pa.
- 4. Western Electric Co., Montgomery, Illinois
- 5. Western Electric Co., Columbus, Ohio
- 6. Western Electric Co., Oklahoma City, Okla.
- 7. Star Expansion Industries, Mountainville, New York
- 8. I.B.M. Corporation, Lexington, Kentucky
- 9. Holly Carburetor Co., Bowling Green, Kentucky

<u>ACKNOWLEDGMENT</u>: We wish to acknowledge the cooperation of The Flexonics Division of Calumet and Hecla for the photographs and permission to discuss their installation.





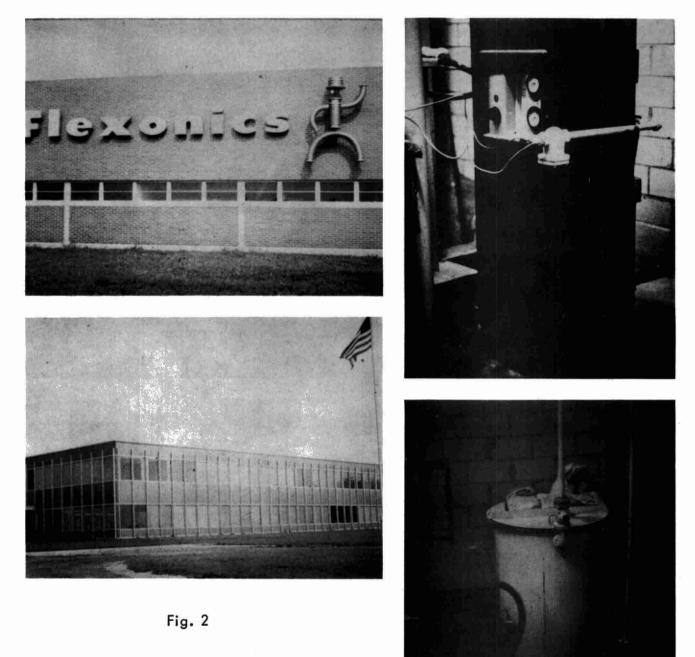


Fig. 5



Fig. 7



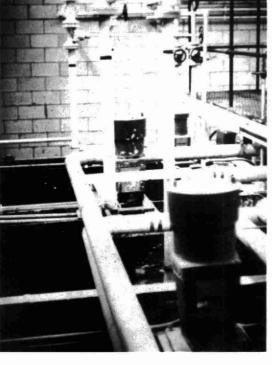






Fig. 8

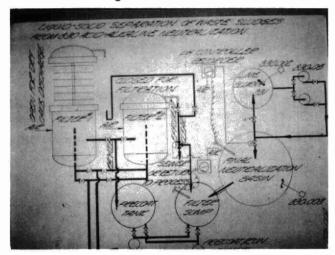
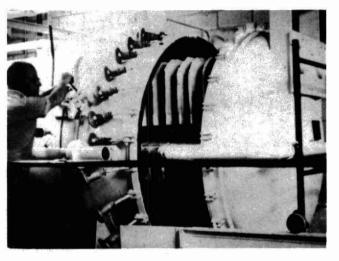


Fig. 11



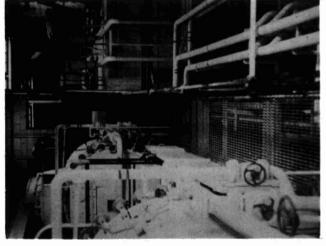






Fig. 12

Fig. 13

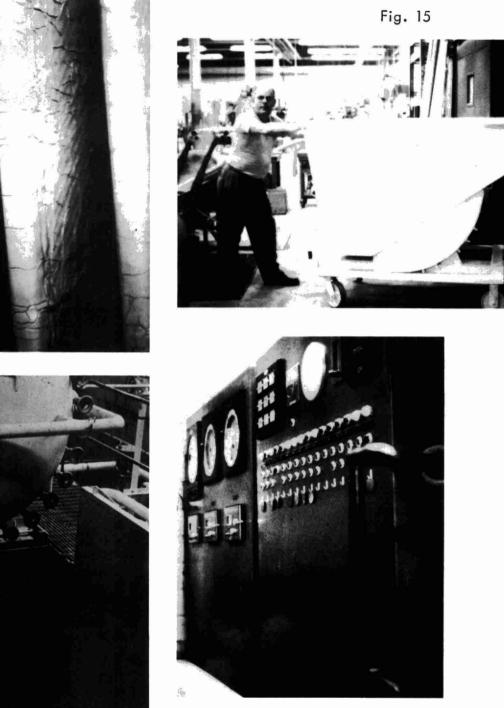


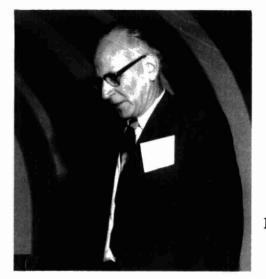
Fig. 16

## PITFALLS IN INDUSTRIAL WASTE TREATMENT

.

by

L. F. Oeming



PITFALLS IN ABATEMENT OF INDUSTRIAL WASTE FOLLUTION

by

L. F. OEMING, Chief Engineer

Michigan Water Resources Commission Lansing, Michigan

According to the information furnished me by Messrs. Berry, Voege and Caverly, this conference is held for a fourfold purpose: to exchange ideas, information and experience on industrial waste problems; to encourage research on apparently insoluble problems; to provide precedents to apply to comparable problems; and to report progress in treatment and disposal programs.

All of these are obviously laudable and I subscribe to them fully. While I have not had the pleasure of attending one of these conferences, your officers have extended the courtesy of supplying me copies of the annual proceedings. The scope and quality of the papers testify to the success of this conference in fulfilling these purposes.

In re-examining the subjects discussed at your prior conferences, I find that highly qualified authorities have given broad coverage to methods of treatment and control for most of the well-known types of industrial wastes. It would therefore be presumptuous for me to attempt to present you with information on specific processes or methods that are novel and unknown to you.

The measures applied in Michigan for the reduction or removal of industrial polluting constituents from streams and lakes do not differ in any marked degree from those practiced in Ontario. While the Ontario pollution control law contains a number of provisions which are not in the Michigan law, the approach of the two administering agencies to abatement of industrial waste pollution has proceeded from the same basic concepts. Under these concepts pollution control is attained by:

1. Reduction or elimination of waste through control of product loss, by-product recovery and re-use of waste water.

2. Application of efficient waste disposal or treatment methods.

3. Efficient use of the assimilating capacity of the receiving waters for effluent disposal.

4. Effective operation and maintenance of control, disposal or treatment facilities.

Requirements for corrective facilities are derived from an evaluation of the characteristics of the receiving waters and an appraisal of the nature and extent of water resources uses to be protected--not on "treatment for the sake of treatment." Volumes of flow and capacities for self-purification are determined for each case in arriving at the effluent restrictions. Stream classification or broad scale application of stream standards have not been a part of our procedures.

The value of these general administrative concepts and procedures has been amply demonstrated by the accomplishments made over the years. As sound as they are, however, their application can not automatically assure completely successful solutions to all problems. Circumstances can and do arise which conspire to defeat the best intentioned plan or program for correction, leading to disappointment and, at times, consternation particularly where sizeable expenditures have been made and the clamor for stream cleanup has been great. Michigan has had its share of these experiences. I propose to draw from them in partial fulfillment of the conference purpose of providing precedents to apply to comparable problems. I intend to direct attention to a few of the more common pitfalls which need to be avoided and adverse factors that need to be recognized in formulating corrective or preventive measures for waste control.

### DEEP WELL DISPOSAL

Disposal of wastes to underground formations has attracted a great deal of interest in recent years. It offers the prospect of completely eliminating the pollution of the surface water and is especially attractive for handling concentrated wastes or wastes which are difficult or impossible to treat. The very simplicity of the term "underground disposal" makes it difficult to convey an appreciation of the obstacles to a successful application. All too often, the proposal has been advances with no more concept than that all that is necessary is to drill a well to a depth below the fresh water horizons, and pour the wastes down the hole. The chances of success will obviously be nil with this approach. However, failures occur in proposals which are advocated by a higher level of knowledge, experience and competency in the fields of geology and hydraulics by neglect of the more subtle chemical and physical factors that project themselves into the system. Many of the failures are comparatively easy to anticipate. They arise by reason of insufficient exploration of the geological structures to determine their capacity to receive wastes, and the magnitude of injection pressures required. Those failures which are less susceptible of anticipation and prevention have been chargeable to sealing of the disposal formation due to its interaction with the wastes. Determination of all the variables that will have a bearing on the success of a particular installation is a task of considerable magnitude.

No established design factors exist upon which a system can be derived and installed. Precedents in the form of successfully operating installations do exist but they have been established only after detailed studies of geological, chemical, hydraulic and physical factors. Information was secured on the location and properties of the disposal strata, the amount and character of liquids contained in the strata, the need for preconditioning the wastes prior to injection and the need and magnitude of pressures involved in introducing the wastes to the formation. The state, in acting on the proposals, has maintained close surveillance to insure that requirements are met which are designed to afford protection against damage to fresh waters or sources of chemical raw materials. These requirements are in the form of specifications on features of input well construction and limitations on injection pressures.

COMBINED TREATMENT WITH MUNICIPAL SEWAGE

The degree of success or failure of abatement through the use of municipal sewage treatment facilities depends upon the reserve capacity available in the plant and on the ability of the process to treat the wastes.

Enthusiasm of municipal officials in encouraging new industry to locate in the community frequently leads to commitments to accept wastes without full knowledge of the problem they are assuming. In a typical case history, the city has recently built a sewage plant to comply with an Order issued by the state. It is gratified with its accomplishment and secure in the knowledge that it has provided some reserve treatment capacity to accommodate growth and confident that it can therefore keep out of trouble with the pollution control

authorities. It is well conditioned to view with favor industry's request for treatment service, and properly so within the limits it can perform. Any concern it may have with the ability of its plant to accommodate the wastes is satisfied by industry's proposal estimating the volume of its wastes to be discharged and their strength usually in terms of oxygen demanding constituents. Negotiations are concluded on this basis and the wastes are accepted into the sewer system. Either as the result of an inaccuracy in estimating the waste loading or neglect of the constituents that will have a destructive effect on the treatment process, there follows an impairment or complete failure of the treatment function and a citation from the state for creating unlawful pollution. Resolution of the dilemma varies from suspension of service to the industry making it necessary to treat separately, pretreating to bring the waste loadings within the capacity of the plant facilities and enlarging or modifying the city's plant. Expenditures are called for which none of the parties expected to make at the time agreements were consummated. Considerable heat is generated in the process of securing correction characterized is diminished? One of several alternatives is presented. Public and private rights to waters of acceptable quality must be surrendered; treatment cost will ascend to such a level that industry may find it impossible to meet them and still remain in business; or ways must be found to supplement the flows at least during critical periods of the year. As to these alternatives, we are convinces that to the extent that natural flow is necessary for maintenance of established equities, the riparian doctrine of reasonable use must be preserved and, if need be, strengthened particularly during summer seasonal periods.

Our concern therefore is directed toward withdrawals of water for consumptive uses. Supplementary irrigation of certain farm crops, golf courses, cemeteries, parks and lawn sprinkling is rapidly increasing. This means no return to the "water bank" after use. If the practice is continued and extended without appropriate controls, it has ominous implications for the future. Present figures on these uses are not particularly alarming, but forecasts portend gradual seasonal depletion of the "water bank." We have estimated that if even as much as 5% of the farm land or other concumptive needs are met by direct withdrawal from drought period flows, streams in many drainage systems would be completely dried up in many summers for weeks at a time. This is when the water is most needed and is now taken. Injury to established uses begins, of course, long before consumptive withdrawals approach the point of stream flow exhaustion. Even as little as a 10% reduction in low flows can readily tip the critical balance toward injurious and unlawful pollution conditions in streams now receiving their maximum safe waste loads. Their recreational value and indispensable use for water supply and waste effluent assimilation would be seriously impaired or completely destroyed.

Statutory authority to control consumptive diversions needs the support of industry as well as the public in order to impart stability to pollution control programs. It would seem contrary to public policy, not to mention the imposition of severe economic burdens on the innocent as well, if heavily loaded stream sections should be shorn of their present waste assimilating capacities. This must be expected if the present trends in the consumptive uses of such waters are not reversed. Many sections of our rivers will be closed to further industrial water using expansion. This factor, more than any other I have discussed here, creates grave problems in securing a greater degree of stability to the pollution control effort.

In conclusion, I have endeavored to describe some aspects of the waste disposal problem which, if overlooked, can result in economic loss as well as disillusionment and embarrassment. I have by no means exhaused the subject and realize that many of you have questions based on your experience that I have not covered. I can only say that I am certain that Dr. Berry and his associates will be happy to rectify any errors of omission on my part.

î.

ENVIRONMENTAL SURVEYS FOR NUCLEAR POWER STATIONS

.

ų

by

Dr. W. E. Grummitt



ENVIRONMENTAL SURVEYS FOR NUCLEAR POWER STATIONS

by

W. E. GRUMMITT

Atomic Energy of Canada Limited Chalk River, Ontario.

### SYNOPSIS

A general review of pre-start-up and operational environmental surveys is presented. Mention is made of the results of the Great Lakes Institute program at CANLU. Experience at Chalk River and at NPD is discussed with particular reference to the types of instruments which are available and to the types of samples which provide the most meaningful information. While total $\beta$  radioactivity at Pembroke, downstream from the AECL Chalk River plant, is not significantly increased, it is shown that Cs-137, and pssibly Sr-90, originating at the plant can be detected at Pembroke by radiochemical analysis. The concentration has never exceeded 3% of the maximum permissible concentration in water for the general population.

In order to ensure the safe operation of a nuclear power station, or other industry, control and monitoring procedures must be established prior to start-up. These procedures must provide a means of preventing or controlling the release of material having a deleterious effect upon man or his environment and, if possible, a means of checking subsequently on whether such a release has taken place unnoticed. In this respect, the nuclear reactor is no different from the pulp mill and problems associated with radioactivity are no worse than those arising from inorganic waste.

Reactors produce very large amounts of radioactivity, but under normal operating conditions the amount released to the environment is so small as to be barely detectable above natural levels. This is achieved by care in design of the plant and by systematic analytical control of all materials released. In addition, a monitoring system should be established in the area surrounding the reactor site. It is this subsidiary monitoring program which I will discuss in this paper. Results will be drawn from experience with existing Canadian reactors for these have a direct bearing on the environmental survey at CANDU. This is the new power reactor being built at Douglas Point on Lake Huron. When complete, it will feed 200,000 kW into the Ontario Hydro system.

In such a program it is necessary to consider the possible long term build-up of radioactivity and to be prepared for accidental releases. In the long term build-up particular . attention must be paid to those radioisotopes with long halflives, e.g. strontium-90, cesium-137 and plutonium-239. Shorter lived radioisotopes, e.g. iodine-131, present the major problems in the case of an accidental release.

At Chalk River and at NPD\*, surveys fall naturally into "on site" and "off site", the latter being the area where unrestricted movement of populations is permitted. Of course, it is preferable for the monitoring in these two areas to be done by different organizations in order to increase public confidence. Provincial and Federal Health Departments have been encouraged to assume responsibility for monitoring outside the plant boundaries. Co-operation of this sort is now at a stage where total responsibility for "off site surveys" will soon be shifted from AECL to the Health Departments.

## Sources of Contamination

The main sources of contamination are fission products, e.g. strontium-90, and capture products, e.g. cobalt-60, from the operation of the reactors. These materials may be transferred as gases or particulates to the atmosphere, or they may be released directly to the ground as dissolved material in solution. Transfer to the atmosphere will generally result in contamination of the soil and the plants which grow on it. Much of the activity released to the environment will slowly accumulate in surface waters unless radioactive decay occurs first. Hence the two rate processes (that is the rate of decay and the rate of transfer to the water) will determine the importance of a particular nuclide in the possible contamination of the environment near the reactor site.

<sup>\*</sup> The main research establishment and the nuclear power demonstration reactor of Atomic Energy of Canada Limited, are referred to as 'Chalk River' and 'NPD', respectively. These are located on the Ottawa River about seventeen miles apart.

Dilute radioactivity in solution is frequently released to surface waters after monitoring. The rate of release can adequately be controlled through the use of water-tight delay tanks such as that shown in Figure 1. This method of disposal is used for reactor cooling water and process wastes.

One further source of contamination is the disposal area, from which radioactivity can be transferred by ground water to surface waters. Inventories are much more difficult to establish in this case and disposal methods are required which will adequately safeguard against unwanted release.

In all cases there may be contamination of biota by the radioactivity in the atmosphere or in surface or soil waters. The extent of this contamination will depend not only on the concentration of radioactivity, but also on the extent to which a particular element enters into biological processes.

# Instruments and Measurements

Having outlined various sources of contamination, we can proceed to consider ways of detecting the activity in the environment. The simplest type of measurement is the detection of  $\Upsilon$ activity on the ground or in the air. Because it does not involve sampling or analysis, this method is appreciably faster than indirect analytical procedures. Methods which involve concentration of the radioactivity are very much more sensitive than direct counting methods but are considerably more complex. Generally these procedures involve filtering to concentrate aerosols, heating to remove water or destroy organic material.

. .

Measurements of 'fallout', in river water and biota are handled in this manner.

Figure 2 shows a portable  $\Upsilon$  survey instrument for mapping accidental releases of activity. Provided the background levels are known beforehand, this instrument can quickly provide information on the distribution of contamination from a reactor accident. At Chalk River and at NPD a number of fixed  $\Upsilon$  monitors are located around the reactor stack, at a distance of approximately  $\frac{1}{2}$  mile, to give an immediate indication of a possible accidental release.

Figure 3 shows a device for collecting samples of ground water from various depths. It consists of a porous plug which can be driven into the ground and through which water can enter. Ground water samples are taken in the vicinity of the disposal area to observe the movement of radioactivity through soil.

A photograph of one of the 'fallout' collectors is shown in Figure 4. It consists of a polythene pail lined with a sheet of thin polythene. This ensures that none of the sample is lost at the time at which it is removed from the pail. 'Fallout' collectors are located in the immediate vicinity of the reactor stacks, at both the NPD and Chalk River establishments. In addition, collectors situated in the villages of Deep River and Chalk River (seven and five miles distant), serve to establish background levels.

Air filtering units are located at the population centers which are situated nearest to the reactors. These indicate changes in the concentration of particulate radioactivity suspended in the atmosphere.

In addition to the foregoing, the following samples are taken at regular intervals. 1) Drinking water from the municipal supplies to the towns between Rolphton and Pembroke. 2) The Process Sewer Outfall, including the reactor cooling water. 3) Fish from the Ottawa River and surrounding lakes. 4) Snowshoe rabbits. 5) Miscellaneous animals trapped in the region. 6) Samples of vegetation which grow near the disposal area. 7) Milk from local supplies.

## Types of Analyses

All samples are checked for  $\operatorname{gross} \beta$ ,  $\gamma$  activity. In addition, the biota, river water, process sewer and 'fallout' samples are analysed regularly for strontium-90, cesium-137, strontium-89 and for gamma emitters such as cobalt-60. Some of the biological specimens are also analyzed for other specific radioisotopes. For instance 10% of the analyses involve a check for iodine-131 and plutonium-239.

## Observations

Controlled quantities of radioactivity are released regularly at Chalk River through the process sewer. However the level in the sewer is never allowed to exceed the maximum permissible drinking water concentration for specific radioisotopes, as established by the International Commission for Radiological Protection. The concentration of strontium-90 in the river as a result of 'weapons fallout' has for several years been at a level of  $\frac{1}{2}$  to 1 pp C/litre (Figure 5). Occasionally it is possible to detect slight increases in the concentration of nuclides such as cesium-137 in river water downstream from the Plant, but at no time has the concentration risen above 3% of the maximum permissible concentration in water for the general population, or above one thousandth of the maximum permissible concentration for industrial workers.

Levels in the river can be correlated with known releases of activity from the plant. The dashed line marked (1 + 2) in Figure 6 is the sum of the 'fallout' and process sewer contributions of cesium-137 to the river. This summed curve gives a reasonable fit to the observed points for Pembroke, though it should be noticed that there is little difference between levels above and below the plant (i.e. Deep River and Pembroke). This type of comparison is possible for cesium-137 only because there is relatively little 'fallout cesium' in the river.

Some of the radioactivity in the disposal area is moving slowly in ground water. At present, this is contributing about 2% as much strontium to the river as is derived from 'fallout'. Cesium moves more slowly than strontium in ground water and consequently has not yet started to move out of the disposal area.

Occasionally the close-in 'fallout' collectors show small amounts of activity over the'fallout' background, but nothing has been detected up to the present time at the sites which are located at five and seven miles from the plant (Chalk River and Deep River). The background due to 'weapons fallout' is shown in Figure 7.

Finally, in the table, typical levels are given for fish and rabbits. As might be expected from the analyses of Ottawa River water, samples of fish caught one mile downstream are very little different from those taken above the plant. Similarly, rabbit bone and flesh appear to be uniformly contaminated as a result of 'stratospheric fallout'.

## CANDU Survey

The CANDU environmental survey is somewhat more complex than that at NPD because of geographical differences, i.e. the proximity of Lake Huron and an extensive agricultural area. Fortunately, however, we are now in a better position to plan the operation as a result of experience gained at Chalk River.

The pre-start-up survey is being undertaken to assess the factors to be considered in the operation of the CANDU generating station. The first phase of this program, undertaken by the Great Lakes Institute, was begun in 1961. It consisted of meteorological, limnological, geological and biological measurements in the area. Fish and animal populations were assessed; wind speeds and water currents were measured. This survey showed very little bottom sediment and very few fish in the Douglas Point area - a somewhat unexpected observation. In the second phase, beginning this year, background levels of radioactivity will be assessed in order to obtain adequate data before startup in 1964.

In conclusion, I would like to draw attention to the need for adequate pre-start-up environmental surveys such as that undertaken at NPD. Such a program allows the detection of minute amounts of radioactivity at levels far below the maximum permissible set by the International Commission for Radiological Protection, and it gives the best assurance that the neighbouring population is being protected from excessive exposure to radiation:

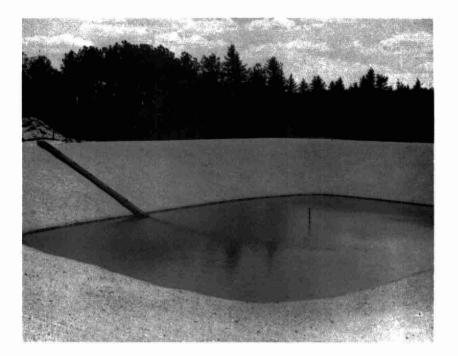
Table	1		

, .

. .

× •

	Distance from	Bone		Flesh	
Location	Chalk River Establishment Miles	Sr-90 pC/g (Wet Wgt)	Cs-137 pC/g (Wet Wgt)	Sr-90 pC/kg (Wet Wgt)	Cs-137 pC/kg (Wet Wgt)
FISH	and the second				
Perch - Rresqu'Ile	12 upstream	0.7	0.49	15	1040
Perch - Toussant Lake	2	2.7	0.29	20	1390
Perch - Holden Lake	20 upstream	2.2	0.24	40	1010
Pike - Sandspit	l downstream	4.1	0.30		
Diologia Contractions					





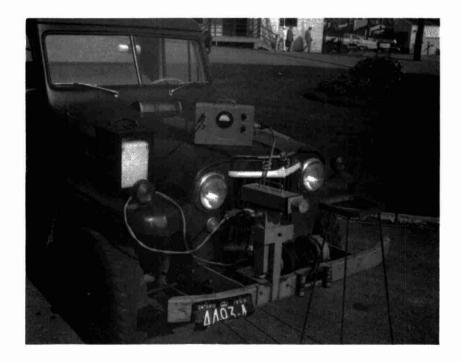


Fig. 2: Portable survey instrument.

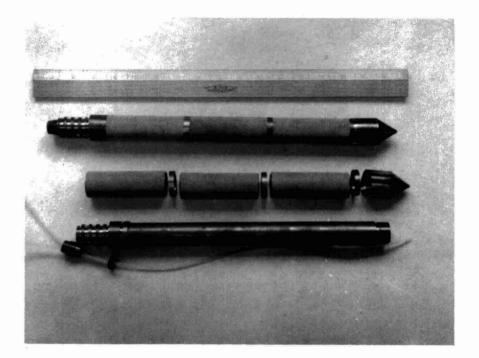


Fig. 3: Ground-water sampler.

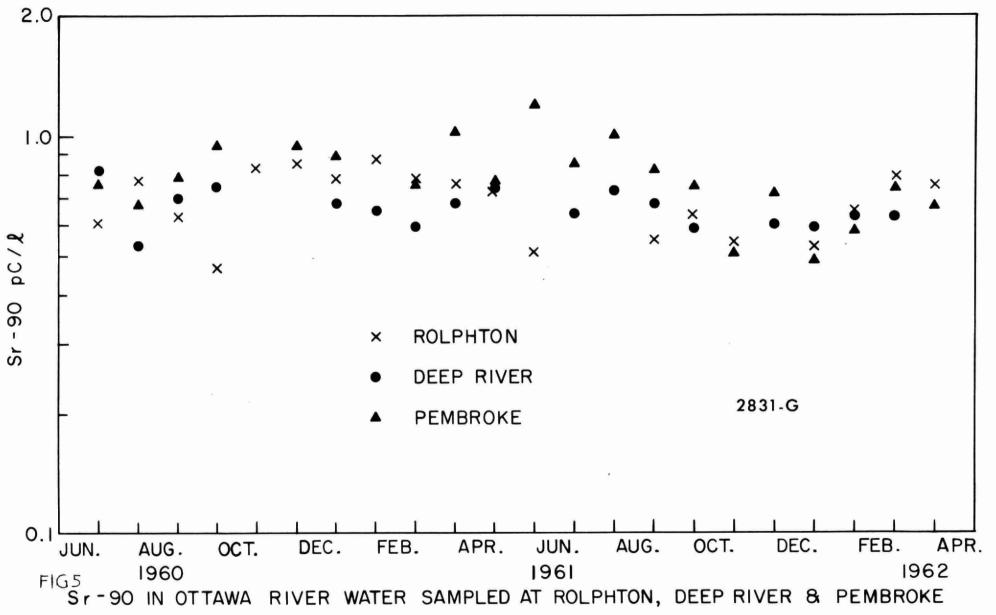


Ł

51

.

Fig. 4: Fallout collector and Yradiation monitor.



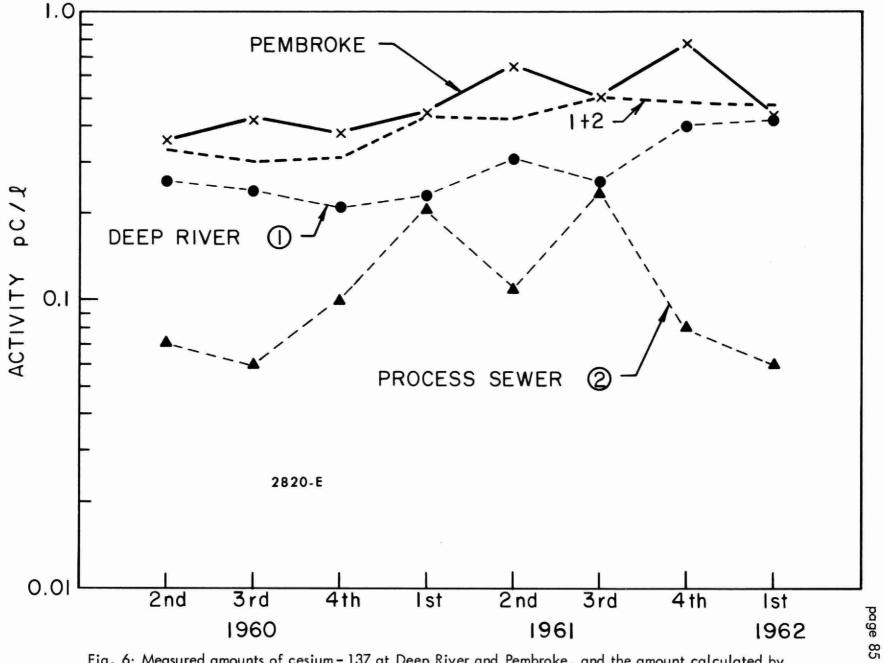


Fig. 6: Measured amounts of cesium – 137 at Deep River and Pembroke, and the amount calculated by adding the process sewer contribution to the Deep River values (curve 1+2).



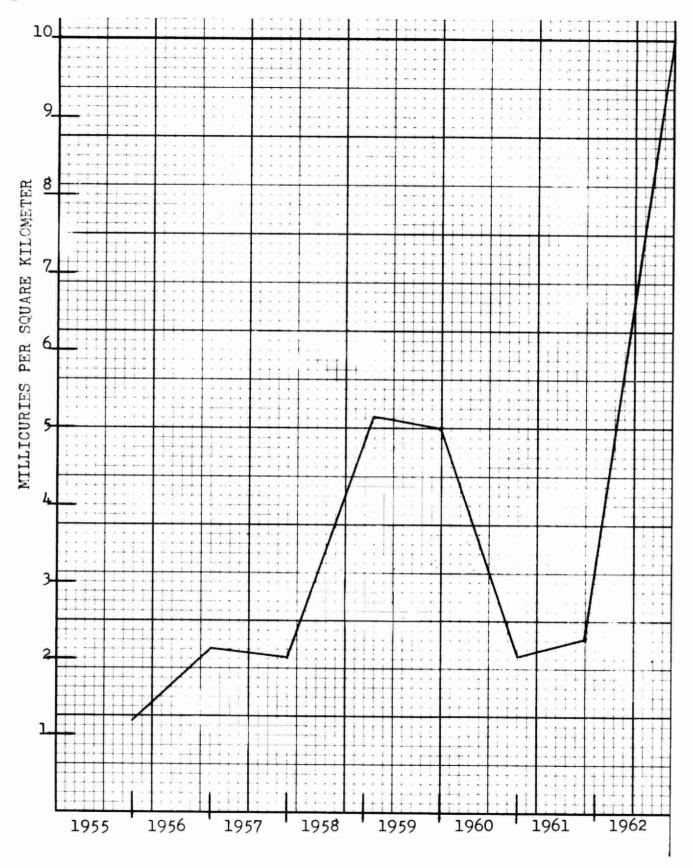


Fig. 7: Strontium-90 from "weapons fallout". Precipitation collected at Deep River, Ont.

PLATING WASTE TREATMENT

.

.

2

.

by

E. W. Hettwer



PLATING WASTE TREATMENT

by

E. W. HETTWER

Northern Electric Company London, Ontario.

### INTRODUCTION

This paper is a description of the facilities and methods used for treating plating wastes at Northern Electric Company, Limited, London works in London, Ontario. In the London plant different types of telephone sets are manufactured, from the well known princess set to the complete telephone booth.

For the treatment of waste, no new or unique methods are used, but approved, efficient procedures are applied in a way which corresponds most to the company's requirements.

Therefore, this paper will bring no new revolutionary ideas on plating waste treatment, but some of the items discussed might be of interest to those thinking of installing similar equipment in the near future.

Introduction (Slide 1) Photo of Northern Electric Plant

The London plant of Northern Electric Company, was built in the years 1958 and 1959. Production started in February 1960. It is located south of London, fronting highway 401. The size of the plant is 380,000 square feet (9-1/2 acres). The staff comprises 1,600 employees.

Manufacturing processes in the plant include plating of gold, silver, chrome, nickel, copper, zinc, tin and anodizing of aluminium. Waste waters from these processes are highly toxic and are treated before they are discharged into the sewer. While the plant was still in its planning stage, it was fully realized that means had to be provided for the treatment of these toxic wastes in a way that today's and perhaps tomorrows requirements for effluents could be met without difficulty.

Directed by these viewpoints, a waste treatment plant was planned and installed below ground level outside the main building.

(Slide 2) Plating and Plating Wastes

Plating in out plating department is done by:

Manual operation (Plating on Racks)	Slide 3
Barrell Plating	Slide 4
Automatic Plating Machines	Slide 5
Anodizing by Manual Operation	Slide 6

These different plating processes yield the following main wastes:

#### Alkali

## Acid

### Cyanide

### Chromate Wastes

Each tank line in the plating department has been provided with three trenches under the tanks for collecting the different rinses:

- (a) The combined acid and alkali rinses.
- (b) The cyanide.

(c) The chromate rinses (Slide 7)

These rinse trenches are connected to a piping system which brings the rinses by gravity flow into the different treatment tanks in the waste treatment plant.

' Tanks containing strong acid or alkali solutions, which are dumped at regular intervals are connected to holding tanks in the treatment plant by special dump lines. In the original installation the rinse trenches and the floor in the plating area were made from trowelled epoxy. However, a survey showed, that this kind of floor protection, either by faulty installation or due to extreme stresses caused by spilled strong acids or other chemicals, showed places of a severe attack. After giving this problem careful consideration, the rinse as well as the exhaust trenches **and** the floor in the plating area were covered with hypalon lined steel sheets. To protect the hypalon lining, the aisles between the tank lines were covered with acid-proof brick.

Control of Plating Wastes

Before thinking of treating plating wastes, careful consideration must be given to the elimination or reduction and control of wastes in the different plating processes.

Besides occasional dumping of spent alkalis or acids used for cleaning, etching or pickling, the main volume of waste comes from rinsing for the removal of the dragged-out cleaning and plating solutions. To minimize the amount of plating solution lost by this process, the plating tank is followed in some cases by a drag-out tank. The plated parts are allowed to drip off over the plating tank, followed by a rinse in the drag-out tank. This is a still tank, made up with de-ionized water. The solution is used to make up losses due to evaporation, spillage or drag-out in the plating tank, or in cases of plating noble metals, the metal is recovered by electrolysis.

For further rinsing the parts are moved into cascade rinse tanks and a final rinse in de-ionized water. Cascade rinse tanks are series of tanks, with fresh water entering the final tank and overflowing from tank to tank, till it leaves, highly contaminated, the first rinse tank and flows in the rinse trench to the piping system, which delivers it to the treatment plant.

The amount of water used for rinsing purposes is automatically controlled by a solu-bridge system. Conductivity cells (Slide 8) in the last rinse tank of the cascade tanks and in each de-ionized water tank, measure the conductance of the rinse water and report it to a control panel. The conductance of rinse water, with a reasonable concentration of contaminants, has been estimated and this value is set on the control panel (Slide 9).

An increase in the contamination of the tank will actuate the control panel to operate a solenoid valve, thus feeding fresh water into the tank. Although this device eliminates operator control of the amount of water used for rinsing, it still pays if the supervisor checks the settings on the control panel from time to time, as some operators have their own ideas on this subject.

By these means the volume of waste and the volume of water to be treated is considerably reduced, thus cutting the costs of plating and waste treatment<sub>e</sub>.

(Slide 10) Treatment of Plating Wastes

In the waste treatment plant, plating shop wastes are treated in a continuous, automatically controlled operation.

The plant treats at present 50 G.P.M. on the average, but is well equipped for handling sudden surges or a future expansion in the plating department and still maintain the proper retention time for the different processes.

The 50 G.P.M. flow of wastes consists on the average of -

2 G.P.M. Cyanide

2 G.P.M. Chromate

46 G.P.M. Combined Acid and Alkali Wastes.

J-0. 15

Each rinse comes separately to the plant and is separately treated. The following will explain each individual process in more detail.

(Slide 11) Cyanide Treatment

Due to the toxicity of cyanide wastes, this particular process always receives a great deal of attention and a fair number of methods have been proposed.

In our case the method of oxidizing cyanides to cyanates, carbon dioxide and nitrogen by chlorine, in an alkaline medium, is employed. The agents used for this process are a 25% caustic soda solution and liquid chlorine. Treatment is carried out at a pH of 10.5. The cyanide destruction tank consists of three compartments in the first two compartments agitators are installed to give a thorough and uniform distribution of the added chlorine and caustic soda. PH and O.R.P. probes (oxidation reduction potential) are installed in the first compartment.

The cyanide rinse enters the first compartment through a baffle with an average pH of 9. The pH probe actuates the caustic feed pump which feeds 25% caustic soda solution from an outside storage tank till a pH of 10.5 is reached and maintained. A pump draws solution from the second compartment, pumps it to the injector of the chlorinator and back into the first compartment. The chlorinator, controlled by the O.R.P. probe, injects chlorine into the line. The injection of chlorine into this sideline only ceases, when the O.R.P. probe in the tank senses the complete conversion of cyanide to cyanate. The second compartment is equipped for the further oxidation of cyanates into carbon dioxide and nitrogen, but as the requirements at present only call for a destruction into cyanates, the second and third compartments are only used to provide sufficient retention time for the conversion.

The location of the probes in the compartment is an important factor. To avoid major deviations from the proper pH or O.R.P. level, probes have to be installed in the place with the most uniform conditions. It was found advantageous to place these probes near the outlet of the compartment.

The effluent of the tank is tested in regular intervals for free cyanide by the benzidine-pyridine method. The tests show that a proper treatment yields an effluent with less than 0.1 PPM free cyanide.

In the literature it is sometimes suggested to treat cyanides at a pH of 9 or even 8.5 with a large excess of sodium hypochlorite. In our case, however, we found that a lowering of the pH under 10 will produce in a side reaction cyanogenchloride, a dangerous, toxic gas. The formation can be explained by the following equation:

> CN - + HOCL \_\_\_\_\_CNCL + OH (1) CNCL + 2OH \_\_\_\_\_CNO- +  $H_2O$  (2) (Slide 12)

In a pH range below 9.5, reaction (1) is very quick, while (2) is slow, therefore the tendency to form cyanogenchloride gas is evident.

To prevent any toxic gases, cyanogenchloride, chlorine or hydrocyanic acid from accumulating in the treatment plant, the cyanide destruction tank is covered and vented by a special exhaust system.

The effluent from the cyanide destruction tank is piped into the final pH tank. Cleaning solutions containing strong cyanides are first dumped by a special dump line into a cyanide holding tank and then bled slowly into the cyanide destruction tank.

(Slide 13) Treatment of Chromates

Chromate wastes are toxic; their treatment consists of a reduction of hexavalent chromium into its trivalent state in an acid medium followed by a precipitation with caustic soda.

Agents used are dump acids, hydrochloric acid, sulphur dioxide and 25% caustic soda solution. The reduction is carried out at a pH of 1.5-3, the precipitation at a pH of 8.5.

Similar to the cyanide treatment tank, the chrome destruction tank consists of three compartments, with agitators in the first and second.

For lowering the pH to a level of 1.5, either dump acid from an acid holding tank, or hydrochloric acid from an outside storage tank is fed to the chrome tank by a feed pump, controlled by a pH probe in the first compartment. Similar to the chlorine treatment in the cyanide tank, a small part of the tank content is pumped to the injector of the sulphinator, where SO2 is injected, and then back into the tank. The sulphinator is controlled by an O.R.P. probe in the second compartment. The amount of SO<sub>2</sub> thus introduced is sufficient to reduce all chromate ion from the hexavalent to the trivalent state.

In the original design, the trivalent chrome was precipitated by introducing caustic soda solution to the third compartment of the chrome destruction tank, followed by a long settling period in a special chrome settling tank.

This was changed however. The effluent leaves the chrome destruction tank with all the chrome reduced to the trivalent state, but not precipitated. It is piped into the final pH tank. The pH in the final pH tank on the average is 10 or higher, due to the effluent from the cyanide destruction tank. Thus the precipitation of the chrome takes place in the final pH tank.

Acid and Alkali Waste Treatment

The combined acid and alkali rinses are piped into the final pH tank. They enter the tank with an average pH of 6-8. In the final pH tank an agitator and pH probe are installed. Means are provided to feed either hydrochloric acid or caustic soda solution. The pH probe will maintain a pH of 8.5 in the tank by feeding either acid or alkali.

Alkali dumps are bled into the final pH tank while acid dumps are held in acid holding tanks for the chrome treatment. We also investigated the use of alkali dumps for the cyanide treatment, but have not so far found it feasible, as the amount of alkali dumped is rather small and its concentration low. Besides some of the alkali cleaners contain wetting agents which would build up excessive foam in the well agitated cyanide tank.

In an extended test run, we investigated the possibility of running the alkali with the cyanide rinse and the acid with the chrome rinse. The result, however, was negative. The acid rinse has an average pH of 4 which is higher than the pH of 1.5-3 needed for the chrome treatment. On the other hand the alkali rinse has an average pH of 9 which is too low for the cyanide treatment. This resulted in an excessive consumption of hydrochloric acid and caustic soda respectively, as we now had to bring a greatly increased amount of water to the proper pH level needed for these two treatment processes.

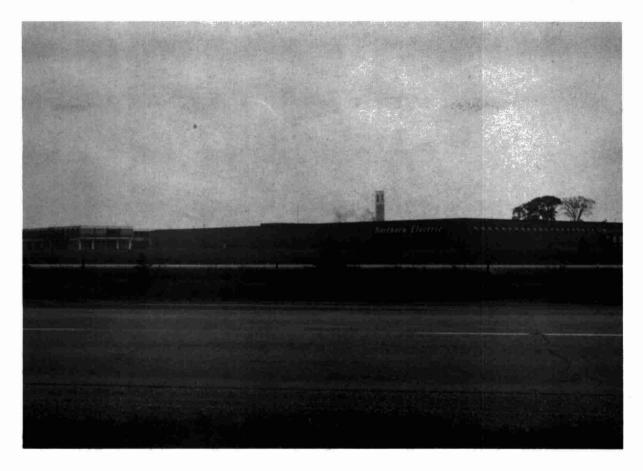
The effluent from the final pH tank is pumped into the storm sewer. It is considered, however, to run the effluent into the sanitary sewer which would bring it into the OWRC sewage plant located in Westminster Township.

. All automatic controls of the plant are combined in a control panel located in the power house. The treatment plant is run by the power house personnel who also do the regular testing of effluents. Only in cases of trouble or special test runs is the laboratory employed in the testing.

The analysis of the final effluent shows on the average:

Hexavalent Chrome:	Less	than	0.5	P.P.M.
Free Cyanide:	Less	than	0.1	P.P.M.
pH:			8	
Solids:			200	P.P.M.

To reduce the amount of solids, a pressure filter has been purchased and will be installed next month. This filter has a filter area of 360 sq. feet, using diatomaceous earth as filter aid. By this installation we hope that our effluent will not only be well treated, but also precipitate free and clear, a joy for every trout to live in.





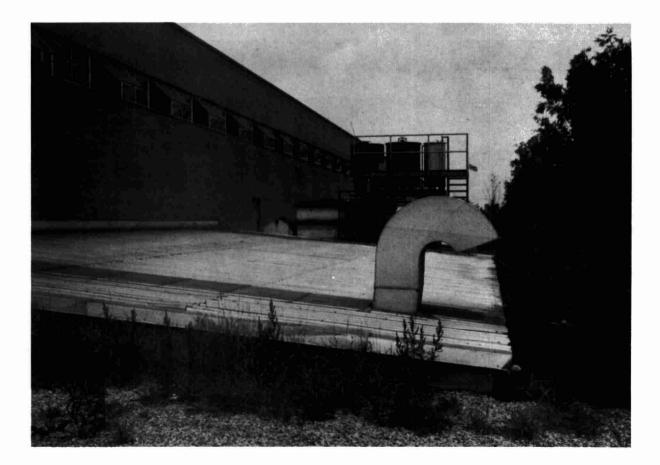




Fig. 3



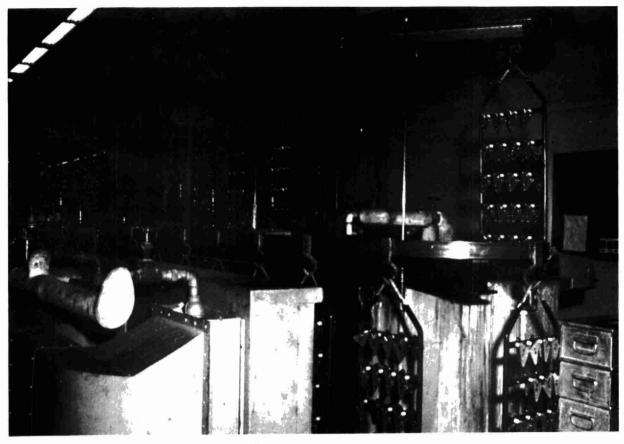


Fig. 5

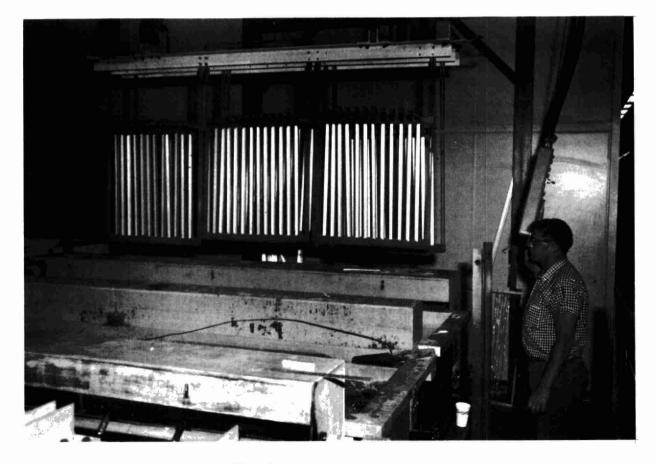


Fig. 6

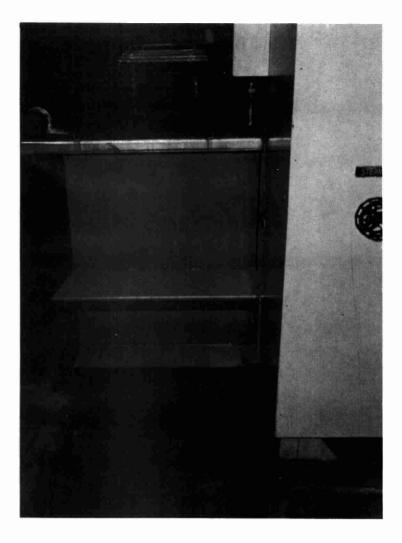


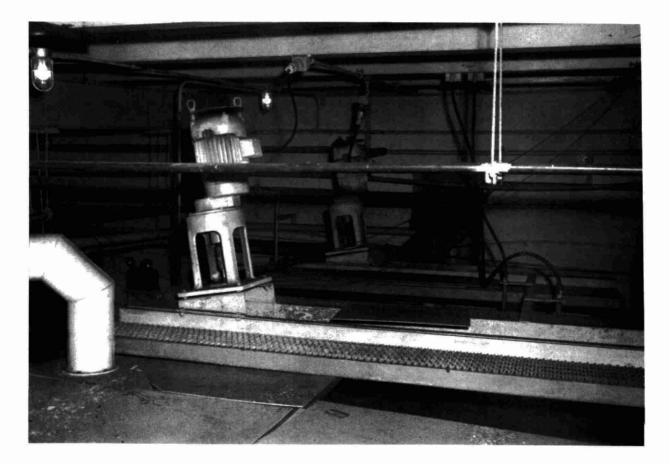






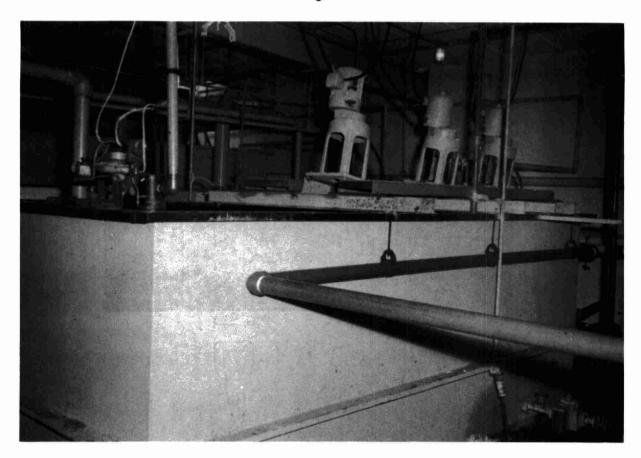


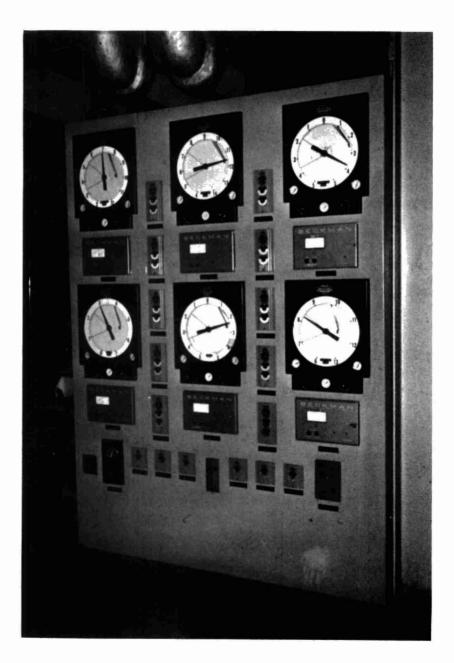
Fig. 10



# $CN^{-} + HOCL \rightarrow CNCL + OH^{-} (1)$ $CNCL + 2OH^{-} \rightarrow CNO^{-} + H_{2}O (2)$

Fig. 12







## IN DUSTRIAL WASTE CONTROL IN METROPOLITAN WINNIPEG

.

by

N. S. Bubbis

### SESSION NUMBER THREE



W. R. Edmonds, Assist. Chief Public Health, Engineering Division, Department of National Health and Welfare. Session Chairman.



INDUSTRIAL WASTE CONTROL IN

METROPOLITAN WINNIPEG

by

N. S. BUBBIS, P. ENG.

Metropolitan Corporation of Greater Winnipeg Winnipeg, Manitoba

The reduction of Pollution of our streams and lakes is an ever-increasing problem of our expanding urban communities and the control of industrial wastes is one of the most important factors in this problem, The Greater Winnipeg Ssanitary District was organized in 1935 to provide treatment for the sewage in the Metropolitan Winnipeg Area. As a result of the establishment of Metropolitan Government on January 1st, 1961, the Sanitary District became the Waste Disposal Branch of the Metropolitan Corporation. The former Sanitary District Act was incorporated and became aucillary to Part VIII of the Metro Winnipeg Act. In this paper I propose to delineate the problem, to review briefly the history of industrial waste control in Metropolitan Winnipeg, outline the manner in which the program was established and the results which have been achieved to date.

Man has always needed air, water and food to survive. He has also had to dispose of his wastes and this was one of the reasons why he established his domicile near bodies of water. As long as society was relatively primitive and communities small, pollution of these bodies of water was not too great a problem. In the last century, with the increasing acceleration, two factors have steadily tended to complicate the pollution problem so that it is now one of the most critical facing urban society. The first of these two factors is the continuing expansion of our industries, using more and more water on the one hand and discharging increasing quantities of waste on the other. The second factor has been that modern society continues to demand a better standard of living with a resultant increase in water use, together with the demand for a reduction of the pollution.

As mentioned, these trends have been accelerating since the last war, and every day brings new processes and new problems. Thirty years ago, detergents, insecticides, plastics, petrochemicals, antibiotics and various synthetic products were either unknown or of little importance. Today these materials are produced by the millions of pounds. Recently, even in the traditionally agricultural west, we have witnessed the growth of the petrochemical industry with its associated difficult waste problems. On the horizon, we see the industrial development of atomic energy and the promise of new and more complex problems.

Now it should be clearly understood that industry is not something separate and apart from the community in which it finds itself. We are all familiar with the jockeying and lobbying that is done in many cases by a municipality and by its Chamber of Commerce or Industrial Development Board to attract an industry to a given area. Tax concessions and other inducements are sometimes made and in most cases the matter of the pollution problem which may result from that particular industry, if given any consideration at all, may be ignored for fear of losing the industry. Needless to say, this is very poor business. On the other hand, it is certainly a very short slighted policy to penalize one industry or discriminate between one industry and another by imposing unreasonable and unrealistic regulations and sewer rental charges.

One method of abating the pollution of streams by industrial wastes is to combine and treat them with the municipal sanitary wastes. This solution, of course, raises several fundamental considerations:

- (1) Are there any objections to permitting industrial wastes to be discharged into the municipal sewer system, and if so, why are they objectionable and can these objections be overcome by proper regulations governing the quantity and strength of these wastes.
- (2) Will industry bear its proper share of the treatment costs and how can this be arranged.

While these questions can be answered in the affirmative, the solutions are not simple, but can be embodied in carefully drawn ordinances.

It will be appreciated that there can be no hard and fast rules which will cover all conditions which may arise. For example, a particular industry of a given size might create no problem in terms of quantity or quality of sewage in a large city. On the other hand, if it were to be located in a town of several thousand people, it might produce wastes equivalent to a population of many times that of the municipality itself and produce shock loads of a very severe nature. Again we have instances where two plants are located adjacent to one another, each producing a waste which, in itself, does not create any problem, but the combination of the two wastes immediately sets up a reaction, giving off odors and gases of an extremely corrosive and offensive nature. From this, it can be seen that a proper sewer ordinance must be designed with particular attention to local conditions. Nevertheless there are a number of provisions which all such ordinances should contain, as follows:

- (1) There is the matter of ensuring that all sewers and other structures are properly constructed.
- (2) They should protect the sewerage system itself and the personnel who are engaged in servicing.
- (3) They should protect the sewage treatment plant and the processes which are used in treating the sewage.
- (4) They should contain a means of charging industry for the additional treatment costs involved in treating the stronger industrial wastes.
- (5) They should outline the method of enforcing the ordinance, that is, by taking out permits, inspections, penalties, etc.

The Metropolitan Corporation's By-Law No. 12 which, while by no means perfect, will illustrate how these provisions can be incorporated into an ordinance, and this is attached hereto as Appendix I. This By-Law was evolved after twenty years of struggling with the industrial waste problem.

Industry uses very large quantities of water and almost all of this becomes highly polluted in processing and then has to be disposed of, a none too easy task, and the simplest solution is to discharge it to the sewers and local water courses. Winnipeg was no exception, and being the centre of an agricultrual area, food processing is one of the major industries and this type of industry produces some very strong wastes. The following examples will give some indication of the magnitude of the wastes contributed by industry. Waste from a slaughterhouse-meat packing plant, of which Winnipeg has 6, will range from a population equivalent of 20,000 to 90,000. The waste produced by a beet sugar refinery with a rated capacity of 2,200 tons of beets sliced per day, results in wastes approximately equivalent to that from 125,000 to 130,000 people.

Prior to the construction of the Treatment Plant, all industrial wastes which could physically be discharged to the sewers were disposed of in this fashion and then into the rivers. As a matter of fact, it was this condition that turned the rivers into virtual septic sewers during the low water years in the 1930's and resulted in the serious nuisance which then prevailed.

It is therefore quite understandable that the practices which had grown up over the years were difficult to break, especially when the only alternative meant the installation of costly equipment to separate the objectionable wastes and further costs in disposing of it by other means. Consequently the District, right from the start of its operations in 1937, was faced with a real problem in dealing with the wastes discharged to the sewers from various industries. In the original act, Section 19, the District was given powers to regulate, control and prohibit the discharge of various materials to the sewers, to impose surcharges on strong sewage and over the years it has gradually evolved a philosophy on the control of industrial wastes which finally culminated in the passing of By-Law No. 80 \* in August 1957.

 \* Sanitary District By-Laws Nos. 38, 65 and 80 became Metro By-Law No. 12.
 Sanitary District By-Law No. 64 became Metro By-Law No. 20.

Initially, the abattoirs and meat packing plants constituted the greatest problem. The fable of their efficiency to the effect that "they use every thing in the pig but the squeal" was unfortunately somewhat exaggerated. The discharge of large quantities of paunch manure, grease, pigs' toe nails, etc. resulted in clogging the sewers and plugging the comminutors and pumps. On reaching the Treatment Plant, the wastes caused further trouble. Frequently, a blanket formed on the top of the claifiers which, in cold weather, would freeze. In the digesters, a scum blanket in excess of 8 ft. in depth formed, which was most difficult to break up. This required the emptying of the digesters, which is quite a dangerous and unsatisfactory procedure.

An educational program was first tried in order to persuade the various industries to co-operate. However, with the outbreak of war in 1939, not very much could be accomplished. Following the war, further steps were taken to try and obtain voluntary co-operation and in addition. By-law No. 38 - A by-law to prohibit the discharge into the sewers within or entering the Greater Winnipeg Sanitary District of certain detrimental materials and slaughterhouse and packing house wastes

was passed in July of 1945. The results were not very good.

By 1950, it was apparent that the District's facilities required enlarging and that a more aggressive control program would have to be instituted if the treatment facilities were to be capable of proper operation and the additional costs were to be paid for on a more equitable basis. While Section 19 of the District's Act provided for the imposition of surcharges for extra strong sewage, these had never been applied. These were considered but the District's Consultants recommended against the implementation of such charges, feeling that they would discourage the various industries from construction pre-treatment facilities, but did recommend that screen chambers at the outlets from each of the packing plants be constructed at the District's expense. The screen chambers were constructed later and in addition, the following two by-laws were enacted in 1954:

- By-law No. 64 A by-law to prohibit the discharge or drainage of sewage within the District into any river flowing through or adjacent to the District.
- By-law Nc. 65 A by-law to prohibit, regulate and control the discharge of industrial and factory waste or excessive amounts of any type of sewage or waste water.

Both of these by-laws made provision for licensing. In the case of By-law No. 64, every person, that is, industry or municipality must obtain a license for any sewer outlet, including storm sewers, into a river. In the case of By-law No. 65, it was mandatory for every industry to obtain a license from the District before discharging any industrial waste or large quantity of sewage or waste water into the sewers. It follows the model by-law developed by the Water Pillution Control Federation and sets out the various types of material prohibited and the standards and normal limits of permitted materials B,O,D, 300 p.p.m. and suspended solids 350 p.p.m. In the case of grease, for industrial waste purposes we have allowed 100 p.p.m. It also gave the General Manager of the District discretion to permit the discharge or sewage of a greater strength under certain specific conditions. This by-law also permits the installation of domestic garbage grinding units in residences but requires that all larger industrial or commercial units be licensed.

While the screen chambers worked reasonably well in preventing large particles such as pigs' toe nails and a certain amount of paunch manure from being discharged into the sewers, it was still found that the effluent from packing plants was of a very high strength, particularly in B.O.D. and grease. It was then decided to review the matter of surcharges and a study of the various methods, regulations and formulae used by similar authorities was undertaken.

The development of equitable rate structures for any utility service is always an extremely complicated matter, and charges for extra strong industrial wastes are certainly no exception. Not only will the charges depend on the quantity and characteristics of the wastes being discharged, on the methods of financing of the sewerage system and sewage treatment works, but will also vary with the type and degree of treatment that has to be given. There will also be the matter of sampling measuring, billing and enforcing the regulations. It will not be possible for me in the time at my disposal to go into this matter in detail, but I would like to indicate certain types of rate structures which have been used.

Generally speaking, there are four types of formulae used in establishing such rates. First we have the one most commonly used, the <u>Flat Rate</u> Formula. This provides that a charge will be levied on a given number of units of sewage discharged to the sewer. As a rule, there is a quantity discount permitted although personally I am not sure that the premise on which this is founded, namely, that it is cheaper to handle large quantities of material, as always correct. It follows, naturally, that the only case where this rate would be equitable to all concerned would be where all of the industrial wastes had the same characteristics as normal sanitary sewage and this, of course, is far from the actual case. The only argument in its favour is that administratively it is very simple.

The second formula is known as the <u>Quality-Quantity</u> or QQ Formula. This formula was developed by a number of the larger cities in an attempt to get away from the basic disadvantages of the Flat Rate Formula, namely, that no consideration was fiven to the characteristics of the sewage. This formula may provide an incentive for industry to reduce the strength of its effluent to reasonable limits. However, it has the disadvantage of applying only to the particular area for which it is developed and as such, cannot be considered as a general formula applicable in all cases.

The third formula is known as the <u>California</u> Formula developed by the California Sewage Works Association. They recommended that each municipality attempt to apply Flat Rate or QQ formula to industry. If this cannot be done, then charges for the additional cost of treatment should be made while taking due cognizance of the other taxes already being paid by the industry. The fourth formula is known as the <u>Joint Committee</u> formula. This was developed by a joint committee of eight organizations, including the Water Pollution Control Federation and the American Society of Civil Engineers. This rejects the tenet of the first three that the entire cost should be borne by the useres and assesses some of the cost to property in general.

A paper titles "Rate Formulae for Industrial Wastes" by Janes M. Symons in the June 1955 issue of WATER & SEWAGE WORKS, **deals** comprehensively with this subject.

The District developed a formula of its own for imposing such surcharges. This was incorporated in By-law No. 80:

"A By-law to provide for surcharges for the discharge of factory and industrial wastes into sewers or rivers within or entering the District."

It was passed in August 1957 and became effective on January lst, 1958. This by-law was a counterpart of By-law No. 65 and was applied in conjunction with it. Both by-laws were subsequently combined in Metro By-law No. 12. Where the District can accept wastes stronger than the set limits and agrees to do so, surcharges are applied in accordance with the Formula.

The District's philosophy in making these surcharges was based on the fact that while industry and the community for a natural partnership, this partnership should be an equitable one. The community naturally wanted to see the of industry since this provided employment for the population and gave an excellent source of tax revenue. Industry on its part naturally wanted to co-operate with the community in order to obtain a market for its products to have available a labour force. But it should not be subsidized or expect to be subsidized by the community in having its stronger wastes treated on the same basis as that of normal domestic sewage. As long as the District could, it was prepared to permit the discharge into the sewerage system of acceptable industrial wastes of higher than normal strength and to impose surcharges for the additional strength. Knowing the basis of the surcharges, industry could then decide for itself whether it was more economical to provide the necessary for itself whether it was more economical to provide the necessary pre-treatment to meet the District's standards or only provide minimum pre-treatment and pay the surcharges.

It might be useful to mention some of the difficulties encountered by the District in applying this by-law and the method of operation. When we were making enquiries originally from other sewage treatment authorities concerning their practices before establishing our by-law, we were rather

interested to learn that in spite of a considerable number of ordinances having been drafted, a great number of these had not been implemented, particularly in the older and larger cities. The main reason for this was apparently due to the concern about the amount of administrative and technical work required to impose these additional charges and also a natural reluctance to tackle this thorny problem with industry.

In regard to the first aspect, we found that all that was required in our case was to set up a small section headed up by professional engineer or chemist, with the only additional help being provided by four or five samplers and the plant laboratory for the analysis of the samples, \$17,000.00 was expended in this program in 1961.

In regard to the second aspect, we found that where an educational program dealing with individual industries had failed, we were able to succeed following the enactment of this by-law and by dealing with all industries in any particular classification at one time.

The regular practice was to call representatives from all industries in a particular category to a meeting and there explain the problems to them, outline the need for this program and the fact that all of them were to be dealt with on the same basis. They were then given a period of time which to install any required or desire pre-treatment facilities, following which surcharges were applied. The construction of a sampling manhole on the sewer outlet from each industry was one of the important requirements. In order not to build up a very large staff, the program was instituted gradually, dealing with those industries which were responsible for the strongest and largert quantities of sewage.

One problem to which we have not been able to obtain a satisfactory solution is that of the actual sampling of the wastes. It will be appreciated that each of the numerous industries in a large city has to be studied separately and samples have to be taken over a period of time at appropriate points not always readily accessible. It is obvious that the strength of the industry's effluent is constantly changing as the processing varies. This is particularly true of seasonal industries who have large peak loads at certain seasons of the year. We have not been successful in devising suitable automatic sampler.

This by-law has now been in effect for just over four years, and during this period of time all the packing plants, slaughterhouses, paper mills, breweries, dairies, tanneries, poultry processing plants and miscellaneous food processing plants such as honey, potato chips, vegetable packing, etc. have been licensed. Surcharges have been imposed upon 31 of them. From our experience with this surcharge by-law, we feel that it has proves successful in controlling and reducing industrial wastes, is based on sound principles, is reasonably equitable and not too difficult to administer. We also believe that industry considers us to have been fair, and has accepted the plan reasonably well, particularly when one bears in mind the natural reluctance to have to spend money on something that was formerly done at no cost and tends to be considered a . nonproductive nuisance.

The following are the general effects of the program:

- (1) There has been a definite reduction in the strength of the sewage going to the sewers. (See Table I). Much of this has resulted from the institution of good housekeeping practices by industry itself. We feel that this has not only benefitted the Corporation, but industry as well, with a considerable quantity of material being salvaged and sold for useful purposes instead of being discharged into the sewers as formerly was the case.
- (2) It has resulted in some decrease in the quantity of sewage contributed by industry. Management watches water consumption more carefully.
- (3) The District had collected approximately \$100,000 in each of the first two years and approximately \$80,000 in 1960 and 1961 from these surcharges and thus the parties who are contributing the higher strength sewage are paying a proportionately higher cost for the required additional treatment. The reduction in the amount of the surcharges, despite an increase in the unit cost of treatment, and the doubling of the number of industries being surcharged illustrates the reduction in the strength of the industrial wastes which is taking place as a result of our program.
- (4) While most of the larger industries with strong wastes have spent a considerable amount of money on the installation of pre-treatment facilities, we have found that most of the smaller industries prefer to pay the surcharges, presumably because they find this more economical.

The Sewage Disposal Branch intends to continue this program until all industries have been completely investigated. In addition, it will be necessary to continue both the regular and spot sampling of the effluent from the various industries in order to make sure that the best possible job is done with the pre-treatment facilities installed, since it has been observed that only by continual vigilance on the part of both the Corporation and top management of industry can the best results be achieved.

In conclusion I can do no better than perhaps to paraphrase the general recommendations which appear in the Practice Manual No. 3, Municipal Sewer Ordinances, put out by the Water Pollution Control Gerderation, as follows:

- Every Municipality should adopt a suitable and complete sewer ordinance, fitted to local conditions, for the control and regulation of the use of the public sewage works.
- (2) Enactment of an ordinance is in itself insufficient to accomplish the desired result. No ordinance can be effective unless it is conscientiously and fairly administered. A cooperative approach by administrative officials will almost always result in friendly compliance with the provisions of the ordinance, but the enforcement procedures and penalties should be employed without hesitancy when necessary.
- (3) The sewer ordinance should be amended as necessary in accord with changing local conditions and technical progress. It should be reviewed periodically, say every five years, and strengthened in such ways as are dictated by administrative experience.
- (4) The ordinance should be supplemented by a thorough sampling program and a permanent and efficient record system.

Finally, despite the additional work involved, the difficulties in sampling and the somewhat empirical nature of the formulae used to base charges, I would venture a prophcy that since the imposition of surcharges for abnormally strong industrial wastes is both equitable in principle and practical in achieving control, more and more sewage treatment authorities will be imposing such charges in the future.

### TABLE I

### COMPARISON THREE LARGE PACKING PLANTS

Packing	Year	No. of Days	Suspended Solids ppm.	5-day B.O.D. ppm.	Grease - ppm.
Plant	<u>Year</u>	Sampled	(Average per year)	(Average per year)	(Average per year)
Α.	1957	3	420	471	152
	1958	6	371	467	130
	1959	3	373	406	194
	1960	11	261	541	117
	1961	12	162	358	109
В.	1957	3	1324	920	335
	1958	3	867	1512	380
	1959	9	325	733	151
	1960	14	245	466	80
	1961	12	312	528	115
С.	1957	3	843	1267	577
	1958	5	453	931	245
	1959	3	356	613	163
	1960	11	324	655	257
	1961	12	405	681	300

Types of Treatment Provided:

1. (a) Manure - Vibrating Screens, Sedimentation tank. Fat - Fat catch basin, Josam interceptor.

(b) Sedimentation tanks, 2 flotation units (Pacific Separators) Vibrating Screens, Rotating drums.

.

(c) 7 Sedimentation tanks, 2 super decanters, 5 Sweco Screens, Rotating drums, Vibrating Screens, Parshall Flume, Automatic Sampler.

.

2. Samples are composites over 24 hours taken every 15 minutes.

June 14th, 1962.

### THE METROPOLITAN CORPORATION OF GREATER WINNIPEG

### BY-LAW NO. 12

A By-law to prohibit, regulate, and control the discharge of industrial and factory wastes or excessive amounts of any type of sewage into bodies of water within or entering the Metropolitan Area or Additional Zone, and to provide for imposing surcharges.

The Council of The Metropolitan Corporation of Greater Winnipeg in meeting assembled enacts as follows:

- 1. In this By-law unless the context otherwise requires, the expression:
  - (a) "Corporation" means the Metropolitan Corporation of Greater Winnipeg.
  - (b) "Director" means the Director of Water and Waste designated by the Metropolitan Council or the person from time to time duly authorized to act in his stead.
  - (c) "Metropolitan Area" means the area described in subsection (3) of Section 3 of The Metropolitan Winnipeg Act being Chapter 40 in the Statutes of Manitoba, 1960.
  - (d) "Additional Zone" means the zone established under subsection (4) of Section 3 of The Metropolitan Winnipeg Act being Chapter 40 in the Statutes of Manitoba 1960.
  - (e) "Person" includes a Corporation aggregate or sole.
  - (f) "The Metropolitan System" means the Metropolitan Sewage Disposal System.
  - (g) "Industrial Waste" shall mean any solid, liquid or gaseous substance discharged, permitted to flow or escaping from any industrial, manufacturing, commercial or business establishment or process or from the development recovery or processing of any natural resource.
  - (h) "Sewage" means domestic sewage or industrial waste or both.
  - "Body of Water" includes any brook, creek, stream, river, lake, pond, waterway, watercourse, canal or other flowing or standing water.

- (j) "Properly Shredded Garbage" means the wastes from the preparation, cooking, and dispensing of food or other manufacturing process that has been shredded to such degree that all particles will be carried freely under the flow conditions normally prevailing in common sewers, with no particle greater than one-half inch in any dimension.
- (k) "Biochemical Oxygen Demand" (abbreviated as B.O.D.) means the quantity of oxygen expressed in parts per million by weight, utilized in the biochemical oxidation of organic matter under standard laboratory conditions for five days at a temperature of 20 degrees Centigrade. The laboratory determinations shall be made in accordance with procedures set forth in "Standard Methods".
- (1) "Standard Methods" shall mean the examination and analytical procedures set forth in the most recent edition of "Standard Methods for the Examination of Water, Sewage and Industrial Wastes", published jointly by the American Public Health Association, the American Water Works Association and the Water Pollutional Control Federation.
- (m) "pH" shall mean the logarithm (base 10) of the reciprocal of the hydrogen ion concentration expressed in inches per liter. It shall be determined by one of the procedures outlined in "Standard Methods."
- (n) "Suspended Solids" means solids that either float on the surface of, or are in suspension of water, sewage, or industrial waste and which are removable by a laboratory filtering device. Quantative determination of suspended solids shall be made in accordance with procedures set forth in "Standard Methods".
- (o) "Gallon" means Imperial Gallon.
- (p) The expression "average sewage" means sewage of the same nature, quality and degree of pollution as the officials of the Corporation shall have estimated the yearly average of the influent to the treatment plant to be after making tests of the usual and appropriate kind for such determination and which estimate has been included in the yearly allocation and precept of the Corporation for the next following calendar year.
- (q) The expression "normal sewage" means factory or industrial waste which has (1) a five day Biochemical Oxygen Demand of 300 parts per million by weight, and
  (2) which contains 350 parts per million by weight of suspended solids, but which does not contain appreciable quantities prohibited without license in Section 2.

- 2. Except as hereinafter provided by license, at an annual fee of Twenty-five (\$25.00) Dollars, no person shall discharge or cause to be discharged any of the following described kinds of sewage, industrial or factory wastes, into any sewer or body of water within or entering the Metropolitan Area or Additional Zone:
  - (a) Any liquid or vapour having a temperature higher than 150 degrees Fahrenheit;
  - (b) any water or waste containing fats, oil or grease of such character or quantity that unusual attention or expense is required to handle such materials by the Metropolitan System;
  - (c) any gasoline, benzene, naphtha, fuel, oil, or other flammable or explosive liquid, solid or gas;
  - (d) any garbage other than "properly shredded garbage" as defined in Section 1 of this By-law; but provided that no shredded garbage from a garbage disposal unit of a greater capacity than one such as may normally be operated by a 1/4 or multiple thereof, HP motor, shall be so discharged without a license under Section 4 hereof;
  - (e) any ashes, cinders, sand, stone dust, mud, straw, shavings, metal, glass, rags, feathers, tar, plastics, wood, paunch, manure, or any other solid or viscous substance which cause difficulty to the Metropolitan System;
  - (f) any paunch manure, or intestinal contents from horses, cattle, sheep or swine; any animal grease or oil; pigs hooves or toenails; any animal intestines or stomach casings, bones; hog bristles; hides or parts thereof; any animal fat or flesh in particles larger than will go through a quarter inch screen; manure; poultry entrails, heads, feet or feathers, fleshing and hair resulting from tanning operations; or any other solid or viscous substance which causes difficulty to the Metropolitan System;
  - (g) any water or waste having a pH lower than 5.5 or higher than 9.0 or having any other corrosive property capable of causing damage or hazard to structures, equipment, and personnel of the sewage works;
  - (h) any water or waste containing a toxic or poisonous substance;
  - (i) any noxious or malodorous substance capable of creating a public nuisance;

- (j) any water or waste containing a radio active substance;
- (k) any industrial wastes whatsoever.
- 3. The Corporation may give a license to any person operating an industrial or factory plant to discharge sewage or factory or industrial waste into sewers or bodies of water within or entering the Metropolitan Area or Additional Zone under specified conditions but no such license shall be given by the Corporation until
  - (a) such person shall have made application in writing for permission to discharge industrial or factory wastes, or sewage into a sewer or body of water within or entering the Metropolitan Area or Additional Zone;
  - (b) such applicant shall have given the chemical and physical analyses, quantity and rate of discharge or sewage proposed to be so discharged and any other detailed information which may be required including all pertinent information relating to any proposed pretreatment before discharge;
  - (c) the application has been approved.
- 4. No person shall discharge or cause to be discharged into any sewer in the Metropolitan Area or Additional Zone, sewage, industrial or factory waste in a greater volume than 100,000 gallons per day without obtaining a license so to do from the Corporation in the manner provided in Section 2 hereof, and having obtained such a license no person shall discharge into any sewer or body of water within or entering the Metropolitan Area or Additional Zone in any one day a greater volume than set forth in the license.
- 5. No Area Municipality shall issue a permit or allow any connection for the discharge of sewage to its sewer system before a license has been issued by the Corporation in writing for such a connection if the sewage to be discharged from such connection will contain any industrial or factory waste or if the sewage as described in Section 4, including waste water to be discharged will exceed 100,000 gallons in any one day.
- 6. As a general guide, the following are some of the characteristics and limits of industrial wastes or sewage which may be permitted to be discharged into a sewer within or entering the Metropolitan Area or Additional Zone. At such times as the Metropolitan System is not overloaded, the Director may in his discretion permit greater degrees of pollution than set out in this section but such permission may be withdrawn on thirty days notice.

- (a) A five-day Biochemical Oxygen Demand not greater than 300 parts per million by weight, or
- (b) containing not more than 350 parts per million by weight of suspended solids, or,
- (c) not containing any appreciable quantity of substances having the characteristics described in Section 2.
- 7. The Corporation further deems it just and equitable that such persons discharging factory or industrial waste into sewers or bodies of water within or entering the Metropolitan Area or Additional Zone should pay an additional quarterly charge over and above the uniform rental charges provided for in The Metropolitan Winnipeg Act to be uniformly raised, on account of the nature of the sewage or waste so discharged, where such sewage or waste has a greater Biochemical Oxygen Demand of 300 parts per million by weight or contains more than 350 parts per million by weight of suspended solids, or contains an appreciable quantity of substances described in Section 2.

Any additional sums so charged in addition to the said uniform rental charges shall be termed a "Surcharge" and shall be ascertained as hereinafter set out.

- 8. The amount of the quarterly surcharge to any sewer user shall be based upon the nature of the sewage, the degree of pollution or both and the number of gallons of sewage discharged into the sewer or body of water within or entering the Metropolitan Area or Additional Zone.
- 9. Any person desiring a license under sections 3 and 4 of this By-law, shall install a sewage meter satisfactory to the Corporation and shall discharge all such sewage through such meter and in default of the license installing and maintaining a sewage meter, the licensee shall be charged for the same number of gallons of sewage as the number of gallons of water supplied to the licensee's premises as shown by the water meter of any area municipality supplying water to the licensee's premises or as may be otherwise supplied to the premises, and if there is no meter measuring the intake of water supplied to the said premises, then the Corporation shall determine the amount of water supplied in any manner or method practicable and the quantity of water so determined shall be used in computing the amount of the surcharge.
- 10. (1) Where necessary in the opinion of the Director, the person making application for a license shall provide at his expense such preliminary treatment as may be

Maria

necessary to change the characteristics of the industrial wastes or sewage to make them acceptable to the Corporation before any license shall be granted.

- (2) Where preliminary treatment facilities are provided for any factory or industrial wastes or sewage, they shall be maintained continuously in satisfactory and effective operation by the applicant at his own expense.
- 11. (1) When required by the Director, the applicant for a license for premises served by a sewer connection carrying factory or industrial wastes shall install a suitable control manhole in the sewer connection to facilitate observation, sampling and measurement of the wastes.
  - (2) Such manhole, when required, shall be accessibly and safely located and shall be constructed in accordance with plans approved by the Director.
  - (3) The manhole shall be installed by the applicant at his own expense and shall be maintained by him so as to be safe and accessible at all times.
- 12. (1) All measurements, tests and analyses and the characteristics of factory or industrial wastes, or sewage or water to which reference is made in this By-law, shall be determined in accordance with the "Standard Methods for the Examination of Water and Sewage" and shall be determined at the control manhole provided for in Section 11 of this By-law, or upon suitable smaples taken at said manhole.
  - (2) In the event that no special manhole has been required, the control manhole shall be considered to the nearest downstream manhole in the common sewer to the point at which the sewer connection of the licensee enters.
- 13. From and after the first day of January, 1961, no person shall discharge sewage containing factory or industrial waste into any sewer or body of water in or entering the Metropolitan Area or Additional Zone where such waste
  - (a) has a five-day Biochemical Oxygen Demand greater than 300 parts per million by weight, or
  - (b) contains more than 350 parts per million by weight of suspended solids, or
  - (c) contains appreciable quantities of substances prohibited without license in Section 2,

without first having received a license from the Corporation permitting him so to do. The said license shall only be issued upon the application of the intended licensee which said application to the Corporation shall set forth such information as may be required by the Corporation. The Corporation shall within three months of the application make such tests and measurements as may be appropriate in order to ascertain the five-day Biochemical Oxygen Demand of factory or industrial waste discharged into the sewers or bodies of water within or entering the Metropolitan Area or Additional Zone by the applicant and also whether such sewage contains more than 350 parts per million by weight of suspended solids and, if so, how much, and whether such sewage contains any appreciable quantity of substances prohibited without license by Section 2, and if so, how much, and all measurements. tests and analyses of the characteristics of such sewage shall be determined in accordance with the "Standard Methods". The surcharge payable by the applicant shall commence with the first day of the next following quarter year and such surcharge shall thereafter be computed on the assumption that all of the factory and industrial waste discharged into the said sewer or body of water by the licensee are as found by such tests.

- 14. The Corporation may thereafter at any time run further tests of the sewage being so discharged by the licensee and may at any time after the filling of the application for license or after the issuance of the license, enter upon the premises of applicant or licensee and gather samples over such period as it may see fit of the factory or industrial waste or sewage being discharged by the applicant or licensee into any sewer or body of water within or entering the Metropolitan Area or Additional Zone, or may make tests upon samples submitted by the applicant or licensee.
- 15. In any billing or account for surcharge rendered to such licensee after the date of taking such further tests showing greater degrees of pollution, shall be computed on the basis that the nature of the sewage so being discharged into the sewer or body of water and the degrees of pollution thereof was as shown by such later tests and not as previously rendered. If any such testing by the Corporation shall show a reduced degree of pollution in the factory or industrial waste so discharged, such new finding shall be used in the computation of the surcharge subsequent to the billing for the current quarter but no reduction shall be made unless at least a full day's operation of the licensee's plant has undergone the test.

16. If the licensee has installed sewage treatment equipment or for any other reason is of the opinion that the nature of the

sewage presently being discharged into the sewer has a substantially lessened degree of pollution than as shown by the prior test, he may request the Corporation to make new tests, such tests to be at his expense. Such tests shall be upon a full day's operation as a minimum. If the Corporation is satisfied that such tests were made when the plant was operating under normal conditions, the result of the latest tests shall be used in computing the surcharge for sewage discharged thereafter in the manner set forth in Section 15 hereof.

- 17. In order to ascertain the surcharge in each individual case the procedure shall be as follows:
  - (a) The Corporation shall cause appropriate tests of the influent entering the sewage treatment plant to be made throughout the year and shall in its yearly allocation and precepts estimate and fix the five-day Biochemical Oxygen Demand in parts per million by weight and the parts per million by weight of suspended solids of the plant influent averaged over the year. Such estimates shall be known as average sewage and shall be used in the next calendar year in computing surcharges. The Corporation shall yearly, estimate and fix in the preparation of its allocation and precepts the costs of treating average sewage in units of 1000 gallons and shall also estimate and fix the cost of removing suspended solids from such average sewage units and the cost of reduction in respect of the said Biochemical Oxygen Demand. It shall then estimate and fix for the next calendar year in such allocation and precepts the cost of treatment of "normal sewage". It shall also estimate and fix in its allocation and precepts yearly, the cost of required chlorination and the cost of treatment for any substance requiring chlorination and the cost of treatment for any substance requiring additional treatment contained or which may be contained in factory or industrial waste.
  - (b) The estimate so included in the allocation and precepts for the next following year shall be used in the computation of the surcharges to be charged to a licensee and the method of such computation shall be as follows:

In all cases the licensee's volume of sewage shall be ascertained as hereinbefore provided. The nature of the sewage and degrees of pollution thereof shall be taken to be as shown in the last test made by the Corporation on the effluent from the licensee's plant, provided that if it be found such last mentioned tests show the effluent to be of a lessened degree of pollution, the results of such tests

shall not be used for the current quarter's billing but shall be used in subsequent billing and if the results of such tests show that the degree of pollution is greater than the previous tests had shown then the billing for the current and subsequent quarters shall be on the assumption that all sewage in that quarter was of the nature and degree of pollution as shown in the last test made. In such computation the Corporation shall by using the cost estimates contained in the allocation and precepts for the current year, ascertain the cost of treating sewage discharged by the licensee into any sewer or body of water within or entering the Metropolitan Area or Additional Zone in units of 1000 gallons, and for each 1000 gallons of sewage discharged into the sewer or body of water, the licensee shall be charged a surcharge whatever the excess in cost may be found to be over the estimated costs of treating a unit of 1000 gallons of normal sewage. At the approximate end of each quarter of the calendar year and at the end of the last quarter of each year, the Corporation shall make a computation of the surcharge in the case of each licensee using the following formula and shall send out a billing therefor. The said formula may be set down as follows:

$$R_{i} = \begin{bmatrix} f_{s} & (S_{i} - S_{n}) + f_{p} & (P_{i} - P_{n}) \\ S_{n} & P_{n} \end{bmatrix} = \begin{bmatrix} R_{n} + (C_{i} - C_{n}) & R_{c} + (X_{i} - X_{n}) \\ C_{n} & X_{n} \end{bmatrix} = \begin{bmatrix} f_{s} & (S_{i} - S_{n}) \\ S_{n} & P_{n} \end{bmatrix} = \begin{bmatrix} R_{n} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (X_{i} - X_{n}) \\ X_{n} \end{bmatrix} = \begin{bmatrix} R_{i} & (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{i} - C_{n}) \\ C_{n} & C_{n} \end{bmatrix} = \begin{bmatrix} R_{c} + (C_{$$

Where  $R_i$  = surcharge per 1000 gals.

- f<sub>S</sub> factor derived from costs of reducing solids.
- fp factor derived from costs of reducing B.O.D.
- Si Suspended Solids in ppm. in the industrial wastes.
- $P_i$  B.O.D. in ppm. in the industrial wastes.
- Ci Chlorine demand in ppm. in the industrial wastes.
- X<sub>i</sub> Substance requiring additional treatment in ppm. in the industrial wastes.
- S<sub>n</sub> Suspended solids in ppm. in the sewage serving as base or normal.
- P<sub>n</sub> B.O.D. in ppm. in the sewage serving as base or normal.
- C<sub>n</sub> Chlorine demand in ppm. in the sewage serving as base or normal.

X<sub>n</sub> - Substance requiring additional treatment in ppm. in the sewage serving as base or normal.

- Rn Unit charge based on cost of treating normal sewage.
- R<sub>c</sub> Unit charge based on cost of required chlorine.
- R<sub>x</sub> Unit charge based on cost of treating any substance requiring additional treatment.
- (c) The Corporation deems it just and equitable that such surcharges should be charged to and collected from the licensee and does hereby require the licensee to pay accordingly forthwith upon receipt of such a billing from the Corporation with a demand for payment thereof, and in default of payment within fifteen days of such demand for payment, the license of such person to discharge factory or industrial waste into any sewer or body of water within or entering the Metropolitan Area or Additional Zone shall be automatically suspended by such effluxion of time and such person shall not so discharge factory or industrial waste into any sewer or body of water within or entering the Metropolitan Area or Additional Zone until payment has been made for such billing and the suspension removed thereby.
- (d) Quarterly billings to licensees shall not be necessary in any case where it is obvious to the Corporation that the quarterly surcharge to the licensee will not be applicable either because the sewage discharged by the licensee does not exceed normal sewage in degree of pollution or in cases where the quarterly billing would probably in the opinion of the Director be Five (\$5.00) Dollars or less, the billings may be made annually but in all other respects the procedure shall be the same.
- 18. Any license given under the terms of this By-law shall be subject to suspension, revocation and cancellation at any time by the Corporation for any reason which to the said Corporation may seem fit.
- 19. Should any Court of competent jurisdiction declare any provision of this by-law ultra vires, then the decision shall affect only such provision so declared to be ultra vires and shall not affect any other part of this By-law.
- 20. This By-law, except Section 13, shall come into force and take effect on the date of the passing thereof and Section 13 shall be deemed to have come into force and effect from and after the 1st day of January, 1961.

DONE AND PASSED in meeting assembled this 28th day of February, 1961.

(SGD.) "R.H.G. BONNYCASTLE" Chairman

(SGD.) <u>"D. C. LENNOX"</u> Secretary

Certified as to form.

"D. C. LENNOX"

Secretary

Approved as to Engineering Details.

"N. S. BUBBIS" Director

# THE EFFECT OF C - 14 AND Sr - 90 ON ANAEROBIC DIGESTION

.

.

,

by

Dr. Werner N. Grune



THE EFFECTS OF C-14

and

Sr-90 ON ANAEROBIC DIGESTION

by

WERNER N. GRUNE

Georgia Institute of Technology Atlanta, Georgia

### INTRODUCTION

It is difficult to predict the fate of radioactive materials in a heterogeneous system, such as sewage sludge, because sludge composition and microbial population are not fully known. Continuous variations in flow and character of the wastes entering a disposal plant are a routine occurrence. Nevertheless, the effluent must be treated to a reasonably uniform quality. Therefore, it is essential to establish the concentrations at which radioactive materials may interfere with the treatment process.

It is also necessary to determine the distribution of activity between the liquid and solid phases in a sludge digester and to know how much activity may escape into the atmosphere in the form of the gaseous end products.

It is not expected that anaerobic decomposition of sewage solids will lend itself to the high degree of treatment or decontamination necessary to meet present standards (1). The adsorptive properties of biological slimes and flocs, to take up and hold radioactivity, seemed earlier to offer considerable promise for concentration of radioactivity and show the way for inexpensive removal of very samll amounts of radioactive materials from relatively large volumes of liquid wastes. Among the biological processes extensively investigated were the activated sludge process, trickling filters, and sewage oxidation ponds. Dobbins (2) and others (3) concluded from these studies that "biological methods will have limited application for the removal of radioactivity from liquids. The extent of the removal of a radioactive element from a liquid waste by biological methods depends upon the biochemical relationship which exists between the element

and the biological system, as well as the chemical composition of the waste."

A dose in excess of 1,000 roentgens is generally necessary to destroy bacteria (4). Therefore, sterilization of the biological systems in sludge is not expected at levels of activity occurring in sewage and waste streams. However, bacterial destruction results when high concentrations of radioactive isotopes are mixed with sewage sludge or when irradiated by a source (5) (6) (7). Exploratory studies at Brookhaven National Laboratory, to sterilize samples of sewage effluent by irradiation, proved that an X-ray dose of 65,000 roentgens caused increased settling of solids from the supernatant, while a dose of 350,000 roentgens contributed additional solids to be present in the supernatant probably by fragmentation of the bacterial cell (8).

Anaerobic digestion and sludge disposal facilities may represent 50% of the capital investment for a waste treatment plant. Operating and maintenance costs for digestion represent from 23 to 36% of the annual budget (9). With the heavy investment in digestion equipment and its importance in the treatment process, it is especially necessary to investigate the digestion process under a variety of operating conditions. As long as the underlying processes in the treatment of sewage solids are still not completely understood, it is difficult to recommend and devise proper treatment. Therefore, a basic investigation of the mechanism of sludge digestion was one of the objectives of the research.

Many studies have been carried out to explain the mechanism of methane fermentation of pure chemical substances and during the anaerobiosis of sewage sludge (10) (11). The mechanisms by which methane is produced by bacteria are still in doubt. Formation of methane has been found to occur both with and without the reduction of carbon dioxide. The conversion of the substrate into the two simple end-products, methane and carbon dioxide, is a unique characteristic of the process (12)

The rapid development and growth of civilian and military uses of atomic energy will increase and compound problems of radioactive waste disposal. In the near future nuclear power plants will be located in widely distributed areas of the United States, from which additional amounts and varied characteristics of waste discharge will flow. In 1960, nine civilian reactors were operated for power production with a combined capacity of 258 electrical megawatts. Nine additional power reactors were under construction in the U.S., adding 271 Mw(e) to the total output. Another eight were under preconstruction development and plans were announced for five more, making a total of 31 projects with approximately 1,580 Mw(e) (13) (14). Previously, the largest A-power plant was the Dresden Nuclear Power Station, located about 50 miles southwest of Chicago, at the confluence of the Kankakee and Des Plaines Rivers. It was designed for an electrical output capacity of 180,000-Kw (180 Mw), is operated by the Commonwealth Edison Co. and went critical on October 15, 1959. However, the Consolidated Edison Co. of New York built a 275,000-Kw atomic power plant at Indian Point on the east bank of the Hudson River, 25 miles north of Manhattan (15). It became the world's largest A-power plant when it went critical late in 1961. This program does not include reactors built by the Atomic Energy Commission or the Nation Laboratories. The development of the nuclear-power industry from 1965 to 1995 has been estimated to increase from 1.5 to 10<sup>4</sup> to 5 x 10<sup>5</sup> Mw(e), accompanied by an increase from 1.5 x 10<sup>6</sup> to 2 x 10<sup>9</sup> gallons per day of radioactive fission-product wastes (16).

The wastes from experimental and power reactors, compounded with quantities of radioactive materials already being discharged from hospitals, research laboratories and industrial establishments, pose challenging problems in waste disposal and environmental sanitation.

A greater concentration of the radioactivity may be found in the liquid phase (supernatant) if digestion of sewage sludge is inhibited or the process otherwise upset. This effect could result in a larger portion of the activity discharged to a stream. With other isotopes, or other chemical forms of the same isotope, a greater percent of the activity may be adsorbed by the sewage solids which after drying, may be used as fertilizer or soil conditioner. In either case the potential hazard of environmental contamination is **a** current problem.

Therefore, one of the most important aspects of this study was to determine the relative concentration of radioactivity in the supernatant and the sludge solids during and after digestion. From a study of these results, levels can be ascertained at which specific isotopes would interfere and possibly inhibit the digestion process. Furthermore, the degree of decontamination afforded by anaerobic decomposition may be assessed at levels below significant radiation damage, as well as any decontamination achieved if the normal digestion process should be destroyed due to radiochemical and/or radiobiological damage.

SPECIFIC OBJECTIVES

The research was divided into two major parts. The first part was carried out to sutdy the effect of concentrations up to 1,000 uc/l (l mc/l) of Carbon-l4 and Strontium-90 on digestion. The results of this phase were to assist the establishment of maximum safe concentrations for plant personnel and for ultimate disposal. The second part was directed toward a study of the relative distribution of C-l4 and Sr-90 in the solid, liquid and gaseous products of

digestion. These studies were performed to learn more about the environmental hazards that may be involved in the disposal of these radioactive wastes to the atmosphere, soil and streams.

Specifically, these investigations evaluated the effects of radioactive materials on digestion and their ultimate fate by:

- (1) Quantitative measurement of daily gas production (total gas produced, expressed as mls/gm of volatile matter added; and as cu ft/lb of volatile matter destroyed.)
- (2) Qualitative measurement of gas production  $(CO_2, CH_4, etc.)$  by gas chromatography.
- (3) The reaction rate of digestion, expressed as k (the velocity parameter of a first order reaction with a lag phase.)
- (4) Measurement of the ultimate gas production, expressed as G.
- (5) Analysis of the autocatalytic nature of digestion by means of a lag-phase, expressed as  $\overline{\phantom{a}}$ .
- (6) Measurement of the rate of volatile matter reduction (for absolute values; for correlation with the rate of gas production and with electrical conductivity measurements.)
- (7) Continuous measurement and examination of the pH to follow closely the progress of digestion and to assist in the evaluation of the radioactive sludges with their controls.
- (8) Continuous measurement and control of a constant digester temperature.
- (9) Continuous measurement of the oxidation-reduction potential of the anaerobic system (in an effort to shed light on the general applicability of this parameter to yield additional information on the progress of digestion.)
- (10) Continuous measurement of electrical conductivity to follow the changes in total and dissolved solids' concentrations (to examine the effect of solids' breakdown in the presence of radioactive materials.)
- (11) Measurement of the distribution of radioactivity between liquid and solid end products from digestion (for various concentrations of initial activity and to follow changes of uptake throughout the digestion period).

(12) Analysis of the gaseous end products, principally  $C^{14}O_2$ and  $C^{14}H_4$  to obtain further information on the mechanism of methane fermentation.

Additional determinations of the characteristics of raw, seeded and digested sludge, gas and liquor, volatile acid production and radioassays of liquids, gaseous and solid end products were included in the control work.

#### EXPERIMENTAL METHOD

For these studies, 17 laboratory digesters were employed in each of nine runs. The period of digestion varied from 26 to 44 days. Seeded sludge volumes of 450, 1500 and 1700 ml were employed. During each run, 12 batch digesters were operated to obtain homogeneous data that would lend itself to statistical analysis. In the other five digesters, containing either 1500 or 1700 ml, the sludge was recirculated through one or more electrode assemblies, including pH, ORP and conductivity cells. Recirculation of sludge from the digesters through the electrode assemblies was accomplished without any loss of  $CO_2$  or  $CH_4$ ; or the entrainment of any air. The details of the experimental method have been presented previously (17) (18) (19) (20) (21).

The composite reactions involved in the anaerobic stabilization of complex organic matter in a well-seeded sludge may be approximated by a first-order reaction. The application of this type of equation is based on the assumption that the reaction velocity k is a function of the organic matter remaining to be decomposed:

$$\frac{dy}{dt} = k (G - y)$$
 (1)

where

y = the amount of gas produced in time t G = Total amount of gas generated during digestion k = reaction velocity constant t = time in days

Intergrating the differential form between the limits of t = 0 and t = t, the equation becomes:  $y = G(1 - 10^{-kt})$  (2)

In general, this equation describes anaerobic digestion adequately. If the amount of seeding material is small compared to the raw solids concentration, an S-shaped or autocatalytic gas production curve is obtained. After an initial lag phase, the rate of gas production increases until about one-half of the total amount of gas is generated. Thereafter, the rate of gas production decreases.

To mathematically characterize sludge digestion, autocatalytic reactions may be treated by fitting the upper part of the curve as a first-order reaction starting some time later than t = 0. This transfer is equivalent to extrapolating the origin of the curve to the end of the seeding lag. The interval between the origin and the extrapolated point is called the time-

1

2

lag. Thomas (22) formulated the first-order reaction with a time lag by the following expression:

$$y = G (1 - 10^{-k(t-\tau)}) = G (1 - C 10^{-kt})$$
(3)  
Where  $\tau = \text{time-lag and } \tau = \frac{1}{\pi} \log C.$ 

#### PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

Part 1: Radiocarbon (C<sup>14</sup>) Studies

EFFECT ON GAS PRODUCTION

The maximum Carbon-14 concentration investigated was 1,000  $\mu$ c/l (1.0 mc/l). Figure 1 shows a family of curves of cumulative gas production from runs XVI, XVII, XVIII and XX, obtained from digesters with plain sludge, from those containing various activities of C<sup>14</sup>-labelled sodium acetate (in the one and two position), and from control digesters to which an equivalent concentration of non-radioactive salt<sup>1</sup> was added.

To present the cumulative gas production curves in mls/gm of volatile solids added for every digester from each of five experimental runs would not be practical. Instead, the gas production data (in terms of mls of gas/gm V.M. added) for each run were expressed as percentages of total gas production from the average plain sludge digester values<sup>2</sup>. These composite curves from 36 digesters are presented in Figure 1.

Although there appear to be some differences in the gas production rate indicated in Figure 1, the results from individual laboratory runs show no significant differences as may be seen in Figure 2. The differences noted in Figure 1 may be attributed to variation in seeded sludge mixture characteristics inherent between individual runs.

Salt in  $C^{14}$  studies refers to solutions containing 2.4, 238, 713 and 2378 mg/l of CH<sub>3</sub>COONa added to the controls to simulate the acetate concentrations added to digesters with concentrations of 1,100, 300 and 1000 µc/l of C-14, respectively.

The seeded sludge varied from run to run, resulting in differences in cumulative gas values. Therefore, the gas values were calculated on a percentage of the plain digesters values. These percentages then could be averaged between runs and plotted to produce a composite chart, showing all data on one plot.

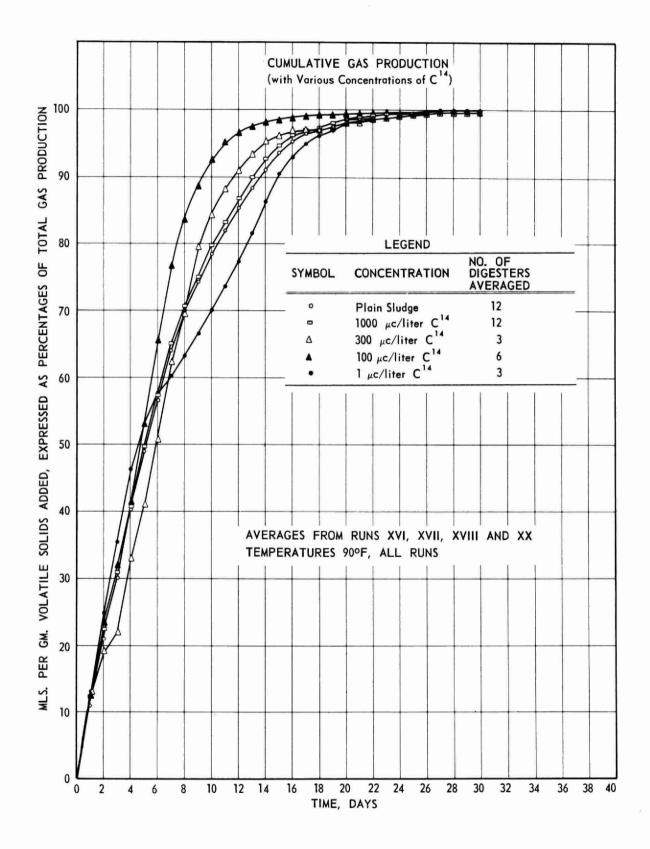


Figure 1.

page 132

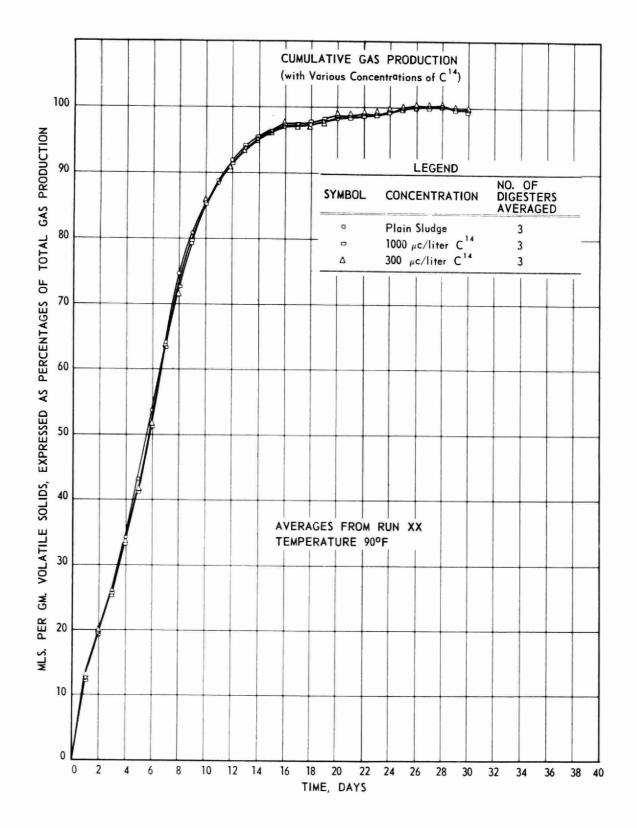


Figure 2.

There appears to be no significant difference in gas production due to the presence of  $C^{14}$ , or equivalent concentrations of salt, when compared with gas production from the plain sludge up to the 1,000 µc/l concentration.

The efficiency of gas production, expressed as cu. ft. per lb. of volatile matter destroyed, was not significantly affected in the presence of 1 to 1000  $\mu$ c/l of C<sup>14</sup> when compared with plain sludge. The quantitative values for Runs XVI through XX are presented in Table 1.

Reaction Velocity Constant

Reaction velocity constants were computed for each of 17 digesters for all five runs with C<sup>14</sup>, and the results from statistical analyses using the t-test for significance are shown in Table II. It may be observed from this table that no significant differences were obtained with concentrations ranging from 1.0 to 1,000  $\mu$ c/l of Carbon-l4 when compared with plain sludge.

Similarly, the control digesters containing the equivalent concentrations of salt (sodium acetate) exhibited no significant difference when compared with plain sludge (P = 22.2%).

As a further test of the relationship on k of sludge mixture (based on the initial volatile matter added), sodium acetate (salt) concentration and  $C^{14}$  activity, a multiple correlation analysis 3 from a total of 60 values yielded the following relationship:

k = 0.0740 - 0.0166M - 0.00000457C salt - 0.0159 (4)  $C_{C-14}$ 

where

M = ratio of seeded sludge mixture, based on the volatile content of raw sludge.

C<sub>salt</sub> = concentration of equivalent, stable sodium acetate, added to the controls, in mg/l, and

 $C_{C-14}$  = concentration of  $C^{14}$  as  $CH_3COONa$ ,  $\mu c/1$ 

3

As a constant  $90^{\circ}$ F incubation temperature was maintained throughout the C<sup>14</sup> series of runs, temperature was not a variable and did not enter into the correlation analysis.

#### TABLE I

# Experimental Conditions, Gas Production and Volatile Matter Reduction

Part I. Radiocarbon (C<sup>14</sup>) Studies

Run	Dig.		EXPERIME	NTAL CO	ONDITIONS	rane ora Britholdson	TOTAL GAS	PRODUCTION	
Period (Days)	No.	Sludge Volume	Sludge Mix-	Inc.	Conc. of Salts(a)	Conc. of	ml/gm V.M.	cu ft/lb V.M.	Reduction Volatile
(Days) Date		(ml)	ture	Temp. OF	mg/1	С <sup>14</sup> (ъ) (µс/1)	Added	Destroyed	Matter(%)
(2496.)		1.75		<sup>0</sup>					20.6
XVI (26) 4/16/59 to 5/12/59	1 2 3 4 5 6 7 8 9 0 1 1 9 3 4 5 6 7 8 9 1 1 9 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	450 1,700	1:1.4	90°	- - 2380 2380 2.4 - - - - -	1,000 1,000 1,000 1 1 1 - - - - - - - - - - - - - - -	282.0 272.7 263.2 267.9 274.5 260.6 301.1 296.7 247.0 253.6 288.6 285.1 294.4 294.8 317.5 274.8 290.7	13.9 13.0 15.0 12.2 13.8 17.8 20.0 11.7 10.0 9.2 12.1 11.2 13.6 25.0 25.6	32.6 33.6 27.6 35.3 36.1 29.6 36.8 23.8 33.9 40.5 40.0 37.6 42.3 34.8 20.4 18.2
xvII (35) 6/3/59 7/8/59 (41) 6/3/59 to 7/14/59	1 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 6 7 8 9 10 11 2 3 4 5 9 10 11 2 3 4 5 10 11 12 12 12 12 12 12 11 12 12 12 10 11 12 12 11 12 13 11 12 11 12 11 11 12 11 12 11 11 12 11 12 11 12 11 12 11 12 11 12 11 12 11 12 11 12 11 12 11 12 11 11	1,700	1:0.7	90°	- - - 2380 2380 2.4 - - - - -	1,000 1,000 1,000 1 - - - - - - - - - - - - - - - - -	287.3 276.0 268.3 274.5 277.9 285.5 298.4 291.9 280.8 283.3 290.4 289.7 243.7 281.6 260.6 269.0 267.8	12.1 12.8 13.4 12.9 13.6 14.6 8.9 9.6 9.8 8.1 11.3 9.3 75.1 25.2 10.1 21.7 38.1	38.0 34.5 29.7 34.0 32.8 27.3 53.6 48.9 46.0 56.1 41.0 49.8 5.2 17.9 41.4 19.9 11.3

(a) Salt refers to a CH<sub>3</sub>COONa solution, see footnote, page 8
(b) C<sup>14</sup> in No. 1 position

đ, . ×\*

## TABLE I (Cont'd)

## Experimental Conditions, Gas Production and Volatile Matter Reduction

Run	Dig.		EXPERIME	INTAL C	ONDITIONS		TOTAL GAS PRODUCTION					
Period	No.	Sludge	Sludge	Inc.	Conc. of	Conc. of	ml/gm	cu ft/lb	Reduction Volatile			
(Days) Date		Volume (ml)	Mix- ture	Temp. <sup>O</sup> F	Salts(a) mg/l	с14(ъ)	V.M. Added	V.M. Destroyed	Matter(%)			
						(µc/1)						
	1 2 3 4	450	1:1.0	90 <sup>0</sup>	-	1,000(1-c) 1,000(1-c)	316.4 282.7	19.9 17.3	25.5 26.2			
	3				-	1,000(1-c)	272.2	12.9	33.3			
XVIII	4				-	100(1-c) 100(1-c)	298.8 309.2	17.6 20.9	27.2 23.7			
(33)	56				-	100(1-c) 100(1-c)	275.1	12.1	35.3			
	7				2380 2380	-	325.9 315.5	23.1 17.0	34.2 29.7			
8/12/59	9				238	-	312.5	18.5	27.1			
to 9/14/59	10 11				-	-	322.5 318.7	21.2 20.3	23.8 25.1			
9/ 14/ 59	12	*			-	-	321.7	21.3	24.2			
	13 14	1700			-	-	317.0 291.5	43.1 82.8	11.8 5.7			
	15				-	-	370.9	291.3	2.0			
	16 17				-	-	319.9 342.9	47.3 91.5	10.9 6.0			
			•									
	1	450	1:2.2	90°	-	1,000(1-c) 1,000(1-c)	165.0 159.4	9.1 8.5	29.1 30.1			
	2 3 4				-	1,000(1-c)	163.8	9.6	24.8			
XIX	4 5				-	1,000(2-c) 1,000(2-c)	161.7 161.6	9.2 8.2	28.1 31.7			
(44)	5 6 7				-	1,000(2-c)	154.0	8.4	26.5			
(44)	7 8			8	2380 2380	-	168.6 184.4	8.8 8.4	30.6 35.1			
	9				2380	-	172.0	9.5	29.0			
9/21/59	10 11				-	-	178.1 181.2	10.0 10.0	28.6 29.1			
to 11/4/59	12	+			-	-	173.0	10.2	27.2			
	13 14	1500 I			-	-	195.7 199.0	10.7 12.2	29.3 26.2			
	15				-	-	233.1 200.1	16.3	22.9 25.6			
	16 17				-	-	232.9	12.5 15.8	23.6			
		*	۲	Υ.								

			14.	
Part	I.	Radiocarbon	(C <sup>++</sup> )	Studies

(a) Salt refers to a  $CH_3^{COONa}$  solution, see footnote, page 8

(b) C<sup>14</sup> in position shown

## TABLE I (Cont'd)

Experimental Conditions, Gas Production and Volatile Matter Reduction

Run	Dig.		EXPERIME	NTAL C	ONDITIONS		TOTAL GAS	PRODUCTION	
Period	No.	Sludge	Sludge	Inc.	Conc. of	Conc. of	ml/gm	cu ft/lb	Reduction
(Days) Date		Volume (ml)	Mix- ture	Temp. <sup>O</sup> F	Salts(a) mg/l	с <sup>14</sup> (ъ)	V.M. Added	V.M. Destroyed	Volatile Matter(%)
Date		(1112)		r	ш8/ т	(µc/l)	Auueu	Descroyed	Maccer(p)
	1 :	450	1:1.2	90 <sup>0</sup>	-	1,000(1-c)	246.4	13.1	30.3
	2	1	1		-	1,000(1-c)		13.7	30.1
xx	3 4				-	1,000(1-c)	248.4	13.3	28.3
	4				-	300(2 <b>-</b> c)	254.9	14.1	29.0
	5 6				-	300(2-c)	244.3	13.1	29.8
(0))					-	300(2-c)	246.8	13.0	28.8
(34)	7				2380		254.5	13.4	30.4
	7 8 9				2380	-	257.8	14.9	27.7
	10				713	-	254.1	15.1	27.1
12/2/59	10				-		259.9	15.8	26.3
to	10	+			-	-	254.4	14.7	27.7
1/5/60	12 13	1500			-	-	250.5 93.0*	15.3	26.3
	14	1,00			-	-	261.2(*)	7.4 27.6	20.1 15.2
	15				_	_	252.6	23.9	17.0
	16				-	-	250.7	38.9	10.3
	17				-	-	217.7	22.0	15.9
	-1		Y			-	<u>(•(</u>	22.0	1).9

Part I. Radiocarbon (C<sup>14</sup>) Studies

\* KCl leakage (\*) Estimated

(a) Salt refers to a  $CH_3^{COONa}$  solution, see footnote, page 8

(b) C<sup>14</sup> in position shown

#### TABLE II

## Average Differences and the Probability (P) of their Occurrences by Chance Alone for k, G and $\tau$ -Values at Various Concentrations of Carrier-free C-14 and Salt (\*) Added to Plain Sludge

Plain Sludge	No. of Digester	Values of k		Values of	G	Values of $\tau$		
C-14 (μc/l)	Pairs	$\overline{d} = \frac{\Sigma(k_h - k_c)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(G_h - G_c)}{n}$	P (%)	$\overline{\mathbf{d}} = \frac{\Sigma(\tau_{\mathrm{h}}^{-}\tau_{\mathrm{c}}^{-})}{1-\tau_{\mathrm{c}}^{-}}$	P (%)	
All Runs 16-20	30	0.00193	22.7	-10.23	22.8	0.0109	74.7	
Run 19 Removed	24	0.00242	21.0	- 9.25	8.76	2.300	63.9	
1000	15	0.00153	52.5	-16.76	26.2	0.0468	44.0	
100	3	0.00217	26.4	- 2.40	12.5	-0.00367	81.0	
1	6	0.00728	17.6	- 3.08	80.2	0.000500	>90	

(a) Comparing Plain Sludge vs. C-14 Containing Sludge

(ъ)	Comparing	Plain	Sludge	vs.	Salt	(*)

Plain Sludge vs.	No. of Digester	Values of k		Values of	G	Values of	τ
Salt (ppm)	Pairs	$\overline{d} = \frac{\Sigma(k_p - k_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(G_p - G_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(\tau_p - \tau_s)}{n}$	P (%)
All runs	15	-0.00178	22.2	14.12	23.3	-0.0950	15.1

(c) Comparing C-14 vs Salt (\*)

C-14 (mc/1)	No. of Digester	Values of k	Values of	G	Values of	τ	
vs. Salt (ppm)	Pairs	$\overline{d} = \frac{\Sigma(k_h - k_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(G_h - G_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(\tau_h - \tau_s)}{n}$	P (%)
All runs	15	-0.00026	87.7	-2.640	71.7	-0.0482	16.2

(\*) Salt refers to solution of  $CH_3COONa$ 

The coefficient of multiple correlation, R, was found to be 0.22, which is not significant. Therefore, no significant dependence of the reaction rates, or k-values, can be assigned to type of mixture, or equivalent salt concentration, or  $C^{14}$ concentration. It also shows that k values can not be predicted with any degree of success by substitution in the regression equation.

As part of the multiple correlation analysis, the partial correlation coefficients, r, for the three independent variables with k were found to be:

- r<sub>M</sub> =-0.15 (partial correlation between type of mixture (seed) and k-values)
- r<sub>S</sub> =-0.11 (partial correlation between equivalent salt concentration and k-values)
- $r_{C-14} = -0.18$  (partial correlation between concentration of C<sup>14</sup> and k-values)

The type of mixture, the equivalent salt, or the  $C^{14}$  concentration did not exert any significant influence on the reaction velocity constant.

However, as noted elsewhere, Run XIX was a typical run because its gas production rate for the first several days was very low for unknown reasons. Since the reaction velocity constant is largely determined by this initial period, another multiple correlation analysis was performed without Run XIX data.

For this case, the regression equation is:

 $k = 0.164 - 0.101M - 0.00000102 C_{salt} - 0.00352 C_{C-14}$  (5)

with a multiple correlation coefficient of R = 0.84.

The partial correlation coefficients were:

 $r_{\rm M} = -0.84$   $r_{\rm S} = -0.049$   $r_{\rm C-14} = -0.080$ 

which shows that mixture exerts a significant effect on the reaction velocity constant.

Also, the coefficient in the regression equation for the mixture significantly affects the k-values ( $t_M = -10.2$ , P<< %) which shows the strong influence of sludge seeding on the k-value.

Ultimate Gas Production and Lag Period

The ultimate gas volume, G, was also not significantly affected by concentrations of C<sup>14</sup> up to 1,000  $\mu$ c/l. The results of the t-tests are shown in Table II.

The results from a multiple correlation analysis from a total of 48 ultimate gas production values, G, yielded the following relationship:

$$G = 152.6 + 162.9M + 0.00289 C_{colt} - 7.616 C_{C_l}$$
(6)

The coefficient of multiple correlation, R, was found to be 0.93, which is significant correlation and shows that values of G can be predicted with some degree of confidence by use of equation (6).

The coefficients of partial correlation, r, for type of mixture, salt concentration and  $C^{14}$  activity with G-values, were found to be:

 $r_{\rm M} = 0.93$   $r_{\rm S} = 0.14$   $r_{\rm C-14} = -0.18$ 

It is evident that of the three independent variables only the seed ration (mixture) exerts a significant influence on G-values.

From an analysis of t-tests of the regression coefficients, with D.F. = 44, the results show that a significant relationship exists only between type of mixture ( $t_M = 17.1$ ; P $\lt$ 1%) and ultimate gas produced.

As shown in Table II, from an analysis of  $\tau$ -values between plain digesters, those containing various levels of  $C^{14}$ , and controls with equivalent salt concentrations, it was established that no significant differences exist.

The results from a multiple correlation analysis of the same basic data for the lag-period  $(\mathbf{x})$  yielded the following relationship:

 $\tau = 0.718 - 0.821M + 0.00000705 C_{salt} + 0.0185 C_{c_1\mu}$  (7)

in which the terms M,  $C_s$  and  $C_{C_1\mu}$  are defined as previously.

The value of R, the coefficient of multiple correlation for the lag-period was found to be 0.88. This shows a highly significant correlation between  $\tau$ -values and any or all of the other three variables. The partial correlation coefficient for the seed ratio (mixture) shows a good correlation ( $r_{\rm M} = -0.88$ ). The partial correlations of  $\tau$  with the concentration of Cl4 ( $r_{\rm C-l4} = 0.058$ ) and with the equivalent concentration of salt ( $r_{\rm S} = 0.046$ ) are poor.

Similarly, the results from tests of the regression coefficients point to the mixture type  $(t_M = -12.1, P \ll 1\%)$  as highly significant but the concentration of  $C^{14}$   $(t_{C-14} = 0.38)$  does not have any real effect. Aside from the fact that the

significance of the mixture (sludge seed) is established, the insignificant correlation between  $t_{-}$  values and  $C^{14}$  was to be expected from the previous discussions of t-tests or  $\neg$ -values from Table II.

Reduction of Volatile Matter and Effect on Volation Acids

The result of  $C^{14}$  studies show that the reduction of volatile matter was not affected by the addition of  $C^{14}$  at the concentrations studied. For batch digesters, the volatile matter reduction ranged from 24 to 56%, as may be seen from Table I.

The volatile acids concentrations did not exceed 528 mg/l (except where KCl leakage from flow cells occurred, when a value as high as 1,153 mg/l was recorded) in any of the digesters during the Cl<sup>4</sup> studies, and was usually below 200 mg/l at the end of the digestion period. Therefore, up to 1,000  $\mu$ c/l or Cl<sup>4</sup> produced no deleterious effect on the volatile acids concentration during digestion.

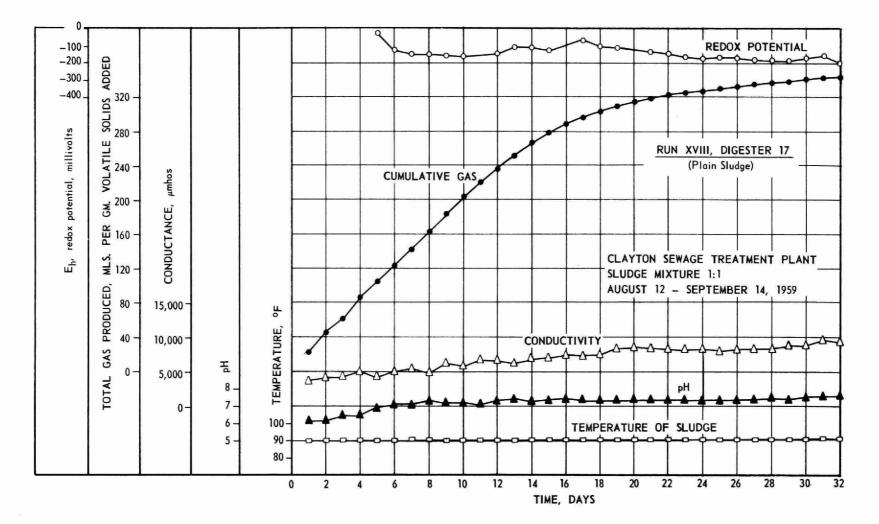
## REDOX POTENTIAL, LIQUID CONDUCTIVITY AND pH

Since  $C^{14}$  was not added to the recirculating digesters, date could not be obtained on the effect of  $C^{14}$  on ORP, conductivity and pH from these experiments.

Previously described procedures (6) were used to continuously record redox potentials and conductivity measurements. No significant differences were found between the redox potentials obtained from the recirculated digesters within the runs. As may be seen from Figure 3, the Eh value of the redox potential curve at the end of the digestion period was -200 mv for digester 17 (Run XVIII). The ORP values for the other recirculated digesters varied from -150 mv to -250 at the end of the 32-day digestion period.

During Run XVIII, the conductivity of the seeded sludge mixture was initially 3,750 umhos and reached a final value of about 9,500 µmhos for digester 17. The final values for the other digesters ranged from 7,000 to 15,000 µmhos but in those cases where the conductivity exceeded 10,000 µmhos, KCl leakage from either ORP or pH flow cells was noted.

The results of continuous pH measurements from digester 17, as shown in Figure 3, illustrate normal pH changes. The initial pH value was 6.2, rising to 7.0 after five days and the final value was 7.5 at the end of the digestion period, showing a well-buffered system. Over the entire  $C^{14}$  series of digestion experiments, the unitial pH values ranged from 5.8 to 6.2 and the final pH values were between 7.2 and 7.5.

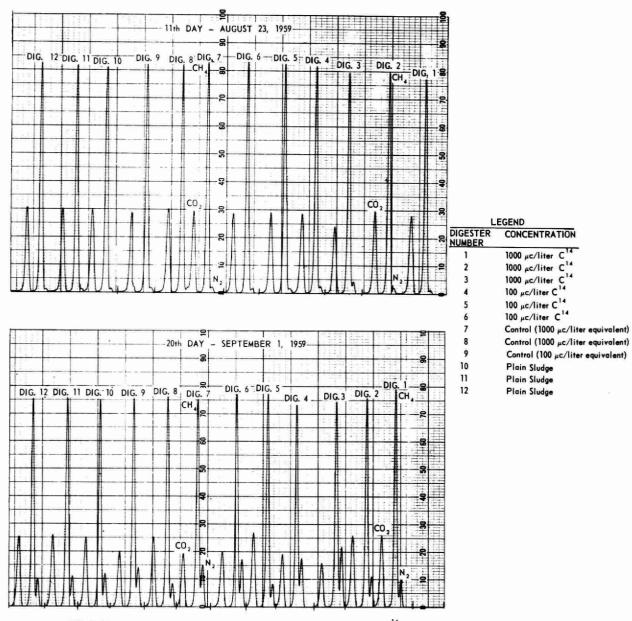


.

.

٠

Figure 3.



GAS CHROMATOGRAPHIC ANALYSIS OF SLUDGE GASES, RUN NO. XVIII - C<sup>14</sup> COLUMN: 71 FT. SILICONE GREASE FLOW RATE: 80 MLS/MIN. SAMPLE SIZE: 1.0 ML. EACH COLUMN TEMPERATURE: 80°F



						0												
								Ru	n XVIII	- C-14	Studie	s						
Dig.		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Nо. Туре		1 mc/1*	l mc/l*	l mc/l*	0.1 mc/1*	0.1 mc/1*	0.1 mc/1*	Salt equiv. 1 mc/1		Salt equiv. 0.1mc/1	Plain	Plain	Plain	Plain	Plain	Plain	Plain	Plain
	234567890123456790122357890	55.2 21.4 38 55.5 22222222222222222222222222222222	52.6 33.7.4 255.6 225.	54.2 45.91 29.5 24.9 25.7 24.9 225.2 23.4 20.5 19.1 18.2 17.5 17.2 18.3 17.4 17.4 17.4	55.6 47.5 30.4 25.5 24.6 25.5 24.6 25.5 25.5 24.6 25.5 24.6 25.5 24.6 25.5 24.6 25.5 24.6 25.5 24.3 22.2 22.2 20.6 20.3 20.6 16.8 18.5 18.5 18.1 18.5 18.1 18.1 18.5 18.1	55.2 48.8 37.6 31.1 27.7 25.3 26.0 26.5 26.0 24.4 25.6.0 24.4 25.9 26.7 25.2 26.9 16.7 16.7 29.2	55.9 50.0 37.9 28.1 25.8 24.9 25.2 25.2 25.2 25.2 25.2 25.2 25.2 25.2 21.9 20.4 20.4 20.7 19.7 19.7 20.1 20.3	56.9 48.728 30.3224.936 224.56.1099914 22266.9991222200 22266.9991222200 188.868 17.5938 16.855938 17.5938 16.938 16.99914 17.5938 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99914 16.99916 16.999	55.4 476.2 306.6 24.6 26.7 26.0 26.1 25.7 22.2 22.2 22.2 22.2 22.2 22.2 22.2	55.35 47.7 36.3 26.7 24.8 24.7 25.7 26.2 25.1 25.1 21.9 20.8 25.1 21.9 20.8 25.7 20.2 19.4 18.3 18.4 19.6 20.4 18.8 18.5	55.6 436.78 306.94 222222222222222222222222222222222222	56.0 49.3 31.3 27.1 225.1 226.1 226.5 226.5 226.5 226.5 226.5 226.5 226.5 226.5 226.5 225.5 25.5	554.74 317.5504476490940310567415	54.0 51.0 52.4 51.9 53.2 22.5 53.4 55.9 22.5 53.4 22.5 53.4 22.5 53.4 22.5 53.4 22.5 53.4 22.5 53.4 22.5 53.4 22.5 53.4 22.5 53.4 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 22.5 5 2.5 5 5 5	54.3 51.3 41.1 33.4 26.9 25.4 24.4 24.2 23.6 25.2 24.4 24.2 23.3 20.5 20.4 20.5 20.2 21.7 20.4 20.5 20.2 21.7 20.4 20.5 20.2 20.5 20.5	59.6 38.3 36.2 49.4 22.2 22.2 22.2 22.2 22.5 51.4 51.0 50.4 9 23.3 34.5 50.4 51.0 50.4 9 23.3 56.7 9 20.2 55.1 45.1 0 50.4 9 20.5 51.4 51.0 50.4 9 20.5 50.4 9 20.5 51.4 51.0 50.4 9 20.5 51.4 51.0 50.4 9 20.5 50.4 9 20.5 51.4 51.0 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 9 20.5 50.4 50.5 50.5	51.3 46.9 35.2 23.32 24.7 24.33 24.33 24.33 24.333 23.42 24.3339 23.22 23.23 3.33	55.3 41.4 52.4

Table	TTT	Per Cent	of	Carbon	Dioxide	in	Sludge	Gas	from	Gas	Chromatographic Analysis
TUDIC		TCI OCHO	OT.	Carbon	DIOVIAC	***	DIUUBC	uus	TIOM	Juno	oniomatographic Analysis

.

\* C-14 in Position 1

٠

1

#### EFFECT ON GAS QUALITY

The gas produced during the C<sup>14</sup> runs was analyzed by gas chromatography. Gas samples from each digester were analyzed daily so that changes in gas composition could be followed as digestion progressed. Chromatograms obtained on two different days from twelve batch digesters are reproduced in Figure 4.

Analysis of the chromatographic curves for digesters 1 through 12 on the eleventh day of Run XVIII, shows that approximately 74% of the gas produced in each digester was methane and 26% carbon dioxide.

Quantitative analysis of chromatograms from the twentieth day shows that in digesters 10, 11 and 12, which contained plain sludge, the  $CO_2$  and  $CH_4$  percentages are practically the same as on the eleventh day, while the  $CO_2$ concentration appears to be lower in most digesters containing salt and radioactive carbon. The results of daily gas chromatograpic analyses from each digester in this run over a period of 32 days are shown in Table III.

To determine if  $C^{14}$  exerted any significant effect on gas quality, statistical analyses to compare CO<sub>2</sub> concentrations in pairs of digesters for each day in each run were performed. The objective of performing statistical analyses on the results of gas composition of paired digesters with and without the presence of radioactive carbon (C<sup>14</sup>) was to determine the statistical significance of any differences in the CO<sub>2</sub> concentration. The comparison in each case was made between the values for the plain versus the C<sup>14</sup> digesters, plain versus the control digesters, or control versus the C<sup>14</sup> digesters. Student's "t" distribution and the "t" test for significance were used.

As in most cases where biochemical reactions are involved, the test for significance is based on the 95 per cent level. Thus, with the use of the "t" distribution, an average of the differences between  $CO_2$  values is considered significant only when such stated differences can be expected to occur by chance alone less than 5 per cent of the time.

The "t" tests were run on various combinations of  $CO_2$ values from digesters 1 through 12 in each of the five  $CI^4$ runs. Comparisons between the  $CO_2$  concentration from 30 pairs of digesters containing  $CI^4$  with those containing plain sludge, showed the  $CO_2$  concentration to be significantly higher in the plain digesters in 22 out of 30 cases. From comparisons of 15 pairs of digesters containing equivalent salt (controls) and containing plain sludge, 13 showed that the  $CO_2$  concentration was significantly higher in the plain sludge digesters. Of eleven comparisons made between digesters containing  $CI^4$  and digesters containing equivalent salt, five showed significantly higher  $CO_2$  concentrations in the  $CI^4$  digesters. Three digesters with ecuivalent salt had significantly higher  $CO_2$  content in the gas, and three showed no significant difference. These statistical analyses show that sodium acetate, either stable or radioactive, lowered the  $CO_2$  concentration in the sludge, but that the  $Cl^4$  and no appreciable effect in the concentrations applied to the seeded sludge. Although differences in  $CO_2$  content were shown to be statistically significant, it should be pointed out that the average difference of the daily  $CO_2$  values from any pair of digesters was only 1 to 3% in most cases, i.e.  $d_{CO_2} \leq 3\%$ . This small difference between  $CO_2$  concentrations, usually below 30% (see Table III,  $CO_2$  after five days), would be hardly noticeable in any treatment plant operation and reflects only a subtle difference.

# DISTRIBUTION OF C14 BETWEEN LIQUID AND SOLID PHASES

The laboratory procedures used in determining the distribution of  $C^{14}$  between the solid and liquid are described in Appendix 1. The results from the five  $C^{14}$  runs are presented in Figures 5, 6 and 7.

The decontamination factors,  $(A_0/A_t)$ , for the solid and liquid phases are plotted separately versus initial C<sup>14</sup> activity and are shown in Figure 5. Of the 28 decontamination factors for the liquid phase, 26 are greater than one. Therefore, the initial C<sup>14</sup> concentration,  $A_0$ , in the liquid phase is greater than the final concentrations, At showing that the liquid must have lost radioactivity to the solid and gas phases during digestion. The decontamination factors for the sludge solids indicate that the initial solids contained less radioactivity than the final solids in 19 out of 28 digesters. Thus, the solids gained radioactivity during the digestion period. These changes may be expected since the C<sup>14</sup> was added to the seeded sludge in the liquid state (as CH<sub>3</sub>COONa). As digestion proceeds some C<sup>14</sup> becomes assimilated into sludge solids and some is released as gas (CH<sub>4</sub> and CO<sub>2</sub>).

Figure 6 shows the initial and final percent uptake of solid to liquid  $(A_s/A_L \times 100)$ . Initially the larger portion of C<sup>14</sup> was in the liquid phase in 16 out of 28 digesters. This result would be expected since the labelled acetate was introduced as a liquid. Actually, considering the wide range of uptake values no real trend in initial distribution of C<sup>14</sup> can be established. The final uptake value at the end of the digestion run is greater than 100% in 25 out of 28 cases which corroborates the findings that the liquid usually has the lower final concentration of radioactivity. Further, each of these 25 uptake values exceeded 600%. Since the initial solid to liquid ratio was always less than 600%, it is shown that the liquid lost radioactivity, while the solid gained, between the start and end of digestion.

Due to the wide scatter of the values on all four graphs and the lack of sufficient data at the 1.0 and 100  $\mu$ c/l

page 146

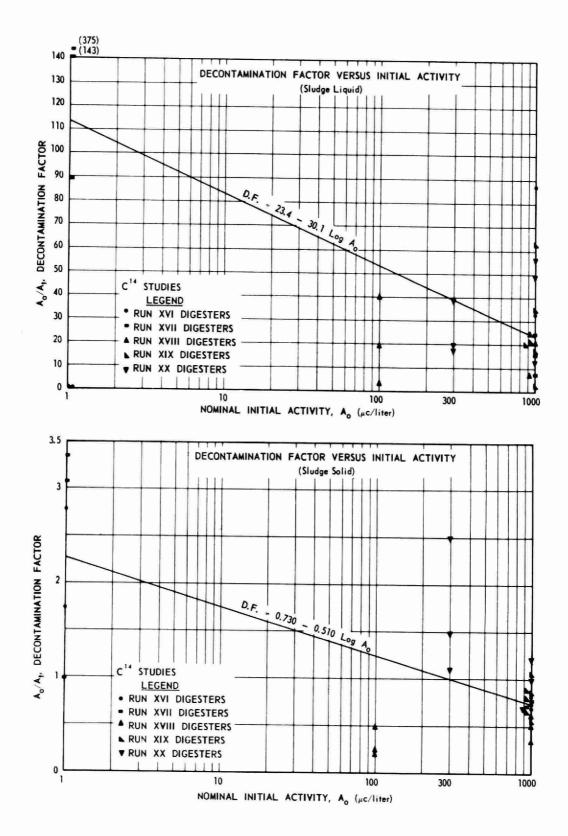


Figure 5.

page 147

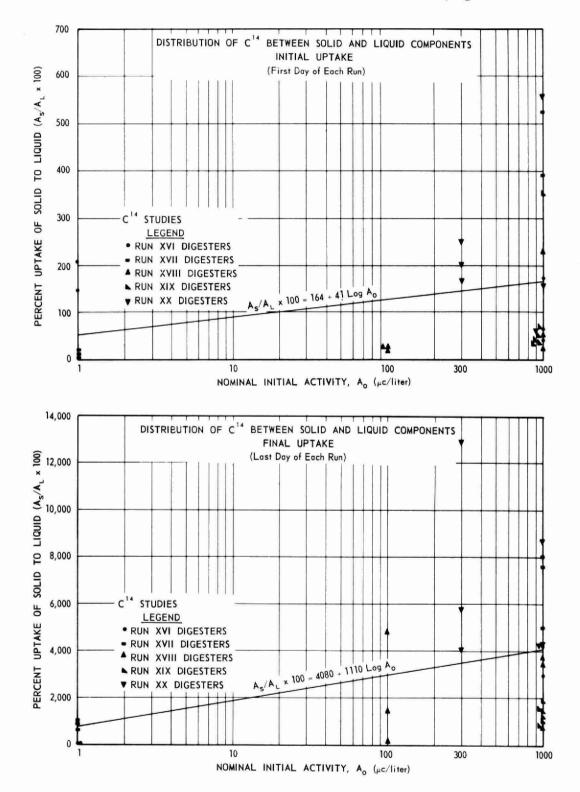
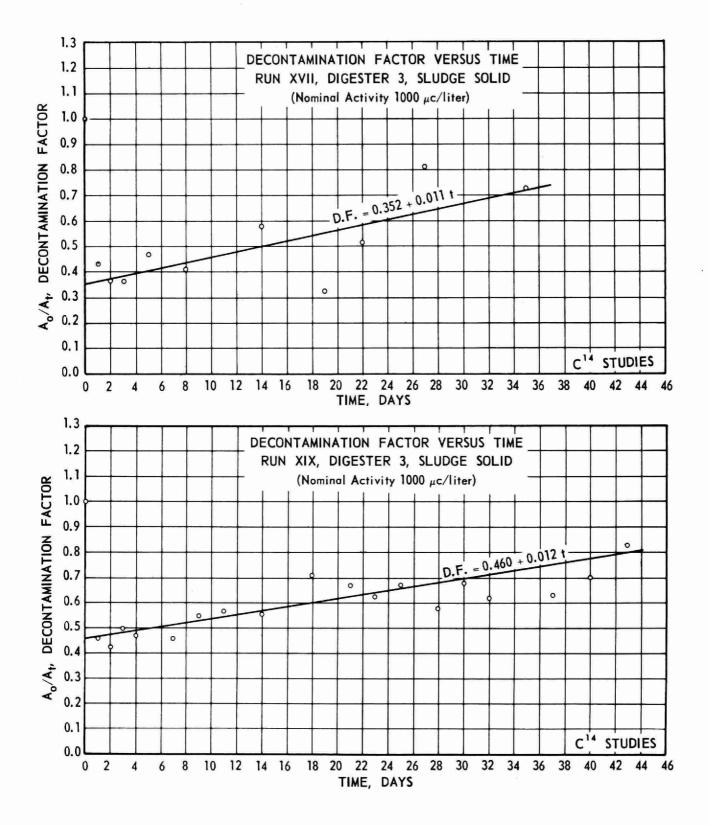


Figure 6.

page 148



activity concentrations, no special physical significance can be assigned to the lines of best fit. The scatter of data can be attributed mainly to the heterogeneity of the substrate sludge and the variation between sludges used in the individual runs.

To follow the distribution of  $C^{14}$  with time, sludge samples were withdrawn every few days from digesters 3 and 6 during all Cl4 runs to determine more clearly the distribution of radioactivity between the solid and liquid as a function of time. Figure 7 presents typical data from Runs XVII and XIX for the decontamination factors of solids for digester 3 which contained 1,000  $\mu$ c/l Cl4. From these graphs it may be noted that the solid gained radioactivity during the first day of digestion due to absorption and adsorption by the biological mass, but lost activity during the remainder of the digestion period, i.e., At for the sludge was decreasing with time. However, the gain over the first day was more than the loss during the remainder of the digestion period. This result agrees with the above observation that the solids gained radioactivity during digestion. In any event, the sludge solids do not end up with a decontamination factor,  $(A_0/A_t)$ , greater than 1. Actually, the solids are starting to pick up  $C^{14}$  at time, t = 0. The radioactive carbon is given off slowly for the duration of the run but represents a net overall gain which may be due to an elutriation effect in the digester. As may be seen in Figure 7, there are day to day variations in the decontamination factors and some of these are fairly large. Further studies of activity distribution are necessary before any functional relationship can be established.

# PRELIMINARY WORK ON METHANE FERMENTATION MECHANISM

The breakdown of carbonaceous material by bacteria into CH4 and  $CO_2$  is a complicated process because of: (1) the wide range of chemical entities which decompose under anaerobic conditions to give CH4 +  $CO_2$ , (2) the large number and variety of microorganisms found to thrive in the cultures, and (3) conflicts arising due to over simplification of the mechanisms of methane fermentation.

Probably the third is the most necessary point of attack on the problem of understanding the process of digestion. It is Known that in a digester the gases form by decarboxylation of acetic acid. Other processes are known to exist, such as the fixation of  $CO_2$  with a production of oxidized substances with a subsequent step of reduction of  $CO_2$  all the way to CH<sub>4</sub> by the reduced substances.

Since acetic acid is always found during methane fermentation, one is inclined to regard it as an important, if not universal precursor, of methane. Three possible mechanisms for the methane fermentation of acetic acid have been suggested by previous workers in this field:

(1) From their work, Omelianskii (23, 24) and Söhngen (25, 26) expected a preliminary decomposition of acetic acid to hydrogen and carbon dioxide, with subsequent reduction of the carbon dioxide to methane by hydrogen.

(2) Barker's work in 1936 (27) entirely supported the theory proposed by Van Niel that methane is formed biologically by the reduction of carbon dioxide.

(3) The reasoning of Buswell and Neave (28) was that methane originates primarily by a simple decarboxylation of acetic acid.

More recent work done on the methane fermentation mechanism with radioactive tracers has shown that the acetate breakdown gives CH4 from the methyl group and CO<sub>2</sub> from the carboxyl group (29)

Methanol also proceeds without labilization of the three hydrogens to give CH4. Pine and Vishniac (15) showed that the "enrichment" cultures, adapted to acetate, change apparent mechanisms when fed with acetate-methanol mixtures or with methanol. They found that with Carbon<sup>14</sup>-labelled acetic acid in the two position the yield of  $Cl^{4}H_{4}$  was 94% and the yield of  $Cl^{4}O_{2}$  was only 2.7% which supports the findings of both Buswell and those of Stadtman and Barker. However, of special interest is what happened when methanol was added to sodium acetate (labelled in the two position). A depression of the  $Cl^{4}H_{4}$  yield to only 52% of the methane due to the addition of methanol during anaerobic fermentation was noted. More significant even is the almost tenfold increase in the  $Cl^{4}O_{2}$ yield which increases to 21.8%. Thus, with the addition of methanol the production of  $Cl^{4}O_{2}$  considerably increases. It would appear that methanol induces an oxidation of the methyl group of the acetate to  $CO_{2}$ . A common intermediate in the acetate and methanol fermentations to methane is proposed to account for some of the reported results.

More recent advances indicate that probably all the reported products and changes of chemical composition are actual. The mechanisms involved however are subject to some discussion. The reduction of  $CO_2$  to  $CH_4$  is now proven. The intermediate steps are far from clear. Likewise the splitting of  $C^1H_3C^200H$  to  $C^1H_4$  and  $C^2O_2$  is also well demonstrated. However, again the mechanism is not clear.

To further define the processes occurring in sludge digestion requires the identification of more of the materials going in and out of the system. Further, realization that any organism which has been shown to be present in sewage and sludge systems can be present in the system allows one to explain almost any phenomena observed in a digester.

Thus, breakdown of glucose to  $\text{CO}_2$  and  $\text{H}_2$  by E. Coli could explain the traces of  $\text{H}_2$  observed by Buswell. The cleavage of CH<sub>3</sub>COOH explains the production of CH<sub>4</sub> and CO<sub>2</sub> with labelling as found by Barker. Some form of CH<sub>2</sub> fixation is shown by Barker and Pine and Vishniac to explain CO<sub>2</sub> reduction to methane as found by many workers for some time. With all these processes occurring concurrently in a plant digester, or a continuously fed digester, it is no wonder confusion arises as long as one part of the picture is taken as "the" way the reaction proceeds.

The ideal manner to further pursue the studies on the mechanism of methane fermentation would be by carefully conducting studies with pure cultures on pure substrates and following the kinetics closely with  $C^{14}$  tracer methodology.

In an effort to shed additional light on the mechanism of methane fermentation, Carbon-14 was fed to the digesters in the form of sodium acetate with  $C^{14}$  labelled in the number one and two positions. The approach taken was a time-rate study of three substrates which were expected to provide an indication of the mechanism of reaction:

- (1)  $CO_2$  as carbonate should show immediate activity in  $CO_2$  production with later production of  $Cl_4H_4$  due to assimilation of the tagged carbon dioxide.
- (2)  $CH_3C^{14}O_2H$  should show immediate carbon dioxide activity with slower production of  $C^{14}H_4$  again due to assimilation of the  $C^{14}O_2$  first produced.
- (3) Cl<sup>4</sup>H<sub>3</sub>CO<sub>2</sub>H should show immediate Cl<sup>4</sup>H<sub>4</sub> activity with very low Cl<sup>4</sup>O<sub>2</sub> activity at any time, if the acetic acid is the immediate precursor of the gases and is not assimilated to build larger molecules within the organism.

From the experimental results it was found that apparently  $C^{14}$  can be and is assimilated to some extent from the two position; and thereafter can reappear as  $CH_{\mu}$  or  $CO_2$ .

The direct reduction of  $CO_2$  by  $H_2$  sounds unlikely during the continuous digestion process; except for very specific bacteria, such as E. Coli fermentation of glucose. The other possible mechanism, leading to  $CH_4$  production by bacteria as suggested by Buswell (12) indicates that  $CO_2$  and  $CH_4$  come from a decarboxylation reaction. However,  $Cl^4O_2$  has been found to give rise to  $Cl^4H_4$ . This shows that either  $CO_2 + 4H_2$   $\longrightarrow$   $CH_4 + 2H_2O$ , or some organism in the <u>cluture</u> is capable of ingesting  $Cl^4O_2$  with the ultimate production of some radioactive compounds which serve as precursors to the  $Cl^4H_4$  formed. Both routes are supported by data from pure culture on pure substrates.

#### EXPERIMENTAL RESULTS

Carbon-14 in the form of  $BaCO_3$ , as received from the Oak Ridge National Laboratory, was converted to sodium acetate by the modified Grignard reagent method according to Calvin, et al (30). A method for the separation of the total CO<sub>2</sub> and CH<sub>4</sub> in the sludge

gas was developed. The CH4 was converted into  $CO_2$  by combustion. After the separation, the  $CO_2$  and the converted CH4 were precipitated as BaCO<sub>3</sub>. The precipitate was transferred to a Millipore Filter and kept in a **desiccator** pending radioassay.

The results from radioassays were troubled by the absorption of moisture by the BaCO<sub>3</sub> which affected the selfabsorption and the  $CO_2$  equilibrium of the samples. Of the five runs performed, the data for Run XVIII was most conclusive as the experimental procedure had become established (in subsequent runs difficulties with the combustion apparatus rendered the data partially invalid).

The sludge in digesters 3 and 6 was dosed with 1,000  $\mu$ c/l and 100  $\mu$ c/l of CH<sub>3</sub>Cl<sup>4</sup>OOH, respectively. This factor of 10, between the C<sup>14</sup> concentrations applied to the sludge initially, was maintained in the gases. The Carbon-l4 labelled CO<sub>2</sub>/CH<sub>4</sub> ratio was plotted for digesters 3 and 6, Run XVIII and the results are shown in Figure 8. The radioassays showed that the Cl<sup>40</sup>O<sub>2</sub> peaks from both digesters came very early and were followed by a second Cl<sup>4</sup>O<sub>2</sub> peak shortly afterwards. The Cl<sup>4</sup>H<sub>4</sub> concentration, although much lower, followed a similar pattern as the Cl<sup>40</sup>O<sub>2</sub> production to about 1,300 mls (about the fifth day). Thereafter, the Cl<sup>4</sup>H<sub>4</sub> concentration continued to increase gradually and this increase was more persistent than for the Cl<sup>40</sup>O<sub>2</sub> concentration. Although the concentration of Cl<sup>4</sup>H<sub>4</sub> never reached the value of the Cl<sup>40</sup>O<sub>2</sub>. concentration, the labelled methane did not fall off or die away, as fast as the Cl<sup>40</sup>O<sub>2</sub>.

The results obtained indicate the following:

- Most of the CO<sub>2</sub> comes from the carboxyl group without first going into CH<sub>4</sub>;
- (2) Some of the carboxyl group decomposes by means of a slower, longer pathway directly into CH<sub>4</sub>.

It is apparent that considerable further research is needed to elucidate on the methane fermentation mechanism with  $C^{14}$ -labelled tracer methodology.

Part II: Radiostrontium (Sr<sup>90</sup>) Studies

100

#### EFFECT ON GAS PRODUCTION

The maximum concentration of radioactive strontium<sup>4</sup> (Sr<sup>90</sup>) investigated was 500  $\mu$ c/l. Figure 9 shows a family of curves of cumulative gas production from Runs XXI through XXIV from digesters with plain sludge, those to which an equivalent concentration of salt<sup>5</sup> was added, and those containing concentrations of 50  $\mu$ c/l and 500  $\mu$ c/l of Sr<sup>90</sup>.

From the cumulative gas production curves, presented in Figure 9, it appears that there is no significant effect exerted by radiostrontium. These curves represent composite data from 31 digesters obtained from four runs, but include only three digesters containing 500  $\mu$ c/l or Sr<sup>90</sup> from Run XXIV. Although the cumulative gas production curve for the 500  $\mu$ c/l shows a lower initial production rate, this information is based on data from a single run only.

Figure 10 shows the cumulative gas production curves for Run XXIV, the only run in which both 50  $\mu$ c/l and 500  $\mu$ c/l concentrations of Sr<sup>90</sup> were examined. These graphs show that the same cumulative gas production characteristics are exhibited by plain sludge digesters, those containing Sr<sup>90</sup> and those containing equivalent salt concentrations. The reproducibility of gas production curves achieved also indicates that the experimental methods were under control.

It may be generally concluded that no deleterious effect on gas production due to  $\rm Sr^{90}$  was exerted at the 50 or 500  $\mu c/l$  activity levels.

As may be seen from Table IV, the efficiency of gas production, expressed as ml/gm of volatile matter added, and cu ft/lb of volatile matter destroyed, was virtually unchanged by the addition of  $Sr^{90}$  or equivalent salt. According to Van Kleeck (31), under favorable conditions of digestion, gas production should be from 11 to 15 cu ft/lb of volatile matter destroyed.

In the foregoing discussion only batch digesters 1 through 12 have been included. The recirculated digesters 13 through 16, were not included because the data obtained could not be compared with batch digesters.

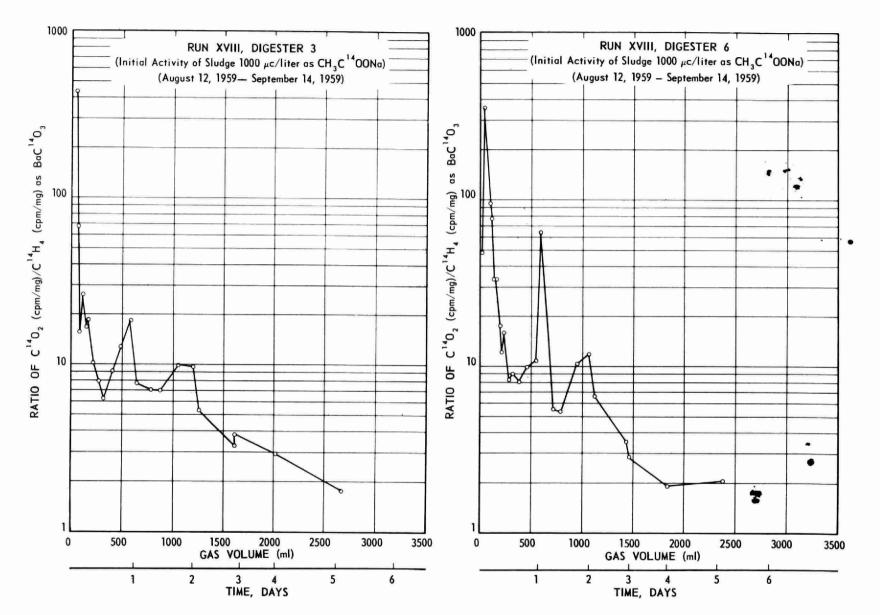
#### Reaction Velocity Constant

IL

Reaction velocity constants were computed for each of 17 digesters in all four runs with  $Sr^{90}$ , and the results from statistical analyses of the k-values using the t-test are shown in Table V.

A high specific activity of  $Sr^{90}$  (30.71 mc/ml) was used in these experiments to reduce the addition of toxic metals to the sludge. The chemical form of the  $Sr^{90}$  solution was  $SrCl_2$  in 1.96 N HCl.

The equivalent salt in these  $\mathrm{Sr}^{90}$  studies refers to an acid solution of 1  $\gg$  of 12 N HCl in 100 ml distilled water to which approximately 1 µgm of  $\mathrm{SrCl}_2$  was added. This equivalent salt solution was added to the controls to compensate for the millequivalents of chlorides added with  $\mathrm{Sr}^{90}$ . The maximum  $\mathrm{SrCl}_2$ concentration added to any digester amounted to only 1.0 mg/1.





4

14

.

.

page 154

.

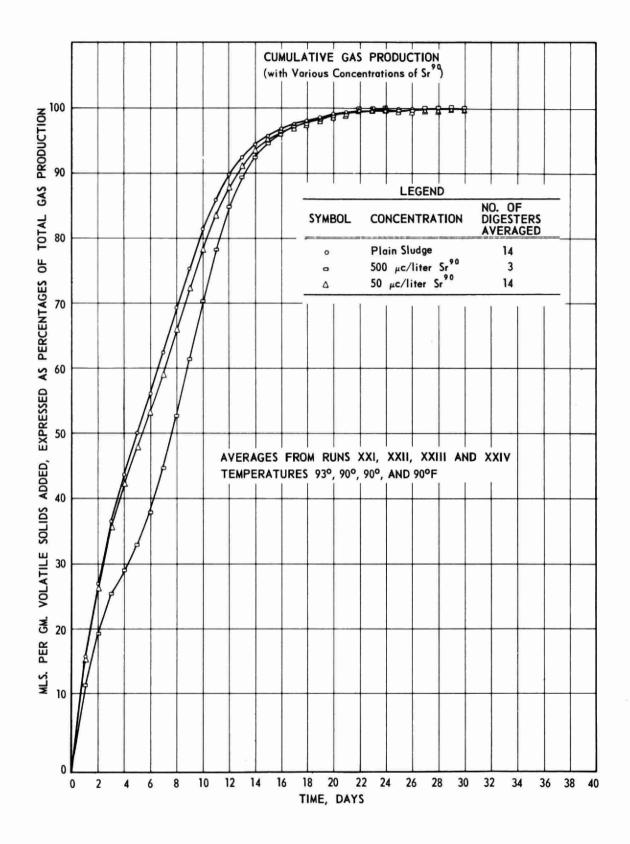


Figure 9.

At first, a significance was found in the comparison between k-values for plain digesters against k-values for all digesters containing various concentrations of Sr90. However, on investigating the data further, it was found that the data from Run XXI was significantly affecting the results5. When the radioactive digesters in Run XXI were compared with plain digesters in that run, a significant difference was found (P < 1%). With Run XXI removed, no significance between k-values of the radioactive and plain digesters was observed (P = 23.1%) for the remaining runs.

To further examine this data and to find if there were any other variables affecting the values of k, a multiple correlation analysis by means of a Burroughs 220 electronic computer was prepared. The data from 47 digesters was used to establish a relationship for k with temperature of digestion, sludge mixture (based on the initial volatile matter added), strontium chloride (salt) concentration and Sr90 activity. The multiple correlation analysis produced the following regression equation:

 $k = 18.56 - 0.196 T - 0.820 M - 0.0130 C_{salt} - 0.0000302 C_{Sr-90}$  (8)

where

- T = digester incubation temperature, °F
- M = ratio of seeded sludge mixture based on volatile content of raw sludge
- C<sub>salt</sub> = concentration of equivalent (stable) strontium chloride added to the controls, in mg/l, and

 $C_{Sr-90}$  = concentration of  $Sr^{90}$  as  $Sr_{Cl_2}$ ,  $\mu c/l_{\circ}$ 

The coefficient of multiple correlation was found to be 0.98, which is highly significant and shows that k-values could be predicted from equation (8) with a high degree of confidence.

From the multiple correlation analysis the coefficients of partial correlation, r, for the four independent variables with k were found to be:

> $r_{T} = -0.98$   $r_{M} = -0.97$   $r_{S} = -0.42$  $r_{Sr-90} = -0.51$

5

The digesters were manually shaken at the start of Run XXI which may account for the difference in the reaction velocity constant.

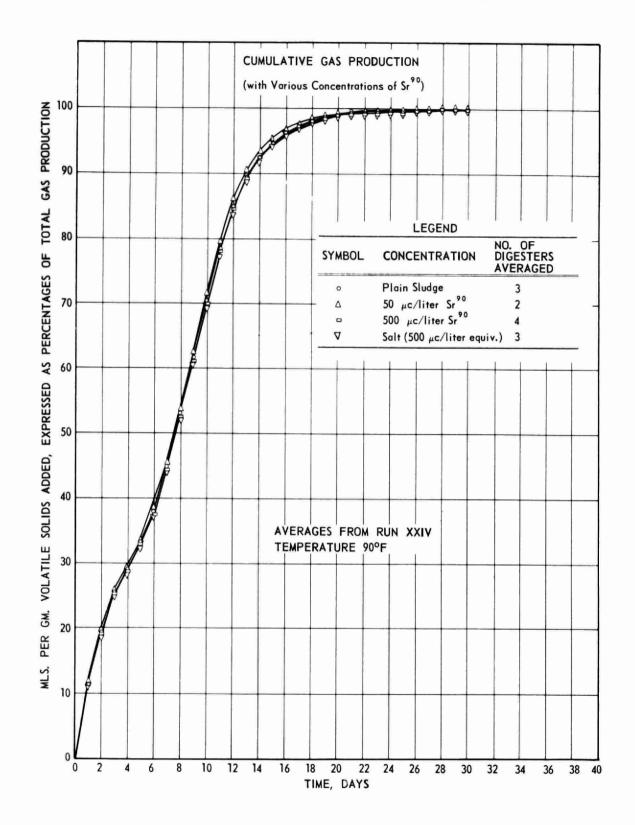


Figure 10.

#### TABLE IV

Experimental	Conditions,	Gas	Production	and	Volatile	Matter	Reduction	

Part II. Radiostrontium (Sr<sup>90</sup>) Studies

Run	Dig.		EXPERIME	NTAL C	ONDITIONS		TOTAL GA	S PRODUCTION	
Period (Days) Date	No.	Sludge Volume (ml)	Sludge Mix- ture	Inc. Temp. <sup>O</sup> F	Conc. of Salts(a) mg/l	Conc. of Sr <sup>90</sup> (µc/1)	ml/gm V.M. Added	cu ft/lb V.M. Destroyed	Reduction Volatile Matter(%)
XXI (34) 2/16/60 to 3/21/60	1 2 3 4 5 6 7 8 9 10 1 2 3 4 5 6 7 8 9 10 1 2 3 4 5 6 1 7 1 2 1 3 1 4 5 6 1 7	450   1500	1:3.5	93 <sup>°</sup>	- - - - - - - - - - - - - - - - - - -	50 50 50 - - - - 10 - -	286.8 280.9 266.0 287.1 293.5 280.4 303.1 289.5 293.8 294.1 298.6 296.5 259.6 270.0 113.0 280.5 210.9	11.6 11.5 11.2 12.2 12.3 11.6 12.6 10.5 12.0 10.2 11.9 12.0 14.7 13.8 9.9 15.1 28.6	39.5 39.1 37.3 38.1 38.6 38.6 38.6 49.3 34.1 39.3 31.4 40.1 328.4 318.4 29.8 11.8
XXII (35) 4/5/60 to 5/10/60	1 2 3 4 5 6 7 8 9 0 1 1 2 3 4 5 6 7 8 9 0 1 1 2 3 4 1 5 6 1 7	450   1500	1:1.0	90°	- - 0.1 0.1 0.1 0.1 - -	50 50 50 - - - - - - - - - - - - - - - -	288.5 285.6 290.3 298.4 305.3 291.2 305.7 298.1 293.4 302.0 297.5 285.5 324.2 303.0 281.1 304.6	11.0 11.1 12.0 12.7 - 14.1 12.8 12.8 12.4 13.1 12.4 13.1 14.9 16.7 15.2 14.8 15.8 16.7	41.9 41.3 38.0 37.6 - 33.1 38.2 37.8 37.0 38.5 38.6 31.2 32.0 27.8 30.6 29.2

(a) Salt refers to a solution of SrCl<sub>2</sub>, see footnote, page 36

TABLE IV (Cont'd)

Experimental Conditions, Gas Production and Volatile Matter Reduction

page 159

Run	Dig.		EXPERIME	NTAL C	ONDITIONS		TOTAL GA		
Period (Days) Date	No.	Sludge Volume (ml)	Sludge Mix- ture	Inc. Temp. <sup>O</sup> F	Conc. of Salts(a) mg/l	Conc. of Sr <sup>90</sup> (µc/1)	ml/gm V.M. Added	cu ft/lb V.M. Destroyed	Reduction Volatile Matter(%)
XXIII (28) 5/18/60 5/14/60	1 2 34 56 78 9011 2 34 56 7 11 12 14 156 7	450 1500	1:1.1	90°	0.1 0.1 0.1 0.1 0.1 0.2	50 50 50 50(b) - - - - - - 10 - 10 - - - - - - - - - -	296.0 286.5 284.8 296.4 293.6 291.9 292.6 288.5 293.1 294.7 295.1 287.8 308.1 303.2 294.8 290.4 304.1	13.0 $12.9$ $11.9$ $12.4$ $11.7$ $12.1$ $12.1$ $12.4$ $12.0$ $13.3$ $13.1$ $16.1$ $14.5$ $13.2$ $14.9$ $13.4$	36.6 35.7 38.1 38.3 40.0 41.6 40.1 38.3 37.4 39.2 35.5 35.2 30.6 33.5 35.7 31.3 36.5
xxIV (33) 7/7/60 8/8/60	1 2 3 4 5 6 7 8 9 9 4 5 4 5 6 7 7 1 1 1 5 6 7 8 7 9 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	450   1500	1:1.0	90° 	- - - 1.0 1.0 1.0 1.0 - - - -	50 500 500 500 500 - - - - 500 - - - - 50 -	301.8 302.3 301.3 299.6 315.4 302.7 312.0 301.9 304.5 307.5 307.2 305.8 308.3 277.1 261.6 292.23 306.7	11.0 12.9 10.1 11.2 14.1 13.0 14.6 14.7 14.9 14.8 15.0 15.3 18.6 27.8 16.7 15.3	43.3 37.5 46.8 42.7 35.8 37.3 32.9 32.7 332.9 32.7 332.8 32.1 26.0 25.1 26.1 26.2 32.2

Part II.	Radiostrontium	(Sr <sup>90</sup> )	Studies	
----------	----------------	---------------------	---------	--

(a) Salt refers to a solution of SrCl<sub>2</sub>, see footnote, page 36
 (b) C<sup>14</sup> included for autoradiographic study

#### TABLE V

Average Differences and the Probability (P) of their Occurrences by Chance Alone for k, G and  $\tau$ -Values at Various Concentrations of Carrier-free Sr-90 and Salt (\*) Added to Plain Sludge

Plain Sludge	No. of Digester	Values of k		Values of G		Values of $\tau$	
Sr-90 (μc/1)	Pairs	$\overline{d} = \frac{\Sigma(k_c - k_h)}{n}$	P (%)	$\overline{\mathbf{d}} = \frac{\Sigma(\mathbf{G}_{\mathbf{c}} - \mathbf{G}_{\mathbf{h}})}{\mathbf{n}}$	P (%)	$\overline{d} = \frac{\Sigma(\tau_c - \tau_h)}{n}$	P (%)
All runs 21-24	18	0.00363	1.70	3.072	13.8	0.0258	8.8
Run 21 Removed	14	0.000879	23.1	-38.96	38.2	-0.00157	70.0
Run 21	4	0.0133	< 1	0.175	> 90	0.131	< 1
500	4	0.00125	65.2	3.275	48.7	0.00225	79.2
50	14	0.00461	1.68	-3.156	19.9	0.0333	8.73
50 (Run 21 Removed)	10	0.00115	26.7	-55.66	39.2	0.00210	71.7

# (a) Comparing Plain Sludge vs. Sr-90

(b) Comparing Plain Sludge vs. Salt (\*)

Plain Sludge	No. of Digester	Values of k		Values of G		Values of $\tau$	
vs. Salt (ppm)	Pairs	$\overline{d} = \frac{\Sigma(k_c - k_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(G_c - G_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(\tau_c - \tau_s)}{n}$	P (%)
All runs 21-24	15	-0.000253	70.7	1.407 .	47 <b>.</b> 3	-0.00183	64.9

(c)	Comparing	Sr-90	vs.	Salt	(*)

Sr-90 (µc/1) vs. Salt (ppm)	No. of Digester	<pre>/ Values of k</pre>		Values of G		Values of $\tau$	
	Pairs	$\overline{d} = \frac{\Sigma(k_h - k_s)}{n}$	P (%)	$\overline{d} = \frac{\Sigma(G_{h} - G_{s})}{n}$	P (%)	$\overline{d} = \frac{\Sigma(\tau_h - \tau_s)}{n}$	P (%)
All Runs	16	-0.00436	2.35	-1.769	57.2	-0.0300	9.80
Run 21 Removed	12	-0.000867	37.5	-4.108	16.3	0.006333	28.7

(\*) Salt refers to solution of SrCl<sub>2</sub>

These results were also confirmed by "t" tests on the coefficients in the regression equation. Applying the null hypothesis that the expected values of the coefficients in the regression equation are zero, it was found that the calculated values differed significantly from zero, or, the hypothesis was rejected.

The results from "t" tests of the regression coefficients with the standard error of the regression coefficients and 42 degrees of freedom, showed that the dependance of k-values on temperature, mixture, salt and Sr<sup>90</sup> concentration was highly significant in each case, (t<sub>T</sub> = -29.5, t<sub>M</sub> = -28.1; P << 1% and t<sub>S</sub> = -2.96, t<sub>Sr-90</sub> = -3.82; P < 1%).

Ultimate Gas Production

The ultimate gas volumes, G, in terms of mls per gm of volatile solids added and calculated as the limiting value by the slope method, were subjected to the same statistical analyses. The results from comparisons between plain, radioactive and control sludge digesters are shown in Table V.

No significant differences of G-values were found for any of the comparisons among plain, radioactive and control sludge digesters.

To determine any real effect on G-values due to Sr<sup>90</sup>, a multiple regression analysis yielded the following regression equation expressing the functional relationship between ultimate gas production, temperature, mixture, salt and Sr<sup>90</sup> concentrations:

 $G = -5899.9 + 65.93 T + 283.6 M + 29.44 C_{salt} + 0.0557 C_{Sr-90}$  (9)

in which the independent variables are defined exactly as for equation (8).

The coefficient of multiple correlation, R, for equation (9) was found to equal 0.78.

This shows that a significant correlation exists between G-values and temperature, type of mixture, salt concentration and concentration of  $Sr^{90}$ .

The coefficients of partial correlation, r, for these independent variables with G were found to be:

 $r_{\rm T} = 0.62$   $r_{\rm M} = 0.61$   $r_{\rm S} = 0.47$  $r_{\rm Sr-90} = 0.49$ 

From examining the partial correlation coefficients the ultimate gas production value is dependent on all four variables.

This conclusion is further supported by the analysis of t-tests of the regression coefficients. All four independent variables were found to be significant at the 99% confidence level.

Effect of Lag Period

As may be seen from Figures 9 and 10, there is no appreciable increase in the lag period,  $\mathbf{\tilde{v}}$ , due to the presence of Sr<sup>90</sup> concentrations from 50 µc/l to 500 µc/l.

From a Student's "t" test analysis of  $\tau$ -values between plain digesters and those containing various levels of Sr<sup>90</sup> and controls with equivalent salt concentrations, it was established that no significant differences exist as may be seen in Table V.

From the multiple correlation analysis the following regression equation was determined:

 $\tau = 78.055 - 0.830 T - 3.535 M - 0.103 C_{salt} - 0.000262$  (10)  $C_{sr-90}$ 

in which the terms T, M, C<sub>salt</sub>, and C<sub>Sr-90</sub> are defined as previously. The coefficient of multiple correlation, R, was found to be 0.93 which shows a highly significant correlation between any or all of the four independent variables and  $\tau$ . The partial correlation coefficients show that the correlation depends greatly on the temperature ( $r_T = -0.91$ ) and the type of mixture ( $r_M = -0.90$ ). The concentrations of salt or Sr<sup>90</sup> appear to exert some influence on  $\tau$ -values ( $r_s = -0.37$ ,  $r_{Sr-90} = -0.49$ ).

The results from t-test of the regression coefficients show that all four independent variables are significant as far as  $\tau$ -values are concerned (P $\angle$ 5%).

Reduction of Volatile Matter and Volatile Acids

The results of  $Sr^{90}$  studies show that the reduction of volatile matter was generally not affected by the addition of  $Sr^{90}$  at the concentrations studied. For batch digesters, the volatile matter reduction ranged from 32 to 47%, as may be seen in Table IV. The volatile acid concentrations did not exceed 830 mg/ldue to any assignable cause and usually remained below 250 mg/lat the end of the digestion period. Therefore, it is unlikely that the addition of Sr<sup>90</sup> affected the volatile acids concentrations adversely.

#### EFFECT ON REDOX POTENTIAL, LIQUID CONDUCTIVITY AND pH

With the identical procedures as in the Cl4 studies and previously reported in greater detail (20)(32), redox potential, conductivity and pH measurements were continuously recorded. Experimental curves for a typical digester (Run XXIII, Digester 15) are shown in Figure 11. No significant differences were found between the redox potential obtained from any of the recirculated digesters within and between runs. The ORP values, obtained from a flow cell connected to a digester containing Sr90, were found to agree closely with the values from the recirculated digester containing plain sludge. As may be seen from Figure 11, the E<sub>h</sub> value reaches -200 mv on the seventh day and at the end of the 28-day digestion period has a constant value of -220 mv. Ultimate values of E<sub>h</sub> ranged from -210 to -250 mv for the Sr90 series of four runs.

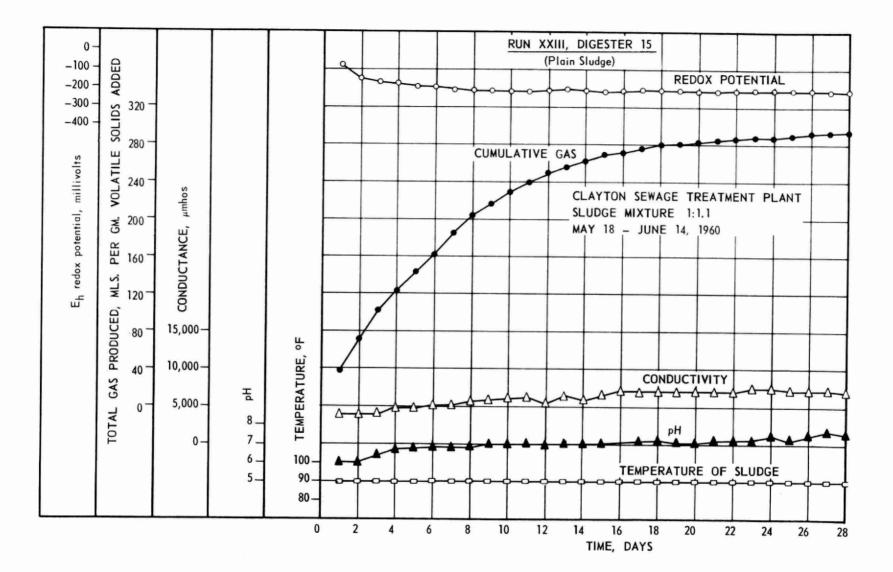
Conductivity values for recirculated digesters, containing  $Sr^{90}$  at concentrations of 10 µc/l and 50 µc/l, showed little deviation from the values obtained from plain sludges. As also shown in Figure 11, during Run XXIII the conductivity of the seeded sludge mixture was initially 3,000 µmhos and reached a final value of 7,000 µmhos for digester 15. Final values for other recirculating digesters were normally in the range of 6,000 to 9,000 µmhos. Although conductivity values for some recirculating digesters containing  $Sr^{90}$  were higher than the values obtained from plain sludge, these differences were attributed to KCl leakage from pH and ORP cells.

The results of continuous pH measurement, as shown in Figure 11, illustrates the normal pH changes. Initially, the pH value was 6.0, rising to 7.0 after five days and reaching a final value of 7.5 at the end of the 28-day digestion period. Initial pH values of the seeded sludge for the  $Sr^{90}$  series ranged from 5.8 to 6.1 and the final values were between 7.2 and 7.6. Since no pH cells were inserted in any of the recirculated digesters containing  $Sr^{90}$ , the effect of  $Sr^{90}$  on pH, if any, could not be evaluated.

The digesters to which an equivalent salt solution had been added exhibited pH, ORP and conductivity values almost identical to those of the plain digesters.

#### EFFECT ON GAS QUALITY

Chromatographic analyses of gases produced during digestion were carried out for all studies with Sr<sup>90</sup>. Samples



.

. .

٠

page 164

.

from each digester were analyzed daily during each run to follow changes in gas composition with digestion progress. Chromatograms obtained on two different days from twelve batch digesters are reproduced in Figure 12.

Analysis of the chromatographic curves for digesters 1 through 12 on the eighth day of Run XXII shows that approximately 75% of the gas produced in each digester was methane and 25% carbon dioxide.

Analysis of similar curves from the twenty-eighth day, as also shown in Figure 12, indicates little change in gas composition with time for the plain, salt or Sr90 containing digesters. Applying the null hypothesis that there exists no real difference in gas quality between digesters, the data shown in Table VI and that from the other three Sr90 runs was statistically analyzed using the "t" test. The data was paired, comparing CO<sub>2</sub> concentrations from digesters with plain sludge, equivalent salt and Sr90 which were analyzed over periods of approximately 30 days. Various combinations of the first twelve digesters were used and the 95% confidence level was chosen for significance.

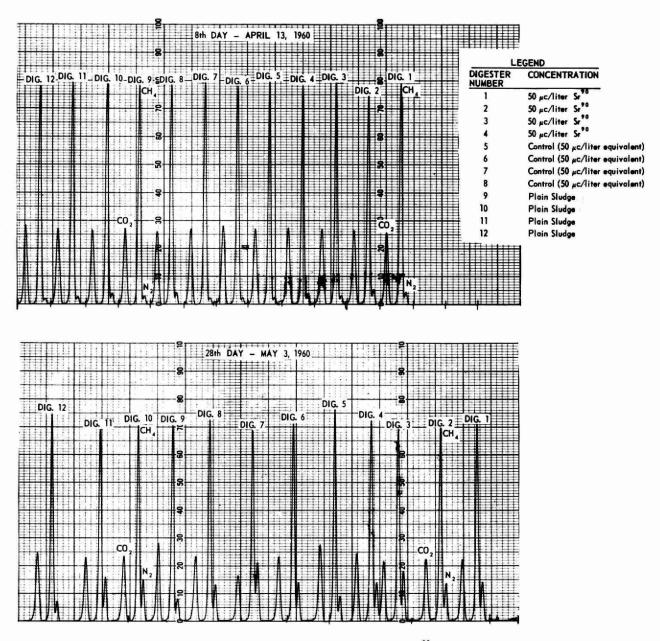
The comparison of  $CO_2$  concentrations from 18 digesters containing  $Sr^{90}$  with those containing plain sludge showed a significantly higher  $CO_2$  concentration in the plain sludge in two cases, in the radioactive sludge in eight cases, and showed no significant difference in the other eight cases. Comparison between digesters containing plain sludge and those containing equivalent salt, as well as between digesters containing  $Sr^{90}$  and those with equivalent salt showed similar inconclusive results. Therefore, the "t" tests confirm the observation that the  $Sr^{90}$  had no significant effect on the  $CO_2$  concentration in the sludge gas at the 10 µc/l to 500 µc/l activity levels.

DISTRIBUTION OF Sr<sup>90</sup> BETWEEN LIQUID AND SOLID PHASES

The procedure used in determining the distribution of  $\mathrm{Sr}^{90}$  in the solid and liquid is described in Appendix 1. The results from four  $\mathrm{Sr}^{90}$  runs are presented in Figures 13, 14 and 15.

The decontamination factors  $(A_0/A_{\pm})$  of the solid and liquid are shown in Figure 13. Since 18 out of 19 values of the decontamination factor for the solid are less than one, the final concentration in the solid is greater than the in ial concentration, showing that the solid phase gained Sr<sup>90</sup> during digestion. No definite trend for liquid decontamination was established since 11 out of 19 digesters had a decontamination factor exceeding one. It appears that in eleven digesters the liquid lost, while in eight degesters the liquid gained Sr<sup>90</sup> (D.F. $\leftarrow$ 1).

page 166



GAS CHROMATOGRAPHIC ANALYSIS OF SLUDGE GASES, RUN XXII - Sr<sup>90</sup> COLUMN: 71 FT. SILICONE GREASE FLOW RATE: 80 MLS/MIN. SAMPLE SIZE: 1.0 ML EACH COLUMN TEMPERATURE: 80°F

				10	IDIE VI		ut of ca	1001 010	xide in	DIUUge	Gas II	om Gas	Chromat	ograph	ie Anai	ysis	
							Ru	n XXII -	Sr-90	Studie	8						
Dig. No.	l	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Туре	50 µc/1	50 µc/1	50 µc/1	50 μc/1	Salt <sup>*</sup> equiv. 50 µc/l	Salt <sup>*</sup> equiv. 60 µc/l	Salt <sup>*</sup> equiv. 50 µc/l	Salt <sup>*</sup> equiv. 50 µc/1		Plain	Plain	Plain	Plain	10 µc/1	Plain	Plain	Plain
Day 1 2 34 56 78 9011234 56 78 9011 2 34 56 78 9011 2 34 56 78 9011 2 34 56 78 931 2 2 2 2 2 2 2 2 2 2 2 2 3 3 3 3 3 3 3	54.6.0.1.2.7.9.6.1.6.7.4.4.5.4.2.9.7.5.5.2.0.5.9.2.8.2.9.0.2 24.5.5.6.6.6.7.4.4.5.4.2.9.7.5.5.2.0.5.9.2.8.2.9.0.2	55.6 51.7	522887132766556554152955593081471	541633496455666666666614306115557740282222222222222222222222222222222222	54.2 50.4 43732 254.4 37332 254.4 266.4 2772 2722 288 29594 87774 27774 266.4 591 265.9 2222 26.4 591	55.6 51.4 3333222222222222222222222222222222222	55.8 50.0 437.6 328.2 24.5 22.2 22.2 22.2 22.2 22.2 22.2 22	54.3 50.7 42.6 8 31.7 25.0 2222222222222222222222222222222222	54.4 51.1 438.3325.8 254.8.160222222222222222222222222222222222222	54.5 56.2244.209.222222222222222222222222222222	5555945092789828886545165594840 22222222222222222222222222222222222	5,1,5,9,8,9,6,5,7,9,8,9,6,3,7,8,1,7,5,5,1,0,8,3,3,8,5,1,9,8,5,5,5,4,4,4,4,4,2,2,2,2,2,2,2,2,2,2,2,2	55.0 55.0 55.1	55.6.1.1.90.7.5.4.7.9.5.5.0.2.7.1.8.1.5.3.5.5.4.7.4.7.4.8.2.5.3 22.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.2.	54.3 53.44.44.40.0 330.79.83.222.222.222.222.222.222.222.222.222.	55.9 49.06 54.05 54.05 54.05 54.05 54.05 54.05 50 50 50 50 50 50 50 50 50 50 50 50 5	page 167 51.8 52.9 54.4 54.4 54.4 55.4 54.4 55.4 54.4 55.4 55.4 54.4 55

.

### Table VI Per Cent of Carbon Dioxide in Sludge Gas from Gas Chromatographic Analysis

\* Control salt approximate Sr-90

.

page 168

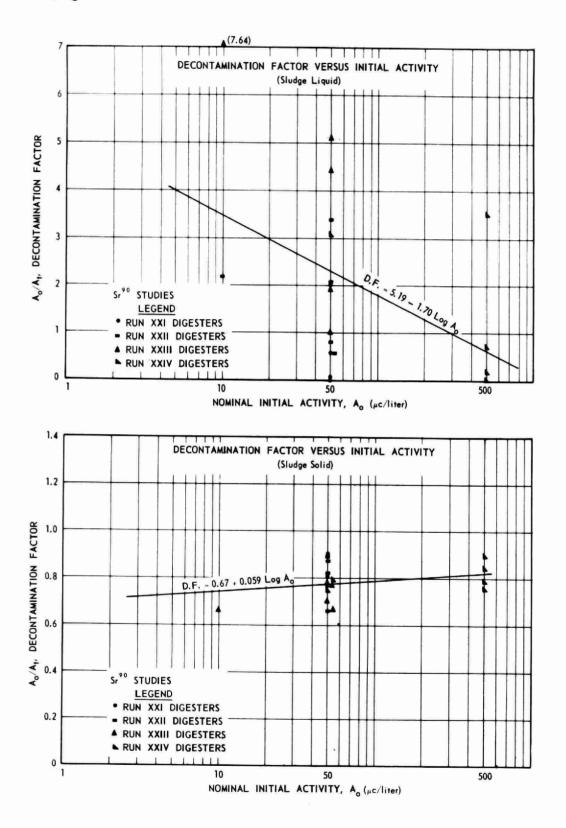


Figure 13.

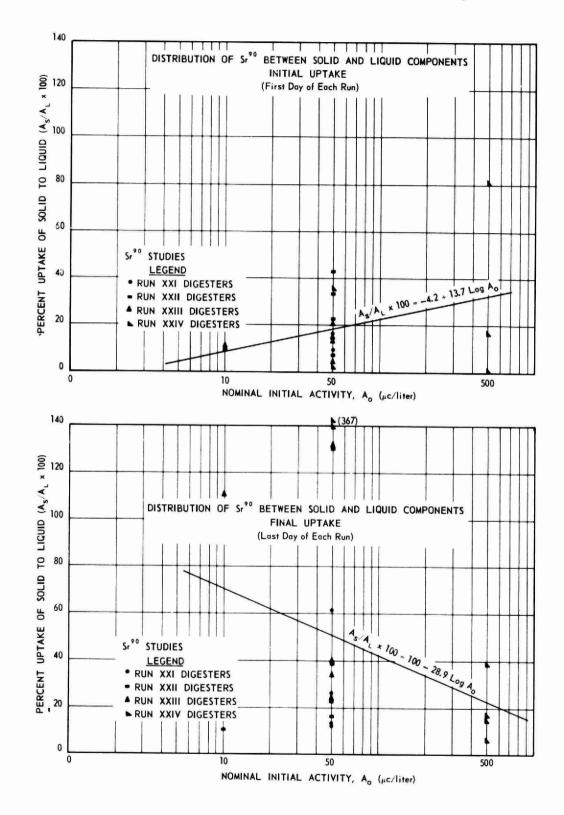
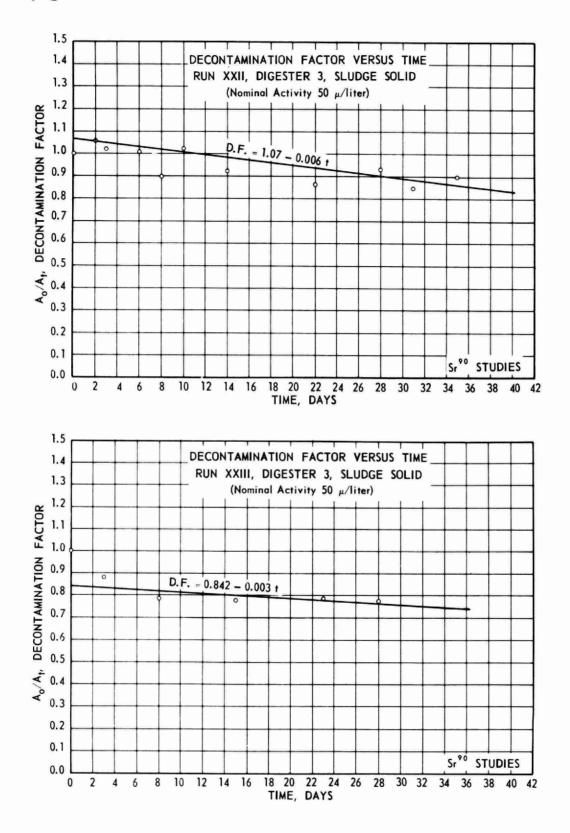


Figure 14.

page 170



In figure 14 the initial and final percent uptake of solid to liquid,  $(A_s/A_L \times 100)$ , are shown. All values of initial uptake are less than 100%, indicating that the liquid contained more of the radioactivity than the solid. Since Sr90 was introduced as a solution of SrCl<sub>2</sub>, the higher concentration in the liquid phase was expected. For 15 out of 20 digesters the final uptake was also less than 100, but since the values are spread over a wide range, no trend could be determined. However, the values for the final uptake factors were generally larger than the initial uptake, indicating that the solid had gained some Sr90 during digestion.

To obtain information about the distribution of  $Sr^{90}$ as a function of time, digester 3 was sampled during each of the four  $Sr^{90}$  runs. Figure 15 presents typical data from Runs XXII and XXIII for the decontamination factors of the solids for digester 3 which contained 50 µc/l of  $Sr^{90}$ . Both curves show a slight linear decrease in decontamination factors confirming the trend of a slight increase of activity by the solid with time.

#### CONCLUSIONS

These investigations on the effects of radioactive materials and their distribution during anaerobic digestion included five runs with concentrations of  $C^{14}$  as CH3COONa up to 1,000 µc/l and four runs with concentrations of Sr90 as SrCl<sub>2</sub> up to 500 µc/l. Based on the analysis of the experimental data, the following conclusions may be reported:

### Results from Carbon-14 Studies

1. The rate of gas production from similarly prepared, seeded mixtures with and without Cl4 was not significantly affected up to 1,000  $\mu$ c/l. There were also no significant differences in the reaction velocity constants between plain sludge and controls (containing equivalent concentrations of CH<sub>3</sub>COONa).

2: Ultimate production of gas, lag-phase period, volatile acids concentration and reduction of volatile matter were not deleteriously affected by concentration of  $Cl^4$  up to 1,000 µc/l.

3. With Run XIX removed from the statistical treatment of the data, it appears that the total gas production may have been somewhat depressed in the presence of Carbon-14. However, the average difference between G-values shows only borderline significance (P = 8.76%) if the test for significance is based on the 95% level.

4. From multiple correlation analyses it was found that a high degree of correlation exists for k, G and  $\tau$ -values with the type of seeded mixture, equivalent salt, and C<sup>14</sup> concentrations as the independent variables.

į

5. Although statistically significant lower  $CO_2$  concentrations were found in most of the digesters containing stable or radioactive acetate, the average concentrations differed by no more than 1 to 3%.

6. To establish the distribution of  $C^{14}$  in the sludge, a study of the decontamination factors,  $(A_0/A_t)$ , for the liquid and solid phases revealed that the sludge solids gained radioactivity during the digestion period. Although this result may be expected since  $C^{14}$  was added to the sludge as  $CH_3COONa$ , the liquid phase usually lost radioactivity during the digestion period, some of the  $C^{14}$  being released as gas  $(CH_4 \text{ and } CO_2)$ .

7. From a preliminary investigation of the methane fermentation mechanism with  $C^{14}$  in the one and two positions of CH<sub>3</sub>COONa, it was found that: (a) most of the CO<sub>2</sub> is derived from the carboxyl group directly, without first going into CH<sub>4</sub>; and (b) some of the carboxyl group is decomposed by a slower, longer pathway to form CH<sub>4</sub> directly.

Results from Strontium-90 Studies

1. No deleterious effects on gas production in the presence of  $Sr^{90}$  concentrations from 10 to 500 µc/l were observed.

2. Ultimate gas production values, lag-phase periods, volatile acids concentrations and reduction of volatile matter were not significantly affected by concentrations of  $Sr^{90}$  up to 500 µc/1.

3. A very high degree of correlation was found for k, G and  $\checkmark$ -values with the incubation temperature, type of mixture, equivalent salt, and C<sup>14</sup> concentration. Incubation temperature and type of seeded mixture (ratio of raw to digested solids) were found to exert the greatest influence of the independent variables on the three parameters: k, G and  $\checkmark$ .

4. No significant differences between ORP, conductivity or pH values from plain, radioactive or control (equivalent salt) digesters were found in the presence of Strontium-90

5. Strontium-90, in concentration from 10 to 500  $\mu$ c/l, exerted no significant effect on sludge gas quality as determined by daily gas chromatographic analyses.

6. From a study of decontamination factors,  $(A_0/A_t)$ , to establish the distribution of  $Sr^{90}$  in sludge, it was found that the concentration of radioactivity in the sludge solids is greater at the end of the digestion period than at the beginning.

### LIST OF REFERENCES

- (1) National Committee on Radiation Protection, "Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and in Water for Occupational Exposure", National Bureau of Standards Handbook 69, U.S. Government Printing Office, Washington 25, D.C. (1959)
- (2) Dobbins, W. D., "Biological Methods for the Removal of Radioactivity from Liquids", Presented at the Nuclear Engineering and Science Congress, sponsored by Engineers Joint Council, Cleveland, Ohio (December 12-16, 1955)
- (3) Straub, C. P., et al, "Sanitary Engineering Aspects of Nuclear Energy", Progress Report of the Committee of the Sanitary Engineering Division on the Sanitary Engineering Aspects of Nuclear Energy, Proc., A.S.C.E., 81, Separate No. 646 (1955)
- (4) Lowe, H. N., Jr., Lacy, Wm. J., Surkiewicz, B. F. and Jaeger, R. F., "Destruction of Microorganisms in Water, Sewage and Sewage Sludge by Ionizing Radiations", J.A.W.W.A., <u>48</u>, 1363 (1956)
- (5) O'Meara, J. P., "Radiation Chemistry and Sterilization of Biological Materials by Ionizing Radiations", <u>Nucleonics</u>, <u>10</u> (February 1952)
- (6) Ridenour, G. M. and Armbruster, E. H., "Effect of High-Level Gamma Radiation on Disinfection of Water and Sewage", J.A.W.W.A., <u>48</u>, 671 (June 1956)
- (7) Dunn, C. G., "Treatment of Water and Sewage by Ionizing Radiations", <u>Sewage Works Journal</u>, <u>25</u>, 1277 (1953)
- (8) Narver, D. C., "Is Sterilization of Sewage by Irradiation Economical?", <u>Civil Engineering</u>, <u>27</u>, 618 (1957)
- (9) Mick, K. L. and Linsley, S. E., "An Examination of Sewage Solids Incineration Costs", <u>Water and Sewage Works</u>, <u>104</u>, 11, 479 (1957)
- (10) Buswell, A. M., "Fermentations in Waste Treatments", <u>Industrial Fermentations</u>, <u>Vol. II</u>, Chapter 14, Chemical Publishing Co. Inc. (1954)
- (11) Pine, M. J. and Vishniac, W., "The Methane Fermentations of Acetone and Methanol", <u>Journal of Bacteriology</u>, <u>73</u>, 736 (1957)
- (12) Buswell, A. M. and Mueller, H. F., "Mechanism of Methane Fermentations", <u>Industrial and Engineering Chemistry</u>, <u>44</u>, 3, 550 (1952)

- (13) "Stretch-Out Ahead for A-Power Building", <u>Engineering-News</u> <u>Record</u>, <u>164</u>, 8, 21 (February 25, 1960)
- (14) "Who's Building the Civilian Reactors?", <u>Nucleonics</u>, <u>18</u>, 1, 19 (January 1960)
- (15) "A-Power Plant Takes Shape on the Hudson", <u>Engineering-News</u> <u>Record</u>, <u>164</u>, 11, 40 (March 17, 1960)
- (16) Weber, F. J., "Status of Regulations of Ionizing Radiation on the Federal Level: Responsibilities of the U. S. Public Health Service", <u>Nuclear Engineering and Science Conference</u>, Preprint Paper No. 21 (April 4-7, 1960)
- (17) Grune, W. N., Bartholomew, D. D. and Hudson, C. I., Jr., "Effects of Radioactive Materials on Anaerobic Digestion", Part I. Radiophosphorus, <u>Sewage and Industrial Wastes</u>, <u>30</u>, 9, 1123 (1958) Part II. Radioiodine, <u>Sewage and Industrial</u> <u>Wastes</u>, <u>30</u>, 11, 1399 (1958)
- (18) Grune, W. N., Philip, R. H., Jr. and Cossitt, R. E., "Anaerobic Process Automation by ORP, Conductivity and Gas Chromatography", presented at the <u>12th Industrial Waste</u> <u>Conference</u>, <u>Purdue University</u>, Lafayette, Indiana, May 14, 1957, <u>Proceedings</u>, pp. 604-635 (May 1958)
- (19) Grune, W. N. and Lotze, T. H., "Redox Potentials in Sewage Anaerobiosis", <u>Water and Sewage Works</u>, <u>105</u>, 1, 37 (1958)
- (20) Grune, W. N., Philp, R. H., Jr. and Borsh, R.J., "Applications of ORP, Conductivity and Gas Chromatography on Sludge Digestion", presented at the 2nd Bio-Oxidation Conference, Manhattan College, April 25, 1957 (New York, N.Y.) "<u>Biological Treatment of Sewage and Industrial Wastes</u>", <u>Vol. II</u>, Chapter 1-8, p. 80-96, Reinhold Publishing Company, New York, N.Y. (1958)
- (21) Grune, W. N., Carter, J. V. and Keenan, J. P., "Development of a continuous Gas Chromatographic Analyzer for Sludge Digestion Studies", <u>Sewage and Industrial Wastes</u>, <u>28</u>, 12, 1433 (1956)
- (22) Thomas, H. A., Jr., "Analysis of the Biochemical Oxygen Demand Curve", <u>Sewage Works Journal</u>, <u>12</u>, 504 (1940)
- (23) Omelianski, W., <u>Zentr. Bakt. Parasitenk.</u>, <u>Abt. II</u>, <u>8</u>, 193, 225, 257, 289, 321, 353, 385 (1902)
- (24) Omelianski, W., <u>Zentr. Bakt. Parasitenk., Abt. II</u>, 11, 369 (1905)

- (25) Söhngen, N. L., Proc. Acad. Sci. Amsterdam, 8, 327 (1905)
- (26) Söhngen, N. L., <u>Rec. trav. chim.</u>, 29, 238 (1910)
- (27) Barker, H. A., "Studies Upon the Methane-Producing Bacteria", <u>Arch. Mikrobiol.</u>, <u>7</u>, 404 (1936)
- (28) Buswell, A. M. and Neave, S. L., "Laboratory Studies of Sludge Digestion", <u>Illinois State Water Survey Bulletin</u>, No. 30 (1930)
- (29) Stadtman, T. C. and Barker, H. A., "Studies on the Methane Fermentation. IX. The Origin of Methane in the Acetate and Methanol Fermentations by Methanosarcina", <u>J. Bact.</u>, <u>61</u>, 81-86 (1951)
- (30) Calvin, M., "Isotopic Carbon", p. 175-179, John Wiley and Sons, New York, N.Y. (1949)
- (31) Van Kleeck, L. W., "The How and Why of Operating Separate Sludge Digestion Tanks", <u>Wastes Engineering</u>, <u>29</u>, 22 (1958)
- (32) Grune, W. N. and Chueh, C. F., "Redox Potential in Waste Treatment - Laboratory Experiences and Applications", presented at the 29th Annual Conference Pennsylvania Sewage and Industrial Waste Associations, August 28-30, 1957, <u>Sewage and Industrial Wastes</u>, <u>30</u>, 479 (April 1958)

### SAMPLE PREPARATION METHODS FOR DETERMINING THE DISTRIBUTION OF RADIOACTIVITY BETWEEN LIQUID AND SOLID PHASES

Approximately four mls of sludge was removed from designated digesters containing radioactivity periodically (on the average twice a week) throughout all runs. Each digester was provided with a withdrawal tube to which a length of Tygon tubing was attached. To withdraw sludge, a length of glass tubing was attached to the Tygon, a syringe attached to the upper end of the glass tubing and the sludge drawn into the glass tubing. After withdrawal, the Tygon tubing was clamped again until the next sludge transfer. These precautions were essential to prevent air from entering the digester. The sludge was transferred from the glass tubing into a clean, dry 10 ml pyrex test. tube and stored in a refrigerator. A portion of the sludge from this test tube was deposited on a planchet and allowed to dry. This sample was called the "mixture" sample and was used as a check on the solid and "liquid" samples described below.

The sludge remaining in the test tube was centrifuged and the supernatant separated from the solid by pouring off into another test tube. The remaining solid was washed and deposited on a planchet. This was called the "solid" sample.

The supernatant was filtered through a type HA filter in a l-inch millipore filter apparatus. One ml of the filtered supernatant was placed on a planchet and dried. This sample was called the "liquid" sample.

These samples were counted in a Nuclear Chicago, Model D-47 gas-flow counter. The gross cpm thus determined were corrected for background to obtain the net cpm count rate.

To correct the net count rate of each sample for self absorption, a self absorption curve was determined. To prepare this curve, the desired radioisotope was added to the sludge and approximately 40 samples were prepared, using the same procedure employed for the preparation of the run samples. The area and weight of each sample was determined and the thickness (mg/sq.cm) evaluated. Using the thickness and net count rate of each of these samples a self-absorption curve was prapared with self-absorption plotted as a function of sample thickness.

### ACKNOWLEDGMENTS

The authors are indebted for the assistance of a number of colleagues who were associated with various phases of this program: Professors J. M. DallaValle, Wm. H. Eberhardt and I. Grovenstein, who gave freely of their time Dr. Wm. F. Atchison and Professor Wm. W. Hines, of the Rich Electronic Computer Center, who assisted Messrs. Neal Aaron and Carlton Neville in the multiple correlation analysis of the data.

Much credit is due to Mr. Roy C. Peek, Jr., who carried out the synthesis of labelled sodium acetate from radioactive BaCO<sub>3</sub> and who also guided much of the experimental work on the methane fermentation studies. Valuable assistance was rendered throughout these investigations by a number of research assistants, including Jack M. Hawkins, who worked most diligently on many phases of the program, and Joseph H. Mehaffey, who handled electrical and instrumentation problems; a number of laboratory and graduate student assistants, including Miss Kay C. Brook, Bruce Bunsen, Neal Aaron, Carlton F. Neville, Marvin A. Turner, Ray A. Smith, John M. Gutermuth, Miss Ann Minkin and George P. Bigelow, who carried out most of the laboratory investigations.

The authors are also indebted to a number of industrial organizations for their splendid cooperation and technical advice. Mr. William H. Williamson, of Industrial Instruments, Inc. provided the conductivity bridge and a 4-point recorder for conductivity; Mr. Frank Mascitti, of Brown Instruments Division of Minneapolis-Honeywell Regulator Company, loaned us a 6-point pH recorder, and Mr. Douglas Dismukes, of the Fischer & Porter Company, cooperated in many ways by supplying ORP cells, flowmeters, redox potential and temperature recorders. The Wheelco Instruments Division of the Barber-Colman Company provided a strip-chart recorder for chromatographic analysis studies.

The research reported herein was sponsored by the National Science Foundation under Research Grant NSF-G5942. The work on gas chromatography was sponsored by the National Institutes of Health under Research Grant RD-4945. We are indebted for the financial support from these agencies, without whose assistance these investigations could not have been conducted.







AFTER DINNER SPEAKERS -- JUNE 26

## EXTREME VARIATIONS IN BREWERY WASTE CHARACTERISTICS AND THEIR EFFECT ON TREATMENT

by

J. T. O'Rourke

## EXTREME VARIATIONS IN BREWERY WASTE CHARACTERISTICS AND THEIR EFFECT ON

### TREATMENT

by

J. T. O'ROURKE

Ryckman, Edgerley, Burbank & Assoc.

and

H. D. TOMLINSON

Washington University St. Louis, Missouri

## J. T. O'ROURKE

INTRODUCTION

Prior to the turn of the century, the problems of waste treatment associated with the brewing industry were not serious since there were a great number of waste sources with only relatively small pollutional loads. Today, however, the industry is producing two and a half times as much beer with only one-tenth the number of breweries that were operating in 1900 (1) (2). It is this twenty-five fold concentration of brewing activities that has imposed some serious problems on existing sewage treatment facilities and has created a need for new or additional facilities in the municipalities where the breweries are located. A single brewery, in a moderately sized community, may double or even triple the total pollutional load of the community in terms of biologically oxidizable material (3). The industry, in general, has done an outstanding job in reducing the strength of their liquid wastes by employing extensive by-product recovery. It has not, however, made much progress in eliminating the soluble organic materials from its final waste streams.

### CURRENT WASTE LOADS FROM THE BREWING INDUSTRY

During 1960, 229 breweries operating in 33 of the 50 states, consumed in excess of four billion pounds of farm products and paid nearly 800 million dollars in federal taxes, while producing some  $9^{4}$  million barrels of beer (2). At the same time this industry discharged between 180 to 500 gallons of waste per barrel of beer brewed containing from 400 to 1200 mg/l of 5-day BOD and from 200 to 500 mg/l of suspended solids (4) (5).

From this current production of beer, it is estimated that the brewing industry discharges between 17 and 47 billion gallons of waste annually, or an average of approximately 82 million gallons per day. It is further estimated that the industry discharges in excess of 430,000 pounds of 5-day BOD per day. This is equivalent to the waste discharged by nearly 3 million persons per day.

### PURPOSE

Since the final composite waste from any brewery is the combination of wastes from various batch type operations, its strength and constituency may vary greatly. The extent of these extreme hourly variations has never been reported. The purpose of this study was two-fold; first, to determine the magnitude of the hourly variations in strength of a total brewery waste and, secondly, to determine the amenability to biological treatment of the composite wastes by the total oxidation principle.

#### SCOPE OF WORK

The first phase of this investigation included the measurement of hourly waste discharges from a typical brewery and the collection of continuous hourly samples for three different types of working days. The continuous hourly samples were collected for three typical working days, namely, a start-up days, (Monday), a mid-week day (Wednesday and Thursday), and a shut-down day (Friday). This method of sampling was used to evaluate the daily variations in total organic load being discharged from the brewery as well as the hourly variations. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were the primary parameters of waste strength used in this phase of the study. Suspended solids, total nitrogen and pH were also used to establish the characteristics of this waste.

The second phase of the work was the determination of the biological oxidizability of the wastes by the complete oxidation modification of the activated sludge treatment process. The overall efficiency as well as the effect of shock loading was evaluated for this type of treatment. The parameters used in this phase of the study were biochemical oxygen demand and suspended solids of the pilot plant effluents. Sludge volume index determinations and microscopic examinations were performed regularly on the mixed liquor to determine the condition of the activated sludge.

### METHOD OF STUDY

Waste Flow Measurement and Sample Collection

The brewery selected for this study was chosen for the following reasons: a) it is of reasonable size with a capacity in excess of one million barrels per year, b) it employs standard or normal brewing and bottling methods, and c) its brewhouse and bottle shop wastes can be measured and sampled independently.

Figure 1 represents the field sampling set-up. The sampling site designated manhole number 1, carried the waste from the brewhouse, racking room and grain drying operations. The site designated manhole number 2 carried the waste flows from the bottling shop operations and few of the fermentation cellars along with a small amount of domestic waste. Waste flow measurements were made with a  $90^{\circ}$  V-notch weir in manhole number 1 and a 24" rectangular weir in manhole number 2. Depth readings were taken manually, at both sites, at one hour intervals, to determine the flow rates. A series of twenty-five consecutive hourly readings was used to plot the waste discharge from the brewery.

An automatic waste sampler, also shown in Figure 1, developed and described by Hodges (6), was used to collect the hourly samples. The hourly samples collected from both waste streams were composited in proportion to the measured flow at each site to make the total brewery waste sample. A twenty-four composite was prepared from the hourly sample composites. All samples were settled for one hour and were carefully decanted into clean sample bottles. This was done to remove excess grain. These hourly samples were analyzed for chemical oxygen demand, biochemical oxygen demand, pH and total nitrogen in accordance with Standard Methods (7). Suspended solids concentrations in the hourly samples were determined by the membrane filter technique (8).

#### Sample Analysis

The COD was determined on all samples collected during the first sampling period to provide information of the total organic load being discharged from the brewery and also to provide a basis for the estimation of the BOD. BOD was determined on all composited samples to determine the total biologically degradable organic material discharged from the brewery as well as the hourly and daily variations. The hourly and daily population equivalent for the wastes were also obtained from this analysis.

At least one series of twenty-four consecutive hourly samples along with some other selected samples, were analyzed for total nitrogen to gain information and insight as to the average BOD to nitrogen ratio for a given day and the ratior at various ranges of BOD.

Suspended solids analyses were performed to predict the range of suspended material to be expected from a brewery practicing the most rigid solids recovery procedures.



FIGURE I. FIELD SAMPLING SETUP

### Pilot Plant Operation

To simulate as nearly as possible actual practice, continuous flow, bench scale activated sludge units, shown in Figure 2, were used in the biological treatment studies. Four units of the same size and design were constructed from clear plexiglas. The size of the units was based primarily on the desired aeration times of up to thirty hours at a minimum flow of about 100 ml/hour. These factors indicated that the units should be in the neighborhood of 3 to 4 liters in volume. The units as constructed has an average volume of 3955 ml. Each unit was equipped with a movable partition to separate the aeration zone from the sedimentation zone. This partition was pinned at its lower end and formed a snug, sliding fit against the walls of the unit. This type of construction enabled the varying of the overflow rate in the sedimentation zone without changing the rate of flow to the unit.

The feeding rates to the pilot plants were controlled by the use of capillary tubes in the closed feed bottles. The capillary tubes controlled the rate of air flow into the feed bottle, and, thus, the rate of feed from the bottle. The rate of flow was easily changed by varying the length of capillary tube.

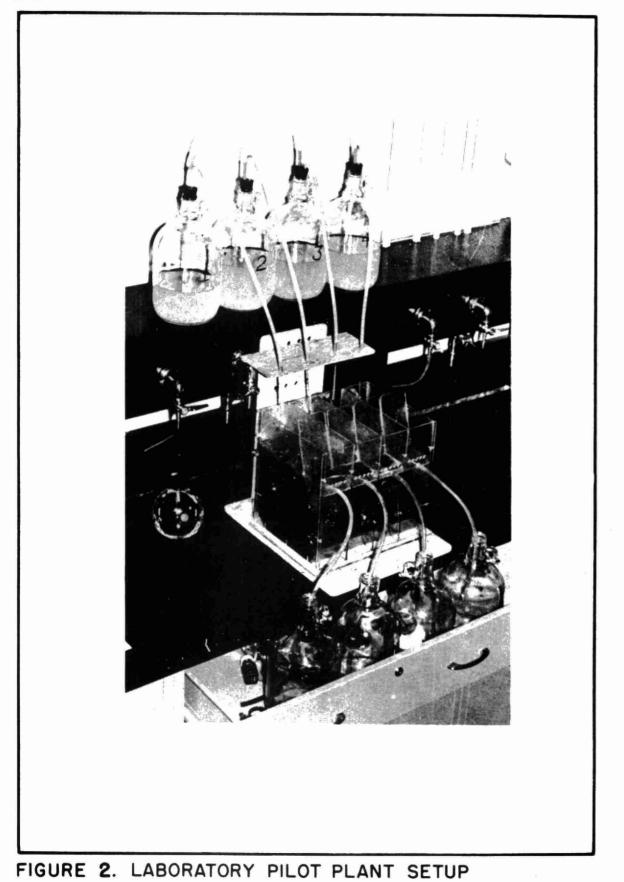
During the acclimation periods, grab samples of brewery waste were fed to all units with loadings ranging from about 20 to 100 pounds per thousand cubic feet of aerator capacity per day. The rates of flow and strength of waste, during these periods, were kept constant until a particular grab sample was depleted. The actual test series was divided into two runs, one without the aid of supplemental nutrients and the second with the BOD:N:P ratio held at 100:5:1 by the addition of inorganic nitrogen and phosphorus.

### DISCUSSION OF RESULTS

Extreme Hourly Variations in Waste Characteristics

Even a casual examination of the results presented here indicates that the rates of water use and waste discharge and the strength of the wastes from the brewing industry are far from uniform. A more complete evaluation of these data points out that these wastes exhibit extreme hourly variations as well as significant variations on a daily basis in pollutional strength. The water use data for a typical year indicates substantial variations in the volume of water used and, consequently, the volume of waste discharged on a monthly basis.

The hourly water used rate as shown in Figure 3 indicates a minimum rate being used in the early morning when the only activity in the brewery was maintenance and cleanup in the bottle shop, while the highest rate occurred just before noon when the brewery was in full operation.



## TABLE I

.

.

# Waste Characteristics of Typical Mid-Week Day

Time	COD mg/l	BOD mg/l	Nitrogen mg/l	BOD/N	Suspended Solids mg/l	Flow MGD	Discharge #/BOD/hr.	Flow Ratio Bottle Shop to Brewhouse
5 - 6 P.M. 6 - 7 7 - 8 8 - 9 9 - 10	548 747 1915 699 1568	376 584 1268 4 <b>0</b> 3 1045			0 80 126 22 0	1.408 1.367 1.425 1.465 1.231	184 277 627 205 451	10.30 8.65 11.65 16.95 16.65
10 - 11 11 - 12 12 - 1 A.M. 1 - 2 2 - 3	1524 1387 812 2340 714	1015 760 468 1400 244	26.9 22.7 31.1	17.4 61.7 8.4	102 74 68 114 38	1.005 0.975 0.945 0.723 0.561	352 257 154 351 47•5	15.10 17.90 11.5 4.5 5.17
3 - 4	3155	1562	45.3	34.4	126	Q.546	296	6.17
4 - 5	2210	1252	38.2	32.8	134	0.553	241	6.3
5 - 6	484	101	19.6	5.1	28	0.576	20.2	8.4
6 - 7	584	295	7.4	39.9	34	1.104	113	8.5
7 - 8	1082	546	11.8	46.3	26	1.484	281	16.0
8 - 9	1605	845	47.0	18.0	82	1.387	407	15.2
9 - 10	1945	1147	27.4	41.8	112	1.616	644	5.75
10 - 11	1190	748	19.6	38.2	92	1.588	412	6.50
11 - 12	8420	4820	9 <b>0</b> .0	53.4	204	1.377	2300	6.84
12 - 1 P.M.	2465	289	4.6	62.8	46	1.575	158	6.27
1 - 2	2110	1120	25.9	43.2	98	1.640	638	5.72
2 - 3	3850	2480	56.0	44.3	174	1.550	1330	8.50
3 - 4	3015	1806	51.2	35.3	178	1.485	930	8.30
4 - 5	5320	3520	45.9	76.7	214	1.378	1680	9.45

## TABLE II

Summary of Hourly Waste Characteristics for

## the Three Day Sampling Period

	•			_
Characteristic	Maximum	Minimum	Average	
Water Use Rate (MGD)	2.240	0.750	1.431	
Waste Discharge Rate (MGD)	1,640	0.546	1.207	
Flow Ratio Bottle Shop/Brewhouse	17.90	4.50	10.29	
pH of Bottle Shop Waste	12.10	2.40		
pH of Brewhouse Waste	7.14	3.64		
Suspended Solids in Settled Waste (mg/l)	214	0	92.6	
Total Nitrogen (mg/l)	90.0	4.6	27.4	
5-day BOD (mg/l)	4820	24	847	
BOD/N Ratio*	96.4	3.4	43.2	
Pounds of BOD Discharged per Hou	r 2300	9.2	355	
Pounds of BOD Discharged per Day	12,355	4,983	8,519	
Total Nitrogen in 24 Hour Compos (mg/l)	ite		15.7	
BOD in 24 Hour Composite (mg/l)			563	
BOD/N Ratic in 24 Hour Composit	е		35.8	

\* Of the samples analyzed for both BOD and total nitrogen

A study of brewery records indicated a general trend toward the consumption of less water per barrel of beer brewed as production increases. This was to be expected since there are certain water demands to be met regardless of the beer production. This trend was slightly offset by the lesser demand for cooling water and lower evaporation rates in the winter months when the beer production is cut back.

The data obtained from the monitoring of the waste streams at the brewery, as shown in Figure 4, indicate that the waste discharge curve for the brewery follows the same general pattern as the water use curve. The minimum and maximum waste discharge rates lagged the minimum and maximum water use rates by several hours, indicating some storage in the brewery. The waste discharge rate from the bottle shop was greater, at all times, than the discharge from the brewhouse, by a factor ranging from 4.5 to nearly 18 times as great. The bottle shop was operating two full shifts with the third being used for cleanup and maintenance, while the brewhouse was operating on a brew basis with the last brew being completed about midway in the second shift. The ratio of bottle shop wastes to wastes was generally higher during the evening hours and brewhouse was greatest after 9:00 P.M. when the brewhouse operations began to slow down. There was another great difference in these waste flows between 7:00 and 9:00 A.M. when the bottling operations were started for another day.

### Extreme Hourly Variations in Waste Strength

pH determinations performed on the hourly segregated samples revealed some interesting and significant information as shown in Figures 5 and 6. The pH of the brewhouse waste varied over a relatively narrow range of 3.64 to 7.14 while the bottle shop waste covered a pH range from 2.40 to 12.10. Generally, the brewhouse waste had a pH between 4.0 and 6.0 which was probably due to the discharge of excess yeast in the washings from fermentation cellars and storage tanks. The high and erratic pH variations in the bottle shop waste can be attributed mainly to the dumping of caustic soaker solutions from the bottle washing operations.

Complete results of the analyses performed on the mid-week day sample are shown in Table I. The maximum, minimum and average values of the waste characteristics for the three day sampling period together with selected analysis of the twenty-four hour composite sample are shown in Table II. The BOD to nitrogen ratio of the samples analyzed covered a wide range of values from 3.4 to 96.4 and had a calculated average of 43.2. Although this BOD:N ratio is considerably less than is required for optimum biological activity, it was felt that since nearly all the nitrogen entering the biological system would be retained in the activated sludge, this waste might be successfully treated without the aid of supplemental nutrients. The twenty-four hour composite sample had a BOD of 563 mg/1.

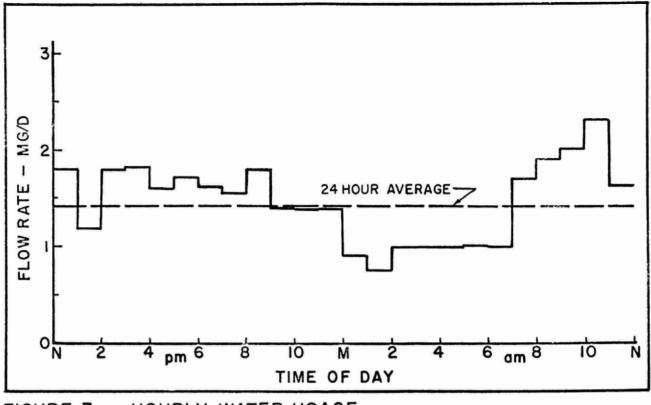
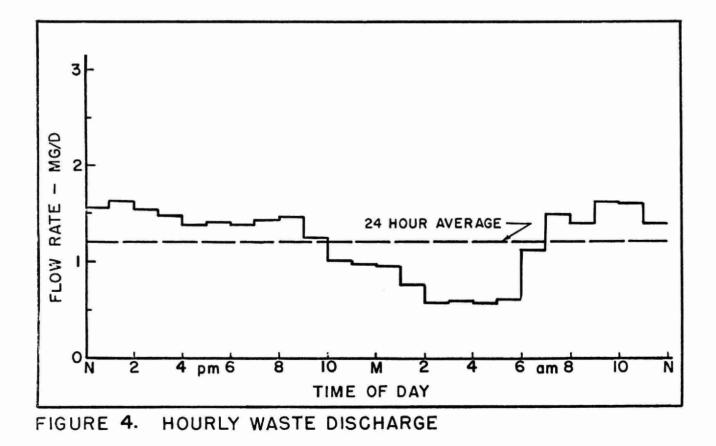


FIGURE 3. HOURLY WATER USAGE



and a BOD:N ratio of 35.8 which further indicated that an evaluation of complete oxidation treatment without the aid of additional nutrients was warranted.

The hourly variations in BOD and COD of these wastes shown in Figures 7, 8 and 9 are primarily a result of the type of processes involved in brewing. The brewing industry employs a number of batch type operations in the production of their products. After the brewing materials are processed in the various units they are removed to the next process and the units are washed and cleaned with the washings being discharged to the sewer.

The wastes discharged on the start-up day were quite weak in comparison with those discharged on the other sampling days. The samples for this type of working day were collected from noon on Monday until noon on Tuesday. The brewery had not been in operation on the week-end prior to the collection of these samples. This partially explains the occurrence of this low organic discharge as there was no possibility of washdown operations being carried over from the preceding day. All the equipment used in the brewing and bottling processes on Friday would have been washed and cleaned prior to the weekend. On this typical start-up day there was very little organic material discharged from the brewery between midnight and 7:00 A.M. This was expected since there was very little activity in the brewery during this period. The grain drying operation was not in operation on the third shift; there was normally little or no brewing on the third shift and the only activity in the bottle shop was maintenance and clean-up. Operations were normal on this day and the sample collected could be considered most typical for this type of day.

Further examination of Figures 7, 8 and 9 reveals a rather cyclic rising and falling in the waste strength during the brewing period of these sampling days. These peaks in organic strength of the waste correspond to some degree with the brew times in the brewhouse.

On the mid-week and the shut-down days the brewery operations were from two to three hours behind schedule due to some mechanical interruptions in the brewhouse. This abnormality, however, merely shifted the organic discharge distribution and did not alter the magnitude nor the erratic nature of the discharge. These difficulties may have accounted for the abnormally high organic discharges after midnight on these sampling days. However, it was found in this study that beer has a BOD in the order of 125,000 mg/l and the first washings from the bottling machinery and from the bottle shop floor, which are discharged during the early hours of the third shift could contribute a substantial BOD discharge. At this high BOD, about 625 gallons of fresh water would be required to dilute one gallon of beer to the BOD range of domestic sewage or approximately 60 gallons to dilute one twelve once bottle that might be accidently spilled. This emphasizes the need for exercising care in the prevention of product spillage and loss.



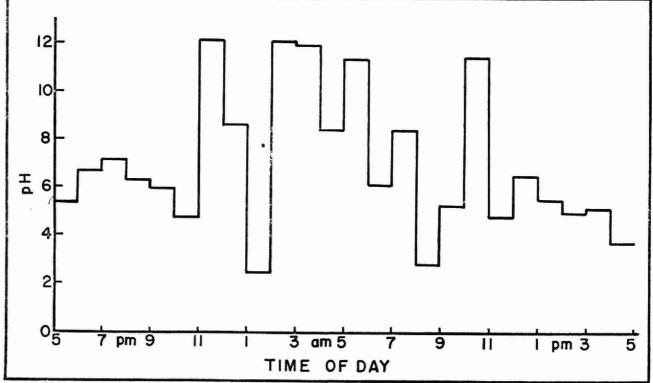
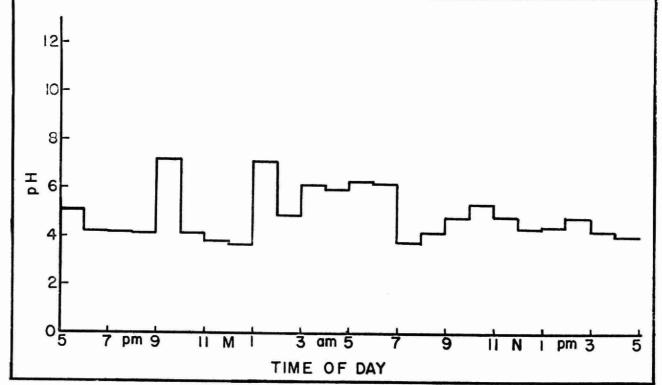
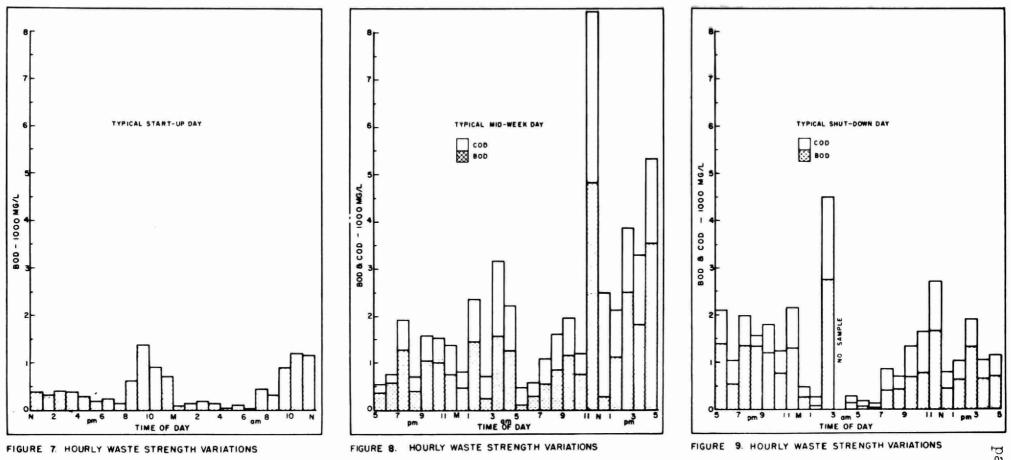


FIGURE 5. PH VARIATIONS OF BREWHOUSE WASTES





page 191

The total hourly BOD load discharged from the brewery exhibited nearly the same variations as shown by the organic concentration of the wastes. Of course, the combining factors of concentration and waste flow did, in some cases, lessen the extreme variations while at other times magnified them. The total hourly load of BOD discharged varied 256 fold while the concentration of biologically degradable materials in the waste had a somewhat lesser variation of 200 fold for the same period.

### Daily Variations in Total Waste Discharge

The total discharge of biologically degradable organic materials per day for the three typical working days sampled had a variation of 240 per cent, as shown in Table III. The range was from approximately 5,000 pounds of 5-day BOD for the start-up day to more than 12,000 pounds for the mid-week day. The discharge for the shut-down day was approximately 8,000 pounds, or just about midway between the other two days. The same quantity of beer 2325 barrels, was brewed on both the start-up and shut-down days, but at the same time better than 3,000 more pounds of 5-day BOD were discharged on the shut-down day. The bottling production was no more than 18% greater on the shut-down day. However, this relatively small difference in bottling production does not offset the discharge of approximately 65% more biologically degradable material. As mentioned above, production was started on Monday with a "clean" brewery while on the Friday sampled there was some possibility of waste carry-over from the preceding working day. The mid-week day produced a greater volume of beer and, This day, consequently, a greater amount of waste materials. like the shut-down day, was preceded by a day of full production which may have accounted for some of the waste discharged.

### TABLE III

Type of D <b>ay</b>	Barrels Brewed	Barrels Brewed Previous Day	# of 5-day BOD Discharged E	Total Popula- tion Quipvalen	Population Equivalent per Barrel t
Start up	2,325	0	4,983	29,200	12.8
Mid-week	3,255	3,255	12,355	72,650	22.4
Shut-down	2,325	3,255	8,217	48,200	20.6

Daily Variations in Total BOD Discharge

The population equivalent per barrel of beer brewed, based on biochemical oxygen demand, was nearly twice as great on the mid-week and shut-down days as it was on the start-up day, averaging 21.5 and 12.8 respectively. Both of these values fall in the range of values reported by other investigators (4) (5).

#### Effects of Extreme Variations on Biological Treatment

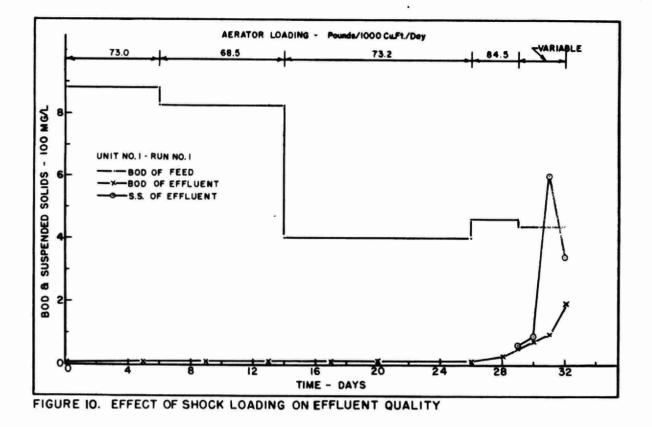
The evaluation of the effects of these extreme waste strength variations on biological treatment was divided into two series of tests. In the first test series, the settled brewery wastes were fed to the pilot plants without the addition of supplemental nutrients. When consistent BOD reductions were observed the units were considered to be acclimated and the variable loading period was started. The feed to the pilot plant units was changed every hour to maintain the natural distribution of 'waste strength variations as they occurred at the brewery.

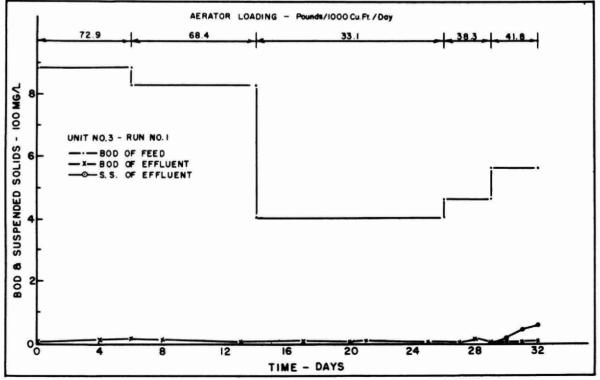
Figures 10 and 11 are representative of the results obtained in this phase of the treatment evaluation. All units, with the exception of Unit 2 gave satisfactory treatment prior to the start of the variable feeding period. In view of the fact that this test series was carried out without the addition of supplemental nutrients it is believed that the dispersed growth in Unit 2 was a result of nutrient deficiency. This difficulty could not have been caused by shock loading since the unit was being fed constant strength wastes at nearly constant flow rates. However, the two units which were fed at variable loading rates experienced a considerable loss in treatment efficiency in a relatively short time after this variable feeding was started. The control unit, on the other hand, continued to produce an effluent with a biochemical oxygen demand consistently less than 17.5 mg/l while being fed a twenty-four composite at a uniform rate of flow. It is felt that the loss of treatment efficiency experienced by Units 1 and 4 was due to the combination of shock loading and nutrient deficiency. The variable loading schedule used in this test series is shown in Table IV.

When it became apparent in run number one that the units were not adjusting to the variable feeding rates, this type of feeding was discontinued and the units were put back on the constant strength feed at constant flow rates. The feeding of inorganic nitrogen and phosphorus was started at this time and continued throughout the remainder of the biological treatment studies. Nitrogen was fed in the form of ammonium chloride and phosphorus was supplied from sodium phosphate. These nutrients were added to the feed, for all units, in sufficient quantities to maintain the BOD:N:P ratio at 100:5:1.

All pilot plant units were fed constant strength wastes at constant flow rates until they were reacclimated to the wastes. During the first two weeks of this reacclimation period, 100 ml of

page 194







fresh domestic sewage was fed per day to aid in the recovery from the dispersed or near dispersed state of growth. Again, the units were considered to be acclimated when consistent BOD removals were observed.

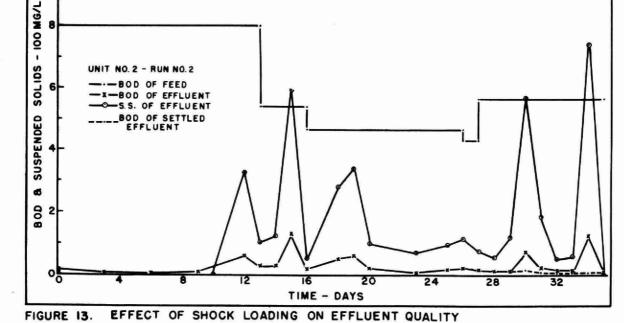
Representative results of this second phase of the treatment evaluation are shown in Figures 12 and 13. In this test series the hourly samples were composited into eight hour shift samples and fed on that basis, as shown in Table V. The results of this study indicated that the variable BOD loading caused by the extreme variations in brewery waste strength had a definite detrimental effect on biological treatment by total or complete oxidation. In both Units 1 and 4 where variable loadings were applied, the units experienced a loss in average BOD removal and an increase in sludge volume index. On the other hand, the control units in both test series, which were loaded at more nearly constant rates did not exhibit the same decrease in treatment efficiency and maintained quite stable sludge volume index values although these values were higher than desired, as shown in Table VI. The close relationship betwen biochemical oxygen demand and suspended solids concentrations in the pilot plant effluents and the low BOD concentrations in the settled effluents, as shown in Figures 12 and 13, indicates that the soluble organic material was effectively removed from solution.

### TABLE V

#### Variable BOD Loading to Pilot Plants

Run	#2
TLATT	TA

	-	Unit #1	******		Unit #4	( 
Time	Flow Rate ml/hr	BOD of Feed mg/l	BOD Loading ptcfpd	Flow Rate ml/hr	BOD of Feed mg/l	BOD Loading ptcfpd
6:00 A.M. to 2:00 P.M.	235	600	61.2	,110	1226	58.5
2:00 P.M. to 10:00 P.M.	235	455	46.4	110	1435	68.5
10:00 P.M. to 6:00 A.M.	120	298	15.5	55	851	20.3



AERATOR LOADING - Pounds/1000Cu.Ft/Day

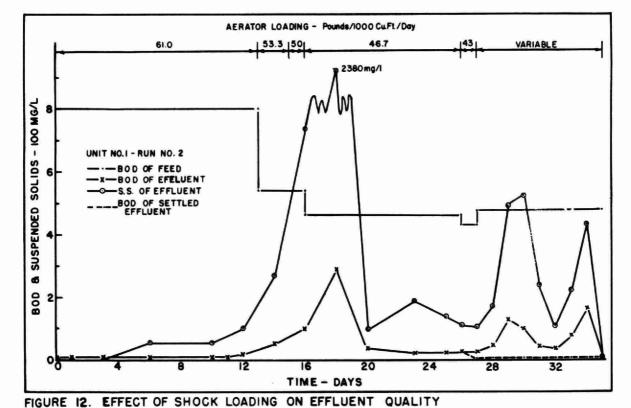
22.2

121

32.3

30.9126

45.8



# TABLE IV

# Variable BOD Loading to Pilot Plants

# Run #1

•	×	ā.				
		Unit #1			Unit #4	
	Flow	BOD of	BOD	Flow	BOD of	BOD
Time	Rate	Feed	Loading	Rate	Feed	Loading
	ml/hr	mg/l	ptcfpd ·	ml/hr	mg/l	ptcfpd
A M						
$6:\frac{A.M.}{00} - 7:00$	400	36	6.25	160	295	20 5
7:00 - 8:00	400	459	79.8	160	546	20.5 37.9
8:00 - 9:00	400	326	56.6	160	845	58.6
9:00 -10:00	400	906	157.0	160	1147	102.0
10:00 -11:00	400	1190	208.0	160	748	51.8
11:00 -12:00	400	1149	200.0	160	4820	334.0
P.M.						<u> </u>
12:00 - 1:00	400	403	70.0	160	289	20,1
1:00 - 2:00	400	325	56.4	160	1120	77.6
2:00 - 3:00	400	407	70.5	160	2480	172.0
3:00 - 4:00	400	399	69.4	160	1806	125.5
4:00 - 5:00	400	277	48.1	160	3520	244.0
5:00 - 6:00	400	189	32.8	160	376	26.0
6:00 - 7:00	400	220	38.2	160	584	40.5
7:00 - 8:00	400	144	25.0	160	1268	88.0
8:00 - 9:00	400	624	108.5	160	403	28.3
9:00 -10:00	400	1382	240.0	160	1045	72.5
10:00 -11:00 11:00 -12:00	220 220	907	8.6.7	100	1015	44.0
A.M.	220	707	67.6	100	760	33.0
12:00 - 1:00	220	102	9.7	100	468	20.3
1:00 - 2:00	220	142	13.6	100	1400	60.7
2:00 - 3:00	220	204	19.5	100	244	10.6
3:00 - 4:00	220	165	15.8	100	1562	67.8
4:00 - 5:00	220	48	4.6	100	1252	54.4
5:00 - 6:00	220	109	10.4	100	101	4.4
						-2

## TABLE VI

# Mixed Liquor Characteristics

	Date 1961	Unit MLSS mg/l	#l svi	Unit MLSS mg/l	#2 SVI	<u>Unit</u> MLSS mg/l	#3 SVI	Unit MLSS mg/1	#4 SVI
Run #1	Aug. 10 16 26 27 28	6500 5940 6500 5160 6380	- 81 116 81	7540 6680 7780 6360 6500	- 116 137 140	9340 7750 7160 7500 8240	- 102 101 100	7440 6820 6440 5380 5600	- 82 93 114
	Sept. 2 3 5 6 8 9 10 12	5120 6060 5220 5020 4940 5520 5440 5600 4240	86 91 117 104 87 110 79 104 78	5760 6680 5280 6840 5700 3840 3900 3520 3620	141 124 152 137 163 256 284 276	7380 8360 8340 7180 7160 6640 6180 6280 6420	92 70 107 123 123 133 123 134 109	5620 6340 4940 5800 5660 6280 5780 6120 6000	77 92 150 128 136 140 154 154 162
Run #2	14 16 19 20 22 29 Oct.	4460 3940 4120 4200 4960 4700	215 177 231 221 194 178	4100 4260 3880 4060 3840 5110	237 162 162 212 230 117	4880 5300 4760 5720 6160 4740	154 175 197 164 156 147	5760 5640 5300 5600 4700 4600	168 170 185 175 208 139
	5 16 23	4780 5460 6400	192 172 151	5180 5880 7380	180 161 131	5140 5940 7620	175 157 126	5360 5820 6760	174 163 140
	Nov. 6 10 11 13 14 15 16 17 19 20 21	5380 5020 4720 4860 4860 4100 3620 3780 3840 3580 3280	180 191 206 200 239 257 238 234 251 281	6820 6200 5840 6060 6400 5740 5400 5360 5420 5480	177 156 168 160 153 207 182 178 177 175 177	5480 6200 5760 5640 6120 5300 5780 5780 5760 5720 5560	177 156 168 174 160 185 161 169 167 168 174	6280 6520 5740 5500 5340 5340 5720 5460 4940 4980 5000	154 149 169 182 184 163 194 191 192

.

The results of the treatment during the variable loading period of second series were generally better than during the corresponding period of the first test series. The addition of nitrogen and phosphorus seemed to all but eliminate the tendency toward dispersed growth in the second test series. In view of the appearance of the mixed liquor during the first series, it is suspected that all the treatment units would have eventually developed a dispersed growth had the first series been continued. Nutrient deficiency is a major cause of dispersed biological growths.

The major difficulty experienced throughout these treatment studies was with the separation of the activated sludge solids from the treated wastes. As indicated by the high sludge volume index values, this sludge was very light and bulky in nature and possessed very poor settling characteristics.

Microscopic examination of the mixed liquor revealed that the sludge was made up of very light, nearly transparent masses of zoogleal growth interlaced with long filamentous strands of fungi and probably sphaerotilus. When the nature of these solids is compared with the heavy, dark granular solids normally present in an efficiently operating activated sludge plant treating domestic sewage, the settling problems discussed here become obvious.

### CONCLUSIONS

In view of the facts brought out in this investigation the following conclusions can be drawn:

- 1. It was demonstrated for the first time that the concentration of biologically degradable organic material discharged from the brewery varied from 24 to 4820 mg/l in hourly composite samples. This is a 200 fold variation in the concentration of these materials on an hourly basis.
- 2. The extreme peaks in BOD concentration correspond quite closely to the brew times in the brewery.
- 3. The organic concentration of brewery wastes, as measured by the COD, varied from 128 to 8420 mg/l in the hourly composite samples, for a variation of 65 fold.
- 4. There was a 240% variation in daily BOD load discharged during a typical work week.
- 5. The combination of the extremely high BOD of beer and the large volume of wastes discharged from the bottling operation contributed a very significant amount of the BOD to the overall pollutional load.
- 6. The 5-day BOD discharged per barrel of beer brewed showed a daily variation of nearly 200% during a normal work week,

having a domestic population equivalent ranging from 12.8 to 22.3 persons per barrel.

- 7. The pH of the hourly composite samples of brewhouse waste varied from 3.64 to 7.10 during a twenty-four hour period. However, the pH of these samples was generally between the range of 4.0 to 6.0. The pH range of the bottle shop wastes, on the other hand, was very erratic, ranging from 2.40 to 12.10. The high pH values for some of the hourly composite samples clearly indicates sizable dumps of caustic soaker solutions.
- 8. The hourly water use rate of the brewery had variations in the order of 320 per cent, while the waste discharge rates varied in the order of 300 per cent.
- 9. The shock loadings resulting from the extreme variation in brewery wastes strengths have a definite detrimental effect on biological treatment by the total or complete oxidation principle.
- 10. Variable loading of the pilot plant units caused an increase in sludge volume index and greatly impaired settling of the activated sludge solids, resulting in high suspended solids concentration in the pilot plant effluents.
- 11. The BOD in the pilot plant effluents was almost entirely due to the suspended activated sludge solids carried out of the sedimentation zone of the treatment units.
- 12. The biological system developed in this study was, however, 99% efficient in the utilization of the soluble biologically degradable organic materials in the brewery wastes.

#### ACKNOWLEDGMENTS

This investigation was supported in part by United States Public Health Service Traineeship Number 61-321.

The most willing cooperation and assistance of the personnel and management at the brewery is sincerely appreciated and acknowledged.

Further acknowledgment is made to the members of the faculty and graduate students in the Environmental and Sanitary Engineering Laboratories at Washington University for their help and suggestions during the course of these investigations. Particular appreciation is expressed for the invaluable assistance willfully rendered during the field sampling phases of this study.

#### REFERENCES

- 1. "Brewing and Malting", <u>4</u>, (475-485), 1958 Edition, Encyclopedia Americana, Americana Corporation, New York.
- 2. Brewers Almanac, 1961, United States Brewers Association, Inc., New York.
- Knoebel, I. G., "Activated Sludge Conditioning With Digester Liquor Cures Plant Overload", Waste Engineering, 29, (240), 1958.
- Mohlman, F. W., "Brewery Wastes", Modern Brewer, <u>21</u>, (35), 1939.
- 5. Rudolfs, W., "Industrial Wastes Their Disposal and Treatment", Library of Engineering Classics, Valley Stream, New York, 1961.
- Hodges, P. B., "Sampling and Flow Measuring Devices for Plant Surveys", Industrial Wastes, 5, (1), 1960.
- 7. "Standard Methods for the Examination of Water and Wastewaters", Eleventh Edition, American Public Health Association, Inc., New York, 1960.
- Engelbrecht, R. S., and McKinney, R. E., "Membrane Filter Method Applied to Activated Sludge Suspended Solids Determinations", Sewage and Industrial Waste, <u>28</u>, (1321), 1956.

A study of brewery records indicated a general trend toward the consumption of less water per barrel of beer brewed as production increases. This was to be expected since there are certain water demands to be met regardless of the beer production. This trend was slightly offset by the lesser demand for cooling water and lower evaporation rates in the winter months when the beer production is cut back.

The date obtained from the monitoring of the waste streams at the brewery, as shown in Figure 4, indicate that the waste discharge curve for the brewery follows the same general pattern as the water use curve. The minimum and maximum waste discharge rates lagged the minimum and maximum water use rates by several hours, indicating some storage in the brewery. The waste discharge rate from the bottle shop was greater, at all times, than the discharge from the brewhouse, by a factor ranging from 4.5 to nearly 18 times as great. The bottle shop was operating two full shifts with the third being used for cleanup and maintenance, while the brewhouse was operating on a brew basis with the last brew being compled about midway in the second shift. The ratio of bottle shop wastes to brewhouse wastes was generally higher during the evening hours and was greatest after 9:00 P.M. when the brewhouse operations began to slow down. There was another great difference in these waste flows between 7:00 and 9:00 A.M. when the bottling operations were started for another day.

Extreme Hourly Variations in Waste Strength

pH determinations performed on the hourly segragated samples revealed some interesting and significant information as shown in Figures 5 and 6. The pH of the brewhouse waste varied over a relatively narrow range of 3.64 to 7.14 while the bottle shop waste covered a pH range from 2.40 to 12.10. Generally, the brewhouse waste had a pH between 4.0 and 6.0 which was probably due to the discharge of excess yeast in the washings from fermentation cellars and storage tanks. The high and erratic pH variations in the bottle shop waste can be attributed mainly to the dumping of caustic soaker solutions from the bottle washing operations.

Complete results of the analyses performed on the mid-week day sample are shown in Table 1. The maximum, minimum and average values of the waste characteristics for the three day sampling period together with selected analysis of the twenty-four hour composite sample are shown in Table II. The BOD to nitrogen ratio of the samples analyzed covered a wide range of values from 3.4 to 96.4 and had a calculated average of 43.2. Although this BOD:N ratio is considerably less than is required for optimum biological activity, it was felt that since nearly all the nitrogen entering the biological system would be retained in the activated sludge, this waste might be successfully treated without the aid of supplemental nutrients. The twenty-four hour composite sample had a BOD of 563 mg/1.

page 202

# INDUSTRIAL WASTE POLLUTION OF STREAMS IN QUEBEC

by

Jean-Paul Gourdeau

# SESSION NUMBER FOUR



R. R. Parker, Vice-President, Beardmore & Company Limited, Acton. Session Chairman.



INDUSTRIAL WASTE POLLUTION

OF STREAMS IN QUEBEC

by

JEAN-PAUL GOURDEAU

Surveyer, Nenniger & Chenevert Consultants Montreal, Quebec

# INTRODUCTION

During the past two years, there has been a great deal of publicity on the pollution of streams in the Province of Quebec. From statements given to the press, one would think that all streams are highly polluted and lakes are being converted into septic tanks, while others were saying that these same streams are very clean and it is unthinkable to provide sewage treatment facilities.

Pollution does exist in certain streams but it is not a general state of affair. That pollution does exist was recognized in December 1955, when after a strong public campaign, the Lieutenant-Governor in council was authorized to form a committee of not more than five persons to study the problem of the pollution of the waters of the public domain of the Province.

This committee was asked to inquire into the nature and cause of the present pollution of these waters, try to find out the remedies therefore, and the measures required to prevent further pollution, and report its findings and suggestions to the Lieutenant-Governor in council. The members of this committee were named on August 1956.

Following a request made by this committee to the Minister of Health, to obtain the necessary data on stream quality, the "Sanitary Engineering Division" of the "Department of Health" undertook to make a study of certain rivers presenting complex and difficult problems for an efficient control of the pollution caused by sewage and industrial wastes.

Unfortunately, the president of this pollution control committee died approximately six months after his nomination and he was replaced only in April 1960. So, officially, this committee did not accomplish too much. But, unofficially, the sanitary engineering division, under the direction of Dr. Theo J. Lafreniere, its Chief Engineer, and Mr. L. Fontaine, its Assistant Chief Engineer, made extensive pollution control surveys in order to gather data on the quality of streams susceptible to be polluted.

Eight rivers were chosen, and for each of these rivers, a sanitary survey of the entire watershed drainage area was made in order to determine the actual and potential sources of pollution. This meant that attention was given to the location of sewage treatment plants, bathing areas, storm drains, sewer outfalls, industrial waste outfalls, and water intakes. To collect these data, visits were made by a sanitary engineer to the secretary-treasurer of each of the municipalities located in the watershed drainage area of the river under consideration. Visits were also made to industrial establishments to determine the pollution load contributed by these sources.

To complete this study, bacteriological, chemical and physical examinations on river water were made by trained personnel equipped with a mobile laboratory. The work included mainly sampling and analyses of river water.

It is my intention today to submit case histories of two rivers in particular which contained appreciable pollution from industrial wastes at the time of the surveys.

## ST. FRANCIS RIVER

The drainage basin of St. Francis river has an area of 3948 square miles and is located in the counties of Megantic, Compton, Frontenac, Wolfe, Stanstead, Sherbrooke, Brome, Richmond, Shefford, Drummond and Yamaska. Furthermore, part of this drainage basin is also located in the United States, in the State of Vermont. The total population residing in this drainage basin is approximately 250,000 persons and 65% of this population is served by sewer systems with outfalls into the St. Francis river or some of its tributaries.

Looking at a map of this area (Fig. 1), we can see that the St. Francis river flows from Lake St. Francis deep in the Eastern townships, to Lake St. Peter, a distance of approximately 135 miles. It winds through a rich, prosperous agricultural and industrial region receiving the influents from a number of tributaries, the most important being the Magog river which joins it at Sherbrooke.

For the most part, it is a narrow and shallow river with a total flow varying from 550 c.f.s. to 80,000 c.f.s. and with a mean flow of 6800 c.f.s. at its mouth. Larger towns located along its banks include East Angus, Sherbrooke, Bromptonville, Windsor Mills, Richmond and Drummondville.

#### Pollution Control Survey

Pollution control surveys have shown that the sources of pollution along this river are abundant and include domestic sewage as well as industrial wastes. This river today is a collecting sewer serving all the municipalities together with the industries located along its complete length as well as the length of its tributaries.

Industry is very active in this region, and consists mainly of pulp and paper and textile industries. These industries are the largest water users but, unfortunately, they also contribute heavily to the river pollution.

The pulp and paper industry produces large quantities of wastes. Paper mill wastes contain cellulose, fillers and bark for the most part, while the pulp mill wastes are high in organic matter as they contain lignins, carbohydrates and resins. In addition, they also contain such toxic materials as sulphites and various chemicals used and produced in cooking liquors.

The textile industry produces wastes both organic and toxic in character. Deterging processes, such as wool scouring, cotton kiering and silk degumming remove dirt, fat, waxes and other materials from the fibres. These are the worst of the textile wastes, since they contain large amount of highly putrescrible organic matter. Bleaching, dyeing and finishing operations produce wastes which may contain organic matter removed from the cloth as well as toxic substances from the various chemicals and dyes in the process.

# Results of the Survey

An extensive river survey was made in 1957 to determine the degree of pollution of the St. Francis river. B.O.D., D.O. and Bacteriological tests were made and the results plotted in order to determine the degree of pollution of this river. Fig. No. 2 shows the B.O.D. variation along the St. Francis river. We can see that the B.O.D. is low and reasonably constant until we reach East Angus. Immediately downstream from East Angus, the B.O.D. sharply increases to 3.4 ppm to decrease until we reach Sherbrooke, where it sharply increases again to 3.9 ppm. The same phenomena occurs at Windsor, at Richmond and at Drummondville where, nevertheless, this last increase is very small.

Graph No. 3 shows the D.O. variation and we can see that where B.O.D. increases, D.O. as expected, decreases and that these variations were observed at the same locations as was noted for B.O.D. variation.

Graph No. 4 shows the bacteriological variation along the St. Francis river. Here again, we see that the coliform count increases sharply downstream from East Angus, Sherbrooke, Windsor and Drummondville.

A careful study of these graphs shows that B.O.D. increases sharply, particularly downstream from East Angus, Sherbrooke and Windsor, and that these increases are more or as pronounced downstream from East Angus and Windsor, even though the population contributing domestic sewage at Sherbrooke is approximately 60,000 persons as compared to 4,500 persons for East Angus and 6,400 persons for Windsor.

The pollution contributed by industry is mainly caused by four pulp and paper mills which produce about 1000 tons of paper per day, and by seven large textile mills.

Bubbling gas resulting from the decomposition of organic matter on the bottom of the river, together with floating debris on the surface and on the banks of this river lead me to believe that industrial wastes were largely responsible for these high B.O.D. values.

# General Observations

It is generally accepted that a river is considered clean when its B.O.D. is below 2 ppm, and that it may be a cause of nuisance when its B.O.D. is more than 4 ppm. From these figures, it can be readily seen that the St. Francis river is a polluted river, as shown by this survey.

Since 1957, one industry in particular spent over \$400,000. to recuperate the bark and burn it instead of discharging it into the river. Another industry has made extensive studies, in order to recuperate as much as possible of the harmful chemical components and, by doing so, reduce the pollution load of its effluent.

But, even though some responsible industries have tried to reduce the pollution of this beautiful river, it must be realized that this control will only have a limited effect on the general condition of this river unless concerted action is taken by municipalities as well as industries. To make the St. Francis river a wholesome river again will not be done through the effort of a few, but only by a real co-operative effort involving positive assistance and goodwill from everyone concerned.

#### ST. CHARLES RIVER

The second river that I wish to discuss is the St. Charles river. This river has its beginning approximately twenty-five (25) miles to the north-west of Quebec City. Its total drainage basin area is two hundred and twenty-two (222) square miles.

At dry weather flows, all the water in this river at Chateau d'Eau is used by the city of Quebec for its potable water supply. It follows that a drainage basin of only eighty (80) square miles is available to supply the necessary water for the dilution of the wastes discharged into this river downstream from the Quebec City water intake.

# Upstream from Quebec City's Intate

The total population inhabiting the drainage basin upstream from the Quebec City water intake is approximately 15,000 persons, including summer residents.

No sewer system has been built; these residents, instead dispose of their sewage by means of individual septic tanks. Furthermore, sanitary inspectors, working for the city, constantly inspect this drainage basin to make sure no sewage is discharged directly into the St. Charles river, or any part of its tributaries.

During the summer months, the waters of the Nelson river and the "Riviere Jaune" are sometimes disinfected at the mouth of these rivers, to maintain fairly good quality of the water in this portion of the St. Charles river. A typical analysis of the river water, at the site of the Quebec City water intake gives the following results:

Color	:	55	ppm	
Turbidity	:	2	mqq	
Alkalinity	:	12	ppm	
Hardness	:	20	ppm	
Dissolved Oxygen	:	9	ppm	
B.O.D.	:	l	ppm	

The coliform counts through varied from 500 to 16,000 per 100 c.c.

From these results, it can be seen that upstream from the Quebec City Water intake, the river water is clear and relatively free from pollution.

Downstream from Quebec City's Intake

Unfortunately, the same conditions do not exist downstream from the Quebec City water intake. The total area of this portion of the drainage basin is eighty (80) square miles, inhabited by approximately three hundred thousand (300,000) persons, of which forty-two (42) percent discharge their domestic wastes into the St. Charles river, forty-two (42) percent discharge their domestic waste into the St. Lawrence river by means of a large collector provided with storm overflows tributary to the St. Charles river, and sixteen (16) percent discharge their domestic wastes directly into the St. Lawrence river. (Fig. No. 5).

The dry weather flow of the river, within the limits of the city of Quebec, is negligible and it is necessary to provide complete treatment before any sewage is discharged into this river. Flow studies made during this survey showed that for the summer 1960, a minimum flow of 7.5 c.f.s. was measured.

#### Pollution Control Survey

In 1960, an extensive pollution control survey made by the "Sanitary Engineering Division" of the Department of Health was made to determine the degree of pollution of this river.

Fig. Nos. 6 and 7 show that the B.O.D. is low upstream from the Quebec City water intake, it then increases to 4 ppm downstream from Lorretteville, and it again stays stable until we reach the limits of the city of Quebec.

At ebb tide, the B.O.D. increased steadily to a value of 16 ppm. This high value was observed in the mouth of the river where a large flow from the St. Lawrence river is available.

At rising tide, the B.O.D. increased sharply to a value of 12 ppm within the limits of the city of Quebec and it decreased to a value of six in the mouth of the St. Charles river. These observations were also confirmed when further tests were made at half rising and half ebb tides, as shown on Fig. 7.

Fig. No. 8 shows the D.O. variation along the St. Charles river. It can be seen that, upstream from Les Saules, the dissolved oxygen content is one hundred and twenty-five (125) percent of saturation. This high oxygen content is due partly because, at this location, the river is a fast flowing stream, but mainly because a rich bloom of algae was observed.

But, within the limits of the city of Quebec, the dissolved oxygen content decreases sharply to a value of twenty (20) percent at ebb tide. Fig. No. 8 shows only mena values, but on a few of the observations made, the dissolved oxygen content was less than zero (0) percent. This means that septic conditions were prevailing in the St. Charles river during part of the pollution control survey.

General Observations

A study of these graphs shows that the highest B.O.D. values obtained were observed in the mouth of the St. Charles river, where there is a very large flow of relatively clean water from the St. Lawrence river.

From this study and from visual observations on the different sources of pollution in this area, I personally believe that this high B.O.D. value can only be caused by a large pulp and paper mill located on the bank at the mouth of this river.

There is no doubt that a certain quantity of the sulphite process wastes are recuperated, and that this company has invested large amounts of money in research for a better utilization of by-products recovered from these process wastes. But a certain percentage of these process wastes are still discharged into the mouth of the St. Charles river.

Up to now, the general consensus of opinion was that, since the St. Charles river is a tidal river, relatively clean water from the St. Lawrence river would provide a good periodic dilution to clean up this section of the river. It was further believed that, if all the municipalities presently discharging domestic sewage into the St. Charles river were to provide sewage treatment facilities, the river would be relatively clean and free from pollution.

From this study, I believe that it will not be sufficient for the municipalities involved to provide sewage treatment facilities. At rising tide, polluted water from the mouth of the St. Charles river is forced back into the river bed, leaving organic deposits and further polluting this section of the river under the tidal influence.

Proof that the river bed is covered by a mat of organic matter was ascertained by a very active gas bubbling action which can be observed at ebb tide. It is really unfortunate that this river, instead of becoming an asset to the city of Quebec, should be allowed to become an open sewer and a menace to the general welfare of the persons residing close by. To illustrate my remarks, I have included the following pictures:

- 1) Fig. 9 shows the bed of the Lairet river
- 2) Fig.10 shows a typical bank of the St. Charles river
- 3) Fig.ll shows a sewer outfall of the city of Quebec
- 4) Fig.12 shows a process waste outfall with accumulation of debris.

A great deal of publicity is given presently to the proposed cleaning up of this river. This is not the first time this has happened. In 1911, approximately two million dollars were spent to start a cleaning action on this river, together with the construction of a dam to keep the water level constant. In 1937, a committee was formed to make a study of the then existing condition of the St. Charles river. It was recommended that a system of collectors, with storm overflows only into the St. Charles river should be built, with a sewage pumping station to force this sewage directly into the St. Lawrence river.

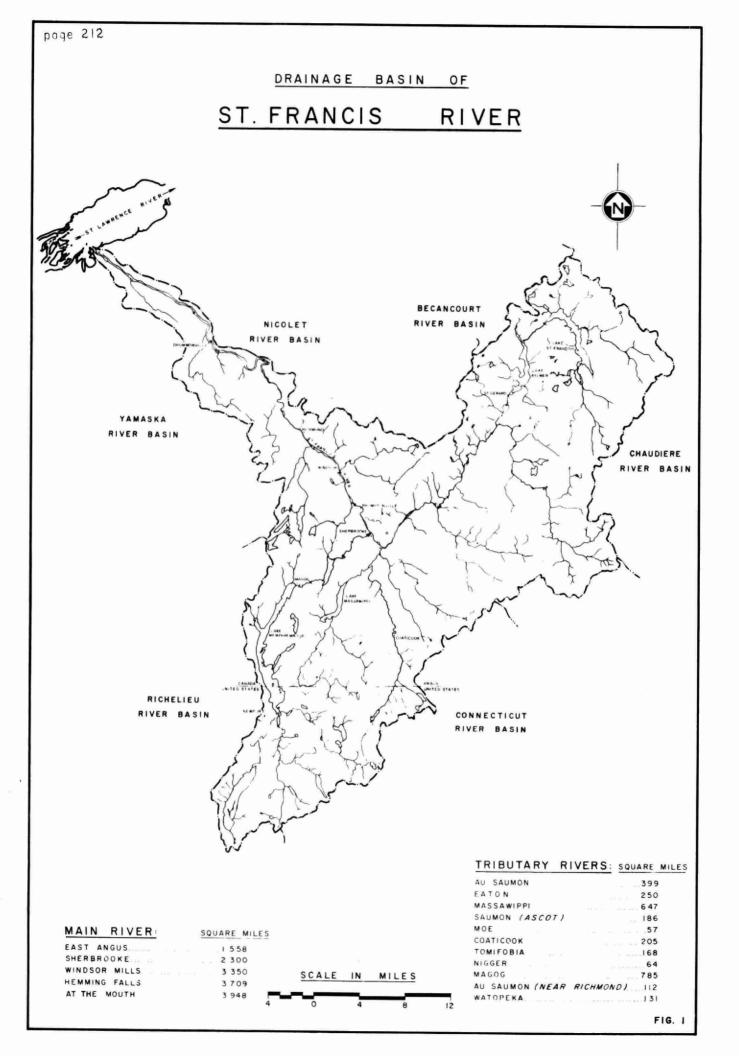
Our consulting engineering firm was retained to prepare the plans and specifications of these collectors and pumping station. Extensive flow studies were carried out, at this time, to locate the sewage outlet, into the St. Lawrence river, at such a point so that the St. Charles river would not be polluted in any way from this outfall. Unfortunately, only part of these collector works were realized. I sincerely hope that, this time, positive action will be taken to remedy the existing situation, not only by the municipalities involved, but also by the industries.

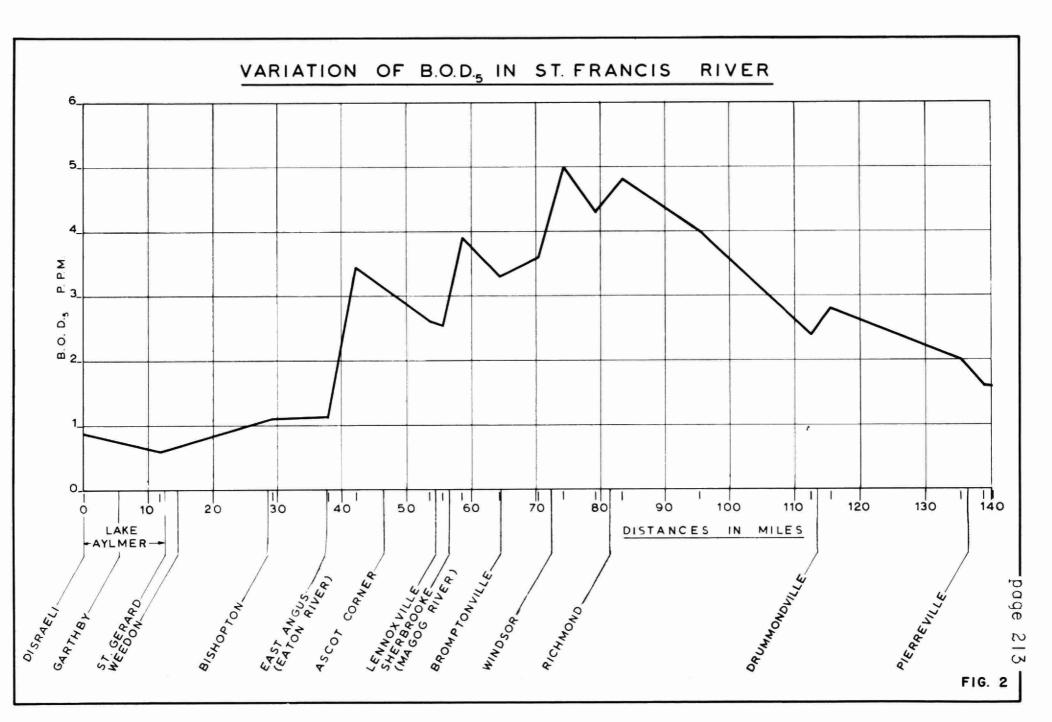
#### Conclusion

That pollution in certain areas of the Province of Quebec exists was proven by the pollution control surveys, which were made by the "Sanitary Engineering Division" of the Department of Health during the years 1957 to 1961. Real progress was made under the former legislation. Sewage treatment plants were built, but stronger powers were necessary to implement a program tending towards a better quality of receiving waters.

Even though the Board members have done all they possibly could, they were not given the necessary technical staff to assist them in carrying out the program of pollution control which they have established.

Government leaders must realize that pollution control will not be solved overnight and the success or failure of a sound planification solely depends on a highly qualified technical staff. This cannot be too strongly emphasized. Otherwise, we may see a set-back instead of a progress in pollution control during the next few years.

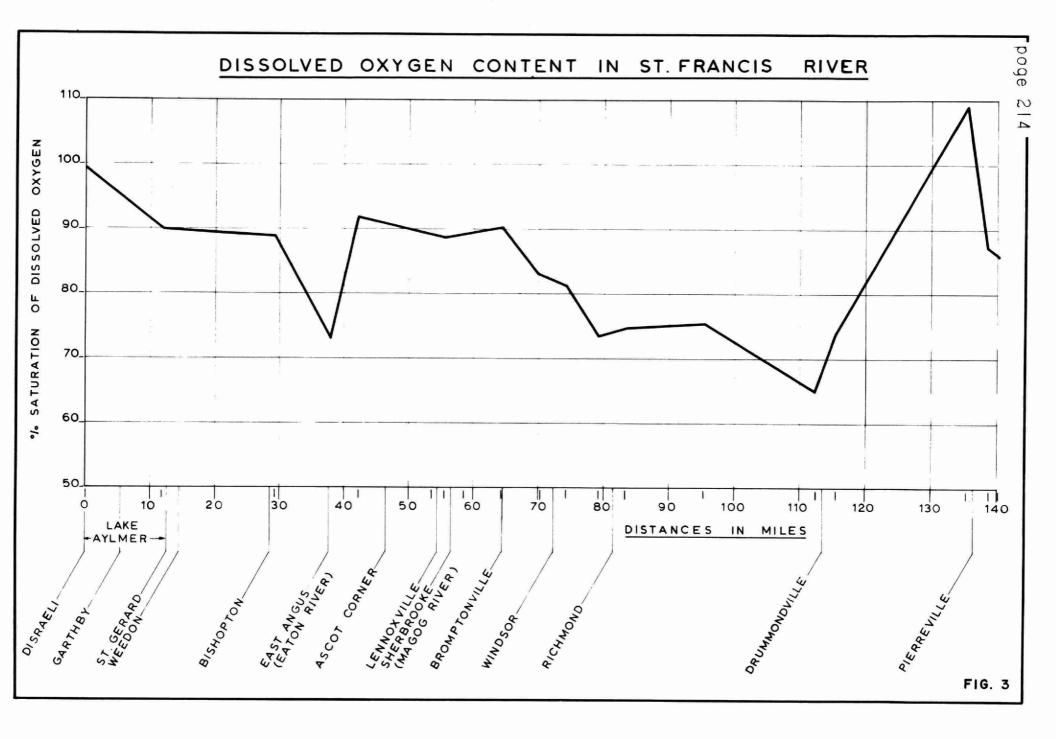




.

.

٠

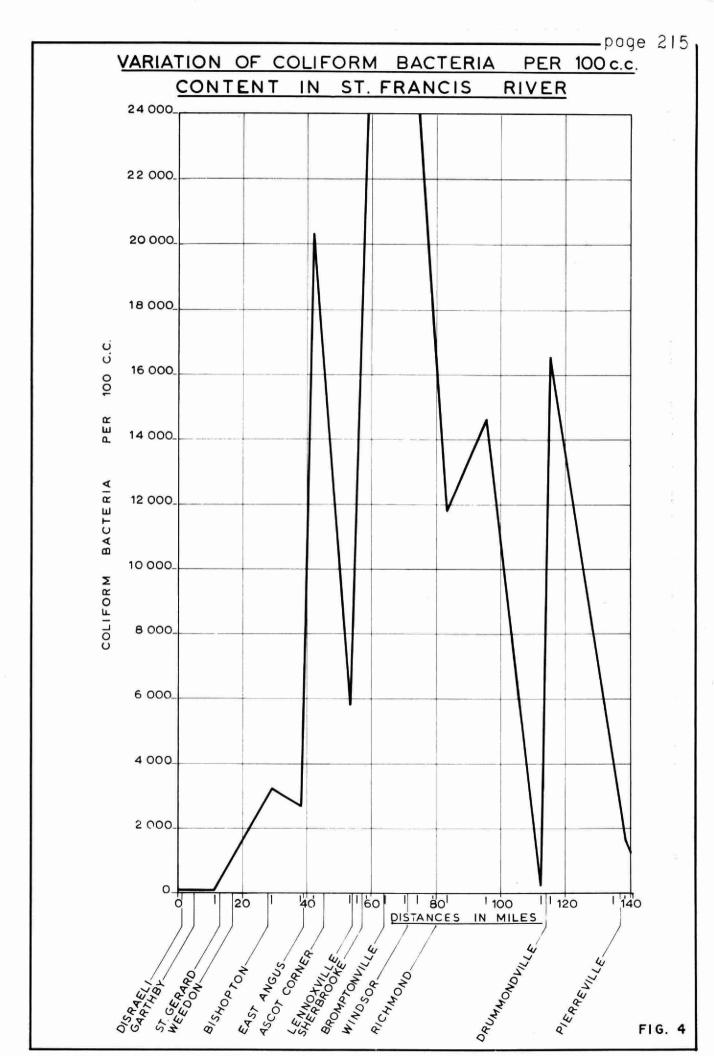


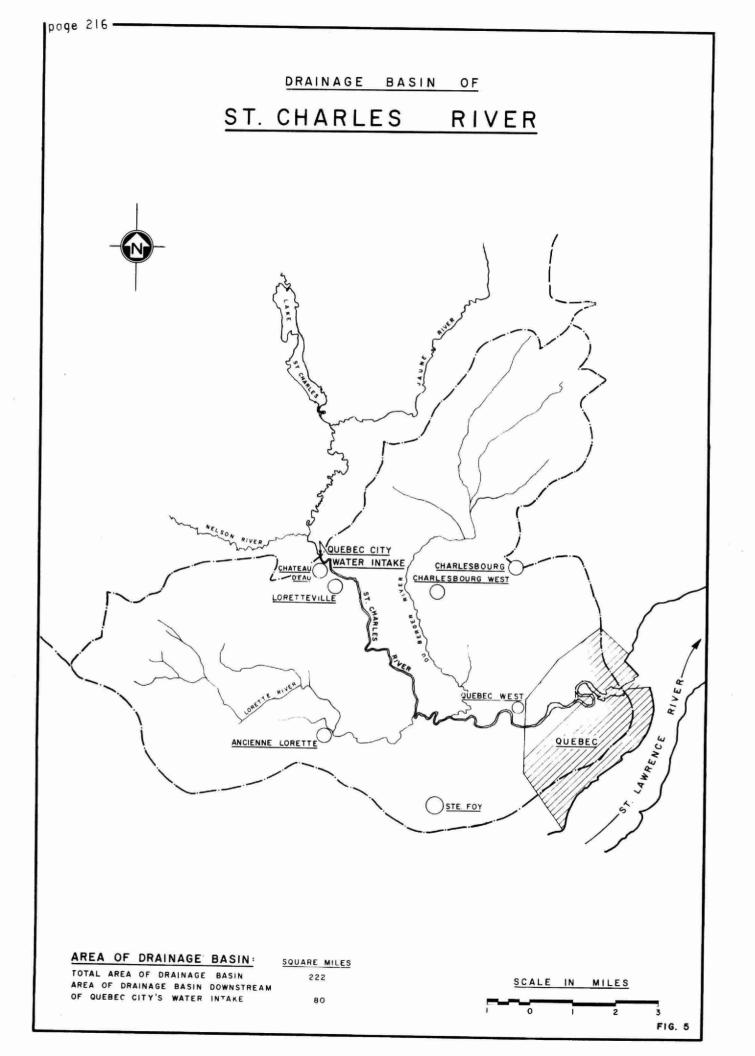
· ·

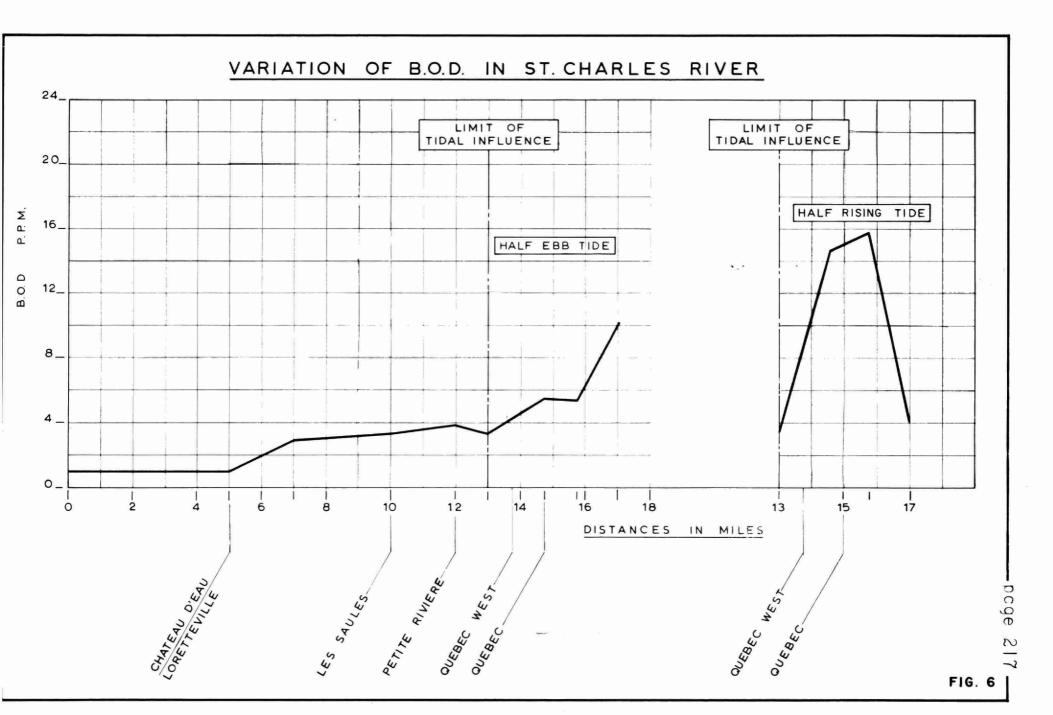
.

۹

• 9

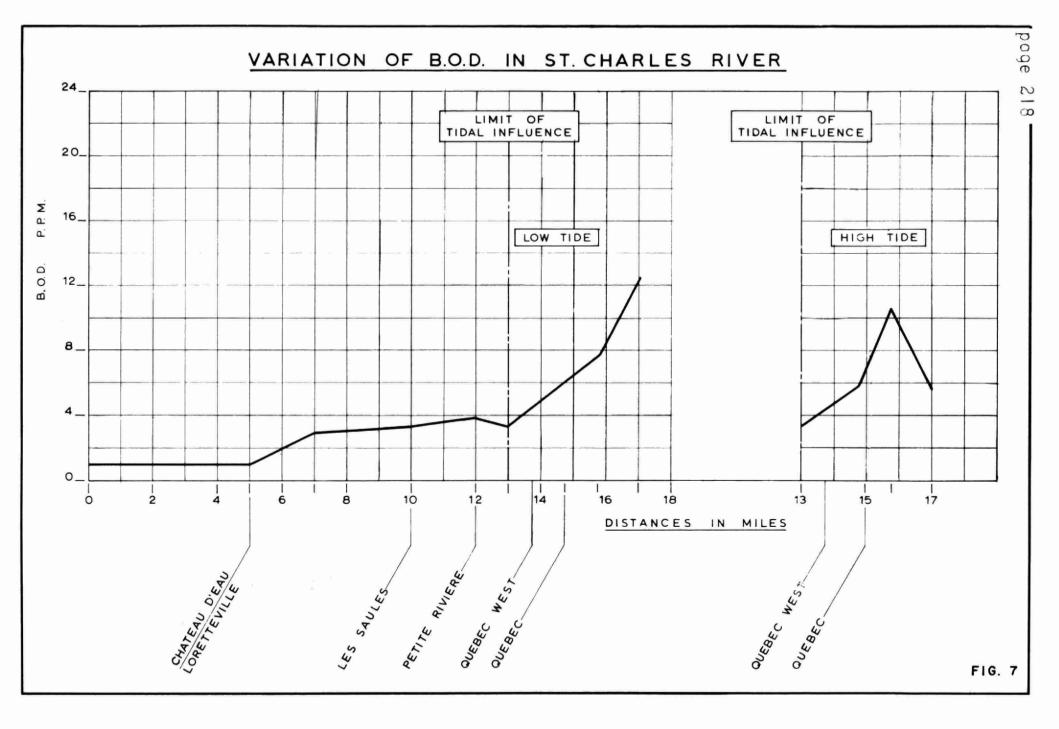






.

 $\overline{v}$ 



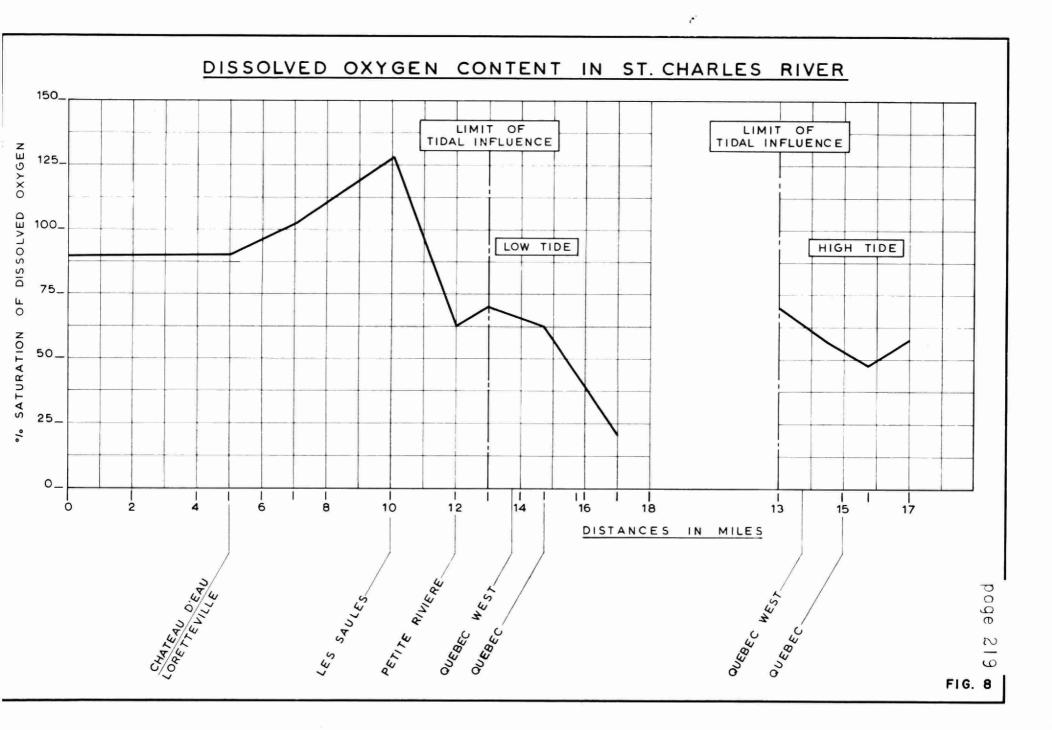
. .

4

•

.

٠



٠

.

.

.

page 220









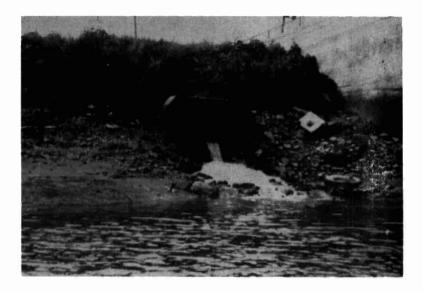


FIG. 11 SEWER OUTFALL



# FIG. 12

PROCESS WASTE OUTFALL AND ACCUMULATION OF DEBRIS







BANQUET -- JUNE 26

# PROCEDURES REGARDING CONTROL OF INDUSTRIAL WASTES IN NEW YORK STATE

by

,

D. B. Stevens

.



PROCEDURES REGARDING CONTROL

of

INDUSTRIAL WASTES

in

NEW YORK STATE

by

D.B. STEVENS

New York State Water Pollution Control Board Albany, New York

Mr. Chairman and Gentlemen, it is my privilege to explain to you people the steps which we in New York State take to control pollution of our waters by industrial wastes.

Our original water pollution control law was passed in 1949 and while it has been amended several times since then, it still remains much as originally drafted. This is now Article 12 of the Fublic Health Law. Under this article, there is set forth a procedure which must be followed in order to classify the waters of the State. Briefly, these are (1) survey of the watershed with respect to physical characteristics of the waters themselves, the use of the lands bordering the waters and the uses of the waters themselves; (2) publication of a report containing a proposed classification of the waters; (3) a public hearing on the proposal; (4) the official classification adopted and filed with the Secretary of State.

Turning now to the classifications, these are based on the best usage in the interest of the public. Basically, there are seven classes for fresh surface waters, two for ground waters and four for tidal salt waters. I said basically there are this number but we do have a few additional special classes. These are caused by one of two conditions. Special standards had been adopted prior to the passage of the water pollution control law for certain bodies of water. These were retained and fitted into the scheme of things. The other condition comes about because certain bodies of water just cannot be made to fit the standards for any class now existent.

Each class is described in terms of a use or combination of uses and specific standards are set for various constituents in the waters. Thus, classification is on the basis of stream standards. The highest class is Class AA and is described as source of water supply for drinking, culinary or food processing purposes and any other usages. Class A waters are similarly described. The basic difference between them is that Class AA waters will reach Public Health Service Drinking Water Standards merely by disinfection while Class A waters will reach these standards after a treatment equal to coagulation, sedimentation, filtration and disinfection.

Class B refers to the best use as bathing and any other usages except as a source of water supply for drinking, culinary or food processing purposes.

Class C has as its best usage fishing and any other usages except for bathing or as a source of water supply for drinking, culinary or food processing purposes.

Class D is for agricultural or source of industrial cooling or process water supply and any other uses except for fishing, bathing or as a source of water supply for drinking, culinary or food processing purposes.

Class E refers to its best usage as sewage or industrial wastes or other wastes disposal and transportation or any other usages except those previously enumerated.

Class  ${\rm F}$  refers to sewage or industrial wastes or other wastes disposal.

Standards are set for each class. Let us see how they change from class to class.

рН	for	$\mathbf{A}\mathbf{A}$	6.5 to 8.5
		Α	6.5 to 8.5
		В	6.5 to 8.5
		С	6.5 to 8.5
		D	6.0 to 9.0
		$\mathbf{E}$	not lower than 5.0
		$\mathbf{F}$	no std.

Dissolved Oxygen

AA 4 ppm Trout 5 ppm A 4 5 B 4 5 C 4 5 D 3 E and F - sufficient to prevent odour nuisances due to anaerobic decomposition. Sewage or Waste Effluents

- AA None which are not effectively disinfected.
  - A None which are not effectively disinfected.
  - B None which are not effectively disinfected. However, this relates only to the bathing season while for A and AA waters it is year round disinfection.

Floating Solids, Settleable Solids,

Sludge Deposits.

- AA None attributable to sewage, industrial wastes or other wastes.
- A None which are readily visible and attributable to sewage, industrial wastes or which deleteriously increase the amounts of these constituents after opportunity for reasonable dilution and mixture with the wastes discharged thereto.
- B, C and D same as A
- E In sufficient amounts to interfere with navigations or cause a public nuisance as defined by the Penal Law.
- F We leave out navigation.

There are a few others but you will notice the absence of specific values for definely toxic materials. This is deliberate because the pH, hardness and buffering capacity has a considerable bearing on the toxicity of many of these compounds or chemicals. For this reason, Class AA, A, B, and C speak of toxic wastes and deleterious substances and states that they shall not be in sufficient amounts as to be injurious to fish life. As a result there are guide figures but the actual criteria is the effect on aquatic life, both the fish and the fish food organisms. Some people have taken these figures as standards instead of a guide.

Turning now to the industrial waste discharge, the important thing is whether or not it is a new discharge. If it is, a new industry or a new effluent line from an old industry, it definitely is a new outlet by our definition. If there was a change within an existing industry which considerably altered the volume or composition of the effluent, it would be considered a new outlet. For all new outlets, there must be a permit from the State Commissioner of Health. This can only be issued after he is certain that the discharge will not contravene the standards established for the receiving waters if they have been classified. If they have not been classified, he must consider the discharge in the light of anticipated classifications.

Now then, how does one obtain a permit?

The first step is to have an engineering study made of the situation and prepare a preliminary report and sketch. This should then be discussed with the Local Public Health Engineer. Who is he? New York State, outside the City of New York, consists of 57 counties, 21 of these counties have their own health departments. If there is an engineer in that county, he is the Local Public Health Engineer or LPHE. If there is no engineer on the staff, the Regional Director of Public Health Engineering who provides assistance here would substitute.

All the cities of over 50,000 population lying outside the counties having their own health departments, also have health departments but only a few have engineers. Most of the cities within these counties have intergrated their health departments with the county unit. There are exceptions to all rules and this is no exception.

These leave 36 counties without county health units. These are grouped into units of from one to four counties and called districts. In each, there is a minature state health department called the District Health Office. Each of these offices has an engineer on the staff and he becomes the LPHE for that district.

Here is a map which shows this in more detail.

In the case of industrial wastes, this material is very minimal as all that is wanted is enough to explain to the LPHE what the problem is and in general how you propose to solve it. He may ask that the scope be expanded to include something else that has been giving trouble to him.

Next comes to actual preliminary report. This provides a full description of the proposed treatment work, design data, water consumption, classification of the receiving stream, the drainage area above the point of discharge, the recorded or estimated seven day average minimum flow in a ten year return period, and uses of the stream below the point of discharge.

The report must also contain the latest VSGS map of the area on which is located the site of the proposed facilities and the outlet pipe to the stream.

The report should also have some reasonable cost estimates for the project.

If this is a modification of an existing plant, that must be discussed in detail, particularly with reference to those portions which will be retained for use.

The matter of flooding with reference to the plant site must be considered and discussed.

The preliminary plans shall include a general map of the area showing existing and proposed sewers, including size and direction of flow, a general plan of the proposed treatment plant site, such drawings as are necessary to indicate the size and capacity of the proposed units and a hydraulic profile through the existing and/or proposed treatment units. The general plan of the treatment plant site shall show the property lines of the property owned or to be acquired and distances to all buildings within 1,000 feet of the nearest unit of the treatment plant.

Two copies of this preliminary engineering report and plan are submitted to the Department through the LPHE. He now reviews the proposal in light of his knowledge of local conditions and sends the material to the Bureau of Water Resource Services in Albany with a memorandum of transmittal. In this memorandum he comments on such things as:

1. The volume and strength of the wastes.

- 2. Stream flow data.
- 3. Downstream uses of the outlet watercourse.
- 4. The need for continuous or seasonal chlorination.
- 5. The suitability of the site as regards:
  - (a) Isolation from habitation and possibility of complaints.
    - (b) Accessibility.
    - (c) Elevation of maximum high waters.
    - (d) Adequacy of the site for future enlargement.

6. Proximity of water supplies.

All of these should be in the engineering report but he looks at these things in light of his personal knowledge of the area.

All of this material is then reviewed in Albany and a letter is returned stating that the proposal is satisfactory or what modifications are necessary in order for it to be satisfactory.

With this notice, work can then be started on any additions necessary to the report, the final detailed plans and the specifications. Where this material has been assembled, it is again submitted to the LPHE for transmittal to Albany. This time there should be two copies of the amended or revised report, one complete set of specifications, three sets of final plans and an application form.

This application form is a request for the approval of the plans and for a permit to discharge the effluent. It must be signed by the owner or proper officials of the company or corporation and show the name and address of the designing engineer and his New York State Professional Engineer's license number.

Just a few words about the final plans. We are now microfilming all plans. Therefore, we want them as black on white. They should not be greater in size than 30 inches by 42 inches or smaller than 16 inches by 20 inches. They should also have a space at least four by seven inches near the title block for placing the stamp of approval. Each sheet shall bear the seal of the designing engineer.

One other point is, we do not approve the specifications, only the plans. Therefore, the plans must contain all the necessary information to indentify and describe the various pieces of equipment. The submission of the specifications is merely to assist in the review of the plans.

When reviewing plans for sewers and sewage treatment facilities, the "Recommended Standards for Sewage Works as Adopted by Great Lakes-Upper Mississippi River Board of State Sanitary Engineers, May 10, 1960" are used. These are quite often referred to as the "10 States Standards" as ten states make up the group. Other states in the United States of America have adopted basically the same recommended standards with slight local modifications.

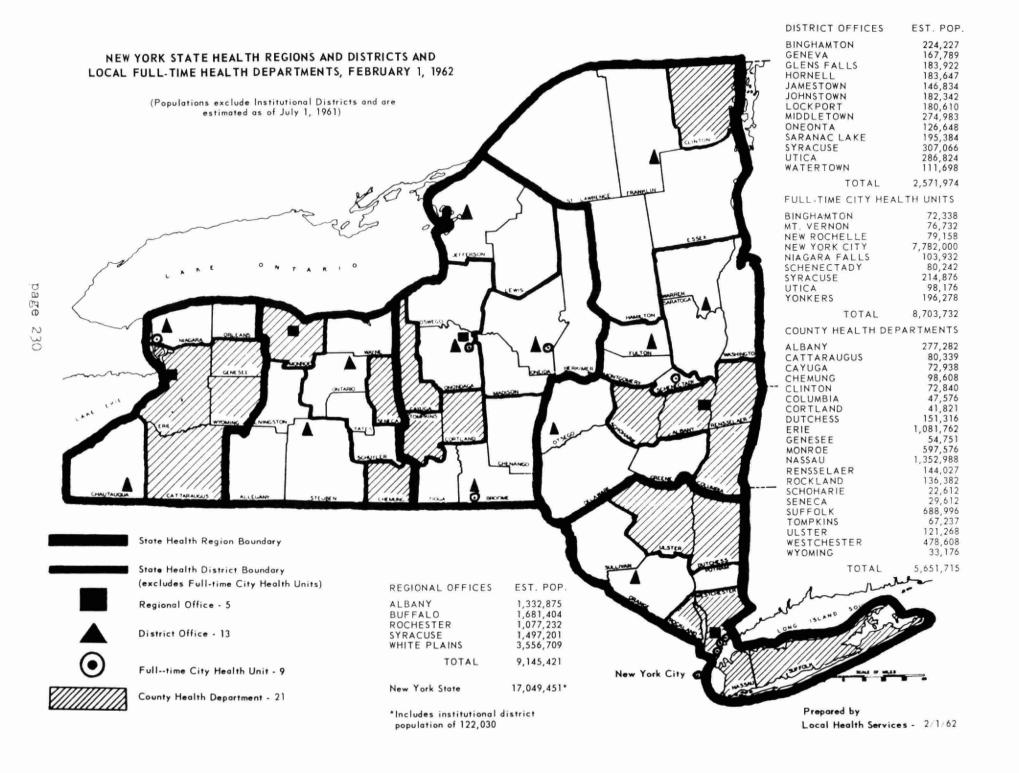
With reference to industrial wastes, it is recognized that no one set of standards could cover the entire field of waste treatment. Engineers submitting plans for industrial waste treatment projects should follow these "Recommended Standards for Sewage Works" as they apply.

So far we have dealt with new sources of pollution. How about the existing sources? In the first part of my remarks, I spoke about the four steps leading to the official classification of the waters. For existing sources, this is a must with two additional steps. The fifth step is the development and adoption of a Comprehensive Pollution Abatement Plan. In this are listed all the known alleged pollutors, some information about them and a recommended program for abatement. This is a published document but the data on each entity are cleared before printing. The sixth step is to sit down with the industry and work with them in setting up a mutually agreeable time schedule for carrying out that portion of the abatement plan relating to their plant. In most cases, this will require reports and plans and these will follow the same steps as outlined for new discharges.

In very brief summary, the steps to be taken would be:

- 1. Retain a competent professional engineer in this field either from within your own organization or from the outside.
- 2. Have your engineer discuss the problem with the Local Public Health Engineer.
- 3. Have your engineer obtain and use a copy of the "Recommended Standards for Sewage Works".
- 4. Submit a preliminary report and sketch to the Local Public Health Engineer.
- 5. With the approval of the preliminary material prepare the final report, plans and specifications along these lines and submit them, together with the application to the LPHE.

6. When approved, start construction.



٠

٠

.

.

.

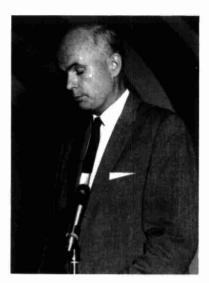
# TREATMENT OF CHROME TANNING WASTES FOR ACCEPTANCE BY AN ACTIVATED SLUDGE PLANT

٠

by

F. Wims

.



"TREATMENT OF CHROME-TANNING WASTES

FOR ACCEPTANCE

BY AN ACTIVATED SLUDGE PLANT

BY

F. J. WIMS, P. ENG.,

MECHANICAL SUPERINTENDENT AND PLANT MANAGER,

COLLIS LEATHER COMPANY LIMITED,

AURORA, ONTARIO.

#### INTRODUCTION :

The leather making process varies quite considerably from plant to plant. There are many reasons for this, but in the main, it is because development in this Industry has traditionally been along empirical, rather than closely scientific, lines. The manufacture of leather is frequently and correctly - described as being more of an art than a science.

In consequence, a paper dealing with the treatment of waste from such a process will be more specific than general. Our particular reference will be to the treatment of the tanning wastes of the Collis Leather Company for acceptance by the Town of Aurora Sewage Treatment Plant.

## GENERAL :

Located at Aurora, Ontario, approximately fifteen miles due north of Metropolitan Toronto, Collis Leather processes calfskins only. (The chrome-tanning method is used exclusively and this, in passing, should be distinguished from the vegetable-tanning process which produces a waste effluent of decidedly different characteristics.) Through the plant's premises meanders a small stream having an average flow of approximately 4.5 c.f.s. This is a branch of the Holland Creek, a tributary of the Holland River, eventually emptying into Lake Simcoe. The stream has long provided the only means of disposal, after treatment, of domestic and industrial effluents in the Town of Aurora. In addition to the tannery, the latter presently

include the wastes from a chicken processing plant, a large drug manufacturer, an anodizing process, and a dairy. Domestic wastes derive from Aurora's population of 8800 as of March, 1962.

All animal skins consist of three layers, namely : the epidermis (i.e., the cuticle or outer layer), a layer of fatty tissue, and the inner layer, or corium. It is the latter from which leather is made and the objective of the tanning process is to strip off the two outer layers and to subject the corium to the action of agents which convert it from a semi-soluble protein to the tough insoluble mass known as leather. The exact nature of this transformation is unknown. A typical flow sheet of the chrome tanning process is shown in Figure I (1).

Qualitative analysis of the composite wastes of a typical chrome tannery effluent will show that it has a high pH, contains dissolved organic material in large amounts, with calcium, sodium, and chromium salts, together with various sulphides also in solution. The wastes will also be heavy in suspended matter including such constituents as hair, bits of flesh, and particles of lime and calcium carbonate.

When such a waste is discharged to a relatively small stream, the action of aeration in passing down the stream results in absorption of carbon dioxide and consequent liberation of volatile ammoniocal substances along with hydrogen sulphide. The dissolved hair and hide material, having been held in solution by the alkaline sulphides, precipitates to build up a layer of readily decomposed organic material on the bed of the stream. Centres of putrefaction are formed in this organic material producing a further liberation of hydrogen sulphide and volatile amines. Warm summer weather aggravates this set of reactions because of the larger amounts of carbon dioxide available from lush vegetation along the stream and the stimulating effect of warm temperatures on the putrefactive bacteria. Further, the solubility of hydrogen sulphide is considerably less in warm as compared with cold water.

Serious pollution has been caused in many parts of the world by the discharge of waste waters from tanneries to streams. The problem is neither isolated nor particularly recent. Complaints against tanneries for fouling streams and town water supplies led to legal action in Richmond (England) in 1280 A.D., in London in 1300 A.D., and such action was successful to the detriment of the local leather trade in Colchester in 1425 A.D.

Tannery waste is frequently a component of the sewage of industrial cities. In very large communities, the proportion present may be so small that no interference with sewage processes is noted, even when the most sensitive forms of biological treatment are used. Experience indicates that where the tannery waste content does not exceed about 10 per cent of the total flow, and the tannery discharge is regular and well distributed, no difficulty with sewage treatment processes is likely to occur.

Regarding sludge digestion, Warrich and Beatty (2) have shown that, where sewage containing vegetable tannery wastes is concerned, tannery solids in the sludge can amount to as much as 40 per cent of the total solids without seriously impairing digestibility. This is not at all true of sludge derived from chrome tannery waste. Such sludge accumulates nearly all of the chromium of the waste, and may carry as much as 5 to 6 per cent chromium on the basis of solids. Any substantial amount of chrome tannery sludge may be expected to interfere with normal sludge digestion.

In many small and moderate-sized communities, tannery wastes have been present in amounts sufficient to disrupt sewage treatment facilities. This (3) has been caused by one or more of the following factors :

- Excessive alkalinity or high pH produced by the lime present in the waste, and resulting in interference with biological treatment processes.
- Hair and fleshing, which form scums on sedimentation tanks, clog sludge-removal equipment, or produce mats in digesters.

 Lime sludge and adherent deposits, which clog sewers, or interfere with proper operation of sedimentation tanks.
 Excessive loads of organic matter which overload the treatment units of the plant.

Most of the tanneries which practice waste treatment of any kind have adopted processes made up of various combinations of storage, sedimentation, and regulated discharge. Some treatments utilize coagulants such as sulfuric acid, carbon dioxide from flue gas, alum, and iron salts. These tend to improve removal of suspended solids, and sometimes colour, but effects little betterment in the B.O.D. All sedimentation treatments create a sludge disposal problem and sometimes this presents more difficulty in handling than the waste itself. The literature (4), (5) reviews many of the analytical results of such treatment but none can be considered sufficiently satisfactory for discharge to a public water course.

While, as indicated, many tanneries do give primary treatment to their wastes, none are presently known to give secondary treatment except where this is done in conjunction with a municipally operated domestic treatment plant. Considerable experimental work (6), (7) has been done on the treatment by biological processes of tannery liquors unmixed with sewage. Some of this work has progressed to the pilot plant stage but, because of the great expense involved, full scale use has never developed.

# History of Treatment At Collis :

For many years, Collis' effluent discharged without treatment of any kind, and with completely unregulated flow, into the branch of the Holland Creek mentioned earlier. As time progressed, however, the area attracted residential growth and much of this, particularly to the north of the town, was of substantial value. Correspondingly, conservation having been neglected, the creek flow diminished alarmingly. At the same time, the public was becoming increasingly aware of the dangers of pollution and of its rights to demand that industry, or any other contributor, institute the necessary measures to eliminate same. Law suits, injunction threates, and related legal costs became almost day to day operating problems for the company.

Efforts were then commenced by Collis to improve the situation. Most of the earlier work appears to have been along trial and error lines. It culminated in a system incorporating settling of the heavier solids, sludge removal, storage of the supernatant from the preliminary settling, additional sedimentation, and dilution before discharge to the stream.

The wastes were conveyed, both by gravity and pumping, as accumulated in the factory, to a small treatment plant on the company's property. Essentially, this consisted of two sedimentation tanks, having a capacity of 25,000 Imp. Gals. each, equipped with baffles for reducing flow velocity and short circuiting, and with scraping mechanism for accumulating settled sludge. Pumps for removal of sludge were also installed.

The supernatant from these tanks passed through an over-flow to two lagoons, each of which had a maximum capacity of approximately 600,000 Imp. Gals. The lagoons were connected in series. Maximum mixing and settling was obtained by means of strategically placed baffles together with judicious positioning of the fill and draw pipes.

The effluent from the final lagoon discharged into what was known as a fresh water pond. This had a surface area of approximately one (1) acre, and an average depth of 20 inches. Filled with fresh water from the creek and existing springs, the pond provided a measure of dilution to the discharge (through a four(4) inch diameter pipe) from the final lagoon. This treatment, of course, immensely improved the quality of effluent entering the stream in comparison with the original discharge of untreated waste. However, the results were still far from adequate and the procedure itself created many critical problems.

One of the major difficulties was the collection, transportation, and disposition of the accumulations of solids, or sludge, in the earthen storage lagoons. It was rarely possible to allow one of the lagoons to stand idle for a long enough period to dry out sufficiently to allow handling with standard equipment. Additionally, hair, fleshings, and other fibrous matter would mat on the surface and dry out enough for, say, a man to walk on it. This crust would generally be about 8 to 10 inches thick but tended to act as an extremely effective seal so that the sludge beneath remained very fluid.

The most effective means of excavating this fluid material was to remove the bucket from a drag line and replace same with an ordinary 45 gal. drum welded into a special bracket. This allowed reasonable efficiency in the excavation process. The material was then hauled in dump trucks to the nearest available dumping site. To prevent spillage on streets and highways, it was necessary to underload the trucks and to take special precautions to seal the tail-gates. Also, the vehicles were thoroughly washed after each day's run to reduce paint deterioration and body corrosion.

Because of very objectionable odour, safety hazards, general messiness, and road damage due to traffic of the heavy

trucks, it was never an easy matter to obtain a disposal site. Procurement generally involved a good deal of bartering and almost invariably it was necessary to shift location from year to year. Mostly, disposal was in blocked off ravines, but occasionally, the sludge was spread over the surface of fallowed fields. Always, the site would be on a marginal farm.

The build-up of sludge had the effect of reducing the volume of the storage lagoons, and, consequently, their sedimentation capacity. This, of course, made it impossible to maintain an effluent discharge of uniform quality. Suspended solids, pH, and - to a lesser extent - B.O.D. increased in close relationship to the accumulation of sludge. Rainstorms, and high spring run-offs, while generally improving the analytical results, produced further lack of uniformity.

Exposed surface area of the storage lagoons and dilution pond was approximately 2 acres. This tended to favour gas evolution and particularly during the warm summer months, very objectionable odour conditions were felt in the residential areas surrounding the plant. Most of the odours were, of course, due to hydrogen sulphide gas. This is most obnoxious under any conditions but the situation always became particularly bothersome during periods of hot, muggy weather when usual air movements were absent. The combination of heat, humidity and H<sub>2</sub>S was more than most residents could endure. The reaction was always angry and its expression frequently explosive. Air contaminants which may be associated with tannery operations include sulphur dioxide, hydrogen sulphide, various mercaptans, and a variety of products, mostly of unknown composition, which result from the putrefactions of organic materials. Many of these materials constitute hazards to health if present in the environmental air in adequate concentrations. They all give rise to strong odour sensations, usually of an unpleasant nature, at low concentrations; and can be detected by olfaction at still lower concentrations.

(One interesting side-light was the action of the sulphide gas on lighter, including white, shades of paint with which a number of houses in the plant area were painted. These turned black owing to the formation of lead sulphide and the company found itself in the house painting business - for free. Local hardwares subsequently began to stock titanium base paints.)

There was usually a period of quiescence during the cool weather months but the trouble invariably flared anew with the arrival of warm weather. This became a time of petitions, headlines in the local press, stormy municipal meetings, and incessantly, the threat of injunction.

Under this pressure considerable experimentation was done with most of the accepted standard remedies. Various odour masking agents were tried, but all of these proved almost entirely ineffective. Good results could be obtained in masking the odours, both qualitatively and quantitatively, under more or less controlled conditions indoors, but duplication in the field was another matter. Here, the physical characteristics, principally density of the various gasses, would come into play and it seemed that even the lightest breeze could effect complete separation.

Of the chemical flocculants, most work was done with ferrous sulphate. Our experience was that its value, under our conditions, was dubious. Most of the heavy, suspended material was settling out, without chemical aid, in the storage lagoons mentioned earlier. The ferrous sulphate produced best results at a dosage of about 0.06% by weight and was added, by the drip method, at the point of feed of the storage lagoons. Because of varying retention periods and inadequate mixing in the lagoons, the results were inconsistent. At best, these did not justify the expense of the material and its application.

The use of chlorine was also thoroughly investigated. Applied directly to the storage lagoons, it had the effect of accentuating local odour conditions. However, when fed at a rate of 150 to 200 ppm at the point of discharge from the diluting pond to the stream, it proved beneficial in lowering the pH and reducing B.O.D. odour conditions along the course of the creek were much improved. At this rate of feed, though the cost of material and application was approximately \$35.00 daily and, for this reason, was confined to the warm weather months. Following this treatment, effluent analysis based on a daily composite sample, taken at random from the weekly test records, shows B.O.D. at 48 ppm; Total Solids : 2400 ppm; Dissolved Solids 1400 ppm and pH 8.4. In 1952, the company decided it was faced with three alternatives :

- to attempt secondary treatment subsequent to its existing, or revised, primary treatment.
- 2) to reach an agreement with the Town of Aurora providing Secondary treatment - in conjunction with the town's domestic wastes - at the existing and/or revised municipal treatment plant.
- 3) To close the Aurora factory and move the company's operation to a locality where the volume and concentration of the company's wastes could readily be handled by existing treatment facilities.

The first alternative was carefully studied but was discarded as being economically impractical. Meanwhile, negotiations continued with the municipality towards acceptance of at least part of the tannery effluent in the Aurora Sewage Treatment Plant.

This latter plant, as it existed in 1952, had a designed capacity - based on a six-hour retention period in the aeration tanks - of 230,000 Imperial Gallons per day. The main plant units were as follows : Grit Chamber and Overflow Chamber, Primary Sedimentation or Settling Tank, Aeration Tanks, Final Settling Tank, Pumphouse Housing Sludge Pump and Blowers and glass-towered Sludge Drying Beds.

A trial agreement was arranged between the municipality and the company to accept the "Soak" and "Bate" wastes in the sanitary sewers beginning on September 9th, 1952. This test

was conducted under the diligent supervision of Mr. A. J. Harris, of what was then known as the Sanitary Engineering Division, Ontario Department of Health, and with the close co-operation of the municipal company engineers.

A typical analysis of "Soak" waste shows 480 ppm 5 Day B.O.D. 8546 ppm Total Solids, 4314 ppm. Dissolved Solids, and a pH of 7.7 "Spent Bating" liquor runs 680 ppm, 5 Day B.O.D., 2626 ppm Total Solids, 2315 ppm Dissolved Solids, and 8.8 pH.

The test was commenced with the discharge of 5,000 I.G.P.D. of the Soak Wastes to the sanitary system. This was pumped at a constant rate over a ten (10) hour day time period. This was continued for a period of one week and then additional quantities of both "soak" and "bate" wastes were added - in daily increments of 1,000 Imp. Gals. - until a maximum of 25,000 Imp. Gals. per day was reached. The pumping time was extended to 14 hrs. daily.

"A close check of the Aurora Sewage Disposal Plant effluent was made after the tannery began discharging the "Soak" and "Bate" wastes to the sanitary sewers. Although the Aurora Sewage Disposal Plant was not considered to be operating at its highest efficiency before the trial period began, these wastes did not increase the total organic nitrogen, free ammonia, suspended solids, 5-day B.O.D. or pH of the plant effluent to any extent". (8)

Concurrently, the company adopted the policy of segregating its Beamhouse Wastes, pumping these to a tank truck and hauling to a disposal site some miles in the country. Daily volume averaged 8,000 to 9,000 Imperial Gallons and these wastes analyzed 10,200 ppm B.O.D., 31,640 ppm, Total Solids, 21,400 ppm. Dissolved, with a pH of 12.1 and 880 Hydrogen Sulphide.

Subsequently, the balance of the tannery wastes consisting of the liquors from the tanning, colouring and finishing departments - were combined with the "Soak" and "Bate" wastes. These were directed as produced to the two 25,000 Imp.Gal. Settling Tanks, described earlier, then passed to an 80,000 Imp. Gal. Settling pond from whence the final effluent was pumped, chlorinated and discharged to the municipal sewers. This addition to the sanitary sewage system was built up gradually to a total daily volume which averaged 175,000 Imp. Gals. Pumping was evenly distributed over a 24-hour period six days a week.

The segregation of the beamhouse wastes, the elimination of the storage lagoons and diluting pond, together with the removal of the tannery wastes from the stream greatly improved conditions in the vicinity of the plant. However, the dry weather flow through the Aurora Sewage Treatment Plant for Aurora sewage and tannery waste combined averaged 550,000 to 600,000 Imperial Gallons per day, of which the Aurora sanitary sewage amounted to approximately 400,000 Imperial Gallons. The treatment plant, although designed in 1932 at a cost of \$47,500. for only 230,000 I.G.P.D. of Sanitary Sewage, performed creditably under this overload. Analysis, by the Ontario Department of Health, on a composite sample of the plant effluent as of November 5th, 1954, showed B.O.D. 39.8, Total Solids 522 ppm, Dissolved Solids 464 ppm and pH 8.46. Analysis, also performed by the Department, on Collis

Leather's effluent as of same date, ran B.O.D. 303, Total Solids 5240 ppm, Dissolved Solids 5050 ppm. These are random checks of the record but can be considered reasonably typical although appreciable variances are also noted.

The overload on the Aurora Treatment Plant, caused principally by the tannery's waste, created very unpleasant odour conditions in the vicinity of the works at time, particularly during periods of hot, humid weather. These were certainly neither as frequent nor as severe as had previously been experienced at the company's premises but definitely demanded correction. Additionally, acceptance of tannery waste resulted in a sludge disposal problem. The sludge, being collected mainly in the primary clarifier, necessitated a change in operating procedure. Previously, the sludge removed from the clarifier was pumped to the drying beds and this method of disposal served very well for the sludge from the municipal sewage alone but proved entirely inadequate to handle the sludge from the combined municipal and tannery flow. The combined sludge proved very difficult to dry. Reasons appeared to be : (a) too large a quantity for the beds; (b) increase in density of the sludge; and (c) the presence of appreciable amounts of inorganic constituents such as lime and common silt which give up their moisture content reluctantly. The Collis leather undertook to collect the sludge as pumped from the clarifier and haul it by tank truck to a remote dump east of Aurora. Volume averaged about 1,500 I.G.P.D. The company did this hauling and disposal at its own expense but - in this period - the municipality made no direct charge to the

tannery for waste treatment.

The problems of over-loading, and a concurrent residential growth, made an addition to the Aurora Treatment Plant imperative. In this connection, lengthy negotiations between Town Council, their Consulting Engineers (Proctor & Redfern), company officials, solicitors for both, and with the Ontario Department of Health - principally Dr. A. E. Berry - acting as impartial observer and technical advisor, resulted in the signing of an Agreement between the Municipal Corporation of the Town of Aurora and the Collis Leather Company Limited on September 26th, 1955. The Agreement :

Some of the more important provisions of the Agreement are noted here :

From the preamble : "....WHEREAS the Corporation's Engineers and the Ontario Department of Health (OWRC) have expressed an opinion that the Municipal Sewage System, as altered and enlarged, will satisfactorily treat the domestic sewage of the Corporation and the other sewage which the Corporation may be committed to treat and the tannery waste, provided that the tannery waste meets with the conditions as in this Agreement provided."

"....AND WHEREAS it is designed by this Agreement to achieve an amicable and permanent solution to the problem of the disposal of the Company's tannery waste through the facilities of the Municipal Sewage System and both parties are pledged to co-operate to the utmost to this end in accordance with the terms and provisions in this Agreement contained and according to the tenor thereof."

From Section (A), paragraph (1) : ".... it being understood and agreed that the Corporation shall not undertake to treat other industrial waste, which the Corporation is not now already committed to treat, without first consulting the Department of Health as to whether or not the same can be treated without disrupting the efficiency of the treatment then existing. The Corporation agrees to submit to the Company, plans of any alterations or extensions before proceeding with same."

From Section (B) subsection (1) and (2) : "1. The Corporation promises and agrees to receive, treat and dispose of the Company's industrial waste, subject to the provisions of this Agreement, on the condition that such industrial waste does not appreciably exceed the following maximum strengths except as specifically noted hereunder :-

a)	B.O.D.	350 ppm
b)	Suspended Solids	250 ppm
a) b) c) d)	Dissolved Solids	6200 ppm
d)	рH	9

This figure pH9 may be exceeded up to an absolute maximum of 9.2 for a period no longer than two days in any one month.

The industrial waste to be analyzed periodically by the Ontario Department of Health and the results so obtained and the interpretation of same by the Department of Health to be binding on both parties.

2. The industrial waste from the tannery not to exceed 250,000 Imperial Gallons in any one day and this flow to be distributed as evenly as possible over a 24-hour period, but in no event shall the flow exceed a maximum allowable rate of

15,000 Imperial Gallons per hour."

From Section (C) subsections (1), (2), (4) and (5): "1. In the event that, in the opinion of the Ontario Department of Health, the Municipal Sewage System becomes clogged, damaged or disrupted and/or in any unsatisfactory working condition by virtue of the Company being allowed its waste to enter such system, the Council of the Corporation shall be at liberty forthwith, after receiving written confirmation from the Ontario Department of Health that such condition exists and is caused by the Company's waste entering into such system, to disconnect the Company's sewer connection with the Municipal Sewage System, other than the connections used for domestic sewage, if in the opinion of the said Department such condition may be best corrected by excluding the Company's waste. The Ontario Department of Health shall be the sole judge as to whether or not the operations of the sewage system shall have become clogged, damaged or disrupted and/or in an unsatisfactory working condition by virtue of the Company entering its waste into such system. On the Company rectifying or correcting the condition causing such clogging, damage or unsatisfactory condition of the Municipal Sewage System, and upon receiving from the Ontario Department of Health its consent to do so, the Corporation shall immediately reconnect the Company's sewer connection with the Municipal Sewage System.

2. In the event that the Company fails to comply with the terms, conditions and provisions of this Agreement and such failure results in a clogging, damaging or disrupting of the Corporation's sewage system, the Company agrees to pay to the Corporation, the

costs of the clearing of such clogging and of correcting such disruption and of the repairing of such damage and, in this connection, the Ontario Department of Health shall be the sole judge as to whether or not the clogging, damaging or disrupting was caused by the failure of the Company to comply with the terms, conditions and provisions of this Agreement. The extent and cost of clearing the clogging or correcting such disruption and of repairing the damage shall be determined by a representative of the Company and by a representative of the Corporation or, in case of a dispute, by an impartial arbitrator appointed by the parties, is possible, or, otherwise, by the Ontario Department of Health.

4. The Corporation shall have a trained operator in charge of the Municipal Sewage System and shall have such sewage system inspected by the Ontario Department of Health at least twice a year, or, whenever requested by the company, to ensure that the maximum efficiency of treatment is obtained and shall put into effect such recommendation of the Ontario Department of Health as will improve the operation of the Municipal Sewage System and thereby improve the efficiency of such treatment, if requested to do so by the company, provided, however, that by implementing such recommendation the costs are reasonable and that the company shall pay one-third of the capital expenditures and operational and maintenance charges incurred thereby.

5. The Corporation agrees to provide the company with copies of any field report submitted by the Ontario Department of Health and to permit representatives of the Company to have access to the Municipal Sewage System at any reasonable time." From Section (D) and subsection (2):

"2. For the disposal of the Company's tannery waste through the Municipal Sewage System during the currency of this Agreement, pursuant to the terms and conditions as contained herein, the Company shall pay and agrees with the Corporation to pay to the Corporation the sum of \$6,605.90 per year for a period of twenty years as set forth in Schedule "A" attached hereto and the Company shall each month also pay one-third of the operating costs (#) of the Municipal Sewage System during the currency of this Agreement." (#) Operating Costs are defined in the Agreement as, "all normal

maintenance charges, repairs and costs of replacements and costs of operation."

Other provisions include:

1. Any new equipment or replacements, costing in excess of \$1,000 in any one year, shall be discussed with the Company, and, if there is any question of the necessity of such new equipment or replacement, the Ontario Department of Health shall be consulted and its opinion accepted.

2. Should the Company be closed for a period of six months at any one time then on notice to the Corporation of this fact, the operating costs only shall cease from the date of the receipt of such notice until the Company shall again open.

3. In addition to the aforesaid payments, the Company shall pay to the Corporation  $7\frac{1}{2}$  cents per 1,000 Imperial Gallons of the Company's tannery waste which the Corporation may be committed to treat in any one day in excess of 200,000 Imperial gallons of tannery waste. At the end of twenty year, the Corporation and the Company

shall review this matter to determine the charge, if any, to be paid for treatment of volume in excess of 200,000 Imperial Gallons in any one day.

4. The Corporation shall not be committed to treat during the currency of this Agreement more than 250,000 Imperial Gallons of tannery waste any one day.

5. After twenty years has expired, the Company shall pay a proportion of the monthly operating costs only, such proportion being the proportion that the daily gallonage of the Company's tannery waste multiplied by one and one-half, bears to the total daily gallonage treated by the Corporation.

6. The Company shall provide a meter to record the amount of the Company's tannery waste, which shall enter the Municipal Sewage System, such meter to be approved by the Corporation's Engineer. The meter readings shall be taken weekly by an employee of the Corporation, such weekly readings to be divided equally by six and the result shall constitute the daily gallonage of waste for the purpose of cost calculation.

7. In the event and to the extent that the Company or its successors should cease to require the facilities of the Municipal Sewage System for the disposal of tannery waste, the Company or its successors shall be entitled to a reduction in the annual payments to the extent that the daily gallonage of sewage treated by the Corporation exceeds 650.000 metered gallons over a period of one year on a yearly average.

8. The Company may appoint a representative to sit at any of the meetings of the Committee of the Council under whose juris-

diction the Municipal Sewage System falls.

9. The Company shall have access to the Corporation's accounts covering the Municipal Sewage System and shall have the right to have such accounts audited.

Reference has been made in the foregoing to the role of the OWRC as counsel and arbitrator. There is little doubt that the Municipality would have refused to enter such an Agreement had this advice and impartiality not been forthcoming. While the technical assistance of the OWRC has been constant and invaluable at all times, the necessity has never arisen during the approximately seven (7) years this Agreement has been in effect for their arbitration.

The Collis Leather Waste Treatment Plant was re-designed and expanded in an effort to provide primary treatment producing results within the limits of the Agreement. It was also planned to achieve greater uniformity of effluent and to have all treatment carried out in a closed structure.

# Collis Leather Waste Treatment (Primary) Plant:

A Flow Sheet of the Collis treatment process is attached. A general description of the process follows:

The wastes from the various processing departments of the factory are collected in conveniently located sumps and pumped through two (2) 6" diameter plastic (Carlon) discharge pipes to

the treatment plant where they enter.

## The Splitter Box:

This is simply a wooden box  $5'-0" \ge 4' - 2" \ge 1'-6"$  with two 12" diameter discharge openings dividing the flow equally into.

# The Two Surge Tanks:

Dimensions of each of these tanks are 50'-0" x 20'-0" x a working depth of 8'-0", giving a capacity of 50,000 Imp. Gals. each. The purpose of the tanks is to provide a surge capacity for the wastes as collected from the various departments of the factory and to obtain uniformity of discharge through thorough mixing. The latter is accomplished by the use of four (4) fifteen h.p. lightning mixers, (2 in each tank) which maintain the fluid in constant and complete agitation. Suction lines lead from the bottom of the surge tanks to

## Two All-Purpose Sewage Pumps (Centrifugal):

These pumps each have a rated capacity of 200 I.G.P.M. at 40 feet head. The pipe valving is so arranged that the pumps can be used singly - providing an alternate - for normal operation, or, in parallel, for emergency service. The discharge piping from these pumps runs to

## The Weir Box:

Where an adjustable v-notch weir is set to maintain a predetermined discharge rate to the settling tanks. An over-flow arrangement sends any surplus back to the surge tanks.

## The Settling Tanks:

The Weir Box discharge flows through a T-trough baffle into the two settling tanks, each having dimensions of 10'-O" x 50'-O" x 8'-O" and a capacity of 25,000 Imperial Gallons. The purpose of the settling tanks is to receive the uniformly-mixed wastes from the surge tanks and to remove by settling as much as possible of the suspended solids. The settled solids know as "sludge" are drawn by means of a scraper conveyor to a collecting sump, located below the tank floor level. This sludge, amounting to approximately 6000 I.G.P.D., is pumped to a tank truck and hauled a few miles into the country for disposal. The supernatant liquor from the settling tanks flows via an overflow pipe (at fixed elevation) to

## The Discharge Sump:

This sump is  $5'-0" \ge 10'-0" \ge 3'-6"$ . Its purpose is to maintain a positive head on the discharge pumps and to provide some temporary holding capacity for changeover of the pumps, removal of obstructions, etc. From this sump, the effluent is picked up by

# The two Discharge Pumps (Centrifugal):

These pumps are duplicates of the all-purpose sewage pumps above and, as previously, the discharge piping allows use of the pumps singly or in parallel.

These pumps discharge to:

## The Weir Box

which is virtually a duplicate of that above. The overflow from this Weir Box goes to the settling tanks while the discharge enters the

## Main Discharge Line

This is a 6" diameter carlon plastic pipe, chosen for corrosion resistance and smoothness of bore. The effluent flows by gravity through this line to a branch of the Aurora Municipal Sewage System. Installed in the main discharge line is

## The Meter

This is a magnetic flow meter, using the Faraday principle of electro magnetic induction; a conductor moving at right angles to a magnetic field generates a voltage directly proportional to the velocity of the conductor. In this application, the raw sewage is the conductor.

The magnetic flow meter consists of a metering transmitter connected by electric cable to a Dynalog receiver (recorder or indicator). The transmitter consists essentially of a length of nonmagnetic pipe. Two metallic electrodes directly opposite each other and flush with the inside of the pipe, detect the millivoltage generated by the moving sewage. This signal is transmitted to the Dynalog receiver.

# After passing through the meter, the waste receives The Chlorine Feed

This is accomplished by means of a Wallace & Tiernan Chlorinator designed to control and indicate the rate of flow of chlorine, to provide a simple means of settling the feed rate at any value within the range of the machine (e.g. Collis chlorinator : 0-200 lbs. per 24-hr. period), to mix the chlorine gas with water, and to deliver the resultant solution to the point of application. (In this case - just beyond the meter.) The normal Collis rate of feed is about 110 lbs. per day over period of flow of about 18 hours.

One very important aspect of the Collis treatment is the segregation of the wastes from the Beamhouse Department. Analysis of these was indicated earlier and showed them extremely high in B.O.D., suspended solids, and pH. This Department is sealed off for drainage purposes and all its wastes are collected in a common sump, from whence they are pumped to a tank truck for haulage to a disposal site. Volume is about 10,000 I.G.P.D.

Hides leaving the beamhouse department receives an over-night wash and the drainage from this operation is treated with Ferrous

Sulphate to precipitate sulphides - before discharge to the Primary Treatment plant. The same procedure is followed with the washings in the hair recovery process. About 100 lbs. per day of Ferrous Sulphate - roughly 50 lbs. for each application - is consumed.

The effluent from the Collis plant is checked twice weekly for B.O.D., Total, Suspended, and Dissolved Solids, pH, Chrome and Sulphides. On a monthly basis, duplicate samples are forwarded to the OWRC laboratory for similar checks. Copies of the latter results are forwarded to the municipality. Analytical results, chosen at random, and covering a period of years, are shown in Table I.

## Sludge Removal and Disposal:

The sludge removed from settling tanks in the Collis Treatment plant has an average pH of 7.3, Moisture 95-96%, Total Splids 4-5%, of which 54 to 58% are organic. Analyses of the inorganic content of the dried sludge shows 7-10% chromium (as  $Cr_2 O_3$ ), 4.5 to 6% chlorides (as Na Cl), 16 to 18% calcium (as Ca Co<sub>3</sub>), 4.5 to 5% Iron (as  $Fe_2O_3$ ), and 2.0 to 4.0% insolubles. Protein content of the sludge averages 30 to 34%.

The sludge is moved along the bottom of the settling tanks by means of a scraper conveyor to a V-shaped sump from which it is removed by a diaphragm type pump to a tank truck. Suction lift is about 10 ft. and discharge head about 10 ft. The tank has a capacity of 1,000 Imperial Gallons and is fitted to a standard dump truck.

Scrap boiler vessels are generally purchased for the purpose.

The scraper conveyor operates at a speed of about 2 1/2 lin. feet per minute and the scrapers are 2" x 4" x 9'6" B.C. Fir. Best results are obtained when scrapers are operated for about 20 mins. before pumping commences and continued until pumps are shut off. About six tank loads of sludge are hauled daily.

The disposal site is located approximately 1 1/4 miles east and 2 miles south of Aurora in Whitchurch Township. In all, six ponds have been built to accommodate the wastes. The ponds are located in ravines with the natural slope of the land forming two sides and dykes constructed across the ravines form the ends. Normally, a rotation from pond to pond procedure is followed to allow drying out. Soil conditions in the area are quite sandy.

Four of the ponds are within 200 yds. of the sideroad and two about 1/4 mile east. There are no water courses in the vicinity of the four ponds but east of the fifth and sixth ponds is a dry stream. Wastes have always been retained in the ponds provided but recently, to minimize possibility of dyke failure and resultant stream pollution, the pond walls have been re-designed. Dyke cross-section on the ponds near the dry water course now show a slope of 1 vertical to 3 horizontal (vertical height varies), a minimum top width of 8 feet, and a free board of 2 1/2 to 3 feet. Slopes are seeded and signs erected warning of the hazards of trespassing.

There are records of complaints from area residents regarding fear of water contamination and odours. OWRC checks of water samples in the vicinity have shown the first to be groundless. However,

there is no doubt that, depending on wind and atmospheric conditions, odours are observed occasionally. The site has been in use since 1948 and, while there has been some residential growth and change in the area, complaints have just been spasmodic in that time.

Besides the sludge from the primary treatment plant, the Collis beamhouse wastes and, from time to time, the digested sludge from the Aurora Sewage Treatment Works, are also disposed of at this site. Volume of the latter is about 2,000 IGPD.

The property on which the sludge is disposed is also used as a municipal garbage dump. It serves three municipalities having an approximate population total of 25,000. Both sludge and beamhouse wastes are simply dumped on the loose, dry garbage as deposited in ravines by the pick-up trucks. About 20% of the sludge and beamhouse wastes are disposed of in this way.

The only effects so far noted have been beneficial. The wastes have a tendency to compact the garbage, to reduce fire hazard, and to impose a measure of control on the rodent population.

The sludge from the Collis Treatment plant is also frequently utilized as a fertilizer. Applications have been on golf courses, park and playground areas, and forage fields.

Meanwhile, subsequent to the signing of the Agreement, the Town of Aurora proceeded with construction of an addition to its Treatment plant. Design was by Proctor and Redfern, Consulting Engineers, Toronto, who had also designed the original plant in 1932, and, having acted in a consulting capacity for the municipality over the years, had a basic background in the problems of tannery wastes.

## The Aurora Sewage Treatment Plant:

The extension to the Aurora Sewage Treatment Plant was completed in 1957, and, as a result, the present sewage treatment plant is actually a combination of two complete activated sludge plants in parallel, with common influent works, raw sludge, pumping station, digester, and sundry facilities.

The smaller plant has been described earlier. The larger plant, the 1956-7 extension, is rated at 770,000 Imperial Gallons per day. The total rated capacity of the two plants combined is 1,000,000 IGPD.

The plant extension follows the standard pattern for Activated Sludge Treatment plants with no indication in the design report that any particular features were incorporated to provide for the acceptance of tannery waste. It is known, however, that a little extra safety factor was added. The clarifiers, aeration tanks, volume of air, and sludge digester have slightly greater capacity than the rated design would normally demand.

Theroretical retention times, under rated conditions, in the Plant Extension, are: for the Primary Clarifier - 2.4 hours, for the Aeration Tanks - 7.0 hours, and for the Secondary Clarifier -3.13 hours. Corresponding retention times for the 1932 plant are: 2.3, 7.2 and 5.1 hours respectively.

Operating records for the plant show an approximate DRY WEATHER FLOW in 1961, of 800,000 I.G.P.D. Storm flows have frequently been recorded at a maximum rate of 2.50 M.G.D. Additionally, at times of excessive flow, by-passing of an unmeasured volume occurs over an average period 39% of the operating time. Efforts are being made by the municipality to separate storm and

sanitary sewers.

Chlorine is applied both at influent works and to the effluent at point of discharge to the carrying stream. Residual maintained at the influent is 2.0 ppm and at the discharge 0.5 ppm. Approximately 120 to 130 lbs. of chlorine are used daily in the treatment.

Plant operators and municipal officials report no untoward difficulties in the operations of the works specifically attributable to tannery waste. It is considered significant that the tanner wastes were accepted immediately the plant came on stream and that these wastes were assimilated as the sludge build-up developed. Following vacation shut-downs, the tannery waste load is returned gradually to the treatment plant and this can be readily done since the tanning operation is a "batch" process.

It had been anticipated that clogging of diffuser assemblies (Chicago Pump Company nozzle type used), undue corrosion, build-up in the trunk system, and formation of scum on the clarifiers would be resultant problems. None of these has occurred.

Very occasionally there has been some hair mat formation in the primary clarifier but this has developed through some mishap at the tannery and was corrected immediately upon notification. The sludge digester has not performed to the degree of efficiency expected. This has not been too serious but has added to the cost of operation and is currently the subject of study. Among the possible causes of comparatively inefficient digestion being checked is the probability that there may be a cumulative effect of the chrome in the tannery waste which inhibits the digestion process. Also, the volume of sludge produced is greater than that usually received from a purely domestic sewage plant of this capacity. No attempt is made to dry the digested sludge. The latter is tanktrucked (about 2,000 I.G.P.D.) to a disposal site in the country.

The overall plant was designed to remove up to 95 per cent of both 5-day B.O.D. and suspended solids. Average removal efficiencies have been about 94 and 77 per cent respectively.

Analytical data on the Aurora Sewage Treatment Plant are shown in Table II.

## Results:

Tabulation of typical results of effluent analyses of the Collis Leather Primary Treatment and of the Aurora Activated Sludge Plant are shown in Tables I & II respectively. These are considered to be reasonably satisfactory.

Perusal of the results will indicate that Collis wastes are above the agreed limit of 350 ppm. B.O.D. about 20% of the time and a similar excess in the Suspended Solids concentration above the maximum agreed limit of 250 ppm is also noted. At no time, however, has the total daily 5-day B.O.D. and Suspended Solids load exceeded the total load permitted by the Agreement.

There has been considerable discrepancy in results between OWRC and Collis laboratories, particularly regarding B.O.D. and Suspended Solids. Methods used are reportedly identical. Investigation is currently underway to correct this situation.

# Costs:

A summary of the total costs of treatment of Collis' industrial waste during the years 1960 and 1961 follows:

COSTS	12 MONTHS Nov. 1960	ENDED Nov.1961	
<ul> <li>A. Charges to company by Municipality: <ol> <li>One third operating costs at</li> <li>Aurora Sewage Treatment Plant:</li> <li>Collis' share Interest &amp; Amortization</li> <li>costs at Aurora Sewage Treatment Flant:</li> <li>Sub-Total:</li> </ol> </li> </ul>	\$6,499.89	\$7,209.84 <u>6,605.90</u> 13,815.74	
<ul> <li>B. Expense of operating Collis Primary Treatment Flant:</li> <li>1) Two (2) trucks - incl. drivers' wages depreciation, gas. licenses, insurance &amp; repairs: (N.B.:One driver also acts as plant operator.)</li> <li>2) Fixed charges - Interest &amp; Amortization</li> </ul>		14,164.22	
<pre>on building and equipment, depreciation same (excl. truck depreciation), taxes: 3) Heating. power &amp; water: 4) Material costs - Chiefly chlorine &amp; ferrous sulphate:</pre>	on 10,522.60 2,168.00 2,657.01	8,414.80 2,097.52 3,229.91	
5) Maintenance, lubrication	<u>552.00</u> 28,547.97 41,653.76	<u>690.28</u> 28,596.73 42,412.47	
<pre>VOLUME OF SEWAGE TREATED: * Cost per 1,000 Gallons of sewage treated: Cost per sq. ft. of leather produced:</pre>	35.6x10 <sup>6</sup> Imp.Gals \$1.17 0.812¢	• #41.2x10 <sup>6</sup> I.G. 1.03 .651¢	
*32.15x10 <sup>6</sup> Imperial Gallons discharged to A 3.45x10 <sup>6</sup> Imperial Gallons tank-trucked to	urora Treatment disposal site.	Works;	

#37.26x10<sup>6</sup> Imperial Gallons discharged to Aurora Treatment Works; 4.00x10<sup>6</sup> Imperial Gallons tank-trucked to disposal site.

DATE	TOTAL	SOLIDS SUSPENDED	DISSOLVE	<u>На</u> <u>D</u>	5-Day <u>B.O.D.</u>	Sulphides <u>as_H<sub>2</sub>s</u>	Chrome as Cr.	Volume (IGPD	COMMENTS
1/29/58 3/6/58 4/22/58 5/15/58 6/12/58 9/23/58 9/23/58	5138 3668 4838 3730 3998 3942 3828	207 104 26 57 23 260 156	4931 3568 4812 3673 3975 3682 3672	8.4 7.8 7.7 7.5 7.8 7.1 7.2	373 272 384 300 308 350 95	nil nil " " 16.0	nil nil " "	173,000 185,000 178,000 190,000 192,000 186,000	Composite " " " " Duplicate to OWRC
2/5/59 3/4/59 6/9/59 10/22/59 11/24/59 12/2/59	3716 4445 4391 4085 4833 6068	75 68 56 304 209 110	3641 4377 4335 3781 4629 5958	6.9 6.8 7.0 6.9 7.3 6.9	260 249 317 290 261 315	l 3 l 2 nil "	2.0 nil " "	168,000 176,000 180,000 187,000 195,000	Composite " " " "
1/14/60 2/24/60 4/12/60 6/2/60 11/22/60 12/29/60	4796 5737 6322 5213 6410 5880	138 298 231 254 308 262	4658 5439 6091 4959 6102 5618	7.4 7.3 8.7 7.6 6.8	264 377 308 326 327 299	" " 1 6 5	5.4 Trace 2.1 nil 2.4 4.3	175,100 162,400 180,000 184,500 167,800 189,600	" No. Soak " 85 lbs. c/2 " Grab - OWRC
1/17/61 2/20/61 5/25/61 10/12/61 10/12/61 11/27/61 11/27/61	6357 6151 5706 5478 5478 5514 5705 5590	271 246 190 160 160 460 240 496	6086 5905 5516 5318 5054 5465 5094	7.2 6.7 6.14 6.5 6.9 6.8 6.9	398 203 344 285 300 259 380	13.2 3.8 6.0 9.7 11.3 11.4 9.4	- 16.0 23.0 37.0	135,890 134,300 115,650 116,000 154,850	Composite No Tanyard " Dup. to OWRC Composite " Dup. to OWRC Composite " Dup. to OWRC
1/3/62 1/3/62 3/12/62 3/12/62 4/5/62 4/5/62	6073 6046 5482 5500 5698 5756	276 490 220 490 241 390	5797 5556 5262 5010 5457 5366	7.4 7.2 7.3 7.0 6.9 7.0	284 460 253 320 305 320	14.3 10.2 16.1 11.6 13.4 7.0	35 19.5 22.5 47.5 32	160,000 169,970 176,400	Composite "Dup. to OWRC " Dup. to OWRC " " Dup to OWRC

 TABLE I

 ANALYTICAL RESULTS - COLLIS LEATHER PRIMARY TREATMENT PLANT

.

(Based on Composite Samples collected over period of plant operation on date indicated) (Results given in p.p.m.)

# Plant #1 - Built 1932 Plant #2 - " 1956-57

# TABLE II

# ANALYTICAL RESULTS - AURORA SEWAGE TREATMENT PLANT ONTARIO WATER RESOURCES COMMISSION

DATE	TOTAL	SOLIDS SUSPENDED	DISSOLVED	рH	5-Day B.O.D.	Chrome as Cr.	Sulphide as H <sub>2</sub> s	COMMENTS
3/26/62 "	1524 552 626	212 30 36	1312 522 590	7.2 8.0 8.0	145 4.0 44	0.7 0.10 0.13	0.0 0.0 0.0	Raw Influent Final Effluent - Plant #1 ""- Plant #2
12/12/61 "	1586 1568 1246	64 88 198	1522 1480 1408	7.9 8.0 7.8	19 44 155	0.44 0.84 1.1	0.0 0.0 0.2	Final Effluent - Plant #1 "" - Plant #2 Raw Influent
9/19/61 "	1586 1170 1186	226 66 108	1360 1104 1078	7.1 7.8 7.5	210 7 26	1.60 0.06 0.18	0.9 0.0 0.0	Raw Influent Final Effluent - Plant #1 ""- Plant #2
7/24/61 "	1386 690 576	156 36 24	1230 654 552		270 14 9	4.00 0.46 0.26	0.7 Tr. Tr.	Raw Influent Final Effluent - Plant #1 ""- Plant #2
7/17/61 "	1142 552 588	214 24 24	928 528 564		175 7 2.8	0.56 0.20 0.17	1.0 Trace 0	Raw Influent Final Effluent - Plant #1 ""- Plant #2
7/10/61 "	1662 550 556	198 14 24	1464 536 543		270 10.0 3.6	0.06 0.7 0.18	0.25 Trace	Raw Influent Final Effluent - Plant #1 ""- Plant #2
11/1/60 "		132 24 50			195 13 19			Raw Influent Final Effluent - Plant #2 ""- Plant #1
9/22/59 "	1714 1136	272 24	1442 1112		190 21			Raw Influent Final Effluent - (sample point not indicated)

# page 264

.

## Conclusions:

The foregoing approach to the treatment of a chrome tanner effluent can be considered a moderately successful one. At any rate, the tannery creek as it traverses the company property has been returned very close to its original unspoiled state. Complaints in the town concerning odour, formerly a torrent, have been virtually eliminated. (Complaints now amount to roughly one or two per year from nearby residents. They occur at times of highly oppressive atmospheric conditions and are attributable to the slow dissipation of air exhausted from those departments using high concentrations of sulphides.)

Well-trained and diligent treatment plant operators are required. Rigid control must be maintained at both the company's works and that of the municipality.

The effect of any changes in the company's process operations on effluent results and treatment facilities must always be carefully considered.

Efficiency of suspended solids removal in the Aurora Sewage Treatment Plant is relatively low. It has been recommended by the OWRC that the effect of trace constituents, such as chrome, in the wastes be investigated in this connection. It has also been recommended that the cumulative effect of chrome on the sludge digestion process be thoroughly studied.

From the company's standpoint, the cost of its primary treatment is not presently prohibitive. Cost reduction in any operation is, however, always a prime object. One aspect of the work now

being done in this regard is the establishment of a research project on the enzymatic process for unhairing and liming. This could completely eliminate the use of sulphides in the leather-making operations and also greatly reduces the amount of lime required. Successful completion of this program could reduce present sewage treatment costs at the tannery by an estimated 50%.

Finally, in an arrangement of this kind, it is axiomatic that a spirit of fair-mindedness and the utmost in cooperation be maintained at all times by all involved.

### **REFERENCES**

(1) (3) - Rudolfe, Willen, "Industrial Wastes - Their Disposal and Treatment", - 146, 154, New York, Reinhold Publishing Corporation (1953)

Warrick, L.F., and Beatty, E.J., Sewage Works Journal 8
 122 (1936)

(4) (5) - Journal American Leather Chemists' Association 36, 121 (1941) and 38, 292 (1943).

(6) - Pennsylvania Department of Health. Tannery Waste Disposal
 Committee. Treatment of Tannery Wastes. Herrisbury, Pennsylvania,
 (1930).

Mohlman, F.W., Treatment of packinghouse, tannery and
 corn-products wastes. Industrial Engineering Chemistry, 1926, 18,
 1076.

Harris, A.J. Report 5Z-GS - 474, Aug. 29 - Oct. 17, 1952.
 Sanitary Engineering Division, Ontario Department of Health. Re:
 Holland River.

(9) - Townshend, A.R., O.W.R.C. Report on Aurora Sewage Treatment Plant, January 1961, p.10.

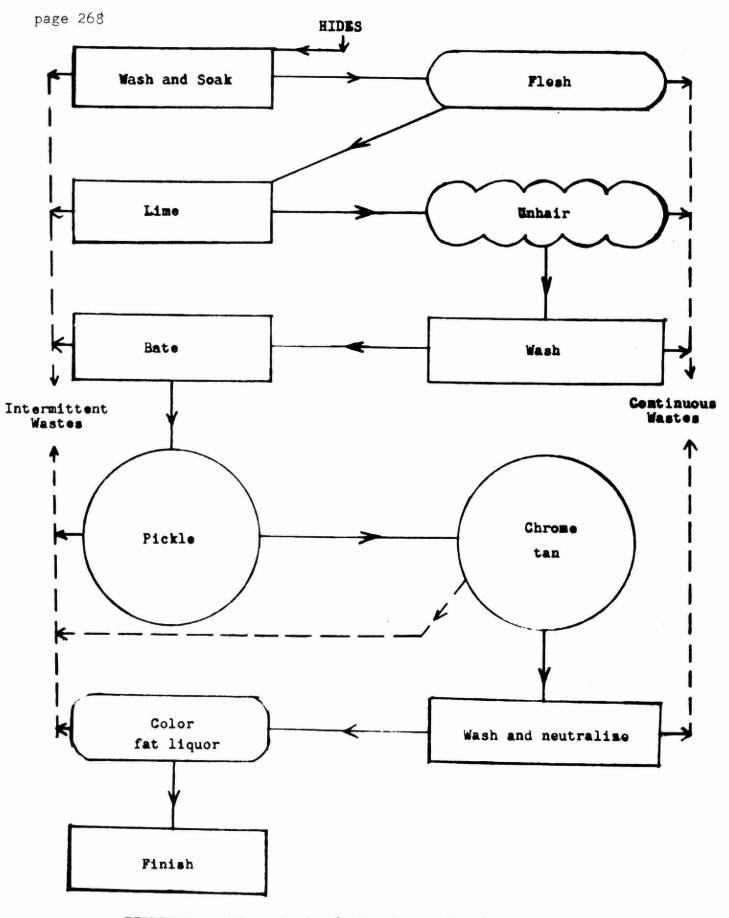
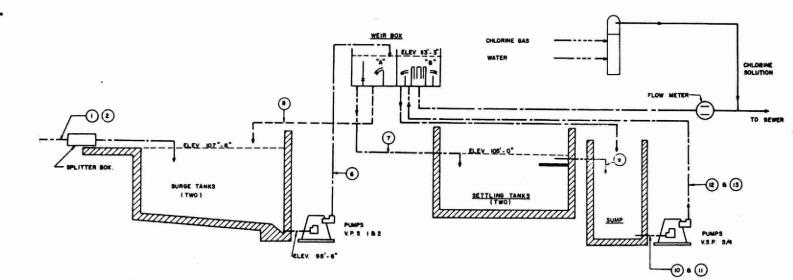
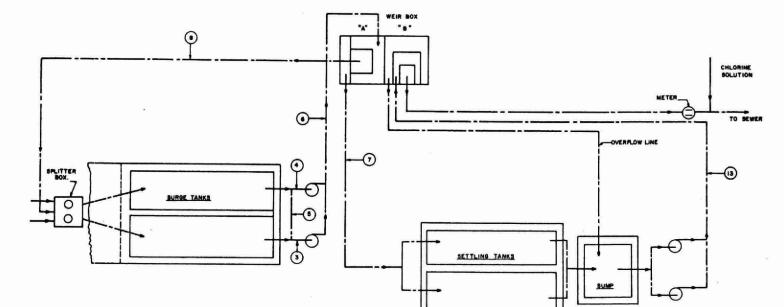


FIGURE I. Flow sheet of the chrome tanning process





	PLASTIC (CARLON ) DISCHARGE PIPES						
3,4	AS SURGE TANK DISCHARGE						
6	DISCHARGE TO WEIR "A"						
7	DISCHARGE TO SETTLING TANKS						
	OVERFLOW TO SURGE TANK						
9	DISCHARGE TO SUMP						
10	A I SUPPLY LINES TO SUMP PUMP						
12	DISCHARGE						
13	DISCHARGE TO WEIR "B"						
	SPLITTER BOX						
	SURGE TANK						
	SETTLING TANK						
	SUMP						
	FLOW METER						
1							
_							
1							
_							

CANADA PACKI UNIT COLLIS LEATI	
FLOW S SEWAGE DISPO	
DRAWN BY	PROJECT No. 58 - 42
DRAWN BY NOT TO SCALE	

REVISED MAY 30, 1962







AFTER DINNER SPEAKERS -- JUNE 26

HYDRAULIC TESTS OF SEDIMENTATION BASINS

by

K. L. Murphy



HYDRAULIC TESTS OF SEDIMENTATION BASINS

by

K. L. Murphy, Department of Civil Engineering, McMaster University, Hamilton. Ontario.

The separation of solids and liquids is an important process in the clarification of water and wastes. The unit process of sedimentation has found wide acceptance as an economical solution to the problem of separation, particularly when a large volume is to be treated.

Although sedimentation basins were used as early as 260 B.C., the majority of basins were designed principally on empirical bases. In a paper presented before the Institute of Sewage Purification in 1942 an anonymous author was quoted to the effect that:

"The construction of settlement ponds is such a simple matter that it scarcely calls for more than a passing mention".

Despite this claim, many workers have tried with mixed success to interpret and predict the phenomena associated with solids separation.

The first to attempt a theoretical analysis of the process was Seddon in 1889 (12). Subsequently many publications including those of Hazen (6), Camp (2) (3), and Fitch (4) have added to the theoretical knowledge of the process. However, most of the hypotheses developed by the workers in this field have been based on certain simplifying assumptions.

One of the most universal of these assumptions has been the concept of a uniform velocity distribution within a basin. Unfortunately, a completely uniform velocity distribution, in both magnitude and direction, is seldom, if ever, encountered. Fluid viscosity, density differentials, and the uneven distribution and momentum of the fluid tend to produce deviations from the "ideal". Various typical flow patterns are illustrated in Figure 1.

page 271

One of the principal approaches to obtain information on the suitability of a particular basin for sedimentation is through hydraulic tracer studies. Inasmuch as it is recognized that in practice, short circuiting, dead spaces, or severe turbulence generally tend to lessen the efficiency of a sedimentation basin, it may be stated that, for best results, the total flow should be retained in the basin for an interval of time that equals or approaches the theoretical detention time. The extent to which this may be accomplished can be determined by the dispersion curve technique. Two techniques are in common usage and will yield essentially similar information. They are:

- the instantaneous dosage or flow-wave technique, and
- 2. the continuous dosage or flow-through technique.

With either technique, a dye, salt, or other tracer whose concentration can be accurately determined, is injected at a known time into the basin influent. Samples of effluent are subsequently collected at known time intervals and the concentration of the tracer plotted against time. With the first method, the time of dosage must be limited to as short a period as practicable if the resultant curve is not to be influenced by the time taken to inject the tracer. This rapid injection could lead to density problems when large quantities of tracer are employed. With the second technique, tracer injection must be maintained at a continuous rate for a period exceeding the difference in retention time for the fastest and slowest water particles.

With both techniques the tracer concentration may be plotted against the elapsed time from the instant of injection to the time of sampling. The curve obtained by the instantaneous dosing technique is illustrated in Figure 2. and is known as the dispersion curve for the basin under the test conditions.

From the analysis of such a curve, various dimensionless hydraulic ratios, involving a comparison to the theoretical detention time (T), have been defined in the literature (9) (11). These ratios may be employed to compare the same basin under different flow rates or basins of different sizes. A summary of the ratios in general use is given below:

- a.  $(t_i/T)$  the initial time ratio-the relative time to the initial appearance of the tracer in the effluent, a measure of the most extreme short circuiting,
- b.  $(t_p/T)$  the modal time ratio the relative time to the peak of the curve, the most probable detention time,

- c.  $(t_a/T)$  the median time ratio the relative time to the centre of the area under the curve, or the time at which 50 percent of the tracer has just left the basin.
- d.  $(t_g/T)$  the mean time ratio the relative time to the centre of gravity of the area under the curve, the arithmetic mean detention time for the tracer.
- e.  $(t_{90}/t_{10})$  the dispersion index the ratio of time for the first 90 percent of the tracer to pass to that time required for the first 10 percent to pass.

It is also possible to obtain a dimensionless dispersion curve which incorporates graphically all of the above ratios. The amount of tracer recovered in the effluent is represented by the area under the dispersion curve. If this area is divided by the theoretical detention time (T), the result,  $C_0$ , is the concentration which would be obtained if the entire dose were uniformly dispersed throughout the basin. If the ordinates of the dispersion curve are divided by  $C_0$  and each abscissa by T a dimensionless dispersion curve is obtained (Figure 3) whose area is unity. Similarly, it would be possible to obtain a dimensionless curve whose maximum ordinate would be unity for an "ideal" basin.

With the continuous dosage technique a dimensionless curve (Figure 4) may also be obtained. Under steady state conditions, when the time of injection exceeds the difference in retention time between the fastest and slowest particles, the final effluent concentration of tracer will be identical to the influent concentration of tracer. Each sample concentration thus is divided by the final effluent concentration attained and each time of sampling by the theoretical detention time. A similar curve can be obtained from instantaneous dosing techniques by accumulating the tracer contained in the effluent for each sampling period. Such a curve is given in Figure 5.

The continuous dosing technique has several disadvantages. It is more difficult to estimate recomery of tracer unless the period of testing is considerably longer than that used with the instantaneous technique. The problem of recovery assumes a position of considerable importance when sampling of the entire flow is not possible. Similarly, it is difficult to establish the modal time ratio  $(t_p/T)$  with this technique as it is represented on the curve by the portion with the steepest slope.

Short circuiting will be seriously aggravated by both mixing and by the occurrence of stagnant areas. If stagnant areas exist a "streaming" of flow will result and the tracer will pass through the basin with only slight dispersion. In

this instance, initial  $(t_i/T)$ , modal  $(t_p/T)$ , median  $(t_a/T)$  and arithmetic mean  $(t_g/T)$  time ratios will be considerably shorter than the theoretical time. The initial appearance of tracer  $(t_i/T)$  is not considered to be as good as a measure of short circuiting as the modal time ratio  $(t_p/T)$  because only a relatively small quantity of tracer actually has this retention time. Because the ratio  $t_g/T$  represents the ratio of the mean time of passage to the theoretical time, this ratio represents the best measure of effective basin volume. If secondary currents exist within the basin, the median  $(t_a/T)$  and the mean  $(t_g/T)$  time ratios will be displaced towards the theoretical detention time, the value of  $t_g/T$  approaching unity when the complete basin volume is utilized.

The variation of  $t_a/T$  with short circuiting is not as large as the variation of  $t_p/T$  and the latter would appear to be of greater value for estimating short circuiting caused by dispersion. The hypothetical "perfect" mixing basin is an example of short circuiting caused by dispersion. Here  $t_i/T$  and  $t_p/T$ are zero while with "infinite" short circuiting  $t_a/T$  is 0.694 and  $t_g/T$  is 1.000.

Dispersion, or scattering about the central tendency, is normally defined in terms of the parameter  $t_{90}/t_{10}$  or the Dispersion Index. Any other equally valid statistical parameters should be as effective.

In sedimentation basins in which most of the volume is effective and thus the  $t_g/T$  ratio approaches unity, a relationship has been found to exist between short circuiting as measured by the ratios  $t_i/T$ ,  $t_p/T$  and  $t_a/T$  and the degree of mixing as measured by the dispersion index  $t_{90}/t_{10}$ . Figure 6 indicates the relationship between the modal time ratio  $(t_p/T)$ and dispersion index for tests conducted at the University of Wisconsin on both a circular (11) and rectangular basin (8) (12) under various conditions.

Under experimental conditions the modal time ratio  $(t_p/T)$  does not always give a similar interpretation of basin performance as the dispersion index. Differences in the "tail" of the curve possibly affect the dispersion index to a greater degree than the modal time ratio. On the contrary, the statistical measure of skewness  $(t_g/T - t_p/T)$  is influenced by the overall shape of the dispersion curve. If this time interval is expressed as a fraction of the mean time ratio  $(t_{\sigma}/T)$ ,

then we have a dimensionless index similar in nature to the dispersion index, but involving the modal time ratio. This index could be termed the Index of Short Circuiting and for the hypothetical "ideal" basin it would have a value of 0.0, while for the "perfect" mixing basin with "infinite" short circuiting it would be 1.0. This parameter utilizes the modal time ratio while at the same time accounts for minor variations in the "tail" of the dispersion curve. As such, it represents an estimate of basin performance which is a composite of that obtained using the modal time ratio (t\_p/T) and the dispersion index (t\_90/t\_10).

Two separate studies at the University of Wisconsin have emphasized the importance of both basin shape and basin appurtenances on the hydraulic performance. Ingersoll (7) and Rohlich (11) have reported on tests of a 10 ft. x 5 ft. rectangular basin, the study sponsored by the American Petroleum Institute. More recently, an investigation of the hydraulic characteristics of a 6 ft. diameter circular basin has been made (11). An overall comparison of the two test basins is available in Figure 6. With comparable overflow rates, and various side wall depths, inlets and outlets the values of the modal time ratio  $t_p/T$  and dispersion index

 $t_{00}/t_{10}$  would indicate that the circular test basin was subject to more severe short circuiting and a greater degree of mixing than the rectangular basin. A similar interpretation is available from the dimensionless dispersion curves, presented in Figure 7. Table 1 lists the values of the various hydraulic parameters for the two basins under the test conditions.

An ideal inlet should introduce the flow into a basin at a moderately low velocity distributed uniformly both horizontally and vertically across the entire basin cross section. With such an inlet the entire basin would be available for sedimentation and the flow conditions of Camp's "ideal basin" would be approached. Conventional inlets do not accomplish this distribution and consequently long narrow basins have proved superior. With long basins a smaller proportion of the total volume is influenced by inlet conditions. Conventional length : width ratios range from 5:1 to 7:1 for rectangular basins. Numerous types of inlets have been tried; simple pipe inlets accomplish neither horizontal nor vertical distribution; full width weirs provide adequate horizontal distribution but fail to give a good vertical distribution. Baffles have been used to attain better inlet distribution. The vertical slat baffled inlet has proved superior to other conventional inlets, (7) (9) Figure 7 and Table 1 indicate the improvement over a simple weir inlet on the rectangular Wisconsin test basin. Mau (9) has indicated the Reynolds' number of the baffle will govern basin performance.

Normally inlet conditions have proved of greater importance than outlet conditions (8) (11). Where extreme underflows exist, caused either by momentum or density currents, inlet modifications have little effect on basin operation. This is particularly true of conventional circular basins and basins which receive a heavy load of suspended solids. Under these conditions relocation of the outlet weir from its normal location on the wall opposite the inlet has markedly improved the basin (1) (5). The earlier observations by Anderson (1) for circular basins are substantiated by the data presented in Figure 7 and Table 1.

The effect of the variation in depth in basin hydraulic efficiency may also be measured by dispersion testing methods. Figure 8 indicates the variations obtained when the depth of the circular basin was varied to give diameter: depth ratios within the range of 6:1 to 2:1 with overflow rates of 1,000, 2,000, 4,000, 8,000 gal./sq.ft./day. The figure indicates that an increase in side wall depth from 1.0 to 1.5 feet caused a substantial increase in the Index of Short Circuiting, particularly at overflow rates in excess of 1000 gal./sq.ft./day. In general, further increases produced further short circuiting but the changes were of lesser magnitude.

Hydraulic testing of sedimentation basins may be employed to ascertain the hydraulic efficiency of the unit under various flow rates, temperature gradients and with various inlets and outlets. Since an improvement in the hydraulic characteristics will in general give an improvement in solids reductions it is possible to evaluate whether a change in basin performance has occurred through a modification to the basin or a change in volume of flow, even when accompanied by a variation in the character of the waste.

The data presented on the circular basin was obtained from a study supported by a P.H.S. research grant from the National Institute of Health, U. S. Public Health Service.

.

.

# TABLE I

# Comparison of Hydraulic Parameters

Basin	Inlet	Outlet Weir	t <sub>i</sub> /T	t <sub>p</sub> /T	t <sub>a</sub> /T	t <sub>g</sub> /T	<sup>t</sup> 90 <sup>/t</sup> 10	tg-tp tg
Circ.	Conv.	Periph.	0.074	0.094	0.609	0.997	18.87	0.906
Circ.	Conv.	Intern.	.098	.138	.691	1.059	12.10	.870
Rect.	Simple Weir	Simple	.063	.175	.724	.921	9.21	.810
Rect.	Vertical Slat	Simple	.165	.605	1.090	1.280	5.29	.527

.

٠

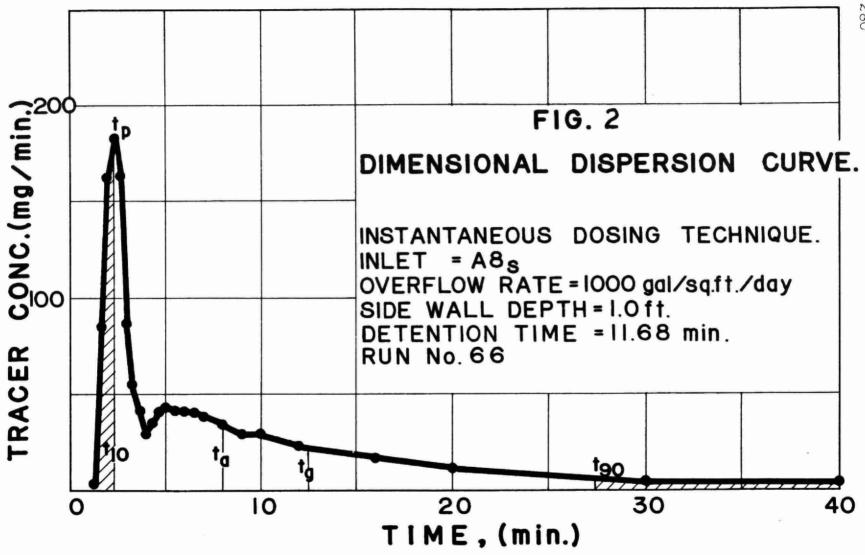
References cited:

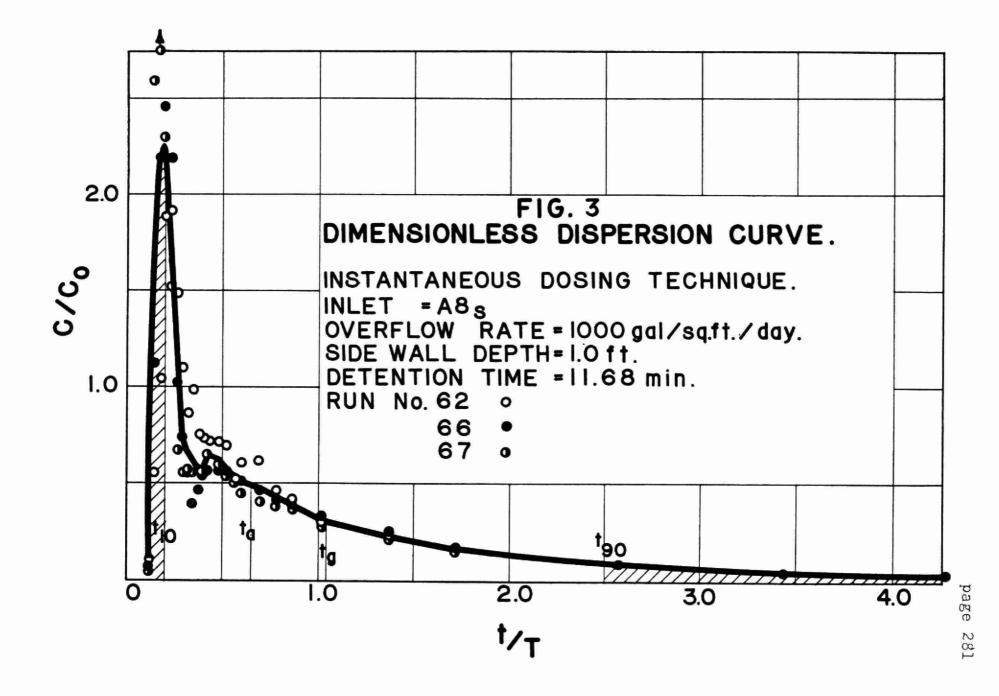
Anderson, N. E.,	"Design of Final Settling Tanks for Activated Sludge", Sew. Works Jour. <u>17</u> , 50-63, (1945).
Camp, T. R.,	"A Study of the Rational Design of Settling Tanks", Sew. Works Jour. <u>8</u> , 742-758, (1936).
Camp, T. R.,	"Sedimentation and the Design of Settling Tanks", Trans. A.S.C.E. 111, 895-959, (1946)
Fitch, E. B.	"Flow Path Effect on Sedimentation", Sew. and Ind. Wastes Jour., <u>28</u> , 1-9, (1956)
Gould, R. H.	"Final Settling Tanks of Novel Design", Waterworks and Sew., <u>90</u> , 133-136, (1943)
Hazen, A.	"On Sedimentation", Trans, A.S.C.E., <u>53</u> , 45-88, (1904)
Ingersoll, A. C.	"A Laboratory Approach to the Behaviour of Oil Water Mixtures in Separators", Unpublished Thesis, University of Wisconsin, (1950)
Ingersoll, A. C.	McKee, J. E. and Brooks, N.H., "Fundamental Concepts of Rectangular Settling Tanks", Trans. A.S.C.E. <u>121</u> , 1179-1204, (1956)
Mau, G. E.,	"A Study of Vertical Slotted Baffles", Sew. and Ind. Wastes Jour., <u>31</u> , 1349-1372, (1959)
Murphy, K. L.,	"Tracer Studies on Circular Basins," Unpublished Thesis, University of Wisconsin, (1961)
Rohlich, G. A.,	"Hydraulic Characteristics of Gravity Type Oil Water Separators", Proc. American Petroleum Inst., <u>31M</u> , 111, 63-85, (1951)
Seddon, J. A.,	"Cleaning Water by Settlement - Observation and Theory", Jour. Assoc. of Engr. Soc., <u>8</u> , 477-492, (1889).
	- ,

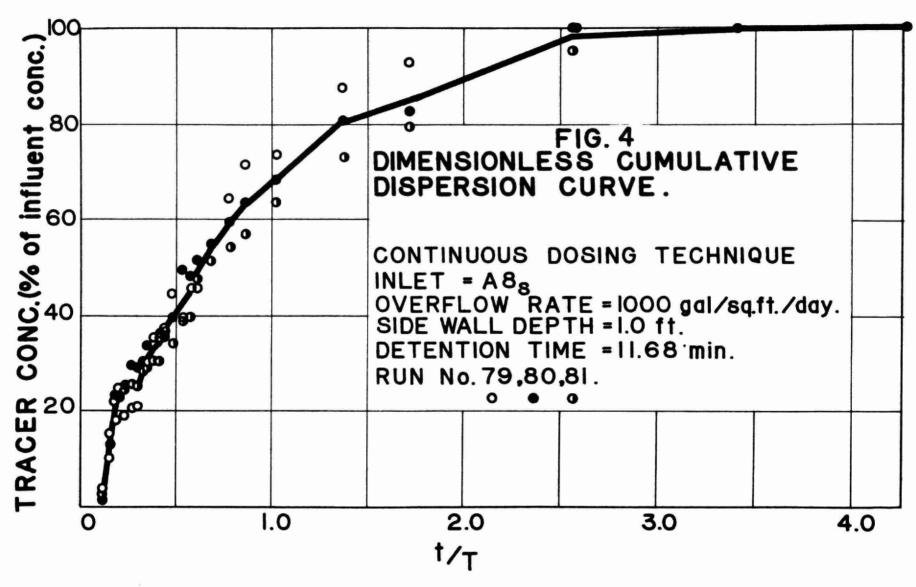
# //XXXXXXXXXXXXXXXXXX /TANKANVANVANA //AXXAXXAXXAXXAXXAXXAXXAXX //XVXVXVXVXXV/A "IDEAL" "TURBULENT" "LAMINAR" "NON UNIFORM" DIAGRAMATIC FLOW PATTERNS .. FIG. 1.

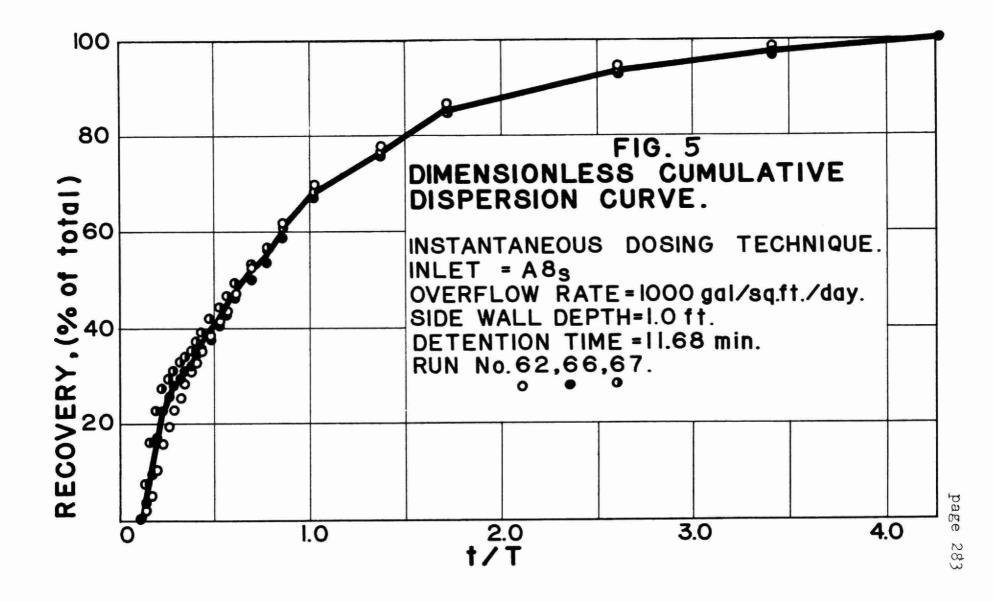
page 279

//8868686866

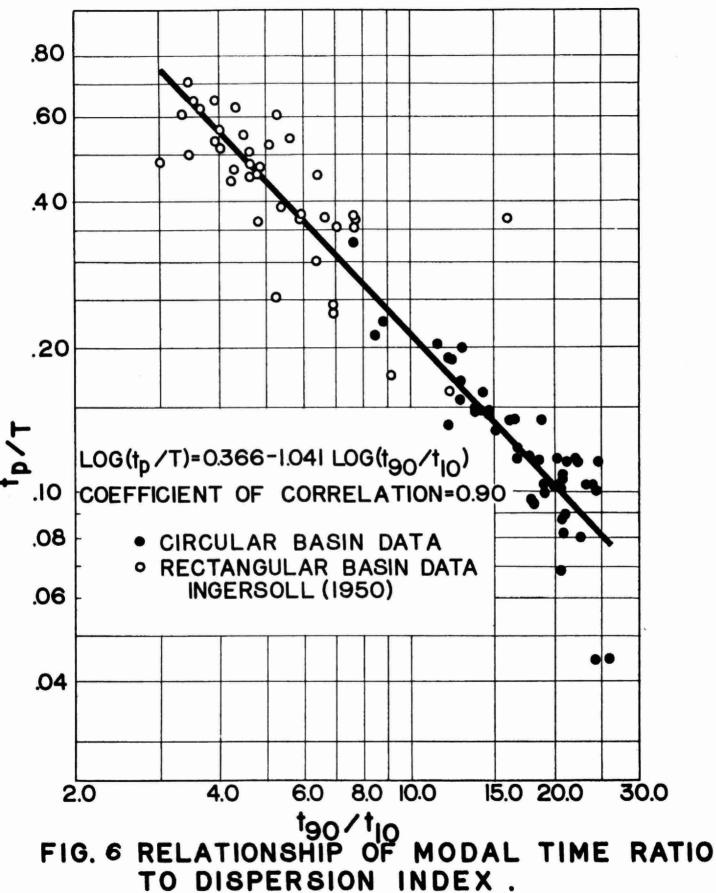


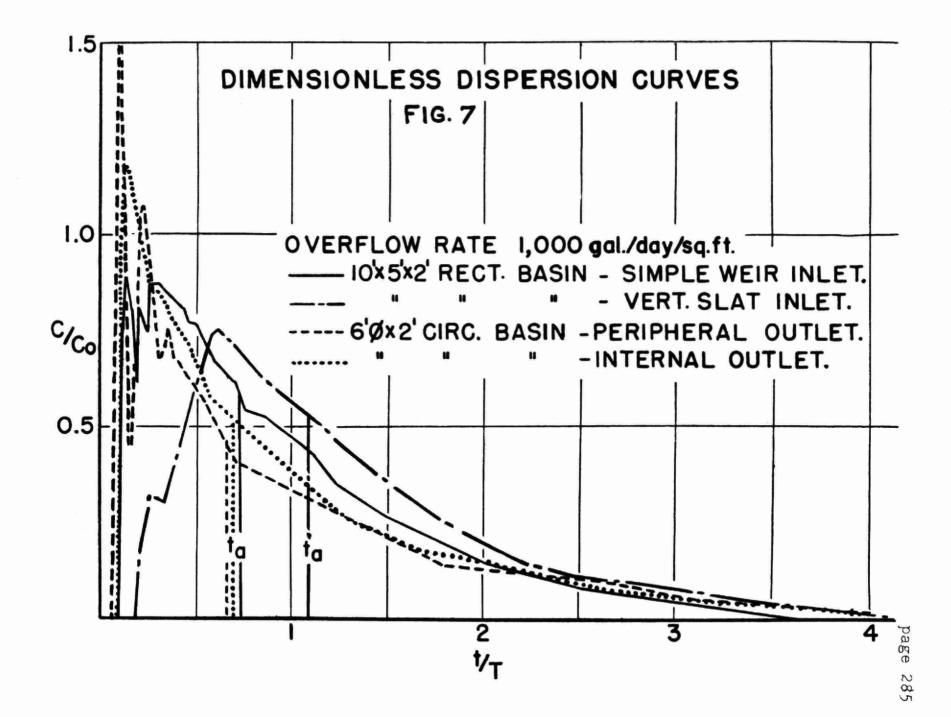


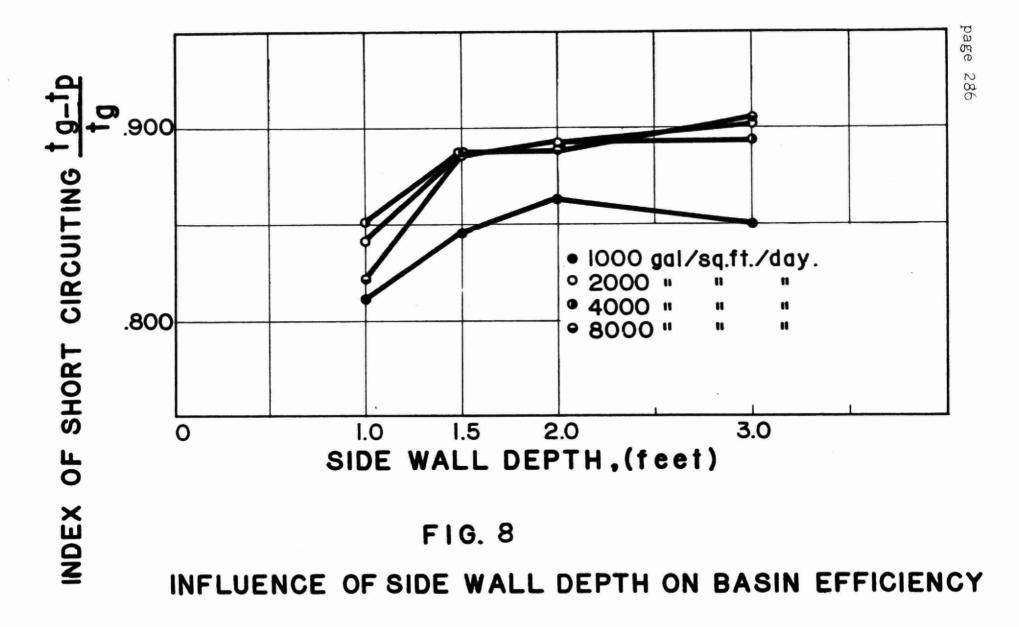












# THE SEARCH FOR BIO-DEGRADABLE DETERGENTS

.

by

.

•

.

Dr. H. Lomas



# SESSION NUMBER FIVE

T. W. Beak, Consulting Biologist. Session Chairman.



"THE SEARCH FOR

BIODEGRADABLE DETERGENTS"

by

H. LOMAS

ONTARIO RESEARCH FOUNDATION

TCRONTO, ONTARIO

#### Summary and Contents

#### I. Introduction

Although the earliest used syndets, and soap itself, are biodegradable, the one with the widest application today is derived from an alkyl benzene with a branched alkyl chain of petroleum origin which is "non-biodegradable".

#### II. Problems Caused by Syndets

- a) Foam in aeration tank
- b) Foam in rivers and canals.
- c) Presence in drinking water.
- d) Interference with sludge settling.
- e) Slowing of rate of sludge digestion.

## III. Properties of Syndets

a) Required desirable properties as syndets

Many of these conflict with the requirements from the pollution aspect.

(i) Low cost and availability of raw materials.

(ii) Economic manufacturing process.

- (iii) High surface activity in low concentrations.
- (iv) Stability to hard water.
- (v) High foaming power and stable foam.
- (vi) Dispersing action on solid dirt particles.
- (vii) Emulsifying action on grease.

(viii) Ready solubility in water in powder form.

#### b) Undesirable properties of syndets in effluent systems

(i) Formation of a more stable foam in the presence of sewage than in pure water.

(ii) Incomplete oxidation.

(iii) Possible effect on growth of bacteria.

(iv) Toxicity of effluent. This is probably much overrated.

#### c) Distinction between bio-degradable and non-biodegradable

It is now generally accepted that the presence of branched alkyl chains considerably reduces the rate of biochemical oxidation.

#### IV. Assessment of Biodegradability

a) Pilot plant tests

It was soon found possible with small scale experiments to show the improvement obtained by using detergent alkylates with less-branched alkyl chains.

b) Large scale tests

Tests were carried out at the sewage plant covering the Luton area in England. Difficulty was experienced in obtaining adequate coverage of the new type syndet, but results were quite significant.

c) Analytical Methods

Estimation of traces of syndets is possible by use of the methylene blue method of Longwell and Maniece, and distinction between branched and straight chain alkyl groups is possible by infrared techniques.

## V. Methods Considered for Reduction of Syndet Pollution

- a) Adsorption on solids.
- b) Use of ion exchange resins.
- c) Froth concentration.
- d) Precipitation with cationic agents.
- e) Extraction.
- f) Adaptation.

#### VI. Synthesis of Potentially Biodegradable Syndets

- a) Raw materials.
- b) Procedures.
- Fatty derivatives economics. Petroleum derivatives. c)
- d)
  - (i) Cracked paraffins.
  - (ii)Alcohols from ethylene with Ziegler catalysts.
  - Alpha olefins with Ziegler catalysts. (iii)
  - (iv) Radiation techniques with n-paraffins.
- e) Sucrose derivatives.
- NOTE: Figures in parenthesis refer to abstracts in Ontario Research Foundation Bibliography titled "Biochemical degradation of detergents".

#### I. Introduction

In the title of this paper the word "detergent" is used. Perhaps, as suggested by Mr. Weaver at the 1960 Conference a better term would be surface active agent or surfactant. However, surfactant covers a much wider field than the range of products with which we are concerned, so in the remainder of the paper the now popular word "syndet" will be used. Syndet, therefore, is the synthetic organic surface active agent used as the active ingredient in cleaning materials, while detergent is the complex mixture of this with builders, alkalis, foam stabilizers etc., as sold to the public.

They synthesis of syndets with the object of imparting biodegradability is a recent development, but a large number of those developed and used during the last thirty years fall into this class. However, by a process of elimination one syndet has become the most widely used of all types in household detergents, namely, dodecyl benzene sulphonate or, commonly, ABS.

It is hoped that this paper will stimulate a wider search for biodegradable syndets so that by another process of elimination the most suitable will be found.

#### II. Problem caused by syndets

The effects of syndets in sewage and effluent systems are by now familiar to all those concerned with these systems.

a) Foam in aeration tanks interferes with their operation and even constitutes a pollution hazard when windblown. The presence of syndets has been shown to reduce airtransfer rates in these systems (17).

b) Foam in rivers and canals is a potential danger to all users of such waterways. Appreciable concentrations of syndets have been found in many rivers (13, 14, 25, 32) and in general they appear to have a half life of 16 days or more (15).

c) Re-use of water in other towns downstream results in appreciable concentrations in drinking water. This has been particularly apparent in Germany, where rivers are a large source of water and towns are close together.

d) Syndets act as dispersing agents and prevent adequate settling of sludge.

e) If the build-up of syndet in the effluent is high, the possibility of toxic effects on fish should be considered. Toxicity claims have, however, in most cases been over-rated.

#### III. Properties of Syndets

#### a) Required desirable properties as syndets

A combination of properties is necessary for a

surfactant to be suitable for use in detergent formulation and many of these conflict with the requirements from the pollution aspect.

(i) Low cost and ready availability of raw materials: This has resulted in the switch to petrochemical sources.

(ii) Economic manufacturing processes: Petrochemical processes lend themselves to the large scale production of alkyl aryl sulphonates.

(iii) High surface activity at low concentration.

(iv) Stability to hard water: This is one of the main reasons for their replacement of soap, and also a reason for their persistence in sewage effluents.

(v) High foaming power and stability of foam: The need for high foam in detergency has been queried and syndets are available with comparatively low foam but the housewife demands suds and there are a number of arguments in favour of foam. Some of the dirt is probably removed by a froth flotation mechanism; the increase in viscosity of foam assists in mechanical removal of dirt; foam is even used as an indicator when the optimum quantity has been added. To maintain foam during the washing of greasy dishes, foam stabilizers are usually added. Fortunately, these are mainly derived from coconut oil, so are readily biodegradable.

(vi) Dispersing action on dirt particles: In order to prevent re-deposition of solid soil particles the syndet should have some dispersing properties. Usually this is obtained by the addition of polyphosphates which do not generally interfere with sewage systems.

(vii) Emulsifying action on grease.

(viii) Ready solubility in powder form.

In the formulae for syndets it is proposed to use the following simple symbols to facilitate description of the various groups in the molecule

	<ul> <li>straight chain alkyl</li> </ul>			
0	-,	polar group - COOH or Na		
•	-	" - SO <sub>3</sub> H or Na		
	-	polyglycol ether chain		

b) <u>Undesirable properties of syndets in effluent systems</u>

(i) <u>Foam</u>

It has been found that foam is produced in sewage effluents

at syndet concentrations below the foaming level for solutions of the syndet in pure water.

Reduction of surface tension alone does not produce stable foam but only reduces the energy required to create bubbles. Stable foam is the result of the formation of an elastic film at the surface resulting in a double air/water interface. Most household detergents contain a foam stabilizing agent which counteracts the adverse effects of grease. These are usually oil soluble materials such as ethanolamides which form an interfacial complex with the amionic surfactant and make them compatible with fatty materials. Other products such as cholesterol and protein degradation products have a similar effect. These are present in sewage and may account for the abnormal degree of foaming which is observed.

#### (ii) Incomplete oxidation

It has been shown that about 50% of the syndet is removed or destroyed during passage through an activated sludge system (28, 38). Most of this is removed by adsorption on the solids present in the system particularly clay-like materials. Most detergents contain ABS, so much of the remainder passes through the system without complete oxidation.

#### (iii) Effects on the growth of bacteria

Inhibition of bacterial growth varies with the ionic type of the syndet. In general they fall into three groups:

- 1. Anionic, which includes soap and ABS.
- 2. Cationic, mainly germicidal surfactants.
- 3. Non ionics, such as the ethylene oxide condensates.

It has been shown that syndets are strongly adsorbed by the cell walls of bacteria (50). Cationics are the most strongly adsorbed, but anionics appear to have a dissolving action on the lipo-protein layers of the cell walls. However, this effect is only apparent in comparatively high concentrations and it is variously reported that the normal concentration of syndet found in effluents has little effect on the bacterial count. It has been shown that ABS has a retarding effect on cellulose decomposition above 10 p.p.m. (22) but it is considered that the effect on digestion in general has been much over-rated (24, 55). c) Distinction between biodegradable and nonbiodegradable syndets

It is now generally accepted that branching of the alkyl groups considerably reduces the biodegradability of syndets (47, 52, 56). The order of attack of micro-organisms on C atoms is (53):

-CH<sub>2</sub>- readily attacked

-CH- less readily attacked

-C- not appreciably attacked

The ABS commonly used in household detergents is made from an alkyl benzene which has been alkylated with tetrapropylene. This alkylating agent gives optimum solubility, stability, detergency etc., and is also inexpensive. The polymerization method used to prepare the tetrapropylene gives a highly branched chain, however, so the final product has a very low degree of biodegradability. By the use of a secondary alkyl benzene in which the secondary carbon atom is near the benzene ring a considerable improvement is obtained. The two alkyl groups can be biodegraded as far as the secondary carbon and the end product is a lower alkyl benzene sulphonate, which has lost most of the surface activity of the original compound.

The older types of detergent were derived from fats and oils and the products such as soaps, fatty alcohol sulphates, Igepons were readily biodegradable. Soaps and Igepons are now used in toilet bars so the development of synthetic bar soaps is not contributing to syndet pollution.

Some of the newer syndets are of the nonionic type, containing long polyglycol ether chains. It has been found that such chains are biodegradable if they are short but those containing long chains are slow in diffusing and penetrating to the enzyme system of the bacteria (48, 52).

# IV. Assessment of Biodegradability

# a) <u>Pilot plant tests</u>

A new type of syndet, Na Dobane JN, with less branching in the alkyl chain, and a sugar-based syndet were tested in water seeded with primary sewage effluent (23). They appeared to have no inhibiting action and the rate of oxygen uptake was increased. In preparation for the large scale tests in the Luton area a pilot plant trial was run (34). The new type detergent was found to be removed in aerobic sewage treatment processes to a much greater extent than ABS.

Lissapol N, a branched alkyl phenol condensed with ethylene oxide has been tested in a sewage medium (20) and no evidence of biochemical oxidation was found. One the other hand no adverse effects on performance of filters etc., was noted except at excessive overloads. This compound is a nonionic agent so has less foaming ability in low concentrations, is less readily adsorbed, and therefore gives less bacterial inhibition than the anionic types.

#### b) Large scale tests

Attempts were made to switch the users of the regular detergent based on ABS to the new type detergent based on NaDobane JN in the Luton area. Market research showed that actually the change-over was slow, but from December 1958 to November 1959 the coverage increased from 58% to 90% (29). In spite of these set-backs, an appreciable improvement was obtained as shown in the Table. This was also confirmed by tests at a point downstream in the river when the quantity of syndet decreased from 318 lbs. per day to 134 lbs. per day between April 1958 and September 1959 (31). Observation of the amount of foam in the river at discharge points also showed a decrease. One point which has not been checked is whether the residual product from the oxidation of the syndet interferes with the estimation of total anionic surfactant. Presumably with a secondary alkyl benzene sulphonate the end product would be isopropyl benzene sulphonate which would not cause pollution troubles but might react with methylene blue.

#### c) Analytical procedures

One of the problems of large scale tests has been the determination of syndets in the small quantities present in effluents, sometimes as low as ).l p.p.m. The method now usually used is that of Longwell and Maniece (57), which involves reacting with methylene blue to form an anioniccationic complex, which is soluble in chloroform. Methylene blue is insoluble so the anionic syndet may be estimated colourimetrically in the extract. This gives total anionic syndet, but it is possible to distinguish between sulphates and sulphonates, as the former are hydrolysed by acid while the latter are not. However, it is not possible to distinguish between straight- and branched-chain alkylbenzene sulphonates by ordinary means but the use of infrared spectra has made this possible. To obtain accurate infrared tests it is necessary to concentrate and this has been accomplished by froth concentration (64), adsorption on carbon (60), or separation as the 1-methylheptylamine salt (61).

#### V. Method for the reduction of syndet pollution

A number of methods have been suggested for the removal of syndets from effluents and a number of these have been tried, but in most cases they are uneconomical.

#### a) Adsorption

A large proportion of the syndet in the sewage is usually found with the solids in the sludge as a result of adsorption at the solid/liquid interface. Some increase in removal may therefore be obtained by increasing the solids content at this stage (37). Addition of clay or similar solids with a high surface area would achieve this effect. Alternatively the filtered effluent can be treated with activated carbon (13, 42). In potable waters 1-2 p.p.m. carbon/l p.p.m. syndet was found to be necessary (44). The amount adsorbed by the solids may be increased by the use of a flocculating agent such as aluminum sulphate (36).

#### b) Ion exchange resins

More effective adsorption and removal is possible with ion exchange resins, but the cost of these materials is very high and also the cost of regeneration.

#### c) Froth concentration

The high solubility of syndets and the low concentration at which they are present in the aqueous phase make handling costs high in most removal processes. A preliminary concentration in a froth concentrator has therefore been suggested and a scheme worked out by Burgess and Wood (45). The process is based on the principle that surfactants are present at a much higher concentration at the liquid/air interface than in the bulk solution. Frothing by means of an air stream followed by skimming the froth from the surface therefore reduces the concentration in the residual solution. The collected froth can then be treated by conventional methods on a much smaller scale (41, 43).

#### d) Precipitation

Household detergents all contain syndets of the anionic type and are therefore precipitated quantitatively by cationic agents added in stoichiometric proportions. This procedure is suitable for small scale treatment but as the amount required is approximately equal to the amount of anionic syndet in the system and cationic surfactants are usually more expensive than anionics, the total cost of treating sewage effluent would be prohibitive.

#### e) Extraction

A method sometimes used in problems of this type is to extract with a kerosine solution of a compound which forms a complex with the material which is to be removed. Water insoluble tertiaryamines are suitable for compounds of an anionic nature, and trilaurylamine has the required properties. It is soluble in kerosine, insoluble in water and therefore not easily lost to the aqueous phase. When the kerosine phase has taken up the syndet to its capacity, the volume is still small enough to make a regeneration procedure economical. In this case dilute alkali is a suitable regenerant.

#### f) Antifoam agents

When foam is the main problem, antifoaming agents, such as petroleum oils have proved effective (39). This does not, of course, remove any of the active material and other troubles may arise at different points in the system.

#### g) Adaptation

By analogy with similar systems it is most likely that a strain of bacteria could be developed which would be capable of attacking branched alkyl groups. Unfortunately straightchain material derived from grease and soap is present in all sewage so adaptation would not be possible when an alternative source of hydrocarbon was available.

### VI. Synthesis of Potentially Biodegradable Syndets

#### a) Raw materials

The larger part of the syndet molecule is the hydrophobic portion, which is usually hydrocarbon in character. This therefore contributes the greater cost. The main sources are natural fats and petroleum, the latter having the advantages of steady supply, low cost and ease of handling. Among natural oils the cheapest are derived from tallow, talloil and soyabean oil, but these are all in the  $C_{18}$  range whereas the optimum chain length is  $C_{12}$  to obtain good detergency combined with solubility. They do, however, give derivatives suitable for use in toilet bars when high solubility is not required. Another disadvantage is that the polar group is a carboxylic acid which requires expensive procedures to convert to the more suitable sulphate or sulphenate group. In contrast the petroleum derived olefins may be readily condensed with benzene and the benzene sulphonated to give true sulphonic acids.

#### c) Fatty derivatives

As mentioned earlier the most useful fatty derivatives are in the C<sub>12</sub> range. These are mainly derived from coconut oil, which is an uncertain market and has a high cost. Conversion to usable material, such as the corresponding fatty alcohols is expensive so the final syndet is also expensive. The cheaper fats, such as tallow, in the form of the corresponding alcohols may be converted to products with more suitable properties by increasing the size of the hydrophills group. This is usually done by condensing with ethylene oxide.

$$ROH + n(CH_2)_2 O \longrightarrow R(OCH_2 CH_2)_n OH$$
$$ROH + 4(CH_2)_2 O \longrightarrow R(OCH_2 CH_2)_L OH$$

or

$$\xrightarrow{H_2SO_4} R(OCH_2CH_2)_4OSO_3H$$

Such products are on the market but are a little more expensive than the petroleum derivatives.

The fatty acids may also be converted to the chlorides and condensed with intermediates such as methyl taurine.

 $\begin{array}{c} CH & CH \\ 1 & 3 \\ RCOC1 + & NHCH_2CH_2SO_3Na \longrightarrow RCONCH_2CH_2SO_3Na \end{array}$ 

These also are biodegradable, and are used in toilet bars but would be too expensive for the standard household detergent.

#### d) Petroleum derivatives

A.B.S. which we have classed as the standard petroleumderived syndet is made from propylene by polymerizing to tetrapropylene, using to alkylate benzene and sulphonating the alkyl benzene to give an alkyl benzene-sulphonic acid the sodium salt of which is "A.B.S." It is the branched tetrapropylene which is responsible for the nonbiodegradability of the end product. Four methods are now available for the preparation of syndets with improved biodegradability from petroleum raw materials.

## (i) Cracking of paraffins

Normal paraffins are readily obtainable from lubricating oil extracts by solvent recrystallization or urea adduction and when suitably cracked yield alpha olefins which may be used to alkylate benzene.

$$CH_3(CH_2)_n CH = CH_2 + \bigcirc \longrightarrow CH_3(CH_2)_n CH \bigcirc I_3$$

Sulphonation of the resulting alkyl benzene give the type of product used in the Luton tests. Although it contains a secondary group it would presumably be degraded to:

CH3 CH which would have considerably less surface

activity than the original material.

# (ii) <u>Alcohols from ethylene with Ziegler catalysts</u>

Alcohols may be produced directly from ethylene by polymerization with a Ziegler type catalyst followed by oxidation and hydrolysis of the high molecular weight alkyl aluminum. The stages in the process are as follows:

	al = 1/3 Al
Polymerization	al R + n $C_2H_4 \longrightarrow al(C_2H_4)_nR$
Oxidation	$al(C_2H_4)_nR + 0 \longrightarrow al O(C_2H_4)_nR$
Hydrolysis	2al $O(C_2H_4)_nR+H_2SO_4 \rightarrow al_2SO_4 + R(C_2H_4)_nOH$

The resulting alcohol may be used in exactly the same way as fatty alcohols to produce fatty alcohol sulphate detergents, by the action of chlorsulphonic acid.

Sulphation  $R(C_2H_4)_nOH + CISO_3H \longrightarrow R(C_2H_4)_nOSO_3H + HCl$ Neutralization  $R(C_2H_4)_nOSO_3H + NaOH \longrightarrow R(C_2H_4)_nOSO_3N_a + H_2O$ 

These are excellent detergents and wetting agents, although many users prefer A.B.S. and having a straight paraffin chain should be readily biodegradable. They differ from the corresponding fatty acid derivatives only in the cost of the raw material and although catalyst cost is at present high, increased production will bring this down considerably. A 100,000,000 lb. per annum plant to make a range of alcohols by this process has just gone on stream.

### (iii) Alpha olefins from ethylene with Ziegler catalysts

One disadvantage of the previous process is the fact that an equimolecular proportion of aluminum alkyl is necessary and recovery of catalyst is not possible. It has been discovered that by use of a second catalyst at a higher temperature, it is possible to displace the higher olefin by ethylene and regenerate the triethyl aluminum. The stages of this process are as follows:

Polymerization  $alR + n(C_2H_4) \rightarrow al(C_2H_4)_nR$ Displacement  $al(C_2H_4)_nR + C_2H_4 \rightarrow alC_2H_5 + CR_2 - CH(C_2H_4)_{n-1}R$ 

The resulting olefins are fractionated, the lower olefins recycled and the aluminum alkyl recovered in the form of its dichloro-ethyl ether complex.

Recycle 
$$alC_2H_5 + CH_2 = CH(C_2H_4)_nH \rightarrow al(C_2H_4)_{n+2}H$$
  
Buildup  $al(C_2H_4)_{n+2}H + C_2H_4 \rightarrow al(C_2H_4)_{n+3}H$ 

The separated olefins in the  $C_{12-18}$  range may then be used for alkylation of benzene in the same manner as tetrapropylene.

Alkylation

$$R CH = CH_2 + CH_2 CH_3 CH$$

Sulphonation

Sulphonation 
$$R > CH \bigcirc + SO \rightarrow R > CH \bigcirc SO H$$
  
 $CH_3 \qquad 3 \qquad CH_3 \qquad 3$   
Neutralization  $R > CH \bigcirc SO H + NaOH \rightarrow R > CH \bigcirc SO Na + H O$   
 $CH_3 \qquad 3 \qquad CH \bigcirc SO H + NaOH \rightarrow R > CH \bigcirc SO Na + H O$   
 $CH_3 \qquad 3 \qquad 2$ 

The properties of the resulting syndet are the same as those of the cracked paraffin derivatives.

#### (iv) Radiation techniques with n-paraffins

During the last war, detergents were made in Germany by the sulphochlorination of paraffins under ultra violet radiation. By this process an alkyl sulphonyl chloride was obtained which could be hydrolyzed to a sulphonic acid.

 $RH + SO_2 + Cl_2 \rightarrow RSO_2Cl + HCl$ Sulphochlorination  $RSO_2C1 + H_2O \rightarrow RSO_3H + HC1$ Hydrolysis  $RSO_3H + NaOH \rightarrow RSO_3Na + H_2O$ Neutralization

Although the optimum range of paraffins was not avail-able, because these were being used for the production of fatty acids, detergents of good quality were obtained by this procedure, and improvements have been made on this continent (65). The process may be worthy of further investigation because of the high reactivity of the sulphonyl chloride group which could lead to a variety of new derivatives.

More recently it has been found that direct sulpho oxidation is possible and this process has been facilitated by the use of gamma radiation (66,67). The ready availability of radioactive by-products from nuclear power plants may make reactions of this type even more feasible. Although there are many intermediate and side reactions the essential process is:

> $RH \xrightarrow{\sim} R^{\circ} + H^{\circ}$  $R^{\circ} + SO_2 \longrightarrow R SO_2^{\circ}$  $R SO_2^o + O + RH \rightarrow R SO_3H + R^o$

The alkyl chain is primary or secondary according to the point of attack of the gamma rays but in either case the resulting syndet is more easily degraded than A.B.S.

#### e) Sucrose derivatives

In addition to the possibility of improving the biodegradability of syndets by changing the nature of lipophilic portion it is also possible to change the hydrophilic portion. Most syndets owe their water solubility to the presence of a carboxyl group, a sulphonic acid group or a polyglycol chain. One of the most water soluble organic solids known is sucrobe and as this is a cheap raw material, attempts have been made to attach to it a hydrocarbon chain. It also has the advantage of ready biodegradability.

Products of this type have been produced from fatty acids by action of their methyl esters on sucrose, and the difficulty of finding a mutual solvent has been met by the development of new solvents such as dimethylformamide and dimethylsulphoxide. Such products are now on the market but sucrose ethers have the disadvantage of being easily hydrolyzed and saponified. It has been shown (70) that the more stable sucrose esters are equal to the best anionic and nonionic syndets available. Unfortunately the processes involved are less simple and more expensive.

#### Conclusion

If it became essential, detergents with the necessary biodegradability could be put on the market immediately, but this would involve appreciable increases in detergent prices. Until costs of the new processes can be scaled down sufficiently there are a few things that can be done to make an appreciable improvement.

1) Partial replacement of A.B.S. with straight chain alcohol sulphates which are now available.

2) The use of alkylates which are less highly branched such as those obtained from cracked paraffins.

3) Froth concentration of sewage effluents.

4) Increase in solids capable of absorbing detergents in the sewage system.

It is obvious that there is still much research to be done but there is no shortage of ideas in the many fields of polymerization, sugar chemistry, radiation chemistry and biochemistry.

In conclusion I would like to than the Ontario Research Foundation for permission to give this paper and Mr. R.H. Shannon of Ethyl Corporation who supplied some of the information on recent developments in the application of Ziegler catalysts to this field.

# SUMMARY OF RESULTS OBTAINED IN LUTON TESTS

• Date	PT/ Coverage in	JN J	Avg. of 3 Tests/week Percent Removed	Wt.in 7 o Sewage	lay period Effluent	Syndet conc. in River 16 miles below
Date April 58 May June July Aug. Sept. Oct. Nov. Dec. Jan. 59 Feb. Mar. April May June July Aug. Sept. Oct. Nov. Dec. Jan. 60 Feb. Mar. April May June				Sewage 4900 4669 4137	Effluent 1026 1145 931	River 16 miles below 318 lbs./day 258 lbs./day 209 lbs./day 197 lbs./day 216 lbs./day 216 lbs./day 151 lbs./day 164 lbs./day 133 lbs./day 141 lbs./day 134 lbs./day
			-		3	а. В.

page 301

# BIBLIOGRAPHY

# BIOCHEMICAL DEGRADATION OF SYNTHETIC DETERGENTS

# Contents

- I. General
- II. Tests on Sewage and Effluent Systems
- III. Treatment of Sewage and Water Containing Syndets
  - IV. Relation between Chemical Structure and Biodegradability
  - V. Analytical Methods
  - VI. Methods of Preparing Syndets

#### I. GENERAL

1. WHAT CAUSED THE SUDS IN THE SEWAGE-TREATMENT PLANT? Anon., Amer. City <u>42</u>, No. 12, 99 (1947) C.A. <u>42</u> 4295h

2. DETERGENTS IN SEWAGE

F.J. Coughlin (Proctor & Gamble); Soap & Chem. Specialties <u>32</u>, No. 2, 51 - 3, 67, 69, 71 (1956) C.A. <u>50</u> 5312f

3. INFLUENCE OF SYNDETS ON SEWAGE TREATMENT

P.N. Degens Jr., (Kg. Shell-Lab., Amsterdam) Congr. mondial detergence et prods. tensioactif, ler, Paris 1954, <u>3</u> 1054-8 (Pub. 1956) C.A. <u>51</u> 18403i

4. SYNTHETIC DETERGENTS

R.E. McKinny and J.M. Symons (M.I.T.) Water and Sewage Works <u>105</u>, 425-7 (1958) C.A. <u>53</u> 8666i

5. DETERGENTS AND THEIR INFLUENCE ON SEWAGE PURIFICATION

W. Winter. Wasserwirtsch-Wassertech. <u>9</u>, No. 1, 15-21 (1959).
C.A. 53 16427

6. HOUSEHOLD DETERGENTS IN WATER AND SEWAGE

P.J. Weaver (Proctor and Gamble Co.) Water and Sewage Works <u>107</u>, 459 - 62 (1960) C.A. <u>55</u> 20271g

7. SYNTHETIC DETERGENTS IN GROUND WATER I AND II

L.G. Campenni, Water and Sewage Works <u>108</u>, 188-91 (1961), 310 - 13 (1961)

- 8. THE INFLUENCE OF DETERGENTS ON WATER ECONOMY
   R. Krüger, Seifen-Ole-Fette-Wachse 86 289 92 1960
   C.A. <u>54</u> 21564d
- 9. NEW CHALLENGE IN WATER CLEANUP

Anon. Chemical Week Aug. 19, 1961, 41-2, 45-6.

10. DETERGENTS IN SEWAGE AND WATER TREATMENT PLANTS

W.K. Griesinger (Atlantic Refining Co.) Soap Chem. Specialties <u>37</u>, No. 3, 295-6 (1961) II. TESTS ON SEWAGE AND EFFLUENT SYSTEMS

11. ANIONIC SYNDETS IN AMSTERDAM SEWAGE

P.N. Degens et al. (Koninkl. Shell Lab. Amsterdam). Sewage & Ind. Wastes 25, 20-5 (1953) C.A. <u>47</u> 4529

12. THE BIOLOGICAL OXYGEN DEMAND OF TEXTILE CHEMICALS

Rhode Island Section Subcommittee on Stream Pollution. W. Stafford et al. Am. Dyestuff Reptr. <u>44</u>, Proc. Am. Ass. Text. Chem. Colorists, P. 355 - 9 (1955) C.A. <u>49</u> 11290b

13. SYNTHETIC DETERGENTS AND WATER SUPPLIES I. SYNTHETIC DETERGENTS AND THEIR PRESENCE IN RIVERS AND RESULTS OF INVESTIGATIONS INTO THEIR EFFECT ON WATER-TREATMENT PROCESSES.

> C. Hammerton; Proc. Soc. Water Treatment Exam. 5, Pt. 2, 145 - 60 (1956) C.A. <u>54</u> 13507b

14. TOXICITY OF SEWAGE EFFLUENT

D.W.M. Herbert (Lab. Research Water Pollution, Stevenage, Engl.) Bull. centre belge étude et document eaux (Liége) No. <u>32</u>, 1 15-20 (1956) C.A. <u>50</u> 13, 343g

15. BIOLOGICAL BEHAVIOUR OF SYNTHETIC DETERGENTS

C.N. Sawyer et al. (M.I.T.) Ind. Eng. Chem. <u>48</u>, 236 - 40 (1956) C.A. <u>50</u> 7484c

16. SYNDETS AND WASTE DISPOSAL

R.E. McKinney (M.I.T.) Sewage & Ind. Wastes <u>29</u>, 654-66 (1957) C.A. <u>51</u> 13275d

17. AERATION SYSTEMS FOR BIOLOGICAL WASTE TREATMENT

W. Wesley Eckenfelder, Jr. Ind. Wastes 2, 9 - 14 (1957) C.A. <u>51</u> 9982i

18. THE EFFECT OF SYNTHETIC DETERGENTS ON THE TREATMENT OF SEWAGE

H. Mann and D.W.M. Herbert (Lab. Research, Water Pollution, Stevenage Engl.) Water & Sanit. Engr. <u>6</u>, 206 - 9 (1957) C.A. <u>51</u> 8339h

19. THE REMOVAL OF ANIONIC SYNDETS BY BIOLOGICAL PURIFICATION PROCESSES

> F.W. Roberts. Water & Waste Treatment J. <u>6</u> 302-3 (1957) C.A. <u>51</u> 18405e

20. EFFECTS OF A NON-IONIC SYNTHETIC DETERGENT ON BIOLOGICAL PERCOLATING FILTERS

> L.W. Oldham. Inst. Sewage Purif., J. Proc. 1958, pt. 2, 136-45. C.A. <u>54</u> 3807a

21. EFFECTS OF SYNDETS ON AERATION PROCESSES

A.L. Downing (Water Pollution Res. Lab., Stevenage, Engl.) Bull, centre belge étude et document eaux (Liége) No. 43 24-31 (1959) C.A. <u>53</u> 22624h

22. DECOMPOSITION OF CELLULOSE IN DETERGENT-CONTAINING WATER

G. Klust and H. Mann (Bundes. Fischerei, Hamburg) Vom Wasser <u>26</u>, 93 - 109 (1959) C.A. 55 21427f

23. BREAKDOWN OF SOME OF THE NEWER SYNTHETIC DETERGENTS IN SEWAGE TREATMENT

P.C.G. Isaac and D. Jenkins (Univ. Durham) Inst. Sewage Purif. J. Proc. 1960, pt. 3, 314 - 29 C.A. <u>55</u> 7720i 24. THE EFFECTS OF ALKYL BENZENE SULPHONATES ON ANAEROBIC SLUDGE DIGESTION

J.W. Hernandez and D.E. Bloodgood (New Mexico Dept. Health) J. Water Pollution Control Federation <u>32</u>; 1300 - 11 (1960) C.A. <u>55</u> 7721c

25. SURVEY OF PHOSPHATE AND A.B.S. CONCENTRATIONS IN ILLINOIS STREAMS

> J.J. Morgan and R.S. Engelbrecht (Univ. Ill.) J. Am. Water Works Assoc.) <u>52</u> 471-82 (1960) C.A. <u>55</u> 27716f

26. ASSESSMENT OF "SOFTNESS" IN A SYNTHETIC DETERGENT BY BIOLOGICAL MEANS

> F.W. Roberts (Sewage Dept., Luton, England). Inst. Sewage Purif., J. Proc. 1960, 469 - 72. C.A. <u>55</u> 26482f

27. EFFECTS OF ANIONIC SURFACE-ACTIVE AGENTS ON WASTE WATER TREATMENT UNITS

> G.W. Malaney et al. (Ohio State Univ.) J. Water Pollution Control Federation 32, 1161-72 (1960). C.A. <u>55</u> 5823

28. ASSIMILATION OF ABS BY AN ACTIVATED SLUDGE TREATMENT PLANT-WATERWAY SYSTEM

> E. Hurwitz et al. (Metropolitan Sanitary District of Greater Chicago) J. Water Pollution Control Federation <u>32</u>, 1111-16 (1960) C.A. 55 3888i

29. THE MANUFACTURERS PART IN THE LUTON EXPERIMENT

G.V.V. Squire (Thos. Hedley & Co. Ltd., Newcastleon-Tyne, Engl.) Inst. Sewage Purification, J. & Proc. 1961, Pt. 1, 27-9.

30. BEHAVIOUR OF A NEW SYNTHETIC DETERGENT IN SEWAGE-TREATMENT PROCESSES

> G.E. Eden and G.A. Truesdale (Water Pollution Res. Lab., Stevenage, Engl.) Inst. Sewage Purification, J. & Proc. 1961, Pt. 1, 30 - 42.

31. DECREASE IN THE CONTENT OF SURFACE ACTIVE MATERIAL IN THE RIVER LEE

> C. Hammerton (Metropolitan Water Board). Inst. Sewage Purification, J. & Proc. 1961, part I, 48 - 9.

32. ABS IN DRINKING WATER IN THE U.S.

AASGP Committee Report (Assoc. Amer. Soap & Glycerine Producers) J. Amer. Water Works Assoc. 53, 297 - 300 (1961) C.A. 55 13721f

33. ABS IN MICHIGAN SUPPLIES

G.E. Oliver (State Dept. of Health, Lansing, Mich.) J. Amer. Water Works Assoc. <u>53</u>, 301-2 (1961) C.A. <u>55</u> 13721e

34. REMOVAL OF SYNTHETIC DETERGENTS IN SEWAGE TREATMENT PROCESSES: TRIALS OF A NEW BIOLOGICALLY ATTACKABLE MATERIAL

> G.A. Truesdale et al. (Water Pollution Res. Lab., Stevenage, Engl.) Water & Waste Treatment J. 7, 441 - 4 (1959)

35. TREATMENT OF POLLUTED WATERS, EFFLUENTS, URBAN AND INDUSTRIAL WASTES

Soc. anon. d'innovations chim. dite Sinnova ou Sadie; Fr. Pat. 1,050,692 (Jan. 11, 1954) C.A. <u>52</u> 20806a

36. THE CONTROL OF THE EFFECT OF SYNDETS ON SEWAGE TREATMENT BY CHEMICAL COAGULATION

> S. Beaver (Peter Spence & Sons, Widnes, Engl.) Congr. Mondial detergence et prods. tensio-actif, ler, Paris 1954, <u>3</u>, 1059-63 (Publ '56) C.A. <u>53</u> 18399

37. SYNTHETIC DETERGENTS IN RELATION TO THE PURIFICATION OF SEWAGE

W.T. Lockett; Inst. Sewage Purif., J. Proc. 1956, 225 - 45. C.A. <u>53</u> 19237

38. SYNTHETIC DETERGENTS: SOME RESULT OF THEIR DEGRADATION

P.E. Spargo (Sewage works, Johannesburg, S. Africa). Inst. Sewage Purif. J. Proc. 1959, Pt. 2, 236 - 40. C.A. 54 21564

39. CONTROL OF SYNTHETIC DETERGENT FOAM BY OIL-BASED DEFOAMANTS

D. Rayner (Sewage Works, Slough, England) Inst. Sewage Purif., J. Proc. 1960, Pt. 1, 27 - 9. C.A. 55 6743

40. EXPERIMENTS FOR REMOVING ANIONIC SYNDETS DISCHARGED INTO RIVER WATERS

> M. Chambon & Andri Giraud. Bull. Acad. Natl. Med. (Paris) <u>144</u>, 631-6 (1960) C.A. <u>55</u> 8715

41. THE ADSORPTIVE PRECIPITATION AND SKIMMING OF DETERGENTS FROM AQUEOUS SOLUTION

> H.P. Kaufman and F. Malz (Deut. Inst. Fettforschung, Münster) Fette, Seifen, Anstrichmittel <u>62</u>, 1024 - 30 (1960).
> C.A. 55 9739g

42. SYNDET REMOVAL FROM DRINKING WATER USING ACTIVATED CARBON

M. Lieber (Nassau County Dept. of Health, Long Island) Water & Sewage Works <u>107</u>, 299 - 301 (1960).

C.A. <u>55</u> 3887c

43. FOAM FRACTIONATION FOR REMOVAL OF SOLUBLE ORGANIC MATERIAL FROM WASTE WATER

> I.A. Eldits (Esso Research & Engineering Co.) J. Water Pollution Control Federation 33, 914-31 (1961)

44. ACTIVATED CARBON FOR TREATMENT OF CONDITIONS ATTRIBUTED TO SYNTHETIC DETERGENTS

> E.A. Sigworth (W. Virginia Pulp & Paper) J. Am. Water Works Assoc. <u>53</u> 1003-6 (1961) C.A. 55 27717h

45. SOME NOTES ON REMOVAL AND DISPOSAL OF SYNTHETIC DETERGENTS IN SEWAGE EFFLUENTS

S.G. Burgess and L.B. Wood; Inst. Sewage Purif. 1962, Pt. 2, 158-68.

- IV. RELATION BETWEEN CHEMICAL STRUCTURE AND BIODEGRADABILITY
- 46. BIOLOGICAL ASPECTS OF THE PROBLEM OF DETERGENTS IN SEWAGE

G. van Beneden; Bull, centre belge étude et document eaux (Liége) No. <u>17</u>, 159-64 (1952) C.A. <u>47</u> 12710f

47. BIOCHEMICAL DEGRADATION OF SYNTHETIC DETERGENTS I. PRELIMINARY STUDIES

> R.H. Bogan and C.N. Sawyer (M.I.T.) Sewage and Ind. Wastes <u>26</u>, 1069-80 (1954) C.A. <u>49</u> 3451h

48. BIOCHEMICAL DEGRADATION OF SYNTHETIC DETERGENTS. II. RELATION BETWEEN CHEMICAL STRUCTURE AND BIOCHEMICAL OXIDATION

> R.H. Bogan and C.N. Sawyer (M.I.T.) Sewage & Ind. Wastes <u>27</u>, 917 - 28 (1955) C.A. 50 4433c

49. EFFECTS OF SYNDETS ON BOD TESTS

W.D. Sheets and G.W. Malaney, Ohio State Univ. Studies, Eng. Exptl. Sta. Bull No. <u>157</u>, 1 - 10 (1955) C.A. 52 623f

50. THE ACTION OF LYTIC AGENTS ON THE SURFACE STRUCTURES OF THE BACTERIAL CELL

> M.R.J. Salton (Univ. Manchester, Engl.) Proc. 2nd Int. Congress Surface Activity, <u>4</u>, 1957.

51. THE C.O.D. VALUES OF SYNDETS, SURFACTANTS AND BUILDERS

W.D. Sheets and G.W. Malaney (Ohio State Univ.) Proc. Ind. Waste Conf., 11th Conf. <u>1956</u>, 185 -96 (Pub. 1957) C.A. 51 13274f

52. THE BIOCHEMICAL OXIDATION OF SYNTHETIC DETERGENTS

R.H. Bogan and C.N. Sawyer (Univ. Washington, Seattle) Proc. Ind. Waste Conf. 1955, 231 -43 (Pub. 1956) C.A. <u>51</u> 8339g

53. SYNTHETIC DETERGENTS AND WATER SUPPLIES II. CHEMICAL CONSTITUTION OF ANIONIC SURFACE ACTIVE COMPOUNDS AND THEIR SUSCEPTIBILITY TO BIOCHEMICAL OXIDATION

> C. Hammerton. Proc. Soc. Water Treatment Exam. <u>5</u> Pt. 2 160 - 74 (1956) C.A. <u>54</u> 13507d

54. EFFECTS OF SYNDETS ON ACTIVATED SLUDGE

R.M. Manganelli (Rutgers Univ.) Proc. Ind. Waste Conf. 11th Conf. (1956) 611-21 (Pub. 1957) C.A. <u>51</u> 13275b

55. SYNTHETIC DETERGENTS AND THE PURIFICATION OF WASTE WATER

N.A. Lykinykh. Materialy Soveshchaniya po Voprosam Ochistki Prom. i Stochnykh Vod, Moscow 1955, 172, (Pub. 1957) C.A. <u>54</u> 9169i

56. SYNTHETIC DETERGENTS WITH THE EASIEST BIOLOGICAL DECOMPOSITION

V.C.E. Burnop and H.J. Bunker (Esso Research Ltd., Abingdon, England) Centre belge étude et document eaux, Bull. trimestr. cebedeau 4, No. 50, 262-8 (1960)

C.A. 55 15963f

## V. ANALYTICAL METHODS

57. DETERMINATION OF ANIONIC DETERGENTS IN SEWAGE, SEWAGE EFFLUENT AND RIVER WATERS

J. Longwell and W.D. Maniece. Analyst, <u>80</u>, 167 (1955)

58. DETERMINATION OF THE SYNDET CONTENT OF SEWAGE SLUDGE

F.W. Roberts and G.R. Lawson. Water & Waste Treatment J. <u>7</u>, 14 - 17 (1958) C.A. <u>52</u> 20797g

59. DETERMINATION OF DETERGENTS IN WATER AND WASTES

J. Nowacki (Inst. Gospodarki Komunalnej, Gliwice, Poland) Gaz, Woda i Tech. Sanit. <u>33</u>, 360 - 3 (1959)

60. DETERMINATION OF BIOLOGICALLY SOFT AND HARD ALKYL BENZENE SULPHONATES IN DETERGENTS AND SEWAGE

C.P. Ogden et al. (Thos. Hedley & Co. Ltd.) Analyst 86, 22-9 (1961) C.A. 55 21625i

61. DETERMINATION OF ALKYL BENZENE SULPHONATES IN SEWAGE

Anon. J. Water Pollution Control Federation 33, 85 - 91 (1961) C.A. 55 8714

62. DETERMINATION OF SURFACTANTS IN WASTE WATER

B. Pohl (Gottwaldov, Czech.) Prumysl potravin <u>12</u>, 230 - 2 (1961)
C.A. <u>55</u> 23880g

63. AVAILABLE METHODS FOR THE DETERMINATION OF SMALL AMOUNTS OF ANIONIC SURFACTANTS IN WATER AND WASTE WATER

> W.K. Fischer (Henkel and Co.) Fette, Seifen, Anstrichmittel <u>53</u>, 14-23 (1961) C.A. <u>55</u> 13723f

64. ANALYTICAL PROBLEMS IN THE LUTON EXPERIMENT

H.L. Bolton and P.J. Cooper (Lab. of Govt. Chemist). Inst. of Sewage Purification, J. & Proc. 1961, Pt. 1, 43 - 7.

#### VI. METHODS OF PREPARING SYNDETS

65. SULPHOCHLORINATION OF PARAFFIN HYDROCARBONS

du Pont. Brit. Pat. 549,512

66. DETERGENTS BY NUCLEAR PROCESSES

J.F. Black and E.F. Baxter (Esso Res. & Eng. Co., Linden, N.J.) Soap Chem. Specialties <u>34</u>, No. 10, 43 - 6, 104-7 (1958) C.A. <u>53</u>

67. RADIATION INITIATED SULFOXIDATION OF HYDROCARBONS

J.F. Black and E.F. Baxter (Esso Research & Engineering Co.) Int. Conf. on the Peaceful Uses of Atomic Energy (2nd) (Geneva) 29, 162 - 5 (1958)

68. LINEAR AND STEREOREGULAR ADDITION POLYMERS

G. Gaylord and H.F. Mark. Chap. VII Ziegler-type catalysts p. 87 - 186. Interscience Publishers, N.Y. 1959.

69. PROCESS NARROWS ALPHA-OLEFIN CUT

Anon. Chem. & Eng. News 1961, Sept. 18, 81.

70. SUCROSE ETHER- AND ESTER-LINKED SURFACTANTS

V.R. Gaertner (Monsanto Chem. Co.) J. Amer. Oil Chemists Soc. <u>38</u>, 410 - 18 (1961)









HEAD TABLE GUESTS -- JUNE 26

# WATER CONSERVATION AND WASTE CONTROL

.

by

R. Hobart Souther



"WATER CONSERVATION AND WASTE CONTROL"

by

R. HOBART SOUTHER, RESEARCH CONSULTANT

CHAS. A. DANA, SCIENCE HALL

GUILFORD COLLEGE, GREENSBCHO

NORTH CAROLINA, U.S.A.

The conservation of water, our most precious natural resource, is necessary if we are to have enough clean water to meet the essential needs of life itself - our industrial technology - agriculture and conservation of fish and wild life resources, as well as recreational facilities.

Fresh water usage in the U.S. has doubled since 1945 from 150 billion to 300 billion gallons daily. By 1980, it is projected to double again to 600 billion gallons a day. This amount is practically as much as the volume of all the streams and rivers in the United States. In many areas, there is now a water shortage, notably in the Ohio River, which at low flow is used almost four times in its flow from Pennsylvania to the Mississippi. When water is reused, pollution control becomes an economic necessity and an integral part of water resources development and use.

Pollution control may be considered in the broader problem of environmental health protection, since the national health may be endangered by certain contaminants.

In this second industrial revolutionary age, we are exposed to new environmental pollutants and conditions - the additive chemicals in drinking water, in processed food, in the air, increased ionizing radiation - that pose new health problems.

These problems in water conservation and pollution control apply not only to the U.S. but to Canada, Great Britain and other European and Asiatic nations - in fact, in all areas where the new industrial revolution and sewage pollution from population centers have increased the need for fresh water beyond the normal supply. When external boundary waters are polluted, it becomes an international problem, just as it is an interstate problem in the Ohio River Valley. Thus, we need such activities on boundary water quality as conducted by the International Joint Commission, United States and Canada.

Here in Ontario is one of the best organizations of any nation, designed to deal effectively with water supplies and waste disposal - The Ontario Water Resources Commission. The OWRC assures maintenance of public water supplies in a safe condition for domestic and other uses, including proper treatment of sanitary and industrial wastes before discharging into streams. It aids in financing modern water and sewage treatment works. There are six commissioners with staff, laboratory and research facilities for water surveys, sampling techniques and fundamental and applied research on sewage and industrial waste.

Realizing the importance of water pollution control, President Eisenhower in one of the last acts of his administration called a national conference on water pollution in Washington, D. C., December 12-14, 1960, with more than 1200 in attendance representing U. S. Public Health, research agencies, industrial, wild life, recreation, engineering, governmental, legal and finance groups. The theme of the conference was "Clean Water -A Challenge to the Nation."

The purpose of the conference was to assess the problem of water pollution to determine its effect on national welfare. and to set realistic goals for its control.

Senator Kerr stated we must no longer endanger the national health or survival by permitting a price tag to prevent action and that we must do what is required. Further, greater research was an absolute necessity as a means to find ways to abate pollu-tion and to do it more rapidly at less cost. Conservative sanitary authorities estimate that \$600 million annually for the next eight years is the minimum required for the construction of disposal facilities of human sewage alone.

These statements show the seriousness of the problem. Pollution is increasing faster in certain areas of the Great Lakes than the success of efforts to control it. Last year, Lake Michigan pollution in the Milwaukee area was so severe that two of the county's 10 public beaches were closed. Cleveland is losing its fight to keep beaches along Lake Erie clean enough for swimming. Other areas including Buffalo present problems.

Conclusions reached at this conference include:

- I. Recommendation of a national credo.
  - A. Users of water do not have an inherent
  - right to pollute. B. Users of public waters have a responsibility for returning them as clean as is technically possible.
  - C. Prevention is just as important as control of pollution.

- II. Streams must be kept as clean as possible, rather than working them to death digesting wastes.
- III. Research must be increased, supported by the Federal Government.

One statement implied that industry was ahead of municipalities in conservation and in safekeeping of water supplies.

But, many felt the great need of more research and training of researchers, engineers, and operators. The majority felt that states should continue control rather than extend Federal authority in pollution control problems. It was stated that industry was obligated to undertake basic research on biotic effect of products they distribute, such as detergents, insecticides, metallic wastes, etc., and let government do it, if the responsibility was not covered by industry.

One statement which I made to the conference stressed the need for further research on treatment of various industrial wastes to adopt the new low cost bio-aeration method developed for textile waste treatment: Proceedings, The National Conference on Water Pollution, Page 598.

Much has been said about the need for funds for more research by the Federal agencies. In my opinion, the present funds would be more useful if greater emphasis was given to the research directly applicable to pollution abatement.

I would like to state that industry has contributed far more than the governmental agencies in research toward cleaning up the streams of the nation. Federal research funds now are largely spent on basic research rather than on the applied research which would give more direct benefits to both industry and municipalities. Lower cost methods of waste treatment are needed to obtain universal acceptance by industry and thus ensure a complete cleanup of the nation's streams. Industry is moving forward in both research and construction to solve its problems, particularly the textile industry which I represent.

The importance of waste water control and water conservation in meeting our essential needs is well recognized by alert and progressive leaders of the textile industry.

Progress in pollution abatement in the past has been handicapped by the relatively high cost of treatment, due partly to use of outmoded conventional processes. Further, claimed difficulty in treating mill wastes biologically has confused researchers seeking cheaper treatment. A paper presented at the 1955 National AATCC Meeting in Atlanta showed that even highly alkaline mill waste and sewage could be satisfactorily treated.

The textile industry has spent millions in research and plant construction, and is becoming more and more aware of its responsibility in promoting further research and building treatment plants to conserve water by using it and returning it to streams as clean as technically possible for other legitimate users.

The National AATCC Committee on Stream Sanitation and the U. S. Public Health Service National Technical Task Committee on Industrial Waste cooperate in disseminating information on the progress of textile waste treatment research. All interested members of the American Association of Textile Chemists and Colorists are invited to participate in the activities of the National AATCC Committee on Stream Sanitation.

An article, "Latest Word on Low-Cost Mill Waste Disposal", in the June, 1960 <u>Textile World</u> states, "Local and state laws are getting tough about mill waste disposal. It's a hard problem. But today, with new methods and better equipment, waste disposal isn't the costly job it once was." The great progress being made in acceptance and application of the lower-cost waste treatment processes, based on prolonged bio-aeration, may be found in more detail in the <u>American Dyestuff Reporter</u>, October 3, 1960, and Proceedings NTTCIW, 1959, Page 54.

These new waste treatment processes, developed by industry, approach the lower-cost oxidation pond treatment (referred to in <u>The Readers Digest</u>, July 1960). Further additional applied research by federal and state agencies in prolonged bio-aeration methods is suggested.

This brings up the particular problems involved in treatment of textile wastes. A comprehensive Industrial Waste Guide to the Cotton Textile Industry, prepared by the National Stream Sanitation Committee of The American Association of Textile Chemists and Colorists, has been published by the U.S. PHS and is available either from the National AATCC Stream Sanitation Committee or the U.S. Government Print Offices, Washington 25, This Cotton Textile Waste Guide gives D. C., price 25 cents. sources, characteristics and pollution effects of process wastes; remedial measures, such as in plant reduction of processing wastes, recovery and reuse of chemicals, substitution of chemicals and good housekeeping; treatment of wastes, such as separation, equalization and storage, screening, aeration, neutralization, chemical, precipitation, chemical oxidation and biological oxidation. Thebiological oxidation processes described are the trickling filter process, the activated sludge process, contact aeration, endogenous respiration and oxidation ponds. (The prolonged bio-aeration or aeration lagoons process which has been proven so successful in experimental treatment of Canton, Cone, Chicopee and Morgan textile plant wastes as a revolutionary low

cost efficient method was just being developed at the time of publication and is described in <u>Textile World</u>, the June, 1960 article, "Latest Word on Low-Cost Mill Waste Disposal.")

Also discussed in the Cotton Textile Waste Guide is sludge disposal, the solution of specific waste problems. Additional waste guides, prepared by the National AATCC Stream Sanitation Committee, now under the Chairmanship of Dr. Percival Theel, are "Waste Guide to the Wool Processing Industry" and "Waste Guide to the Laundry Industry", referred to in <u>American Dyestuff</u> <u>Reporter</u>, October 3, 1960.

Numerous publications about research and improved methods in Textile wastes treatment indicate that no other industry in the past few years has made more progress in reducing stream pollution. This achievement has resulted largely from active AATCC membership participation in the objectives of the National AATCC Committee on Stream Sanitation, which was originally formed to promote, encourage and inspire further research in stream pollution abatement as well as for the exchange of information among members of our association, and to cooperate in the work of the National Technical Task Committee on industrial waste.

A meeting held in Atlanta at the National AATCC Convention in 1954 brought forth two new concepts in waste treatment which have since been widely publicized. One was set forth in a paper by Duane Snyder reporting pollutional abatement results from the substitution of low BOD warp sizing chemicals, such as carboxy methyl cellulose for those of high BOD characteristics, such as starch and gums. Another new idea was reported in a paper presented by another textile research laboratory showing that highly alkaline mill wastes combined with sewage could be successfully treated in trickling filter and activated sludge processes without chemical adjustments. Certain published data prior to this time said this could not be done. John Brown of Cannon Mills reported on experiments in treating combined mill waste-sewage. which have since been applied very successfully to treatment of such mixtures in an enlarged trickling filter plant designed originally for treating only sewage.

These early findings accentuated the need for further research to obtain better and cheaper aeration methods. It was brought out in one case history that treatment of mill waste in a conventional trickling filter-activated sludge system would cost \$180,000 per year compared to treatment cost of less than \$60,000 per year in a recently developed bio-aeration lagoon system, with efficiencies in both processes above 90 percent removals of BOD.

Current textile waste research in general is directed toward further improvements in prolonged bio-aeration processes. An example is a study which I recently conducted for Penick and Ford, Ltd. Inc. with results showing that it is more economical

to treat strong desizing wastes along with dye and other wastes in bio-aeration processes than to substitute low BOD sizings for starch.

The acceptance by regulatory agencies of recently developed low cost prolonged bio-aeration processes for the treatment of textile wastes has resulted in accelerated programs of pollution abatement in a large number of mills throughout the industry, particularly in the South.

This new low cost complete treatment method, developed under my direction at Cone Mills, has been adapted for use by Cone Mills at Haw River and Greensboro plants, and by other textile groups, including Burlington, Caton, Chicopee and Morgan-Jones.

A textile plant using this streamlined process will pay approximately \$7,000 per year in operating costs to treat about a half-million gallons daily of extremely strong wastes, five times the normal strength of sewage. By comparison, some cities would charge about \$47,000 per year to treat the same volume in a conventional trickling filter or activated sludge municipal system. The capital cost of the new type of waste treatment plant could be amortized in four years with such savings.

A proposal for furtherresearch by federal agencies for application to wastes from other industries, such as chemical, pulp and paper, soap and glycerine has been submitted to The National Technical Task Committee Research Project Subcommittee. Experimental results on textile waste have shown more than 90% removal of pollutants, at 1/6 to 1/3 the cost of conventional activated sludge or trickling filter treatments now in use by most municipalities. (<u>Textile World</u>, June, 1960) Correlations of tank solids with efficiency show good results in 2000-6000 ppm solids range.

Another new technique is the biosorption process, which can be successfully applied to conventional activated sludge plants, increasing capacity 200 to 300 percent, at very little increase in capital cost.

These are a few of the highlights in textile waste treatment research. The treatment of any industrial plant waste is a specific problem because it largely depends on the size and standards set on receiving stream, volume and strength of wastes to be treated, nature and characteristics of waste, including toxicity. Whether to treat in a municipal plant will depend on over-all costs and joint benefits of joint treatment. The new low cost one-stage prolonged bio-aeration process costs considerably less than treatment in a joint municipal plant.

Construction costs range around \$25.00 per lb. BOD/day for treating dye and starch desizing wastes, either separately or combined with sewage, in the new biological aeration processes compared with \$100.00 per lb/day for treatment of the same wastes in conventional activated sludge, trickling filter, or combined processes. (Proceedings Fourth Southern Municipal and Industrial Waste Conference, 1955, Page 69.) Operating costs in the new bio-aeration methods range around 0.6 cents per 1b. BOD/day and about 1.8 cents per 1b. BOD/day in conventional processes. Construction costs of oxidation ponds may run to \$170.00 per 1b BOD per day, but operating costs are extremely low.

My research in experimental treatment shows that the new and simple aerobic process which eliminates expensive sludge digestion equipment removes up to 95% of BOD in starch desizing wastes at an amazingly low construction cost of approximately 1/6 as much as in a conventional or municipal waste treatment process. It thus becomes more economical to treat desizing wastes, along with dye and other finishing wastes in this onestage aerobic process than to use low BOD substitutes for starch to reduce the pollution load on stream or in conventional treatment plants. These data indicate the best answer yet to the greater research stressed by Senator Kerr as needed to find ways to abate pollution faster and cheaper.

More and exciting research in the future, to seek further improvements and efficiency in treating industrial wastes, is visioned. A great need still exists for continued research on aerobic treatment of starch desizing waste and for more intensive study on various factors influencing treatment efficiency, such as types of micro-organisms, various nutrients and pollutional loadings, if starch is to compete better with substitutes. Synthetic detergents do not respond to bio-treatment and experimentally may be removed by foam producing techniques, or as the British are proposing, in changing their molecular structure to make them more biologically reactive. The German Public Health Service will not permit synthetic detergents in effluents to streams. Dyes which lower the surface tension respond to removal by foaming techniques. Civic groups in California object to oxidation ponds because of mosquitos. The Mosquito Control Association is asking for relief.

A bibliography relating to research leading up to development of the new bio-aeration process is appended. "An Industrial Waste Guide for the Textile Industry", as previously mentioned, gives an excellent approach to the solution of specific waste problems.

In solving a textile waste water treatment problem, the following should be considered:

 Seek lowest cost satisfactory method through research - whether oxidation ponding, trickling filters, activated sludge or prolonged bioaeration.

- Study present in-plant processes to conserve water, reduce pollution load and eliminate toxic chemicals such as chrome and bactericides.
- 3. Conduct research, with all necessary guidance, to determine waste characteristics and correct size of treatment plant needed for each mill waste, if utmost economy is desired. Few plants if any can treat wastes alike because mill wastes differ in pH and amount of pollutants.
- Cooperate fully with state authorities in giving information to obtain acceptance of any new methods.

Since capital and operating costs of the new type waste treatment plants are considerably lower than conventional trickling filter or activated sludge plants, other industrial groups and cities treating industrial waste may be expected to follow with similar low cost bio-aeration plants. Industry will thus fulfill its obligation in conserving water and keeping streams as clean as possible, by accelerating pollution abatement programs through advances in research and greater acceptance of its responsibilities from resultant economies.

The need for industrial waste treatment including textile wastes is becoming increasingly urgent. Problems should be approached by a study of their magnitude, in-plant changes to reduce pollution loads and volumes; by reduction and subsitution of chemicals such as inorganic for organic and by good housekeeping. Analyses and laboratory pilot plant studies should follow to determine treatability and the most economical process for treatment.

When this is done, the textile industry will have learned to conserve its available water supply, use it to full advantage and return it to the stream in a condition suitable for other legitimate users. In doing so, it will thus fulfill its obligations to the National Credo and thus provide enough clean water to meet the essential needs of life.

## REGIS TRATION LIST

### NINTH ONTARIO INDUSTRIAL WASTE CONFERENCE

H. E. Archibald, Manager, R. K. Kilborn & Associates, 36 Park Lawn Rd., TORONTO 18, Ontario.

G. C. Armstrong, Department of Lands & Forests, Fish & Wildlife, TORONTO, Ontario

A. Assaly, Engineering Development Dept., Pulp & Paper Research, Institute of Canada, 3420 University St., MONTREAL, Quebec.

S. Aston, Chief Chemist, Courtauld's (Canada) Ltd., Montreal Rd., CORNWALL, Ontario.

M. E. Bailey, Manager, Industrial Products, B. F. Goodrich Canada Limited, 409 Weber St. W., KITCHENER, Ontario.

F. W. Bainborough, Sales Engineer, Dorr-Oliver-Long, 1810 Yonge St., TORONTO, Ontario.

S. M. Baker, Plant Engineer, The Proctor & Gamble Co. of Canada, Burlington St. E., HAMILTON, Ontario. P. E. Barolet, Waste Treatment Engineer, Northern Electric Co., Ltd., P. O. Box 6123, MONTREAL, Quebec.

R. G. Barrens, Engineering Technician, Ontario Water Resources Commission, 801 Bay St., TORONTO, Ontario.

T. W. Beak, Consultant, Box 220, COLLINS BAY, Ontario.

J. C. Bell, Process Chemist, Polymer Corp. Ltd., SARNIA, Ontario.

G. Belyea, Salesman, Nelson Chemical Co., 12345 Schaefer, DETROIT, Michigan.

Dr. A. E. Berry, General Manager, Ontario Water Resources Commission, 801 Bay Street, TORONTO, Ontario.

W. L. Bishop, Branch Manager, Chemical Developments of Canada, LONGFORD MILLS, Ontario.

P. J. Blundy, Eng. - Pollution Control, British-American Oil Co. Ltd., CLARKSON, Ontario. B. R. Boardman, R. K. Kilborn & Associates, 36 Park Lawn Rd., TORONTO 18, Ontario.

E. Bodnar, Toronto Twp., COOKSVILLE, Óntario.

J. Boese, Manager, Boese R. R. #2, ST. CATHARINES, Ontario.

O. J. Bolduc, The Austin Company, Chicago Heights, Illinois, U.S.A.

G. Boucher, Sanitary Sales Engineer, Dorr-Oliver-Long, 635 Dorchester West, MONTREAL, Quebec.

F. T. Bowley, Contracting Engineer, Horton Steel Works Ltd., 25 Adelaide St. W., TORONTO, Ontario.

W. Brechin, Gen. Supts. Office, Canada Packers Limited, 2200 St. Clair Ave..W., TORONTO 9, Ontario.

F. Bremner, Engineering Department, Dow Chemical Co. of Canada Ltd., P. O. Box 1012, SARNIA, Ontario.

N. W. Bremner, Supervisor Chemical Section T.S.&P. Canada Ltd., Dow Chemical Co. of Canada Ltd., SARNIA, Ontario. HAMILTON, Ont

R. W. Brouillette, Field Sales Engineer, B. F. Goodrich Indust. Prod. Co., MARIETTA, Ohio, U.S.A.

W. F. Brown, Industrial Waste Control Eng., Metropolitan Toronto, Metropolitan Toronto Dept. of Works, 55 Eglinton Ave., TORONTO 12, Ontario.

N. S. Bubbis, Director & Chief Engineer, Metro Waterworks & Waste Disposal Division, 455 Ellice Ave., WINNIPEG 2, Manitoba.

J. E. Buchan, Manager, Union Carbide Can. Ltd., Bakelite Division, Box 396, BELLEVILLE, Ontario.

N. C. Burbank Jr., Editor, Industrial Water & Wastes Magazine, Scranton Publishing Company, Dept. of Civil Engineering, Washington University, ST. LOUIS 30, Missouri.

D. P. Caplice, Industrial Waste Engineer, Ontario Water Resources Comm., Laboratory Division, c/o 801 Bay St., TORONTO 5, Ontario.

D. F. Carrothers,
Section Manager, Soap Products-Product Research,
The Proctor & Gamble Co. of
Canada Ltd.,
P.O. Box 589,
HAMILTON, Ontario.

Page 327

W. B. Caswell, Engineer Process, Regent Refining, c/o Regent Refining, Port Credit, TORONTO, Ontario.

T. R. Chambers, Product Supervisor, Dow Chemical of Canada Ltd., SARNIA, Ontario.

D. S. Caverly, Assistant General Manager, Ontario Water Resources Comm., 801 Bay St., TORONTO, Ontario.

L. Commerford, Manager, Sanitation Equipment, Rex Chainbelt (Canada) Ltd., 1181 Sheppard Ave. E., WILLOWDALE, Ontario.

J. H. Connor, Assistant to the Managing Director, R. J. Davies, Eimco Process of Canada, International Business Machines, 165 Cartwright Avenue, TORONTO, Ontario.

J. S. Couse, Assistant General Manager, Crane Canada Ltd., Engineering Products Group, 1355 Martingrove Rd., REXDALE, Ontario.

G. M. Cox, Senior Laboratory Technician, City of London, City Engineer's Office, LONDON, Ontario.

R. W. Crain, Waste Treatment Engineering, Industrial Filter & Pump Co., 5625 Leitch Avenue, LaGrange, Illinois, U.S.A.

W. S. Cramp, Technical Services, St. Lawrence Corp. Ltd., 840 Sun Life Bldg., Dominion Square, MONTREAL, Quebec.

T. W. Cross, Project Engineer, Swift Canadian Co. Ltd., 1960 St. Clair Avenue West, TORONTO 9, Ontario.

N. Czornyj, Chief Chemist, Sun Oil Company Limited, P. O. Box 307, SARNIA, Ontario.

844 Don Mills Road, DON MILLS, Ontario.

H. M. Davis, Canadian Breweries Ltd., Research Division, 369 Lakeshore Blvd. East, TORONTO, Ontario.

A. V. DeLaporte, R. R. #2, OAKVILLE, Ontario.

C. S. Dutton, Associate Partner, Proctor & Redfern Consulting Engineers, 75 Eglinton Ave. East, TORONTO 12, Ontario.

Page 328 W. R. Edmonds, A/Chief Public Health, Engineering Division, Dept. National Health and Welfare, 1440 St. Catherine St. W., Room 318, MONTEFAL 25 Outbeen 45 Spencer St., OTTAWA, Ontario. A. C. Elliott, Steel Co. of Canada, HAMILTON, Ontario. D. Fowler, Sewage Treatment Plant Supervisor, City of London, Hamilton Road, R. R. #8, LONDON, Ontario. H. J. Gauer, Soaps Processing Manager, Lever Brothers Limited, 299 Eastern Ave., TORONTO, Ontario. G. J. Gaukroger, Chief Metallurgist, The McKinnon Industries Ltd., Plant 1, Ontario Street, ST. CATHARINES, Ontario. M. A. Gendron, Consulting Engineer, Gendron Lefebvre & Assoc., 10125 Blvd. St. Laurent, MONTREAL, Quebec. A. G. Gillespie, Vice-President, Flygt Canada Ltd., 8230 Mayrand St., MONTREAL, Quebec.

J. P. Gourdeau, Room 1012, MONTREAL 25, Quebec.

Dr. W. E. Grummitt, Section Head, Atomic Energy of Canada Ltd., CHALK RIVER, Ontario.

Dr. W. N. Grune, Professor-Sanitary Engineering, Georgia Institute of Technology, School of Civil Engineering, ATLANTA 13, Georgia.

A. J. Harris, Assistant Director of Laboratories, Ontario Water Resources Commission, 801 Bay St., TORONTO, Ontario.

J. J. Heffernan, M. M. Dillon & Co., 88 Eglinton Ave., East, TORONTO, Ontario.

G. Henry, Consulting Engineer, R. R. Anderson & Associates, 194 Wilson Ave., TORONTO, Ontario.

J. C. Henshaw, Supervisor of Tech. Services, Crane Canada Ltd., Cochrane Water Conditioning Div., 1355 Martin Grove Rd., REXDALE, Ontario.

E. B. Hettwer, Chemist, Northern Electric Co. Ltd., Communications Equipment Div., P. O. Box 5081, LONDON, Ontario.

Page 239

D. E. Hibbard, Civil Engineer, H. J. Heinz Co. of Canada, LEAMINGTON, Ontario.

J. D. Hisey, Partner, Hisey & Barrington, 31 Yonge St. N., RICHMOND HILL, Ontario.

B. G. Hooper, Sales Engineer, Dorr-Oliver-Long Ltd., 1819 Yonge St., TORONTO, Ontario.

D.E.H. Hubbs, Technical Development, National Silicates Limited, P. O. Box 69, TORONTO 14, Ontario.

C. C. Hunter, Chief Chemist, Imperial Oil Ltd., SARNIA, Ontario.

D. J. Inglis, Manager, Pollution Control Division, Flygt Canada Ltd., 8230 Mayrand Street, MONTREAL 9, Quebec.

H. W. Izzard, Technical Consultant, National Sewer Pipe Limited, P. O. Box 18, OAKVILLE, Ontario.

R. A. Johnston, Assistant Professor, Ontario Agricultural College, Dept. of Microbiology, Ontario Agricultural College, GUELPH, Ontario. D. Jones, Manager, Technical Section, Canadian Pulp & Paper Association, 2280 Sun Life Building, MONTREAL 2, P. Q.

J. B. Kinney, Director - Consultant, Wallace & Tiernan Ltd., 925 Warden Ave., SCARBOROUGH, Ontario.

P. Knight, Montreal Branch Manager, Eimco Process of Canada Ltd., 315 Dorval Ave., Dorval, Prov. of Quebec.

J. W. Koshurba, Asst. Sewer Engineer, Corporation City of Hamilton, 115 West 31st St., HAMILTON, Ontario.

C. A. Laferriere, Desjardins & Sauriol, Consulting Engineers, 400 Labelle Blvd., CHOMEDEY, Quebec.

E. O. LaFontaine, Senior Civil Engineer, C. G. Russell Armstrong, 317 Bartlet Building, WINDSOR, Ontario.

A. J. Lafreniere, Steel Co. of Canada, HAMILTON, Ontario.

R. Laak, Public Health Engineer, Ontario Dept. of Health, 67 College St., TORONTO 2, Ontario. Page 330

A. Lalonde, Beauchemin, Beaton, LaPointe, 4611 Place Neuilly, MONTREAL, Quebec.

J. C. Larmond, Asst. Maint. Superintendent, General Motors of Canada, OSHAWA, Ontario.

L. B. Leppard, Physicist, Ontario Dept. of Health, 67 College St. (Annex) TORONTO, Ontario.

H. Lightwood, Section Head, Sewer Department, Township of Scarborough, 2001 Eglinton Ave. East, SCARBOROUGH, Ontario.

Dr. H. Lomas, Research Associate, Ontario Research Foundation, 43 Queen's Park Crescent, TORONTO 5, Ontario.

L. S. Love, Engineer, Babcock Wilcox & Goldie McCulloch, Cornation Blvd., GALT, Ontario.

R. B. Marshall, Mgr. Quality Control - Prod. Research, H. J. Heinz Co. of Canada Ltd., LEAMINGTON, Ontario.

Dr. W. J. Martin, Director of Medical Services, Cyanamid of Canada Ltd., P. O. Box 240, NIAGARA FALLS, Ontario. J. McCormack, Co-ord. Lab. Services, British American Oil, 800 Bay St., TORONTO, Ontario.

B. W. McCrae, Project Manager, Giffels & Vallet of Canada Ltd., 1550 Ouellette Ave., WINDSOR, Ontario.

Dr. H. M. McFarlane, Supervisor, Wastes & By-Products Section, Pentral Research Division, Abitibi Power & Paper Co., Ltd., SAULT STE. MARIE, Ontario.

J. A. MacKenzie, Executive Engineer, H. G. Acres & Co. Ltd., 1259 Dorchester Road, NIAGARA FALLS, Ontario.

S. A. McWilliams, Industrial Design & Development, Pumps and Softeners Ltd., 148 Cummer Avenue, WILLOWDALE, Ontario.

C. B. Macrae, Sanitary Drainage Engineer, Twp. of Etobicoke, 550 Burnhamthorpe Rd., ETOBICOKE, Ontario.

G. Maloney, Waste Treatment Engineer, Schwinigan Chemicals, 600 Dorchester St., Room 319, MONTREAL, Quebec.

K. M. Mayall, Biologist, Department of Lands & Forests, Conservation Authorities Branch, 454 University Ave., TORO NTO, Ontario. W. J. Miller, Technical Control Superintendent, Chief Engineer, Canadian International Paper Co., Michigan Water Resources Comm., 200 Mill St., Station B, LANSING, Michigan R. H. Millest, .Co-Supervisor-Ind. Waste Branch, Ontario Water Resources Comm., J. T. O'Rourke, Associate Engineer, Ryckman, Edgerley, Burbank and Associates, Room 300, Laboratory Division, 801 Bay Street, TORONTO 5, Ontario. Coronet Building, 225 S. Meramec Ave., ST. LOUIS 5, Missouri. R. E. Mills, Pollution Control Chemist, Naugatuck Chemicals Division, Dominion Rubber Co. Ltd., H. D. Paayila, ELMIRA, Ontario. Technical Director, KVP Company Limited, ESPANOLA, Ontario. R. F. MacDowall, Salesman, Canadian Johns-Manville Co. Ltd., R. R. Parker, Vice-Presiden Vice-President, PORT CREDIT, Ontario. Beardmore & Co. Limited, ACTON, Ontario. J. V. Morris, Project Engineer, James F. MacLaren & Assoc., 2115 Keele Street, J. A. Parratt, International Business Machines, 844 Don Mills Rd., TORONTO 15, Ontario. DON MILLS, Ontario. K. L. Murphy, R. Phoenix, Industrial Waste Branch, Ontario Water Resources Comm. Assistant Prof., McMaster University, Dept. of Civil Engineering, Laboratory Division, McMaster University, c/o 801 Bay St., TORONTO 5, Ontario. HAMILTON, Ontario. F. Muter, R. O. Pickard, Assistant Sewer Engineer, Field Sales Manager, B. F. Goodrich Canada Ltd., Corp. City of Ottawa, R. R. #4, KITCHENER, Ontario. 111 Sussex Dr., OT TAWA, Ontario. J. Norman, S. R. Price, M. M. Dillon & Co., LONDON, Ontario. City Engineer, City Hall, Queen St., NIAGARA FALLS, Ontario.

D. B. Redfern, Proctor & Redfern, Consulting Engineers, 75 Eglinton Ave. E., TORONTO, Ontario.

J. D. Reid, President, Napier-Reid Limited, 35 Marlborough Ave., TORONTO 5, Ontario.

J. M. Rigney, Assist. District Engineer, Ontario Water Resources Commission, J. Scott, Information Officer, Ontario Water Resources Commission, 801 Bay St., TORONTO 5, Ontario.

L. A. Robb, Plant Chemist, Ethyl Corp. of Canada Ltd., P. O. Box 160, CORUNNA, Ontario.

J. H. Root, Commissioner, Ontario Water Resources Commission, Groundwood Control Engineer, 801 Bay St., TORONTO, Ontario.

O. Rylski, Toronto Twp., COOKSVILLE, Ontario.

T. H. Safford, Associate, Chas. T. Main, Inc., 129 West Trade Street, CHARLOTTE, North Carolina.

E. Sanderson, Supervising Engr., Sewage & Waste Treatment, Foundation Eng., Corp. Ltd., 8 Spadina Rd., TORONTO, Ontario.

R. B. Schaffer, Chemist, T.S. & D. Dow Chemical Co., MIDLAND, Michigan, U.S.A.

G.T.G. Scott, Partner, Canadian-British Engineering Consultants, 3089 Bathurst St., TORONTO 19, Ontario.

801 Bay St., TORONTO 5, Ontario.

K. G. Seabright, Production Superintendent, Cities Service Refining (Canada) Ltd., Box 520, OAKVILLÉ, Ontario.

Ontario Paper Co. Ltd., THOROLD, Ontario.

R. H. Shannon, Manager, Chemical Products, Ethyl Corp. of Canada, 48 St. Clair Ave. W., TORONTO, Ontario.

R. Shaver, Process & Production Division, Refining Department, Texaco Canada Limited, 1425 Mountain St., MONTREAL 25, Quebec.

K. Shikaze, Chemical Engineer, Ontario Water Resources Commission, Laboratories & Research Div., 801 Bay St., TORONTO, Ontario.

C. A. Smith, Manager, Properties & Construction, Canadian Canners Limited, P. O. Box 540, 44 Hughson St. S., HAMILTON, Ontario.

R. E. Smith, Assistant Professor, Ontario Agricultural College, GUELPH, Ontario.

A. M. Snider, Chairman, Ontario Water Resources Comm., WATERLOO, Ontario.

R. T. Southgate, Dorr-Oliver-Long, TORONTO, Ontario.

R. H. Souther, 1700 N. Elm St., GREENSBORO, North Carolina.

D. B. Stevens, Assoc. Chemical Engineer, New York State Dept. of Health, 25 Gardner Terrace, DELMAR, N.Y.

W. D. Stevens, Sales Manager, Metallurgical & Process Equipment, Canadian Locomotive Co. Ltd., 140 Ontario St., KINGSTON, Ontario.

R. C. Stewart, Industrial Wastes, Field Engineer, Ontario Water Resources Comm., Industrial Wastes Branch, 801 Bay St., TORONTO, Ontario. W. Stirling, Maintenance Superintendent, General Motors of Canada Ltd., North Plant, OSHAWA, Ontario.

H. Stokes, Chief Engineer, Swift Canadian Co. Ltd., 1960 St. Clair Ave. W., TORONTO, Ontario.

D. Stokoe, Engineer, J. F. MacLaren Associates, 321 Bloor St., TORONTO, Ontario.

J. K. Sullins, Technical Director, The Mead Corporation, KINGSPORT, Tennessee.

W. M. Swann, Township Engineer, Township of Etobicoke, 550 Burnhamthorpe Rd., ETOBICOKE, Ontario.

C. W. Tanner, Sales and Service, Brooks Chemicals Inc., 649 Westmount Cres., LONDON, Ontario.

R. E. Thompson, Director of Water Purification, Metro Toronto, 25 Guildcrest Dr., SCARBOROUGH, Ontario.

G. H. Thompson, Sanitation Engineer, Corp. City of Kitchener, City Hall, KITCHENER, Ontario.

# L. M. Tobias, Engineer, Ontario Water Resources Commission, Dominion Foundries & Steel, Depew St. Plant Operations Division, 801 Bay St., TORONTO 5, Ontario. H. D. Tomlinson, Associate Director, Environmental and Sanitary Engineering Div., Washington University, ST. LOUIS 30, Missouri. A. R. Townshend, Assist. Supervisor of Plans, Ontario Water Resources Commission, 801 Bay St., TORONTO, Ontario. A. Tramley, Sales Manager, Fennia Limited, 2521 St. Remi Road, DORVAL, Quebec. F. A. Voege, Director, Laboratory Division, 801 Bay St., TORONTO, Ontario. H. L. Walker, Process Engineer, British American Oil Co., 800 Bay St., TORONTO, Ontario. W. B. Waugh, Chemist, Canadian Oil Companies Ltd., Sarnia Refinery, P. O. CORUNNA, Ontario. J. A. Watson, Plant Engineer, The McKinnon Industries, ST. CATHARINES, Ontario.

Page 334

W. R. Weir, Depew St., HAMILTON, Ontario.

P. W. Williams, Canadian Johns-Manville, PORT CREDIT, Ontario.

C. Wilson, Control Chemist, Dryden Paper Company Ltd., DRYDEN, Ontario.

J. Wilson , Rex Chainbelt Canada Ltd., WILLOWDALE, Ontario.

F. J. Wims, Collis Leather Company, AURORA, Ontario.

J. D. Willis, Design Engineer, City of Brantford, City Hall, BRANTFORD, Ontario.

M. Yatabe, Engineer, Gore & Storrie Limited, 980 Yonge St., TORONTO 5, Ontario.

K. Zettel, Ontario Sales Manager, B. F. Goodrich Canada Ltd., 17 Ludgate Dr., REXDALE, Ontario.

TD 897.5 .057 1962 copy 2 9th Ontario waste management conference : proceedings / 76573