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10th
ONTARIO
INDUSTRIAL WASTE
CONFERENCE

Proceedings

JUNE 1963

SPONSORED BY

THE WATER AND POLLUTION ADVISORY COMMITTEE

TO THE

ONTARIO WATER RESOURCES COMMISSION

CONTENTS

PREFACE

D.S. Caverly
General Manager,
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Conference Chairman.

This Proceedings contains the technical papers presented at the Tenth Ontario Industrial Waste Conference held in June 1963 at Delawana Inn, Honey Harbour, Ontario.

The Water and Pollution Advisory Committee is grateful to those who prepared and presented papers and to those who participated in the discussions. Many advances made in our knowledge of industrial waste treatment would not have been possible without meetings of this kind and the Committee is thankful for the opportunity of promoting a better understanding of the many complex problems.

Conferences like this serve for the exchange of information and new ideas among industry, designers, universities and governments. Progress in Ontario so far has been good but greater efforts are needed to meet the increasing number and complexity of industrial wastes.

The committee recognizes the cooperation given by industry in these matters and is hopeful that greater progress will be made.

Further information may be obtained by writing to the Water and Pollution Advisory Committee, Ontario Water Resources Commission, 801 Bay St., Toronto 5, Ontario.

THE SOLVENT EXTRACTION OF PHENOLIC COMPOUNDS FROM WEAK AMMONIA LIQUOR

by

A.C. ELLIOTT

SESSION ONE

Dr. N.C. Burbank, Jr.,
Washington University
Session Chairman

"THE SOLVENT EXTRACTION OF PHENOLIC COMPOUNDS FROM WEAK AMMONIA LIQUOR"

by

A.C. ELLIOTT

The operation of a fully integrated steel plant requires enormous quantities of water. The Steel Company of Canada, Hamilton Works, pumps from Burlington Bay an average of 170 million gallons of water per day. Fortunately, only a small percentage of this total volume of water is in contact with the plant's products and, therefore, contaminated. The larger percentage of the water is used for cooling purposes only, and apart from a slight increase in temperature, is discharged in its original quality.

However, in processes where water is an integral part of the operations, water pollution problems do arise. Such a process is found in the production of large quantities of metallurgical coke and in the refining of the raw coke oven gas. More specifically, in this process the steel industry is confronted with the problem of controlling the emission of phenolic compounds entrained in the weak ammonia liquor. At Stelco, this problem was, in the past year, resolved with the start-up of a new phenol recovery plant. This plant, built at a cost of $550,000 applies the solvent extraction principle to phenol recovery which will be described herein.

A brief review of the coking procedure and the formation of the phenolized weak ammonia liquor will be helpful in the presentation of this paper and will also acquaint those who may not be familiar with this process.

The by-product method of carbonizing coal serves a twofold purpose. The primary function is the mass production of metallurgical coke for use in the Blast Furnaces. The other is the recovery of valuable coal chemicals that absorbs part of the operating expenses of the coke plant.

At Stelco, the present coking facilities consist of three batteries, with a total of 191 underfired and regenerative by-product ovens. Coal coking is a batch operation requiring a 17 ton coal charge per oven and a carbonization period of about 17 hours. As carbonization proceeds under the influence of high temperatures, the volatile constituents are driven from the coal matrix. When the treatment of the coal is completed, the end doors of the ovens are removed and the coke is pushed out. A total of 270 ovens are pushed in a 24-hour schedule, or approximately one every 5.5 minutes. The annual production of metallurgical coke exceeds 1,200,000 tons.

Slide I --- General Picture of the Batteries

Slide II --- Battery Being Pushed

The other function of the coking operation is the recovery, separation and refining of the volatile and gaseous matter evolving from the coal. We will confine ourselves to the flow pattern of the gaseous constituents and the separated organic fractions.

Each individual oven is provide with a single coke gas exhaust duct. Liberated raw coke gas leaves the oven through the exhaust duct and is transferred to the collecting main. The volatile products consist essentially of coke gas, water vapour, ammonia, tar and light oil. These fractions occur in sufficient volume to permit an economic recovery of useful products.

As the raw coke gas progresses through the collecting mains, its temperature is reduced from 1600°F to 190°F by a series of spray systems. The cooling liquid used for spraying is the accumulated condensate from the volatile coal products and is known as ammonia flushing liquor. This liquor, with entrained condensable matter, is separated from the gaseous stream in the downcomer and decanter system. The liquor is returned to the hot tar drain tanks and the coke gas is drawn through the primary coolers by the exhausters.

Slide III --- Flow Diagram -- By-Product System

From the exhausters the coke gas is forced through a series of electrostatic tar precipitators to eliminate the last traces of tar material. In the subsequent operation, the gas is scrubbed with sulphuric acid to fix the ammonia vapours of the coke gas and to produce ammonium sulphate. The ammonium sulphate solution is concentrated and crystallized.

The Light Oil Scrubber completes the gas refining process. Benzol, Toluol, and Xylol fractions are the main coal chemicals which are washed from the coke gas. In this last stage, a light oil solvent is employed to absorb the coal chemicals in a gridded countercurrent scrubber tower. The saturated solvent is continuously pumped to the Benzol Plant for distillation of the hydrocarbons.

The purified coke gas, containing the fixed gases; hydrogen, methane, ethane, and carbon monoxide, is boosted by centrifugal boosters to 7 p.s.i.g. for plant usage. Distribution of the fuel is accomplished through an extensive pipeline system. The coke ovens themselves are a major consumer of the gas and depend upon it as fuel for supplying the necessary heat in the endothermic reaction of destructive distillation.

At this particular point we have to return once more to the ammonia liquor flushing system. Certain organic compounds evolved during the coking process are absorbed and concentrated in the weak ammonia liquor. As we mentioned earlier, this liquor, along with the effluent from the primary gas coolers, is re-cycled to the decanter tanks. These tanks provide a crude separation of the heavy tar compounds from the carrier liquor. The effluent from the tar tanks is split into three separate flow systems. The first system recirculates the liquor to the spray nozzles in the collector mains. In the second system the liquor is cooled and re-cycled to the primary gas coolers. Within the gas coolers the gas temperature is reduced to 95°F to condense the residual light tar constituents. Finally, the surplus from the drain tanks is diverted to a second decanter tank for final cleaning and then transferred to the Phenol Recovery Plant. This surplus of liquor is created by the continuous condensation taking place in the collector mains. The withdrawn liquor contains a high concentration of phenolic fractions which must be removed before discharging the liquor to the lagoon.

The quantity and the particular phenolic fractions produced in the coking process vary, depending essentially on the coal, temperature, and carbonization period. A comprehensive analysis of our ammonia liquor indicated the following compounds:

Slide IV --- Analysis of Ammonia Liquor to Phenol Plant

The crude tar acids recovered from the liquor were found to contain the following phenolic fractions: see Page 12

Slide V --- Phenolic Constituents in Ammonia Liquor

Identification was made through fractionation and chromatographic separation. Since the phenol fractions are essentially monohydric in nature, the solvent extraction method appeared to be the correct technical approach to remove the phenolic material.

Slide VI --- Shot of Phenol Plant

The phenol extraction of the waste ammonia liquor is performed before the ammonia still. The main components of the Recovery Plant are: a phenol extraction tower, two caustic reactors, product storage facilities and adequate settling and pumping equipment.

Slide VII --- Storage Tanks

The sequence of the process is best illustrated with a schematic flow diagram:

Slide VIIIa and VIIIb --- Flow Diagram of Phenol Plant

Phenol laden ammonia liquor is withdrawn from the Hot Tar Drain Tanks, through the final decantor and into the settling tanks. The amount of liquor withdrawn is in proportion to the condensate make. From storage, the liquor is pumped through either a heat exchanger or liquor cooler to control the temperature at 100°F. Subsequently, the pressurized liquor is injected into the extractor through a bank of distribution pipes located near the top of the tower. Simultaneously, light oil solvent, from the re-circulating tank, is pumped through a similar distribution manifold near the bottom of the extractor. Buoyancy differences between the two liquid phases permit the light oil solvent to percolate upward through the descending liquor. Because intimate contact between the two liquids is essential for high extraction efficiency, the extractor was supplied with a wood grid packing to create a tortuous flow pattern. In the exchange process, the tar acids are dissolved by the light oil from the liquor. From the base of the extractor the dephenolized liquor flows up a vertical stand pipe and through an overflow weir box to the ammonia still for further processing. In case the ammonia still cannot accommodate the entire flow, the dephenolized liquor backs up and is channelled through an overflow pipe to the dephenolized liquor storage tank. The phenolized light oil overflows from the top of the extractor and is piped by gravity through two caustic washers connected in series. In each reactor, the oil is evenly distributed below the caustic charge and bubbles through the Raschig ring packing where the phenol reacts to form sodium phenolate. Oil leaving the top of the No. 1 Reactor compartment is transferred through an external inverted loop system to the distributors of the second reactor for a final clean-up wash. The dephenolized light oil overflows from the top reactor and is returned to the oil recirculating compartment located in the base of the reactor tower. The light oil may now be pumped back to the extractor system.

Phenol rich light oil is allowed to percolate through No. 1 Reactor until 86 per cent caustic conversion has been achieved. This is equivalent to a caustic consumption of 0.397 pounds of sodium hydroxide per pound of phenol removed.

The oil circulation is then temporarily interrupted to permit the dumping of the weak carbolate product to the concentrator. Excess water and entrained light oil are vaporized from the carbolate before storing the product. The vapours are recovered in a closed-loop vent system which is tied directly to the coke oven gas suction main. The partially converted caustic in No. 2 Reactor is dropped to No. 1 Reactor. A fresh charge of 240 grams per litre of caustic soda is then automatically mixed and pumped to the second Reactor. Oil circulation may now be resumed to extract and convert phenolic material from the weak ammonia liquor.

The Static Phenol Recovery Plant is a compact installation capable of treating 150,000 U.S. g.p.d. of phenol laden waste liquor from the By-Product facilities. The plant operating efficiency is 98% plus, removing about 2,500 pounds of phenolic material per day. The discharge effluent to the ammonia still contains less than 50 p.p.m. By design, the process requires a minimum amount of supervision and utility service. On a regular two-hour basis, the operator scrutinizes the oil and liquor flow rates, checks the extractor temperature and records the liquor levels in the settling tanks. In addition, on the day shift, a number of pertinent samples are collected and analyzed by the laboratory. The laboratory advises the supervision on the reactor condition and indicates the nearness of the next carbolate dump. These duties complement the operator's regular responsibilities, consuming about one hour per eight-hour shift. For a carbolate dump, however, the shift operator is assisted by a helper for draining the reactors and replenishing their charge. A typical set of operating analyses are shown in Slides IXa and IXb. The history of phenol conversion for the same period may be followed in Slide X. The slope of the curve represents the rate of phenol conversion. Once the phenol content in No. 1 Reactor has built up to about 190 grams per litre, the reaction rate declines rapidly as indicated by the tail-end of the curve. Consequently, the phenolized light oil migrates through the carbolate solution in No. 1 Reactor without the necessary conversion taking place. Because the final clean-up wash in No. 2 Reactor has not sufficient capacity to extract the residual phenols from the light oil, a steady rise occurs in the amount of phenols recirculated with the light oil. This reduces the light oil's solvency for phenols and impairs the efficiency of the ammonia liquor phenol extractor. Hence, the plateau represents an optimum conversion, where it is desirable to discharge the bottom reactor containing 225 grams per litre of phenols and recharge it with the less saturated carbolate solution from the top reactor. The light oil circulation pump is stopped approximately 30 minutes ahead of the dump. This allows the light oil to separate from the caustic. The original 4,300 I.G. caustic charge will have expanded to about 7,000 I.G. with an 86% caustic conversion. The carbolate mixture is then drained by gravity to the concentrator until light oil carbolate emulsions appear at the try valve on the reactor. The try valve is located just above the carbolate drain. Concentration of the carbolate continues until the volume is reduced to about 3,300 I.G. The time required for cooking the raw product is about 60 hours. The concentration progress is followed with a periodic specific gravity check. Once the phenolate's specific gravity has reached 1.26, the operation is judged complete and a product sample is removed for final chemical analysis. A typical product description is shown in Slide XI.

The time required for dropping and recharging the reactors is about three hours. To recharge the top reactor, a 50 per cent caustic solution is mixed with dephenolized ammonia liquor in a common header and pumped to the reactor. Each flow is measured and controlled so as to yield a caustic solution of 240 grams per litre of sodium hydroxide. The volume required for recharging the reactor is 4,300 I.G.

Slide XIIa and XIIb

The effectiveness of any liquid to liquid extraction system depends on the particular solvent used. A number of available solvents were investigated. The light oil fractions from the Benzol refining process satisfied the requirements of miscibility, density, and good solvency for phenols. In addition, this solvent is readily available from our own By-Product facilities. Essentially, the solvent is a carbon disulphide free mixture of aromatic and paraffinic compounds. Slide 13 shows a typical distillation analysis. Aromatics, because of their excellent phenol solvency, constitute the main fraction. Unfortunately, however, some sulphur bearing compounds dissolve in the light oil during the extraction process. These tramp elements react to consume the caustic at the expense of the phenolate in the reactors and cause a slight contamination of the product. The light oil make-up to the Phenol Plant averaged over six months' continuous operation amounted to 2.76 gallons per 1,000 gallons of processed ammonia liquor.

To prevent the formation of light oil emulsions in the Extractor, it is essential that the heavy tar fractions are separated from the ammonia liquor.

Most existing phenol extraction processes use filtration methods to clean the raw ammonia liquor. However, 80% of the operating costs of such installations are consumed by the filtering equipment alone; hence, other means of separating the tar material were appraised by a comprehensive engineering report. The conclusion was that settling tanks, affording long retention periods, were adequate for our particular raw ammonia liquor. In case the liquor characteristics should change, provisions have been made in the plant layout to incorporate filtering equipment.

Aside from providing liquor storage facilities, the settling tanks serve as final gravity tar separators. Three tanks, adequately sized to hold two days of process liquor, may be used in rotation. While one tank is filling, the second tank is settling and the third tank is supplying the feedstock for the Phenol Recovery Plant. Liquor feedstock is pumped from the tank well above the tar drain valves. Because of the effective separation in the decantor system, only traces of tar are found in the settling tanks. No tar and emulsions problems have so far occurred. Centrifuging the liquor was initially considered, but judged too complex in operation and maintenance. In addition, the tank system permitted us to use not only two existing tanks but also to use them as liquor reservoirs. It is advantageous to pump feed liquor to the Recovery Plant independently of the liquor make and thus eliminate expensive flow control instrumentation. A periodic adjustment of two hand valves is sufficient to maintain the desired liquor volume and liquor to light oil ratio. From experience, in normal operation, a liquor to light oil ratio of 1--1.26 was found adequate to substantially reduce the phenolic concentration of the ammonia waste liquor.

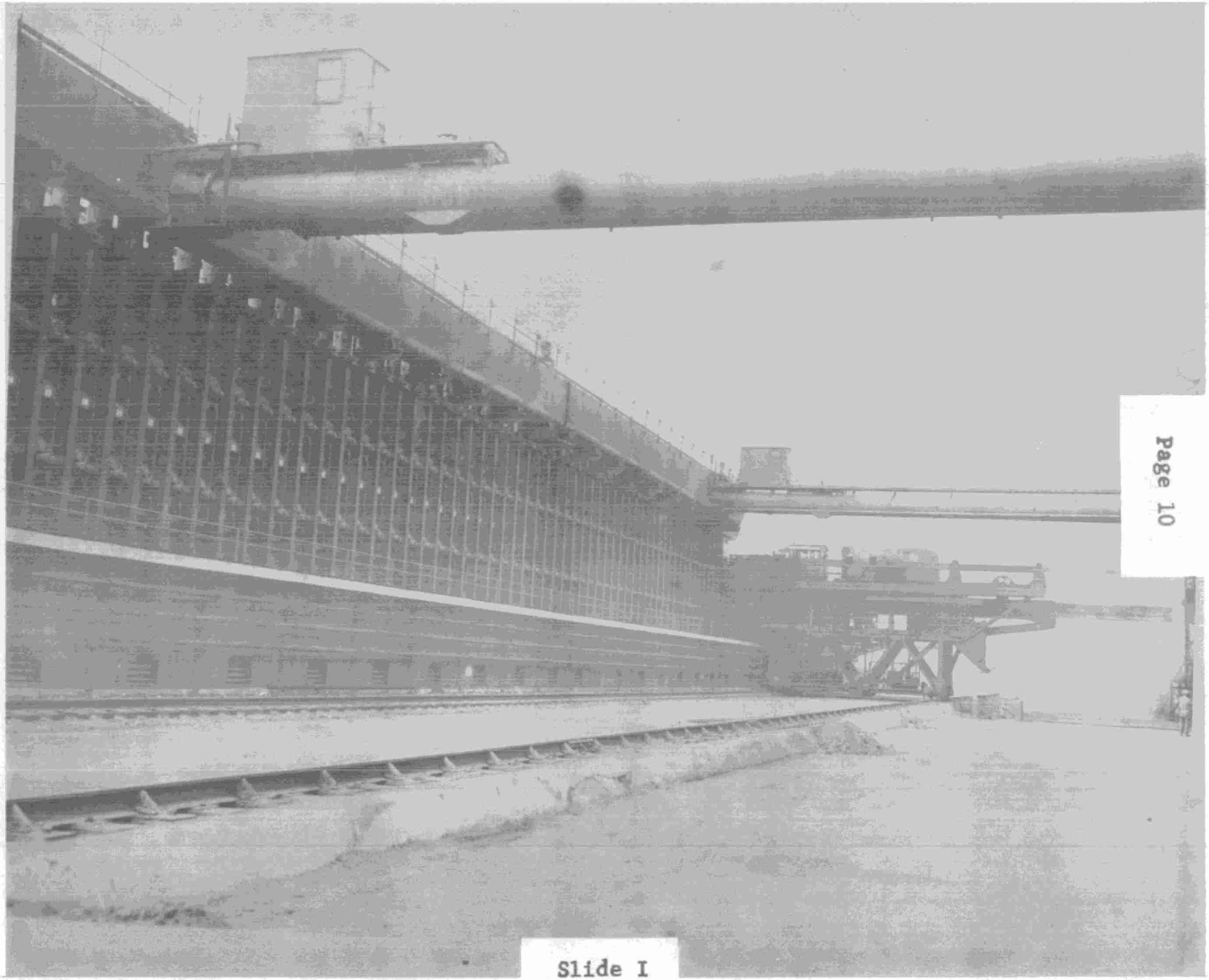
The dephenolized light oil solvent from the top reactor contains traces of dispersed carbolate material. If the tramp material is allowed to accumulate, troublesome emulsions are formed. The previously described solvent circulating tank is adequately sized to provide the necessary retention time for the solvent and carbolate phases to separate. At regular intervals, the precipitated carbolate is drained to a holding tank. In addition, the discharges from the much drains and inspection try valves are also channelled to the same tank. Periodically, the accumulated mixture may be pumped to the concentrator for light oil recovery, or used as an additive in a fresh caustic soda mix for the reactor. Currently, the latter approach is followed. The collecting network eliminates the discharge of oil and caustic solutions to our sewer system.

In summary, the Phenol Recovery Plant effectively reduces the phenolic emission by 98%. Subsequent treatment of the waste liquor in the 'ammonia still' further reduces the phenolic pollutant, resulting in an effective over-all reduction of 99%. The recovery of a saleable product from this operation was an important consideration in the decision to construct a static solvent extraction system. Utility and labour requirements are low. The plant has been in operation for over a year with no serious difficulties experienced during this time.

In concluding, we would like to mention that the steel industry has other water pollution problems to contend with. Fortunately, however, much time, energy, and money is being spent to resolve these problems and the progress resulting from these efforts is very satisfactory. The regeneration of waste pickle liquor is now technically feasible and appears as an economically practical solution to the disposal of this contaminant. Stelco engineers are now conducting a detailed study of this process with the intention of integrating it soon into its new pickling operations. Improved techniques in the settling of mill scale fines are now being investigated. This research project, conducted by the Mellon Institute and sponsored by the American Iron and Steel Institute, consists of model studies of pit design parameters with reference to optimum overall dimensions, entry and exit ports, the use of baffles and chemical coagulants to increase scale settling efficiency.

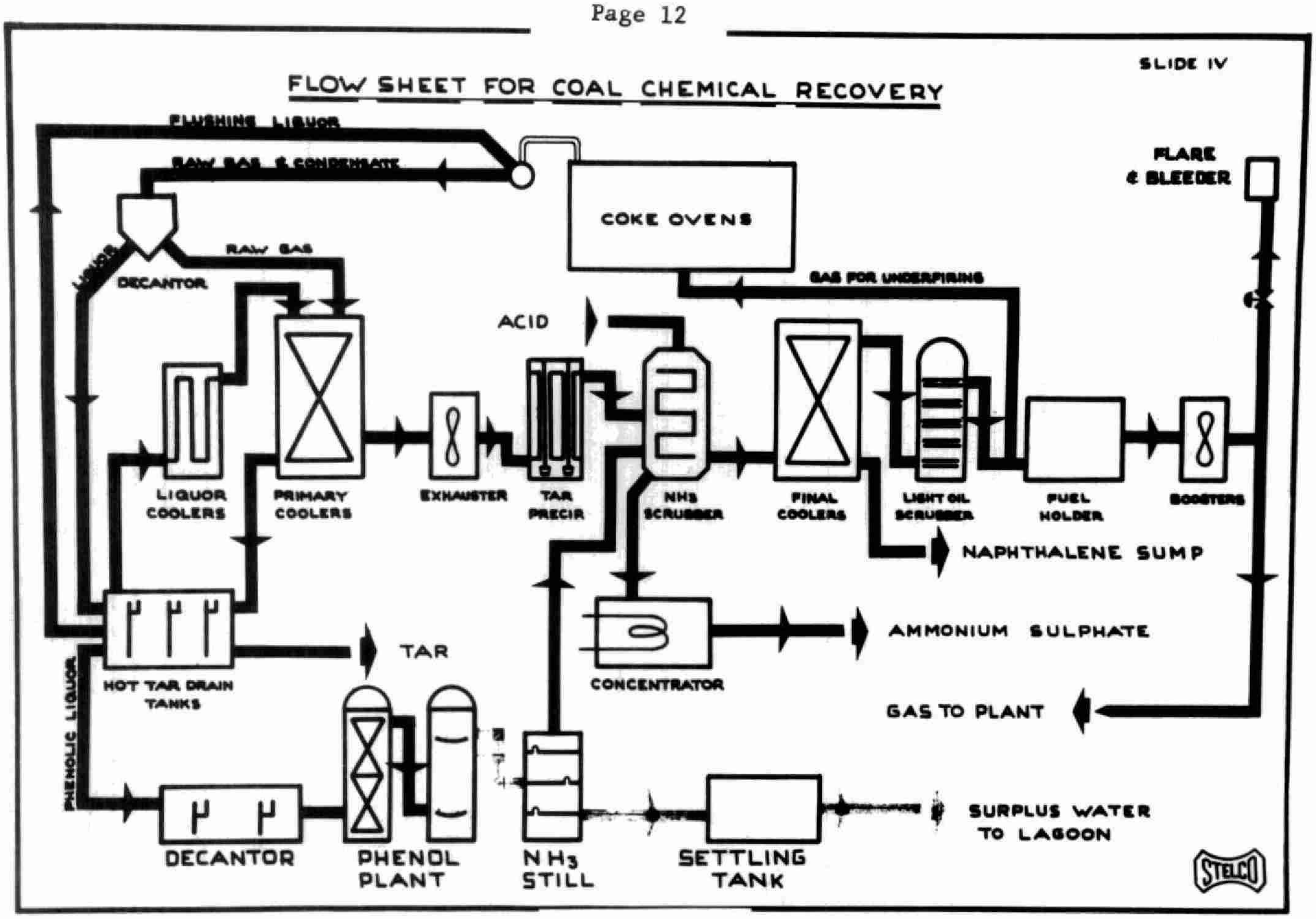
When a proposed closed water recirculation system is adapted to Stelco's Coke Oven's Final Coolers, Stelco cyanides and phenol emissions will be almost completely eliminated.

These few points are an indication of Stelco's and the steel industry's willingness to co-operate in the abatement of water pollution. We sincerely hope that from such co-operative efforts, an improvement in the quality of our water resources will result.



Slide I

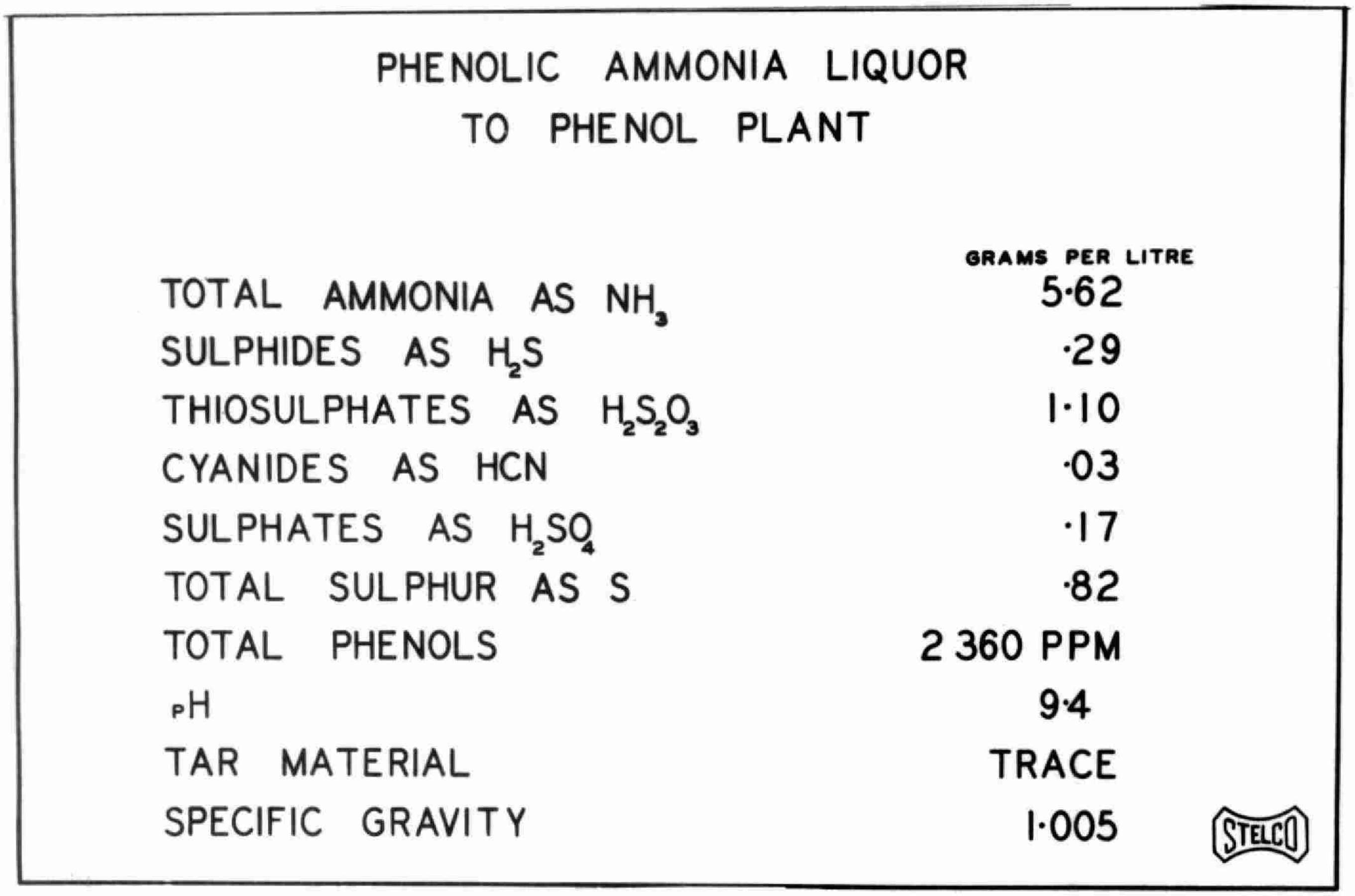
Slide II



SLIDE IV

FLOW SHEET FOR COAL CHEMICAL RECOVERY

Slide III

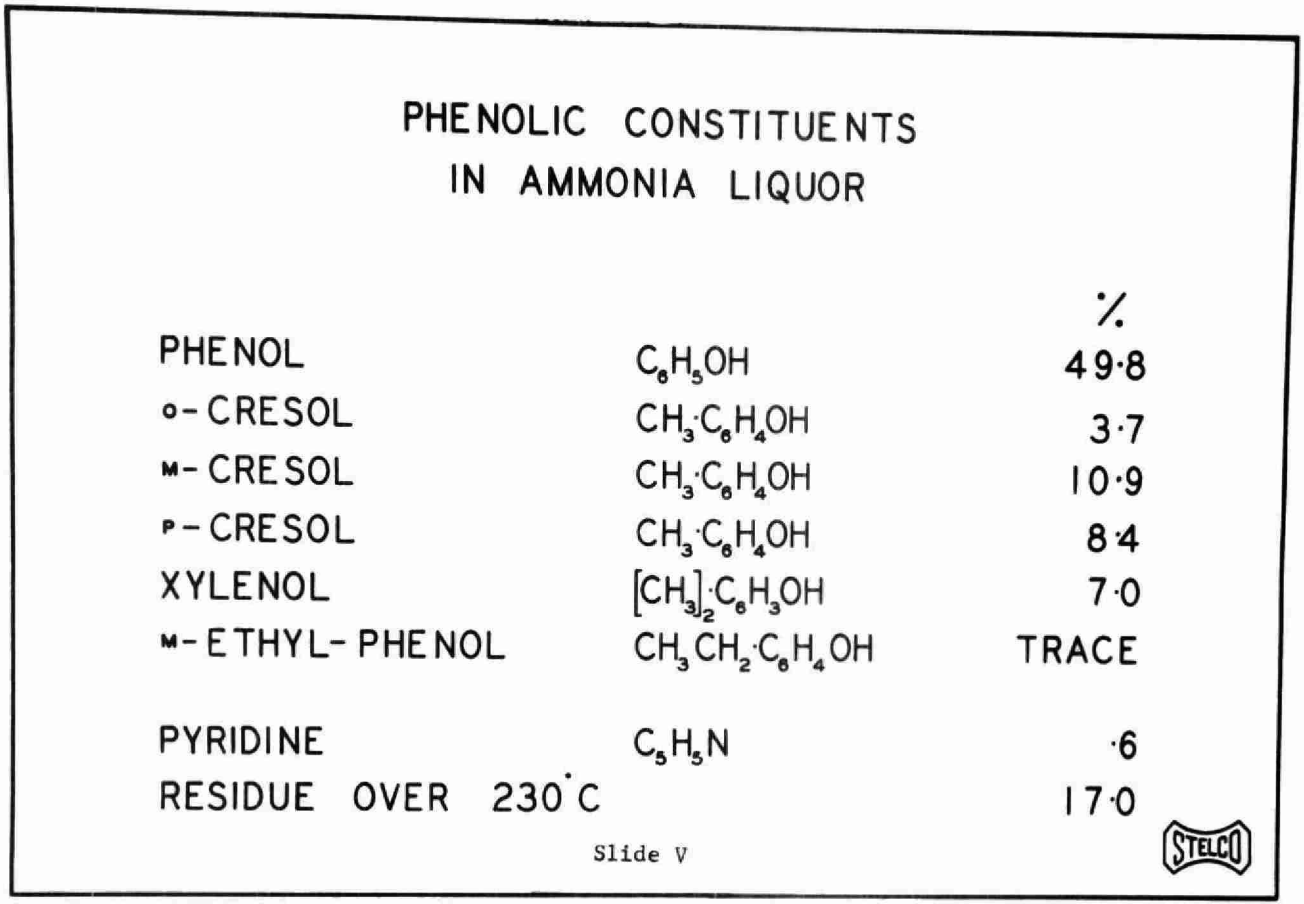


PHENOLIC AMMONIA LIQUOR TO PHENOL PLANT

	GRAMS PER LITRE
TOTAL AMMONIA AS NH_3	5·62
SULPHIDES AS H_2S	·29
THIOSULPHATES AS $H_2S_2O_3$	1·10
CYANIDES AS HCN	·03
SULPHATES AS H_2SO_4	·17
TOTAL SULPHUR AS S	·82
TOTAL PHENOLS	2 360 PPM
pH	9·4
TAR MATERIAL	TRACE
SPECIFIC GRAVITY	1·005

STELCO

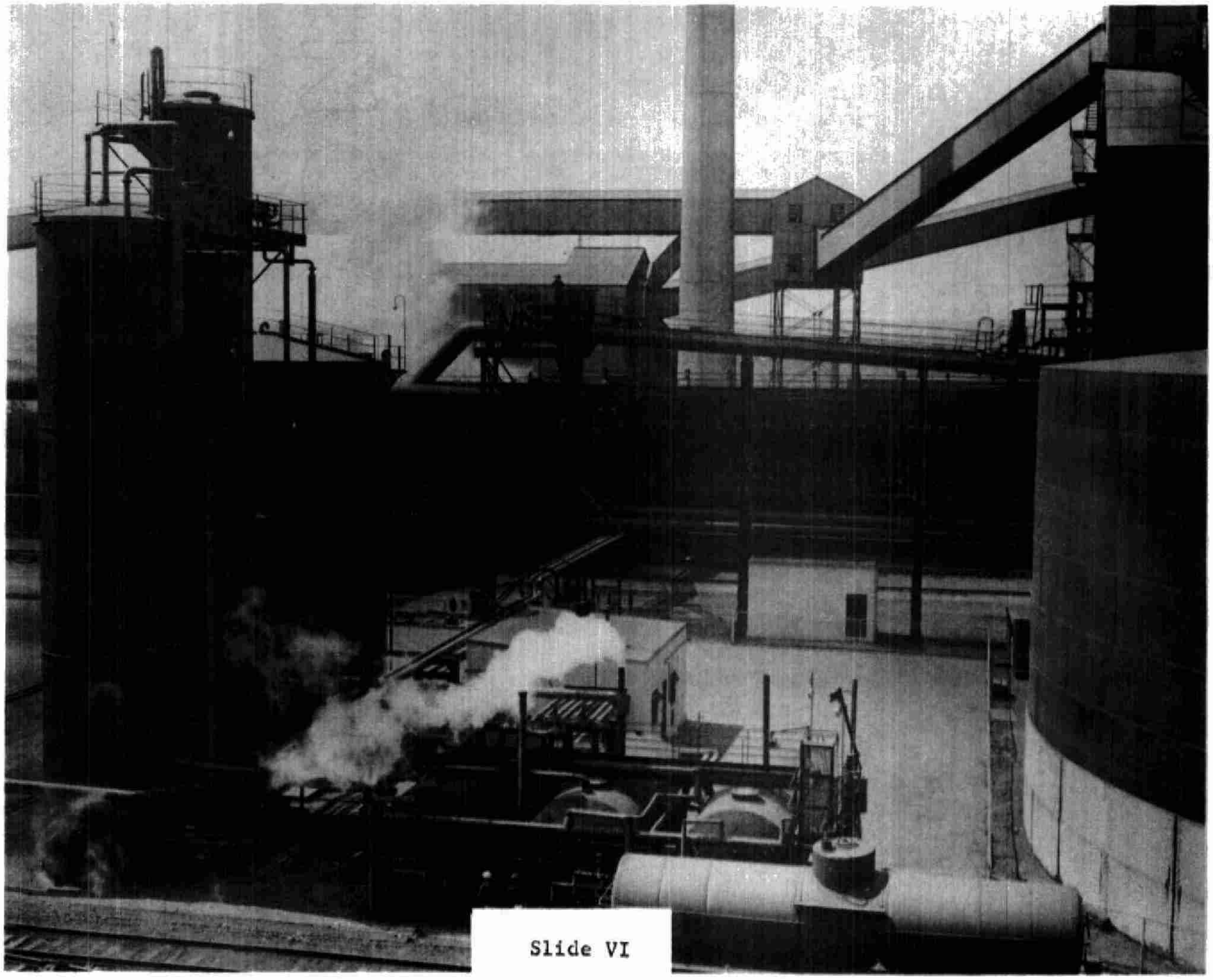
Slide IV



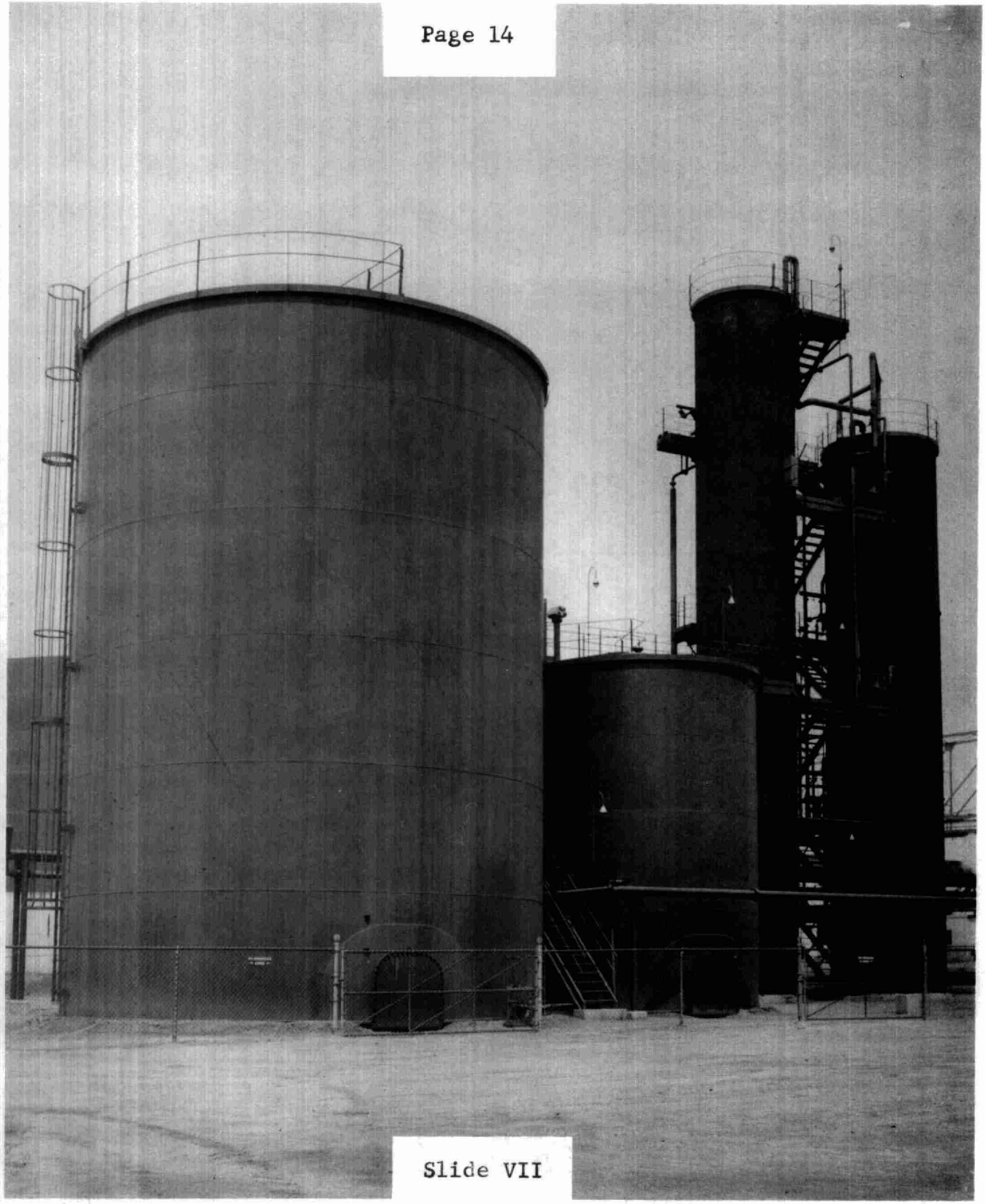
PHENOLIC CONSTITUENTS IN AMMONIA LIQUOR

		%
PHENOL	C_6H_5OH	49·8
o-CRESOL	$CH_3{\cdot}C_6H_4OH$	3·7
m-CRESOL	$CH_3{\cdot}C_6H_4OH$	10·9
p-CRESOL	$CH_3{\cdot}C_6H_4OH$	8·4
XYLENOL	$[CH_3]_2{\cdot}C_6H_3OH$	7·0
m-ETHYL-PHENOL	$CH_3CH_2{\cdot}C_6H_4OH$	TRACE
PYRIDINE	C_5H_5N	·6
RESIDUE OVER 230°C		17·0

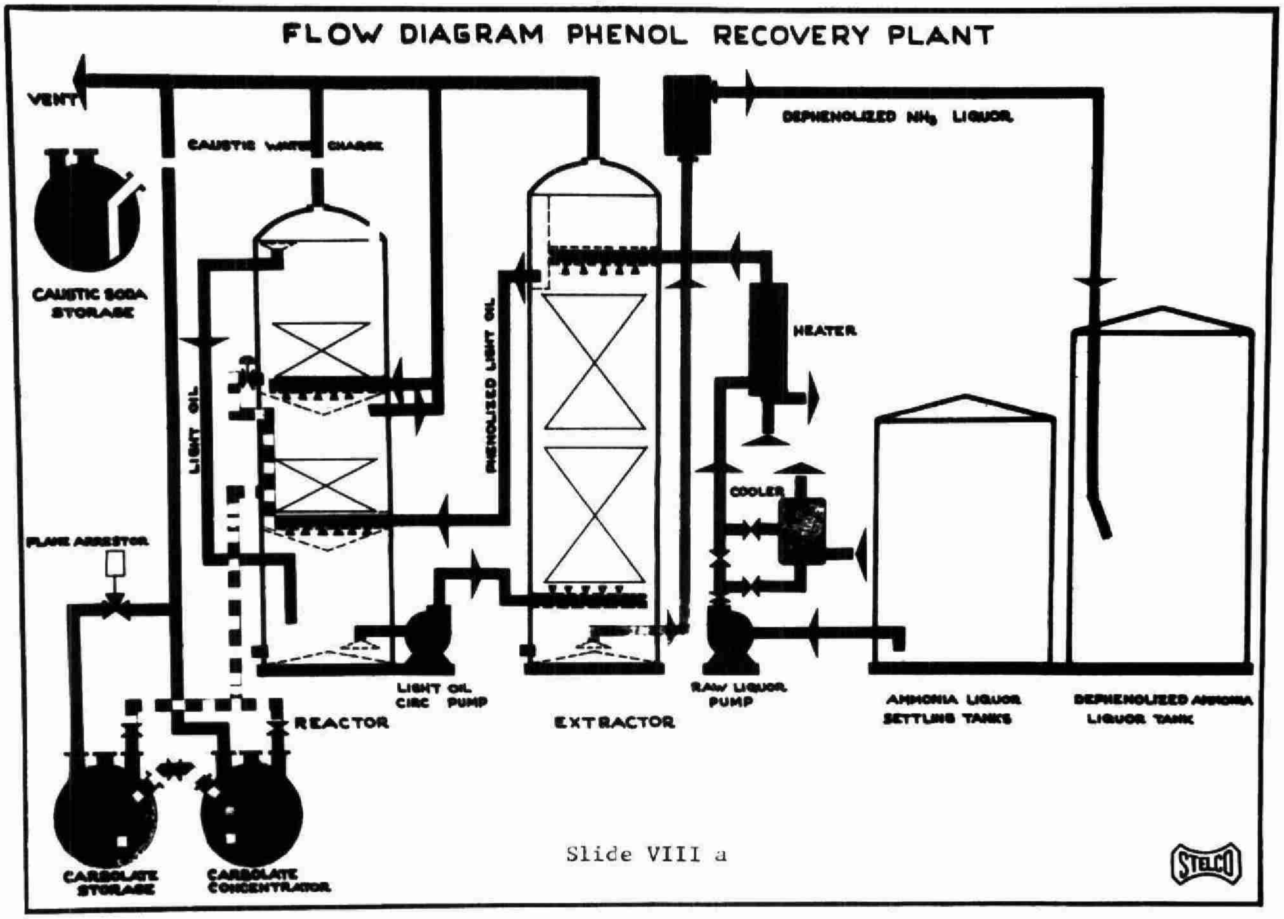
Slide V



Slide VI

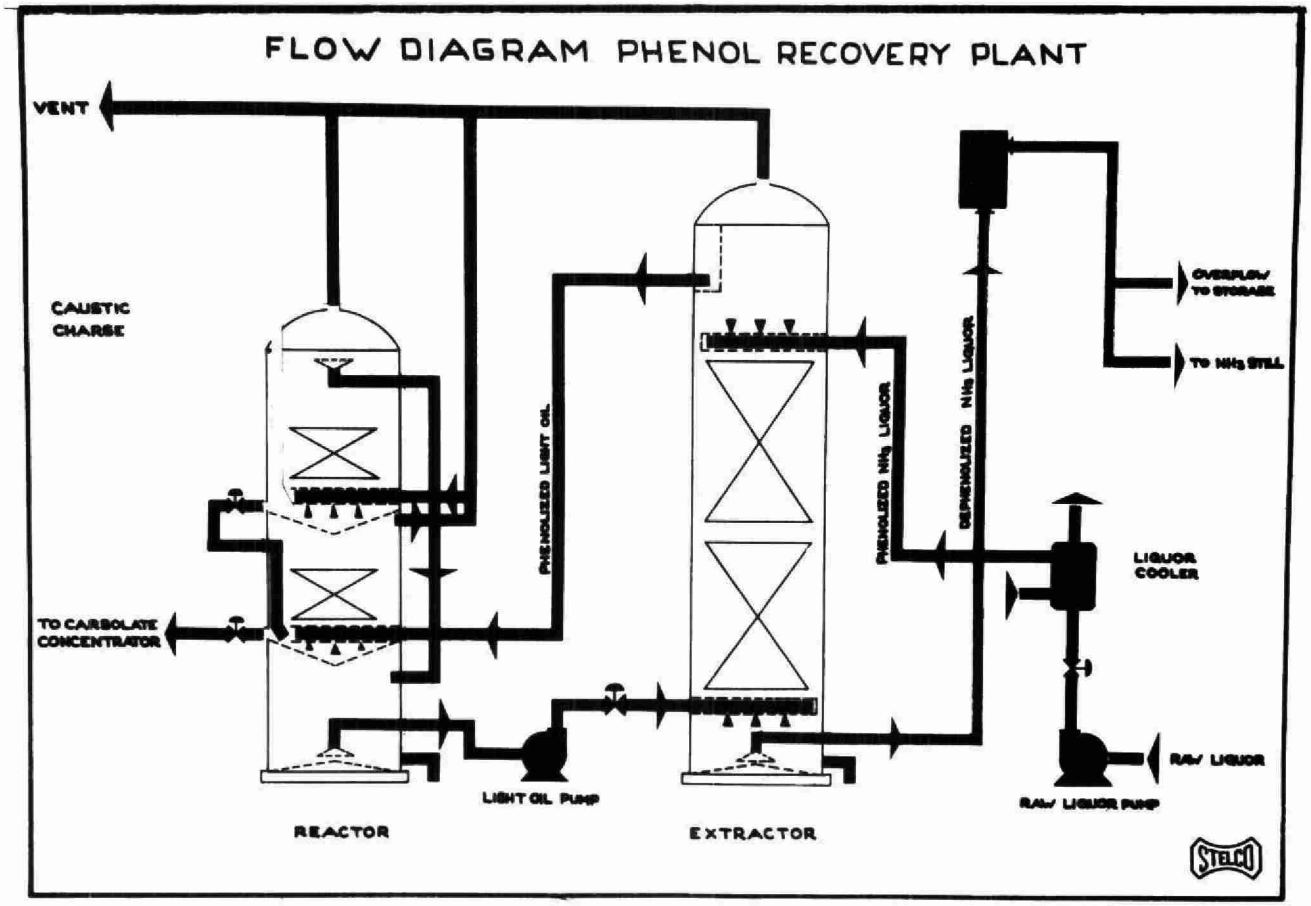


Slide VII



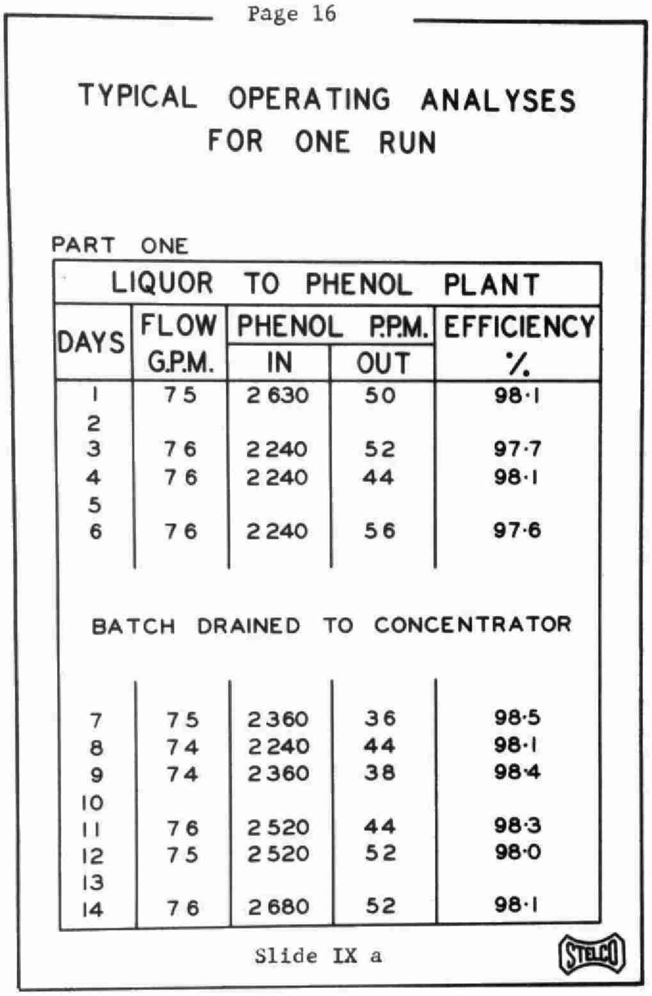
FLOW DIAGRAM PHENOL RECOVERY PLANT

Slide VIII a



FLOW DIAGRAM PHENOL RECOVERY PLANT

Slide VIII b



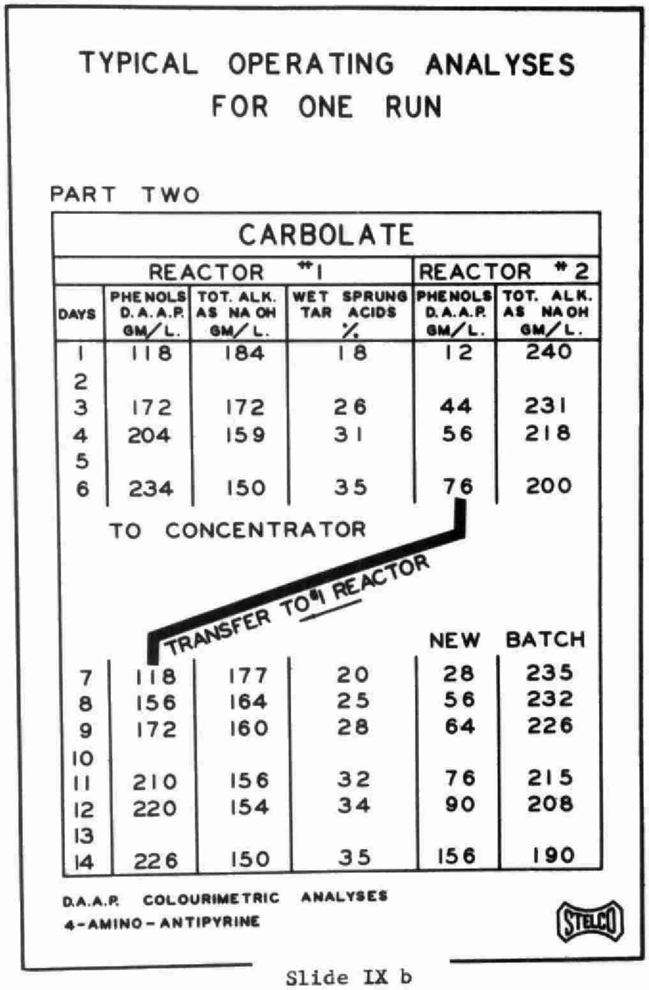
TYPICAL OPERATING ANALYSES FOR ONE RUN

PART ONE

LIQUOR TO PHENOL PLANT

DAYS	FLOW	PHENOL P.P.M.		EFFICIENCY
	G.P.M.	IN	OUT	%
1	75	2 630	50	98·1
2				
3	76	2 240	52	97·7
4	76	2 240	44	98·1
5				
6	76	2 240	56	97·6
BATCH DRAINED TO CONCENTRATOR				
7	75	2 360	36	98·5
8	74	2 240	44	98·1
9	74	2 360	38	98·4
10				
11	76	2 520	44	98·3
12	75	2 520	52	98·0
13				
14	76	2 680	52	98·1

Slide IX a



TYPICAL OPERATING ANALYSES FOR ONE RUN

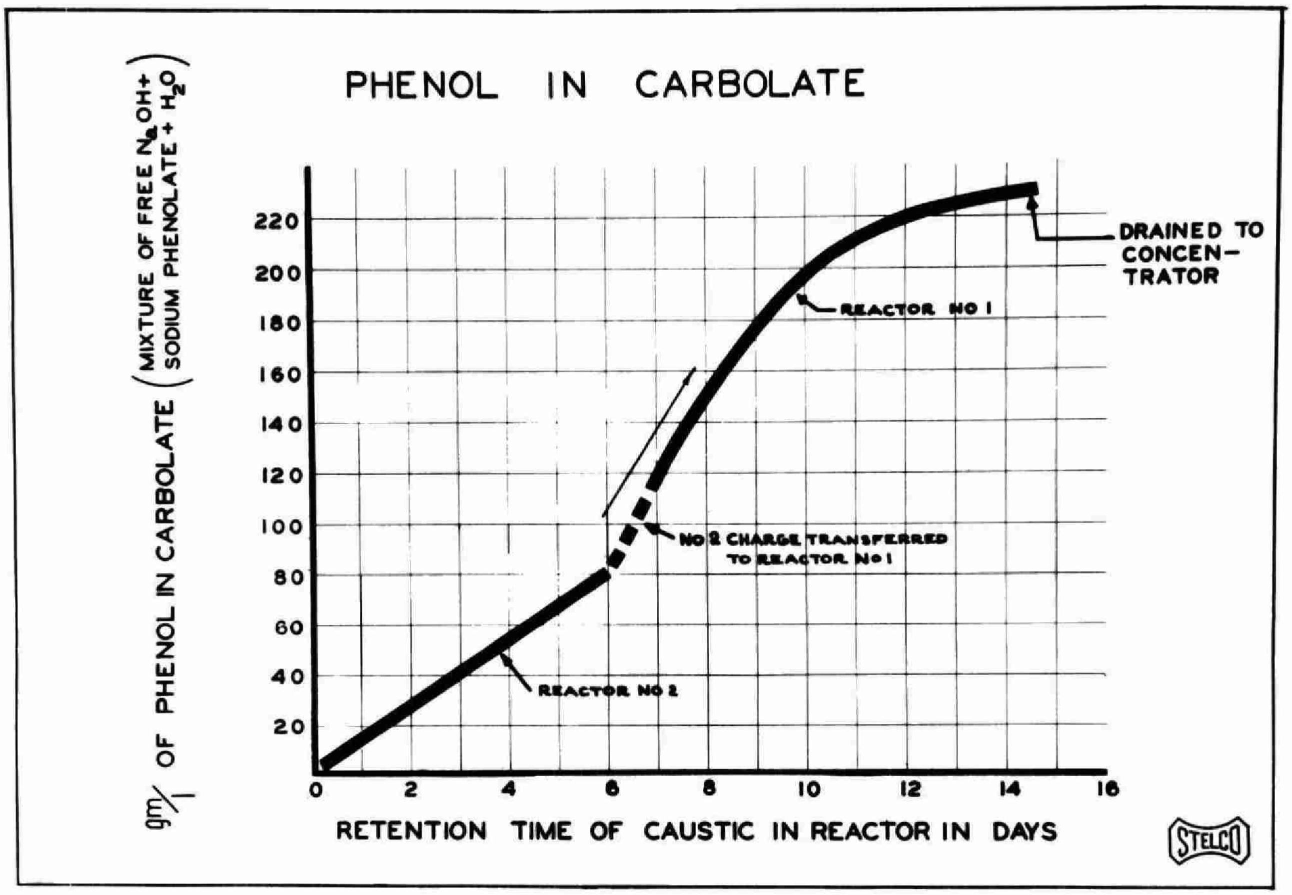
PART TWO

CARBOLATE

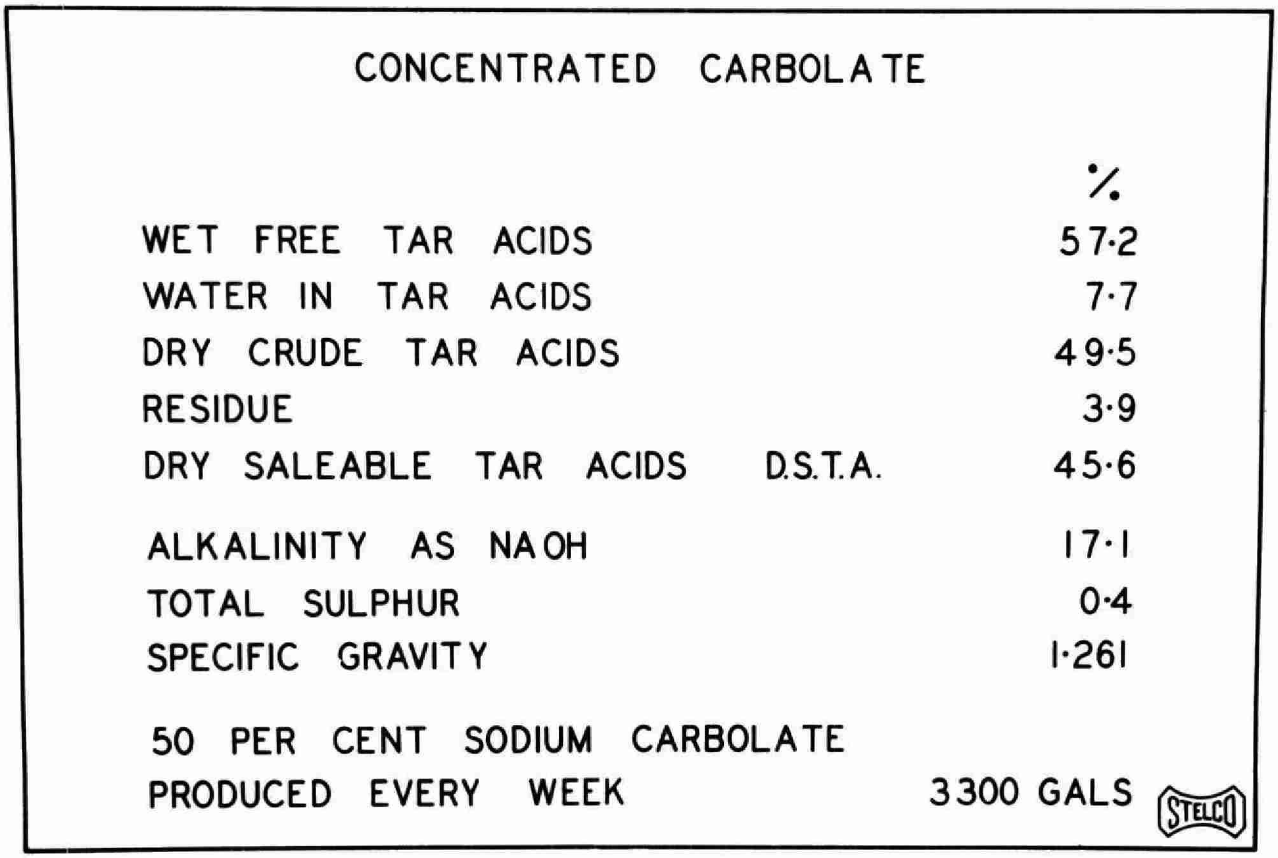
	REACTOR #1			REACTOR #2	
DAYS	PHENOLS D.A.A.P. GM/L.	TOT. ALK. AS NA OH GM/L.	WET SPRUNG TAR ACIDS %	PHENOLS D.A.A.P. GM/L.	TOT. ALK. AS NA OH GM/L.
1	118	184	18	12	240
2					
3	172	172	26	44	231
4	204	159	31	56	218
5					
6	234	150	35	76	200
	TO CONCENTRATOR				
				NEW	BATCH
7	118	177	20	28	235
8	156	164	25	56	232
9	172	160	28	64	226
10					
11	210	156	32	76	215
12	220	154	34	90	208
13					
14	226	150	35	156	190

D.A.A.P. COLOURIMETRIC ANALYSES
4-AMINO-ANTIPYRINE

Slide IX b



Slide X

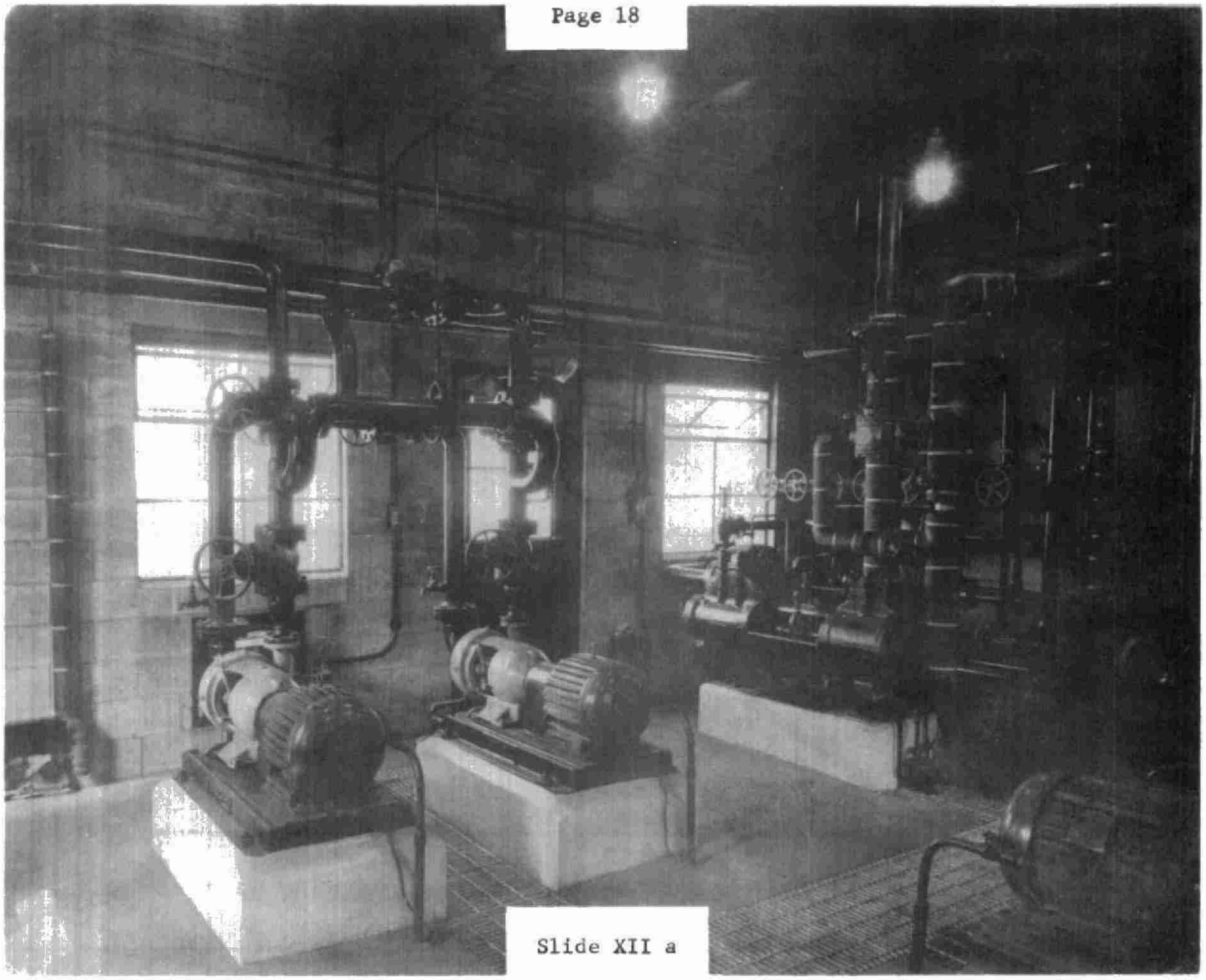


CONCENTRATED CARBOLATE

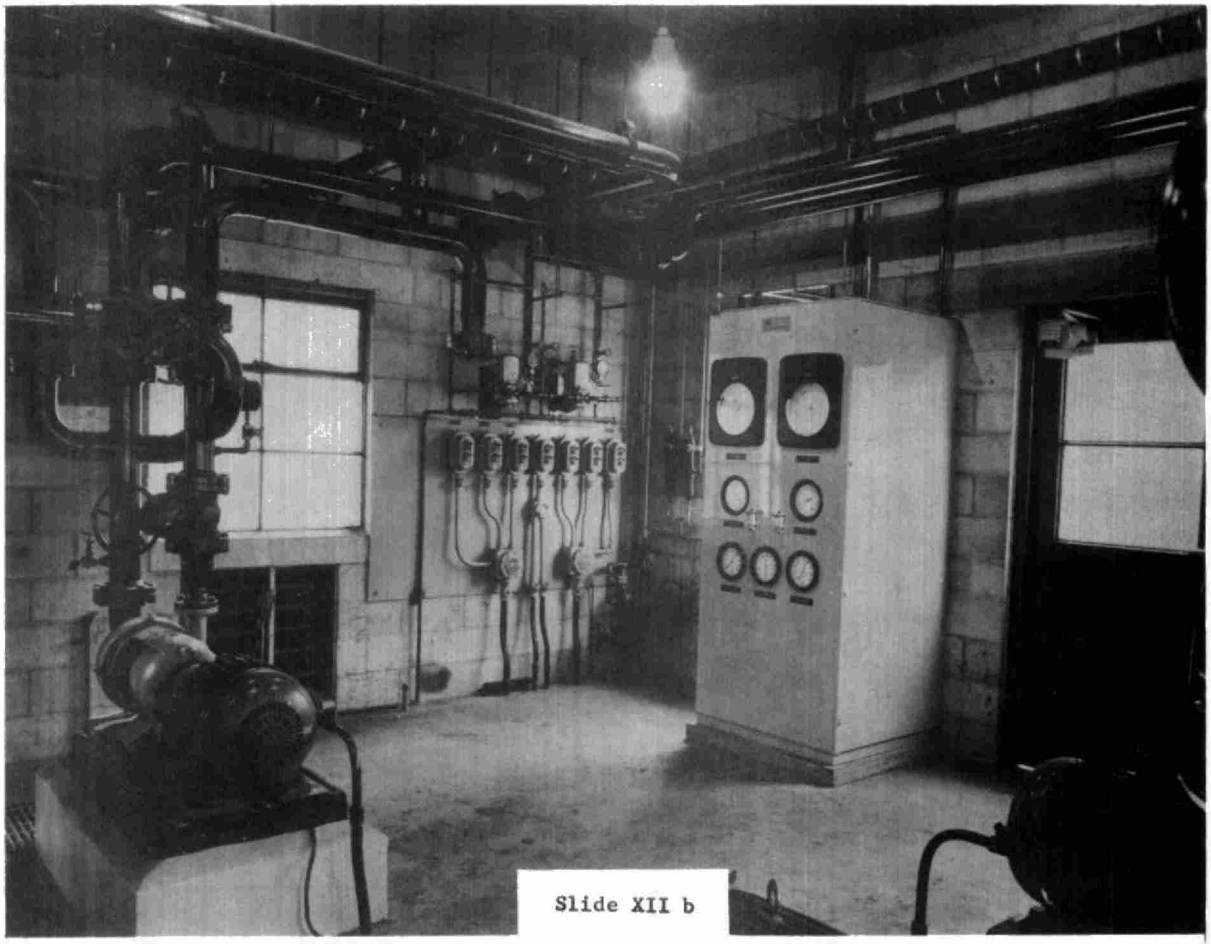
		%
WET FREE TAR ACIDS		57·2
WATER IN TAR ACIDS		7·7
DRY CRUDE TAR ACIDS		49·5
RESIDUE		3·9
DRY SALEABLE TAR ACIDS	D.S.T.A.	45·6
ALKALINITY AS NAOH		17·1
TOTAL SULPHUR		0·4
SPECIFIC GRAVITY		1·261

50 PER CENT SODIUM CARBOLATE PRODUCED EVERY WEEK 3300 GALS

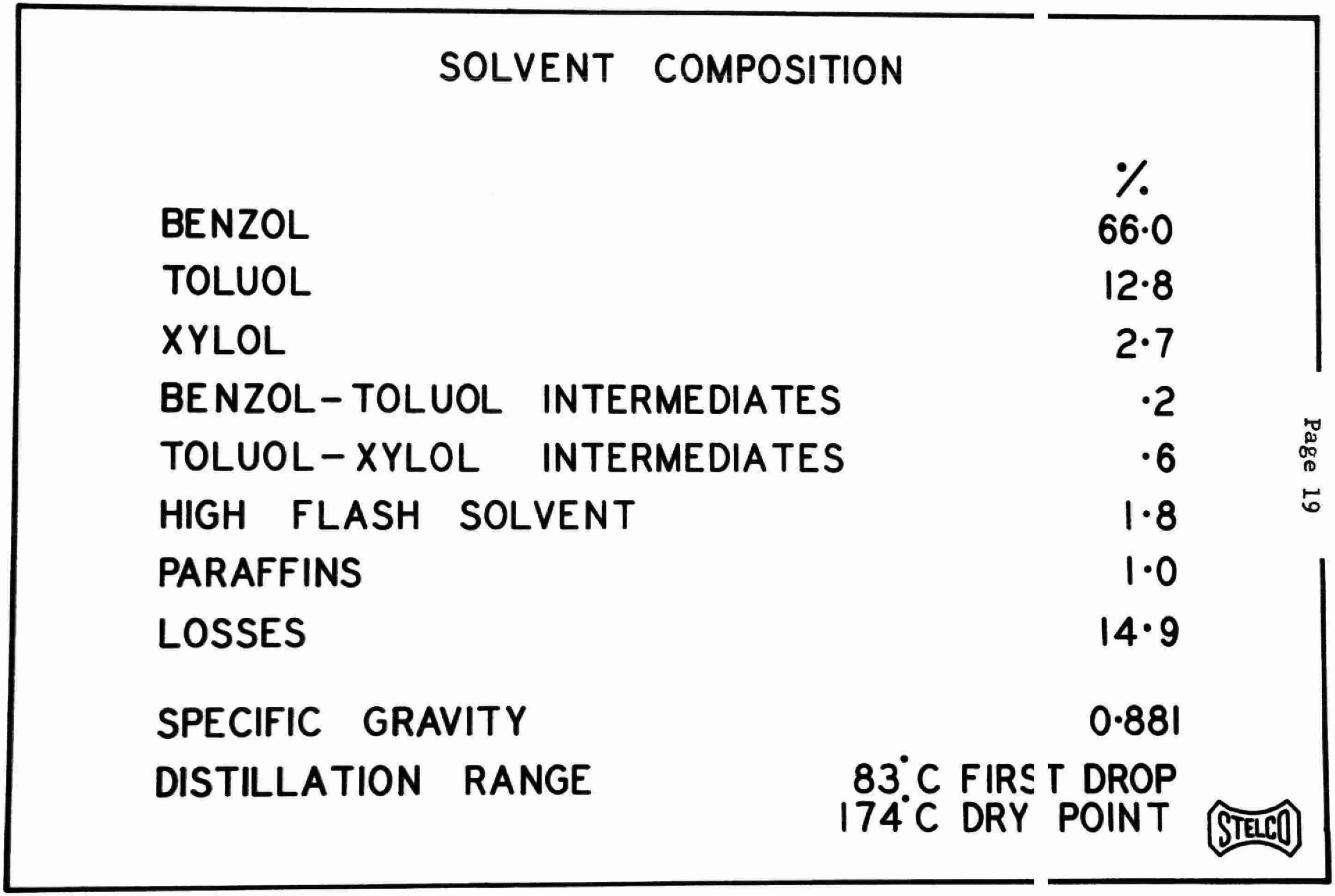
Slide XI



Slide XII a



Slide XII b



SOLVENT COMPOSITION

	%
BENZOL	66·0
TOLUOL	12·8
XYLOL	2·7
BENZOL-TOLUOL INTERMEDIATES	·2
TOLUOL-XYLOL INTERMEDIATES	·6
HIGH FLASH SOLVENT	1·8
PARAFFINS	1·0
LOSSES	14·9
SPECIFIC GRAVITY	0·881
DISTILLATION RANGE	83°C FIRST DROP 174°C DRY POINT

Slide XIII

ACKNOWLEDGMENT

The authors wish to thank Mr. Al Schuldt, General Duties Engineer, Utilities Department, for his contribution in assembling the technical data and preparing the slides.

Thanks are also due to Mr. S. Anslow, Superintendent, Coke Ovens, and his staff, for their co-operation; to J. Williams, Development Engineer, for technical advice; to G. Gates, Engineering Department, for his excellent photographs and colour slides; and to B. DePagter, Engineering Department, for the preparation of the flow diagrams.

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WASTE WATER TREATMENT AT REGENT'S PORT CREDIT REFINERY

by

R. A. SHAVER

"WASTE WATER TREATMENT AT REGENT'S PORT CREDIT REFINERY"

by

R.A. SHAVER

Potable water is essential to human life. Among other uses, an abundant water supply is also necessary for the operation and growth of industry.

This paper deals with a rather unusual control situation in which an oil refinery discharges its industrial effluents to a point in a lake only 1600 feet from an intake to a water treatment plant supplying potable water to a town of 6,000 population.

The refinery of Regent Refining Canada Limited, a subsidiary of Texaco Canada Limited, is located on the shore of Lake Ontario, near the mouth of the Credit River, in the Town of Port Credit, 14 miles west of downtown Toronto.

Present crude oil refining capacity of the plant is 35,000 bbls per day. Processing includes atmospheric and vacuum distillation, visbreaking fluid catalytic cracking, catalytic polymerization, catalytic reforming and product treating. Petrochemical production includes benzene, toluene, xylene and normal hexane.

Smaller scale effluent control problems of the plant prior to its acquisition by Texaco in 1957 were accentuated by expanded refinery capacity to 20,000 bbls per operating day, and by the construction of a Fluid Catalytic Cracking Unit by the end of that year. Phenol concentrations reached a maximum of 390 ppb, and it became difficult to avoid the occasional high oil content in the effluent. Most of the refinery wastes were combined in a single sewer system. Two small oil traps in the plant processing area were used for waste oil water separation. The separator effluent flowed to the shale pit, an old disused shale quarry of 8,000,000 gals. capacity. This provided additional oil separation and some natural oxidation of the effluent before discharge to Lake Ontario.

Sour phenolic condensate from overhead receivers on the Fluid Catalytic Cracking Unit, Atmospheric Distillation and Visbreaking Units was fed to the Sour Water Stripper. In this 2 ft. 6 in. Diam. x 33 ft. tower, containing 10 bubble cap trays, hydrogen sulphide was removed from up to 40 USGPM of sour water by stripping with hot Fluid Catalytic Cracking Unit flue gas. Phenolic water from the Stripper was used as Desalter charge water, resulting in an 80% to 90% removal of phenols from the water by the crude oil.

IMMEDIATE IMPROVEMENTS

In 1958 and 1959, some improvements were made to -

1. prevent accidental spills of spent caustic to plant sewers, and

2. increase oil removal efficiency of the plant oil-water separator and shale pit.

Caustic treating areas were paved and dyked and collecting sumps installed to remove spent caustic spills to storage. Underground spent caustic pipelines were relocated above ground for better leak detection. Spent caustic of commercial value was sold and the balance trucked away for outside disposal.

The plant oil-water traps were combined into one separator to improve oil separation and skimming, and some cooling water effluent was removed from the oily water feed to the separator.

In addition to these improvements, plant experiments utilizing biological oxidation and shale pit water aeration were started. Laboratory tests were also conducted to evaluate chemical oxidants for phenols destruction.

PILOT PLANT ACTIVATED SLUDGE BIOLOGICAL OXIDATION UNIT

In July 1959 a pilot plant Biological Oxidation Unit of the complete mixing, sludge return, activated sludge type, was borrowed from the Ontario Water Resources Commission to conduct tests on phenolic water in the refinery.

The unit, an Infilco"Aero-Accelator", 6½ ft. Diam. x 10 ft. high, was designed to oxidize approximately 7 pounds of phenols per day by the bacterial action of activated sludge. Figure 2 is a flow diagram of the pilot plant.

Waste water batches were prepared and air mixed in a 290 bbl. charge tank. Feed to the pilot plant accelator was through a centrifugal pump, flow recorder control valve, and steam heated fin-tube heat exchanger. Treated Aero-Accelator effluent flowed by gravity to the effluent tank where it was thoroughly aerated before intemittent discharge to the sewer.

Figure 3 shows a cross section of the cylindrical Aero Accelator and illustrates the flow of feed into the bottom center of the vessel, below a hood forming an aeration zone of 194 cu. ft. At this point, back pressure controlled plant air was introduced through a diffuser ring and dispersed by a turbine type mixer aerator above the ring. The turbine mixer also acted as a radial flow type pump to completely mix the waste water, air and activated sludge within the aeration zone. The large bubbles of incoming air were broken up into fine bubbles for rapid oxygen absorption. The lifting action of the air bubbles conveyed the mixed liquor up the inner draft tube where the flow discharged through gates with adjustable openings. The mixed liquor then moved down the annular space between the draft tubes to the clarification zone. There a throughput volume of clarified effluent was displaced from the mixed liquor by the waste entering the unit. This effluent was displaced upward and flowed over the discharge peripheral weir into an effluent launder.

The activated sludge, separated from the effluent, was carried into the mixing zone beneath the hood by the recirculating volume of mixed liquor. The recirculated flow was controlled by varying the area of the gate openings at the top of the inner draft tube. Although a timer-actuated blowdown was provided to control solids concentration, this was used only once during the test runs.

Eighteen months operation of the pilot plant unit under various experimental conditions resulted in a practical knowledge of just what such a unit could and could not do, and produced useful ideas and data for the design and operation of a full sized plant unit.

Certainly the widest experience was obtained in starting up the pilot plant, for this was done all too frequently during the first year of operation. It seemed that two or three weeks was just about the longest period that sludge could be expected to survive the sharp changes in temperature, as well as the changes in sulphides, phenols and caustic concentrations inflicted during some of the experiments.

Table I shows typical pilot plant start-up data recorded from the time of addition of 1,000 gallons of sewage sludge from Toronto's Glendale Sewage Treatment Plant, through the gradual acclimitization period, and up to a feed of 2½ lbs. of phenols per day within three days. At this point the unit was oxidizing 50% of the maximum effective loading of 5 pounds of phenols per day achieved during the plant tests.

Early efforts to build up sludge content in the unit and to increase loadings were unsuccessful. During some runs it was believed that high applied air rates were causing endogenous respiration of the bacteria. A successful continuous run of over 3 months was finally achieved without further addition of sewage solids. Although applied air was steadily reduced, sludge did not increase sufficiently to permit operation of the intermittent sludge blowdown.

Table II shows data recorded during attempts to operate the pilot plant at maximum load.

Other pilot plant work involved general operating changes under various conditions, solution of foaming problems, use of chemical flocculants, addition of nutrients, and treatment of gravity de-oiled FCCU process water along with the regular charge of flue gas stripped phenolic condensate.

Another experiment of interest was to determine how much flue gas stripped and neutralized caustic could be treated in the pilot plant.

A test run was made by adding successively higher volume percentages of caustic in the phenolic condensate feed to the unit. The caustic contained 1.5% free NaOH and 97 - 190 ppm phenols. Nutrient was added at a rate of 6 ozs. of disodium phosphate per 300 bbls.

Less than 2.3% of neutralized caustic in the feed seemed to have little effect on the activated sludge, although 3 - 4 times the normal air rate was required. See Table III.

The pilot plant work was finally discontinued in January 1961.

It was concluded from the pilot plant test runs that with a properly designed and instrumented unit to provide adequate control of feed composition, feed rate, temperature, air, etc., little difficulty should be experienced in operating a full sized Bio Unit to 99% phenols removal efficiency. Treatment cost would also be lower than other known methods of phenols destruction.

PLANS FOR MAJOR IMPROVEMENTS TO WASTE WATER COLLECTION & TREATMENT

Improvements in the effluent during 1959 were very encouraging. There had been a three-fold decrease in average effluent phenols compared with the previous year, and the maximum effluent phenols result for 1959 was only 1/5th of the maximum effluent phenols content for 1958.

In spite of this improvement, it was realized that major changes to the waste water collecting and treating facilities would have to be made in order to meet the effluent phenols objective of 20 ppb, and to adequately handle future increased waste water flows with additional plant expansion.

Several complete waste water phenols surveys were conducted in the refinery during early 1960. Each survey involved analyses of samples taken at more than 20 locations in the plant. The data provided a complete refinery waste water phenols balance under different operating conditions. These were used as a basis to set the design capacity of a phenols destruction unit and to predetermine the expected refinery effluent phenols content when the unit was in operation.

A plan was then approved to -

A. Complete the segregation of all oily process water, storm water and once-through cooling water into three separate sewer system, the purpose being -

  1. To reduce the aqueous extraction of phenols by large quantities of relatively clean water in contact with oil in the sewers and separator.

  2. To reduce to a minimum the quantity of process water requiring oil-water separation. This would reduce the required separator size and keep the waste water stream flow to a minimum should some future post-separator treatment be required.

B. To construct a modern gravity separation type oil-water separator with API design features, to handle oily process water and storm water separately.

C. To construct a Biological Oxidation Unit to oxidize phenolic compounds in separately gathered phenolic waste water.

Early in 1961 an area of approximately 1 acre was cleared near the Lakefront for construction of the waste water treating facilities.

During the next six months 4,000 ft. of trunk sewer line of 18 in., 24 in., and 36 in. size were laid to carry segregated waste water streams to treatment facilities.

The new API Oil-Water Separator was completed and operating in June 1961. The Biological Oxidation Unit was placed on stream the following month. Total cost of the project was $450,000.

Vacuum Unit barometric condensers were also replaced by surface condensers to remove a large source of emulsified oily waste water.

WASTE WATER FLOW

Figure 4 is a flow diagram of waste water in the refinery.

Oily process water and storm water are fed to separate channels of the new API separator. The combined separator effluent flows to the shale pit retention basin. FCCU oily process water is settled in its own separator adjacent to the new API separator, where oil is removed. The effluent is then pumped to the Bio-Unit for phenols oxidation. Cooling water effluent flows directly to the shale pit, which also serves as an emergency oil trap in the event of a leak in a cooler. Sour condensate from the Fluid Catalytic Cracking, Atmospheric Distillation and Visbreaking Units is flue gas stripped, a necessary treatment before biological oxidation is possible. The Sour Water Stripper effluent is charged to the Bio-Unit. Bio-Unit effluent then flows to the shale pit from which all plant effluent water flows under an oil retention baffle and over a weir to Lake Ontario.

API OIL-WATER SEPARATOR

The oil-water Separator consists of three channels, each designed to accommodate a flow of 1500 USGPM. (See Figures 5 and 6)

Each channel has a short pre-separation bay, 19 ft. long, equipped with a manually cleaned trash rack and tilt pipe skimmer. This is followed by a main separating section for each channel measuring 116 ft. long from the inlet vertical slot distribution baffle to the effluent oil retention baffle and tilt pipe skimmers. Channels are each 16 ft. wide with an operating water depth of 4 ft. 9 in. Overall Separator length is 149 ft., overall width is 52 ft.

Oily process water flows into No. 1 channel and storm water flows from tank fields and paved units into No. 3 channel. The Separator effluent flows to the shale pit where it combines with cooling water effluent to the Lake (Fig. 7) An inlet manifold and gating arrangement permits the use of No. 2 channel for either oily process water or storm water and allows for continuous operation of the Separator while any channel is taken out of service and pumped dry for maintenance. The oily process water channel is equipped with moving flights to keep the surface free of oil and the bottom clear of sediment. Sludge hoppers are built into the floor of each Separator channel near the influent end. Sludge pumps, to keep these troughs emptied, will be installed in the future if needed.

Skimmed oil from the Separator flows by gravity into an oil sump having a capacity of 150 bbls. Settled water in the sump is returned from the sump to the No. 1 channel inlet, while recovered oil and emulsion layer is pumped to one of two 2,000 bbl. capacity steam heated emulsion breaking tanks adjacent to the Separator. These tanks are also used for oil recovered in the FCCU process water separator. Separated water bottoms from these tanks may be phenolic, hence they are returned to the inlet of the FCCU process water separator, the effluent of which is treated in the Bio-Unit.

BIOLOGICAL OXIDATION UNIT

The Biological Oxidation Unit consists of 4 vessels located within a 90 ft. x 90 ft. paved and dyked treating unit site. (Fig. 8) Cost of the unit was $160,000 not including utility tie-ins, sewers and other offsite items. Offsite feed preparation installations include the previously described flue gas sour water stripping tower located at the Fluid Catalytic Cracking Unit, as well as a single channel, 52 ft. long x 10 ft. 6 in. wide x 7 ft. deep, API oil-water separator for FCCU oily process water.

Bio-Unit charge water from the sour water stripper and FCCU separator is pumped to one of two 30 ft. diameter x 40 ft. high, 5,000 bbl. charge tanks, equipped with propeller mixers, while the contents of the second tank, previously tested for phenols and sulphides are fed to the treating vessel. (Fig. 9) High level alarms on the FCCU separator effluent basin and two charge tanks are set to prevent overflow of phenolic water to the Lake.

The treating vessel is an Infilco "Aero Accelator" complete mixing, sludge return, activated sludge unit, 32 ft. diameter x 14 ft. 3 in. high with an aeration volume of 4,940 cu. ft. (Fig. 10) The vessel internals and the operating principles involved are similar to those in the pilot plant Biological Oxidation Unit. Foam breaker paddles were attached to the aerator shaft just above the water surface in the inner draft tube. Sides of the inner draft tube were also extended three feet to contain foam. The unit was designed to oxidize 100 lbs. of phenols per day at 300 USGPM hydraulic flow.

Effluent from the Aero Accelator vessel flows into the 30 ft. diameter x 16 ft. open top effluent aerated retention tank. This provides over four hours retention at maximum design flow. (Fig. 11) A 5 HP "Vortair" surface aerator mixer is designed to dissolve 480 lbs. of oxygen per day into the retained water before discharge to Lake Ontario via the shale pit.

Every practical effort was made to instrument the Biological Oxidation Unit to ensure smooth operation with a minimum of attention, and to provide adequate recorder control to aid in determining the causes of upsets if they occur. Remote alarms were installed to alert the operator of unusual conditions that could result in escape of phenols to the Lake.

Air is supplied to the Aero Accelator by two rotary positive displacement blowers, each delivering 105 scfm air at 6 psig. One of these is provided with a variable speed drive to permit closer adjustment of air. A rotameter in the air line indicates air flow to the Accelator. A remote alarm in the FCCU Control Room 500 feet away signals any air blower interruption. Phenolic water feed to the Accelator from the charge tanks is on flow recorder control. A temperature sensing element located in the Accelator inner draft tube records activated sludge aeration zone temperature, and controls steam input to the feed preheater. Failure of the Accelator turbine mixer also sounds an alarm in the FCCU Control Room.

The aerated retention tank was included as a necessary part of the unit to aerate the unit effluent before discharge to the Lake. This removes additional BOD and phenols from the Accelator effluent before discharge to the Lake. It also helps to oxidize small amounts of activated sludge that may carry over from the Aero Accelator. The retention tank also detains the flow of effluent containing higher than normal phenols during mild Accelator upsets and gives the operator time to detect such upsets and to take corrective measures.

The Biological Oxidation Unit was started up on stripped phenolic condensate feed on July 16, 1961. A 3,500 gallon quantity of activated sludge from a local refinery effluent treatment plant and 2,000 gallons of sewage treatment plant sludge were added. The unit came on stream smoothly, building up to approximately 4,000 ppm dry MLSS* at half the design phenols loading within two weeks. Dissolved oxygen and all other tests were normal.

On July 28, 1961 gravity separated oily process water from the FCCU separator was gradually added to the feed. Accelator center draft tube dissolved oxygen dropped off to zero, but phenols oxidation capacity steadily continued to increase up to design load.

Efforts have since been made to obtain a dissolved oxygen reading in the Accelator. These have not succeeded, although air inputs of up to a maximum of 210 scfm have been used. The lack of dissolved oxygen has not impaired phenols removal ability of the unit, or its remarkable flexibility in coping with rapid two-fold changes in phenols loading conditions.

The Biological Oxidation Unit has operated continuously without further addition of sludge, since its start-up July, 1961, until it was shut down as planned during the recent scheduled refinery shutdown, April 25, 1963.

Table IV shows typical operating range conditions for the unit, as well as some high influent loading test data.

Under normal operating conditions, two pounds of granular ammonium phosphate are added per day to supply nutrient to the bacteria.

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* Mixed Liquor Suspended Solids (dry), or the concentration of activated sludge carried in the Accelator inner draft tube.

Some oil enters the Accelator in the charge, but the maximum analyzed has not exceeded 12 ppm.

Operating costs for the Bio Unit at 100 lbs. phenols per day capacity work out to 35¢ per pound of phenols. This includes labour, electricity, steam, nutrient, laboratory and maintenance costs. Not included are sour water stripping and waste gas incinerator operating costs of 91¢ per pound of phenols.

Table V shows conditions during the start-up of the Biological Oxidation Unit last month. A 2300 gallon quantity of refinery waste treatment plant activated sludge was added to the Accelator along with 2300 gallons of raw sludge from Glendale sewage plant. Insufficient phenolic water was available to bring the unit up to its design phenols capacity during the first week, but it is notable that only 36 hours was required to acclimatize the sludge to 49% of the design phenols capacity of the unit.

CONTINUING EFFLUENT CONTROL WORK

In January 1963 the Port Credit Refinery crude oil capacity was expanded to 35,000 bbls per day. Facilities for the production of normal hexane and nitration grade toluene and xylenes also came on stream.

Segration of storm and oily process water is provided at the new Units which are paved throughout. The segregated sewers on the new units are tied into their respective offsite trunk sewers leading to the new API separator. Older unit areas in the plant are gradually being serviced with required sewers and are being paved.

EFFLUENT RESULTS

The average oil content of the plant effluent since June, 1961 is 2.9 ppm.

Phenols in plant effluent were close to the 20 ppb objective in the first few months of Bio Unit operation. Following this period the Sour Water Stripper had to be shut down periodically due to inefficient incineration of stripper off gases that were causing an odour nuisance in the local area under adverse wind and weather conditions.

During these periods phenolic water has been charged to the Desalters. This situation has now been remedied with the start-up this month of a new combined heater-waste gas incinerator. Incinerator performance data is insufficient for presentation at this time.

For the past few years we have noticed a gradual increase in the phenols content of our refinery water intake. Believing that our effluent may be recirculating in the lake to our intake located 1,000 ft. to the north-east, a daily phenols analysis of refinery intake water was started in January, 1962. This was followed by a phenols survey of the Lake front and lower Credit River area in the fall of 1962.

A limited survey of this type imposes certain restrictions in the interpretation of results that indicated the possibility of an unidentified significant outside source of phenols.

Additional phenols surveys covering a wider local water area are now needed. These should be augmented by surveys of Lake and River currents in the area.

There is also a need to improve the accuracy of the phenols test in the low parts per billion range.

In the meantime, our intake water is now being analyzed daily. Although the average difference between our influent and effluent phenols results is below the OWRC objective of 20 ppb, the policy of our Company is to continue to improve waste water treatment where necessary and to keep pace with refinery expansion to ensure a satisfactory effluent.

REFERENCES

(1) American Petroleum Institute Manual on Disposal of Refinery Wastes, Vol. 1, Waste Water Containing Oil, 6th Ed. - 1959

(2) Biological Treatment of Petroleum Refinery Wastes, prepared for the API Committee on Disposal of Refinery Wastes by R.E. McKinney, 1962.

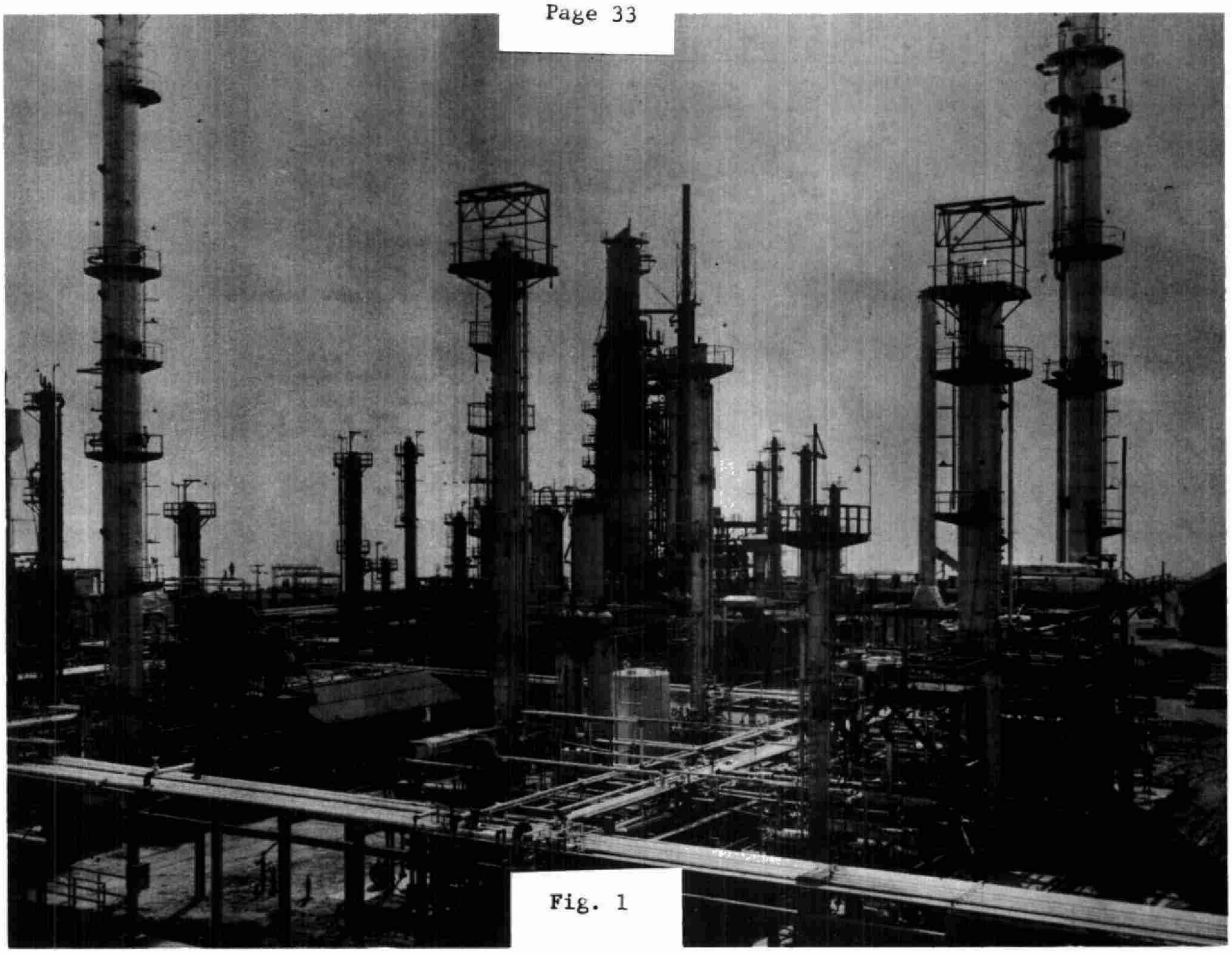


Fig. 1

FIG. 2
PILOT PLANT BIOLOGICAL OXIDATION UNIT
FLOW DIAGRAM

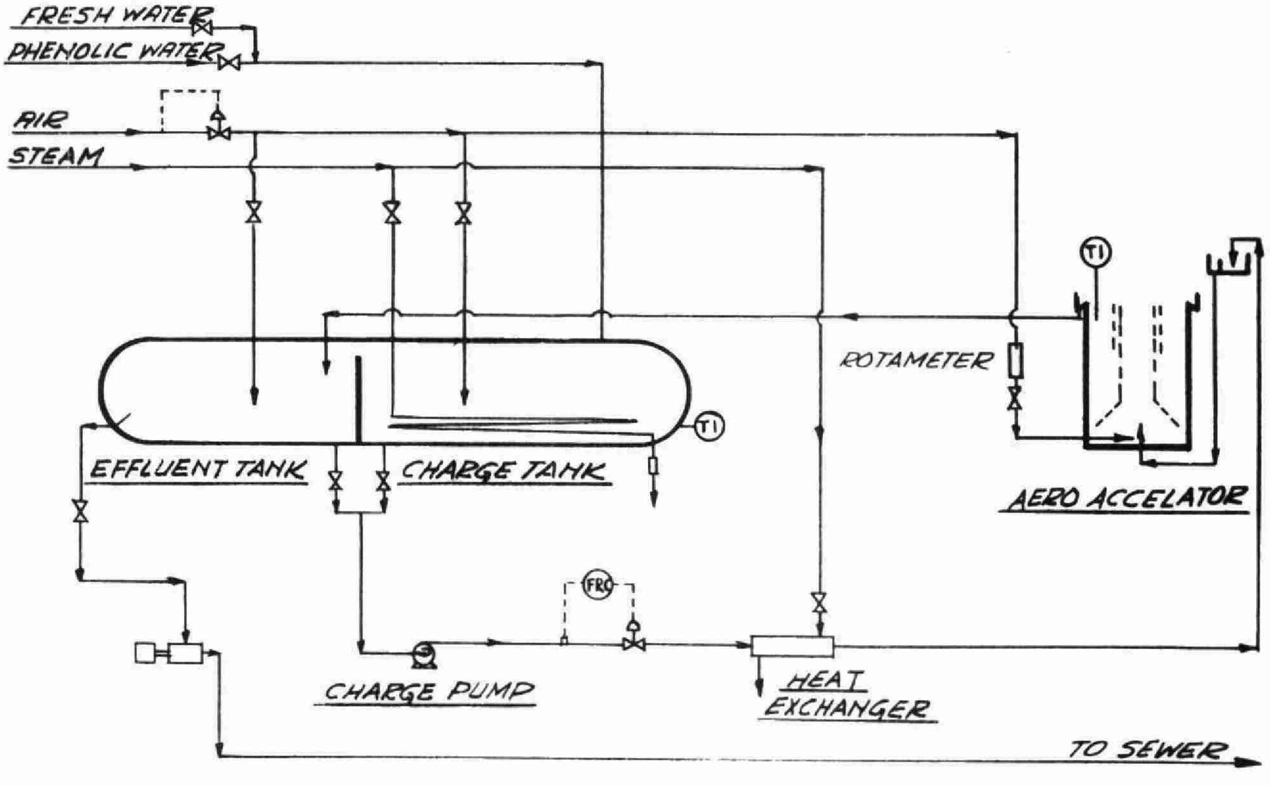


FIG.3 - PILOT PLANT "AERO ACCELATOR"

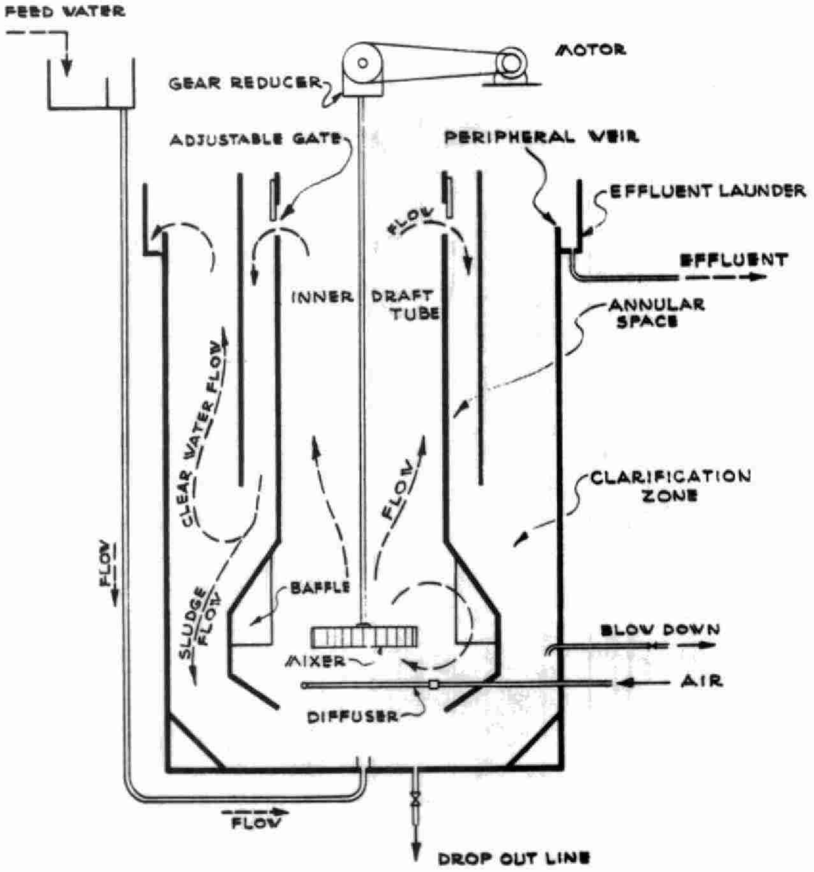


TABLE I
PILOT PLANT BIOLOGICAL OXIDATION UNIT
TYPICAL START UP DATA

TIME IN HOURS FROM INITIAL START-UP	0	4	10	20	25	27	45	49	52	58	68
RAW SEWAGE SLUDGE CHARGED TO ACCELATOR (USG)	1000	-	-	-	-	-	-	-	-	-	-
RAW SEWAGE - SLUDGE VOLUME, 1/2 HR. SETTLING (%)	50	-	-	-	-	-	-	-	-	-	-
CHARGE TANK WASTE WATER PHENOLS (PPM)	20	-	20	-	-	-	-	-	-	91	-
CHARGE TANK WASTE WATER NITROGEN (PPM)	65	-	-	-	-	-	-	-	-	-	-
INTERMITTENT FEED (HRS DURATION AT 2 - 4 USGPM)	2	-	1	-	-	-	-	-	-	-	-
PHENOLS CONCENTRATION IN ACCELATOR (PPM)	6.5	5.6	-	0.6	-	-	-	-	-	-	-
CONTINUOUS FEED RATE TO ACCELATOR (USGPM)	0	0	0	0	1.5	0.5	0.5	2.0	5.0	1.0	2.5
APPLIED AIR - SCFM	10	10	10	10	8.9	8.9	8.9	9.3	9.3	9.3	9.3
ACCELATOR TEMPERATURE (°F)	102	104	-	106	102	100	94	95	98	98	102
SLUDGE VOLUME, 1/2 HR. SETTLING (%)	-	25	-	30	25	25	25	25	25	25	20
DRY MIXED LIQUOR SUSPENDED SOLIDS (PPM)	-	-	-	-	2768	-	-	3200	-	-	1935
DISSOLVED OXYGEN (PPM)	-	0.6	-	0.4	-	-	1.4	-	-	-	1.7
INLET PHENOLS (PPM)	-	-	-	-	9.5	9.5	6.7	6.7	6.7	91.0	91.0
OUTLET PHENOLS (PPM)	-	-	-	-	0.1	0.5	0.4	0.4	0.2	-	0.9

TABLE II
PILOT PLANT BIOLOGICAL OXIDATION UNIT
OUTLINE OF DATA FROM MAX. APPLIED PHENOLS LOAD TESTS

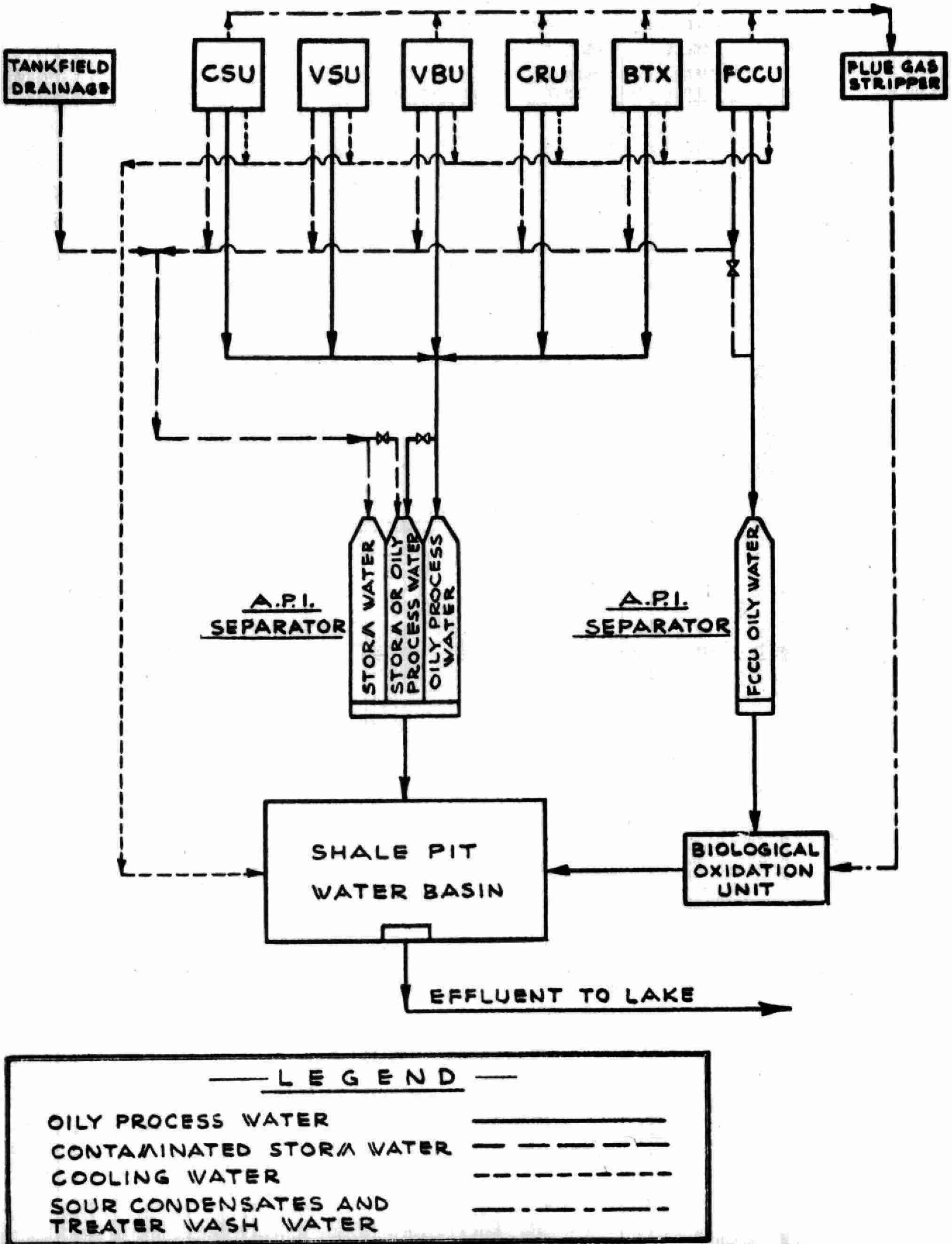
FEED RATE (USGPM)	**AERO ACCELATOR INLET PHENOLS (PPM)**	**AERO ACCELATOR OUTLET PHENOLS (PPM)**	**OXIDIZED PHENOLS (LBS. PER DAY)**	**APPLIED AIR (S.C.F.M.)**	**MIXED LIQUOR SUSPENDED SOLIDS (PPM)**
3.2	112.0	0.8	4.3	5.6	-
4.6	86.4	0.8	4.7	2.4	4450
2.4	154.0	2.8	4.4	2.4	4450
6.0	91.0	3.5	6.3	2.4	2500
6.0	96.0	1.4	6.8	2.0	2500
6.0	60.2	2.4	4.2	2.0	2500
5.4	210.0	38.0	11.1	2.0	2500

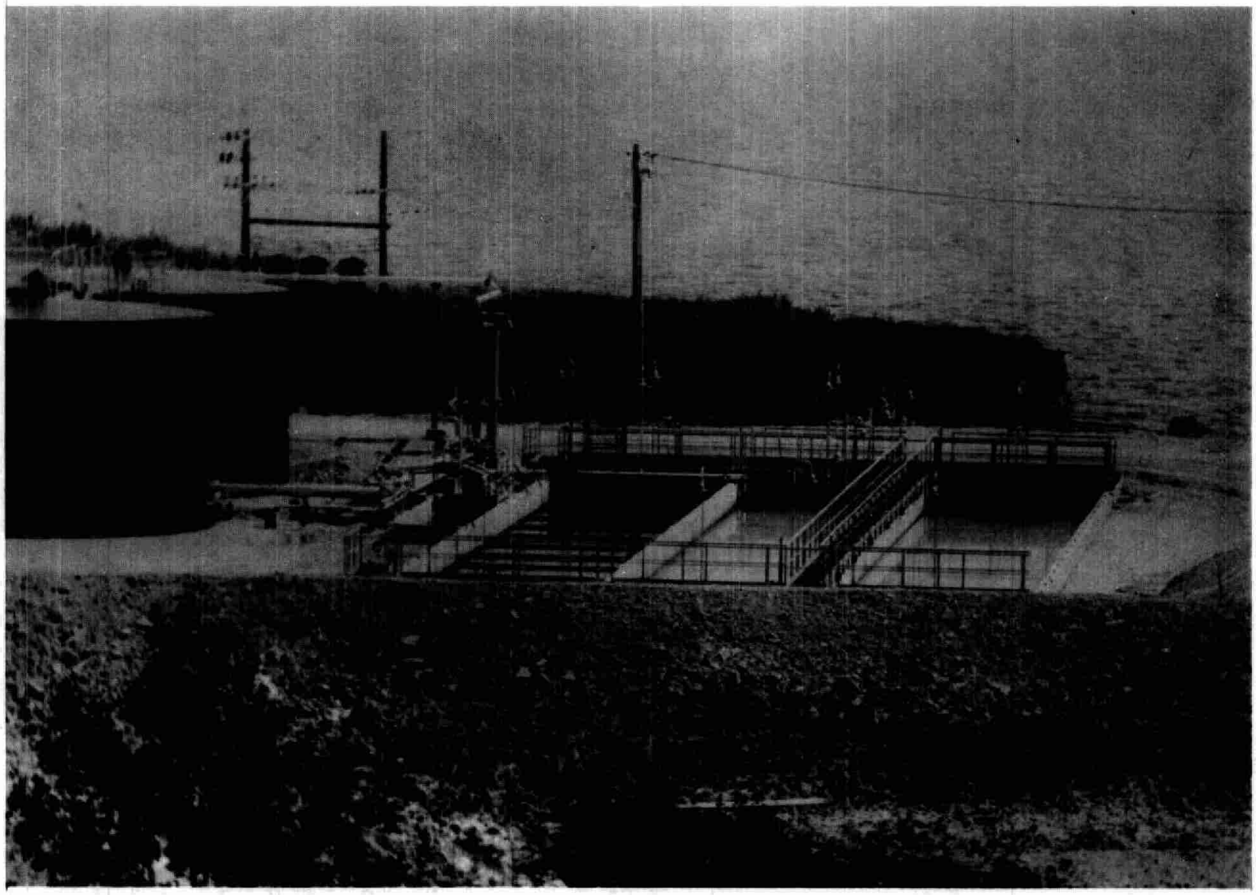
TABLE III
PILOT PLANT BIOLOGICAL OXIDATION UNIT
NEUTRALIZED CAUSTIC TEST RUN

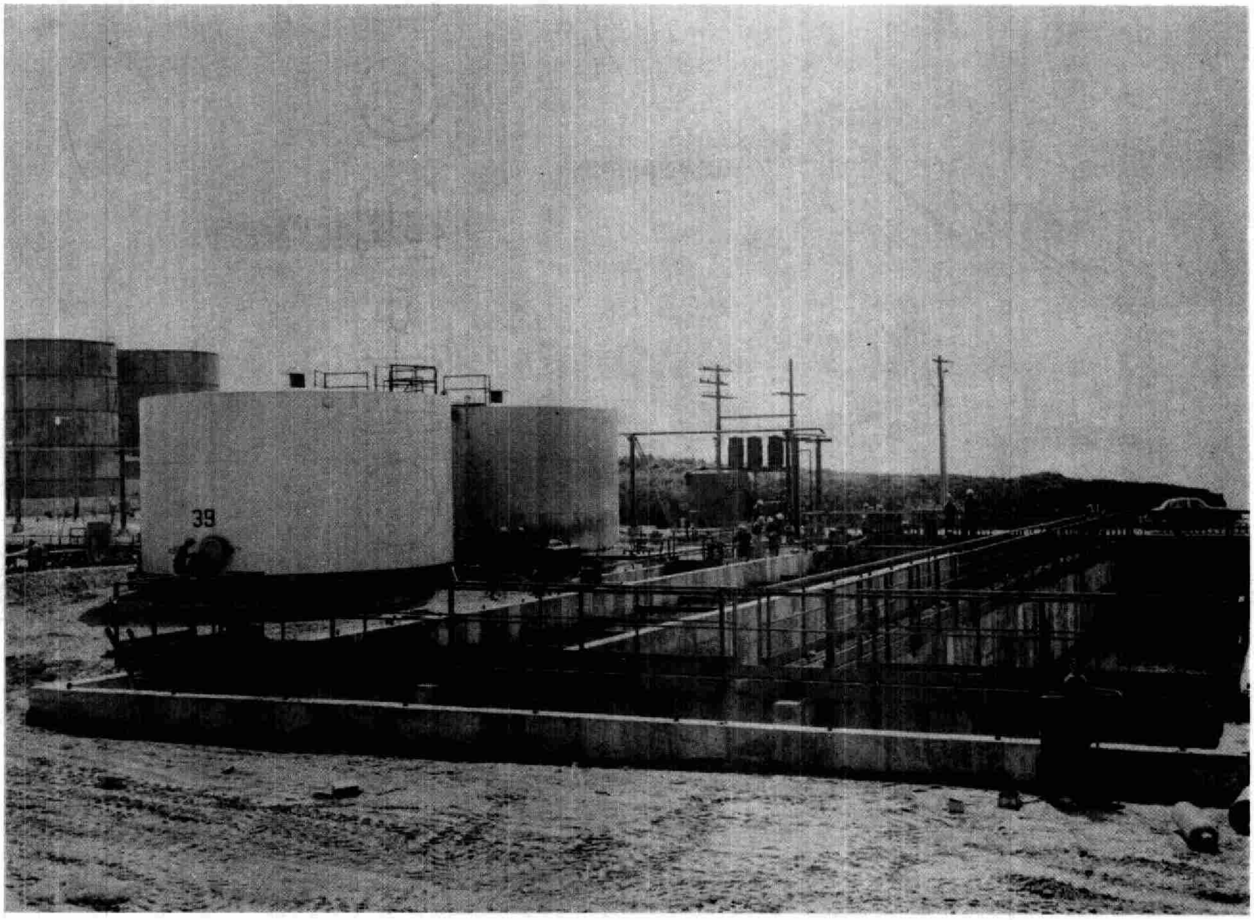
DAY	**NEUTRALIZED CAUSTIC ADDED TO FEED**	**INLET B.O.D.**	**INLET PHENOLS**		**OUTLET PHENOLS**	**AIR**	**ACTIVATED SLUDGE**		**OUTLET D.O.**
	(VOL.%)	**(PPM)**	**(LBS/DAY)**	**(PPM)**	**(PPM)**	**(SCFM)**	**(VOL.%)**	**MLSS (PPM)**	**(PPM)**
1ST	0.48	-	4.0	123	0.11	9.4	39	4045	-
2ND	"	-	4.0	114	11.4	9.4	30	3840	2.0
2ND	0.34	255	4.0	114	5.7	9.4	-	-	-
3RD	"	-	4.0	117	0.93	9.4	32	4080	3.5
4TH	"	-	4.0	106	1.1	9.4	31	2620	-
4TH	"	-	4.0	124	0.95	9.4	-	-	-
5TH	"	-	4.0	108	0.99	9.4	31	4025	-
6TH	0.66	-	4.0	147	0.49	9.4	32	4156	-
7TH	"	-	4.0	132	0.93	9.4	-	-	-
8TH	1.3	-	4.0	142	1.3	9.4	33	2670	4.0
9TH	"	207	3.6	103	1.5	9.4	34	3660	2.0
10TH	"	-	3.6	105	1.3	9.4	33	3750	-
10TH	2.3	217	4.0	-	2.3	9.4	-	-	-

FIG.4

FLOW DIAGRAM OF WASTE WATER FACILITIES AT REGENT REFINING (CANADA) LIMITED



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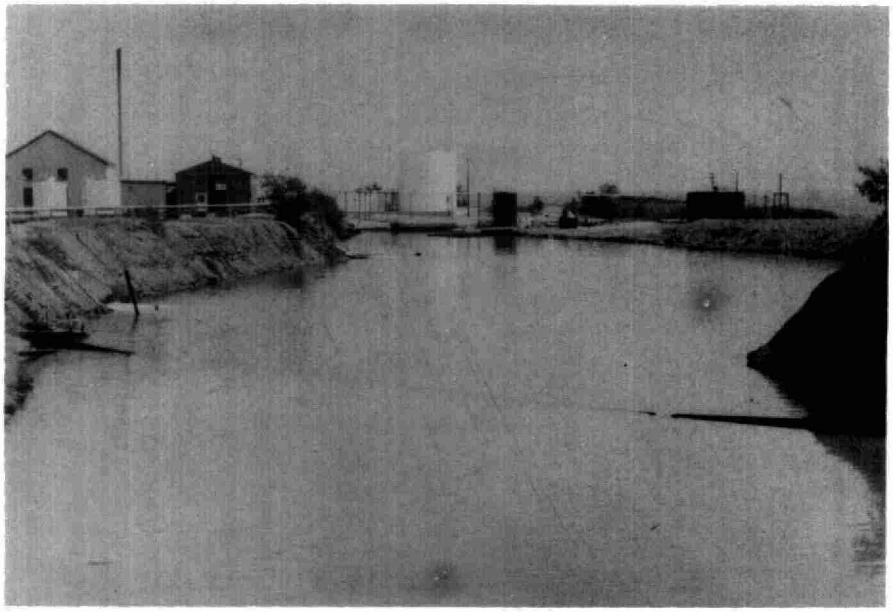


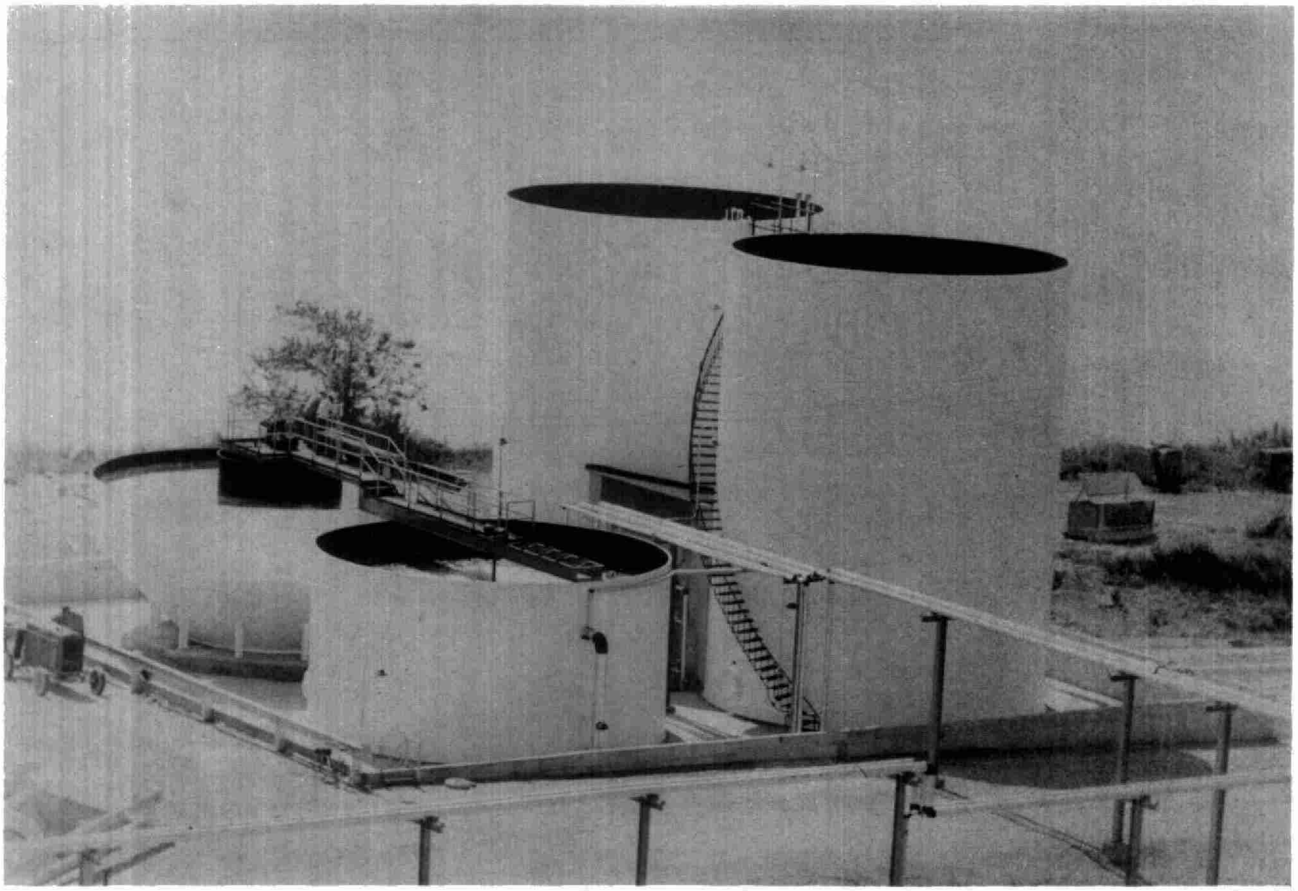
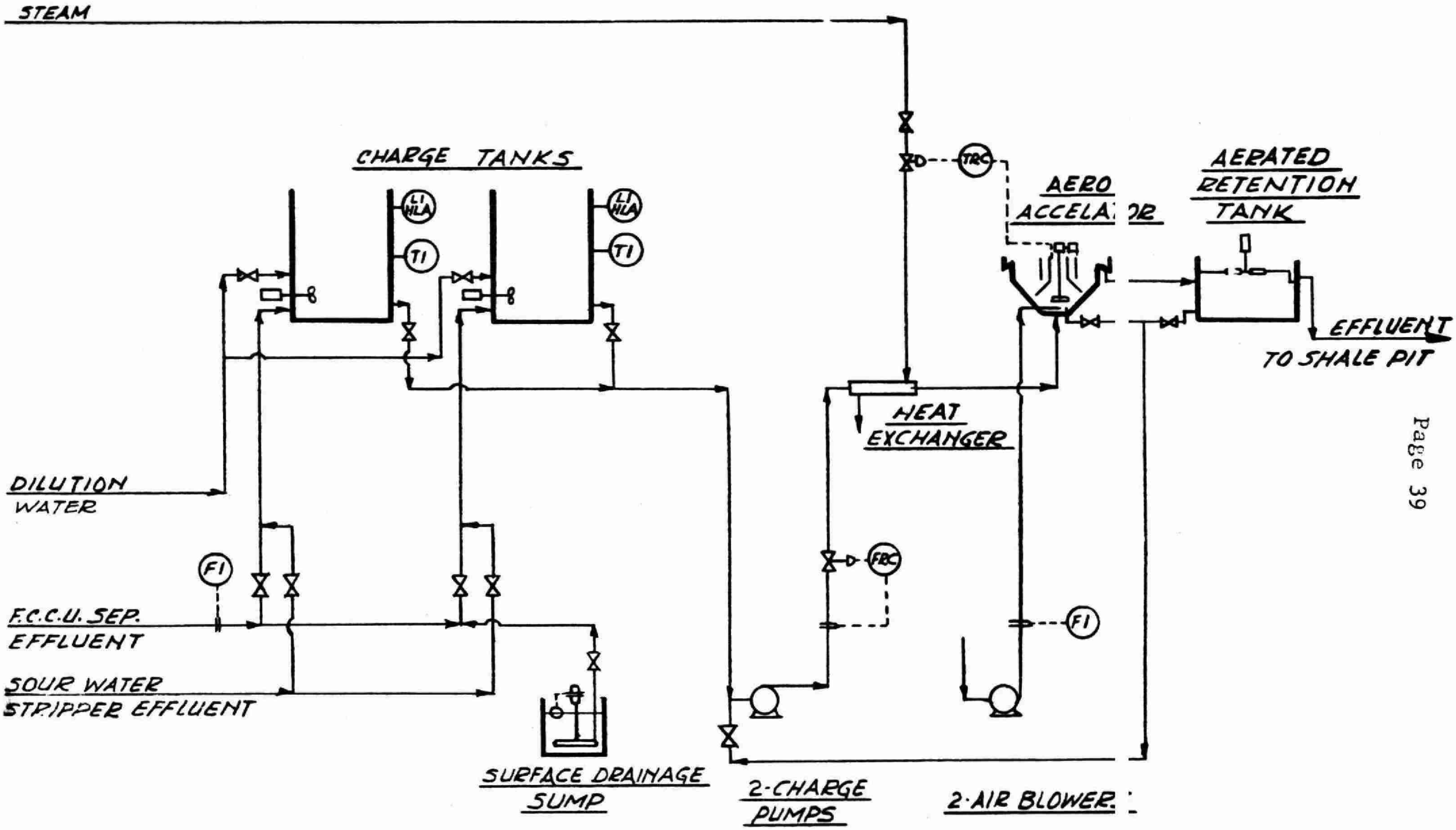
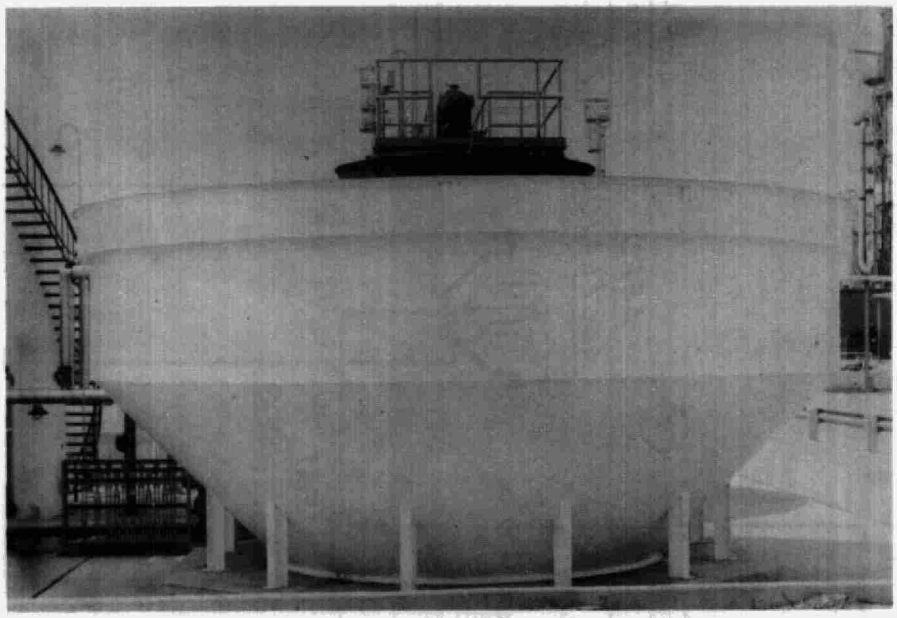


FIG. 9

BIOLOGICAL OXIDATION UNIT FLOW DIAGRAM





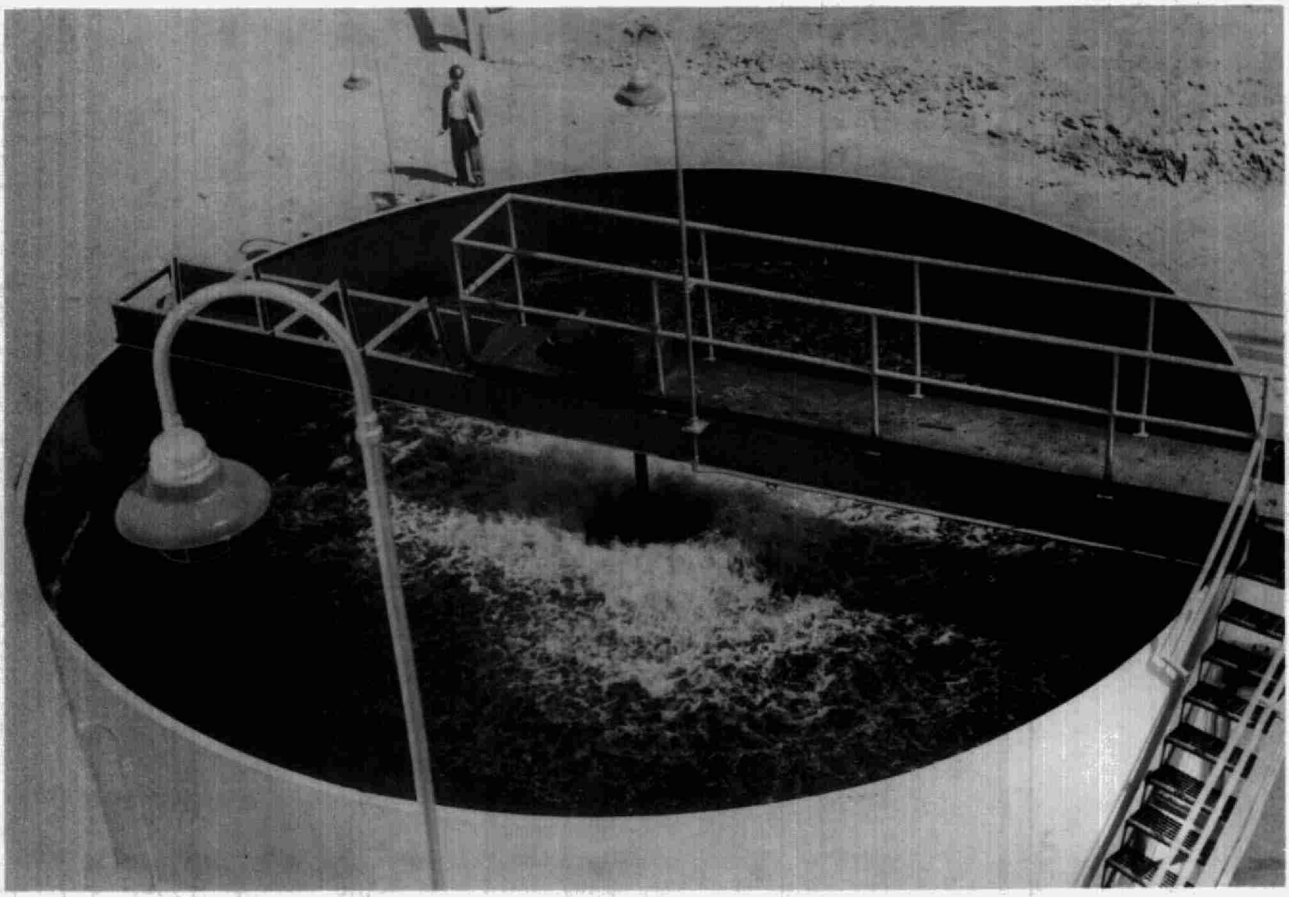
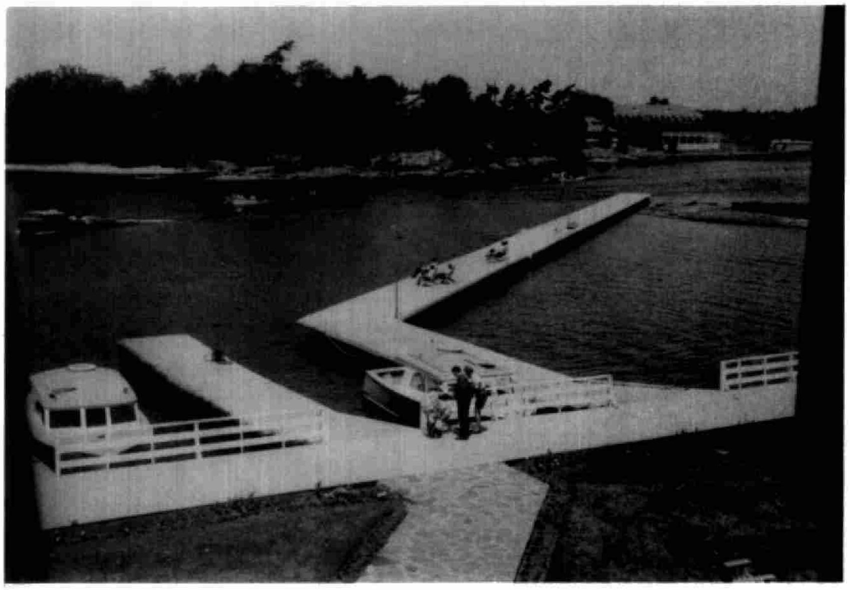


TABLE IV
BIOLOGICAL OXIDATION UNIT
TYPICAL OPERATING CONDITIONS AND HIGH INFLUENT LOADING TEST DATA

- CONDITIONS -	OPERATING RANGE (TYPICAL)	HIGH INFLUENT LOADING TEST DATA		
		A	B	C
FEED RATE (USGPM)	90 - 195	102	154	295
AIR (SCFM)	110 - 200	150	174	198
NUTRIENT (LBS AMMON. PHOS. PER DAY)	2	6	6	6
ACCELATOR TEMPERATURE (°F)	90 - 103	97	95	100
ACCELATOR D.O. (PPM)	0	0	0	0
SLUDGE VOLUME, 1/2 HR. SETTLING (%)	5 - 35	5	22	14
DRY MLSS (PPM)	2000 - 6000	4000	8830	2890
ACCELATOR PHENOLS IN (PPM)	20 - 75	44	79	56
ACCELATOR PHENOLS IN (LBS./DAY)	20 - 140	54	145	198
ACCELATOR PHENOLS OUT (PPM)	-	0.6	0.5	8.6
RETENTION TANK PHENOLS OUT (PPM)	0.2 - 1.4	0.1	0.4	6.6
ACCELATOR B.O.D. IN (PPM)	-	442	402	292
ACCELATOR B.O.D. OUT (PPM)	-	181	232	242
RETENTION TANK B.O.D. OUT (PPM)	-	76	124	132
ACCELATOR C.O.D. IN (PPM)	-	760	860	513
ACCELATOR C.O.D. OUT (PPM)	-	236	485	500
RETENTION TANK C.O.D. OUT (PPM)	-	220	210	272
RETENTION TANK D.O. OUT (PPM)	0.1 - 5.0	4.7	0.1	0

TABLE V
BIOLOGICAL OXIDATION UNIT
START UP CONDITIONS-MAY 1963

TIME	FEED RATE	AIR	ACCELATOR PHENOLS			SLUDGE VOLUME 1/2.HR. SETTLING	DRY MLSS	FEED C.O.D.	DISSOLVED OXYGEN
(HRS. FROM START)			INLET		OUTLET				
	(USGPM)	SCFM	(PPM)	(LBS/DAY)	(PPM)	(%)	(PPM)	(PPM)	(PPM)
0	-	160	44.1	-	-	-	-	-	-
16	45	160	39.2	21	4.7	8.5	-	-	-
24	29	160	39.2	14	1.0	9.0	-	-	-
36	120	156	33.6	49	0.3	10.0	-	-	-
48	150	158	21.0	38	0.4	9.0	-	-	-
60	150	158	21.0	38	0.3	9.0	-	-	-
72	165	156	35.0	69	0.3	8.0	-	-	-
84	120	156	35.0	51	0.3	9.0	-	-	-
96	120	158	30.8	45	0.3	8.0	2786	944	4.8
108	135	174	35.0	57	0.4	9.0	-	-	-



THE VIEW

BIOLOGICAL TREATMENT OF PULP AND PAPER MILL WASTES

by

E. L. BARNHARDT

SESSION TWO

J.J. Heffernan
M.M. Dillon & Company
Session Chairman

"BIOLOGICAL TREATMENT OF PULP AND PAPER MILL WASTES"

by

E.L. BARNHARDT

INTRODUCTION

The Bleached Board Division of the West Virginia Pulp and Paper Company is headquartered in Covington, Virginia. The Covington Mill produces "primarily" high quality bleached board from kraft pulp and corrugating medium from neutral sulfite semi-chemical pulp. The total paper and board production is about 1,000 T/D.

An integral part of a concentrated effort to improve stream conditions below the mill led to the construction of an activated sludge waste treatment plant in 1955, only after pollution reduction at the source had reached the point of diminishing returns. As operating experience with the plant was gained and improvements added, it was possible to treat greater portions of the mill waste. Figure I illustrates the increasing BOD loadings the plant has accepted since startup and also demonstrates the ability of the system to treat the wastes effectively.

The original plant consisted of one 100' diameter primary clarifier for the sedimentation of wastes with high suspended solids content and activated sludge treatment for the settled wastes and a major portion of the low solids Bleach Plant flow which entered the secondary system directly. The paper machine wastes, some of the Bleach Plant flow and a few miscellaneous wastes did not receive treatment initially. In 1959, in order to increase the plant's capacity and efficiency, diffused air aeration units were replaced by dual rotor turbine aerators and a second 100' diameter primary clarifier and an equalization tank were added to the facilities. Immediately after the expansion, additional wastes from the paper machines and more miscellaneous flows were accepted for treatment. All wastes were then mixed in the new equalization tank and the total flow equally split between the two primary clarifiers.

Figure II is a schematic flow diagram and material balance of the treatment system as it exists today.

It is the purpose of this paper to review the treatment performance from January 1958 to the present.

PRIMARY TREATMENT

Prior to July 1959, only those waste streams with high suspended solids content received primary treatment (Figure III). During that period the clarifier overflow rate varied from 1,150 gal./ft.^{2}/day to 1,420 gal./ft.^{2}/day resulting in an average reduction in suspended solids of 81%. From July 1959 to July 1960, the overflow rate varied from 1,280 to 1,420 gal./ft.^{2}/day. This included all waste flows after mixing in the equalization tank and equally split between the two primary clarifiers. The suspended solids reduction during this period averaged 79%. Over the period August 1960 to present, the average reduction in suspended solids was 78.2%. Because of the increased waste flows, the average overflow rate for the latter period had increased to 1,520 gal./ft.^{2}/day with a range of 1,370 to 1,670 gal./ft.^{2}/day. This represents an increase of 20% over the July 1959 to July 1960 period. This increase in overflow rate, however, resulted in less than one percent decrease in suspended solids removal efficiency.

A statistical analysis of primary tank BOD removal (Figure IV) for the same periods shows increased removal efficiencies at the higher overflow rates. The removals increased from 19.6% in the period before June

1959 to 25.4% during the June 1959 to July 1960 period and averaged 28.3% from August 1960 to the present. These data indicate that high concentrations of organic suspended materials contained in paper machine wastes and bleaching wastes are being removed by primary clarification alone.

The variation in suspended solids and BOD removal efficiencies for the three periods are summarized in Table I.

TABLE I

PRIMARY TREATMENT PERFORMANCE

Period	Average Overflow Rate Gal./ft.^{2}/Day	Suspended Solids Removal % Frequency		
		10	50	90
Jan. 1958-June 1959	1,285	78.5	81.0	83.6
June 1959-July 1960	1,350	76.3	78.9	81.5
Aug. 1960-Present	1,520	75.3	78.1	81.2

Period	Average Overflow Rate Gal./ft.^{2}/Day	BOD Removal % Frequency		
		10	50	90
Jan. 1958-June 1959	1,285	15.0	19.6	24.2
June 1959-July 1960	1,350	20.8	25.4	30.0
Aug. 1960-Present	1,520	23.2	28.3	33.4

BOD REMOVAL

The removal of BOD from simple substrate has been observed to exhibit zero or first order kinetics at low concentrations of BOD. In complex wastes such as those from pulp and paper mills, however, the constituents are subject to varying reaction rates. This results in a decreasing overall rate of removal of the various components. The overall rate of BOD removal can, therefore, be defined by a retardant type reaction. This form of equation was employed to define BOD reduction through the aeration tanks. The plot to determine the rate coefficients for numerous runs in which samples were withdrawn at the end of each bay in the aeration tanks are shown in Figure V. The results of several tube studies made in the laboratory are also included in the data. From this plot the following relationship was developed:

(1)

$$100\,\frac{le}{lo} = \%\ \text{BOD remaining} \qquad \frac{100}{1+kS_a t}$$

in which

k = reaction constant

S_a = average mixed liquor solids

t = aeration detention time

le = filtered effluent BOD

lo = BOD of waste after mixing in aeration tanks

It should be noted that in Equation (1) the % BOD remaining is based on the BOD applied to the aeration tank after mixing with the return sludge.

$$lo = \frac{la + r\,le}{(1+r)}$$

in which

r = the return sludge recycle ratio, R/Q

la = primary settled BOD

The rate coefficient k is related to temperature, nutrient levels and to variations in the characteristics of the waste and activated sludge. Temperature and nutrient effects are discussed in subsequent sections of this paper.

Daily variations in waste and sludge characteristics exert a profound effect on the oxidation rate. Figure VI shows the daily variation in the k rate computed from Equation (1) for the daily reported results of April 1960 and April 1961. The results are based on filtered effluent BOD values. It will be observed from Figure VI that the average k rate for April 1960 is 1.60 but may vary over the 10% to 90% probability range from 0.75 to 2.40. There was considerably less variation in the k rate during April 1961. Since the nutrient level and the temperature were similar, no obvious explanation exists for this difference. Further study would be required to define more closely the factors which affect the daily k rate and hence BOD removal relationship.

The variation in % BOD reduction in secondary treatment for these same months is shown in Figure VII. For the April 1960 results the average % BOD removal efficiency was 81.0. The spread between the 10% and 90% probability was 76% to 86% BOD reduction. A similar spread exists for the months of April 1959 and April 1961. The principal reason for the slight increase in effluent BOD in 1961 as compared to 1960 is an increase in effluent suspended solids. It should be noted that during the 1961 period the average difference in BOD between the filtered and unfiltered effluents was 15.5 ppm and the average effluent suspended solids was 88 ppm. This would indicate approximately 0.175 ppm of BOD is exerted per ppm of effluent suspended solids.

Since it has been demonstrated that secondary effluent suspended solids substantially influence the BOD removal, it is significant when comparing oxidative efficiency to consider only soluble BOD removal. In April 1959 the filtered effluent BOD was 43.8 ppm with a corresponding percent reduction of 80.7%. In April 1960 and 1961 the filtered effluent averaged 22.9 and 21.2 ppm, respectively, with a corresponding BOD reduction of 88.9% in both cases.

EFFECT OF NUTRIENT LEVELS

While the difference in BOD removal in 1960 and 1961 in Figure VII can be explained by increased effluent suspended solids, the lowered efficiency attained in 1959 can also be explained, but because of a different variable. That variable is nutrient feed. In 1959, only 1.48 lbs. of nitrogen/100 lbs. of BOD removed was added, while in 1960 and 1961 the feed rate was approximately tripled to 4.87 and 4.41 lbs., respectively. The results of this comparison are presented in Table II.

TABLE II

Month	Nitrogen Added Per 100 lbs. BOD Rem.	Temperature °F	Per Cent Reduction 10%	50%	90%
April 1959	1.48	105.0	69.5	74.5	80.0
April 1960	4.87	104.5	76.0	81.0	86.5
April 1961	4.41	100.0	74.0	78.6	85.0

It is obvious that increasing the nutrient level yields an overall increase in secondary performance. In view of the fact that the aeration retention period was far less in 1960 and 1961, the comparison is even more striking.

There is also correlation which can be presented on the effect of temperature on BOD reduction at various nutrient feed rates. Figure VIII demonstrates this effect. This plot was obtained by grouping plant operating records into temperature and nitrogen feed levels with large enough span to detect significant variation in BOD reduction. The data demonstrate that at lower aeration tank temperatures the nitrogen feed rate may be less than at the high temperatures without seriously impairing BOD removal efficiency. It is also evident from analysis of plant operating data that at nutrient levels about 4.5 lbs. of nitrogen/100 lbs. BOD removed that the advantage of increased nutrient level is less marked (Figure IX)

OXYGEN UTILIZATION

The aeration system at Covington consists of two aeration units being fed in parallel. Each unit is divided into four aeration compartments which are operating in series. Figure X depicts the oxygen requirements for the plant in each of the aeration compartments. As will be noted, almost 70% of the oxygen must be supplied in the first two aeration compartments and 40% is consumed in the first compartment.

FINAL SEDIMENTATION

From previous data presented in this paper it was noted that the effluent suspended solids normally contribute about 15% to 20% of the effluent BOD. The solids removal efficiency of the final clarifiers is therefore of considerable importance. Figure XI is a statistical comparison of effluent suspended solids concentration taken during three periods of increasing flow conditions. Table III summarizes these data.

TABLE III

FINAL CLARIFIER PERFORMANCE

Period	Average Influent Flow MGD	Average Overflow Rate GaL/ft.^{2}/Day	Average Effluent Susp. Solids
Jan. 1958-June 1959	15.0	660	76
July 1959-July 1960	21.2	940	81
Aug. 1960-Present	24.0	1060	90

Although it is recognized that other variables exert influence on the effluent suspended solids concentration, it can be noted from the plot in Figure XI that the substantial increase in overflow rate from 660 gal./ft.^{2}/day to 940 gal./ft.^{2}/day resulted in an increase in average effluent suspended solids of only 5 ppm. A subsequent increase from 940 gal./ft.^{2}/day to 1060 gal./ft.^{2}/day, however, allowed a 9 ppm increase to occur.

COST

The cost of operation of the Covington Waste Treatment Plant is about $1.26 per ton of paper produced (Table IV). This ratio has remained fairly constant since 1955 only because the higher costs incurred by increased nutrient feed, labor, maintenance power and defoamer have been offset by decreased charges for depreciation and increased paper production. However, another realistic and appropriate measure of treatment efficiency, cost-wise, is the actual cost of removing BOD. (Figure XII and Table V) This cost has declined from a high in 1956 of 6-1/2 cents per pound of BOD removed to the current low of 2-1/2 cents per pound last year. This is a reduction of almost 62%.

CONCLUSIONS

From the analysis of the plant operating results in the period 1958 to 1962, it can be concluded that:

1. The primary clarifier suspended solids removal, with inclusion of additional mill flows and the additional primary clarifier, is about the same as previous operation with one clarifier and lower flows. An improvement is noted in primary BOD removal efficiency. Suspended solids and BOD removals presently average 78% and 28% respectively.

2. The effect of aeration detention time and mixed liquor solids on BOD removal during bio-oxidation treatment can be expressed by the relationship developed from Figure V (Rate Coefficient Plot)

$$\text{\% BOD remaining} \quad \frac{100}{1+kS_a t}$$

3. The rate coefficient k is influenced by variations in waste characteristics, temperature and nutrient level.

4. At temperatures greater than 100° F the BOD removal efficiency is impaired.

5. The effect of nitrogen deficiency on BOD removal is greatest at the highest temperatures.

6. Increasing the nitrogen feed above 4.5 lbs. N/100 lbs. BOD removed exerts only a slight influence on BOD removal.

7. During the last period under investigation, the final settling tanks were operating under maximum hydraulic design conditions.

TABLE IV

COST OF OPERATION

POLLUTION ABATEMENT DEPARTMENT MONTHLY AVERAGE

	Amount Dollars	Per Cent of Total
Operating Labor	3,500	9.2
Maintenance	3,880	10.3
Operating Supplies	390	1.0
Power	3,655	9.7
General Expense	600	1.6
Salaries	2,400	6.3
Depreciation	12,200	32.3
Chemicals	9,500	25.1
Research & Development	1,700	4.5
Total	37,825	100.0

TABLE V

COST OF BOD REMOVAL

Year	Cost Dollars/Month	BOD Removed lbs./day	Cost/lb. of BOD Removed
1956	$28,090	14,410	$0.065
1957	33,200	17,940	0.062
1958	28,970	23,890	0.040
1959	33,160	20,020	0.055
1960	34,720	39,670	0.029
1961	31,180	41,200	0.025
1962	35,000	46,050	0.025

FIGURE I

CHRONOLOGICAL PLOT OF BOD LOADING

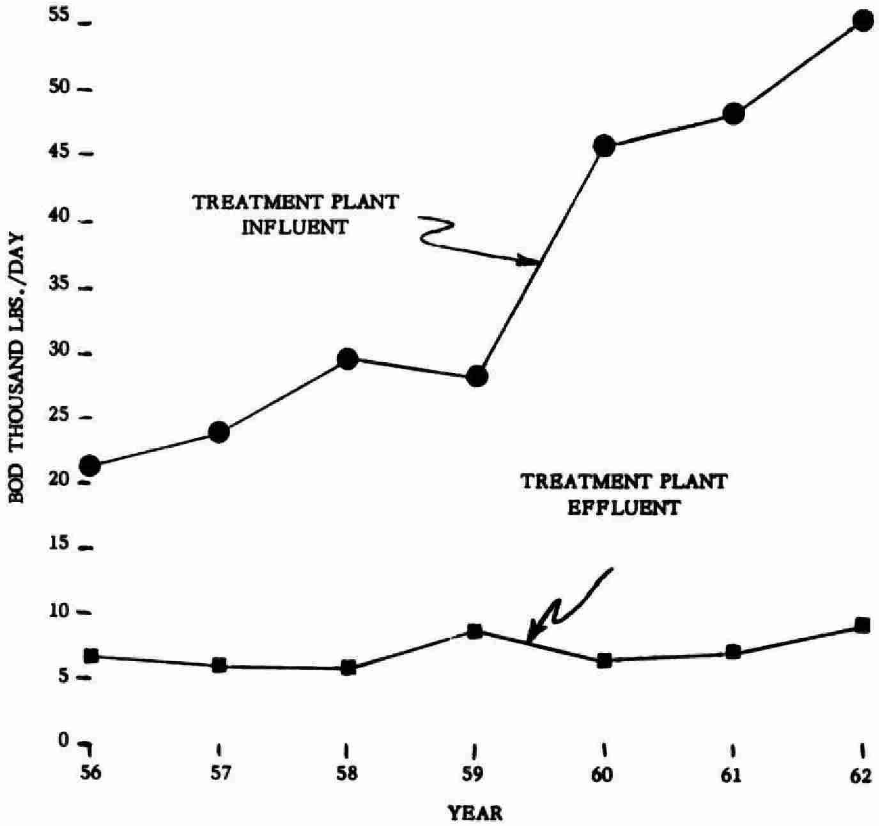
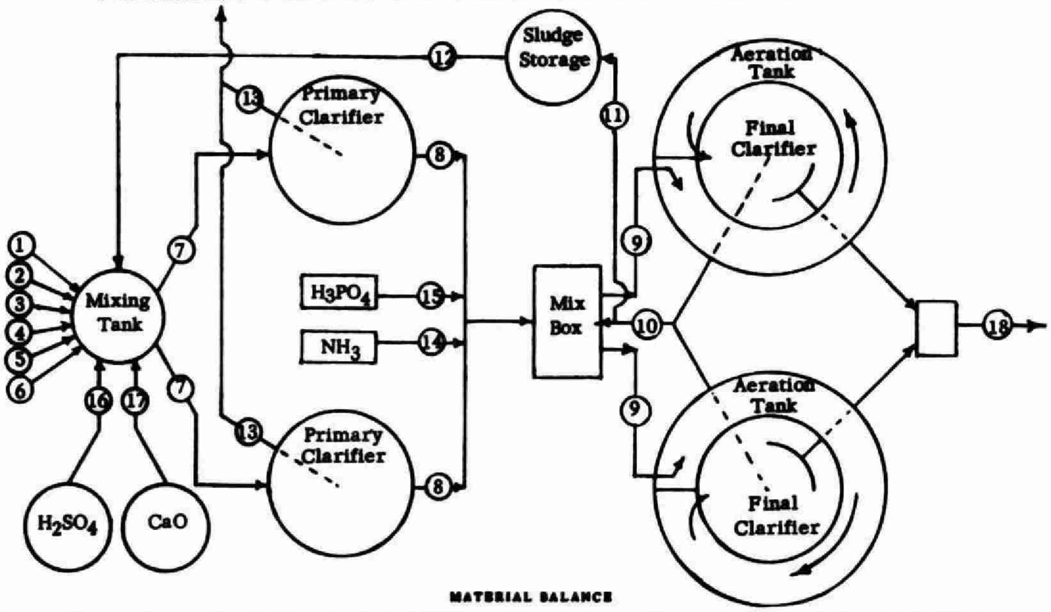


FIGURE II

SCHEMATIC FLOW DIAGRAM AND MATERIAL BALANCE



MATERIAL BALANCE

LINE	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
FROM	Bleach Room	Settling Pond Eff.	East Side	SC and Fly Ash	Paper Mill	Paper Machine Backwater	Mixing Tank	Primary Clarifier	Mixing Box	Final Clarifier	Final Clarifier	Sludge Storage	Primary Clarifier	NH_3 Tank	H_3PO_4 Tank	H_2SO_4 Tank	CaO Tank	Final Clarifier
TO	Mixing Tank	Mixing Tank	Mixing Tank	Mixing Tank	Mixing Tank	Mixing Tank	Primary Clarifier	Mixing Box	Aeration Tank	Mix Box	Sludge Storage	Mixing Tank	Disposal	Primary Effluent	Primary Effluent	Mixing Tank	Mixing Tank	Jackson River
BOD ppd	17, 400	1, 900	14, 700	5, 100	9, 000	1, 300	51, 300	38, 800	-	-	-	-	-	-	-	-	-	6, 300
SS ppd	5, 800	3, 700	64, 500	32, 600	49, 400	1, 600	192, 400	42, 000	752, 500	710, 500	36, 500	34, 800	145, 300	-	-	-	-	34, 500
FLOW mgd	8.65	1.75	8.35	2.17	4.78	1.16	26.5	25.7	34.3	8.62	.44	.44	0.78	-	-	-	-	25.73

Average for months Nov.-Dec. 1962 and Jan. 1963

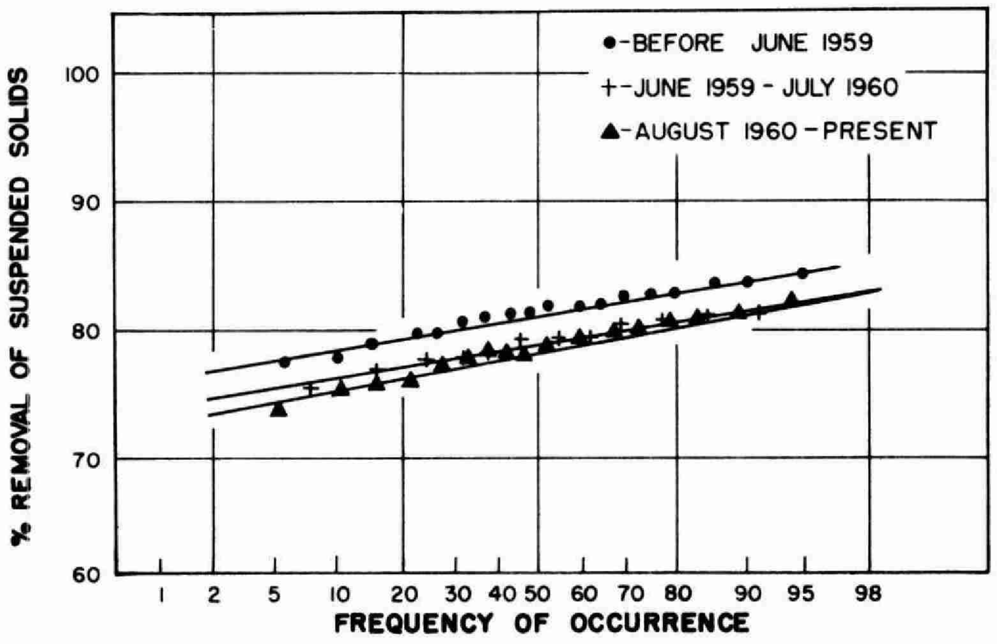


FIGURE III

STATISTICAL COMPARISON OF PRIMARY TREATMENT EFFICIENCY - SUSPENDED SOLIDS REMOVAL

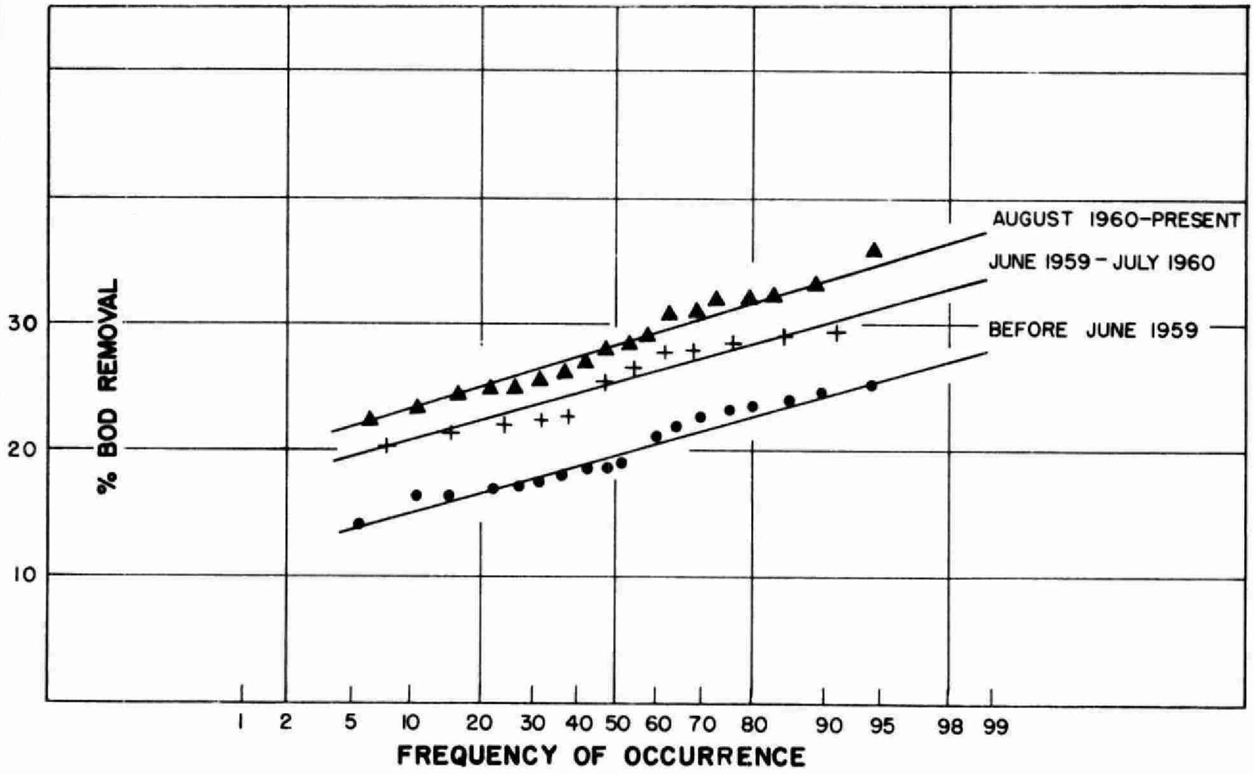


FIGURE IV

STATISTICAL COMPARISON OF PRIMARY TREATMENT EFFICIENCY - BOD REMOVAL

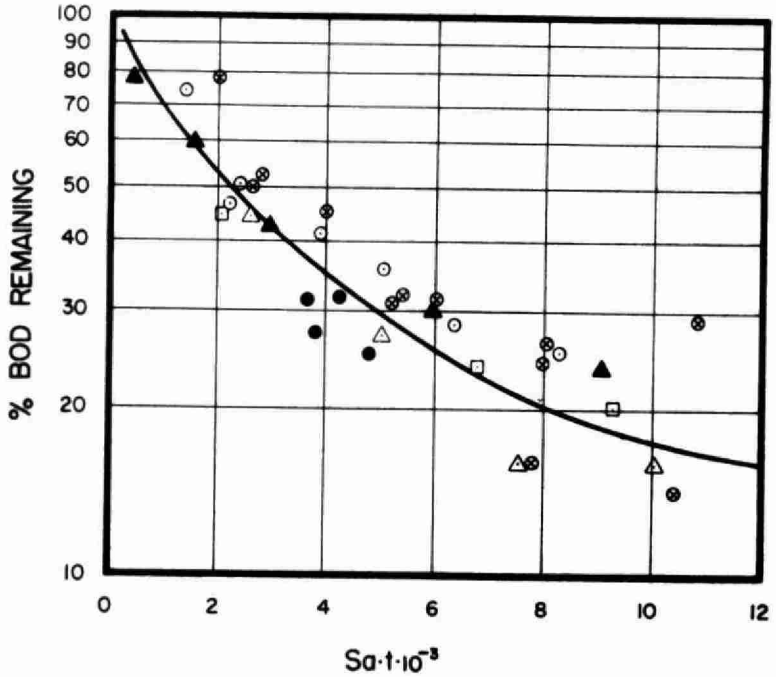


FIGURE V

CORRELATION OF PLANT BOD REMOVAL DATA

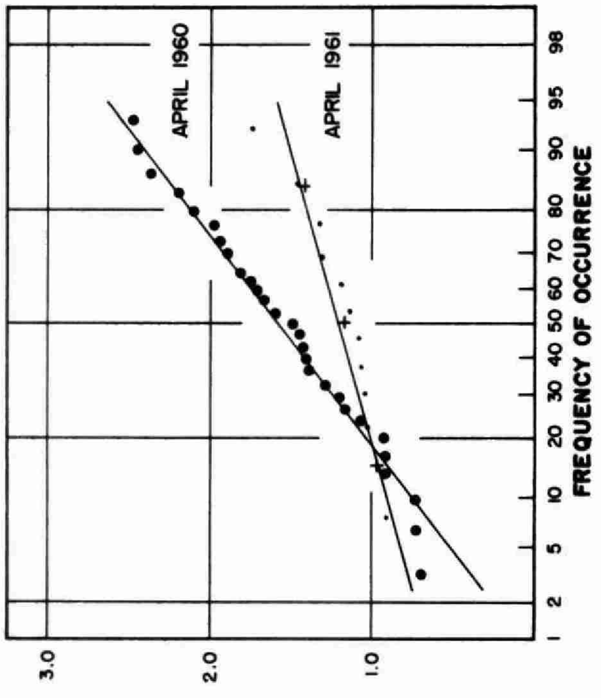


FIGURE VI

STATISTICAL ANALYSIS OF PROCESS REACTION RATES - DAILY VALUES FOR APRIL 1960

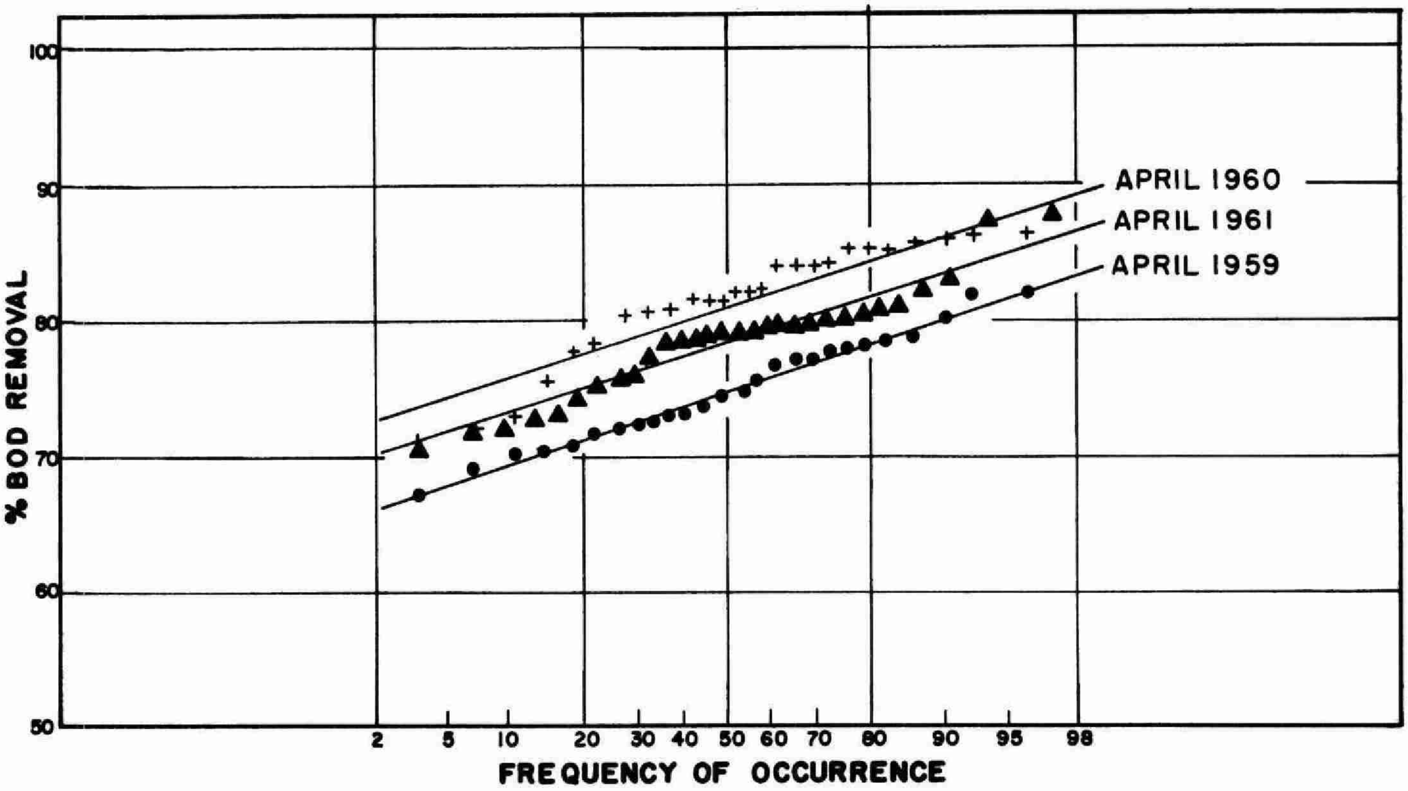


FIGURE VII

STATISTICAL COMPARISON OF SECONDARY TREATMENT EFFICIENCY - BOD REMOVAL

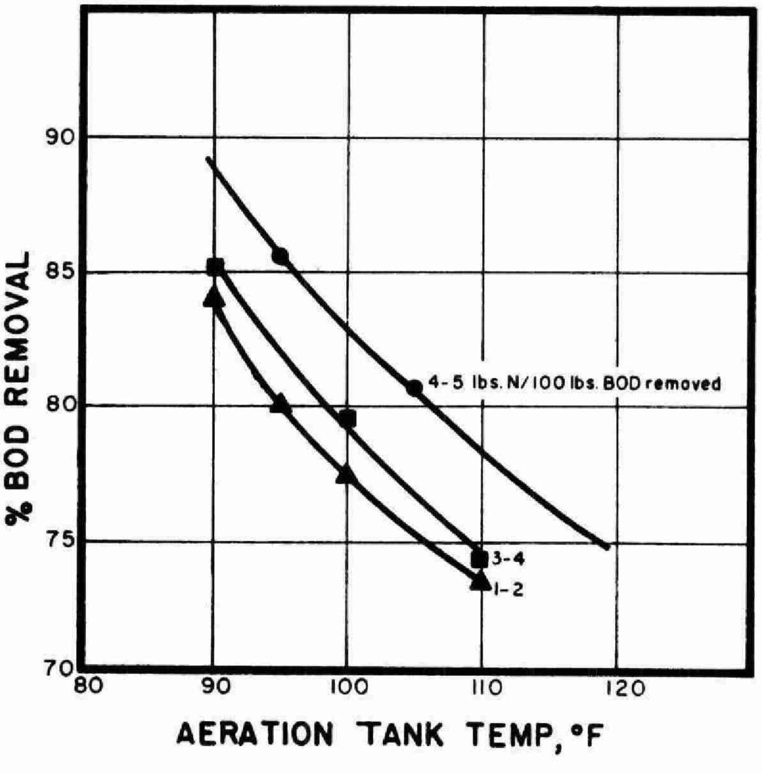


FIGURE VIII

EFFECT OF AERATION TANK TEMPERATURE ON BOD REMOVAL

AT VARIOUS NUTRIENT LEVELS

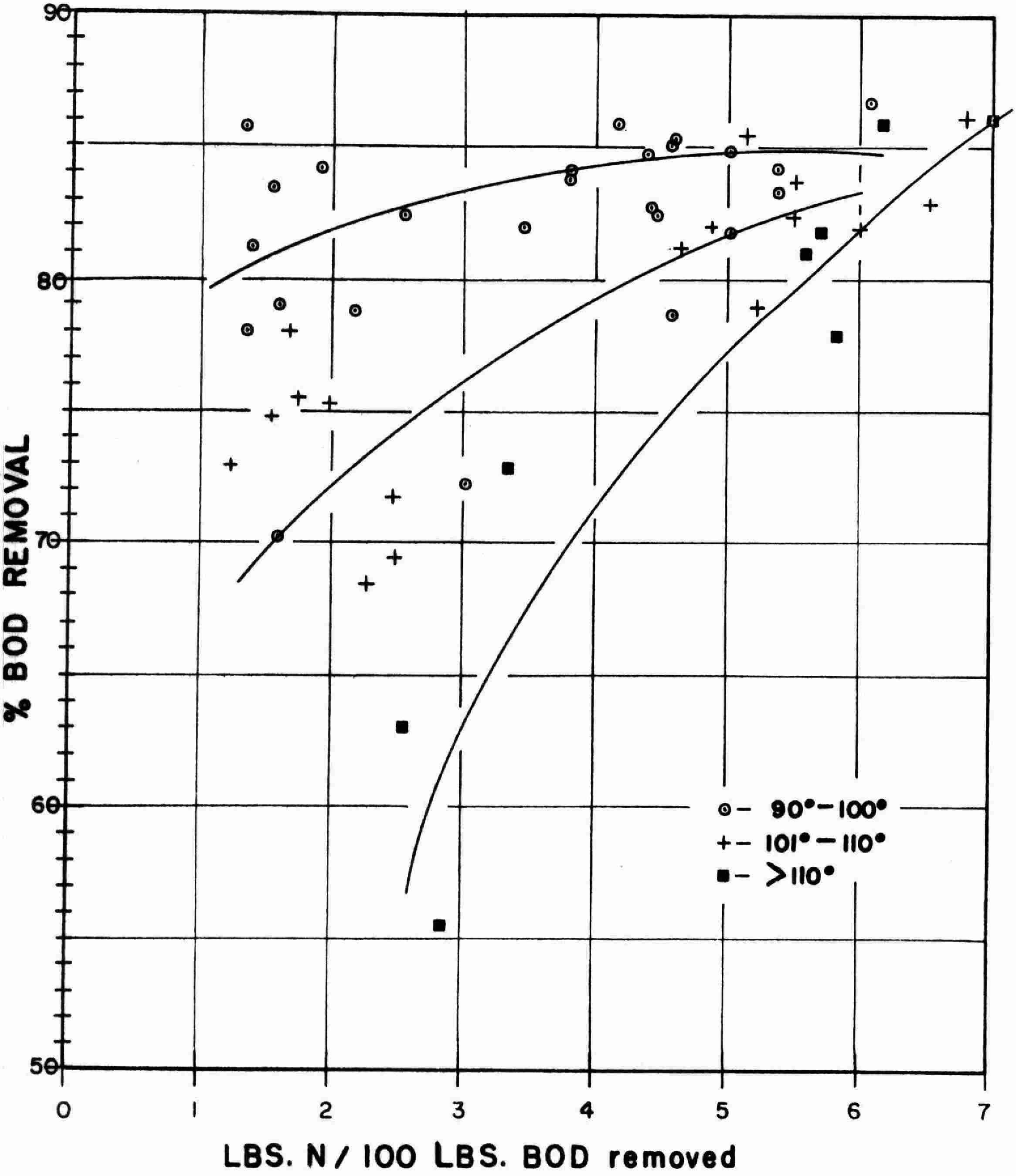


FIGURE IX

RELATIONSHIP BETWEEN BOD REMOVAL AND NUTRIENT LEVEL AT VARIOUS AERATION TANK TEMPERATURES

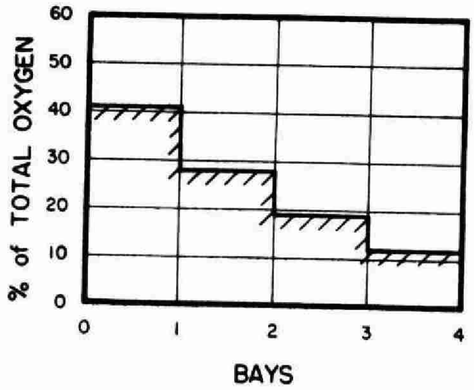


FIGURE X

VARIATION IN OXYGEN DEMAND DURING TREATMENT

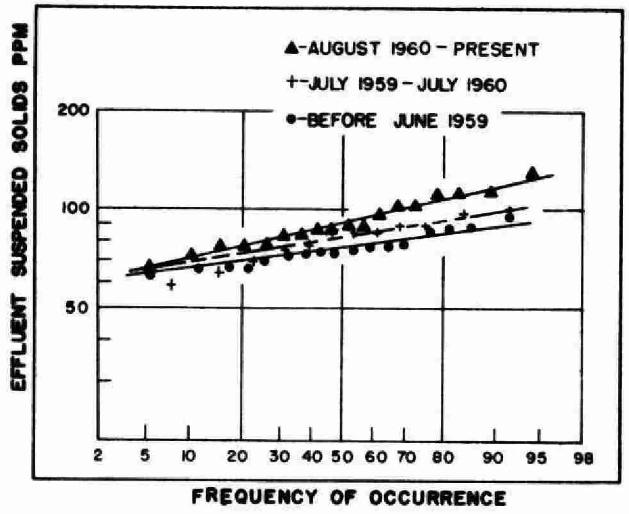
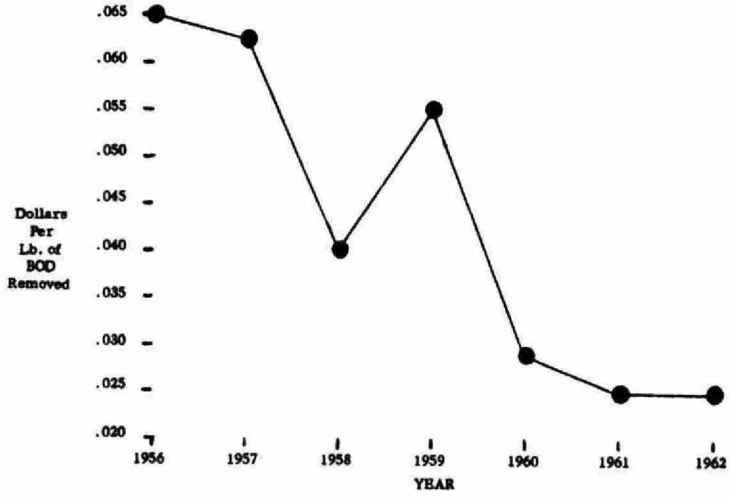


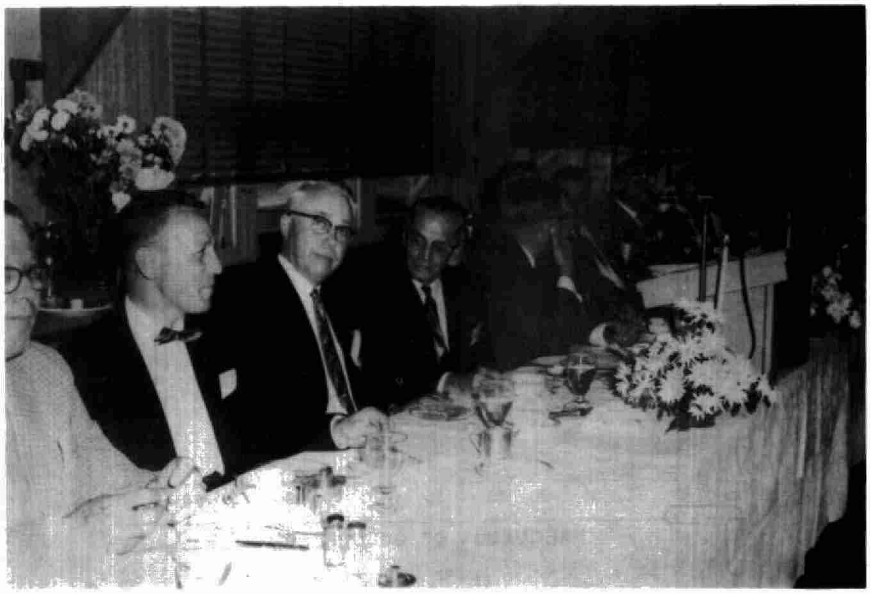
FIGURE XI

STATISTICAL COMPARISON OF EFFLUENT SUSPENDED SOLIDS CONCENTRATION

FIGURE XII

COST OF BOD REMOVAL





HEAD TABLE

A STUDY OF THE SUITABILITY OF THE 4-AMINOANTIPYRINE METHOD FOR THE DETERMINATION OF PHENOL EQUIVALENTS IN PULP AND PAPER MILL EFFLUENTS

by

H.M. McFARLANE

"A STUDY OF THE SUITABILITY OF THE 4-AMINOANTIPYRINE METHOD FOR THE DETERMINATION OF PHENOL EQUIVALENTS IN PULP AND PAPER MILL EFFLUENTS"

by

H.M. McFARLANE

ABSTRACT

An investigation of the suitability of the 4-aminoantipyrine method for the determination of phenol equivalents in pulp and paper mill effluents has been carried out. It has been found that the results obtained are seriously affected by the type of sample involved, the condition of the apparatus and the conditions in the laboratory being used. It is concluded that the method should be applied with caution to wastes containing suspended or colloidally dispersed cellulosic matter.

INTRODUCTION

In the "Objectives for Water Quality in the Province of Ontario" adopted by the Ontario Water Resources Commission, it is stated that the presence of phenolic substances in water causes objectionable tastes and odours and can taint the flesh of fish. It is suggested that adequate protection will be provided if the average phenol content of the water is kept below 2 p.p.b., and that this result will be attained if plant effluents are kept below 20 p.p.b. phenol or phenol equivalents.

Gurnham (1) states than an unpleasant taste is produced by as little as 0.1 p.p.m. phenol in water, and that on chlorination 1-5 p.p.b. phenol produce medicinal tastes in water supplies. Klein (2) reports that fish will not be present in waters containing 0.2 p.p.m. phenol and that 0.002 p.p.m. (2 p.p.b.) will give a perceptible taste to chlorinated water supplies.

Kinney (3) has expressed considerable doubt that the relationship between phenol content and taste and odour is valid. However, until such time as there is general agreement with his thinking, the premise on which regulations concerning phenols are based must be accepted.

It should be pointed out that the work described in this paper was not aimed in any way at questioning the validity of the regulations concerning phenol. Rather it was directed at determining the suitability of one analytical method for the determination of phenol equivalents in the effluents from one industry.

Over the past five or six years, engineers of the Ontario Water Resources Commission have carried out several surveys of mill effluents at various mills of the Abitibi Power and Paper Company, Limited. One of the standard analyses carried out has been the phenol test and on occasion, levels of this material close to 100 p.p.b. have been reported. While the technical personnel of the Company are aware that phenolic materials can be formed from wood in some of the pulping processes, there has been, nevertheless, some question as to the validity of the test procedure when applied to pulp and paper mill effluents.

The particular method of analysis used in the work reported here was the 4-aminoantipyrine method as described in Standard Methods (4). Since pulp and paper mill effluents can contain a great variety of complex organic chemicals, it was felt that the entire procedure, including the preliminary screening, should be followed. Rather than use actual mill effluents, synthetic effluents were prepared. For instance, spent sulphite cooking liquor is known to contain lignin degradation products which might be phenolic in nature; but, it also contains a variety of simple sugars which are obviously non-phenolic. Solutions of such sugars were, therefore, carried through the test procedure. Pulp and paper mill effluents can also contain colloidally dispersed carbohydrate material (hemicelluloses) and suspended fibres. Such suspensions and dispersions were prepared as described later.

EXPERIMENTAL

As mentioned previously, the phenol contents of the various solutions were determined using the 4-aminoantipyrine method. The procedure described in Standard Methods (4) was followed as closely as was physically possible. Four sets of all-glass distillation apparatus were used. Each set was heated by an individually controlled electric heater. Optical densities were determined using a Bausch & Lomb Spectronic 20 with 1-inch tubes. Standard phenol solutions were made up and standardized as described in the method (4).

The scheme of analysis may be conveniently divided into three sections:

(a) the preliminary screening procedure;
(b) the colour development and extraction;
(c) the photometric reading.

Briefly these sections may be described as follows:

(a) Preliminary Screening

Copper sulphate is added to the sample and the pH is adjusted to less than 4.0 with phosphoric acid. The sample is distilled in an all-glass apparatus. Phosphoric acid and copper sulphate are added to the distillate which is then extracted with chloroform which dissolves the phenol. The phenol is then extracted from the chloroform solution into IN NaOH.

(b) Colour Development and Extraction

Ammonium chloride is added to the alkaline extract and the pH is adjusted to 10.0 ± 0.2 with ammonium hydroxide. The colour developing reagents, 4-aminoantipyrine and potassium ferricyanide, are added and after three minutes the colour is extracted into chloroform. A blank is carried through these same steps.

(c) Photometric Reading

The absorbance of the sample is read against the blank at 460 mmu in a suitable spectrophotometer.

Standard phenol solutions are carried through sections (b) and (c) and an absorbancy-concentration curve is plotted. Concentration of the unknown is determined from this curve.

Materials tested were as follows: D-glucose, L-arabinose, D-fructose, D-galactose, D-mannose, D-xylose, D-galacturonic acid, bleached hardwood sulphite pulp, bleached softwood sulphite pulp, groundwood pulp and lowyield unbleached softwood sulphite pulp. With the exception of the galacturonic acid which was practical grade, all chemicals used were reagent grade.

HOT WATER EXTRACTION OF PULP SAMPLES

Thirty grams (oven-dry basis) of each pulp was slushed in 1500 ml. of boiling distilled water. The slushed samples were then vacuum filtered using No. 4 Whatman filter papers. The pulp pads were washed with sufficient boiling distilled water to give total filtrates of about 2000 ml. The solids contents of the filtrates were determined. The pulp pads were air-dried.

Analytical data on the pulps used are given in Table I.

RESULTS AND DISCUSSION

A series of standard phenol solutions was prepared and the colour was developed and extracted. Transmittances in one-inch tubes were measured at 460 mmu with the blank being set at 100% transmittance. Results are shown in Table II and Curve 1 of Figure 1.

Some two months later, when a new supply of 4-aminoantipyrine was obtained, a new set of standards was prepared and the transmittance measured as before. Results are shown in Table II and Curve 2 of Figure 1.

While the differences between the two sets of results are significant, the effect on the conclusions reached is not important since the samples tested were, for the most part, compared with each other.

EFFECT OF ENVIRONMENT AND APPARATUS ON RESULTS

At the beginning of the investigation the work was carried out in a laboratory usually reserved for water and waste studies. This is a large room fitted out with most of the standard laboratory fixtures. Shortly after the work began, another program involving the use of large amounts of phenol was started. Realizing the dangers of contamination, the phenol analysis project was restricted to one sink and one end of the long central bench. All apparatus for the project was set aside and was not used for any other work. The new program was restricted to the other end of the laboratory. However, it soon became apparent that the analytical work was being affected. For instance, when distilled water was put through the entire procedure, apparent phenol contents varying between 0 and 10 p.p.b. were obtained. Various sugar solutions gave results of duplicate determinations with apparent phenol contents varying between 15 and 70 p.p.b.

The phenol analysis project was then moved to another room in which very little work of a chemical nature is normally carried out. Some improvement in results was obtained, but not sufficient to be satisfactory.

Two sets of the distillation apparatus were rinsed with distilled water, steamed out and then one litre of distilled water was distilled through each. The other two sets of apparatus were treated in a similar manner with a dilute NaOH rinse first. Four blank determinations were carried out using the entire preliminary screening procedure. Apparent phenol contents varied between 5 and 25 p.p.b.

Following this, four additional blank determinations were carried out. In this trial the distillation was normal, the preliminary screening extractions were eliminated, the colour being developed directly in the distillate and then being extracted.

Apparent phenol contents were less than 2 p.p.b. in all four cases. This indicated that the prior contamination had occurred in the beakers, flask, extraction funnels, etc., used in the preliminary screening extraction.

Up to this time, the method of washing glassware had been to use a household detergent followed by thorough rinsing with tap water and distilled water. A polyphosphate cleaner was obtained and all glassware was washed using this material. Four blanks were then carried through the entire procedure and apparent phenol contents were again all below 2 p.p.b. It was felt that all sources of contamination had been eliminated.

EFFECT OF SAMPLE COMPOSITION ON RESULTS

Following the elimination of sources of contamination, no difficulty was experienced in obtaining good checks between duplicates of samples containing dissolved material only. However, when the samples contained colloidally dispersed or suspended organic matter, widely divergent results were at times obtained. Results are summarized in Table III.

Examination of Table III shows that with the exception of galacturonic acid, none of the sugars tested gave rise to any significant "apparent phenol". When the wood pulp samples were suspended in water and treated, results tended to be quite variable. The same was true of the hot water extracts of the pulps.

Comparison of Tables I and III shows that no correlation exists between the phenol level and the only benzenoid constituent of the pulps - the lignin. However, during the work it was noticed that pronounced baking occurred on the sides of the distilling flasks when extremely high phenol values were obtained, e.g. with both the bleached hardwood sulphite pulp and its hot water extract. It is felt that some if not all the phenol obtained with other samples was due to a similar cause.

Referring to the galacturonic acid, it is known that such substances decompose on heating in acid medium to give carbon dioxide, furfural and other unknown materials (5). Similar decompostions will take place with the pulp samples since uronic acids are known to occur in hemicelluloses (6). It is quite possible that the unknown decompostion products of the uronic acids could give rise to a positive phenol test.

CONCLUSIONS

The work described here has shown that one of the standard methods for the determination of phenol in plant wastes should be applied with caution to any effluent containing suspended or colloidally dispersed carbohydrate material. Cleaning of the apparatus used and conditions in the laboratory should be watched carefully if contamination of the sample is to be avoided.

If phenol content is to continue to be one of the criteria with which effluent quality is judged, it seems certain that extensive research on a more widely applicable method of analysis is need. In this connection, a brief report on an alternative method of phenol determination has been noted (7). While details of the procedure are not known, it is possible that some of the difficulties described here would be avoided, since the distillation step is eliminated.

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TABLE I

COMPOSITION OF PULPS USED IN PHENOL TESTING

Type of Pulp	Species	Lignin (%)	Pentosan (%)	Mentanol Soluble (%)	Solids Content Of Hot Water Extracts (ppm)
Bleached hardwood sulphite	Unknown	1	6-10	0.7	126
Low-yield sulphite	Black spruce	1.8	4.4	1.2	106
Bleached softwood sulphite	Black spruce	1	4.0	0.7	102
Groundwood	Spruce ?	25	-	-	-
Refiner groundwood	Black spruce	25	-	0.7	82

TABLE II

ABSORBANCIES OF STANDARD PHENOL SOLUTIONS AT 460 mmu

Phenol	Absorbancy*	
p.p.b.	Trial 1	Trial 2
0	0	0
10	0.051	0.036
20	0.102	0.066
30	0.180	0.097
40	0.244	0.122
50	0.328	0.143
60	0.409	0.177
70	0.456	0.208
80	0.523	0.256
90	0.602	0.284
100	0.620	0.328

$$*\text{Transmittancy} = \frac{\text{Transmission of solution}}{\text{Transmittance of solvent}}$$

$$\text{Absorbancy} = \log_{10} \frac{1}{\text{Transmittancy}}$$

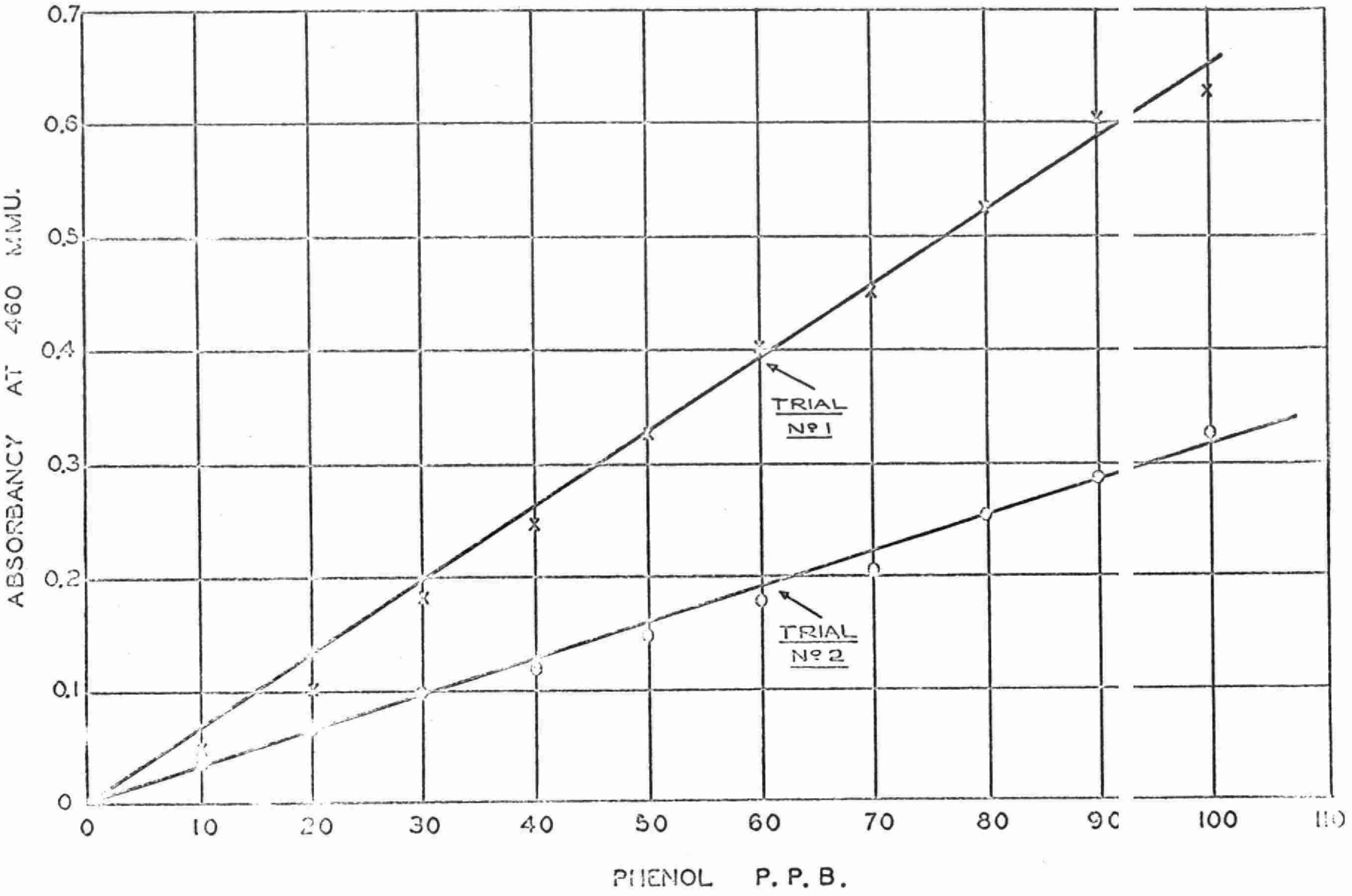
TABLE III

PHENOL EQUIVALENTS OF SUBSTANCES OCCURRING IN PULP AND PAPER MILL EFFLUENTS

Material	Description	Phenol Equivalents: Calc'd on solution or suspension p.p.b.	Phenol Equivalents: Calc'd on solid p.p.m
D-glucose	15 g./1.	0	0
L-arbinose	5 g./1.	0	0
D-mannose	5 g./1.	0	0
D-xylose	5 g./1.	0	0
D-fructose	5 g./1.	1	0.2
D-galactose	5 g./1.	1	0.2
α-D-galacturonic acid	5 g./1.	5	1
Bleached hardwood sulphite	10 g./1.	16	1.6
	2 g./1.	4-100	2-50
Low-yield sulphite	10 g./1.	4	0.4
	2 g./1.	7-26	3.5-1
Bleached softwood sulphite	10 g./1.	3	0.3
	2 g./1.	0-7	0-3.
Groundwood	10 g./1.	16	1.6
	2 g./1.	4-12	2-6
Hot water extracts	Bleached softwood sulphite	8-81	63-63
	Low-yield sulphite	4-34	38-32
	Bleached softwood sulphite	9-29	88-29
	Refiner groundwood	4-47	49-57

FIGURE I

CALIBRATION CURVES FOR PHENOL DETERMINATION



WASTES SAMPLING

by

P. B. HODGES

"WASTES SAMPLING"

by

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This paper is part of the story of a waste reduction program in a large chemical plant - the story of how it proceeded in order to "get the facts" and of the wastes monitoring scheme established to help provide a continuing wastes reduction program.

BACKGROUND

The W.G. Krummrich Plant of Monsanto Chemical Company is situated opposite St. Louis on the Illinois side of the Mississippi River about one mile from the river. It produces about 65 chemical products simultaneously, mostly organic intermediates derived from the basic raw materials salt, sulphur, and benzene.

In most chemical processes, besides the products desired, come by-products, often useless or in quantities so small that recovery is not economically justified. Also, usually an excess of one or more of the raw materials must be added to make the chemical reaction proceed smoothly so the final product must be separated from both the by-products and the unreacted ingredients. Chemical plants normally, therefore, have highly complex problems of waste disposal involving several times the number of different materials actually produced for sale.

We have always been interested in minimizing wastes and recovering by-products because that's good business. Monsanto as a company has always striven to be a good neighbor and to be accepted in all of the communities in which it operated. In our plant, we have been careful to treat known toxic wastes to make them harmless before sewering and to minimize sewering of any wastes which might be objectionable.

In 1955, a report of a two-year study of pollution problems in the St. Louis section of the Mississippi River was issued along with recommendations to the municipalities and industries for improvements. With the increasing emphasis on protection of water resources throughout the country and the likelihood that the municipalities and industries in the local area would move to improve the river, we then had additional reasons beyond the economic factors for reducing wastes. We therefore intensified our efforts in this direction and entered into a formal waste reduction program in early 1956.

This program brought out the need for continuous sampling of waste streams. In the various production departments, actual amounts of materials in waste streams were generally unknown or had been calculated by difference from material balances where only the main product streams had actually been measured. For the plant as a whole, grab samples of effluents in the trunk sewers had been taken on an occasional basis but such grab samples obviously could not present a true picture of total losses. Specific information was needed.

<u>For the plant as a whole</u>:

1. To show size and extent of pollution problems.
2. To establish a base line by which to measure progress in abatement.
3. To enable discussion of the problems with control agency officials on a factual basis.

<u>For the individual production departments</u>:

1. To obtain data to justify technical studies and projects to eliminate or reduce waste.

2. To monitor operations so that unusual losses could be detected quickly and appropriate corrective action taken promptly.

No commercial sampling equipment could be found which we felt would adequately meet our particular needs despite numerous inquiries to companies who we thought might sell the necessary equipment.

In addition to waste stream sampling, flow measurements were needed. For the plant and for most of the departments, conventional measuring devices such as orifice and weirs were impractical.

Both sampling equipment and flow measurement methods had to be devised. In the case of the sampling equipment, numerous difficulties have had to be overcome in order to develop inexpensive, reliable samplers requiring little attention. It is hoped that this work will be of assistance to other plants having similar problems.

Continuous Vacuum Samplers

The first need of the pollution control program was to sample the main plant sewers at four (4) points, all of which were distant from electric power. Use of electricity was questionable because of moisture, fumes and possibility of flammable vapors. The sewers were deep (15-20 ft.). To meet this need, we devised and built a low-cost continuous vacuum sampler using a stainless steel oxygen tank (1). Figure #1 shows a sketch of this sampler. Operation is as follows:

a) The tank (1) is evacuated to 20 mm Hg. (or less) by taking the unit, which is readily portable, to a vacuum source such as a laboratory pump or multi-stage steam ejectors and connecting hose (3) to the source.

b) The evacuated unit is returned to the sampling site and is connected by the rubber stopper to the filter flask (13) which should be suspended in the sewer manhole out of direct sunlight. The polyethylene tube (15) from the sewer runs through the side arm into the flask so that the water drip rate is readily visible and so that siphoning cannot occur (do not permit any part of tube (15) to be higher than the flask side arm.)

c) The filter flask is then evacuated by means of the hand pump (10) to the point where water barely starts to drip from the tip of the tubing (15). Too high vacuum can be relieved slowly by the needle valve vent (9) until the desired drip rate is attained.

d) Valve (6) is closed and the sampling continues by displacement of air through the sight feed bubbler with needle valve (5) into the vacuum tank (1). The needle valve (5) is adjusted to give the flow desired. This adjustment need never be changed unless dirt or water is inadvertently drawn into the valve.

With the unit shown, sample sizes can be controlled from one to three liters in twenty-four (24) hours. If larger samples are desired, larger vacuum tanks should be used. In order that the sampling rate be reasonably constant over the twenty-four (24) hour period, the vacuum tank volume should be greater than twice the sample size desired and the filter flask should be protected from extreme temperature changes.

To discourage tampering, the hand vacuum pump can be disconnected daily and a cover locked over the bubbler, valves and gage.

Total materials cost for each unit, including the hand vacuum pump, is about $55.

In our installation, four samplers were installed and a small gasoline engine powered vacuum pump on a station wagon was provided, eliminating the necessity for moving the samplers. The four sampling stations, although nearly a mile apart, can be tended in a total of about forty-five (45) minutes per day, including taking the samples to the laboratory.

This sampler has proved to be quite dependable, is corrosion resistant and is well suited for our use. It has its obvious limitations -- the flask must be protected from extreme temperature changes, the small sampling tube trailing downstream will not draw in proportionate amounts of settleable solids and the joints must be kept tight.

ELECTRIC CONTINUOUS SAMPLER

When sampling of operating department waste streams was started, the need for a low-cost dependable and low-maintenance electric sampling pump became apparent. Since there were many points where we desired to install samplers, those qualities became major considerations in our work. No commercial sampling equipment was found which we felt possessed all of those qualities.

In 1956, the Becher laboratory pump was introduced and we tried it for our use. The pump is now called "Rota-Flex" and is sold by Cole-Palmer Instrument and Equipment Company in Chicago, Illinois.

As received, the pump was direct coupled to a 1/20 HP, 1550 RPM shaded pole enclosed motor. This speed was much too high for our use so we have used various speed reduction devices to drive the pump at about 30 - 100 RPM, depending on the sample size desired (2-6 gal. per day).

Frequent difficulties were encountered in early use of the pump. Figure #2 shows the internals of the Rota-Flex Pump. The two Nylon rollers move in a planetary motion pressing against the Tygon tube and thus force liquid through the tube. Only one Nylon roller is used in the pump as built and no provisions are made for easy lubrication. With slight bearing wear and wearing of the plastic parts a "dead spot" would develop as the single Nylon roller passed between the tube ends (note position of top rotor.) The "dead spot" caused highly irregular flow at the low speeds used. This was overcome by adding the extra Nylon roller, drilling holes through both rollers and providing a homemade steel roller spacer as shown.

To minimize wear in the pump a 7/32" hole was drilled and tapped in the end cover for this 1/4" x 28 thread grease fitting. A heavy Silicone grease is injected about every two weeks by a grease gun.

Figure #3 shows the sampler as we have been using it for 24 hour composites. The 1/50 HP gearmotor turns at 40 RPM.

With the combination of the cone step pulley and the small spring loaded adjustable pitch pulley, a wide range of operating speeds are easily obtained.

As finally developed, this sampling pump arrangement was inexpensive (about $70 for parts), was quite dependable and required little maintenance except for lubrication, and occasional replacement of the Tygon tube, tube guard and Nylon rollers. The pump served us very well as long as a small group of trained people was doing the sampling.

However, as our wastes sampling and control program developed, we came to realize that the person collecting the sample could quickly gain considerable information merely by observing the appearance and, perhaps, odor of the waste. We also came to the conclusion that the production departments, who make the waste and who necessarily have to control wastage, should do their own wastes sampling. This would give them the quick information gained from collecting the sample and would assist them in acceptance of their responsibility for reducing wastes.

In order for the production departments to assume the waste sampling job, we needed equipment that required almost no maintenance. This was provided by using a Randolph pump shown in Figure #4 with the cover removed. This is a "squeegee" type pump considerably larger than the Rotaflex. Because the tube has no sharp bends, there is little tendency for blockage from solids. We do occasionally use a plastic ring insert on each side of the pump tube to keep it centered.

Figure #5 shows the pump and drive unit. The 2 RPM gear motor drives the pump at between 1-2 RPM through a spring loaded adjustable-pitch pulley and adjustable motor base arrangement. The unit is sturdy, simple and normally runs for months at a time with no attention whatsoever except to collect the samples.

We use three-sixteenths inch (3/16") I.D. or 1/4" I.D. polyethylene tubing for sample intake from the waste stream and for delivery to the sample receiver.

Teflon tubing can be substituted advantageously for the polyethylene tubing in cases where blockage is likely to occur. In sampling streams containing large solids, the intake tube is allowed to trail downstream, thus avoiding blockage of the end of the tube. Such an arrangement obviously does not give samples fully representative of the settleable solids content of the stream. Alternate solutions to the sampling problem must be found in those instances where large amounts of heavy or large solids are present and must be representatively sampled. Covers should be provided to keep rain and dust out of the equipment. In the summertime, the cover should be raised enough to permit air circulation around the shaded pole gear motors which tend to run hot. In freezing weather, electrical plastic heat tapes and light bulbs are used as necessary and, along with the heat from the motor, keep the equipment from freezing. Three-wire, grounded wiring should be used throughout except for the heat tapes, where grounding is not possible.

AUTOMATIC SHIFT SAMPLER

Early in our sampling program, the need for taking samples representing periods shorter than twenty-four (24) hours became evident. For the needs of production supervision in monitoring their operations, shift samples were necessary so that unexplained large losses could be investigated. This was handled on a short term basis by having available personnel pick up the samples from the continuous pump samplers at the end of each shift. This technique was, of course, practical only for limited numbers of samplers over short periods of time. As the sampling program increased, the time interval distributor was developed to satisfy the need for practical shift sampling.

A description of this automatic shift sampler follows (see Figure #6)

1) The wooden framework is made of 3/4" weather-proof plywood braced by corner irons. The size shown is for collection of 10 x 1 gallon samples. The pumping unit is similar to that described in the section "Electric Continuous Sampler" and illustrated in Figure #5 except that it is fastened vertically to one end of the framework. Purpose of this type mounting

is threefold: (a) it is compact, (b) it keeps the working parts off the ground, and (c) it discourages tampering and theft. The pump motor and speed reducer are bolted to the Plywood base using self-locking nuts. Bolt heads are between the plate and the wooden framework. The pumping unit can be locked onto the framework through the heavy bolts shown, which are drilled out on the ends to permit use of padlocks. Parts, therefore, can not readily be removed except by first unlocking the pump base.

2) The sample flow is delivered to the distributor via a 3/16" I.D. Tygon tube which is loosely supported by a wire attached to the framework.

3) The distributor assembly is shown in Figure #7. ¼" O.D. Saran tubing shown was selected as the discharge tube because it is quite rigid and will turn readily in the guide. Operation of the distributor is very simple. The plastic alligator clip acts as a threaded nut. It is held against the 3/8" steel rod by the rotation of the ¼" threaded bolt shaft which also moves the Saran discharge tube lengthwise down over the plastic pipe trough shown. With the timing arrangement described below, the intervals between the Lucite dividers represent exactly 8 hours. The Lucite dividers are made by sawing 1/8" thick discs off a 1" diameter rod and then grinding one side to a knife edge. The distributor trough is rigid 1" I.D. plastic pipe split longitudinally. ¼" x 20 thread holes are tapped in it to take the ¼" O.D. polyethylene tubes which discharge into the bottles. The tubes are pressed into the plastic pipe and are held by the threads. The dividers are cemented in place.

4) The timing arrangement consists of the ¼" threaded bolt turned by the small chain and sprocket drive shown in Figure #6. The drive is powered by a IRPM timing motor.

5) Details not illustrated are: (a) the use of Teflon tubing, ¼" I.D. x 3/8" O.D. to act as bearings for the ¼" threaded bolt, and (b) Teflon washers to act as thrust bearings for

the ¼" threaded bolt and 60 tooth sprocket. Also not shown is a ½" portion of the ¼" threaded bolt at the extreme left where the threads are filed off smoothly. This permits the plastic clothespin to ride freely at the end of its travel without damage to the threads gradually worn into it.

The arrangement described above allows collection of 10 x 8 hours shift samples without attention. In event samples at other time intervals are desired the sprocket ratio and distributor trough can be altered as necessary. Figure #8 shows the sampler as altered to collect 24 x 1 hour samples where we need information on losses at short time stages of a process. Total cost for parts of the entire unit as shown is about $140 exclusive of bottles and electric cord. We now have 25 of these samplers (mostly of the automatic shift sampler type) in use at our plant and expect even more to be used as the waste reduction program progresses. This is proving to be a very valuable tool for production supervision in pin-pointing losses to definite times, areas and process conditions.

Results of the sampling are used in various ways, depending on the particular need. For example, a daily graphical report is widely distributed through the plant showing phenolic type losses by departments. Individual production departments sometimes show their results graphically on large charts in control rooms or offices so that trends can be readily noticed and corrective action can be taken promptly.

With the many samples collected and analyzed daily, analytical costs would be prohibitive if we had to depend on standard methods. Our primary immediate concern in wastes control is phenolics. We use a Technicon Autoanalyzer for the phenol determinations and find that it performs well for our purposes. It automatically analyzes a sample each 6 minutes with excellent reproducibility and acceptable accuracy. We have very recently purchased the necessary components for the Autoanalyzer to adapt it for C.O.D. analyses and are now in the process of putting it into operation. We do not yet have information available on its performance in our use.

Flow Measurement

Many techniques are used for measuring flows and the description of most of these methods are readily available. One excellent reference is published by ORSANCO and is titled "Planning and Making Industrial Waste Surveys".

In our case, obtaining flow data proved to be almost as difficult as obtaining our continuous samplers. Our quite old sewer system was simply not designed for ease of measuring flows. Installation of flumes or weirs was impractical and would have been very expensive because our sewers are deep and the slope is so small that in many cases we just could not stand the necessary drop over weirs. Levels changed frequently in the sewers when we knew flows had not changed appreciably so we could not tell much from levels.

One of the techniques described in the ARSANCO reference mentioned previously is measuring flows by the salt water dilution method. An assayed solution of NaCl is injected at a constant, measured rate into a stream. Samples are taken of the stream far enough downstream that the salt water is thoroughly mixed and the samples are analyzed for salt content. The dilution factor times the salt water solution flow rate equals the stream flow. This method is useful and easy to use as long as the Cl concentration in the waste stream is very low or is constant. At our plant, discharges of wastes containing chlorides are normal so the method as such has very limited application.

Working with our laboratory, we developed a method for injecting LiCl solution of known strength at a constant rate into the sewers and then we sampled and measured the dilution of the Lithium downstream. As in the salt water dilution method, from the injection rate and the dilution factor the sewer flow can be calculated quite accurately. Lithium is foreign to our wastes and it has a unique property in that it can be assayed accurately and quickly by flame spectrophotometry in low concentrations of around 2 ppm. Figure #9 shows our equipment for injecting the Li Cl solution. The 20% Li Cl solution is stored in the drum and is pumped to the constant head overflow by the small plastic centrifugal pump. The injection rate is adjustable by means of the stop cock. The operator is measuring the injection rate and will then move the funnel under the stream so that the solution will flow into the sewer via the hose. After a few minutes pumping, several grab samples (usually about 6-10) will be taken downstream for later assay for Li concentration. We have found that generally only about 15-20 minutes total pumping of the solution is necessary. At the end of the injection period the pumping rate will again be measured to be sure that it didn't change. We usually try to add the 20% Li Cl solution at a rate which will give about 6000: 1 dilution in the stream.

Important points in using this method are:

(1) The Li Cl should be added to a fast moving part of the stream. If, for example, it is added in a manhole with a static head of water, the Li Cl should be added via a hose to the outlet of the manhole. The hose should be sufficiently large to avoid trapping of air which could cause irregular flow of Li Cl to the stream.

(2) Sufficient distance must be allowed between the addition and the sampling points to be certain that the Li Cl is completely mixed in the stream. The minimum distance is a matter of judgment and depends on turbulence of the stream. Erratic laboratory test results on the six grab samples would, of course, indicate insufficient mixing.

To conserve laboratory manpower, we have adopted the practice of running several tests at about the same time and arranging for measuring all of the dilution in one series of spectrophotometer measurements.

The flow measurement technique described is, of course, useful for instantaneous flow measurements only. It is also useful for calibrating or testing more conventional flow measuring devices.

Proportional-to-Flow Sampling

Generally speaking, in wastes sampling, it is desirable that samples be collected proportionally to flow of the waste stream. There are many ways of accomplishing this - the most usual is to provide a flume, weir or other primary measuring device with a recorder and integrator.

The integrator operates a sample collection device such as a dipper, a solenoid valve, a small pump or perhaps drains the contents of the plug of a large valve through which waste is flowing. In any case, the integrator, after the passage of a predetermined number of gallons in the waste stream, activates the device which collects a fixed amount of waste sample each time it operates.

Other means used are; (1) to pass the entire waste stream through a siphon arrangement and collect a fixed-amount sample each time the siphon operates, (2) to use a dipper operating at fixed time intervals. The dipper is so constructed that it collects an amount proportional to flow as measured by level in the primary sensing element - the flume or weir. (3) to use a pneumatically operated piston partially immersed in the waste stream. The piston and cylinder are designed so that each discharge delivers an amount proportional to the stream flow, again as measured by height of water in the flume or weir.

In our particular case, we were fortunate in that our operations are mostly continuous and waste flows are relatively constant. We did not require proportional to flow sampling to give us the needed basic information on sewered losses. One method, which we learned from Prof. H.D. Tomlinson, then of Metcalf and Eddy, is illustrated in Figure #10. We used this method to measure small, variable-flow process streams. Stainless steel weir boxes were made up using 60° or 90° V-notch weirs or, in one case, a Rettger height-proportional-to-flow weir. Levels were recorded by the bubbler method using the small diaphragm air pump to furnish the air. Air flow was regulated by the needle valve and bubbler. Back pressure from the bubbler tube was recorded on the 0-20" water pressure recorder. Hourly composite samples were collected and were then composited according to the average flow as measured during the corresponding time interval. The composite sample could then be considered as having been collected reasonably proportional-to-flow. In some cases, all 24 samples were analyzed and lbs. of material lost each hour were calculated.

As our in-plant waste treatment and waste control work progresses, we are becoming increasingly interested in providing proportional-to-flow sampling in certain area. We are operating at greatly reduced levels of waste discharge and the needs for accuracy are becoming proportionally greater. We have recently tried a somewhat different approach as follows:

(1) Figure #11 pictures a weir which we placed in a sewer manhole having a split tile at the invert level. Note the large opening at the bottom of the weir to prevent solids accumulation. The weir is equipped with a bubbler tube stilling well so we can measure level on the upstream side. This weir is anything but standard so we calibrated it in place at various flows using the Li Cl dilution method described earlier and obtained a curve of flow vs. water level (or air pressure in the bubbler system).

(2) Figure #12 shows the device for converting the air pressure signal into proportional-to-flow sampling. The copper cam is driven by a 1 RPM timing motor. As air pressure is exerted on the mercury pool in the well it raises the mercury level in the plastic standpipe which in turn raises the plastic float with carbon stem. The carbon contacts the cam, closes a low voltage circuit and actuates a relay which in turn operates a sampling pump during the contact period. The shape of the copper cam was designed and formed in accordance with the characteristics of the weir and the mercury level system. The contact is made during that portion of the cam cycle directly proportional to the flow in the sewer between zero and full flow.

We, therefore, have proportional-to-flow sampling.

Figure #13 shows the device in operation. So far, it is working very well. We do not anticipate any particular problems with the proportioning device. We may have trouble with the frequent starting and stopping of the gear motor driving the sampling pump. If we do, we will let the sampling pump run full time and use the relay signal to divert the sample stream either to the bottles or back to the sewer in proportion to the sewer flow.

If this scheme works out as well as we expect, we can convert several of our sampling installations to become proportional-to-flow at very low expense.

ACKNOWLEDGEMENT

The method described for measuring flows by dilution of Li Cl solution was developed by Mr. D.B. Hines of Monsanto Chemical Company, St. Louis, Missouri.

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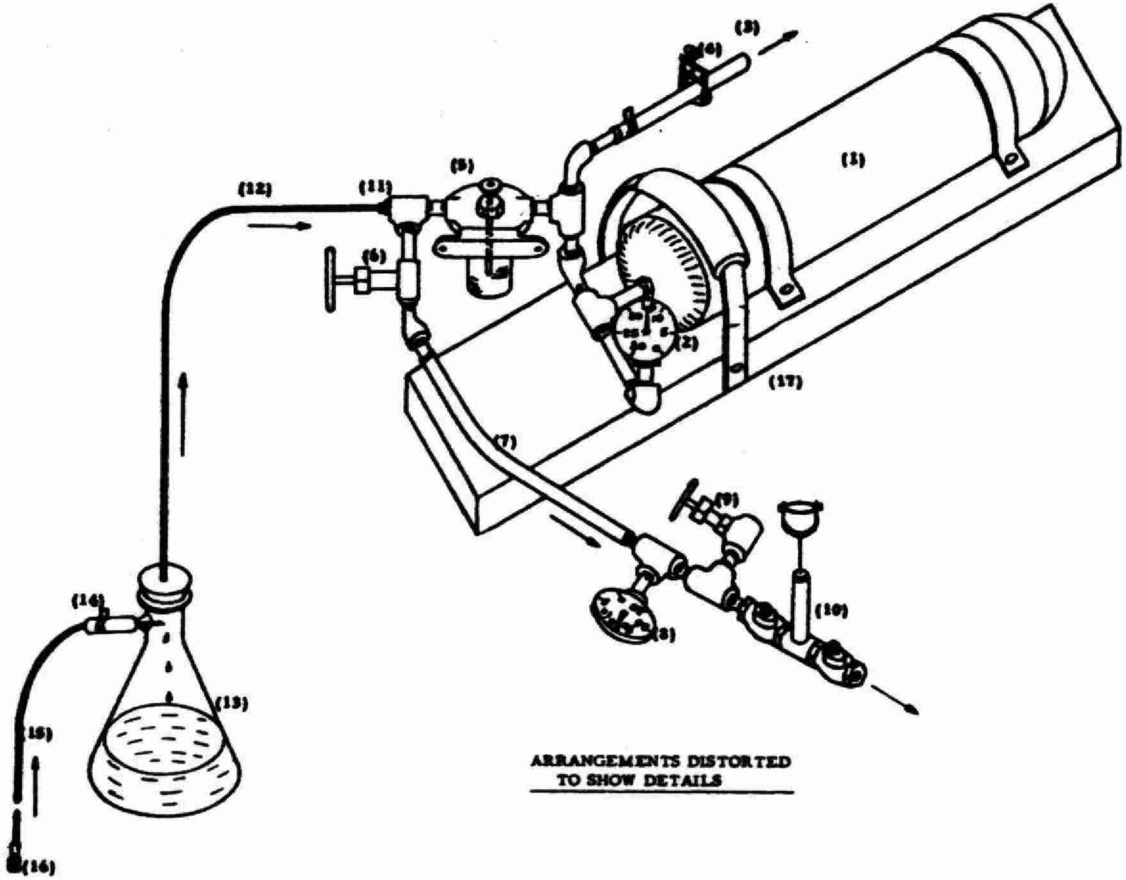
(2) "Planning and Making Industrial Waste Surveys", prepared by the Metal-Finishing Industry Action Committee of the Ohio River Valley Water Sanitation Commission, Cincinnati, Ohio, April, 1952, page 8.



ARRANGEMENTS DISTORTED
TO SHOW DETAILS

LEGEND

(1) 6" x 24" STAINLESS STEEL YGEN TANK

(2) 2-1/2" VACUUM GAGE - 0- Hg.

(3) RUBBER VACUUM HOSE - C NNECT TO VACUUM SOURCE

(4) HEAVY DUTY HOSE CLAMP

(5) SIGHT FEED BUBBLER WIT NEEDLE VALVE - FLUID IS TRANSF MER OIL

(6) 1/4" BARSTOCK VALVE

(7) RUBBER HOSE CONNECTIO TO HAND VACUUM PUMP

(8) 2-1/2" VACUUM GAGE - 0- Hg.

(9) SMALL NEEDLE VALVE

(10) SMALL HAND VACUUM PUM

(11) 1/4" O.D. TUBING CONNEC OR TO 1/4" I.P.S. FEMALE FITTING

(12) 1/8" I.D. x 1/4" O.D. POLY THYLENE TUBING

(13) 4 LITER VACUUM FILTER ASK

(14) HEAVY HOSE CONNECTION O ARM OF FLASK

(15) 1/8" I.D. x 1/4" O.D. POLY THYLENE TUBING FROM SEWER - TH OUGH ARM OF FLASK

(16) 1/4" TUBING CONNECTOR - SE AS TUBING WEIGHT

(17) MOUNTING BOARD WITH CA RYING HANDLE AT POINT OF BAL NCE

FIG. #1 - CONTINUOUS VACUUM SAMPLER (1)

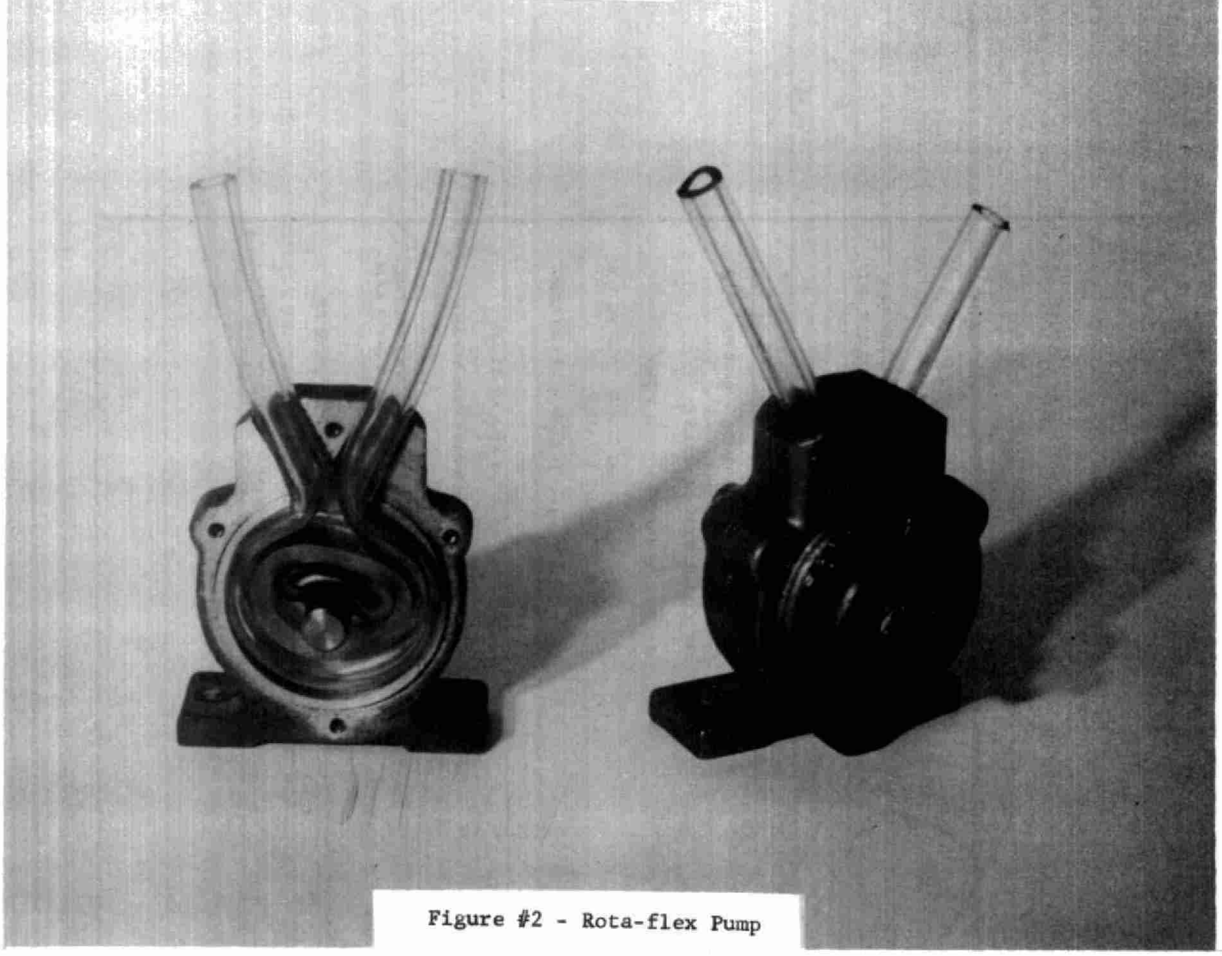


Figure #2 - Rota-flex Pump

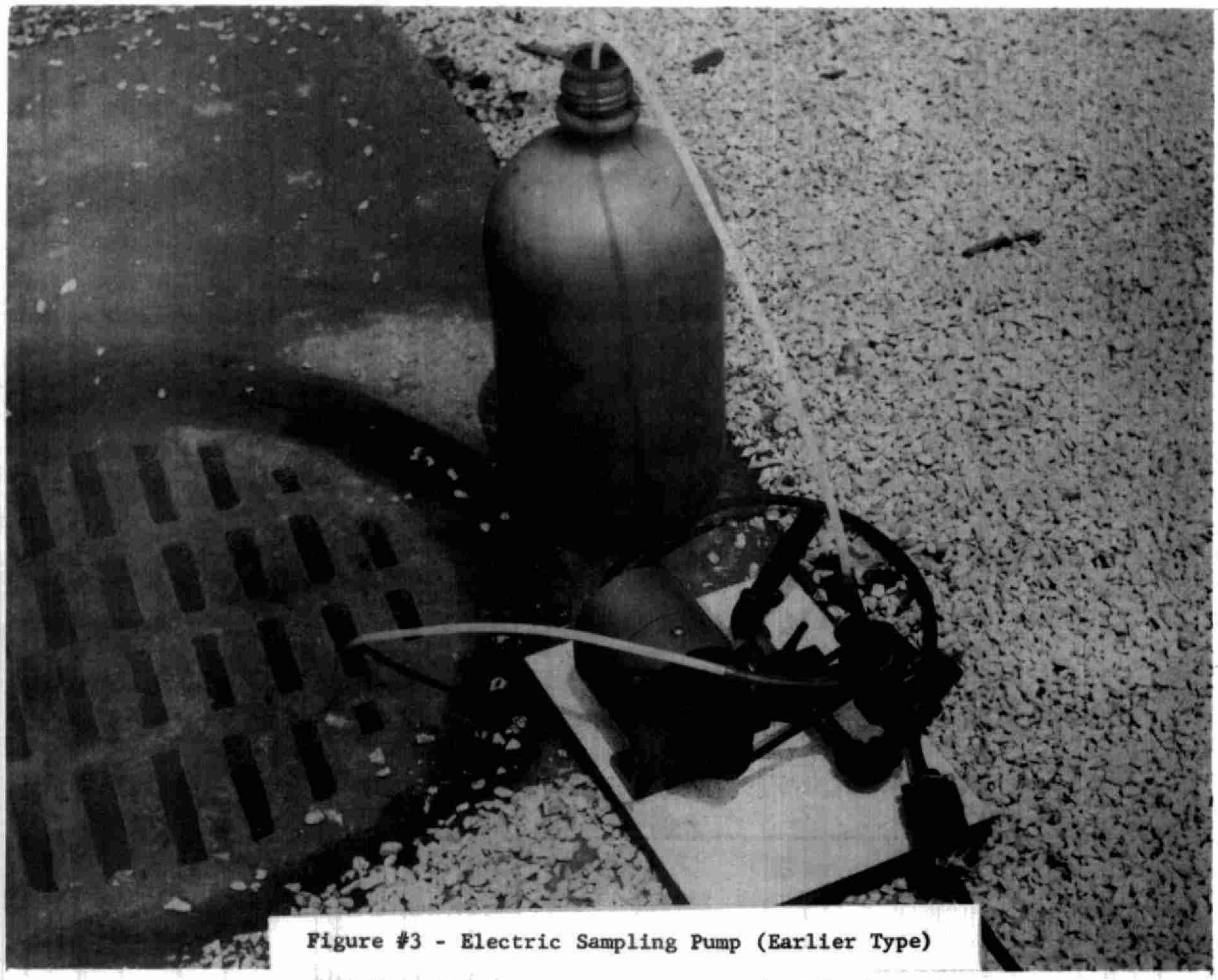


Figure #3 - Electric Sampling Pump (Earlier Type)

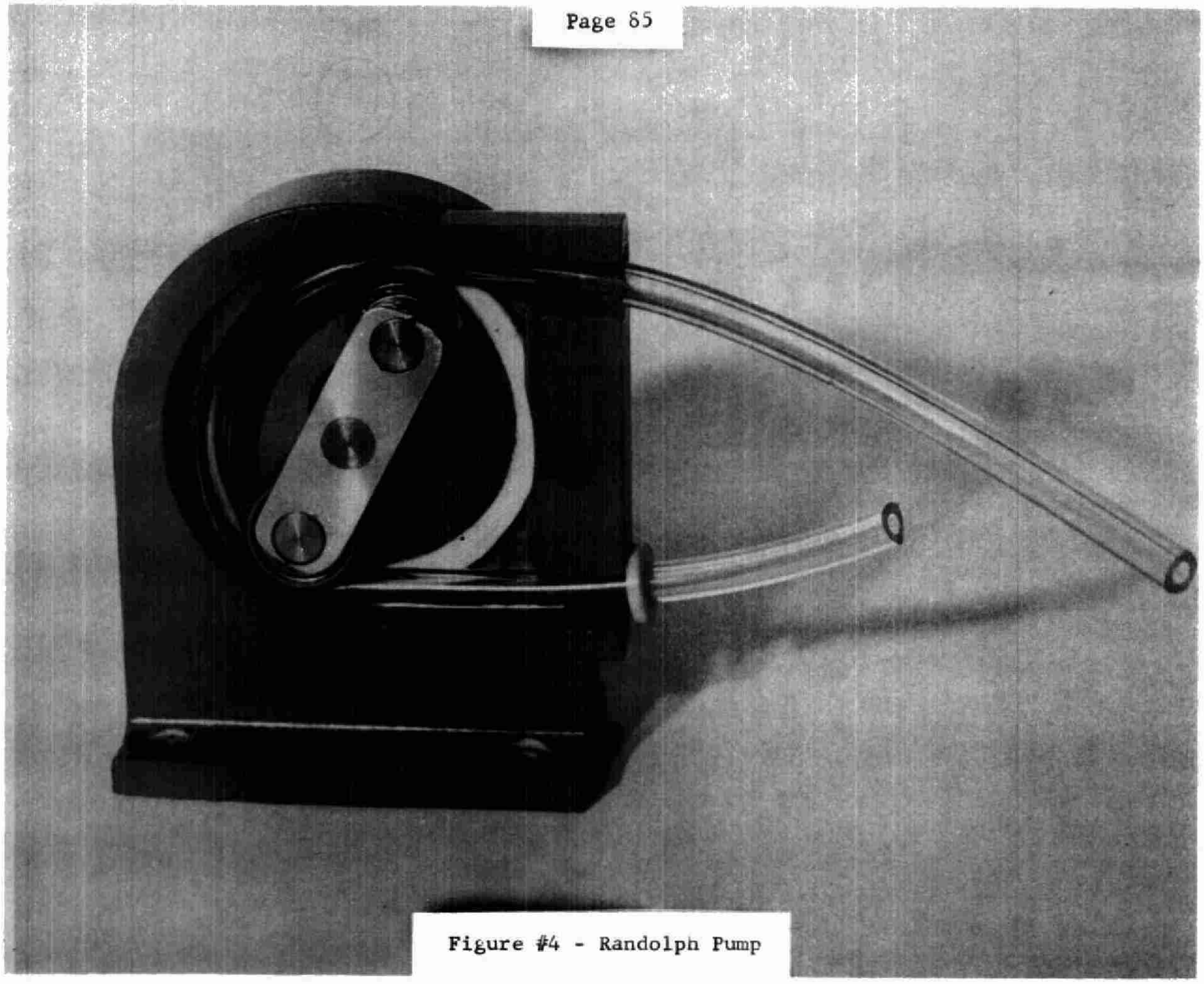


Figure #4 - Randolph Pump

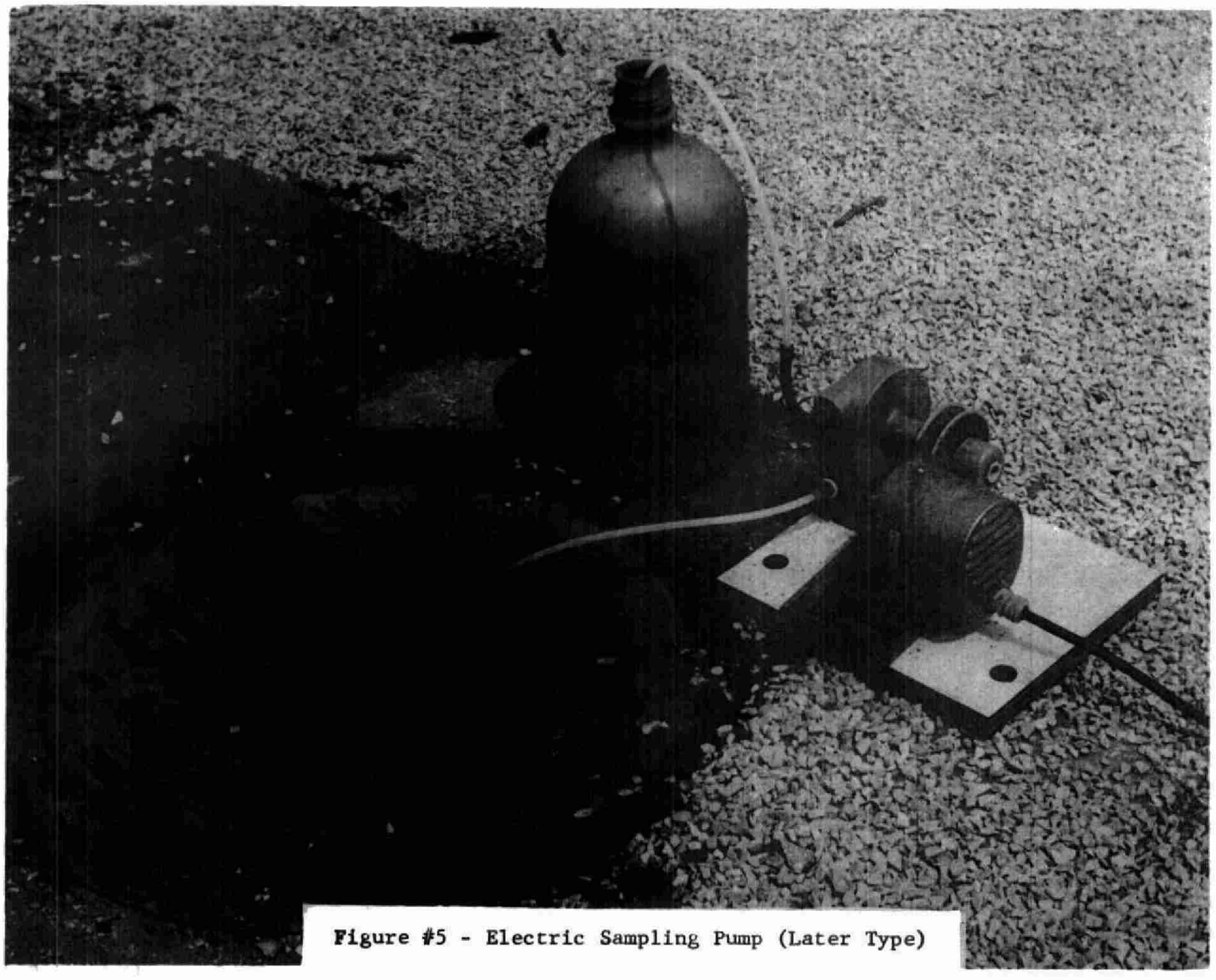


Figure #5 - Electric Sampling Pump (Later Type)

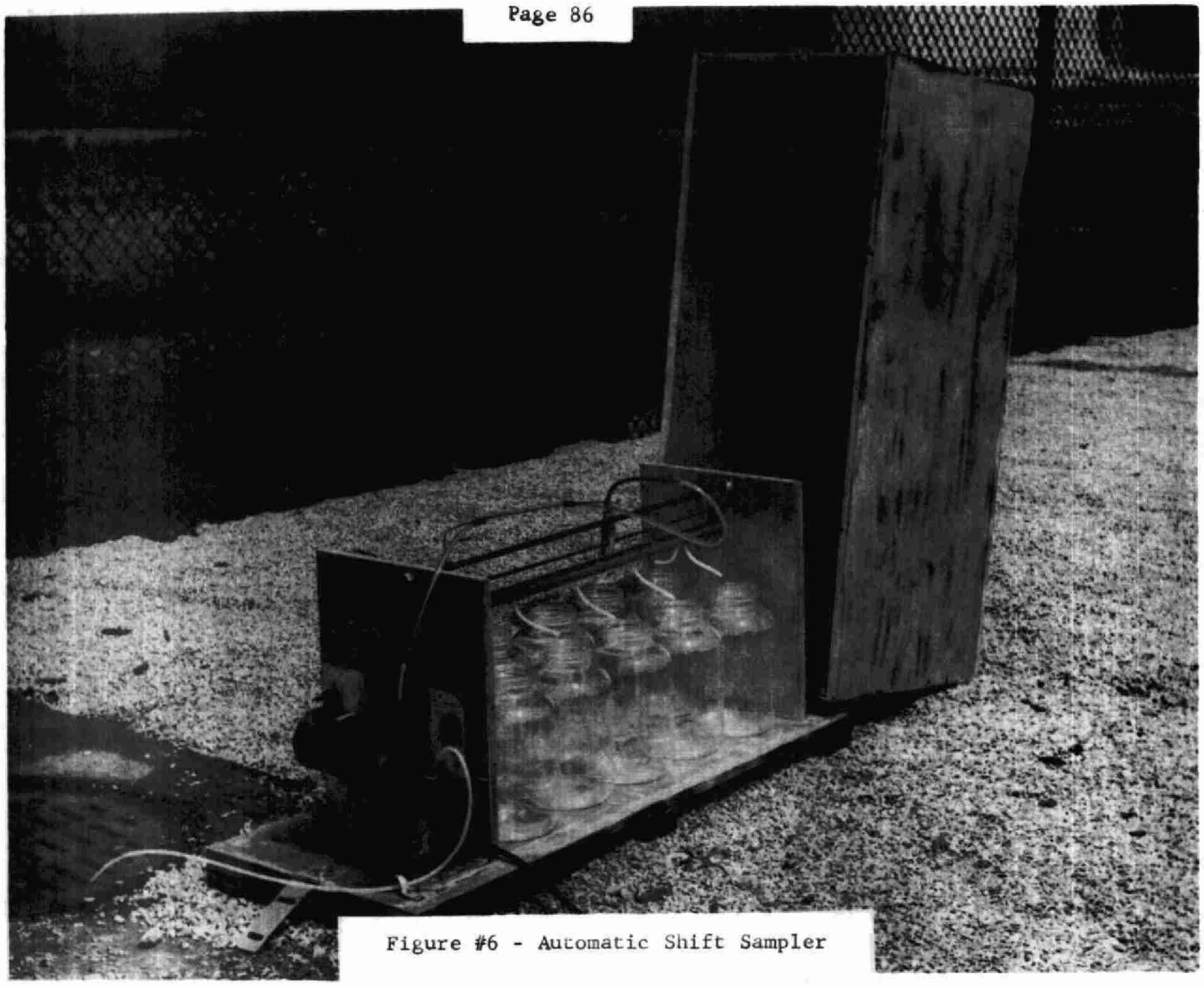


Figure #6 - Automatic Shift Sampler

Figure #7 - Distributor

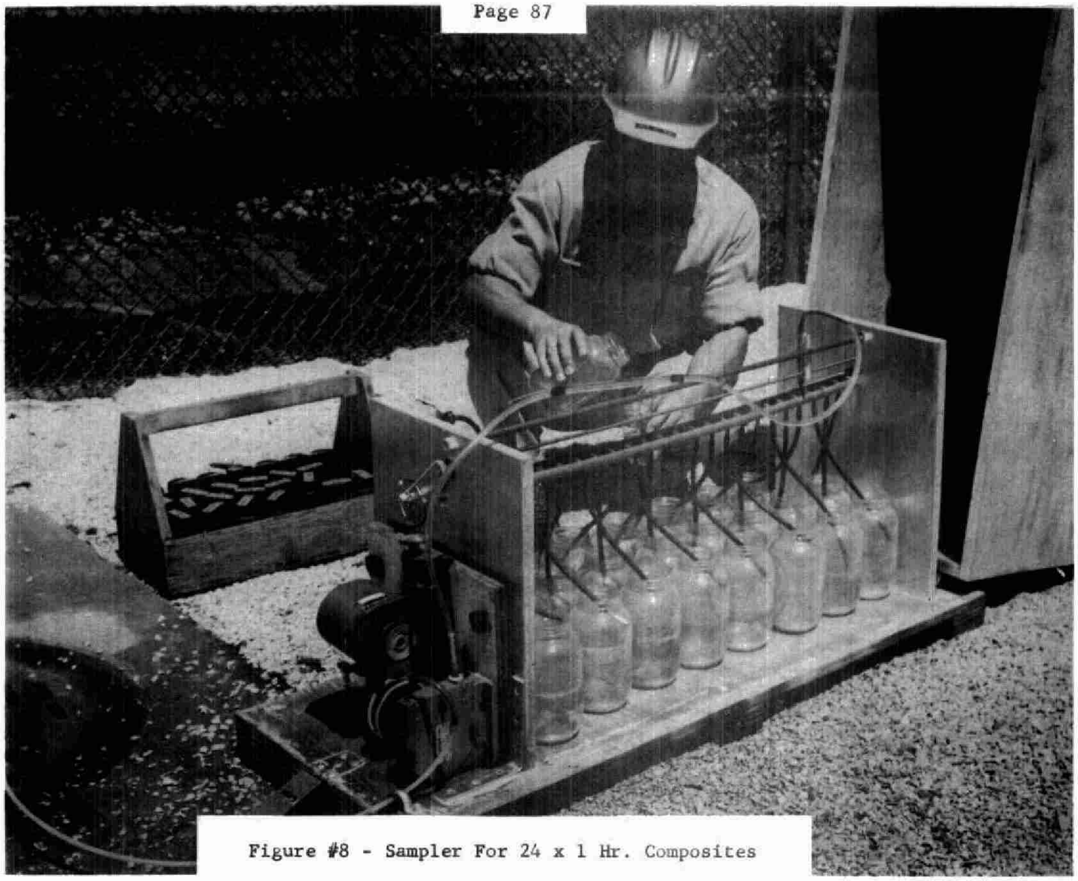


Figure #8 - Sampler For 24 x 1 Hr. Composites

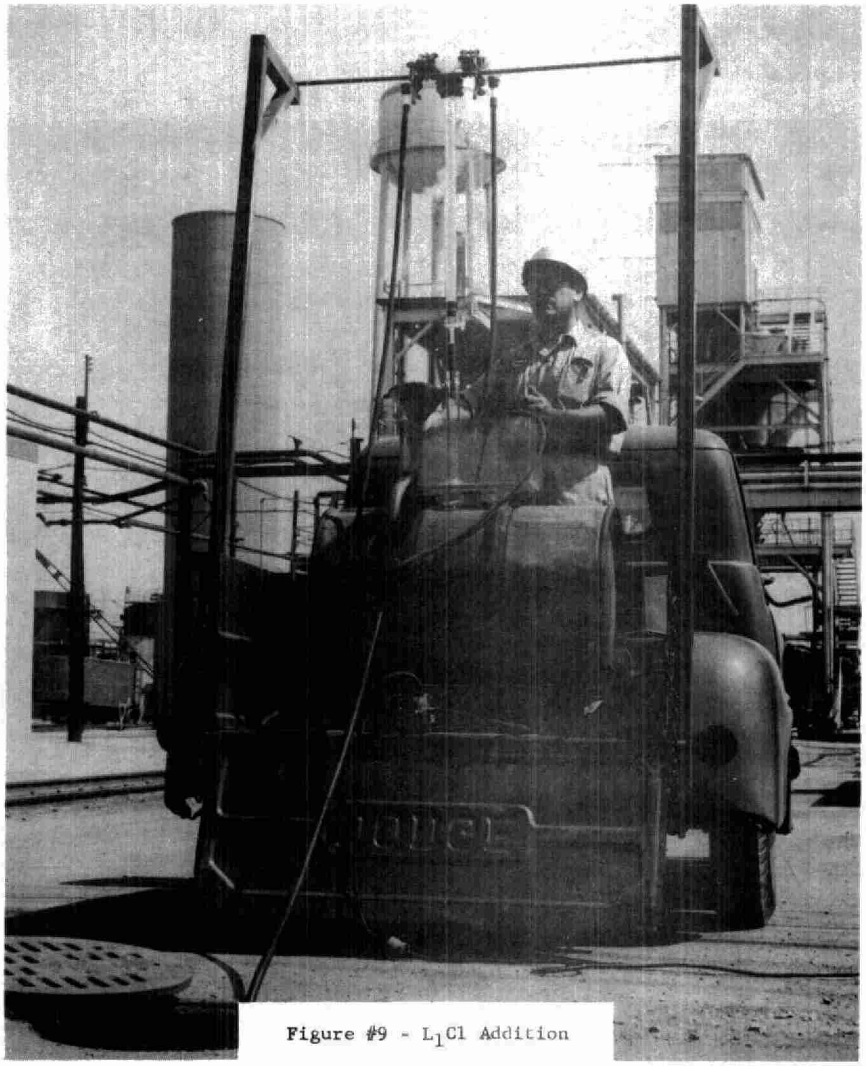


Figure #9 - L_1Cl Addition

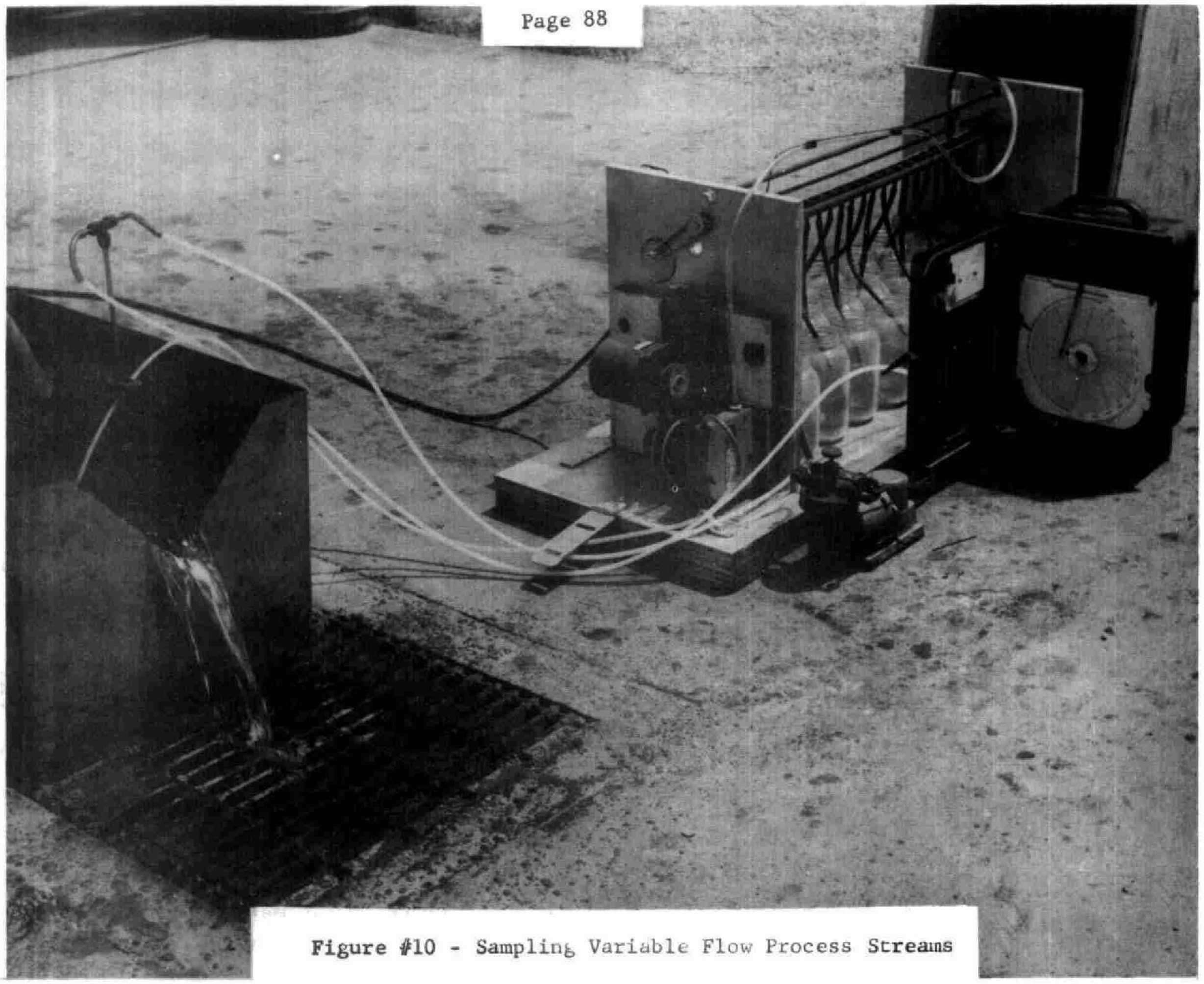


Figure #10 - Sampling Variable Flow Process Streams

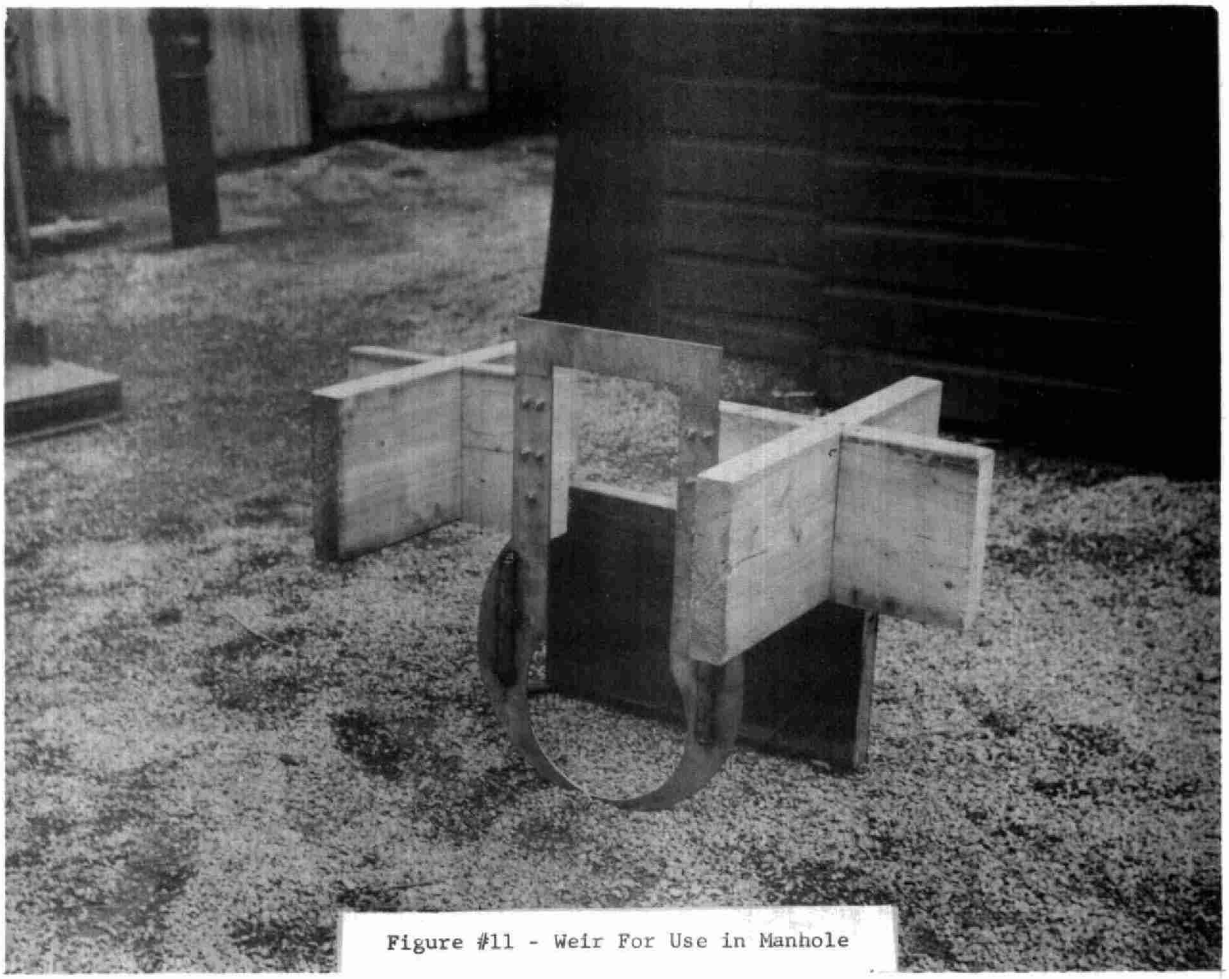


Figure #11 - Weir For Use in Manhole

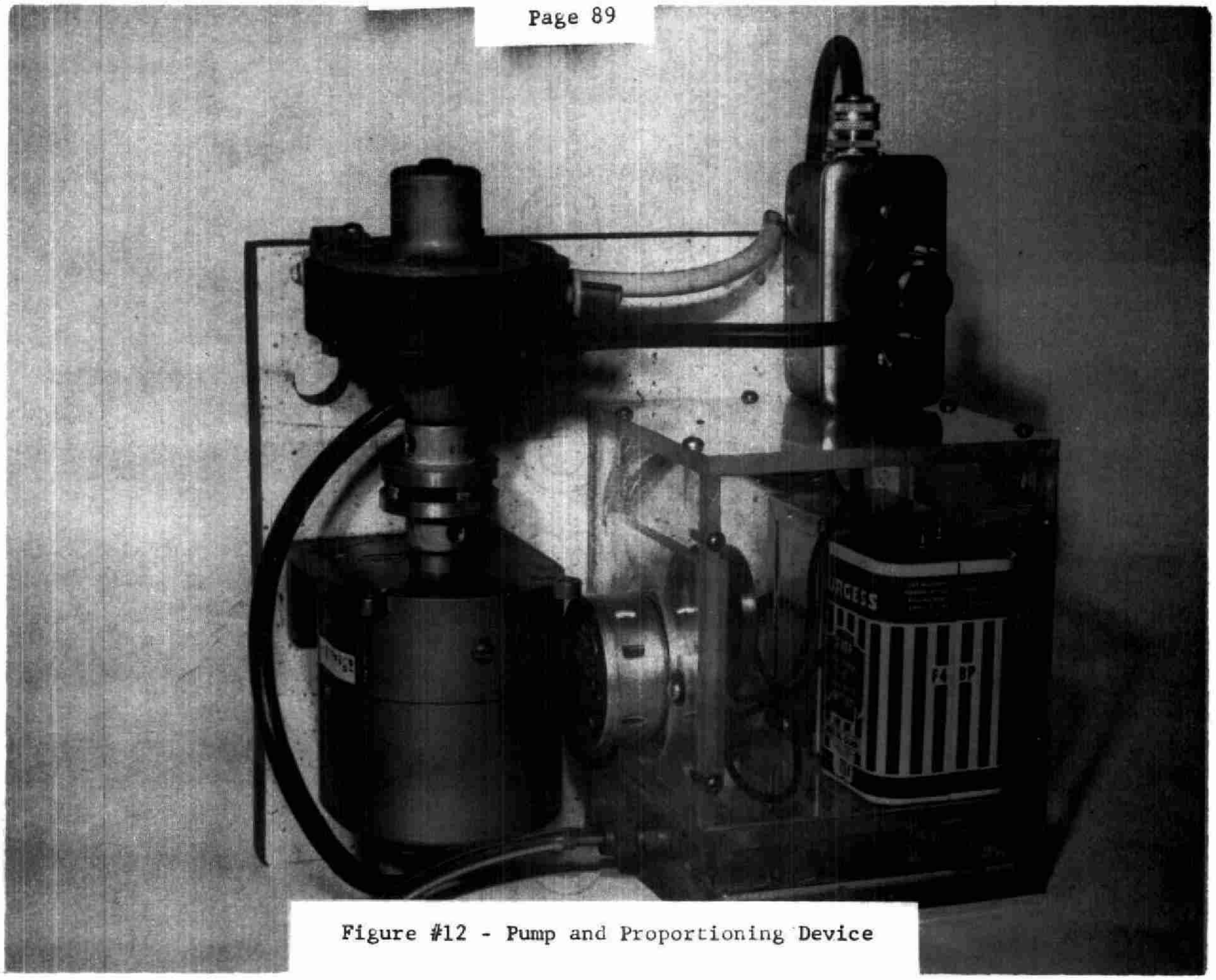


Figure #12 - Pump and Proportioning Device

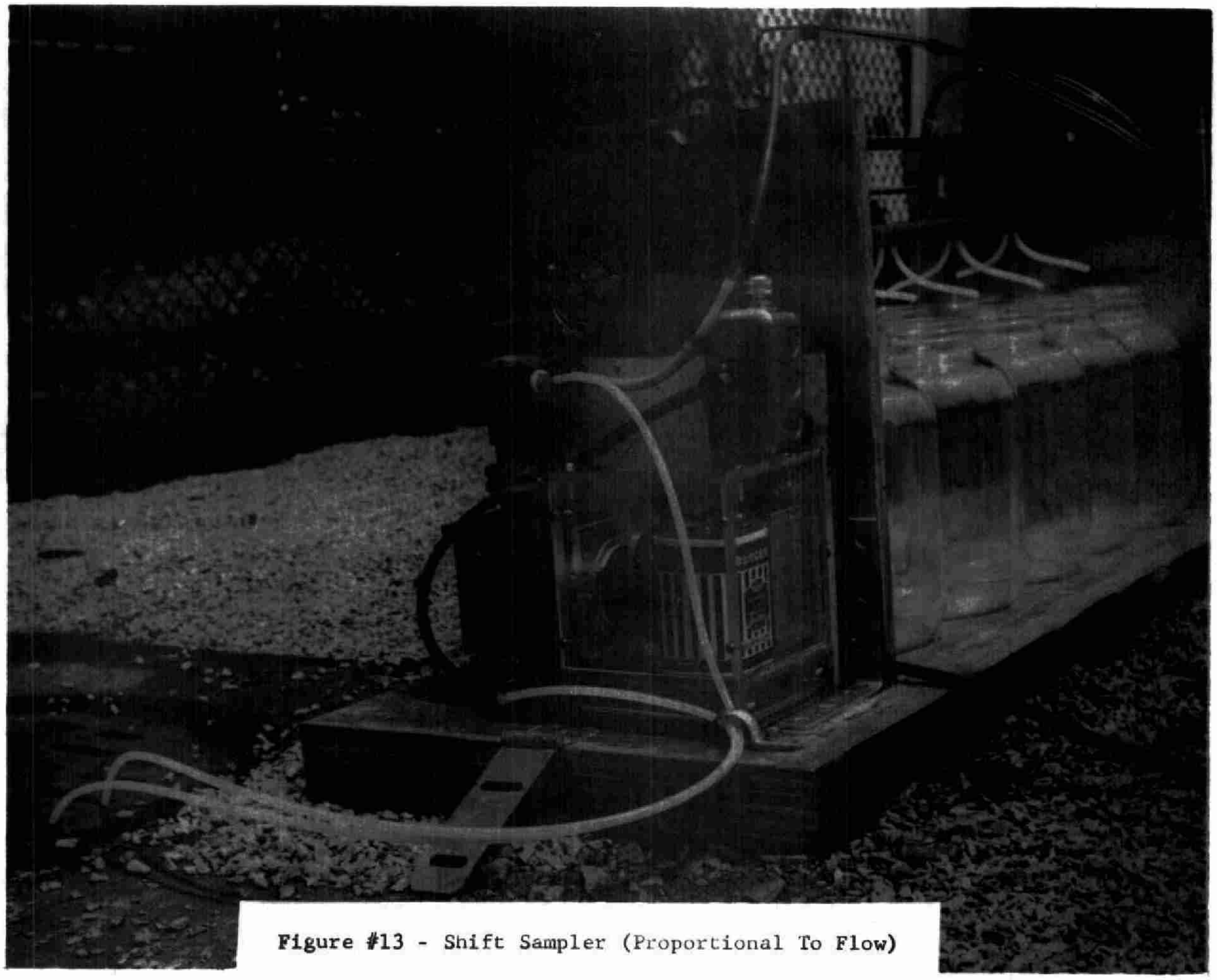


Figure #13 - Shift Sampler (Proportional To Flow)

SOME CONSIDERATIONS OF FOOD INDUSTRY WASTES PROBLEMS IN QUEBEC

by

A. L. VAN LUVEN

"SOME CONSIDERATIONS OF FOOD INDUSTRY WASTES PROBLEMS IN QUEBEC"

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The two great industrial provinces of Ontario and Quebec have many similar problems in processing the products of farms, forests and mines, and in the treatment and disposal of the wastes which result from these industries. This paper attempts to deal only with the wastes that result from the Food Industries in Quebec.

Due to the relative youth of our Quebec Water Purification Board, we have a great deal to investigate and much to do about these problems. Consequently we have very little factual information to indicate the progress made to date in the pollution-abatement of the wastes from the food industries in Quebec.

While we do not have much basic information of our own to disclose, we feel that we can contribute toward laying a foundation for better mutual understanding of the requirements for successful handling of industrial waste problems.

It is my intention in this paper to try to indicate the size of the problem from the technical point of view while, simultaneously, appealing for a cooperative progressive program which I am sure would be welcomed by all of us.

I shall try to give you some of the background of the food waste problems in Quebec, and comment on the probable conditions that exist in these industries, in the light of the present day technology for dealing with food industry waste.

First of all, let us consider the numbers and locations of these food industries because the geography has a great influence on the economics of the problem, which is extremely important.

Following this, we shall consider some of the technical procedures that may lie ahead for these cities, towns, villages and their food industries.

NUMBER OF FOOD INDUSTRIES IN QUEBEC

Slaughtering and meat packing	98
Animals oils & fats	2
Sausage & sausage casing	27
Poultry processing	45
Butter and cheese plants	429
Pasteurizing plants	180
Condenseries	11
Ice cream manufacturers	9
Process cheese	8
Fish products	58
Fruit and vegetable canners	133
Feed manufacturers	342
Flour Mills	5
Breakfast cereals	4
Biscuit manufacturers	17

for example, in a modern well operated dairy, may be much less than shown here).

Industry	Range of B.O.D. per units (pounds)	Volume of Waste Per Unit (Imp. gals.)	Unit
Meat Packing	3.0 - 4.0	360 - 800	1 hog
Dairies & Cheese	32 - 570	125 - 1225	1000 lbs raw milk
Canneries	6 - 300	2100-21000	100 cases of #2 cans
Sugar refineries	21 - 39	2400-4000	ton of beets
Beverages	24 - 40	5300-19200	1000 cases
Distilleries	17 - 205	500,000	1000 bu. of grain
Breweries	2 - 7	125 - 860	bbl. of beer
Pultry killing	50 24 with blood recovery	2600-12000	1000 broilers

MEAT PACKING INDUSTRY

The following table will show how the meat packing industry is distributed throughout the province, and, at the same, it will show what the meat packers, as a whole, are facing in treating their wastes.

Population in the Municipality	Meat Packing Plants
Over 1,000,000 (Montreal)	25
170,000 (Quebec)	5
50,000 - 60,000	4
40,000 - 50,000	2
30,000 - 40,000	4
20,000 - 30,000	4
10,000 - 20,000	9
5,000 - 10,000	18
2,000 - 5,000	13
Less than 2,000	14
Total	98

From these figures it would appear that approximately 50% of the meat packing waste problem occurs in towns with less than 20,000 people; i.e. considering only the number of plants and not the amount of business being done by each.

Without favouring larger units, commenting only on the technical aspects of the waste problems, there is an inescapable and significant fact here that must be brought out, if we are to look at these waste problems realistically.

From these figures, it is quite likely that about 50% of these packing plant wastes are produced in non-integrated or poorly integrated packing houses, which may not recover many of the by products such as blood, tankage, casings, hair, etc. In non-integrated plants there are frequently quite limited facilities for saving blood (which has extremely high B.O.D.) for separating manure from fat wastes (so that both may be recovered more efficiently) and for more utilization of the animal raw materials. Larger and well integrated packing houses produce an infinite variety of smoked meats, cooked meats, essential animal oils, animal foods, casings, dried hog hair, hoof & horn meal, glands, extracts, and then frequently blend some of their own raw materials with those from outside sources, to provide an even greater variety of products, all of which greatly reduce waste and lead to the old saying that "little is lost except the squeal".

The intense competition in the packing industry has a special significance in the handling of their waste problems, in my opinion. This situation suggests that the industry, as a whole, can not afford losses and will endeavour to keep their recoveries at a high level. This is true; however the keen competition also means that each individual plant must keep its costs in line with those of its competitor. This frequently leads to the ditching (sewering to you) of low value, unwanted materials that would otherwise be costly to handle; in fact some plants may not possess adequate facilities to handle these nuisance materials.

In the handling of packing-house waste there is absolutely no doubt that the waste problem is reduced tremendously by proper segregation of the wastes within the plant. These wastes should be separated into

- manure wastes
- fat wastes - then recover fat & protein & reuse the water
- clear water wastes (reuse as much as possible)
- blood wastes with a minimum of water
- domestic sewage

Segregation of this packing waste not only increases the amounts of materials recovered but also enhances the quality of fats and of protein solids that are recovered.

It is not the purpose of this paper to consider the handling of these industrial wastes in much detail, although I shall try to indicate the types of problems. There is no doubt in my mind that the individual packing house or rendering establishment can greatly reduce its waste problems and the problem of the municipality at large by adopting what we commonly refer to as proper "IN - PLANT" procedures.

These "In-Plant" procedures should be the very first approach to the problem because the results thereby obtained will have a very significant bearing on the handling of the problem from then on. For further remarks along these lines I refer you to my paper entitled, "Treatment of Packing House Wastes", published in the proceedings of the 6th Ontario Industrial Waste Conference.

Having given adequate preliminary "IN - PLANT" treatment to the various waste flows to accomplish as much recovery as is economically possible, the plant waste may be treated by the activated sludge process, by trickling filters, by lagoons (anaerobic, aerobic or facultative) or by the anaerobic contact process followed by aerobic lagoons.

There is only one further comment about treatment methods that seems appropriate at this time. For several years now we have known of the possibility of handling paunch manure wastes by using a wet-combustion method. If this method can be perfected it will improve the waste picture in the packing houses to a very significant degree.

It is usually more suitable for both the industry and for the municipality if the plant wastes are handled in the municipal sewer system after the wastes have received reasonable preliminary treatment to reduce the strength and equalize the flow.

In my opinion, municipalities would be well advised to protect their sewage systems by having proper municipal sewerage By-laws, keeping in mind that the object is to work with industry and not place them in non competitive situations.

Dairy Industries

In this section we include pasteurizing, butter and cheese, process cheese, condenseries, and ice cream manufacture. As shown above, there are 637 plants engaged in the manufacture of these products in Quebec, and their locations according to populations are as follows:

Population in the Municipality	Number of Dairy Plants
Over 1,000,000 (Montreal)	26
170,000 (Quebec)	9
80,000 - 90,000	1
60,000 - 70,000	5
50,000 - 60,000	6
40,000 - 50,000	1
30,000 - 40,000	16
20,000 - 30,000	26
10,000 - 20,000	34
5,000 - 10,000	50
2,000 - 5,000	132
Under 5,000	331
Total	637

It is apparent from these figures that there is an over-whelming percentage of these dairy industries located in small municipalities. 73% in municipalities with less than 5000 people and 52% in municipalities with less than 2000 people.

This is almost certain to mean small plants without modern equipment, without modern means for affecting good recovery of wastes, probably lower yield of products, less financing ability and far less integration than in larger units.

In addition, the smaller municipalities are far less likely to have sewage treatment plants that are capable of handling the strong wastes that come from large and small dairies alike.

Again, with the dairy industry, as with the packinghouse industry, "IN-PLANT" control and reduction of losses before the wastes even go near a sewer, are extremely important parts of this problem. It is certainly realized by every responsible management in this country that throwing raw materials away is a loss of money to them; repetition of this theme in this paper is not intended as a dig at these industries, but rather it is suggested (and I hope you will accept it this way) that here is an essential part of the problem that should be reviewed by all concerned in order that we may solve our difficulties to the mutual advantage of all.

Trebler & Harding in 1955 in a paper entitled "Fundamentals of the Control & Treatment of Dairy Wastes" reported that dairy wastes are about the easiest ones to treat by biological methods because milk & milk products are nature's most nearly perfect foods for microorganisms as well as for man. The solids consists of proteins, fats and carbohydrates in various proportions depending on the type of process. The waste usually have a relatively high B.O.D., little of which is removed by sedimentation. By making allowances for these factors, milk wastes can be treated successfully by existing biological methods in any municipal sewage treatment that has <u>sufficient</u> secondary treatment capacity.

Klein reported in 1958 that pretreatment to remove sand and fat from dairy waste is desirable. Where only primary treatment is available, preaeration can be used to oxidize lactose which is soluble. With secondary treatment, pre-aeration is not mandatory but an increase in the rate of sludge-pumping from the secondary clarifier to the primary influent is recommended. Klein stated that the formation of lactic acid lowers the pH and interferes with the settling and digestion of sludge. Klein also stated that, provided the sewage treatment plant is designed with sufficient reserve capacity and with high recirculation of sludge, accidental spills of milk or of by-product can be handled successfully in activated sludge plants. Also he reported that the direct feeding of such concentrated by-products as whey, skim milk and buttermilk to municipal sludge digesters has been done without inhibiting digestion and has resulted in increased gas production.

Milk wastes have been treated on conventional trickling filters, by diluting with cooling water or effluent to provide a B.O.D. concentration to the filter of 200 - 300 ppm. However, this practice may result in "ponding" and fly nuisance.

Aeration may be batch or continuous with or without return sludge. The main requirements are sufficient tank volume to give the detention necessary for the process used, proper tank shape to promote mixing, sufficient height above the water line to contain foam, and a minimum temperature drop through the tank.

Compared with filters, aeration tanks have lower first costs and occupy less space but more power is needed per pound of B.O.D. removed and difficulties such as foaming and sludge bulking can occur. Aeration tanks can take shock loads if there is sufficient reserve capacity of well-aerated sludge.

Klein described a milk waste plant, consisting of primary and secondary sedimentation, a two-stage high rate filter, chlorination and unheated digester, which was designed to relieve the load on a municipal sewage treatment plant. The milk waste consisted of waste from receiving, weighing, can washing, separating, pasteurizing, butter-making plus cooling water and condensate from evaporating and drying. It was found that the trickling filter produced very bad odours; a great deal of grit was getting into the system from the washing of milk trucks and the unheated digester did not function until heating was installed. It was also found that the dairy wastes were much stronger than had been calculated and that the surge flows required correction in order to make the plant work properly.

Eldridge and others have pointed out that the activated sludge will produce very good results on dairy waste, giving 85% removal, treating wastes of over 1000 ppm B.O.D. although the air requirements may be as much as 3600 c.f. per lb. of B.O.D. and the retention in the aeration tank may be quite long. Several writers have emphasized the importance of grit removal for dairy wastes and equalization of wastes (sometimes using an aerated equalization tank followed by 24 hour aeration in the mixed liquor tank).

The disposal of whey from the production of cheese is a problem that requires a great deal of attention especially since from every 1000 lbs of milk there are 900 lbs. of whey. About 20% of the whey in the U.S. is converted to powdered whey with attendant removal of the protein & butter fat portion. Whey can also be disposed of by spray irrigation but this method is not advisable with our Quebec climate and generally heavy soils.

In the handling of milk wastes it is frequently necessary to offset acid conditions by neutralization with lime at the rate of about 1 lb of lime per 1000 gallons of waste. Sometimes dairy plant wastes contain excessive amounts of caustic cleaning chemicals.

VEGETABLE CANNERS & PRESERVERS

There are 130 of these plants in Quebec, and they are dispersed according to population as shown in the following table.

Population in the Municipality	Canning Plants
1,000,000	24
170,000	3
50,000 - 60,000	3
40,000 - 50,000	4
30,000 - 40,000	1
20,000 - 30,000	13
10,000 - 20,000	12
5,000 - 10,000	9
2,000 - 5,000	19
Under 2,000	45
	133

These establishments are primarily engaged in manufacturing canned & dried fruits and vegetables, fruit and vegetable juices, soups, preserves, jams & jellies, pickles, cider and sauces.

In the canning industry the wastes results from water from heat sterilizers, cooling of sealed containers, washing of the products, blanching, spillage and cleaning of equipment and floors. There are also the solid wastes.

The common methods of treatment have been, in the past, screening, sedimentation, biological filtration, lagoons and land irrigation. Cannery wastes are non-toxic but they are highly organic and consist of carbohydrates, fats and proteins with B.O.D. values of 240 to 6000 ppm. and suspended solids ranging from 20 to 3500 ppm. The pH is normally 6.2 to 7.6 although silage liquor can be very acid.

Fruit & vegetable wastes under rapid anaerobic decomposition give off H_2S, organic acids and nitrogen decomposition products.

The chief difficulty with all methods of handling cannery wastes is odour control; sodium nitrate is frequently used to prevent odours and to satisfy 20 to 37% of the B.O.D. Sodium nitrate is quite expensive for this application.

Spray irrigation has frequently been used for the disposal of canning wastes, however spray irrigation requires a minimum area, proper slope conditions, good fertility of the soil so that it will support good cover crops and the operation must be well managed. The addition of solids to these canning wastes makes the irrigation project much more difficult.

Screening of canning wastes is almost universal but these screened solids are frequently responsible for difficult operational problems due to:

(1) Cost of disposal.

(2) Odour problems that result from the storage of these solids.

(3) Fly problem

(4) Problem of finding a suitable disposal ground.

There has been considerable work on the comminution of these wastes and including them in the liquid wastes for disposal by spray irrigation; this has been partially successful with pea canning wastes although there are definite mechanical problems due primarily to the fiber. Stones and tramp metals also present a problem in comminution of these wastes.

In the past it has been found that the treatment of combined municipal and canning plant waste has limited application due to the sudden large volumes from the cannery which throw municipal plants out of balance. This has been particularly true when using activated sludge plants in small towns; these small plants, of course, recover very slowly from shock loading.

There has been considerable success with lagoons preceeding highrate trickling filters. Anaerobic digestion of the cannery sludges is satisfactory providing the wastes are limed to a pH of, at least, 6.5.

Apparently cannery wastes can be handled in aerated lagoons of 10 feet depth, at a loading of about 300 lbs. BOD/acre/day using about 0.7 c.f.m. of air per 1000 gallons of waste (supplying about 1.1 pounds of oxygen per pound of B.O.D.) and obtaining 50 to 80% removal of the B.O.D. The bottom sludge in these lagoons has a fairly high benthol demand.

Norgaard et al compared (a) anaerobic digestion followed by either activated sludge or high-rate trickling filters (b) primary settling plus either single or two high rate trickling filters and (c) activated sludge both with and without primary settling. Norgaard found that the activated sludge with primary settling, sludge reaeration and with supplementary feeding of ammonia during the peak season gave a high degree of treatment with moderately high loadings. The other processes investigated were unsatisfactory.

Sugar Refineries

Quebec has 3 sugar refineries, 2 of which are in Montreal and 1 in a town which has a population of 2870. These refineries are primarily engaged in the manufacture of cane sugar, beet sugar, sugar syrups, molasses and beet pulp.

The main problems in this industry are due to the seasonal operation and large quantities of wastes.

A typical sugar beet manufacturing process consists of "fluming" the beets to the plants, removing stones and tramp metal in traps, washing and slicing the beets, extracting the sugar in diffusion cells, storing and draining the spent pulp for later sale as a feed, filtering and concentrating the sugar juice (using carbon dioxide and lime), crystallizing the sugar and separation of sugar from the molasses.

In modern refineries the wastes are separated into three streams to facilitate treatment and disposals as follows:

(1) Flume and process water which is screened over vibrating screens with 0.1" openings, at a loading of about 30 gals. per sq. ft./ minute.

The screenings are then disintegrated and pumped to the pulp silo. The screen underflow may then be run into lagoons connected in series and having an operating depth of about 3 feet.

These lagoons will effect about 15% reduction of B.O.D. and 94% removal of suspended solids with a holding time of about 24 hours.

The flume & process waters contain approximately 50% of the total B.O.D. in wastes & almost all of the suspended solids.

(2) Pulp silo Drainage.

The spent pulp, from the diffusion cells, after washing and dewatering over screens, is stored in silos.

In small towns, the drainage from these silos should be stored throughout the season in laggons and then gradually be fed into a treatment system. The degradation of B.O.D. affected by lagoons is neglible and these wastes are strongly acid.

(3) Lime Wastes.

These wastes may also be lagooned.

The manufacture of cane sugar results in less wastes than the production of beet sugar because the extracted cane is suitable for direct use as fuel, and the sugar itself requires less purification. Inefficient operation of the sugar mills can lead to a considerable waste problem.

THE BEVERAGE INDUSTRY

Here we are including only those establishments that are primarily engaged in manufacturing non-alcoholic beverages and carbonated mineral waters or concentrates and syrups for the manufacture of carbonated beverages.

It is interesting to note that in the U.S. in 1954 there were 4643 soft drink production establishments by comparison with 180 in Quebec in 1962. On this basis Quebec may be over populated with soft drinks firms or perhaps there are some business opportunities left in the U.S. Another interesting fact is that coca-cola accounts for 56.6% of the carbonated drinks.

This industry is also quite seasonal and some of the smaller plants virtually suspend their operations during the colder months. The disposition of these plants in Quebec is as follows.

Population in the Municipality	Soft Drinks Plants
Over 1,000,000 (MOntreal	19
170,000 (Quebec)	6
80,000 - 90,000	1
60,000 - 70,000	3
50,000 - 60,000	5
40,000 - 50,000	2
30,000 - 40,000	9
20,000 - 30,000	26
10,000 - 20,000	34
5,000 - 10,000	28
2,000 - 5,000	24
Under 2,000	23
	180

It is noted that 75% of these plants are in towns of less than 30,000 people, and 26% in towns with less than 5,000 people.

The essential ingredients of carbonated soft drinks are water, sugar, carbon dioxide, acids, flavours, colours and salts. The water that is employed by this industry must be almost completely free of suspended matter, odour, air, alkalinity, and any other substance which could destroy the delicate flavours, colours and appearance of the bottled drink or cause difficulty in the plant operation.

The sources of the wastes in this industry are wastes from mixing and blending of the sugar solution, sludges from the back washing of filter units, alkaline cleaning solution from bottle washing (this is used for 5 or 6 weeks then replaced). In the washing of bottles there is a great deal of left-over drinks, straws, discarded cigarette butts, soil, mould and other miscellany. If the bottles are labelled, these must be removed or the suspended solids in the wastes will be considerably increased. There are also intermittent wastes from periodic cleaning of syrup mixing tanks, syrup storage tanks, filters etc.

These wastes have a pH from 10-11.4, B.O.D. from 250 - 660 Mg/1., suspended solids from 160 to 340 Mg/1. and total alkalinity 290 Mg/1.

The sanitary wastes are not a large proportion of the total for this industry. The maximum daily B.O.D., suspended solids and alkalinity may exceed the average by 200% although the variation in the daily flow apparently ranges from 75 to 125% of the average.

Using the American production figures which were reported by Porges, it is possible that the wastes from all the soft drink establishments in Quebec would be equivalent on a B.O.D. basis to the wastes from a city of 39,000 people and on a typical summer day these wastes might be equivalent (in total) to a town of 58,000 people. Remember, I said previously that approximately 26% of the total soft drink waste problem occurs in towns with less than 5,000 people.

There is a possibility that something might be done in the future about reclaiming some of the sugar from the returned, unused drinks, and using this reclaimed sugar for animal feeds.

DISTILLERIES

These are establishments which are primarily engaged in producing such alcohol beverages as whiskey, brandy, rum, gin and commercial ethyl alcohol.

There are 7 distilleries in Quebec located in towns with population as follows:

Population in the Municipality	Distilleries
Over 1,000,000	2
20,000 - 30,000	2
10,000 - 20,000	1
2,000 - 5,000	2

I had hoped to know the production of many of these Quebec industries but unfortunately time was too short. However I do have some figures of interest which may provide some guides.

One large distillery produces about 18000 gallons per day of total alcohol, from approximately 5000 bushels of grain per day (i.e. corn, rye and malt).

Distillers, I believe, usually calculate their probable yields on the basis of producing from each bushel of grain about 3.5 gallons of proof alcohol, 18 lbs of dried distiller's solubles plus carbon dioxide, yeast and heat.

In order to produce 18000 gallons per day for 6 days/week, this company creates about 2.5 Imperial M.G./week of wastes containing about 0.5% total solids. Distiller's dried grains & distiller's solubles are very valuable feed materials the recovery of which greatly reduces the strength of the wastes. These dried grains possess an 85% total digestible nutrient which surpasses such feeds as soya bean oil, corn gluten, cotton seed and meat meal; their value has been well demonstrated from feeding tests with cattle. Distiller's dried solubles, the evaporated drum dried portion of the stillage, finds its main use in feeds for poultry & various concentrates.

Without the recovery of distillers grains & solubles the B.O.D. of distillery waste is about 20,000 lbs per 1,000 bushels of grain, whereas with complete recovery we obtain B.O.D. strengths of approximately 200 lbs per 1,000 bushels of grain;

The wastes from well-managed modern distilleries are large in volume but weak and mainly a problem in hydraulics. They have been treated on trickling filters; it does not seem likely that these wastes would harm an activated sludge process.

BREWERIES

The published data for Breweries in the United States indicate a waste water flow of 9 to 13 gallons per gallon of brew at a B.O.D. of 420 to 1200 ppm.

There are 4 breweries in Quebec all of which are in large centres of population. There are 2 in Montreal, 1 in Ville LaSalle and 1 in Quebec City. Thus the Quebec Brewery wastes will not have as much <u>relative</u> influence on the operation of sewage treatment plants as will be the case for most of the other food industries. The trend toward concentration of the brewing industry has been quite marked in the United States. Since 1900 the number of American breweries have been reduced by 1/10.

Even for large sewage treatment plants, brewery wastes present a problem, due to the extremely wide variation in almost every property of the wastes. The concentration of biologically degradable organic matter may vary from 24 to 4800 mg/l. from one hourly composite sample to another - i.e. 200 fold variation. In addition to these wide variations in B.O.D. and suspended solids, the pH may vary from 2.4 to 12.1 for certain waste streams, and the water consumption may vary by 300% from hour to hour.

These features mean certain shock loading for any moderately sized or small sewage treatment plant and perhaps some difficulty for even large plants unless corrective measures are taken.

Brewery wastes require the addition of nitrogen and phosphorous nutrients for biological treatment, in order to maintain the B.O.D.: N: P ratio at 100 : 5 : 1. Apparently there has been good sucess in treating brewery waste alone on trickling filters and by activated sludge using aeration periods of 3 to 6 hours. Therefore, there are good reasons for believing that, with the proper adjustments, well-designed municipal sewage treatment plants would be able to handle brewery wastes.

Poultry Processing

There are 45 of these plants in Quebec and their disposition according to population is as follows:

Population in the Municipality	Poultry Plants
Over 1,000,000 (Montreal)	9
50,000 - 60,000	2
10,000 - 20,000	2
5,000 - 10,000	3
2,000 - 5,000	13
Under 2,000	16
Total	45

There are 63% of these plants in municipalities with less than 5000 people, 36% of them in very small places.

The rapid growth of the broiler growing industry has naturally caused these plants to be located near the sources of the poultry in order to reduce transportation and handling costs.

There are no unusual problems in dealing with poultry wastes because of the actual properties of these wastes. The difficulties arise because these plants are generally located in small municipalities where the water and sewage facilities are already inadequate without the added heavy burden from poultry killing operations.

It is distressing indeed to local officials who desire to locate a poultry industry in their small town, to learn that the industry may require as much as 200,000 gallons of water over a 12 - 14 hour period and that the waste treatment facilities in most instances must provide secondary treatment for an equivalent population of 5500 people, (i.e. a moderately sized poultry killing operation of 20 to 25,000 birds per day).

The improvements in processing efficiency have enabled poultry processors to handle as much as 6000 - 7200 birds per hour, and effect yields of about 74%. For calculations, allow 3 to 3½ lbs per bird as the live weight of broilers.

The wastes from poultry processing will depend on the type of operation; for example, a plant may operate without holding the birds overnight, thus reducing the manure and feed wastes; a plant may produce - New York Pack which, in the trade, means "not eviscerated"; blood may or may not be saved; the operation may be manual or it may employ "Flow-away" systems for one or both of feathers and offal; Flowaway systems may recirculate the water.

There are great differences in the waste strength according to these foregoing alternatives. For example, a flowaway system may use 12000 gallons of water per 1000 birds while a manual system may only use 2600 gallons for 1000 birds. Recirculation will reduce the water consumption by 35%. Blood saving may reduce the B.O.D. by 60%.

It is essential that poultry killing plants save feathers, offal, (by rotary or vibrating screens), blood and grit from the gizzards. A Bar screen with ½" opening should be welded into the plant sewer at the point of exit to prevent flushing of large solids into the sewer system.

It is interesting to note that there may be as much as 3000 lbs. of grit from the gizzards of 50,000 birds.

The flow from poultry killing plants is intermittent, which creates a problem in small towns. The processing period is usually about 8 hours; this is followed by 4 to 8 hours of cleanup and the poultry plant frequently operates only 4 days per week.

The Engineer who proposes to design a sewage treatment plant for a very small town with a poultry plant, or for the poultry plant alone, must plan for lengthy shutdown periods in the poultry plant followed by a shock load after the shutdown period.

It has often been found economical to design extended aeration activated sludge plants on the basis of treating the flows as received. However if the poultry waste flow is proportionately too large, aerated equalization tanks can be provided.

Teletzke stated that lagooning of poultry wastes was not successful in one instance. Trickling filters have been successful for a combination of poultry and municipal wastes, but trickling filters are not advisable in our climate.

Teletzke reported that an extended aeration process gave 90% removal of B.O.D. and 79% removal of suspended solids when operating on 24 hour aeration, 15 lbs of B.O.D. per 100 lbs of mixed liquor suspended solids, M.L.S.S. at 5000 ppm, 45 lbs. B.O.D./1000 c.f. of aeration tank, and 100% return sludge, using 1500 c.f. of air/lb. B.O.D. removed.

CONCLUSIONS

(1) The activated sludge process is applicable for all of the food waste problems in Quebec. This means one of the forms of the activated sludge process but it does not mean that the activated sludge process must be used.

(2) Whenever possible, these food plant wastes should be mixed with municipal sewage for treatment.

(3) Great care must be taken in establishing the actual conditions and the most suitable design conditions when dealing with food wastes.

(4) In most cases, these waste flows must be discharged into the municipal system at a uniform strength and at a constant rate of flow.

(5) "In-Plant" treatment is invariably essential for these industries.

(6) Every one of these industries would be well advised to have their waste problem and its relationship to the municipal sewage problem studied by an Engineer.

(7) Municipalities would be well-advised to adopt well-considered By-laws to protect their sewage treatment systems, remembering at all times that their local industries often must meet wide competition.

(8) Municipalities must be realistic in dealing with their industrial waste problems particularly at the planning stage.

(9) Good cooperation based on thorough mutual understanding of the several facets of these problems, by all concerned, will go a long way toward obtaining good design data, sufficient flexibility and capacity in the sewage treatment plant, a community on guard against faulty construction and finally a sewerage system that really works as planned.

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BIOLOGICAL TREATMENT OF CERTAIN ORGANIC INDUSTRIAL WASTES

by

J. M. FAIRALL

SESSION THREE

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Department of National
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Session Chairman

"BIOLOGICAL TREATMENT OF CERTAIN ORGANIC INDUSTRIAL WASTES"

by

J.M. FAIRALL

The basis of design for biological treatment of municipal wastes has not been satisfactory for strong industrial wastes. Lagoons and aerated ponds are being used frequently where adequate land is available, but in many cases it is more economical to treat strong industrial wastes in biological systems at high loadings and these systems will be discussed in this paper.

EJECTOR AERATION

In the early fifties a modified activated sludge process was applied to wastes from the dairy industries. Dairy wastes have been treated on high rate trickling filters with more or less success, particularly when the intermittently discharged wastes are passed through a flow equalization tank ahead of the filters. It became necessary to aerate the wastes in the tank in order to control odors and make the trickling filter treatment more effective. Activated sludge treatment of milk wastes had been tried but difficulty was encountered with plugging of the gas diffusion devices. A solution to the problem of treating dairy wastes was developed by aerating the wastes in a tank with a detention time of about 10 hours, based on an average rate of flow. The wastes were thoroughly mixed in the tank by recirculating the wastes through ejectors which sucked in air from above the liquid surface. Later, compressed air was supplied in order to accommodate heavier loads. The treated wastes were settled and some sludge was returned to the aeration tank.

Two of the earlier ejector aerator systems were built by Dean Milk Company at Huntley and Chemung, Illinois.(165) The one at Huntley was loaded at about 66 lbs. of BOD/day/1000 cu. ft. of aeration tank volume, and used around 925 cu. ft. of air per lb. of BOD removed. The other unit, at Chemung, was loaded at 118 lbs./day/1000 cu. ft. and required 935 cu. ft. of air per lb. of BOD removed.

Abbott Laboratories also built a similar aeration plant for pharmaceutical wastes which was later modified. (140)

There were two notable sequences to these dairy waste treatment units. From the beginning a longer aeration time was provided for dairy wastes than for municipal wastes. Frequently the tank volume was equal to the total daily flow of waste and this detention time was extended to develop into extended aeration plants for sanitary wastes and industrial wastes. The Department of Agriculture became interested in the dairy waste treatment plants and the basic work of Porges (168) and Hoover pushed forward the application of activated sludge processes by Eckenfelder (169) and others.

TRICKLING FILTERS

Pharmaceuticals

Following World War II the production of antibiotics boomed and in the early fifties the treatment of wastes was becoming of great concern.

In the production of antibiotics such as penicillin, streptomycin, and terramycin, a fungi is grown aerobically in a fermentation broth made up of corn liquor, lactose, and mineral salts. At the end of the fermentation cycle the biological activity may or may not be inhibited, the fungi mycelium is separated from the broth by vacuum filtration and the antibiotic in the filtrate is extracted with a solvent such as amyl acetate in an acid solution. The solvent is stripped from the spent broth, the degree of stripping depending on the value of the solvent and the toxic effect on subsequent waste treatment processes, and the broth is discharged as a waste product. The filter cake may be disposed of as a solid waste. Waste solvent may be disposed of by incineration.

The spent broth has a pH between 2 and 3 and a BOD between 4000 and 13,000 mg/l. The nutrients in the spent broth are sufficient to support biological treatment processes.

Fine chemicals are often manufactured at the same plant as the antibiotics and these organic chemical wastes may or may not be segregated from the spent broth. Sanitary wastes are generally segregated and settled before being combined with the spent broth. Clean waste cooling water is segregated and not treated.

In 1945 The Upjohn Company decided to build a plant for the production of penicillin and streptomycin about six miles south of Kalamazoo, Michigan. The receiving stream was Portage Creek flowing into the City of Kalamazoo at rates of flow from 10 to 20 cfs. Pilot plant studies indicated penicillin-free wastes to average around 13,000 ppm BOD and streptomycin wastes to average 2500 ppm BOD, with spoiled batches containing as high as 20,000 ppm BOD. (89)

In the spring of 1948 a waste treatment plant was placed in operation. The plant consisted of 2 aerated holding tanks with 10-hr. detention, 2 rectangular sedimentation tanks, 2 90-ft. diameter trickling filters arranged for either series, parallel, or alternating double filtration, final sedimentation, chlorine contact tank, and sludge digestion tank with sludge drying beds. (89)

The aeration tanks were typical of the early trickling filter plants treating antibiotic wastes, the aeration serving to strip the spent solvents from the wastes and equalize the wastes to some degree. Various flow arrangements were tried with the trickling filters with routine operation being established as parallel flow at 500 gpm each, half being primary effluent and half recirculated filter effluent. The average load was 2540 lb./acre/ft./day with recirculation ratios varying from 2 to 9. The average filter removal was 90%. (113)

In July, 1949, Lederle Laboratories at Pearl River, N.Y. completed their first trickling filter for the treatment of pharmaceutical wastes. (90) Initially, wastes were treated on this high rate filter preceded by a primary clarifier. Recirculation of about 3 to 1 was practiced. Subsequently an aeration tank with 4.5 hours detention time was constructed ahead of the clarifier. Normal summer temperature in the tank was 85° - 95°F. Sludge was disposed of by filtration and incineration. (90) During the winter of 1950-51, Lederle experienced difficult operation when the filters ponded. (112) Other pharmaceutical houses have had similar experience on rock or slag filled filters and this has led to use of the activated sludge process. Since then, Lederle has converted the aeration tanks ahead of the trickling filters into the activated sludge process operating in parallel with the filters. (148) The filter capacity has been enlarged and operates as two stages. These activated sludge tanks are lightly loaded compared with those to be discussed later.

During the winter of 1950-51, Merck & Co., at West Point, Penna., put a two-stage trickling filter plant into operation. Operations have been reported for the 1952 season when the filters were not up to design load. (103) On the primary filter the hydraulic rate was 12.5 mgad and the BOD loading was about 27.2 lbs/day/1000 cu. ft.

In 1952, American Cyanamid Co. at their Willow Island, W. Va., plant put a trickling filter plant into operation to treat wastes from fermentation manufacturing processes. (104) The first units are two aeration tanks with 12-hr. detention followed by two primary clarifiers. The two high-rate trickling filters are filled with blast furnace slag, and are followed by clarifiers. The filters were operated at 17.9 gals/day/sq. ft. The primary filter was loaded at 64.5 lbs BOD/day per 1000 cu. ft. and the secondary filter was loaded at 29.9 with 60% removal in each stage. Final sludge was recirculated to the aeration tanks.

Following an extensive pilot plant program (99), Mereck & Co. at Elkton, Va., installed two trickling filters in parallel. The design hydraulic load was 7 mgad (116 gpd/sq.ft.) and the design BOD load was 70.4 lbs/day/1000 cu. ft. for an expected 70% removal at 30-32°C (149).

Subsequently these filters were operated in parallel following an activated sludge plant which will be discussed later in this paper. As second stage treatment these filters were operated at about twice the hydraulic load with a slightly greater BOD load at 18-34^{o} C. (149)

All of these filters have used rock or slag media. The wastes are very strong and it has been difficult to go to high hydraulic rates without loading them excessively biologically and plugging the media, as some of them have done. Dilution by recirculation will reduce the strength of the wastes but this tends to cool the filter and winter operation has sometimes been difficult due to low temperatures of the recirculating liquid.

Kraft Pulp

The Rome Kraft Company has constructed a trickling filter to treat waste white water and black liquor from their integrated kraft pulp and paper mill near Rome, Georgia. (163)

Black liquor is discharged to a strong waste lagoon from where it is pumped at a metered rate to a surge tank and blended with white water and filter effluent. Nitrogen and phosphorous supplements are added to the surge tank effluent as it is pumped to the rotary distributor of the trickling filter.

The filter tower is filled with PVC medium. The octagonal-shaped tower is 80ft. in diameter and about 30 ft. tall. The depth of medium is 20 ft. The medium is supported on epoxy-coated steel grating resting on trapezoidal shaped beams. Recirculating effluent may be taken from the bottom of the tower.

Effluent flows by gravity to a conventional circular clarifier, with sludge being returned to the surge tank. This sludge return may be eliminated following operating experience. Settled effluent passes to an existing aeration tank and then to a series of five lagoons before being discharged to the Coosa River.

Based on extensive pilot plant tests, the filter was designed for an average load of 600 lb. of BOD/day/1000 cu. ft. applied at 210 mgad with a recirculation ratio of

0.5. Design temperature was 52°C and a removal of 50% was expected. Initial operation was at 500 to 650 lb. BOD/day/1000 cu. ft., dosed at 200 to 260 mgad without recirculation. Temperatures never exceeded 48°C. Removal ranged from 46 to 58% with a mean of 51%.

ACTIVATED SLUDGE

Pharmaceutical and Fine Chemicals

In 1949, Heukelekian published the results of some bench scale research on the treatment of antibiotic wastes by aeration with dispersed growths. In 1954, Eckenfelder and O'Connor (105) (169) published an early paper indicating a different viewpoint of the activated sludge process from that used in the design of conventional municipal plants and also mentioned the use of the turbine aerator.

The pharmaceutical industry had not been entirely satisfied with the performance of trickling filters with rock media and the turbine aerator being adopted from the fermentation industry, made the activated sludge process more understandable to the industry.

Merck & Co., at their Danville, Penna. laboratory carried on extensive pilot plant studies using a turbine aerator. (108) A design was proposed at 780 lbs. BOD/day/ 1000 cu. ft., for 70.5% removal.

Late in 1958 construction was completed on an activated sludge plant at the Elkton, Va., plant of Merck & Co. Following flow equalization and neutralization of chemical wastes, settled sanitary wastes are mixed with the neutralized wastes and the combination is aerated in two aeration tanks in series or parallel. Each tank is provided with two turbine aerators. The aerated effluent flows to a modified air flotator for sludge separation. The clear effluent flows to the two trickling filters in parallel, which were previously discussed. The floated sludge is either recirculated to the aeration tanks or wasted to an aerobic digester. Modifications have been made to this plant in order to improve operation.(149)

Abbott Laboratories, North Chicago, Ill., had been treating their wastes in two aeration tanks equipped with ejector aerators. Following extensive pilot plant tests (140) one of the aeration tanks was equipped with turbine aerators. (150) This construction was completed in June 1958. Raw wastes are discharged to one unmodified aeration tank for flow equalization and solvent stripping, using air supplied through the existing jets. The equalized wastes flow to the modified tank consisting of three compartments in series, each equipped with two turbine aerators. For the operating conditions reported (150) the turbines in the third compartment were turned off and only half as much air was supplied to the sparger rings as to those in the first two tanks. The aerated wastes were settled in a gravity sedimentation tank and some sludge was recirculated to the first aeration compartment to control the mixed liquor solids. Waste sludge was thickened in a flotation unit.

Average operating data indicated a loading of 475 lbs. of BOD per day per 1000 cu. ft. of tank volume for 78.5% BOD removal with a power consumption of 0.35 to 0.45 kwh per lb. BOD removed. With the ejector aerators the power consumption had been 0.56 kwh.

EXTENDED AERATION

Earlier in this paper it was indicated that in treating dairy wastes, flow equalization tanks were used ahead of the trickling filters or aeration tanks, when conventional activated sludge was the treatment process. By combining the two tank volumes, dairy waste treatment has developed extended aeration where the detention time is around 24 to 36 hours. (167)

In the pharmaceutical industry, which is also treating a soluble substrate, the flow equalization tanks are still required ahead of the trickling filters and the aeration tanks. In at least one case antibiotic wastes are being treated by complete mixing activated sludge or extended aeration. (146) This is the Paoli, Penna. plant of Wyeth Laboratories. (172)

PILOT PLANTS FOR CONTROL

The exact details of treatment will vary from plant to plant and industry to industry so that the same treatment process cannot be applied identically and economically to two different plants. The required degree of treatment will vary as well as land values, existing equipment and existing available services. Because of these factors it is difficult to make comparisons such as those attempted in this paper.

All of these pharmaceutical and fine chemical plants have had some matters in common:

1. The waste treatment plant has been developed from pilot plant studies.
2. Production has increased during construction of the waste treatment plant or shortly thereafter.
3. Production operations have been modified and the characteristics of the wastes have changed.
4. Completely new production lines have been contemplated or added with different wastes.

Instead of abandoning the pilot plant once the full scale plant is constructed, a number of manufacturers have maintained the pilot plant in order to study proposed modifications or new waste characteristics, and to study the causes of treatment plant upsets.

Lederle Laboratories (148) has two pilot trickling filters, one of which is 6-ft. in diameter, and a continuous flow 3 compartment activated sludge pilot.

Abbott Laboratories (141) have developed a shaken flask test for batch operation and have built a bench scale continuous flow unit for use in various investigations.

Wyeth Laboratories (172) continues to use their pilot plant to observe the effect of variations in operation.

BIOLOGICAL TREATMENT OF CERTAIN ORGANIC WASTES

Activated Sludge

PLANT	YEAR	#BOD/DAY # MLS	C.F. AIR $\# \text{ BOD}_R$	# BOD/DAY 1000 CU. FT.	% BOD REMOVED	REF.
DEAN MILK, HUNTLEY	1950		925	66	85-97	165
DEAN MILK, CHEMUNG	1950		935	118	75-85	165
MERCK & CO., ELKTON	1958	1.42-3.41	281-442	419-723	39-45	145
ABBOTT LAB., N. CHICAGO	1958	2.2	284	475	78.5	150
LEDERLE LABS., N. CHICAGO	1961			120	>80	148

Trickling Filters

PLANT	YEAR	GPD SQ. FT.	# BOD/DAY 1000 CU.FT.	% BOD REMOVED	REF.
UPJOHN CO.	1948	110	58.4	90	113
LEDERLE LAB., PEARL RIVER	1950	611	77	80	112
MERCK & CO., WEST POINT	1952	288	27.2	91	103
AMERICAN CYANIMID	1952				
MERCK & CO., ELKTON	1958	322	77.6	53	149
LEDERLE LABS., PEARL RIVER	1961		90	>80	148
ROME KRAFT	1962	4600-5980	500-650	46-58	163
PRIMARY		17.9	64.5	60	104
SECONDARY		17.9	29.9	60	104

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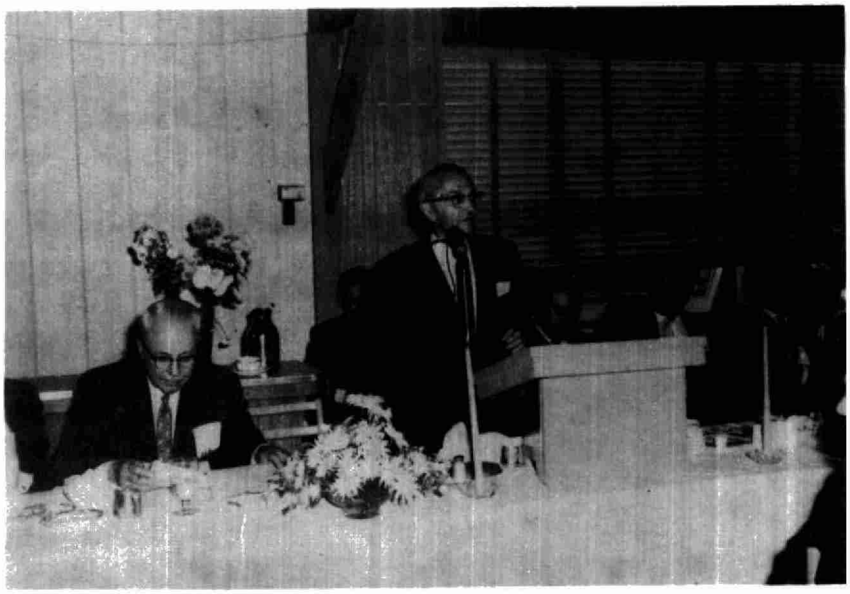


AFTER DINNER

SPEAKERS

BY PRODUCT RECOVERY OF ATOMIC ENERGY WASTES TO TREAT COLLOIDAL SYSTEMS AND SUSPENSIONS

by

W. N. GRUNE

"BY PRODUCT RECOVERY OF ATOMIC ENERGY WASTES TO TREAT COLLOIDAL SYSTEMS AND SUSPENSIONS"

by

W.N. GRUNE

I. INTRODUCTION

A. Background

This project, which was initiated March 1, 1962, is designed to investigate the effects of high energy ionizing radiation on a wide range of colloidal systems. The systems under investigation include lyophobic and lyophilic sols, aerosols, foams and emulsions. Significant parameters are investigated before and after exposure to radiation to ascertain effects, and results evaluated with emphasis on possible practical applications.

B. General Comments on Colloidal Systems

The size of solute particles in ordinary solutions is generally between 1 and 10 A, or 0.1-1 mu. Many systems, however, contain particles considerably larger which may range in size from the upper limits for ordinary solutions to several microns in size. Systems which are composed of dissolved or dispersed particles ranging from about 1 mu up to several microns in size are known as colloids. Such systems, therefore, occupy a position between true solutions, i.e., those having low-molecular solutes, and coarse mixtures. Colloids are usually considered to be heterogeneous, consisting of two phases: (1) the disperse medium, and (2) the disperse phase. All types of colloidal dispersions are known, a few of which are:

1. Solid in liquid (sols)
2. Liquid in liquid (emulsions)
3. Gas in liquid (foams)
4. Solid (or liquid) in gas (aerosols).

Theoretical analyses concerning the stability of colloidal dispersons have led to the conclusions that the potential energy function characterizing the system has a maximum when the particles are separated by an optimum distance and decreases very rapidly at smaller distances. The height of this potential energy barrier determines the stability of the system and is markedly affected by the presence of potential-determining ions in the system. In the case of lyophobic colloids, the addition of electrolytes to the system decreases the height of the potential barrier, eventually reaching a critical value causing the dispersion to coagulate. The critical potential is presumably related to the zeta potential, and hence the electrophoretic mobility of the sol. It is anticipated that ionic radiolytic products resulting from irradiation should have an effect on the suspended solid by altering the structure and potential of the electrical double layer as well as the surface conductance of the sol particles.

II. SCOPE OF THE PROBLEM

The generation of colloidal systems of considerable nuisance value is a common occurrence in the operation of the forces of nature, in functioning of equipment, and in industrial processes. In meeting the nuisance problems of such system, many devices of chemical mechanical and electrical nature have been employed. The addition of electrolytes to lyophobic hydrosols, the use of alcohols and silicones as antifoam agents, the supercentrifuge for breaking emulsions, and the Cottrell precipitator for smokes are typical examples. The effects of radiation on colloidal systems, however, have not been previously explored systematically. There have been isolated studies of specific systems, but the results obtained have not produced conclusions which can be applied to colloidal systems in general.

Some potential uses which may arise from these investigations are:

A. Eliminating nuisance problems created by colloidal systems occurring naturally (as in municipal water purification), in industrial processes, and in the functioning of equipment by treatment with ionizing radiation resulting in the coagulation of such dispersions.

B. This study should lead to a better understanding of the behavior of smokes, dusts, droplets and condensation nuclei, which could be useful in predicting the behaviour of military smoke screens and various meterological phenomena in the neighborhood of nuclear explosions.

C. Procedures and/or possible precautions should result from this study regarding manufactured and industrial products which are likely to be exposed to ionizing radiation during the course of production.

III. EXPERIMENTAL APPROACH

As a result of the very broad scope of this program, this research project was divided into three phases. These include:

A. Solid-Liquid Systems
B. Aerosols
C. Foams and Emulsions

Following is a brief description of the experimental approach taken under each of the three phases:

A. Solid-Liquid Systems

1. General

Applicable, stable dispersions are prepared and characterized by determination of significant parameters. These parameters are re-determined after exposure to ionizing radiation (beta and gamma from isotopic sources and X-rays) to ascertain effects. These parameters include: pH, conductivity, turbidity, zeta potential and particle size. Effects are then correlated with various parameters, e.g. radiation dosage.

2. Sol Preparation

Lyophobic hydrosols are prepared with the following characteristics in mind:

- a. easily prepared
- b. reproducible
- c. stable for prolonged period of time
- d. capable of being prepared over a range of surface potentials, including both positive and negative values.

Types of sols which have been investigated for applicability using the above criteria include aluminum oxide, stannic oxide, barium sulfate, ferric sulfide, ferric oxide, and silver iodide. Of these aluminum oxide, ferric oxide, and silver iodide have been found to be most suitable.

Future plans include the preparation of titanium oxide, chromium oxide, and vanadium oxide. A general view of the laboratory area and equipment is shown in Figure 1.

3. Electrophoretic Mobility Determinations

Determinations of electrophoretic mobilities are accomplished using a modified Briggs-type microelectrophoresis cell mounted on the stage of a Zeiss microscope with illuminator, resting on a vibration-free polyfoam shock absorber, and a special constant-current power supply. These items of equipment are shown in Figure 2, and a close-up of microelectrophoresis cell is shown in Figure 3.

The optical system found to be most effective for these determinations has consisted of a 30X ocular and a 20X achromatic objective.

4. Irradiation Technique

Irradiations are carried out in circular glass petri dishes. The dosage is delivered to the samples by a 140 kv peak (5 ma to 10 ma) standard G.E. therapy type X-ray unit which has been previously calibrated. Two views of the X-ray facility are presented, Figure 4 is photograph of the electric control panel, lead lined door leading into the separate X-ray room with part of the X-ray unit shown, while Figure 5 is a close-up of the X-ray unit head in position for irradiation of the sol which is held in the covered petri dish.

B. Aerosols

Liquid and solid aerosols produced by combustion, atomization and vapor condensation techniques are being employed. The particle sizes of these aerosols range from a few hundreths to a few tenths of a micron in diameter. The effect of radiation on these aerosols is studied by providing a constant aerosol supply to a system containing a section for exposing the aerosol to X-radiation. The aerosols are passed through the system with and without exposure to X-radiation and are analyzed for differences in particle electrostatic charge and particle size distribution. Several analytical methods are employed, the principal ones being ion counter measurements and electron micrographs.

Figure 6 shows the shielded chamber and auxiliary equipment including the aerosol generator, ion counter, constant temperature bath, and X-ray unit.

C. Foams and Emulsions

A great number of emulsion and foam systems have been examined as to composition, methods of preparation, stability, effects of heat and pH, for the purpose of establishing standards.

Macroscopic observations of settling rate and other gross parameters of emulsions are supplemented with microscopic observations of particle size distribution and in situ observations of effects of irradiation via closed circuit television microscopy. Observations of foams are generally confined to gross effects and low power measurements of bubble size distribution.

Figure 7 shows the available means for observing in situ the microscopic effects of radiation on these materials provided via closed circuit television. This phase of the study has been recently broadened by the inclusion of electrophoretic effects.

IV. RESULTS

A. Solid-Liquid Systems

Initial studies were conducted using an aluminum oxide sol. The sol was prepared by spontaneous peptization methods and characterized by determination of pH, conductivity, turbidity, concentration, and electrophoretic mobility. Radiation dosages up to 2500 roentgens had little or no perceptible effect on the aluminum oxide sol. Though the conductivities of the irradiated samples vary to a small extent, these differences fall within the range of experimental error and cannot, therefore, be regarded as significant. The sol was found to be stable over a pH range from 2 to 8. Table I shows some of the results obtained with aluminum oxide sol.

There appears to be some indication that a threshold value of radiation dosage exists at which the Fe_2O_3 sol coagulates sufficiently to permit settling. Since this value is related to the concentration of Fe_2O_3 in the dispersed medium (sol concentration) it was considered expedient to irradiate the most dilute sample (19:1) to investigate a threshold value for this sol concentration. For this purpose, 75 ml of the dilute sample was irradiated, and a total dosage of 1.14×10^5 roentgens was delivered. The turbidity, expressed as per cent transmittance, of the control was 2.9 as compared to 1.5 for the irradiated sample. Though the sol did not coagulate sufficiently to induce settling, comparison with the turbidity of the control revealed that some coagulation did occur. Some of the results with ferric oxide sols are shown in Table II.

Present studies are concerned with increasing the total dosage delivered to achieve the critical value, for a given concentration, which will effect sufficient coagulation to induce settling of a ferric oxide sol.

B. Aerosols

Aerosols of solid particles of such substances as poly(methyl methacrylate), sodium chloride and silica have been prepared by atomization of dilute solutions and suspensions. Particles in these systems were found to be electrostatically charged both positively and negatively as a result of the atomization process. Exposure to

TABLE I

Effect of Irradiation of Aluminum Oxide Sol

lask No.	Dosage (roentgens)	pH		Specific Conductance (L_8, umho/cm)		Turbidity (% Transmittance)		Electrophoretic Mobility ($\frac{u - cm}{volt-sec.}$)	
		Before	After	Before	After	Before	After	Before	After
27	118	3.65	3.80	2,780	2,740	84.0	91.5	7.85	(b)
28	590	3.65	3.78	2,780	2,740	84.0	92.0	7.85	(b)
29	1,180	3.65	3.80	2,780	2,780	85.2	92.0	7.85	(b)
30	2,360	3.65	3.78	2,780	2,780	81.2	89.5	7.85	(b)
31	4,720	3.65	3.75	2,780	2,820	84.9	92.0	7.85	(b)
32 (a)	---	3.65	3.60(c)	2,780	2,560(c)	84.0	90.0(c)	7.85	(b)
33 (a)	---	3.65	3.80(c)	2,780	2,780(c)	84.0	90.0(c)	7.85	5.02(c)
34 (a)	---	3.65	3.82(c)	2,780	2,780(c)	86.0	89.9(c)	7.85	5.02(c)

NOTES:

(a) Controls
(b) Particles could not be seen
(c) Received identical treatment, except for irradiation

TABLE II

Effect of Irradiation of Ferric Oxide Sol

Flask No.	Time Irradiated (Minutes)	Dosage (Roentgens)	Specific Conductance (L_s, umho/cm)	Turbidity (% Transmittance)
60	0	0	104.2	0
61	302	1.21×10^5	121.2	0
67	0	0	---	2.9
66	260	1.04×10^5	---	1.5
68	0	0	19.8	53
69	80	3.20×10^4	17.5	54

X-radiation significantly reduced their electrostatic charge.

The carrier gas has a pronounced effect on the discharging of silica aerosols exposed to ionizing radiation. When air and helium were used as carrier gases the total positive electrostatic charge on the particles was reduced by approximately 75 and 80 per cent, respectively, and the total negative electrostatic charge was reduced by approximately 75 and 85 per cent, respectively. However, with argon as the carrier gas the total positive electrostatic charge on the aerosol was reduced by only about 25 per cent upon exposure to X-radiation while the total positive electrostatic charge was reduced by approximately 95 per cent. The reason for the unusual behavior of argon as opposed to air and helium is not understood at this time.

The discharging mechanism for aerosols of solid particles is apparently by particle capture of the gas ions produced from the carrier gas by the ionizing radiation. This is strongly indicated by the fact that the smaller aerosol particles are neutralized preferentially as shown in Figure 8. (It should be remembered that in the ion counter which was used to obtain these size distributions the particles with no electrostatic charge do not appear in the size distribution). The greater mobility of the smaller particles possibly leads to a greater probability of ion capture.

C. Foams and Emulsions

Normal settling rates and settling characteristics (striation resulting from particle size classification) have been observed and recorded photographically. The settling rate is greatly increased by ultraviolet irradiation, and in proportion to the period of irradiation. Irradiation with a 200 watt quartz mercury lamp at 16 inches for 60 minutes was followed by complete clarification of the emulsion within a period of 8 hours. This represents a twenty-five fold increase in settling rate over the normal. No increase in settling rate has been observed as a result of X-ray irradiation.

Figure 9 shows a close-up of microscope in irradiation chamber; a part of the equipment devoted to emulsion studies.

V. CONCLUSIONS

A. Solid-Liquid Systems

Radiation dosages up to 30,000 roentgens appeared to exert no measurable effect on aluminum oxide sols prepared by spontaneous peptization methods. During the ferric oxide sol studies, radiation dosages up to 120,000 roentgens were applied and appeared to induce some coagulation as exhibited by doubling the transmittance from 2.9 to 1.5 per cent for the control and the irradiated sample, respectively. However, the concentration of the ferric oxide sol seems to play an important role.

B. Aerosols

The conclusions that can be drawn from the research on aerosols to date are:

(1) Upon exposure to ionizing radiation, electrostatically charged aerosols invariably undergo a reduction in charge.

(2) The degree to which the particles are discharged and the relative quantities of positive and negative charges that are neutralized depend upon the nature of the carrier gas.

(3) The smaller aerosol particles are discharged preferentially by ionizing radiation. This is so despite the fact that all the particles in the size range studied are believed to carry only single charges.

C. Foams and Emulsions

In the case of emulsions, it is felt that the effect of ultraviolet irradiation, resulting in increased settling rate, is due to loss of zeta potential, which is not observable immediately in the individual emulsion particles. If such is the case, application of microelectrophoresis techniques, in conjunction with closed circuit television microscopy, should lead to effects observable during the course of ultraviolet irradiation.

VI. FUTURE PLANS

A. Solid-Liquid Systems

Work of the future includes a continuation of irradiation studies employing lyophobic hydrosols with eventual extension to lyophobic organosols as well as lyophilic systems. Varying parameters other than radiation dosage and utilizing increased dosages (from isotopic sources) will constitute a major portion of future endeavors. These parameters include ionic strength (and hence conductivity and electrophoretic mobility), pH, and turbidity. Since the ferric oxide sols seemed to react to coagulation at dosages of just about 10^5 roentgens, the immediate objective will be to pursue higher radiation dosages, followed by applying dosages of the same order of magnitude to the aluminum oxide sols.

B. Aerosols

Present studies as well as those for the immediate future include the behavior of aerosols of liquids exposed to ionizing radiation. The evaluation of the filterability of aerosols with and without exposure to ionizing radiation is also of present concern. Some Russian research on the gamma irradiation of transformer-oil mists (1) has shown an increase of approximately 40 per cent in the number of mist droplets retained by cotton-wool filters. This was attributed to aerosol coagulation.

Future plans include the study of X-radiation on systems of solid nuclei and condensable vapors. Attempts will also be made to correlate the data obtained on the electrostatic behavior of aerosols in the presence of ionizing radiation with theoretical concepts of aerosol charging by ion capture.

C. Foams and Emulsions

The study of emulsions will take two major directions: (1) microscopic observations during the irradiation will be modified by the addition of microelectrophoresis techniques, and (2) the scope of gross observations will be increased by the inclusion of a wide variety of emulsion systems, including both commercial and laboratory preparations.

Studies of foams will continue along lines previously laid out, with emphasis on standard foams produced by the fritted disc device.

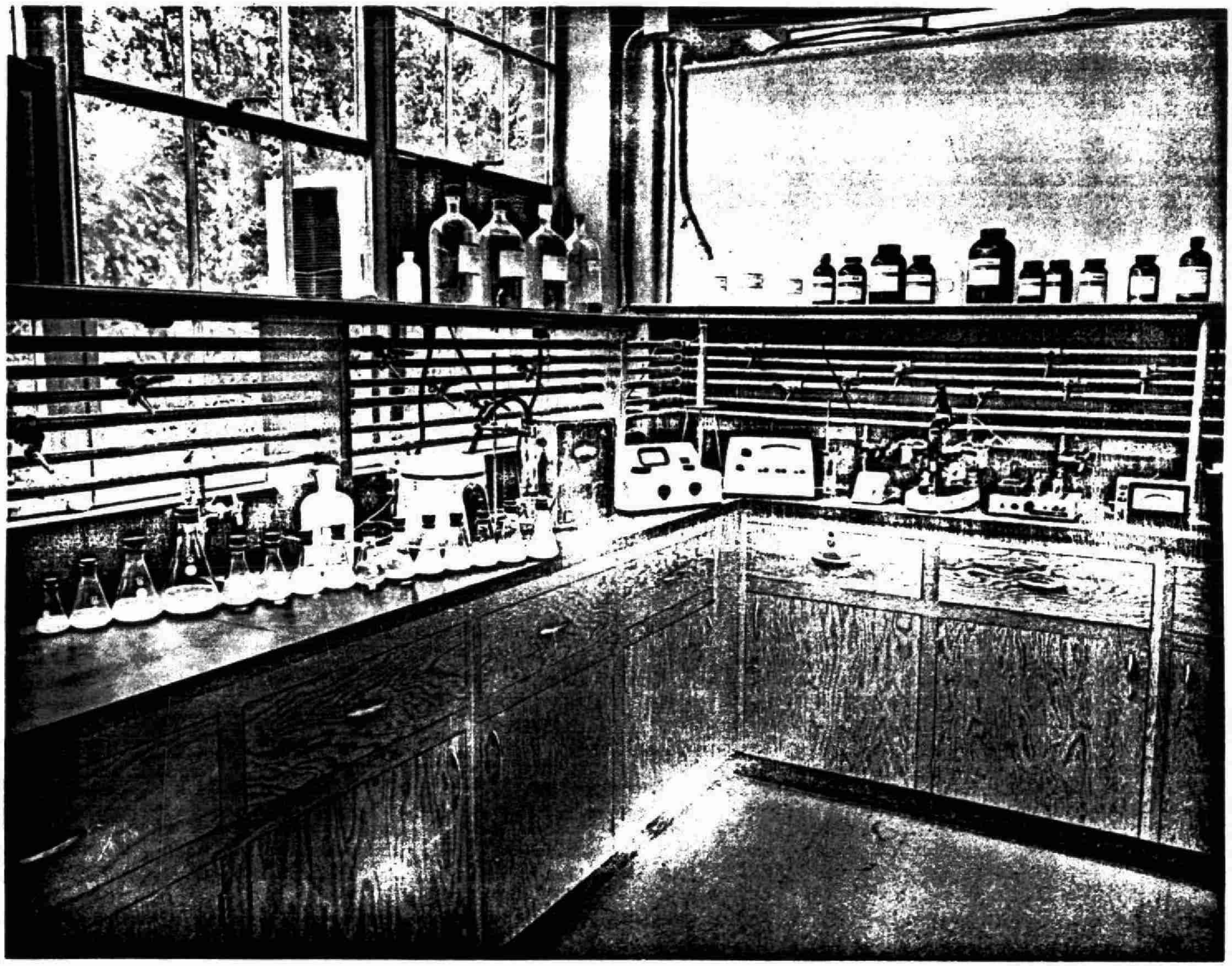


Figure 1. View of Laboratory Area and Equipment Devoted to Solid-Liquid Studies.

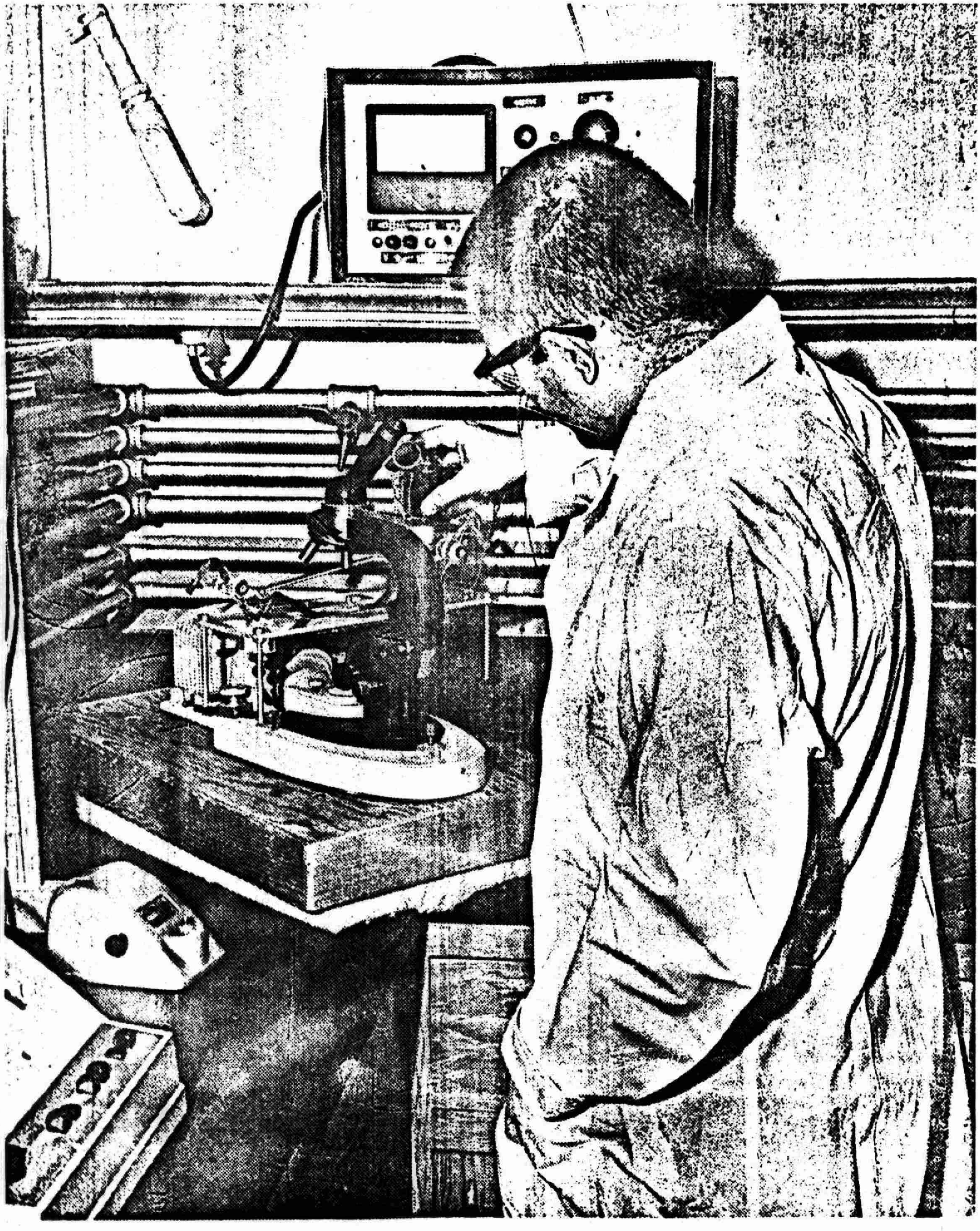


Figure 2. View of Microelectrophoresis Apparatus and Power Supply

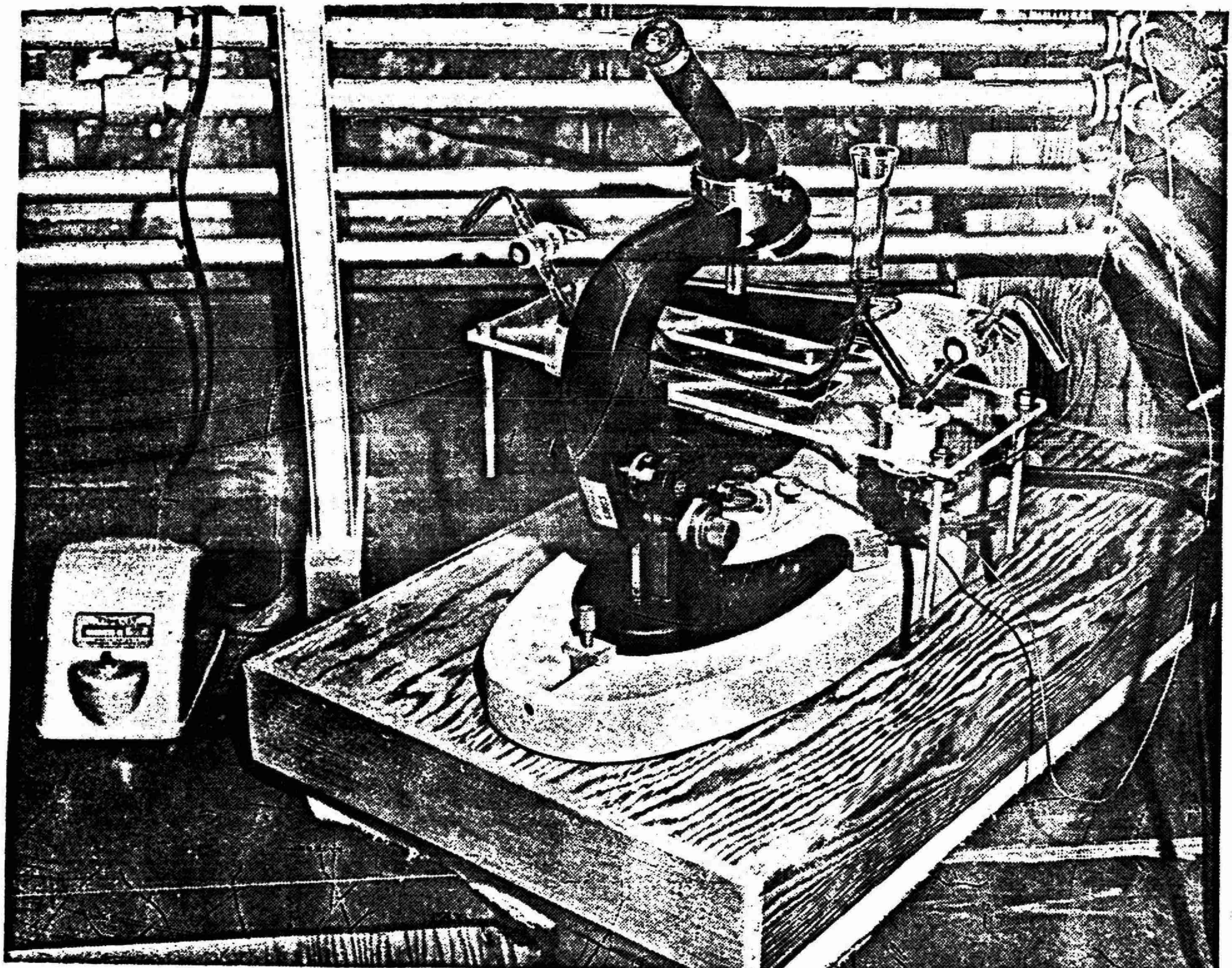


Figure 3. Close-up of Microelectrophoresis Apparatus

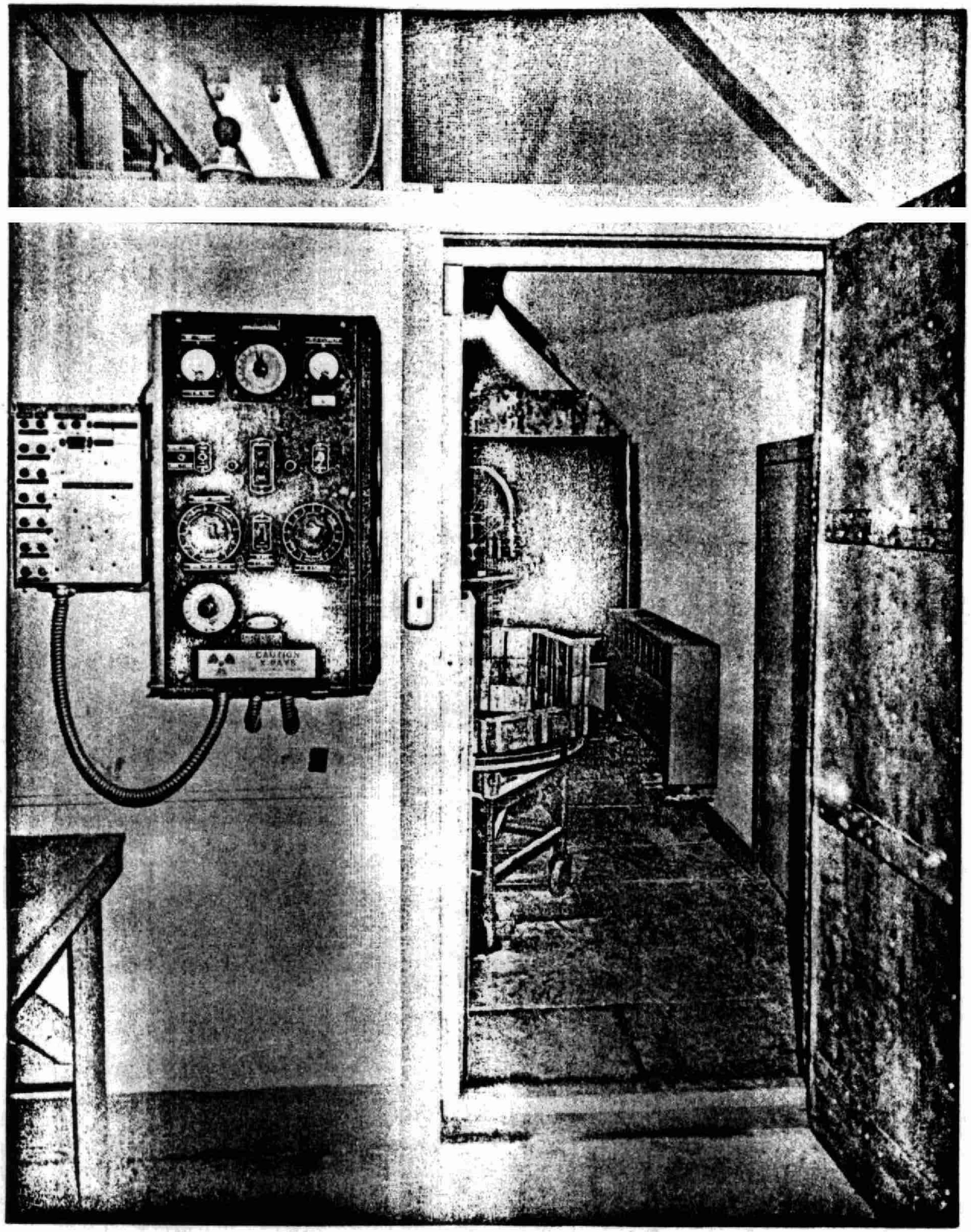


Figure 4. View of Control Panel and X-ray Room

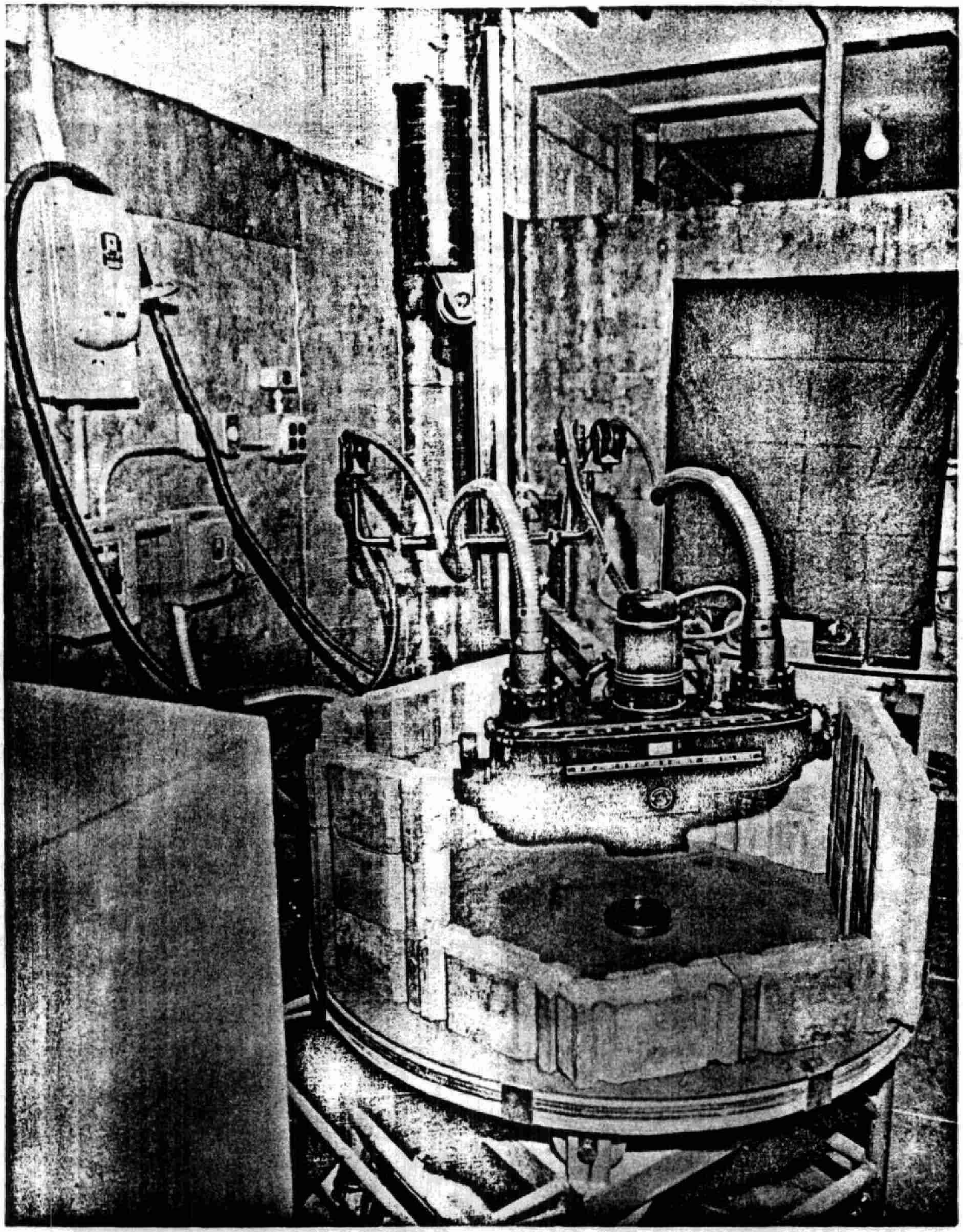


Figure 5. X-ray Facility with Sample in Place

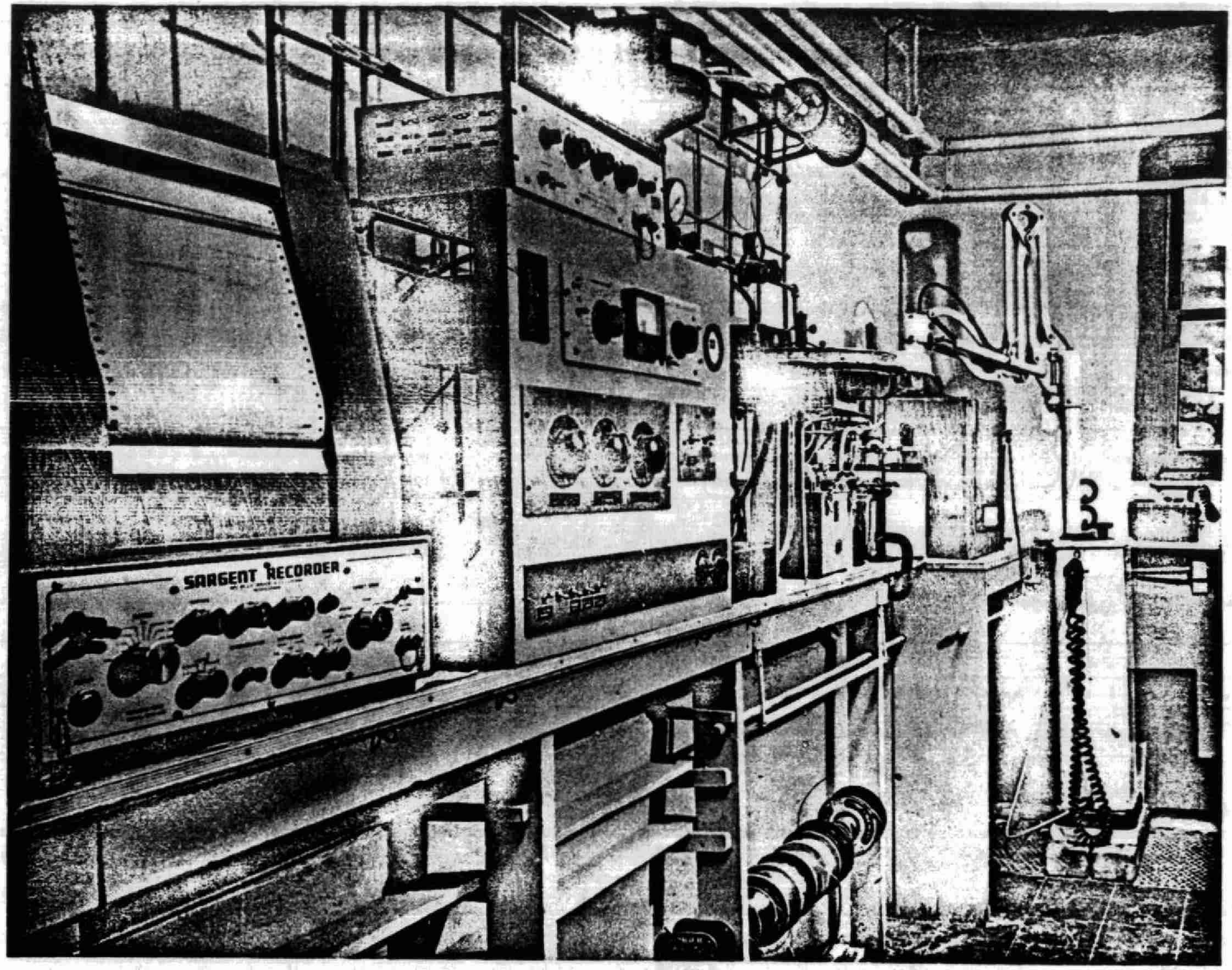


Figure 6. View of Laboratory Area and Equipment Devoted to Aerosol Studies.

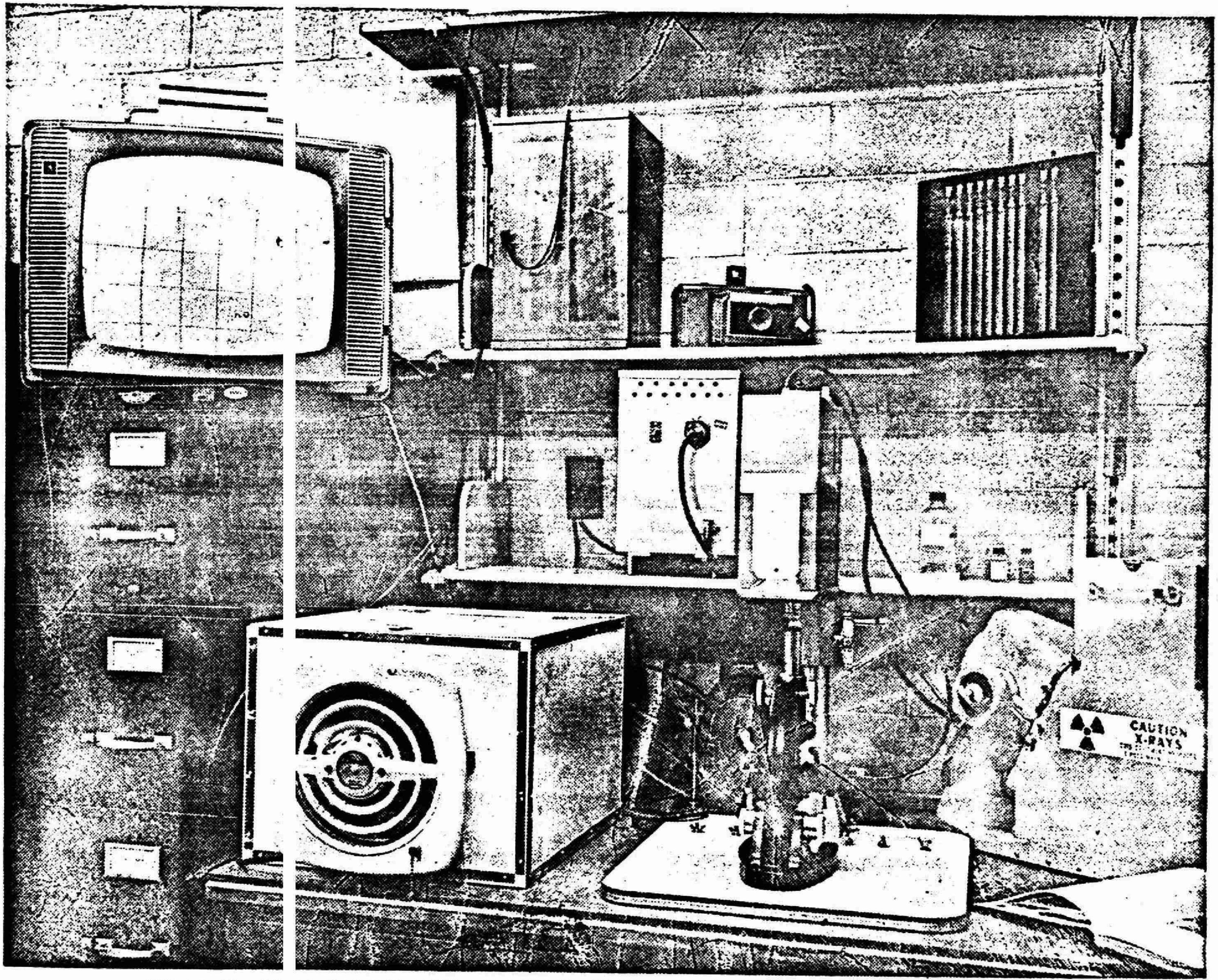


Figure 7. View of the Facility for Study of Microscopic Effects of Radiation on Emulsions

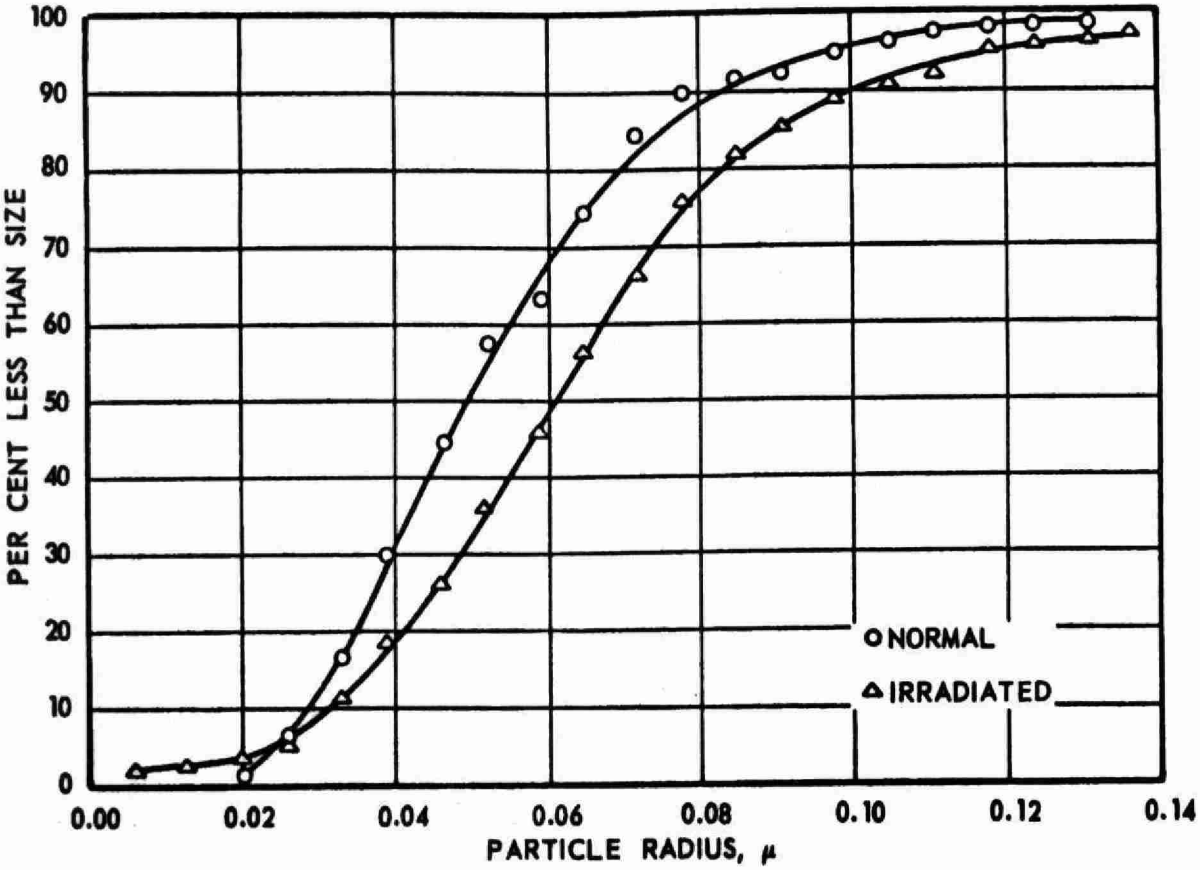


Figure 8. Particle Size Distributions for Normal and Irradiated Poly (methyl methacrylate) Aerosols.

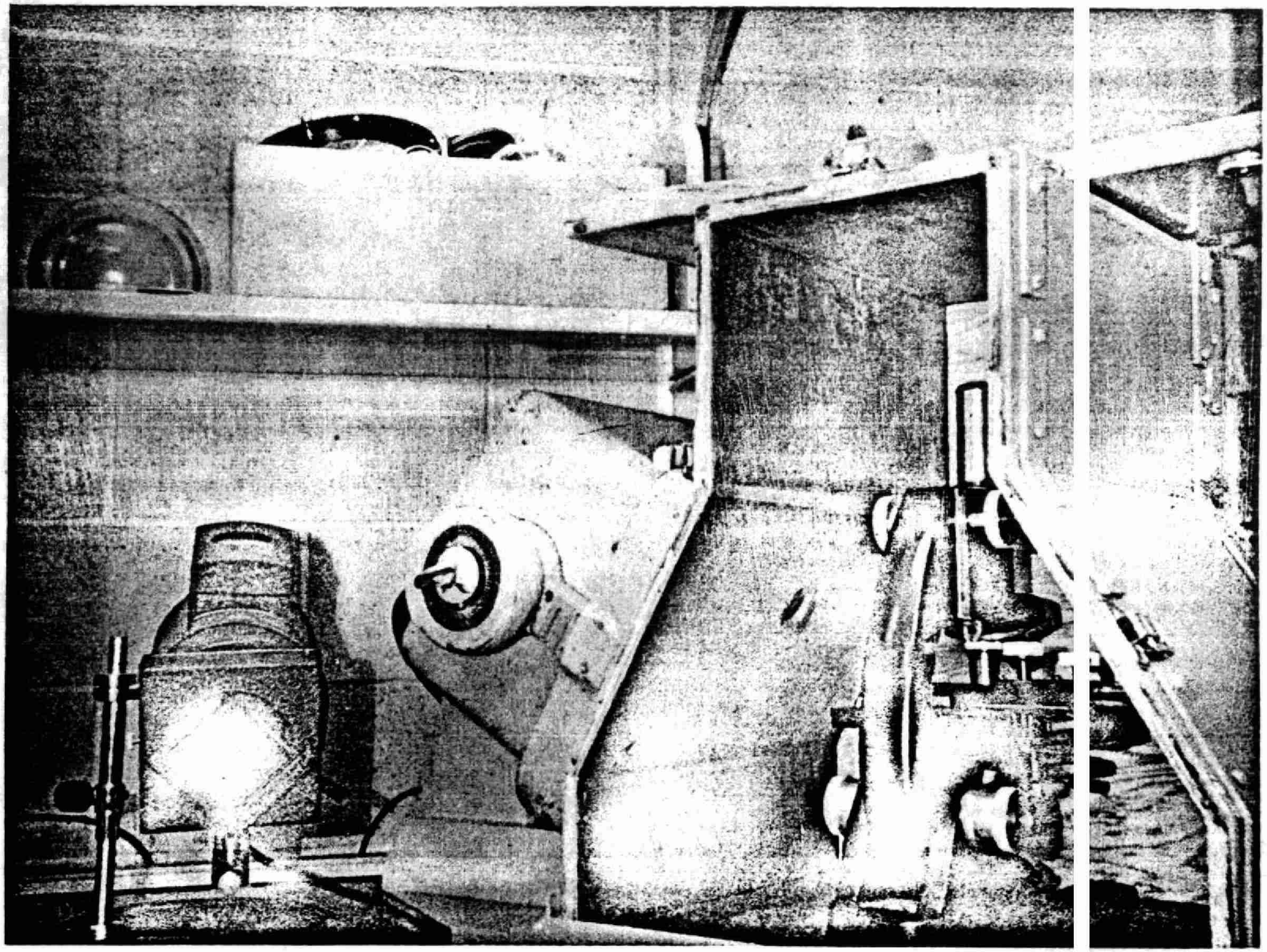


Figure 9. Close-up of Microscope in Irradiation Chamber; a Par of the Equipment Devoted to Emulsion Studies.

AFTER DINNER

SPEAKERS

TREATMENT OF WASTE LIQUIDS FROM THE MANUFACTURE OF CELLULOSE MEAT CASING

by

J. W. PFAFF

"TREATMENT OF WASTE LIQUIDS FROM THE MANUFACTURE OF CELLULOSE MEAT CASING"

by

J. W. PFAFF

A. THE PROBLEM

Waste liquids from the manufacture of cellulose meat casing contain sulphuric acid, traces of carbon bisulphide, sodium sulphate, sulphur in the form of a colloid and small particles of cellulose which form when waste viscose is discharged to the acid sewer. In addition, there are small quantities of carbon black and dyes which are occasionally discharged when colouring systems are cleaned. Because cotton is used in place of wood pulp in the preparation of the viscose, the concentration of sulphites is quite low. The result of this mixture is a liquid having a pH of approximately 2.5 and a suspended solids content that varies depending on the discharge of waste viscose. The pH occasionally goes to approximately 9 if large amounts of viscose or caustic are dumped.

B. PRELIMINARY WORK

Experimental work was carried on over four years on varying scales. Initially, work was concentrated on neutralizing only. A lime slurry was fed directly to the sewer under control of a pH measuring system. This system gave a widely fluctuating control, primarily due to the lack of reaction time, proper mixing and sampling, and was at best troublesome and unreliable.

The next step involved finding a method of removing solids and achieving better pH control. After working with two firms in the water treatment field and after a study of several samples, a pilot plant with a capacity of approximately 20 GPM was rented. This plant was based on the flotation principle and worked quite well when the concentration of viscose was right, but when the viscose concentration was low, the floc would not float and it was decided to use a settling system, because there was no way of controlling the amount of viscose present. This pilot plant was run for a while longer to obtain information on methods of pH control and to try to predict sources of trouble in a full scale system.

Lime was used as the neutralizing agent for most of the test run, but soda ash was used on a trial basis to see if any benefit could be derived from its use. With the pilot plant set up, no significant value in the use of soda ash was noted and because it costs approximately two and a half times as much as lime, lime was chosen as the neutralizing agent for a full scale plant.

C. THE FULL SCALE PLANT

The detailed design of a plant to handle 200 Imp. G.P.M. was started in February of 1962; construction started in May and the initial runs were made in late October. Satisfactory operation as far as effluent was concerned, was achieved by the latter part of November, but small changes were made on a continuing basis to improve the function of some components and reduce the attention required. The plant has no full time operator, but a mechanic makes a routine check about every hour and replenishes the chemical feed tanks as required. This system of operation appears to be satisfactory and as the operating personnel gain experience and further minor changes are made, the attention required can be reduced further.

The plant itself is contained in a building 48 ft. x 40 ft. and 20 ft. high under the trusses with a section 28 feet high over the holding tank. The schematic layout of the plant is as shown on the diagram.

All waste liquid is collected in a trench in front of the machines and flows by gravity to the acid sump A, which is acid brick lined. The sanitary sewage from the plant is not put into this system but discharges to the Town sewer system. Cooling water and rainwater are discharged to a separate storm water system.

Liquid is pumped from the sump by one of the pumps B while the other is on standby with automatic changeover. These pumps are in a pit and operate on flooded suction because experience showed that gases coming out of the fluid kill the prime, using even a low suction lift. The pump flow is controlled by sump level through an air-operated control system, which introduces some delay to iron out small surges in flow.

The pump discharges into holding tank C which holds the liquid for approximately fifteen minutes at design flow and agitates the liquid with a twin propeller mixer. The upper propeller is kept near the surface to aerate the liquid. Lime slurry is pumped into this tank under control of a pH recording controller system. The combination of lime and aeration is effective in eliminating the sulphurous odours. The level of this tank is controlled by a system similar to that used on the sump and small surges can be further reduced. The pH controller is set between 6.5 and 7.0 and gives a pH in the final effluent between 8.0 and 8.5.

The holding tank discharges by gravity to the clarifier D which is a standard design clarifier that was sandblasted and coated with a coal tar epoxy coating. This unit operates on the sludge recirculating principle and has a heavy duty sludge scraping system. The rotational speed of the sludge scraper was doubled after it jammed in the sludge bed. This speed increase seems to have solved the jamming problem.

The sludge formed in the clarifier is blown off into a collecting tank E which is agitated only to make pump out easier. The blow-off is timed with an electric timer and the rate is manually adjusted to hold an approximately constant sludge blanket level. When this tank is filled, it's automatically pumped out into decanting tank F.

In the decanting tank the sludge is allowed to sit. The particles settle to the bottom and a clear supernatant is left. The supernatant is pumped back to the clarifier and the sludge is pumped to a pit in the yard. The cycle in this decanting tank is timer controlled, with the settling time adjusted to give the longest time allowed by the rate of blow-off. Approximately four hours is the ideal time; beyond this very little settling takes place.

The sludge formed consists chiefly of calcium sulphate, some unused lime, sand impurities from the lime, colloidal sulphur and small particles of viscose. It is heavy and slimy but has no odour. The disposal of the sludge is the worst problem. Filtering was considered but did not proceed because the experience of the American Viscose Company which was outlined in a report on an almost identical problem, indicated that this was costly and bothersome. Some experimental work with a centrifuge, showed that quite a dry residue could be obtained. This was not pursued further because the capital cost of an automatic discharge system was high and difficulties were foreseen in handling the solids which were like peanut butter in consistency. At present, the sludge becomes fairly heavy in the pit and can be handled with a front end loader and dump trucks lined with polyethylene.

The pit banks were built up to five feet in thickness resulting in a mass of frozen sludge last winter. The depth will be limited to eighteen inches next winter. At this depth a heavy front end loader can pry out and break the frozen sludge in chunks. A pit approximately 40 feet by 150 feet and three feet deep will hold about three months' summer sludge and about one month's frozen sludge. Cleaning takes about one and a half days. Drying the sludge with waste heat from the incinerator was unsuccessful due to lack of temperature and surface in the dryer and it was not pursued further.

The plant auxiliaries include the lime slurry system and the chemical make-up and feed systems as well as a stacker type crane for unloading bagged lime which is received on pallets.

The lime slurry is made up using approximately 1,200 pounds of lime in 3,000 gallons of effluent water. This lasts 20 to 24 hours. This slurry is pumped with a 1,200 RPM all iron centrifugal pump and is fed to the holding tank or recirculated.

The coagulant aids are made up in batch form and pumped in with standard design piston metering pumps. The chemical system has low level alarms which give the operators ample warning of low tanks. Alarms are used to signal failure or abnormal conditions for the main components.

Tank G is a surge tank. When the acid filters are backwashed high flows beyond the capacity of the plant result. These high flows are collected in the surge tank and drained from it at approximately 7 GPM to the acid sump.

The effluent from the clarifier is run to the plant storm sewer where it is mixed with an approximately equal volume of cooling water and then discharged to a natural creek flowing along the plant property. Generally speaking, the plant operates well most of the time. Occasional sludge boils occur due to temperature change, but this does not have too long an effect on the effluent.

The start up did not present any serious problems. There were some difficultires, chiefly in the original lime slurry circulation system to overcome plugging. Operation has settled down to a set routine. There is scaling in the holding tank that flakes off and plugs lines if it is not knocked off about once a month to keep the pieces small and brittle. The clarifier coated with about 1/8" of scale, but this has not presented any problem and was probably due to poor pH control at the start as it is not building up now.

Different coagulant aids are being tried in an effort to reduce the chemical cost. This cost and the cost of sludge removal represent the major expenses beyond depreciation. These are approximately as follows:

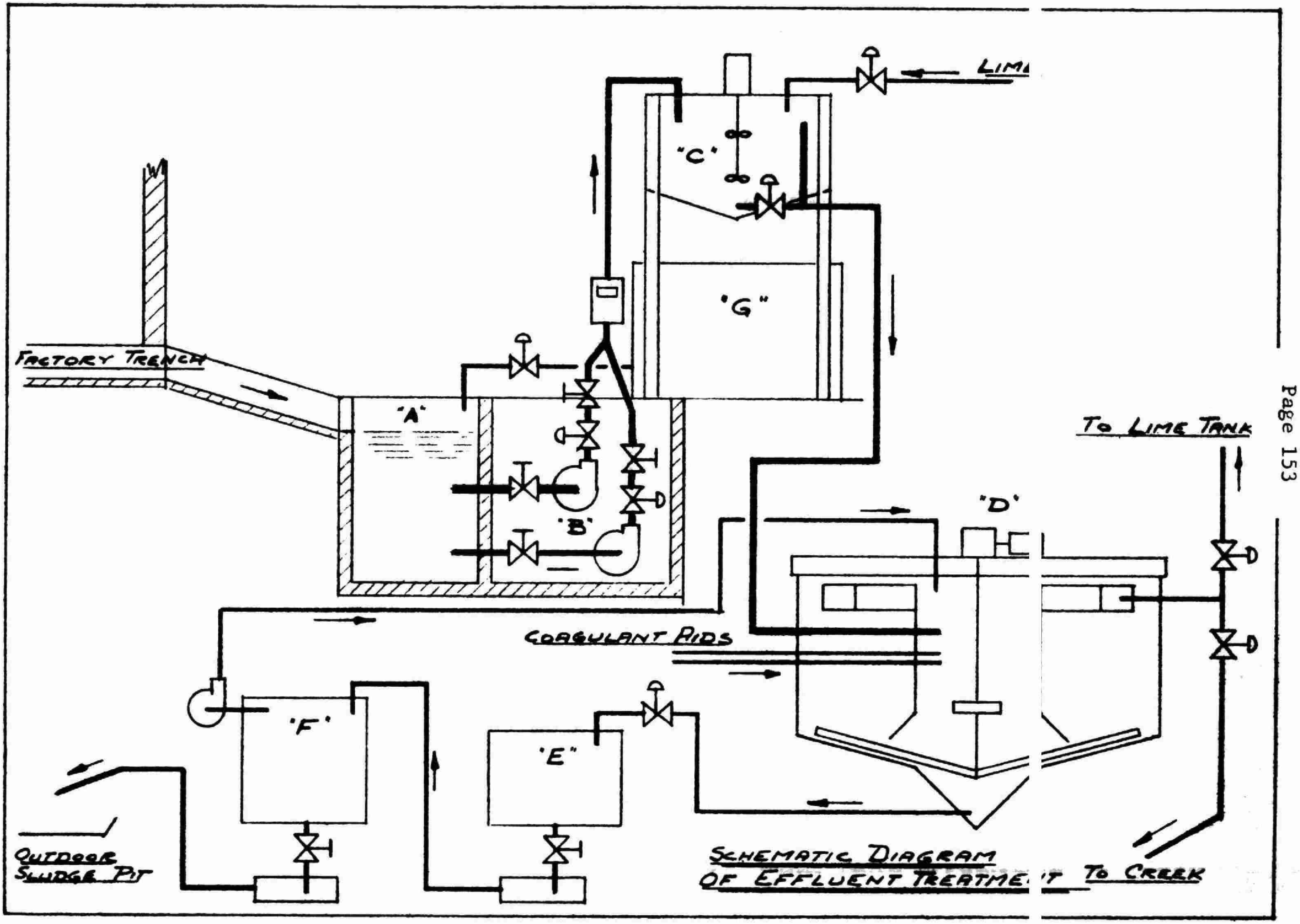
Lime	7.9¢/1,000 gal.
Alum	0.7¢/1,000 gal.
Coagulant Aids	1.1¢/1,000 gal.
Chemical Total	9.7¢/1,000 gal.

Sludge removal is estimated at $ 1,000/yr. or about 1.9¢/1,000 gallons.

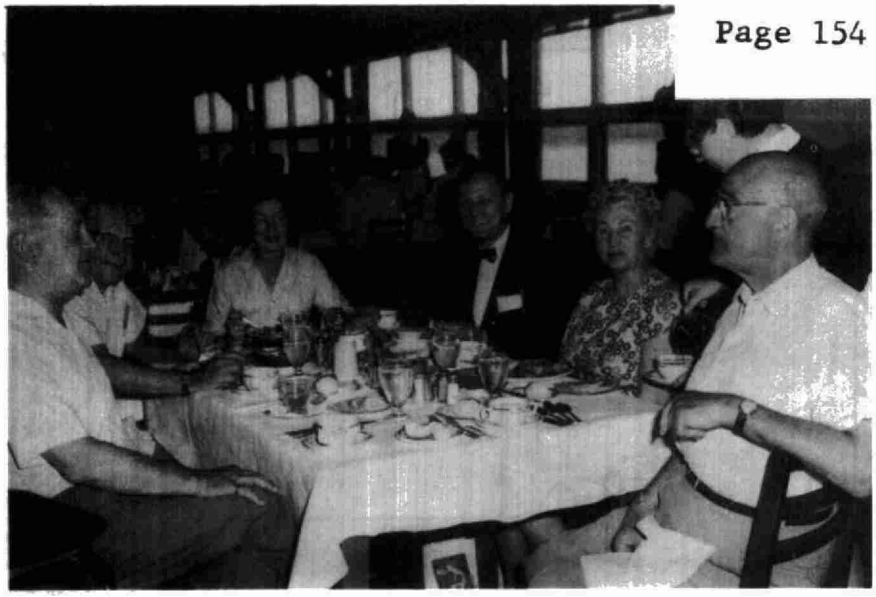
Labour is presently about 6¢/1,000 gallons but should decrease.

The total cost then is about 17.6¢/1,000 gallons.

The foregoing covers the main parts of our system and their function. We hope it has been interesting to you. Thank you for your attention and if there are any questions, I will attempt to answer them.



SCHEMATIC DIAGRAM OF EFFLUENT TREATME T



THE BANQUET

VARIATION OF ORP IN AN ACTIVATED SLUDGE PLANT WITH INDUSTRIAL WASTE LOAD

by

J. T. O'ROURKE

SESSION FOUR

Dr. A.E. Berry
Canadian Institute On
Pollution Control

Session Chairman

"VARIATION OF ORP IN AN ACTIVATED SLUDGE PLANT WITH INDUSTRIAL WASTE LOAD"

by

J. T. O'ROURKE

INTRODUCTION

During the past two decades many investigators have considered the use of oxidation-reduction potential (ORP) measurements for the control of operations in sewage and industrial waste treatment systems. Early studies by Moore, et al (1) developed basic formulations for ORP relationship to bacterial systems by using pure cultures in sewage. The same author, as did others (2,3,4,5), also investigated oxidation-reduction potential development in activated sludge systems. The degree of activity of biological systems has been related to ORP measurements by some investigators (6). There are also several studies reported in the literature of the relationship between anaerobic treatment and ORP, as well as the control of anaerobic systems by this parameter (7,8).

Waste treatment plant odour control, aeration control in activated sludge processes, digestion monitoring and influent monitoring are among the wide variety of applications for oxidation-reduction potential measurements. Influent monitoring is one of the most important considerations in the control of industrial waste treatment processes. In the role of influent monitoring, ORP measurements can render a valuable service to chemical treatment processes as well as to biological treatment processes. It would alert the plant operator to any abnormal conditions in the plant influent stream - for instance, a heavy "slug" of oxidizing or reducing compounds that could possibly upset a chemical or biological treatment process. The above is by no means meant to detract from the value of ORP measurements as an in-plant control parameter in activated sludge systems. The exemplification of the value of ORP as an in-plant control parameter is to be the primary objective of this paper.

OXIDATION-REDUCTION POTENTIAL

In general terms, ORP is a basic relation between the ratio of the concentrations of the oxidants and reductants in any chemical or biological system. A qualitative comparison between ORP and dissolved oxygen is presented in Figure 1. The rate of change of ORP is much greater at very low levels of dissolved oxygen. In a given system at higher levels of dissolved oxygen, the ORP does not change as rapidly with a change in concentration of oxidants. The normal ranges of ORP of the various biological environments - namely, aerobic, anaerobic and facultative - are also shown in Figure 1.

The basic reaction of the oxidation-reduction potential is expressed mathematically as

$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{oxidants})}{(\text{reductant})}$$

where E_h = potential measured

E_o = voltage in millivolts of the reference electrode

R = universal gas constant

T = absolute temperature, degrees K

n = number of electrons transferred

F = Faraday's constant

(oxidants) = concentration of oxidants present in system

(reductants) = concentration of reductants present in system

The standard oxidation-reduction potential is normally related to a hydrogen reference electrode. However, due to the inherent difficulties encountered with the hydrogen reference electrode, it has been common practice to utilize other reference electrodes. The reference electrodes which have found the greatest application are the calomel electrode and the silver-silver chloride electrode. In order to equate the calomel or the silver-silver chloride electrode to the standard hydrogen electrode, it is necessary to correct for the differential voltage or E_o in the preceding equation.

There are a number of conditions which affect the potential itself as well as the rate of changes of potential in these systems. In biological systems such as activated sludge the following factors have been cited by Rohlich (9) as being significant:

1. Ratio of concentration of oxidant to the concentration of reductant,
2. Temperature of system,
3. Tendency of materials to be oxidized or reduced, and
4. Hydrogen-ion concentration

Other researchers (6,7) have stressed the fact that ORP is a measure of the intensity of a system rather than its capacity for oxidation or reduction.

Throughout the years, there has always been some confusion as to the conventions used in reporting oxidation-reduction potentials. Much of this "befuddlement" is clarified in a report by Kehoe and Jones (10). These authors outline the various reference electrodes and their relationship to the standard hydrogen electrode and the various noble metal electrodes in use. They also point out the limitations of ORP measurements as well as the precautions to be exercised in the calibration of the measuring devices.

A complete discussion of the theory of oxidation-reduction potential is beyond the scope of this study. However, these principles are more fully discussed in periodicals and text books on electrometric measurements (7,11).

HISTORY OF BELLEVILLE, ILLINOIS SEWAGE TREATMENT PLANT

The sewage treatment plant at Belleville, Illinois, where this study was made, began operations in 1940 (12). By 1950 the plant was enlarged to accommodate increases in both industrial and residential waste loads. All of the existing units in this conventional activated sludge plant were enlarged and high-rate roughing filters were installed between the primary sedimentation and aeration facilities. No intermediate sedimentation facilities were provided for the "sloughed" solids from the filters.

Extremely low sludge density indices and large populations of Sphaerotilus created tremendous operating difficulties. These difficulties were attributed to the high carbo-hydrate content of the influent waste and the erratic organic load received at the treatment plant. These operational problems culminated in the decision in 1956 to convert the existing conventional activated sludge plant to the Kraus nitrification process. Since 1956 this plant has continued to use the Kraus modification method with only minor changes in plant piping.

A schematic diagram of the current sewage treatment facilities at Belleville, Illinois is presented in Figure 2, and the detention times for the various units of the treatment plant are given in Table I. The "roughing" filters shown in Figure 2 were not in use during the period of study. These units are placed in operation around May of each year and taken out of service about December. This time period coincides with the periods of increased organic loading on the system.

The normal volume of nitrified sludge is approximately 0.5 MGD of which 0.45 MGD is return activated sludge and the remainder, or 0.05 MGD, is digester liquor. This mixture of return activated sludge and digester liquor is aerated for a theoretical detention period of twenty-four hours.

TABLE I

DETENTION TIME IN TREATMENT UNITS

BELLEVILLE, ILLINOIS

Treatment Unit	Capacity (ft^3)	Average Detention Time (hrs) Week Days	Week-end
Primary sedimentation	40,000	1.07	1.45
Aeration	197,000	5.27 (3.67)*	7.16 (4.50)*
Nitrification	65,000	24 **	24 **
Trickling Filters	71,000	--	--
Final sedimentation	101,400	2.40 (1.87)*	3.68 (2.32)*

* Based on raw waste flow plus recirculation

** Based on secondary sludge return and digester liquor.

Selected average operational results for the calendar year of 1962 and for the month of March, 1963 are presented in Table II. It is of interest to note the high operational efficiency as indicated by the reductions in both BOD and suspended solids.

The plant is currently treating an organic load equivalent to a population of approximately 135,000 per day, of which approximately 35,000 is contributed by the domestic population of the city, while the remaining 100,000 is from industrial and commercial sources. The majority of this industrial waste load is from a local brewery.

The breakdown of water users in Table III will serve to outline the proportion of the industrial contributors. The above-mentioned contributors are the major waste sources. There are also many other smaller "typical" commercial and industrial contributors.

DESCRIPTION OF FIELD STUDIES

From operating data at this plant it was known that the total organic load during the week was four to five times as great as the weekend load. The measurement of chemical oxidation demand (COD), dissolved oxygen (DO) and ORP were selected as those parameters of most significance in the study of a waste treatment plant utilizing the Kraus modification of the activated sludge process. The condition of extreme weekly cyclic loading to the plant (without changes in plant operation) represented an opportunity to observe the resultant change in DO and ORP. Other tests which were made included pH, temperature and BOD of selected composite samples.

As most of the large waste contributors operated on a five-day week, the studies were made on Sunday and during mid-week to illustrate best the effects of the extreme variation.

On both types of day (mid-week and Sunday) the above-mentioned analyses were made on the plant influent, primary sedimentation basin, primary effluent channel, aeration basin and final effluent at various time intervals. More detailed evaluation on the change in DO and ORP through a typical aeration basin were made on each day.

TABLE II

AVERAGE OPERATIONAL RESULTS

BELLEVILLE, ILLINOIS SEWAGE TREATMENT PLANT

Characteristic	Raw Sewage	Final Effluent	Percent Reduction
BOD, mg/1			
1962	385	16	95.8
March 1963	355	16	95.5
Suspended Solids, mg/1			
1962	279	14	95.0
March 1963	259	18	93.1
Flow, MGD			
1962	5.05	--	--
March 1963	5.65	--	--

TABLE III

MUNICIPAL WATER USE BY INDUSTRIAL AND COMMERCIAL ESTABLISHMENTS

Type of Industrial or Commercial Users	Working Days Per Week	Daily Water Use gals/Working Day
Brewery	5	1,360,000
Slaughtering	5	19,600
Foundries	5	96,000
Hospitals	7	212,000
Schools	5	76,500
Convalescent homes	7	23,800
Bottling works	5	23,200
Motels and recreation	7	69,700
Miscellaneous	5	159,000

Hourly flow measurements were obtained from a continuous recorder and totalizer on the plant influent line.

DISCUSSION OF RESULTS

The variation in flow rate and organic loading rate as measured by COD throughout the study period is presented in Figure 3. The average flow rate on Sunday was approximately 5 MGD and varied from 4.0 MGD to 5.7 MGD. The week-day average flow rate was approximately 6.9 MGD with a minimum rate of 4.8 MGD and a maximum rate of 8.8 MGD.

The range of COD in pounds per hour for Sunday was from 234 to 517 with an average of 324, while the week-day COD loading ranged from 2,680 pounds per hour to a low of 175 with an average of 1,330. This represented a gross variation of 15 fold in organic loading throughout the study period.

As previously mentioned, temperature and/or pH can influence ORP values. Consequently, both temperature and pH observations were made at the same time as the ORP determination. All of these analyses were performed at each unit throughout the plant. Inasmuch as the temperature through the plant did not vary more than 1° Centigrade, and the pH did not vary more than 0.6 units during the study, the effect of these variables was insignificant.

The change in flow rate, as well as organic loading, had a direct effect on the DO and ORP in the various units of the plant. The DO and ORP throughout the treatment plant for a typical Sunday and week-day are presented graphically in Figure 4. As would be expected, the trend of ORP through the plant was closely related to the DO.

The raw sewage arrived at the sewage treatment plant in a non-septic condition on both week-day and Sunday as indicated by both DO and ORP values. In spite of a relatively short detention time in the primary sedimentation basin, the DO and ORP was markedly reduced. This rapid reduction of ORP and DO in the primary can be attributed to the readily degradable nature of the raw sewage. The DO and ORP increased as the waste discharged over the effluent weirs of the primary sedimentation basin. The effluent from the aeration basin contained a relatively high ratio of dissolved oxygen to soluble degradable organic material as indicated by the ORP and DO. Due to the continued biological activity in the final clarifier, although at a reduced rate, without the benefit of additional air supply, there was a significant decrease in both ORP and DO.

Of particular interest is the change of ORP and DO through a typical aeration basin. With the extremely heavy week-day organic load, the ORP decreased to a minimum of 0 millivolts at approximately the one-fourth point through the basin. Beyond this point of minimum ORP in the basin, the potential rapidly increased to +130 millivolts at the effluent end of the basin. In contrast, the ORP on Sunday did not decrease at any point in the aeration basin. Instead, there was an increase in ORP to a maximum of +130 millivolts just beyond the mid-point of the aeration basin and remained stable throughout the remainder of the basin. These results indicate that reserve aeration capacity was available on Sunday, while on the mid-week day the full aeration capacity was needed to obtain the same degree of stabilization as indicated by the ORP. The DO values through the aeration basin for the mid-week day and Sunday further substantiate the complete utilization of the basin capacity on the week-day.

Samples of mixed liquor were collected at the inlet and outlet ends of an aeration basin. ORP was determined immediately upon collection and after thirty minutes. The ORP of the sample from the inlet of the aerator decreased from +20 millivolts to -85 millivolts, while the outlet sample decreased from +130 millivolts to only +95 millivolts during the same time period. This difference in change of ORP represents first, the stabilized condition of the effluent, second, the activity of the microorganisms in the mixed liquor, and third, the high rate of biological utilization at the inlet to the basin.

The settleability of the sludge in the mixed liquor from the aeration basin is indicated graphically in Figure 5. The volume of the compacted sludge after only fifteen minutes was 30 percent of the original volume of mixed liquor. The relatively low value of 58 percent volatile material in the mixed liquor, resulting from the addition of digester liquor through the Kraus process, contributes to the rapid settling rate.

The high rate of biological conversion of soluble organic material to rapidly settling cellular material resulted in approximately 96 percent BOD removal and 94 percent suspended solids removal during the study.

SUMMARY

The 15 fold variation in organic loading at the Belleville, Illinois sewage treatment plant which utilizes the Kraus modification of the activated sludge process created a significant variation in dissolved oxygen and ORP levels throughout the plant when comparing week-day operations with weekend operations. ORP values in the aeration basin ranged from a minimum of -5 to a maximum of +130 millivolts during the weekly cyclic loadings received at the plant. At various points in the aeration basin throughout the study the DO varied from 0 mg/1 to a high of 6.2 mg/1.

A critical review of ORP and DO data obtained, relating to the aeration basin in particular, indicated that the plant was operating at a level during the week which utilized practically all of the aeration capacity. On the other hand, there appeared to be excess aeration capacity used on weekends as evidenced by high DO and ORP attained only part-way through the aeration basin. By the use of ORP it would be possible to regulate or adjust not only the volume of air supplied but also the point of greatest need for increased air supply during periods of heavy organic loads.

The measurement of the rate of change of ORP to indicate the activity of mixed liquor is possible and was demonstrated in this survey.

High reductions in soluble organic material and suspended solids have been accomplished at the Belleville, Illinois sewage treatment plant by the employment of the Kraus modification of the activated sludge process, even though approximately 75 percent of the organic material discharge to sewer system is from industrial sources.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Mr. Irvin G. Knoebel, Superintendent, Sewage Treatment Plant, Belleville, Illinois and to his very capable assistant, John Rathweiler, for the cooperation and many suggestions as well as for the benefit of their experience, without which this paper would not have been possible. Appreciation is expressed to Mr. Robert Rock, Research Associate, Washington University, for giving up his otherwise free time to assist in the collection of portions of the field data.

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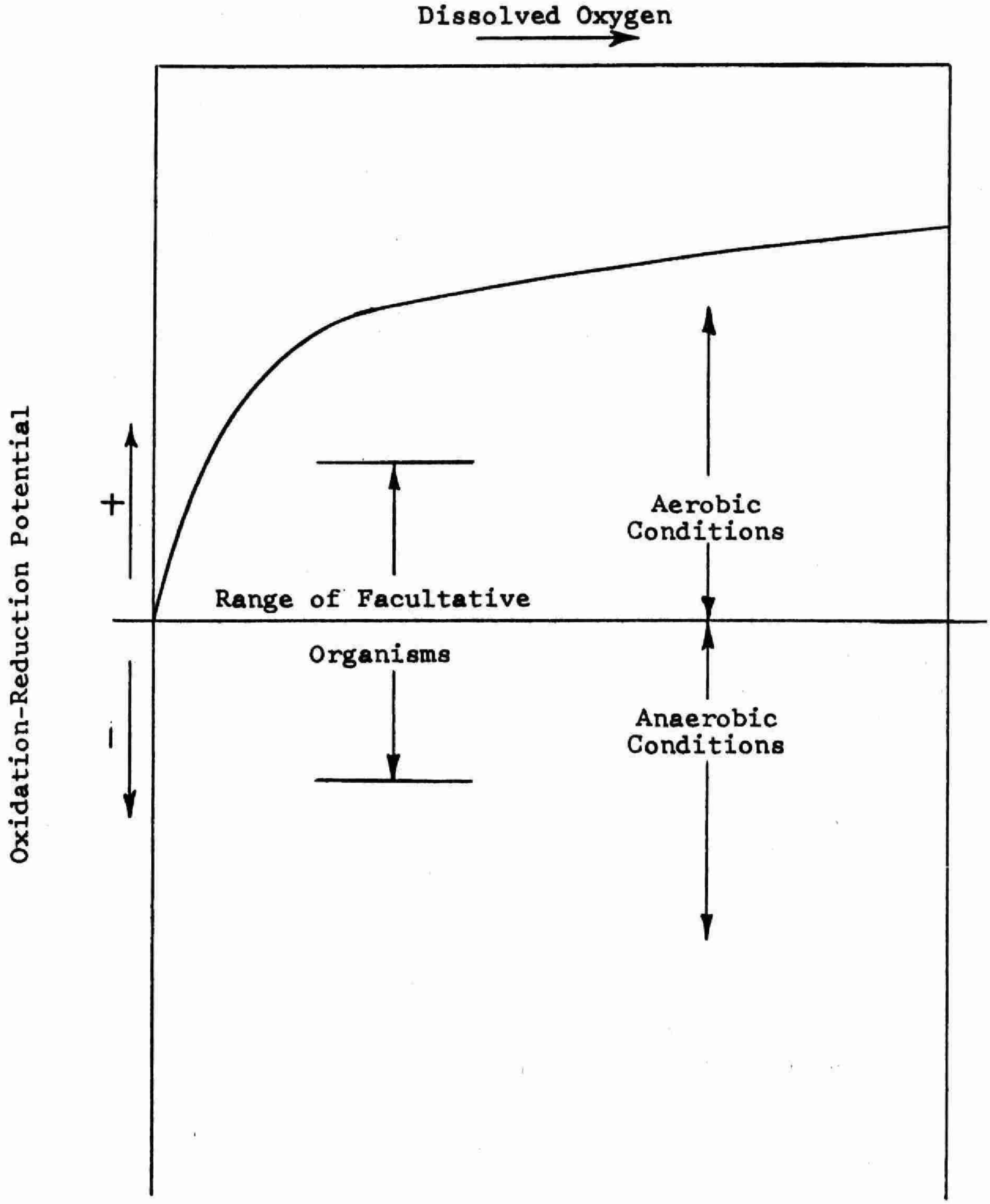


FIGURE 1 QUALITATIVE RELATIONSHIP BETWEEN ORP AND DO

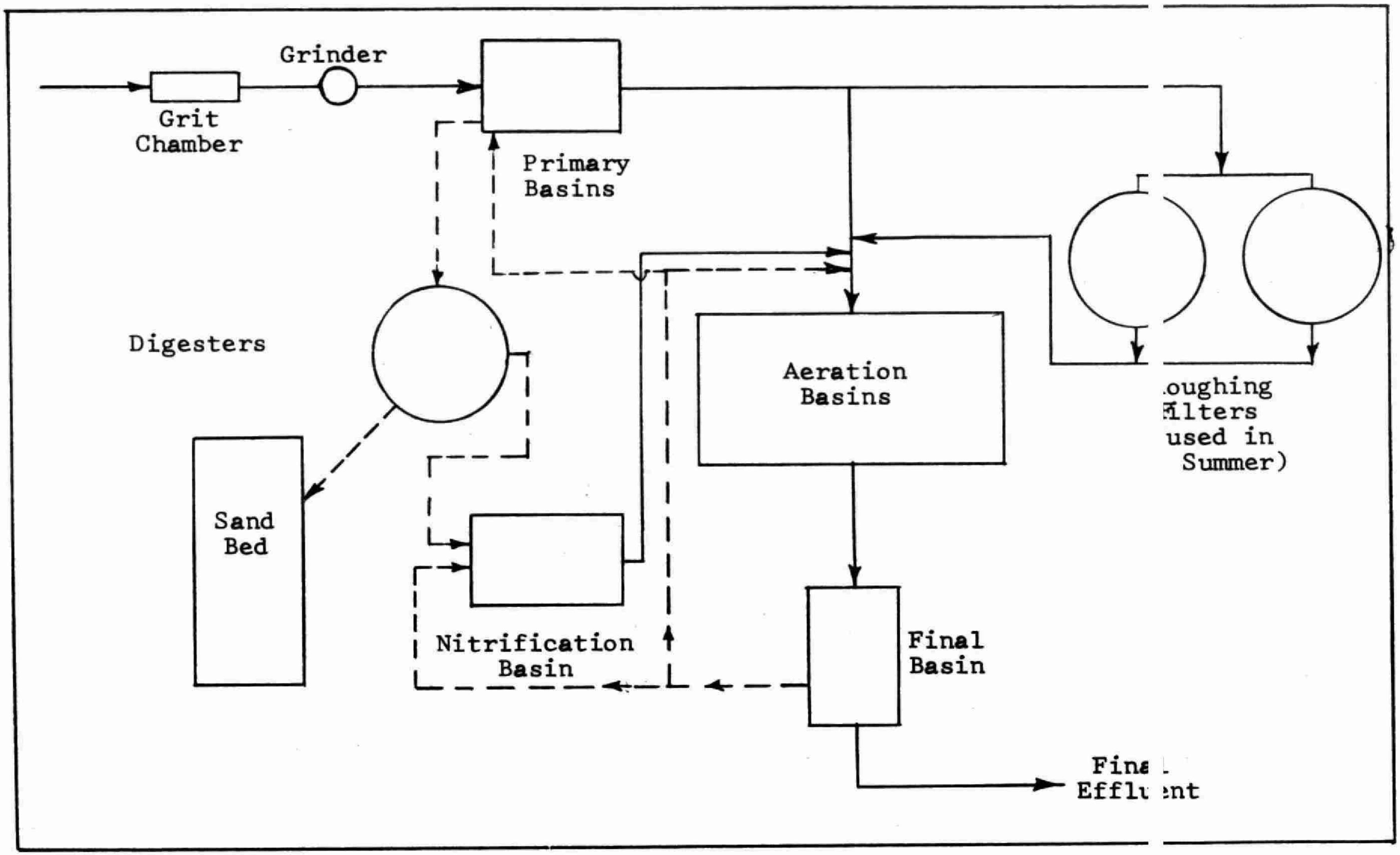


FIGURE 2 SCHEMATIC DIAGRAM OF ACTIVATED SLUDGE PLANT AT BELLEVILLE, ILLINOIS

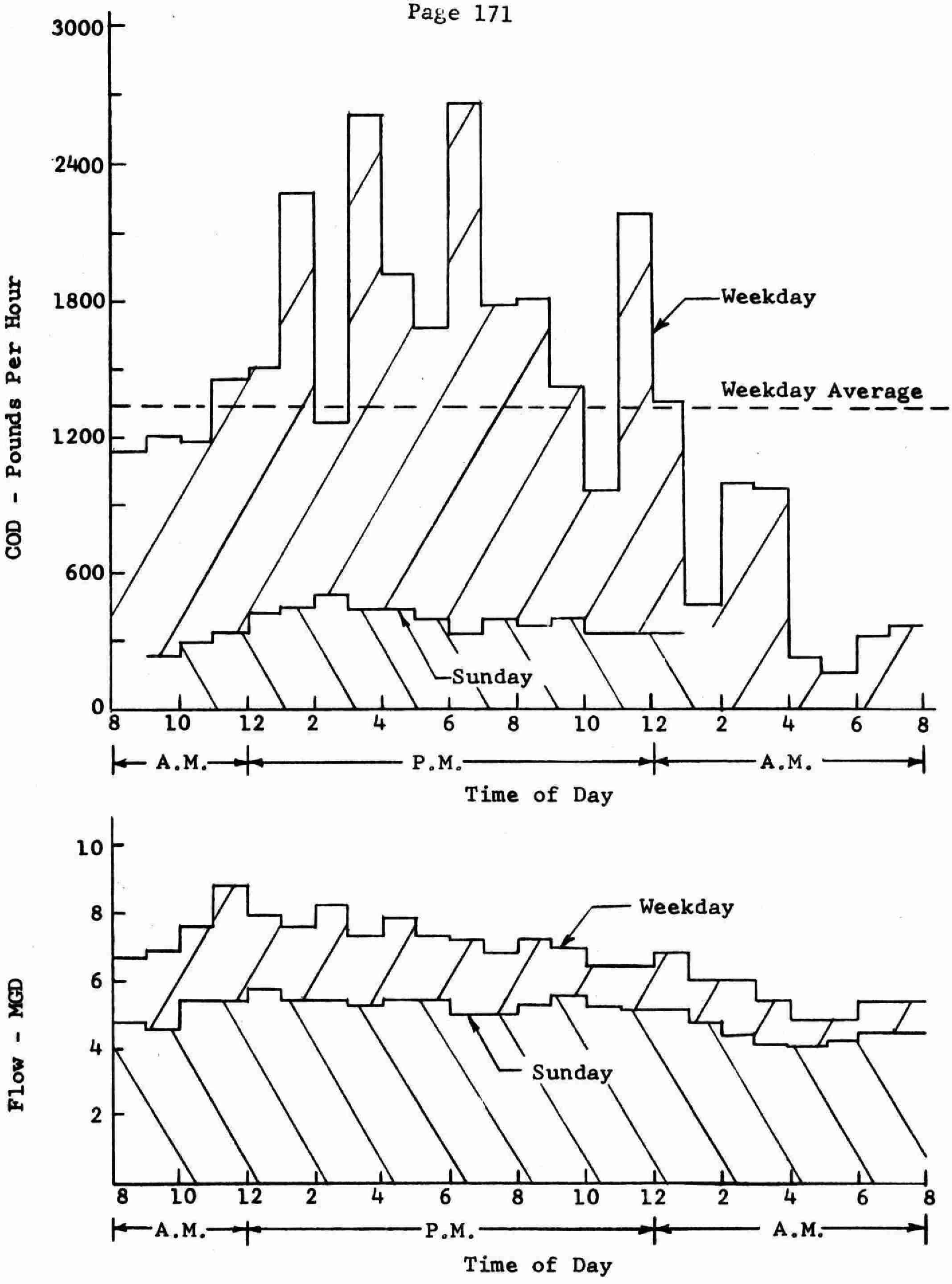


FIGURE 3. VARIATION IN FLOW RATE AND COD LOAD AT SEWAGE TREATMENT PLANT AT BELLEVILLE, ILLINOIS

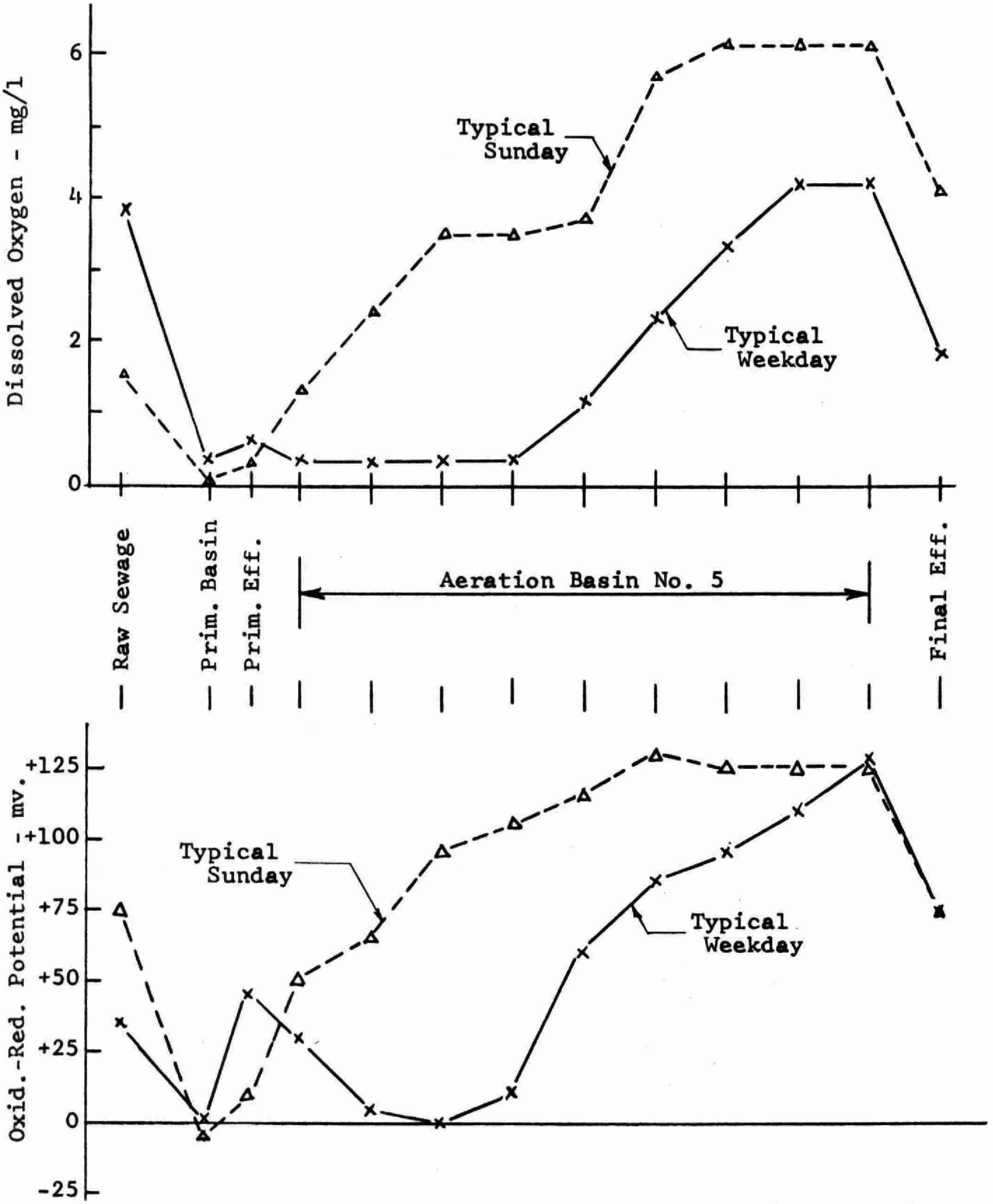


FIGURE 4 VARIATION OF DO AND ORP THROUGH TREATMENT PLANT

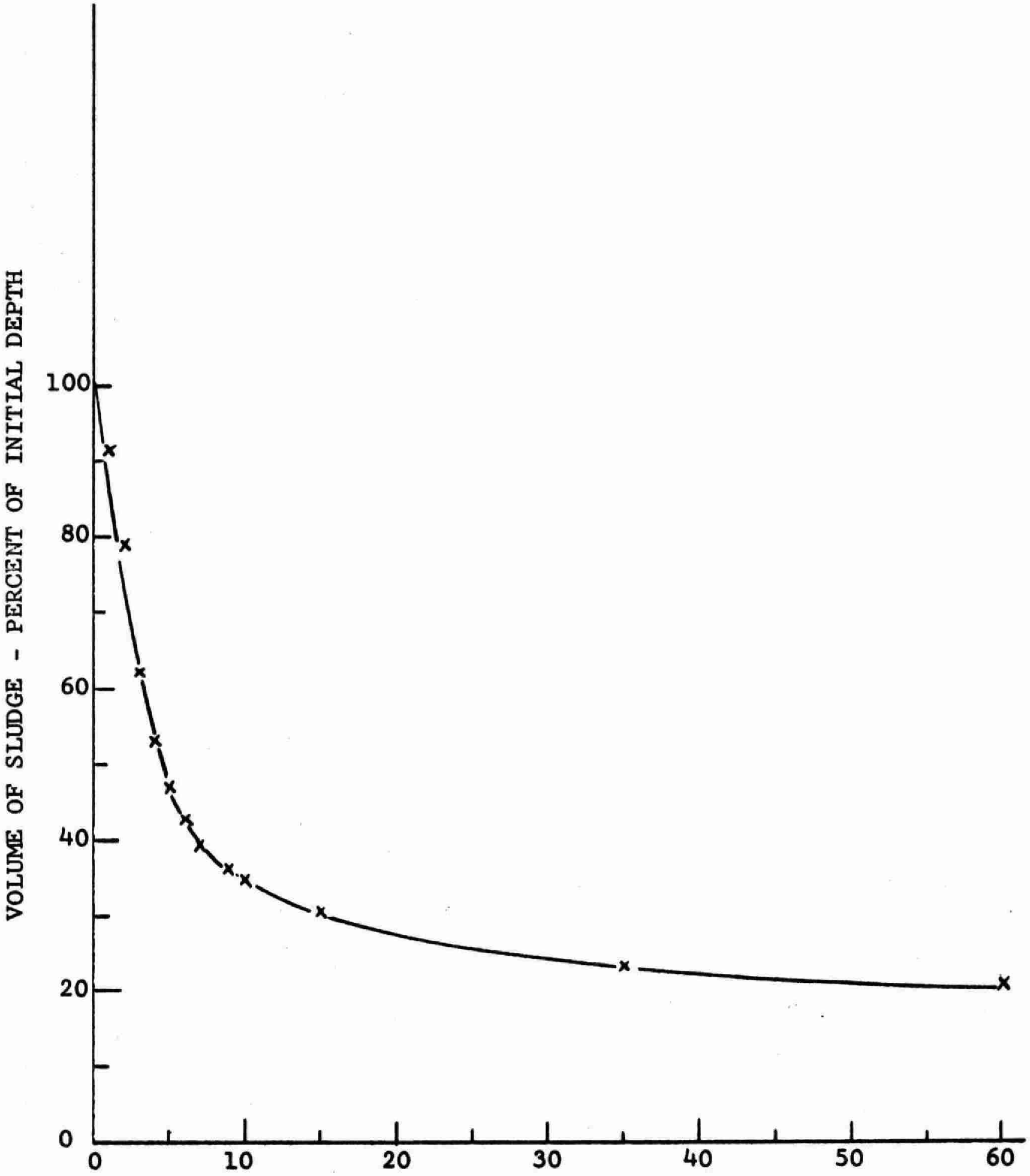
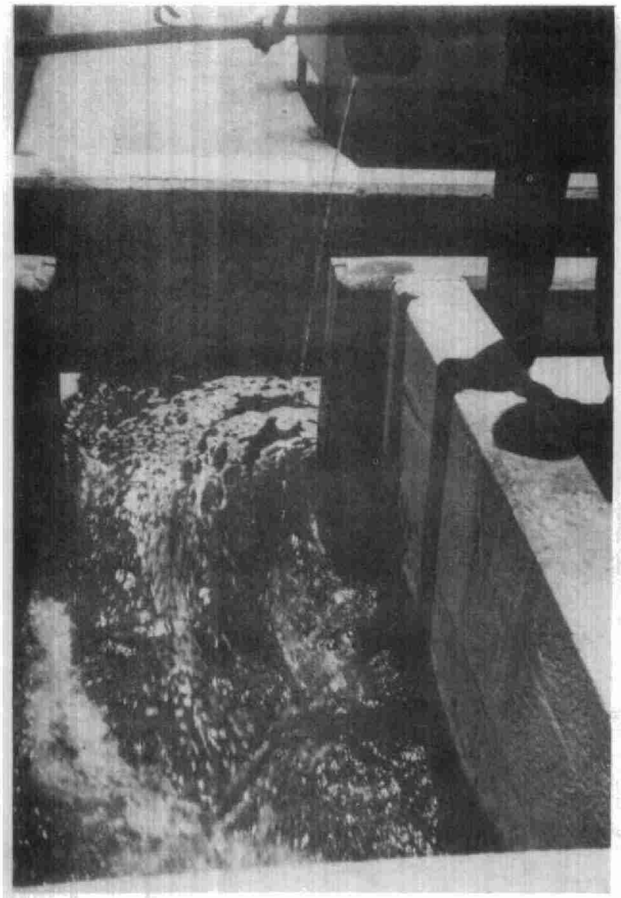
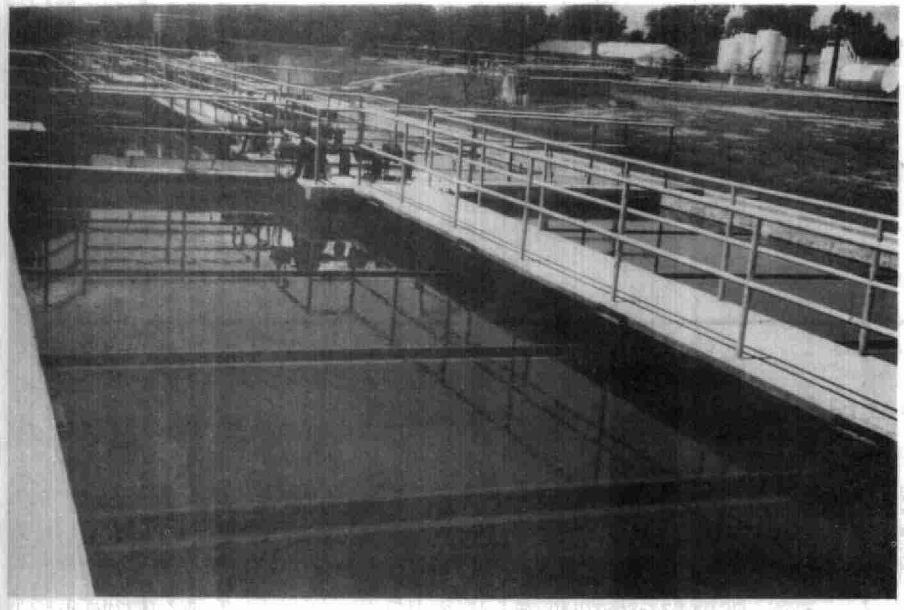
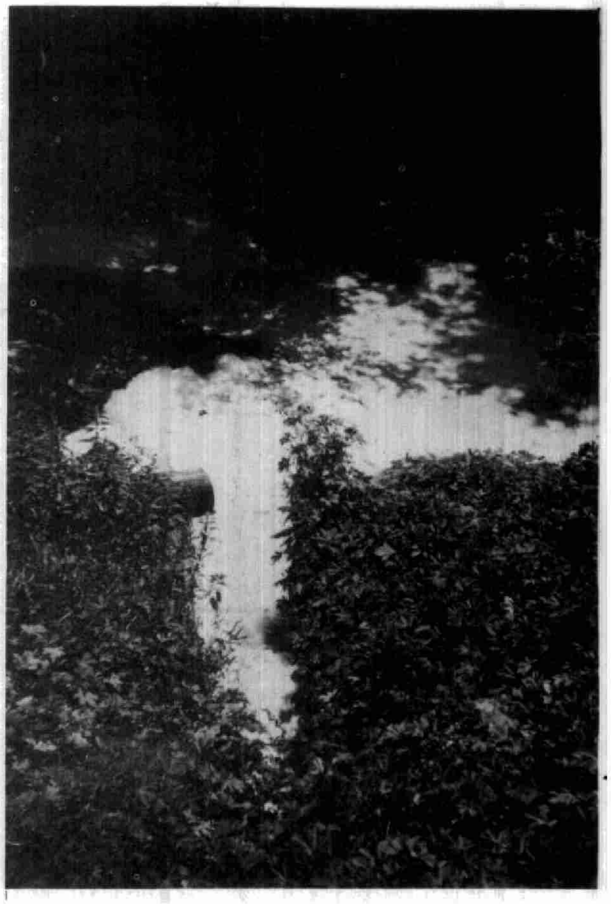
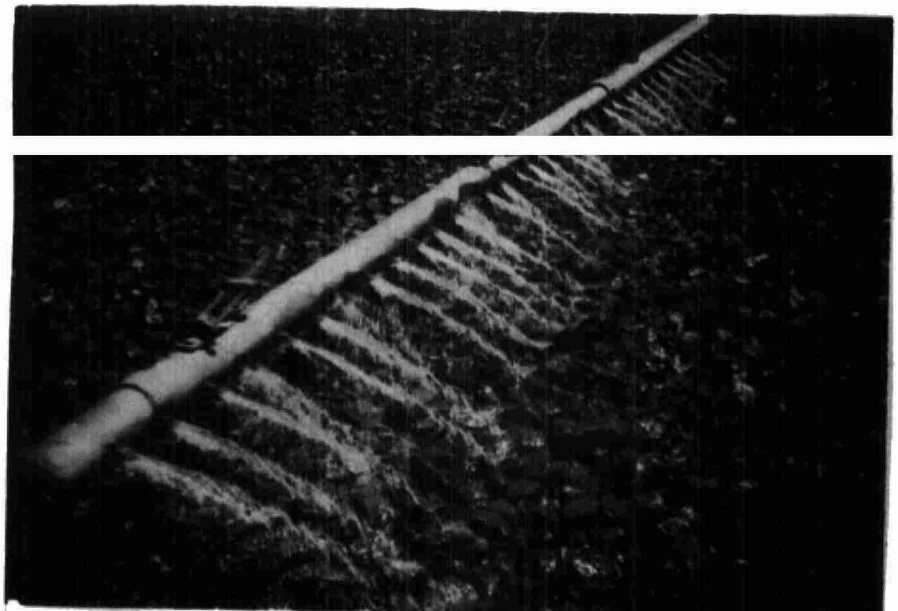


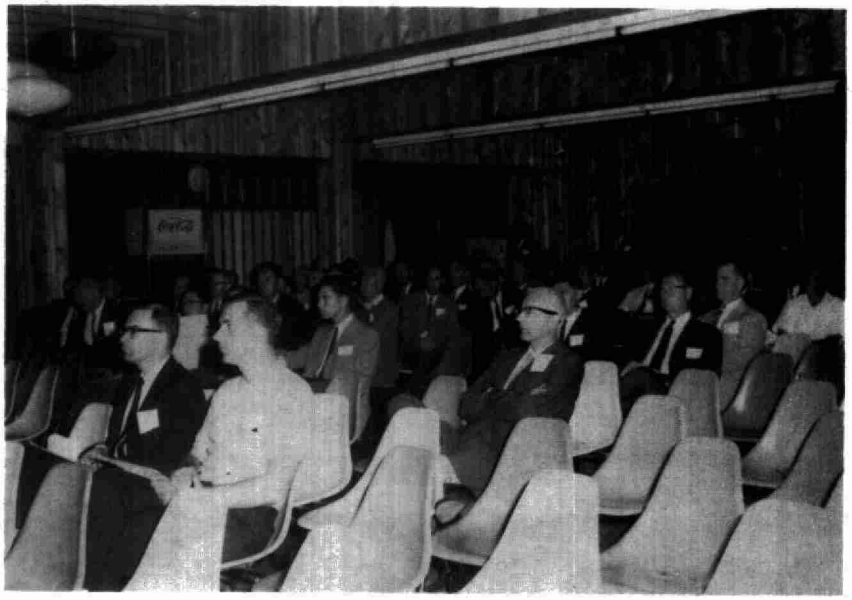
FIGURE 5 SETTLEABILITY OF ACTIVATED SLUDGE FROM BELLEVILLE, ILLINOIS PLANT

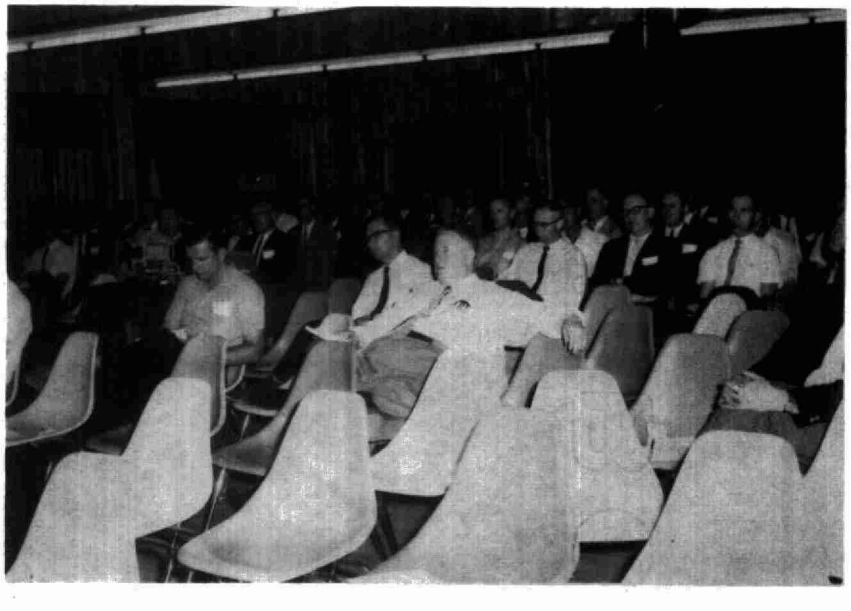












TECHNICAL SESSIONS

THE POTENTIALITY OF ACTIVE CARBON IN THE TREATMENT OF INDUSTRIAL WASTES

by

E. A. SIGWORTH

"THE POTENTIALITY OF ACTIVE CARBON IN THE TREATMENT OF INDUSTRIAL WASTES"

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Industrial wastes constitute such a wide variety of compounds that Moore and Turcotte (1) have stated, "No design for an industrial wastes treatment project can be 'taken off the shelf.'" Active carbon is one of the many potentials resting on the shelf of the designing engineer, but all too frequently it is relegated to an obscure position on the shelf and ignored or forgotten. This is probably due to the misconception that active carbon is an expensive treatment. In some cases this is quite true, yet in other instances it is the least expensive of all presently known methods.

With the recent development of new chemical compounds which resist biological degradation, active carbon is being given much more serious consideration in the wastes treatment field. Foaming problems associated with the use of synthetic detergents have been widely publicized and are well known to all of you here. Also equally well known is the fact that the active component of these detergents, alkyl benzene sulphonate (ABS), resists biological degradation in waste treatment plants. Wastes from laundries, particularly the new coin-operated units, are being seriously considered by health officers. In fact, in some States, regulations are in existence governing the ABS content of such wastes. As a result many firms have developed package units for treatment of laundry wastes, and the most successful units for providing the desired degree of treatment involve the use of powdered active carbon, usually in conjunction with alum coagulation. Granular active carbon units are being seriously studied as a tertiary treatment for domestic wastes, but this can admittedly be quite expensive when all additional costs are considered.

Existing uses

Active carbon is presently being employed in a number of industrial applications for reclaiming solutions which otherwise might constitute wastes. An example is the dry-cleaning industry where active carbon is utilized to treat the used solvent for removal of color, fats, oils, etc., thus permitting re-use of the solvent for further cleaning. The usual practice is to pump the carbon slurry into a pressure filter to form a carbon layer through which the solvent is circulated continuously. Small establishments may use 2 to 5 pounds of carbon per week, which is certainly inexpensive when compared to alternatives of distillation or discarding the solvent.

Another wide-scale use of active carbon is in the plating industry for reclamation of electro-plating solutions. Organic additives to electro-plating solutions will decompose in time, at the temperatures involved, and cause difficulties. These decomposed organic compounds are removed at intervals with active carbon, permitting reconstitution and re-use of the plating solution. Similar applications have been employed in treatment of dye wastes and pickle brines.

Active carbon has also been employed for reclamation of spent hydrochloric acid, spent sulphuric acid, spent thiosulphate in sulphur-dye wastes, transformer oil, ethylene chloride, and aniline from diphenylaniline wastes. Even in the food industry materials such as scrap candy, pickle brines and maraschino cherry syrup have been re-used after treatment with active carbon. A very recent addition to this list is a di-decyl ester of phthalic acid which had been used for cleaning metering pumps. All of these applications have resulted in economical savings through re-use of valuable products, and el [illegible] their discharge as wastes into water courses.

There are many other potential uses for active carbon in the treatment of organic industrial wastes, particularly now that so much attention is being directed to the effect on water quality when such wastes are discharged into rivers and streams. A more thorough knowledge of the principles involved in the use of active carbon will undoubtedly suggest economic solutions to many waste disposal problems.

Types of Activity

The Langmuir theory proposes that the active carbon surface consists of different types of patches arranged in a checkerboard pattern. In our experience we have confirmed that there are at least three different types of active patches. One type will adsorb odours, phenol and iodine, and these might be visualized as the blank squares shown in figure 1. The other two types, illustrated by cross-hatched areas, will adsorb various dyes and color bodies from solution. Since types of active surfaces will vary among different grades of active carbon, proper selection of specific grades is essential to obtain optimum results.

Influent of Solubility on Adsorption

A very important factor involved in the use of active carbon is that adsorption is a fight against solubility. Thus compounds having a low degree of solubility are readily adsorbed, while highly soluble compounds are adsorbed to a much lesser extent. Although there are a few exceptions to this rule, it is quite generally applicable where active carbon is to be used.

Thus we can generalize by saying that since most organic compounds are sparingly soluble in water, these are readily adsorbed on active carbon. However the degree of solubility is still an influencing factor. For example benzene is sparingly soluble in water and therefore readily adsorbed. When we convert benzene to phenol by adding a hydroxyl radical (OH) to the ring, the solubility is increased resulting in a lower degree of adsorption. Then if phenol is neutralized with caustic soda, solubility is further increased by formation of the sodium phenolate salt, which is not appreciably adsorbed. In addition to phenol (carbolic acid) most other organic acids such as acetic, benzoic, formic, maleic, oxalic and tartaric are capable of removal with active carbon. Neutralization of any of these acids with an alkali would decrease adsorption.

The pH of the solution thus assumes importance for optimum adsorption of organic compounds. In the case of organic acids the pH must be maintained at a sufficiently low level to prevent formation of the corresponding salts. In the specificcase of phenol, adsorption diminishes appreciably as the pH is raised to 8.6 and higher.

In contrast with organic acid adsorption, aniline is poorly adsorbed from an acid solution. Removal is greatly increased as the pH is raised to 7.0, beyond which adsorption remains constant. (2) From the experiences with organic acids it would seem logical that higher pH values would be favorable for the adsorption of organic bases. This has been confirmed by studies on propyl and butyl amines showing maximum removal as the pH was raised to 12.0.(3) pH is also important in adsorption of inorganic chemicals, but this will be discussed later.

Affect of Solvent

In the case of organic compounds best efficiency is to be expected from a water solution because of lower solubility. However, in chemical processing, higher solubilty is often required necessitating the use of other solvents such as alcohol, ether, carbon tetrachloride, etc. Since degree of solubility can differ with the various available solvents, proper selection is important particularly if active carbon is to be used in subsequent processing. A high degree of solubility would be desirable where carbon is to be utilized to remove unwanted impurities. However, if the solvent is to be stripped for recovery of the dissolved chemical, then a lower degree of solubility would be preferred. Re-use of solvent, through purification with carbon can prove a real economy, while at the same time reduce or completely eliminate a waste problem.

Influence of Time

Time of contact varies from a few minutes to several hours if full utilization of the carbon is to be obtained. Some academic studies have indicated a period of days before adsorption equillibrium is established. Such protracted time periods are usually not practical in commercial usage, so three hours is usually a maximum allowable period of time. With powdered active carbons, adsorption is reasonably complete in a matter of 15 to 30 minutes. In some instances, such as low temperature or high viscosity, longer times are beneficial. With granular active carbons longer times are required for the impurities to reach the internal active surfaces. Where granular active carbons are utilized in percolation columns, residence time of the liquid in the carbon bed becomes a very important factor.

Influence of Temperature

Theoretically, elevated temperatures result in increased molecular motion, thus giving increased opportunities for impurities to contact and be adsorbed on the active surfaces of carbon. This theory is born out in actual practice in many applications, such as removal of colour from sugar solutions and vegetable oils. Care must be exercised that temperatures are not carried to the point of damage to the material being treated, such as caramelization of sugars.

On the other hand volatile compounds are more readily removed at lower temperatures. This is particularly evident in the adsorption of materials from air or other gases. In fact active carbons utilized in gas purification can frequently be regenerated by heating or steaming the carbon column to volatilize the adsorbed materials.

Influence of Concentration of Solution

The last traces of any impurity are most difficult to remove by adsorption. Conversely best results are obtainable when the impurity is present in high concentrations. Therefore maximum carbon efficiency is obtained if it can be utilized before any dilution takes place.

This is illustrated in table 1 and figure 2 showing adsorption studies on different concentrations of phenol in water. Figure 2 shows the results in table 1, plotted on log-log paper using $\frac{X}{M}$ values as the abscissa and C values as the ordinate, where X is the weight of phenol adsorbed, M is the weight of carbon used, and C is the concentration of phenol remaining in the solution. Thus the adsorption isotherms show the amount of phenol adsorbed on carbon at varying degrees of removal.

The top line shows results with a starting concentration of 2% of phenol, and may be visualized as typical of a segregated waste from a complex industrial operation. Removal of 90% of phenol, (namely a residual concentration of 0.2%) is represented at the far left end of the adsorption isotherm where the $\frac{X}{M}$ value is about 160 milligrams per gram of carbon.

If the specific waste is not segregated, but is permitted to blend with wash water and other wastes, we might expect a dilution ratio of at least 10 to 1. This stage is illustrated by the next line, where the starting concentration is 0.2%. Here it will be noted that the amount of phenol adsorbed by a unit weight of carbon has dropped noticeably to about 130 milligrams of phenol per gram of carbon.

Next let's presume the industrial wastes are discharged to a sewage treatment plant where further dilution takes place. Considering a further 10 to 1 dilution at this stage, the phenol concentration would be reduced to 0.02% and adsorption is illustrated in the third line. A further drop in the $\frac{X}{M}$ value is quite evident.

Finally let's consider that the sewage effluent is discharged to a stream where a further dilution of 100 to 1 takes place before the water reaches the intake of a downstream water treatment plant. The bottom line illustrates this condition with the phenol concentration being only 0.0002% (2ppm). To accomplish 90% removal of phenol at this stage of dilution the $\frac{X}{M}$ value has dropped to about 20 milligrams per gram of carbon, as compared to 160 in the top isotherm. Thus it is evident that greater carbon utility is attainable by treatment at the point of highest waste concentration.

Desorption

Adsorption differs from normal chemical reactions in that materials retained on the carbon are usually in their original condition and not changed chemically. Thus the potential exists for releasing these adsorbed impurities so the carbon can be re-used, and possibly recover the adsorbed impurities as valuable compounds.

Although potentials exist for desorption of active carbons used in gas adsorption, present discussions will be limited to carbons which have been utilized to treat solutions.

Theoretically, odorous compounds are volatile in nature, and therefore should be released by the application of heat. Unfortunately, early efforts in the water field to regenerate granular active carbon units by steaming techniques resulted in such limited success that this treatment was abandoned in favor of complete replacement of virgin active carbon.

An extremely important consideration in desorption is that conditions which are poor for adsorption should be good for desorption. Returning to the principle that adsorption is a fight against solubility, it is therefore logical that changing conditions to increase solubility should result in desorption. This suggests two basic factors, namely changing the pH of the eluting liquid or changing the solvent.

These conditions are illustrated in the case of phenol in Table II. Since phenol is more readily adsorbed at a low pH utilization of a high pH should result in release of phenol as the phenolate salt. Results show that raising the eluting pH to 11.0 removed less than one quarter of the phenol held on the carbon. Although other independent investigators have demonstrated practically 100% recovery of organic acids by a simple change of pH, it is evident from these studies that phenol is held on the carbon more tenaciously.

Investigations were therefore extended to include a change of the solvent, in which benzene was chosen as the eluting solvent. Results show recovery of nearly 70% of the adsorbed phenol. This, therefore, offers the possibility of recovery of a valuable product through adsorption and desorption techniques.

A third potential for desorption is the addition of a more readily adsorbable material which will replace and thus release adsorbed material to the eluting solution. This principle is illustrated in the additional results recorded in Table II. Here benzene is considered as being more adsorbable than phenol and therefore should result in elution. Results, without pH adjustment, show about 64% desorption of the phenol. Combining the principle of utilization of a more adsorbable compound with transformation of the phenol to a more soluble state, resulted in desorption approaching 68%.

Early work on the concentration of penicillin is an excellent example of adsorption and desorption. Penicillin was adsorbed as penicillic acid. The carbon slurry was then adjusted with alkali to form the penicillin salt. Then amyl acetate, being a more readily adsorbable material, was added to accomplish further release of the penicillin salt from the active surface of the carbon. The eluent from this concentration stage resulted in a solution containing several hundred times the original concentration.

An extremely interesting situation developed in this work on penicillin. The consumer insisted on being supplied a quality of carbon which would retain the greatest amount of penicillin. As the process became less secretive it developed that the most important factor was the amount of penicillin which could be eluted from the carbon. With this subsequent knowledge it was learned that a less active carbon could accomplish almost equal adsorption, but much greater proportions were released in the desorption stage. Thus a process which would probably still be in existence today is a thing of the past. This is mentioned to illustrate the need to consider the varying degrees of active surfaces available on different grades of active carbons.

Methods of Application

Active carbons are available in many particle sizes ranging from a very fine powder to coarse granules. Powdered forms of carbon are most extensively used in industry because of their ready adaptability, with minor expenditures for equipment. The manner of use is illustrated in figure 3. The liquid to be treated is pumped into the mixing tank, powdered carbon is added, and agitated for the proper period of time (usually 20 to 30 minutes). The mixture is then pumped through the filter press and run to storage. Granular active carbons are usually employed in a percolation system, in which the granules are placed in a large column and the solution is pumped upward or downward through the carbon bed. These columns are usually 3 to 40 feet deep, and rate of flow will vary from ½ gal. to as much as 5 gals. per square foot per minute.

Inorganic Compounds

It has been only very recently that information has come to light indicating potentials for active carbons in the treatment of inorganic compounds. Most organic compounds, as previously mentioned, are capable of adsorption by active carbon. In contrast active carbons are quite selective in their removal of specific inorganic substances. Here again, with some notable exceptions, the degree of solubility plays a role similar to that of organic compounds.

Metallic ions such as sodium, potassium, calcium and magnesium are not appreciably adsorbed with active carbon. Under optimum conditions, copper, zinc, nickel and cadmium are only slightly adsorbed; gold, lead and iron are appreciably adsorbed, and antimony is strongly adsorbed. Molybdenum, silver and tin are adsorbed to such an extent that the carbon might be smelted for recovery of the metal.

Studies indicate that pH of the solution is of paramount importance for optimum results in metallic ion adsorption. Iron, copper, zinc, nickel, cadmium, lead and silver are best adsorbed at pH of 5.0 to 7.0. Removal fails off as the pH is lowered and usually none of these, except silver, are adsorbed at a pH of 2.0 or lower. Molybdenum is strongly adsorbed at a pH of between 2.0 and 3.0 with practically no adsorption at 0.5 or less and also at pH levels above 4.5. Tin appears to be strongly adsorbed at pH levels of 0.5 to 2.0, with efficiency falling off as the pH is lowered. Antimony is strongly adsorbed even at a pH below 0.

Rather extensive studies on molybdenum indicate that the type of acid used can also influence the best pH to obtain optimum adsorption. That the degree of stripping is tied in closely with pH and the acid used, is graphically illustrated in Figure 4. The milligrams of molybdenum adsorbed per gram of carbon are plotted against pH, where 60% stripping is obtained. Results with three different carbons are shown. Solid lines illustrate curves for sulphuric acid, demonstrating that optimum results are obtained at a pH of 2. Dashed lines show similar curves for hydrochloric acid, and here the optimum pH appears to have shifted to 3.0. This is particularly evident with the more active carbon A, where nearly 16% loading was obtained.

Since molybdenum is not appreciably adsorbed below a pH of 0.5 or above a pH of 4.5, these are conditions which can be considered for desorption. Studies conducted with a dilute caustic soda solution resulted in better than 90% elution of molybdenum from the carbon. Furthermore the resulting solution contained 40 times more molybdenum than was present in the starting solution. Readjustment of the carbon to a lower pH should permit re-use of the carbon for further adsorption and desorption operations.

Utilization of strong acid for desorption was not studied, but offers potentials for separation. For example adsorption at a pH of 2.0 should result in the removal of molybdenum, tin, antimony, and small amounts of silver. Any iron, copper, zinc, nickel and cadmium would remain in solution since they are not adsorbed at this pH.

If the carbon containing the various adsorbed metals is treated at a pH of 0.5 we might expect to elute all of the silver and molybdenum, and possibly some of the tin. If the carbon is then treated with a solution at a pH of below 0, it is probable that all of the tin would be removed, leaving only antimony on the carbon. These possibilities have not been investigated, and therefore are conjectures based on studies of individual compounds. Nevertheless they suggest potentials for selective separation through controlled conditions of adsorption and desorption.

Other inorganic compounds which are capable of adsorption are --- gold, hexavalent chromium (which is partially adsorbed and partially reduced), chlorine, bromine, iodine and permanganate.

In evaluating laboratory results it is well to bear in mind that plant scale applications of active carbon usually are more efficient than those obtainable in small scale laboratory experiments. In fact it is usually possible to use half the laboratory dose in plant operations. If economics are questionable, based on laboratory results, pilot plant studies should be conducted to determine whether greater efficiency is possible in plant practice.

Conclusion

Although active carbons are presently utilized for the treatment of a fairly large number of industrial waste products, many other potentials exist for such a versatile purification tool. Greater knowledge of the principles involved in the use of active carbon should suggest applications which might disprove the belief of some individuals that treatment costs are too high to justify application to industrial wastes.

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TABLE I

Phenol Adsorption Studies

Initial Concentration ppm	Carbon Dosage(M) gm/liter	Phenol Removed(X) mg.	Phenol Remaining(C) mg.	$\frac{X}{M}$ mg/gram
20,000	70	13,482	6,518	193
20,000	80	15,259	4,741	191
20,000	90	15,823	4,177	176
20,000	100	17,008	2,992	170
2,000	10.0	1,366	634	137
2,000	14.0	1,725	275	138
2,000	16.5	1,835	165	111
2,000	18.0	1,874	126	104
200	1.0	94.4	105.6	94.4
200	1.4	126.6	73.4	90.4
200	2.0	163.6	36.4	81.3
200	2.5	180.6	19.4	72.2
2.0	0.037	1.30	0.70	35.2
2.0	0.057	1.55	0.45	27.2
2.0	0.062	1.63	0.37	26.3
2.0	0.082	1.75	0.25	21.3

TABLE II

Desorption Studies

Phenol concentration on carbon equivalent to 123 mg/gram

Elution Medium	% Phenol Eluted
Water - pH 11.0	23.9%
95% Water, 5% Benzene, pH 5.9	64.3%
95% Water, 5% Benzene pH 11.0	67.7%
Benzene	69.0%

FIGURE 1—Langmuir Theory

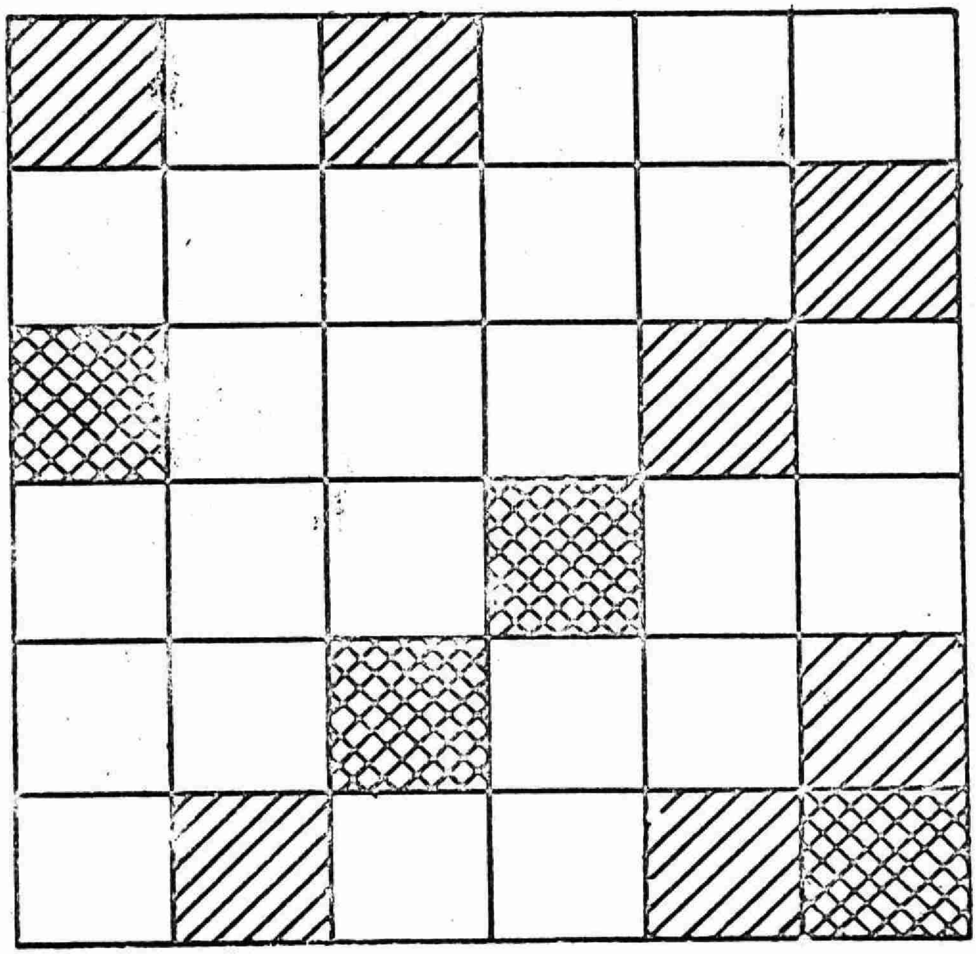


FIG. 2
PHENOL ADSORPTION ISOTHERMS OF DIFFERENT CONCENTRATIONS

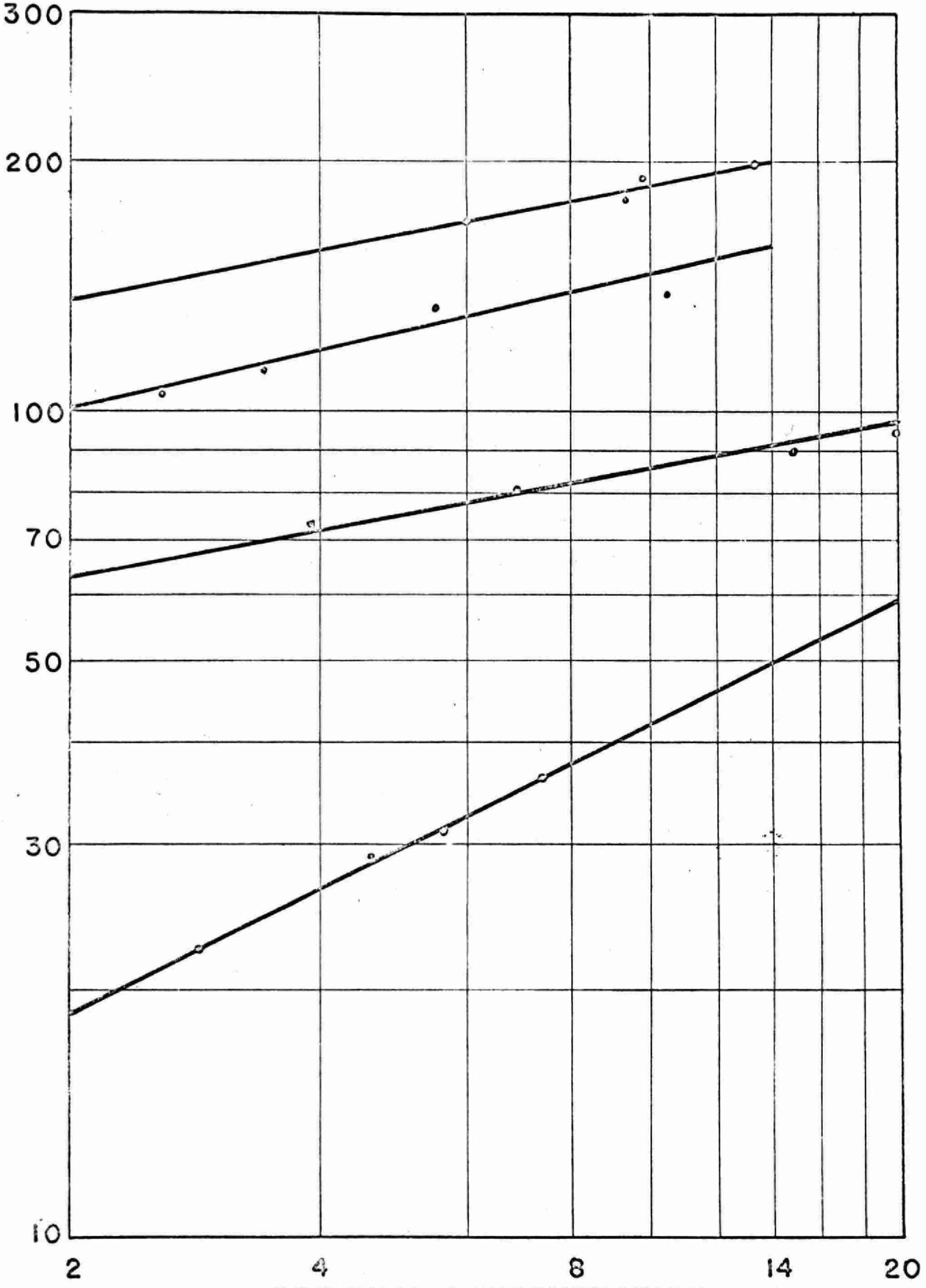


FIGURE 3

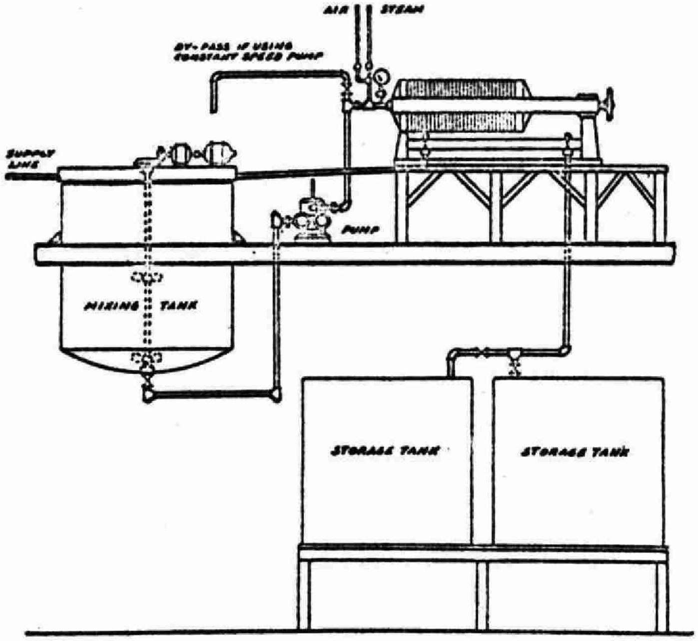
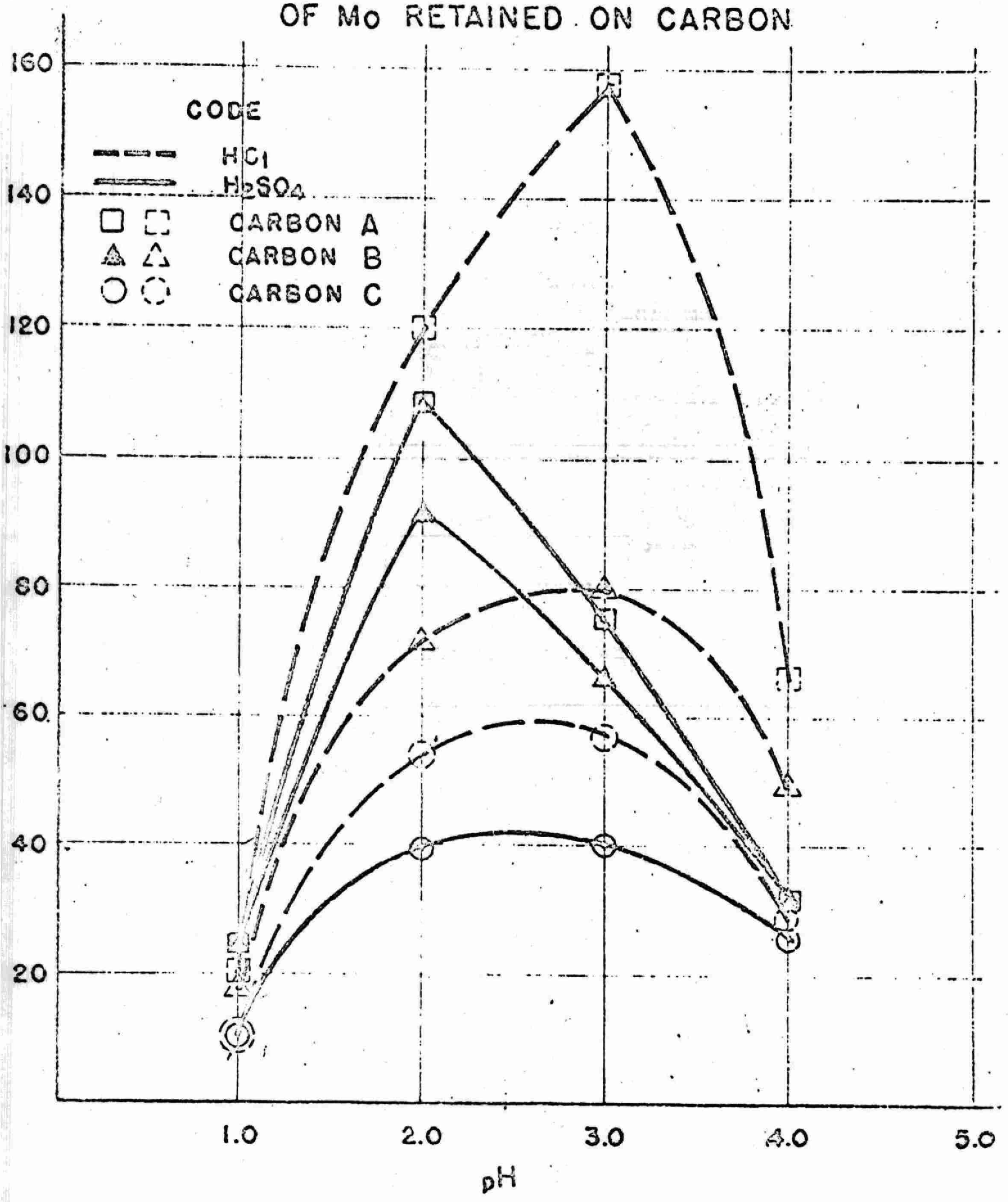

AIR
STEAM
BY-PASS IF USING
CONSTANT SPEED PUMP
SUPPLY
LINE
PUMP
MIXING TANK
STORAGE TANK
STORAGE TANK

FIGURE 4

INFLUENCE OF pH AND ACID USED, ON AMOUNT OF Mo RETAINED ON CARBON



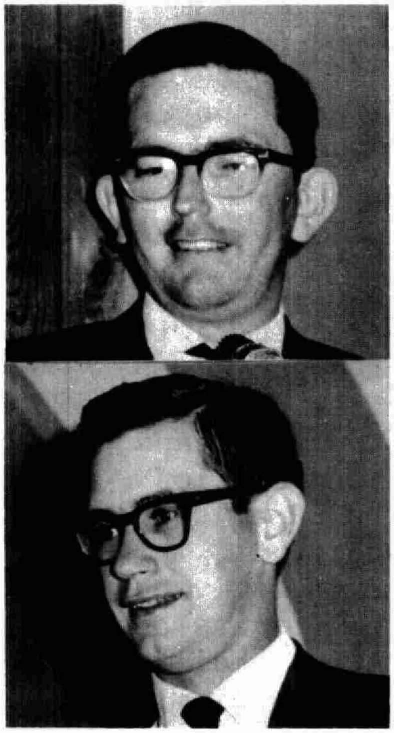
ACTIVATED CARBON ADSORPTION
A UNIT PROCESS IN LIQUID INDUSTRIAL WASTES TREATMENT

by

NUGENT MYRICK

and

G. S. DAWKINS



"ACTIVATED CARBON ADSORPTION A UNIT PROCESS IN LIQUID INDUSTRIAL WASTES TREATMENT

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The philosophy of waste water treatment appears to be changing from one of only achieving a minimal treatment of the waste to one based on the complete removal of all pollutants. That is, the present goal of waste water treatment is apparently to remove any material which has the potentiality of being harmful to man and his environment.

Through detailed engineering studies, high quality waste water plant effluents can be achieved. These engineering studies may reveal that several unit operations and processes will be required to treat the waste economically. One very economical process is bio-oxidation; however, it should be remembered that the design of this process is based on an optimum rate of biochemical oxidation of the waste and therefore, does not yield an effluent free of organic matter. For the treatment of these very dilute organic waste treatment process streams or raw waste streams to obtain a high quality waste effluent, an adsorptive system may offer a relatively economical solution to the treatment problem. In this paper a basic review of the fixed bed adsorber is presented in addition to the engineering analysis of the completely mixed adsorber.

In the treatment of liquid industrial wastes, adsorption is a physical phenomenon which occurs when the pollutant molecules are brought into contact with a solid surface. If the interaction between the solid adsorbent, activated carbon, and the condensed organic pollutant molecule is weak, the process is termed physical adsorption and is due probably entirely to van der Waal forces.

At equilibrium adsorption, the number of molecules adsorbable on the surface is a function of (1) the temperature of the system; (2) the concentration of the organic pollutant; (3) the nature of organic pollutant molecules with respect to the degree of polarity, molecular weight and molecular structure; and (4) the nature of the adsorbent's chemical composition and surface configuration. Secondarily, the pH of the adsorbent solution effects the molecular state, the solubility of the adsorbate, and the degree of activity of the surface of the adsorbent. Organic pollutants are normally more easily adsorbed under acidic than basic pH conditions. Also, agents such as colloidal turbidity particles may effect the adsorption process by physically blocking the pore structure of the adsorbent. The equilibrium state of adsorption has been described by several theoretical models. The theories of these models include capillary condensation, a solid surface on which there is either a mono- or multi-molecular layer of molecules and others. The proposed theories and the resulting equations tend to adequately describe adsorption isotherms for some systems over specific ranges but no one equation has been derived that applies to all adsorptive systems.

The empirical Freundlich adsorption equation and its plot on logarithmic paper, commonly known as the Freundlich adsorption isotherm, may be used to select the minimum activated carbon dosage when other variables are held constant. This equation correlates adsorptive capacity per unit weight of activated carbon, X/M, with the concentration of adsorbate remaining in solution at equilibrium. The Freundlich equation is usually written:

$$^{X}/_{M} = KC^{1}/_{n} \qquad (1)$$

or in the logarithmic form:

$$\log\ (^{X}/_{M}) = \log K + \frac{1}{n} \log C \qquad (2)$$

where: X = units of adsorbate removed by the activated carbon

M = weight of activated carbon in the system

C = concentration of adsorbate remaining unadsorbed at equilibrium.

The two constants K and $^1/_n$ are particular to the system, i.e., to both the activated carbon used and the nature of the adsorbate. The equation in a logarithmic form is a straight line having a slope of $^1/n$ and an intercept of K at C = 1.

In Figure 1, Gaut[1] has presented a Freundlich adsorption isotherm for phenol at 25°C. This isotherm has a slope of $^1/n$ equal to 0.316 and a constant, K, equal to 16.5. Therefore, the adsorptive capacity ($^X/M$) is 16.5 $C^{0.316}$. The activated carbon used to obtain this isotherm was Darco HDG, a product of Atlas Chemical Industries, Wilmington, Delaware.

Activated carbon adsorbers in waste water treatment are used primarily when the adsorbable material, the adsorbate, is present in a very low concentration, or when it is specified that the adsorbate concentration be reduced to a very low value. A very high ratio at equilibrium between the adsorbate concentration on the adsorbent and the adsorbate concentration in the effluent makes an adsorptive process preferable as a waste treatment process.

To evaluate the applicability of an activated carbon adsorber to the treatment of complex multicomponent industrial waste streams, experimental adsorption isotherms using various types of carbons should be determined. The selectivity is based on the relative size and characteristics of the adsorbate. Actually, it is this phenomenon of selectivity which makes an adsorptive process more applicable to waste treatment than distillation due to the fact that azeotropes may be broken and compounds which possess the same volatility as water may be separated.

THE FIXED BED ADSORBER

The fixed bed adsorber is a semi-continuous unsteady state operation. To evaluate this operation, consider a waste stream which contains a strongly adsorbable pollutant at concentration, C_o. The waste stream is passed upwards through a relatively deep fixed bed of adsorbent which initially is free of adsorbate. The organic pollutants are readily adsorbed in the initial layer when the adsorber is first placed in operation. The adsorption wave profile is established as the pollutant flows through the bed. The pollutant effluent concentration is in equilibrium with the activated adsorbent. The transition zone, in which the pollutant concentration of adsorbable components is decreasing, is termed the transfer zone. The length and shape of this zone is a measure of the rate of adsorption. If the rate is infinitely rapid, a square wave would be produced as shown in Figure 2a. However, mass transfer rates are finite and the velocity profile through the bed is not constant; therefore a typical adsorber concentration profile would be better represented by Figure 2b. The given profile indicates that the bed is about half exhausted. The wave front will pass through the adsorber until the effluent concentration from the adsorber is the same as the inlet concentration. At this point, the bed is totally exhausted and the adsorbent must be regenerated before the bed can be re-used. The breakthrough point occurs when the effluent concentration rises above the equilibrium value.

An exact mathematical solution to the unsteady state problem is impractical and has been accomplished only for several special cases. Treybal[2] presents an easily used method due to Michaels[3]. The method allows the prediction of the length and shape of the mass transfer zone in a fixed bed from the equilibrium adsorption isotherm. This method is based on the following assumptions:

1) adsorption from dilute feed mixtures,

2) the equilibrium adsorption isotherm is concave to the solution concentration axis,

3) the mass transfer zone is constant in height as it travels through the column, and

4) the height of the adsorbent bed is large, relative to the height of the mass transfer zone.

These assumptions are not too restrictive for most waste-water treatment applications.

In Figure 3 a typical continuous effluent concentration profile is presented. The length of the mass transfer zone Z_a can be calculated using Equation (3).

$$Z_A = Z \quad \frac{\theta\ A}{\theta_E - (1-f_m)\theta_B}$$

where: Z = packed bed depth

$\theta\ A = \theta E - \theta B$

$\theta\ E$ = time to adsorber exhaustion

$\theta\ B$ = time to breakthrough

f_m = fraction of mass transfer zone not loaded with adsorbate

C_E = concentration of effluent at exhaustion

C_B = concentration of effluent at breakthrough

Barry[4], in a review of fixed bed adsorbers, states that f_m is often approximately 0.5 but may vary from 0.35 to 0.65. This variation depends on the shape of the effluent curve.

The length of the mass transfer zone is independent of bed depth. To study the mass transfer zone, adsorbent particle size, type of adsorbent, type of waste, pH of the waste stream, and bed temperature are held constant. Then the velocity and waste concentration effects on the mass transfer zone can be experimentally evaluated.

The amount of pollutant removed by the fixed bed prior to breakthrough can be predicted using the equilibrium adsorption isotherm to find the adsorbed pollutant concentration in equilibrium with the feed stream and making a correction for the mass transfer zone.

Consideration should also be given to the falling off of adsorption with prolonged usage if regeneration is planned. Adsorbent life tests will provide the necessary information.

The type of regeneration methods needed to make the adsorbent reusable will depend on the nature of the adsorbent and the waste treated. Generally laboratory work is needed to check a proposed method.

THE CONTACT ADSORBER

The contact adsorber is a one or two stage batch operation. The waste stream and the adsorbent are placed together, mechanically agitated and allowed to come to equilibrium. Separation is usually achieved by a filtration or a sedimentation process.

A number of schemes ranging from single-stage batch to continuous multistage operation are well described by Treybal[2]. Usually, equilibrium is closely approached in a single stage, so the analysis is based on the assumption that stage efficiencies are unity. The method of analysis is similar to that used in other separation processes such as distillation and extraction[5].

Economy in operation is often achieved by a countercurrent operation where the inlet feed meets the nearly spent adsorbent. This method requires a minimum amount of adsorbent for a desired separation. Figure 4 presents a schematic diagram for a three stage countercurrent contact process. The familiar stair-step diagram is used to determine the stream concentrations after each stage. Although shown in the schematic diagram as a continuous operation in practice it is more often run batchwise.

The resistances that must be overcome to achieve adsorption are:

1) resistance to mass transfer of solute through the liquid film,

2) resistance to diffusion of solute through the pores, and

3) resistance to adsorption on the surface.

In a well agitated system the second resistance is usually controlling. For this reason the maximum feasible temperature is usually employed to reduce the solution viscosity and reduce this resistance, thus allowing equilibrium to be achieved in a shorter time. This more than compensates for the small negative effect on the adsorption equilibrium caused by the increased temperature.

THE COMPLETELY MIXED ADSORBER

A completely mixed adsorber is defined as one in which both the waste stream and the adsorbent are fed and removed continuously and enough agiatation is provided to approximate instantaneous mixing. The following analysis is presented below to describe this system taking non-ideality of mixing into account and utilizing adsorbent age distributions.

The completely mixed adsorber is easily subjected to engineering controls in that the activity of the adsorbent can be established and maintained, and secondly the effluent quality can be predicted to give a designed degree of removal of the pollutants. Since the adsorbent is continuously fed and removed, a continuous regeneration system would be feasible. However, the type and size of the regenerative system would be considerably different from the semi-continuous scheme required for a fixed bed adsorber.

A completely mixed bench scale adsorber[6] which is ideal for laboratory experimentation is shown in Figure 5. Air is used to achieve almost complete mixing. The granular adsorbent is fed into the top of the adsorber and removed at the side opening. An internal clarifier is used to separate the adsorbent from the effluent.

In the completely mixed adsorber, the pollutant concentration in the system is constant and equal to the effluent concentration. Since the adsorbent remains in the system a varying length of time ranging from approximately 0.1 to 4 turnovers, equilibrium between the adsorbent and the solution is not uniformly achieved. Most conditions which effect rate of adsorption and hence the amount adsorbed as a function of time can be specified. These variables are operating temperature, pH of the system, type of adsorbent, type of pollutant, adsorbent particle size and desired effluent waste concentration. It is necessary to experimentally determine an adsorption isotherm at the desired effluent waste concentration, keeping the above mentioned variables constant, in order to predict the amount of pollutant removal for a completely mixed adsorber. These adsorption isotherms are a function of time and give the amount adsorbed per gram of adsorbent.

The effect of non-ideal mixing in the completely mixed adsorber can easily be taken into account by using the exit age distribution, $E(\theta)$, as defined by Danckwerts[7]. This exit age distribution is defined as the fraction of material in the exit stream between the ages θ and $\theta + d\theta$. The term, θ, is in dimensionless time units and is given by:

$$\theta = t\, Q/V \qquad (4)$$

where: t = time

Q = flowrate of waste through the system

V = liquid volume in the system

For an ideal reactor where mixing is perfect the following relation can be shown to hold.

$$E(\theta) = e^{\theta} \qquad (5)$$

By using tracer or step function techniques on an actual mixing vessel, the exit age distribution can be determined experimentally when mixing is not ideal. These techniques are fully described in the current literature[8,9].

The mixing achieved in the experimental completely mixed adsorber was studied for several flow rates using the washout method. An initial concentration of methylene blue dye was placed in the reactor and the disappearance of the dye was observed for a time period equivalent to four displacements of the reactor volume at the stated flow rates. If ideal mixing was achieved the plot of log dye concentration versus time should be linear with a slope of $-\theta$ as indicated by Equation (5). An approximately linear relationship was found in the plot of the experimental results in Figure 6. The time for one turnover, i.e., the time required to make $\theta = 1$ from Equation (4), is predicted from the known adsorber volume and flow rate and compared with the value obtained from the slope of the lines in Figure 6. This comparison is presented in Table I.

TABLE I

Q, ml./min.	Predicted Turnover time, min.	Measured Turnover time, min.
100	57.5	56
200	28.8	25

The total amount of pollutant adsorbed per unit of adsorbent, A_{Total}, may be described by the following equation,

$$A_{Total} = \int_{0}^{\infty} A(\theta)\ E(\theta)\ d\theta \qquad (6)$$

where $A(\theta)$ is the amount adsorbed per unit of adsorbent at the design conditions as a function of time and can be obtained from the adsorption isotherm. The term $E(\theta)$ is defined by Equation (5) and can be obtained experimentally or from Equation (4). The integral in Equation (6) is normally evaluated graphically or numerically. Although the range is from 0 to ∞, the contribution to the integral for $\theta \succ 4$ can be neglected.

The required feed rate of the adsorbent can be predicted using the following material balance relationship:

$$M \times A_{Total} = Q\ (C_o - C_f) \qquad (7)$$

where: M = rate of addition of adsorbent, grams/minute

Q = rate of addition of waste-water stream, liters/minute

C_o = original pollutant concentration, grams/liter

C_f = exit concentration of pollutant, grams/liter

A_{Total} = total quantity of pollutant adsorbed per unit of adsorbent.

CONCLUSIONS

Adsorption is a unit process which is relatively economical in the treatment of very dilute waste-water streams. A basic review of the fundamental design considerations of both fixed bed and contact adsorbers was presented.

The engineering analysis for a completely mixed adsorber system was presented. This type of an adsorber is easily subjected to engineering controls in that the activity of the adsorbent can be established and maintained. Secondly, the effluent quality can be predicted to give a designed degree of treatment of the waste-water stream.

ACKNOWLEDGEMENTS

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APPENDIX A

Nomenclature for parts to the Completely Mixed Adsorber presented in Figure 5.

1. Effluent tube
2. Cover with effluent tube support and adsorbent feed tube support
3. Internal clarifier support
4. Internal clarifier
5. Internal cone for recirculation baffle
6. Adsorber
7. Fritted glass disc for air distribution
8. Internal cone support
9. Influent tube
10. Air inlet tube
11. Adsorbent exit port

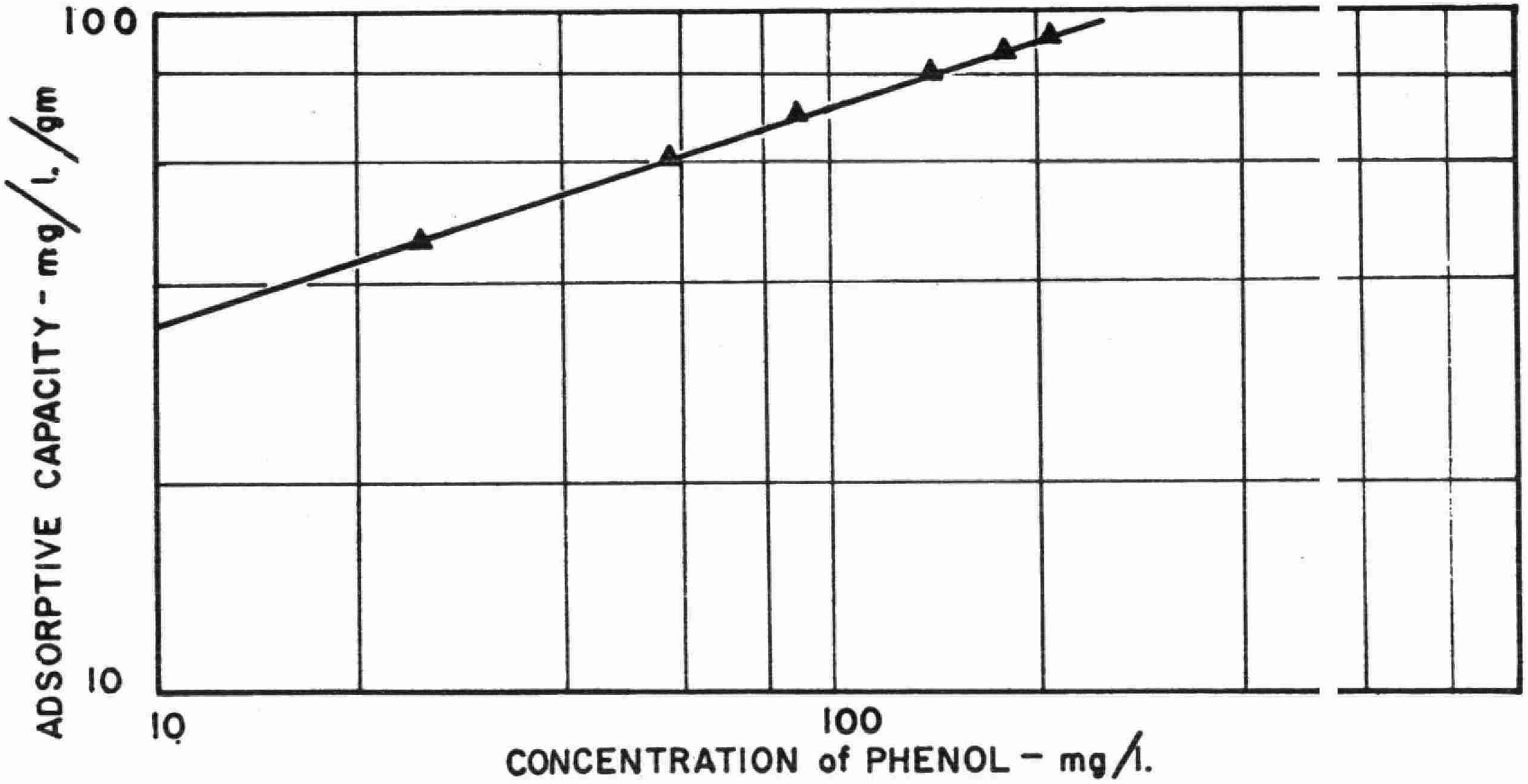
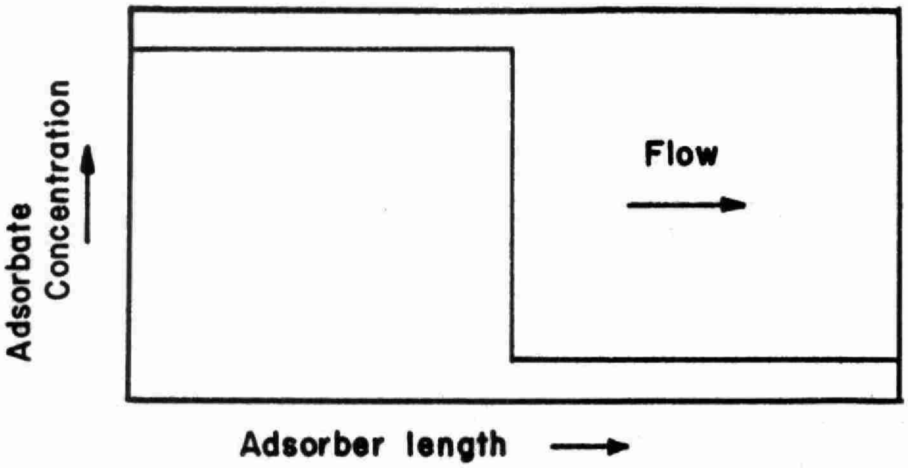
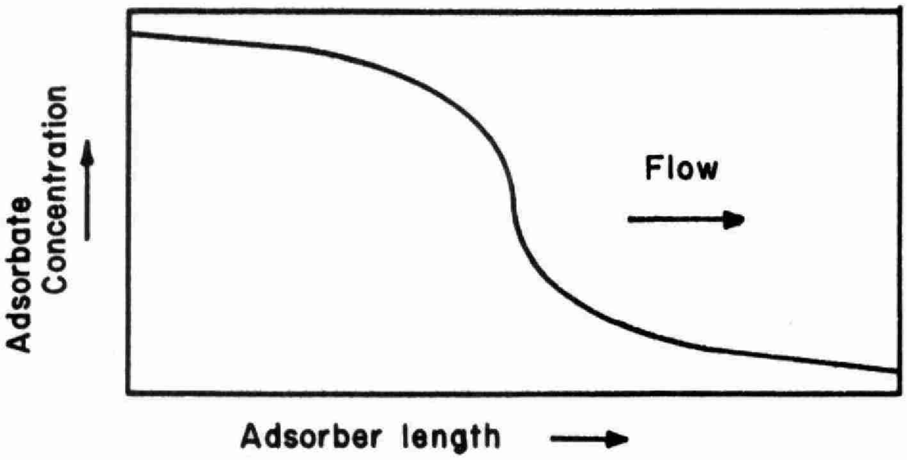


Figure 1. FREUNDLICH ADSORPTION ISOTHERM



a.) Infinitely rapid adsorption rate



b.) Typical adsorption rate

Figure 2 MASS TRANSFER ZONE PROFILES

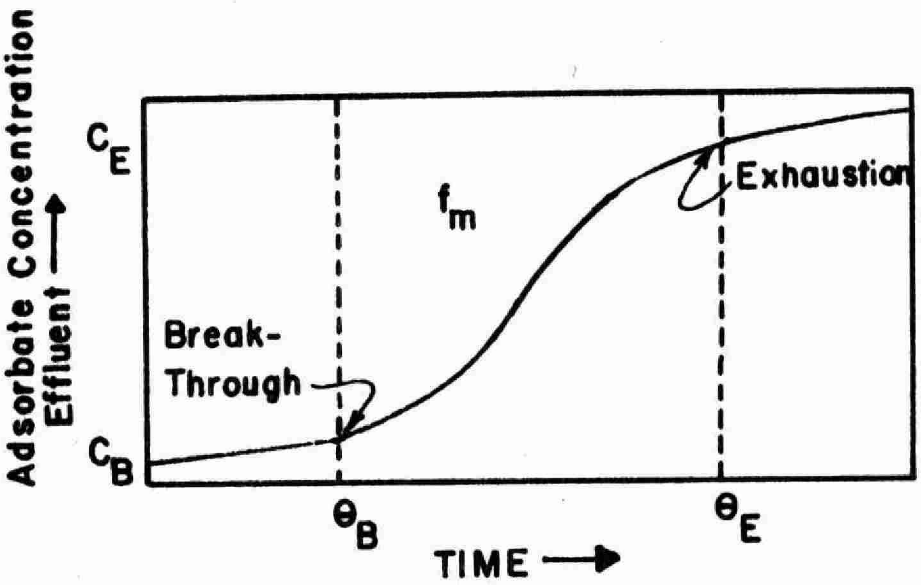


FIGURE 3 CONTINUOUS EFFLUENT CONCENTRATION PROFILE

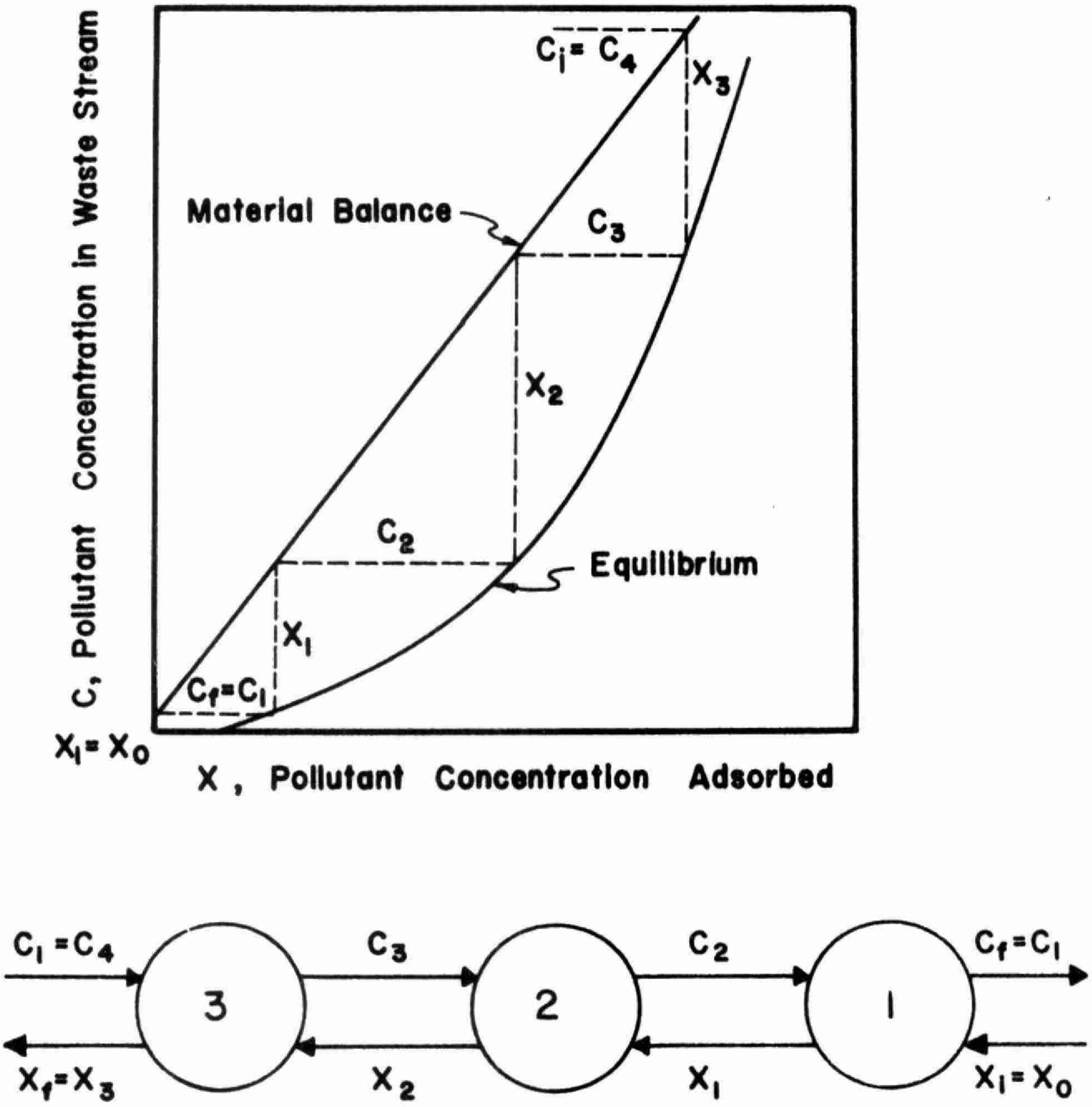
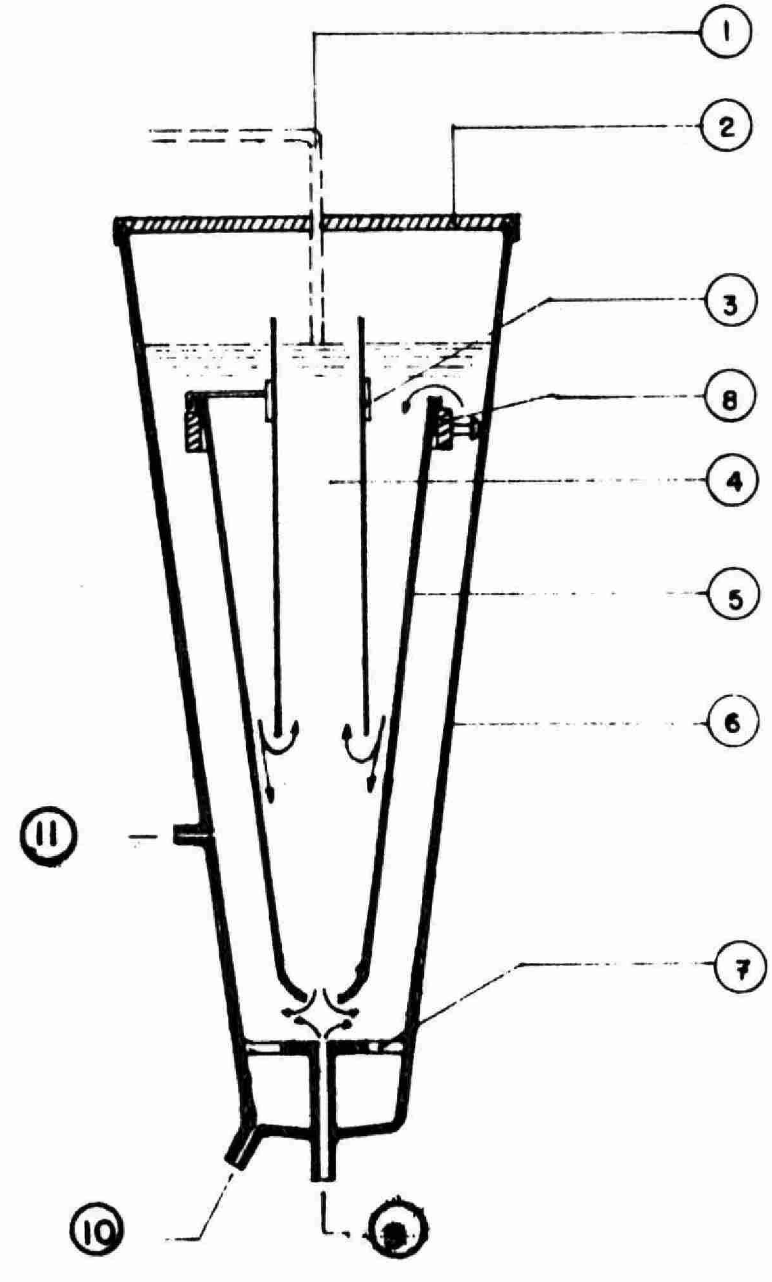


Figure 4. THREE STAGE COUNTERCURRENT OPERATION



NOMENCLATURE, APPENDIX A

Figure 5 COMPLETELY MIXED ADSORBER

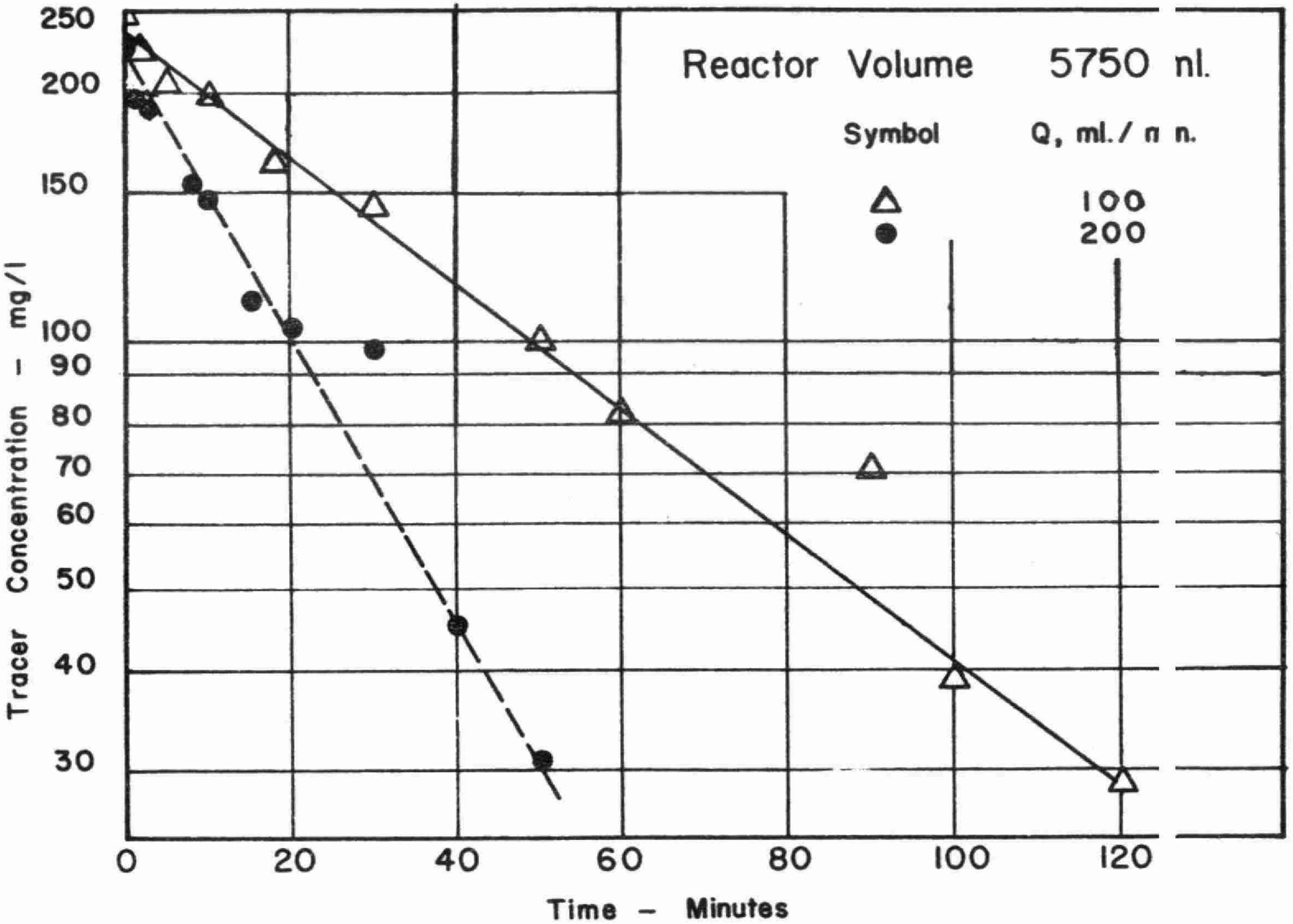


Figure 6 TRACER WASHOUT CURVES

WASTE DISPOSAL IN PHOSPHATE FERTILIZER PLANT OPERATION

by

N. MEYERS

SESSION FIVE

K. L. Murphy
McMaster University

Session Chairman

"WASTE DISPOSAL IN PHOSPHATE FERTILIZER PLANT OPERATION"

by

N. MEYERS

This paper is concerned with the disposal of wastes from two plants operated by the Electric Reduction Company at Port Maitland Ontario. These plants are located on the Grand River just above its juncture with Lake Erie.

The Dominion Fertilizer plant was built in 1958 and was originally designed for the production of single superphosphate fertilizer. This material contains about 18% of phosphorus pentoxide, the active ingredient, and about 65% of inert gypsum. In keeping with the trend to higher analysis fertilizers, the Dominion Fertilizer Company, which in 1959 had become a wholly owned subsidiary of the Electric Reduction Company, converted the plant so that triple superphosphate as well as the single superphosphate could be produced. Triple superphosphate contains 48% phosphorus pentoxide and negligible amounts of gypsum. It is therefore less costly to store, ship and apply. It is, however, more costly to make since phosphoric acid rather than sulphuric acid is used in its manufacture.

In order to supply the needs of the Dominion Fertilizer Company, a plant to make wet-process phosphoric acid was built at the same site in 1961.

Additional acid capacity was incorporated to supply other fertilizer manufacturers since this is the only acid plant of its kind in eastern Canada. The rated plant capacity is about 400 tons of concentrated acid a day which is equivalent to 200 tons of phosphorus pentoxide. It may be mentioned here that the other principal method of making phosphoric acid is by burning elemental phosphorus. This thermal process gives a much purer but more expensive acid which is not competitive with wet-process acid in making low cost fertilizers. The Electric Reduction Company has for many years produced thermal acid and the production of wet-process acid represents a natural extension of its technology.

Wet-process acid is made by the reaction of phosphate rock, which is essentially a type of calcium phosphate, and sulphuric acid. The other product of the reaction is gypsum, or calcium sulphate dihydrate, which is filtered out of the acid. Most of the impurities in the rock remain in the acid. These include fluorine, iron, aluminum and organic matter as well as many others. At Port Maitland, calcined rock was chosen for acid production since the organic matter is carbonized during calcination and a clear light green acid rather than the usual viscous dark brown one is produced.

In addition to gypsum, several other materials are discarded from the acid plant. I would like now to describe these materials and their formation. The principal waste, as far as bulk is concerned, is the gypsum which is produced at the rate of 900 tons/day. Gypsum itself is a relatively insoluble inert white solid which, as made in the acid plant, consists of fine crystals with a grey appearance due to a small amount of carbon formed during rock calcination. At the end of the filtration, the cake is washed off the filter with water and transported as a slurry to the lime treatment area. This treatment of the gypsum is made necessary by the presence of about two tons a day of soluble phosphoric acid left in the cake by incomplete washing. Four to five tons of phosphate is also present as insoluble dicalcium phosphate that has co-crystallized with the gypsum. Both forms represent a loss of product and plant conditions are carefully controlled to minimize them. In addition to the loss of saleable product, these materials represent an added expense since they must be treated before being discharged. They are undesirable in the effluent for two reasons; firstly, they are acidic and may lower the pH beyond the safe limit for aquatic life, and secondly, they provide readily available phosphorus which may increase the fertility of the water to the point where undesirable algae will proliferate.

Another important component of the effluent stream is fluorine. The phosphate rock carried into the plant approximately twenty two tons of fluorine a day. This dissolves in the acidic solution to form hydrofluoric acid which attacks silica or silicates to form fluosilicic acid and water. Fluosilicic acid, in turn, partly decomposes to re-form hydrofluoric acid and a gas, silicon tetrafluoride, which is the source of the characteristic odour encountered in these plants. By elimination of HF from the latter two equations, the reaction can be formulated as fluosilicic acid and silica producing water and silicon tetrafluoride. This is a convenient formula since free hydrofluoric acid is present only in trace quantities in these solutions. I will digress for a moment to describe the acid plant flow sheet in more detail. Sulphuric acid and rock enter the acid tanks along with recycled acids from the cooler and the filter. After digestion is complete, the acid containing 30% phosphorus pentoxide is filtered and concentrated to 54%. The gypsum is washed three times, first with 14% acid to give 22% acid for recycling, second with 5% acid to give 14% acid, and finally with water to give 5% acid. Some silicon tetrafluoride gas is evolved in the acid production tanks, in the vacuum evaporator cooler and in the vacuum filter. Since it is toxic and cannot be released to the atmosphere, it is scrubbed from the off-gases by water. It reacts chemically with the water to form silica and fluosilicic acid in a reversal of its method of formation. The vapour pressure of silicon tetrafluoride above the scrubber liquor is negligible until the concentration of fluorine reaches a few percent. At present, the fluorine concentrations of these scrubber liquors at the acid plant are only about 100 ppm and the total amount of fluorine collected from these sources is a little over half a ton a day.

A similar evolution of silicon fluoride takes place when the acid is concentrated. A flame of natural gas submerged in the acid heats it to boiling and drives off water, silicon tetrafluoride and also hydrogen fluoride. The scrubber for this system collects over thirteen tons of fluorine a day and the effluent liquor is a 1 ½% solution of fluosilicic acid. This stream is combined with the other contaminated wastes for lime treatment. It accounts for about 80% of the lime requirement and is therefore a major factor in the waste disposal program.

Fluorine is also present in the gypsum filter cake in amounts of five tons a day. X-ray spectrography indicates that it is present mainly as calcium fluosilicate. This material is slightly soluble in water and the fluofilicate ion from it hydrolyses in neutral or alkaline solutions to form silica and hydrofluoric acid. This reaction takes place on treatment with lime, and in addition, the hydrofluoric acid reacts with the lime to form insoluble calcium fluoride.

To sum up the situation at the acid plant, there are five important quantities to be taken into account. These are:

1. The solids, which consist mainly of gypsum.
2. The phosphate, which can influence water fertility.
3. Fluorine, which can be toxic in rather low concentrations.
4. Acidity, which can be harmful to aquatic life and
5. Water, which carries the other materials to the public waterways.

Turning now to the fertilizer plant waste disposal, a similar set of materials is found. In this plant, phosphate rock reacts with sulphuric or phosphoric acid to form single or triple superphosphate. The waste products are principally rock dust and silicon tetrafluoride which are sucked out of the reaction area by the ventilation system. As before, the air stream is scrubbed with water to remove contaminants. The scrubber liquor contains rock dust, silica, fluosilicic acid and phosphoric acid released from the rock dust by the fluosilicic acid. Here again the important quantities to be reckoned with are solids, phosphate, fluoride, acidity and water.

All plants for the production of phosphate fertilizer and phosphoric acid are faced with similar disposal problems. The disposal methods used vary from one plant to another according to the particular circumstances involved. For acid plants, the most primitive method is to discharge the wastes into a large land basin, a tidal river or a sea.

In at least one case, enough water is added to the effluent before disposal to dissolve almost all of the gypsum. This method is, of course, only applicable in the few locations where very large quantities of water are available.

When there is too little water to dilute the effluent sufficiently, the first component to become objectionable is the gypsum. Hence, the first step in improving the effluent is to provide a system for removing the solids. The usual procedure is to allow the solids to settle out in a large shallow pond or lagoon, after which the clear water overflows to the nearest watercourse. Dykes may be built in the lagoon to guide the water and avoid short-circuiting to the exit. Little effort has been directed toward studying the efficiency of settling basins since it is known that collection efficiency increases with size and the construction of a sufficiently large basin is usually feasible.

The clear overflow from such a lagoon contains phosphoric and fluosilicic acids. If their concentrations are objectionably high, the addition of lime slurry either before or after settling not only neutralizes these acids but also precipitates them fairly completely. Phosphoric acid forms an insoluble calcium phosphate while fluosilicic acid is hydrolyzed to silica and calcium fluoride, both of which are insoluble. These three materials settle out with the gypsum in one case, or are discharged to the watercourse in the other. At a pH of 7, the fluoride concentration is 10 to 15 ppm. In order to reach 1 ppm of fluoride, the effluent must be made basic by adding enough lime to reach a pH of 9. Some improvement in the quality of the effluent can also be effected if it is diluted with uncontaminated water before being discharged. Obviously the volume of effluent water before dilution should be reduced to a minimum to make this method feasible.

The ultimate step in effluent treatment is to recover the material in it so that little or no waste is discarded. All of the wastes mentioned, including the water can be recovered and used. Re-use of slightly contaminated water before it is treated not only reduced the load on the treatment system, allowing it to work more efficiently, but also reduces the quantity of other wastes carried along with it to the watercourse. Special corrosion-resistant equipment may be needed to handle this water if it is highly acid. It may be preferable to treat the water before reuse to avoid corrosion if the equipment on hand will not withstand the untreated water.

The recovery of gypsum involves washing out any undesirable impurities and drying. Only the barest minimum of treatment can be justified economically since low cost gypsum is usually available from other sources, and the end-product, plaster or wallboard, must be made from the least expensive raw material in order to be competitive. Recovery may be undertaken in spite of the low profitability to avoid the disposal problem.

Soluble phosphoric acid in the gypsum may be recovered by further washing of the cake. The economic limit is reached when the value of this additional acid is equal to the expense of recovering it. The recovered acid may be used in place of water for washing the gypsum, or for diluting the sulphuric acid since these streams eventually finish up in the phosphoric acid.

Fluosilicic acid may be recovered in several ways of which the following are typical examples:

1. The concentrated (93%) sulphuric acid supplied to the acid plant is diluted to the required 55-70% with recycle phosphoric acid (22% P_2O_5). The high acidity and temperature cause the evolution of silicon tetrafluoride which is captured as a fairly pure and concentrated fluosilicic acid.

2. Sodium carbonate is added to phosphoric acid to precipitate sodium silicofluoride which may be sold as such or converted to other products.

3. The fluorine-containing gases evolved in the acid evaporation process are stripped of fluorine in a modified scrubber system whose end-product is a fluorine compound in a commercially usable form (eg. a 15-25% fluosilicic acid).

The greatest difficulty in each case is to produce a saleable product at a price competitive with fluorides from fluorspar. Since the largest consumption of fluorides has been in the form of such products as cryolite, aluminum fluoride, hydrofluoric acid and calcium fluoride, it has been necessary to remove the silica from the fluosilicic acid, or to accept a small market. In recent months, the growing interest in fluosilicic acid for water fluoridation offers an economic outlet for a sizeable part of this phosphate plant by-product.

The remaining recoverable material, rock dust, may be returned to the process as feed stock if it can be obtained in an easily-handled form.

In summary, it can be stated that the recovery of waste products from phosphate plants has, up to the present, offered small economic rewards. It is unlikely that the market picture will alter, except in the case of fluorides which are undergoing rapid development.

We now turn to the waste treatment methods in use at the present time at Port Maitland. Here, all uncontaminated streams such as cooling water are discharged directly to the sewer. All other streams from the acid plant are combined and neutralized with lime slurry. The resultant mixture, about 2,500 Imperial gallons per minute, is pumped to an artificial lagoon which was created on former swampland by enclosing the area with a dyke. The solids, gypsum, silica, calcium fluoride and calcium phosphate settle out in the lagoon while the supernatant liquor overflows to a small creek which empties into the Grand River. This neutralization and settling treatment, which is entirely for the purpose of avoiding water pollution, has an operating cost of about $160,000 per year, in addition to its capital cost of $300,000.

The Grand River which receives the effluent, has a flow of 75,000 IGPM at its period of lowest ebb and about 5 ½ times that when in full flood. The pH is 8.2, the fluorine is 0.3 ppm and the calcium is 800-900 ppm. Because of these properties, the river is able to neutralize and precipitate rather large quantities of acid plant wastes.

During the first few months of operation, the disposal system worked reasonable well. The pH at the neutralizing tank was maintained at 7 and samples of lagoon effluent showed a fluorine concentration of 10 ppm. After dilution by the Grand River, the calculated fluorine concentration was about 0.6 ppm, of which 0.3 ppm was due to the naturally occurring fluorides in the river.

The level of suspended solids in the lagoon effluent was not measured during this period. It was later discovered that the efficiency of solids removal was 99.8% which corresponds to 70 ppm in the effluent. This is much higher than the recommended level of 15 ppm. It was observed that there was a good deal of channelling so that only a small portion of the lagoon was effective in settling the solids. An increase in the water level was used to increase the effective area and a later analysis showed only 6-10 ppm of solids. The chemical composition of the solids has not been determined since only very small samples have been collected. The material tends to clog the filter very easily resulting in a tedious separation problem.

Several months after the plant start-up, the pH of the effluent from the lagoon dropped below the desired level. The lime flow to the neutralizing tank was increased to bring the pH up from 7 to 10 or 11. In spite of this, the pH at the outlet of the lagoon dropped as low as 3.5 which is well below the recommended range of 5.5 to 9.5. It may be noted here that the pH of the river at the Dominion Fertilizer plant which is downstream from the acid plant was 7.9 to 8 during this time. The river seems capable, therefore, of absorbing the acidic effluent without undue difficulty.

On investigation of the lagoon, it was found that untreated lime being deposited at the inlet and a further increase in lime to the neutralizing tank was of no benefit. The high acidity of the outlet, meanwhile, was allowing the escape of fluoride and phosphate. This state of affairs seems to be due to insufficient reaction time in the neutralizing tank.

We have been adivsed that the fluorine level should be below 1-2 ppm following dilution by the river. Calculations show that this condition is being met. Plans are now being prepared for the recovery of about 65% of the fluorine by modifying the concentrator scrubber system. This will reduce the load on the neutralizer by over 80% and increase the residence time by 8%. We are also evaluating methods of reducing the volume of effluents by re-use of some of the water. As a temporary measure the concentrator scrubber liquor will be neutralized separately from the rest of the effluents since laboratory tests indicate that precipitation of fluorides should be more efficient with this arrangement.

The effluent from the Dominion Fertilizer plant is treated by settling which removes about half the solids. Due to the low flow rate of about 40 gallons per minute, however, the total amount of the contaminants introduced to the river are smaller than for the acid plant. At times, local concentrations are high and this is accentuated by the discharge location of the effluent stream in a quiet bay.

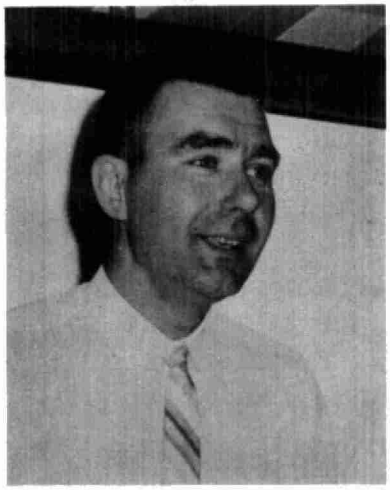
Various plans have been proposed for dealing with this effluent. At this moment, the leading contender is to transfer the scrubber liquor to the acid plant treatment system. The solids would first be separated and returned to the process as feed stock while the liquid would be recycled to the scrubber to give a smaller amount of concentrated liquor. This concentrate would be taken to the acid plant in tank trucks for treatment. The final result would be a complete elimination of aqueous wastes at the Dominion Fertilizer plant and a much improved effluent at the acid plant.

In conclusion I would like to thank all of those who have contributed the advice and information that has made this paper possible.

AVOIDANCE OF SUBLETHAL MINING POLLUTION BY ATLANTIC SALMON

by

J. B. SPRAGUE



"AVOIDANCE OF SUBLETHAL MINING POLLUTION BY ATLANTIC SALMON"

by

J. B. SPRAGUE

INTRODUCTION

Pollution from base-metal mines is a new but growing problem in New Brunswick. While the mines are a welcome addition to the province's economy, there is some danger that they will harm fish in freshwater or estuaries. The Atlantic salmon (*Salmo salar* L.) fishery has been a large and continuing source of income, both from the commercial catch and more especially from money brought in through development of angling. Accordingly, there is an attempt to exploit mining potential without polluting rivers enough to disturb the sensitive salmon.

One of the base-metal mines is on a tributary of the Northwest Miramichi River, a noted angling river of the east coast. Here the Fisheries Research Board had been carrying out basic research on salmon life history for several years before mining pollution affected the river. By coincidence, pollution entered the Northwest Miramichi between two salmon counting fences, and therefore movements of fish up and down the river could be fairly closely followed. Unusual downstream movements during the spawning migration were in fact the first sign of trouble caused by mining pollution. In previous years there had been almost no downstream movement.

The object of research described here is to find the "safe" level of copper-zinc pollution for fish movements. This was investigated by the continuing program in the Miramichi, to which a water sampling program was added, and by sustaining laboratory experiments. The "safe" level, once determined, could be used as an objective in designing waste treatment facilities.

The study was an interesting one because of the opportunity to compare little-known avoidance reactions in nature with laboratory tests of avoidance. Furthermore, an earlier worker (Jones, 1947) had concluded that fish of another species usually did not avoid copper, but swam into it, and in strong concentrations became stupefied.

Results from the Miramichi strongly suggested avoidance as shown in Table I. Usually there are between 1,000 and 8,000 adult salmon moving up the Northwest Miramichi River during spawning migrations in the warm part of the year. Before the mine came into being, only 1 or 2% of these fish returned downstream through our counting fence. A similarly low percentage prevailed up to 1959, through a short period when the mine and concentrator were operating. In 1960 the mine was reopened, and acid water which had filled the shafts was pumped into a tributary of the Northwest Miramichi. Since this was a sulphide ore, oxidation had produced free acid in the minewater, and this in turn had helped to dissolve more heavy metals.

Pollution in 1960 apparently caused more than 20% of the migrants to return downstream compared to the usual 1 or 2%. In spite of waste control efforts at the mine, disturbed migration was also apparent in 1961 and 1962.

Laboratory studies of lethal concentrations

As a point of reference for work on avoidance, we determined lethal concentrations of copper sulphate and zinc sulphate for young salmon, and that the toxicity of mixtures was predictable. A search of the literature had revealed a heterogeneous array of "lethal concentrations", some of them differing by factors of almost 1,000.

Lethal tests were conducted in fibreglass tanks with constant flows of water. Glass, plastic, and other non-toxic materials were used to construct the apparatus.

TABLE I

YEAR	MINING ACTIVITY	% OF SALMON RETURNING DOWNSTREAM
1954 - 1956	Before Mining	1 - 2%
1957	Mining and Milling	3%
1958 - 1959	No Activity	1 - 2%
1960	Pumping	22%
1961	Exploration	14%
1962	Mining and Milling	10%

Table I - Disturbance of salmon migration in the Northwest Miramichi River as related to mining activity on a tributary.

Results are for the period when the salmon-counting fence was operating, usually between May and November. In some years, such as 1962, records of fish movements are approximate since the fence was partly destroyed or open during freshets.

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Tests were run in air-saturated water of 15° or 17°C, pH 7.3, and total hardness of 20 mg/l $CaCO_3$, which is very soft but characteristic of the Miramichi region (Sprague and Carson, 1963). Desired levels of toxicant were maintained in the test-tanks by adding stock solutions of copper sulphate and/or zinc sulphate to the inflowing water by means of low-capacity pumps made of non-toxic materials. Time to 50% mortality in a group of young salmon was determined at each constant concentration of toxicant.

Results showed that the highest concentrations which just failed to cause 50% mortality were 48 µg/l of copper or 600 µg/l of zinc (Sprague, 1963 A). These incipient lethal levels (Terminology of Fry, 1947) of copper and zinc apply only for the type of water used in these tests. In particular, the incipient lethal levels (ILL'S) become higher in water of greater hardness (Lloyd and Herbert, 1962).

The toxicities of the two metals may be compared by expressing them as fractions (or multiples) of the respective ILL'S, a system developed by Lloyd (1961). Results of lethal tests have been expressed in this way in Fig. 1. Zinc kills the fish faster than copper at comparable multiples of the ILL. The toxicity of mixtures of copper and zinc solutions has been expressed by adding the fraction of ILL for copper to that for zinc. There is potentiation of toxic action in the mixtures, that is, the fish die more quickly than if the toxicities were merely additive. However it is possible that the ILL for mixtures is attained by simple addition of the fractions of ILL of the two components. This is being tested at the time of writing.

Of interest is the sharp cut-off between lethal and non-lethal concentrations of copper and zinc solutions. These incipient lethal levels correspond almost exactly with the 50 µg/l and 700 µg/l ILL's of copper and zinc for rainbow trout in water of the same total hardness (Lloyd and Herbert, 1962). Since the agreement is almost exact, it seems reasonable to adopt the relationship between ILL and total hardness of water which has been determined by Lloyd and Herbert, and we have done so in the work described below.

Field studies of lethal concentrations

Although copper and zinc were usually in sublethal concentrations in the Northwest Miramichi River after cross-stream mixing, lethal levels were sometimes reached in the polluted tributary and tests with caged fish in this tributary resulted in mortalities. Water samples taken at the same time were analysed for copper and zinc. These field experiments showed reasonable agreement with lethal times expected from the laboratory experiments. This indicated that zinc and copper alone were responsible for death of caged fish in the polluted tributary. No evidence has been brought to light of any other significantly-toxic pollutant in downstream sections of the tributary.

Laboratory experiments on avoidance

Having determined the incipient lethal levels in the laboratory, tests were designed to show what fraction of the ILL's would be detected and avoided by young salmon. Young fish were used because of ease of handling, but it seems reasonable that any sense of detection found in the young would also be present in the adult salmon.

The apparatus used in these tests is shown in Fig. 2. It was essentially a trough made from a Plexiglass tube of 14.6 cm diameter. A constant flow of water went into each end of the trough and drained from the centre. Toxicant could be added to the water going into one side or the other by means of a variable-speed peristaltic pump. Tests with dye showed that there was a sharp separation between the two waters at the midline of the trough so that the fish had a distinct choice. In operation, the doors seen at the sides were almost closed, and a cover placed on top to avoid visual disturbance of the fish. After the fish was accustomed to the apparatus, a very weak concentration of toxicant was created on one side. An observer recorded the fish's movements for 10 minutes by pencil, left or right across the width of a moving strip of kymograph paper. Successively stronger concentrations of the toxicant were tested on the same fish, using sides chosen randomly. Then the whole procedure was repeated with another fish. The sensitivity of the method was improved by using only records in which the fish was actively swimming and therefore could display its avoidance, if any.

Four tracings of fish movements are shown in Fig. 3. Each tracing represents 10 minutes of time from top to bottom. The movements of the fish are indicated and also the midline of the trough separating the two types of water. At the top of each tracing is shown the strength of copper solution and which side it was on. The percentage of time spent in the normal water is written at the bottom, and whether or not the choice of sides was significant at the 5% level.

The first tracing in Fig. 3 shows random movements of the fish along the trough, indicating that it cannot detect this small amount of copper, or else does not object to this concentration. However, the fish seems to avoid 0.2 ILL, that is 20% of the incipient lethal level. Avoidance of 0.65 ILL and 2.05 ILL is very definite. Statistical significance of the last avoidance could not be tested because the fish did not enter the copper solution three times as required by the mathematical test. This strongest concentration of copper would cause death in about 15 hours.

Results for solutions of copper sulphate, zinc sulphate, and mixtures are displayed together in Fig. 4. Results in more detail are being prepared for publication separately (Sprague, 1963 B). Inspection of Fig. 4 suggests that there is distinct median avoidance of all three conditions at 0.06 to 0.07 ILL, and at the remarkably low level of 0.02 ILL for mixtures of copper and zinc. Degree of avoidance of the three types of solution seems roughly the same in the range of 10 to 100% of the incipient lethal level, that is 0.1 to 1.0 ILL as fractions.

Thus it is apparent that young salmon will avoid copper and zinc in the laboratory, but it should be pointed out that there was no particular motivation for fish to stay at either end of the apparatus, and therefore no particular reason for fish to stay in the solutions of metal.

How do these findings apply to nature, where there may be considerable motivation for fish to move through a section of water during migration? The findings at the counting fence in the Miramichi River should answer this question.

Field experiments on avoidance

These results may be regarded as the proof of the pudding. First of all we should look at the undisturbed salmon movements during a year before the mine was developed, and we have chosen 1955 as a typical example. The left side of Fig. 5 shows that there is a large spring run of salmon, little activity during the summer, then a smaller and less regular autumn run. In general, movements of fish coincide with changes in river flow. This is especially noticeable in the autumn of 1955, when the first movements of fish came at the time of a fair-sized freshet. During the entire year, 2% of the salmon which moved upstream came back down through the fence, a fairly negligible proportion.

Movements past the counting fence during the warm season of 1960 are shown on the right-hand side of Fig. 5, along with river flows. The degree of pollution was estimated by adding the fraction of Ill for copper to the fraction of ILL for zinc for a given day. The hardness of water is taken into account since this determines which values are used for the ILL's on a particular day. No other environmental identities are thought to have influenced the ILL'S greatly during the warm season.

At first glance, one might say that pollution aids migration, because upstream fish movements tend to be greater at times of increased pollution. However, this is because both are related to a third factor - river flow. There is normally increased upstream movement of fish during freshets, as was shown in 1955. However, pollution also tended to increase at these times, presumably because rain and increased streamflow washed metal-bearing wastes into the water. We feel that the fish moved upstream at these times in spite of the pollution, not because of it.

There is some indication in Fig. 5 that very high pollution levels of 0.8 and 0.9 ILL in early July 1960 caused a cessation of upstream movement. However this cannot be proved, since the failure of salmon to arrive at the counting fence during this period may have been caused by something other than pollution.

The significant thing in 1960 is the unusually large downstream movement totalling 22% of the fish which had previously gone upstream. This downstream movement seemed to occur when pollution exceeded about 0.425 ILL. This "safe limit" was obtained by simply laying a straight-edge across the degree of pollution in Fig. 5, and raising or lowering it until peaks of pollution above the straight-edge seemed to match significant downstream movements.

The high pollution in July of 1960 came during and after acid mine-water was pumped from the shafts. Waste treatment was initiated in mid-summer, but a small rainfall and freshet in mid-September apparently washed a large amount of waste downstream and caused a severe rise in dissolved metals. The autumn rains and freshets did the same thing.

Similar results for 1961 and 1962 are shown in Fig. 6. In these years, there seemed to be disturbance of migration when pollution exceeded 0.35 and 0.4 ILL. Unfortunately the wet summer of 1962 interfered with operation of the counting fence many times, and for many of the most interesting periods, records of salmon movements are only minimum estimates.

Discussion

We are following both salmon movements and degree of pollution in the river for one more year, 1963, and expect that the results will confirm in general the findings of previous years. We are well aware that migrating salmon are not simplified clockwork machines in their response to degree of pollution, and we realize that there are many factors governing their movements, most of them not related to pollution. Nevertheless, the reasonable agreement among the three estimates of "safe" level of pollution, based on separate years, gives us some confidence in the results. It might be mentioned that no consistent correlation of movements with pollution was found until we used this method which took into account all three factors: water hardness; copper; and zinc.

The Conclusions So Far Are These:

1. Atlantic salmon do detect copper and zinc in solution at very low concentrations of less than 10% of the incipient lethal levels.

2. Copper and zinc are at least additive in their effects on fish, and may potentiate each other in some circumstances.

3. Degree of copper-zinc pollution in a river can be fairly easily calculated and expressed as a single number, at least in respect to effects on fish.

4. Migration of Atlatnic salmon is liable to be disturbed if copper-zinc pollution exceeds 35-45% of the incipient lethal level.

Acknowledgments

We would like to thank many of our fellow-employees of F.R.B., especially E.J. Schofield, R.J. Gibson and R.H. Currie, who operated the counting fence and collected water samples, often under adverse conditions. W.V. Carson carried out the ticklish job of analysing for extremely low concentrations of copper and zinc. Thanks are also due to Miss Ann Ramsay for patience in carrying out the laboratory tests of avoidance. Dr. R.W. Boyle and A.Y. Smith of the Geological Survey of Canada gave helpful advice on chemical procedures and analysed some of our 1960 samples for metal. J.E. Peters of the Department of Northern Affairs and National Resources supplied data on river flows before it was published.

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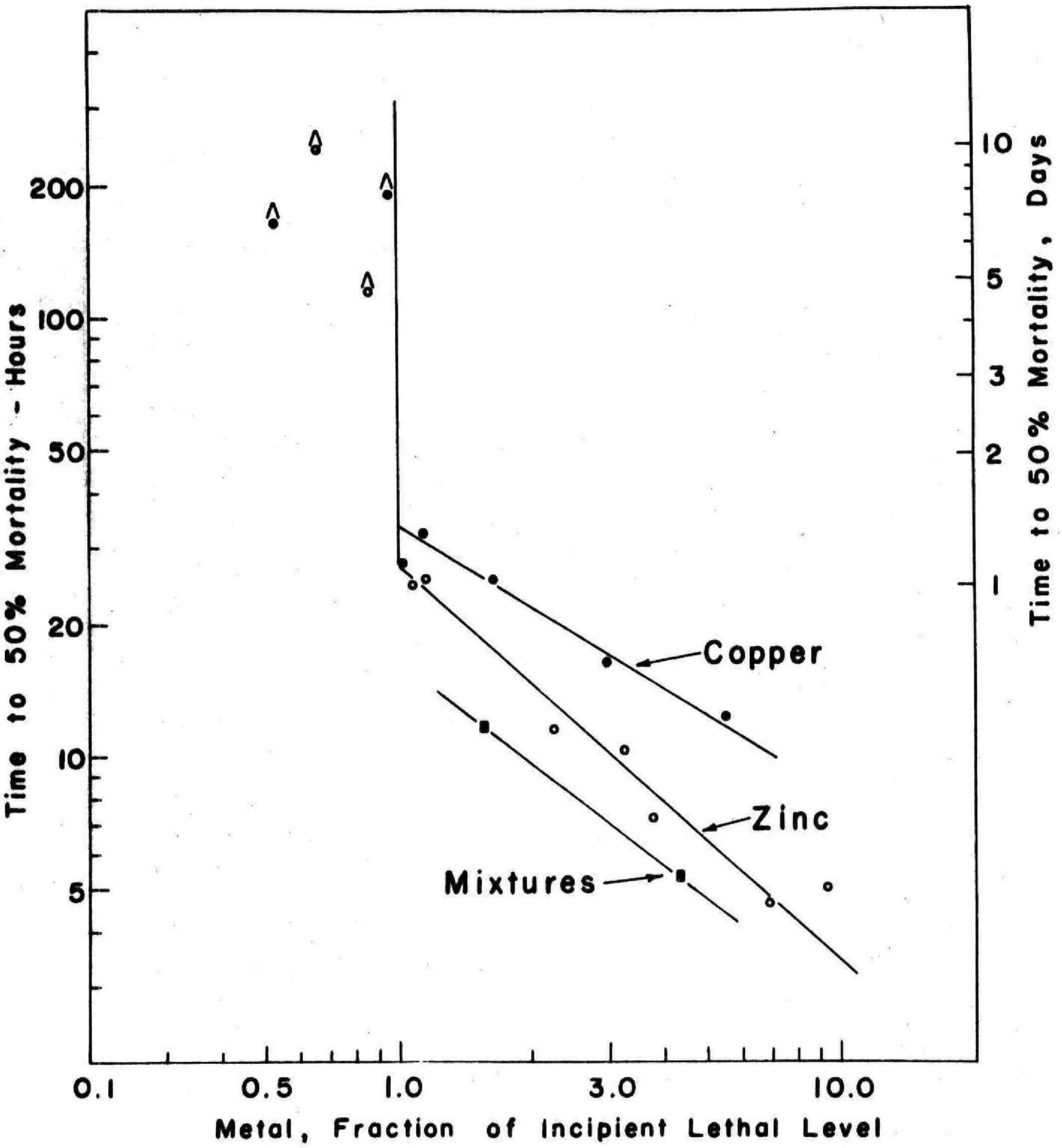

Fig. 1. Comparative toxicities of copper sulphate, zinc sulphate, and mixtures to young Atlantic salmon in water of 20 mg/l total hardness.

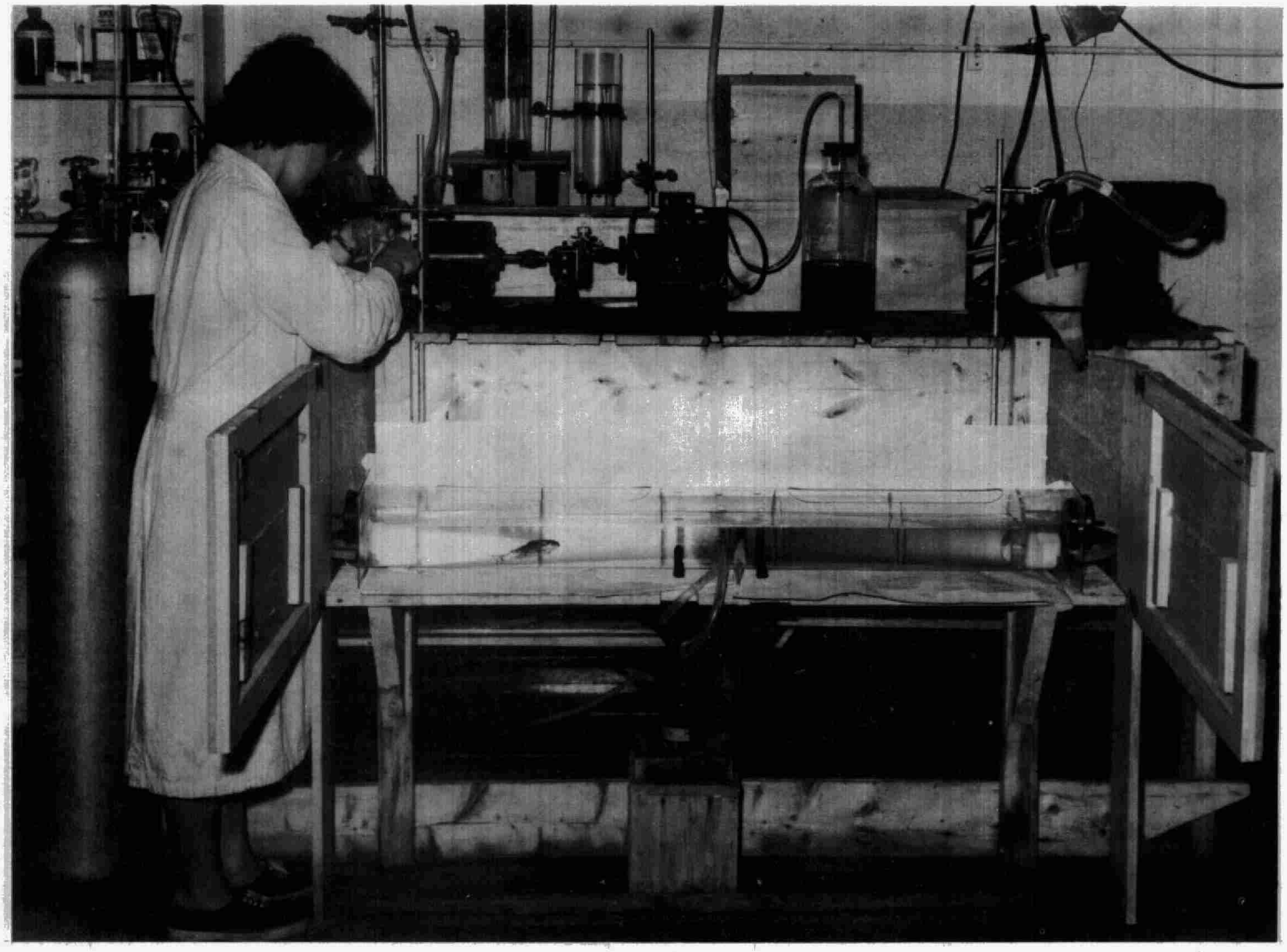

Fig. 2. Apparatus used for testing avoidance shown by young salmon in the laboratory. The fish was given a choice between normal water at one end of the plastic trough, and water containing toxicant at the other end. In the picture, some dye may be seen in the right hand side of the tube. This was added to demonstrate that there was quite a sharp separation of the two types of water half-way along the trough.

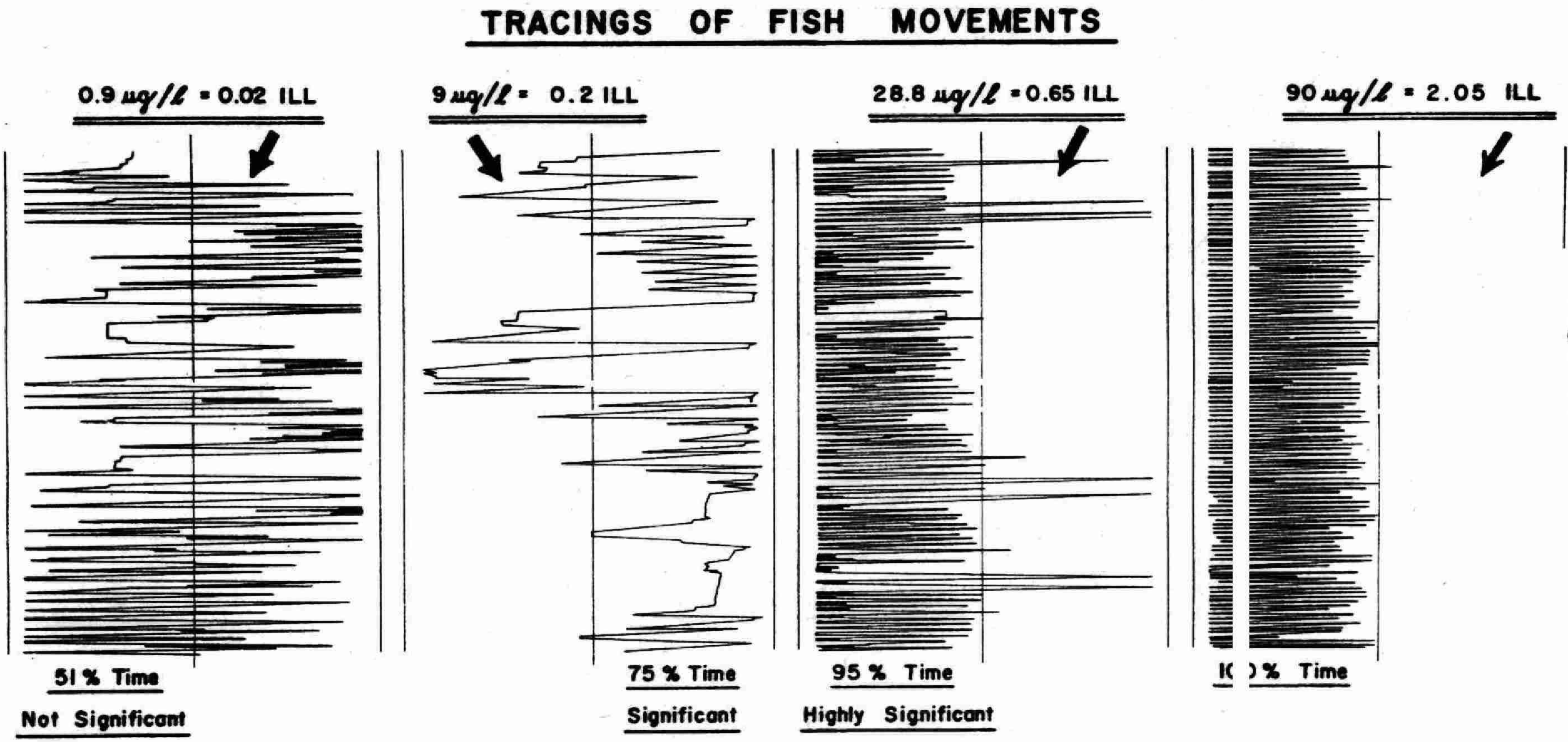

Fig. 3. Tracks of fish moving along the avoidance trough in four different concentrations of dissolved copper. Each record represents 10 minutes. Further explanation in text.

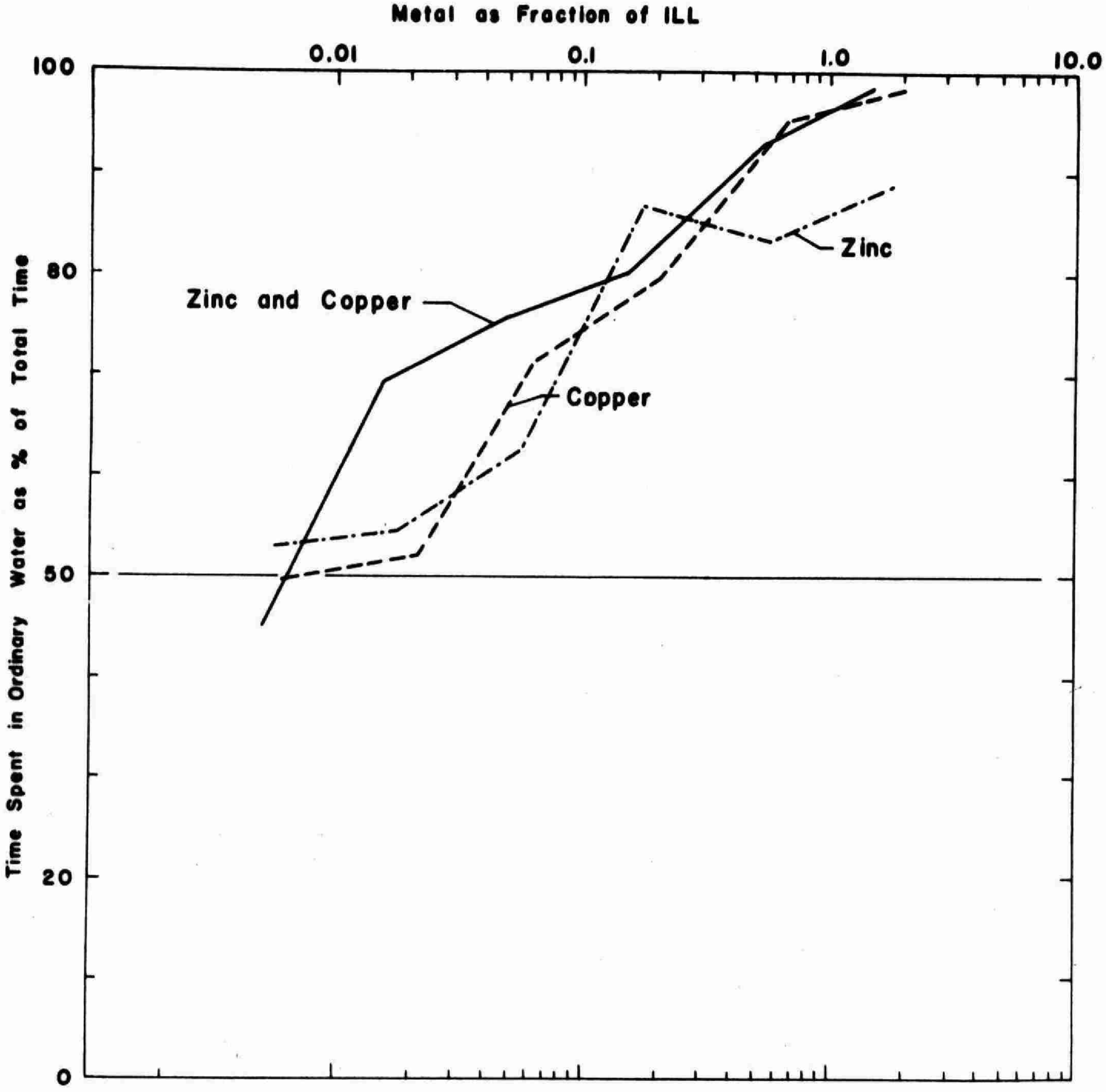

Fig. 4. Median avoidance response of several fish to metal solutions of various strengths. Concentrations are expressed as fractions of the incipient lethal levels. Random movements of fish would result in a score of 50% of time in ordinary water, while a higher score suggests avoidance. Medians for copper are based on 6 fish at each concentration, for zinc on 7 to 26 fish, and for mixtures on 5 to 5 fish.

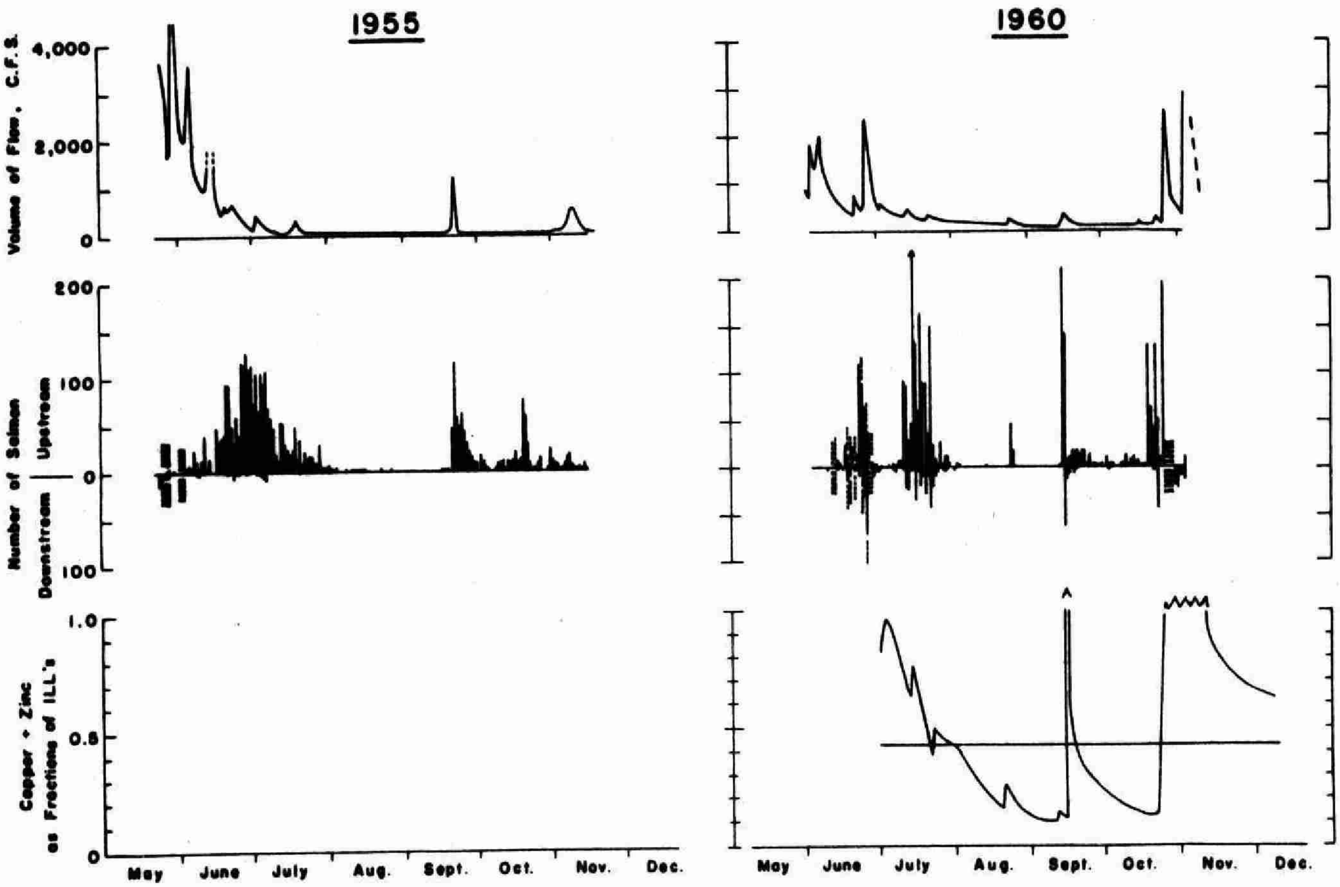

Fig. 5. Migratory movements of adult salmon in the Northwest Miramichi River in 1955 and 1960, with associated environmental conditions. Typical seasonal pattern of movements is represented by 1955, when there was no mining pollution. Number of fish moving upstream or downstream past the counting fence are shown for each day by a vertical line. Broken lines indicate that the fence was partially open, and more fish may have passed either way on these days. Flow in the river is typically a large spring freshet and smaller autumn freshets which are variable in size and timing. Pollution is expressed as the fraction of the incipient lethal level of copper which was present in the river, added to the fraction of the incipient lethal level of zinc.

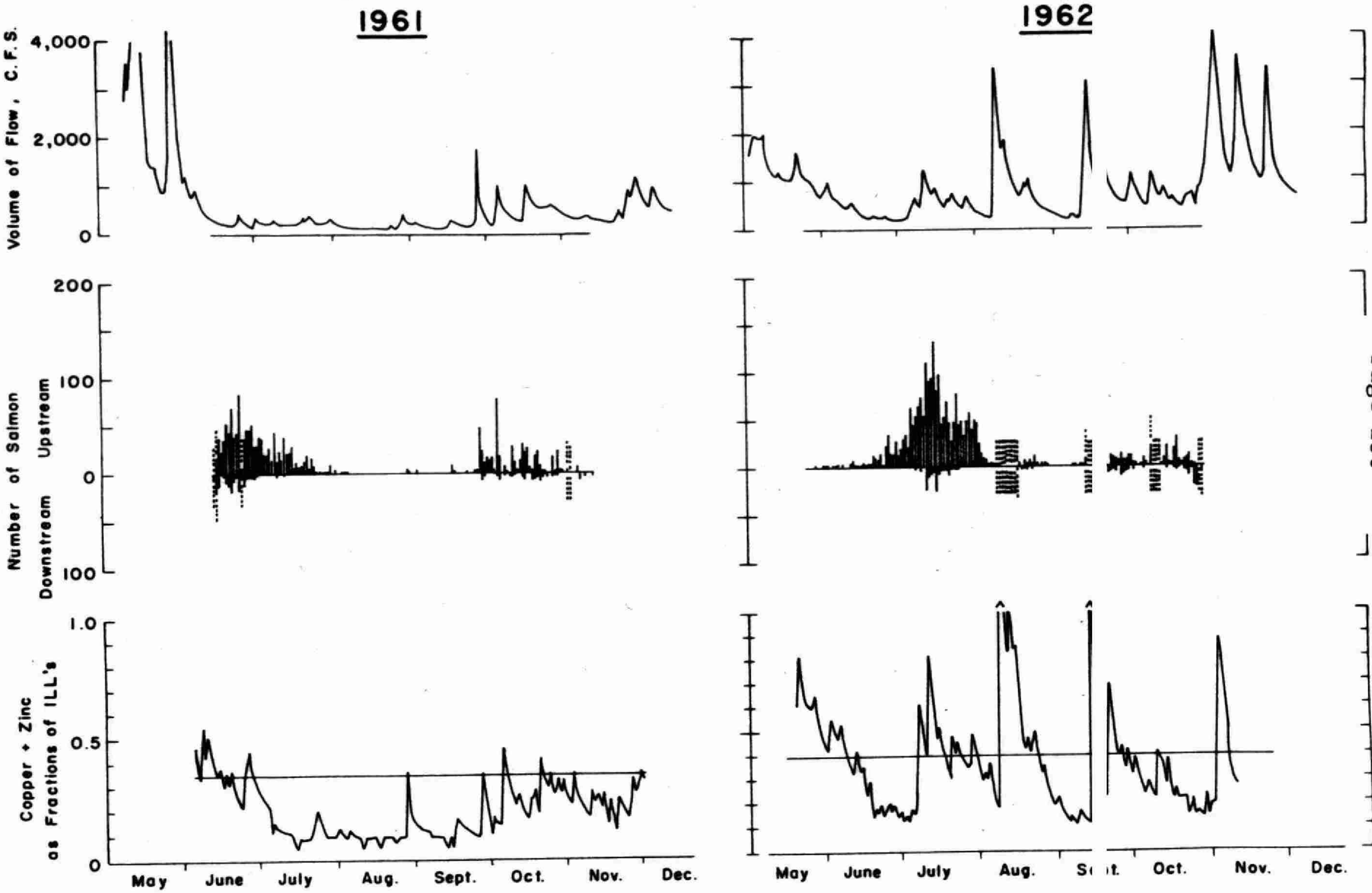

Fig. 6. Daily movements of adult salmon in 1961 and 1962 past the counting fence in the Northwest Miramichi River, correlated with river flow and degree of pollution.

INDUSTRIAL WASTE RESEARCH PROGRESS

by

R. E. FUHRMAN

"INDUSTRIAL WASTE RESEARCH PROGRESS"

by

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The mountainous problem of water pollution control on our continent manifests itself wherever we find concentrations of population. From experience, we know these populations are the result of opportunities for employment brought about by the continued industrialization of our countries. The industrial revolution, which is credited with United States expansion during the 19th century, still continues to exert its influences and it certainly is every bit as effective in Canada as it is in the United States.

It is not our purpose here to analyze these developments and the relations between industrial growth and population, but we do well to notice that these do go hand in hand. In the United States, it has been often observed that the beginning of the century found one-third of the population living in metropolitan areas. By 1960 this proportion had reached two-thirds and by 1980 it is expected to be three-fourths. Probably a similar migration is taking place in Canada and these bare figures seem interesting but not particularly absorbing until we note the effects of such compound growth of industries as well as the immediate communities which support the industries.

In the United States the census population is now approaching 190 million. The proportion of this population served by community drainage systems is approximately two-thirds or about 125 million. Provision of such drainage and provision for the treatment of the collected wastewaters to control water pollution in the receiving waters is a task of gigantic proportions. Gigantic, at least, are the problems of financing and management. The technology of the engineering designs, construction and operation are fairly well established and readily followed. By this I do not imply that these practices are static, but the provision of community drainage facilities has almost always been based on maximum economy of construction of long-lived conduits. Where these principles have been set aside, failures have often resulted with bitter lessons to all concerned with the project. On the other hand, municipal wastewater treatment practices have progressed over any period of recent history you care to take. If you question this, I urge you to look at the advertisements in any of our technical magazines at 10 or 20 year intervals. For those old enough, the progressive steps will be readily apparent. Even though the field is often criticized as not progressing by one breakthrough after another, a fair evaluation of this progress shows that more service is squeezed from the cost of facilities now than at earlier periods. It is unfortunate that the declining value of the dollar masks these improvements to some extent and usually only the trained eye can bring all the variables into focus.

Within relatively recent years in the United States, the pollutional load of industry has been equated, for practical purposes, to the domestic pollution burden. This indeed must be done rather roughly because many industrial wastes do not lend themselves to the usual yardstick of measuring BOD's of domestic waste-waters. However, a great many industrial wastes do have organic matter which decomposes by bacterial action and when this is the case, BOD comparisons may be made with proper precautions. The great difference in industrial and domestic wastewaters in this regard is the seemingly infinite number of complex materials in the wastewaters of industry. It is a familiar occurence to be reminded of the abundant complexities, and how we know so little of many new trade wastes which are "coming on the line" almost daily. For the purpose of this discussion, there is no intention on my part to provide details of the wastes created by new industrial processes of any recent period.

CURRENT INDUSTRIAL WASTES RESEARCH

In the June issue of the magazine "Industrial World" (1) there is a most interesting article entitled "Industry Attacks Water Pollution". The article mentions several products of modern research and development and it features the ORSANCO robot monitoring system. For the information made available by this system to be measured and recorded automatically is indeed a marvel. At 27 stations the variables recorded include dissolved oxygen, fluoride content, hydrogen ion concentration, temperature, specific conductance and others. In addition there are 70 stations measuring radioactivity of the river's flow.

Included in the article are several summarizing aspects of various industries and their current practices concerning the reduction or treatment of their industrial wastewaters. These are briefly summarized in the following paragraphs.

PULP AND PAPER

For many years the National Council for Stream Improvement has been the research arm for the pulp and paper industry. Research costs are now at a level of 10 million dollars per year. Recovery of paper fibres and suspended solids have increased considerably through processes of sedimentation, contact reaction, flotation and filtration. About a million tons of fibre are now reclaimed each year by U.S. mills. "White" water is being re-used quite generally. Since 1945, the effluent discharge of U.S. mills has been reduced 2% in spite of a doubled production through this period.

PETROLEUM REFINERIES

The American Petroleum Institute reports a reduction in the overall water requirement by that industry from 8 to 5.5 gallons of water per gallon of crude oil capacity for the decade ending with 1959. Research studies of the past have indicated that separate treatment of waste waters from varying processes gave the highest overall level of treatability of these wastewaters. The industry has invested $160 million in treatment facilities and now has plans for a further investment of $30 million. The bold leadership in refinery waste treatment offered by the Cities Service Company plant at Bronte, Ontario, is an excellent example of the application of modern research and development techniques.

COAL MINING

The practice of flushing coal washings to the nearest stream became uneconomical many years ago. The recovery of these fines from the streams not only improved navigation but it recovered solid coal dust that could be marketed. This is now done on these wastes at the plant in settling basins so that briquettes result. The economy has been a helpful partner to research in this advance.

METAL WORKING PLANTS

Pickling and plating tank wastes are strongly acid solutions. Here again, economy often helps in the recovery of valuable metals from the plating solutions. Examples are on record where the recovery of metals more than pay for the treatment process. All of us engaged in water pollution control may well wish for more such instances.

CHEMICAL PLANTS

In this field we find a complexity of discharges, the removal or treatment of which challenges the best research brains. Many of the products are desirable because of their stability. As a result of this stability, the decomposability of their wastes under the conditions of wastewater treatment or the receiving waters is a deterrent to economical discharge. Until research is able to crack many of these problems, unusual solutions such as dumping at sea or injection into deep geological formations will continue in spite of their high cost.

There is an abundance of research work evident in a story (2) recently reported by Mr.G.A. Howell, assistant to the Administrative Vice-President-Engineering of the U.S. Steel Corporation. To reduce the usual volume of water of between 45 thousand and 65 thousand gallons required to produce a ton of finished rolled steel, the Geneva works of the U.S. Steel Corporation at Provo, Utah, re-used water 10 times to reduce water consumption to about 10% of the normal figure. As such industries are constructed more and more in areas of water shortage, such practices can be expected to increase. Even in other areas, with the cost of water rising, an intermediate solution may prove to be economical. All of these developments depend on research to lead the way and each one in itself is an indicator of progress through research.

The multitudinous uses of water in a steel mill give a seemingly unending challenge for improvement. Water sprays and settling tanks are used to recover blast furnace flue dust. Special pits are used to recover the iron oxide scale formed by hot rolling. Pickling liquors demand neutralization, while biological treatment is used to remove phenolic wastes of coke plants, and oil skimmers and flotation methods recover lubricants.

In the Geneva plant, domestic wastewater is thoroughly treated to such a high degree that it can be returned to the plant's raw water supply for industrial washing and flushing. The treated water system supplies water for steam condensing, furnace cooling and heat exchange. Similarly it serves coke production, furnaces and the hot rolling mill. Hot used water is returned to a large reservoir for cooling and recycling to these units. The report closes with the statement "In many respects the effluent water is superior to that of the surface waters entering the plant. Normally the irrigation and ditch waters are turbid and high in organic content. By means of its clarification facilities the plant is actually improving the water."

The Geneva mill is a much more recent installation with water economy built into it than the now classic example of the Fontana, California, plant built by Kaiser during World War II. The U.S. steel industry laughed at Kaiser when he built this plant in the desert, but, through water economy, he has found a way to make the desert bloom in a new fashion.

In a recent report, the proximity of the Shell oil refinery at Anacortes, Washington, and a commercial oyster bed offshore in Puget Sound required the Washington State Pollution Control Commission to set high standards for treatment of refinery effluent.

Over several years of operation, this has been an outstanding success and last year the Shell refinery was granted an award for its accomplishment in water pollution control. Facilities installed include separation of wastes within the plant and a combination of treatment and control to offset the pollutional character of the various process wastes.

The oily process wastewater is subjected to two steam-stripping units for removing hydrogen sulphide, mercaptans and ammonia from sour process waters to eliminate the personnel hazard and odours. In addition to the oil removal, the wastewater is subjected to pH control and biological treatment prior to discharge.

Demineralizer drainage receives dilute acid wash water and it is held in a surge basin as an aid to pH control in the biological treatment. As a final measure of protection, rain water drainage from all parts of the refinery passes through a mechanical oil skimmer and trash bar screen.

ROLE OF RESEARCH

These examples could be repeated over and over, and it may well be asked what is the relation of this to progress of research in industrial wastes. It has been the pattern of research in this field to be done rather quietly by industries because of the proprietary value of such developments. However, the approach by some industries through centralized research activities has contributed major gains in the pulp and paper industry, the petroleum industry, the canners industry, the meat packing industry, the dairy industry, the steel industry, the electroplating industry, the MCA, the soap and detergent industry and the laundering industry, to mention only a few. A list of industrial organizations carrying on research in the field of industrial wastes is indeed imposing and it appears to include every industrial activity which might be involved in water pollution control. For this reason, it may be honestly observed that virtually all aspects of the pollution problem by industrial wastewaters is under the scrutiny of some research work going on somewhere. In our technical literature is an overall compilation of industrial expenditures for research and development work as well as for actual treatment plant construction and operation. By its nature, the treatment of industrial wastewaters is so related to product manufacture, by-product manufacture, and wastes, that developments are of such value to the developer that he would not want to share this information with his competitor. No one could advocate a different policy in this respect and, for the sake of economy, we are obliged to encourage the reduction or elimination of a waste through improved methods within an industry before resorting to the treatment of industrial wastewater per se. So, an industry faced with a water pollution control problem should first engage in a sound research and investigation program to minimize waste and simplify its problems of wastewater treatment. When it reaches this point, it should not delay with the necessary physical installation to comply with its water pollution control responsibilities. Continuation of its research program can still pay off in the future as processes are perfected and as further development of a plant occurs.

The progress of industrial waste research has been amply described by Mr. A.J. Steffen, Manager of Sanitary Engineering, Wilson and Company, Chicago. He has stated: (3)

"Millions of dollars are being spent by industry in industrial wastes research, much of it on utilization and conservation of wastes. This cost rarely appears in the records as research in pollution control because it is usually classified as product research.

"In waste treatment research, industry has certain inherent advantages over the municipal sewage field. For example, industrial waste treatment studies can be conducted on a semi-plant scale, and, if need be, on a full-scale trial-and-error basis--procedures generally not adaptable to municipal financing. Such studies have been stimulated in the postwar years by the work of industrial chemists and process engineers who have assumed responsibilities in the sanitary engineering field. They tackle each problem as a process problem, often breaking away from conventional treatment practices to develop entirely new processes.

"Postwar efforts have led to significant breakthroughs in industrial waste treatment--microbiological oxidation, disposal by irrigation, development of synthetic trickling filter media, the anaerobic contact process, air flotation, the use of ion exchange for removing dissolved ingredients, and disposal of sludge by wet oxidation, to name a few. Some of these processes, developed in the industrial field, have been adapted to the treatment of municipal sewage, notably microbiological oxidation and sludge disposal by wet combustion".

It is worthy to note that several of the United States have provided financial aid for industries proceeding with industrial wastes treatment problems. During the last 12 years, the following states have enacted legislation which gives a measure of tax relief for actual installations. These include Maine, Massachusetts, New Hampshire, North Carolina, Vermont, Virginia, and Wisconsin.(4) Measures are perenially proposed for Congressional relief from federal taxes for such purposes, but so far none of these has been enacted. These signs indicate that research in the field could well be done with good returns both in production and compliance with water pollution control requirements.

Perhaps no segment of industry has had the publicity given basic and applied research than has the field of radioactive waste disposal. Literature in our field is replete with descriptions of this work. Obviously, the reason for this is that the work in this field is either done directly by the government or under its direct supervision and management. At the same time it may be observed that solutions of the problems of radioactive waste disposal have been the most challenging of any yet encountered. The disposal problems of the field therefore are credited to the nature of these wastes rather than the lack of competition for solution to these problems.

FUTURE ROLE OF RESEARCH

Recognizing that research is the starting point for any water pollution control problem in industry, it is gratifying to see the close relation that has developed between the water programs and plant management in many industries. Just as the availability of water may influence the location of a new plant, it has a continuing influence on plant management, control and expansion. Only by a continuous research program can a plant keep up with the changes of its own industrial complex. The trend of meat packing closer to the farm and consolidation of canning and dairy plants are examples of major industry changes.

Rising costs in themselves have given stimulation to waste treatment research. Dollar returns can be high and the highest return is likely to come from an industry-wide research program. Use can be made of research work carried on by others in universities, in government and other organizations as well as by individuals. This would probably include, in the U.S. at least, the most important service of the U.S. National Technical Task Committee on Industrial Wastes.

Industrial wastes research deserves great credit for the progress that has been made in water pollution control. This progress is continuing now at a high rate and there is every reason to believe that its rate will continue and probably increase with continued expansion of our countries. It is the key to a major part of water pollution control progress in the years ahead.

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