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Papers Presented

at

Seventh Ontario

INDUSTRIAL

WASTE

Conference

JUNE 5th, 6th, 7th, 8th

1960

AT

Delwana Inn, Honey Harbour, Ontario

Sponsored By

THE WATER AND POLLUTION ADVISORY COMMITTEE
OF THE
ONTARIO WATER RESOURCES COMMISSION

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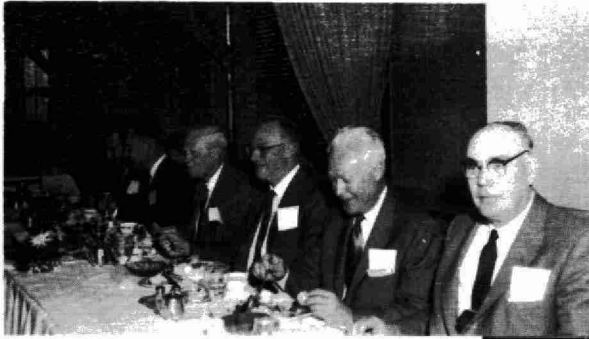
ONTARIO WATER RESOURCES COMMISSION

C O N T E N T S

	Page
PREFACE	1
WASTE DISPOSAL FROM URANIUM OPERATIONS IN THE ALGOMA WATERSHED	2
- K. D. Hester, and G. R. Yourt, Rio Tinto Mining Co. of Canada Limited, Management Services Division	
RECENT DEVELOPMENTS IN THE HANDLING OF RADIOACTIVE WASTES	17
- I. L. Ophel, Environmental Research Branch, Atomic Energy of Canada Limited, Chalk River, Ontario.	
INCINERATION FACILITES AT DOW, MIDLAND	22
- C. L. Sercu, Manager, Waste Control and Utilization, Dow Chemical Company, Midland, Michigan. U.S.A.	
COLOUR MEASUREMENT	30
- N. L. Nemerow, Professor J. C. Bryson, Graduate Student, and R. H. Brock, Jr., Instructor, Department of Civil Engineering, University of Syracuse, New York, U.S.A.	
POLAROGRAPHIC SCANNING OF INDUSTRIAL WASTE SAMPLES	42
- W. W. Ullmann, J. D. Porter and W. W. Sanderson, Division of Laboratories and Research, New York State Department of Health.	

DETECTION AND MONITORING OF PHENOLIC WASTE WATER	56
<ul style="list-style-type: none"> - A. D. McRae, Loss and Waste Controller, Engineering Division, Imperial Oil Limited and F. H. Griffiths, Chief Chemist, Edmonton Refinery, Imperial Oil Limited and R. G. Lane, Chemist B., Sarnia Refinery, Imperial Oil Limited. 	
LIME NEUTRALIZATION OF METAL BEARING ACID WASTES	63
<ul style="list-style-type: none"> - V. S. Tadsen, Director, Research and Development, The Gibsonburg Lime Products Company, Gibsonburg, Ohio. U.S.A. 	
HOUSEHOLD DETERGENTS IN WATER AND SEWAGE	71
<ul style="list-style-type: none"> - P. J. Weaver, Member, Research Steering Committee of the Association of American Soap and Glycerine Producers, Inc. The Proctor and Gamble Company, Cincinnati, Ohio. U.S.A. 	
THE USE AND CONSTRUCTION OF OXIDATION PONDS FOR INDUSTRIAL WASTE TREATMENT	84
<ul style="list-style-type: none"> - J. H. Neil, Supervisor, Biology Section, Division of Laboratories and Research, Ontario Water Resources Commission, Toronto, Ontario. 	
WASTE STABILIZATION PONDS IN ONTARIO, DESIGN AND CONSTRUCTION	91
<ul style="list-style-type: none"> - J. J. Heffernan, M.M. Dillon and Company, Toronto, Ontario. 	
APPLICATION OF FLOTATION PRINCIPLES TO SEVERAL INDUSTRIAL WASTE TREATMENT PROBLEMS	98
<ul style="list-style-type: none"> - J. W. Pratt and E. R. Vrablik, Process Engineers Inc. Palatine, Illinois. U.S.A. 	

	Page
WASTE ASSIMILATION CAPACITY PROCEDURES	110
- C. J. Velz, Chairman, Department of Environmental Health, School of Public Health, University of Michigan, Ann Arbor, Michigan.	
SOLIDS REMOVAL PRACTICES IN THE PAPER INDUSTRY	121
- R. O. Blosser, Resident Engineer, Kalamazoo College, Kalamazoo, Michigan	
INDUSTRIAL WASTE TREATMENT AS A FACTOR IN THE LOCATION OF WET PROCESS INDUSTRIES	126
- T. H. Safford, Southern Representative, Chas. T. Main Inc., Charlotte, N.C. U.S.A.	
WATER POLLUTION	135
- G. A. Selke, Commissioner of Conservation, State of Minnesota. U.S.A.	
BRITISH PRACTICE IN THE TREATMENT OF TRADE WASTES AND EXAMPLES OF ITS EFFECT ON SEWAGE TREATMENT PLANT DESIGN	141
- G.T.G. Scott, Partner, Canadian British Engineering Consultants, Toronto, Ontario.	
METROPOLITAN TORONTO'S APPROACH TO INDUSTRIAL WASTE	153
- C. V. Williams, Engineer, Department of Works, Municipality of Metropolitan Toronto, Toronto, Ontario.	
REGISTRATION LIST	162



HEAD TABLE
Seventh Ontario
Industrial Waste Conference
1960

P R E F A C E



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

Conference Chairman.

The Seventh Ontario Industrial Waste Conference was again sponsored by the Water and Pollution Advisory Committee of the Ontario Water Resources Commission. This meeting took place at Delawana Inn, Honey Harbour, Ontario, on June 5th, 6th, 7th and 8th, 1960.

The proceedings of this Conference are distributed as a contribution towards the widespread program for improving existing methods in industrial waste treatment. The papers are printed in the order in which they were given. A list of those who attended the Conference is also included. A study of the papers is recommended for all who are concerned with industrial wastes.

The Water and Pollution Advisory Committee is grateful to all who contributed in any way to this program of papers and discussions. It is recognized that these problems are of great magnitude, and it is gratifying that authorities in the field are willing to give their time for the preparation of papers and presentation of them at these meetings. The Ontario Water Resources Commission is glad to be of service in attacking these problems.

For further information write to:

The Water and Pollution Advisory Committee,
Ontario Water Resources Commission,
East Block, Parliament Buildings,
TORONTO, Ontario.

2.

WASTE DISPOSAL FROM URANIUM OPERATIONS
IN THE ALGOMA WATERSHED



V.R. Dixon, Vice President
H.J. Heinz Company
Chairman,
Session No. 1

By

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ABSTRACT:

The Algoma Watershed is delineated. The treatment and disposal of process wastes from uranium operation in the watershed is discussed in detail. The effect of process waste disposal on the water supply system is reviewed.

The health aspects of waste disposal are considered.

The only deleterious effect on the river system from uranium operations appears to be the increased hardness of the water, necessitating more chemicals or special treatment for boiler water feed.

I. INTRODUCTION

1. The Area

The area to be discussed in this paper is primarily a section of the drainage basin of the Serpent River. The drainage basin lies in Ontario's Algoma District, almost exactly half-way between Sudbury and Sault Ste. Marie. The section under consideration covers an area about 240 square miles. It lies between twelve and twenty-four miles north of Lake Huron, and extends about twenty miles east from the boundary line between the Sault Ste. Marie and Sudbury Mining Division.

For the last seven years this area has been the scene of one of the world's great mining developments. It contains the world's largest known deposits of uranium and, in spite of the huge tonnages presently being mined, only a small fraction of the ore deposits have been treated.

2. History

The first diamond drill went down in the Algoma District in April of 1953. The drill hole was just off Highway 17, about half-way between Sudbury and Sault Ste. Marie on a property called Peach Uranium Mines. This drill hole eventually became the basis for the Pronto Uranium Mines property, about fifteen miles east of Blind River.

After this drill hole had proved the existence of commercial grades of uranium ore, the famous Algoma District "back-door staking bee" was organized in May, June and July of 1953. During this time, approximately 1,400 claims (about 56,000 acres) were staked in the area being considered. These claims were on the radioactive pebble conglomerate outcrops in the Algoma District which followed quite closely the Serpent River system.

As soon as the news of the uranium strike got out in mid-July 1953, another 8,000 claims were staked in the area. After many financial transactions, these claims eventually made twelve uranium mines, feeding eleven uranium mills. The tonnages, names, start-up dates and several shut-down dates of these mills are included in Table I-1.

3. The Problem

As indicated in Table I-1, by May of 1958, the residue from approximately 34,000 tons of ore per day had to be disposed of in the tailings areas. The acid consumed in treating this ore was approximately 80 pounds of sulphuric acid and four pounds of nitric acid per ton of ore. In general, the treatment employed is to neutralize the acid with lime, and settle the solids in dammed areas, allowing only the clear neutral overflow to enter the river system. About 1,500 tons of acid had to be neutralized

every day after May of 1958. A total of approximately 170,000 tons of water per day was required for the treatment of this ore or about 25,000 gallons per minute. These figures delineate the magnitude of the problem of waste disposal and water supply in the uranium operations in the Algonia watershed.

4. Pronto System

Pronto Uranium Mine is only one mile from the highway and is not connected with the water source for the other plants. It had a completely separate waste disposal problem to any other of the mills. The original design of the system was to pick up water in one arm of Lake Lauzon to feed the mill and the townsite, and discharge the tailings through the tailings pond area to another arm of the lake. This meant that Pronto was really circulating the water through a giant settling basin, acidifying it and neutralizing it in the mill, and then returning this water with its high contents of salts to a reservoir for re-use.

5. Elliot Lake Area

The main disposal problem, however, was in the northern section where the ten other mills were built. These mills were all considerably larger than Pronto and the treated liquid wastes from all of them drained into the same river system, the Serpent River. From the Serpent River also, the feed water for the townsites, the mills and the boiler plants was taken.

The magnitude of this disposal problem was recognized long before the first mill started up, and in October 1956 representatives from all the mines in the area were called together by the Honourable Mr. Kelly, then Minister of Mines for Ontario, to discuss "the domestic and process water supply and the disposal of their mine tailings and sanitary wastes". The outcome of this meeting was a report by R.M. Way and Company, Consulting Engineers, and a map reproduced in part in Figure I-1 showing the drainage basins in the area and the proposed tailings disposal areas.

The map indicates how the mines in the middle belt, Stanleigh, Milliken, Lacnor (formerly named Lake Nordic) and Algom Nordic would receive and recirculate water containing the disposal materials from all the mines in the top section. The townsite of Elliot Lake has been isolated as much as possible from contamination by the disposal effluent from the uranium mines.

6. Elliot Lake Area - Disposal

Algom-Quirke at the head waters of the system, is in the most favourable position of all the mines. Originally Quirke obtained its process water from the Serpent River. Later a pump house was located in Dunlop Lake, and this is the present source of its water.

The tailings overflows from Quirke, Denison, Spanish American and Panel all drain into Quirke Lake. Here they are diluted by the full flow of the Serpent River and carried down along this stream through Kindall Lake, Whiskey Lake, the north side of the east arm of Pecors Lake then out through the south side of the east arm and south towards Lake Huron.

The disposal from Can-Met and Stanrock is carried down through Half-Moon Lake, May Lake and Hough Lake into the north-west arm of Pecors Lake. The disposal from Stanleigh and Milliken flows through Crotch Lake, McCabe Lake and into May Lake where it follows the Can-Met and Stanrock flow back into Pecors Lake.

The disposal from Lacnor and Algom-Nordic flows into lower Buckles Creek through a drainage system and from there to Nordic Lake and down through a long series of lakes to eventually reach the Serpent River and drain into Lake Huron.

The capacities of the tailings ponds vary with the disposal area considered. The disposal area at Algom-Quirke, for instance, was originally designed to take over twenty-five million tons of tailings. This would be suitable for almost twenty-five years life of the mine at the 3,000 tons a day rate.

The Algom-Nordic tailings area, on the other hand, must continually be built up by means of dams in order to contain the necessary tailings. This has been going on since the beginning of operation. These dams were originally sand and gravel, and were sealed by the tailings themselves. Later, dams were built by hydrocloning the tailings. The sand is used for the dam, and the dam then made impervious by the slime overflow.

7. Elliot Lake Area - Water Supply

The water supply for the mines in the top belt, Spanish American, Stanrock, Can-Met, Denison and Panel comes from Quirke Lake.

The mines in the middle belt have a more complicated supply problem (see Figure 1-2). From the north-west arm of Pecors Lake a pump station moves approximately 10,000 gallons of water per minute into Buckles Creek. The upper water shed of Buckles Creek is diverted by means of a canal into North Nordic Lake, then to Westner Lake. Three hundred to four hundred and fifty million gallons per month are pumped from here to Dumbell Lake. Pump stations at Dumbell feed Milliken, Stanleigh and Lacnor, each station pumping about 2,000 I.g.p.m. to the mine concerned. Algom-Nordic obtains its water from North Nordic Lake, although the twenty or so families on the Algom-Nordic townsite obtain their water from Ryan Lake.

The middle belt is a critical part of the system since the effluent from eight mines is being treated and returned to Pecors Lake and is then used again as fresh water in the process. This should indicate the efficiency of our disposal system, as this lake acts, as Lake Lauzon did at Pronto, as a giant receiving basin through which the water supply is

recirculated. Of course, considerable dilution also occurs here from stream flows.

II. MILL PROCESSES

1. Plant Flowsheet

The process waste from the uranium operations comes from several sources. A typical flowsheet is presented in Figure II-1. The heavy line shows the uranium flow and the light solution and solids disposed of or recirculated.

The underground mining operation requires process water for drilling and for laying dust. This water, plus underground seepages, must be pumped to surface and discarded. At most plants this is sent to tailings without any further treatment.

The ore is crushed dry using a jaw crusher and two cone crushers in series. The cone crusher discharge is ground wet, first in open circuit rod mills and then either in ball mills or pebble mills in closed circuit with a mechanical classifier. Classifier overflow is about 55 per cent minus 200 mesh. This product is settled to about 55 per cent solids in Dorr thickeners. The thickener overflow is generally returned to the grinding mills to conserve heat and water. However, some of this overflow is sent to waste. At one plant, Quirke, mine water is employed as feed water to the grinding circuit.

The thickener underflow is filtered using a disc filter and then leached (at about 65 per cent solids) in pachucas or agitators by sulphuric acid. The acid addition ranges from 55 to 90 pounds of 100 per cent acid per ton of ore. Live steam is used to heat the pulp to between 45°C. and 70°C. Up to six pounds per ton of sodium chlorate is required at some mills. The pulp is agitated by air or by mechanical means.

The leach discharge solution runs about 50 grams free acid per litre and contains many dissolved salts, mostly iron and aluminium sulphates. The acid must be partially neutralized with slaked lime to between one and five grams per litre so that the uranium may be picked up on an ion exchange resin. In this pH adjustment step, calcium sulphate is precipitated as a solid.

The pulp is then dewatered in acid thickeners. Thickener underflow is filtered and washed twice on drum type filters. The cake from the last filter stage is repulped, generally in water, and goes to waste.

The overflow from the acid thickeners, containing nearly all the uranium, is clarified and passed through an ion exchange resin. The passage through the resin removes the uranium and the waste product is called barren effluent. This is divided into two portion, the "royal barren" and the "waste barren". The waste barren may be used as a wash on the filtering stage but the majority of it goes to the tailings neutralization

area. Here lime is added to a pH of about 8.0 with vigorous aeration before disposal to the tailings ponds.

The royal barren contains a small amount of uranium and in many plants this is recirculated. This is generally done by liming to a pH of about 7.0 and returning the liquor to the neutral thickeners. The solids containing the uranium settle and the solution overflows to waste.

The ion exchange resin is stripped of its uranium with a nitric acid solution. The uranium is precipitated out in two stages using lime in the first stage, and either magnesia, ammonia or caustic soda in the second. The precipitate is thickened, filtered and sent to a drying plant. The overflow from the thickener is brought up to the necessary strength by nitric acid additions and returned to ion exchange. At times it is necessary to bleed some of the nitrate overflow to maintain a solution balance in the eluate circuit. This is already at a pH of 7.0 and is sent out to tailings.

Summarizing then, the material sent to tailings from a uranium plant consists of:-

- (1) mine water,
- (2) neutral thickener overflow containing some nitrates,
- (3) solids residues from leaching at 55 per cent minus 200 mesh,
- (4) neutralized waste barren, and
- (5) intermittent nitrate bleeds from the eluate circuit.

Partial solution analyses of these materials and approximate flows for a 3,000 tons per day mill are given in Table II-1.

2. Mine Water

In general, the mine water receives no treatment. At most properties, the uranium content of this water is low and the pH about 6.5. Combining this water with the mill tailings in the tailings pump box or tailings lines is adequate disposal treatment.

At Algom-Quirke, this water is employed in the grinding circuit, because of the relatively high uranium content (0.015 gm/l U_3O_8 or 15 p.p.m.) of the water and the low pH (4.5).

3. Neutral Thickener Overflow

At some plants, the excess neutral thickener overflow goes direct to tailings also. This overflow contains some fine slimes and has a very low salt content. At other plants it is combined with the tailings and goes through the tailings neutralization section.

4. Tailings Neutralization and Barren Neutralization

At all plants in the area, the acid wastes are neutralized with slaked lime. The lime is a high calcium type and is a mixture of shaft and rotary kilned lime. It is bought as a minus 1-1/2 inch material, and is handled in bulk, being transported in covered hopper rail cars and trucked to the mill site in covered trucks.

The discharge from the plant storage bins is slaked in Dorr slakers or in ball mills. The slurry from the lime holding tanks is circulated through a ring main. Automatic pH control is used on the lime slurry feed from the ring main.

The two types of tailings treatment used in the Elliot Lake area are:-

- (1) Separate neutralization of barren and solid tails in agitators, and
- (2) Neutralization of the combined barren solids and barren solution in pachucas.

Two typical plants which epitomize the methods used at the various plants in the area are considered.

In the first case, agitators were employed in two separate circuits.

The solids, as a 50% to 60% solids slurry are at a pH of about 3.0. Having been water washed, they contain little acid and few dissolved salts. They are pumped to a circuit consisting of three - 18 feet diameter by 20 feet high agitators in series. In the first agitator, lime is added through a pH controlled feeder to bring the pH to 5.0. The pH is raised to 8.0 in the second agitator. The third agitator acts as a surge and is generally nearly empty. Discharge from the third agitator goes to the tailings pump box.

The solutions, mainly waste barren, contain considerable quantities of dissolved salts (see Table II-1) and require the majority of the lime. The pH of these solutions is about 1.7 to 1.8. The treatment circuit consists of four agitators in series all 18 feet diameter by 20 feet high.

A manually controlled flow of lime goes to the first agitator. The pH in the second agitator is increased to 5.0 and controlled there automatically. The pH in the third agitator is raised to 8.0 and again the fourth agitator acts as a surge tank ahead of the tailings box; vigorous aeration continues in the fourth tank, however.

Aeration is a most important part of the process. Gypsum scale builds up quickly on the tanks even when aeration is vigorous, but the build up is exceedingly rapid when no aeration is employed. For example, at one plant barren and lime were fed together in a mixing box. This flow (about 400 I.g.p.m.) passed through a short piece of eight inch diameter pipe to the aeration tanks. Within eight hours, the eight inch pipe was almost completely blocked. Copious aeration appears to prevent the supersaturation of the solutions with gypsum, and therefore at least slows down the gypsum scaling process.

The neutralization reaction can be followed by the colour in the tanks. The first two tanks are brownish, indicating a mixture of calcium sulphate and ferric hydroxide. The third tank, at pH 8.0 is a dark green, showing ferrous hydroxide precipitation. The surge agitator has brownish indications, showing that the oxidation of the ferrous ion is nearly complete. The air oxidation of ferrous to ferric goes on quite rapidly at these high pH's. Contact time for the whole circuit is between 1-1/2 and 2 hours.

Considerable mechanical problems occurred in the waste barren neutralization section with this type of tailings neutralization circuit because of the gypsum scaling noted above. At some mills, also insufficient contact time was provided in the plants to give complete neutralization at this stage.

The second method of treating the tailings is to combine both the solutions and solids and agitate them together in pachucas. This combination cannot be made in agitators because agitators will not mix very low density pulps. There is a tendency to sand out and the agitator rakes become stuck. With the pachuca, however, since air is used for agitation and is introduced at the apex of the conical bottom, much more dilute solutions may be thoroughly agitated and so this method can be used for tailings disposal.

The pachucas have the additional advantage of not scaling. Apparently the ore particles act as nuclei for the calcium sulphate and thus prevent supersaturation.

At one typical plant, three pachucas in series, each 15 feet in diameter and 35 feet high with 60 degree cones are used for combined barren and tailings neutralization. The slurry enters the first pachuca at a pH approximately 2.0 and is adjusted to a pH of 6.5 by an automatically pH controlled lime feeder. The pH electrodes are on the discharge of the tank. No more lime is added, but the slurry is thoroughly aerated in the remaining two pachucas. The slurry leaves the mill at a pH of about 6.5.

Contact time with the 30% solids slurry is about one and one-half hours.

5. Disposal of Process Waste (Pumping, Dam Feed)

The combined solid and solution tailings after neutralization collects in a tailings box and is pumped from here to the tailings disposal area. This can be one to four stage pumping or even gravity disposal, depending on the pressures required. The pumps are generally rubber lined centrifugal type. Pipe lines are steel rubber lined, steel, or wood stave. The tailings lines may be as long as 7,000 feet.

As an example, one tailings pump at Algom-Quirke consists of a 10" x 8" S.R.L.-C. pump run by a 50 horsepower motor pumping about 1,500 U.S. gallons per minute approximately 3,000 feet through a 10" tailings line.

6. Reactions During Neutralization

The leaching reactions in the mill and the chemical reactions in the tailings treatment step determine what contaminants occur in the water from the tailings ponds.

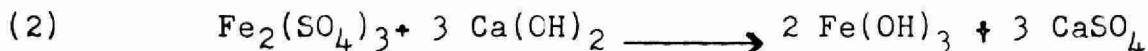
The leaching reactions dissolve iron and aluminium from the ore as well as uranium. Nearly all the uranium is removed on the ion exchange resin. The major dissolved materials entering the barren neutralization tanks are, therefore, sulphuric acid, iron and aluminium sulphates, plus some chlorides and nitrates. The liming step is designed to remove the iron and aluminium completely, and neutralize all the acid.

The main chemical reactions which occur in the neutralization tanks are, in chronological order:-

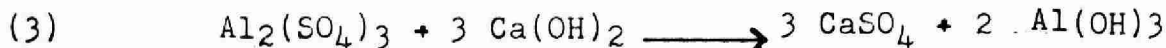
The neutralization of sulphuric acid by hydrated lime



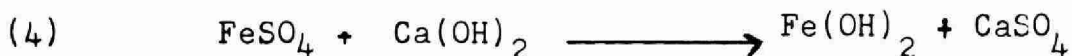
The neutralization of the ferric hydroxide, virtually complete at a pH of about 4.0.



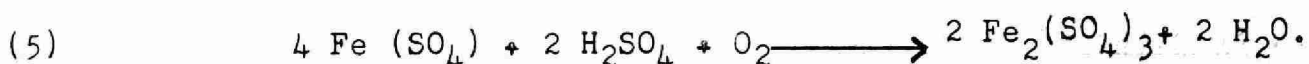
The neutralization of the aluminium sulphate



The neutralization of the ferrous hydroxide



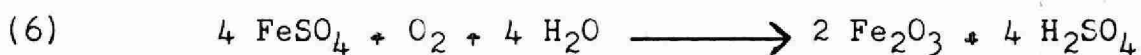
This will not be complete until nearly pH 9.0. The vigorous aeration of the solutions will, however, oxidize the ferrous ion to ferric.



and the ferric sulphate is then neutralized, as above, at a lower pH.

Reaction (5) should be completed before the solutions leave the mill, and therefore vigorous aeration and contact time are most important in the tails treatment.

Compare reactions Nos.(2) and (4). In reaction No. (2), three lime atoms are required for two iron atoms while in reaction No. (4) only two lime atoms are required for two atoms of iron. As the ferric iron form is the stable one, if ferrous iron salts are sent to the tailings ponds and are oxidized to ferric, a drop in pH occurs, as sulphuric acid is produced.



This will drop the pH of the tailings pond discharge.

III. STREAM ANALYSES

1. Start-up Problems

The effect of a uranium mill start-up on the watershed is shown in Figure III-1. This figure illustrates the change in values of the pH, the total dissolved solids, and the total hardness occasioned by a mill start-up. These analyses were run by the staffs of one of the mills.

Mill 'A' came on stream in the fall of the year. The usual start-up troubles occurred but the tailings neutralization area was operating satisfactorily by approximately March. The tailings effluent discharged into the Serpent River. The water came down the river to a pump house and this water was returned to the mill.

In late May - early June, mill 'B' started up. The tailings were discharged into the Serpent River through a temporary settling basin and affected the water supply. The effect is shown graphically in the above Figure. Note the very rapid rise of the total dissolved solids and the total hardness curves. These would rapidly rise to a limit, depending upon the hardness and dissolved solids in the effluent thrown out and, of course, the diluting stream flow. In approximately the middle of October these values began to improve, when the permanent disposal area came into operation.

Meanwhile the pH had dropped drastically from about 6.4 down to approximately 4.5.

Because of this problem, the owner of Mill 'A' decided to obtain process water from another source. The change is shown as occurring at the beginning of November.

2. Selected Water Analyses

Table III-1 indicates selected analyses of waters taken at various times in the various sections of the area. The analyses were done by the staff of the Industrial Waters Section of the Mineral Processing Division of the Department of Mines and Technical Surveys of the Dominion Government. The section is headed by Dr. J.F.J. Thomas.

We may consider items 1 and 6 as representative of the virgin water in the area.

The first sample was cut from Lauzon Lake before any Pronto effluent had gone into it and the Dunlop Lake sample should not be contaminated in any way since it is at the head waters of the system.

Items 2 and 3 show a grab taken at Lake Lauzon well down the lake from the place of entering tailings. There has been an increase in hardness, but the effect is by no means drastic.

Item 4 is taken from the Pronto mill tap which draws its water from Lauzon Lake.

Item 5 is an indication of the water now being taken from Elliot Lake. This was cut from a service station tap.

Item 7 is water from Ryan Lake, which is used by the Algom-Nordic townsite.

Item 8 is a sample of the water presently being drawn from Quirke Lake.

Item 9 is a cut from the discharge from Pecors Lake. As mentioned earlier, this lake received the tailings effluent from all the plants with the exception of Lacnor (Lake Nordic), Algom-Nordic and Pronto.

Item 10 indicates a cut taken lower down the Serpent River and shows the diluting effect of the extra streams on Item 9.

To indicate somewhat more precisely the effect of the tailings disposal on the water supply, the intake to the Pecors pump house station has increased from a hardness of 24 p.p.m. in the summer of 1958 to 75 p.p.m. in the summer of 1959 to 120 p.p.m. in February of 1960. This hardness increase, of course, is because of the recirculation of water through the lake.

3. Weekly Sampling Program

It became evident in late 1958, after all plants were producing, that there was need for a regular check of effluents. An arrangement was agreed upon between government departments concerned and representatives of the mining companies to have weekly samples analyzed for solids, turbidity, hardness, pH, acidity (CaCO_3), iron and nitrates. The following locations

were chosen: Dunlop Lake (virgin water), Serpent River (two locations) and the tailings overflow from each mill. (Sampling for organics, uranium and radium will be discussed later under Health Aspects).

The samples were collected by mine personnel and forwarded by engineers of the Ontario Department of Mines to the Laboratory of the Ontario Water Resources Commission.

Periodical reports of all these weekly samples, and occasional specimens taken by the Commission's engineers, were forwarded to each manager along with a letter, signed by Dr. Berry, containing recommendations for improvement and credit for progress as the readings indicated.

This practice began February 2, 1959 and has continued since. It has been a most informative and helpful program.

To illustrate the levels of the tailings dam overflow from a typical mill, Table III-2 compares the averaged effluent of nine mills in early 1959 and early 1960.

In addition to this control, some mines run their own analyses on daily or weekly grabs taken from sections of their tailings area, and other pertinent locations.

IV. HARDNESS EFFECTS

1. Treatment at Milliken.

In considering the increase in hardness of the waters in the area, it is wise to compare this with other water sources. The "Water Conditioning Handbook" published by The Permutit Company of New York indicates natural sources of water vary from as below 10 p.p.m. hardness to above 1,800 p.p.m. hardness. Waters at the upper limit are potable (after the human system becomes used to them) but are unsuitable for industrial use.

The water hardness in Lake Ontario and Lake Michigan runs about 125 p.p.m., somewhat higher than our present water sources.

To indicate the treatment chemicals required, and their variations with hardness and pH, the raw water analysis of the feed water to Milliken Lake Uranium mines is shown in Figure IV-1. The quantity of treatment chemicals required is shown in Figure IV-2.

2. Pronto Water Softening

It has already been necessary to install a Zeolite Water Softening plant at Pronto Uranium Mines Limited, because of the very high hardness of the water.

The hardness of the raw water fed to the Pronto plant had increased from a low of 12 p.p.m. for virgin water to 250 p.p.m. by December 18th, 1957. The pH was 6.8. It was decided at this time to install two water softening units. These went into operation in late April, 1958. Approximately 70% of the water was softened by these units at a rate of about 15,000 gallons of raw water per regeneration. The raw water by June, 1958 had increased to some 270 p.p.m. hardness and the regeneration gallonage had gone down to about 12,500 per unit.

After the diversion of tailings effluent to Lake Huron in the summer of 1959, the regeneration gallonage increased to some 40,000 gallons on a hardness of 90 p.p.m. by February, 1960.

Chemical treatment costs were down to about \$4.00 per million pounds of steam in February 1960 from a high of approximately \$20.00 per million pounds in June, 1958.

V. HEALTH ASPECTS

1. Radioactivity

Uranium in drinking water has been monitored monthly for several years by engineers of the Department of Health for Ontario. Radium has been checked less frequently because of technical difficulties.

The most recent MAC's (maximum allowable concentration) suggested for public drinking water by the Division of Industrial Hygiene (Ontario Department of Health) are 500 - 1,000 micrograms per litre (parts per million) for natural uranium and 5 - 10 micromicrograms per litre for radium -226.

In regard to uranium, the large majority of tap water readings in the Algoma watershed have been less than 10 and 100, and an occasional one over 100. Samples of tailings overflow taken quarterly usually register less than 100. Analysis of water pumped from mines yield concentrations usually from one to several hundred; a few exceed a thousand micrograms per litre. In one concentrator, the uranium is recovered by using mine water in the milling process.

Almost all assays of radium in tap water have been less than 5 micromicrograms per litre. Tailings overflows range up to 7. Radium in mine water varies mostly from 1 to 50 micromicrograms per litre. Readings taken where the Kennebec River (of which the Serpent is a tributary) crosses Highway 17 have been under 10. This appears to indicate that there is no build up of radium downstream from the mining operations.

It should be noted that the radioactive tolerances mentioned above are based on life time exposure.

2. Drinking Water

Weekly samples are taken of various tap waters and analyzed by the Department of Health for organic contamination that might occur from overflows or seepages of sewage systems or other origins.

Drinking water supplies for office, plant, underground and domestic use are chlorinated with up-to-date equipment, using chlorine gas.

3. Sewage Disposal

Domestic and plant sewage is disposed into septic tanks and tile beds and in several instances pumped into tailings ponds.

During the construction period there were problems with organic contaminations from temporary and inadequate lavatory facilities; these conditions are past history. Apparently there was no definite evidence to indicate that they were directly responsible for the hepatitis epidemic which occurred in the area in 1957. The latter was attributed mainly to laxities in personal hygiene.

4. Nitrates

Johnston (1) reports the occurrence of a blood condition, among infants, caused by certain well waters containing high concentrations of nitrates. Apparently the first known fatality occurred in Saskatchewan in 1948 where the water contained 1,320 parts per million NO_3 as N. Reference is also made to the condition in livestock.

It bears mention that the disease is associated with well waters, usually also contaminated with organics rather than from disposal of nitrates from chemical processes in surface waters. No cases of a blood condition have been attributed to nitrates in the Serpent River system.

The recommended MAC for infants is 10 parts per million nitrate nitrogen. Readings from samples of virgin water from Dunlop Lake, several from the Serpent River on its way to Quirke Lake, and one of the overflow from each tailings pond usually range from 0 to 1, 1 to 10 and 10 to 70 p.p.m., respectively.

5. Fish Life

No studies have been made by the mining companies into the possible effects of effluents on fish. However, it is known that they have been thriving in effluent waters. Minnows have been observed in the tailings ponds themselves where total hardness levels are up to 2,500 or more.

(1) Johnston, R.A. - "The Incidence of Nitrates in Rural Ontario Well Waters" Trans. First Industrial Waste Conference.

Some fishermen in the area feel their catch in several of the lakes in the system this year has been the best to date. This includes lakes in the "inner chain" which, because of a smaller flow than in the main Serpent River, is affected more by the effluents.

VI. CONCLUSIONS

The problems of industrial wastes and water supply posed by uranium operations in the Algoma District have been outlined and discussed in detail.

The contaminants, including the uranium, may be all precipitated by increasing the pH to approximately 8.0 and aerating. If this is done, and the effluent material settled, then the water may be hard but it is quite suitable for use.

The deleterious effect of this hard water on plant and animal life appears to be non-existent. At several places part of the problems with tailings disposal have been increased because beavers tried to put dams at the wrong spot in the tailings ponds. Fish and frogs live and thrive in the tailings disposal waters, so these treated waters are certainly not harmful to animal life.

Part of the disposal problem in the Elliot Lake area is being reduced by the stretch out of uranium deliveries to 1966. Fewer operations will thus be disposing of effluent. As indicated in Table I-1, only seven mines will be disposing of waste by the end of this year to the Serpent River basin rather than ten as previously.

It may be necessary for some of the mines still operating to install water softening plants to treat their boiler water. It is indicated, however, that the disposal procedures followed, when properly practised, adequately protect and preserve the natural and human resources of the region.

VII. ACKNOWLEDGEMENTS.

The writers acknowledge the co-operation and services provided by various Government Departments, Ontario Water Resources Commission, Department of Health particularly the Division of Industrial Hygiene, the Ontario Department of Mines and the Federal Department of Mines and Technical Surveys.

The data and assistance received from the Mine Managers and their Staffs is greatly appreciated.

The authors wish to thank the Management of the Rio Tinto Mining Company of Canada Limited for permission to present this paper.

TABLE I-1

START-UP DATES, MILLS, TONNAGES AND SHUT-DOWN DATES.

<u>TONS</u>	<u>MILL</u>	<u>START-UP</u>	<u>SHUT-DOWN</u>
1,500	Pronto	September, 1955	April, 1960
3,000	Quirke	September, 1956	
3,000	Nordic	January, 1957	
6,000	Denison	May, 1957	
4,000	Lacnor	September, 1957	June, 1960
3,000	Panel	February, 1958	
2,000	Spanish American	May, 1958	February, 1959
3,000	Stanleigh	March, 1958	
3,000	Stanrock	March, 1958	
3,000	Milliken	April, 1958	
2,500	Can-Met	March, 1958	March, 1960

TABLE II-1

TYPICAL ASSAYS AND APPROXIMATE FLOW RATES OF DISPOSED MATERIAL

Material	Approx. Igpm. for 3,000 tons/day mill	U ₃ O ₈ gm/l	SOLUTION ASSAYS gm/l									
			pH	H ₂ SO ₄ gm/l	Fe ⁺³ gm/l	Fe ⁺⁺ gm/l	NO ₃ gm/l	Al ⁺⁺⁺ gm/l	SO ₄ gm/l	Ca ⁺⁺ gm/l	SiO ₂	Cl
Mine Water	250	0.015 to 0.002	6.7	-	-	-	-	-	-	-	-	-
Neutral Thickener Overflow	50	0.001	6.7		<0.01	<0.01	6.0	<0.1	-	-	-	-
Barren Solids (as a pulp)	2 tons/Minute solids 350 I.g.p.m. solution	varies,	but	never greater than waste barren below								
Waste Barren) Royal Barren)	600 I.g.p.m.	{0.004 {0.010	1.8	1.0	0.5	2.5	0.5	1.0	20.0	-	0.2	0 to 0.7
Uranium Thickener Overflow	1 gallon/min.	0.005	7.0	0	<0.01	<0.01	50.0	-	25.0	1.0	-	0 to 1.5

TABLE II-2

REACTIONS DURING NEUTRALIZATION

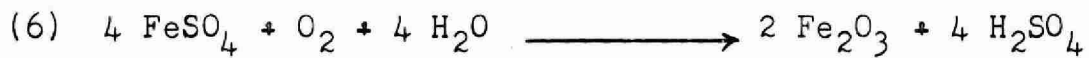
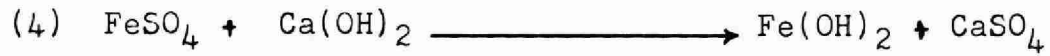
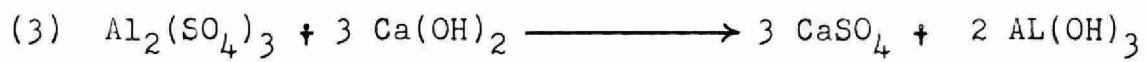
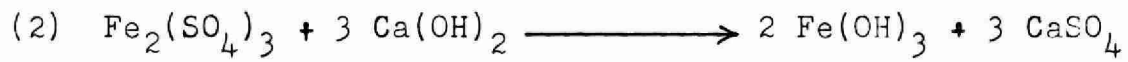
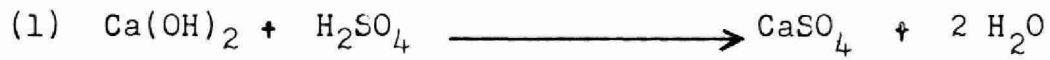


TABLE III-1

SELECTED ANALYSES OF WATER.
SAMPLES FROM ELLIOT LAKE AND VICINITY

Courtesy - Dr. J. F. J. Thomas of the Dept. of Mines and Technical Surveys.

SAMPLE FROM	ITEM NO.	DATE	pH	ANALYSES IN PARTS PER MILLION							
				Total hardness (∞ CaCO ₃)	Mg	Ca ⁺⁺	Total Fe	SO ₄	NO ₃	SiO ₂	Chloride
Lauzon Lake before Pronto Start-up	1	August 3, 1955	7.0	14.6	1.3	3.7	-	8.0	Trace	2.1	1.0
Shore of Lauzon near Highway 17	2	August 6, 1958	6.8	24.1	1.8	6.7	-	18.7	0.6	1.6	1.0
Shore of Lauzon near Highway 17	3	Sept.25, 1959	6.8	32.3	2.3	9.3	0.08	24.9	0.3	2.6	5.1
Pronto Mill Tap	4	Sept.29, 1959	6.4	170	18.2	38.6	0.3	167	0.3	2.9	26.9
Elliot Lake Tap (in Service Station)	5	Sept.25, 1959	7.0	45.3	2.4	14.4	0.07	34.6	0.8	2.5	9.4
Dunlop Lake	6	Sept.24, 1959	6.5	12.1	0.6	3.9	0.04	6.8	0.1	1.5	0.2
Ryan Lake, Water Source for Nordic Townsite	7	Sept.25, 1959	7.0	18.6	1.1	5.6	0.1	7.1	0	2.0	3.5
Quirke Lake	8	Sept.29, 1959	6.4	97.6	3.4	33.9	0.25	90.7	0.6	2.4	8.8
Canal near Nordic Trailer Park, from Pecors Lake	9	Sept.25, 1959	6.8	83.9	4.4	26.6	0.23	75.9	1.0	3.0	6.0
Serpent River, near Elliot (Depot Lake, Highway 108)	10	Sept.25, 1959	6.7	72.6	4.0	22.7	0.05	65.0	2.5	1.6	6.4

TABLE III-2

COMPARISON OF EFFLUENT ASSAYS - 1959/1960

<u>Material Analyzed in p.p.m.</u>	<u>First Quarter 1959 Feb. 2 - Mar. 10</u>	<u>First Quarter 1960 Jan.20 - Mar.14</u>
NO ₃	48.9	17.2
Hardness	1,746	969
Total Fe	7.5	13.7
pH (Lab.)	5.5	5.8
Turbidity	24.1	16.7

RECENT DEVELOPMENTS IN THE HANDLING
OF RADIOACTIVE WASTES



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INTRODUCTION

While it is true that the widespread use of nuclear power will depend largely on economic factors, it is equally true that inability to control the radioactive by-products would severely restrict the places at which nuclear power plants could be built. For this reason the atomic energy industry has in recent years spent an increasing amount of research and development work on the treatment and permanent storage of radioactive wastes.

This paper will outline some of the recent Canadian effort in this field, particularly as it applies to reactors for generating nuclear power.

ELIMINATION OF HIGHLY RADIOACTIVE LIQUID WASTES

One of the most interesting, and unheralded, developments in the Canadian nuclear power research program is the possibility of completely eliminating the highly radioactive liquid wastes which are associated with the chemical processing of irradiated reactor fuel. Almost all of the radionuclides produced by a reactor are contained within the uranium fuel. When the fuel is processed to recover the 'unburned' uranium the highly radioactive fission products are unwanted by-products of the process. Since the waste fission products are now dissolved in highly corrosive liquids their subsequent handling and containment is a difficult and expensive matter.

The development of a high integrity natural uranium oxide fuel for the NPD-2 and CANDU reactors means that chemical processing of the irradiated fuel is a doubtful economy (1). So much of the fissionable uranium-235 is 'burned' during the lengthy residence time in the reactor that the cost of recovering the depleted uranium by expensive chemical processing (under current conditions) is more than the value of the reclaimed fuel.

The high-level radioactive waste problem then becomes one of handling and storing encased solid material rather than treating highly dangerous liquids. If the fuel is stored in

accessible vaults it will still be available in the future if new, cheaper methods of recovering uranium or other useful by-products are developed.

FIXATION OF WASTES IN NEPHELINE-SYENITE GLASS

The possibility of the Canadian nuclear power program generating large quantities of high-level liquid wastes in the near future now looks remote. However, if the need to handle such wastes does arise we will have available a method of fixing the fission products in a solid inert form. This process, which involves the mixing of the fission product solution with powdered nepheline syenite and the subsequent fusion of the mixture into a hard glass, has been developed by the Chemical Engineering Branch of Atomic Energy of Canada Ltd. (2).

Development of the method has reached an advanced stage and at the present time the Environmental Research Branch and the Chemical Engineering Branch are jointly engaged in field testing the storing of the glass blocks directly in the soil.

Storage of bare glass in wet soil was chosen as the test condition because this is the most unfavourable of the various storage methods that have been considered. In a large scale process it is more likely that dry storage in a concrete or rock vault would be used.

Two field experiments are in progress at the present time. The first, which was started in August 1958, comprises twenty-five nepheline syenite glass hemispheres weighing 2 kg each and containing a total of 300 curies of mixed fission products. The blocks are buried in a known configuration below the water table and the radionuclides leaching from the glass are monitored by means of special ground water samplers and soil samplers placed 'downstream' from the blocks⁽³⁾. Leaching rate of the glass is very low - in the order of 10^{-7} gms glass per square centimetre per day - and this test has resulted in only barely detectable amounts of radionuclides in the soil twelve inches from the blocks. Sampling will be continued for some years.

A second field test was started in May, 1960. The blocks used contain a total of 1000 curies of fission products and are expected to produce more easily detectable concentrations of radionuclides in the ground water and soil. After several years monitoring, the soil 'downstream' from the blocks will be intensively sampled to obtain an accurate estimate of the total amount leached from the glass under these conditions. The Chemical Engineering Branch is simultaneously carrying out leaching tests in the laboratory which will help in the interpretation of the field test results.

STORAGE OF SOLID WASTES

At Chalk River the disposal of solid materials contaminated with significant amounts of radioactivity is based on dry storage in concrete containers⁽⁴⁾. Only those materials contaminated with minor amounts of radionuclides are placed directly into the soil. With these amounts the cation exchange capacity of the soil is sufficient to hold back the radioactive cations. However, this type of disposal used up considerable areas of ground and an incinerator is being developed for installation in the near future. Ash from the incinerator will be mixed into concrete.

The containers for the more contaminated wastes are built as six inch thick concrete-walled trenches set below ground level. After being partly filled with waste the trench is filled with sand and a water-proof concrete lid is cast in position. The whole container is then covered with dry soil. Special disposals, such as radioactive ion-exchange resin columns, are made into below-ground sections of waterproofed concrete pipes.

LIQUID WASTE HANDLING

The dispersion of very low-level liquid wastes into the Ottawa River has been described in some detail elsewhere (5,6). Other liquid wastes with somewhat higher concentrations of radionuclides are not directed to the river but receive special treatment.

Wastes containing medium levels of radioactivity along with very low concentrations of salts are handled in covered seepage basins. In these the water drains away through the soil and the cationic radionuclides are retained by the ion-exchange sites on the soil particles. The covering, consisting of eight feet of crushed rock, acts as a shield against radiation, prevents access by wildlife, discourages plant growth and eliminates air contamination.

These basins have handled large volumes of waste and have performed quite satisfactorily. A small percentage of the radionuclides have migrated in the ground water for several hundred feet, over a period of years. For this reason, this method would not be used in closely settled areas. Ion exchange treatment on resin columns is a suitable alternative for this type of waste although somewhat more expensive. The feasibility of borehole injection into shallow underground strata is being considered.

Medium-level radioactive wastes containing high concentrations of acids, detergents, etc. can not be treated by ion exchange. Nor are they suitable for seepage basins, since the excess cations will displace the radioactive cations from the exchange sites on the soil particles and destroy the

adsorptive capacity of the soil. Such wastes have been treated at Chalk River by making them into a rather poor quality concrete within 55-gallon drums. These drums are stacked inside a large concrete container. The whole assembly is then converted into a large solid concrete monolith by pouring high quality concrete around and over the drums. Such monoliths were first constructed in 1956 and while they contain several thousand curies of fission products within the drums only minute amounts of radioactivity have been found outside the structures.

POWER REACTOR WASTE TREATMENT

All of this experience has resulted in the development of a sound system for handling radioactive wastes at our future nuclear power sites. The system is based on the principles of containment for all hazardous amounts of radionuclides and controlled release of minor quantities.

Irradiated fuel would be temporarily stored in water-cooled basins in which the water is recirculated through ion-exchange columns. It will later be transferred to permanent dry storage.

Low-level radioactive liquid effluents will be collected and dispersed on a batch system. Each batch will be sampled and analyzed before being released at a controlled rate into inactive dilution water from the power plant condensers. Only pre-diluted wastes will be released to the environment.

Liquid wastes such as ion-column regenerants which are unsuitable for dispersal will be evaporated to small volumes and placed in concrete monoliths. Condensate from the evaporator is returned to the recirculating ion-exchange system.

To reduce land area requirements low-activity solid wastes will be incinerated and the ash made into concrete. Non-combustible material and more highly contaminated solids will be placed in concrete trenches.

Such a waste handling system can be used in densely populated areas without hazard to the surrounding population. Preliminary cost estimates for construction and operation of such a facility associated with a large power reactor indicate that treatment costs should not exceed one per cent of the cost of the generated electric power.

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INCINERATION FACILITIES AT DOW, MIDLAND

by

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The Dow Chemical Company plant at Midland, Michigan produces 83,000 tons per month of complex chemicals. These production facilities in turn produce tons of waste products both solid and liquid which must be burned, buried or treated.

50 million gallons per day of water wastes are treated in an activated sludge treatment plant. 80,000 pounds per day of Biochemical Oxygen Demand are satisfied in this treatment plant and some 7,500 pounds per day of phenols are biologically oxidized before the wastes can be discharged to the river.

Many oils, solvents and still residues are kept out of the sewer system and must be burned. Over 250 Dempster loads of these waste tars per week are generated at Midland. This represents a total of over 500,000 gallons per month of still residues, waste solvents, washes and contaminated products that must be destroyed. Over 1700 drums and similar containers of semi liquid and solid waste chemicals are produced monthly, in addition to almost 17,000 cubic yards per month of other refuse.

To safely and efficiently destroy burnable wastes, Dow put into operation in 1959 a two million dollar incineration plant to handle 81 million BTU per hour of liquid tars and 60 million BTU per hour of solid refuse. Storage mixing and blending facilities for both liquid and solid wastes are included as are scrubbing facilities for fly ash and acid gases.

This huge expenditure was necessary because of the tremendous quantities of combustible solid and liquid wastes that must be destroyed with a minimum of air and water pollution. These wastes have been the subject of extensive research, investigation re-use, reduction and even possible sale of these waste products. Many thousands of dollars have been recovered, yet this large incineration plant was needed to properly dispose of the remaining wastes that have no value.

Refuse at Dow consists of plastics, paper, boxes and other solids of high BTU content, plus many non-burnable solids.

Most of the waste products from laboratories are extremely hazardous. Toxic, reactive or explosive, these items, although usually small in volume, are frequently the hardest disposal problem.

Safe and efficient disposal of all of these materials is now accomplished by control of the collection, handling, and incineration of the wastes. Collection and handling are determined by volume, character and hazards involved in the material. Control of the incineration of these wastes is accomplished by blending, mixing or even burning the material separately, in a well designed incinerator. Investigation, design and construction of adequate facilities to handle these wastes took five years. The clean incinerator stacks at Midland are proof that all the Dow combustible waste materials can be incinerated without further nuisance to the community.

Solid tars from the production plants at Midland originally were buried, and, as the plant expanded, many of these wastes had to be rehandled and moved again. To eliminate this problem, the tars were hauled from production to a hand-stoked vertical tar incinerator. A rotary kiln was installed in 1948 with an ash recycle system to aid in burning these hard tars. It soon became obvious that the rotary furnace could burn a tremendous amount of solid refuse, paper, boxes, drums of chemicals, with a minimum of effort. The ash recycle was giving problems, and was abandoned, as it had been proved that the tars could be hauled in liquid form and pumped to the incinerator more efficiently than being handled as a solid.

The Dow Midland plant was expanding at a rapid rate and there were a lot of construction materials to dispose of at this time. Gradually, the original 10' diameter by 25' long kiln became overloaded and much refuse had to be burned on an open dump. The kiln was not equipped with secondary combustion or air control and all feeding was done by hand, so most of the time a plume of black smoke poured from the stack. All refuse was introduced to the kiln through a 4' diameter open hole in the floor. This is actually the simplest and most economical way to feed a kiln as the operator can view the fire at all times. Ignoring air pollution and safety considerations, this is an expedient way to get rid of just about any type of combustible waste.

The Air Pollution Control and Safety Departments at Dow were much troubled over this operation, but there was no safer incineration process available. Landfill of the solid wastes had been attempted, but this was costly, gave the opportunity for ground water contamination and the danger of fire in the fill area was always present. Incinerator catalogs did not have a master plan to solve all of the handling and air pollution problems resulting from burning these heterogeneous wastes. Most types of furnaces could not satisfactorily burn plastics. The wastes from the polystyrene plant melt and burn at the same time. It was visualized how this viscous material would then drop through grates and harden upon

cooling, plugging the grates and building up on hearths. In the rotary kiln, the melting plastic mingles with the ash or sticks to the sides of the kiln and burns completely. This was observed in the existing rotary kiln incinerator, but tremendous quantities of black smoke were also observed, belching from the stack. Having determined the amount and character of the material to be burned, an investigation was initiated to determine cost and basic design of an incinerator that would satisfy all requirements.

A literature study produced the Volund patent on a rotary kiln incinerator, which patent rights are held by the International Incinerator Company of Atlanta, Georgia. Further investigation of the municipal rotary kiln type incinerator in Atlanta, Georgia indicated that this type of unit could satisfactorily and continuously burn garbage and refuse with a minimum of smoke and odor.

The incineration problem at Dow Midland is quite different from a normal municipal situation. Chemical wastes, plastics, still residues and even plant rubbish have a much higher BTU content than ordinary garbage and refuse. The hydro-carbon nature of most of the wastes produces a very dense black smoke and occasionally a drum or can of chemicals will explode in the fire. These characteristics prompted change in the basic design of a usual Volund incinerator. Cognizant of the complexity of the problem, and with the cooperation of Dow engineers, International Incinerators, Inc. agreed to design a rotary kiln incinerator for this unusual problem. Placed in operation in January 1959, the unit operates satisfactorily and does destroy all of the Dow Midland solid combustible wastes and many of the liquid wastes without smoke or odor problems. A stationary tar furnace complete with off-gas scrubbing facilities was placed in operation in the spring of 1958 and has noticeably reduced the odors in the Midland area caused by the burning of combustible liquid wastes.

These liquid wastes called "tars" are by-products, contaminated chemicals or bad batches that cannot be reclaimed economically, for which there is no market and, therefore, are wastes. These materials, which vary from light solvents to very heavy still residues, then must be disposed of as cheaply as possible without causing other safety, air or stream pollution problems. Some of these residues and slurries are very high in water content as they have been removed from waste water streams emanating from production processes. These materials cannot be satisfactorily treated in the biological treatment process of the Dow liquid waste treatment plant, and must be destroyed by incineration.

All waste tars are hauled to the incinerator area in Dempster Dumpster tanks. The trucks drive up a ramp and dump into the top of agitated holding tanks. Large hoppers are provided on top of the tanks to prevent spillage during the rapid dumping process which normally takes two to three minutes to transfer 700 gallons of tar. Bar screens in the bottom of the hoppers collect debris, gravel or large solids that

may happen to be present in the Dempster tanks.

The holding tanks are 10 feet in diameter, 12 to 15 feet high, agitated with top entering turbine agitators with right angle gear reducers having output speed of 68 rpm. Single impellers are 41 inches in diameter, with six blades 5 inches wide. These agitators have no bottom support which eliminates the need for draining the tank for maintenance. Fifteen tanks, totaling 110,000 gallons of inventory are used to hold, mix and blend tars.

Over 400 drums per month of burnable hydrocarbons are hauled to the incinerator area for disposal. Drums are unloaded to a drum dock and the contents are drained to an agitated holding tank. These tars originate in over a hundred and twenty production or laboratory areas. Some of these sources have 3 or 4 different kinds of tars which cannot be mixed, so close control of the handling and dumping of these tars is an absolute necessity. There is always the danger of unhydrolyzed or reactive materials being present which might result in an explosion or fire.

All requests for hauling wastes are phoned to the incinerator office. Any request not contained in a catalog is turned over to supervision. A check of the strange material is then made with the source to determine handling precautions and burnability. If necessary, special handling and disposal techniques are applied. All information necessary to haul and dispose of the waste is written on a dispatch slip and radioed to a truck in the pickup area.

When the truck gets to the incinerator, the driver stops at a microphone and calls out the tar by building number. Loud speakers carry the message to the operating areas, and the driver is told where to dump the materials.

Ten tanks are heated and insulated, to keep the contents above 80°C., to maintain fluidity. Two of these tanks are used to hold and blend certain high BTU, low ash, low chlorine tars that are then rehailed to the powerhouse where they are burned as fuel. The remaining tanks are used for solvents and contaminated waters and slurries that must be destroyed. Contents of the tanks are mixed and pumped with Sherzer centrifugal pumps through traced and covered pipelines to either the rotary kiln incinerator or a stationary liquid tar burner.

Single strainers with 1/4 inch openings are located on the suction side of the pumps. Liquid tars are then pumped to a duplex strainer with 1/8 inch openings located at the tar furnace. This strainer collects any solids that may form in the pipeline.

The tar furnace is a rectangular suspended wall type furnace 10' x 25' x 10' high. A penthouse on top of the furnace houses dampers which allow gases to go to an 8' x 60' high stack or to acid gas scrubbers. Liquid wastes are pumped to four low pressure air atomizing oil burners.

This type of oil burner lends itself to the range in viscosity and heating value of the waste tars. To burn these tars successfully it is necessary to atomize the combustible liquid and then bring it into contact with the proper amount of air. In the low pressure air oil burners, this is accomplished by using 16 or more ounces of air pressure, part of which spins through a set of stationary vanes, picking up the oil from the oil nozzle, converting it to a gaseous mixture and giving it forward velocity. When this mist leaves the atomizing head, it is mixed with the remainder of the primary air. Adjustment of air volume and pressure is extremely simple, and is determined and adjusted by the operator with each different liquid. The tar nozzles are large, will pass a 1/8 inch particle, and also are very easily cleaned. Cleaning is done by rodding the orifice or disassembling the few parts in the atomizing head.

As long as the liquid has sufficient calorific value to support combustion, these nozzles do a wonderful job of preparing the liquid for combustion. Fuel pressure required at the oil burners is normally from 2 to 5 psi. To minimize build up of tar in the lines, a fuel recycle system is used, which includes a pressure sensing element, a diaphragm valve and a pressure controller. Pressure is set on the burner side of the recycle system and the diaphragm valve passes sufficient fuel to maintain this pressure. The major part of the fuel pumped to the furnace is recycled back to the tar tanks.

Air for the nozzles is supplied by a 20-ounce blower. Flame eyes actuate manual reset valves which automatically close on flame failure. A time delay allows initial energizing of the system. This includes a gas pilot, touched off by a spark plug, which ignites fuel oil pumped through the tar burner. This is then weaned to the tar mixture to be burned. This entire system shuts down in the event of flame failure.

All tars are burned in suspension, but a secondary air blower pressures jets which blow across the floor of the furnace. This supplements the induced secondary air, maintains turbulence and burns up any heavy solids that deposit on the floor. Very little ash forms in this furnace, indicating good combustion.

Hot gases at upwards of 1700°F. are vented through the penthouse to the stack. Both furnace and stack are lined with hard burned super duty firebrick. When burning tars contain large concentrations of chlorine or sulfur, the gases are diverted through two vertical packed towers.

These scrubbers are 11½ feet in diameter with 11 feet of 1½ inch berl saddles. 10,000 scfm. of gases are pulled through each scrubber with open type wheel fans. Gases are discharged to a top house of plastic packing which acts as an entrainment separator. All metal surfaces are rubber lined and the masonry in the scrubbers is acid proof brick.

Water for scrubbing is obtained from a weak phenol sewer adjacent to the area. The water containing possibly 10 ppm. phenol is pumped from a sump with two 3-stage vertical turbine pumps. Each pump is powered by a 20 hp. vertical solid shaft motor, and each will deliver 700 gpm. at 87 feet total head. Distribution of the scrubbing water is by means of V notch weirs across the top of the column. The water is screened in a strainer before going to the scrubbers. Effluent water from the scrubbers is discharged to the sewer system with all neutralization and oxidation being done at the waste treatment plant. Scrubbers operate satisfactorily, discharging a minimum of acid gases to the atmosphere.

The tar furnace was designed by Bigelow Liptak, in co-operation with Dow engineers. Many preliminary designs were available, as there are several reputable waste oil incinerator firms in the country. This particular unit appeared to best solve the Midland problem at the lowest cost. After one year of operation, the unit is still operating as expected.

The new Dow rotary kiln incinerator was designed to burn 110 tons per day of mixed refuse, including plastics, rubbish and drums of chemicals. This capacity was to be attained using two rotary kilns with each kiln handling a minimum of 60 million BTU per hour. Stack effluent criteria included smoke density of not more than 2 on the Ringleman chart for not more than four minutes in any one-half hour and not more than 0.85 lb. dust per 1000 lb. flue gas at 50 percent excess air.

Design of this unit was started in September 1956 and construction was completed in December 1958. As finally put into operation, the incinerator consists mainly of a refuse pit, crane feed to a feed conveyor, special feed equipment for drums, rotary kiln, air control, secondary combustion, water spray system, residue conveyor and stack.

All refuse, except full drums and paks of hazardous material, is dumped into a refuse pit. This pit is 20 x 54 x 20 and will hold 800 cubic yards of burnables. An overhead crane of 3½ ton capacity, 52 ft. lift, 42 ft. span for 84 ft. long runway was installed to mix the refuse and elevate to the charging hopper. A 2 cubic yard bucket designed for incinerator service completes this piece of equipment.

From the charging hopper the refuse falls by gravity onto a drag chain conveyor located inside a feeder housing. A 7 inch high x 5' - 9" wide channel flights on this conveyor move the refuse to the feed chute where the refuse falls by gravity into the fire. Speed of the conveyor is variable, obtained with a Louis Allis Varispeed drive, controlled from the operating panel.

Paks and drums are dropped down the feed chute with a hydraulically operated feed device. This gives maximum protection to the operator. A large vent over the feed chute opens to the

outside of the building, to relieve any explosions that might take place in the kiln. Primary combustion air is damper-controlled through the top of the feeder and travels down the feed chute to the kiln. The entire feeder is under negative head from the stack, the refuse in the charging hopper maintaining the closure at the hopper opening.

Liquid tars are fired horizontally into the kiln from both sides of the feed chute to help maintain temperature and to burn up the smoke. Modified low pressure air atomizing oil burners complete with flame safety equipment are installed on the seal plate at the feed end of the kiln. Piping has been installed to be able to pump contaminated waters and wet slurries through the oil burners. Screening, pumping, recycle and flame safety equipment is similar to that on the liquid tar furnace previously described.

Adding all of these liquid and solid fuels to a fire would seem to cause poor combustion. In practice, the problem is the opposite. The liquid fuels are needed to provide a hot flame to burn up the liberated carbon particles from the combustion of the plastics. Also, the refuse tends to minimize the radiant heat problem developed during the burning of roughly 8 gpm. of tars in the kiln. The kilns are 12'-9" OD x 35'-0" long. Temperatures in excess of 2000°F. are achieved in the kiln, with 9 inches of Varnon refractory protecting the shell. An 8000 CFS fan producing 10 inches static pressure forces over fire air through a series of nozzles located on the sides and bottom of feed chute. This gives turbulence to the gases and cools the seal plate.

As the refuse is moved horizontally in the kiln, all of the organic matter is destroyed, leaving an inorganic ash. This ash or residue includes drums, tin cans and slag. A 3 inch slope is provided through the length of the kiln, which aids in moving the solids to the discharge end. While turning, this ash, slag or other material drops into a residue conveyor trough that contains 3 feet of water. The residue drag chain conveyor in the bottom of the trough contains 12 inch channels 5 feet wide on 7 foot spacing, which moves the material out from under the kiln, up an incline and across a bar screen. This separates the metal and the ash into different Dempster boxes for hauling and disposal.

Leaving the kiln, the gases impinge on refractory surfaces that cause a swirling action in the secondary combustion chamber. This added turbulence with the additional detention time is sufficient to burn up the smoke. No secondary fuel or after burners are used. Thirty feet from the kiln, the gases pass through the first of two banks of water sprays. Approximately 300 gpm. of water is sprayed through 54 nozzles, which knocks down the fly ash. This ash is then sluiced to the residue conveyor and discharged with the other ash.

The secondary combustion chamber is lined with 21 inches of refractory through the turbulent areas. As the gases slow down, the walls decrease to 9 inches of suspended,

super duty brick. The cooled gases then pass under a refractory lined motorized damper, to a 12' ID by 200' high chimney. The chimney is lined for the full height with Varnon firebrick. A target wall, 35 feet high, is carried up independently of the main lining.

The rotary kiln incinerator as installed represents invested capital of \$1,350,000. Completion of the second unit plus capital already spent on the tar furnace, scrubbers, tanks, etc. will bring the total over \$2,000,000. Future planning includes utilization of the heat to dry and burn the sludge from the water waste treatment plant. This slurry normally has a very obnoxious odor. Drying and burning thus poses many additional problems even though this is the most economical way to destroy these wastes. Waste disposal sludge amounts to 40 tons per day of dry solids or 400 ton per day of wet slurry.

The incineratory equipment described is functioning very well. Large volumes of wastes are being handled safely without contaminating the atmosphere. Dow feels that incineration is expensive but necessary, in the age of expansion, in order to better get along with a watchful community.

C O L O R M E A S U R E M E N T

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INTRODUCTION

The presence of colored compounds in waste waters creates a somewhat different problem in stream sanitation than that of gross organic pollution.⁶ Colored streams affect the mental rather than the physical health of observers and users. It is already well established that mental and physical health are closely related. For example, the medical profession claims that constant awareness of his condition and its eventual outcome can have a bad psychological effect upon the patient. In a similar manner, the presence of colored matter in streams makes the observer anxious for the safety and welfare of the downstream users. Thus, a stream relatively free from physical pollution but containing foreign colored matter may be classed as "polluted" in the eyes of the general public. It is then of the utmost importance to reduce the color of wastes being discharged to rivers. Before one can reduce the color of wastes, a suitable method of color measurement must be available. Standard Methods for the Examination of Water, Sewage, and Wastes¹ recommends the use of (A) platinum cobalt color standards, (B) spectrophotometric, and (C) photometric methods. Platinum cobalt standards involves a visual color comparison with known typical stream color standards. Any slight change in hue or addition of turbidity make a visual color comparison by this method impossible. The spectrophotometric method involves the utilization of lights of unit wave lengths comprising the entire visible spectrum (400-700 μ). Only transmitted, or its reciprocal (absorbed) light is measured by this method. The human eye, however, observes reflected light. Photometric methods make use of three color filters (amber, green and blue). The relative amounts of light passing through

each filter from the sample color provide the basic information from which the color measurement is obtained. This, too, measures transmitted light and is subject to the same errors caused by turbidity as the spectrophotometer. For a more complete discussion of these three methods the reader is directed to an original paper by Coss and Nemerow.²

Since reflected color is normally observed when standing on a bank or bridge overlooking a river, other means of color measurement must be used. Most streams - polluted or non-polluted - contain a certain amount and type of turbidity. Since turbidity affects the reflected color, the method used to measure color must include the effects of turbidity (See Fig.4). In addition, the new method must also include some means of measuring color differences. Color differences are objectionable to viewers under certain conditions and to certain degrees. Most state stream standards specify "none (color) in quantities such that the stream becomes objectionable".

The authors have been studying two possible methods of measuring reflected color to demonstrate color differences.

(1) Use of Stream Colorimeter^{7,3} and (2) Photographic means.

1 - STREAM COLORIMETER

Two major pieces of apparatus were used in carrying out this study. One, the Streamviewer, is a device for simulating a natural stream in its natural surrounding; and the other, the Stream Colorimeter² is a device for measuring the color of liquids by reflected light.

The Streamviewer³ is a box constructed of one-half inch plywood with dimensions of 24 inches from front to back, 25 inches from side to side, and 20 inches from top to bottom. The box has a viewing slot in the front which permits a person to see the interior. A trough is fitted to the bottom of the box at the rear and in line of sight for a person looking through the viewing slot. A circulating pump is fitted to the trough so that water in the trough can be kept in constant motion. The interior of the box is designed to represent a rural, summer scene from the Drowning Creek region near Hoffman, North Carolina. The rear wall of the interior is a painting in water colors made from color photographs of the region mentioned. The bottom is painted to represent grass. A daylight-type fluorescent lamp is used to light the interior. When appropriately colored water is put into the trough, the apparatus in operation represents a stream in its natural setting to the viewer. (See Fig.1).

The Stream Colorimeter is essentially the Photovolt Photoelectric Reflection Meter, Model 61C with the 61C-D search unit available from the Photovolt Corp., (Figs. V, VI, VII). To this basic instrument are added two special containers, one reference container and one sample container. Also, a more sensitive galvanometer or a photocell current amplifier is added. Hunter's tristimulus color components (filters), amber, blue, and green are used. The sample of liquid to be measured is put into one container and distilled water is put into the reference container.

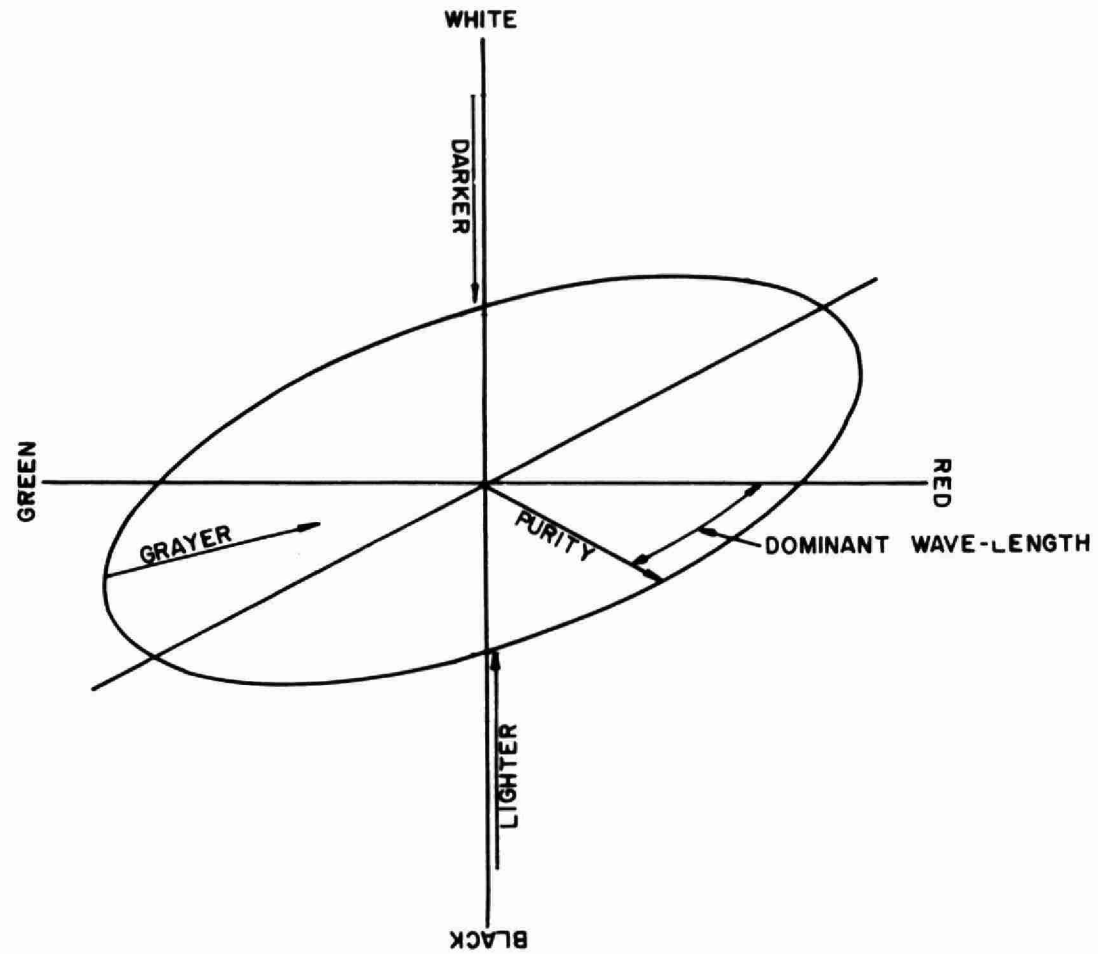


FIGURE 2 A CONCEPT OF COLOR-PERCEPTION SPACE

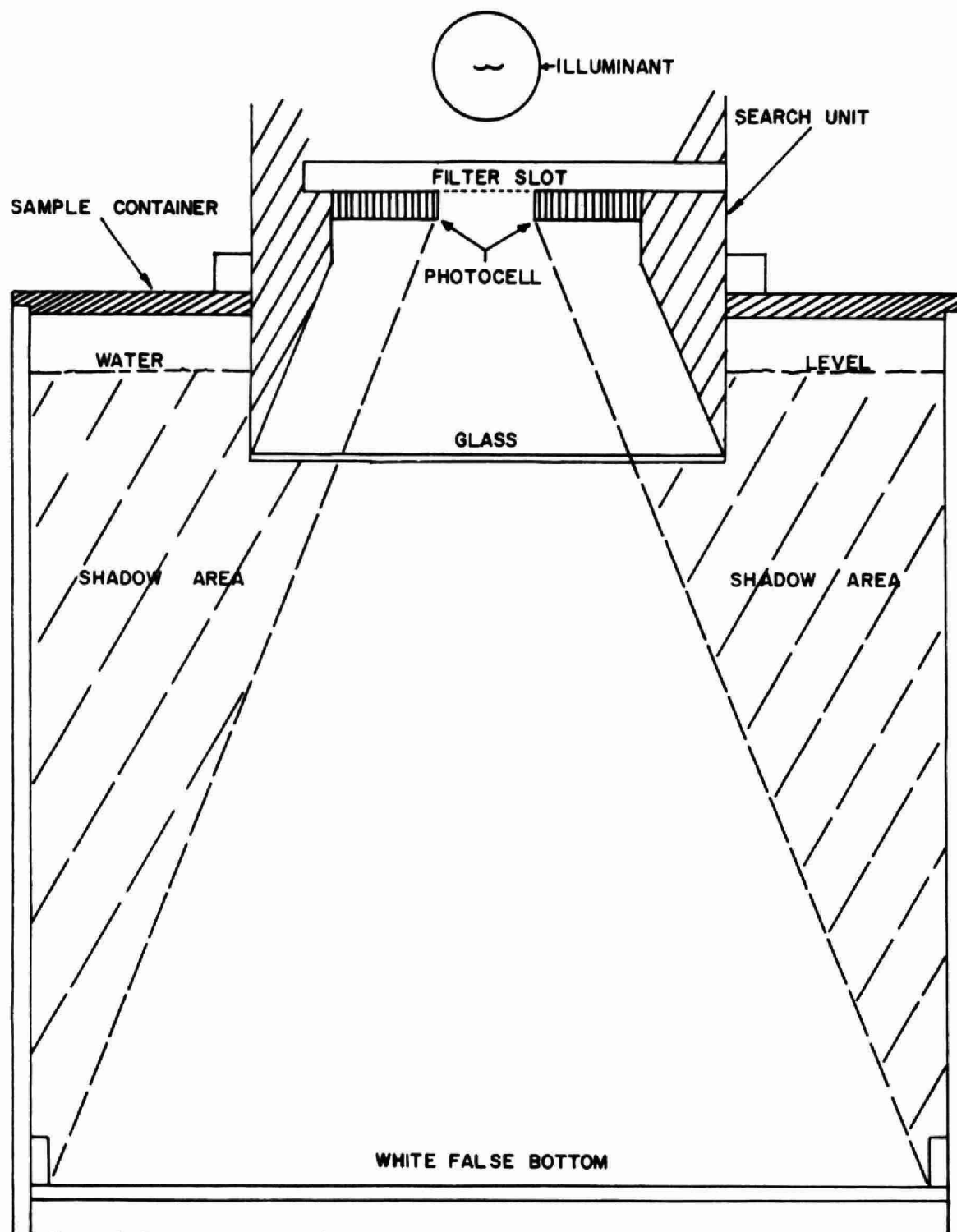


FIGURE V. APPROXIMATE FULL SCALE VIEW OF FINAL APPARATUS COLOR-MEASURING COMPONENTS AND SAMPLE CONFIGURATION.

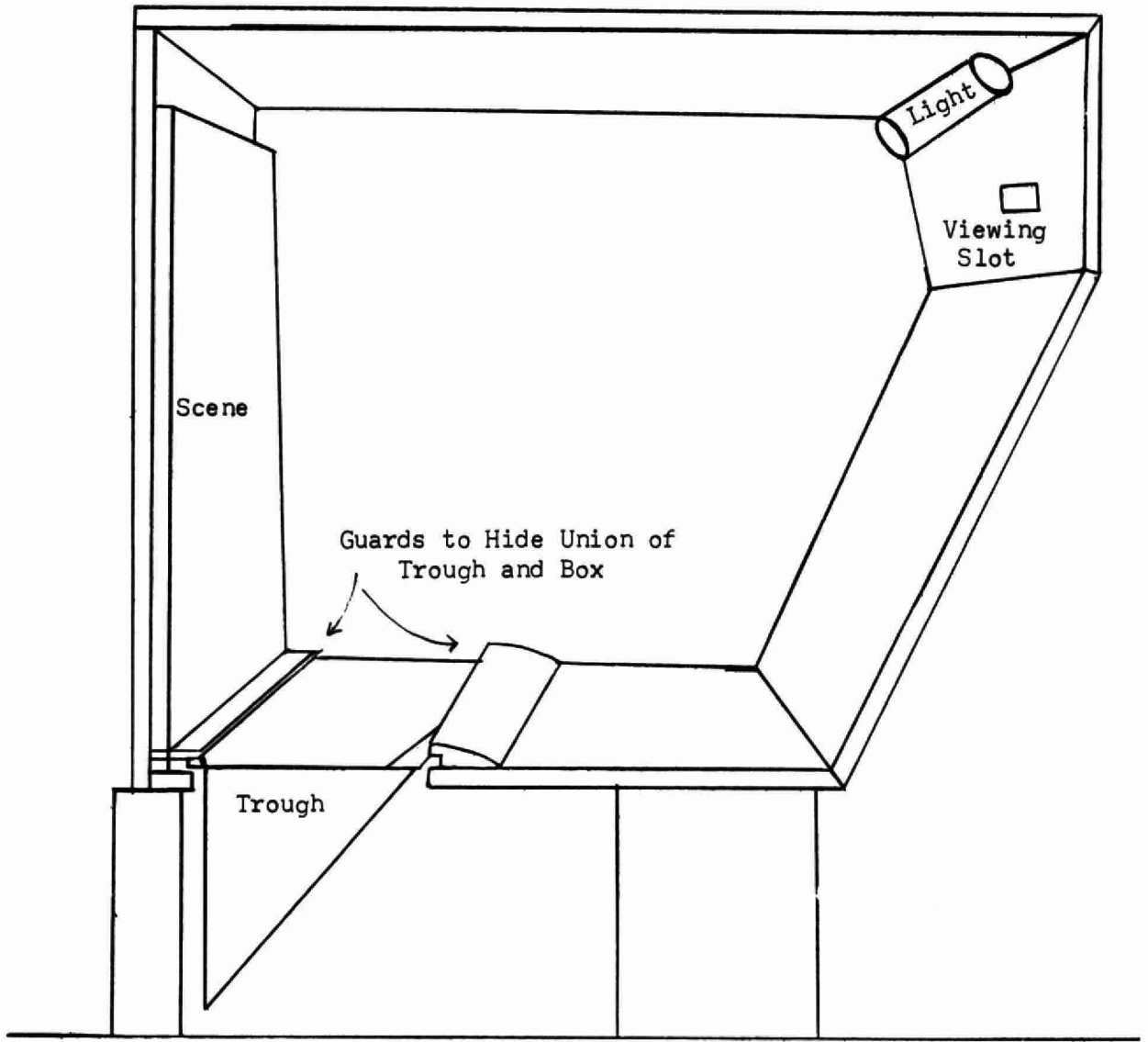


FIG. 1 STREAMVIEWER (Pump not shown)

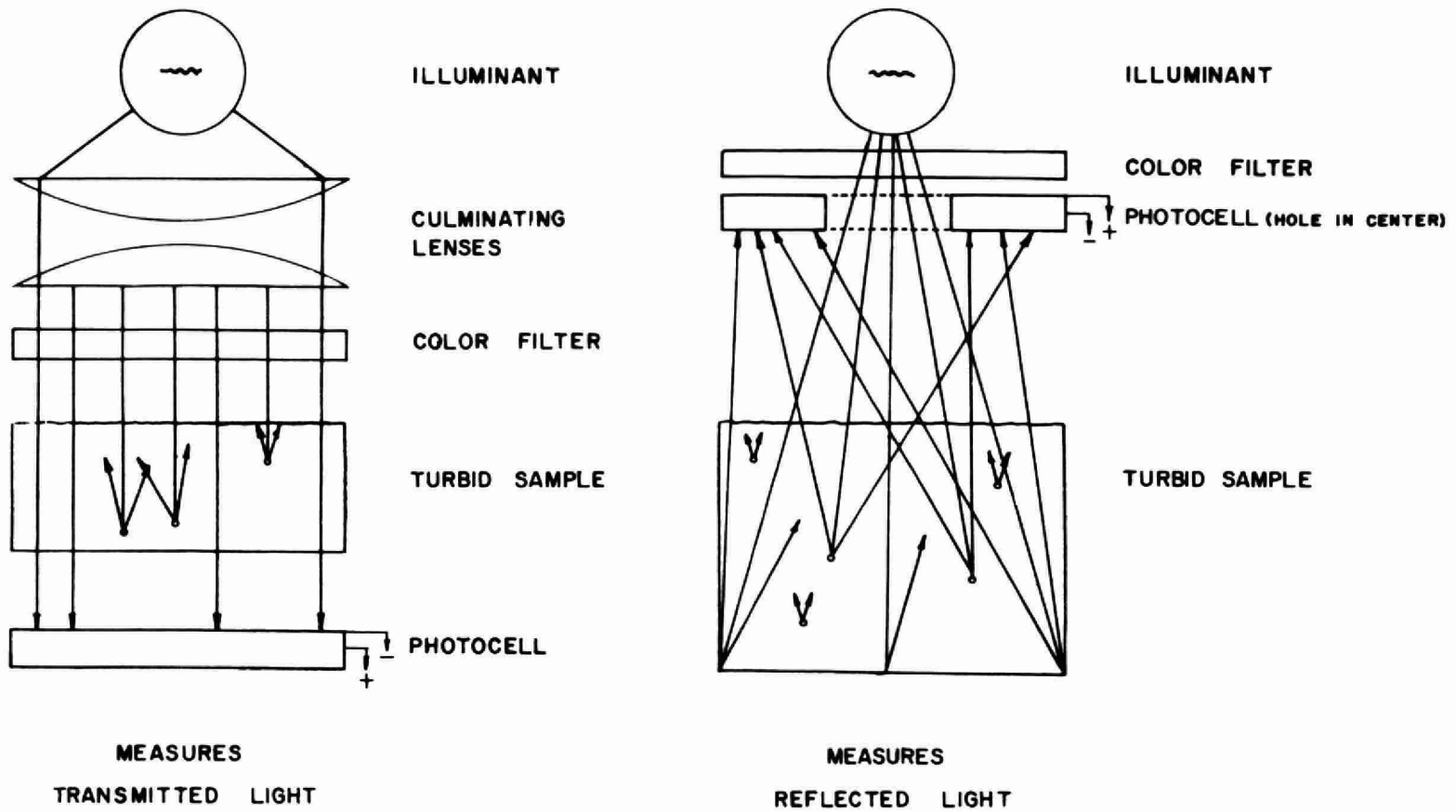


FIGURE 4. COMPARISON OF COMPONENT CONFIGURATIONS OF INSTRUMENTS MEASURING TRANSMITTED LIGHT & INSTRUMENTS MEASURING REFLECTED LIGHT

With one filter in place, the search unit is introduced into the reference solution; and the galvanometer is adjusted to read 100 per cent. The search unit is then transferred to the sample solution, and the percentage of light refelected by the sample is read from the galvanometer dial. This process is repeated with each of the three filters. These three filter readings can then be used to define the color of the sample in terms of dominant wave length, luminance, and purity in accordance with the procedure adopted by the International Commission on Illumination (C.I.E.)⁴

Dominant wave length indicates the particular hue involved in the visible spectrum; luminance refers to its brightness; and purity refers to its grayness. These are illustrated clearly in Fig. 2.

DESIGN OF THE STUDY

In outline the experimental procedure consisted of using the Streamviewer to present the water from a natural stream (the color of which had been measured) to a subject. To this stream were added small amounts of a colorant until the subject objected to the color. At this point a sample of the objectionable water was removed for subsequent measurement of color. This process was repeated with each of six colorants. Twenty subjects followed this same procedure. All color measurements were made using the Stream Colorimeter.

The water used in the trough of the Streamviewer was matched to a sample of water taken from Drowning Creek during a period of average summer flow and average summer color conditions. Records of the Geological Survey, United States Department of the Interior, Raleigh, North Carolina, were used to establish the averages mentioned above.

Twenty male students of North Carolina State College were used as subjects. These studens were residents of the Drowning Creek region of North Carolina.

Colorants used were textile dyes obtained from the Textile School, North Carolina State College. Six colorants - a red, a blue, an orange, a green, a yellow, and a violet dye - were used.

The data collected consisted of the 20 colors found objectionable for each of the six colorants added. The colors found objectionable were compared to the standard color (color of the natural stream) to establish the relationship.

RESULTS

The Hunter-Scofield color-difference formula⁵ was used to determine the difference between the standard color and each of the colors objected to. This formula gives color-difference values in terms of the National Bureau of Standard's unit of color difference which is defined as a "... unit of color

difference so small that measured differences of less than one unit represent perceptually unimportant color differences in most commercial transactions". (5,p. 519). The formula was empiracally derived and is expressly intended for use with the Hunter tristimulus filters. A Complete description of the formula and a sample problem appear in a later section of this paper.

The twenty color-difference scores for each colorant added were tested to determine if they conformed to the normal distribution curve. This involved testing the score distributions for kurtosis and for skewness. The distributions of scores for each of the colorants added was found to be essentially normal. Fig. 3 shows the distribution of the color-difference scores. Each graph in Fig. 3 shows the score frequencies on the vertical axis and the standard deviations from the mean score value on the horizontal axis.

The normal distribution curve was adopted as the model for obtaining a "5% OP" (Objectionable Point) score. The procedure for obtaining said score was as follows: the arithmetic mean and the standard deviation of the distribution were computed; these values were used in the formula

$$5\% \text{ OP} = \text{Mean} - 1.65 \text{ standard deviation}$$

The area under the normal distribution curve from a point 1.65 standard deviations from the mean to the most extreme score on the same side of the mean included 4.95 per cent of the total population. Thus, as applied here, less than 5 per cent of the population from which our sample was drawn will object to any color-difference value which is smaller than the 5% OP score given. Fig. 8 shows the area about the standard color defined by the 5% OP score for each of the six colorants used. The 5% OP scores on each of the axes are the values derived in this study. The lines connecting these points are estimates of the 5% OP scores which would be found if other colorants were used.

DISCUSSION

It is emphasized that this study is concerned with demonstrating a method. The values obtained apply only to the population sampled. To employ this method in setting standards for the control of color pollution, it would be necessary to give careful consideration to the sample of individuals who gave the judgements of "objectionable". Likewise, the interior of the Streamviewer would have to be modified in accordance with local conditions.

It is pointed out that the 5% OP score is an arbitrary value used in this study. By employing the normal curve model, it is possible to obtain the 1% OP score, the 10% OP score, or any other OP score from 1 to 100 per cent.

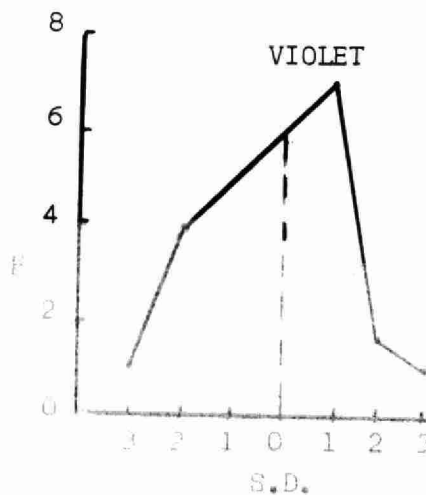
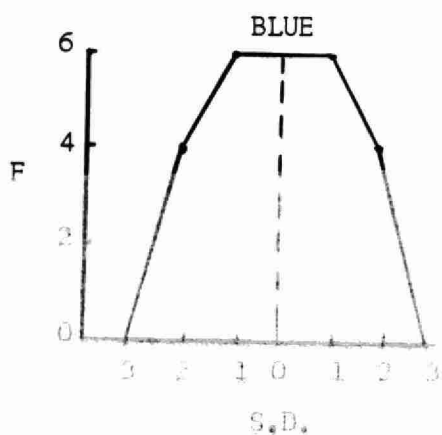
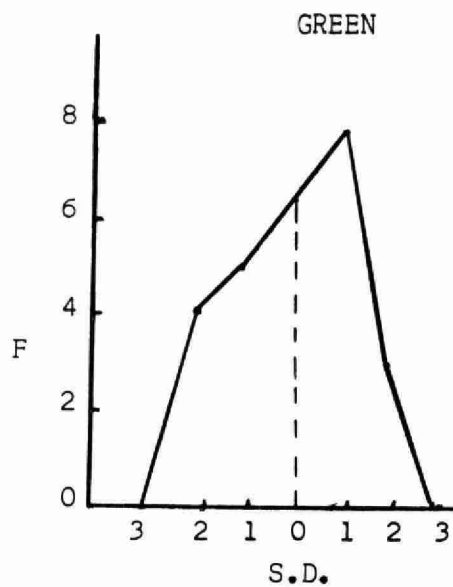
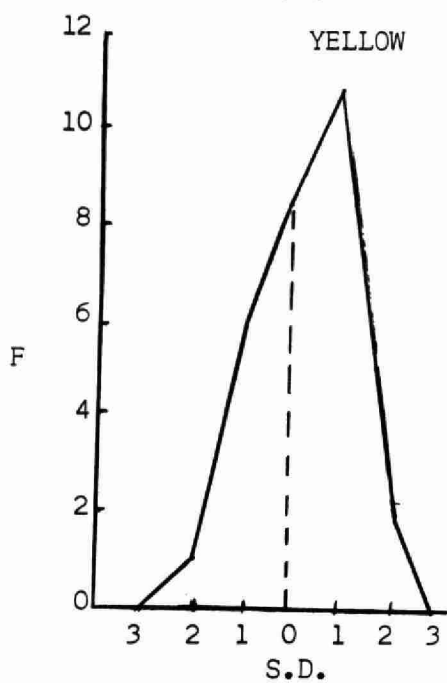
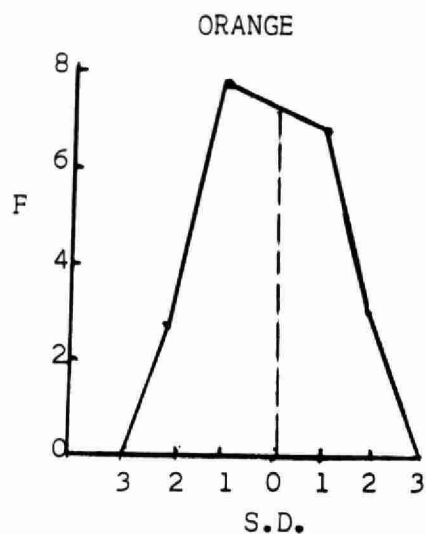
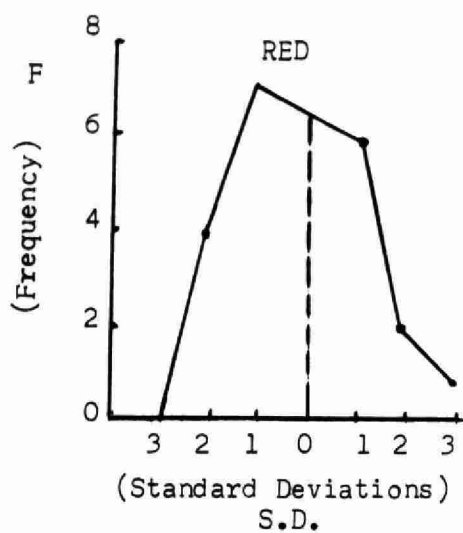


FIG. 3. DISTRIBUTION OF COLOR-DIFFERENCE SCORES

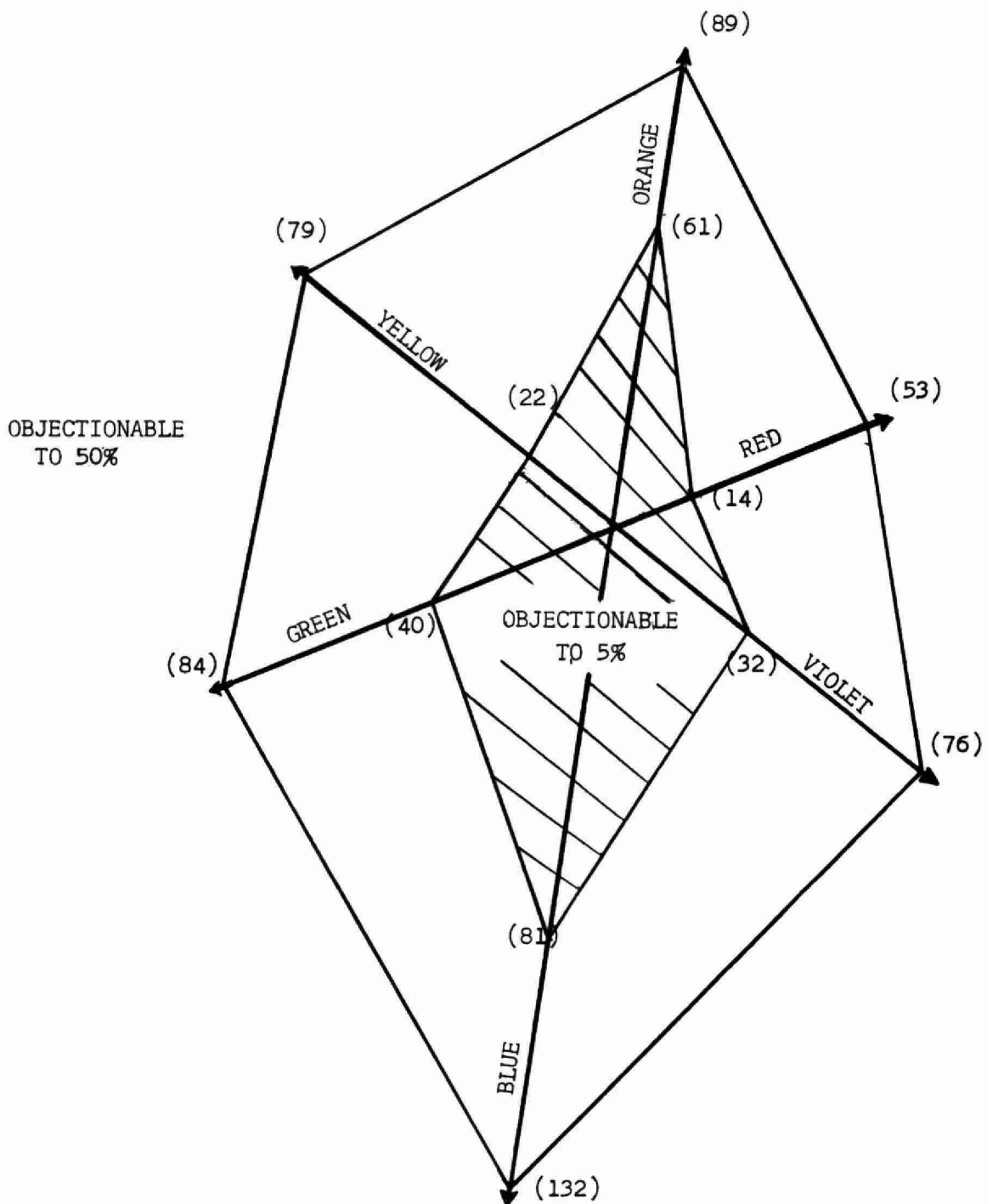


FIG. 8. RELATIONSHIP OF 5% OP SCORES AND MEAN SCORES TO THE ORIGINAL COLOR OF THE SAMPLE STREAM

Scale: 1/32 inch equal 1 NBS unit of color difference

APPLICATION OF RESULTS

Conditions:

1. An industry discharges a purple dye waste continuously into a stream.
2. The stream has an average flow of 20 cfs (cubic feet per second), a seven day once in ten years minimum flow of 8 cfs. The waste discharged varies from 1 mgd (million gallons per day) to 3 mgd with an average of 2 mgd.

Problem:

1. How is a standard set for this stream (5% OP score)?
2. How much color must be removed from this waste to meet the stream standard?

Steps to be taken:

1. Measure the color of the stream at minimum flow conditions. Use the Stream Colorimeter and obtain the tristimulus filter values.

Example: A (Amber) 94
 B (Blue) 71
 G (Green) 91

2. Draw a sample from the population which is in contact with the stream.

Example: 20 subjects

3. Add dye waste to original stream using Streamviewer apparatus. Keep record of amount of colorant added.
4. When subject finds the color of the water objectionable, record the amber, blue, and green filter readings and the ratio of the volume of colorant to the volume of water in the trough.

Example: Subject objects when A-84, B-65, G-80 and ratio is 2.40 parts of colorant to 5.00 parts of water.

5. Work color-difference formula to find color-difference score between original color of stream and each of the colors objected to.

Example:

I. General formula

$$\Delta E = \left[(L_0 - L_1)^2 + (a_0 - a_1)^2 + (b_0 - b_1)^2 \right]^{\frac{1}{2}}$$

$$L = 100 (G)^{\frac{1}{2}}$$

$$a = \frac{A - G}{A + B + 2G}$$

$$a = 7L \alpha$$

$$\beta = \frac{.4 (G - B)}{A + B + 2G}$$

$$b = 7L \beta$$

Sub "o" indicates values for original color of stream
 Sub "1" indicates values for color found objectionable.

ΔE is the color difference in National Bureau of Standard's color units.

II. Specific problem

Original color	Objectionable color
A 94	A 84
B 71	B 65
G 91	G 80
$L_0 = 953.54$	$L_1 = 894.43$
$\alpha = .0086$	$\alpha = .0129$
$\beta = .0231$	$\beta = .0194$
$a_0 = 57.43$	$a_1 = 80.77$
$b_0 = 154.25$	$b_1 = 121.46$
$\Delta E = [(59.51)^2 + (-23.34)^2 + (32.79)^2]^{\frac{1}{2}}$	
$\Delta E = (5161.38)^{\frac{1}{2}}$	
$\Delta E = 71.84$	

6. Rank color differences and ratio of colorant to stream water.

Example:

ΔE value	$\frac{\text{vol of colorant}}{\text{vol of stream}}$	ΔE value	$\frac{\text{vol of colorant}}{\text{vol of stream}}$
126	2.94/5	72	2.40/5
122	2.90/5	72	2.40/5
114	2.82/5	70	2.38/5
99	2.67/5	62	2.30/5
93	2.61/5	53	2.21/5
87	2.55/5	49	2.16/5
86	2.54/5	48	2.16/5
83	2.51/5	47	2.15/5
82	2.50/5	42	2.10/5
79	2.47/5	25	1.93/5

7. From the E scores determine the 5% OP score.

Example: Mean ΔE score - 75.50

Stand. Devia. = 26.47

$$5\% \text{ OP} = 75.50 - (1.65) (26.47) = 32.00 + \Delta E$$

8. Determine the colorant-to-stream ratio which gives the 5% OP score.
(Linear interpolation)

Example:	ΔE value	ratio
	42	2.10/5
interpolate	(32)	(2.00/5)
	25	1.93/5

9. Determine industry's present volume ratio at minimum stream flow and maximum discharge rate.

Example: 8 cfs = 5,170,176 mgd (min. stream flow)

3,000,000 mgd (max. discharge rate)

Ratio (rounded for computational ease) is 3/5.

10. Compare the present ratio in step 9 with the desired ratio in step 8 and determine how much colorant must be removed. The assumption is that the volume ratio, 3/5, cannot be changed and that the amount of colorant in the discharge must be reduced.

Example: Present ratio - 3/5

Desired ratio - 2/5

Here it is necessary to remove one third of the colorant from the waste so that the amount of colorant presently found in two parts of waste will be the same as that found in three parts of waste after the reduction is effected.

11. As the rate of flow of the stream changed, the percentage of waste to be removed will change. As the rate of discharge changes, the percentage of waste to be removed will change. As the concentration of colorant in the discharge changes, the percentage of waste to be removed will change. The percentage of waste removed, no matter what conditions of the factors mentioned above prevail, will always be of a magnitude so that a color difference value of $\Delta E = 32$ or less is maintained in the stream between points above and below the place where the industrial discharge enters the stream.

SUMMARY

Twenty subjects observed one at a time as a simulated

natural stream was changed in color by the addition of each of six different colorants. Every subject indicated when the color of the stream became objectionable for each of the colorants. A color-difference formula was used to determine how greatly the objectionable colors differed from the original color of the stream. The distribution of scores for each of the colorants was examined and found to be normally distributed. Using the normal curve model, 5% OP scores were determined for each of the separate colorants. These 5% OP scores represent color differences between the original stream color and the color resulting from the addition of a colorant which are objectionable to fewer than five per cent of the population represented by the sample used. A specific application is presented to illustrate the possible use for the results obtained.

CONCLUSIONS FROM STREAM COLORIMETER METHOD

The point at which the color of a stream becomes objectionable as a result of the addition of a colorant can be qualified in terms of a number. This number represents the difference between the original color of the stream and the certain color objected to.

The color-difference scores for the addition of any certain colorant were found to be normally distributed in the sample used in this study.

From the findings it is inferred that the normal curve model can be employed to determine color differences which will be objectionable to certain percentages of the population.

2 - PHOTOGRAPHIC METHOD

This consists of a means by which photographs are taken of streams above and below the point of suspected pollution which will show the effect of organic matter pollution through tonal changes on the photographs.

If photographs are taken at two points on a stream for the purpose of registering a pollution differential there are obviously variables other than pollution which will cause a change in the photographic tone. The main variables involved are stream depth, color of the stream bottom, physical condition of the water surface, angle at which the photo was taken, and light intensity. The assumptions are made that both camera and film are identical in each case; and that film processing procedures are standard.

Thus, unless many of these variables are eliminated the problem becomes impractical. By taking a sample at each point in the stream and placing them in identical containers, the above variables may be eliminated through the recording of both samples with a single exposure. Each container would be made of the same colored material and have the same depth. The water surface would be calm in both cases, and the relative light intensity and picture taking angle identical.

The containers to be used when the pictures are taken will play an important part in the experiment. They should be as deep as practically possible since tonal variations caused by pollution are to be measured, and quite logically the tone evident at the surface of a polluted solution will become darker as the depths of the liquid increase. The rate of tone differential due to depth will be less for the purer solution; and therefore some advantage will be realized through the use of deep containers.

The above mentioned containers were photographed in the field close to the area where the second sample was taken. This reduced the transporting of samples and equipment to a minimum.

Different films or filters, whether used in combination or not, will give a variety of results. Also any given film or film and filter combination will act differently depending on the light intensity at the time the picture was taken.

After an adequate container is decided upon the problem reduces itself to one of photographing the samples under different film, filter, and light conditions, to determine the best combination. It may very well prove that the above combination will be peculiar to the type of pollution.

The pictures for this initial study were taken by a Kodak Signet 35 mm. camera.

Two types of color film were used initially. (Filters were not used.)

1. Ectochrome - 32 (accent blue and green)
2. Anscochrome - 32 (accent orange and red)

The initial experiment utilized the following types of containers:

- Ten quart galvanized pails (2)
- Two liter laboratory beakers (2)

The results of the first set of pictures will establish a basis for consideration of additional films and/or filters. The following six slides illustrate photographically the effects of pollution in the Creek.

The sites selected were on a small creek just upstream and downstream from a small primary sewage treatment plant. No other sources of pollution are known to exist at these sites. However, samples were collected on a day following heavy rains. An abnormal amount of natural turbidity arising from soil erosion was evident in the creek. Because of this turbidity any color effect from the sewage pollution was minimized. In fact, some doubt existed as to whether any sign of color pollution could be shown under these conditions.

If under these conditions, a color change could be shown, the

authors feel it could certainly be demonstrated under normal receiving water conditions.

Polluted and non-polluted samples were also analyzed in the laboratory to determine the degree of correlation between tonal color difference and pollutional characteristics. The following sanitary analyses were carried out:

1. Dissolved oxygen
2. B.O.D.
3. Visible color (spectrophotometer 400-7-- Mu)
4. Total organic matter - ash
5. pH
6. Temperature
7. Suspended solids
8. Turbidity

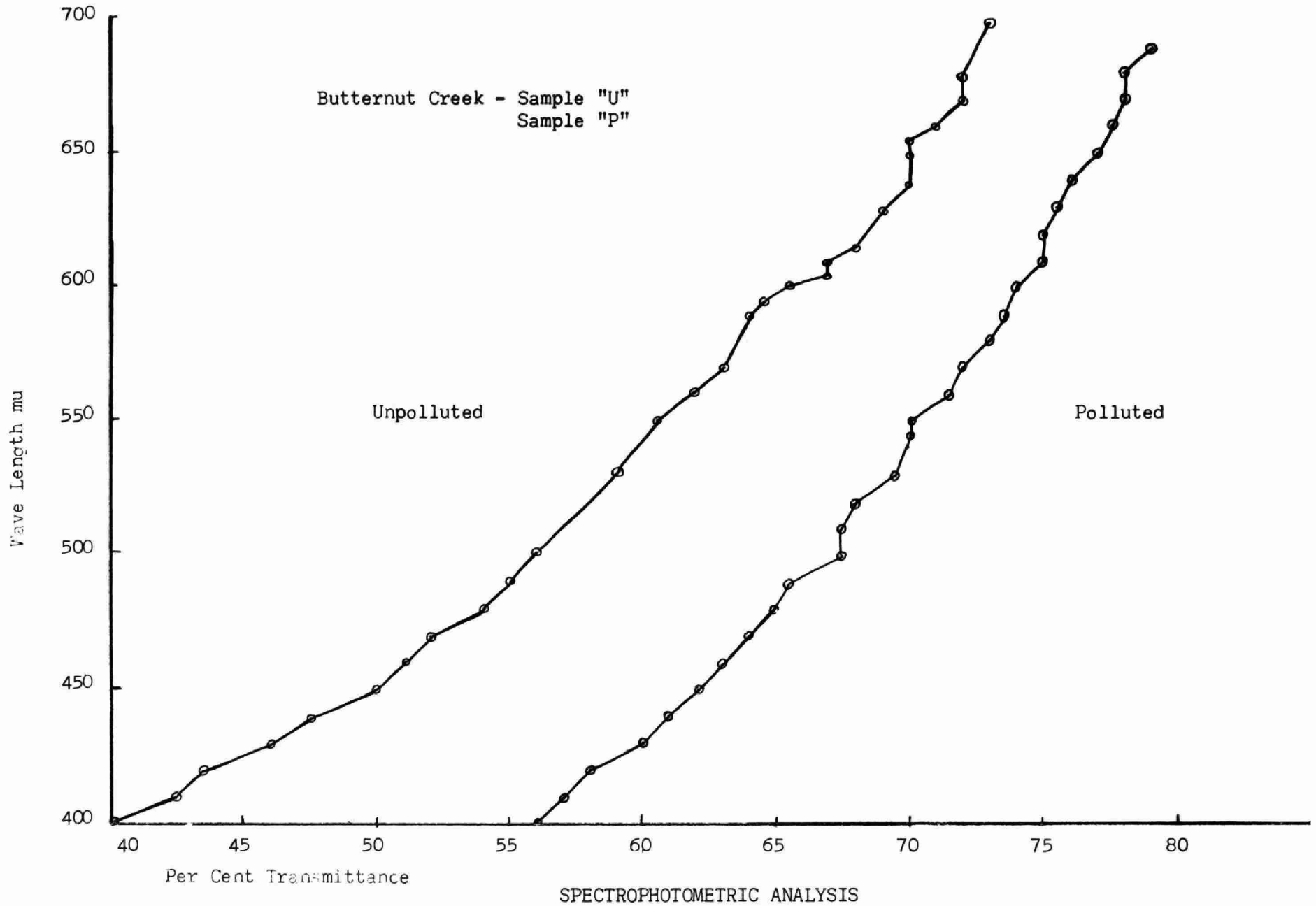
The analytical results are expressed in Table I. Transmitted color results are shown in Fig. 9.

DISCUSSION OF PHOTOGRAPHIC METHOD

Some slight visual color differences were evident on the photographs. This existed despite the fact that the naked eye could neither detect color difference in the stream nor the beakers. In this instance the anscochrome film showed slightly better color differences between upstream and downstream samples. However, the ectochrome depicted better site differences. Therefore, a detailed film type study appears justified. Color differences were also more readily visible in the 2 liter beaker samples than in the galvanized pails. Evidently the additional light obtained by transmission and reflection through the sides of the glass beakers enhanced detection of color differences. This indicates that a more comprehensive study of the container design and material should be carried out. Color differences in the beaker samples were noticed both when viewed from a line of sight horizontal to the beakers and from a location directly over the beakers. Selection of the exact location for taking the picture can only be determined after many additional experiments. It also appears that a high intensity of light may be desirable when taking the photographs. Polaroid film taken and developed immediately may be useful in determining whether a significant color difference and therefore proper sampling point exists.

The sanitary analysis shows that there is a significant difference in the quality of upstream and downstream water samples. For example, the BOD of the downstream (polluted) sample was about 5 times that of the upstream sample. On the other hand, the upstream sample contained more turbidity and suspended matter than the downstream sample. This is even more dramatically illustrated by the spectrophotometric analysis (Fig.9) showing a decrease in transmitted light at all visible wave lengths in

Fig. 9



the upstream sample. However, no difference in dominant wave lengths is evident from the spectrophotometer analysis. A more sensitive means of detecting color differences - such as the Stream Colorimeter - may be necessary in this case. The fact that the photographs showed differences in purity of samples and the spectrophotometer also illustrated this phenomenon - while neither showed a difference in hue is quite interesting. It suggests that a color difference as indicated by the one characteristic, purity, may be the most significant change due to sewage pollution.

SUMMARY

Existing methods of color measurement are described briefly. Two innovations in color measurements are presented along with supporting data. Color differences rather than color concentration are emphasized in both newer approaches. Stream Colorimeter and Photographic Methods both offer considerable promise for measuring and quantifying color differences. A considerable amount of research is called for in the two new methods of color measurement described herein.

TABLE I
Sanitary Analyses of Upstream and Downstream
Creek Samples

	Upstream (Non-polluted)	Downstream (Polluted)
Temperature (°C)	17	15
pH	7.9	7.8
Dissolved Oxygen (ppm)	9.0	8.3
B.O.D. (20°C 5 day)	2.7	12.2
Total Solids (ppm)	521	617
Total Ash Solids (ppm)	419	486
Total Organic (ppm)	102	131
Suspended Solids (ppm)	174	108
Suspended Ash (ppm)	154	90
Suspended Organic (ppm)	20	18
Total Dissolved Solids (ppm)	347	509
Dissolved Ash (ppm)	265	396
Dissolved Organic (ppm)	82	113
Turbidity (ppm)	50	43.5

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POLAROGRAPHIC SCANNING OF INDUSTRIAL WASTE SAMPLES

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The discharge of metal-bearing wastes by industries to our nation's waterways is a matter of increasing concern to public health authorities. These waste often contain metals in various combinations with anions and other cations. The standard technics for their analyses are time consuming. Therefore, a screening technique to eliminate analysis for metals that may not be present and to indicate those that are present is much to be desired. If it will also indicate the optimum sample volume for standard analysis, it will be of added value. With these needs in mind, a study was conducted on the use of the polarograph.

HISTORICAL (1)

The analytical technic known as polarography was originated and developed about 1926 by Professor Jaroslav Herrovsky at Charles University, Prague, Czechoslovakia. The principle is based upon the unique properties displayed by an electrolytic cell consisting of a nonpolarizable reference electrode, a readily polarizable electrode in the form of a mercury drop falling from a capillary, and an electrolytic solution containing small amounts of electro-reducible or electro-oxidizable material. When an increasing electromotive force is impressed across such a cell and the resulting current plotted as a function of the applied voltage, a curve is obtained whose extension along the current axis is directly related to the concentration of the trace material, and whose inflection point is located at a voltage characteristic of that material.

THEORY

The metals most frequently encountered in wastes of this type, and therefore included in this study, were copper, zinc, lead, silver, nickel, cobalt, chromium, cadmium, and iron. The level of significance was taken to be 0.01 mg./l. Including a tenfold concentration of the sample, the method would be required to detect concentrations of 0.1 mg./l. or, as expressed in molar terms, from $0.5 \times 10^{-6}M$ (lead) to $2 \times 10^{-6}M$ (chromium). The lower limit of polarographic detection using ordinary equipment and the dropping mercury electrode is said to be about $10^{-6}M$.⁽¹⁾ This suggests that the concentrations of interest lay at or just below the lower limit of detection.

The mercury pool electrode mentioned in a series of papers from Cornell by Cooke and his associates seemed more promising. Work in this laboratory with a manually operated Fisher Electropode⁽²⁾ showed that current potential curves obtained at a mercury pool cathode in a stirred solution could give information about the identity and concentration of several metals down to concentrations of several hundredths milligrams per liter, assuming a tenfold concentration of sample. In unstirred solutions the sensitivity is decreased and the current becomes a function of the rate of voltage increase.

A Sargent model XXI polarograph became available in the summer of 1958 and led to a reorientation of the work in two directions. First the sevenfold increase in current sensitivity of the new instrument permitted reconsideration of the dropping mercury electrode. Second, automatic voltage scanning and recording made it possible to obtain meaningful curves at a mercury pool electrode in an unstirred solution.

Apparatus and Materials

A. Polarograph

Fisher Electropode - manually operated with no recorder

Sargent model XXI recording polarograph

B. Reference Electrode

The reference electrode consists of a small helix of #24 silver wire chloridized by brief anodic treatment in dilute HCl. As a matter of routine it was rechloridized at the start of every working day. A brief rinsing in distilled water after the anodic treatment is the only further preparation required.

Direct measurement showed that in nearly saturated KCl solutions the Ag/AgCl electrode was about 25 millivolts negative to the saturated calomel electrode (SCE), which is the usual standard in polarography. All half-wave potentials in this report are, unless otherwise stated, referred to the silver-silver chloride electrode in nearly saturated KCl. To convert them to the basis of the SCE, add -0.03 v.

It should be emphasized that the pool and the dropping mercury electrode (DME) were usually negative to the reference electrode. In some solutions it was possible and desirable to start the

voltage scan at a slightly positive potential (positive with reference to the Ag/AgCl electrode), but what is referred to as an "upward" scan took the potential of the pool or DME always toward larger negative values, and the "downscan" was from large negative values to small negative values, to zero and sometimes to positive potentials. Half-wave, half-peak, and other potentials are marked + or - depending upon the sign of the pool or dropping electrode.

C. Cell

This cell (See Figure 1) was designed to permit the DME and pool electrode to be used interchangeably without disturbing the solution. It was constructed from a 6-inch Pyrex test tube. A sintered glass bubbler, made from Pyrex glass powder between 140-200 mesh, (3) was sealed in the bottom. This bubbler permits the passage of nitrogen through the solution for de-aeration. A two-way stopcock permits the passage of nitrogen either through or over the solution when polarograms are being made.

When the pool electrode is used, mercury is added to form an annular layer in the bottom surrounding the bubbler tube. Its area, which within limits is not dependent upon the amount of mercury added, is roughly 0.8 cm.² A platinum wire passing through the bottom of the cell permits connection of the mercury pool to the polarograph lead.

When the DME is to be used, the capillary, held in a rubber stopper, is simply inserted through the top of the cell.

D. De-aeration

Oxygen is readily reduced at a mercury cathode and must be removed from solutions prior to polarographic analysis.

Tank nitrogen is frequently used for de-aeration prior to polarographic analysis. The high sensitivity of the pool electrode demands that the traces of oxygen, contaminating commercial nitrogen, be removed. Commercial nitrogen passed through a spiral wash bottle containing vanadyl sulfate solution, (4) then through a fritted glass bubbler into the bottom of a centrifuge bottle containing vanadyl sulfate solution, and finally through a second bubbler into a centrifuge bottle containing water, meets these requirements. The outlet tube of each of the two centrifuge bottles contains a simple trap to catch spray carried by the gas stream. Before the wash bottle, the system is connected to a pressure relief device. All connections are made with Tygon tubing. (5) In more recent work this method was abandoned. The nitrogen is now passed over copper turnings at 450°C. A furnace for this operation is commercially available.

Two drops of 95-per-cent ethanol are added to 10 ml. of the solution under examination to reduce the size of nitrogen bubbles, and thus increase the speed of aeration. (1)

As will be seen later, it is necessary to replace the solution in the cell by another solution without disturbing the mercury. The new solution must be substantially free from oxygen before it is added. This is accomplished by a pre-deaeration cell made from a Pyrex test tube by attaching a side arm and sealing a fritted glass bubbler in the bottom.

E. Mercury

Mercury was purified by shaking with nitric acid. Persistent irregularities at the pool electrode were reduced by adding the mercury from a burette.⁽⁶⁾ The mercury is now purified in a commercial "Oxifier" and then filtered through a gold leaf filter.

F. Other Materials

Double distilled water stored in polyethylene bottles was used throughout the study. All chemicals were C.P. or reagent grade with the exception of the ammonium hydroxide. All of the commercially available ammonium hydroxide tested at this laboratory contained small amounts of heavy metals. Therefore, it was prepared by passing cylinder ammonia through double distilled water until an approximately 7 M solution was obtained. In later work, the ammonium-sulfate supporting electrolyte, prepared by the neutralization of sulfuric acid with ammonium hydroxide, was purified from traces of heavy metals by extraction of dithizonates into carbon tetrachloride.

PROCEDURE

A. Care of Cell

All glassware, including the cell, is washed with 6 M nitric acid followed by several rinses with distilled water and finally with double distilled water. Care should be taken, when emptying the cell, that the potassium chloride in the side arm does not enter the main body of the cell.

B. Cell preparation

Saturated ammonium sulfate solution is added to the side arm to fill about half of its height (See Figure 1). A saturated KCl solution is then added carefully to the outer end of the side arm to just push the ammonium sulfate solution up nearly to the junction of the side arm with the cell. The chloridized silver wire described previously is inserted into the KCl solution. Double distilled water is added to the cell to a level just below the junction of the side arm. About eight drops of saturated ammonium sulfate solution and two drops of ethyl alcohol are added to the cell. Nitrogen gas is bubbled through the solution in the cell for a few minutes to prevent oxygen in solution from entering the side arm when the level in the cell is subsequently raised. Additional water is added to close the junction between the solutions in the cell and the side arm, and nitrogen is bubbled through the

solution for several minutes more. Next, the mercury pool is added from a burette to form a layer on the bottom. The face of the bubbler should not be covered. Nitrogen is then bubbled through the liquid in the cell for an additional few minutes. In all, the bubbling time should be at least ten minutes.

C. Upward Scanning

The initial run with the pool electrode usually gives an irregular curve with a high residual current. Basic salts or oxides of mercury or of contaminating metals are probably involved in this effect, and perhaps also traces of "grease" or other organic substances. A preconditioning of the mercury eliminates most of these troublesome irregularities. This is accomplished by running about two automatic voltage scans on a distilled water blank prepared as described in section B.

When the supporting electrolyte was ammonium sulfate, scans were from +0.2 v. to -1.8 v. When ammonium hydroxide - ammonium sulfate was used, scans were from 0.03 to 2.0 v. Before actually running a curve with automatic scanning, it is worthwhile to scan the voltage up and down rapidly several times by hand. This serves to remove some of the worst irregularities.

Next run a curve with automatic voltage scanning by-passing the nitrogen over the solution. A sensitivity of 0.020 $\mu\text{a}/\text{mm.}$ is suitable and the voltage should be carried up until the current goes off-scale. Return the per cent span dial to zero and repeat. The second curve is usually lower and smoother than the first.

D. Downward Scanning.

Downward scanning of the voltage is often instructive, since it tends to redissolve or strip from the mercury pool the metals deposited into it during the upward scan. These stripping or anodic waves may be more characteristic than the cathodic waves or peaks found on the upscan.

In interpreting downscan curves, both the voltage and the current axes must be read backwards. The positive time direction along the chart now corresponds to a decreasing applied voltage, and a current rise from right toward left on the chart now means an anodic current, since the DME switch is in the positive position.

E. Preparation of Sample.

One hundred ml. of sample is brought to fumes with 0.1 ml. concentrated H_2SO_4 . If necessary to remove organic matter, concentrated HNO_3 is added drop-by-drop until the sample becomes clear. Excess HNO_3 is removed by washing the sides of the flask with double distilled water and again bringing to fumes. Fuming also removes chlorides which produce serious interference in the determination of copper.

After the flask has cooled, the acid is neutralized with

metal-free ammonium hydroxide and the excess ammonia removed by boiling until the odor of ammonia disappears.

Make the solution up to about 10 ml., filter, and add to the deaeration cell. Add 2 dps. of 95-per-cent ethanol and de-aerate for 10 minutes. Remove the distilled water blank from the polarographic cell with a pipette without disturbing the mercury. To protect the mercury from oxygen, keep a good current of nitrogen flowing while the blank solution is being removed and while the sample is transferred from the pre-deaeration cell.

F. Polarograms

Bubble nitrogen through the solution in the cell for a few minutes to ensure removal of traces of oxygen which may have found access during the transfer. Meanwhile, make a quick manual voltage scan to precondition the mercury. By-pass the nitrogen over the solution and scan at least two upward and one downward curves with automatic scanning. Two curves are recommended as a minimum because irregularities removed in the preconditioning process may recur after transfer of a new solution to the cell, and also because the waves for certain metals seem to be higher and more distinct after the first upward scan. By making two or three scans, the risk of mistaking an accidental and transitory irregularity for a significant wave is reduced.

If the DME is to be used, insert the dropping electrode into the cell (with the nitrogen still by-passed over the solution) so that it dips into the upper part of the solution. Adjust the height of the reservoir to give a drop time of 4 or 5 seconds, and run a polarogram at suitable sensitivity.

After suitable curves have been run with $(\text{NH}_4)_2\text{SO}_4$, sufficient ammonium hydroxide is added to make the solution about 0.4 M in NH_3 . Nitrogen is bubbled through the solution for a few minutes to insure good mixing and remove any oxygen that may have been entrained with the ammonium hydroxide.

If the DME has added so much mercury to the pool that the fritted bubbler is covered, suck out the excess with a drawn-out rubber bulb pipette.

After curves have been run in the presence of free ammonia, it may sometimes be advantageous to add about 300 mg of ethylenediaminetetraacetate (EDTA-the disodium salt was used). This powerful complexing reagent pushes the reduction potentials of most of the metals involved in this study to such negative values that they no longer give reduction waves. Curves run at the pool electrode in the presence of EDTA give little or no information, but at the -DME, copper and lead give waves at more negative potentials than without it. If interferences in other curves have left doubt concerning the presence or absence of these two metals, curves run at the DME after addition of EDTA may settle the question. Otherwise,

addition of EDTA is not worthwhile. The foregoing statements apply when EDTA is added to an ammonium sulfate solution containing excess ammonia. Its effect on curves obtained under other conditions has not been examined.

G. Interpretation of Polarograms

1. At the DME. There is extensive literature on the interpretation of conventional polarograms. (1,5) Half-wave potentials, $E_{1/2}$, were read off at the half-way point of the rise as determined by inspection or by a rough measurement. No correction was made for current resistance (IR) drop across the resistors in the measuring circuit.

Wave heights in favorable cases were easily measured vertically through the half-wave potential between straight-line extrapolations of the sections of the polarogram immediately preceding and following the wave. When the wave being measured was immediately preceded or followed by another wave, this procedure was less certain, but the wave heights were usually good enough for present purposes.

2. At the pool electrode. The literature gives much less help in interpreting curves obtained at the pool electrode.

A peak is obtained at a pool electrode in a quiet solution. The decrease in current following the peak is due to depletion of the reducible species in the neighborhood of the electrode in the absence of stirring. They also found that peaks were higher the greater the scanning rate.

In this report the term "wave" is often used in a general sense to include peaks.

Half-wave or half-peak potentials, $E_{1/2}$, were located by inspection or with the aid of a rough measurement of height. They were usually not uncertain by more than about 0.01 v.

Measurement of wave heights was less certain because of the variety of shapes encountered. When the current rise was immediately preceded by a minimum and/ or followed by a maximum, measurement was made from a horizontal tangent drawn at the maximum or minimum. Otherwise, a preceding or following straight segment of the curve was extrapolated as well as possible, and the wave height was measured vertically along the ordinate through the half-wave potential.

Stripping waves or peaks (more properly, valleys) obtained when the voltage was scanned downward were measured similarly.

RESULTS

A. Effect of Contaminants

In order to distinguish between features of polarograms made

by the metals being studied and the effects of substances accidentally present, the behavior of the latter was investigated.

1. Oxygen. Dissolved oxygen gives two waves at the DME.⁽⁵⁾

The first comes quite near the start of the voltage scan, at around -0.1 v.; the second, with a more gradual rise, has a half-wave potential between -0.9 and -1.0 v. At the pool electrode oxygen has a similar effect.

2. Chloride. Use of a sulfate-supporting electrolyte in place of chloride makes it possible to start the voltage scan at a more positive potential. In such a sulfate solution, therefore, chloride is an objectionable contaminant. It makes its presence known at the pool cathode by a very high, narrow peak between +0.2 and 0 v.

3. "Grease". Occasional sharp peaks observed at the pool electrode at potentials more negative than -1.1 v. were perhaps caused by traces of fatty oil. Dispensing of the mercury from a burette in which it has stood for at least 24 hours, appeared to eliminate all or nearly all of the effects attributed to grease.

4. Hydrogen ion. The final rise due to hydrogen reduction occurs at a less negative potential at the pool electrode than at the DME.⁽⁷⁾ The higher the hydrogen ion concentration, the less negative the potential at which the reduction of hydrogen ion begins. Therefore in strongly acid solutions, little useful information can be obtained at the pool electrode.

A possible source of contaminating acidity may be overheating of the ammonium sulfate in the preparation of the sample.

B. Discussion of Metals Individually and in Certain Combinations

Tables 1 and 2 summarize the results of the study of individual metals and certain combinations. These data were obtained from samples containing known concentrations of metals in double distilled water. All were treated by the method described for the preparation of samples, i.e., by successively (1) evaporating 100 ml. of sample to fumes with 0.1 ml. concentrated sulfuric acid; (2) adding excess ammonium hydroxide; (3) boiling off excess ammonia; and (4) diluting to 10 ml. The resulting solutions were about 0.18 M in ammonium sulfate. Additional curves were obtained in these solutions after successive addition of (1) enough ammonium hydroxide to make the solution about 0.4 M in ammonia and (2) about 100 mg. of EDTA.

All potentials in the following tables are with reference to the Ag/AgCl, saturated KCl reference electrode and unless otherwise stated are half-wave potentials.

Numbers marked "ppm/ua" are reciprocally related to wave-heights. From them estimation of the approximate concentration responsible for a wave or peak is possible. For most of them a wide variation is indicated. This is the actual variation found in a number of runs. When the number of comparable runs is small, the variation found may be misleadingly small. These reciprocal wave-heights should be regarded as only a very rough indication of concentration because of : (1) lack of standardization of conditions; (2) uncertainty in measuring heights from the curves; (3) influence of neighboring waves or peaks on the one being studied. When no reciprocal wave-height is given for the solution containing excess ammonia, it may be assumed to be about the same as that for the ammonium sulfate solution without excess ammonia.

Recent work has been aimed at improving the accuracy and precision. Although this work is still not complete we are hopeful that we will be able to determine quantitatively lead, zinc, cadmium, nickel and copper in concentrations as low as 0.01 p.p.m. with a standard deviation of about ± 10 per cent.

Voltages enclosed in parentheses and marked* apply to anodic stripping observed when the potential is scanned downward. No reciprocal wave-heights are given with these, since, in general, stripping waves are of about the same magnitude as the cathodic waves found on the upscan.

A more complete discussion of the phenomena summarized in tables 1 and 2 may be found in the work by Porter.⁽⁸⁾

Figures 2a, b and c show the characteristic behavior at both the DME and the pool cathode of cadmium, copper, lead, zinc, and nickel. The solution analyzed was prepared to contain the following metals by the prescribed procedure.

Cu	0.2 mg/l
Pb	2.0
Cd	0.1
Zn	10.0
Ni	0.5

Curve 1 of Figure 2a shows the polarograms of this solution made at the DME with ammonium sulfate as the supporting electrolyte. The wave for copper is several times as high as would be expected for this concentration; contamination may be suspected. The lead and zinc waves are normal. The cadmium is too dilute to be detected with certainty. The nickel which is about at the limit of detectability is overshadowed by the high zinc concentration.

Curve 2 shows the characteristic more negative initial rise caused by the excess ammonia promoting anodic oxidation of mercury. The wave at -0.42 v. may be due to either copper or lead since they overlap in ammoniacal solutions. Complexing by ammonia has deferred the reduction of zinc permitting the wave for nickel to be seen. For curve 3, 300 mg. of EDTA has been added to the solution. The initial rise is still more negative. EDTA makes the reduction potentials of nearly all metals so negative that their waves are lost in the final rise due to hydrogen reduction. Of the metals present only lead gives a wave.

In figure 2b are shown the polarograms for upscans at the pool electrode. Curve 1 shows the polarogram when the solution was 0.18 M in ammonium sulfate. The copper and lead waves are typical. The low cadmium concentration shows up distinctly though its wave is smaller than it would be if not preceded by a high lead peak. When the scan reached -0.68 v. the sensitivity was reduced to 0.2 of the previous value or to 0.100 $\mu\text{a}/\text{mm}$, so that the zinc wave could be recorded. Even in the absence of zinc it is doubtful if nickel would have given a distinct wave in this solution.

Curve 2 represents an upscan of the solution with a pool electrode in the presence of an excess of ammonia. The first reduction wave of copper is very small because of the high peak preceding it. This peak is probably due to reduction of mercury which had been anodically oxidized just before the start of the upward scan. To avoid development of such peaks the potential should not be allowed to become unnecessarily positive. Ammonia increases the separation between cadmium and lead which is advantageous when there is a large amount of lead and little zinc. The nickel and zinc waves are also separated by ammonia as they are at the DME.

Figure 2c shows the stripping curves obtained at the pool electrode. Curve 1 was run in a solution which was 0.18 M in ammonium sulfate. The high zinc concentration gives a very deep stripping wave (off scale). Cadmium is barely noticeable at this sensitivity. If the potential had been left at about -0.8 v. for a short time to dissolve most of the zinc out of the pool, and if the scan had been continued downward at the higher sensitivity, the cadmium wave would have been more evident. The lead and copper stripping waves are typical.

Curve 2 was run on the same solution in the presence of excess ammonia. The zinc and cadmium dissolve at a more negative potential in the presence of ammonia. However, cadmium shows up better here than in curve 1 because of the increased sensitivity. The strong anodic lead wave may hide the more negative of the two copper waves since they have nearly the same potential. The less negative copper wave is typical.

APPLICATION TO ACTUAL SAMPLE

A comparative study was conducted on nine metal-bearing samples which had been submitted to this laboratory for analysis. Comparison was made between the results obtained using the quiet mercury pool electrode, the dropping mercury electrode, and the colorimetric procedures used in this laboratory.⁽⁹⁾ The results are given in table 3. The investigation was restricted to the analysis of lead, copper chromium, zinc, nickel, and cadmium. Iron and silver cannot be determined by the procedure as it now stands. Cobalt was not found polarographical in any of the samples examined.

The results of this study show that copper, nickel, cadmium, lead, and zinc can be determined on a semi-quantitative basis polarographically. Chromium, however, was detected in only two of the nine samples examined and appeared in the hexavalent form. Apparently in seven of the nine samples examined, the chromium in the presence of organic matter was all reduced to the trivalent state during fuming with sulfuric acid. Waves due to trivalent chromium may have merged with the final rise.

Of the six metals investigated, the determination of copper gave the most nearly quantitative results. Chromium interference was expected since the two have similar half-wave potentials. Only in sample #473 did the chromium obscure the copper wave and this was easily resolved by a backscan since chromium does not give a stripping wave. Lead, on occasion, (samples 471, 472, and 474, table 3), gave positive results polarographically where none was obtained colorimetrically. This may have been due to the absorption of lead by the cell from a previously examined sample. However, these results were all 0.10 ppm or less. Since the procedure is to be used as a screening technique prior to wet analysis, these occasional false readings will cause little difficulty. Cadmium did not interfere with the determination of lead even when cadmium was 100 times as great as the lead concentration (sample 458, table 3).

Zinc and nickel were easily distinguished in all combinations studied. An upscan in the presence of excess ammonia caused sufficient separation of their half-wave potentials to permit them to be easily distinguished.

In general, the results as shown in table 3 indicate that the quiet pool electrode is more versatile than the dropping mercury electrode. Concentrations ranging from 0.01 to 6.0 ppm were determined using the quiet pool by merely changing the sensitivity or by raising or lowering the curve by the controls provided for this purpose. The dropping mercury electrode is of value for extremely high concentrations such as were found in sample 405, table 3. However, for some unknown reason most of the results obtained with the dropping mercury electrode were considerably higher than the results obtained using either the quiet pool electrode or the standard laboratory procedures.

Figures 3a and 3b are typical of the polarograms obtained in the examination of actual samples. Curve 1 corresponds to an upscan in 0.18 M ammonium sulfate using the mercury pool electrode. Typical waves for chromium, copper, cadmium, and zinc are obtained although the half waves for cadmium and zinc are shifted about 0.04 v. to the negative. The concentrations obtained from wave height measurements for chromium, cadmium, and copper were in good agreement with the results obtained by wet analysis. The zinc wave was, however, about three times as high as would be expected.

Curve 2 was obtained by an upscan at the pool electrode with an excess of ammonia. Two copper waves of equal height can be observed. The wave at -0.34 v., however, could be caused by the presence of lead if it were not for the fact that no lead was detected in curve 1. Well formed curves were obtained for both cadmium and zinc and the determined concentrations agreed quite closely with those values obtained by wet analyses. The curve for nickel, although somewhat obscured, is still detectable.

Figure 3b shows the polarogram obtained at the DME for the same sample in excess ammonia. A well formed curve was obtained and copper, cadmium, nickel, and zinc were easily identified in concentrations quite close to those obtained by wet analysis.

By proper selection of the type of curves to run, the average time to complete the screening procedure was from two to three hours. Most of the data secured in this study (table 3) could have been obtained merely running up-and-down scans with ammonium sulfate supporting electrolyte and an upscan with excess ammonia added. The dropping mercury electrode need only be used when high concentrations of one or more of the metals are present.

CONCLUSIONS

Polarography can be used as a screening procedure for the determination of copper, lead, nickel, cadmium, zinc, and possibly cobalt, although this latter has not been studied sufficiently. It was unsuccessful for the determination of iron, chromium, and silver.

The method required from two to three hours to complete. The results although semi-quantitative indicate which metals are present and permit the selection of proper sample volume for wet analysis. Although at present the method has not been in use for a sufficient period to permit an estimate of the time saved, indications are favorable.

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LEGENDS

- Figure 1. Polarographic cell for dropping mercury electrode.
- Figure 2a. Upscan of synthetic sample with dropping mercury electrode.
- Figure 2b. Upscan of synthetic sample with quiet pool electrode.
- Figure 2c. Downscan of synthetic sample with quiet pool electrode.
- Figure 3a. Upscan of sample #457 with quiet pool electrode.
- Figure 3b. Upscan of sample #457 with dropping mercury electrode.

Table 1

Half-wave Potentials and Current Concentration Ratios
of Metals at the Mercury Pool Electrode

	In $(\text{NH}_4)_2\text{SO}_4$	+ NH_4OH	+ EDTA
Cd	0.52 to 0.56 v. 0.6 ± 0.3 ppm/ua *(0.50 to 0.53 v.)	0.66 to 0.70 v. *(0.64 to 0.68 v.)	no wave
Pb	0.34 to 0.37 v. 2.0 ± 1.0 ppm/ua *(0.31 to 0.35 v.)	0.38 to 0.42 v. *(0.37 to 0.39 v.)	no wave
Zn	0.96 to 0.98 v. 0.5 ± 0.2 ppm/ua *(0.89 to 0.92 v.)	1.18 to 1.22 v. *(1.16 to 1.18 v.)	no wave
Ni	no wave	0.91 to 0.92 v. 0.4 ± 0.2 ppm/ua *(stripping behavior variable)	no wave
Cu	+0.02 to +0.06 v. 0.5 ± 0.3 ppm/ua *(+0.07 to +0.09 v.)	2 waves: (1) 0.12 to 0.15 v. (2) 0.38 to 0.42 v. each wave about 0.6 to 2.8 ppm/ua *(0.08 to 0.12 v. 0.36 to 0.38 v.)	variable
Co	1.01 v. (range of potentials 0.25 ± 0.1 ppm/ua *(stripping behavior variable)	1.02 v. not known, probably about ±0.02 v.) 0.40 ± 0.02 ppm/ua *(0.36 to 0.40 v.)	no wave
Cr (VI)	+0.10 v.; no wave or peak if even a trace of excess acid is present *(no stripping wave)	high sharp peak just following initial rise *(no stripping wave)	probably no wave
Cr (III)	0.86 to 0.88 v. inadequately studied	not studied	not studied
Fe (III)	no clear indication obtained under these conditions		
Ag	not studied; it seems likely it would be reduced before the initial rise and would raise the entire curve.		

* Half wave potential of anodic strip

All potentials are negative unless marked +

Table 2

Half-wave Potentials and Current Concentration Ratios of
Metals at the Dropping Mercury Electrode

	In $(\text{NH}_4)_2\text{SO}_4$	+ NH_4OH	+ EDTA
Cd	0.57 to 0.59 v. 28 ± 5 ppm/ua	0.67 to 0.74 v.	no wave
Pb	0.37 to 0.40 v. 100 ± 20 ppm/ua	0.43 to 0.47 v.	1.13 to 1.17 v. abt.100 ppm/ua
Zn	0.98 v. 12 ± 2 ppm/ua	1.19 to 1.22 v.	no wave
Ni	1.01 to 1.03 v. 12 ± 2 ppm/ua	0.91 to 0.95 v.	no wave
Cu	+0.02 to +0.05 v. 13 ± 2 ppm/ua, usually	2 waves: (1) 0.17 v., often not seen (2) 0.38 to 0.45 v. each 25 ± 5 ppm/ua, usually	0.47 to 0.51v. 20 ± 10 ppm/ua
Co	no wave	1.15 to 1.20 v. 10 ± 2 ppm/ua	no wave
Cr (VI)	0.02 \pm v. $1.7 \pm$ ppm/ua	tends to merge with initial rise	no wave
Cr (III)	not adequately studied -- probably no waves under these conditions		
Fe (III)	possibly about 1.3 v.	1.35 v.	no wave in presence of 0.4 M NH_4OH ; small wave at about 1.3 v. when nearly neutralized with sulfuric acid
Ag	not studied		

All potentials are negative unless marked +

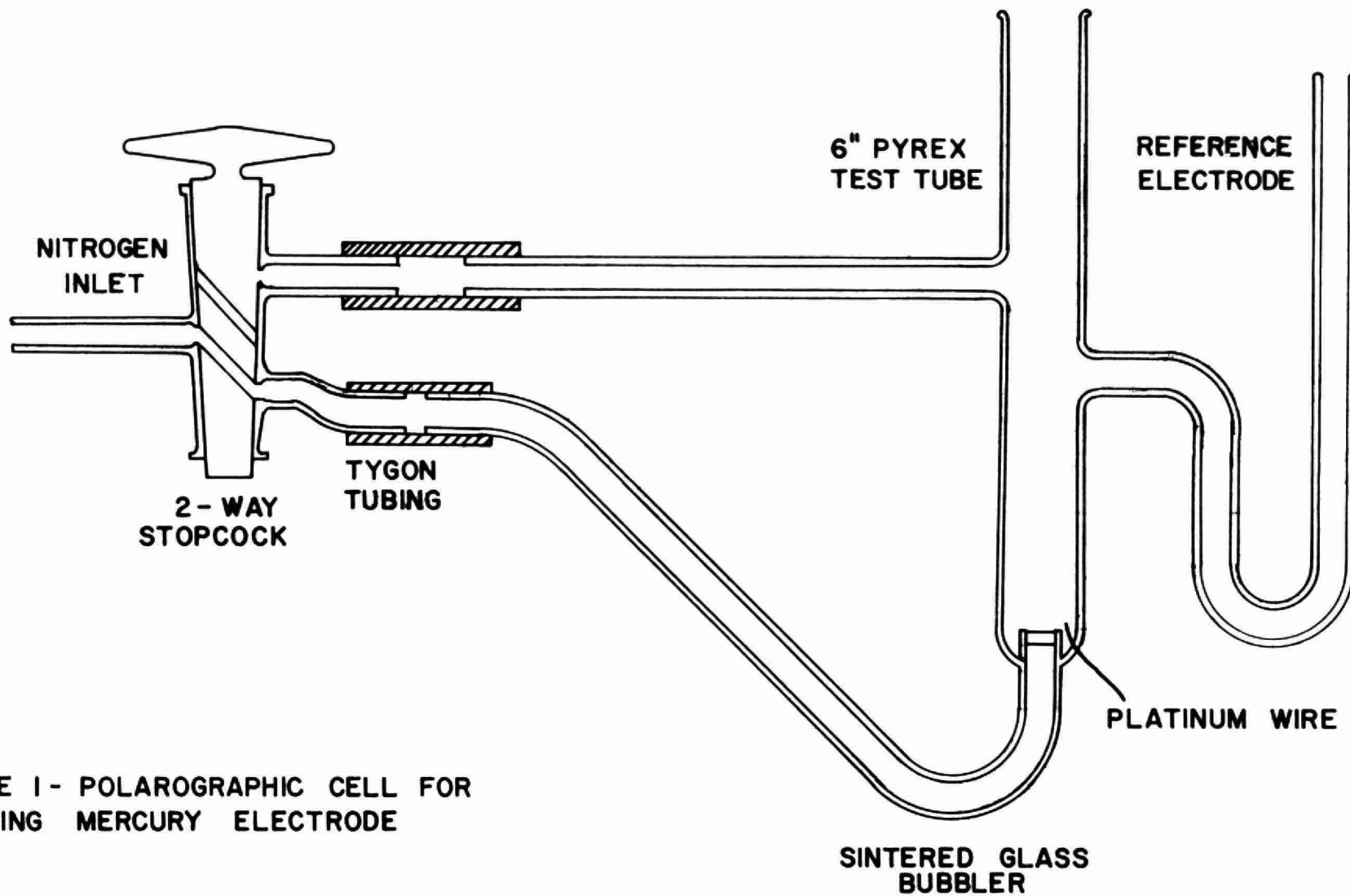
Table 3

Results of Comparison Study between
Polarographic Methods and Standard Methods of Analysis

Sample No.	Copper (ppm)			Chromium (ppm)			Cadmium (ppm)			Lead (ppm)			Nickel (ppm)			Zinc (ppm)		
	QMP	DME	WET	QMP	DME	WET	QMP	DME	WET	QMP	DME	WET	QMP	DME	WET	QMP	DME	WET
471	0.05	-	0.05	0	-	0.14	0.01	-	0.05	0.03	-	<0.03	<0.01	-	<0.05	0	-	-
472	0.03		0.03	0	-	0.04	0.01	-	0.06	0.03	-	<0.03	<0.01	-	<0.05	0	-	-
473	0.30		0.32	0.94	-	1.0	0.05	-	0.20	0.10	-	0.05	tr.	-	<0.05	tr.	-	-
474	0.07		0.06	0	-	0.12	tr.	-	0.06	0.08	-	<0.03	<0.01	-	<0.05	0	-	-
457	0.39	0.26	0.45	0.01	0	0.03	1.8	3.6	2.6	0	0	-	0.08	0.07	0.11	0.55	0.64	0.50
458	0.7	1.7	1.07	0	0	<0.02	6.1	13.8	3.0	0.06	0	0.02	0.10	0.34	0.25	0.93	0.68	0.64
405	-	13	7.8	0	0	0.11	2.4	4.5	1.9	0.8	-	0.7	-	1.7	1.2	-	8.4	4.5
38	0.58	0.68	0.24	0	0	4.7	0.99	8.1	1.6	0.05	-	0.02	0	0	-	0	0	-
489	0.05	-	0.04	tr.	-	0.78	0.10	-	0.08	0.01	-	0.01	0.04	-	0.10	0	-	-

QMP = Quiet Mercury Pool

DME = Dropping Mercury Electrode



**FIGURE 1- POLAROGRAPHIC CELL FOR
 DROPPING MERCURY ELECTRODE**

POLAROGRAPHIC ANALYSIS

synthetic sample

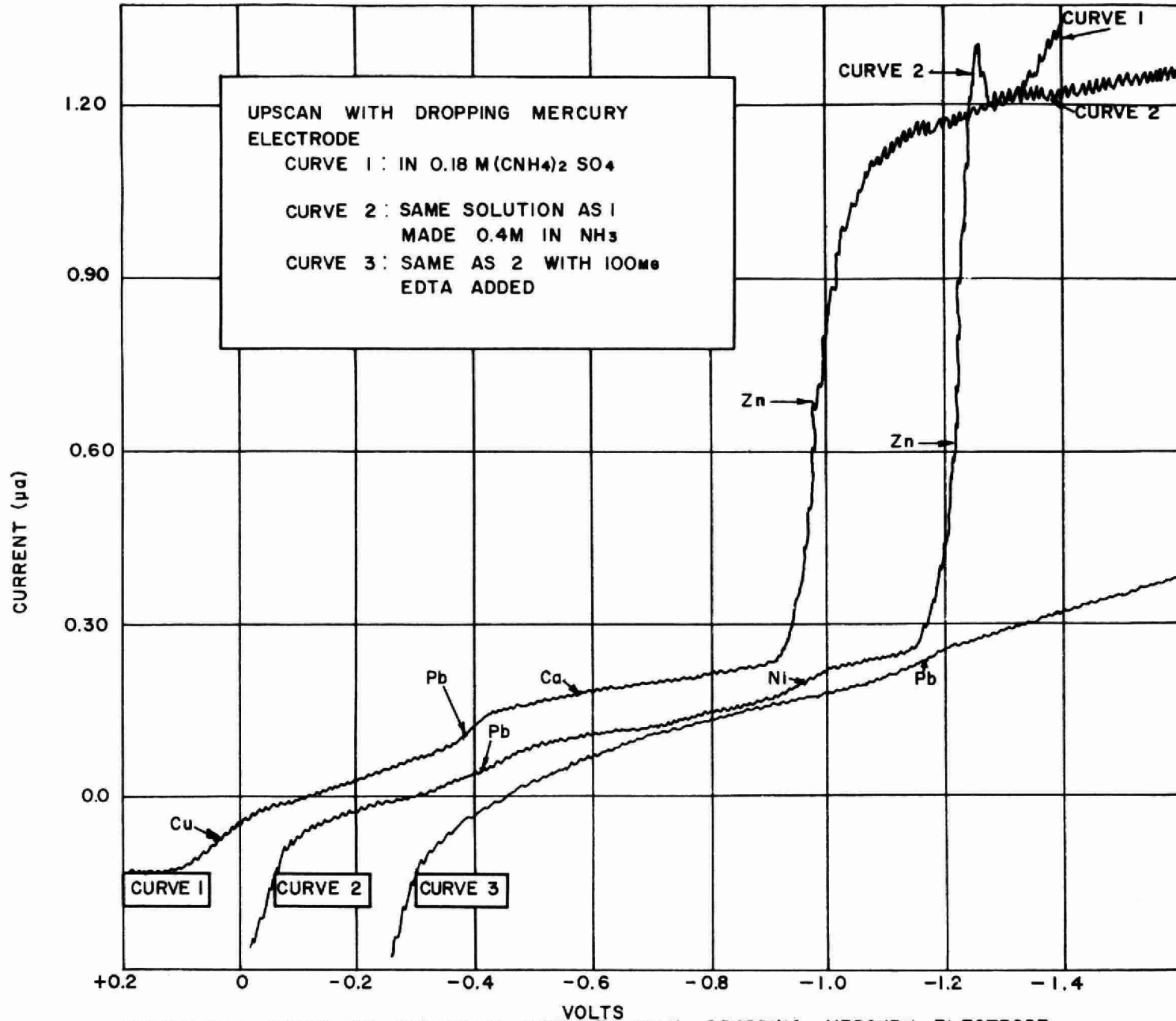


FIGURE 2A : UPSCAN OF SYNTHETIC SAMPLE WITH DROPPING MERCURY ELECTRODE

POLAROGRAPHIC ANALYSIS

synthetic sample

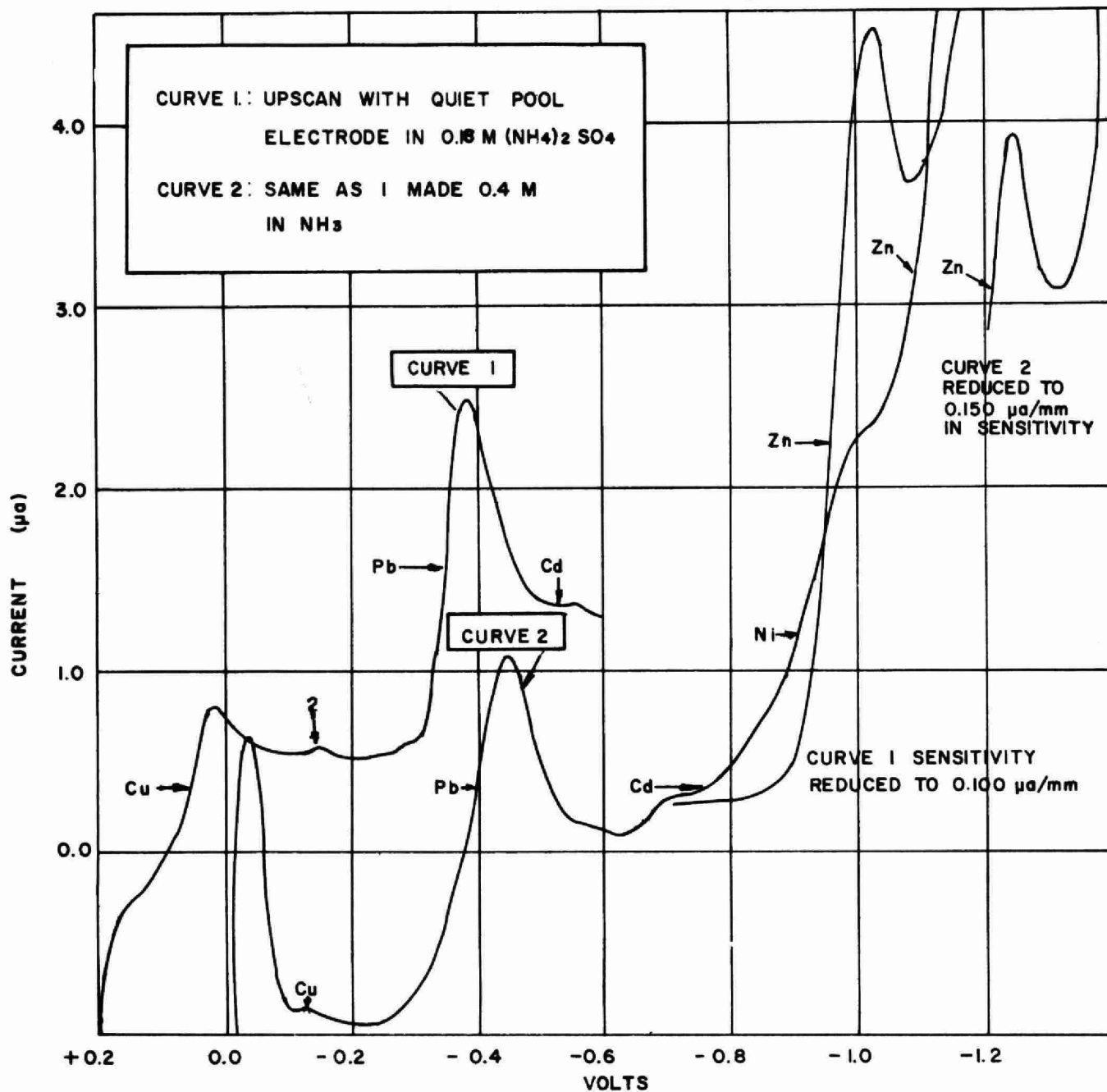


FIGURE 2B - UPSCAN OF SYNTHETIC SAMPLE WITH DROPPING MERCURY ELECTRODE

POLAROGRAPHIC ANALYSIS

synthetic sample

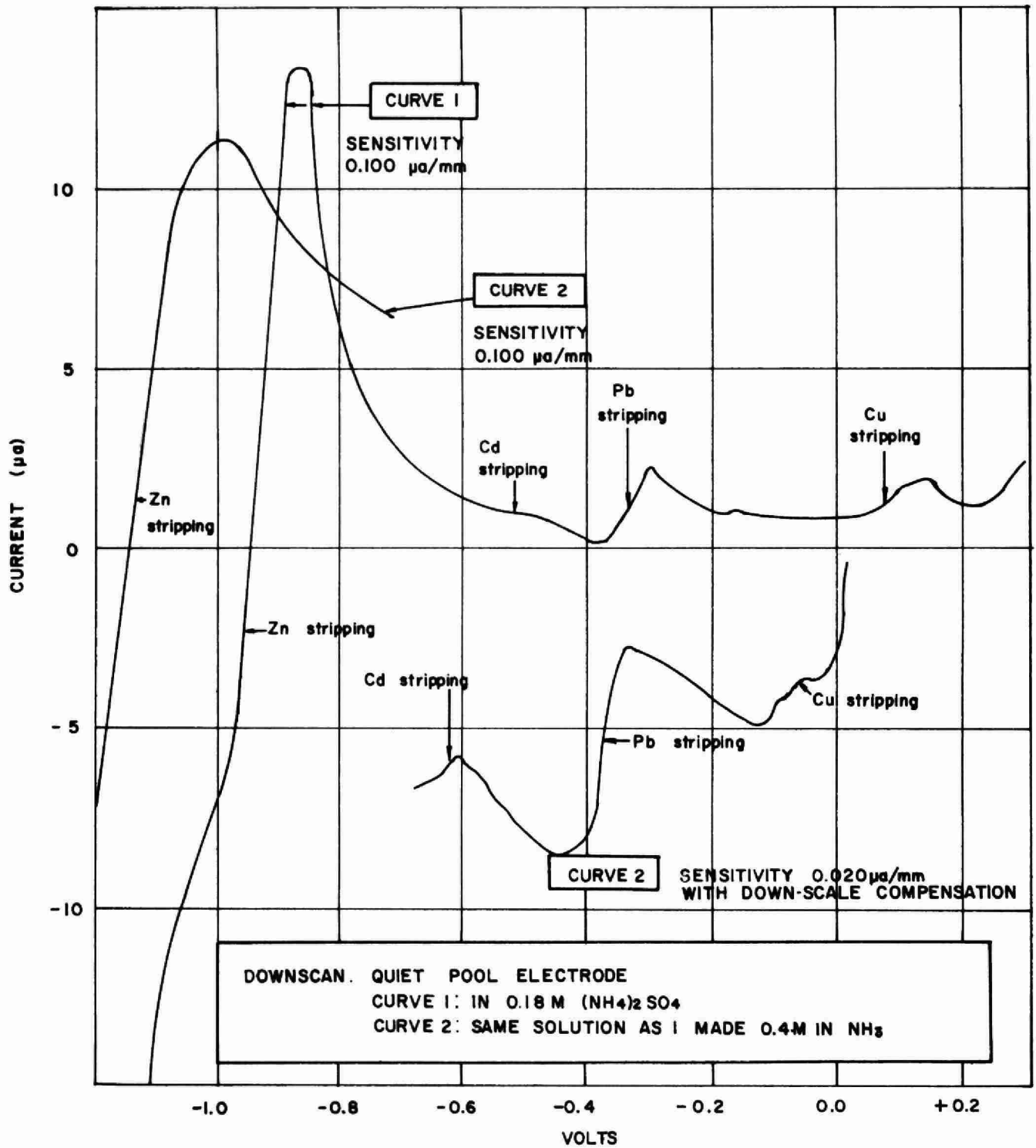


FIGURE 2C - DOWNSCAN OF SYNTHETIC SAMPLE WITH QUIET POOL ELECTRODE

POLAROGRAPHIC ANALYSIS

sample 457

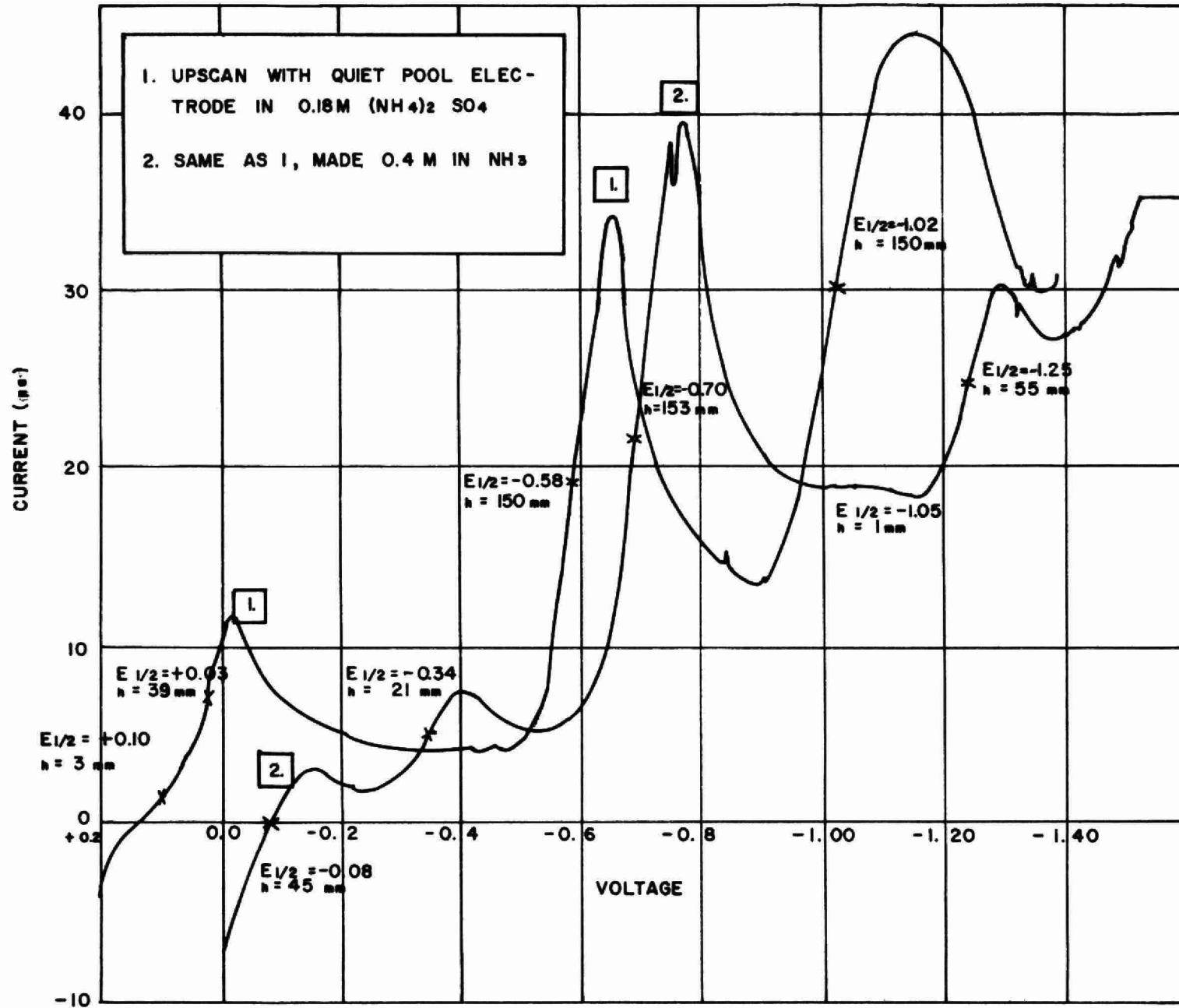


FIGURE NO. 3A - UPSKAN OF SAMPLE NO. 457 WITH QUIET POOL ELECTRODE

POLAROGRAPHIC ANALYSIS

sample 457

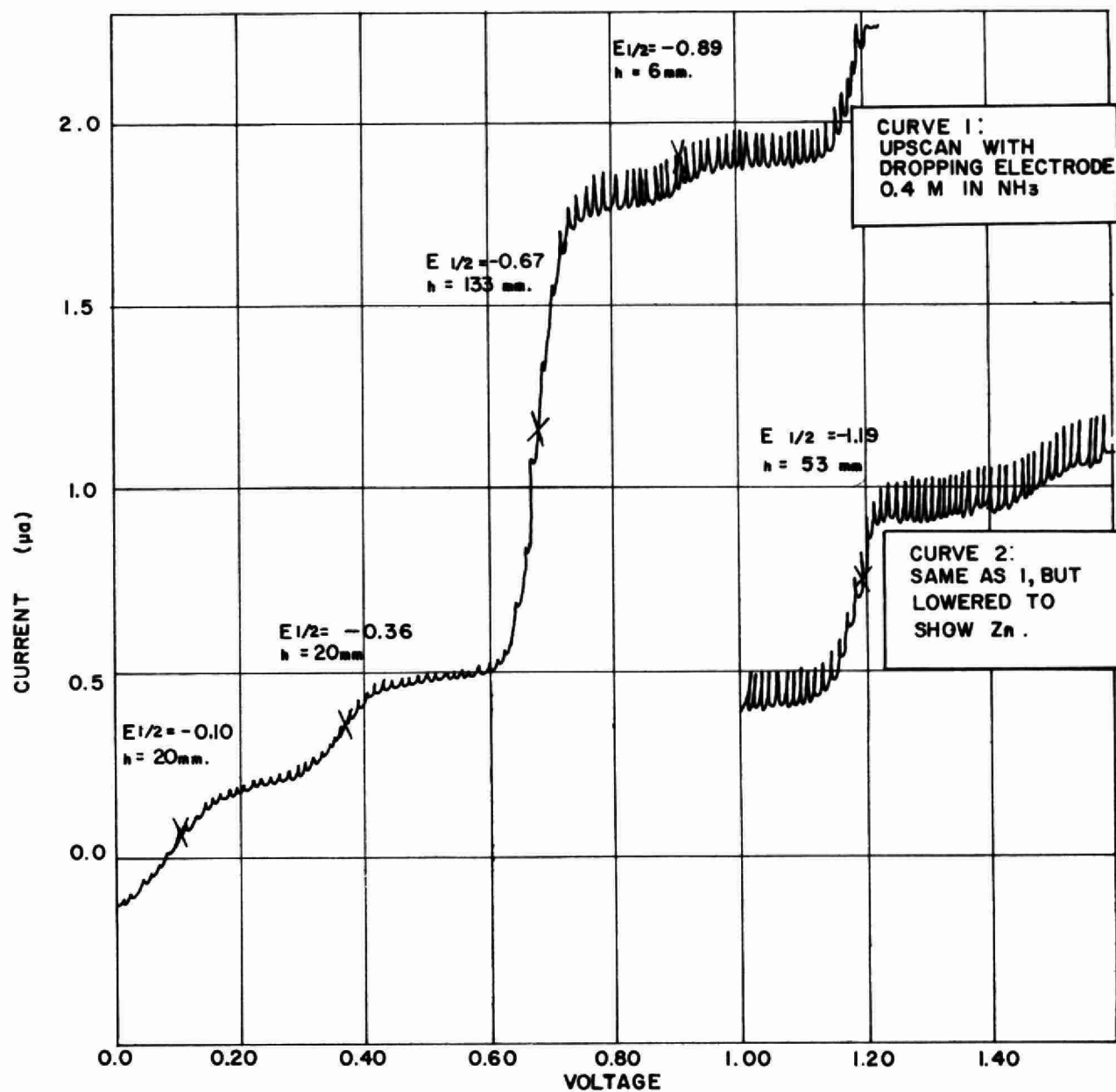


FIG. 3B - UPSCAN OF SAMPLE NO. 457 WITH DROPPING MERCURY ELECTRODE

"DETECTION AND MONITORING OF PHENOLIC WASTE WATER"

By

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ABSTRACT

Restrictions on discharge of phenolic compounds to boundary waters has led Imperial Oil Limited to provide facilities for continuous detection of phenolic contaminants in phenol plant cooling water and subsequent automatic diversion of the water from the sewer to impounding facilities prior to disposal. The principle of the equipment was originally conceived by Dr. G. Gutzeit and his associates of General American Transportation Co.

Detection is by continuous colourimetric analysis employing the Gibbs Indolac method. Equipment is provided for continuous mixing of sample and reagents, photo-electric measuring and recording of phenol concentration and warning to operating personnel should major contamination occur.

Contaminated water is diverted to impounding tanks automatically by motor driven valves. These valves are operated by the recorder on the phenol detector which is equipped with a switching relay. When the phenol concentration in the cooling water reaches a predetermined level the valve on the cooling water return header closes as the valve on the line to the impounding tanks opens.

Impounded water is burned in two vertical type incinerators.

DETECTION AND MONITORING OF PHENOLIC WASTE WATERINTRODUCTION

With present-day industrial growth, a corresponding increase in the severity of pollution problems has arisen. This factor cannot and has not gone by unnoticed by the general public, who has demanded that some action be taken to decrease or erase completely, many of these problems.

Pollution problems have been studied on Municipal, Provincial, and Federal levels. Following these studies, several objectives for pollution control have been set along with recommendations for meeting these objectives.

Sarnia, Ontario, which is located on International boundary waters, has experienced a tremendous industrial growth over the past twenty years. As a result of this growth, the characteristic problems mentioned above were born.

In 1952, members of local industry formed the St. Clair River Research Committee to discuss common pollution problems and exchange proposed solutions to these problems. The situation at Sarnia is perhaps even more critical due to the fact that the city is located on an International waterway. All such waterways come under the jurisdiction of the International Joint Commission, which is composed of three Americans and three Canadians appointed by their respective governments. Governments of the Provinces and States bordering these waters are committed to carry out the findings of the I.J.C. The Ontario Water Resources Commission, therefore, solicits the cooperation of local industry in maintaining conditions in the St. Clair River Acceptable to the I.J.C.

In a report tabled by the I.J.C. in 1951, it was stated that "Adequate protection should be provided for these waters if the concentration of phenol or phenolic equivalents does not exceed an average of 2 parts per billion and a maximum of 5 parts per billion at any point in these waters following initial dilution. This quantity in the receiving waters will probably be attained if plant effluents are limited to 20 parts per billion of phenol or phenol equivalents".

Imperial Oil Limited at Sarnia soon realized that phenolic compounds were the most serious pollutants with which the Refinery had to deal. The major source of phenolic compounds at the Refinery are: Phenol Plant, Catalytic Cracking Unit sour water, and Treating Plant wash waters.

In 1955 a Biological Oxidation Unit was commissioned at Imperial's Sarnia Refinery to destroy 600 pounds per day of phenolic compounds from the aforementioned sources. However, a serious spill of phenolic water from the Phenol Plant in December, 1955, revealed the necessity for some means of early detection and proper monitoring of phenolic waste water.

At Imperial's Sarnia Refinery a Cooling Tower was installed on the process cooling water system at the Phenol Plant to reduce the volume of water discharged to the river from this plant. The blow-down from this tower is discharged to one of the oil-water separators and then to the St. Clair River. A device for detecting phenol contamination of the cooling water was necessary so that the blowdown could be directed to the Biological Oxidation Plant should the phenol content of the cooling water exceed 10 ppm.

A similar problem existed at Imperial's Refinery at Edmonton, Alberta, where waste waters are discharged into the Saskatchewan River. Authorities have limited the daily output of phenol in these wastes to 2 pounds in winter and 16 pounds in summer. As a result the whole Refinery has been put on a cooling tower system. Cooling water from each unit is returned to a common cooling tower and then recirculated. A volume of water is continuously purged from the cooling tower to the river and fresh makeup is added. It is important, therefore, to detect any phenol contaminated water and direct it away from the cooling tower. The Phenol Plant is the main source of potential contamination and the installation of detecting and monitoring equipment on the cooling water return line from the Phenol Plant to the cooling Tower was justified.

DETECTION

A. Preamble

The detection of phenolic materials in waste waters requires some means of continuous analysis based on one of the standard analytical methods. The General American Transportation Corporation of Chicago drew our attention to an instrument employing a nitrous acid-mercuric nitrate reagent (Millons Reagent) which was quite suitable for continuous analysis of waste water for phenol.

B. THE INSTRUMENT

(a) Principle

The instrument quantitatively mixes sample and reagent. After allowing sufficient time for colour development the resulting colour solution is passed through one of two optical cells. A sample containing no colour reagent is passed through the other optical cell. Light of wave length 400 millimicrons is passed through the optical cells and the intensity measured by two matched photoelectric cells. The difference in light intensity, which is proportional to the amount of phenol in the sample is recorded on a chart.

(b) Description

The Phenol Detector was built by the Instrument Department of the Sarnia Refinery. The waste water sample and the reagent are mixed by two stainless steel micro-bellows pumps. A coil is supplied to give a residence time of approximately five minutes for colour development before entering the optical cell. A similar pump

charges the sample to the reference cell. The optical cells are matched Aminco absorption cells. A 6 volt sealed-beam lamp provides the light source which is passed through two 410 millimicron light filters. The transmitted light is measured by two matched Weston photo-electric cells and the difference in intensity is recorded on a circular chart by a Brown Recorder. The recorder is calibrated so that it sounds an alarm in the Phenol Plant Control Room when the phenol concentration of the cooling water exceeds 10 ppm.

(c) Initial Service and Problems

After testing the instrument in the laboratory it was put into service on the cooling water return line from the Phenol Plant to the Cooling Tower. Performance was not too satisfactory due to the following limitations:

- (1) The 3:1 ratio of sample to reagent was difficult to maintain with the resultant formation of a yellow precipitate in the lines and the measuring cell.
- (2) Millons reagent is costly (approximately ten dollars per day) and difficult to prepare (500 grams of concentrated HNO_3 are added slowly with stirring to 500 grams of mercury. After the reaction subsides, 800 mls. of distilled water are added and the resultant solution is mixed thoroughly.)
- (3) Daily servicing by an instrument man was required due to fouling of the instrument with sediment.

(d) Modifications

Subsequent to the installation of the Phenol Recorder at Sarnia, a similar instrument was built and put into the same service at the Imperial Edmonton Refinery. They experienced similar problems to our own and offered the following modifications as a solution:

- (1) Millons reagent was replaced with Indolac (Gibbs Method), correspondingly the filters were changed from 400 μ to 625 μ .
- (2) Facilities were installed for buffering the sample prior to the addition of Indolac.

The use of Indolac reagent, which is easily prepared, eliminated the problem of precipitation. However, new problems were introduced. Gas bubbles were released upon the addition of Indolac to the sample, causing large fluctuations in the recording circuit as they passed through the optical cell. Buffering to pH 9.6 caused the formation of a carbonate precipitate on the walls of the measuring cell.

The addition of a drip pot in which the sample, buffer, and Indolac are mixed solved the problem of air bubble formation by acting as a venting vessel. The drip pot had certain other advantages which led to its installation at the point of mixing the buffer with the stream.

These advantages are:

- (a) It facilitates the setting of pumping rates since all pumps are discharging at atmospheric pressure rather than against the pressure of some other pump.
- (b) It affords a visible check on all three pumps so that if one pump should lose suction it may easily be identified and suction resorted.

A Zeolite water softener and filter were installed in the sample line ahead of sample pump suction. This eliminated the problem of hard water precipitation and foreign materials getting into the instrument.

The extra pump required for addition of the buffer solution was made available by feeding the reference cell with line pressure directly from the sample source, thus eliminating the pump for reference feeding.

With the above modifications having been completed, the continuous phenol recorder at the Edmonton Refinery is now giving satisfactory service.

MONITORING

A. Preamble

In addition to detection, facilities are also required for diverting, storing, and disposing of phenol contaminated waste water. At Sarnia Refinery it was only necessary to divert the water from the sewer to the already existing Biological Oxidation Plant. Edmonton Refinery, however, required additional impounding and disposal facilities.

B. Diversion

Contaminated cooling water is diverted automatically by means of the closure of a sixteen inch motor controlled valve on the cooling water return header and the opening of a twelve inch motor controlled valve on the line to the impounding facilities. The diversion valves are operated by the recorder on the phenol detector which is equipped with electric switches, the operating point of which is adjusted by means of a set point adjustment. A set point indicator is provided on the recorder chart. The switching action is double pole double throw for operation of the motorized valves. The reversing relays on the motor driven valves are operated by the phenol recorder and connected so that as one valve opens the other closes.

C. Impounding

Contaminated water is diverted to two storage tanks which have a combined capacity of 20,700 bbls.

D. Disposal

The impounded water is burned in one of two phenolic waste water incinerators at a temperature of 1500°F. to ensure complete combustion of dissolved contaminants. Incineration of phenolic water shows a better economy in the specific locality as compared with flue-gas stripping and biological oxidation.

R E A G E N T SIndolac Solution

- prepared fresh daily by dissolving six tablets of Indolac (2,6 - dibromoquinonechlorimide) in 1.5 litres of distilled water.

Millon's Reagent

- prepared by slowly adding 250 ml of concentrated HNO_3 to 500 gms of mercury. Add an additional 250 ml of concentrated HNO_3 after reaction subsides. Finally add 800 mls of distilled water and mix thoroughly.

Buffer Solution

- prepared by dissolving 10 gms boric acid and 15 gms of KCl in 1 litre of water and adjusting pH to 9.6 with NaOH. Three litres per day required.

R E F E R E N C E S

1. "Biological Oxidation of Phenolic Waste Water", a paper by McRae, A.D., Ross, W.K., and Sheppard, A.A., presented to a Session on Waste Disposal During the 21st mid-year Meeting of the American Petroleum Institute's Division of Refining, in the Sheraton-Mount Royal Hotel, Montreal, Quebec, Canada, May 16, 1956.
2. "Continuous Phenol Recorder", a paper by Fern, G.R.H. presented at the Refinery Technical Conference, Engineering Division, Imperial Oil Limited, Sarnia, Ontario, Canada, November 4-8, 1957.
3. "Automatic Phenol Detector", a paper by Griffiths, F.H., presented at the Refinery Technical Conference, Engineering Division, Imperial Oil Limited, Sarnia, Ontario, Canada, November 3 - 7, 1958.
4. "Phenol Wastes Treated by Coal Adsorption and Oxidation" by G. Gutzeit and G.A. Enyart, Wastes Engineering, September, 1955, Page 443.

FIGURE 1
PHENOLIC WATER DIVERSION SYSTEM

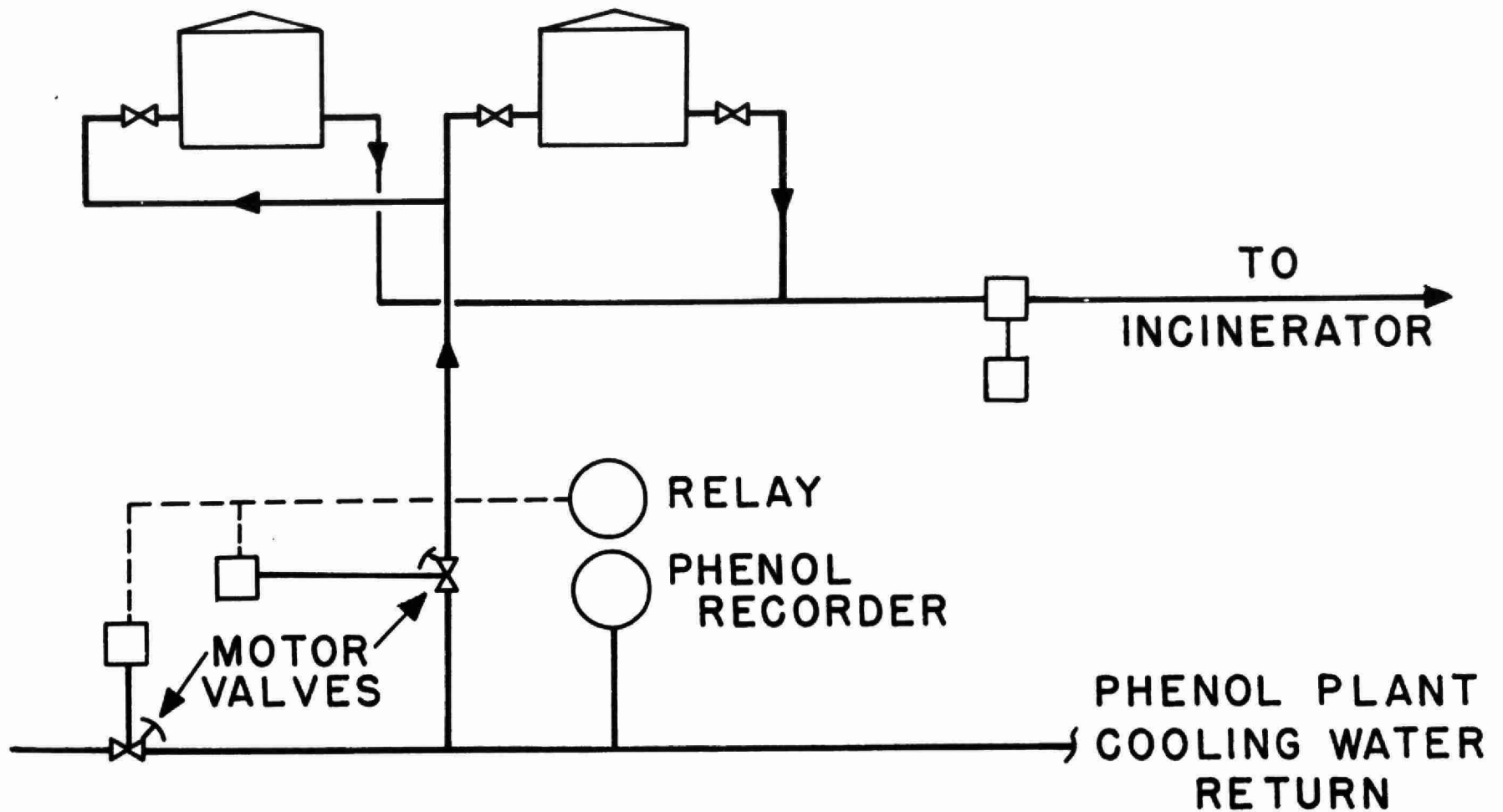
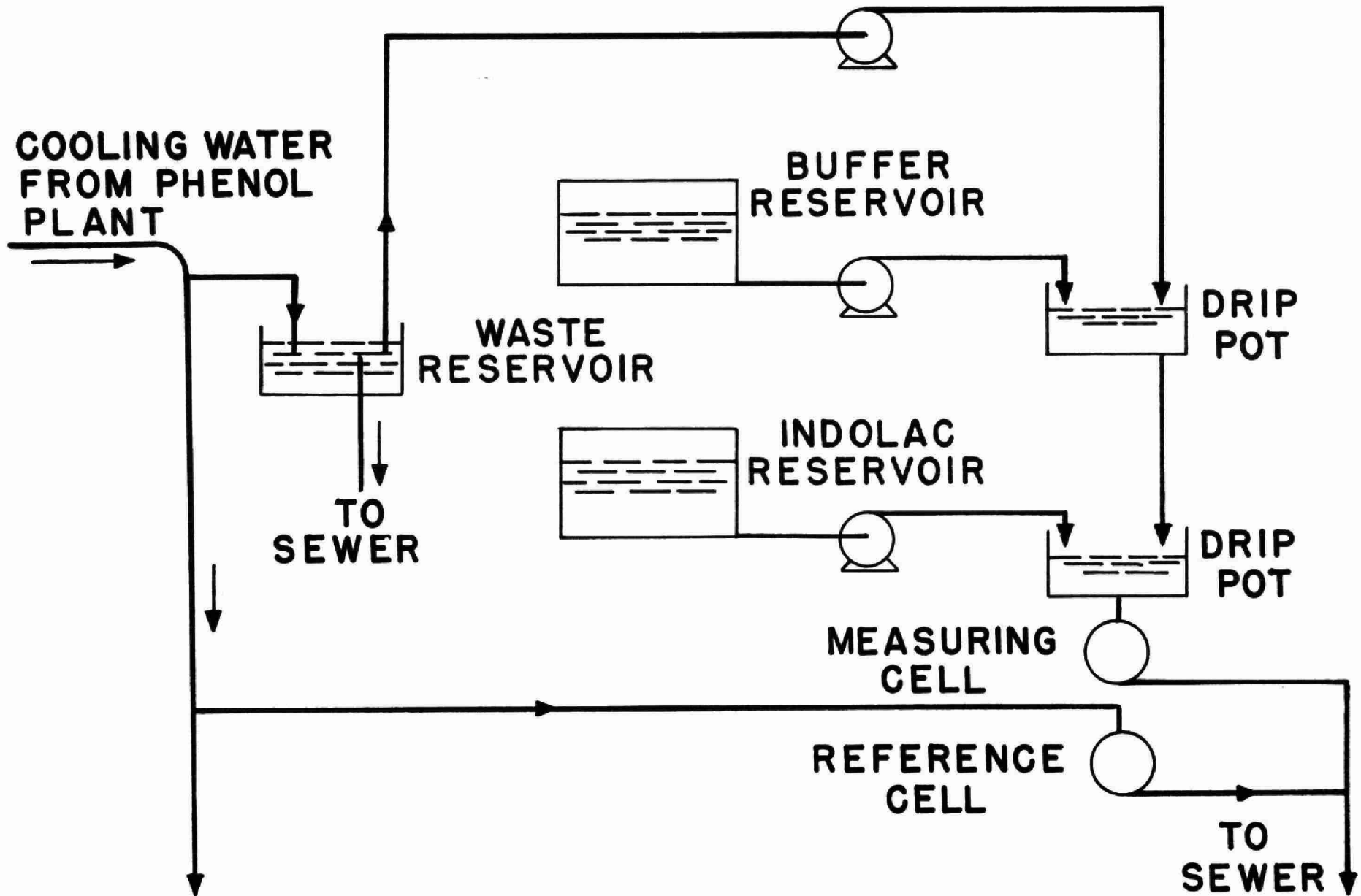
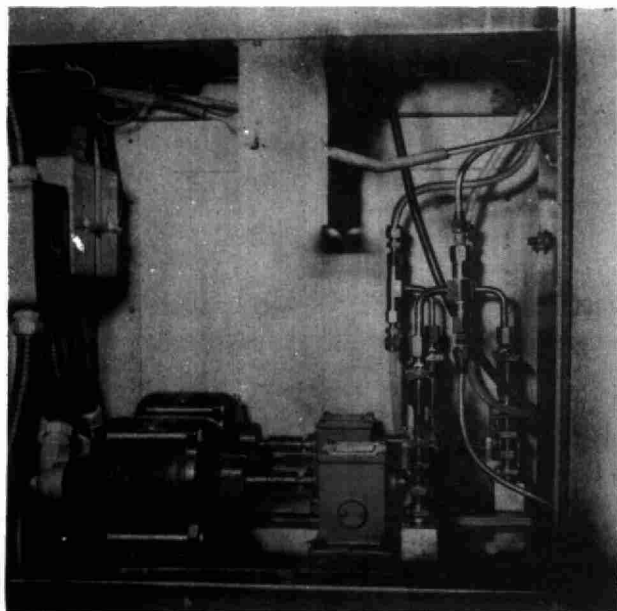
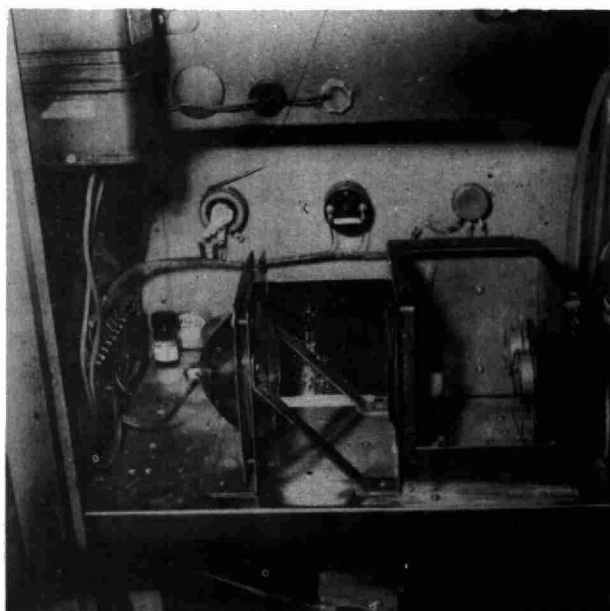


FIGURE 2
PHENOL DETECTOR - FLOW PLAN

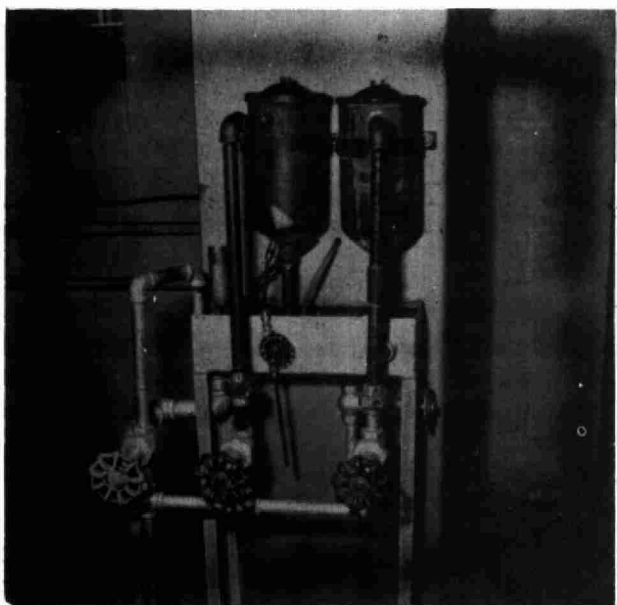




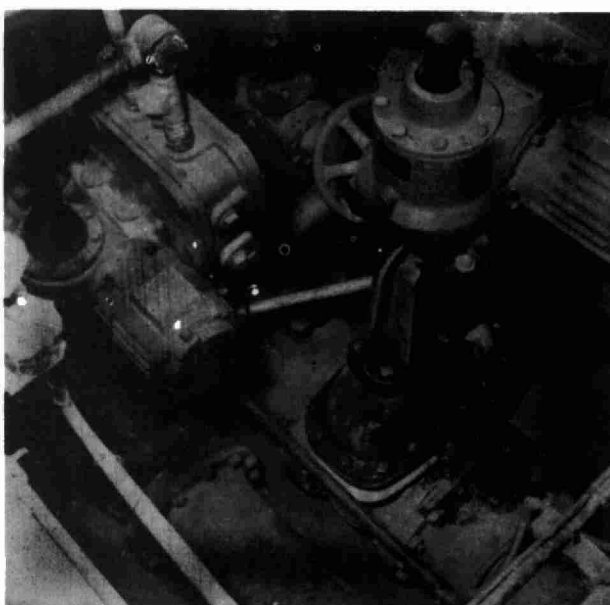
Pumps - front pump circulates the buffer and Indolac, rear pump circulates the sample.



Light source, filters, and glass cells.



Oil filters, put into service as zeolite water softeners



General view of the diversion valve

LIME NEUTRALIZATION OF METAL BEARING ACID WASTESV. S. TADSENDIRECTOR RESEARCH AND DEVELOPMENTTHE GIBSONBURG LIME PRODUCTS COMPANYGIBSONBURG, OHIOU. S. A.

Where recovery acid and acid soluble constituents from certain types of metal processing wastes is impractical from an economic standpoint, lime neutralization of those constituents is often used. Waste treatment of this type constitutes an expense item to be added to the cost of the plant's product. As such, it is important to keep treatment costs minimal. Because lime neutralization is a very broad subject¹, the scope of this paper is limited to reporting experimental work done with freshly slaked dolomitic quicklime^a, and is further limited

^aA typical analysis of the quicklime used in this work is:

SiO ₂	0.32%	CaO	57.37
Fe ₂ O ₃	0.08	MgO	41.37
Al ₂ O ₃	0.25	SO ₃	0.08

L.O.1. 0.52

This quicklime has a high slaking rate. Its calculated equivalent weight is 24.3 as compared with 28 for pure CaO.

to three phases of lime neutralization directly associated with the design for and cost of acid waste treatment, namely:

- 1) The effect of quicklime slaking procedures on reaction rates.
- 2) The effect of mixing rates on reaction rates.
- 3) The effect of mixing rates on sludge settling rates and volumes.

Dolomitic quicklime is composed of calcium and magnesium oxide in equimolar ratio associated with varying amounts of impurities and must be slaked before using for waste neutralization. Lime hydrate thus formed is only slightly soluble² in water and to obtain practical concentration is supplied to a treatment process as a slurry. We are dealing, then, with solid-liquid interfacial reactions. These reactions may be complicated in practice by the formation of reaction products on the surface of the lime crystallites.

The reaction rate of dolomitic lime with acids^b is slow as compared with high calcium limes or caustic soda.

^bFor simplicity, any substance having a hydroxyl ion demand will be called an acid.

This slower reaction, under certain conditions, may be advantageous as we shall discuss later.

Theoretically, to increase the reaction rate of dolomitic lime slurries with acids the simplest expedient would be to increase the specific surface of the lime hydrate.³ This could best be done by controlling slaking conditions. Figure 1 shows the effect of slaking temperature on the plus 200 mesh residue of 10% dolomitic lime slurries. The plus 200 mesh residue is related to the average particle size in the slurry. This has been confirmed by sedimentation procedures and microscopic particle count. Slaking residue is a simple index that can be used to determine slaking conditions^c that will produce a lime hydrate of high surface area.

^cThe procedure used was to add 10% by weight of minus 20 mesh quicklime to water at the selected temperature contained in a modified Dewar type flask equipped with a mechanical stirrer, stirring for 20 minutes, then purging the slurry on a 200 mesh (74 micron) testing sieve, washing the residue on the sieve for 10 minutes with a water spray, drying and weighing the residue. Percent residue is based on the original weight of quicklime.

The slaking conditions, including temperature, concentration, rate of agitation, and time, that result in a minimum residue should produce a lime hydrate slurry having the highest surface area, and therefore, reaction rates.

To confirm this lime slurries prepared at different temperatures, all other slaking conditions being held constant, were reacted with 0.46% sulfuric acid (0.094 equivalents per liter) under constant conditions^d.

^dThe acid solution was prepared and placed in the mixing tank, the impeller positioned, and its speed set at 100 r.p.m. Meanwhile, the theoretical amount of lime plus 10% was added to ten times its weight of water at the selected temperature. The slaking apparatus described earlier was used. After slaking for 20 minutes the entire mass was poured into the acid solution. The pH of the mixture was observed continuously using a Beckman Model H-2 meter equipped with an alkali resistant glass electrode and a calomel reference cell.

Figure 2 shows the effect of lime slaking temperature on the reaction rate of dolomitic lime slurry with 0.46% sulfuric acid. Sulfuric acid was used in these tests because of its preponderant industrial usage. Observe the reaction rate increases rapidly with increasing

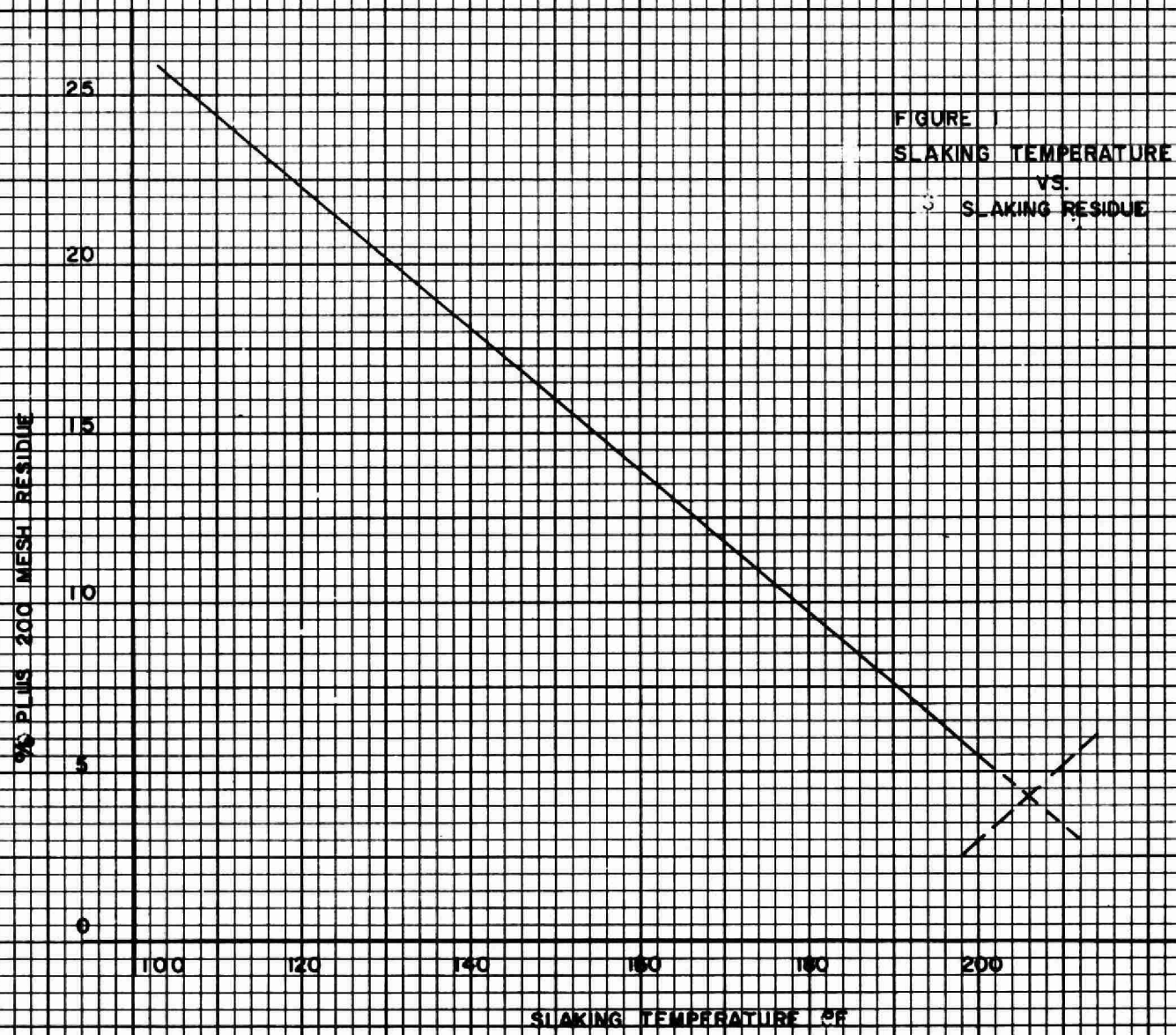
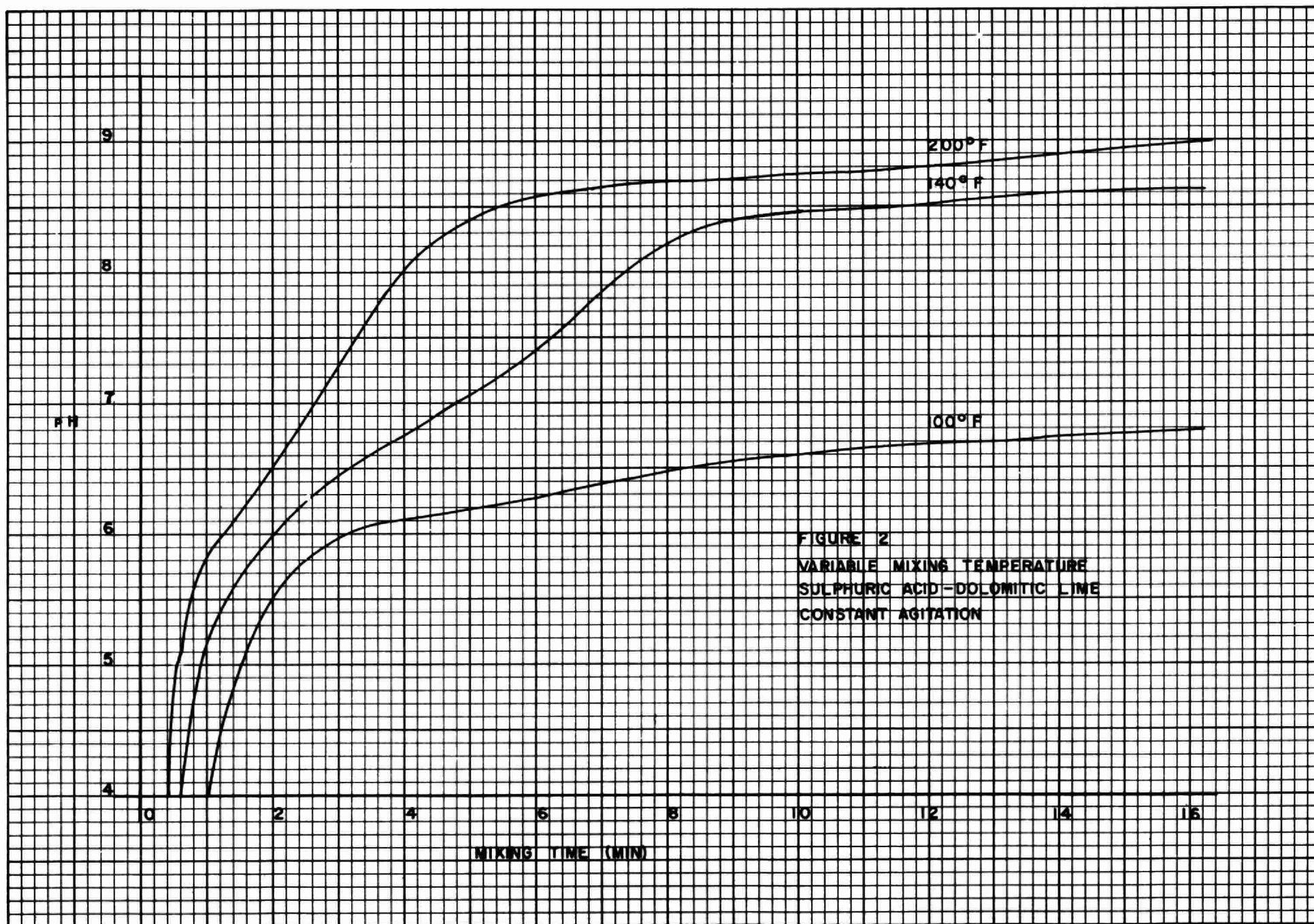


FIGURE 1
 SLAKING TEMPERATURE
 VS.
 SLAKING RESIDUE



slaking temperature. Slaking at the higher temperatures converts substantially all of the magnesium oxide to the more soluble magnesium hydroxide. Deamore and Machin⁴ have shown the crystallites of magnesium hydroxide are small as compared with those of calcium hydroxide. This results in a larger specific surface and offsets the very low solubility ² (0.01 g/l) of magnesium hydroxide to a large degree. The presence of sulfate ion, and the resulting formation of slightly soluble calcium sulfate on the surface of the lime particles has a retardant effect on the reaction.

This series was run at a constant lime-acid ratio and it is quite apparent the ratio could be reduced when using optimum slaking conditions, thus leading to reduced lime consumption and other less obvious operational economies.

The second phase of this study was to determine the effect of agitation or mixing speeds on lime-acid reactions. Theoretically, increased turbulence in the mixing tank should result in higher reaction rates between the slightly soluble solid phase lime and the liquid phase acid. This thought is further enhanced by the possibility of increased liquid shear tending to disrupt the formation of reaction products on the surface of the lime particles. High turbulence is contrary to the design of many waste treatment plants which largely follow the old low velocity flow principles for potable water treatment.

To study the effects of agitation on reaction rates and floc formation a standard turbine impeller⁵ and mixing tank design was used. It consisted of a 4 inch diameter, four flat blade turbine impeller operating on the central axis of a 11.5 inch diameter by 16 inch high cylindrical mixing tank with four one inch wall baffles installed at 90° to each other. The turbine was operated at a distance of 4 inches from the bottom of the mixing tank and driven by a variable speed drive. Rushton⁵, Mahony⁶, Oldshue⁷, and Sachs⁸ have studied the flow pattern of such mixing devices extensively. Such a device is capable of being upsized accurately. All subsequent neutralization runs were made on 16 liters of solution having a total hydroxyl ion demand of 1.5 equivalents.

The first series was to determine the effect of mixing speeds on the neutralization rate of sulfuric acid by dolomitic lime slurry prepared by slaking at 180°F. This slaking temperature was used throughout the following work because early in this series it was found that slightly erratic results were obtained from slurries prepared at higher temperatures, probably due to boiling during slaking adversely affecting the particle size of the lime hydrate. Figure 3 shows the results of three neutralization runs using impeller speeds of 100 rpm, 150 rpm, and 300 rpm. Observe the curves more upward and to the left, and the terminal pH raises significantly with increasing mixing speed. At the higher mixing speeds a substantial reduction could be made in the quantity of lime required to obtain a satisfactory terminal pH. It should be pointed out that the magnesium hydroxide portion of the lime is reacting quite rapidly and completely under these conditions. This is in opposition to much published literature.

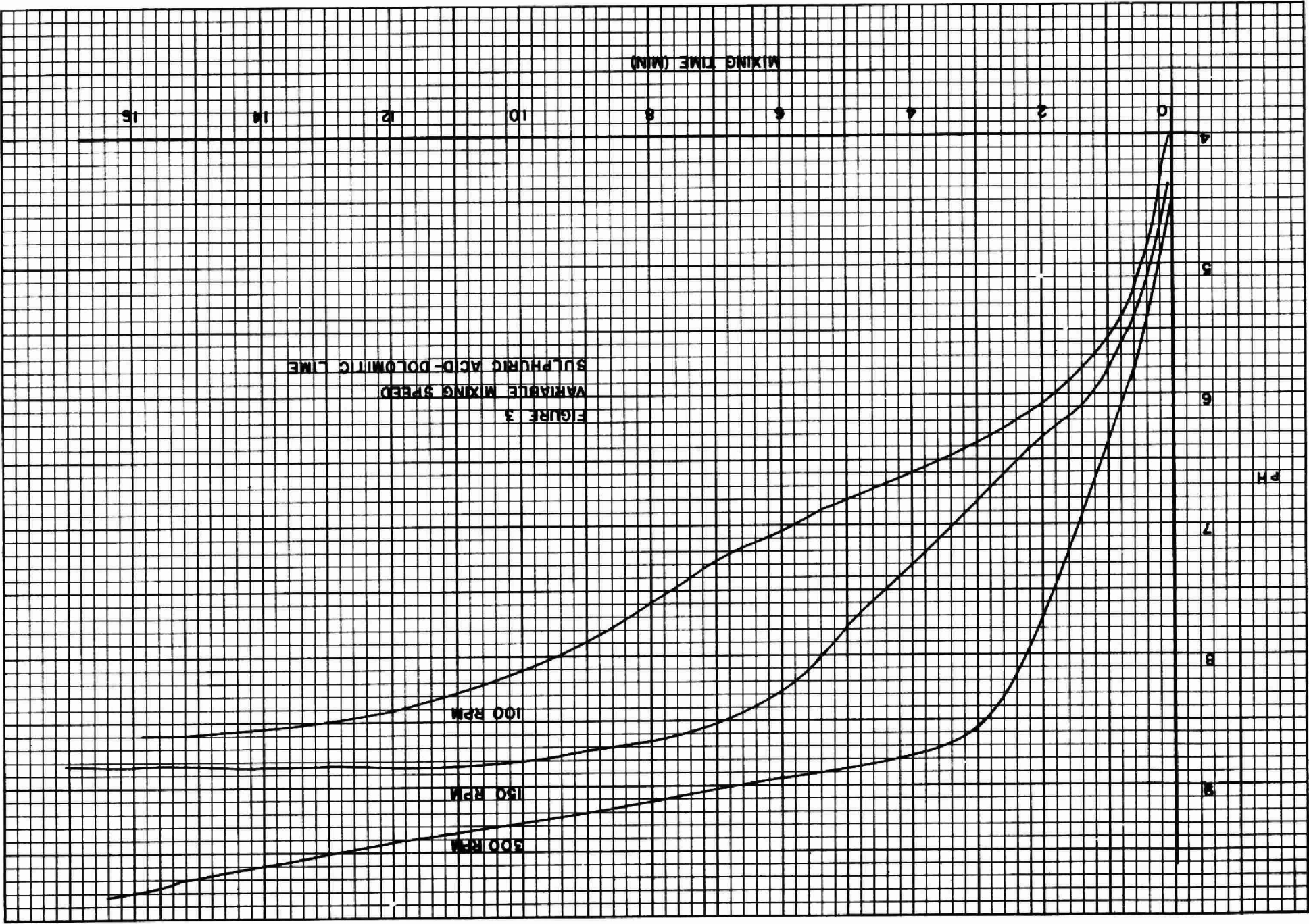
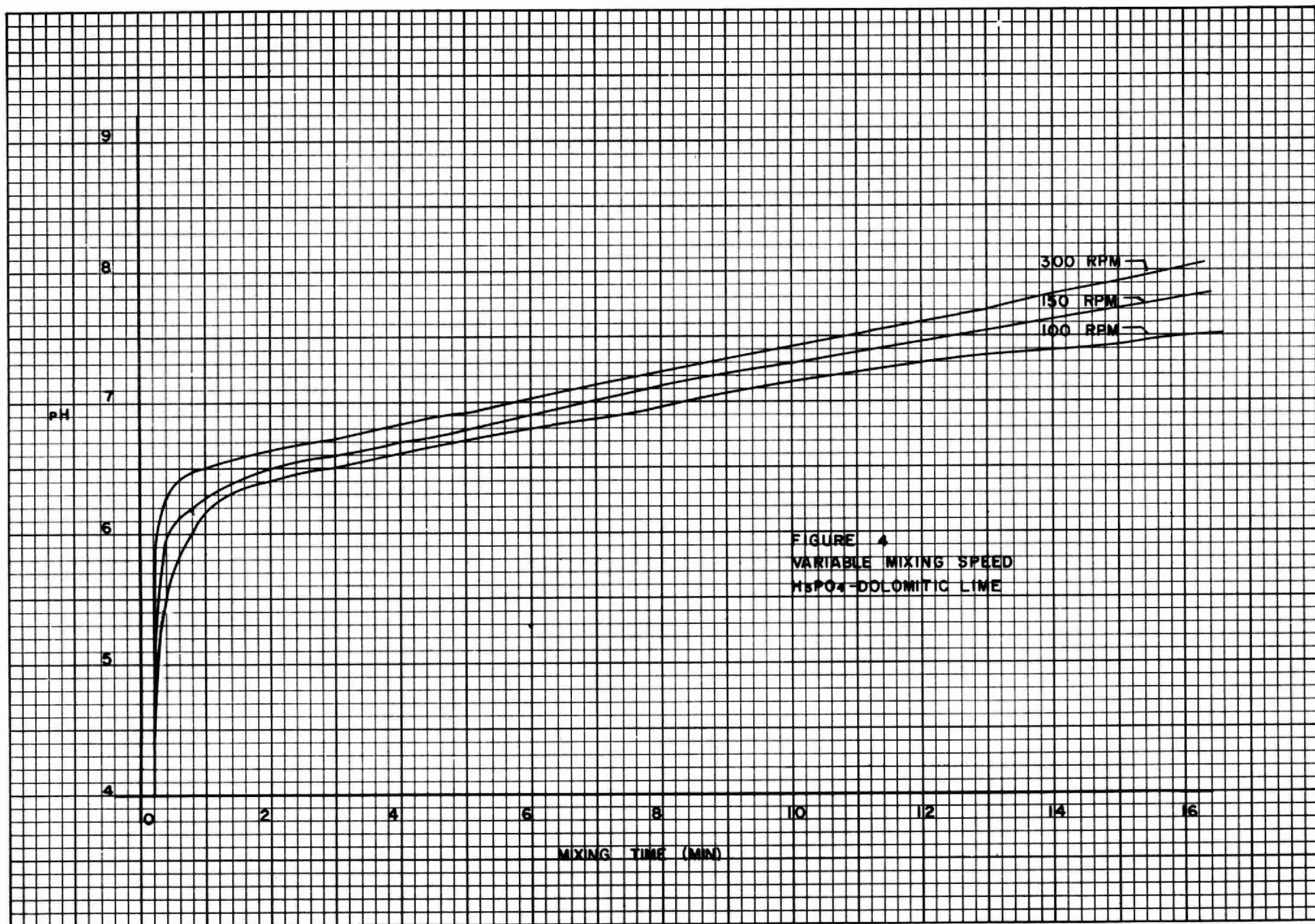


FIGURE 3
VARIABLE MIXING SPEED
SULPHURIC ACID-DOLOMITIC LIME



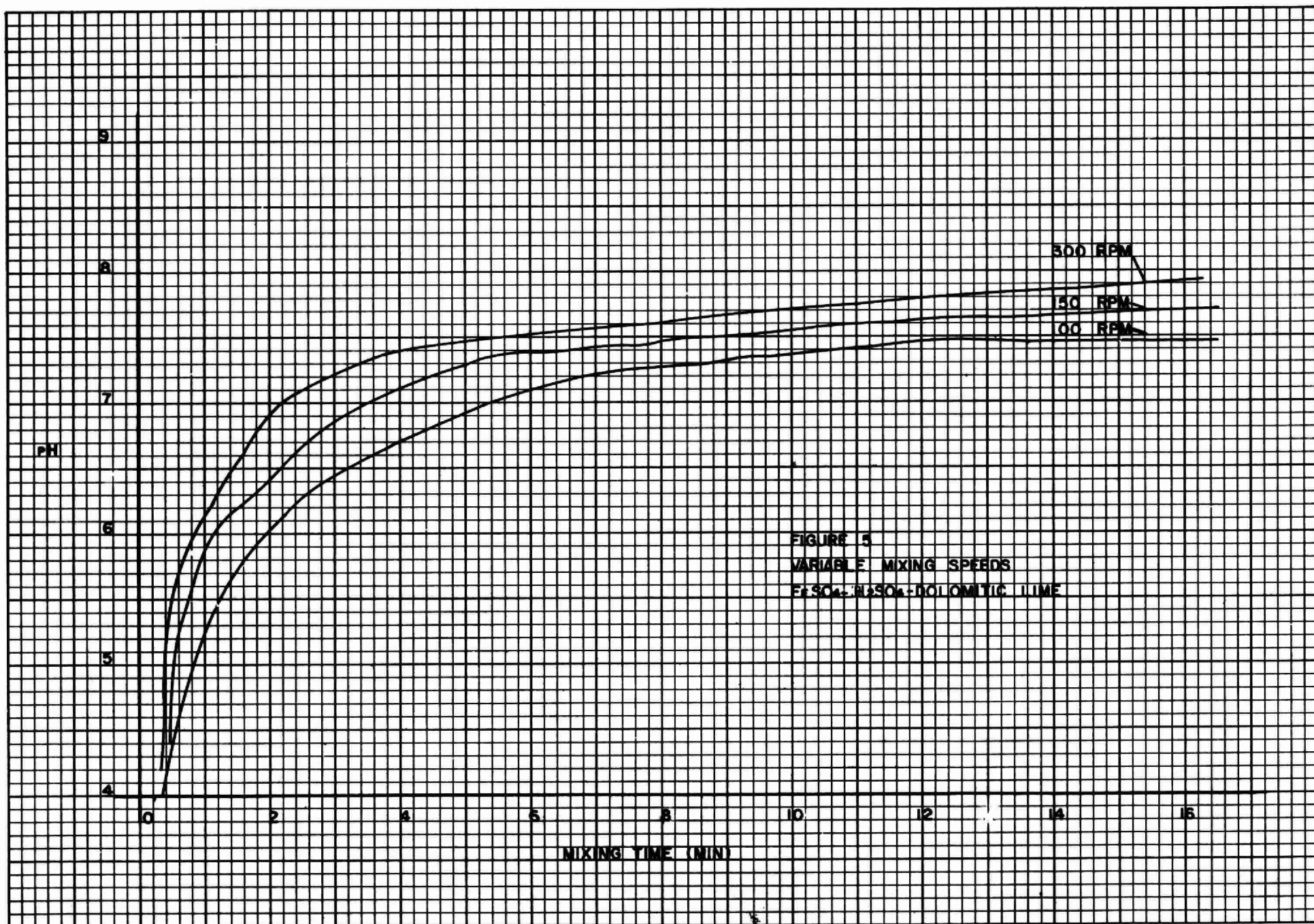
The formation of calcium sulfate exhibits a small retardant influence on the reaction at higher impeller speeds while the other major reaction product, magnesium sulfate, is completely soluble and has no retardant effect. The degree of ionization of the second hydrogen ion of the sulfuric acid has an observable influence. A study of the reactions of the hydrochloric acid with dolomitic lime confirmed these thoughts.

The second series studied the influence of mixing speeds on the reaction of dolomitic lime slurry with phosphoric acid. This was thought important because of the extensive use of phosphates for pre-painting treatment of many metals and for rust inhibiting treatment of steels. The results of this series are shown in Figure 4. Observe that mixing speeds, in the range used, have little influence on the reaction rate or the terminal pH. The formation of flocculant reaction products has some influence, but the major influence is the low degree of ionization of the second and third hydrogen ion, and the resultant small driving force existant between this and the magnesium hydroxide. The curves rise steeply in the first half minute because the lime concentration is 230% in excess for the first stage of ionization of the phosphoric acid. The curves then break sharply to the right under the influence of the second stage of ionization.

In the balance of this series studying the influence of mixing rates on neutralization rate and the physical interference of reaction products, 0.75 equivalents of various metal sulfates or acids were mixed with 0.75 equivalents of sulfuric acid, thus the total hydroxyl ion demand is 1.5 equivalents for each mixture.

Figure 5 represents typical reaction rate curves for a ferrous sulfate-sulfuric acid mixture. The reaction rate is increased and the terminal pH is raised with increasing impeller speeds. Ferrous hydroxide forms a very tenacious floc and traps lime readily. The hydroxyl ion demand of ferrous ion reaches its maximum at pH 6 and the curves break over at this point. The driving force for this latter reaction is small and it is probable that much higher turbulence is required to break the floc film and promote higher reaction rates. Investigation of this is being continued.

Figure 6 shows the effect of substituting chromic acid for a portion of the ferrous sulfate. At the initial pH of the solution chromic acid oxidizes the ferrous iron to ferric, and the plus 6 chromium content is reduced to chromic. Plus 6 chromium can not be precipitated by direct neutralization whereas chromic ions form a very insoluble hydroxide. The reduction of plus 6 chromium by ferrous sulfate in acid solution and consequent precipitation is a common method of removing chromium from acid wastes. The curves again move upward and to the left with increasing turbulence. This reaction is influenced by the pH at which chromic and ferric ions have their maximum hydroxyl ion demand. Ferric ion has a maximum hydroxyl ion demand at pH 3.4 and chromic ion at pH 5.8. The hydroxyl ion demand of this reaction mixture is very high in the low pH range and the early floc formation retards the solution



MIXING TIME (MIN) 0 2 4 6 8 10 12 14 16

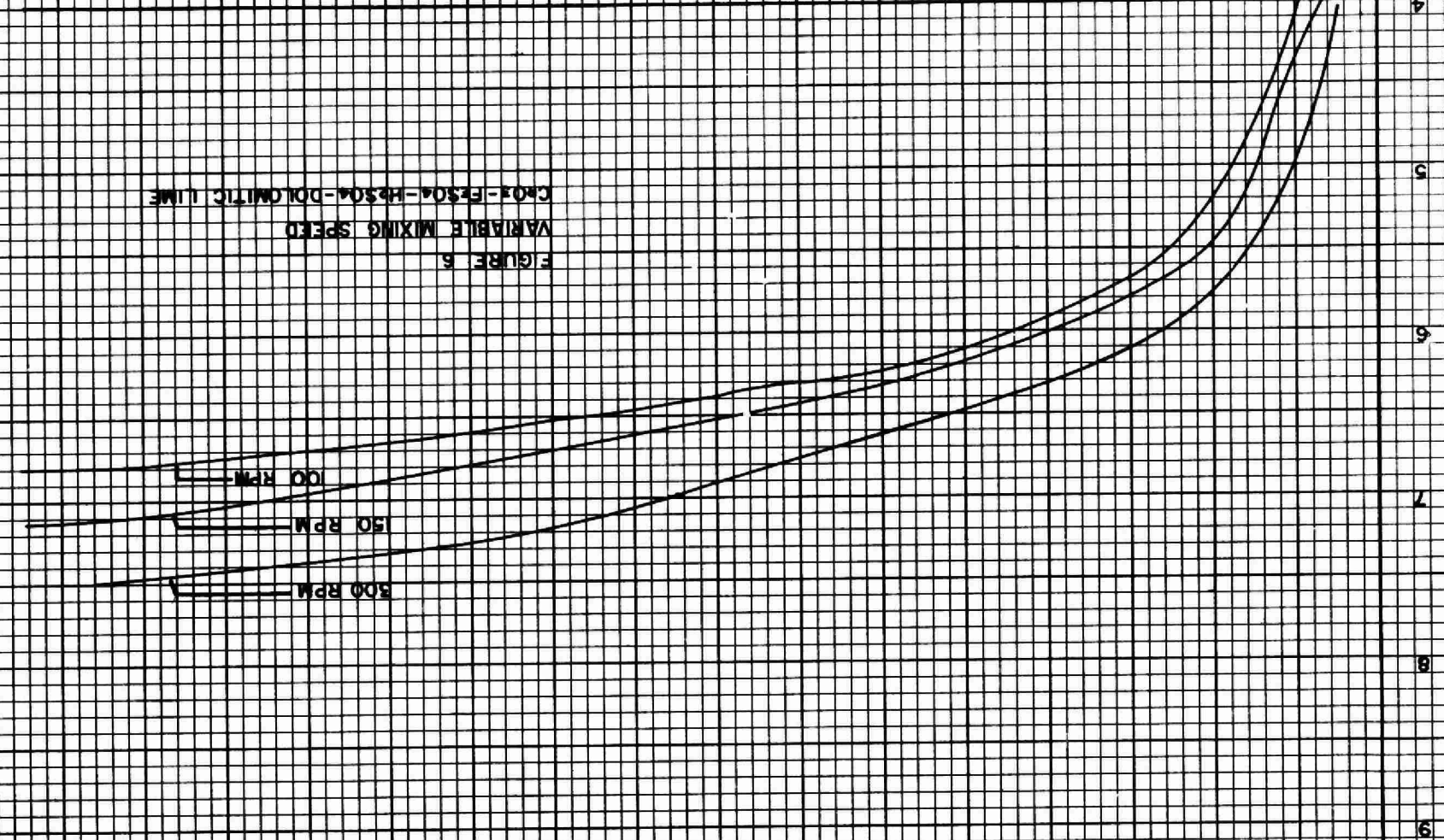


FIGURE 6
VARIABLE MIXING SPEED
CO₂-ES₂O-H₂SO₄-DOLOMITIC LIME

100 RPM
150 RPM
500 RPM

pH

of lime. Referring to the curves, we notice the pH is still rising after 16 minutes of mixing. Laboratory work showed that prolonged agitation of this mixture, as well as most others in the series, would produce a terminal pH between 9 and 9.4.

It would be well to compare Figure 6, a reaction having a high hydroxyl ion demand in the low pH range, with Figure 7, representing the nickel sulfate-sulfuric acid-lime reaction which has a hydroxyl ion demand in the high pH range. This latter figure would appear to show a very high reaction rate, with little difference due to mixing speeds. This reaction mixture initially contained 0.75 equivalents each of nickel sulfate and sulfuric acid plus 1.65 equivalents of lime. The hydroxyl ion demand for forming nickel hydroxide is reached at pH 8.1. During the very early stages of neutralization there is a lime excess of 120% reacting with the acid only. When a pH of 8 is attained the curves break sharply with the formation of nickel hydroxide demanding hydroxyl ions as rapidly as the remaining lime, mostly magnesium hydroxide, will give them up. The driving force for this reaction is very small and considerable time is required to complete the precipitation of nickel hydroxide. Knowledge of these hydroxyl ion demand levels is most essential to design effective and economical automatic pH controlled systems for industrial waste treatment. If sampling points are placed wrongly or retention times are too short, much lime could be wasted or a poor quality effluent obtained.

The reaction of copper sulfate-sulfuric acid and dolomitic lime is the most interesting of those studied. Cupric ion has its maximum hydroxyl ion demand at pH 5.4. The hydroxide gel is very tenacious and is an excellent clarifier. Interpreting the reaction curves in Figure 8, we find at the lowest turbulence the sulfuric acid is neutralized and copper hydroxide is formed. The hydroxide then flocs and traps the unreacted lime, holding the pH of the mixture constant. Note the time scale and mixing speeds are different from all previous figures. At 250 rpm impeller speed, changes take place in the floc with increased turbulence causing a lime release and a rise in pH after 35 minutes of mixing. At 300 rpm this floc change takes place much sooner and the pH rises rapidly to near the equilibrium point of pH 9 within 30 minutes. It is probable that higher turbulence would be beneficial to this reaction. This is being investigated. Further, it would be of fundamental interest to determine what changes take place in the copper hydroxide floc that would account for the observed behavior.

Some of the behavior of flocs and sludges can be interpreted by microscopy. The physical density of a floc can be determined qualitatively by its optical and physical density will be. Higher density leads to better settling rates and improved sludge compaction.

Figure 9 is a photomicrograph (50 μ = 1 inch) of a well formed ferrous hydroxide-calcium sulfate floc four hours old. The density of this floc makes it quite easy to study optically.

The solids content is about 5%. Figure 10 is the same floc photographed with polarized light. This shows well developed acicular calcium sulfate crystals. The work of Faust and Orford⁹

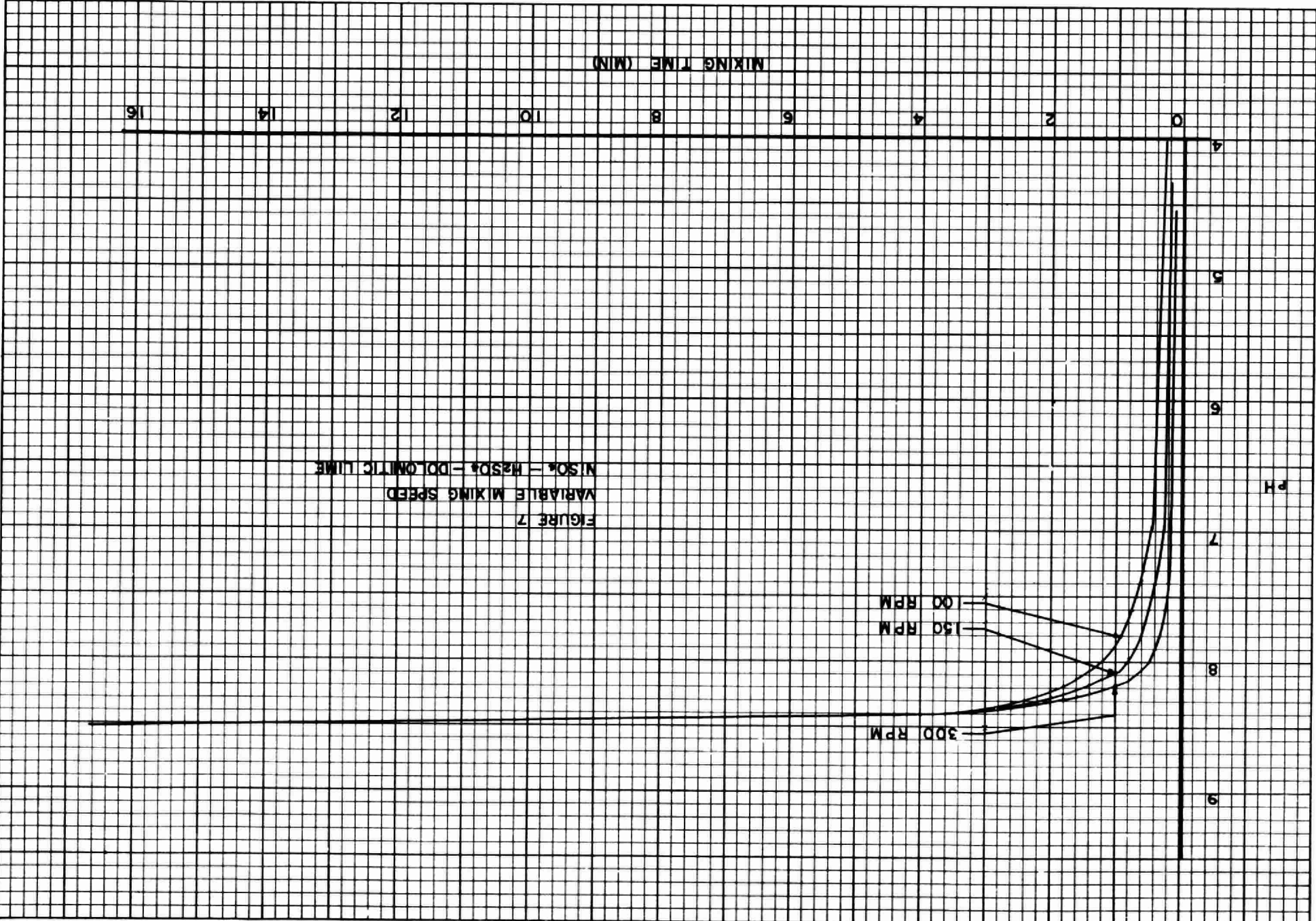
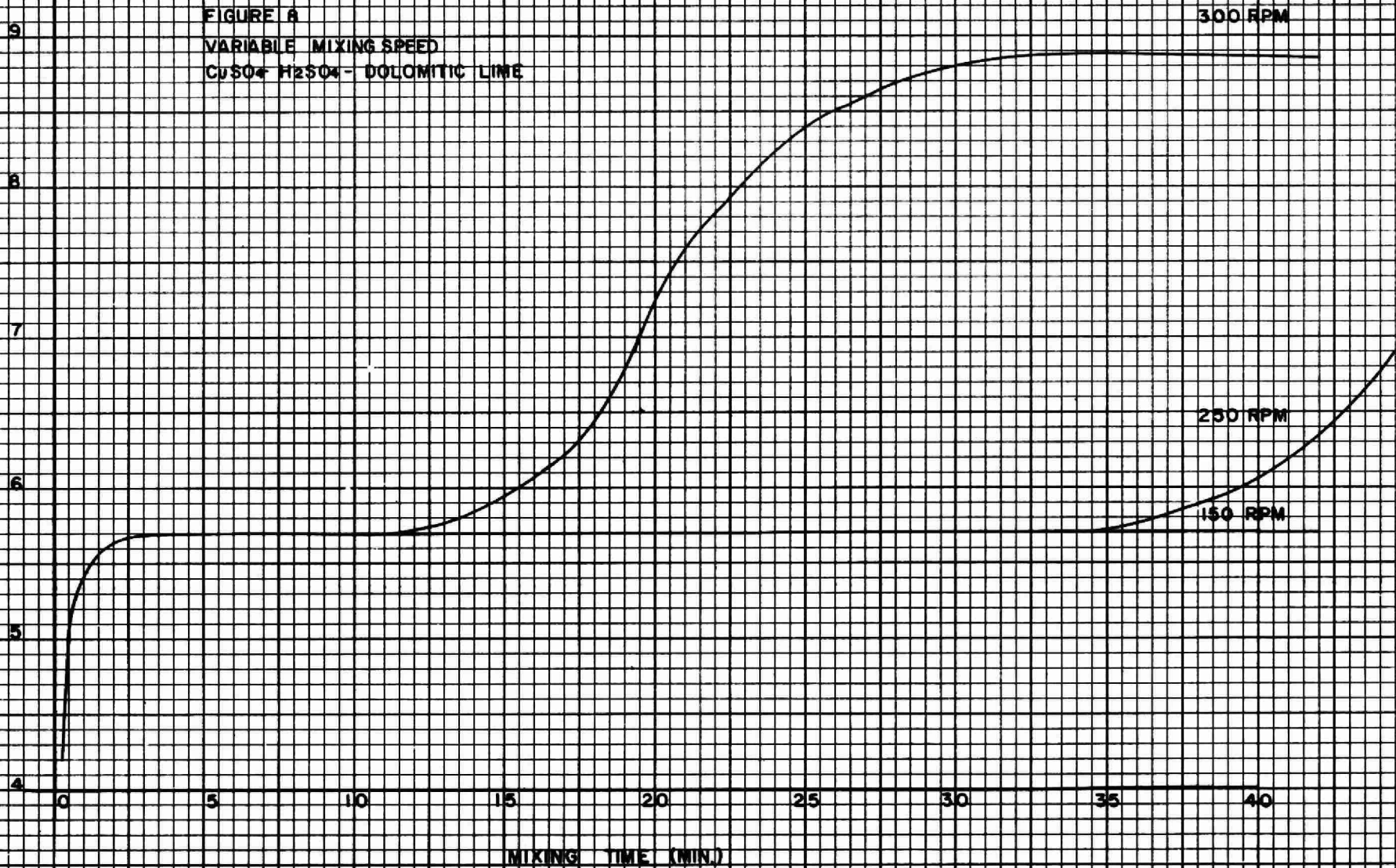


FIGURE 7
VARIABLE MIXING SPEED
NISO₄ - H₂SO₄ - DOLOMITIC LIME

FIGURE 8
VARIABLE MIXING SPEED
CuSO₄ - H₂SO₄ - DOLOMITIC LIME



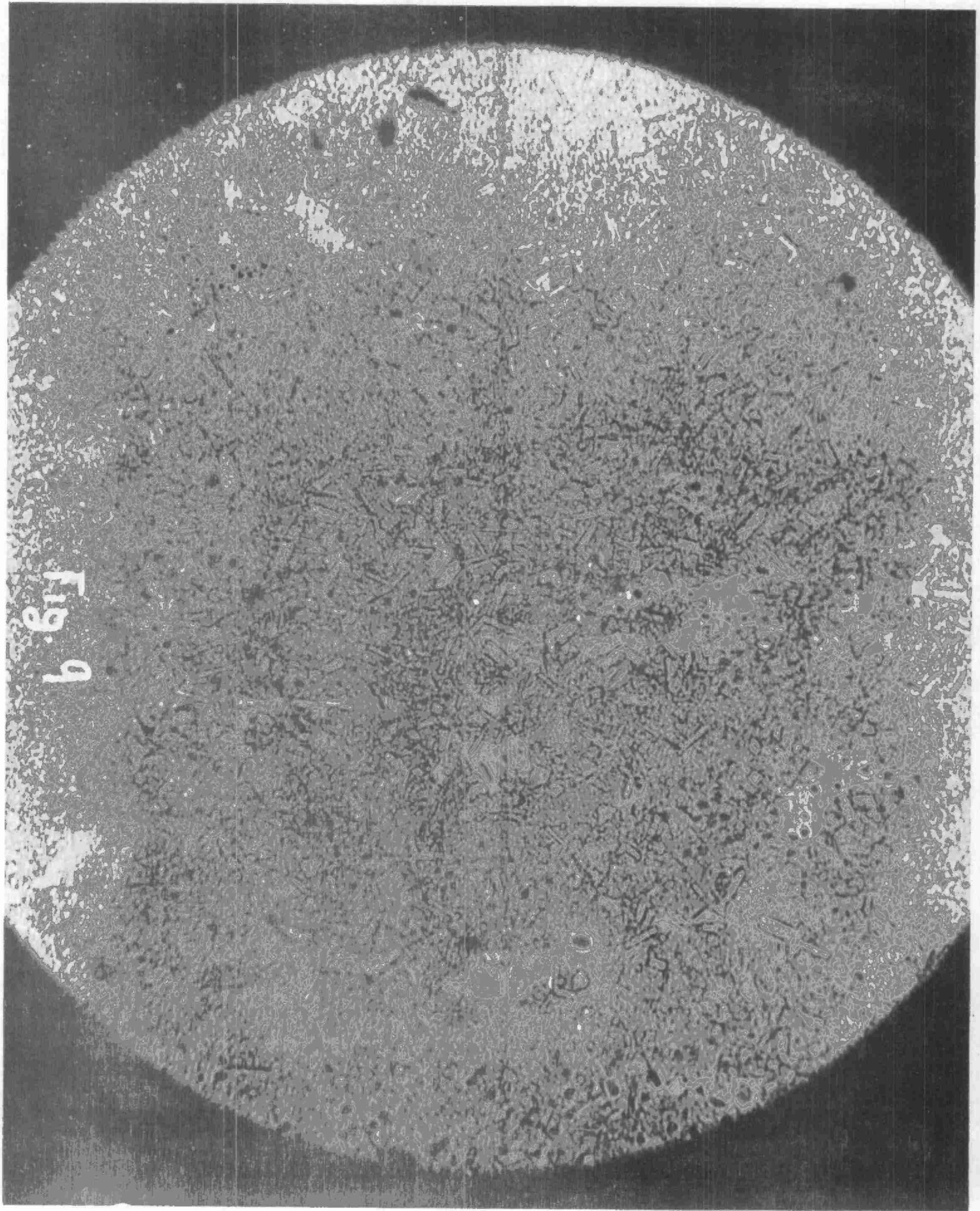
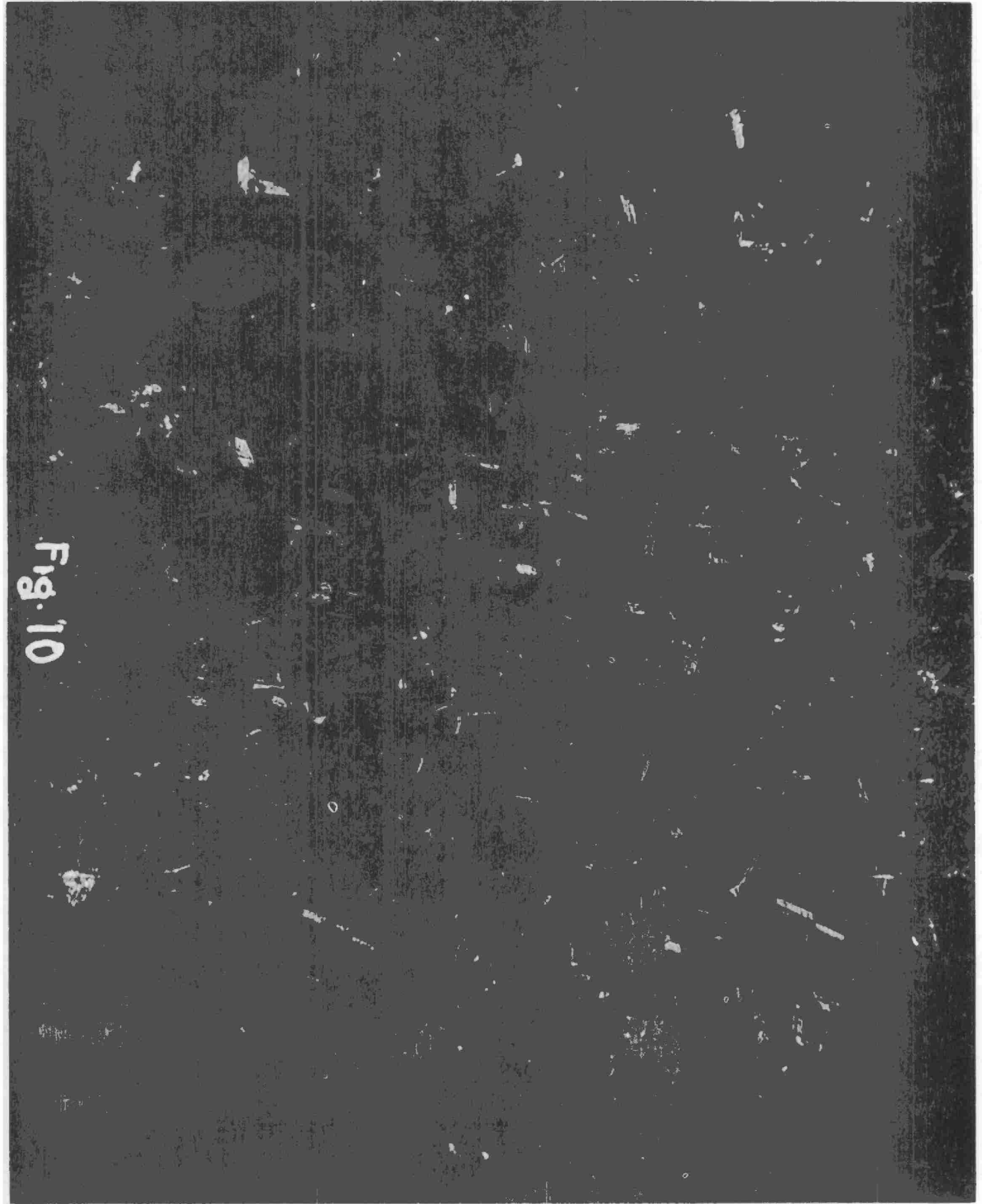


Fig. 9

Fig. 10



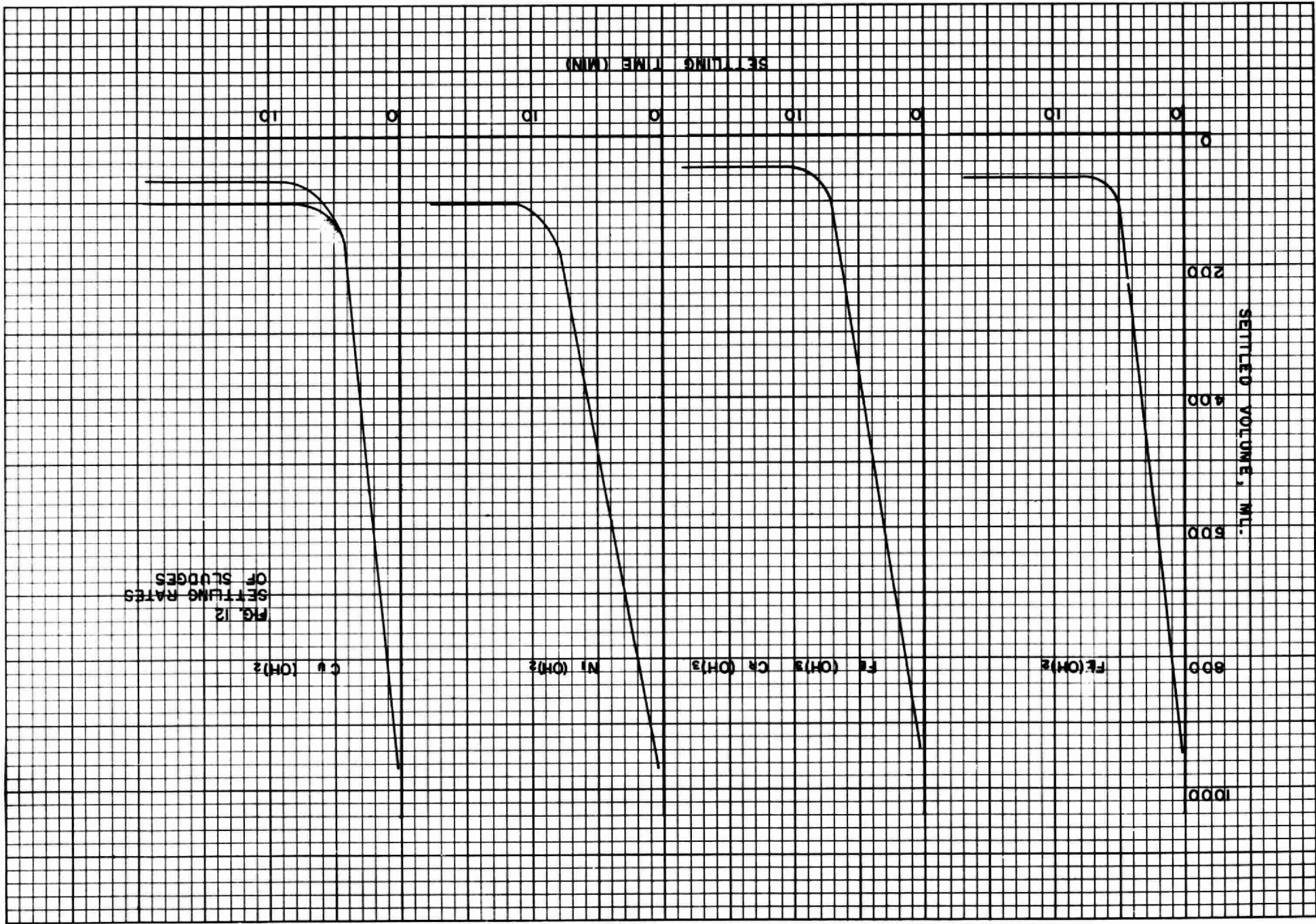
has shown when sulfuric acid is neutralized with lime, this acicular crystal form of calcium sulfate does not have the most desirable settling characteristics. Seeding with sludge improves the settling characteristics by producing larger acicular crystals, but seeding with native gypsum produces a rosette crystal form having a high bulk density. This results in high settling rates and greatly reduced sludge volumes. Crystal seeding is less effective when a hydrous metal floc is included in the system, but should be given careful study in all cases where sludge volume, settleability, or filterability are important. The physical trapping of any high density material, i.e., crystals formed in the reaction, foreign material brought in with the waste, or even excess lime, will improve settling rates and compaction. The floc in Figure 10 is considered well formed because it shows minor optical properties when only four hours old.

The rate of formation of hydrous metal floc has a great influence on its physical characteristics. Figure 11 shows electron micrographs of ferric hydroxide floc at 140,000 diameters (35,000 x e plus 4x optical). The floc at the right was formed rapidly and shows the fibrous pattern of a gel. This is similar to a metal floc formed by rapid precipitation with caustic soda, soda ash, or a highly reactive high calcium lime. The floc in the micrograph on the left shows the beginnings of crystallinity. This floc was formed over a four hour period by the addition of lime water to ferric chloride with vigorous agitation. Sub-crystalline floc, as on the left, hold less water, is more dense and has good settling characteristics. In this respect, the slower reaction rates of dolomitic lime may be advantageous.

The third phase of this study was to determine the effect of agitation rates on floc settling rates and sludge volumes. Increased turbulence does increase the reaction rate of dolomitic lime with acids. If this increased turbulence would result in major changes in floc character that would increase settling times beyond practical limits, then the previous studies would be of little value in waste treatment.

Samples of sludges were prepared by repeating the mixing rate procedures described previously. Thirty minutes after the lime slurry was added to the acid a 1000 ml. sample was siphoned from the mixing tank at the plane of the impeller into a graduated cylinder during sampling. This was a good indication that the floc was not damaged by the higher mixing turbulence. To improve the reliability of the settling rate data, the siphoned sample was agitated severely immediately prior to the start of readings. Samples must be at ambient temperature to prevent thermals being set up in the graduate and disturbing the floc meniscus. Figure 12 plots settled volume against time for the various mixtures. Except for copper hydroxide, the settling rate curves for each mixture were nearly identical for all mixing speeds. The copper hydroxide curves show a reduction in settled volume with increased mixing speed. This confirms the thought that a major change takes place in this floc that is a function of time and mixing turbulence. In all cases the settled sludge volume is low because only one half of the sulfate ion has been precipitated as calcium sulfate, the balance remaining in solution as magnesium sulfate, and the flocs have high densities.

Fig. 11



From the curves in Figure 12 we must conclude high mixing turbulence in the range of these studies does not destroy hydrous metal flocs as formed by reactions with dolomitic lime slurries. Copper hydroxide floc is definitely improved by high turbulence. Observations show the various flocs reform or gather extremely rapidly after agitation is stopped. This high agitation principle is an innovation in waste treatment plant design.

Future work includes studies of higher agitation rates and their attendant effects, seeding the various mixtures, and, copper hydroxide behavior during mixing.

In summary, we have shown

- 1) Optimum slaking conditions for a dolomitic quick-lime will produce a highly reactive lime hydrate,
- 2) The reaction rate of dolomitic lime hydrate with acids, or metal bearing acid wastes, can be raised by increased turbulence in the mixing tank, and
- 3) The increased mixing turbulence has no detrimental effect on the settling characteristics of the hydrous metal flocs studied.

ACKNOWLEDGEMENT

This work was suggested by Mr. C.C. Cupps of the Rockwell-Standard Corporation who has applied these principles to plant practise and has largely confirmed these experimental findings.

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HOUSEHOLD DETERGENTS IN WATER AND SEWAGE

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Former Director
Laboratories and
Research
Ontario Water
Resources Commission

Chairman
Session No. 3



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I am happy to be here today to discuss the role of household detergents in water and sewage, and to tell you something of the research program being carried out in the U.S. by the Soap Association on this matter. As some of you may know, this activity has been underway now for some five to six years. During this time many of us in the detergent industry have had an opportunity to observe and better comprehend the problems faced by those in the water and wastes treatment field, and while we still are a long way from being skilled sanitary engineers, I think we have at least some grasp of the scope of the problems you people face. We hope that our efforts on just one of these many problems -- the detergent question -- will be helpful in pointing the way towards the solving of others.

I believe a word on exactly why I am here might be in order. Mr. Fred A. Voegel of the Ontario Water Resources Commission first approached Procter & Gamble of Canada Ltd., with the thought that because of the increasing use of synthetic detergents, and the resultant claims about increased foaming and phosphate discharges, it would prove of interest to get the manufacturers' viewpoint on the question. At P&G's suggestion, he contacted the U.S. Soap Association, which has sponsored over a quarter of a million dollars in research on this question, and requested a speaker. I am here today in response to that request.

I made a visit to the Ontario Water Resources Commission's new laboratories about a month ago, at which time I had a most interesting meeting with Mr. Voegel and Mr. Duncan. They told me that the problems in Canada which are believed to be related to synthetic detergents really boil down to two areas -- foaming in sewage treatment plants and increased algae growth. Where possible I shall try to relate U.S. experience to these problems. At the same time, you may also be interested in some first-hand information on the research projects which are related to other aspects of the detergent question, and I shall plan to touch on these as well. Before getting into these aspects, however, at Mr. Voegel's suggestion I should like to spend a little time discussing the chemical makeup of synthetic detergents, since this is a specialized and somewhat complicated field and the terms which are used are frequently confusing.

DETERGENT DEFINITIONS

By definition, a detergent is anything that cleanses. As such, ordinary soaps, the new "synthetic" detergents, plain water, even sand when used for scrubbing, can all be classified as detergents. What really interests us, however, are the synthetic detergents which have become so popular since World War II, and how these relatively new materials compare with the soap products which the housewife has used for years. The following simplified comparison between the two types of product may help to point up the similarities between the two, and make them both more understandable.

In Figure 1, which shows a representation of the two major types of packaged household washing products which the housewife might purchase, both the "synthetic" and the "soap" products are labelled as "detergents". Definite points of similarity exist between the two, in that the large proportion of each contains a surface active agent and a phosphate builder. The surface active agents, or surfactants as they are also called, differ between the two, as does the exact chemical identity of the phosphates. Also, the amounts or percents of each are obviously different. Nevertheless, in the broad sense they both contain the same basic types of materials which, when properly formulated, combine to get out the dirt.

Now, this next concept is important to understand, because a misunderstanding frequently leads to misleading reporting of results. After a packaged product, either soap or synthetic detergent, is used for laundering, and released down the drain, it loses its individual brand identity, and must be considered on the basis of the individual components - i.e., the "surfactant" portion and the "builder" portion. Different manufacturers market different formulations in terms of percent of individual components, but the chemical nature of the components themselves may be the same. Thus, once in water or sewage, only the components can be considered.

This is logical from the viewpoint of practical effect, too. For example, as will be brought out later, it is the surfactant portion of synthetic detergents which has been associated with frothing, not the phosphate builder portion. And the phosphates have been associated with algae growth, not the surfactants. Thus, they should always be considered separately.

In line with this, it is important that the components be named correctly, and I would like to go on with the comparison of the packaged soap and synthetic detergents in order to make certain the terminology is completely understood.

The surfactant portion of either product is an organic agent which at laundering concentration lowers surface tension and penetrates between the soil particles and the cloth, thus helping to remove the soil when the fabric is agitated in the washing machine. It also is the material which makes the "suds".

In the soap detergent the surfactant portion is called by the same name - "soap", a name applied to it for many centuries before

chemists finally identified its specific chemical structure. To be technical, it is the sodium or potassium salt of a fatty acid derived from a natural fat or oil. In the soap detergent this surfactant material may be as much as 90% of the formulation. Thus, there isn't a great deal of difference in terms of percent between the "surfactant" portion and the entire package soap product, and calling this surfactant "soap" does not lead to serious confusion.

In the synthetic detergent, however, as the slide shows the surfactant portion is a much smaller percent of the entire product than in the case of the packaged soap detergent. In this case to call this surfactant portion by the same name as the entire packaged product - i.e., "detergent" - can lead to real confusion. This is a problem which has shown up many times in the literature, where persons may say "detergent" but actually mean "surfactant", with the result that the interpretation of the reported findings is in error.

For clarity, therefore, we strongly recommend that the terms "synthetic detergent", "detergent" or "syndet" be reserved for the complete packaged product; and the term "surfactant" or "surface active agent" be used for the organic sudsing agent. When this is done, the problem is automatically straightened out, and the reporting and interpreting of data are clarified. The specific surfactant material most widely used in household synthetic detergents, and which has been the subject of most of the U.S. research, is known as ABS (alkyl benzene sulfonate). This material, I understand, amounts to approximately half of the synthetic surface active material used in Canada.

The phosphate builders present in both packaged household soap and synthetic detergents are mildly alkaline complex phosphates which, because of their soil suspending and hardness sequestering properties, help "build" the formulation into a product which will do the best (now known) job of getting dirt out of clothes. The specific phosphate compounds used in the packaged synthetic and soap detergents are not very different.

One interesting point which might be mentioned in passing is that in the U.S. the combined per capita consumption of packaged detergents and soaps has remained about the same during the years when detergents replaced soaps in the home. Total consumption, of course, has increased as the population increased. Actually, less surfactant from synthetic detergents enters the sewers today than did the surfactant "soap" thirteen years ago, because there is so much less surfactant in packaged detergents. I understand that this also is true in Canada.

ANALYTICAL ASPECTS

Another point which I feel merits a brief discussion deals with the analytical aspects of the detergent question. There are several methods available for the determination of ABS in water and sewage. The most widely used is the methylene blue

colorimetric procedure, which was published in the October 1958 JAWWA (1) by the AWWA Task Group on Analytical Methods for ABE. However, as the Task Group cautions in its report, this method is subject to interferences, and at times can give misleading results. The Task Group therefore recommends that questionable results be checked by the referee procedure developed by the Soap Association (2) which is also included in the Task Group report. This method, based on infrared principles, is long, and consequently not normally used for routine checking. It definitely should be used if there is any question about results, however. Incidentally, both of these methods recommended by the AWWA Task Group are expected to appear in the next issue of Standard Methods.

Improved methods for phosphates are also now available. A procedure developed by a Soap Association committee was published in the December 1958 issue of the JAWWA (3).

ALGAE PROBLEMS

The first of the two Canadian problems which I should like to discuss is the question of algae growth. I am aware that some hold the opinion that phosphates derived from detergents have caused a significant increase in algal blooms. As it happens, the Soap Association has not sponsored any research on this particular problem, and thus I can only discuss it today on the basis of what I have learned from the literature, and from talking with experts in the field. However, if nothing else, this review has impressed upon me the fact that a good deal still needs to be learned about the causes of algal blooms, and it certainly would be preliminary to try to pinpoint these causes at this time.

A seminar on algae (4) was given last April at the Taft Sanitary Engineering Center in Cincinnati which certainly confirmed, at least to me, this position of uncertainty. I believe you might be interested in a brief recap of some of the pertinent comments made at this meeting.

For example, one speaker (Prof. H.K. Phinney, Oregon State College) gave a paper on a problem which exists at Klamath Lake in Oregon. This lake receives essentially no domestic wastes, yet for over 60 years summer algal blooms have been intense. This is a case where natural enrichment causes the growth. Repeated chemical analyses of the water from many sampling stations failed to establish chemical factors which might explain the problem. The water was low in calcium, very low in dissolved phosphorus, high in chloride. Thus, very important sources of nutrients other than domestic sewage definitely indicated. It would certainly be our recommendation that such possibilities of natural enrichment be investigated when attempting to learn the causes of algal blooms.

Somewhat along the same line, another speaker at this seminar (Prof. R.O. Sylvester, Univ. of Washington) pointed up the

extreme importance of drainage from forests and agricultural lands as sources of nutrients which can cause algae blooms. He presented data which showed that considerable amounts of both nitrogen and phosphorus result from run-off following rainfall, with agricultural lands showing the higher amounts, as would be expected.

Other interesting points brought up in this seminar included the statement (by Dr. R.W. Krauss, Univ. of Maryland) that so little is known concerning the nutritional requirements of algae, that even knowing the chemical makeup of waters, it is impossible to predict growth. At one point he also noted that polyphosphates are not suitable growth factors for algae. The types of phosphates used in detergents are, of course, polyphosphates.

Another speaker (Dr. Provasoli, Haskins Laboratory) noted that vitamins are required as growth factors with certain algae, and recommended that this factor be given increased attention. Still another speaker (Dr. G.W. Lawton, Univ. of Wisconsin) reported that at the end of the first year of the diversion of domestic wastes around Wisconsin lakes, essentially no difference in the chemistry of the lake water is evident, although several new strains of algae have appeared. It is recognized, however, that this is a relatively short time in which to expect significant chemical changes.

All in all, the seminar pointed up the fact that a great deal needs to be learned before all of the factors controlling algal growth are known. The Proceedings of this seminar are to be published, probably in about six months, and if anyone is interested, he should request a copy directly from the Taft Center.

Still on the algae question, there are at least two additional literature references which bear on the question of phosphate contribution to algae growth. The work of Gerloff and Skoog at the University of Wisconsin(5) indicated that both the nitrogen and phosphorus contents of samples collected during periods of algae blooms in Wisconsin lakes were in the range of "luxury" consumption; in other words, they were very much higher than the minimum levels necessary for algal growth. The concentration of algae which might be considered a good lake bloom is quite low, approximately 10 mg of algae per liter.

Consequently, very low phosphorus concentrations apparently can support substantial blooms in natural waters. This raises questions as to the true significance of phosphorus derived from detergents, since without the detergent contribution sufficient phosphorus may already have been present from land drainage and other sources.

Also, there is some evidence that if the phosphorus content is increased beyond the minimum levels necessary to support good algal blooms, a heavier bloom does not result. Work by Dr. Fitzgerald at Wisconsin showed that there was no difference in the growth of one strain of algae (*Chlorella pyrenoidosa*) whether it was in an effluent containing 7.3 ppm phosphorus or in the same effluent with three-quarters of the phosphorus removed (i.e., to 1.8 ppm)(6).

So much for the literature on algae growth factors. I would like to add that although a great deal remains to be learned concerning the relative importance of the various nutrients, there does appear to be general agreement that regardless of source nitrogen and phosphorus are factors. Thus it would appear desirable to remove them, and one way which has been suggested is through use of oxidation ponds. This is not a novel suggestion, and its possibilities may have been considered for Canada. To us, however, it does look like a most interesting approach.

The review article by Fitzgerald and Rohlich on stabilization ponds(6) discusses the effectiveness of these ponds in removing nutrients. They report that ponds can achieve 75-90 percent reduction of ammonia nitrogen, 60 percent organic nitrogen and 96 percent phosphorus. The phosphorus, incidentally, is believed to be precipitated out by the increased pH of the ponds, rather than removed by absorption by the algae. They point out that it might be possible to harvest the algae and sell it as a food supplement, chicken feed, or as a source of industrial raw materials. Harvesting, of course, would permanently remove any nutrient materials from the water which might be later released from dead algal cells.

This, then would appear to be an intriguing possibility as a tertiary step in sewage treatment. We noted with interest the comment of your Dr. A.E. Berry in his talk on "Research in Canada" at the recent AWWA Annual Meeting, suggesting that research should be carried out on a large, as well as laboratory, scale. In line with this, we hope it will be possible for Canada to put this suggestion of tertiary treatment to practical test in the field.

FROTHING PROBLEMS

The second of the two Canadian problems believed associated with detergents, or more accurately the surfactant material from detergents, is that of frothing on sewage treatment plants. In this area the Soap Association has sponsored some research, and we may be able to provide you with more helpful information than in the case of algae. The project to which I refer is on the causes of frothing, and the means by which it can be eliminated or controlled, at the University of Wisconsin.

In many ways, this has been the most difficult of the various projects sponsored by the Association, because separating out, and even identifying, the various factors involved is a considerable problem. Some of these factors still haven't been established; however, much progress has been made.

To date the Wisconsin Project has established that while the surfactant ABS is one of the factors which contributes to frothing, many other either independently or combined also are involved. For example, low suspended solids concentrations

promote frothing, as has been recognized since the San Antonio studies a number of years ago.(7) Protein degradation products, present in almost every domestic sewage, also contribute to the frothing problem. In addition, elevated temperatures (over 70°F.) and high pH values are somehow involved. Aeration rates play a role, and the conditions during low flow periods, particularly at night when ABS levels in the influent are certainly low, somehow promote the problem.

The degree to which each of these, and undoubtedly other, factors is contributing to frothing still has not been established. Nor is the actual mechanism known by which such materials as ABS and complex nitrogen compounds do contribute. It certainly isn't the simple matter of lowering surface tensions, because at the low concentrations of 10 ppm or under the surface tensions are hardly affected. To our knowledge, no one has ever established a relationship between frothing and surface tension measurements in aeration tanks.

You may be interested in the studies which currently are in progress at Wisconsin, and which will close out the project when completed. They have designed a rather unique laboratory-scale continuous-flow activated sludge plant (Figure 2) in which an experiment is being run which will permit statistical interpretation of the factors being tested. These factors are (1) suspended solids, (2) detention period, (3) aeration rate, (4) ABS in feed, (5) BOD in feed, and (6) nitrogen: BOD ratios. High and low conditions or concentrations of each factor are included. A total of eight separate runs is required, and since each run requires as much as three to six weeks, and some have to be repeated, completing the study takes a long time.

It is not planned to submit the data to statistical analysis until the entire test is complete. However, it is interesting to note in passing that the incomplete results suggest that reduced frothing may be associated with lower aeration rates and extended detention periods. This cannot be considered conclusive at this time, however. Overall, it is hoped that out of this work may come the defining of operating conditions which will minimize frothing for the factors which exist and cannot be controlled, at any given time.

I might add that in the U.S., which frothing is recognized as a nuisance problem, it has not been generally associated with poorer plant performance. Operators keep it under control by maintaining high solids levels in the aeration tanks, or with sprays or de-foamants. Much of the Wisconsin work, incidentally, has been published in Sewage & Industrial Wastes.(8)

OTHER SOAP ASSOCIATION RESEARCH

I mentioned earlier that the Association has supported other research which was not directly connected with problems which might exist in Canada. This research has been carried out in both the water and sewage treatment fields.

For example, projects at the Massachusetts Institute of Technology⁽⁹⁾ (10) and the University of California (11) have dealt with the fate of ABS in sewage treatment, and with attempts to improve the 50% or better which currently is removed in primary and secondary treatment. The MIT people demonstrated up to 80% removal on a laboratory basis with a "complete mixing" modification of the activated sludge principle; however, one attempt to modify an existing plant to this system has not yet been successful. The California people have demonstrated, also in the laboratory, as high as 90% removal by deliberately frothing effluent from aeration tanks, followed by removal and separation disposal of this froth; this technique has yet to be applied to an operating plant. Both processes offer the promise of improved ABS removal if they can be adapted to large scale practice.

The area of water treatment has received considerable attention in the Association's research program. At Johns Hopkins University, (12) a project was carried out to determine effective and economic means for removing trace quantities of ABS from water supplies, should it ever become desirable. A number of materials which might serve as ABS adsorbing agents were evaluated, with activated carbon turning out to be easily the most effective. It was also found that different carbons have different effectiveness. In brief, it appears that for ABS concentrations in the range of 0.2 to 2.0 ppm, from 40 to 90 ppm of a good carbon will remove 90% of the ABS in the water supply.

Incidentally, I might point out that, at least in the U.S., the levels of ABS in surface waters are very low, (0.5 ppm and under.)⁽¹³⁾ The results of a weekly monitoring program which has been carried out since 1954 by Procter & Gamble on the Ohio River just below Cincinnati have shown an average of only 0.16 ppm apparent ABS, and there has been no tendency to increase during this entire period.⁽¹⁴⁾ Similarly, two surveys of the drinking waters of 32 major U.S. cities serving an estimated population of 25 million have shown an average ABS content of 0.03 ppm with samples ranging only from 0 to 0.14 ppm.⁽¹⁵⁾ These are certainly low, and insignificant levels, and may very well be representative of Canadian cities.

The other Association project in the water area has dealt with the phosphate component of synthetic detergents, not as it relates to algae growth, but as this component might affect water treatment. This project was carried out at the University of Illinois. Studies were undertaken to (1) survey typical streams in the State of Illinois for the amount and type of phosphate present, and (2) determine whether the existing concentrations might have any effect on conventional water treatment operations. This latter phase stemmed from laboratory work which had suggested that the complex phosphates used in detergents could, at relatively high concentrations, interfere with coagulation and settling.

The survey of Illinois streams, using the improved phosphate analytical procedures developed by the Association, showed that phosphate concentrations were low, with the complex phosphate generally less than 0.5 ppm as P₂O₅, and the ortho phosphate

content about the same. It was also determined, and this is very important, that almost half of the total phosphate present comes from the drainage of agricultural land. This concurs with the findings reported at the algae seminar which were discussed earlier.

Laboratory studies on coagulation and settling showed that the 0.5 ppm level of complex phosphates had an effect on this process which was barely perceptible, and that this could be overcome readily by either a moderate increase in coagulant dosage or an increase in settling time.

Other laboratory studies showed that the complex phosphates had an effect on this process which was barely perceptible, and that this could be overcome readily by either a moderate increase in coagulant dosage or an increase in settling time.

Other laboratory studies showed that the complex phosphates will degrade to the simple ortho form in the presence of stream biota, the rates of degradation varying according to the physical, chemical and biological conditions encountered. Overall, the Illinois work showed conclusively that the phosphate levels found in Illinois streams have no practical significance on water treatment, and further that only a portion of the phosphates present can be detergent-derived. If these findings are in the same order as levels found in Canadian stream, it would appear that the same conclusions would apply as far as water treatment is concerned.

The Illinois work has been published in four separate papers which some of you may be interested in reading. (16) (17) (18) (19)

SAFETY OF SYNTHETIC DETERGENTS

Questions are raised from time to time concerning the toxicological aspects of ABS, and occasionally, the polyphosphates.

The Soap Association has made a thorough review of the literature concerning ABS toxicity. This review, entitled "ABS and the Safety of Water Supplies", is scheduled to be published in the June issue of the JAWWA.(20) The literature, covering acute and sub-acute toxicity experiments, shows in all cases an adequate factor of safety for ABS, considering the levels in water supplies.

In addition, a two-year chronic study of the effect of ABS in rats has been completed by Hazelton Laboratories and P&G, and is scheduled for early publication in Toxicology and Applied Pharmacology.(21) In this chronic study, levels of 1000 ppm and 5000 ppm were fed in the diet, and the weight equivalent of 1000 ppm was fed in drinking water, to three different groups of rats. No evidence of toxicity was noted, and it was the conclusion of the authors that "to the extent that animal tests provide a basis for the assay of toxicity to humans, it would appear that considerable amounts of ABS (much in excess of the amounts that might find their way into the drinking water) could be consumed over long periods without harm".

Of interest also are the limits being proposed for the current revisions of the U.S. Public Health Service Drinking Water Standards.(22) A limit of 0.5 ppm ABS is proposed, based on aesthetic rather than safety reasons. The two reports mentioned above have been submitted to the Toxicology subcommittee of the USPHS reviewing these Standards, and the fact that the ABS limit has been publicly proposed without toxicological comment suggests that they agree with us that the factor of safety demonstrated by the rat feeding experiments is more than adequate.

On the question of the safety of phosphates, the U.S. Food & Drug Administration has cleared both the polyphosphates used in detergents, and the ortho form to which polyphosphates degrade, for use as food additives.(23) This would appear to establish without question the safety of these materials.

CONCLUSIONS

This, then, briefly covers the activities of the Soap Association regarding the various questions raised in the U.S. on detergents and their role in water and sewage. Only in part does this work relate to the problems you have experienced in Canada. However, I hope that the information on algae developed from the literature, and the recommendation that oxidation ponds be tried for removal of nitrogen and phosphorus, will prove helpful.

In general, we believe the Association research program has shown that synthetic detergents are not responsible for all of the problems of which they were once accused.

The fact that ABS is removed to an appreciable extent in secondary sewage treatment has been established, and methods for improving that removal in sewage treatment, as well as removing it from water, have been devised.

In aeration tank frothing, ABS is by no means the only contributor; in fact, the other factors are so important that merely by themselves they might create a definite problem.

ABS has been shown to have a toxicological factor of safety many times the concentrations which might occur in water supplies. Phosphates also are known to be safe.

Phosphates have been shown to cause no serious problems in water treatment plant operations.

The role played by phosphates derived from synthetic detergents in promulgating algae blooms is not clear. It is evident, however, that natural drainage from agricultural lands and forests can contribute significant amounts of nitrogen and phosphorus to streams and lakes, and these sources should be considered along with domestic wastes when studying specific problems.

In any event, the Association's broad research program is continuing, and as more facts are developed we hope that they can be used both to eliminate any problems where detergents are involved, and to further answer the many other problems of concern to the people in this extremely important field.

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PACKAGED HOUSEHOLD:

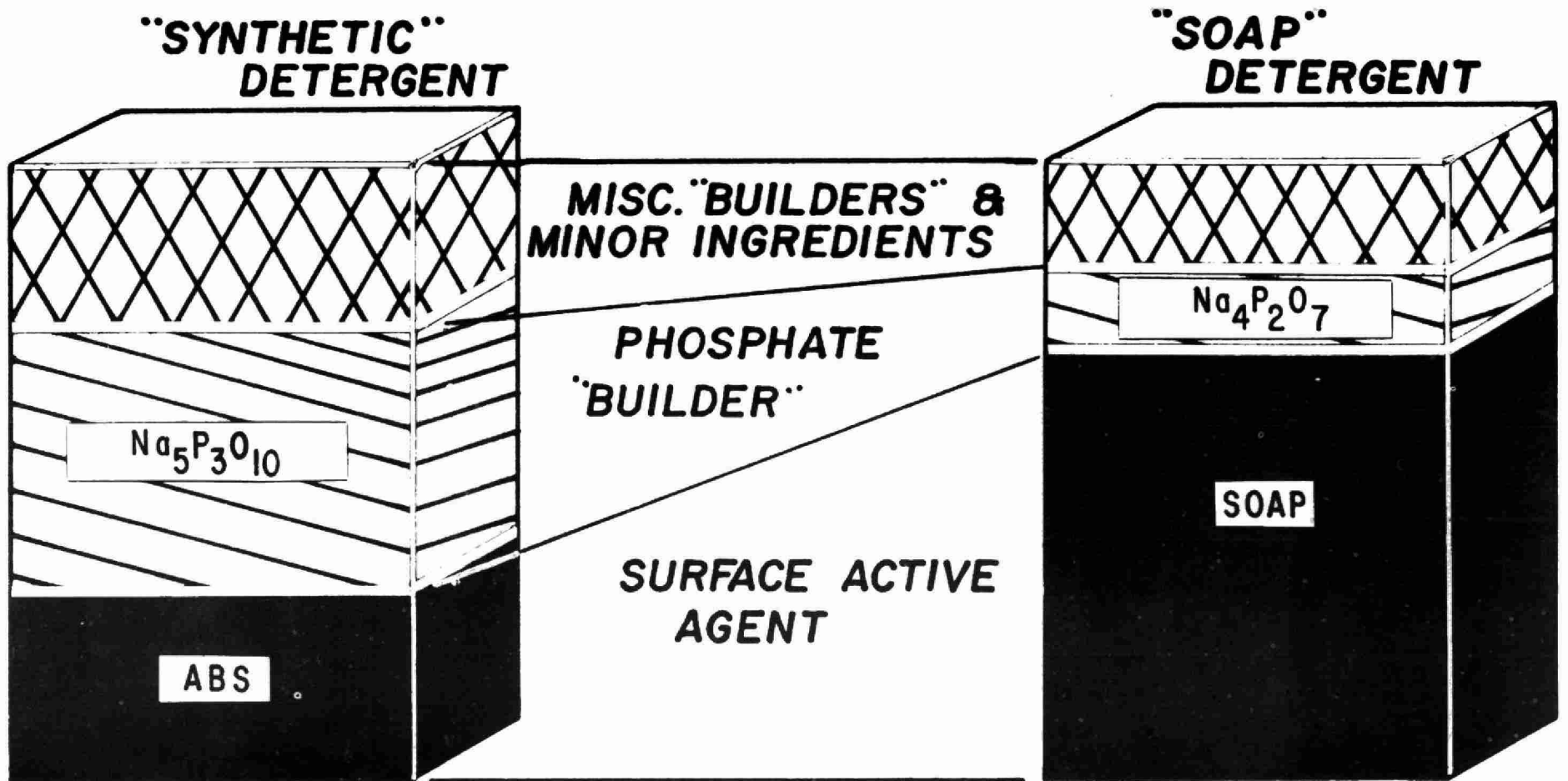


Figure /.

Representation of two major types of packaged household washing products.

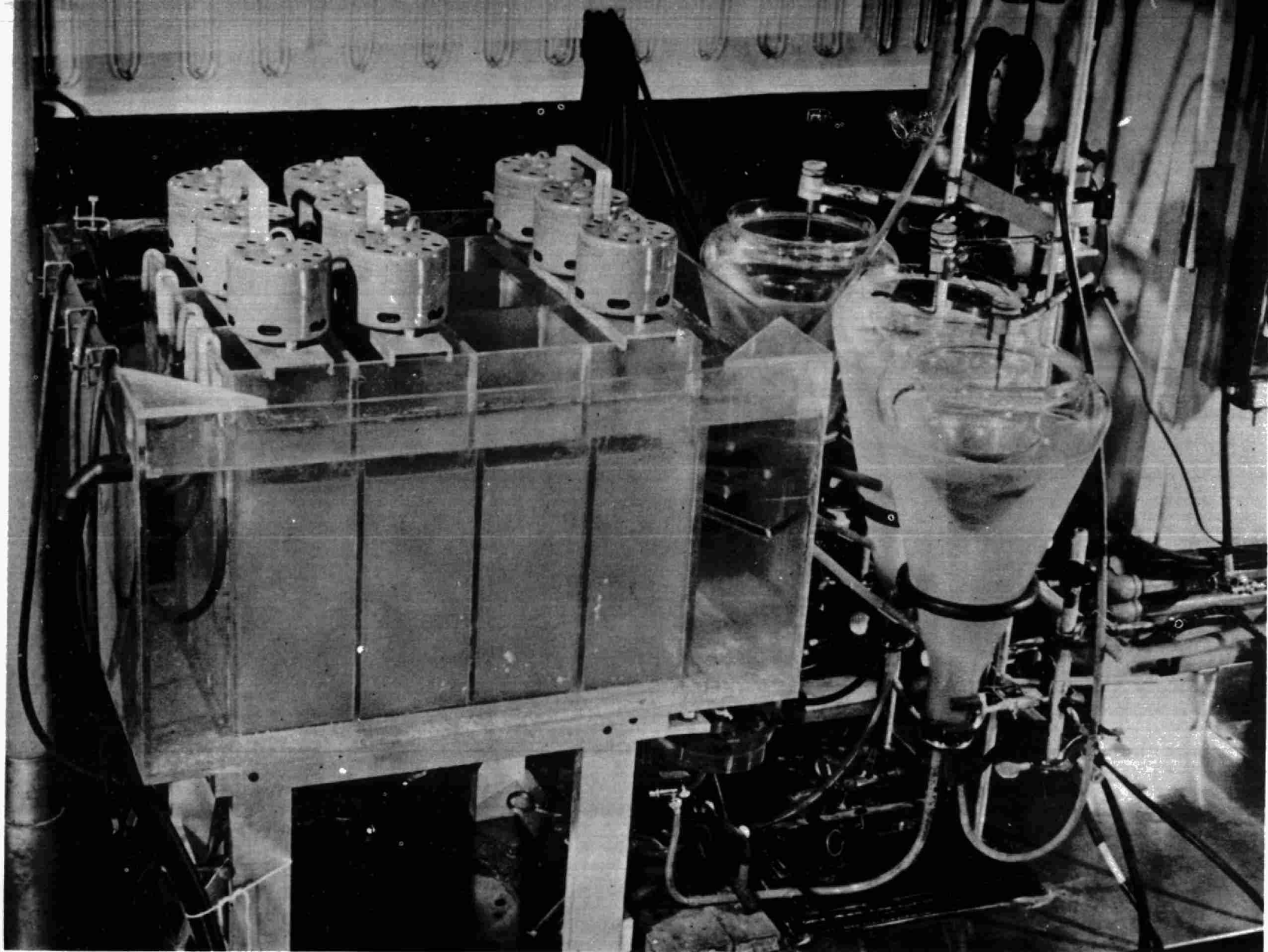


Figure 2. Laboratory-scale experimental activated sludge unit developed at the University of Wisconsin. Unit consists of three separate systems in parallel, with diffused air aeration tanks (immersed in constant temperature water bath) shown in left center, and final settling tanks at right. Note that one set of mechanical stirrers, used to assist in holding solids in suspension, was removed when photograph was taken.

THE USE AND CONSTRUCTION OF OXIDATION PONDS
FOR INDUSTRIAL WASTE TREATMENT



by

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The purpose of this paper is to put forward a method of waste treatment that has not previously been discussed at this conference. The reason for its appearance on this programme is two-fold. Firstly, it is intended to provide an idea for consideration, and secondly, as it is not a panacea for waste treatment, some of the pitfalls will be noted.

Gentlemen, first let me say that here is a process for the treatment of an industrial waste where you get something for nothing, and it is conceivable that you end up with a marketable product. Your capital outlay increases not depreciates in value. The system automatically adjusts itself to changes in the wastes it receives and little or no maintenance is required. All that you have to do is to create a favourable environment for a few kinds of 'bugs' to grow. When I say the capital outlay increases, by this I mean that the land acreage used for the ponds generally increases in value. The ratio of volumes of effluents to the receiving ponds smooths out any short term variations in flows, or strengths of wastes, thus, it operates automatically. The statement that no maintenance is required is based on the fact that algae never need to be oiled and as bacteria are not noted for requiring clean surroundings, the maintenance costs are low. It was also mentioned that a marketable product is developed. All that is required to sell this product is to devise a means of economically removing the algae from solution.

Previously, it was said that to achieve this utopia of waste treatment all that had to be done was to create a favourable environment - this is the crux of the operation of the biological process that takes place in an oxidation pond.

Before further discussion the environmental factors, a little of the history and some information on the basic principals involved in the treatment of the waste by this means would seem to be of value. The original oxidation ponds came into being many years ago when certain western towns used the nearest slough as a receptacle for the town sewage, undoubtedly with some feeling of guilt and much against the wishes of the health officials. It was noticed, however, that odours seldom developed and samples of the effluent showed a remarkable reduction in BOD, solids and bacterial

counts. From this observation a scientific interest developed to determine why the sewage received such good treatment and how the efficiency of the process might be improved.

An examination of the literature indicates that almost all, of quite an extensive list of publications, have occurred since about 1954. Probably the U.S.P.H.S. has done more work than any other group but information has also come from Australia, New Zealand, Israel, Sweden as well as Canada.

As a result of these studies the theory of how the treatment is provided has been quite well worked out and while more studies are needed, considerable worthwhile information is available for those who are building and operating oxidation ponds.

Most organic materials are subject to bacterial degradation. This is a change from complex substances to stable compounds or the elemental form. The process of breakdown is mainly the result of bacterial action where a whole series of different bacteria perform one step in the process. As degradation takes place, oxygen is required in the chemical reactions. If the waste is strong and oxygen is not being supplied in sufficient quantity, the process will use up the available supply and the reaction will become anaerobic. Under these conditions, a new set of "bugs" take over and obnoxious odours will be omitted.

Secondary methods of sewage treatment are so designed that oxygen is provided in the water at all times. In the activated sludge process, air is blown into the sewage and on trickling filters large surface areas enable oxygen to be absorbed. In oxidation ponds instead of blowing air into the sewage or trickling it over rock beds, the oxygen is provided by green plants known as algae by the process of photosynthesis.

Algae are very simple plants often composed of only one cell or a group of unspecialized cells. The algae are so primitive that they do not have any true roots, leaves or stems and reproduce only by simple division or spore formation. There are many thousands of species of algae that live in almost any environment where water and sunlight are available. The species which grow in oxidation ponds, however, are very limited as only those which find a polluted environment acceptable are able to exist. In the oxidation ponds the world over only four or five types of algae are common and of these, one is almost always the dominant organism. Under favourable conditions the algae multiply rapidly by simple cell division in a geometric progression. Thus once it begins to grow, it very rapidly populates the environment to the limit of its carrying capacity. The resistant stage of this alga is very hardy and can dry up and be blown around with the dust so that it is almost universal in distribution.

The bacterial degradation which was previously mentioned creates a rich supply of nutrients in the pond including various available nitrogen forms, a plentiful carbon dioxide supply, phosphorous and other essential elements and in this rich environment heavy concentrations of algae grow. Algae, like other plants, grow and multiply by combining carbon, nitrogen, phosphorous and indeed

most of the known elements into living protoplasm. The force promoting this reaction is derived from sunlight and altogether it is known as photosynthesis. The reaction utilizes the waste carbon dioxide from the bacterial decomposition and produces oxygen. Thus the circuit is completed and is essentially a self-sustaining one where bacteria break down the organic material and use oxygen and algae utilize the waste products and provide the oxygen. When the rate of decomposition uses oxygen at a rate in excess of the replenishment of the oxygen supply, the ponds are overloaded and will become anaerobic.

From the foregoing, it is evident that certain requirements must be met before an effective growth of algae can be developed. These requirements constitute the favorable environment that I spoke of previously. Of prime importance is sunlight, as it is the source of energy driving the process that produces oxygen. A second requirement is a suitable food complex. Of particular importance is a source of carbon which generally supplied by the carbon dioxide released from decomposing organic substances. Nitrogen in a form available to the plants such as ammonia or nitrates must be present. Phosphorous is also of prime importance and some basic or non-limiting supply of many other elements must be available in a form suitable for use. Temperature exerts a controlling influence on the rate of the reaction. Certain of the algae are quite capable of operating at temperatures approaching 32° and for this reason the process need not stop in cold weather. The rate of oxygen production may not be as great but as the bacteria are also slowed down the process remains in balance although it requires a longer period for treatment. The pH is also of importance slightly alkaline being the most favourable but again a range from about 6 to 10 will produce algae cultures.

The oxidation ponds were originally developed for the treatment of domestic sewage and most of the research studies have been directed towards the flora and fauna of the ponds and to establishing design criteria and loading standards. As a result, there is now available quite good criteria for the successful operations of these structures on sewage. The recommendation which the Commission use is that the loading should not exceed seventeen pounds of BOD per acre per day or in other words one acre of ponds for every 100 persons. This recommendation is determined by a period in the spring immediately after the ice leaves when the pond changes from an anaerobic to an aerobic state. Heavier loading than this will cause obnoxious odours to develop and persist for a period of time depending on the weather and the degree of overloading.

The facilities at Camp Ipperwash, an army camp near Sarnia, provide a good example of how these ponds operate on domestic wastes. Here five acres of pond area divided into two cells provides the complete treatment for sewage for a variable population. Normally during the fall, winter and spring season a camp of about 500 persons is maintained, this provides a loading that approximates our recommendations. In summer time, however, the camp strength may go to 2000 which is four times the recommended dosage but as this coincides with the period of maximum efficiency, effluents of

suitable quality for discharge are obtained, i.e. below 20 ppm BOD and solids. From dozens of samples that have been taken during three years of operation, only two have been more than 20 ppm. BOD and both of these occurred just in the period of spring breakup. No serious odours have ever developed.

The experience with industrial waste treatment in oxidation ponds has been less successful not because the process is not adapted in some instances for treating these wastes but because none appear to have been built with sufficient capacity. There are two ponds in Ontario working on chicken killing wastes that have been in operation for almost three years. These are purely for the treatment of industrial waste so that a discussion of their operation seems pertinent. The first lagoon to be built in connection with the chicken killing process had a total area of 3.7 acres. The water used was approximately 60,000 gallons per day and the mean strength of the waste was 768 ppm. BOD. When the pond was first put into operation some odours were noted but before long the warm summer weather promoted an extremely dense growth of algae. The odours disappeared and no serious problems occurred until the following spring. At that time, very obnoxious odours developed causing some distress in a nearby hamlet. Subsequently, a second lagoon of 5.7 acres making a total area of 9.5 acres was added. This covered all the land that was available for ponds and while the 49 lbs. of BOD per acre per day loading was still excessive the ponds now operate fairly successfully as intermittent odours develop only during a period of about one month from the time of break-up until the algae return the ponds to an aerobic condition. The BOD results of the effluent from these ponds have seldom been sufficiently good to allow a direct discharge as the normal effluents are approximately 50 ppm. The plant, however, is situated in a gravel strata and the total discharge from the ponds can be absorbed into the ground in a nearby pit. It is thought that if these ponds were doubled in size a satisfactory effluent would be obtained for discharge to the nearby water-course.

The second chicken killing plant has been somewhat more successful in the operation of their ponds. This plant is somewhat smaller, processes fewer birds, and consequently has less acreage in ponds. The loading on a pounds of BOD per acre basis is not less, however, and in spite of this most of the results with the exception of the early spring, have been of sufficiently good quality for discharge.

An experimental oxidation pond for the purpose of studying the effectiveness of this method of treating a tannery waste has been operated since late last summer. This pond of about half an acre was not designed and built for this purpose but so far has proven quite satisfactory. Initially sewage was fed in order to establish an algal population before tannery waste was applied. In spite of the fertility imparted by sewage and subsequent commercial fertilizer applications, no strong algae growth developed. The algae did, however, appear to be increasing in numbers and early in September tannery wastes at the rate of ten lbs. per acre per day were fed. It was soon evident that little change occurred in the BOD, suspended solids, pH, color, turbidity,

alkalinity, or algae counts, and for this reason the feed rate was increased to 20 lbs. per day. This did not effect the pond either and subsequently the feed rates were increased to 30 and then to 50 lbs. per acre per day. The BOD in the pond remained consistently below 10 ppm. and a low but stable algae population remained. Early in December a sharp increase was noted in the BOD and by early January, the ponds contents had increased to 64 ppm. At that time, it was decided to stop feeding the tannery waste and to follow the decrease of the BOD under the ice. The condition of the pond did not warrent further applications until shortly after the ice disappeared. Increasing concentrations of tannery wastes are now being applied in order to determine the maximum loading that will still provide an effluent suitable for discharge. This tannery waste has a relatively high BOD initially being about 800 ppm. and a chloride content of about 2000 ppm. The pH tends to be rather high, and a heavy turbidity is noted in their other holding lagoons. So far the adverse characteristics of this waste has not significantly effected the treatment provided in this pond. Thereis, however, a definite possibility that inhibition of the process will occur as the concentration of inorganic substances builds up. More information resulting from this experiment as to whether oxidation ponds are a suitable method for treating tannery wastes will be available by the end of the summer.

Recently a series of three ponds was built for the treatment of a potato chip waste. This effluent has a strong BOD in the influent and is primarily carbohydrate in nature. As these facilities only began operation this spring, little information is available yet. From the two sets of samples that have been taken, however, it is interesting to note that a pond which was designed for anaerobic action has developed an intense algae bloom. Odours are evident, and this is not surprising as the pond contents have a BOD of about 600. The second lagoon in the series has only recently been filled and a recent sample of the contents indicate a BOD of 56 ppm. A third cell in the series has not yet filled but it seems likely that the effluent from this will be satisfactory for discharge. Because of the pure carbohydrate nature of the waste it would seem that some of the essential algal nutrients will soon be in short supply. If this occurs, some fertilizing elements may have to be added to satisfy the requirements of the algae. These structures were constructed on an experimental basis and have a total of about 15 acres. No previous design criteria were available for treating a waste of this kind and more land has been provided for expansion, should this be necessary.

From the examples that have been discussed there appear to be a few conclusions that can be drawn as a guide to future installations of this type. Firstly, it would seem that this method is particularly well adapted to seasonal operations. The maximum efficiency is obtained during the warm months and a good treatment has been noted with loadings up to 100 lbs. BOD per acre per day perhaps only a quarter or a third of the land area is necessary when the maximum load comes at that time. Their use is questionable where the media is unsuitable for the growth of algae or where the waste may have either a bacteriacidal or algicidal action. Pure canning wastes are normally almost pure carbohydrate and for this reason are an unbalanced media. There is, however, the possibility

of mixing it with sewage to provide a balanced feed. The Commission is presently constructing a 75 acre lagoon area for the town of Listowel to treat combined sewage and cannery waste.

The use of oxidation ponds where a significant quantity of milk waste is included does not appear to be satisfactory. The literature reports a number of instances where ponds receiving milk waste that were not overloaded, produced little algae and were malodorous. Unfortunately, no specific information is available as to what proportions of the load would be satisfactory.

Certain wastes may inhibit the growth of algae through the interruption of some essential process. Of particular importance here are wastes that are highly coloured or maintain a colloidal suspension as this seriously limits the phototrophic zone.

Some wastes may be directly toxic to either the algae or the bacteria. Both are required and any interference will spoil the usefulness of the ponds. An interesting example of this was a pair of small ponds receiving a small quantity of waste having some cyanides, phenols and a high BOD. Ordinarily this with the inorganic nutrients that were available should have been sufficient to develop a good bloom of algae and to provide a satisfactory reduction in the waste components. In spite of good algae growth there was little improvement in the effluent. It was concluded on a subsequent investigation that while the algae grew well and produced oxygen the bacterial action was inhibited and for this reason very little improvement was noted.

In considering waste treatment processes, oxidation ponds and spray irrigation systems are two valuable methods, each providing a solution to different problems. The criteria for loading is pounds of BOD per acre of pond per day for oxidation ponds and gallons or inches of liquid per acre per day in spray irrigation systems. From these criteria it is evident that the BOD is the limiting factor in the ponds and the Hydraulic loading on the land. Within limits, therefore, spray irrigation systems are most suitable for moderate flows having a high BOD and oxidation ponds more favourably disposed to less excessive BOD concentrations and greater flows. A few simple calculations on the land are required to treat by either method readily determines the economics in most instances.

It has been the intention of this paper to discuss some of the possibilities and limitations of the oxidation pond as a method of waste treatment. It is evident that while they have been proven to be effective in treating sewage, their use on industrial wastes is relatively new. Unlike sewage each type of industrial waste is different and careful consideration must be given to determine whether it will provide an adequate environment for the specific biological community that is developed in effective oxidation ponds. More observations and experimentation are necessary to establish this as a method which has adequate

loading criteria and will provide predictable results. It does, however, offer considerable hope in some fields where no other method is now available.

Early in this talk it was mentioned that a product of value resulted in treating wastes in an oxidation pond. This is the algae which are developed and the next logical step is the harvesting and utilization of the algae themselves. These plants that grow in such large quantities, are rich in proteins, carbohydrates, and fats, and would make a valuable supplement for animal feeds. There remains only the technical problem of separating these minute cells which may occur in excess of 25,000 per drop from the water.

While we have not yet solved the problem of turning sewage or industrial wastes into a useful products, a very satisfactory product has been harvested in the far eastern countries for centuries. There, each home has its own private oxidation pond behind the house. The out-house is built over the water and the pond is continually fertilized by the family. The organic solids are broken down by the bacteria, utilized by the algae and the algae in turn eaten by the minute animals. These minute animals form the food of larger animals which are in turn consumed by carp and other cultivated fish. In due time these fish are harvested, eaten and before long the cycle is completed.

Gentlemen - This is Conservation!

WASTE STABILIZATION PONDS IN ONTARIODESIGN AND CONSTRUCTION

By



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Prior to 1954 he was with the Department of National Defence and since that date has been with M. M. Dillon and Company Limited, specializing in municipal engineering.

This paper deals with the design and construction of stabilization ponds, and while the design criteria may differ slightly depending on the nature of the waste to be treated - be it domestic sewage or a particular trade waste, the construction principles are much the same.

INDUSTRIAL WASTES

The criteria for domestic sewage treatment are fairly well resolved. For a particular trade waste capable of treatment solely by an oxidation process, it is necessary to know in some detail the B.O.D. characteristics and the probable flows which can be expected if the industry's production is seasonal or fluctuating for any reason. With this, it is possible to determine theoretical sizes. More often, it has been the practice in Ontario for an industry to secure sufficient land so that it may increase the number of cells in the lagoon system to meet actual operating conditions.

DEVELOPMENT

Probably no new development in the water pollution control field has quite caught the fancy of the Ontario people as has the advent of the sewage lagoon, or oxidation pond or stabilization pond as they are now called.

While the success of the stabilization pond has been known in Europe and in the United States for many years, it was only comparatively recently that the first of these treatment facilities was actually designed and operated in this Province. Some ponds had been developed mostly as a stop-gap measure to deal with seasonal cannery wastes, but these were temporary facilities and were not intended to provide the high degree of treatment that was to be achieved with later designs.

It was in 1954 that M. M. Dillon and Company was faced with a somewhat unusual set of circumstances in a military camp. The design population fluctuated widely, the quality of native soil (or sand) would not permit of sand filtration and as is often usual, the budget was limited. Considering all factors, a stabilization pond appeared to be the answer.

PRECEDENT

A check of the records in Ontario showed no precedent. The literature, however, did reveal some success in the State of North Dakota and based mainly on the experience of this State and reports from Western Canada, it was decided to embark on the venture.

With the hesitant approval of the Sanitary Engineering Division of the Department of Health (now the Ontario Water Resources Commission) the design was completed and shortly after, the ponds were put into operation. The success was almost immediate and these ponds have performed very well for the past four years - so well that the installation has been a model for other municipalities and their consultants.

It is worth noting that other firms of consulting engineers in Ontario have followed close on our heels and they too have made significant contributions in this field.

What then are the requirements for sewage stabilization ponds?

LAND

The early basic criteria of 10 acres per 1,000 population, even when modified to acceptable present day standards, indicates that available land is probably the most significant requirement.

Unless sufficient land at low cost and within a reasonable distance of a community or industry is available, the idea of ponds can be dismissed. Even apparently worthless farm land can grow speculatively in value to the point that it cannot be considered.

There comes a point in an economic study where it may be cheaper to consider some of the other means of treatment.

LOCATION

If possible, the ponds should be at least $\frac{1}{4}$ mile from the nearest habitation. Where this is not possible, close siting may be acceptable when wind direction and screening are favourable. Properly loaded, the ponds should be able to lose ice cover in Spring and overturn with a minimum of odour. However, there may be a period of unsettled weather at this time, with possible refreezing and lack of sunlight resulting in a switch back to anaerobic conditions. This may produce objectionable odours.

SURFACE AREA

The determination of required surface has been the subject of much scientific and non-scientific speculation.

Initially, one acre per one hundred population was used. This has since been modified both in the U.S. and in Canada. While lengthy formulas are available, it is probably easier to use one of the simpler criteria i.e.

- (a) 20 to 30 lb. B.O.D. per acre per day
- (b) 1 acre per 200 to 250 population
- (c) 120-140 days storage capacity

Since the area required is interdependent on a number of other factors, it is wise not to rely on any one criteria but rather to consider the case in point, make adjustments to suit local conditions, and ensure that agreement is reached with the regulatory bodies.

CELLS

Desirably two or more cells should be constructed so that flexibility of operations is possible.

These cells should be designed such that series, parallel or single cell operation can be maintained.

Certain authorities favour series operation where the first cell can be operated as an anaerobic pond. While this may be satisfactory, and result in a very high B.O.D. reduction in the first cell, the possibility of odour development is greater and for the unattended installation (and this is obviously an ultimate) a parallel operation or a lightly loaded series operation is essential.

It goes without saying that the very large cell, say 10 acres or greater, should be broken up into more than one cell to

to reduce the wave action which if allowed to develop over a wide area, could cause undesirable erosion to the dikes forming the sides.

It has been stated that pumped recirculation from one pond to another is useful to permit seeding of a pond deficient in algae and other reasons, but such a refinement would appear only to complicate the set-up, and indicates that some attendant must be available to carry out this function.

SHAPE

Ponds need not be constructed to a rectangular pattern. The contours of the land should be carefully considered and maximum use made of existing conditions.

One of the great expenses is the cost of earth moving and the use of existing, naturally consolidated embankments should not be overlooked.

Depth considerations may rule out certain natural ground features, however many successful ponds have been built simply by damming up an old dry watercourse and preventing the ingress of surface water.

DEPTH

Authorities seem evenly divided between 3 ft. and 5 ft. for optimum depths.

A number of factors affect depth:

- (a) Light penetration
- (b) Rate of mixing by wind
- (c) Prevention of growth of bottom weeds
- (d) Rate of overturn in Spring
- (d) Possible anaerobic conditions

and these factors so conflict with one another that it is probably sufficient to say that 3 ft. to 5 ft. will provide satisfactory conditions in almost every case.

We have had good results with a depth of 5 ft.

COMMINUTION

Wherever possible, it is wise to provide coarse screening and grinding facilities for raw sewage. This can be accomplished by a manually cleaned bar screen and automatic comminuting devices of which many are on the market.

The screening and grinding will serve the two-fold purpose of protecting pumps, if a force main is involved, and will reduce most wastes to a size that they will be more easily distributed through the stabilization pond.

INLET

The simplest type of inlet is usually the most generally successful. If the inlet pipe is carried to the centre of the cell, and if provision is made to prevent scour from it (should it be a force main) or if consideration is given to the prevention of an undesirable build-up of sludge, the installation will work.

Regardless of whether the pond is fed from the centre or from one end by a series of pipes, no evidence exists that there have been serious build-ups of sludge at these points. It would appear that the constant circulation within the pond from inlet to outlet and the wind action has been sufficient to evenly distribute the sludge over the entire bottom.

A submerged inlet, however, is recommended in all cases.

OUTLET

Variation exists in the type of overflow or outlet structure.

Since most ponds must be constructed to allow for overflow to a receiving stream, it is essential that a simple yet effective structure be designed.

We have withdrawn liquid from the top of the pond and have simply inserted a metal pipe with its invert at the design high water mark. This is simple but has the disadvantage that any floating material can be discharged.

The use of a manhole in the dike or berm, divided by stop logs with the inlet near or at the bottom of the pond permits withdrawal from beneath the surface and has the added advantage of permitting the maintenance of any desired level in the pond.

Again, the withdrawal from a number of points across a pond may have certain scientific advantages, but it has been proven that a simple single point is also quite satisfactory.

EARTHWORK AND LINING

Most native soils encountered in the area in which it is proposed to construct ponds are satisfactory for resultant impermeability.

It is not desirable that liquid be able to move from one cell to another through the dikes or berms, nor should the rate of percolation through the bottom exceed $\frac{1}{4}$ " per day. To overcome this it may be necessary to line the pond with an impermeable material or treat it chemically.

Our experience at Ipperwash Military Camp in this regard is interesting. Early investigations showed that the lagoon area was very fine sand with a light overburden. We had hoped that this sand would permit of the construction of a slow sand filter, but it was apparent after testing that the uniformity coefficient was such that this was impossible.

Obviously then, we had to provide a lining of some sort. Fortunately, native clay was available within a short distance and one cell was lined with a four to six inch blanket of this. As a trial, the second cell was not lined, the assumption being that the sludge would "blind" it in a short time and high percolation could be accepted for a while.

In fact, this theory was true and within a few months, this cell performed exactly as the first.

PROTECTION

It is wise to ensure that the entire pond area is fenced and adequately posted with warning signs.

If near a built-up area, the unwary is apt to stumble into a pond on a dark night and our experience has also shown that some of the over-exuberant populace have chanced to utilize the pond for swimming purposes.

MAINTENANCE

There is no sewage treatment facility which can be so easily maintained. This is probably the greatest selling point - if selling is necessary!

Nothing can be worse than a mechanical treatment plant in the hands of an incompetent or unskilled operator. The stabilization pond runs itself.

The grass on the dikes should be mowed periodically - once a month at least - for appearance if for nothing else. Inspections should be made for leaks around overflow pipes. Burrowing animals such as muskrats may be a problem, but traps soon catch these and might even turn the installation into a profitable trapping operation!

Mosquito breeding has been suggested as a problem, but this too can be overcome by introduction of a selected specie of top-water minnow. It may be necessary to try several species to

obtain the one best suited to the local environment.

COST

What does a stabilization pond system cost?

A good pattern for this Province has not yet been established, but it is worth noting that this type of treatment can sometimes be instituted for only 25% of the cost of the more conventional mechanical plants.

Our experience on actual ponds constructed and on estimates made for new installations shows that the cost will be approximately \$20 to \$25 per capita. This does not include such facilities as pumphouses or sewers required to bring the influent to the pond area. Figures available from the United States show an average cost of \$15 per capita in the northern states. As in a conventional plant, the unit cost is higher for the small ponds and decreases for larger ponds.

CONCLUSION

In Ontario, the stabilization pond is here to stay! After a slow start, public acceptance has been gained to the point that every small community looks to this system as the solution to their problem of reducing the pollution of existing watercourses.

The limitations of the system are few. Even an apparent high land cost becomes acceptable when the low annual cost of operation and maintenance is considered.

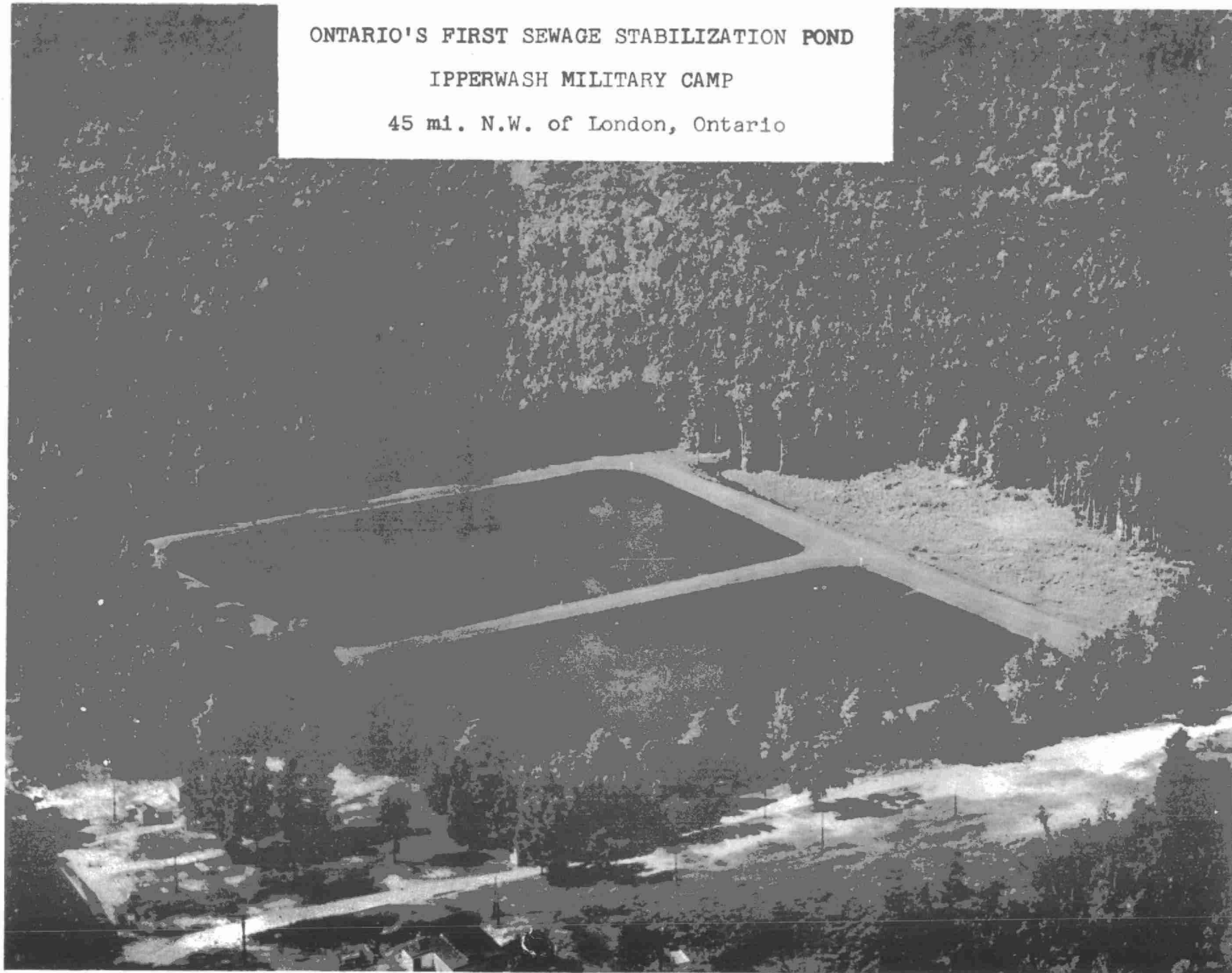
But, regardless of the tone adopted by this author in attempting to de-bunk scientific theories, the sound developed design principles cannot be overlooked and the careful thought of the competent professional engineer - be he a municipal employee or a consultant should be sought by those contemplating the construction of stabilization ponds.

The hand and mind of the engineer are essential for adequate surveys for maximum use of land, for hydraulic considerations, for soil permeability studies, for proper specifications, and most important of all - on-site job control during construction.

ONTARIO'S FIRST SEWAGE STABILIZATION POND

IPPERWASH MILITARY CAMP

45 mi. N.W. of London, Ontario



APPLICATION OF FLOTATION PRINCIPLES TO
SEVERAL INDUSTRIAL WASTE TREATMENT PROBLEMS

By

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and

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Palatine, Illinois



Jack Pratt

INTRODUCTION

Flotation is a unit operation for the separation of liquids or for the separation of solids from liquids.

The separation of phases by sedimentation is limited at times by the presence of extremely fine particles or globules which do not have a significant settling or rising rate, or the phases may not differ appreciably in density from the parent liquid. Flotation is generally free from these limitations for the removal of fine particles or globules is largely based upon the surface properties of the phase to be removed and not upon its size. Also, the apparent density of the phase which is to be removed is reduced by the adsorption or absorption of gas bubbles, thereby causing the gas-solid or gas-liquid agglomerate to rise.

Although different gases may be employed in the flotation process, air is the gas most commonly employed.

Dissolved-air flotation generates the air bubbles by the precipitation of air from a solution super-saturated with air.

Dissolved-air flotation may be classified into two categories depending upon the pressure which exists when the air is allowed to precipitate. When the air is dissolved under atmospheric pressure and allowed to precipitate out of solution under vacuum, the process is called vacuum flotation. Pressure flotation encompasses systems where the air is dissolved under elevated pressures and allowed to precipitate out of solution under atmospheric pressure.

Dissolved-air pressure flotation has been more widely used than vacuum flotation due to the limited pressure drop available with vacuum flotation (maximum theoretical pressure drop is 1 atmosphere) and the construction cost of proper vacuum facilities.

THREE METHODS OF FLOTATION

There are three methods of accomplishing flotation:

1. Adhesion of an air bubble to a suspended solid particle.
2. The trapping of air bubbles in a floc structure as the bubbles rise.
3. The absorption of an air bubble in a floc structure during formation of the floc.

Figure 1 illustrates the three methods of flotation.

For proper flotation under Method 1, there must be a contact established between the suspended phase and the air phase. The required contact may be established by either precipitating the air bubble on the suspended solid surface or by collision between the suspended solid and the air bubble. The former method is preferred because of the more positive method of contact.

The suspended solid is usually in a static state of movement, whereas the bubble is dynamic and actually has flow lines established around it. Therefore the suspended solid and the air bubble have viscous motion, and the suspended solid will tend to simply follow the flow lines established around the air bubble, and no contact will result. These flow lines are prominent, and unless the rising bubble contacts the suspended solid directly, the suspended solid will not be removed.

The maximum possible contact for Method 1 may be established by dissolving the air into the stream that contains the suspended phase so that, when the air precipitates out of solution, the surface of the suspended phase, due to surface tension, acts as a plane for bubble nuclei formation. Also, to increase the probability of contact, a degree of turbulence may be created by restricting the bubbles and stream being processed for a period of time.

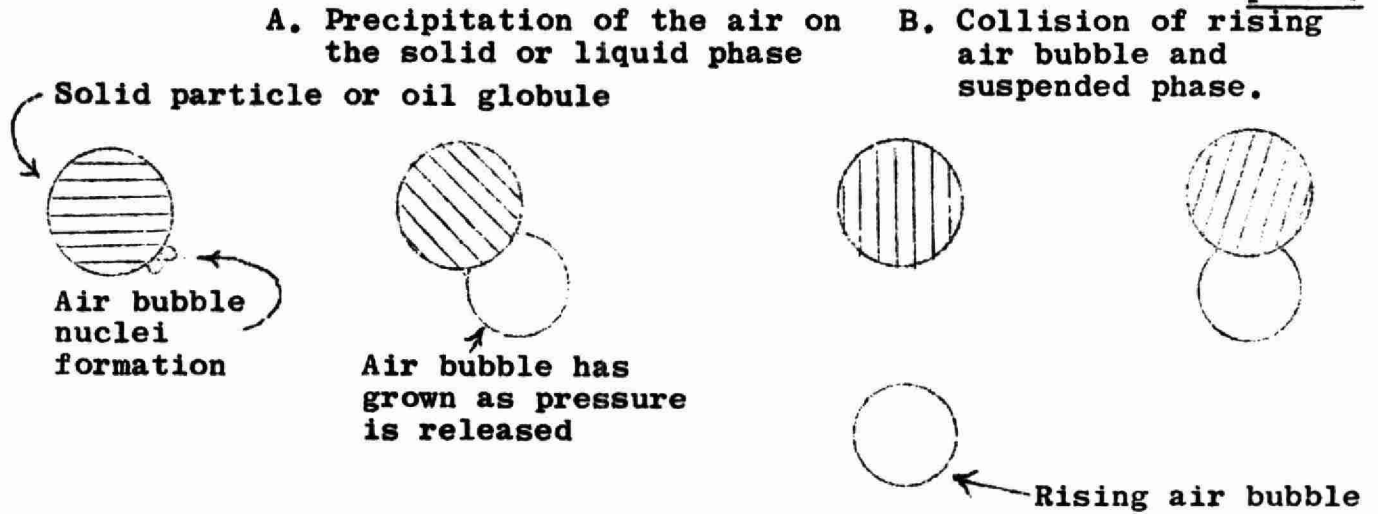
Method 2 is dependent upon the floc structure having a sufficiently irregular surface that a rising bubble may trap itself in the surface irregularities. A situation exists with this method which is analogous to a condition encountered under Method 1, which is the probability of contact between the rising air bubble and the relatively static floc structure. To increase the probability of contact, it has usually been found necessary to increase the size of the floc structure. The larger the floc diameter, the greater the probability that a rising air bubble will trap itself and not miss the floc structure or "flow around" the floc structure because of flow lines established around the rising air bubble.

Method 2 could be classified as a "screening operation". A great degree of discrepancy exists between laboratory and field results due to the "screening operation" of Method 2. In the laboratory the screening action is very prominent because of the static nature of the tests, whereas in the field the screening action

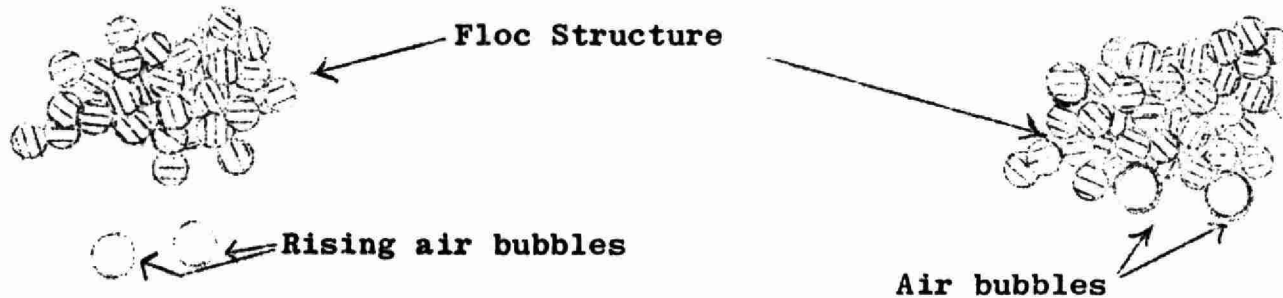
FIGURE 1

THREE METHODS OF DISSOLVED-AIR FLOTATION

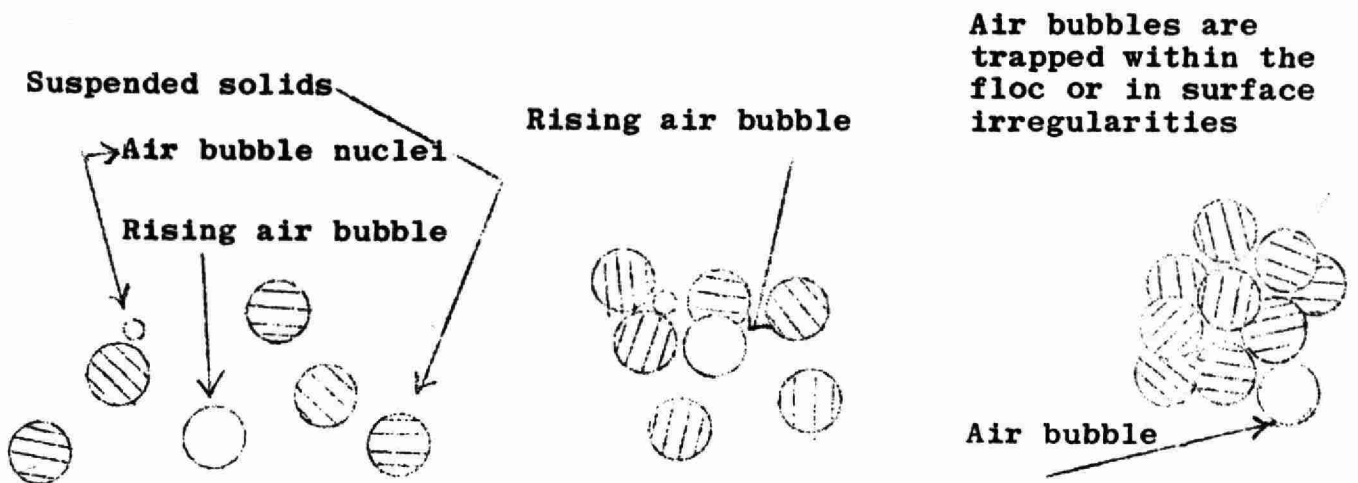
Method 1. Adhesion of an air bubble to a suspended liquid or solid phase.

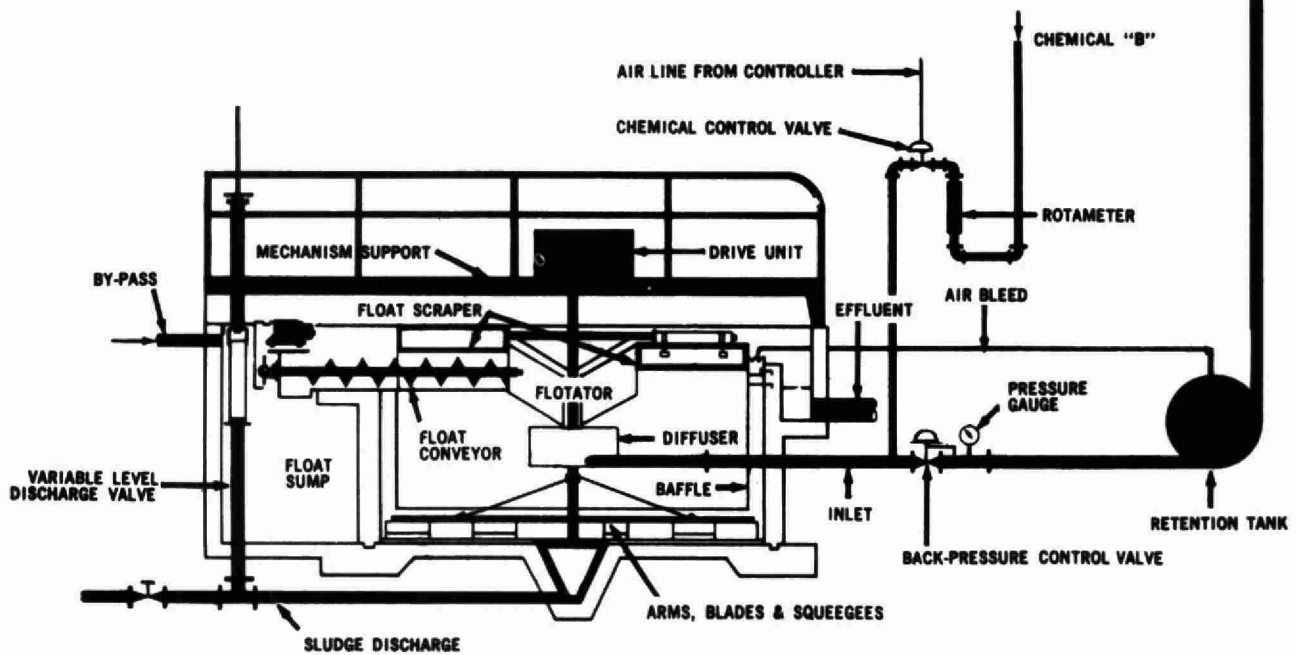
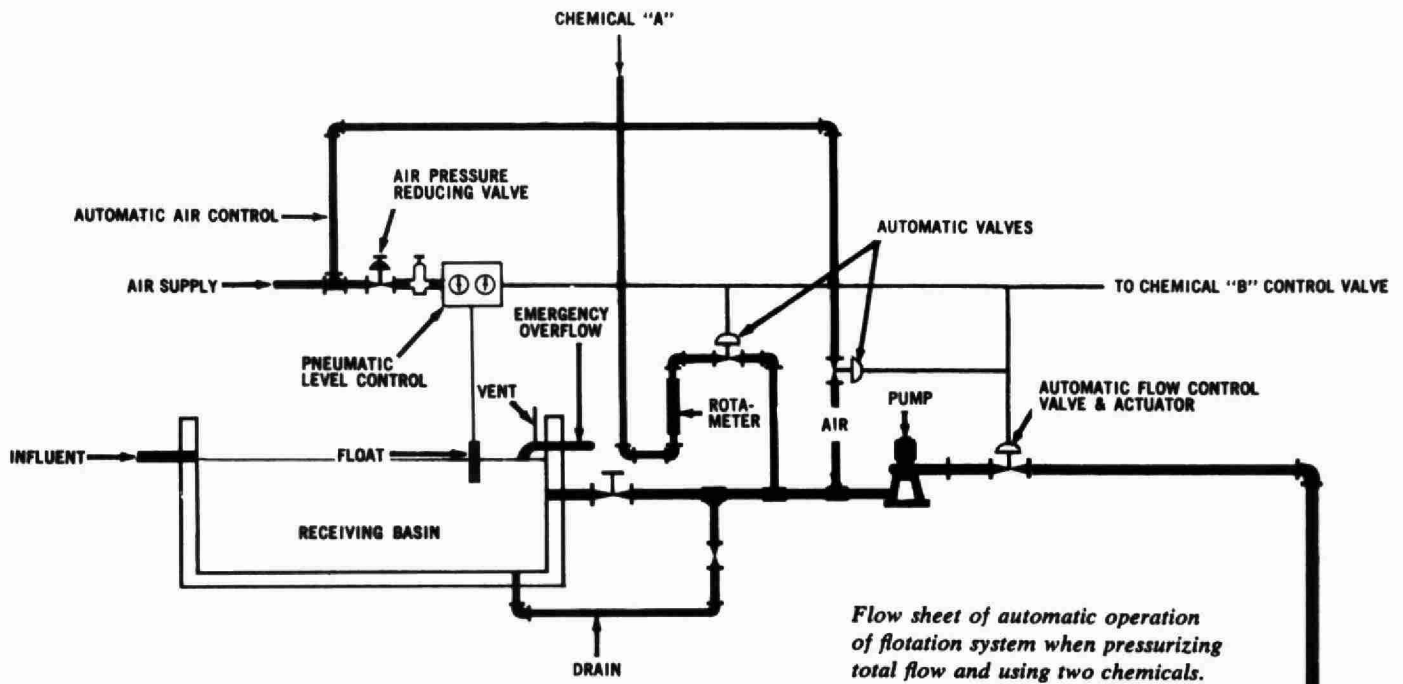


Method 2. The trapping of air bubbles in a floc structure as the air bubbles rise.



Method 3. The absorption and adsorption of air bubbles in a floc structure as the floc structure is formed.





is not appreciable due to the dynamic nature of the flowing treatment process.

Method 3 encompasses the formation of a floc around not only the suspended solid but also around the air bubbles. This permits the formation of nuclei on the surface of the suspended solid, trapping of rising gas bubbles in the surface irregularities of the floc and absorbing air bubbles in the floc structure itself. The formation of the floc around the air bubble or bubbles is accomplished by forming the flocs after the pressure has been released and the air is precipitating out of solution. The time necessary for the proper degree of flocculation required for dissolved-air flotation is usually less than 10 minutes, and the required retention times may be properly designed in Flotators.

Based on Stokes' Equation, if gas bubbles are united with the floc by a process of adsorption only, then doubling the diameter of the agglomerate would increase the rate of rise two-fold.

A limitation to increasing the diameter of the gas-solid combination exists, for as the combination is increased in size, the bulk density increases and may approach or exceed the bulk density of the liquid. This is one limitation to dissolved-air flotation by Method 2.

Again citing Stokes' Equation, the effect of doubling the diameter would increase the rate of rise four-fold if the bulk density of the agglomerate is maintained constant. This may be accomplished by absorbing the gas bubbles into the floc structure as the floc is formed (Method 3).

DESIGN OF DISSOLVED-AIR FLOTATION SYSTEMS

A flotation system utilizing the pressurization and de-pressurization sequence consists of the following elements:

1. Pressurizing pump
2. Air injection facilities
3. Addition of chemicals (if necessary)
4. Retention tank or contact vessel (if necessary)
5. Back pressure regulating device
6. Flotation unit

These are inter-related as shown by Figure 2.

1. Pressurizing Pump

The pressurizing pump creates an elevated pressure such that the increased solubility of air can be achieved in accordance with Henry's Law. Air is injected into the suction side of the pump. For achieving the maximum air solubility possible, two stages of pumping may be employed with air injection between stages. The usual range of pressures employed is from 30 to 60 psig.

2. Air Injection Facilities

One of the most effective methods to place air into solution is by injecting the gas into the suction side of the pressurizing pump.

Air volumes up to approximately 4 to 8% of liquid volumes may be injected into the suction side of a centrifugal pump without air binding. Submergence of the pump inlet is critical to air binding. A low submergence allows air binding to occur at a lower air rate. Air injection at a particular discharge rate lowers both discharge rate and discharge pressure. At constant air addition and high liquid flow rates, pump capacity decreases rapidly with increasing discharge pressure. Pump capacity diminishes less rapidly at higher liquid flows and pressures.

Eighty to 110% of the air required for saturation may be added to the pump suction without air binding.

Approximately 35 to 45% of the air added is dissolved when the air is added to the pump suction. To obtain 80 to 90% of theoretical air solubility, two stage pumping is employed with the injection of air between stages.

3. Addition of Chemicals

The addition of chemicals, when required, is a most significant step in the flotation process. Chemicals may be injected, depending upon where they are most efficient into various points along the process piping from the pressurizing pump to the Flotator.

The use of flocculating chemicals such as alum, activated silica, ferric chloride, etc. to form flocs which include air bubbles has been applied.

4. Retention Tank or Contact Vessel

The retention tank is used to afford time for injected air to attain maximum possible saturation, holding time is 30 to 60 seconds. Any free air in the flow is removed in the retention tank prior to entrance to the Flotator.

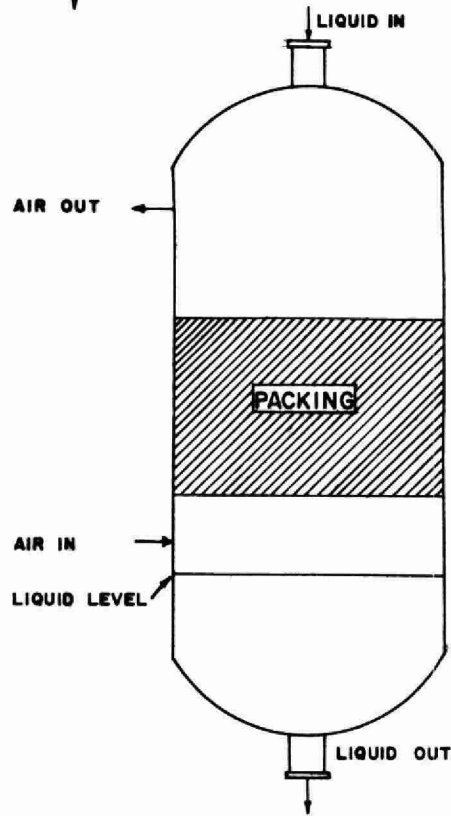
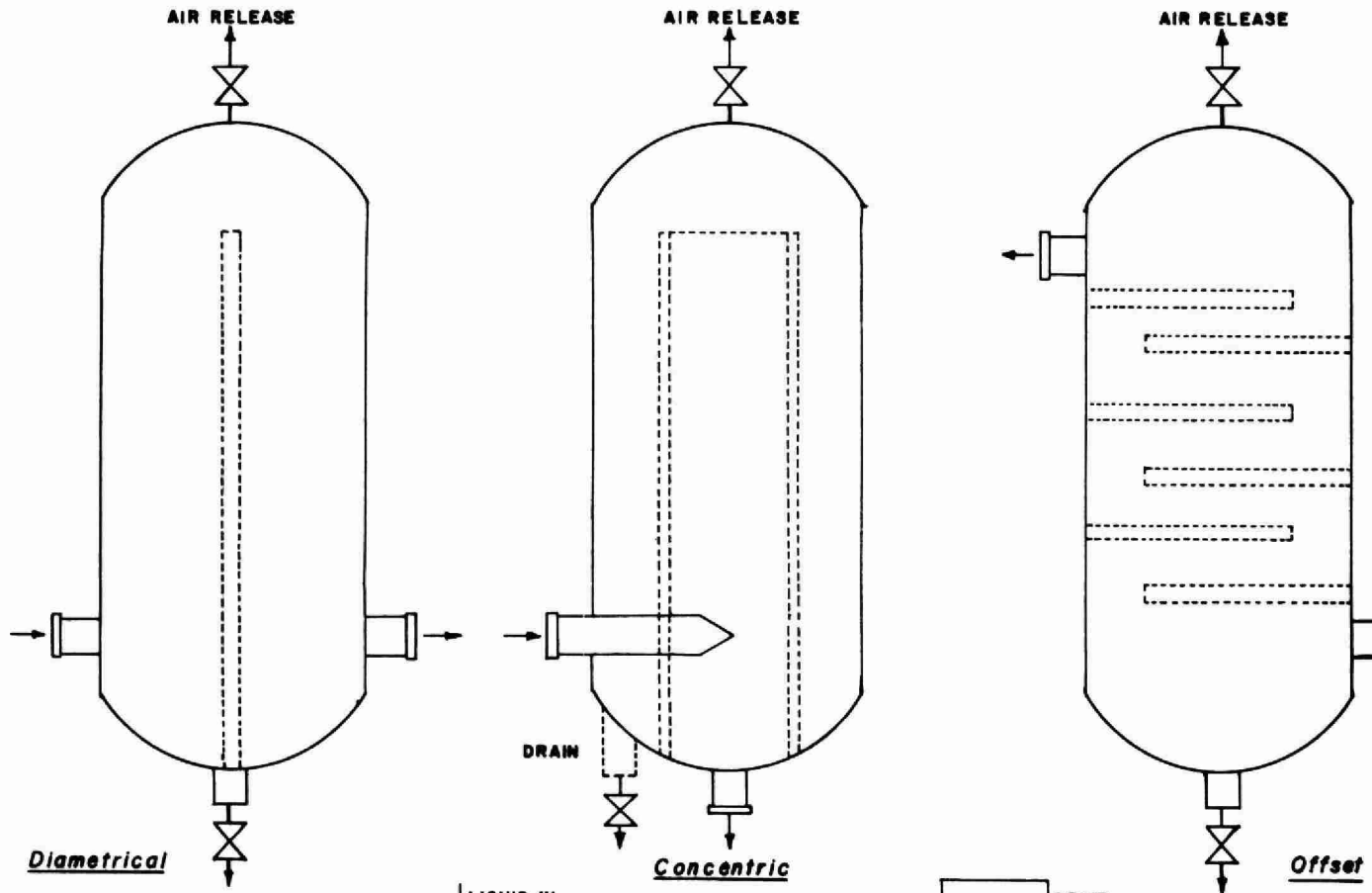
If the free air is not removed, Flotator efficiency will be greatly impaired. Figure 3 illustrates various retention tank baffling arrangements. Each arrangement has a specific application, depending upon the ease of gas solubility and nature of the process stream.

If two stages of pumping are employed, because of increased efficiencies, retention tanks or contact vessels are not necessary. The static designs are employed when air solubility values, at the elevated pressure, below 50% of theoretical are acceptable. The dynamic designs are

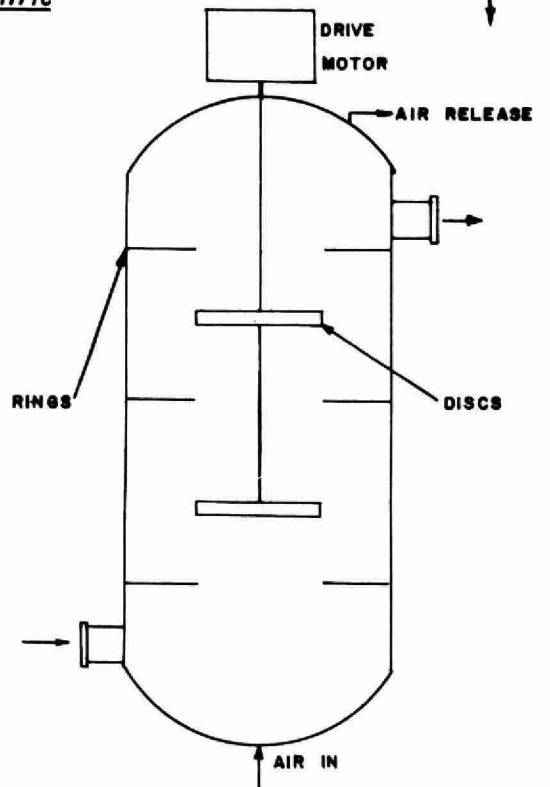
FIG. 3

RETENTION TANK ARRANGEMENTS

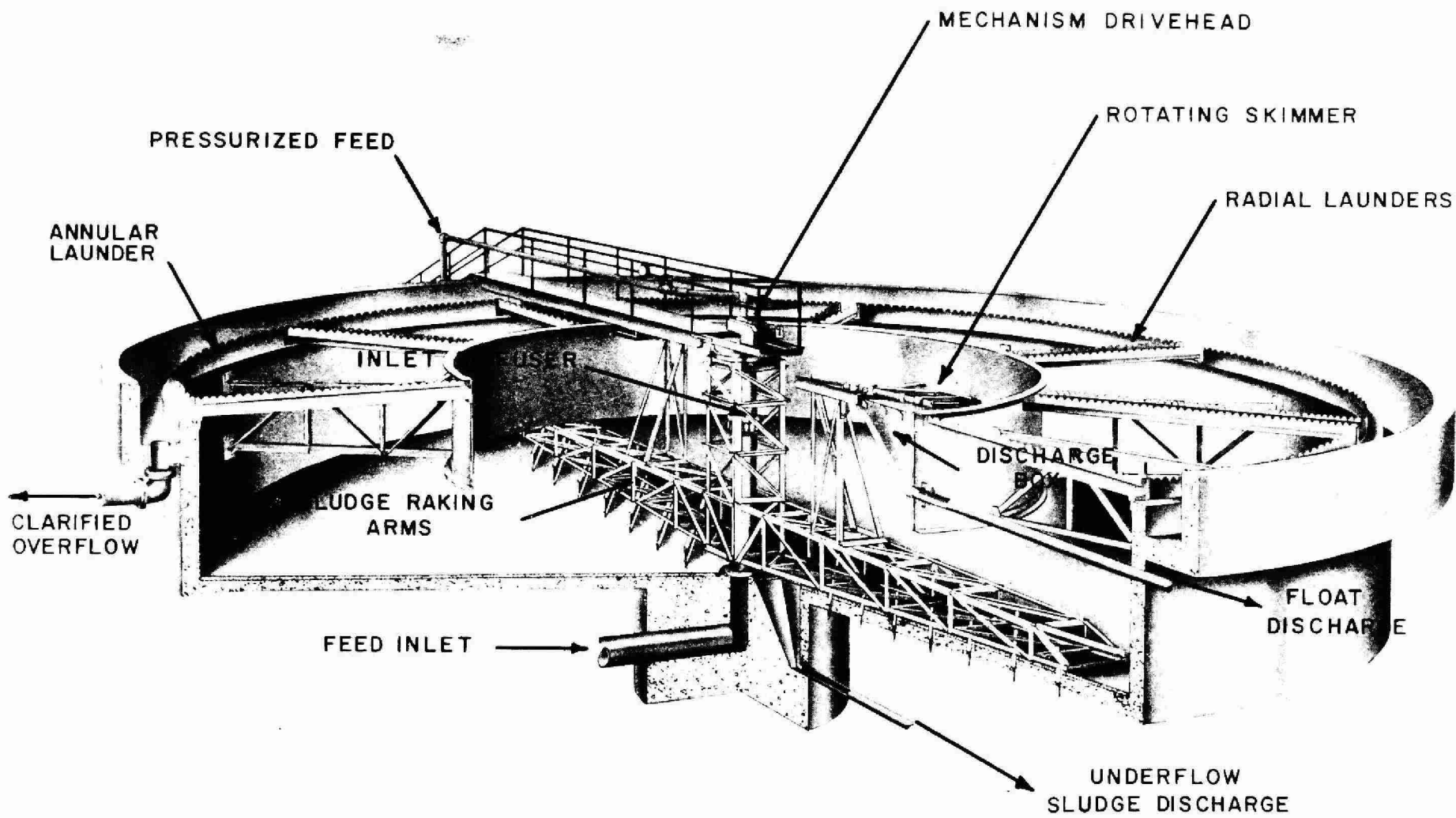
STATIC DESIGNS



Packed Tower Design



Dynamic Design



FLOTATOR CLARIFIER

employed for achieving air solubility values greater than 90% of theoretical. The solubility values are based on the amount of air dissolved in the retention tank effluent and do not include any free air, present as finely dispersed bubbles. The free air present in the static type retention tank discharge represents approximately 33% of the total air present in the discharge. The turbine type retention tank has indicated aeration efficiencies of 90% or greater. The packed tower has not yet been investigated, but it is felt that extensive retention times, i.e. large towers, will be necessary in order to obtain 90% plus aeration efficiencies.

5. Back Pressure Regulating Device

The back pressure regulating device maintains as nearly constant a discharge head on the pressurizing pump as is possible. Usually a Saunders-type flexible diaphragm valve is employed. If a constant, non-corrosive flow is anticipated and no large solids are present, a plug or gate valve may be employed.

6. Flotation Unit

Dissolved-air Flotators may be classified as either Flotator-Clarifiers or Flotator-Thickeners.

- A. Flotator-Clarifiers accomplish flotation in an inner circular compartment which is surrounded by a circular clarification zone.

Clarification units in sewage and waste treatment plants are normally sized for average flows on the basis of overflow rate and detention. The concentration of suspended solids is relatively small and most of these solids settle quickly to the sludge zone. However, the near-colloidal material has a slow settling rate and requires the greater part of the tank area and volume for its removal.

By removing the slow settling solids through flotation, the Flotator-Clarifier materially reduces the size of the clarification compartment. The suspended particles that settle slowly, tend to float, or stay in suspension are floated, concentrated and skimmed from the center flotation compartment. The heavier solids settle to the bottom where a conventional raking mechanism moves them to the center for discharge. This new concept in clarification has been proven in a number of installations to operate with excellent results.

Flotation and sedimentation are easily accomplished by properly designing the diameters of each compartment. Figure 4 illustrates a Flotator-Clarifier.

- B. Flotator-Thickeners have only a flotation compartment. They are designed to remove floatable solids plus any solids which are non-floatable and may settle during

the retention time allowed for flotation.

Figure 5 illustrates a Flotator-Thickener. The design shown by Figure 5 also highlights the submerged tangential feed-well design which offers uniform distribution of the feed into the entire contents of the tank. The direction of motion imparted by the tangential inlet permits maximum utilization of the volumetric contents of the feedwell. It is in this feedwell that proper contact is made between the suspended solids and their air bubbles. Retention time in the feedwell is designed to accommodate floc formation around the air bubbles as well as the suspended solid or liquid phase. By placing the feedwell inside the flotation tank, once the air-solid bond is formed, the agglomerate is allowed to flow into the flotation compartment with essentially no turbulence, which would not be the case if the agglomerate had to pass through a perforated baffle or under a solid baffle. The adhesive bonds which are formed in addition to the flocs are fragile, and excessive turbulence or shear would destroy the bond or the floc structure.

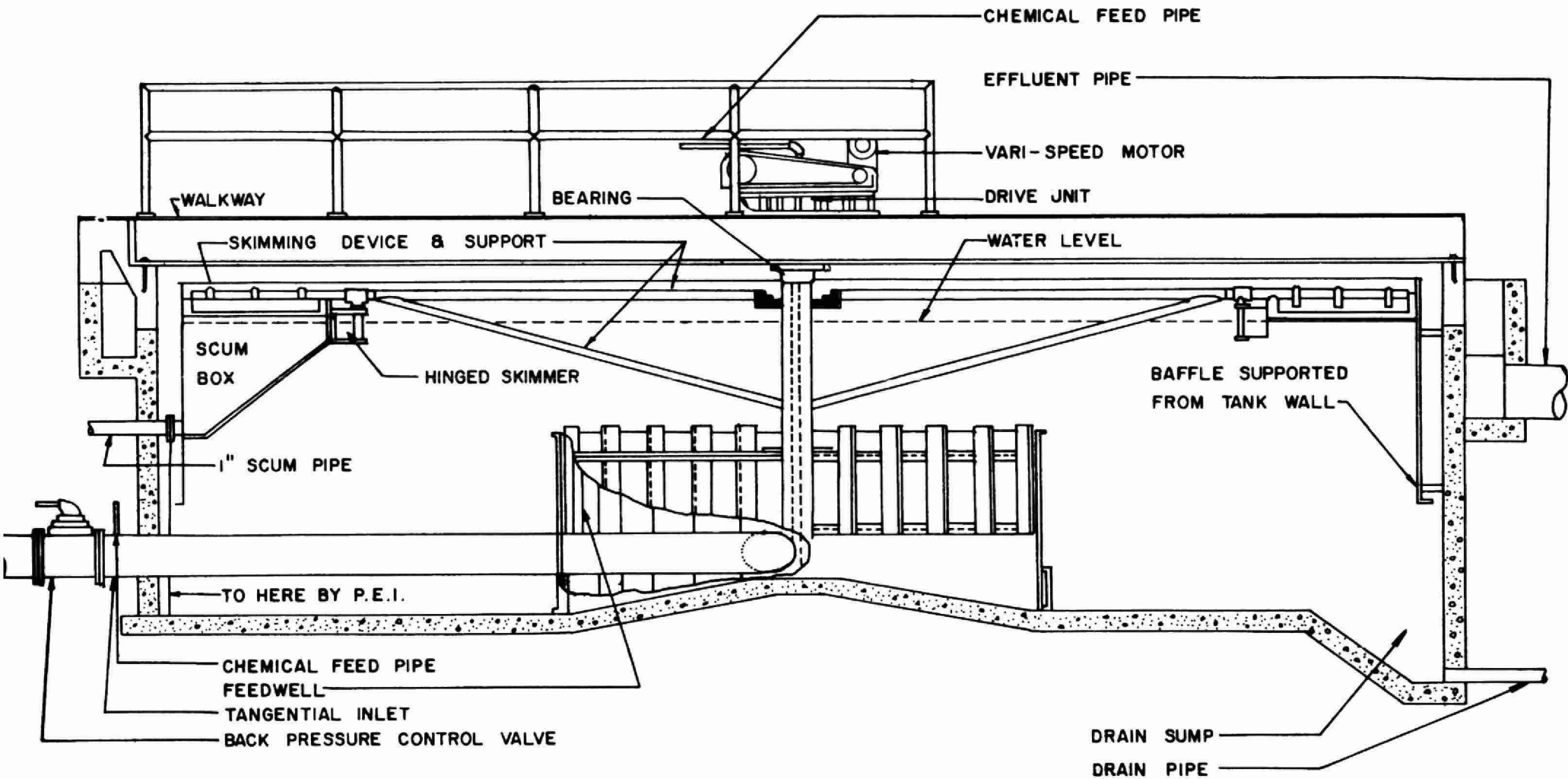
- C. Common Design Features - An important design feature is the horizontal run of pipe going straight into the feedwell; the absence of any elbows minimizes coalescence of air bubbles.

Total pressurization and partial flow-pressurization are two possible arrangements which may be made for dissolved-air flotation.

When total pressurization is employed, the entire waste stream is pressurized. Operation of a flotation unit where only a portion of the feed or a portion of the flotation unit effluent is pressurized is termed partial pressurization. The stream that is pressurized under a partial pressurization system is blended into the unpressurized stream.

The blending of the pressurized stream with the unpressurized stream represents a critical step in the dissolved-air flotation process. The concentric partial pressurization piping used in connection with the submerged tangential inlet is shown by Figure 6. The pressurized stream is contained within the inner pipe and flows at a velocity which exceeds the velocity of the unpressurized flow, which is contained in the outside pipe. The pressurized stream, due to the difference in velocities, diffuses in a jet stream pattern into the unpressurized stream and thereby permits maximum blending of the two streams. The

FIGURE 5
FLOTATOR - THICKENER



pressurized pipe is terminated a calculated distance from the entrance to the feedwell, a design feature which results in all of the diffusion taking place in the pipe line. The feedwell is for uniform distribution of the feed, to permit more gas bubble-suspended solids contact, and also to minimize short-circuiting and streaming within the flotation unit.

THREE SYSTEMS OF FLOTATION

Three systems used for partial and total pressurization are shown by Figure 7.

In the total pressurization system, variations in flow, if they exist, are regulated by an automatic back pressure valve which receives a signal from a level recorder placed in the pressurizing pump sump.

If large variations in flow exist, a method indicated by the partial pressurization of feed diagram shown on Figure 7 may be employed. Any flow which cannot be handled by the pressurizing pump is allowed to overflow the pressurizing pump sump and flow by gravity directly to the Flotator. Several field installations have indicated the beneficial aspects of this type of design.

A second method of partial pressurization consists of pressurizing a portion of the Flotator effluent and blending this stream into the unpressurized feed. Caution must be exercised in employing this system if a constituent is present in the effluent which represents a phase that is unfloatable. If the portion of the effluent leaving the flotation unit is not sufficient for removing the unfloatable matter at a rate equal to the quantity of unfloatable matter entering the flotation machine, a buildup of the unfloatable matter will occur. When equilibrium is finally achieved i.e. when the quantity of unfloatable matter entering the unit equals the quantity leaving in the effluent stream, the quantity of unfloatable matter being recirculated may be of such a significant amount that flotation is greatly impaired.

To obtain the power consumption and quantity of gas required for either partial or total pressurization, a straightforward example may be employed. There are two criteria which may be used in the sample calculations. One is that the same solids-to-air ratio is desired and the other, which is based on the probability of gas-bubble-suspended solid collision, is that the concentration of gas bubbles per unit volume of liquid should be the same. Table I indicates the calculations employed and is based on several assumptions: (1) the feed is either saturated or unsaturated with the gas phase, (2) 100% saturation of the air phase is accomplished

FIGURE 6

PARTIAL PRESSURIZATION FEEDWELL

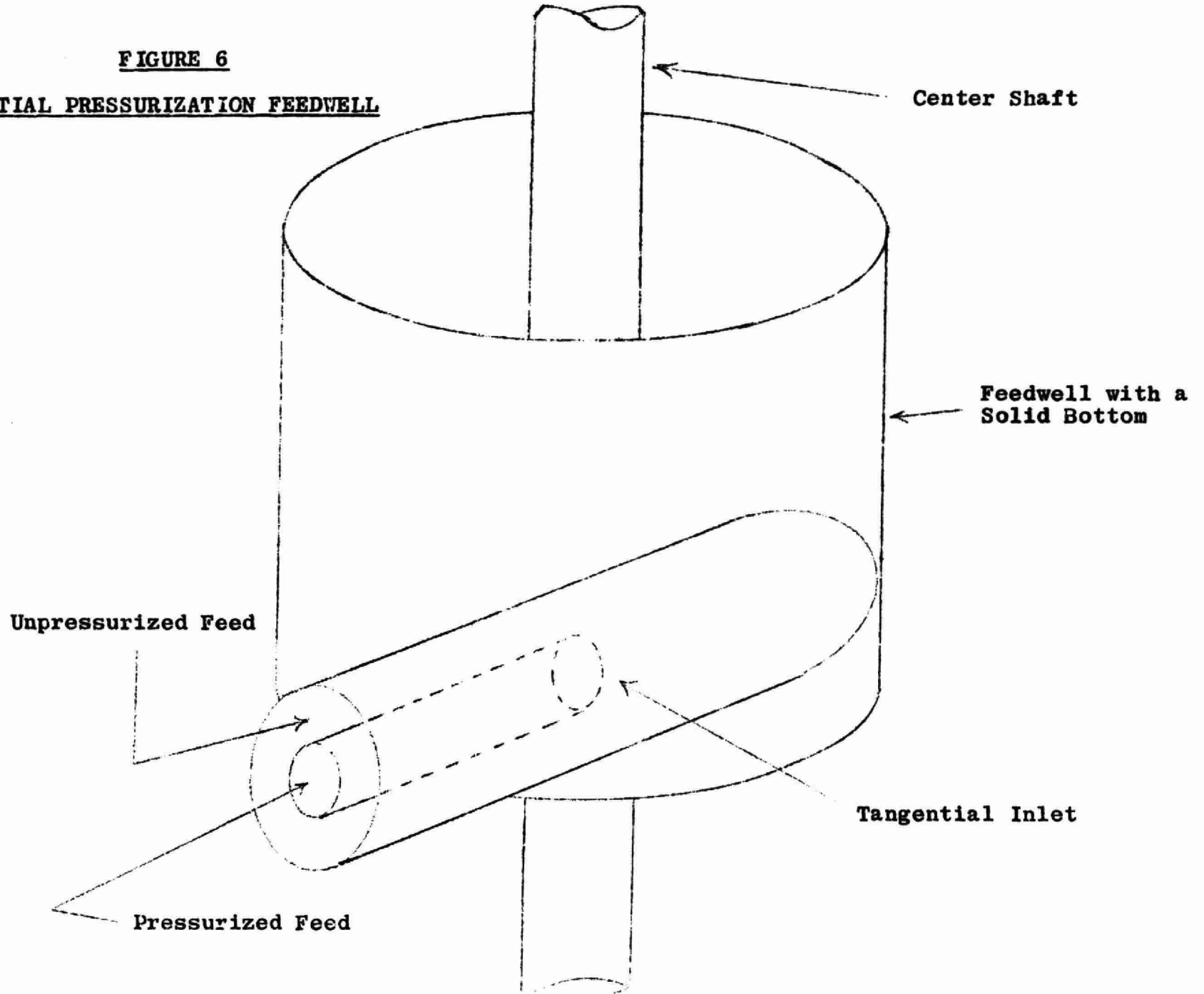
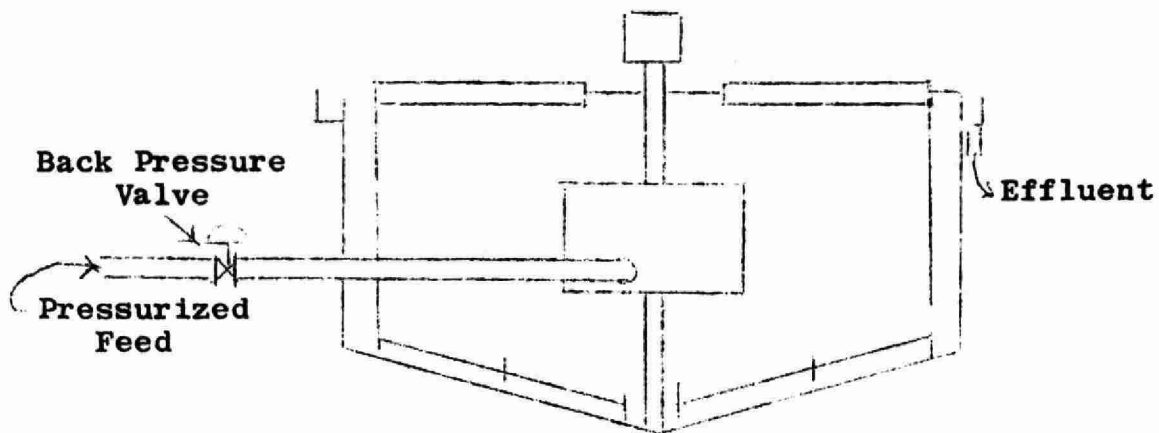
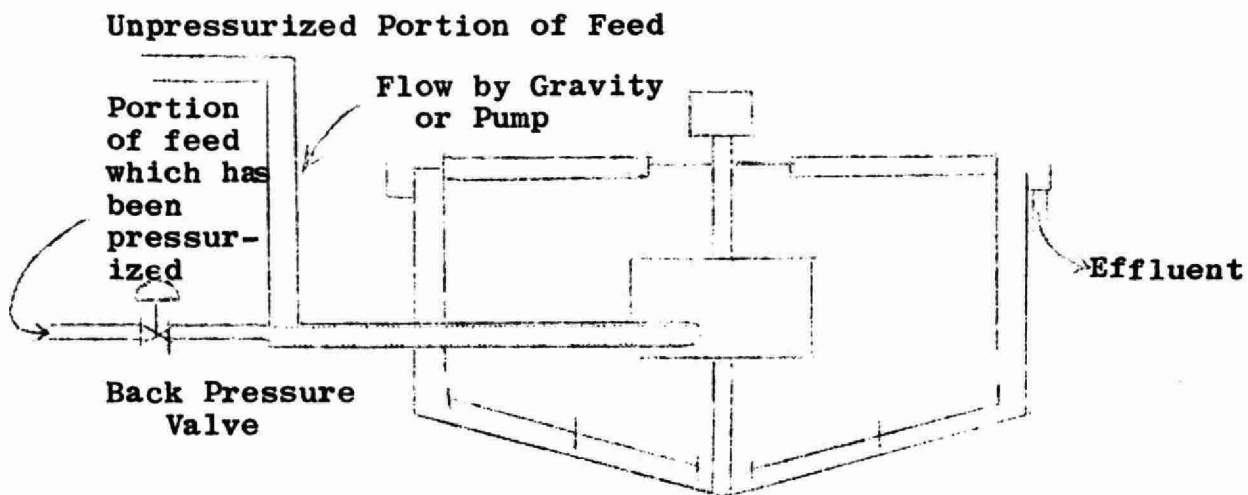


FIGURE 7

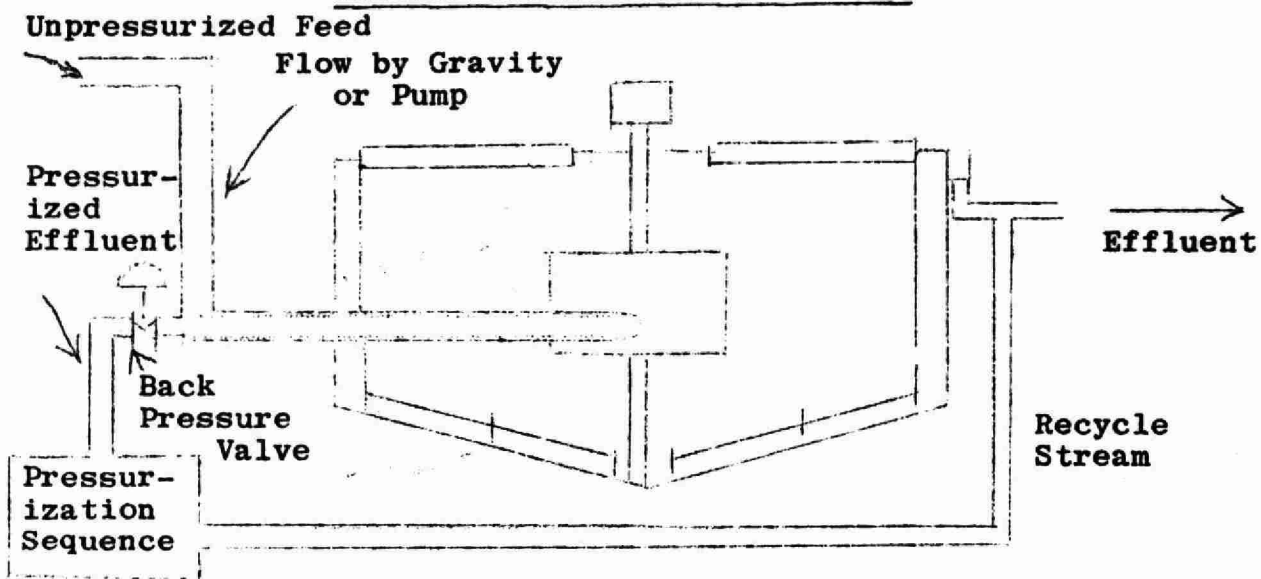
Methods Employed For Partial And Total Pressurization



Total Pressurization



Partial Pressurization of Feed



Partial Pressurization of Effluent

by the pressurizing system, (3) Henry's Law applies, and (4) the flow leaving the flotation unit is either saturated or partially saturated with the gas phase.

The results of Table I indicate that, with recirculation of the effluent or pressurization of only a portion of the feed, higher aeration pressures must be resorted to in order to maintain the same solids-to-air ratio that may be obtained with total pressurization. It is significant that if recirculation of the effluent is employed and it is desired that the concentration of air bubbles be the same as when total pressurization is employed, greater amounts of gas must be dissolved and consequently greater aeration pressures employed.

The partial pressurization system is employed where higher solids to gas ratios are permissible and where the required concentration of gas per unit volume of liquid is also low.

A disadvantage to partial pressurization of the effluent results because the flotation surface area must be increased to accommodate the quantity of flow being recirculated. Field experience has shown that the limitation to the sizing of a flotation unit is usually a hydraulic one. Laboratory tests, under static conditions, have indicated that overflow rates of 5 to 6 gpm per square foot of surface area should be permissible, whereas field operations indicate that the correct hydraulic rate is 1.5 to 2.5 gpm per square foot. Therefore, if 50% by volume of the effluent is recirculated, the flotation unit would have to be increased in surface area by almost 50% as the surface loading must be maintained at its maximum permissible hydraulic loading of approximately 1.5 to 2.5 gpm per square foot.

The maximum permissible surface loading rates are a function of tank diameter, rate of rise of the gas-solid agglomerate, and fluctuations in feed characteristics.

DESCRIPTION OF DISSOLVED-AIR FLOTATION SYSTEMS

Examples of dissolved-air flotation units are discussed and shown by photographs contained in this section.

The examples chosen illustrate total pressurization as well as the two different methods of partial pressurization. The photographs indicate the special engineering designed into flotation units - engineering which is based on the specific requirements of the particular problem.

Oil Refinery Waste

The photograph illustrates a 40 foot diameter unit which is handling over 1000 GPM of flow from a 40 foot diameter preskimming clarifier. The system utilizes total pressurization; however, any flow which cannot be handled by the pressurizing pump simply overflows the sump preceding the pressurizing pump and gravity flows to the flotation unit where the unpressurized stream is effectively blended with the pressurized stream.

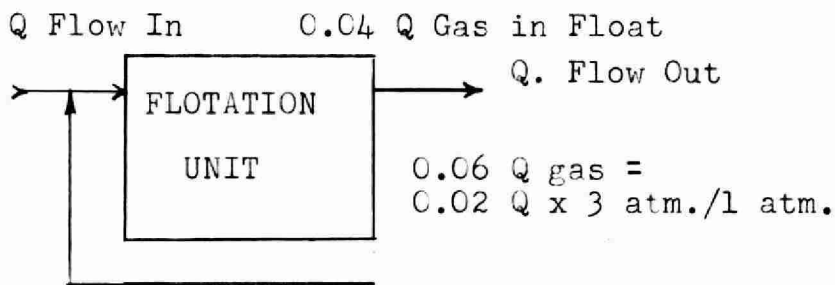
TABLE 1

SAMPLE CALCULATIONS OF GAS QUANTITIES AND PUMP PRESSURE

REQUIRED FOR TOTAL AND PARTIAL PRESSURIZATION

BASES: For examples of partial pressurization, either 50% of the feed is pressurized (Item 2 below) or an effluent stream equal in volume to 50% of the feed is pressurized (Item 3 below). Flow rate has a volume equal to Q. The solubility of gas in the liquid is equal to 0.02 Q by volume at atmospheric pressure (solubility similar to air in water). Initial assumption is made that three atmospheres (absolute) required for total pressurization. Values in brackets indicate operation where the flow leaving the flotation unit is saturated with the gas at atmospheric pressure.

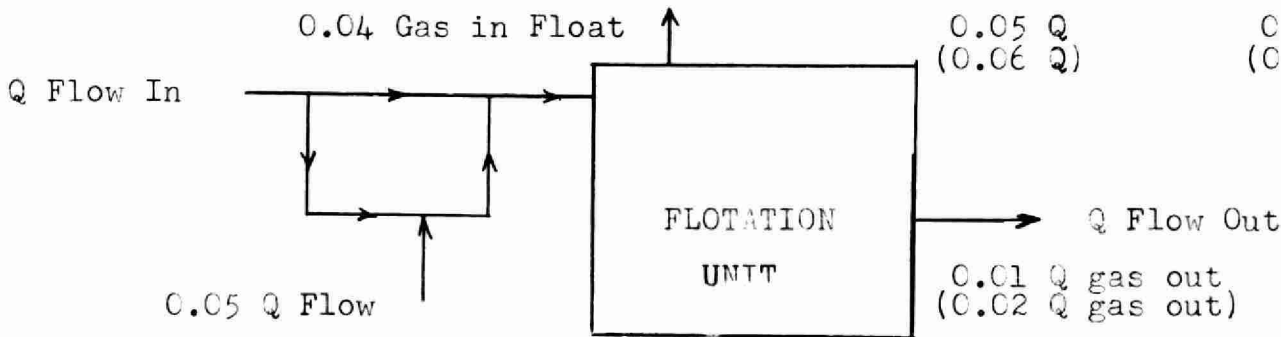
1. Total Pressurization.



<u>Amount of Gas Required For</u>	
<u>Constant Solids/Air Ratios</u>	<u>Constant Air/Liquid Volume Ratio</u>
0.06 Q	0.06 Q

Pump Discharge Pressure, Atmospheres Absolute
3 Atmospheres

2. Partial Pressurization of 50% of Feed.



0.05 Q	0.05 Q
(0.06 Q)	(0.06 Q)

5 Atmospheres
(6 Atmospheres)

$$0.05 Q = 0.04 Q + 0.02 \text{ (0.5Q)}$$

$$(0.06 Q = 0.04 Q + 0.02 \text{ (1.0Q)})$$

Over 80% of the free-oil going to the flotation unit is removed as float, and the float consists of 80-90% oil by volume. Tests conducted on both the pressurizing pump feed and Flotator effluent indicate that the pump does not increase the emulsified oil content of the process stream.

Flotator effluents, with no chemical addition, range from 50-60 ppm total oil of which 25 ppm is emulsified oil. If chemical addition were employed, Flotator effluents would be less than 25 ppm total oil.

Other oil refinery waste treatment plants, which are not pictured, include two 35 foot diameter Flotators which employ the total pressurization method and are preceded by two 90 foot diameter pre-skimming tanks. The Flotators reduce the total oil content, without any chemical treatment, from 100-125 ppm to 30-45 ppm. Total flow to the Flotators is 2000 GPM.

Another refinery installation consists of a 24 foot diameter Flotator which treats the effluent from a 30 foot diameter preskimming clarifier. The Flotator handles 500 GPM of waste water. For this particular installation total pressurization is employed, and the Flotator recovers 80-90% of the free oil in the Flotator feed without chemical addition. The float removed from the unit is approximately 100% oil, by volume.

Where chemical treatment of the refinery waste is necessary, Flotator designs similar to Figure 5 have been recently installed.

One of the most important advantages of flotation units for the treatment of a refinery waste is that the Flotator is capable of producing an effluent of 30-60 ppm total oil without any chemical treatment. If effluents of 25 ppm total oil are required, then chemical treatment must be used. However, where biological treatment units are to follow the flotation units a 30-60 ppm total oil Flotator effluent is acceptable.

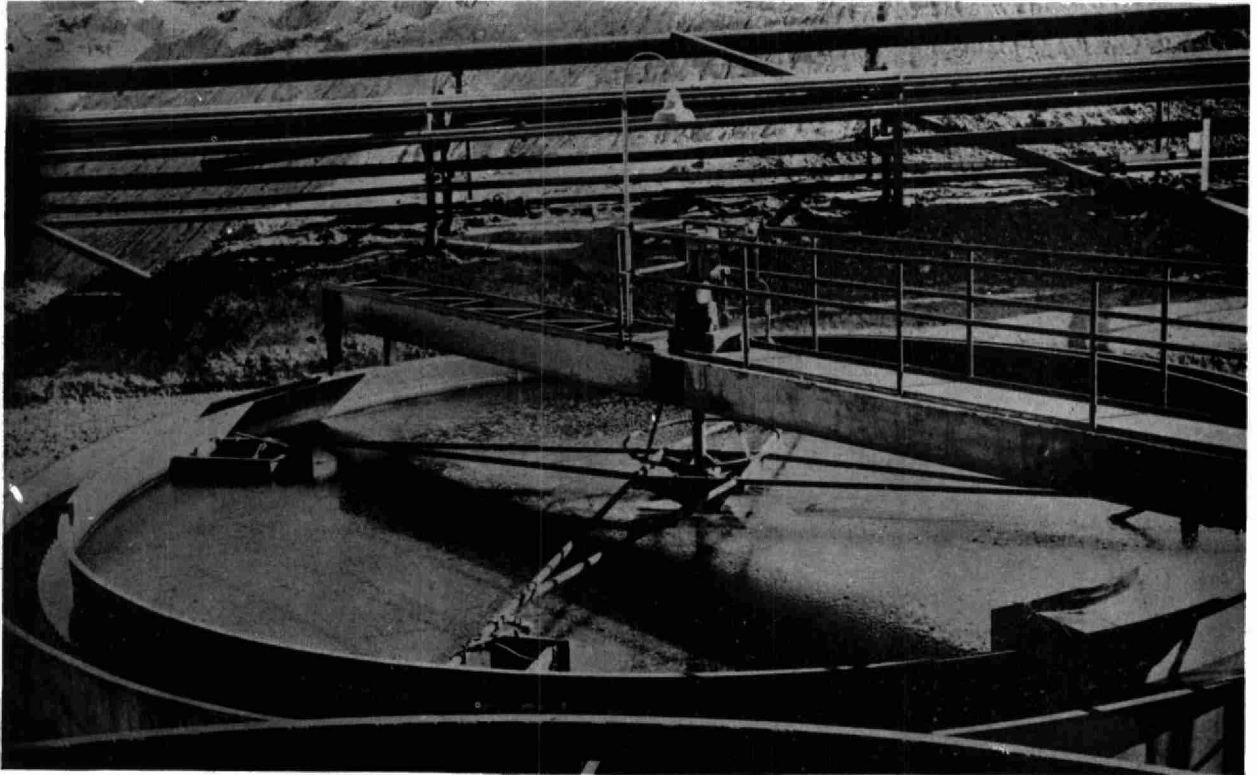
Rendering Plant Waste

This unit is 6 feet in diameter and handles a flow slightly less than 100 GPM. The unit is capable of removing 90% + of the total fat contained in a feed which averages 4000 ppm total fat. The 5-day BOD is reduced by over 90%, from 7000 ppm to 500 ppm. The Flotator skimmings contain 10% solids which partly consist of 20% crude protein and 60% crude fat (on a moisture free basis). In this instance, total pressurization is employed.

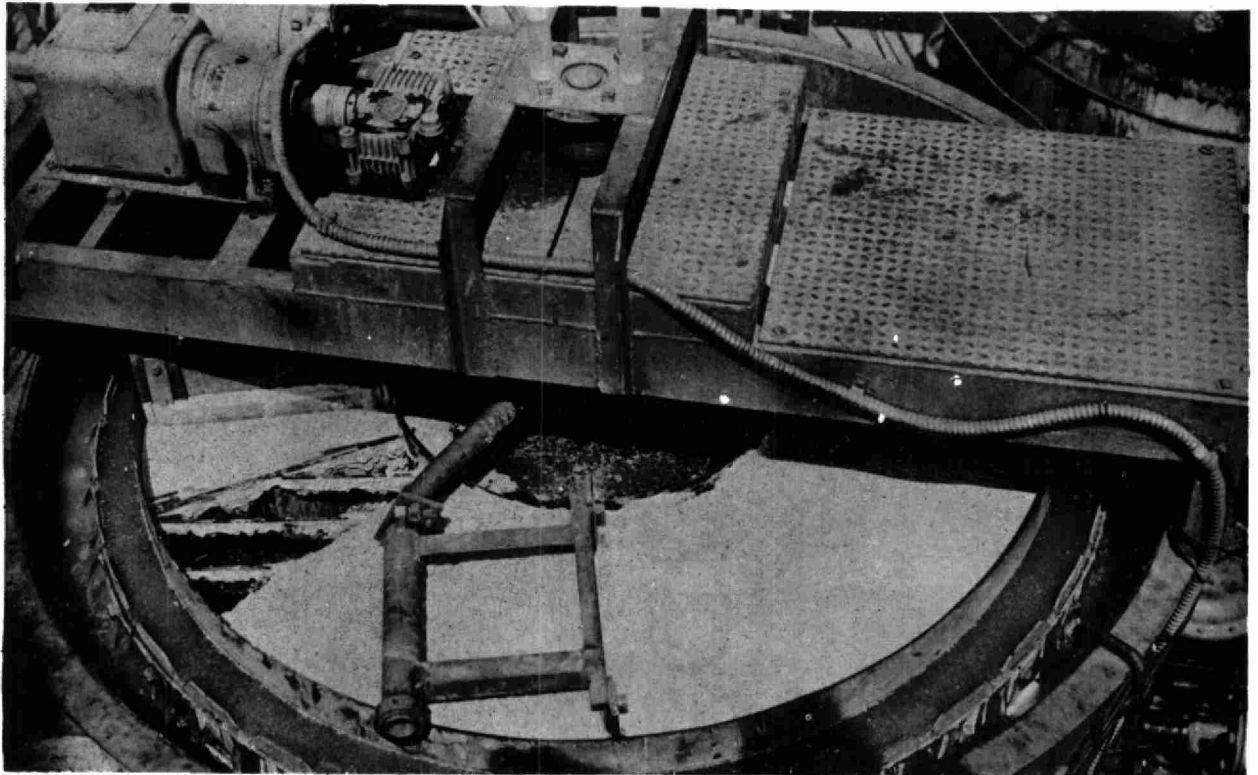
Steel Mill Oily Waste

The flow to this total pressurization Flotator-Clarifier is approximately 200 GPM. The flotation compartment has a diameter of 10 feet and the overall diameter is 20 feet.

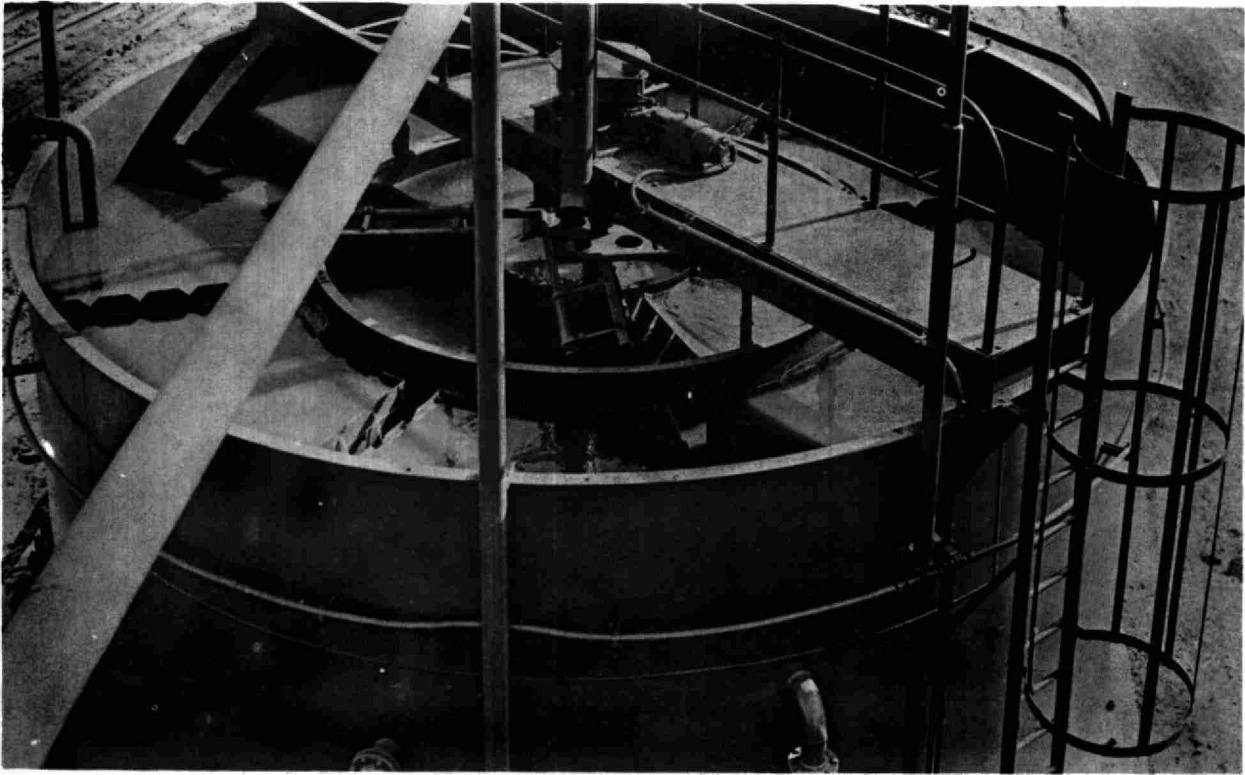
The application is to recover oil and oil-coated particles by flotation and to allow mill scale to settle out in the clarification compartment. Approximately 90% of the free oil is removed in the flotation compartment.



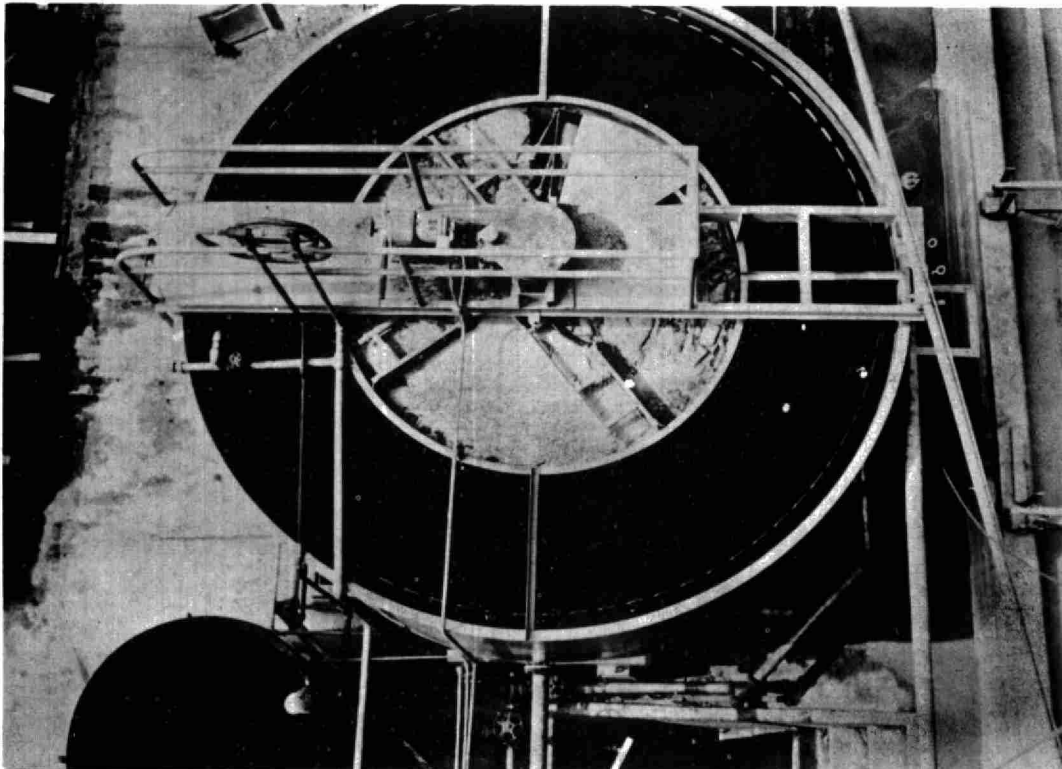
OIL REFINERY WASTE



RENDERING PLANT WASTE



SHEET MILL OILY WASTE



SLAUGHTER HOUSE WASTE

Slaughter House Waste

A rate of 250 GPM is fed to this 9 foot diameter flotation compartment in this 16 foot diameter Flotator-Clarifier.

Results have indicated 95% plus removal of ether-soluble matter (initial values approximately 4000 ppm), 90% plus removal of suspended solids (initial values approximately 6000 ppm) and a 50% plus removal of 5-day BOD (initial values approximately 3000 ppm).

This unit is a total flow pressurization system.

Sewage With Oil-Bearing Industrial Waste

Each unit has an 18 foot diameter flotation compartment and a 35 foot overall diameter. The Flotator-Clarifiers are partial pressurization units with effluent recirculation and are rated at 700 GPM per unit. The flotation operation removes 95% plus of the free oil contained in the oil-bearing industrial waste.

The application of a Flotator-Clarifier as a primary treatment unit in a sewage treatment plant, where the domestic sewage contains a floatable industrial waste, represents a very advantageous adaptation of flotation to the characteristics of sewage.

Sewage With Seasonal Fruit Cannery Waste

A flow of 130,000 GPD is fed to this 32 foot diameter by 13 foot SWD partial pressurization (of the effluent) Flotator-Clarifier. A fruit cannery waste is present in the sewage, and the removal of the bulk of solids in this waste is accomplished by the flotation process.

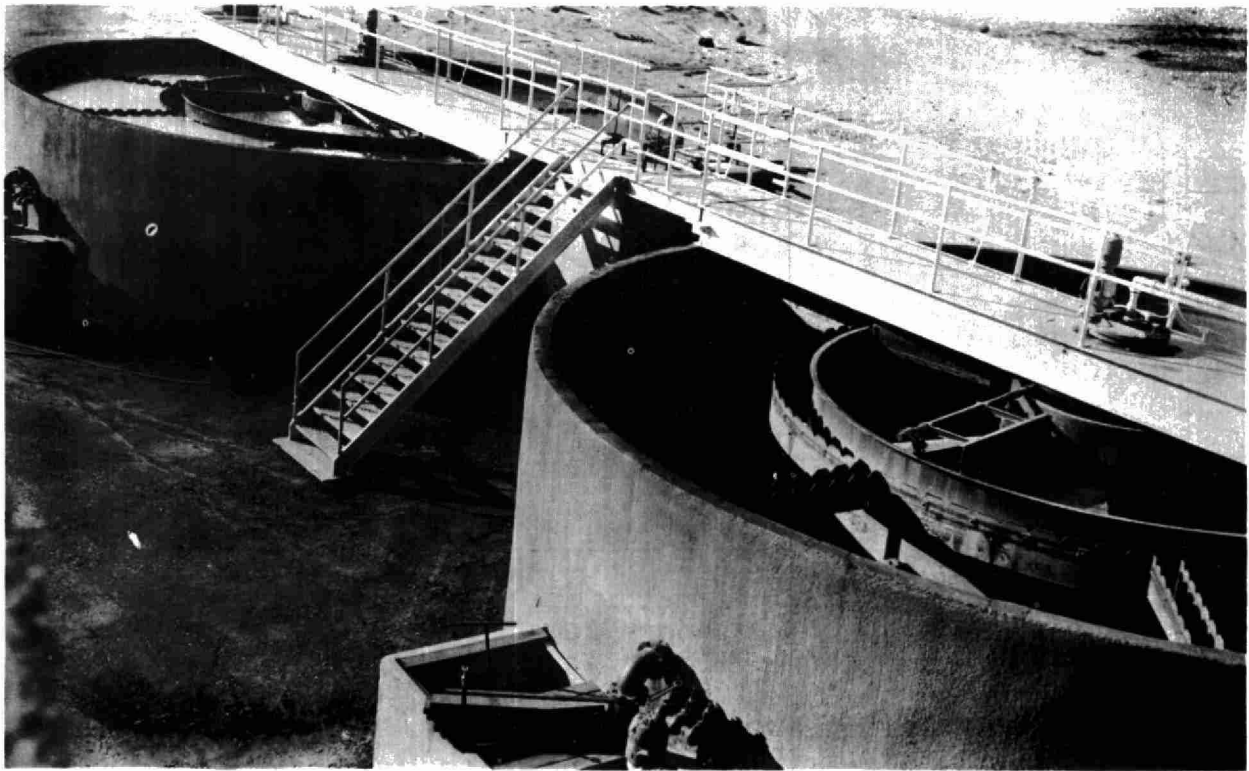
BOD (5-day) removals vary from 42 to 73.5%; suspended solids removals vary from 57.3 to 88% with a float averaging 9.5% solids of which 75.5% are organic. The underflow averages 1.1% solids and 55.7% organic.

Waste Activated Sludge

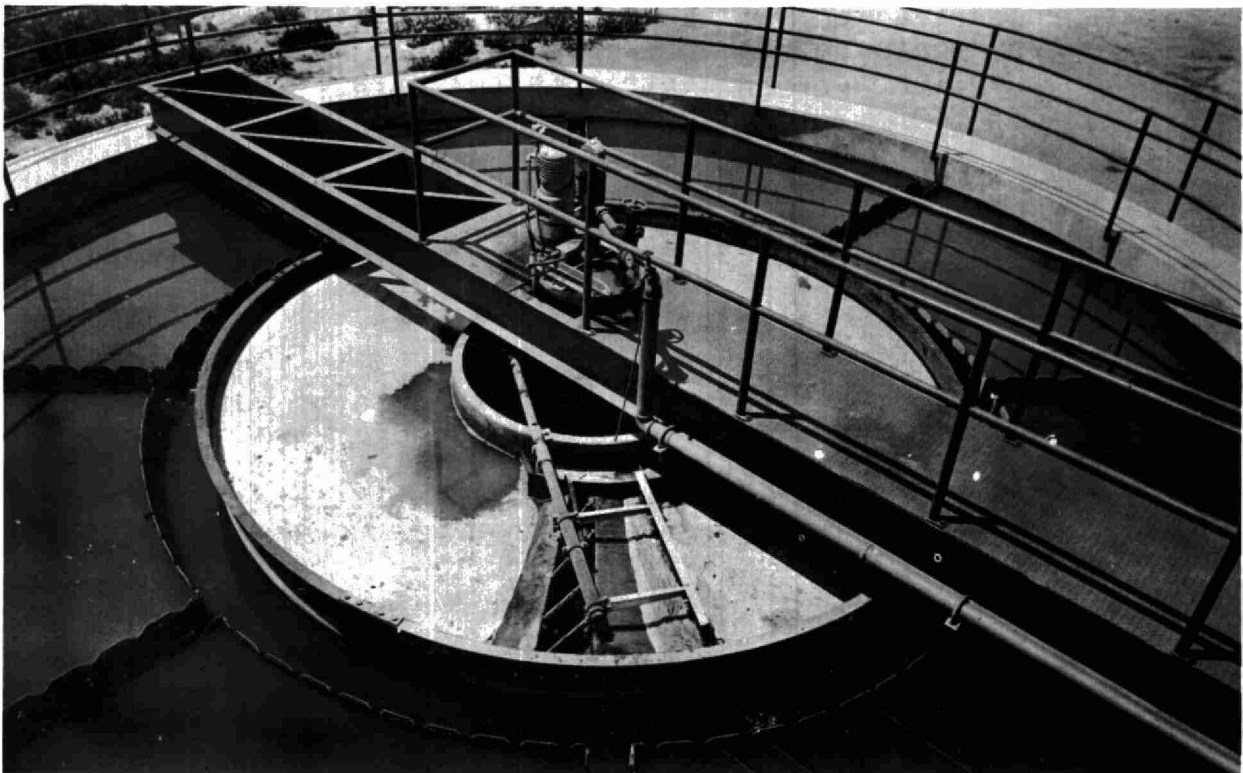
The 8 foot diameter total pressurization Flotator which is shown concentrates a 5000 ppm waste activated sludge stream to a 3 to 4% float. Percent recovery of suspended solids is over 90%. The dissolved-air flotation unit is capable of obtaining solids concentrations 2 to 3 times greater than what can be obtained by sedimentation in a final clarifier.

The unit is fed at a rate of 60 GPM.

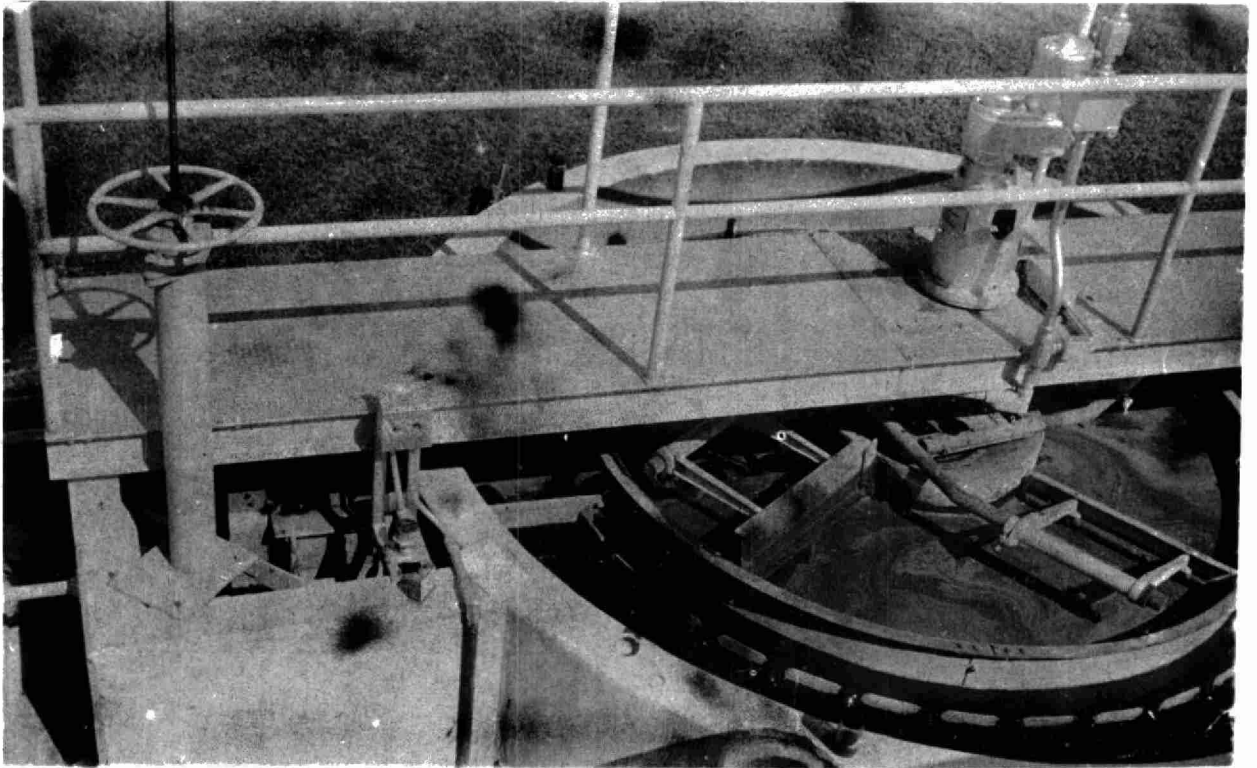
Additional installations not pictured include a 16 foot diameter total pressurization Flotator handling 250 GPM of 3000-5000 ppm feed. The float from this unit has averaged 4 to 5% solids and the suspended solids recoveries are 85-90%.



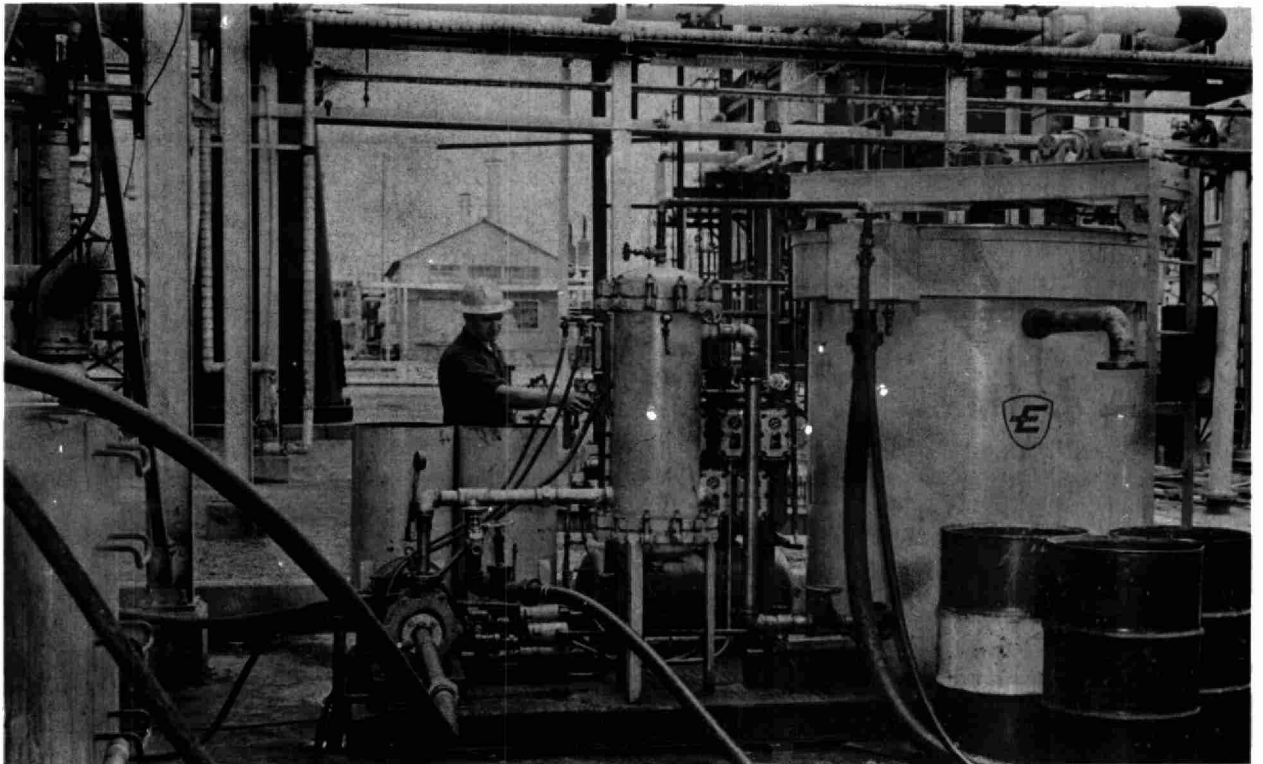
SEWAGE WITH OIL BEARING INDUSTRIAL WASTE



SEWAGE WITH SEASONAL FRUIT CANNERY WASTE



WASTE ACTIVATED



PILOT PLANT FLOTATOR

Pilot Plant Flotator

The pilot plant Flotator unit shown is fabricated on a structural steel base supporting all the necessary equipment for complete dissolved-air flotation investigations. The components which contact the process liquid are all fabricated of stainless steel. All that is necessary for the operation of this unit is a feed line, electricity, and pressurizing pump seal water. The unit has facilities for feeding two chemicals and has its own pressurizing pump and all necessary metering devices. Both total and partial pressurization investigations may be made.

Aircraft Maintenance Waste

A preskimming clarifier is followed by a 13 foot diameter by 10 foot SWD Flotator designed for optimum operation of 267 GPM with a hydraulic capacity of 900 GPM. Partial pressurization of Flotator feed is employed with excess flows overflowing the pressurizing pump sump and mixing with the pressurized stream in the Flotator.

The waste is composed of wash water, free oils, solvents and other wastes from aircraft maintenance shops.

Activated silican and alum are employed to reduce the ether-soluble oil from 200 ppm in the Flotator feed to 20 ppm in the effluent.

Chemical treatment is employed using 30 ppm alum and 10 ppm activated silica.

Primary Sewage Treatment Plant (A cut-away drawing of this unit is shown by Figure 4 of this paper)

The Flotator-Clarifier is 70 feet in overall diameter and has a 9 foot SWD.

Partial pressurization is employed with a portion of the effluent being pressurized and blended with the influent.

The float from this unit contain 6.7% solids which are 87.6% volatile and the underflow contains 3.7% solids which are 79.5% volatile. This illustration together with a previous Flotator-Clarifier illustration indicates considerably higher organic content in the float than in the underflow of a Flotator-Clarifier.

The application of flotation principles to several industrial waste treatment problems is summarized by Table 2.

TABLE 2
APPLICATION OF FLOTATION PRINCIPLES TO SEVERAL
INDUSTRIAL WASTE TREATMENT PROBLEMS

<u>Type of Waste</u>	<u>Constituent to be Removed</u>	<u>% Removal</u>
<u>Total Pressurization</u>		
Oil Refinery	Oil	80-95 (no chemical treatment)
Rendering Plant	5-day BOD	90
	Fat	90+
Steel Mill	Oil	90
Slaughter House	Suspended Solids	90+
	Ether Soluble Matter	95+
	5-day BOD	50+
Waste Activated Sludge	Suspended Solids	90+
<u>Partial Pressurization of Forward Flow</u>		
Oil Refinery	Oil	80 (no chemical treatment)
Aircraft Maintenance	Oil	90
<u>Partial Pressurization of Effluent</u>		
Sewage With Oil Bearing Industrial Waste	Oil	95+
Sewage With Seasonal Fruit Cannery Waste	Overall 5-day BOD	42 - 73.5
Primary Sewage	Overall Suspended Solids	57.3 - 88
	High Organic	6.7% Float S.S.
	Suspended Solids	(87.6% volatile)
		3.7% Underflow S.S.
		(79.5% volatile)

CONCLUSIONS

The purpose of this paper was to present the fundamental principles of dissolved-air flotation and to indicate how these principles are applied for designing flotation units for the treatment of Industrial Wastes.

Examples have been cited of various installations, and pictorial illustrations have indicated the engineering that is required in designing a dissolved-air flotation installation.

Dissolved-air flotation is no longer an experimental process. The fundamental principles are known and extensive field work has established the necessary design correlations. The results of laboratory tests, realizing the hydraulic limitations of flotation units, may be used to effectively size flotation units. It is still the better part of good engineering judgment, however, to select flotation as a treatment process only with a background of experience, judgment and equipment that is competently and properly designed not only on functional but on mechanically and hydraulically sound bases.

WASTE ASSIMILATION CAPACITY PROCEDURES

Lou F. Warrick
 Water Supply &
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 Service
 Chairman
 Session No. 4

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INTRODUCTION

In a modern urban technological society, waste assimilation capacity of streams is one of the most important aspects of use of water resources. This asset, to be used intelligently, must be defined in quantitative terms. Generally, four types of problems are at issue, determination of the best possible site selection for new mill locations, evaluation of potentialities for expansion at existing sites, analysis of proposed plans for pollution alleviation, and critical appraisal of the competitive position of waste disposal in multiple water uses associated with proposed river developments. There is no substitute for thorough detailed studies in developing definitive answers for these kinds of problems. Since organic was usually the major problem, the waste assimilation capacity procedures presented in this paper are oriented to that type of waste; however, much of the subject matter is more widely applicable.

Five major phases are usually entailed in evaluation of waste assimilation potential of a stream: (1) determination of the magnitude and characteristics of the wastes; (2) appraisal of the natural hydrologic setting; (3) adoption and verification of self-purification factors involved; (4) forecasts of stream conditions expected for ranges of waste loading under various probabilities of stream runoff; and (5) critical appraisal of the impact of man-made river developments, existing and proposed.

Source of Wastes

Location, magnitude, and characteristics of existing municipal and industrial waste sources are best obtained by a well designed on-shore survey. In addition to the usual measurements of volume and concentration of constituents, special consideration should be given to unusual sources. In the BOD work a check should be made for immediate demand and a differentiation made between the portion of BOD in settleable solids form subject to deposit and that in colloidal and dissolved form. In addition to the standard 5-day BOD, rate curves should be run on the wastes and on representative river water samples

taken downstream. Industrial operating schedules and product output provide a basis for evaluating variation expected in waste load. Where a new mill or an expansion is involved, estimates of waste loads are based upon pilot results or loading per unit of production bases upon prior experience.

Attempting a quantitative measure of waste load through water course sampling is an inadequate substitute for an on-shore survey. Water course sampling results should be reserved as a check against the direct measurement of the sources.

Hydrology

The degree to which waste assimilation capacity can be quantitatively defined is dependent to a large extent upon the detail with which the hydrology of the specific drainage basin is determined. Hydrologic phenomena are highly variable in time and place; hence, waste assimilation capacity of a river is not a fixed static quantity, but rather a range in potential tied to hydrologic change. Fortunately, however, though variable, hydrologic changes occur in the long run in a quite orderly fashion, and can be defined by statistical analyses of long term records. Knowing the nature of variation and probabilities of occurrence, one can make rational decisions about levels of use of the water resource. Three hydrologic variables are particularly pertinent, climate, stream runoff, and physical characteristics of the river channel.

Climatic Setting

The climatic setting establishes the unique differences between drainage basins. Physiographic land forms, geology, topography, vegetative cover, land use, rainfall, and temperature all play a role. Since the critical condition with respect to waste assimilation capacity usually is coincidence of high temperature and low stream flow, temperature deserves special consideration.

Air and Water Temperature.

Temperature of the river water is of primary importance as it plays a triple role, affecting the rate of stabilization of organic matter, the dissolved oxygen saturation capacity of the water, and the rate of reaeration. As temperature rises the rate of satisfaction or organic matter increases, thereby increasing the demand upon dissolved oxygen of the river, and, unfortunately, as temperature rises the oxygen saturation capacity of water decreases. Off-setting this to some extent, with rise in temperature, is the increase in diffusion of dissolved oxygen within the body of water.

Long term records of water temperature are usually not available, and while methods are available ⁽¹⁾ to derive water

 (1) Forecasting Heat Loss in Ponds and Streams. C.J. Velz and J.J. Gannon. J. Water Pollution Control Federation, 32:392 (1960).

temperatures from meteorological records, the computations are extensive in developing a long term series. However, temperature of surface water of streams parallels reasonably the monthly mean air temperature, and for many practical problems the patterns developed from statistical analysis of long records of monthly mean air temperature serve as a reasonable approximation. This is illustrated in Figure 1, showing a comparison of air and water temperature records for the lower Arkansas River. Based upon statistical analysis of the 66 year record of air temperature at Pine Bluff, Ark., Curve A shows the most probable monthly average air temperature expected and the shaded band, about the most probable, indicates the range within which monthly average air temperature can be expected for 80 percent of the years. Observed river water temperatures taken at Little Rock, Ark., for a 6 year period are also shown on Figure 1 for the respective months through the seasons of the year as the mean, and the maximum, and the minimum monthly averages. It will be noted that in most instances these water temperature data fit well within the pattern described by the 66 year record of air temperature.

From the statistical analysis of records of stream runoff, the period of most frequent occurrence of drought flows can be identified in relation to the seasonal temperature pattern, as shown on Figure 1. For the lower Arkansas, the severe drought stream flows occur most frequently in late September and early October after the seasonal peak in temperature has passed, which is a distinct advantage. While this is a common pattern, in some climatic settings the seasonal peak of temperature coincides with the drought stream flow frequency distribution, which is a disadvantage to waste assimilation capacity.

In the severe northern latitudes the critical season may be winter when ice cover prevents reaeration from the atmosphere. The seasonal pattern developed from monthly mean air temperature records assists in identification of the period when ice cover can be expected.

Stream Runoff Characteristics

The size of the river, or the amount of stream flow available, is the most important asset in waste assimilation. In addition to very unequal geographical distribution, the quantity of stream flow tomorrow will be different from today, varying through the seasons from year to year with extremes of flood and drought. While the average flow of a river may appear good, the real restriction limiting the quantity of water available for use is the uncontrolled natural drought flow. Two statistical evaluations aid in judging availability, the seasonal pattern of runoff, and the determination of the drought flow probabilities for the critical warm weather summer-fall season. To illustrate these and show how different one drainage basin can be from another, I have drawn from studies we have made on a river in the Atlantic Coastal Plain Referred to as River "A" (drainage area 2,465 square miles) and on a river in Michigan of practically the same drainage area, referred to as river "B".

FIGURE 1
LOWER ARKANSAS RIVER

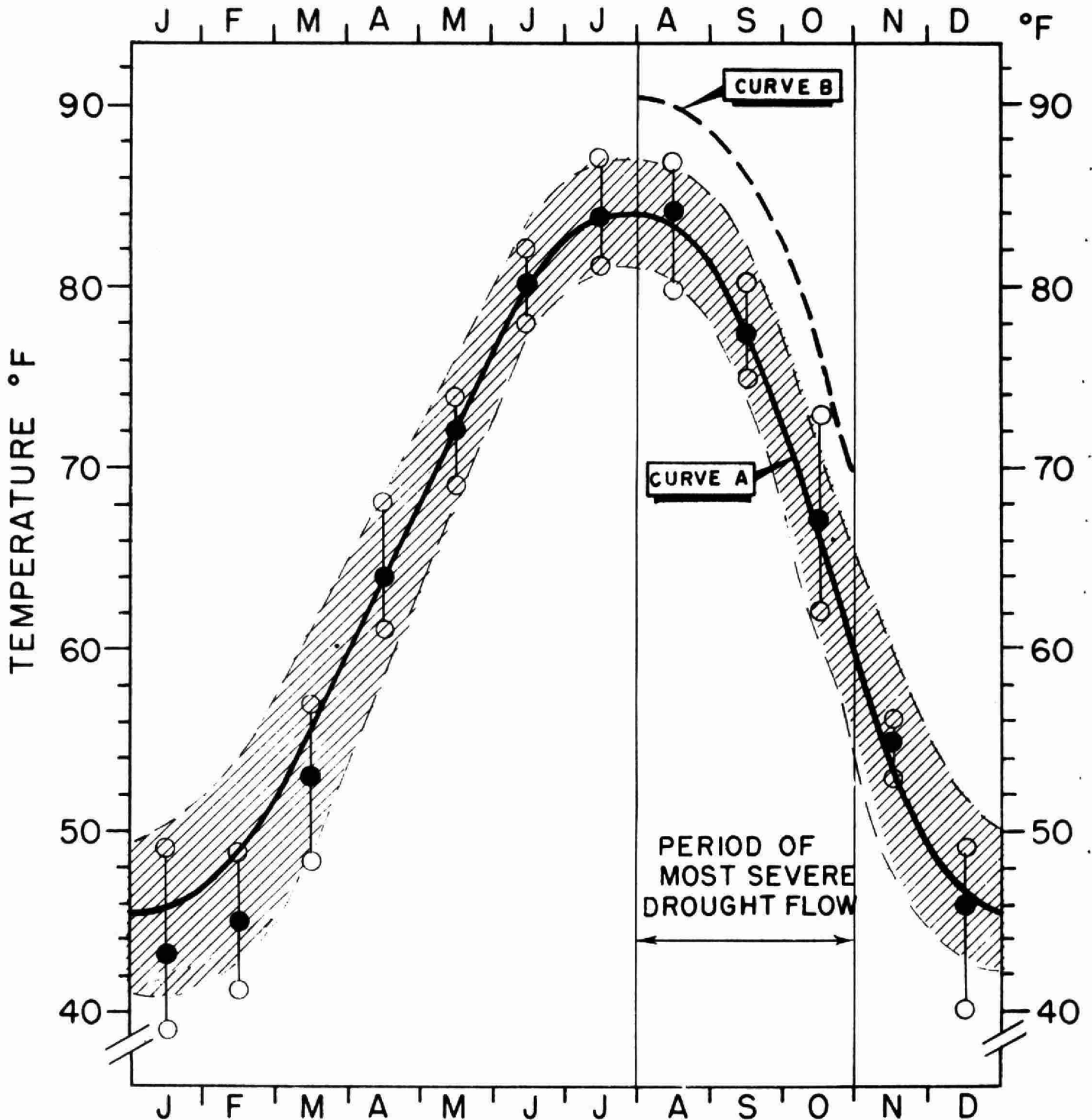
COMPARISON SEASONAL PATTERNS OF AIR AND WATER TEMPERATURE

CURVE A : MOST PROBABLE MONTHLY AVERAGE AIR TEMPERATURE RANGE
 RANGE IN MONTHLY AVERAGE AIR TEMPERATURE FOR 80 % OF YEARS

MAX. ○
 AVE. ●
 MIN. ○

CURVE B : CRITICAL WEEKLY AVERAGE

OBSERVED RIVER WATER TEMPERATURE

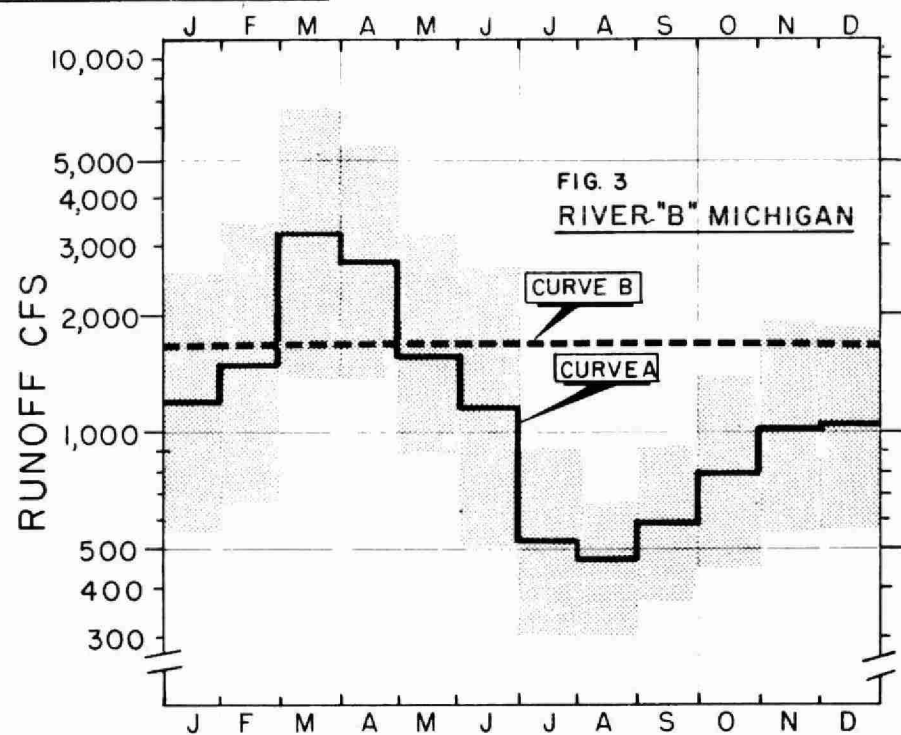
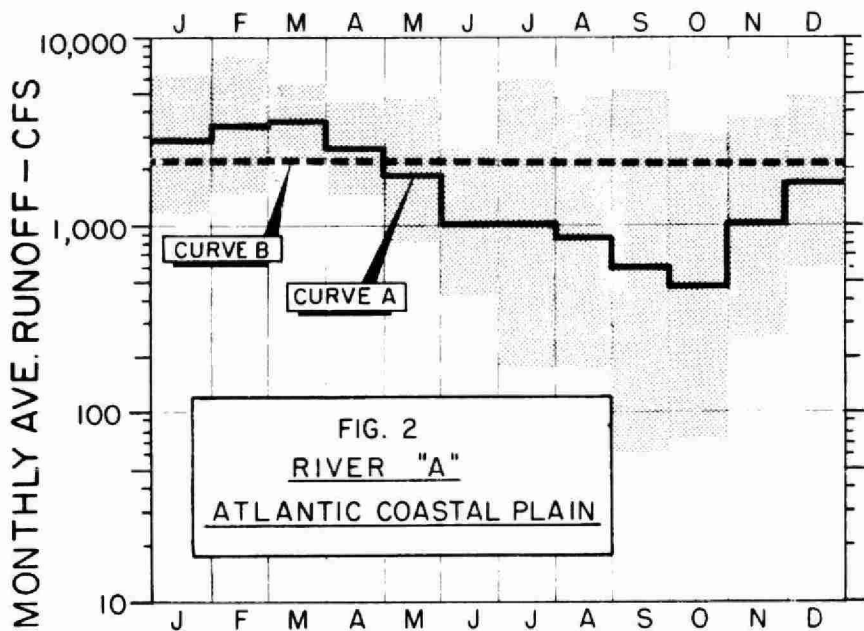


SEASONAL PATTERN OF RUNOFF

CURVE A MOST PROBABLE MONTHLY AVERAGE

CURVE B MEAN FOR PERIOD OF RECORD

■ RANGE WITHIN WHICH MONTHLY AVERAGE CAN BE EXPECTED FOR 80% OF YEARS



Seasonal Pattern of Runoff

Analyses of long-term monthly average discharge records at stream gaging stations reflect the seasonal pattern of runoff and deviations expected. The variation of discharge for any month from year to year is usually great and generally approaches a logarithmically normal distribution. Analyzing each month of the year separately provides the most probable monthly average discharge and the expected ranges, from which the seasonal pattern can be constructed.

Figures 2 and 3 illustrate such seasonal patterns for River "A" and River "B", respectively. The most probable monthly average is represented by Curve A and the shaded belt about the most probable is the range within which monthly average discharge can be expected for 80 percent of the years. The average discharge for the period of record is good, River "A" at 2,150 cfs and River "B" somewhat less at 1,540 cfs. Both have high winter-spring flows and low flows in the summer-fall season. The most probable or normal drought flow of River "A" is expected in October at 470 cfs and for River "B" in Michigan is practically identical with this, but is expected earlier in the season, in August. However, similarity of the two rivers ends here. A significant aspect to consider is the degree of variation expected above and below normal such as indicated by the 80 percent confidence range shown by the shaded band. Referring to River "A", for the critical drought month of October, while the most probable runoff is 470 cfs the upper limit of the 80 percent range can be expected as high as 3000 cfs and the lower limit can be expected to fall as low as 60 cfs. In contrast to this, River "B" in Michigan for which the most probable drought month is also 470 cfs, the 80 percent range in variation is much narrower extending up to 600 cfs and falling to 320 cfs.

River "A" in the Atlantic Coastal Plain is an example for a stream generally high in runoff, with high flow in many years continuing through the summer-fall season with high potential, but occasionally subject to extremely severe droughts drastically restricting potential if growth is geared to the drought flow.

Drought Flow Severities and Probabilities

Since the time of passage through the critical reach of a river is generally less than a month, in addition to the seasonal pattern of stream runoff developed from monthly average discharges, from the standpoint of waste assimilation capacity it is of importance to know the probabilities of severe drought flows expected for shorter periods such as the minimum weekly averages. Selection of such minimum flows for the warm weather season for each year of record develops a series of extreme values which generally are in close agreement with the statistical theory of extreme values (2). Figure 4 shows plots of such minimum flows for River "B" in Michigan on extremal probability paper; Curve A the distribution for the minimum consecutive 30 day average drought flows, Curves B, C and D the minimum consecutive 15, 7 and one day averages, respectively. From these probability

(2) The Return Period of Flow Flows. E.J. Gumbel. Annals of Mathematical Statistics, 12:163 (1941).

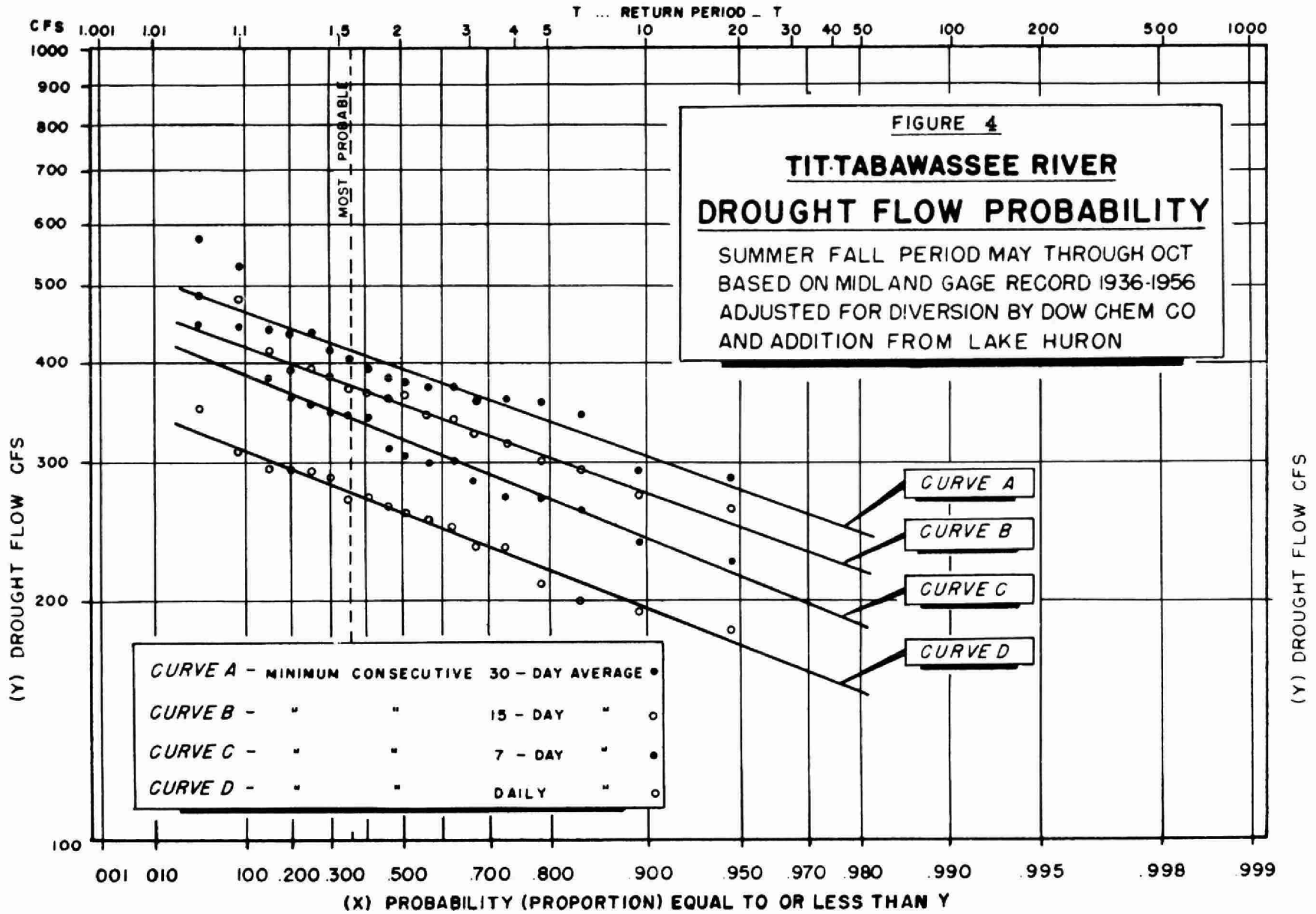
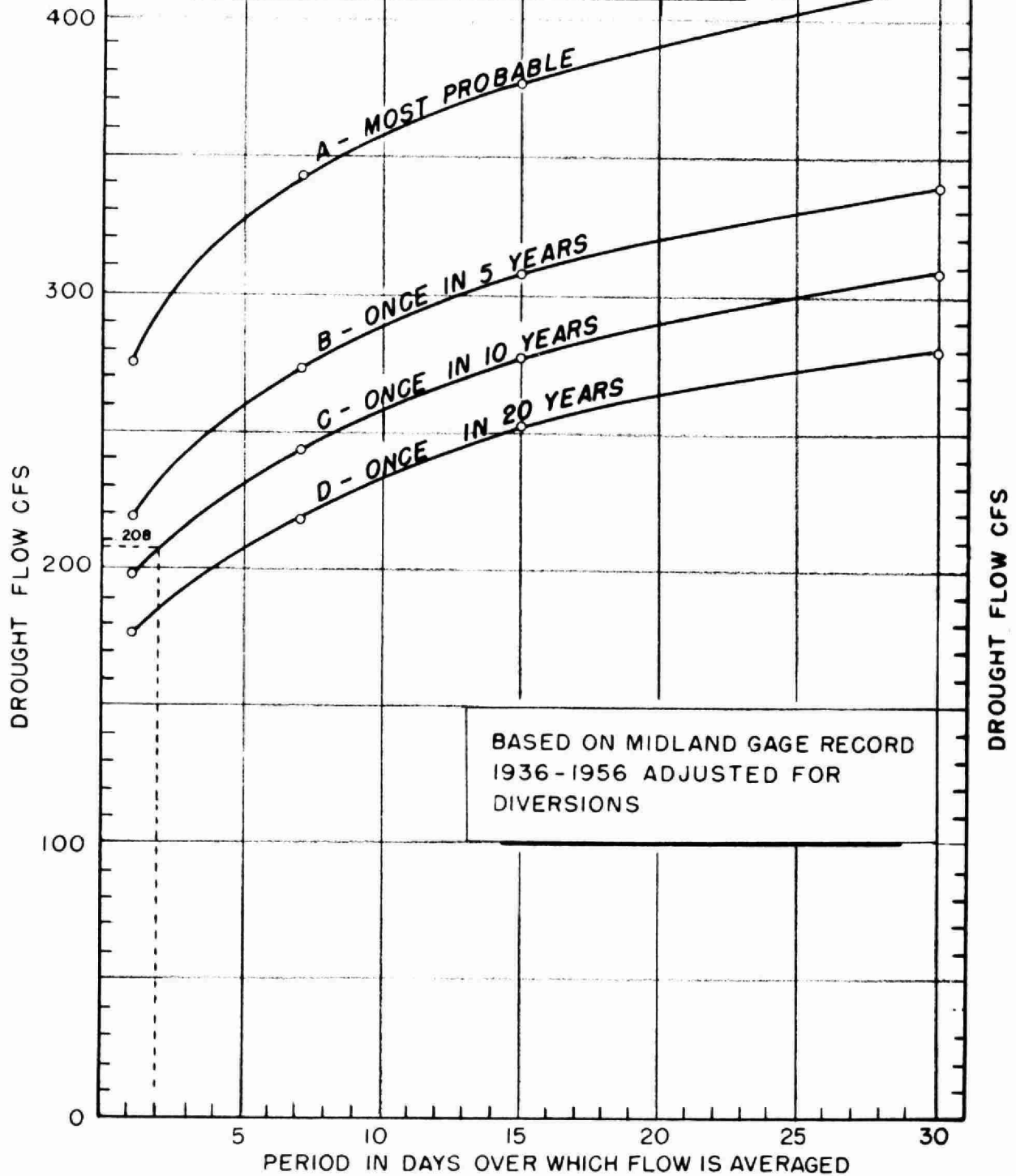


FIGURE 5

**TITTABAWASSEE RIVER
DROUGHT FLOW CHARACTERISTICS
AT MIDLAND, MICH.**

RELATION BETWEEN SEVERITY AND PERIOD OVER WHICH DROUGHT FLOW IS AVERAGED



distribution curves it is possible readily to obtain the drought severity for any probability of occurrence such as the most probable or the once in 5, 10 and 20 year frequency. Expected drought flow severities for these frequencies are summarized in Table 1.

TABLE 1

EXPECTED DROUGHT FLOW DURING SUMMER-FALL SEASON
RIVER "B" IN MICHIGAN

Drought Frequency	Minimum Daily Average Cfs	Minimum 7-Day Average Cfs	Minimum 15-Day Average Cfs	Minimum 30-Day Average Cfs
Most Probable	274	341	375	414
Once in 5 Years	219	271	306	338
Once in 10 Years	197	242	276	307
Once in 20 Years	177	217	251	278

In turn, from the probability distribution curves, the relation between severity and duration of drought flow can be established as shown on Figure 5. This provides a graphic concept of the entire drought flow structure expected on the Michigan River "B" during the warm weather season as an average flow over any number of consecutive days from one to 30 days duration; Curve A, the most probable drought expected in any year, and Curves B, C and D, drought expected on the average in the long run once in 5, 10 and 20 years, respectively. It will be noted that as the period over which stream discharge is averaged, is shortened, available stream flow declines or drought severity increases. Each stream has its unique drought flow framework within which man-made activities and water uses must be viewed.

Similar analyses of drought characteristics of River "A" in the Atlantic Coastal Plain also demonstrate distributions in accord with the theory of extreme values but which are quite different in severity from that of the Michigan River "B".

TABLE 2

EXPECTED DROUGHT FLOW SUMMER-FALL SEASON
RIVER "A" IN ATLANTIC COASTAL PLAIN

Drought Frequency	Minimum Daily Average	Minimum Monthly Average
Once in 5 years	44 cfs	115 cfs
Once in 10 years	24 cfs	59 cfs

For example, comparing Tables 1 and 2, the once-in-ten-year drought flows on the Michigan River "B" as minimum 30-day average and one-day average are 307 cfs and 197 cfs respectively, while on the Coastal River "A" they are 59 cfs and 24 cfs respectively. Certainly, there is not much prospect for industrial development on River "A" if it is geared to these natural drought flows. But before abandoning River "A" as an industrial site, the general high level of runoff otherwise available suggests substantial potential, consideration of which is discussed later.

Physical and Hydrologic Characteristics of the River Channel

An aspect of hydrology usually not fully appreciated is the physical characteristics of the stream channel, whether deep and slow moving or shallow and rapid. Occupied channel volumes, widths, depths, surface and cross-sectional area, and hydraulic factors including the important element of time of passage from reach to reach are essential to the quantitative determination of deoxygenation and reaeration along the course of the river. If such data are not available they now can be obtained readily in the field employing portable echo sound equipment, by channel cross-section sounding at about 500 foot intervals along the course. Each runoff regime produces its corresponding channel characteristics; having field measurements for one runoff condition, based upon appropriate stage rating curves, adjustments can be made in channel characteristics for other probabilities in stream flow.

Adoption and Verification of Self-Purification Factors

The third phase of evaluation of waste assimilation capacity procedure is the adoption of deoxygenation and reaeration fundamentals to the specific stream under study in order to determine the resultant self-purification capacities. Our approach (3) is to consider deoxygenation and reaeration separately; the liabilities and assets are then combined to determine the resultant dissolved oxygen profile along the river. The liability side, deoxygenation, is determined from the integration of the waste loads down the river at the pre-determined rate of decomposition and at the time of passage computed for the specific runoff regime, taking account of any abnormalities such as immediate demand, sludge deposits, or biological extraction. The assets side, reaeration, is based upon Phelps's fundamental law(4) using the factors of runoff, occupied channel volume, depth, water temperature and stream turnover as determined from the physical

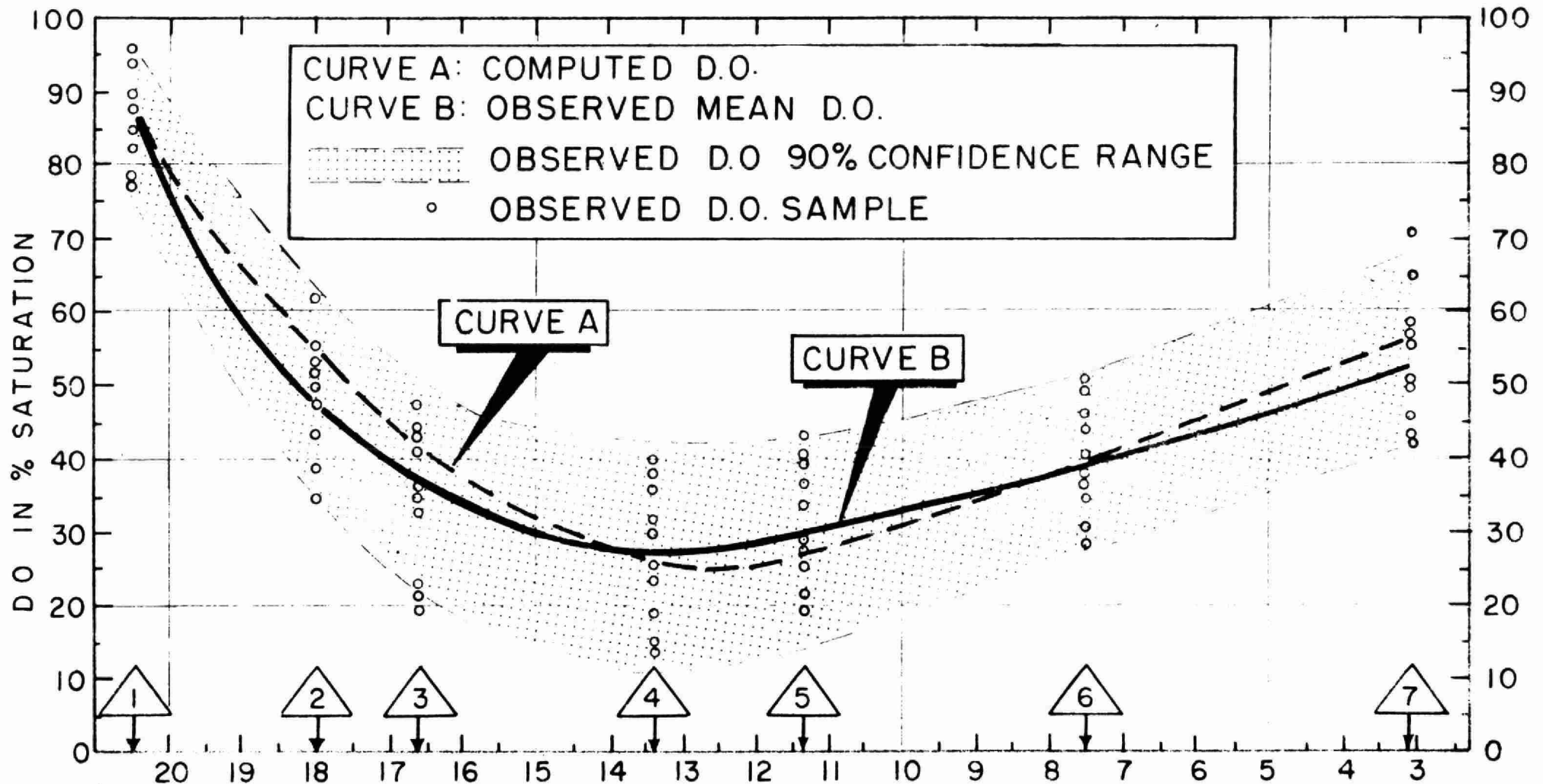
(3) Factors Influencing Self-Purification and Their Relation to Pollution abatement. C.J. Velz, Sewage Works J., 19:629 (1947); 21: 309 (1949)

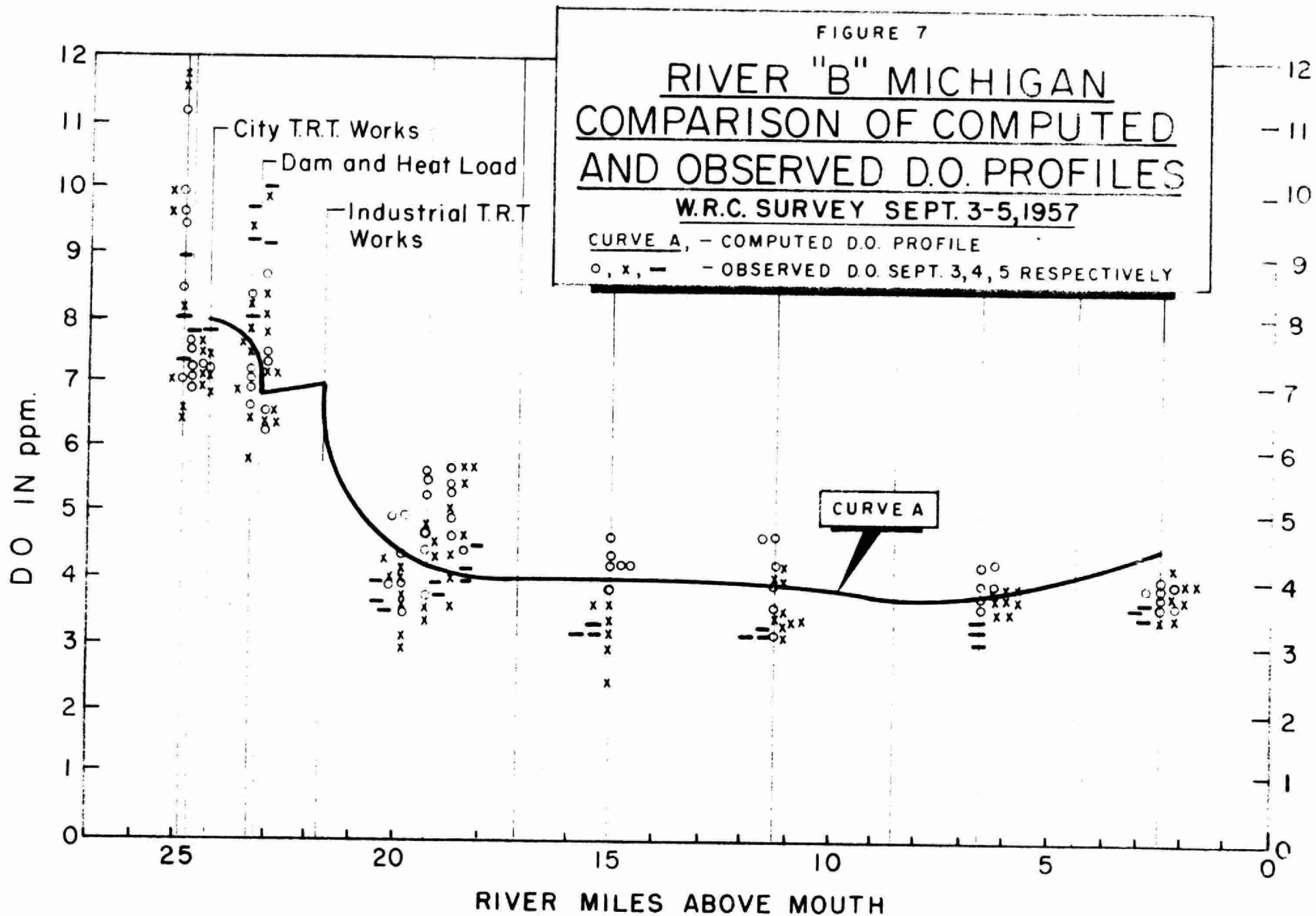
(4) Stream Sanitation. E.B. Phelps, Wiley (1944).

FIGURE 6

COMPARISON OF COMPUTED AND OBSERVED
DISSOLVED OXYGEN PROFILE
RIVER "C" - MICHIGAN

AUGUST 11-12, 1954, TEMP 17.5 TO 20.5°C; AVERAGE RUNOFF 225 CFS.





and hydraulic characteristics of specific reaches of the river, taking into account initial dissolved oxygen in the stream flow and that contributed from tributaries along the course.

This procedure provides a basis for direct comparison between observed river sampling results and an independently computed dissolved oxygen profile under the same conditions, thus providing a verification of the self-purification factors adopted. For a verification to be significant it is axiomatic that conditions be comparable, and that observed water course sampling reliably reflect a known pollution loading and steady runoff regime. Rivers are dynamic and water course sampling must be more than taking grab samples now and then under highly variable conditions. For statistically significant results a carefully designed and well executed program of intensive sampling is required⁽⁵⁾.

Three examples drawn from among our river studies illustrate the validity of this approach and the high degree of verification that can be obtained from refined computations and good stream survey data. Figure 6 shows the observed dissolved oxygen profile for River "C" in Michigan based upon an intensive round-the-clock 3-day survey, providing 18 samples at each sampling location. Curve B represents the mean of the observed data and the shaded band, the 90 percent confidence range based upon variation of the individual sample results. Curve A represents the independently computed dissolved oxygen profile under conditions which prevailed during the intensive survey period, taking into account the prevailing loads and self-purification characteristics involved. It was noted that the computed dissolved oxygen profile (Curve A) is in close agreement with the mean of the observed D.O. sampling results (Curve B).

Figure 7, similarly, represents comparison between computed and observed dissolved oxygen profiles on River "B" in Michigan. This represents a complex situation of municipal sewage, industrial wastes, and a heavy heat load. Again, the observed survey data represent an intensive water course sampling program over a 3-day period, reflecting 18 or more individual sample results at each sampling location. Curve A represents the independently computed dissolved oxygen profile for the conditions which prevailed during the survey period, and it will be noted there is generally good agreement between the observed and computed results.

Similarly, Figure 8 represents a comparison of computed and observed dissolved oxygen profiles on River "D" in Virginia, solid lines representing the independently computed D.O. profile and the circles the observed based on sampling data. These profile illustrate dramatically the importance of taking into consideration abnormalities associated with sludge accumulation. The upper profile represents conditions in which, preceding the sampling period, the runoff hydrograph permitted a prolonged period of accumulation of sludge approaching equilibrium levels with consequent sharp decline in D.O. The lower profile represents conditions under approximately the same waste loading

⁽⁵⁾ Sampling for Effective Evaluation of Stream Pollution. C.J. Velz. Sewage and Industrial Wastes, 22:666 (1950).

FIG. 8.

**RIVER "D" VIRGINIA
COMPARISON OF COMPUTED
AND OBSERVED D.O. PROFILES**

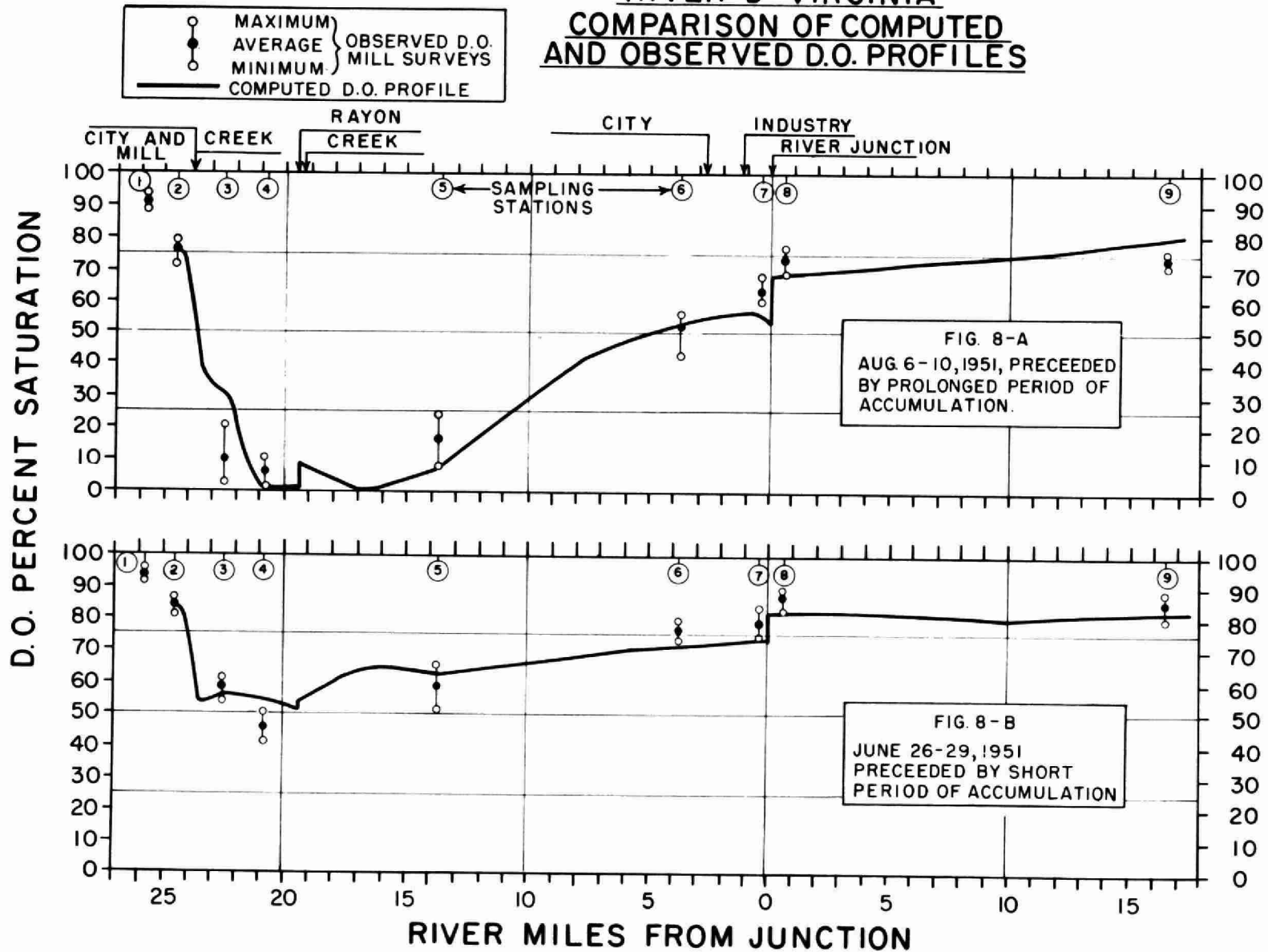
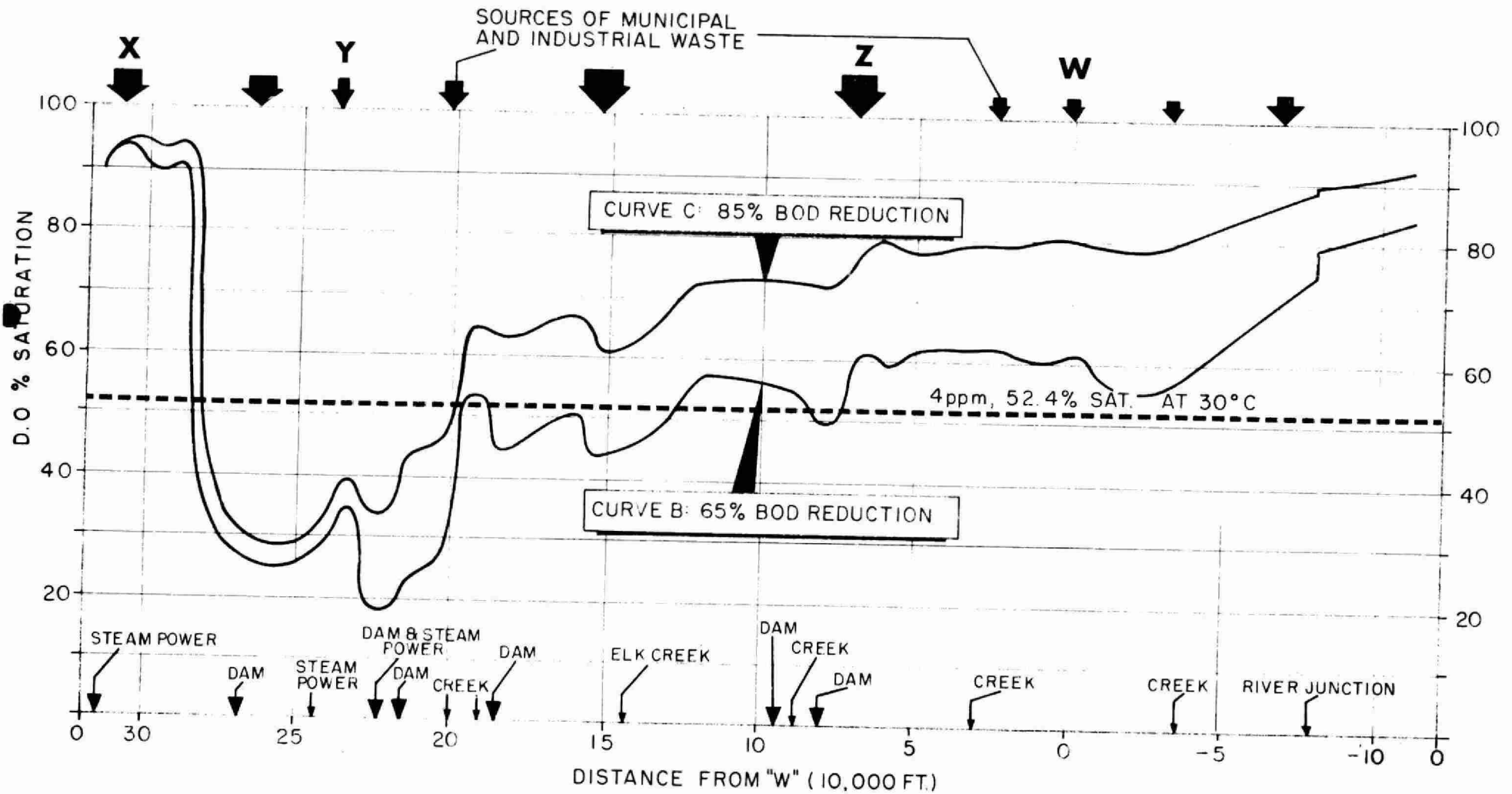


FIG. 29
RIVER "E" OHIO
FORECAST DISSOLVED OXYGEN PROFILES, 1975 LOADS, RELIANCE
UPON TREATMENT ALONE, NO REGULATION OF STREAM FLOW
 10-YR. DROUGHT RUNOFF AT "Z" 316 CFS



and runoff but preceded by only a short opportunity for sludge to accumulate with consequent less severe decline in D.O. Taking such conditions into account in our refined methods of computation, it will be noted that there is good agreement in both instances between the computed and observed results.

At this point I should like to emphasize that there is no short-cut to evaluation of waste assimilation capacity. A considerable body of detailed information and computations are involved if definitive quantitative answers are to be developed. In our experience the widely used oxygen sag equation bases primarily on observed stream conditions and then applied to other stream conditions is not adequate for evaluation of most situations encountered today. Likewise, reliance on statistical correlations of observed stream sampling data taken under one set of conditions is not adequate to project expected results for quite different conditions. We believe that the sound approach is to break the problem down into its respective aspects, considering in each area the fundamental factors involved.

Forecasts of Stream Conditions.

With self-purification characteristics defined and verified on a fundamental basis, it is possible to forecast stream conditions expected for various waste loadings over the whole range of stream runoff expected. Such forecasts define the range in waste assimilation capacity available, from which the relation between stream runoff and allowable waste loading can be established. It is then possible to appraise the desirability of the river location as a site for a new mill, for expansion at an existing site, or to evaluate the effectiveness of various pollution abatement proposals.

The objective is maximum utilization of water resources without waste or abuse. As competition for limited water resources intensifies, greater attention is directed toward utilization of a larger proportion of the total annual capacity of the stream, not just the minimum available during the drought season. To this end, two methods of increasing waste assimilation potential offer promise: storage of stream runoff with regulated release to augment flow during the drought season, or storage of industrial waste with regulated release in accord with seasonal variations in natural stream flow. Excerpts from studies we recently made illustrate the potential of these two approaches.

River "A" in the Atlantic Coastal Region discussed above, which, it will be recalled, has a high average runoff but suffers from occasional severe droughts, is a good example of the potential of waste storage and regulated release. For this location, some 40 dissolved oxygen profiles were forecast for all seasons of the year in order to evaluate the possibilities of lagoon waste storage as a means of utilizing a larger proportion of the annual waste assimilation capacity. Waste assimilation capacity during drought periods is drastically limited, and computations show that even employing the highest degree of waste treatment technically

feasible, the drought flows would support only a small mill production capacity. But the forecasts further disclose that if the total annual waste assimilation capacity of the stream could be utilized each year it would provide annual mill production potential 10 to 50 times that possible under restricting drought conditions. It was further found that moderate lagoon waste storage capacity opened possibilities of this location as a site for a mill of considerable capacity. As an illustration of the potential of stream runoff storage and flow regulation, reference is made to a highly developed urban-industrial complex in Ohio along River "E". Figure 9 represents the computed dissolved oxygen profiles expected under once in 10-year natural drought runoff for two plans of sewage and waste treatment for 1975 loads; Curve B, 65 percent reduction in BOD and Curve C, 85 percent reduction. Drought conditions on this river are extremely severe with the once in 10-year drought of 133 cfs, 223 cfs, and 316 cfs at locations "X", "Y", and "Z", progressively downstream. Under these conditions of extreme low flow, even with a very high degree of treatment, desirable dissolved oxygen conditions in the critical reaches of the river cannot be maintained.

Figure 10 shows forecasts of dissolved oxygen profiles for a combination of moderate treatment, removing settleable solids subject to deposit, in combination with low flow regulation of the stream, Curve A increasing the dry weather flow from 316 cfs to 800 cfs at location "Z", and Curves B and C for additional increments of augmented flow in the lower reach. Comparing the shape of these profiles with the previous profiles under drought conditions and high degree of treatment (Figure 9), a dramatic difference is apparent, particularly in the upper reach of the river, with substantial improvement in dissolved oxygen conditions.

As the trend toward urban-industrial concentration continues, reliance upon waste treatment alone will not be adequate, and more consideration to drought alleviation through stream flow regulation will be necessary for continued economic growth dependent upon multiple water use.

Impact of River Developments on Waste Assimilation Capacity

Evaluation of the impact of existing and proposed river developments on waste assimilation capacity is of increasing significance in the competitive use of water resources. Depending upon how planned and operated, man-made river developments such as hydro and steam power plant, dams, reservoirs, navigation works, and stream diversions can be either beneficial or detrimental to waste assimilation potential. Hence, industry and government agencies responsible for satisfactory waste disposal must be constantly on the alert as to the effect of existing and proposed river developments. Often a little fore-planning can result in mutually beneficial results; when irreconcilable conflicts are presented, rational decisions can be based only upon quantitative appraisals of the benefits and the damages. Time does not permit a detailed documentation, but a few situations may illustrate the importance of this phase of waste assimilation evaluation.

FIG. 10
RIVER "E" OHIO
 FORECAST DISSOLVED OXYGEN PROFILES, 1975 LOADS
 PRIMARY TREATMENT WITH AUGMENTED STREAM FLOW

CURVE A: 10 YR. DROUGHT FLOW AUGMENTED BY HEADWATER STORAGE TO 800 CFS AT "z"
 CURVE B: ADDITIONAL INCREMENT FROM ELK CREEK STORAGE TO 1,000 CFS AT "z"
 CURVE C: ADDITIONAL INCREMENT FROM ELK CREEK STORAGE TO 1,100 CFS AT "z"

SOURCES OF MUNICIPAL
 AND INDUSTRIAL WASTE

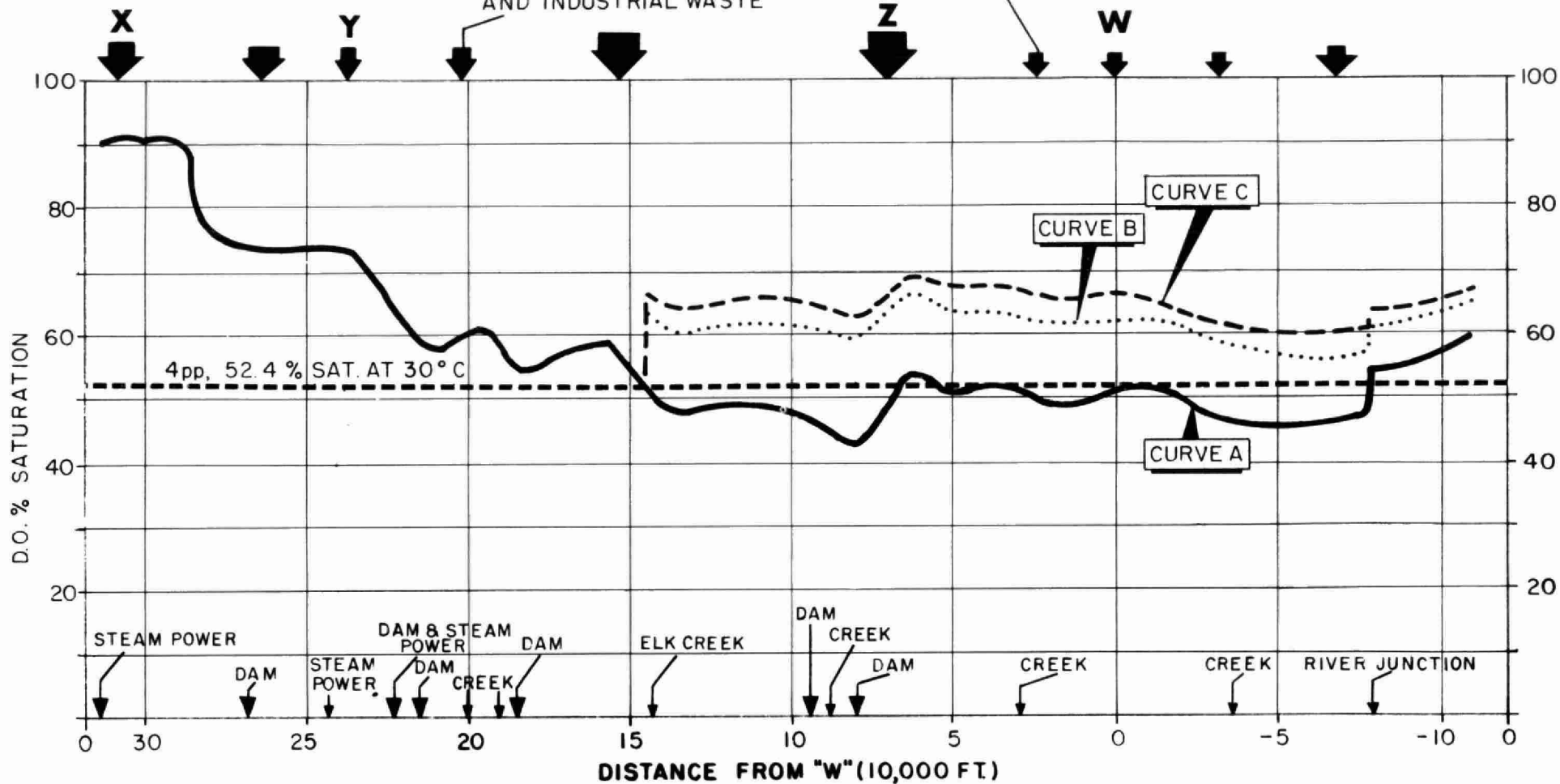
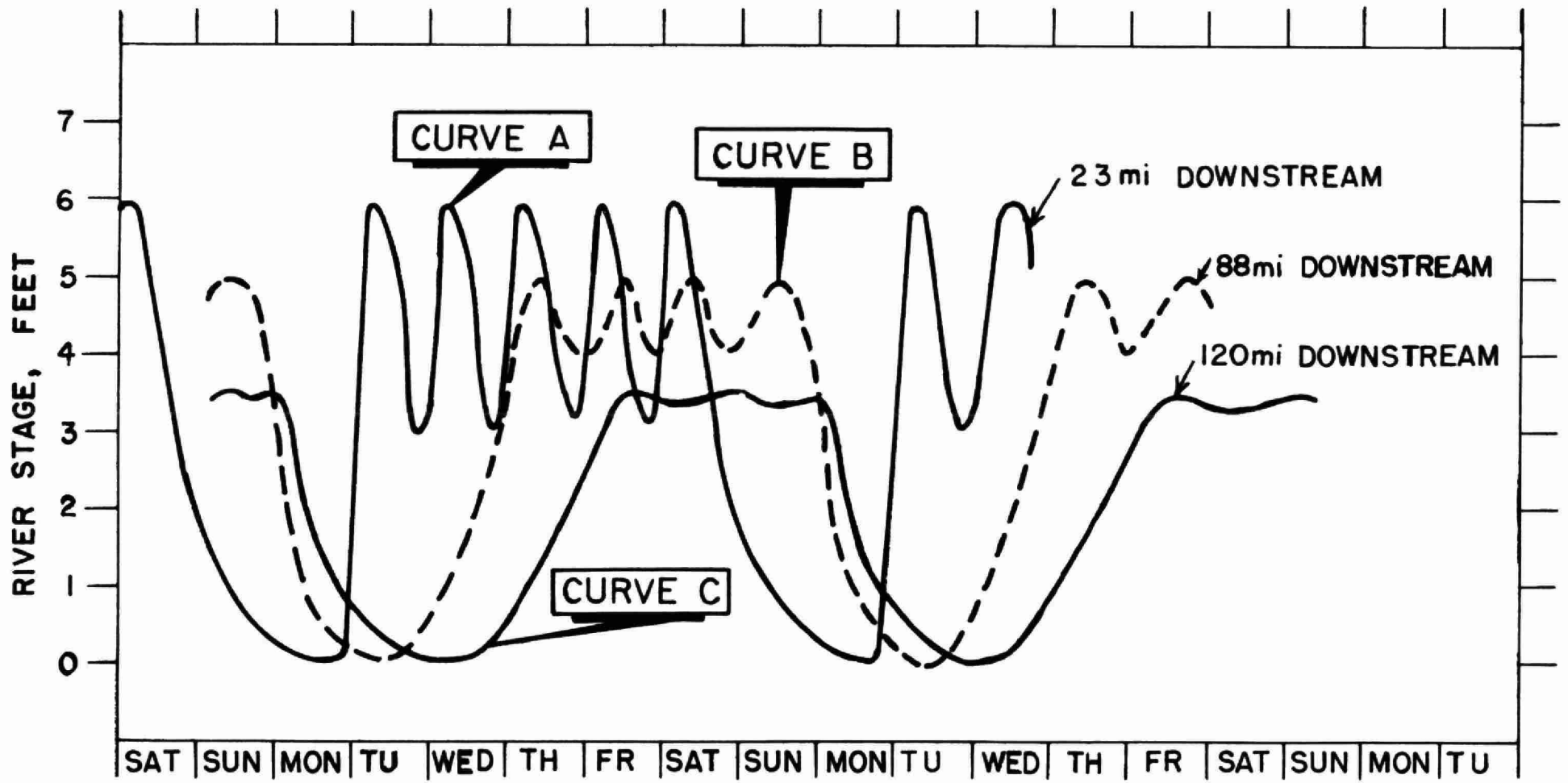


FIGURE II
RIVER F - SOUTH CAROLINA
TYPICAL FLUCTUATION IN RIVER STAGE
INDUCED BY HYDRO POWER PLANT
DURING ORDINARY LOW RUN OFF



One difficulty to cope with is the diurnal and weekend pulsations in discharge induced by modern hydro power plant practice. The trend is to rely upon the hydro power to meet the peak power demands, using steam generation to carry the base load. In some cases this results in drastic reduction of natural waste assimilation capacity. A dramatic illustration is represented in Figure 11 for River "F" in South Carolina, where continuous measurements of change in stage were recorded at three locations downstream from a large hydro power plant. Curve A represents the change in stage at a location 23 miles downstream, Curve B at a location 88 miles downstream, and Curve C at a location 120 miles downstream. The diurnal fluctuations during week days are sharply defined in the upper reaches, and the marked decline in stage associated with the weekend shut-down is reflected all along the course as low flow for periods of over 2 days.

While it is not to be expected that the pattern of hydro power operation in combination with steam generation will be changed, it is possible to iron out these diurnal and weekend pulsations in discharge by the installation of a relatively small reregulating reservoir below the main hydro power plant. In the self-interest of the utilities in promoting industrial customers, such reregulators may become standard practice in plans for hydro power developments.

In addition to the hydro power developments, of increasing importance is waste heat discharge from steam power plants. Large quantities of condenser water are needed, and since about 50 percent of the energy input is dissipated in the condenser water, a substantial rise in river temperature during the drought season may result, adversely affecting waste assimilation capacity and aquatic life. Multipurpose storage and stream flow regulation to increase dry weather runoff is a good corrective.

Upstream storage reservoirs developed on a multipurpose basis with consideration to drought alleviation through low flow regulation during the critical warm weather low runoff season can be a distinct asset to waste assimilation capacity, as was illustrated for the Ohio River "E" (Figure 10). However, in connection with reservoirs, particularly those with deep submerged outlets, the discharge below the dam may contain little or no dissolved oxygen. Without a sufficient intervening stretch to rebuild to normal level of dissolved oxygen through reaeration, down-river users can be seriously affected. Proper design to permit taking water at different levels to insure satisfactory dissolved oxygen can overcome this difficulty.

Navigation works, through construction of dams or deepening of the natural channels, may drastically reduce waste assimilation capacity of the stream by increasing the demand on oxygen resource through longer time of passage and by reduced reaeration. Navigation works are often promoted on the basis of stimulating industrial development; actually they may be a serious handicap to industrial growth through curtailment of natural waste assimilation capacity.

Diversion of water resources for supplemental irrigation, a practice rapidly extending into the humid areas, unless compensated by storage, is an extremely serious threat to industrial development. These consumptive uses of water are greatest in the season when there is the greatest need to conserve the waste assimilation capacity in the stream.

Conclusion

In conclusion, if water management is to move forward on a rational basis, free of waste, abuse, and arbitrary action, it must be guided by facts, the quantitative definition of waste assimilation capacity of each particular stream. Intelligent, rational planning implies comprehensive evaluation in advance of adoption of any abatement proposal. It also implies an element of prevention with thorough evaluation before location and construction of new mills or expansion at existing sites. Time, effort, and resources devoted to comprehensive evaluation of water resources and waste assimilation capacity will be repaid many fold in avoiding conflicting water developments and in avoiding pollution problems.

SOLIDS REMOVAL PRACTICES IN THE PAPER INDUSTRY

By



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You have just heard an excellent paper on the waste assimilation capacity of streams. As was pointed out by Dr. Velz each stream has a certain capacity to assimilate waste loads. This ability to assimilate a waste load is dependent on a number of interlinking factors which include the hydrological characteristics of the stream and the temperature of the stream.

I wish to emphasize that each river or possibly a section of a river may require a different degree of treatment than another river. Seasonal runoff patterns may be such that treatment is only a short term summer requirement. Hence, the type of solids removal and degree of solids removal practiced may vary from one location to another. I will, therefore, cover in this paper some of the methods employed in the paper industry to reduce the solids load in paper mill effluents. These practices cover a wide spectrum and it is not uncommon to find multiple employment of one or more methods discussed. Many solids removal practices involve the collection of hydrous sludges composed of organic and inorganic materials. The problem of solids removal and sludge disposal are closely associated and the consideration of one without the other is almost impossible.

Internal Measures to Reduce Solids Losses

A Substantial reduction in solids losses from many operations can be accomplished by internal measures. While internal measures may not be classified as waste treatment, in many cases they have contributed substantially to a reduction in solids losses. In most cases, solids loss reduction should start internally and be followed later by external measures.

The means to accomplish fibre recovery and the accompanying solids loss reduction are many. Lardieri recently covered in detail the subject of "Recovery of Useable Solids". While each operation is a distinct problem of its own some practices can be applied almost universally. One of the simplest and yet more constructive steps that can be taken is stock chest level control to prevent overflow to the sewer. Any of several

positive detection or warning devices can be used to detect full chests so that overflows are prevented.

The reuse of high solids content waters in stock preparation in practically all cases has resulted in a reduction in solids losses. While there are some grades which do not warrant extensive reuse of water within the mill, these grades are few and far between, for the practice finds use in mills which manufacture a wide grade of products. Common uses for the unclarified white water include beater makeup and beater dump, cylinder and wire showers, dilution at jordans, consistency regulators and the like. The success of a good water reuse system usually hinges on white water tanks of proper design and adequate capacity to supply peak loads.

It is becoming more common place to isolate the rejects from screens and other dirt removal equipment, dewater the fibre on screens or in wooden boxes, then haul this material directly to the dump. This practice not only isolates rejects from possible contamination of white water which could be reused but usually affords a substantial solids loss reduction.

Savealls have contributed substantially to solids loss reductions in the paper industry. The types used include drum screen, inclined screen, flotation, vacuum type and gravity sedimentation units. Each has its merit. The simpler screen savealls are the cheapest but in due turn usually recover less material. Gravity, flotation, and vacuum type savealls produce the best effluents but are more expensive to install. Certain types of operations lend themselves better to saveall operation and reclamation of the reclaimed fibre and reuse of the clarified water. In general, it can be said that the fewer the grade changes the more effective the saveall operation. Good saveall operation and subsequent good solids recovery can usually be traced almost directly to savealls of adequate size placed where they can be easily supervised and maintained and used in conjunction with a surge tank arrangement.

For some operations, savealls serve the dual purpose of fibre reclamation and final treatment units.

External Measures

It is generally implied that the solids recovered by savealls are reused in the mill. In many cases external treatment of mill effluents is necessary to satisfy treatment requirements.

Where barking is practiced there is, in some cases, a chance to reduce the solids load discharged to the stream by relatively simple means. The obvious preliminary step is to haul the bark to dumps rather than discharge to the stream. Wet barking operations usually carry a high load of large particulate matter in the effluent that can be readily screened or removed by settling in simple earthen settling ponds.

The removal of settleable solids, settleable solids being defined as those suspended solids which are removed by 1 hour or 2 hour settling in the laboratory, is usually the first step in

a pollution abatement program where external treatment is required.

Exclusive of those cases where savealls on the sewer in contrast to savealls in the white water system are used, gravity sedimentation is a common method of settleable solids removal. Both earthen basins and concrete or steel tanks are used.

Earthen settling beds are usually built in parallel with one in use while one or more are having the sludge dewatered by seepage prior to excavation. Design criteria are not firm for this type of operation but one must allow for storage of a substantial volume of sludge and maintain a width that will allow cleaning with a crane. For maximum rate of seepage in dewatering the sludge accumulation, a porous subsoil of gravel is beneficial and, under all circumstances, the bottom should be well above the ground water table.

The use of mechanical clarifiers for removal of settleable solids is common. These clarifiers, similiar to those used in domestic sewage treatment, are round or rectangular in shape with mechanical sludge removal mechanisms. Both shapes are used; the round tanks being predominant. Design criteria are usually expressed in surface loading rates of gal/ft²/day and in detention time. Surface loading rates in the range of 500-1000 gal/ft²/day are employed depending on the nature of the waste.

Detention times in due turn range from 1½ to 5 hours. Detention time may appear to be high in some cases due to the depth of tank employed. For example, depths of 10-12 feet are common and beneficial in providing a period for sludge storage compaction. The collection mechanisms for these units resemble those found in conventional sewage clarifiers but are generally of heavy duty construction capable of handling torque loads normally associated with thickener operations.

In practically all cases, sludge is pumped from mechanical clarifiers as opposed to gravity draw off. Sludge pumping, if properly designed, provides a more dense sludge and reduces supervision time involved. Variable speed screw pumps have found wide spread use as sludge pumps. Centrifugal pumps are used but leave much to be desired in selecting pumping rates even when time actuated due to the variation in line head loss, and therefore variation in discharge rate, involved when pumping fibrous slurries.

Sludge Disposal

The science of solids removal is probably more straight forward and more advanced than sludge dewatering and sludge disposal. While there is some semblance of correlation in settleability between most mill effluents, the sludge from different operations varies tremendously.

The removal of settable solids must therefore also involve consideration of their disposal.

Land disposal is the common method of final disposition of the sludges from the paper industry. The methods of processing prior to and actual disposition on the land, however, cover a wide spectrum.

Where large land areas are available the pumping of sludge to large man made or natural basins is practiced. While this method of disposal is cheap and simple there remains the problem of an odor nuisance.

In many cases sludge drying beds are used to partially dewater sludge prior to hauling it to land disposal. These beds are porous bottomed units set above the water table. A bed is usually designed to hold one month's sludge. After filling, a minimum two month period is used for partial dewatering of the sludge prior to excavation.

Some sludges can be vacuum filtered at reasonable loading rates. Other sludges are almost impossible to thicken to the point where filtration is either practical or possible.

In an effort to devise a means to handle some of the sludges which are extremely difficult to dewater, we have extensively explored the field of centrifugation. Both the disk type and conveyor type centrifuge have been investigated in the laboratory and in the field. The conveyor centrifuge appears to be better adapted to sludge dewatering than the disk centrifuge.

Extensive test work with the conveyor centrifuge has indicated that solids recovery is probably the limiting feature of the equipment. Solids recovery in the range of 90% can be obtained with the proper feed rates, however. Factors which were shown to affect solids recovery included bowl speed and feed sludge solids content. An increase in either or both resulted in a better solids recovery. Cake solids content of the dewatered sludges tested were comparable to vacuum filter cakes. Power requirements for centrifuging are in the range of 0.7 HP/Gal/minute. This power cost is compensated for in many installations by the need for an apparently small amount of supervision.

While final disposition of most all paper mill sludge after some type of dewatering is on the land, problems are involved. Both the esthetics and space required must be considered. Waste treatment in congested areas leads to sludge disposal problems particularly where odors are involved. The quantity of land required for sludge disposal becomes preponderously large in some cases and what appeared to be adequate acreage at one time is now filled with sludge.

The possibility that recovery of these solids might be feasible in some instances has been investigated by the Council and by individual mills. It suffices to say that while

they can be used in certain products, neither the demand nor the financial attractiveness of any scheme has led to an expansion beyond the laboratory.

There is little doubt that land disposal will continue to be a dominant method of sludge disposal. For those instances where land disposal of raw sludge is not possible, we have investigated the feasibility of sludge burning. Of those sludges tested, it appeared that the physical handling problems encountered could be met. The heat balances encountered with paper mill sludges are not as favorable as those of domestic sewage due to the lower BTU content of the organic matter present. The lower heat values in due turn require drier sludge cakes than normally associated with domestic sewage sludge if heat requirements are not exorbitant. This fact guides our thinking on sludge dewatering and we are now investigating the use of continuous pressure filters which show promise of producing drier sludge cakes.

Summary

The reduction or removal of suspended solids from mill effluents has many aspects. The degree of removal or reduction will depend on local conditions.

Settleable solids removal is a three phase project involving removal, dewatering, and disposal; each a problem in itself.

STATEMENT OF THE PROBLEM

Obviously, in the selection of a site for a new industry the starting point must be the requirements of the new plant. It seems superfluous to point out that it is imperative to have a definite statement at the outset of the study of the requirements of the plant as initially and as ultimately planned. However, it is surprising how difficult it is to obtain this information and how frequently requirements are changed after the site study is underway.

Controlling factors governing the selection of a wet process site include:

- (a) The availability of raw materials.
- (b) Transportation in relation to raw materials and markets.
- (c) The quality and quantity of labor available.
- (d) Community facilities.
- (e) Taxes at the local and state level.
- (f) Power and fuel.
- (g) Character and type of land in the site itself.
- (h) Quantity and quality of process water.
- (i) Quantity and quality of the wastes discharged.
- (j) Quality and quantity of water available in the receiving stream for the assimilation of wastes to be discharged which is interrelated with the regulations and standards of the stream control agency of the state in which the site is located.

All of the factors discussed above except waste disposal have always been of importance and now waste disposal has become so important it might be said that something new has been added to the problem of site selection.

Items (a) to (f) inclusive, while most significant, are beyond the scope of this paper and will not be discussed further.

The size and topography of the site is of major importance since in many cases the most feasible method of solving the waste disposal problem is by storage in shallow basins which may serve both as equalization tanks and oxidation lagoons, or by storage in reservoirs which provide a substantial amount of impoundment with release controlled in proportion to the ability of the stream to assimilate pollution. Frequently lagoons may be only one of the treatment devices but will have a significant bearing on the overall

performance and cost. Another important consideration is that changes in process or upgrading of regulatory standards may require more complete treatment than those currently envisioned. All these factors underscore the importance of acquiring ample acreage for lagoons to care for current and future needs.

WATER SUPPLY

Because the amount of industrial waste is a function of water supply requirements and because the quality of raw water available is related to the quality of the stream for assimilation purposes, surface water supply merits special consideration in this paper as a site requirement. (Obviously, in the case of underground sources, consideration of the quality of the water in the receiving stream is independent of water supply.)

The usual general requirements of an industrial water supply specify that it should be virtually free of suspended matter and turbidity, low in color and hardness, free of objectionable tastes and odors, and low in iron, with a pH in the vicinity of 7.0. The above applies to industries using water for process purposes which is the problem we are primarily concerned with. There are in addition a number of industries that use water very largely for cooling and for these industries low and uniform temperature are most important although the permissible tolerances of chemical constituents can be higher.

Formerly the quality of water available in its natural state was a much more important factor in site selection since many older industries were located to take advantage of a lake or stream which provided water of sufficiently good quality to be used without treatment, but generally speaking, today's requirements are sufficiently exacting that few natural waters are good enough to be used without treatment.

There are, of course, many exceptions to the above and currently considerable study is being given to the possibility of using different grades of water for appropriate uses in a wet process plant.

Generally speaking, once the quantity of water for processing requirements has been established, the determination of the quantity of waste to be handled is comparatively simple. Obviously, certain deductions can be made to cover uses which contain no pollution of which cooling water is the most important. However, it should be noted that the addition of large amounts of heat to cooling water may complicate the stream pollution problem.

Setting up the quality of the waste, i.e., the amount of pollution resulting from various processes, is apt to be troublesome, particularly if the source of information happens to be an old mill situated on a stream where are a number of different outlets discharging in locations difficult to gage. In many cases, it is necessary to calculate pollution loads from data and experience at other mills manufacturing similar products, and this is always necessary in a case of a newly formed company.

CAPACITY OF THE RECEIVING STREAM TO ASSIMILATE INDUSTRIAL WASTE

From our previous discussion the selection of a site is now reduced to this form; that the total pollution load to be discharged into the stream from the proposed plant in its initial and ultimate size has been established. The next step is to select several tentative locations. In many cases this can be done as office study with the aid of local development agencies as are maintained by many states and by railroads and other utilities. Speaking practically, in the southeast area of the United States there are a limited number of sites which contain these important elements; namely a large tract of land with suitable topography located on a good sized stream, with access to major highway and railroad facilities, and reasonably near a city or town large enough to supply adequate community resources such as schools, hospitals, housing, recreational facilities, etc. As an indication that such sites are becoming scarce, several larger industries having need for large wet process sites have acquired such sites for future development.

In the consideration of how much treatment of the industrial waste is required it is obviously necessary to determine the assimilation capacity of the stream on which the site is located. In general dissolved oxygen is the most important analytical constituent and in most cases there is adequate published data for preliminary studies. After an initial elimination has been made, it may be necessary then to have analyses made to determine the quality of the water in the receiving stream at those sites which are still under consideration.

At sites below larger impoundments with low level outlets which may be either discharge gates or hydraulic turbines, consideration should be given to the possibility of depressed dissolved oxygen flows resulting from the discharge of bottom water. This condition is giving engineers in the southeast serious concern since the assimilation capacity of these conditions is very much lower than would be normally expected. Many of you are familiar with the work of Mr. Milo A. Churchhill, Chief of the Stream Pollution Control Section, Tennessee Valley Authority and the extensive studies which led to the remedial measures taken at the Roanoke Hydroelectric development of Virginia Electric and Power Company on the Roanoke River in North Carolina.

The current programs of stream flow measurements are so extensive that at the present time we very rarely lack sufficient flow data to make adequate estimates of stream flow at a given site. Having done this then the question arises as to what figure of stream flow will be used to test periods which may be critical with respect to maintaining a proper oxygen balance in the receiving stream. Various figures which have been used include:

- A. The minimum daily average flow.
- B. The minimum consecutive five day average flow.
- C. The minimum average calendar month.

In recent years there has been a trend among regulatory bodies to accept a condition based on an occurrence 9 years out of 10 with a possible deviation of one year out of 10. This figure is arrived at statistically by the skewed probability analysis. It should be pointed out parenthetically that Dr. Velz, whom you have heard this afternoon, through his work for the National Council for Stream Improvement, has had a great deal to do with the acceptance of this 9 years out of 10 basis. In one state where we have worked the language of the act creating the regulatory body contains the language "reasonable and capable of attainment" and this in turn has been defined administratively as an occurrence 9 years out of 10. Several other states have also accepted this basis and hopefully it is reasonable to suppose that it will become of rather general acceptance.

In the past many regulatory bodies have established the minimum daily average flow which seems unduly severe and particularly if the stream is subject to diurnal fluctuations due to the operation of hydro plants above.

Along with the determination of the stream flow to be used it is also necessary to have data regarding stream velocities which in turn determine the time of transit as a prerequisite to a computation of the sag point of the dissolved oxygen profile.

In the Southeast there is a factor of growing importance effecting the quantity of stream flow available for assimilation, namely the increasing use of water for irrigation. In this area it has been proved economically feasible on high value crops such as cotton and tobacco, particularly in view of current acreage restrictions. Because irrigation is largely a consumptive use it is obvious it can reduce low flows materially and thus upset the balance of waste assimilation factors in the stream so a forecast of possible use for irrigation should be included in stream flow estimates.

AMOUNT OF TREATMENT REQUIRED

Having determined the stream flow data to be used and the estimated pollution load, computations can be made of the quality of the water which will result below the site and thus determine the degree of treatment required. As was pointed out earlier, the size of the site and its topography is a most important element. In most cases since the most obvious and economical solution to achieve the degree of treatment required is by holding tanks and/or lagoons, it is essential that large areas of relatively level land be available. In terms of capital investment required to build and equip a new plant, the cost of land, if acquired at the time the site is under consideration, is usually relatively small. In a rather extensive study which was made some years ago by our office on a pulp mill location, at the outset a basic requirement of 400 acres for a plant site and 4,000 acres for lagoon areas was established which was estimated as ample for current and future needs.

The lagoon area does not need to be high grade land; clearing may not be necessary, in fact trees may be an asset. Frequently low cost land in the flood plain can be used, but if such land is used the design of the dikes must provide for covering vegetation to provide adequate root structure on the dikes so they can withstand an occasional overflowing without failure. Obviously, in such cases a calculated risk is taken that the dikes may be overtopped by a flood during the first years before vegetation is established. Other considerations in the design of lagoons will not be gone into since design is beyond the scope of this discussion.

It is very advantageous to own land on both sides of the river. In the first place this prevents claims resulting from adverse ownership and second it permits a diffuser pipe to be laid across the width of the stream to the other shore which is most helpful to provide equal dilution across the stream and keep stratification at a minimum.

For textile mills, where dyeing and finishing are done, a holding tank and/or a lagoon will be helpful in the following ways:

- (a) Reduce the shock effect of batch discharges by reducing the effect of heavy concentrations of injurious constituents. Where different colors are used, the tank will blend these colors to a more neutral and thus less unsightly shade.
- (b) In many woolen mills, the dyes tend to be acid, the finishing processes alkaline, and the mixture may be somewhere near neutral with a resultant deposition of sludge. For many types of textile wastes, storage in shallow lagoons will result in considerable B.O.D. and color removal. The addition of settled sanitary sewage frequently helps this process besides providing an economical solution to this problem.
- (c) If lagoons can be built in gravel or sand deposits as occur in some river valleys, percolation into the soil will provide natural filtration and a consequent lessening of the amount of waste discharged into the stream. This obviously requires regular cleaning of the bottom.

In discussing the use of lagoons in connection with pulp mills, and pulp and paper mills, it is important that the drain piping be laid out so that the wastes may be separated according to their pollution content. For a new mill, this can be incorporated in the original design. If this has to be done in an existing mill or later in a new mill, it involves a difficult, expensive job and the changes involved to segregate and collect this waste may cost as much as the treatment plant itself.

In a bleached sulphate mill wastes may be classified as:-

- (a) Wastes containing suspended matter primarily fibers.
- (b) Potentially toxic wastes but not necessarily oxygen depleting.
- (c) Wastes which cause oxygen depletion in the receiving stream.

To remove the fibers and toxic materials, ("a" and "b" above), lagoons affording, say one day detention, will catch the fibers, keep them out of the river, and also this period of detention will render mercaptans harmless, the principal toxic constituent. This type of lagoon, which may be termed a "fiber trap", should be built in duplicate to facilitate cleaning. In some cases, fiber removal can be better effected in a mechanical clarifier in the form of a shallow circular concrete tank.

Provision should also be made so that "spills" can be isolated and diverted into small lagoons to prevent the emergency dumping of black liquor of such strength as to cause serious oxygen depletion in the stream. This type of lagoon is particularly useful in the start-up period of a plant when mistakes in operation are more liable to occur. With the results of "spills" impounded, steps can be taken to dispose of these potentially very harmful wastes in an orderly fashion with a minimum of shock on the receiving stream.

To take care of the oxygen consuming wastes, largely "brown" wastes from the sulphate mill, shallow oxidation lagoons which afford capacity for a number of days storage are both helpful and relatively inexpensive. Available data indicates that 30 days storage in lagoons five feet deep will result in B.O.D. reduction of 50% or over under the climatic conditions prevailing in the Southeast.

Still another type of most effective lagoon is what might be termed impoundment lagoons, which are, in effect, basins of sufficient size to impound wastes in times of stream flow too low to take the normal loading for release when stream flows are high enough to maintain the dissolved oxygen above allowable limits. Such lagoons are in effect storage reservoirs and, in some cases, approach water supply and water power reservoirs in size, so that, if this type of what is frequently termed massive impoundment is used, the amount of land required is very great. As Dr. Velz has stated this type of impoundment can make possible the complete assimilation resources of the stream on an annual basis.

With the number of sites reduced by the elimination of those with some marked defect, before a final decision regarding a site is made, it is most helpful to have informal discussions with the appropriate stream sanitation officials.

These men in addition to intimate knowledge of local conditions will frequently make what amounts to an informal ruling on the basis of their own state laws and administrative procedures regarding the adequacy of the scheme of treatment proposed for a particular site. In many cases conferences may be desirable also with officials of state recreation, fish and game boards. To the writer it is important to bear in mind that in addition to a knowledge of the law, it is most helpful to know in what frame of mind the law is administered.

With tentative solutions of the waste disposal problem arrived at, this phase of the site selection problem can then be evaluated along with other significant factors. Usually the final determination is the function of top management acting on recommendations of the engineer. While estimates of the cost of development of various sites can be made with the dollar a common denomination, there may be intangible factors of which community facilities are significant which will implement a final decision.

In conclusion, in the selection of a site for a large wet process industry, the problem of mill effluent disposal has become one of the significant factors requiring evaluation. Consideration of this problem involves determination of the initial and ultimate pollution loads which will have to be disposed of and the assimilation capacity of the receiving stream, which in turn effects the degree of treatment required. Since one of the most feasible methods of reducing the pollution load on the receiving stream involves the use of lagoons and since lagoons require extensive areas of land, it is important that at the site selected the initial purchase of land at the site selected should be large enough to permit sufficient lagoon capacity for the ultimate capacity of the plant.

WATER POLLUTION

by

George A. Selke,
 Commissioner of Conservation,
 State of Minnesota.

Guest Speaker

IMPORTANCE OF WATER

A civilization cannot survive without water. Wise use of our water supplies is necessary to insure our standard of living; to perpetuate our way of life. Water pollution, therefore, is a serious threat to our society -- a problem which presents a challenge which must be met. The problem has been magnified by growth.

1. During the past 50 years, the United States has more than doubled its population, concentrated two-thirds of it in urban communities, increased the number of automotive vehicles from 1,000 to 70 million, multiplied total industrial production by 900 per cent.
2. Tremendous expansion of chemical industries. We have over 500,000 distinct chemical compounds in use in industrial production today, while 20 years ago there were only a few hundred.

OUR DEMAND FOR WATER

The United States daily uses an estimated 300 billion gallons of water. Industry and power generation require about 46 per cent of this total. Agricultural irrigation accounts for the largest share of the remaining 54 per cent. Households use is slightly less than 5 per cent.

INCREASED LEISURE TIME --- and the population explosion have placed unrepresented pressures on our waterways from the recreational standpoint.

- A. Polluted Waters are esthetically objectionable: unfit for fish and wildlife; unpleasant for swimming, boating, other recreational outlets.

LIFEBLOOD OF PRODUCTION --- 600,000 gallons of water are required to make one ton of synthetic rubber; 65,000 gallons for a ton of steel; 510,000 gallons to make 1,000 yards of woolen cloth; one million gallons to produce 1,000 barrels of aviation gasoline.

POPULATION EQUATIONS

1. Municipal Wastes -- In 1920, municipal wastes had a "population equivalent" of 40 million persons. Today, even though 105 million persons are served by 6,500 sewage treatment plants costing \$8 billion, the population equivalent of discharged municipal wastes has risen to 75 million persons.

We have lost ground in reducing total municipal pollution discharges into our waters.

2. Industrial wastes -- In 1920, industrial pollution from organic wastes had a "population equivalent" of 17 million people. Today, the polluting effects of these wastes are estimated to be double those of municipal wastes -- or a population equivalent of 150 million persons.

3. The Future -- By 1980, it is predicted 90 per cent of the population growth will be urban in character, bringing with it the problem of disposing of huge volumes of complex municipal and industrial wastes into limited watercourses of relatively fixed assimilating capacity.

Sewage outlets and water intakes are being wedged closer together and reuse of water must be increased.

Example of problem: Chicago pours into the Illinois waterway, each day, effluent which has the population equivalent of more than 1 million persons and contains 1,800 tons of contaminants.

AREAS OF CONCERN -- SOME ILLUSTRATIONS

In most instances, we have sufficient information to cope with the problem of pollution, but we are moving very slowly...

1. Raw sewage, garbage and industrial wastes from stockyards and slaughterhouses continues to pollute our rivers.
2. The Androscoggin river of New Hampshire and Maine has been described as the most polluted water of its size in America.
3. For the past 10 years, it has been common knowledge that the Animas, a tributary of the Colorado river, was contaminated by radioactive wastes from uranium milling operations.
4. Some general causes of water pollution:

Failure to treat all sources of sewage or waste...
 Intentional and accidental bypassing of untreated pollutants...
 Overflows of raw sewage and storm water mixtures...
 Unexpected sharp overload of otherwise adequate facilities...
 Failure of authorities to require waste collection and treatment.....
 Incompetent or poorly supervised plant personnel... Interruption of stream flow on which the treatment process depends for dilution water.....

AREA OF RESPONSIBILITY

For the most part, official responsibility for environmental health activities properly rests with the level of government closest to the people capable of performing the function.

1. The role of industry in the control of environment health hazards is increasing.
2. Over the next decade social and economic forces will increase the potential of environmental health hazards.
3. It is becoming increasingly apparent that the essential elements of our surroundings -- the Water we drink, the air we breathe, the food we eat, the shelter which protects us, man's pursuit of a fuller life via his occupation, recreation, transportation, social organizations -- have a definite and complex inter-relationship.

COMPONENTS OF ENVIRONMENT

Three major areas of health concern are recognized:

1. The biological component -- including living things of the plant and animal kingdom, ranging from the food upon which life depends to those micro-organisms responsible for disease. (The health related problems of water pollution now include a new array of water pollutants.)
2. The physical component -- encompassing the non-living things and physical forces affecting man, such as water, air, food, chemicals, heat, light and radiation.
3. The social component -- which includes cultural values customs, attitudes, economic status and social and political organizations.

NON-BIOLOGICAL HEALTH HAZARDS

These include social factors, nuclear energy, air and water pollution, which compound the problem of environmental health.

1. Our increased use of materials and products is attended by increasing quantities of potentially toxic substances.
2. It is the total and cumulative exposure of the individual to ionizing radiations that is important no matter how the separate components reach him.
3. Increasing urbanization, the growth and coalescence of large metropolitan complexes and new patterns of living multiply the sources of environmental hazards.

4. Difficulties of controlling water pollution are intensified by the multiplicity of political subdivisions, with varying financial structures and philosophies of public responsibilities. Intensive public education on the vital role water plays in our society is necessary.

COMPLICATIONS IN CONTROL

1. Industrial Chemicals

- A. The problems of insuring pure water in adequate amount is complicated by an assortment of organic chemicals, many of industrial origin that find their way into our waterways. These chemicals adversely affect plant and animal life and diminish recreational resources.
- B. Industrial wastes must be identified and great effort exerted in order to cope with them. Example: Soap, formerly not a problem, is being replaced by synthetic detergents which now are contaminating our water supplies. The impact of this problem is particularly acute in metropolitan areas.

2. Nuclear Reactors

- A. There are now 500 nuclear reactors in the United States, most of them concerned with the production of power.
- B. Presently, there is no method of disposal of high level wastes which contain high amounts of curies (measure of radiation) per gallon of liquor -- and which have a life ranging from 25 to 4,000 or 5,000 years.
- C. There is no tradition in disposal. The current solution is a simple one: Hold it!
- D. By 1980, we will have an additional 65 to 70 millions gallons of high-level waste. Intense studies are underway to determine "What to do with it." Low-level wastes are now being discharged to the environment.

3. Ionizing Radiation

- A. Little public concern is shown over the problem of ionizing radiation. The amount of radiation being distributed in the United States is greater than at any time in the history of the world.
- B. There are some 130,000 Roentgen-ray machines in use in the United States today. Until very recently, these had not been scrutinized with respect to the health impact on the operator, the patient, or the industrial user.
- C. Within the past 12 years, elements have been produced

that never existed before. Radioisotopes have moved rapidly into medical and biological research and into industrial use.

INTERNATIONAL BOUNDARY WATERS

1. Of great international concern is the problem of the pollution of our common boundary waters. These waters include the St. Clair River, Lake St. Clair, Detroit River, St. Mary's River from Lake Superior to Lake Huron, and Niagara River from Lake Erie to Lake Ontario.
 - A. Large populations and great industries have developed along their shores. It is important to evaluate the nature and extent of pollution; the remedial measures necessary.
 - B. The cumulative effect of uncontrolled waste disposal into these boundary waters could seriously reduce their capacity to perform many beneficial and necessary functions vital to the health, recreation and economy of people on both sides of the border.

RESEARCH IS NEEDED

1. We require more information about the pollutants to which the consuming population is exposed.
2. We need more precise data on the health status and incidence of illness and disability in the population.

RESPONSIBILITY IN INDUSTRY

1. Many industries are showing a sense of moral and economic obligation - a "pollution consciousness."
 - A. Great Northern Oil, in the Twin City industrial complex invested \$1 million on waste treatment control; National Container Corp., of Owens-Illinois Glass Company spent \$500,000 on waste treatment ponds; Champion Paper and Fibre Company of Canton, North Carolina, is spending several million dollars to stop waste flowage into the Pigeon River; Caterpillar Tractor Company of Peoria, Illinois, is sponsoring a national advertising campaign stressing the importance of water to industry; American Cyanamid constructed a \$4.5 million waste treatment plant at Bound Brook, New Jersey.

POLLUTION AND THE FUTURE

1. The growth and economy of a nation is highly dependent upon its water resources.
 - A. Our future prosperity hinges on our ability to reuse water from all sources. Water is the life-blood of production.

- B. The old adage, "You never miss the water until the well runs dry" is still true.
- C. We need to inform the public, industry, government officials and the children in our schools of our marvelous water resources - and the need to conserve our waters.

BRITISH PRACTICE IN THE TREATMENT OF TRADE WASTES
AND EXAMPLES OF ITS EFFECT ON SEWAGE TREATMENT PLANT DESIGN



L.W.C. Sturgeon,
 Director,
 Welland & District
 Health Unit.

Chairman
 Session #5

by



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The development of British practice in the control and treatment of trade wastes over the past hundred years has been governed in no small measure by Government legislation. Before considering this legislation, however, it might be well to look briefly at the physical background to the problem.

Great Britain is for the most part a densely populated country, very much industrialized, with no large bodies of water except the sea. The rivers and lakes are very small by Canadian standards. The densest industrial concentration tends to grow up on or near the coal fields, producing diversified industries in association with large populations; more scattered development tends to produce the specialized factory with the relatively small associated population. Both of these conditions present their own particular problem in trade waste disposal in the absence of adequate diluting streams.

I am given to understand that, under the common law of Great Britain, anyone may discharge their waste water into the natural drainage course of the area subject only to such action as a riparian owner might take to recover damages. This was the general practice up until the middle of the nineteenth century and its effect on the natural water courses of the country can well be imagined. W.T. Sedgwick in "Principles of Sanitary science and Public Health" quoting Dr. Budd, states:-

"For the first time in the history of man, the sewage of nearly three millions of people has been brought to seethe and ferment under a burning sun in one vast open cloaca lying in their midst."

"The result we all know. Stench so foul we may well believe had never before ascended to pollute this lower air. Never before at least has a stink risen to the height of an historic event. For months together, the topic almost monopolized the public prints. "India is in revolt and the Thames stinks", were the two great facts coupled together by a distinguished foreign writer to mark the climax of a national humiliation."

This 'Historic stink' resulted in action by the Government who set up the British Royal Commission of Sewage Disposal in 1857. This body issued its first report in 1865 which was followed by the Public Health Act of 1875.

The Public Health Act placed on local authorities the duty 'to provide such public sewers as may be necessary for effectually draining their district' and 'to make such provision by means of sewage disposal works or otherwise as may be necessary for effectually dealing with the contents of their sewers'. It also prohibited them from discharging foul water until it had 'been so treated as not to affect prejudicially the purity and quality of any stream, water course, canal, pond or lake'.

The Public Health Act was followed in 1876 by the Rivers Pollution Prevention Act. The administration of this latter Act fell to a large number of different authorities such as Catchment Boards, Drainage Boards, Fishery Boards and the like. Their powers were not very great or well defined and they were all to be found operating in the drainage area of the same river. Although this was not a very satisfactory piece of legislation, it did result in many industries taking some action to treat their wastes or to divert or to seek to divert them into the sewers of local authorities, where these existed.

The duties of these various Boards were subsequently taken over by Rivers Boards under the Rivers (Prevention of Pollution) Act of 1951. This has had the effect of placing the whole of any river and its tributaries under the control of a single authority for all purposes, including the conservation of water resources and the prevention of pollution.

However, under the Public Health Act of 1875, local authorities were allowed to refuse to accept any trade waste which might interfere with their method of disposal or for which they had insufficient capacity either in their sewers or their disposal works. This unfortunate state of affairs was perpetuated in various revisions of the Public Health Act even as late as 1936.

As will be appreciated, the practical results of this situation which persisted for some sixty years, varied very much in different parts of the Country. They depended in general on whether local authorities were anxious to attract industry, whether they had the money to spend on sewers and sewage disposal, whether they were sensitive about the pollution of their rivers, and whether the particular authority responsible locally for implementing the Rivers Pollution Prevention Act had the will to enforce it.

A 'co-operative' authority would accept and treat the trade wastes either free or by agreement with the industries concerned to pay for the service. Sometimes, as a result of so doing, they found it difficult to maintain the standard of their effluent.

An 'unco-operative' authority would refuse to accept trade wastes, in which case the industries were left to treat them by themselves. This was often difficult and expensive whereas it might have been easy to treat these wastes in association with domestic sewage. The amount of treatment that trade wastes received

from the factory owners prior to discharge would obviously depend on their sense of civic duty and/or the willingness of the various river authorities to take them to court.

In practice, things were not as bad as one might suppose. A great deal of research was carried out by sewage treatment plant staffs under local authorities and by others, into the treatment of trade wastes with domestic sewage. There are numerous cases of successful co-operation between local authorities and industries and a good example of the enterprising approach to this problem in some quarters is the acceptance of wool scouring wastes into the sewers by the textile towns in the West Riding of Yorkshire. The grease contained in these wastes was extracted and sold for the manufacture of lanolin and for other purposes.

A great many voluntary agreements were made between local authorities and industries, sometimes providing for payment either of a capital contribution towards new works or of an annual charge. But the position was, however, unsatisfactory. Local authorities often found themselves saddled with bad agreements and new industries had no certainty that their wastes, other than domestic, would be taken into the public sewers even if they were prepared to pay for the service.

The authorities concerned with this problem gave much thought to the possibility of evolving some system which would be both workable and provide definite reasonable rights to both parties. The result was the Public Health (Drainage of Trade Premises) Act of 1937. The intended effect of this Act is:

- 1) To give industries the right of access to public sewers subject to certain conditions,
- 2) to give local authorities safeguards in the acceptance of trade wastes into their sewers, and
- 3) to put upon the Minister the responsibility for ensuring equitable arrangements between these two parties in the event of dispute.

When this Act was passed, the Minister in question was the Minister of Health. However, in the re-organization following the establishment of the National Health Service, all duties under this Act were transferred to the Minister of Housing and local Government.

Under this Act, extensive powers were conveyed on the local authority. They are enabled to pass by-laws governing the discharge of trade wastes into the local sewerage system and they are enabled to enter into agreements with industries for the treatment of trade wastes. However, ultimate authority is still vested in the Minister of Housing and Local Government whose responsibility it is to ensure that equitable arrangements are made between the parties concerned.

The Public Health Act of 1937 also provides that no trade

waste may be discharged from any trade premises into a public sewer until a "Trade Effluent Notice" has been served on the local authority by the owner or occupier of the premises.

This notice, which is in effect an application to discharge trade wastes into the sewerage system, must give details of the nature and composition of the trade waste, the maximum quantity which it is proposed to discharge in any one day, and the highest rate at which it is proposed to discharge it. On receipt of such a notice, the local authority may specify a date before which the effluent may not be discharged and may then either give its consent to the discharge unconditionally, which it would presumably do if it had already made by-laws and the proposed discharge complied with them, or it may give its consent subject to such other conditions as it thinks proper to impose. These conditions would be with respect to the following:-

- a) The point in the sewerage system at which the discharge may be made.
- b) The nature or composition of the trade waste; that is to say the local authority may require the trade waste to be pretreated.
- c) The maximum quantity which may be discharged in any one day.
- d) The highest rate at which it may be discharged.
- e) Any other matter with respect to which by-laws may be made under the Act.

The industry is protected in some measure in that, in any case, no condition may be made which is inconsistent with any by-laws which are already in force. The result of this is, of course, that most local authorities have refrained from making by-laws and to date they have not been pressed to do so by the Ministry concerned.

In practice, therefore, local authorities lay down new conditions to meet each individual case. The industry concerned has further protection in that, if it is aggrieved by any conditions made by the local authority, it may appeal to the Minister who may annul or modify it to what is considered reasonable or, of course, dismiss the appeal.

From the above rather brief description of this Act, it would appear that local authorities have things very much their own way provided that they are reasonable in their demands. However, there is a further provision which has caused a certain amount of dissatisfaction among the officials who have to operate the Act, and has had considerable bearing on the design of treatment plants for both domestic sewage and for trade wastes.

The provisions to which I refer arise from a natural dislike of retrospective legislation which may deprive someone of an old established privilege. The Act provides that the present of a local authority to the discharge of any trade waste is not

necessary if a waste of the same nature or composition was lawfully discharged from the premises concerned into the sewer at some time within the period of one year prior to March 3rd, 1937. Thus, an industry may have a prescriptive right to continue to discharge a difficult trade waste into the public sewers, and so long as no increase in the quantity or change in the composition is made, the industry cannot be made to pay more than was in fact being paid prior to the passing of the Act. The Act came into force in July, 1937 and, therefore, had not been in operation very long before the outbreak of war. Conditions during the next years were rather exceptional so it is only since the war that an opportunity has existed to assess its value.

From the point of view of the local authorities, the perpetuation of the rights of industries to discharge wastes into the sewers, without consent or condition, has created anomalies. For example, those authorities who in the past have complied with official recommendations and accepted trade wastes into their sewers in an attempt to protect the rivers from pollution, now have inadequate control over such discharges. On the other hand, authorities who refused to accept trade wastes prior to the passing of the 1937 Act, now possess the advantage of full control of all such discharges into their sewers.

In many cases when discharges of trade wastes received the consent of the local authority forty or fifty years ago, it was not possible to foresee the changes which have taken place in sewage purification technique, nor the high standards of river purity which are now being required. Many existing discharges have an inhibiting effect on bacterial processes, thus preventing the local authority from following the most advantageous and economical practice in treatment. Also, where additional works are necessary to produce a satisfactory effluent, present day costs are out of all proportion to those ruling at the time when the discharge was originally accepted.

From the point of view of industries, discharges allowed under statutory rights may be putting such a strain on the sewage purification plant that the local authority is compelled to impose more stringent conditions on the discharges from other factories not possessing such rights. In such instances, if reasonable control could be obtained over all discharges, the local authority would be in a position to offer other factories in the district more favourable conditions in regard to pretreatment.

Two examples of how the regulations under this Act have affected the design of sewage treatment plants may be of interest. In each case the method of treatment was much the same but was adopted for very different reasons.

The first case involves sewage treatment for a town of some 20,000 population with engineering wastes of a volume equal to the domestic flow. The wastes under consideration tend to be weak, but do include oils and metal salts which are inhibitive to the action of the activated sludge process and percolating filters.

In this particular instance there had been no discharges of trade wastes of any significance prior to the passing of the Drainage of Trade Premises Act in 1937. No industries, therefore, had prescriptive rights, and the local authority was able to make restrictions and prohibitions for the engineering wastes to be discharged from two large automobile manufacturing plants. These prohibitions and restrictions are set out in Appendix I to this paper and may be of interest.

To comply with these requirements the factories concerned agreed to install pretreatment plants, and these took the form of oil recovery units, which incidentally are paying for themselves, and chlorination units for the elimination of cyanides. So long as the standards set up by the local authority were maintained, no adverse effects on the sewage treatment plant would be expected. However, it was appreciated that even with facilities for inspection of the factory pretreatment plants, and the best of intentions on the part of the industrialists, accidents might occur which could put the sewage treatment plant out of action. Although in such event the local authority would have cause of action against the industries, this would be poor recompense for the damage and inconvenience which might be caused. It was, therefore, decided that the sewage treatment plant must be so designed as to minimize the effects of any such accidental discharges.

The sewage treatment plant under design was to discharge to a very small stream, the average dilution being about two to one. In summer this dilution reduces to almost nil. The local Rivers Board, therefore, insisted on an effluent having no more than ten parts per million of B.O.D. and fifteen parts per million of suspended solids at all times. It will be appreciated that this is a high standard to maintain continuously, and the possibility of an upset by accident 1 shock loads was a very serious matter.

A sewage treatment plant based on the activated sludge process is perhaps more vulnerable to such conditions than a percolating filter plant. However, it was decided that whichever of these two was adopted, some form of protection was necessary and that this could best be provided by a first stage of high rate recirculation in percolating filters.

As there was plenty of natural head available, and in other respects the site was suitable for percolating filters, these were adopted for the final treatment also. This decision was influenced in addition by the local authorities desire to have a plant which could be operated by one eight-hour shift per day and remain unattended at night. By this means, labour costs could be minimized.

In order to comply with the requirements of the local Rivers Board, it was desirable that as much of the storm water reaching the plant as possible, should also have full treatment.

Since the site was suitable, the storm tanks were provided in series with the full treatment works instead of in parallel as is more usually the case.

This arrangement is shown in Figure 1, and it will be seen that the contents of the storm tanks pass forward for full treatment automatically as the storm flow falls off. This ensures that the tanks are empty to receive the next storm when it occurs. The size of these tanks is such as to contain the flow arising from a normal rainstorm in the drainage area so that only under exceptional circumstances do they overflow to the receiving stream.

In designing the first stage high rate filters with their sedimentation tanks, the guiding principle was not only to effect the maximum removal of B.O.D., before the peak flow passed to the second stage treatment, but also to provide as much dilution as possible for any shock load of a toxic nature. The recirculating pumps were, therefore, arranged to maintain a uniform flow equal to three times the dry weather flow through this stage. That is to say, when one dry weather flow is being received at the works, the rate of recirculation is two dry weather flow. The rate of recirculation reduces automatically as the flow into the works increases. This control is achieved by means of the measuring flume between the storm tanks and the primary sedimentation tanks.

The recirculation is taken from the bottom of the intermediate sedimentation tanks and so includes all the humus produced in this stage which then resettles in the primary sedimentation tanks. All the sludge produced is, therefore, concentrated in these primary tanks for discharge to the digestion tanks.

In two stage plants of this type it is thought by many people that intermediate settling is unnecessary, and that humus can very well be accepted directly in the second stage of treatment, whether this be activated sludge or percolating filters. In this case, however, it was felt that the presence of these intermediate tanks with a reasonable detention period was a further safeguard against shock loads.

The design data for the whole plant was as follows:-

Dry Weather Flow	-----	2 M.G.D.
Maximum Flow for Full Treatment	-----	6 M.G.D.
Storm Tank Capacity	-----	500,000 gallons
Primary Sedimentation	-----	2 hours' detention at maximum flow.

Intermediate Sedimentation -----	1½ hours' detention at maximum flow.
Final Sedimentation -----	2 hours' detention at maximum flow.
Primary Filters Dosing Rate -----	2,400 gals/ cu. yd diluted flow = 800 gals/cu.yd. raw sewage at D.W.F.
Secondary Filters Dosing Rate -----	200 gals./cu.yd on D.W.F. 600 gals/cu.yd on max. flow.
Recirculation -----	0 to 5 M.G.D., in 1 M.G.D. Steps.

From these figures it will be seen that the overall dosing rate in the filters is 160 gallons of crude sewage per cubic yard. This compares quite well with the loading of an orthodox percolating plant.

In the second case, a first stage of high rate filtration was adopted but for quite a different reason.

In this case also, the population served was about 20,000 and the trade wastes were equal or rather more in quantity than the domestic flow. They were, however, very strong, having a B.O.D. of between 800 and 900 P.P.M. They were derived from tanneries which had a prescriptive right under the Act to discharge their wastes untreated to the sewers. These wastes were generally very alkaline, and the pH of the resulting mixture with domestic sewage was eleven or more.

Because of the very high pH, settlement in primary tanks was very poor. Very little reduction in B.O.D. by these means was possible and subsequent oxidation was difficult. Experiments were made with a view to neutralizing these trade wastes at their source. These experiments showed that this would be a very expensive procedure.

A pilot plant was installed at the sewage treatment plant and the results obtained showed that a high rate filter with recirculation of the effluent would reduce the pH to approximately seven. At this value, a reasonable settlement could be effected and a reduction of B.O.D. to about 250 P.P.M. was possible.

A first stage of percolating filtration was, therefore, adopted with a dosing rate of 1,000 gallons of sewage per cubic yard. Recirculation was as in the previous example but a rate of four times D.W.F. was maintained in the primary settling tanks. In this case, intermediate settlement was not provided partly because no shock loads were involved and partly on account of site conditions and an over-riding need for economy in the design of this particular plant.

A flow diagram for this installation is shown in Figure II.

The whole of the filter effluent is returned to the inlet to the primary settlement tanks and the effluent from these tanks, which is at a steady rate of four times the dry weather flow, is split automatically. The splitting device allows a flow equal to the incoming flow of sewage to pass forward to the second stage filters. The remainder is sent back to the first stage filters and so back to the primary settling tanks.

The second stage of treatment could equally well have been by activated sludge or percolating filters. Percolating filters were chosen for a number of reasons. As in the first example, it was desired to have no night attendants, the site was suitable and there were in existence some filters which could be incorporated in the design to provide some of the required capacity. This stage of filtration is on orthodox lines. Rectangular beds, with travelling distributors, were adopted to suit the site. The dosing rate is 125 gallons per cubic yard per day on dry weather flow.

In this plant, the storm water tanks are in parallel with the full treatment plant. They are in fact existing hand cleaned primary sedimentation tanks adapted for the purpose. This was dictated by considerations of economy and the fact that there was no special reason to cater for toxic conditions in the storm water, as in the first example.

These two examples do, I believe, serve to show how the problems of local authorities, in dealing with trade wastes in their sewage treatment plants, are affected by current legislation.

No doubt improvements to this legislation will be made in years to come, but the progress achieved by British authorities during the past eighty years does indicate that a serious effort has been made to control industrial wastes and reduce river pollution.

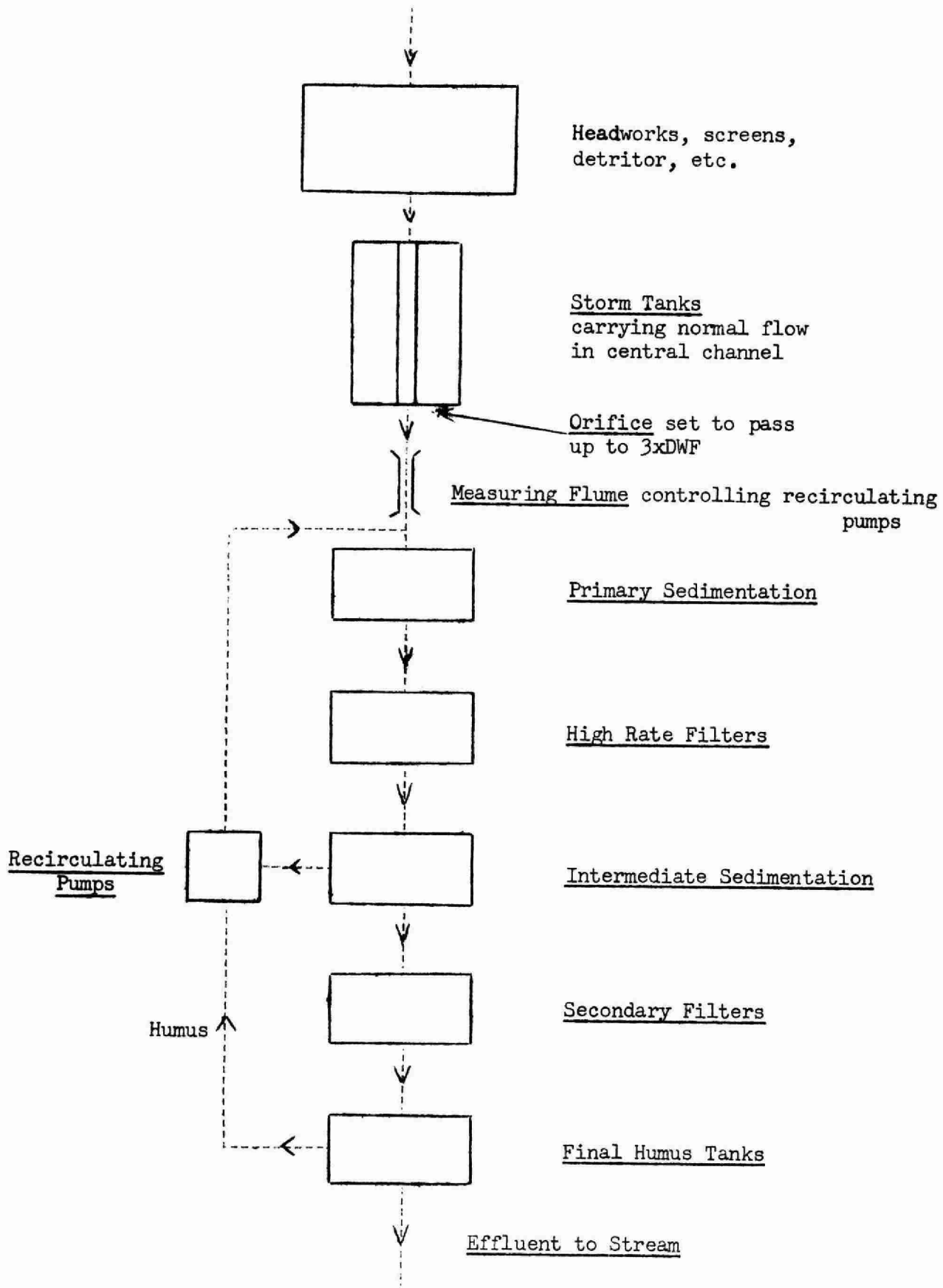


FIGURE I

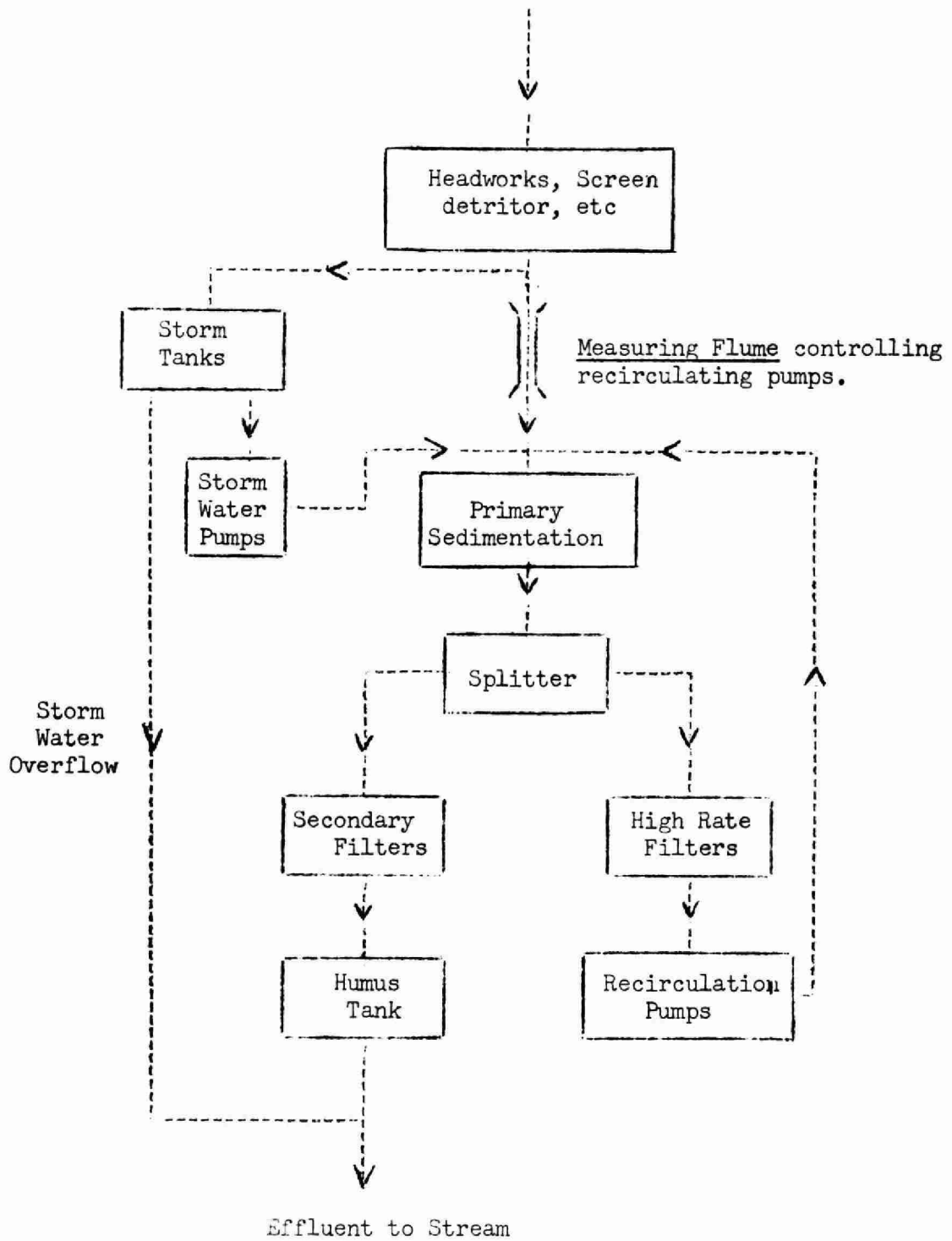


FIGURE II

APPENDIX I.

BOROUGH OF -----

TRADE WASTE AGREEMENT WITH MESSRS. -----MOTORS LTD.

PROPOSED HEADS OF AGREEMENT

1. Point of Discharge

The Trade Wastes to enter the Corporation's sewerage system at Manhole A.9.

2. Quantity.

The quantity of Trade Waste to be discharged to the sewers shall not exceed 220,000 gallons in any one day.

3. Rate of Flow

The rate of discharge shall not exceed 30,000 gallons per hour.

4. Measuring

The Company shall install a recording meter to measure the flow of Trade Wastes separately from domestic sewage.

5. Balancing

If required to do so, the Company shall provide means for regulating the flow so that it may be spread equally over twenty-four hours or be proportioned to the sewage flow to the treatment works.

6. Internal Drainage

The factory drainage system shall be so arranged that the contents of any plating or pickling bath cannot be discharged accidentally or otherwise without adequate dilution or neutralization.

7. Characteristics of the Trade Effluent

(1) Definitions.

Maximum concentration means the concentration of constituents ascertained by analysis of a mixture of four samples of equal volume taken in any period of thirty minutes at intervals of ten minutes.

Average concentration means the concentration ascertained by analysis of a mixture of 8 samples of equal volume taken at intervals of not less than one hour in any day of which two shall have been taken between the hours of Midnight and 7 A.M., and six between the hours of 7 A.M., and Midnight.

(2) Prohibitions.

The Company shall not discharge to the Sewer:-

- (a) Materials which evolve toxic gases or substances capable of producing noxious odours, which are harmful to men working in the sewers;
- (b) substances which may produce inflammable or explosive gases in the sewers;
- (c) residues of wool, hair, oakum, rags or coarse bodies capable of causing obstruction or encrustation of public sewers;
- (d) Residues or sludges resulting from purification of wastes;
- (e) substances which by reason of their nature and quantity adversely affect the biological conditions in the Ousel Brook;
- (f) (i) An effluent of which the pH value is less than 7.0 or more than 9.5 except between the hours of 7.0 a.m., and 7.0 p.m., when the permitted range shall be 6.5 to 9.5.
(ii). An effluent such that the oxygen absorbed from an N/80 solution of permanganate exceeds 100 parts per million in a shaken sample of the effluent or 60 parts per million in a settled sample of the effluent.

(3) Restrictions.

The Company shall not discharge to the sewer an effluent containing more than the following amounts of the stated substances:-

Constituent	Concentration in parts per million.	
	Maximum	Average
Total solids in suspension of which the loss on ignition must not be less than one-half	450.00	300.00
Coarse mineral solids settled in 30 seconds	Nil.	
Mineral or other oil or emulsions thereof.	*	

(3.) Restrictions (Continued).

* (A settled sample after acidification and standing for one hour must not develop a separate layer of mineral or other oil of measurable depth.)

<u>Constituent</u>	<u>Concentration in parts per million</u>	
	<u>Maximum</u>	<u>Average</u>
Tar	Nil	
Bitumen or derivatives thereof	Nil	
Alcohol	2.00	1.00
Amyl Acetate or derivatives	2.00	1.00
Trichlorethylene	2.00	1.00
The following constituents in solution:-		
Cyanide (as Cn) (free titratable)	1.25	0.50
Chromium (as Cr) (Hexavalent)	1.50	0.75
Copper (as Cu) (when tested at pH 7.8)	2.00	1.00
Zinc (as Zn) (when tested at pH 7.8)	2.00	1.00
Nickel (as Ni) (when tested at pH 7.8)	2.00	1.00
Iron (as Fe) (when tested at pH 7.8)	15.00	10.00
Aluminum (as Al) when tested at pH 7.8)	15.00	10.00
Sulphates (as SO_3)	200.00	175.00
Silicates (as SiO_2)	150.00	100.00
Phenols (as C_6H_5OH)	9.00	6.00

8. Processes

The Company shall not vary the processes producing a trade effluent in any way likely to affect the trade effluent without first notifying the Corporation.

9. Capital Contribution

The Company shall pay to the Corporation a capital sum in respect of the duplication of the sewer between points X and Y equal to the difference in cost between a 12 inch diameter sewer and a 15 inch diameter sewer.

10. Annual Charges

The Company to pay to the Corporation for all trade waste discharged, an amount to be calculated according to the following formula:-

$$A + B \frac{(M)}{(DM)} = \text{Pence per 1,000 gallons}$$

Where A = the cost in pence to the Corporation of their sewerage system per 1,000 gallons of sewage treated

Where B = the cost in pence to the Corporation of treatment per 1,000 gallons of sewage treated.

10. Annual Charges. (Continued)

Where M = McGowan figure for the trade waste.

Where DM = McGowan figure for theSewage.

11. Termination

Subject to the provision for prior determination hereinbefore contained, this Agreement shall remain in force until determined by the mutual consent of the parties hereto, provided that if either party wishes to amend the Agreement in any particular, then that party shall be at liberty to give to the other party three months' notice in writing at any time of the desired amendment, and in default of agreement between the parties as to the making and operation of the said amendment the matter in dispute shall be referred to the arbitration of the Minister of Housing and Local Government.

METROPOLITAN TORONTO'S APPROACH TO INDUSTRIAL WASTE

By

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 Municipality of Metropolitan Toronto

Pollution Control is a problem which concerns the majority of municipalities and industries today. Can the expense required in providing proper facilities to meet the desired standards be justified? The growing demand by the general public and government agencies for waste control is being aided by Industry's increasing awareness that it is also sound business practice.

With the need for pollution control facilities, has come research into methods to improve treatment and reduce its cost. This problem has been studied by many authorities across the continent and has occupied Metropolitan Toronto since its inception. Several codes to control the discharge of industrial waste have been recommended, rewritten and adopted by various centres in the past few years. Proposed codes have been discussed at many technical conferences such as this, with increased concern and appreciation of the problem. Industrial waste then, and its control, is a matter of prime interest, not only to the body which must provide the treatment facilities, but also to Industry which uses the municipal sewerage works.

We wish to review the factors which should be considered in the establishment of effective regulations for controlling the discharge of industrial wastes into municipal drainage systems. The problems that have been encountered in drawing up and enforcing existing codes on this continent makes it apparent that a single regulation, particularly for sanitary sewers, which will apply to all localities and situations, will be difficult to obtain because each individual case differs, depending on the size of the Municipality, the design of the sewer system, the number and type of industries and the nature of the treatment plant. However, a uniform code for the Province as a whole would be, in our opinion, very desirable.

We feel that generally the duty of a municipality is to accept and treat all liquid wastes, originating within the tributary area, which do not cause damage to the sewers or affect treatment plant operation. This provides the following advantages:

1. Better control is achieved in one combined plant, rather than in a number of separate smaller plants, some of which might be privately owned. Large treatment plants such as our Main and Humber warrant the employment of more qualified men.

2. It is sometimes more economical to treat a combination of industrial wastes and domestic sewage than to treat each one independently, because of dilution, flow equalization, blending and other factors. Also the unit costs for both construction and operation are reduced as the size increases.

3. It also relieves Industry, as much as possible, from the responsibility of treating wastes and allows it to concentrate on its normal function.

If Industry is permitted to discharge its waterborne waste to the public sewer system, then it must be prepared to co-operate with the public agency in solving any problems which may arise because of that waste and must recognize the necessity for some measure of control. Two approaches which may be considered are as follows:

1. The whole control is set out as inflexible limits beyond which a discharge will not be permitted.
2. Only some substances are controlled by inflexible limits, with the remainder being unlimited but the excess above specified amounts paid for at rates to cover the extra cost of treatment.

The first method has been adopted by a number of municipalities in both the United States and Canada. In these instances, the regulations are outlined in detail and are justified largely on the basis that the treatment plant is overloaded or the sewer system has inadequate capacity.

The second method is one which is gaining in popularity as it permits the maximum use of the municipal sewage treatment facilities, and at the same time provides the control that is necessary to protect these works.

For the purpose of this discussion, industrial wastes can be grouped in four main categories:

1. Wastes, sufficiently clean and innocuous to go directly to the natural water courses and the lake, such as rain water, unpolluted drainage, industrial cooling water or industrial waste water within limits.
2. Materials that must be excluded because they damage the sewerage system, are harmful to humans or animals or cause a public nuisance.

MATERIALS TO BE EXCLUDED FROM STORM SEWERS

- (a) Liquid or vapour having a temperature higher than 150°F.
- (b) Water which may contain more than 10 parts per million of fat, oil, greases, or other ether-soluble materials or lubrication oils.
- (c) Gasoline, benzene, naphtha, fuel oil or other inflammable or explosive liquid, solid or gas.

- (d) Garbage or floating objects of any kind.
- (e) Ashes, cinders, sand, mud, straw, shaving, metal, glass, rags, feathers, tar, plastics, woods, cellulose, paunch manure of any other solid, viscous, or colloidal substance capable of causing obstruction to the flow in the sewers.
- (f) Waters or wastes having a pH lower than 6.0 or higher than 9.5 and not remaining within these limits on dilution or having any other property capable of causing damage or hazard to structures, equipment or persons.
- (g) Waters or wastes discharged from industrial processes containing suspended solids exceeding 15 ppm or which are incapable of passing through a $\frac{1}{4}$ " screen.
- (h) Noxious or malodorous gas or substance capable of creating a public nuisance, including hydrogen sulphide, and carbon bisulphide.
- (i) Waters or wastes in which the B.O.D. exceeds 20 ppm.
- (j) Coloured waters or wastes which require a dilution in excess of 4 to 1 to dissipate the colour till it is not determinable by the colour test.
- (k) Waters or wastes in which the Coliform Bacteria count exceeds 2,400 per 100 ml.
- (l) Waters or wastes containing toxic or poisonous substances in sufficient quantity to injure or constitute a hazard to humans, animals, fish or fowl.

MATERIALS TO BE EXCLUDED FROM SANITARY SEWERS

- (a) Liquid or vapour having a temperature higher than 150°F.
- (b) Ashes, cinders, sand, earth, mud, straw, metal, glass, pigments, rags textiles, tar, wood products, paper fibre and plastics, or other viscous or colloidal substance capable of causing obstruction to the flow in sewers or other interference with the proper operations of the sewage treatment plants.
- (c) Animal wastes such as hair, wool or fur, feathers, intestines or stomach casing, paunch manure or intestinal contents, hides or parts thereof, hooves, toenails, horns, bones and fleshings.
- (d) Waters or wastes which may contain more than 150 parts per million, by weight of fat, oil or grease of animal or vegetable origin, or 15 parts per million of

oil or grease of mineral origin or tar.

- (e) Waters or wastes having a pH lower than 6.0 or higher than 9.5 or having any other corrosive property capable of causing damage or hazard to structures, equipment and personnel of the sewage works.
- (f) Gasoline, benzene, naphtha, fuel oil, acetone, solvents or other inflammable or explosive liquid, solid or gas.
- (g) Noxious or malodorous gas or substance capable of creating a public nuisance.
- (h) Waters or wastes containing substances of such character and quantity that unusual expense or attention is required to handle such materials at any sewage works under the control of the Municipality.

3. Materials not excluded, but restricted in amounts because of their harmful effects on the biological processes used in the treatment plants or those materials which pass through the plant without change and are not desirable in the receiving waters.

MATERIALS NOT EXCLUDED BUT TO BE RESTRICTED IN AMOUNTS
IN STORM AND SANITARY SEWERS

Maximum permissible limits in discharge to sewers

	<u>Storm</u>	<u>Sanitary</u>
Phenolic Equivalents	15 ppb	50 ppb
Cyanides	0.0 ppm	5 ppm
Cadmium as Cd	1.0 ppm	5 ppm
Chromium as Cr	1.0 ppm	5 ppm
Copper as Cu	3.0 ppm	5 ppm
Zinc as Zn	15 ppm	15 ppm
Iron as Fe	17 ppm	17 ppm
Chlorides as Cl	1000 ppm	1500 ppm
Solphates as SO ₄	1500 ppm	1500 ppm
Sulphides	none	5 ppm

Phenol and phenolic equivalents are restricted to 15 ppb in storm and 50 ppb in sanitary sewers. It is assumed that phenols in the sanitary flow will be removed at the treatment plant and diluted so that the effluent will contain 15 ppb. Further dilution by the receiving waters should then reduce the concentration before it reaches a water intake to a point below that which will seriously affect the water supply.

It was brought out by N.J. Howard and R.E. Thompson (1) that concentrations of phenol as low as 3 and 4 ppb, when combined with chlorine in water can be tasted. In higher concentrations chlorophenols impart a disagreeable taste sometimes referred to as "iodine" taste.

To ensure that Metropolitan Toronto's drinking water is free of these tastes, hourly taste tests are taken and superchlorination is applied to the filtered water whenever there is a possibility of phenol being present. This practise was started by Howard and Thompson (1) as early as 1927.

Phenolic equivalents refer to derivatives of phenols which form chlorophenolic complexes. These arise chiefly from petroleum refineries, coal tar and plastic manufacturing industries. Phenolic equivalents also result from the biological decomposition of waste sulfite liquor and certain types of algae.

4. The fourth class of wastes are those for which the sewage treatment plants are designed to treat. This classification covers almost all industrial wastes and the municipal sewage treatment plant is the right and proper destination for them.

We have found that prohibited materials reach the sewers in some cases intentionally, and in others, inadvertently. The amounts of the materials found vary from a relatively small, single occurrence to a large continuous flow lasting several days.

For example: recently a foreman employed in a factory, that manufactures rubber cement for an artists supply firm, had a batch of rubber dissolved in toluol. Because a wrong colour was mixed, he dumped the batch down the sewer, thinking he was making a final disposition of his mistake. By the time this reached the treatment plant the solvent had dissipated, leaving the sticky rubbery mass to clog the screens and pumps. Investigation by our Industrial Waste Control Branch pin pointed the infraction to one company. The company management was shocked to hear of this and took appropriate action, so that it would not happen again.

Waste lubricating oil is one of the materials dumped to the sewers intentionally. We have had to undertake several clean up jobs at sewage treatment plants from this cause. Since the flow is intermittent the source is often difficult to trace. Our experience with fuel oil, on the other hand, has been that even though the flows were heavy and continuous they were accidental happenings. Usually, these were due to leaks and when traced to the source, the offending parties were grateful when we drew attention to their loss and arranged to correct the situation immediately. Mineral oils not only affect the operation of the pumps, comminuters, etc. but also disturb biological action by coating micro-organisms. They often foul stream.

The damage to sewers by acid wastes is also a problem of considerable proportions. The damage not only affects the industry's private drain but also the sewer outside the plant property. A cave-in or a blocked sewer is often the first indication that the sewer has been damaged.

In several instances the industry concerned has been charged by the Municipality for the cost of repairing the sewer. Sewage treatment plants are sometimes affected by acid wastes despite the dilution factor.

In our laboratories, we subjected test specimens of concrete to the action of solutions covering a range of pH from two to eleven. This test was carried out on concrete with a mix by weight of 2 parts water, 3 parts cement, 9 parts sand. The cement was cured for 24 hours at 70°F and the specimens were weathered outside for 30 days. After this period they were washed to remove grime and dust, dried at 103°C for 6 hours and then weighed before placing in the various solutions. The pH in the solutions were originally made up with buffer solution and corrected at least once a day.

As expected, in acid solutions there was a degradation of the concrete blocks. Solutions nearly neutral or alkaline did not affect the specimens noticeably. It should be noted from the table that the loss of weight in the sample of concrete in 22 days was over 2% with pH 6. The loss was six times this amount with pH 5 and fifteen times, with pH 4.

EFFECT ON CONCRETE OF BUFFERED SOLUTIONS OF ACIDS AND BASES

DURATION OF TEST	APPROX. pH of SOL.	INTL.WT. OF CONCRETE BLOCK	FNL.WT. OF CONCRETE BLOCK	CHANGE IN WT. PER GM.	% CHANGE
22 days	3	38.197gm	24.316gm	-13.881	-36.35
" "	4	43.504 "	28.863 "	-14.641	-33.66
" "	5	42.076 "	36.087 "	- 5.989	-14.24
" "	6	43.921 "	42.922 "	- 0.999	- 2.28
" "	7	50.475 "	50.703 "	+ 0.228	+ 0.45
112 "	8	42.326 "	42.291 "	- 0.035	- 0.083
" "	9	43.752 "	44.075 "	+ 0.323	+ 0.74
" "	10	39.819 "	39.656 "	- 0.163	- 0.409
111 "	11	39.876 "	40.070 "	+ 0.194	+ 0.49

The disposal of waste pickle liquor from acid pickling presents a problem in Metropolitan Toronto as it does in many other areas. Present methods of disposal include neutralization with alkali, dumping at sea or in land fills. The former method is costly, as it requires excessive amounts of neutralizer and still involves removal of the sludge. Much research has been carried out in this field, particularly in the United States, Great Britain and Germany. Waste pickle liquor has a pH of 1 to 2 and a ferrous sulphate content varying up to 20%.

Considerable effort is being made with waste pickle liquor as with numerous industrial wastes, to try to convert it into a useful

product or by-product. The Ontario Research Foundation is at present working on such a programme in conjunction with an industry in the Metropolitan area.

Our own laboratory has carried out experimental work to determine the feasibility of admitting waste pickle liquor direct to the treatment plants at a controlled rate. However, owing to the toxicity of iron (3) on biological processes and the cost of installing special feeding equipment, this procedure has not yet been found to be feasible.

We in Metropolitan Toronto are very pleased at the general attitude of Industry in accepting its responsibility towards treatment of wastes. Some have installed excellent equipment on their property to deal with this problem. However, as has been indicated it is our opinion that the great majority of industrial wastes can and should be treated in the municipally owned sewage treatment plants which are designed to handle them. The additional cost incurred in treating these excessive wastes should be assessed fairly among the various industries involved.

Many have requested information on the cost which the Municipality would charge them to treat their particular waste in order that they may decide whether or not it would be more economical to arrange for their own treatment. The basis for assessing Industry's share for treatment of industrial waste has not as yet been finalized but several possibilities exist.

FLAT RATE METHODS

1. A percentage of the water bill irrespective of strength or quality.
2. A rate schedule for volume of waste discharged, irrespective of strength or quality.
3. A rate based on the type of industry.

The chief objection to these methods is that they do not permit equitable apportionment of costs as far as strength or quality of discharge is concerned.

QUALITY-QUANTITY METHOD

Charges are related to the volume of flow and the strength of the waste.

In Cincinnati, Ohio, the charge is based upon volume, plus excessive strength of waste above a norm. The Allegheny County, Pa., formula is based upon volume plus an additional formula to take care of the extra load of suspended solids, B.O.D. and chlorine demand imposed by handling industrial wastes, whereas in Buffalo, New York, surcharges are based solely on chlorine demand.

METHOD BASING CHARGES ON ASSESSMENT

This approach regarding sewerage surcharges commences with the premise that everyone who has property in the municipality is paying for waste treatment in his taxes.

Calculations based on the normal strength of domestic sewage, assuming 4.3 persons per household and an average of \$5,000 residential assessment, show that per assessment dollar, householders contribute approximately 0.08 lb. B.O.D. and 0.08 lb. Suspended Solids in their domestic sewage. Thus, Industry should also be entitled to treatment of the same amount of B.O.D. and Suspended Solids per assessment dollar. Some municipalities however, are willing to go further by granting Industry free treatment up to five times the domestic load i.e. approximately 0.4 pounds B.O.D. and 0.4 pounds Suspended Solids per dollar assessment.

Sewage treatment costs range from 1 to 2 cents per pound B.O.D. or per pound Suspended Solids in the Metropolitan treatment plants. In practical application, the surcharge system using an assessment factor of 0.4 and treatment costs of 2 cents per pound works as follows:

A small meat packing plant has an assessment of \$400,000. The company is entitled annually to free treatment of 400,000 times 0.4 or 160,000 lbs. B.O.D. and the same amount of Suspended Solids.

If the company discharges 40,000,000 gallons per year with an average load of 900 ppm B.O.D. and 1000 ppm Suspended Solids, the B.O.D. load is 360,000 pounds and the Suspended Solids load 400,000 pounds.

$$\begin{aligned} \text{Surcharge for B.O.D.} &= (360,000 \text{ lb.} - 160,000 \text{ lb.}) \times \$0.02 \\ & \quad 200,000 \times 0.02 = \$4,000 \end{aligned}$$

$$\begin{aligned} \text{Surcharge for S.S.} &= (400,000 \text{ lb.} - 160,000 \text{ lb.}) \times \$0.02 \\ & \quad 240,000 \times 0.02 = \underline{\underline{\$4,800}} \end{aligned}$$

TOTAL SURCHARGE FOR THE YEAR
WOULD BE

\$8,800

At present our programme of waste control involves the inspection, sampling and testing not only of industrial effluents but also of streams, storm sewer outlets and lake front points. Last year a total of 1540 samples of industrial effluents was taken on which our laboratory made 7,900 tests. Records of the results of these tests are filed separately for each industry in order to maintain a complete history of their effluent.

Our programme is also one of acquainting Industry with the problems involved, and of obtaining their co-operation in taking a sound approach toward the entire matter of industrial waste. Much remains to be accomplished but progress is gradually being made towards the establishment of a uniform code, permitting the maximum use of the existing municipal sewerage facilities by Industry and at the same time providing the Municipality with the necessary control. At present, and until the uniform code is put into effect, the different area municipality by-laws provide any authority required.

To assist an industry, hearings or meetings are held between Metropolitan Toronto and company officials with representatives of the area municipality and the Ontario Water Resources Commission present, to discuss the problems arising from the waste of that particular company. This ensures that there is complete understanding between all parties concerned and at the same time frequently produces a solution that is satisfactory to all. It is through such co-operation of all interested agencies and companies that our streams and lakes will be safeguarded for the recreation, health and welfare of all citizens.

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