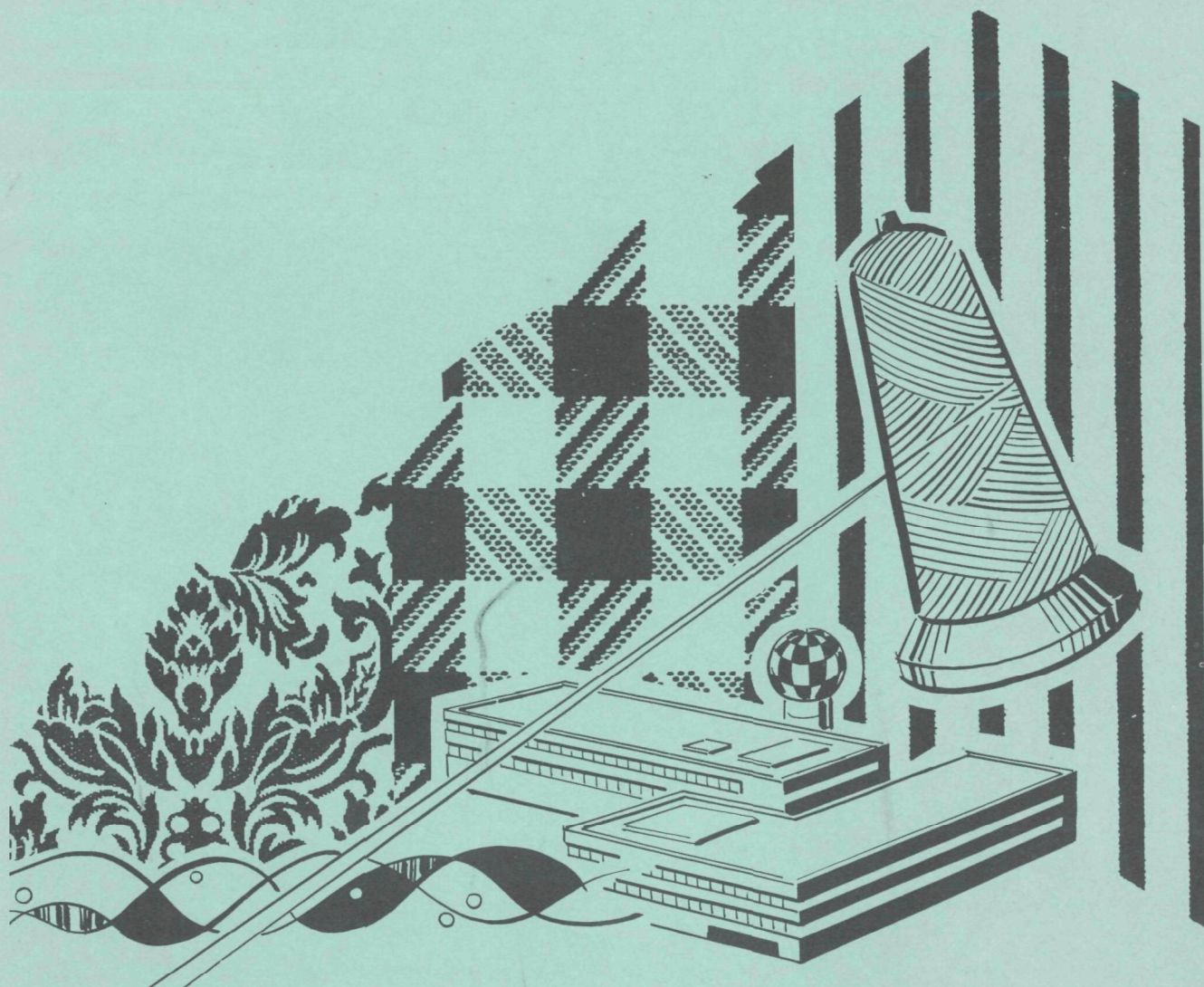


Zinc Precipitation and Recovery

From Viscose Rayon Waste Water



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ZINC PRECIPITATION AND RECOVERY

FROM VISCOSE RAYON WASTE WATER

by

American Enka Company
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for the

ENVIRONMENTAL PROTECTION AGENCY
WATER QUALITY OFFICE

Project No. 12090 ESG
January 1971

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ABSTRACT

In May, 1968, the Industrial Pollution Control Branch of the Water Quality Office/Environmental Protection Agency, initiated a research and development grant with American Enka Company to perfect an improved process for the precipitation and recovery of soluble zinc in rayon manufacturing wastewaters.

In the production of viscose rayon, zinc sulfate is used as a component of the acid spinning bath. Zinc is lost in a dilute form when the acid spun yarns are washed with water and at various points in the spinning bath system. The novel zinc recovery system involves the initial neutralization of the waste stream to pH 6.0, sedimentation of insolubles, the crystallization of zinc hydroxide in a high pH environment, the sedimentation of zinc hydroxide and the solubilization of the zinc with sulfuric acid.

This novel recovery system was operated at a 600 - 1000 gpm rate with 70 - 120 mg/l of Zn in the feedwater. The system can maintain an effluent concentration of Zn less than 1 mg/l, which corresponds to 98 - 99% removal efficiency. The unique zinc hydroxide sludge is easily concentrated to 5 - 7% solids by sedimentation and to 10% solids by centrifugation. The sludge particles obtained by this process are spheroids of 4 - 8 microns average diameter.

A recovery of 2,000 pounds of zinc daily assures recovery of the 12.5 to 14.0 cents/lb. of Zn operating and maintenance costs. The cost of zinc oxide purchased by Enka amounts to 15.6 cents/lb. of equivalent Zn.

This recovery plant was awarded a Finalist prize for achievement in water pollution control in the 1970 Gold Medal Awards, single-plant category, by The Sports Foundation, Inc.

This report was submitted in fulfillment of Grant Project 12090-ESG between the Water Quality Office/Environmental Protection Agency and American Enka Company.

Key Words: Industrial wastes, textile fibers, heavy metals, chemical precipitation, flocculation, operating cost

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SECTION I

CONCLUSIONS

The following conclusions can be drawn from this study, which covers work done in a laboratory, pilot plant and industrial scale over a period of several years:

1. The efficient and economical recovery and reuse of waste soluble zinc from viscose rayon plant wastes has been proven under industrial conditions.
2. The efficiency of the precipitation and recovery of soluble zinc exceeds 95%, which is higher than that of other known methods such as ion exchange.
3. Dense, easily handled sludges, which are susceptible to simple disposal as a solid, or to recovery for reuse, can be obtained by precipitation of soluble metals as hydroxides if the operation is carried out under controlled conditions.
4. The effluent water from the recovery plant is extremely clear water of constant, slightly alkaline pH and it is essentially free of toxic metal content. It can be reused to advantage where its high hardness and salt content is not an impediment, such as water for flushing and cleaning purposes, pump seal water, etc. Its soluble zinc content is less than 2 ppm.
5. When lime is used for neutralization, the value of the recovered zinc easily pays for the operating costs. Depending mainly on the zinc recovery capacity of the plant, the acid to zinc ratio in the feed, and the price of lime, the value of the recovered zinc may also pay part or all of the capital investment costs.
6. Under American Enka Company's plant conditions, it is easy to obtain a zinc hydroxide concentration of 5 to 7% by settling alone, and without the use of coagulant aids in the precipitation reactor. Using centrifugation, a non-flowing solid exceeding 10% zinc hydroxide can be obtained. The presence of cellulose floc affects the settleability and density of the sludge.
7. The particles of the unique dense zinc hydroxide sludge appear in scanning electron micrographs as spheroidal particles with a diameter of 4 - 8 microns. They are formed only as a result of very repeated adsorption or precipitation of soluble metal on existing hydroxide particles, followed by pH adjustment with alkali.
8. Addition to the acid wastes of various dilute alkaline wastes effects a saving in lime consumption.

9. There is technology already available in the electrolytic zinc industry to remove impurities which may be found undesirable in the recovered acid zinc sulfate.
10. The operating and maintenance costs for recovery of the soluble waste zinc depend on the sulfuric acid/zinc sulfate ratio in the waste and on the amount of zinc recovered daily. When recovering 2000 pounds Zn daily from a waste with a ratio of 5 to 6, the operating and maintenance costs are 12.5 to 14.0 cents/lb. Zn. The cost of purchased zinc oxide is 15.6 cents/lb. of equivalent Zn.
11. The zinc recovery plant was awarded a Finalist prize in the 1970 Gold Medal Awards, single-plant category, by the Sports Foundation, Inc. These Awards are presented for achievement in the field of water pollution control and related water conservation or development.

SECTION II

RECOMMENDATIONS

1. It is advantageous, both economically and process-wise, to collect the waste flows at their source in a concentration as high as possible.
2. The neutralization plant should be designed to use the cheapest lime available that is technically acceptable under conditions of reuse.
3. The clear water effluent from the recovery plant should be reused or otherwise mixed with other plant effluents so that the pH 9.5 - 10 will be reduced before discharge to the stream. If the other effluents are not acid enough to reduce the pH, the effluent could be contacted with waste combustion gases, such as those generated by a steam boiler, or by any other acid material.
4. The concentration of the wastes fed to the neutralization plant should be equalized as much as possible, to aid pH control. An expensive feedforward pH control system should not be necessary and may actually create more problems than it solves.
5. All operations should be made as automatic as possible, to save expense.
6. The clarifier underflow should be thickened sufficiently so that the impurities can be disposed of as a solid waste.
7. Although apparently simple, a lime slaking system can be a source of many problems, and therefore, it should be designed carefully by using all available information from established lime consumers.
8. It appears advantageous to concentrate the hydroxide sludge by using centrifugation, so as to reduce the soluble calcium and excess water in the recovered zinc sulfate.
9. The basic principles of the precipitation process should be applicable to waste treatment problems other than pollution by soluble metals. For example, dense iron, aluminum, calcium, and other sludges could be used to remove suspended impurities, including dispersed oil particles, or colored compounds in various wastes from textile, cellulose pulp, and other industries. Previous attempts to develop this type of process have been frequently impeded by the difficult sludges which were obtained.

If waste acid mine waters were treated in a similar fashion, not only toxic soluble metals could be eliminated but also excessive sulfate ion could be reduced by gypsum precipitation.

SECTION III

INTRODUCTION

PURPOSE AND OBJECTIVES

The purpose of this project, "Zinc Precipitation and Recovery from Viscose Rayon Wastewater" was to perfect a process for removing soluble zinc from industrial effluents in order to protect fish and other aquatic organisms in the receiving stream.

A new process for precipitation of soluble zinc had been developed by American Enka Company through the pilot plant stage, and a large-scale plant had been designed, built and operated for a very short time. At this point, the Industrial Pollution Control Branch of the Water Quality Office, Environmental Protection Agency, offered Enka a research and development grant to help perfect the process, in exchange for making all the process information publicly available.

In order to perfect the process, the following objectives were defined:

1. To install appropriate equipment to collect and channel waste streams containing soluble zinc into the treatment plant so that a significant amount and concentration of zinc could be treated.
2. To perfect the operation by which the excess acid is neutralized and the soluble zinc is precipitated and removed from the waste streams.
3. To improve the quality of the recovered zinc and the water effluent so that they may be reused in manufacturing processes.
4. To determine the capacity of the plant and its investment and operating costs.
5. To improve plant efficiency and economics. Operating costs are to be reduced by the use of rayon plant wastes that are alkaline in nature and by the use of lime for acid neutralization.
6. To use all of the technology developed, in order to demonstrate its value.

BACKGROUND INFORMATION

To the best of our knowledge, all viscose rayon producing companies use zinc in the manufacture of practically all of their rayon products. The amount of zinc used depends on the type of product which is being made and the particular company's special knowledge about making its products. In general, it can be said that textile yarns and most staple fibers are spun using fairly small amounts of zinc sulfate, while industrial yarns, such as those used in the manufacture of automobile tires, conveyor belts, braided hose, etc., are spun using larger amounts.

The zinc which is used in the viscose rayon process is not consumed in any of the viscose reactions. It is merely lost, either being carried out by the spinning filaments and then lost in the subsequent washing operations, or it is lost by splash and drip from the machinery involved. In addition, some zinc is lost in the washing of filters and other equipment.

It is estimated that more than 50 million pounds of zinc sulfate are consumed annually by the rayon industry while producing more than one billion pounds of product.

Other industries discharge zinc to the streams. For example, a large ground-wood pulp mill can use up to five tons of zinc daily (12) because zinc dithionite is used as a bleaching agent in the production of newsprint. Zinc salts are used commonly now as a chemical treatment in recirculating water systems and are discharged to the streams in the blowdown of the system. And, of course, the electrochemical industry also wastes a large amount of zinc and other dissolved metals annually.

It has been estimated that in British industrial areas an average of 23% of the total toxicity of mixed pollution for fish is contributed by zinc and copper (3).

However, in spite of the importance of pollution by zinc and other soluble metals, the reduction of inorganic wastes in the U.S. has been running only about 27%, versus about 57% reduction in organic wastes (1). There are several reasons for this lower figure, and probably the most important are the two following.

There are few time-proven, well-developed techniques generally applicable to inorganic pollution, as compared to organic pollution, where various established systems for biological digestion have been used for a long time and are continuously being perfected.

Economic reasons are perhaps even more important. Although the output of inorganics, and hence the corresponding wastes, has been increasing at 1.5 - 2.0 times the gross national product, the price of inorganics has been dropping recently at about 2.5% per year (1). In the face of this reduction in prices, the investment in inorganics waste treatment facilities will have to increase from the present \$82 million to at least \$135 million by 1974, according to a recent federally sponsored survey.

The process developed by American Enka Company with EPA aid should have application to reduce stream pollution in any industry where the waste water contains metals which form insoluble hydroxides. It is a practical process which produces a dense, easily handled sludge which can be recovered in concentrated form for its metallic value. The process takes advantage of the fact that acid wastes need to be neutralized anyway before discharge to a stream, and therefore, neutralization and precipitation of dissolved metals from acid wastes by this process is more economical over-all than by other available processes.

It is probable that this process can be used also for removal of dispersed oil particles and other suspended particles, or removal of color from textile wastes or wood pulping wastes, by precipitating iron, aluminum or other hydroxides in a dense, easily concentrated sludge. It could be used also to neutralize acid mine waters with lime, precipitating their toxic mineral content and, at the same time, reducing the excessive sulfate ion concentration by simultaneous precipitation of calcium sulfate. The difficult type of sludge obtained in many precipitation processes has often impeded the successful development or utilization of these processes in the past (32, 33, 34).

As part of the general background information on zinc recovery, some of the other available processes found in the literature will be mentioned.

For example, the Dutch Holima process precipitates the zinc as the carbonate on inert nuclei which can be screened off and discarded. A recent patent (9) describes the use of sodium carbonate or bicarbonate to precipitate zinc carbonate. It is recommended for viscose rayon solutions in which the ratio of the weight percentages of zinc and sulphuric acid is at least 1:3.

Precipitation of the zinc using lime is well known (10, 11), and has been used in plant scale for years in Europe and the U.S. But, a dense, recoverable zinc precipitate has never been mentioned. Usually, combined plant wastes are treated with lime, and the resulting sludge containing zinc, calcium, cellulose, etc., is discarded to lagoons.

Ion exchange processes appear frequently in the literature (5, 6, 8, 10, 11, 15, 16). Some of their disadvantages are:

1. The effluent, still highly acid, has to be neutralized anyway before discharge.
2. Acid and sodium ions compete for the adsorption of zinc on the resin, reducing its capacity as much as 50% when the sodium and hydrogen ions amount to 15 grams/liter (11, 16, 17). A spill of concentrated acid bath must be collected and diluted with soft water before it reaches the resin.
3. Certain amines and spinning agents poison the resin and reduce its capacity.
4. Efficient adsorption of impurities such as calcium, magnesium, iron, lead, copper, etc., often prevent reuse of the zinc without further chemical separations.
5. The efficiency of zinc removal is low. By using a recycle regeneration system, the efficiency of recovery will average 92% (11).

A Russian process may be mentioned (7). It precipitates and discards the zinc as zinc sulfide by using hydrogen sulfide from the waste rayon spinning gases.

A German process (22) uses an activated sludge system to reduce the zinc content of waste waters to 6 - 10 mg./l. It was more effective in hard waters. The zinc is discarded together with the biological sludge.

And, of course, if the concentration of zinc and other chemicals warrants it, the acid waste solutions can be concentrated by evaporation and then reused. For steam economy, multiple effect evaporators are preferably employed (11).

SECTION IV

HISTORICAL REVIEW

The toxic effect of zinc on fish and other lower organisms growing in the stream has been well documented in the literature (2, 3, 4, 31).

Therefore, for a long time the American Enka Company rayon plants sought to reduce the amount of zinc lost from the spinning processes by collecting those waste flows that were sufficiently concentrated to be susceptible to evaporation of excess water and reuse for further processing of the chemicals dissolved in it. However, no reasonably economical processes were known which would eliminate or recover the zinc from very dilute waste solutions.

At the suggestion of personnel from the Stream Sanitation Committee of the North Carolina Department of Water Resources, a method of treating the acid and zinc bearing industrial wastes together with the sanitary sewage waste was tried in 1964, on a pilot plant scale basis. Enka was told that there were certain extended aeration systems treating combined sanitary and industrial wastes with an initial pH as low as 3.0 or less. During the aeration treatment, the pH was elevated sufficiently to precipitate and settle out heavy metals such as zinc together with the biological sludge. A 20-gallon aeration unit provided with a 1/2 HP mechanical aerator was rented and a small clarifier and a feed storage tank were manufactured at Enka. During the tests, a BOD reduction of 80 to 85% was obtained in the presence of 25 to 30 ppm of zinc metal at a pH of 3 to 4. Unfortunately, the biological environment did not result in a pH increase, there was no appreciable reduction in the zinc content and the trials were suspended.

During the early part of 1965 Enka's Central Engineering Department was requested to study all of the information available and to present a detailed program of action to be taken in the immediate future.

Ion exchange and neutralization with precipitation were the two processes mainly considered, and the recommendation given was to proceed with a neutralization-precipitation method while studying further the possible attractiveness of ion exchange for certain selected waste streams. The following considerations were set forth in a report published in March, 1965:

1. If ion exchange would be chosen, it could not be used to treat all of Enka's acid wastes. A considerable portion of these wastes was contaminated with substantial amounts of magnesium, and it would be strongly adsorbed by the ion exchange resins.

NOTE: It is also known that zinc cannot be recovered efficiently from solutions relatively high in acid and sodium salts (11, 16, 17).

2. The acidity of all zinc bearing wastes treated by ion exchange would not be reduced, and the effluent would still need to be neutralized to maintain a satisfactory pH in the receiving stream. This results in double treatment costs, over-all, before the plant effluent can be discharged to the streams.

3. Certain impurities in the waste streams to be treated by ion exchange, in addition to magnesium, such as lead and other metals, calcium hardness, etc., would be retained by the exchange resin and problems related to regeneration of the resin and reuse of the zinc could be expected. The Permutit Company had warned Enka certain spinning agents and organic compounds such as amines would poison the exchange resin and seriously reduce its capacity. Dilute spin bath samples were sent to Permutit for testing, and a subsequent report confirmed the presence of compounds which affected the resin's exchange capacity.
4. The neutralization-precipitation method was judged to be more economical over-all, more flexible and easier to operate.
5. Other dilute sources of pollution could be treated at the same time, such as waste lye from the rayon plant dialyzers and dilute waste viscose from equipment cleaning operations. When these wastes are acidified, cellulose and hemicelluloses precipitate and a potential source of BOD pollution can be eliminated. At the same time, the waste alkali content is utilized to neutralize part of the waste acid.

Company Management accepted the recommendations of this report and several companies were contacted for their experience handling light hydroxide sludges.

Infilco, Inc. provided Enka with data on its pilot plant tests precipitating a dense type of ferrous hydroxide sludge using waste pickle liquor and acetylene sludge in order to obtain a reduction in the oil content of the waste water from a steel cold reduction mill. The pilot runs were carried out using a 3-1/2-ft. diameter "Densator" reactor.

Since laboratory tests confirmed that a dense zinc hydroxide sludge could be obtained using the same principles used for ferrous hydroxide, American Enka rented a similar "Densator" pilot unit to develop the process through the pilot plant stage. This unit operated from December, 1965, until May, 1966. The description of the unit and an outline of the results obtained is given in Section V.

Concurrently with the operation of the pilot unit, an industrial sized recovery unit was designed.

The North Carolina State Stream Sanitation Committee issued in May, 1966, a permit for American Enka Corporation to construct and operate the new plant.

To reduce expenditures to a minimum until the new process could be proven, it was decided to initially use the zinc waste flow from one of the rayon plant waste trenches. This trench carried about one-third of the zinc waste water. When the process was developed, the other zinc bearing flows would be collected for treatment.

In addition, to simplify the operations and technical problems, it was decided that initially only caustic soda would be used for acid neutralization.

The plant started operating in May, 1967.

When the decision was made to use initially an open trench as the plant feed, the zinc concentration in the trench was about 100 ppm. By mid-1966, the concentration had halved; and at the plant start-up date, the average concentration was about 6 ppm of zinc. This was due to the fact that most of the production of industrial yarns, which are spun using a high zinc bath, was transferred to another company plant, as well as a reduction in the market for this product.

The completed plant was run for a short time and then shut down. The zinc losses from the rayon plant were so reduced at that time that the zinc concentration in the receiving streams was well below the maximum allowable figure specified by the State of North Carolina.

During the time that the plant was run, essentially all the zinc was precipitated, but the concentration of impurities was so great in relation to that of zinc, especially light cellulose floc, that the zinc was not reused for lack of the means to purify the final zinc sulfate solution. There were other problems concerning the operation of the plant, chief among these being a very poor pH control during neutralization, preliminary to clarification of the feed solution.

In May, 1968, the Water Quality office of the Environmental Protection Agency, then named Federal Water Pollution Control Administration, offered American Enka, through its Industrial Pollution Control Branch, a research and development grant to complete the development of the process. It was specifically requested that Enka operate the plant at first using only caustic soda for neutralization. Lime would then be used when the new equipment designed to prepare and add lime slurry would be available.

A new collection system for acid wastes was built in order to be able to have a reasonable zinc concentration in the feed solution. A dilute viscose collection system was also constructed. A new pH control system recommended by Foxboro Company was installed. Suitable means were provided for adding a coagulant aid to help clarification. A small rotary belt vacuum filter was purchased to filter the recovered zinc sulfate solution initially, and to concentrate further the clarifier underflow, if so desired. Suitable lime handling, storage and slaking equipment were also provided.

During early September, 1969, the improved plant started operation using caustic soda for neutralization. By mid-October, the recirculating zinc hydroxide sludge concentration had increased to 6,500 ppm of zinc and sludge was being concentrated by further settling and then was being dissolved with sulfuric acid. The initial recovered product was pumped back to the neutralization tank for reprecipitation because it was dirty, but soon afterwards the product was sent to the rayon plant for reuse.

During the first half of December, 1969, the plant was shut down to make necessary instrument and other equipment modifications and repairs. By that time, the recirculating Densator sludge concentration had increased to about 10,000 ppm of zinc. The recovered zinc sulfate concentration was approximately 3.5 to 4.1%, after adding excess acid for dissolution of the sludge.

During the end of February and first part of March, 1970, the plant was started again in operation. During the shutdown, several pipelines were left improperly drained and considerable freeze damage resulted during a period of sustained cold weather.

The plant continued to operate using caustic soda for neutralization until the end of May, 1970, when the lime equipment became ready for operation. By that time, the recirculating sludge concentration had increased to about 17,500 ppm of zinc.

During June and July the lime equipment was giving trouble most of the time, and many changes had to be made to improve its continuous operation.

Except for occasional short periods of shutdown for minor repairs or changes, the plant has operated continuously using lime for neutralization from August, 1970, through the end of the year. Operation has been generally satisfactory.

During the period of neutralization with lime, the concentration of the recirculating Densator sludge has fluctuated between 20,000 and 29,000 ppm of zinc, about 3.0 to 4.4 percent of zinc hydroxide. Subsequent settling, before dissolution, yields a concentration usually in excess of 5.0% zinc hydroxide. This concentration was the goal that Enka had set for itself when the plant was being designed.

SECTION V

DESCRIPTION OF PILOT PLANT STUDIES

From December, 1965, until May, 1966, American Enka operated a pilot plant "Densator" reactor rented from Infilco, Inc.

A sketch of this unit is shown in Figure 1. It is 3.5 ft. in diameter and approximately 10-ft. high. The primary zone, where the acid feed contacts the recirculated sludge, is located in the top 2.5-ft. of height. The secondary zone, where caustic soda is added to the mixture flowing from the primary zone and reacted with it, consists of an inner cylinder 18 inches in diameter extending from near the top of the Densator to approximately one foot from the bottom. In the lower annular section the sludge separates from the clear water which overflows to the sewer. The sludge is pumped out of the bottom and into the primary zone again. A variable speed agitator is mounted on top of the unit and provides agitation to the primary and secondary zones and to the sludge at the bottom of the unit. Enka was told that the unit should handle a waste water flow of 10 gals./min.

Acid waste from a rayon plant waste water trench, with a pH between 2.0 and 4.0, was pumped to a 3,000-gallon storage tank, the acid was neutralized with caustic soda to a pH of 6.5 and the solution was allowed to settle overnight. Additional zinc sulfate was added when desired.

The concentration of zinc in the feed was varied from about 35 to 165 ppm. There seemed to be somewhat better results with the higher than with the lower concentrations.

The maximum feed flow used could not exceed 5 to 6 gals./min. Since on a few occasions there was some loss of zinc sludge in the overflow, even this flow may have been too high. 5 gals/min. corresponds to 0.635 gals./min./sq. ft. rise in the annular sludge settling section. The large-scale Densator was subsequently designed for a maximum up-flow of 0.44 gals./min./sq. ft., but even this flow has never been reached in practice due to other equipment limitations.

Cellulose floc in the feed affected adversely the density and settleability of the sludge. To reduce this contamination, the Densator feed was filtered through a filter press dressed with cotton flannel.

The sludge was recirculated to the primary zone at a rate of 2 gals./min.

A "Superfloc" coagulant aid seemed to help the settleability of the sludge at a dosage rate of about 0.5 ppm. Unfortunately, there is no record of which type of American Cyanamid "Superfloc" was used. "Separan" NP-10 coagulant aid did not appear to help at dosage rates between 0.1 and 0.5 ppm. "Separan" is sold by Dow Chemical Company.

PILOT PLANT DENSATOR

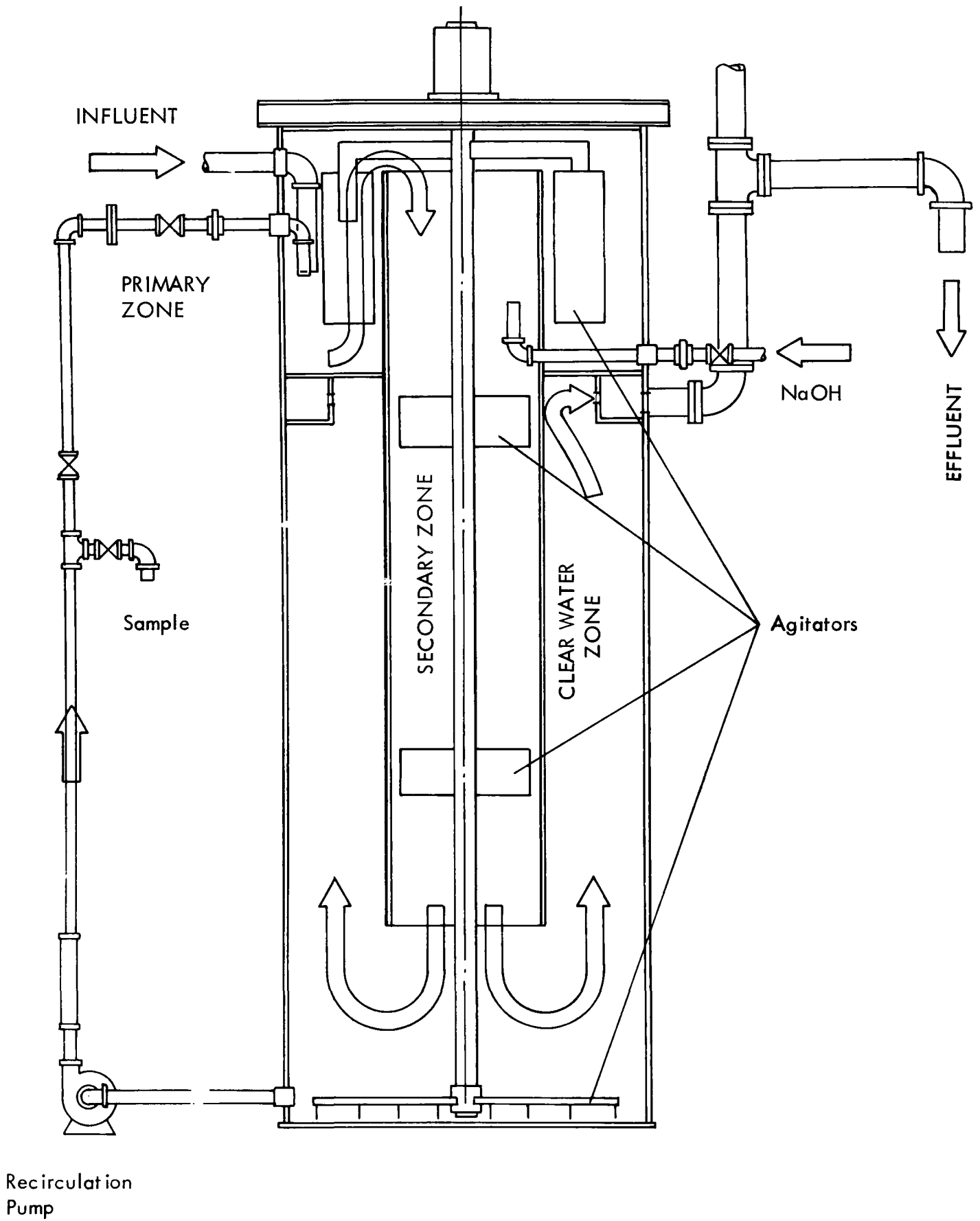


FIGURE 1

Using a feed rate of 5 gals/min., a sludge recirculation rate of 2 gals./min., a feed concentration of 165 ppm of zinc and 0.5 ppm of Superfloc, a sludge with 35 to 44 grams/liter of zinc hydroxide could be regularly obtained. Once a concentration of 50 grams/liter was reached.

The volume of sludge could be reduced to about half by subsequent settling aided by gentle stirring.

No noticeable difference was observed whether the pilot unit was operated continuously or batchwise.

During most of the tests, the pH in the primary zone was 8.3 - 8.6, and it was 9.5 - 9.8 in the water effluent.

SECTION VI

FLOW DIAGRAMS AND DESCRIPTION OF THE RECOVERY PLANT

The Enka process is different from other similar hydroxide precipitation processes in two respects:

- (a) Unlike other companies who have added lime to neutralize acid and precipitate zinc in one step and have then stored the resulting unusable sludge in lagoons, American Enka has divided the process in two steps. First, the expensive neutralization step is carried out with lime and the solution is clarified of all insolubles. Then zinc is precipitated with caustic soda in a relatively pure state.
- (b) The precipitation is carried out in a manner unique in the field of metal hydroxides, so as to obtain a new form of dense sludge with special properties. It can be easily washed to eliminate or reduce soluble salts, can be centrifuged without difficulty, stored as a solid or reused as a chemical.

Briefly, the process can be described as follows:

Sulfuric acid and zinc-bearing wastes are collected at various points in the Rayon Plant and pumped to one main pit. Various waste alkaline flows are collected and added to the acid wastes, to reduce other types of pollution and for reasons of economy. The composite wastes are neutralized with lime to a pH just below 6.0, the pH at which zinc begins to precipitate. Some calcium sulfate may precipitate and it, with or without the aid of a coagulant aid, helps to clarify the solution as it flows through a clarifier, where the insolubles settle out and are concentrated for disposal in the plant dump.

The clarified solution now flows to the primary zone of the Densator reactor where it is contacted with a high concentration of previously precipitated zinc hydroxide, up to 50 or more times the metal concentration in the feed solution. During this contact, most of the dissolved zinc in the feed adds onto the existing particles. Alkali is added in the reactor's secondary zone to complete the reaction and to restore the pH back to 9.5 - 10.0. If desired, a coagulant aid can also be added here to obtain an even greater sludge density and improved settleability.

From the secondary zone of the reactor, the mixture flows to the annular section, where the solids settle and are separated from the clear, essentially zinc-free effluent. The settled sludge is scraped into a center well where it is kept mildly agitated for pumping back to the primary zone of the reactor or to be removed for further concentration in a separate vessel. This next vessel is provided with even milder agitation and here the sludge settles normally to a concentration of 5 to 7% of zinc hydroxide. The zinc is then dissolved with acid and reused in the rayon plant.

By comparison, if the same acid feed solution were treated with caustic soda to a pH of 9 - 10 without the presence of previously precipitated hydroxide sludge and then allowed to settle for as much as 18 hours, the zinc hydroxide concentration in the settled material would be less than one-half of one percent.

The characteristics of the untreated acid wastewater, the treated effluent and the recovered zinc sulfate are summarized in Table I.

TABLE 1
CHARACTERISTICS OF PLANT FLOWS

Raw Wastewater

Sources:

Acid yarn wash water, filter backwash water, spin machine pot spray water, spin bath spillage, etc.

Dialyzer waste lye, containing caustic soda and hemicellulose

Viscose filterpress and storage tank wash water, containing sodium cellulose xanthate, caustic soda, sulfides, etc.

Characteristics:

Flow: 600 - 1000 gpm

pH: 1.5 - 3.0

ZnSO₄: 70 - 120 mg/l as Zn

H₂SO₄: 800 - 2000 ppm

Na₂SO₄: 0.20 - 0.25%

MgSO₄: 60 - 150 mg/l as Mg

Cellulose and hemicellulose: less than 1%

H₂S, Na₂S, ZnS, S, Fe, Pb, surface active agents, etc: less than 0.1%

Treated Effluent

pH: 9.5 - 10.0

ZnSO₄: 1 mg/l as Zn

CaSO₄: less than 0.2%

Na₂SO₄: 0.20 - 0.25%

MgSO₄: 50 - 150 mg/l as Mg

Fe: 0.3 mg/l

BOD: 24 mg/l (mostly from surface active agents)

COD: 60 mg/l (mostly from surface active agents)

Recovered Zinc Sulfate:

ZnSO₄: 8.5 - 11.0%
H₂SO₄: less than 1.5%
Mg: 0.5%
Fe: 0.1%
Pb: 0.02%

A detailed description of the process follows below. The flow diagrams for the process are shown in Figures 2, 3 and 4. The underlined numbers shown in the three figures refer to the equipment item numbers as described in Section XII. A description of the acid and alkali collection systems is also given in Section XII.

The mixture of acid and alkaline wastes, which is preponderantly acid, is pumped by pump - 1 through a plastic pipeline for a distance of a few thousand feet to the neutralization tank, item - 2.

The zinc concentration in the recovery plant feed is approximately 70 - 120 ppm and the normal flow is 600 to 1000 gals./min.

The feedforward pH control system with feedback trim, item 3, measures the pH and volume of the incoming flow and adds the required amount of alkali. If the resulting pH differs from the set point pH, the controls will correct the flow of alkali accordingly.

Normally, lime slurry is added for neutralization through control valves CV-1 and CV-2, shown in Figure 3. However, in case of a shutdown of the lime system, caustic soda solution from the rayon plant can be added through control valves CV-11 and CV-12. The fluid pressure of either alkali at the respective control valves is kept uniform by using a suitable head tank placed above the level of the valves.

The caustic soda head tank also feeds soda solution to the Densator, through a rotameter adjusted manually. Because the large amount of hydroxide sludge in the Densator acts as a buffer, changes in the pH are very gradual. Manual adjustment of the soda flow once, or at most twice, per day has been found to be sufficient. The original plan was to meter the alkali automatically by using a Hach colorimetric zinc analyzer, but this has never been tried out because it was considered unnecessary.

It would be less expensive to add lime slurry to the Densator also, but there would be some calcium precipitation which would contaminate the zinc sludge. In those cases where this calcium contamination would not be objectionable, lime slurry should be used for reasons of economy.

Practically all the alkali added to the Densator is consumed for precipitation of the hydroxide sludge. The preliminary neutralization to a pH of 5.0 - 6.0 has essentially completed the reaction with acid to the neutral point. See Figure 5.

ENKA ZINC RECOVERY

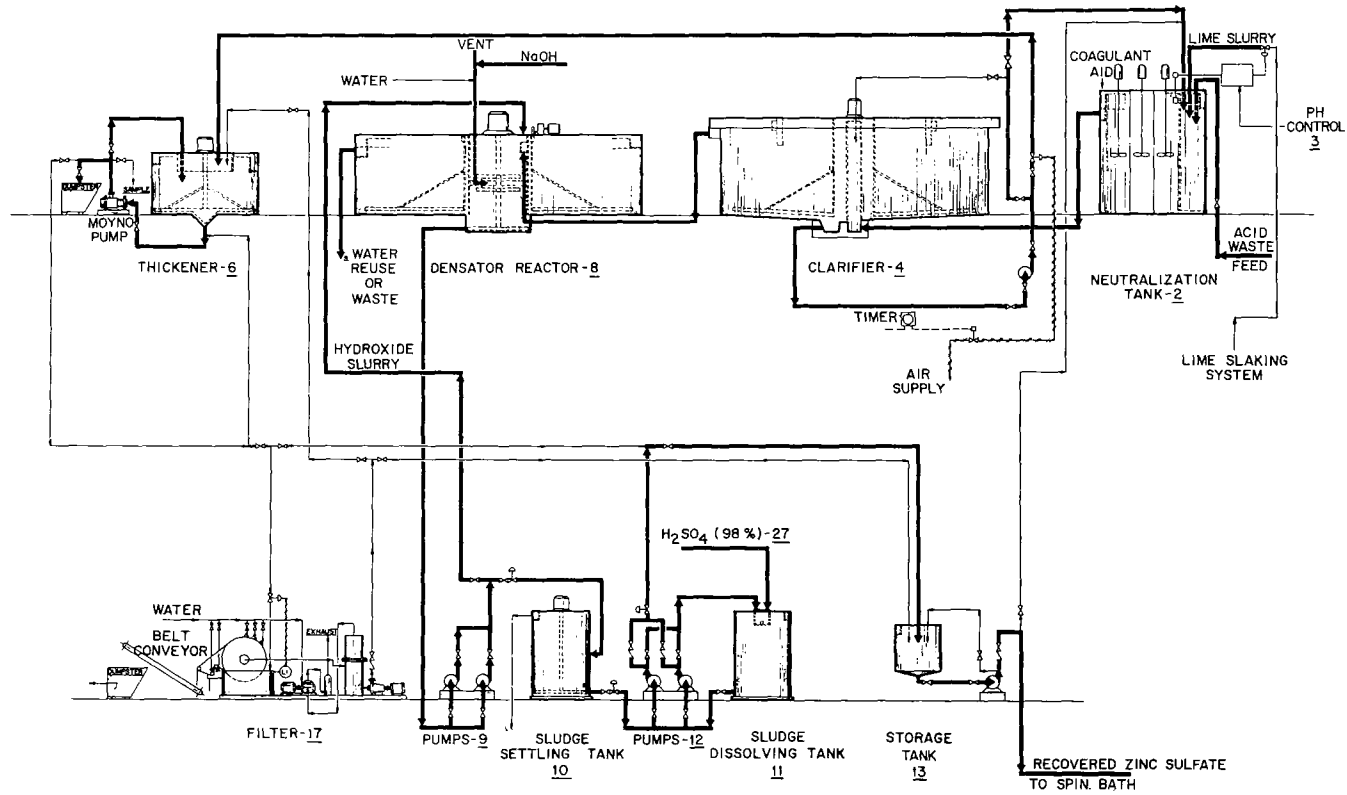


Figure 2

ALKALI SUPPLY AND pH CONTROL SYSTEM

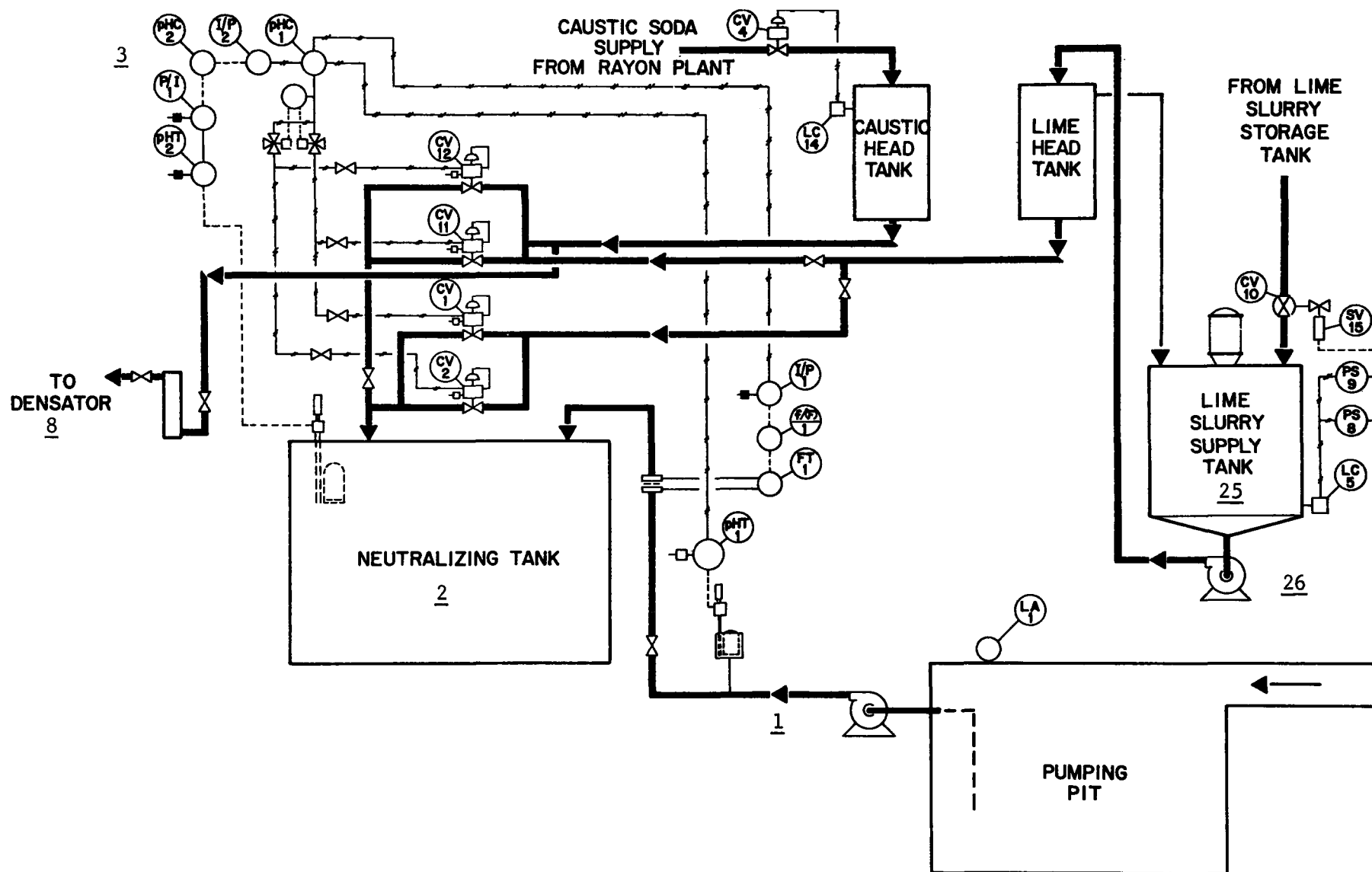


Figure 3

LIME SLURRY MANUFACTURE AND SUPPLY SYSTEM

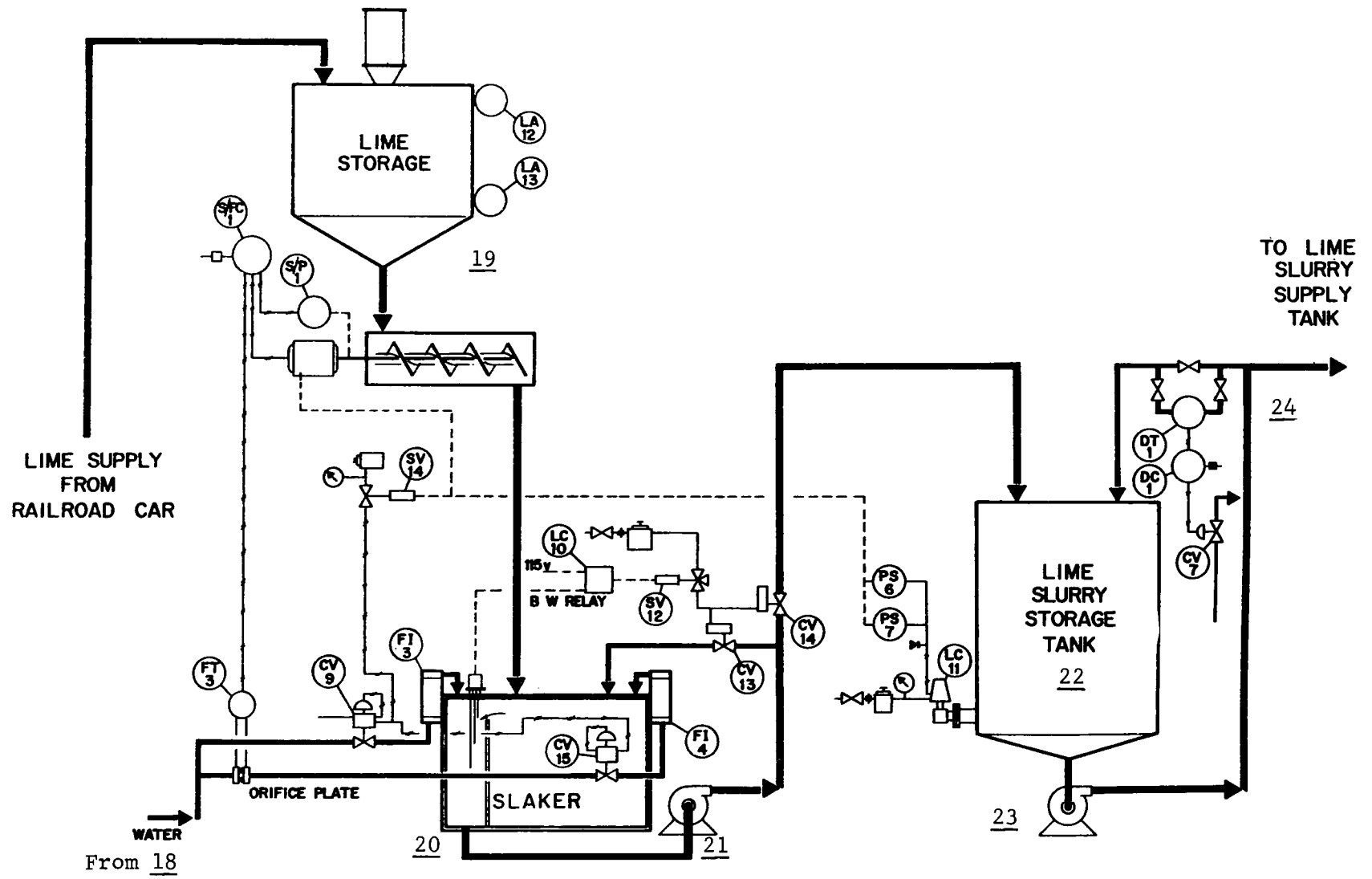
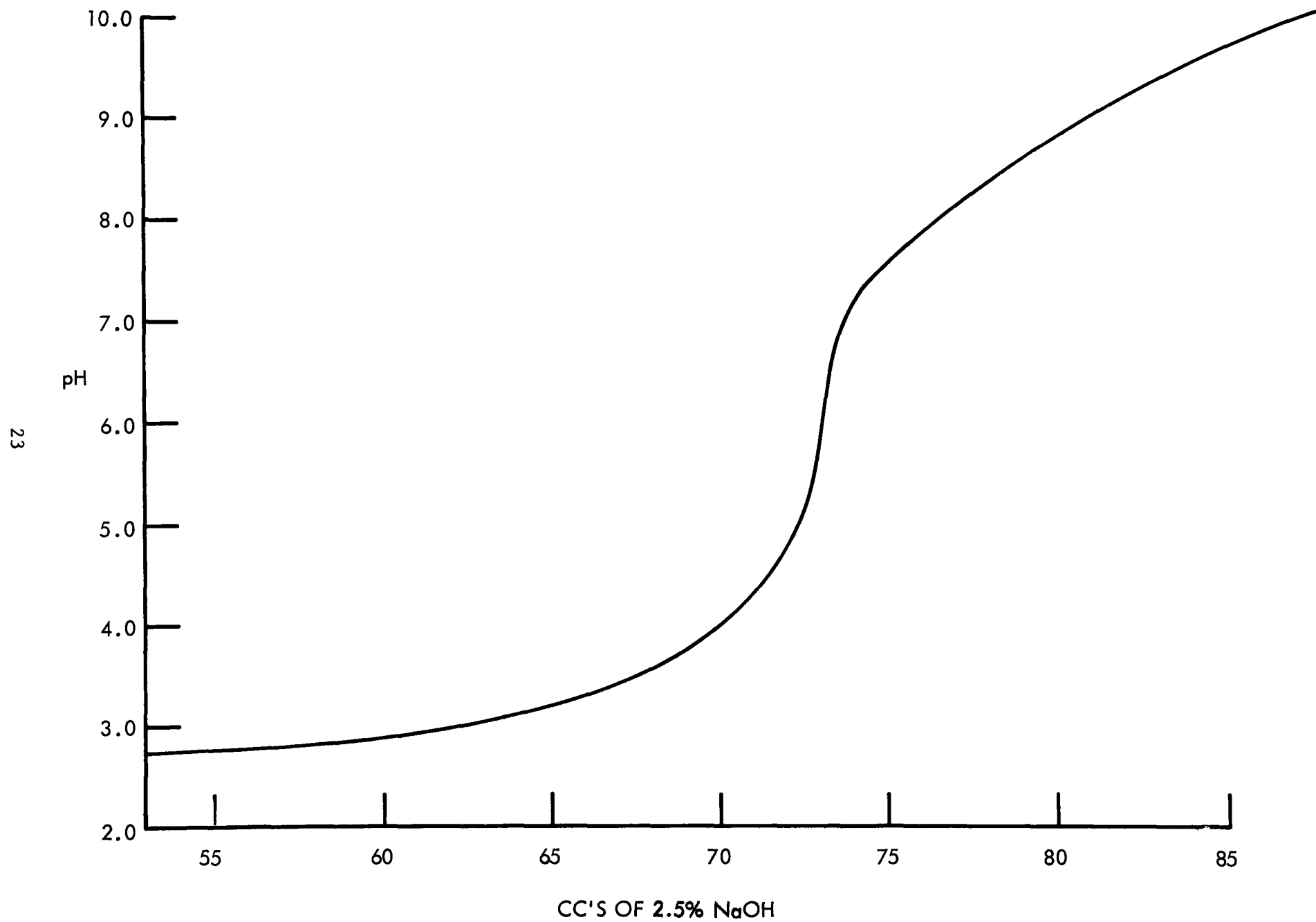


Figure 4

TITRATION CURVE OF DILUTE ACID WASTE FROM RAYON PLANT



CC'S OF 2.5% NaOH

Figure 5

The preparation of the lime slurry is as shown in Figure 4. The rotary kiln quicklime, with a maximum pebble size of 3/8", is fed to the slaker - 20, by means of a rotating screw placed under the lime storage tank - 19.

The water feed to the slaker is split into 2 flows, a slaking water flow, through control valve CV-15 and rotameter F1-4, and a dilution water flow through control valve CV-9 and rotameter F1-3. The slaking water actually flows through a small heat exchanger placed in the slaker itself, where it is heated somewhat by the outflowing slaked lime slurry, which is at 170 - 190 deg. F. However, because this exchanger supplied by the slaker manufacturer is quite small, we have added a 24 KW electric heater with thermostat in the slaking water line. This heater is not shown in Figure 4, but it is described in Section XII.

The liquid level in the slaker is controlled by level controller LC-10, which returns the lime slurry pumped by pump - 21, back to the slaker, or feeds it to the storage tank - 22, through its action on control valves CV-13 and CV-14.

The setting of the lime screw feeder speed is set manually to provide more than the average lime slurry consumption rate. The slaking water rate is adjusted to give a slaking chamber temperature of 170 - 190 deg. F and the dilution water rate is adjusted to give a lime slurry composition of 10 - 12% calcium hydroxide.

Whenever the liquid level in the storage tank - 22 reaches a preset height, the level controller LC-11 turns off the lime screw feeder and the slaking and dilution water flows. When the liquid level drops to another preset height, the lime and water feeds to the slaker are turned on again.

During slaking, if the temperature should exceed 190 deg. F, a high temperature switch adds additional slaking water during 3 minutes.

Because the lime storage tank - 19, the slaker - 20, and the slurry storage tank - 22 are placed some distance away from the zinc recovery plant itself, beside a railroad siding, the slurry is pumped continuously by pump - 23 through a long underground pipeline to the recovery plant site and back to tank - 22 in a closed loop. The flow velocity in this loop is kept high to prevent sedimentation and coating of the inside pipe walls.

To control further the lime slurry concentration, a liquid density meter and controller - 24 has been placed in the slurry recirculation loop and it may add dilution water through control valve CV-7 as required to maintain any desired density level within the range 1.03 to 1.08 at 85 deg. F. In practice, we use this instrument to indicate the density, but we have not found it necessary to use it as a density controller. However, we are considering purchasing by-product "carbide lime" from acetylene manufacture for at least part of our lime requirements, if the quality and cost is satisfactory. Since this calcium

hydroxide would be in the form of a concentrated slurry, the density controller would be very valuable then for adjusting automatically the slurry concentration.

The lime slurry is added normally to the first or second compartments of the wooden neutralization tank - 2. Each of the 3 compartments is provided with vigorous agitation. The solution leaving the tank should have a pH preferably about 5.5. As it flows out of the tank, coagulant aid solution is added if required, especially when caustic soda is used for neutralization. When lime is used and calcium sulfate is precipitated, the subsequent clarification of the solution is much improved and coagulant aid addition should not be necessary.

Besides sulfuric acid and zinc sulfate, the feed solution also has sodium sulfate, magnesium sulfate and small amounts of organic cationic and non-ionic rayon spinning aids. Some other impurities are cellulose floc, sulfur, zinc sulfide, hydrogen sulfide, and traces of iron and lead. Except for part of the iron and lead, and some sodium sulfide, which flow to the Densator, most of the latter impurities are eliminated in the clarifier - 4. Of course, when calcium sulfate solubility, about 0.2%, is exceeded during neutralization, calcium sulfate precipitate also appears in the clarifier underflow. This gypsum precipitate helps to carry down with it the other suspended impurities during clarification. In order to exceed the maximum solubility concentration of calcium sulfate, the sulfuric acid concentration in the feed must be about 0.16% or higher. To increase the amount of gypsum being precipitated, part of the clarifier underflow can be pumped back to the acid feed, to dissolve its gypsum content before lime is added for neutralization. This addition can be made to the first compartment of the neutralization tank if the lime is being added to the second compartment, as we prefer doing. The first compartment is preferably used as an acid concentration equalizing section.

The clarifier underflow that is not recirculated is sent to a thickener - 6 for concentration, prior to disposal in a waste dump area. Provision has been made to concentrate further the thickener underflow, if desired, by pumping the sludge by means of a Moyno pump - 7 to a rotary vacuum belt filter - 17.

Some of the suspended impurities are attached to air or gas bubbles, and tend to float initially when the neutralized feed solution flows into the clarifier - 4. To prevent this scum from floating directly to the clarified effluent weir, a 38-ft. diameter floating baffle, extending about 4 - 5 ft. down from the water level, retains the impurities until eventually they lose their bouyancy, settle and are removed in the underflow.

The clarified solution flows to the Densator reactor - 8 where it contacts recirculating sludge in the primary zone, receives caustic soda solution in the secondary zone and the sludge is separated from the clear effluent in the annular zone, as already explained.

Periodically or continuously, as desired, sludge is removed in the settling tank - 10, where the sludge is retained for several hours and its density is thereby increased. As the sludge flows to the settling tank, relatively soft neutral plant water is added to dilute and wash away much of the calcium dissolved in the water which accompanies the sludge. If desired, the sludge in the settling tank could be rinsed further with soft water to reduce even more the calcium content of the final sludge recovered, but we find this second step unnecessary for our requirements. Centrifugation of the sludge would accomplish a similar purpose and would increase sludge density also.

Settled sludge is removed in batches to dissolving tank - 11, and concentrated acid is added to it for dissolution of the solids. A Havig mixing pot is suspended on top of the tank and serves as a primary reaction chamber, protecting the tank's rubber lining. The acid is added with a metering pump. To reduce the attention required from the operator, the acid pump can be turned off automatically by means of a preset timer, or even by means of a pH controller set to turn the pump off when the pH reaches a value of 1 or 2. By experience, at a pH of about 1.5, there is about 0.5% free acid.

If there are enough impurities in the acidified sludge to warrant it, the acid solution can be filtered in rotary vacuum belt filter - 17 before being transferred to storage tank - 13 for reuse. This was actually done when the process was run while using caustic soda for neutralization, but the filtration rate was quite slow. Later, a new pipeline was installed between the dissolving tank - 11 and the first compartment of the neutralization tank - 2. The zinc sulfate solution was allowed to settle, and any settled turbid portion was returned to the start of the process for reclarification and reprecipitation. Since the acid to zinc ratio is low in this solution, the only added cost of reprocessing is the caustic soda required for reprecipitation.

SECTION VII

DISCUSSION OF OPERATIONAL PROBLEMS AND RESULTS

ZINC RECOVERY EFFICIENCY

The efficiency of the zinc recovery process depends on the concentration of the soluble zinc in the acid feed. This is due to the fact that unless there is an abnormality in the Densator operation, such as an accidental low pH, the soluble zinc in the clear effluent remains essentially constant. Therefore, the higher the soluble zinc concentration in the feed, the higher the percent efficiency of zinc recovery.

In Table 2 the final soluble zinc concentration can be observed during one period in which the more accurate but laborious atomic absorption technique was being used to determine the zinc concentration in the clear Densator effluent. This particular period was chosen for the Table because there were repeated pH problems due to the lime feed tank level control and clogging of a lime slurry pipeline, resulting in a very low pH in the clarifier and a moderately low pH in the Densator. Only the zinc content in the clear Densator effluent was determined by atomic absorption. A titration with ethylene diamine tetraacetic acid at a buffered pH of 6.8 was used for the other zinc analyses shown. The analytical procedure is described in Section XII.

It can be seen that on October 8 and 12, and on November 5, the solution in the clarifier was very acid. Enough additional caustic soda was added to the Densator to compensate for the lower pH, and only on November 5 did the Densator pH become too low. At that time, the zinc in the effluent increased to 10.9 ppm. The rest of the time the zinc remained below 2 ppm and its concentration did not correlate with the zinc concentration in the clarifier solution flowing into the Densator, which varied from 64 to 126 ppm.

Using 85 ppm as the average zinc concentration in the clarifier, or the feed to the Densator, and 1.08 ppm as the average zinc concentration in the effluent (excluding the November 5 figure), the average percent loss can be calculated as 1.27%, for a zinc recovery of 98.7%.

If the average zinc concentration in the clarifier had been 150 ppm instead, the zinc recovery figure would correspond to 99.3%, as the zinc concentration in the effluent would not be expected to change.

EFFLUENT WATER QUALITY

The effluent water is normally very clear. It does contain about 2,000 - 2,500 ppm of dissolved sodium sulfate, which is present in the feed to the plant, and somewhat less than 2,000 ppm of dissolved calcium sulfate, corresponding to the solubility of gypsum in the presence of this amount of sodium sulfate (23). Atomic absorption analysis of this effluent also indicates 50 - 150 ppm of magnesium, 0.3 ppm of iron and no other metals except for about 1 ppm of zinc. In addition, there is a small quantity

TABLE 2

LABORATORY ANALYSES OF PLANT pH, ZINC AND MAGNESIUM

	<u>Feed</u>			<u>Clarifier</u>		<u>Dens. effl.</u>		<u>Dens. sludge</u>		
	<u>pH</u>	<u>ppm Zn</u>	<u>ppm Mg</u>	<u>pH</u>	<u>ppm Zn</u>	<u>pH</u>	<u>ppm Zn</u>	<u>pH</u>	<u>ppm Zn</u>	<u>ppm Mg</u>
10-7-71	1.9	73	127	5.4	85	9.8	0.88	9.9	21,580	3,840
10-8-71	1.6	80	122	<u>3.3</u>	79	9.75	1.05	9.85	25,040	4,620
10-9-71	1.95	92	98	6.5	64	9.95	1.50	9.95	26,810	4,990
10-12-71	1.7	77	133	<u>3.2</u>	81	9.65	0.83	9.75	25,110	3,450
10-13-71	1.75	77	115	5.2	126	9.65	1.20	9.8	26,090	4,430
Shutdown 10-14 until 11-4 to modify lime feed tank level control and piping										
11-4-71	1.7	67	119	6.0	71	10.1	1.07	10.1	17,650	3,040
11-5-71	1.7	154	91	<u>3.1</u>	105	<u>8.0</u>	<u>10.9</u>	8.5	20,600	2,890
11-6-71	1.9	56	90	6.0	85	10.1	1.20	10.1	18,500	2,970
11-9-71	1.8	74	120	6.5	67	10.1	0.92	10.2	23,280	3,650

of soluble organic rayon spinning agents, non-ionic and cationic, which are added in the rayon manufacturing process. These agents, plus possibly some soluble cellulose decomposition products, contribute a small amount of organic contamination to the effluent. 26 BOD determinations averaged 24 ppm. Five COD determinations averaged 60 ppm, while the corresponding BOD determinations averaged 27 ppm, or an average COD to BOD ratio of 2.2.

This water is suitable for reuse wherever the high sulfate and high hardness is not an impediment; for example, as cleaning and flushing water, pump seal water, etc. It has been used for all water needs in the zinc recovery plant except for lime slaking and diluting water, and for the safety shower and eye wash station.

Any unused effluent water should be mixed with other plant effluents to reduce its pH of 9.5 - 10.0, or acidified in some inexpensive way.

As a matter of interest, Figure 6 has been included to show the effect on Hominy Creek, the small stream receiving American Enka's effluents, during the operation of the zinc recovery plant while neutralizing the acid with caustic soda and recovering about one-half of the zinc consumed by the rayon plant. The points which are shown correspond to one grab sample per week and therefore show considerable variation. It is interesting to note though, that the average zinc concentration was reduced by more than 50%. We believe that this is due to the well-known effect of zinc adsorption by the silt solids in the stream (19, 20, 21). The large pH variations are believed to be caused mostly by the rinse water of boiler feed water demineralizers. These discharges will be equalized in the near future.

REUSE OF ZINC

The recovered zinc has been used for many months in the rayon plant. Because the zinc contains some magnesium, it is used in a rayon bath that contains both zinc and magnesium. This bath is the same one that contributes the magnesium to the recovery plant feed.

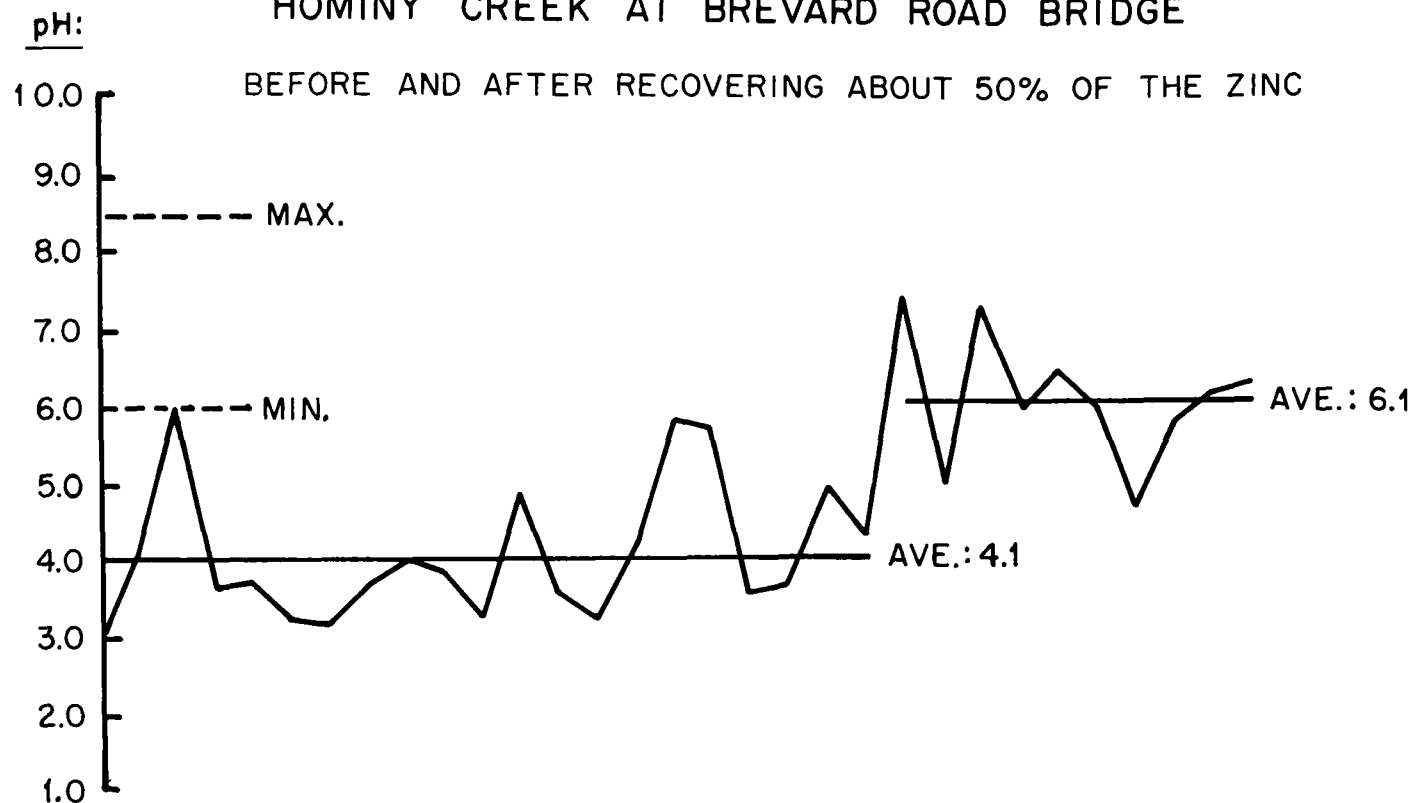
The average concentration of the magnesium in the recovered zinc sulfate solution is about 5 percent based on zinc sulfate.

If the caustic soda solution added to the Densator would be considerably more dilute than 21%, and if the pH in the Densator were kept at 9.0 - 9.5 at all times, there should be no appreciable concentration of magnesium hydroxide in the zinc sludge. Most of the magnesium hydroxide is precipitated between 9.5 pH and 11.0 pH (27).

Some of the iron in the feed solution is precipitated in the clarifier, some in the Densator, and there is apparently still a small amount in the effluent. The average concentration in the recovered zinc sulfate solution is 2.58% based on zinc or 1.04% based on zinc sulfate. This amount of iron is apparently of no consequence to the rayon plant operation.

HOMINY CREEK AT BREVARD ROAD BRIDGE

BEFORE AND AFTER RECOVERING ABOUT 50% OF THE ZINC



P.P.M. Zn:

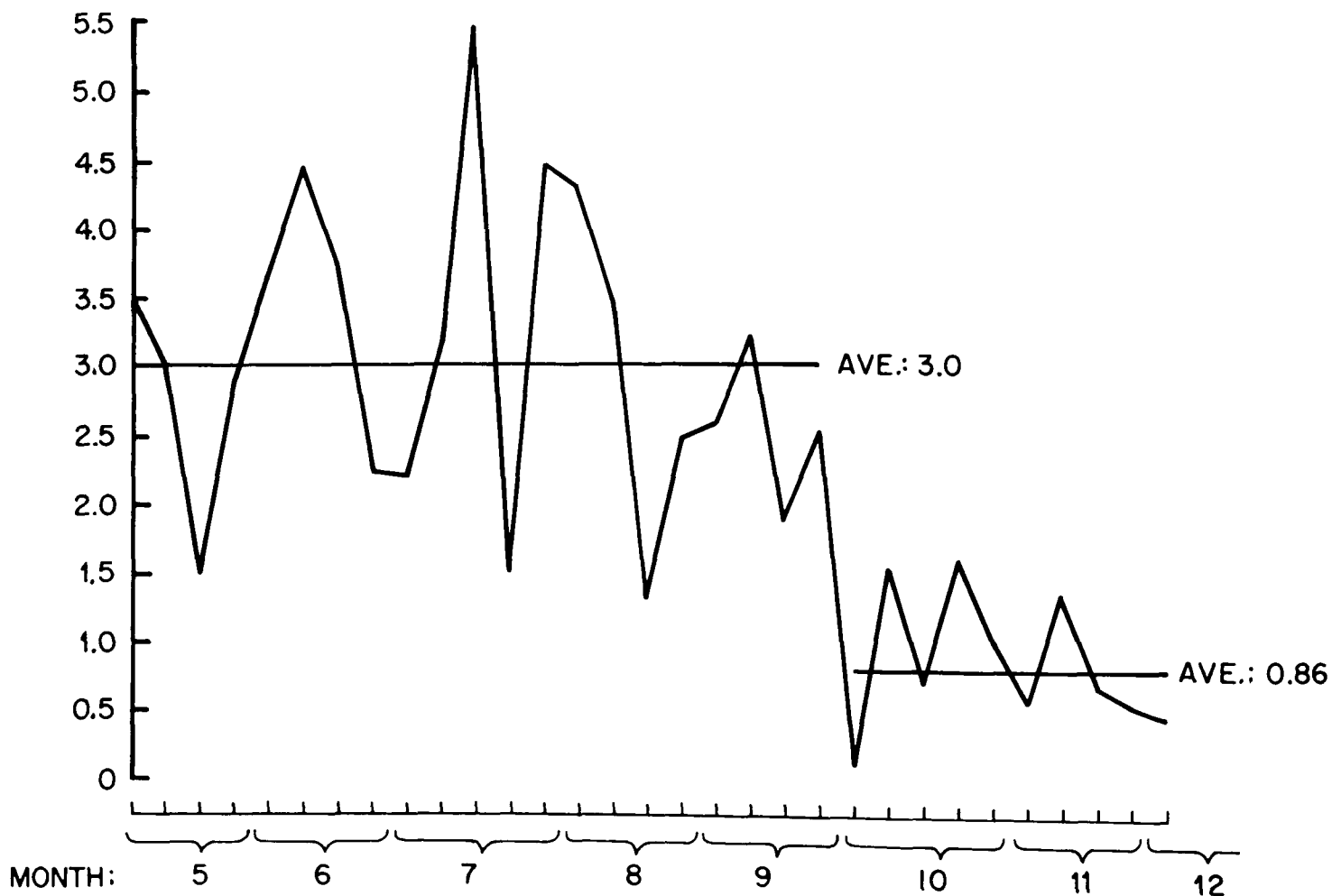


Figure 6

Part of the iron originates from the concentrated sulfuric acid, which may have as much as 75 ppm when it is used.

It is possible that if a greater percentage of zinc lost by the rayon plant had been recovered during the development of the process, it might have become desirable to purify the recovered zinc sulfate and reduce its iron content. The process which would be used is well known and includes oxidation of the iron to the trivalent state, precipitation using careful pH control, coagulation and separation of the hydroxide. Purification of iron as well as other impurities from an acid solution of zinc sulfate before the solution is sent to the electrolytic cells is a normal procedure in the electrolytic zinc industry (14, 24).

There can be as much as 0.55% of lead in the recovered hydroxide sludge, based on the weight of zinc, or 0.22% based on zinc sulfate. However, the lead content in the solution pumped back to the rayon plant is about 0.15% based on zinc sulfate.

The lead in the hydroxide sludge dissolves more difficultly than the zinc. For example, if sulfuric acid is added to the sludge until a pH of 3.5 is obtained, about 92% of the zinc is dissolved but only 15 - 20% of the lead. At a pH of 2.5, about 95% of the zinc is dissolved, but only about 33% of the lead.

All the calcium present in the hydroxide sludge appears to be dissolved in the water which accompanies the sludge, and amounts to about 600 ppm. During the past tests we found it necessary only to add fresh soft water to the sludge as it is transferred from Densator to settling tank, diluting thereby the concentration of calcium in the water. In the near future, when we plan to collect and recover most of the zinc lost by the rayon plant, we will probably find it desirable not only to wash the sludge with soft water, but also to centrifuge the sludge and increase its solids content. This will reduce further the calcium content, as well as the water that must be evaporated when the recovered zinc is added to the rayon spinning baths. Centrifugation in the laboratory produces a hydroxide sludge of more than 11% concentration.

If a small amount of light cellulose floc carries over from the clarifier, it is retained by the Densator sludge. If some of this cellulose is sent back to the rayon spinning bath together with the recovered zinc sulfate, it can be noticed that the spin bath filters will require more frequent backwashing, and that the concentration of cationic spinning agent in the bath will be reduced, requiring a greater flow of make-up solution.

Therefore, if there is appreciable turbidity in the recovered zinc sulfate solution, the insoluble material is allowed to settle and this impure portion is returned to the neutralization tank for subsequent clarification and zinc reprecipitation.

Initially, when caustic soda had to be used for neutralization, there was more cellulose carry-over and the rotary vacuum belt filter was used for purification of the final solution. However, filtration rates were very low and the operation was very undesirable.

SOLUBLE ZINC CONCENTRATION VERSUS SOLUTION pH

The "solids contact" process, on which Enka's zinc precipitation step is based, has been used mostly for lime softening in water treatment plants. When applied to the precipitation of metal hydroxides in the manner developed by American Enka, several unusual effects have been discovered.

The unusual shape and density of the zinc sludge particles are discussed in Section VIII, under the title "Scanning Electron Microscope Studies."

Another unusual characteristic seems to be the special relationship between pH and soluble zinc in the presence of Enka's dense zinc hydroxide sludge. For example, caustic soda was added to 285 ppm of soluble zinc sulfate until a pH of 9.5 was reached and most of the zinc was freshly precipitated. When more caustic soda was added, some of the zinc began to redissolve already at a pH of 10.0. This is shown in Table 3 which lists the soluble zinc, as determined by EDTA titration.

TABLE 3

SOLUBLE ZINC VERSUS pH IN ABSENCE OF SLUDGE

pH:	3.0	9.5	10.0	10.5	11.0
ppm Zn:	285	2.0	7.2	42.9	118.3

However, the results are different in the presence of dense sludge, as shown in Table 4. Densator sludge was taken from the primary zone, with a pH about 9.0. To aliquot samples of this sludge, sulfuric acid or caustic soda was added to obtain pH values in the range between 8.5 and 10.5 and the samples were allowed to settle. The soluble zinc in the liquid above the settled sludge was then analyzed, this time using atomic absorption for greater accuracy.

TABLE 4

SOLUBLE ZINC VERSUS pH IN PRESENCE OF SLUDGE

pH	<u>After settling 2 hours:</u>		<u>After settling 24 hours:</u>
	<u>ppm Zn</u>	<u>Turbidity</u>	<u>ppm Zn</u>
8.5	6.1	turbid	0.66
9.0	2.6	sl. turbid	0.22
9.5	2.6	sl. turbid	0.20
10.0	2.2	sl. turbid	0.17
10.5	0.1	clear	0.13

Considering the samples settled during 2 hours only, it was evident that the heavier magnesium precipitation obtained at a pH of 10.5 helped to settle the suspended zinc hydroxide.

The soluble zinc in the samples settled during 24 hours, which were all clear above the sludge level, shows the real equilibrium condition. Even at a pH of 10.5, no zinc hydroxide had been dissolved. Indeed, the soluble zinc had the lowest value at this pH.

The table shows that the pH in the Densator effluent should be at least 9.0. At a pH above 10.0, magnesium hydroxide precipitates heavily and actually aids the rate of settling of the sludge. However, since the value of the recovered magnesium is only 5.3 cents per pound, the caustic soda required for its precipitation costs 24% more than the value of the magnesium recovered. For this reason, we maintain a maximum pH value of 10.0 in the Densator effluent. The settling of the Densator sludge can be aided also, of course, by using a coagulant aid such as the "Superfloc" used in the pilot plant tests.

Table 5 below shows that an acid solution of zinc sulfate can be neutralized up to a pH of 6.0 without precipitation of any of the zinc as hydroxide. The soluble zinc has been analyzed by both EDTA titration and atomic absorption, but the latter is considered to be much more exact.

TABLE 5
SOLUBLE ZINC VERSUS pH IN THE CLARIFIER

<u>pH</u>	<u>ppm Zn (EDTA)</u>	<u>Atomic absorption</u>	
		<u>ppm Zn</u>	<u>ppm Fe</u>
3.0	184	172.0	1.9
4.0	183	172.0	1.9
5.0	182	172.0	1.5
6.0	180	172.0	0.85
7.0	157	150.0	0.26

The table also shows that 55% of the iron has precipitated at a pH of 6.0. No attempt was made previous to the analysis to make sure that all iron was in the ferric form and some of it must have been divalent iron.

Although no soluble zinc will precipitate at the normal pH of 5 to 6 maintained in the clarifier, insoluble zinc sulfide in the acid feed does settle out and is collected in the clarifier underflow. This underflow normally contains 1.0 to 1.5% of solids. Although there is available only a limited number of underflow solids analyses, these solids usually contain 10 - 15% of zinc and 0.5 - 1.5% of iron, analyzed and calculated on a dry basis. It is estimated that the insoluble zinc amounts to about 5% of the total zinc in the acid feed to the plant.

The remainder of the clarifier underflow solids consist mainly of gypsum, sulfur and cellulose floc.

USE OF COAGULANT AID IN THE CLARIFIER

Laboratory tests using a number of different coagulant aids for easier settling of the cellulose floc and other clarifier impurities indicated that Calgon No. 227 and Nalcolyte 672 seemed to aid settling. However, plant-scale tests showed that only the Nalco product worked satisfactorily. It is a slightly anionic polyacrylamide of very high molecular weight. The average addition rate is about 3 pounds per million gallons of flow, or a concentration of about 0.35 ppm.

A solution of 12.5 pounds of Nalcolyte 672 dissolved in 700 gallons of water is metered to the neutralized solution before the clarifier. It is further diluted with about 5 gals./min. of water flow before the point of addition.

Agglomerates of insoluble material often float on the surface of the clarifier and are retained by the floating baffle until they eventually sink. An analysis of this material showed about 0.4% of zinc sulfide.

The average turbidity of the clarifier effluent is less than 5 Jackson turbidity units.

LIME SYSTEM AND pH CONTROL

The lime system holds the dubious distinction of having been the most difficult one to get to operate satisfactorily. The feedforward pH control system was the second one most difficult.

The difficulties encountered with the lime system will be outlined first, as follows:

1. The slaking and diluting water from the rayon plant was found to have a too low and too variable pressure. A pressure-boosting water pump had to be installed in the line to the slaker.
2. The control of the slaker was designed originally to operate differently from that described in Section VI. Referring to Figure 4 the slaking water flow was continuously measured by an orifice meter FT-3 and the reading was fed to a controller that continuously adjusted the velocity of the lime feed screw to give a preset ratio of lime to water. This ratio could be changed manually. This proved to be a very unsatisfactory way to maintain a constant slaking temperature. The level in storage tank (22) was measured by a DP cell, and level controller LC-11 was supposed to regulate both water control valves CV-9 and CV-15 to maintain a constant tank level and an approximately constant lime slurry concentration. Moreover, the control valve CV-15 was not supposed ever to close completely below a certain flow, so that the lime screw drive reducer would never operate below its minimum designed speed. These relationships were too difficult to achieve in practice.
3. The lime slaker was supplied to Enka with all the diluting water addition at the grit removal chamber. Since there is no agitation at that point, other than the slow revolving of the grit removal screw, the dilution water did not mix with the creamy slurry from the slaking chamber. The thick slurry carried out with it most of the grit instead of it being removed in the grit chamber by the screw. This grit created problems in pipelines, tanks, and especially in all the control valves. The second slaking chamber had to be converted to a dilution chamber and the intercommunication at the bottom of the dividing wall between the chambers was closed.

The sloping bottom in part of the grit removal chamber then began to collect slowly mounds of grit above the reach of the removal screw. This collection of grit would interfere with the flow of slurry, and the liquid would back up and spill out through the grit removal opening instead of being pumped to the storage tank. The return flow pipe for slurry, through valve CV-13, was then provided with suitable nozzles inside the grit removal compartment to wash down the grit accumulations.

4. The level control electrodes, placed at the slaker outlet, would bridge across with lime and stop operating. Each electrode was covered, except for tip, with Tygon plastic tubing to prevent electrical short-circuiting.
5. Because all lime slurry tank outlets were at the tank bottoms, the fine grit which even now flows with the slurry has no safe place to collect and be removed. The grit gave problems with the pH control lime feed valves and would also clog the pipeline whenever the valves temporarily closed. The outlet of the lime slurry supply tank was changed to the straight side of the tank and suitable valves and flushing water were placed at the bottom nozzle to permit flushing out the deposited grit.
6. It was found initially that the lime feeder screw was really too large for our lime usage and a sprocket and chain reduction was added to the drive.
7. A most difficult problem occurred, while operating the initial slaker control system, when the slaking mixture would get too thick, or start to boil, and the slaking compartment would bridge over and fill up with lime. The lime flow would back up and overflow, spilling over the whole slaker and surroundings.
8. A high-temperature alarm and switch were added so that whenever the slaking compartment temperature exceeded a preset value, usually 195 deg. F, a solenoid valve would add an additional flow of water to the slaking compartment during a period of 3 minutes, thereby reducing the temperature and diluting the thick slurry. This control was found very useful.

Compounding the problems during the production of lime slurry were the problems with the feedforward pH control system, which required excessive attention and never operated really satisfactorily.

Although the concentration of acid in the feed varied continuously, within a maximum pH range of 1.5 to 3.0, the flow was very constant over the short term, varying slowly from one day to the next. To prevent initial difficulties this was done on purpose, allowing any excess acid being collected to overflow at the pumping pit. A typical graph of the feed pH is shown in Figure 7 showing that the normal pH changes were within 0.5 pH unit. To be able to operate correctly, the recording pen had to be adjusted so as to read in the middle of the chart, and the pH of 6.0 in the chart is really 1.5.

The initial recommendation to add the neutralizing alkali at the inlet box to the first tank compartment had to be changed due to excessive lag time. The alkali had to added very close to the compartment mixer.

The feedback trim could not correct the alkali addition in such a way as to prevent continous cycling of the pH, sometimes over several pH units, and still be able to respond satisfactorily when there was a sudden greater pH change.

A typical pH graph, as measured by the second set of electrodes after lime neutralization, is shown in Figure 8.

It was found that the pH graph was similar whether the first set of electrodes for the feedforward control were operating or not, so that they were eventually removed and the corresponding pH transmitter switch placed on "check," so as to "read" artifically a constant feed pH.

The only way to obtain a much improved pH control was to use the first tank compartment as an equalizing tank, so as to feed to the second compartment a nearly constant acid composition and then add the alkali to this second compartment. The feedforward electrodes remain inoperative and the feed-back trim electrodes, placed in the second compartment, control the alkali addition. This controller is provided with reset and derivative action. A typical graph using lime neutralization is shown in Figure 9.

Our conclusion is that although it may be possible to make our feedforward pH control system work if sufficient specialized and experienced personnel would work on it, it appears to us to be too difficult to adjust and control to be satisfactory for our purposes.

If sufficient feed concentration equalization is provided, a feedback controller is satisfactory if there is good agitation for a short lag time. The neutralization can be carried out in one step, as done at Enka, or in more than one step (25), for a greater factor of safety.

It is very desirable to have an agitated compartment or tank, subsequent to the neutralization step, to even out any pH fluctuations.

For the sake of the record, it should be mentioned that each neutralizing alkali is added at Enka with two control valves in cascade so that the smallest opening of the larger one equals the largest opening of the smaller one. The Foxboro valves are as described in the following table:

TABLE 6

TYPE OF ALKALI FEED CONTROL VALVES

Use:	Lime	Lime	Soda	Soda
Diameter:	2 in.	1 in.	1-1/2 in.	1/2 in.
Type:	AS split body	F7 parabolic needle (K)	AS split body	F7 needle (J)
Cv:	46	2.25	25	1.13

The large caustic soda valve was adjusted so that it could never open more than halfway.

It should be mentioned here that only high calcium lime is suitable for good pH control. Limes with high magnesium content react more slowly and the pH keeps increasing over a long period of time.

Figure 7
Typical Graph of Plant Feed pH (6 in scale = 1.5 pH)

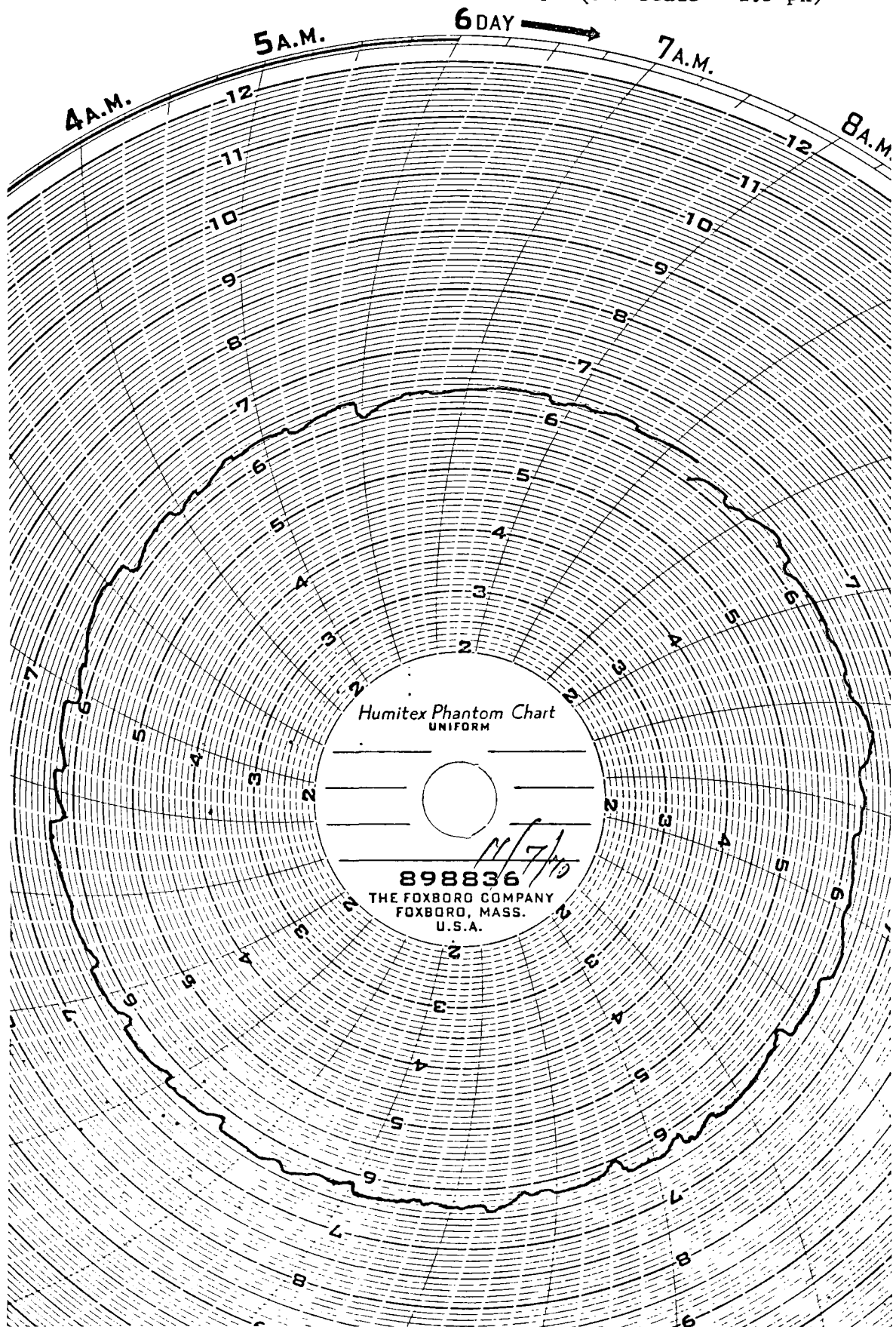


Figure 8
Typical Graph of pH After Lime Neutralization
While Using Complete Feedforward System

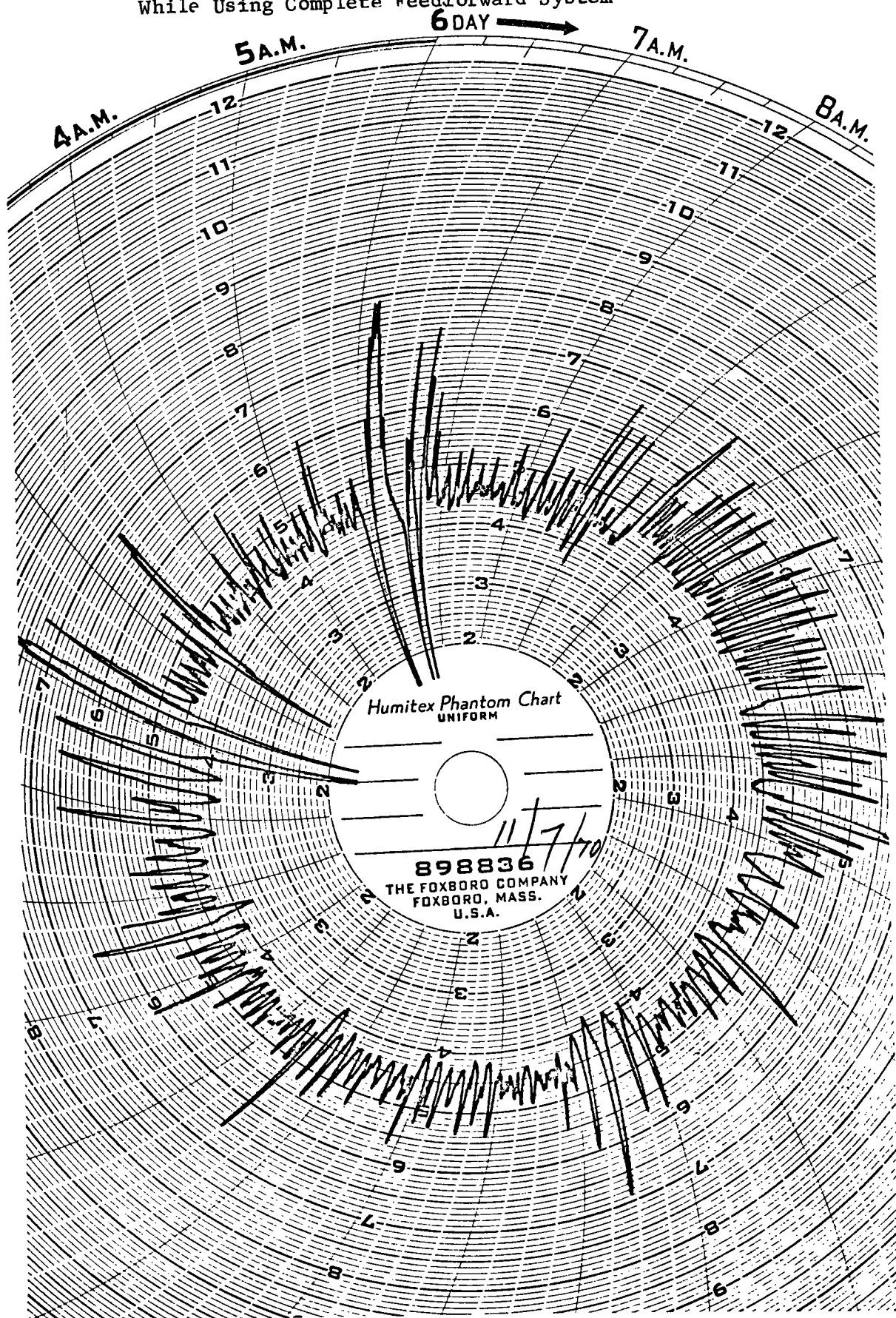
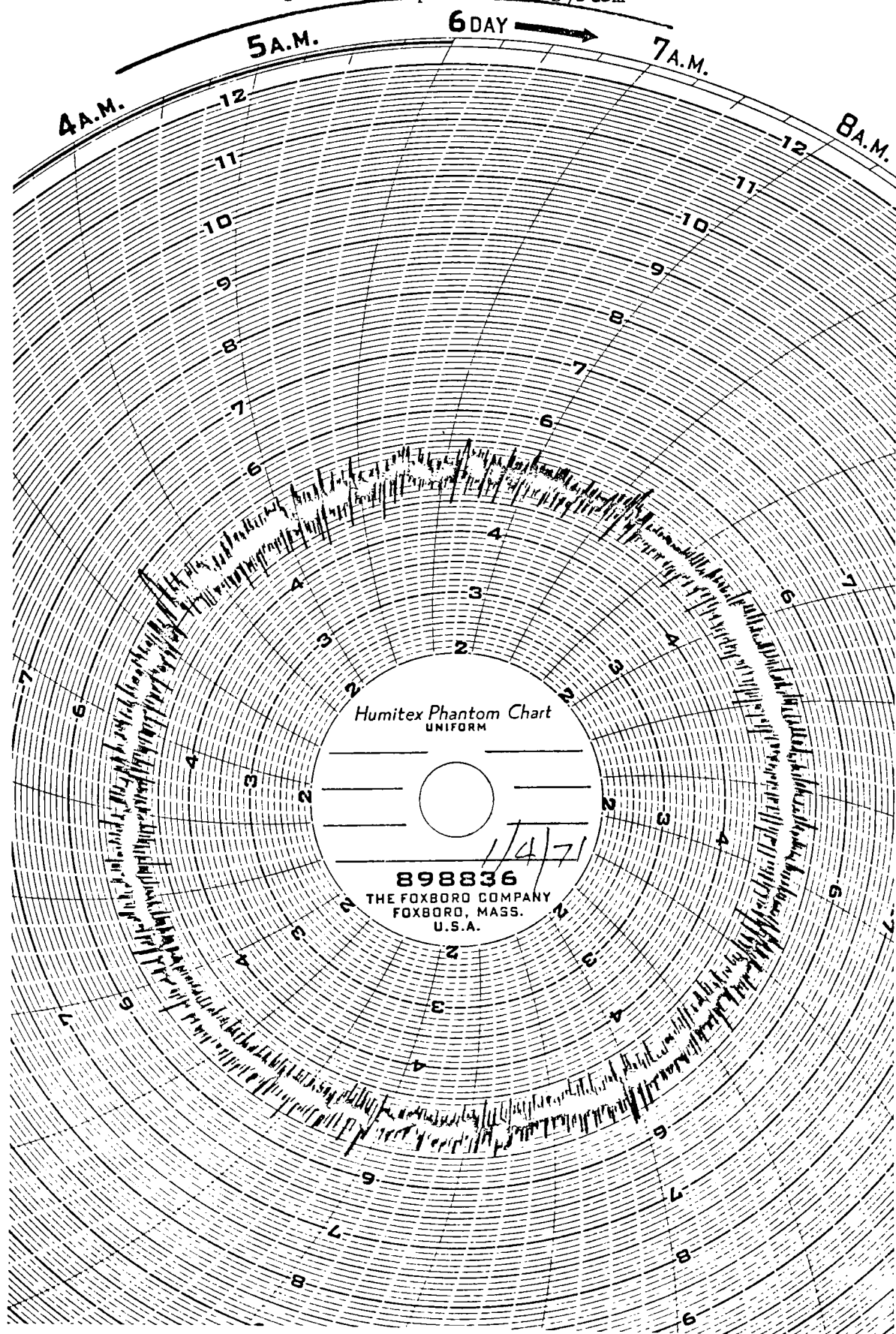


Figure 9
Typical Graph of pH After Lime Neutralization
While Using Modified pH Control System



SECTION VIII

SCANNING ELECTRON MICROSCOPE STUDIES

As part of an attempt to understand better the mechanism by which Enka's unique form of dense zinc hydroxide is formed and to be able to visualize the actual appearance of the individual sludge particles, the Physics Research Department of American Enka took many photos of the recovery plant sludge and various laboratory-made sludges using a scanning electron microscope. A selection of the photos is described and shown below.

All samples of sludge were first washed well with distilled water, to eliminate dissolved salts which would become solid when the sludge samples were air dried. Therefore, the particles shown should be only the sludge particles. It is true, of course, that the appearance of the sludge particles is susceptible to change when drying. However, since all sludges were washed and dried in the same way, it should be possible to detect different results by comparison.

The appearance of the actual recovery plant sludge from the Densator is shown in Figures 10, 11 and 12 at 1,400, 4,800 and 5,500 magnification, respectively. The particles can be seen to be fairly rounded, smooth and with a very dense appearance.

A series of laboratory precipitations was carried out using pure chemicals, in an attempt to observe any gradual changes in the appearance of the precipitate. Chemically pure zinc sulfate was dissolved in distilled water to give a solution with 500 ppm of zinc. This high concentration was chosen to try to accelerate the production of the dense sludge. Pure caustic soda solution was added to obtain a pH of 9.5. The suspension of zinc hydroxide was centrifuged very gently to accelerate settling, but not enough to agglomerate the precipitate. The clear solution was decanted, additional zinc sulfate solution was added to the sludge, and the process repeated again and again. After 10 precipitations, the dried sludge appeared as shown in Figures 13, 14 and 15 at 500, 1,075 and 5,400 magnifications, respectively. The two higher magnifications show the sludge particles as loose leaflets. The photo at 500 magnification shows irregular chunks which probably resulted from drying a thick layer of sludge. These chunks are not rounded or smooth as are the particles found in the recovery plant sludge.

After 30 successive precipitations, the dried sludge appears as shown in Figures 16, 17 and 18 at 550, 1,100 and 6,200 magnifications, respectively. The photos of the two smaller magnifications show that the leaflet particles appear to be agglomerating together, while the photo at the greatest magnification shows that the sludge particles are indeed composed of leaflets.

After 60 precipitations, the dried sludge appears as shown in Figures 19, 20 and 21 at 500, 1,180 and 5,850 magnifications, respectively. The photos of the two smaller magnifications show that the agglomerates are now becoming more rounded; and, the photo at the greatest magnification shows how the surface of the sludge particles is becoming very dense, with the leaflets barely visible now.

It is possible to imagine that after many more precipitations, the sludge particles can become as rounded and dense as shown in the photos of the sludge from the recovery plant.

Three more photographs are worthy of showing, although we are not certain of the proposed explanation for the unique appearance of these sludge particles. They are shown in Figures 22, 23 and 24 at 5,200, 10,750 and 22,000 magnifications, respectively. Two or three months before the photos were taken, a sample of the recovery plant solution was taken from the clarifier. Caustic soda was added until the zinc precipitated, and then the sample was kept in a stoppered bottle for occasional exhibition to demonstrate graphically the difference between freshly precipitated sludge and Enka dense sludge. It is speculated that during the long storage at room temperature, the precipitated zinc hydroxide rearranged its shape into the special crystals with pointed needles. Since the experiment has not been repeated for confirmation, we cannot be certain of the explanation proposed, especially considering that the original solution was the impure plant feed, instead of pure zinc sulfate as was used for the 60 successive precipitations. However, if the explanation is correct, as we are inclined to believe, it could be said also that the dense round shape of the particles in the Enka plant sludge cannot be obtained simply by long sludge storage time, since the shape of the crystals obtained would be entirely different. Indeed, over the 2 to 3 months of storage, the single-precipitation sludge obtained from the plant solution did not appreciably increase in density.

From Figures 10, 11 and 12 it can be calculated that the dense sludge particles average 4 - 8 microns in diameter. Based on the size of the particles shown in Figure 15, it appears that fresh, normally precipitated zinc hydroxide is in the form of thin curved platelets about 2 microns in diameter. This configuration explains the slower settling velocity and the lower final density normally obtained with zinc hydroxide precipitates.

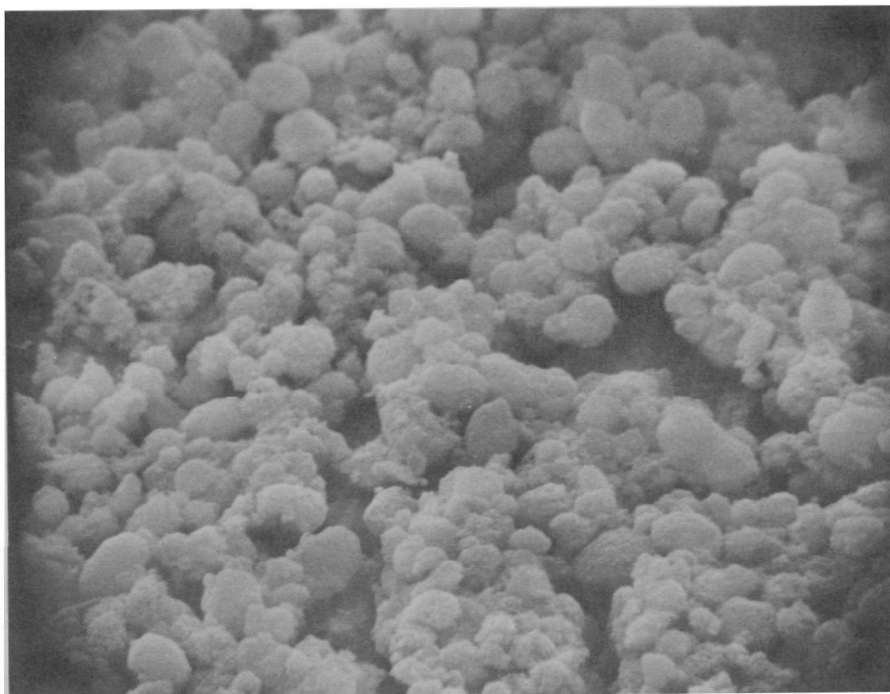


Figure 10: Recovery Plant Sludge (1,400 X)

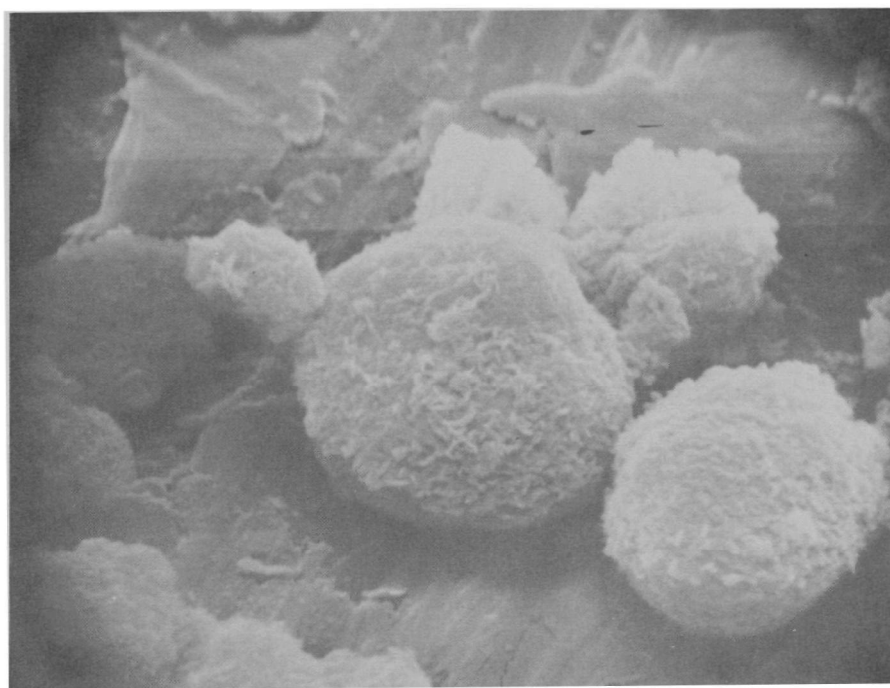


Figure 11: Recovery Plant Sludge (4,800 X)

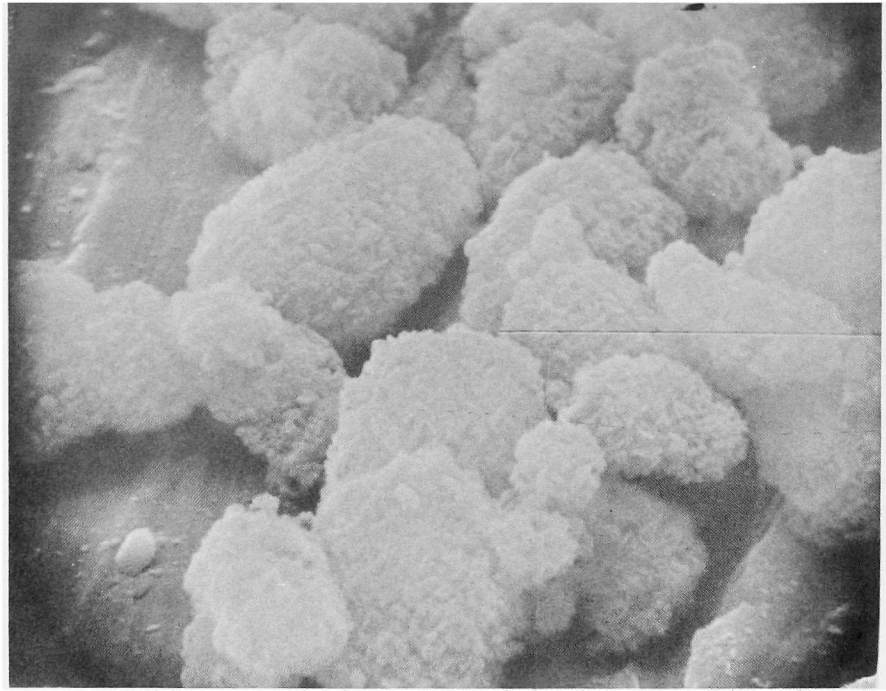


Figure 12: Recovery Plant Sludge (5,500 X)

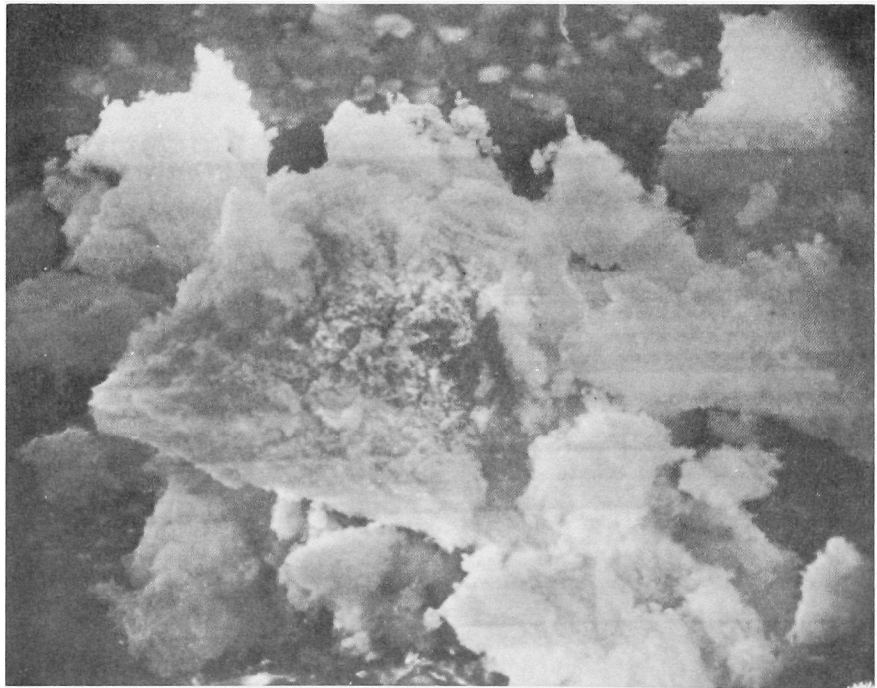


Figure 13: Laboratory Sludge after 10 Precipitations (500 X)

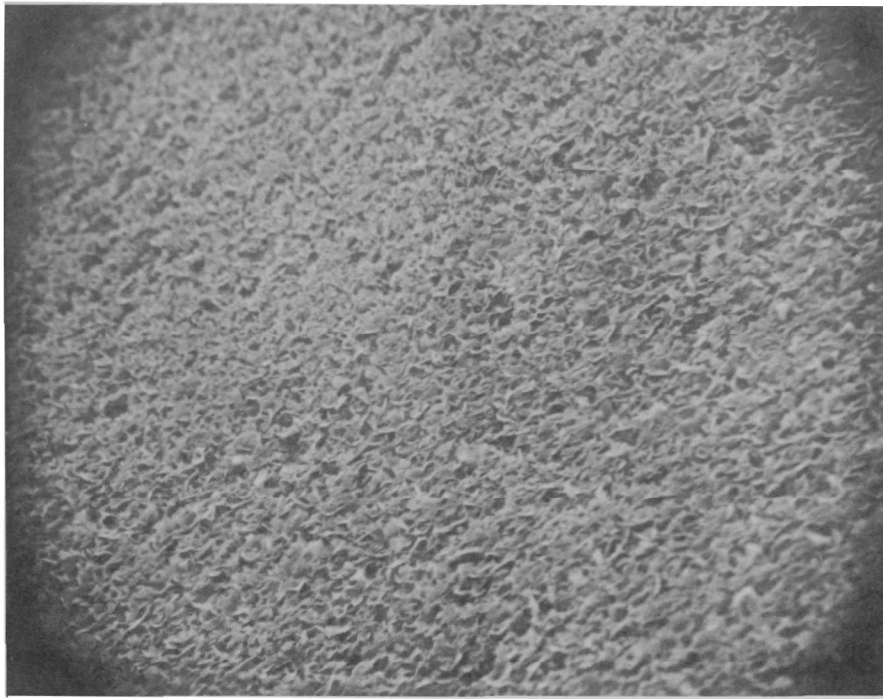


Figure 14: Laboratory Sludge after 10 Precipitations (1,075 X)

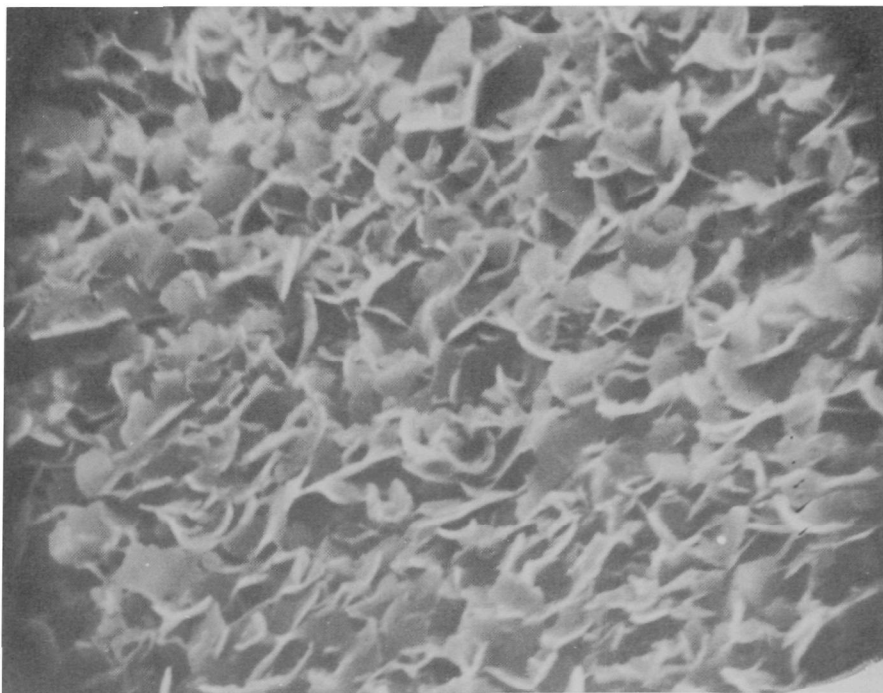


Figure 15: Laboratory Sludge after 10 Precipitations (5,400 X)



Figure 16: Laboratory Sludge after 30 Precipitations (550 X)



Figure 17: Laboratory Sludge after 30 Precipitations (1,100 X)

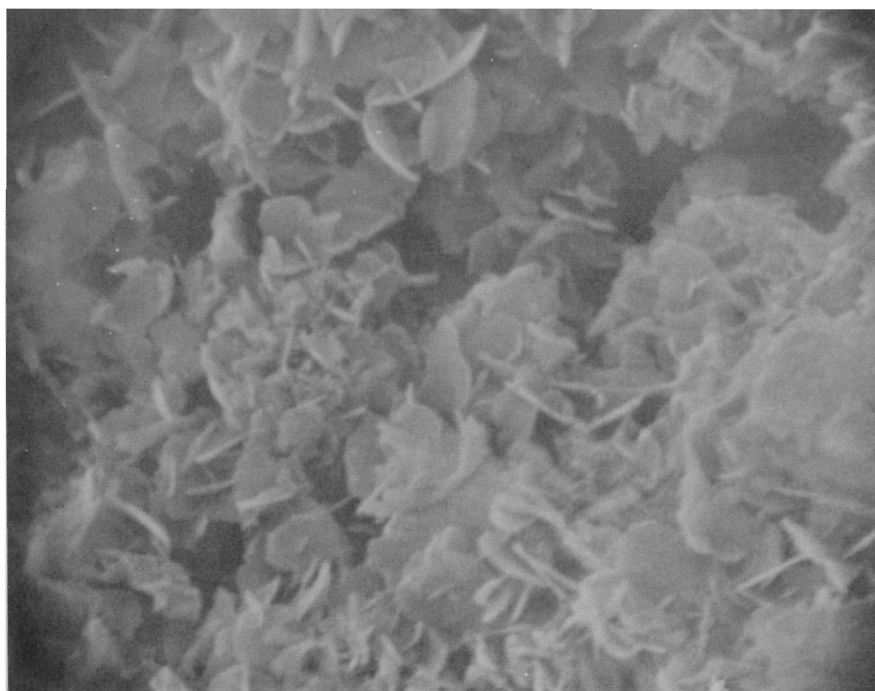


Figure 18: Laboratory Sludge after 30 Precipitations (6,200 X)

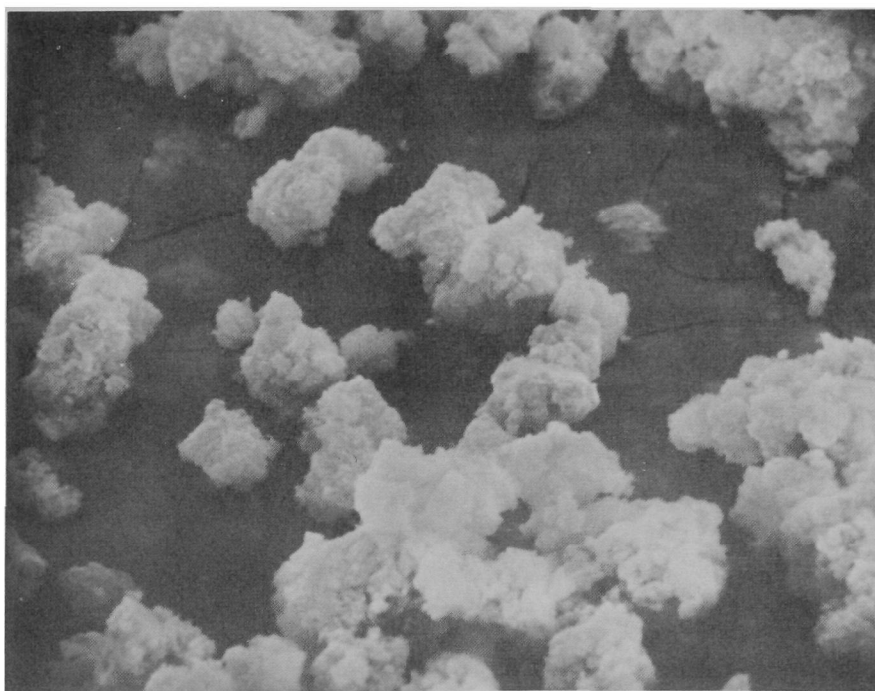


Figure 19: Laboratory Sludge after 60 Precipitations (500 X)

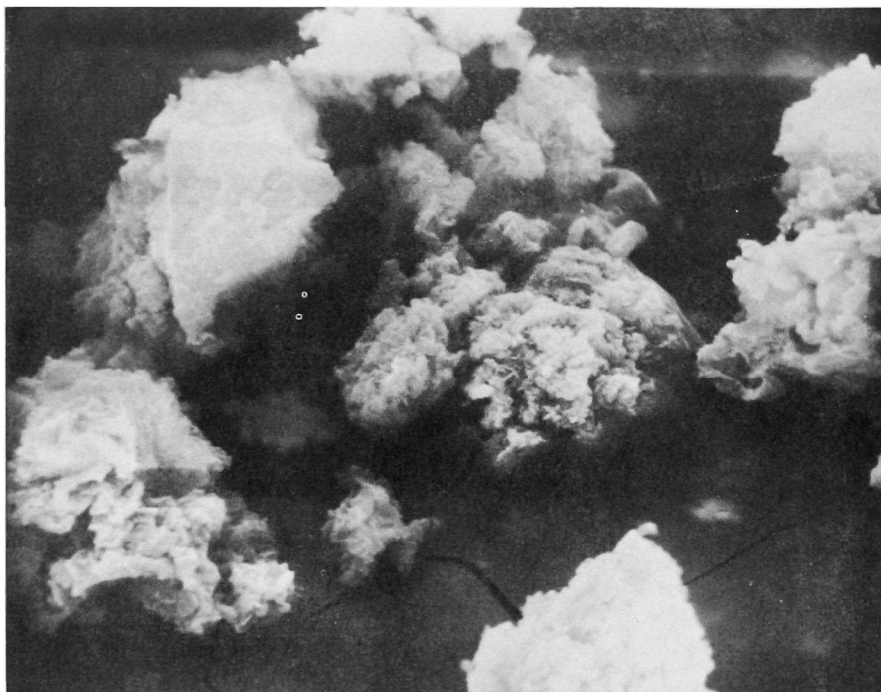


Figure 20: Laboratory Sludge after 60 Precipitations (1,180 X)

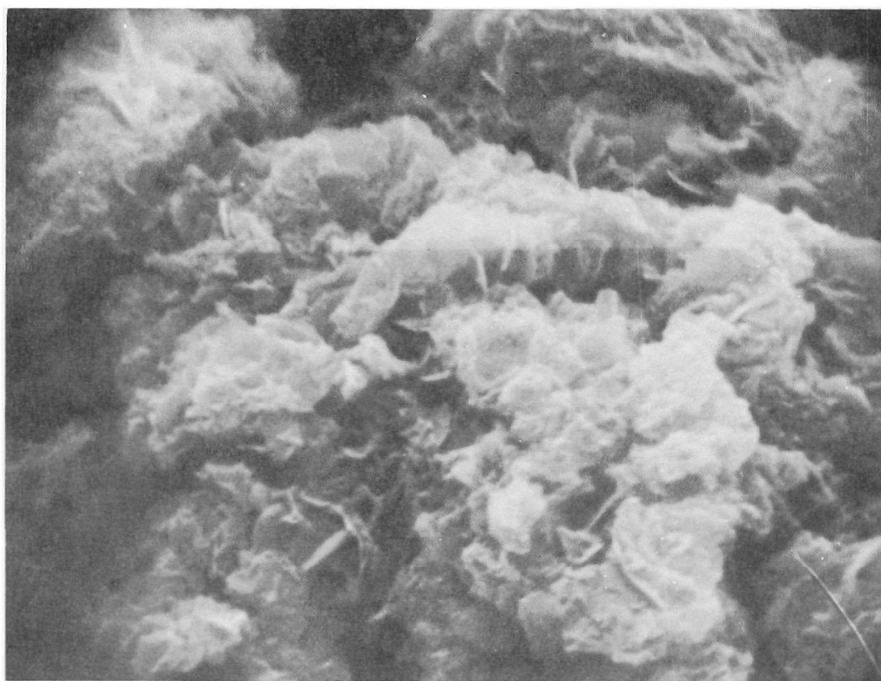


Figure 21: Laboratory Sludge after 60 Precipitations (5,850)

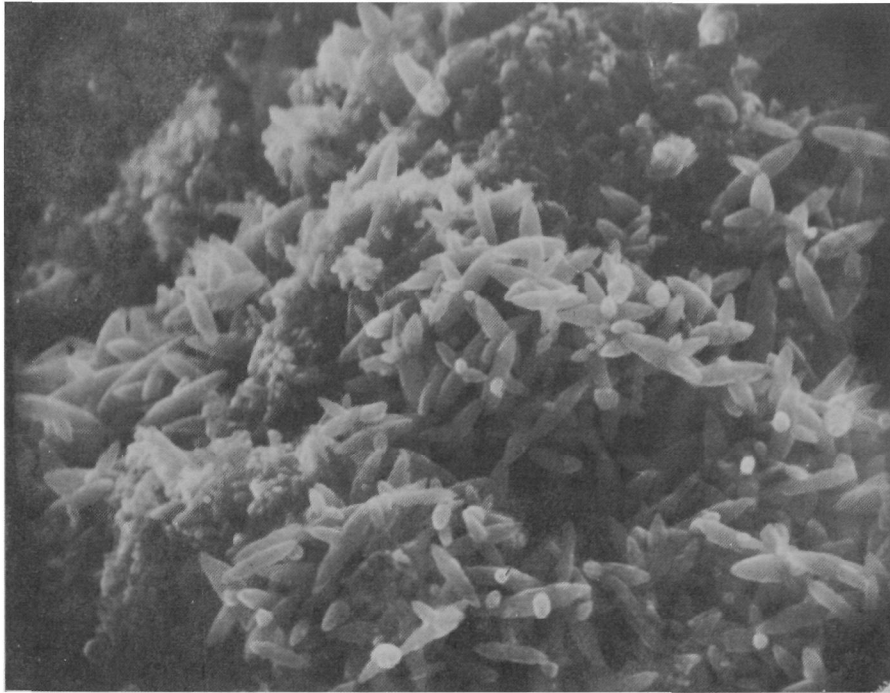


Figure 22: Plant Solution. Precipitated Once and Aged (5,200 X)

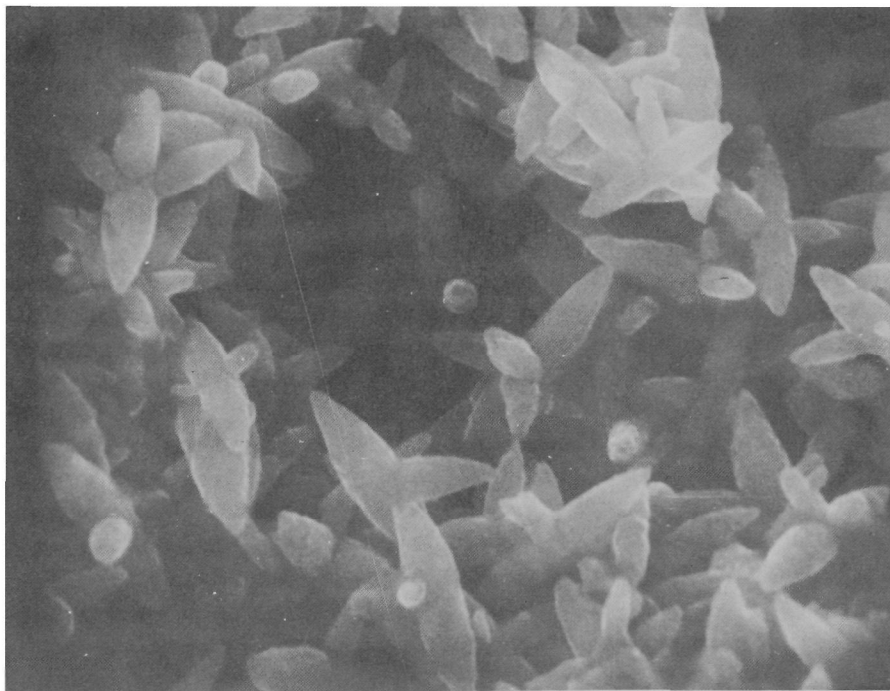


Figure 23: Plant Solution. Precipitated Once and Aged (10,750 X)

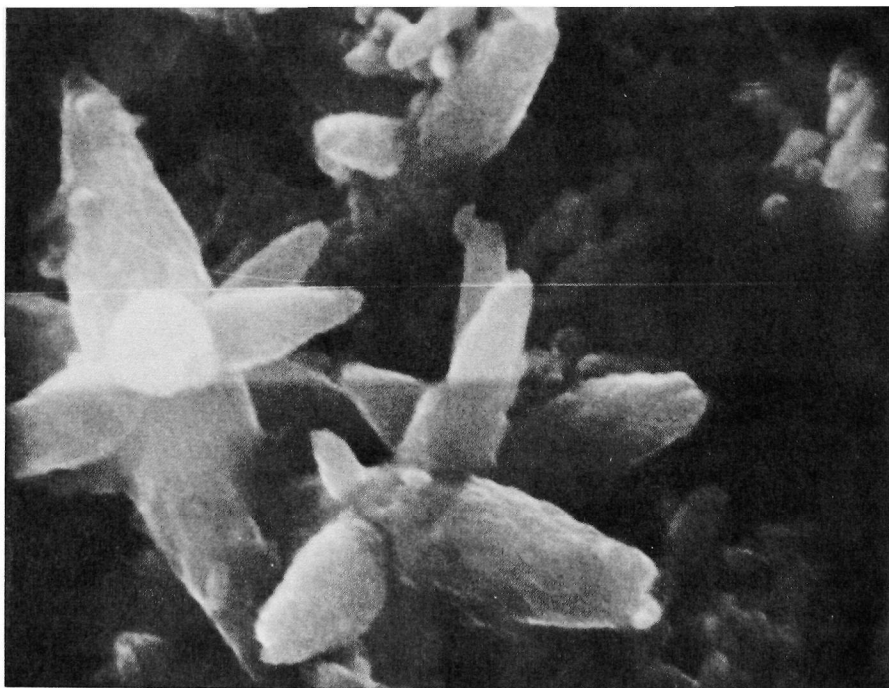


Figure 24: Plant Solution. Precipitated Once and Aged (22,000 X)

SECTION IX

COSTS

CAPITAL INVESTMENT COSTS

The investment of equipment for installation of the acid and alkali collection systems will be shown separately from that corresponding to the recovery plant proper, since there should be a collection system for any comparable kind of zinc recovery or treatment plant.

	<u>Recovery Plant</u>	<u>Collection Systems</u>
Period before R and D grant	\$370,000	---
Period during grant	<u>240,000</u>	<u>120,000</u>
Total	\$610,000	\$120,000

The engineering cost, or the cost of technical services related to the design and construction, of the recovery plant and the collection systems was not recorded separately.

Period before R and D grant	\$ 65,000
Period during grant	<u>130,000</u>
	\$ 195,000

If the design and construction had not been carried out during two separate periods, each with different purposes, and if this project had not been primarily a research and development project, the engineering cost should have been appreciably lower. In addition, because of lack of experience with the handling and slaking of lime, the design and construction of parts of the lime installation and its instrumentation was changed more than once, adding to engineering and construction costs.

Capital investment costs for a new similar future plant could be reduced by doing the following:

- (a) Instrumentation costs which mounted to about \$44,000, can be reduced considerably using a properly designed feedback controller and two small neutralization tanks, together with preliminary acid feed concentration equalization.
- (b) The rotary vacuum belt filter installation, which was purchased partly as a safety measure, to be able to filter out cellulose floc when using the caustic soda neutralization system, or to dry further the clarifier underflow mud after suitable thickening, could be dispensed with. The thickened mud can be dumped directly without further filtration, saving approximately \$40,000.

- (c) If neutralization with lime is carried out under such conditions that there is calcium sulfate precipitation, probably the coagulant aid addition would be unnecessary and the corresponding make-up and addition system, costing about \$8,000, could be saved. Of course, operating costs would be reduced also to the extent of the daily cost for the coagulant aid.
- (d) There may be some additional cost savings if instead of a Densator, which includes a reactor core section and an annular settling section with expensive scraper design, a separate small reactor tank and a clarifier of standard design would be substituted.

Some of these savings would be offset, however, by increased costs for the remainder of the equipment, due to escalation.

It should be pointed out here that the investment in a similar recovery plant depends mostly on the magnitude of the acid flow to be treated, rather than the amount of zinc to be recovered. Therefore, it is very worthwhile to collect the waste zinc flows at their source with the highest concentration feasible.

OPERATIONAL COSTS

The cost to operate the zinc recovery plant depends mostly on the amount of acid that must be neutralized per unit of zinc recovered. The ratio of sulfuric acid to zinc sulfate in the plant feed, called ratio R in this report, depends on the usually secret composition of the rayon spinning and regenerating bath formulas used by the rayon spinner, and the actual proportion of the different types of rayon spun in each plant, as each type usually employs a different formula. For example, textile filament yarns are usually spun in baths with a high acid to zinc sulfate ratio, while high-tenacity industrial yarns and some types of specialty fibers are spun using a lower ratio. Furthermore, for each type of rayon product the ratio varies depending on the source of the waste. For example, the ratios are different for the spin bath filter backwash, the spinning pot spray water and the first yarn cake wash.

The over-all ratio R for this plant has usually been about five to six when adding waste alkaline flows to the waste acid flow. Otherwise, the ratio has been about six to seven.

The cost of chemicals is the following:

- (a) High-calcium rotary kiln quicklime, 95% available lime, costs about \$20 per ton.
- (b) Caustic soda solution, available to the recovery plant as a 21% solution costs about 2 cents per pound of 100% NaOH.
- (c) Rayon grade zinc oxide, available to the rayon plant at 12.5 cents per pound.
- (d) Nalcolyte 672 coagulant aid costs \$2.32 per pound. It was added at the rate of 3 pounds per million gallons.

For the consumption of electrical power see Section XII, Appendix. The corresponding average electrical cost, at 0.7 cent per kilowatt-hour, is \$22.40 per 24 hours.

The cost of labor and supervision under normal operation is assumed to be one-half man, about \$5,000 per year. This amounts to \$13.70 per day. His duties would be to check the equipment and instrumentation, to acidify a batch of zinc hydroxide sludge and to pump the recovered zinc sulfate to the rayon plant. The latter two operations can be made so as to turn off themselves automatically.

Because there appears to be little maintenance required for this plant, maintenance costs are assumed to be one percent of capital costs. If the latter are taken as \$600,000, maintenance costs would amount to \$16.40 per day.

Using the given figures, it can be easily shown that if only caustic soda is used for neutralization, instead of lime, the value of the recovered zinc would not even pay for the cost of the caustic soda used. Per pound of zinc recovered:

Cost of soda for neutralization:

$$\frac{(R) (161.4) (80)}{(65.4) (98)} (0.02) = (\$0.0404) (R)$$

Cost of soda for zinc precipitation:

$$\frac{(80) (0.02)}{(65.4)} = \$0.0245$$

Value of the zinc recovered:

$$\frac{(81.4) (0.125)}{(65.4)} = \$0.1555$$

To be able to pay for just the cost of the caustic soda, the ratio R for sulfuric acid to zinc sulfate in the feed to the plant cannot exceed the following value:

$$(0.0404) (R) + (0.0245) = (0.01555)$$

or,

$$R = (0.1310)/(0.0404) = 3.24$$

As mentioned before, the ratio R for our plant is 5 or higher.

If lime is used for neutralization, as is being done under normal operation, the cost of the lime, per pound of zinc recovered would be:

$$\frac{(R) (161.4) (56) (0.01)}{(65.4) (98) (0.95)} = (\$0.01485) (R)$$

or,

2.7 times less than the cost of caustic soda for the same purpose.

When using lime, it is assumed that the precipitation of calcium sulfate after neutralization makes the use of coagulant aid unnecessary to obtain satisfactory clarification.

If the amount of zinc recovered daily is called Z, the ratio R at which the value of the zinc pays for the operating and maintenance costs in the Enka Plant is given by the following formula:

$$(\text{cost of lime}) + (\text{cost of soda}) + (\text{cost of labor}) + (\text{cost of electrical power}) + (\text{maintenance cost}) = (\text{value of zinc})$$

$$(0.01485) (R) (Z) + (0.0245) (Z) + (52.50) = (0.1555) (Z)$$

The corresponding values of Z and R are shown in the table below:

TABLE 7

MAXIMUM ACID TO ZnSO_4 RATIO AT VARIOUS RECOVERY CAPACITIES TO PAY FOR OPERATING AND MAINTENANCE COSTS

Lbs. zinc/day (Z):	1000	2000	3000	4000
Max. R to pay O. & M. costs:	5.28	7.05	7.64	7.95

A minimum recovery of about 1000 pounds of zinc daily assures payment of the operating and maintenance costs.

The maximum flow that can be handled by the Enka Plant is believed to be about 1200 gals./min. The plant bottleneck is the size of the clarifier, which is 74 feet in diameter. To obtain good settling of the suspended impurities, including cellulose floc, the upflow velocity should not exceed about 0.28 gal./min./sq. ft., and preferably even lower, 0.24 gal./min./sq. ft.

Based on the pilot plant tests, the Densator should be able to operate satisfactorily at about 2000 gals./min., equivalent to 0.425 gals./min./sq. ft. To handle this flow, the Enka clarifier should have a diameter of 95 feet, or another additional clarifier with a diameter of 60 feet should be provided.

Due to the fact that even the very dilute zinc wastes must be collected and treated, it is doubtful that the Enka Plant's concentration of zinc in the composite collected wastes flows would ever exceed about 150 ppm. Therefore, the maximum present capacity for zinc recovery of the plant is about 2,160 pounds of zinc per day, corresponding to a flow of 1200 gals./min. and 150 ppm of zinc. If a larger diameter clarifier were available, the plant capacity for zinc recovery would be about 3,600 pounds of zinc per day.

At a zinc recovery capacity of 2000 pounds daily, operating and maintenance costs would total 12.5 and 14.0 cents/lb. of zinc at a ratio R of 5 and 6, respectively. At a plant capacity of 3,500 pounds daily, these costs would be 11.5 and 12.9 cents/lb., respectively. The cost of purchased ZnO is 15.6 cents/lb. of equivalent zinc.

To pay for amortization of capital, greater plant capacity would be required, as shown in the following calculations.

Amortization payments corresponding to a capital investment of \$600,000, at 20 years and 7% interest, would amount to \$155 per day. To include this cost, based on a larger sized plant, the required capital investment will be estimated to increase as the 0.6 power of the increase in plant size as given by the increase in the plant feed flow. The concentration of zinc in the feed flow is assumed constant at 150 ppm.

Therefore, the amortization cost, expressed in terms of the amount of zinc recovered (Z), would be:

$$\left[\frac{(Z) (10^6)}{(150) (8.3) (1200) (1440)} \right]^{0.6} (\$155.00) =$$

$$(Z/2160)^{0.6} (155) = (1.55) (Z)^{0.6}$$

To determine the electrical costs, assume that they are directly proportional to the flow, or to the amount of zinc recovered:

$$(Z/2160) (\$22.40) = (Z/96.5)$$

Maintenance costs of 1% would increase as the capital investment increased, and would amount to:

$$(Z/2160)^{0.6} (\$16.40) = (0.164) (Z)^{0.6}$$

The cost of labor is assumed constant.

Cost of insurance and taxes, as well as general overhead items such as research, etc., are not included.

Therefore, the corresponding formula for this case would be:

$$(\text{cost of lime}) + (\text{cost of soda}) + (\text{cost of labor}) + (\text{cost of elec. power})$$

$$+ (\text{maintenance cost}) + (\text{amortization cost}) = (\text{value of zinc recovered})$$

$$(0.01485) (R) (Z) + (0.0245) (Z) + (13.70) + (Z/96.5) +$$

$$(0.164) (Z)^{0.6} + (1.55) (Z)^{0.6} = (0.1555) (Z)$$

The corresponding values of plant flow, Z and R are shown in the table below and in Figure 25.

TABLE 8

MAXIMUM ACID TO $ZnSO_4$ RATIO AT VARIOUS RECOVERY CAPACITIES
TO PAY FOR OPERATING, MAINTENANCE AND AMORTIZATION COSTS

<u>Flow</u> <u>(million gals./day)</u>	<u>Z</u> <u>lbs./zinc/day</u>	<u>Max. R to pay</u> <u>O., M. and Amortiz. Costs</u>
1.6	2,000	2.14
3.2	4,000	3.70
4.8	6,000	4.41
6.4	8,000	4.85
8.0	10,000	5.13

If lime would be available at a lower cost, the economics of the process would improve greatly. For example, a kraft pulp mill (28) purchases limestone and calcines it to quicklime in a rotary kiln at the rate of 120 tons per day. A portion of the quicklime, with 90% calcium oxide, is available to its waste treatment plant at cost, \$15.35 per ton. If quicklime were available at this cost for Enka's zinc recovery, the new values of R would be as shown in the following table and in Figure 25.

TABLE 9

MAXIMUM ACID TO $ZnSO_4$ RATIOS AT VARIOUS RECOVERY
CAPACITIES TO PAY FOR OPERATING, MAINTENANCE AND
AMORTIZATION COSTS IF CHEAPER LIME IS AVAILABLE

<u>Flow</u> <u>(million gals./day)</u>	<u>Z</u> <u>lbs./zinc/day</u>	<u>Max. R. to pay</u> <u>O., M. and Amortiz. Costs</u>
1.6	2,000	2.65
3.2	4,000	4.57
4.8	6,000	5.45
6.4	8,000	6.00
8.0	10,000	6.35

Although a minimum recovery plant of about 10,000 pounds of zinc daily capacity is required to pay all operating, maintenance and amortization costs using our present lime costs, only about half that capacity is required if the lower priced lime were available to Enka, although the price reduction is only about 19% based on available calcium oxide.

In an attempt to lower lime costs, Enka is investigating the possibility of using "carbide lime," the by-product of acetylene manufacture.

In the case of other industrial plants, it may be easier to collect acid wastes with a higher concentration of zinc than is the case at Enka. To show the effect of increased zinc concentration on the economics of this process, the maximum R ratio in the feed that will allow recovery of all operating, maintenance and amortization costs at different plant capacities has been calculated again. Capital investment costs have been assumed to vary as the 0.6 power of the

increase in plant size as given by the increase in the plant feed flow. The new values of R are as shown in the following table and in Figure 25 and correspond to a zinc concentration of 300 ppm in the feed.

TABLE 10

MAXIMUM ACID TO $ZnSO_4$ RATIOS AT VARIOUS RECOVERY
CAPACITIES TO PAY FOR OPERATING, MAINTENANCE AND
AMORTIZATION COSTS IF Zn CONCENTRATION IN FEED IS DOUBLED

<u>Flow</u> <u>(million gals./day)</u>	<u>Z</u> <u>lbs./zinc./day</u>	<u>Max. R to pay</u> <u>O., M. and Amortiz. Costs</u>
0.8	2,000	4.38
1.2	3,000	5.07
1.6	4,000	5.50
2.4	6,000	5.98
3.2	8,000	6.28

It can be seen that the economics improve greatly in this case. Therefore, in certain instances it may be better not to dilute the acid wastes with alkaline wastes, so as not to increase the recovery plant flow, even if the resulting R ratio becomes greater.

The use of a cheaper lime improves the economics to a greater degree at the larger plant capacities. On the other hand, when the amount of zinc to be recovered is relatively small, it is then most important to treat the zinc in the most concentrated form.

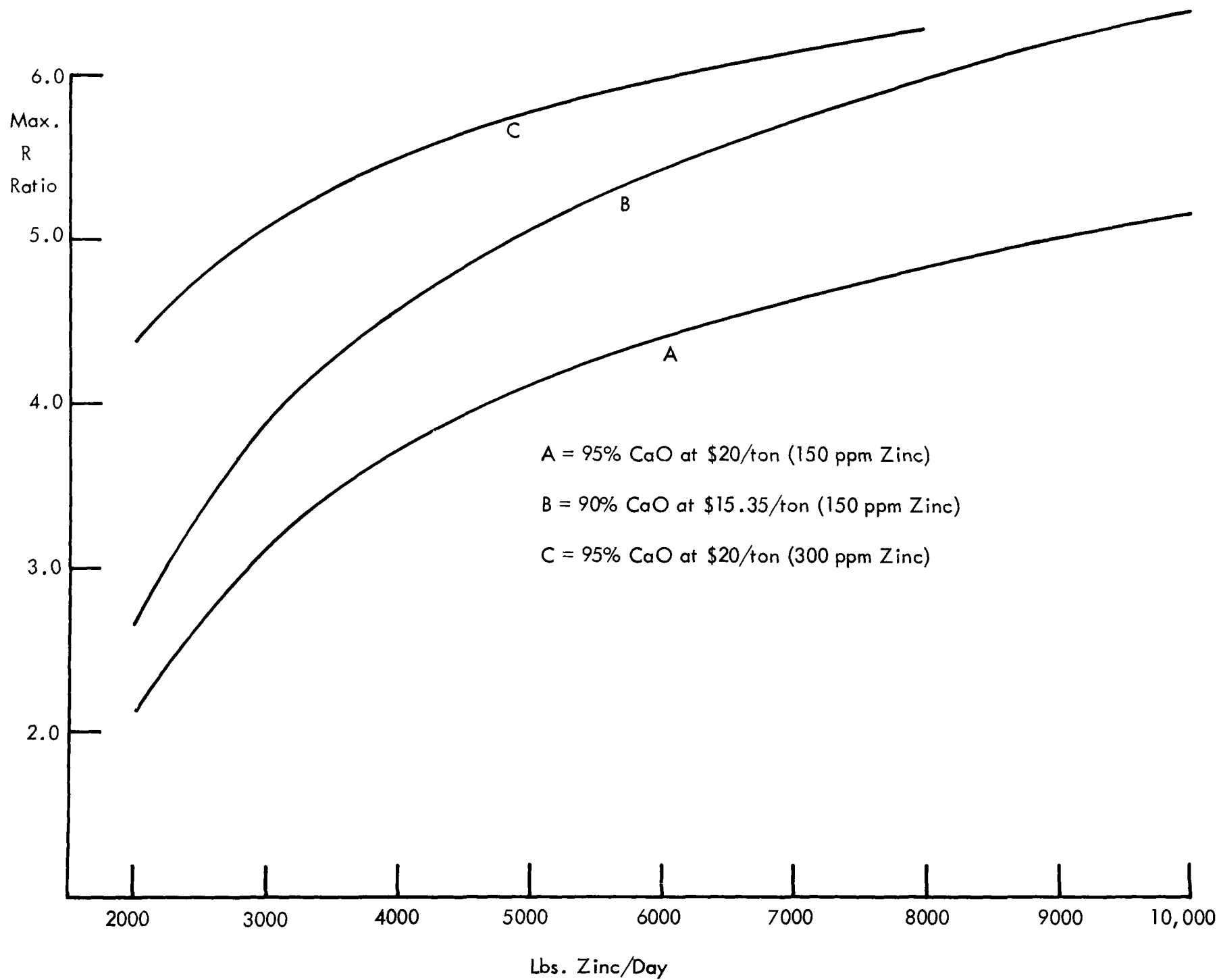


Figure 25

SECTION X

ACKNOWLEDGEMENTS

As is usual with a study project of this magnitude, the assistance and advice of many persons was essential for its successful completion.

The foresight and encouragement of the top management of American Enka Company, who sought for years a solution to the zinc pollution problem, is gratefully acknowledged.

We acknowledge the aid and encouragement of the personnel of the Water Quality Office of the Environmental Protection Agency, mainly Mr. William Lacy, head of the Industrial Pollution Control Branch, Mr. Charles Ris, the Project Manager, and Mr. Edmond P. Lomasney, the Project Officer who patiently followed and helped for so long with the many details of the project.

On the American Enka side, the Project Director was Mr. Frans van Berkel, Enka Vice President and Technical Director.

The Project Coordinator for the grant, and Enka Project Engineer, was Mr. David M. Rock.

The Management of Central Engineering, the department with the major responsibility for the development of the project, always offered all possible aid for its successful completion. Mr. Grady Allman was responsible for the design of the plant. He also substituted for the project engineer whenever Mr. Rock was absent.

The management and personnel of the Enka rayon plant were cooperative and helpful at all times. Mr. B. V. Hill, Manager of the Chemical Laboratory, ran all the tests with the Densator pilot plant. Subsequently, he was responsible for the analytical work, and lately also for running the recovery plant. Mr. Fred Walker operated the recovery plant most of the time, including many nights and weekends and showed much ingenuity in solving many starting-up problems.

We gratefully acknowledge also the valuable work done with the scanning electron microscope by Dr. J. Parker, Manager of Physical Research, and Dr. Nancy Watkins. For the many indispensable analyses made by using atomic absorption techniques, grateful thanks are due to Mr. J. P. Price.

And last, but certainly not least, we acknowledge the efficient and patient typing of Mrs. Ruth Ownbey, who typed this report as well as all the voluminous correspondence concerning the zinc recovery project.

Space limitations prevent us from mentioning many more who rendered valuable assistance to this project.

SECTION XI

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SECTION XII

APPENDICES

DETAILED LIST AND DESCRIPTION OF MAIN ITEMS OF EQUIPMENT

EQUIPMENT USED IN WASTE COLLECTION SYSTEMS

Acid Wastes

The waste acid flows from various sources are collected as follows:

The spinning pot spray water applied to the outside of the centrifugal pots in rayon cake spinning machines is collected in underground sumps or pits and pumped to the main outside pumping pit. The pumps are actuated by a liquid level switch.

When the rayon spinbath filters are backwashed, the initial flow carries with it some spinbath which is impregnating the filter medium, as well as much of the trapped suspended impurities. By using timers, switches, and effluent flow-diverting valves, the first six to ten minutes of backwash flow is collected and sent to the main outside pumping pit.

The first water wash applied to the rayon yarn cakes after spinning also carries with it acid and zinc solution impregnating the cakes. By using timers, switches, and effluent flow-diverting valves, the first six to ten minutes of wash flow is collected and sent to the main outside pumping pit.

Other sources of acid and zinc waste solutions, such as drains and losses from the spinning machines and the spinbath storage tanks are also collected in sumps and pumped with pit pumps to the main outside pumping pit.

The wetted parts of all pumps and valves used in this acid service are all rubber, neoprene or similar acid resisting elastomers, Karbate, PVC or PVDC, or alloys such as Hastelloy-C, Carpenter-20, Durimet-20, or Worthite. Most of the piping is PVC or Fiberglass-reinforced Atlac-382 polyester resin.

The main outside pumping pit is made from concrete lined with acid-resisting brick. Screens made from thin redwood slats are provided to remove any large material, such as rags, pieces of wood, etc., that may be present accidentally.

Alkaline Wastes

Certain dilute alkaline wastes are collected and added to the acid wastes at the main pumping pit. This is done to eliminate an additional source of stream pollution and to neutralize partly the acid in the zinc recovery plant feed for reasons of economy, since the lime consumption is reduced thereby.

Any available waste lye from the rayon plant caustic soda dialyzers is added to the acid in the main pumping pit. This waste lye normally contains one to two percent of caustic soda and a similar concentration of hemicellulose.

Alkaline wash water generated from the periodic washing of rayon viscose tanks, filter presses, etc., is collected in a common pit tank provided with steel screens removable for cleaning. The water and viscose mixture is pumped to a concrete pit by means of a Viking heavy duty Model IQ-288 rotary pump provided with a Viking B-size, 6.27/1 helical gear reducer and a 7-1/2 HP - 1800 RPM motor.

In this pit, the water-viscose mixture is further diluted with waste water by using an Eastern Model VG-7 mixer with a 14-inch diameter propeller driven at 420 RPM by a 2 HP motor.

The diluted mixture is now pumped with ordinary centrifugal pumps to an outside buffer tank of 12,000 gallons capacity which is placed close beside the main acid pumping pit. The alkaline solution flows by gravity at a nearly constant rate into the acid pit. The large 14-foot diameter by 12-foot high steel buffer tank is provided with a Chemineer agitator Model MDP-75-426 consisting of a 42-inch diameter turbine impeller placed on the 2-1/2-inch diameter x 142-inch long shaft at a level 36 inches from the tank bottom and another 33-inch diameter impeller placed at the end of the shaft. The 304 SS impellers and shaft are driven at 68 RPM by a 7-1/2 HP motor and reducer.

During the time when the sodium cellulose xanthate from the viscose solution is in contact with acid, while in the main pumping pit or in the long 10-inch diameter FRP pipeline from the pumping pit to the recovery plant itself, the xanthate has sufficient reaction time to decompose to insoluble cellulose floc, sodium sulfate and sulfur by-product compounds. This reaction should be completed before the first pH adjustment, when lime is added to neutralize the acid.

All the pipelines for dilute waste viscose collection inside the rayon plant, and up to the large outside buffer tank, are provided with Victaulic couplings at frequent intervals, for easy disassembly in case of plugging.

Recovery Plant Equipment

Item

- 1 Two 10" x 8" Denver SRL Frame Four pumps, soft-rubber-lined, centrifugal, closed impeller, with overhead hinged motor base, water gland type, with replaceable pressure molded impeller and casing liners, cast iron split case and flanged ring clamps. All wetted metal parts other than ceramic sleeves are Carpenter-20 alloy. Slide type base, drive guard, an 8-groove V-belt drive and 50 HP motors. All designed originally to pump 2,000 GPM at 50 feet of TDH. However, V-belt pulleys were changed subsequently, to pump about 1,000 GPM at a similar head.

Item

- 2 One open top, pressure creosoted Douglas Fir tank 32-feet I.D. and 20-feet nominal stave length. Staves and bottom are machined from 3" lumber and given an 8-pound pressure treatment of creosote oil. The tank is banded with 3/4-inch diameter mild steel rods and malleable iron straight pull draw lugs; the bands are epoxy-coated and mastic was used to coat the lugs, nuts and threads. One set of 4-inch x 8-inch pressure treated Douglas Fir chine joists are spaced at the bottom at approximately 16 inches center-to-center distance. Approximate tank volume is 100,000 gallons. The tank is subdivided by radial partitions into three approximately equal sections. Each section is provided with an agitator, described as follows:

Denver Equipment turbine-type agitator with 5-blade, rubber-covered impellers, driven by a 25 HP TEFC motor

NOTE: Initially, the alkali required for neutralization was added in the first compartment of the wooden tank. Subsequently, the first compartment was allowed to function as an acid concentration equalizer, and the alkali addition is now made into the second compartment.

- 3 One complete Foxboro feedforward pH control system. The influent flow is measured and characterized to a fractional power relationship. The characterized flow signal is combined with the influent pH measurement and the reagent valve characteristics to produce an equation which is the process model:

$$M_B = f(F) + \left(\frac{1}{\log R} \right) (r_B - \text{pH}), \text{ where}$$

M_B = reagent valve stroke, % of max.

$f(F)$ = characterized influent flow signal

R = rangeability of reagent valve

r_B = feedback term, supplied from a non-linear controller

pH = influent pH

The influent flow and pH position the reagent flow control valve to deliver the precise amount of reagent required to neutralize the acid in the influent. As the influent conditions change, the amount of reagent is adjusted accordingly. The reagent flow computation (actually, valve position) is altered by the output of a feedback controller where gain is automatically adjusted as a function of the error existing between the set pH and the final measured pH.

The main items of equipment purchased from Foxboro are:

- (a) Model 613 DM d/p cell transmitter with Model 610 AR Power Supply Unit.
- (b) Flow Characterizer Model 66 N.
- (c) Two Model 69TA-1 Current-to-air Transducers.
- (d) Two Model 40 PH Recorder Controllers with Type JJ Pneumatic Transmitter.
- (e) Model 52A-SP4 Pneumatic Indicating Controller with External Reset.
- (f) Model 62H-4E Special Non-linear Controller.
- (g) Model 66F Pneumatic to Current Convertor.

More details on the pH control instrumentation are given in the main body of the report.

Item

- 4 One Infilco BF Clarifier drive mechanism size BF-100, with Philadelphia reducer and pinion assembly and 1/2 HP, 900 RPM motor. Scraper RPM is 3 RPH.

One clarifier tank with steel sidewalls, 74-foot diameter and 14 feet high set on a concrete sloping-bottom pad. Inside surfaces were coated with a thin layer of type H Fiberglass mat and bisphenol-A (Atlac 382) polyester resin.

One clarifier floating baffle approximately 38-foot, 7-inch diameter, made from eight straight FRP (Atlac 382) panels, each 16 feet long. Polyurethane foam blocks are attached to provide bouyancy. Panel height is about 5 feet.

- 5 One clarifier underflow centrifugal pump: Dean Bros., 1-1/2" x 3" - 6-DL-200 inline pump, 316 SS, rated for 50 GPM at 35 ft. TDH. Motor is 1 HP, 1750 RPM.

- 6 One thickener mechanism: Type B Eimco Heavy Duty to handle 6 tons/day of solids. Continuous operation at 8,000 ft.-lbs. of torque and peak loading of close to 12,000 ft.-lbs. Rake speed of 0.33 RPM. All wetted parts are mild steel with 3/16-inch thick natural rubber covering, or FRP.

One 20-foot diameter x 8-1/2-foot high thickener steel tank with flat bottom. Inside surfaces coated with coal tar epoxy.

Item

7 One Type SSQ Moyno sludge pump, to pump the thickener discharge. Pump has 316 SS body and internals, Buna N lined stator. Rated for 10 GPM of 50% gypsum slurry at 25-ft. TDH. Motor is 1-1/2 HP, 900 RPM.

8 One Infilco Densator Reactor: outside tank is 80-ft. inside diameter by 13-ft. 6-in. side depth, with concrete bottom. Inside tank and concrete bottom centerwell (4-ft. deep) are 20-ft. diameter. All inside surfaces coated with Bitumastic No. 33 and all outside surfaces with Bitumastic No. 50.

Center mixer drive is 1 HP U.S. Varidrive with a #9 CVD Winsmith reducer. Top section with 2 paddles 7 feet long by 1 foot high. Middle section with 4 paddles 4 feet long by 9 inches high. There is also a cutter bar rotating 1 inch above the bottom well surface. Normal shaft RPM is 2.5.

Scraper drive is 1-1/2 HP U.S. Varidrive with a #10 CTDO Winsmith reducer provided with torque limit device. Normal RPH is 2.

9 Two Fairbanks Morse "Paper Stock" sludge recirculating centrifugal pumps, Fig. 5460 P, 4-in. horizontal end suction, for 400 GPM maximum flow at 32 ft. TDH. Motor is 5 HP and 1200 RPM.

10 One 4,000-gallon sludge settling steel tank 8-ft. diameter by 11 feet high, covered on the inside with 1/4-inch thick "Triflex" rubber. Provided with a Nettco agitator having two flat blades each 3 inches wide, 3 feet, 7-11/16 inches long and 5/8 inches thick, rotating 3 inches above tank bottom at 3 RPM. Drive has a 1/2 HP-900 RPM motor, 3 V-belts, and a Nettco Model T-115 reducer with 100/1 ratio, and a 2-3/6-in. diameter steel shaft.

11 One 4,000-gallon sludge dissolving steel tank similar to item 10 above, but without agitator. Provided on top with a Haveg mixing pot to react the recirculating sludge with the concentrated sulfuric acid being added by means of a Milton Roy diaphragm type metering pump.

12 Two LaBour sludge recirculating and dissolving pumps, rated to pump 50 GPM, at 80 ft. TDH, of a sludge with 1.2 - 1.8 sp. gr. and 70 - 700 centipoise viscosity. The pumps are size 15, type DZT, made from Elcomet-K alloy.

13 One recovered zinc sulfate storage tank of 1,000 gallons capacity, constructed of Fiberglass reinforced polyester resin (Atlac 382).

14 One acid-resistant centrifugal pump, used to transfer recovered zinc sulfate to the rayon plant for reuse, capable of pumping 20 GPM at 156-ft. of TDH. Pump was manufactured by Worthington, with all wetted parts made from Worthite alloy, and is Model 1-1/2 CNG 104. Motor is 10 HP, 1800 RPM.

Item

- 15 Two coagulant aid solution preparation and feed tanks, each with 750 gallons capacity, constructed of Fiberglass reinforced polyester resin (Atlac 382). Each tank is provided with an agitator having one 12-inch diameter propeller revolving at 350 RPM and a 1 HP - 1750 RPM electric motor.

The coagulant aid powder is added, for dissolution, by means of a funnel and a Schutte-Koerting mixing-eductor Type 227.

- 16 One coagulant aid solution metering pump, a Model FR-131A, Milton Roy Simplex pump designed for a maximum flow of 18.3 gallons per hour against a discharge pressure of 6.5 lbs./sq. in. Wetted parts are 316 type SS with Teflon diaphragm. Drive motor is 1/4 HP.

- 17 One Eimco pilot plant filtering equipment assembly mounted on a common platform and consisting of:

- (a) One 3-ft. diameter x 1-ft. face rotary vacuum belt filter with 9.4 sq. ft. of filtering area, made of Eimco-Met plastic. The drum has 8 sections. The belt is polypropylene cloth material.
- (b) Eimco-Met plastic tank for 33-1/3% submergence of the filter drum.
- (c) One mechanical variable speed drive connected to a chain drive, and designed to allow drum speeds of 1.0 to 10 minutes per revolution. Motor is 1/4 HP.
- (d) One swing type, pin mounted oscillating arc agitator with rake assembly driven through arcs by a crank disc and connecting rod arrangement. Drive is with a 1/2 HP gearmotor and chain drive, designed for an agitation speed of approximately 19 cycles per minute.
- (e) Two cake wash pipes with spray nozzles.
- (f) One cake discharge roll and one take-up and wash roll. Two cloth wash pipes with spray nozzles. One cloth tracking mechanism, an Edge-Track alignment system.
- (g) One vacuum receiver tank, 15-in. diameter x 5-ft. high, made of Eimco-Met plastic.
- (h) One Worthington 1-1/2 - CNG - 74 Worthite alloy filtrate pump rated for 20 GPM at 60' TDH. Motor is 1-1/2 HP, 1800 RPM, TEFC.

Item

- (i) One Nash CL-402 water sealed rotary cast iron vacuum pump with V-belt drive and water trap silencer, rated for 362 CFM at 20-in. Hg and 1170 RPM. Motor is 20 HP, 1800 RPM, TEFC.

NOTE: In addition to the above assembly, there is also an inclined belt conveyor to collect the filter cake discharge and to drop it into a 3 cu. yd. Dempster Dumpster container, provided with a T-2 bail, which is placed outside the pump and filter house.

The belt conveyor is 14-in. wide and 8-1/2-ft. long. The structure is of 304 SS and the belt is Goodyear Pylon 140. Belt speed is 50 ft./min. The drive motor is 3/4 HP.

- 18 One Dean Brothers plant water pressure booster pump, Type PH-231, size 1-1/2" x 3" - 11-1/2, rated for 65 GPM at 140 ft. TDH. Motor is 10 HP, 1750 RPM.

- 19 One Sprout-Waldron and Company 6-in. Schedule 40 "Pneu-Vac" negative pressure system designed to unload pebble quicklime weighing 55 to 60 lbs./cu. ft. and 3/16-in. to 3/8-in. diameter, dry and free-flowing. The material is to be delivered directly from the railroad car to the intake of the system under uniform feeding conditions by an adjustable opening in the hopper car manifold, and conveyed over a maximum combined vertical and horizontal distance of 100 ft., with not more than two 90 degree rigid elbows, or their equivalent, on the negative side of the conveying line. The system is designed to unload the specified lime at about 50,000 to 60,000 lbs. per hour. The components of the system are listed below:

- (a) One tandem portable hopper car unloader for a 6-in. diameter line.
- (b) Three sections of 6-in. diameter x 10-ft. long non-toxic rubber hose.
- (c) 6-in. Schedule 40 pipe, elbows, couplings, etc.
- (d) One filter-receiver, Flex-Kleen Model 84-CT-30, 17-in. mercury design, continuous and automatic, with 300 sq. ft. of cloth area, to handle 60,000 lbs./hr. of 3/8-in. pebble quicklime conveyed by 1400 CFM of air at ambient temperature. Includes suitable connections and instrumentation.
- (e) One rotary valve, 16 x 14, square inlet and outlet, cast iron construction, with inspection panel. Capacity is 1.2 cu. ft. per revolution, with design clearance of 0.002/0.003 inches radially. Provided with a 1-1/2 HP - 155 RPM motor and a guarded roller chain drive to operate the airlock at 45 RPM.

Item

- (f) One Butler bolted steel tank, 12-ft. diameter x 56-ft. high to store 4350 cu. ft. of 60 lbs./cu. ft., 3/16-in. to 3/8-in. pebble quicklime, based on a 45 degree angle of repose. Includes a 60 degree hopper with 12-in. diameter opening, rack-and-pinion operated slide gate, two Bin-Dicators, etc.
- (g) One conveyor screw, 6-in. diameter x 12-ft. long, with sprocket and chain drive, to deliver about 86 to 860 lbs. of lime per hour. Driven by a U. S. Varidrive motor of 1 HP.
- (h) One blower assembly, rotary positive displacement single stage unit, Roots-Connersville 816-RAS-60, with 8-in. diameter inlet and outlet, to operate at 1390 RPM and inlet flow of 1320 CFM ambient air at 16-in. Hg vacuum. Provided with guarded V-belt drive and a 75 HP motor, snubber, etc.

- 20 One BIF detention type lime slaker, with 77.4 gallons total volume in the two main slaking chambers, each chamber provided with one 1-1/2 HP and V-belt driven propeller agitator, 10 gallon grit removal chamber provided with a removal screw driven by a 1/4 HP motor and a gear reducer to rotate at 4.4 RPM, a small heat exchanger to preheat the slaking water with the hot lime slurry, and two rotameters to measure the flow of slaking and dilution water. Slaking capacity is approximately 700 lbs. lime/hr.

NOTE: The grit is discharged to a 3 cu. yd. Dempster Dumpster container provided with a T-2 type bail.

A Chromalox NWH-3 electric heater with 24 KW capacity (50 watts/sq. in.) has been provided to preheat additionally the slaking water.

- 21 One Goulds centrifugal pump, Model 3196, size 1 x 2 - 8, 316 SS, to transfer the slaked lime slurry from the slaker to a storage tank, rated for 35 GPM of 12% slurry at 180 degrees F maximum and 40 ft. TDH. The drive is a 1-1/2 HP, 1800 RPM motor.
- 22 One 8,000-gallon capacity lime slurry storage tank provided with a Chemineer turbine type agitator driven at 87 RPM by a 5 HP electric motor and reducer.
- 23 Two Goulds centrifugal pumps, Model 3196, size 1-1/2 x 3-13, Group M, 316 SS construction, rated for 50 GPM of 12% lime slurry at 270 ft. TDH, and driven by a 10 HP, 1800 RPM motor.

Item

- 24 One lime slurry density meter, Hallikainen Instruments' Model No. 1373 Gravitrol Density Analyzer, with 316 SS sample loop and SS flex bellows, 1.4 inch I.D., density range of 1.03 to 1.08 at 85 degrees F and a maximum of 80 PSI, linearly related to a pneumatic output signal.
- 25 One lime slurry feed tank with 750 gallons capacity, provided with a turbine type agitator driven by a 1 HP motor and reducer. RPM of mixer is 30.
- 26 One Dean Brothers lime slurry feed centrifugal pump, size 1" x 2" - 8-1/2, type PH-231, rated for 32 GPM of 12% slurry at 65 ft. TDH, and driven by a 3 HP, 1800 RPM motor. Pump material is 316 SS.
- 27 Two 434-gallon (each) Dempster Dumpster portable carbon steel tanks, for concentrated sulfuric acid storage and transportation, 40-in. diameter, designed for 98 PSIG pressure.
- 28 One Wayne 2-stage tank mounted air compressor, to supply air for instrumentation use. One B-6-A Lectrodryer has been provided also, to dry the compressed instrumentation air.

NOTE: All pumps for lime slurry operation (items Nos. 21, 23 and 26) had to be equipped with Rott Durametallic mechanical seals with internal water lubrication injected between the seal rubbing faces.

SECTION XIII

APPENDICES

ELECTRICAL POWER REQUIRED FOR MOTORS AND HEATERS (EXCLUSIVE OF IN-PLANT COLLECTION SYSTEMS)

<u>Item</u>		<u>Rated Cap./Unit</u>	<u>Breakdown by use</u>	
			<u>Continuous</u>	<u>Intermittent</u>
<u>1</u>	Recovery plant acid feed pumps at main pit: (2) ea.	50 HP	50	--
<u>2</u>	Lime System:			
	(a) Water Heater	24 KW	24 KW	--
	(b) Vacuum Pump for Lime Unloading	75 HP	--	75
	(c) Rotary Valve for Lime Unloading	1-1/2 HP	--	1-1/2
	(d) Lime Feeder Screw	1 HP	1	--
	(e) Slaker Mixers (2) ea.	1-1/2 HP	3	--
	(f) Grit Removal Screw Drive	1/4 HP	1/4	--
	(g) Slurry Pump, Slaker to Storage Tank	1-1/2 HP	1-1/2	--
	(h) Slurry Storage Tank Agitator	5 HP	5	--
	(i) Slurry Recirculation Pumps (2) ea.	10 HP	10	--
	(j) Slurry Feed Tank Agitator	1 HP	1	--
	(k) Slurry Feed Pump	3 HP	3	--
<u>3</u>	Water Pressure Booster Pump	10 HP	10	--
<u>4</u>	Neutralization Tank Agitators (3) ea.	25 HP	75	--
<u>5</u>	Clarifier:			
	(a) Scraper Drive	1/2 HP	1/2	--
	(b) Underflow Pump	1 HP	1	--

<u>Item</u>		<u>Rated Cap./Unit</u>	<u>Breakdown by use</u>	
			<u>Continuous</u>	<u>Intermittent</u>
<u>6</u>	Densator			
	(a) Scraper Drive	1-1/2 HP	1-1/2	--
	(b) Mixer	1 HP	1	--
	(c) Sludge Recirculation Pumps (2) ea.	5 HP	5	--
<u>7</u>	Sludge Settling Tank Agitator	1/2 HP	1/2	--
<u>8</u>	Sludge Circulation and Dissolving Pumps (2) ea.	3 HP	--	3
<u>9</u>	Concentrated Acid Metering Pump	1/2 HP	--	1/2
<u>10</u>	Clarifier Underflow Thickener			
	(a) Scraper Drive	1-1/2 HP	1-1/2	--
	(b) Mud Pump	1-1/2 HP	1-1/2	--
<u>11</u>	Rotary Vacuum Belt Filter			
	(a) Drum Drive	1/4 HP	--	1/4
	(b) Agitator	1/2 HP	--	1/2
	(c) Vacuum Pump	20 HP	--	20
	(d) Filtrate Pump	1-1/2 HP	--	1-1/2
	(e) Belt Conveyor	3/4 HP	--	3/4
<u>12</u>	Coagulant Aid System			
	(a) Agitators (2) ea.	1 HP	2	--
	(b) Metering Pump	1/4 HP	1/4	--
<u>13</u>	Zinc Sulfate Return Pump	10 HP	--	10

<u>Item</u>	<u>Rated Cap./Unit</u>	<u>Breakdown by Use</u>	
		<u>Continuous</u>	<u>Intermittent</u>
<u>14</u> Air Compressor	1 HP	1	--
<u>15</u> Pump Room Heaters	10 KW	--	10 KW (winter)
	15 KW	--	15 KW (winter)
	5 KW	--	5 KW (winter)
Total HP (motors)		175-1/2	113
Total KW (heaters)		24	30
Total equiv. KW		155	114

Neglect area lighting and other minor miscellaneous loads.

Assuming average continuous operating load is 75% of the rated load: $(155) (0.75) = 116 \text{ KW}$

Assuming the average intermittent load operates only one-fifth of the time, at 75% of the rated load:
 $(114) (0.20) (0.75) = 17.1 \text{ KW}$

At a cost of 7.0 mils/KWH, the average daily electrical cost is: $(133.1 \text{ KW}) (0.007) (24 \text{ hrs.}) = \22.40

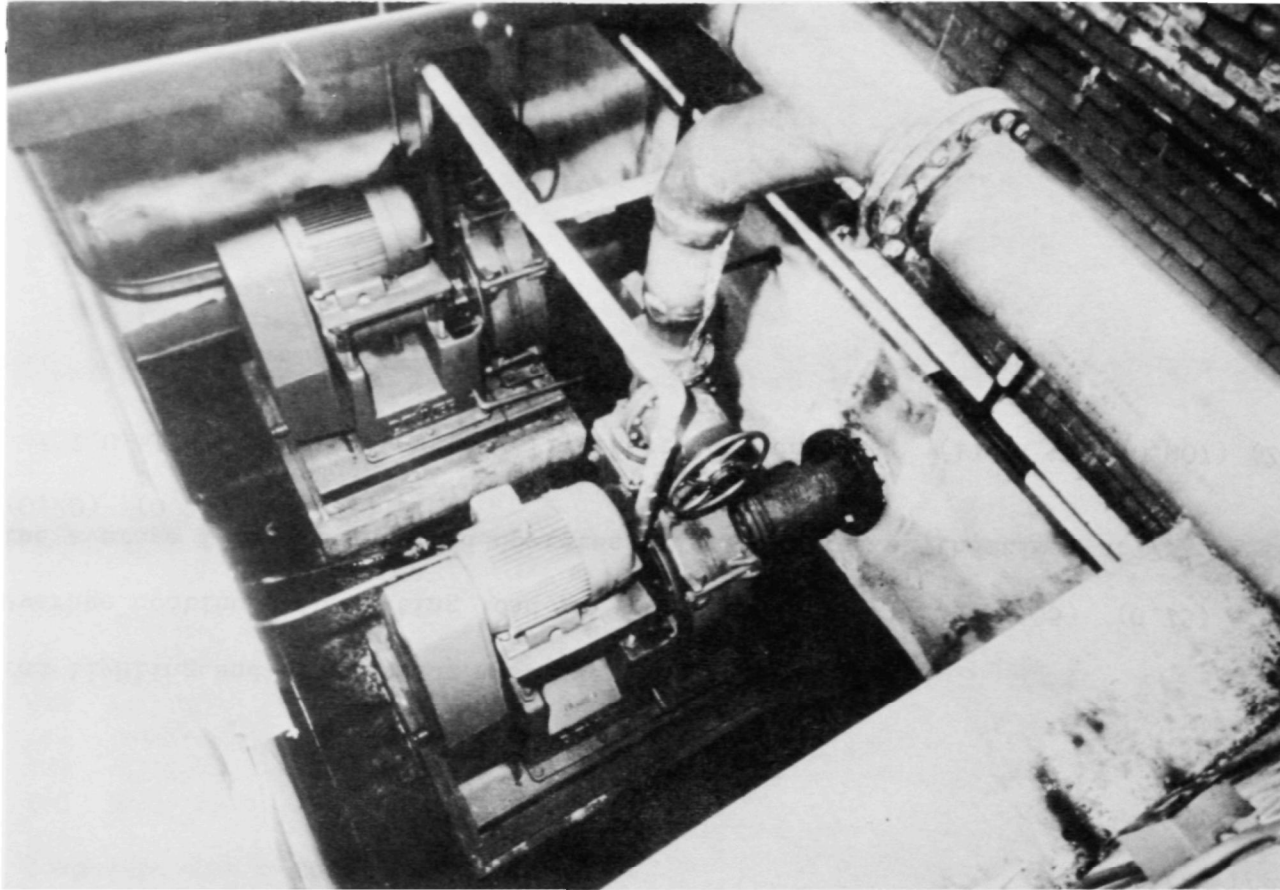


Figure 26: Main Acid Feed Pumps (Item 1) by the Collection and Pumping Pit



Figure 27: Air View of Waste Treatment Area. Zinc recovery Equipment can be seen at lower left.

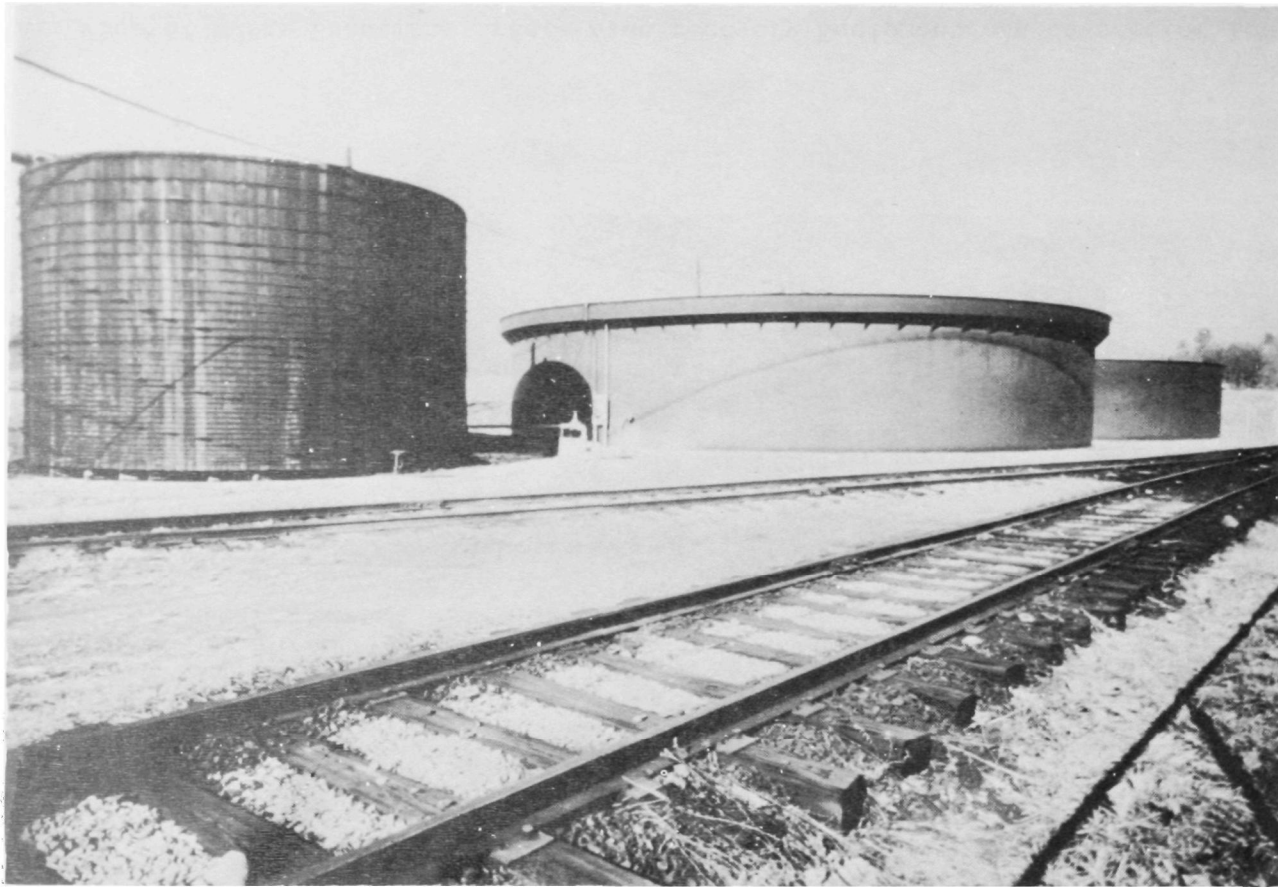


Figure 28: The Neutralization Tank (Item 2), Clarifier (Item 4) and Densator (Item 8) can be seen from left to right.

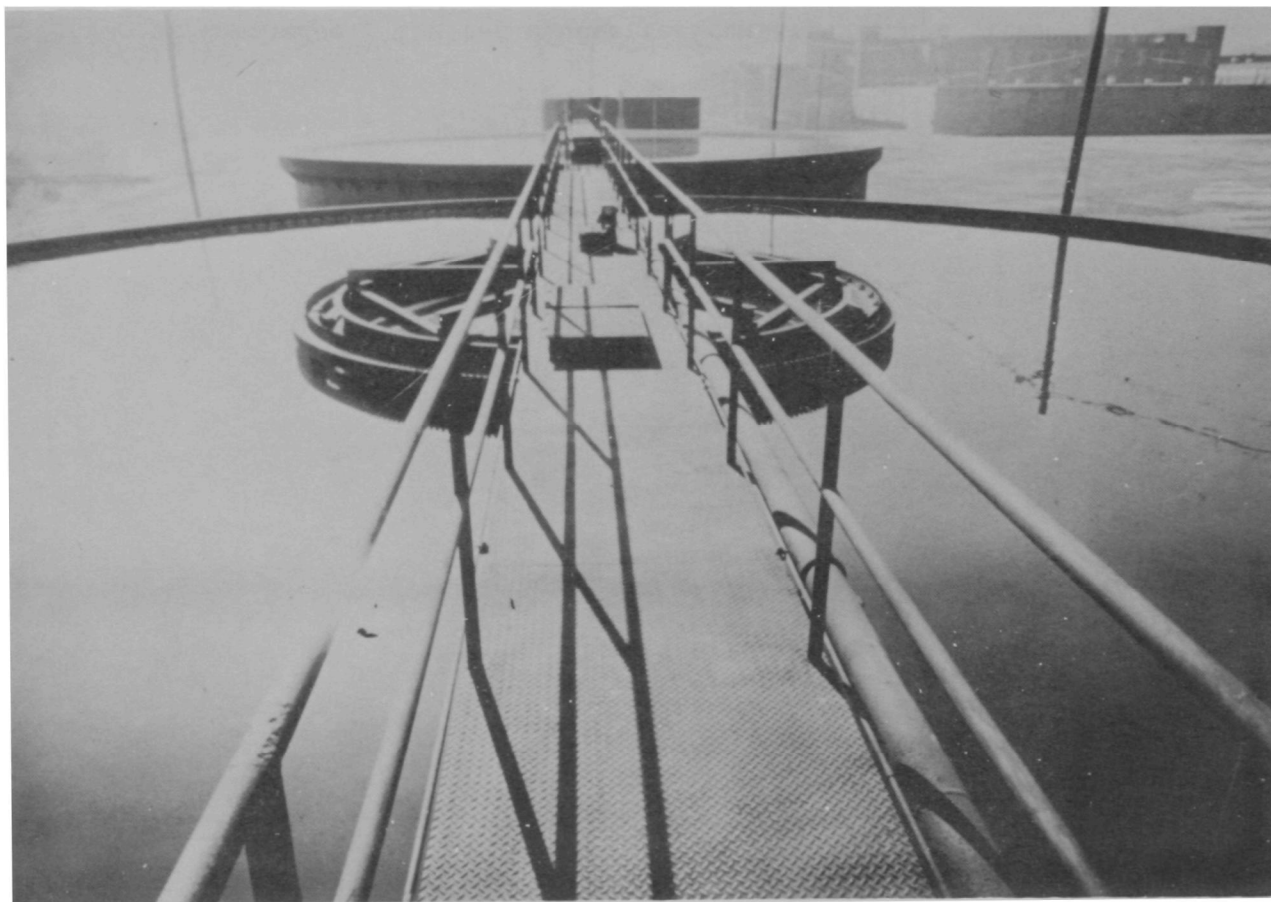


Figure 29: View of the Densator from its walkway

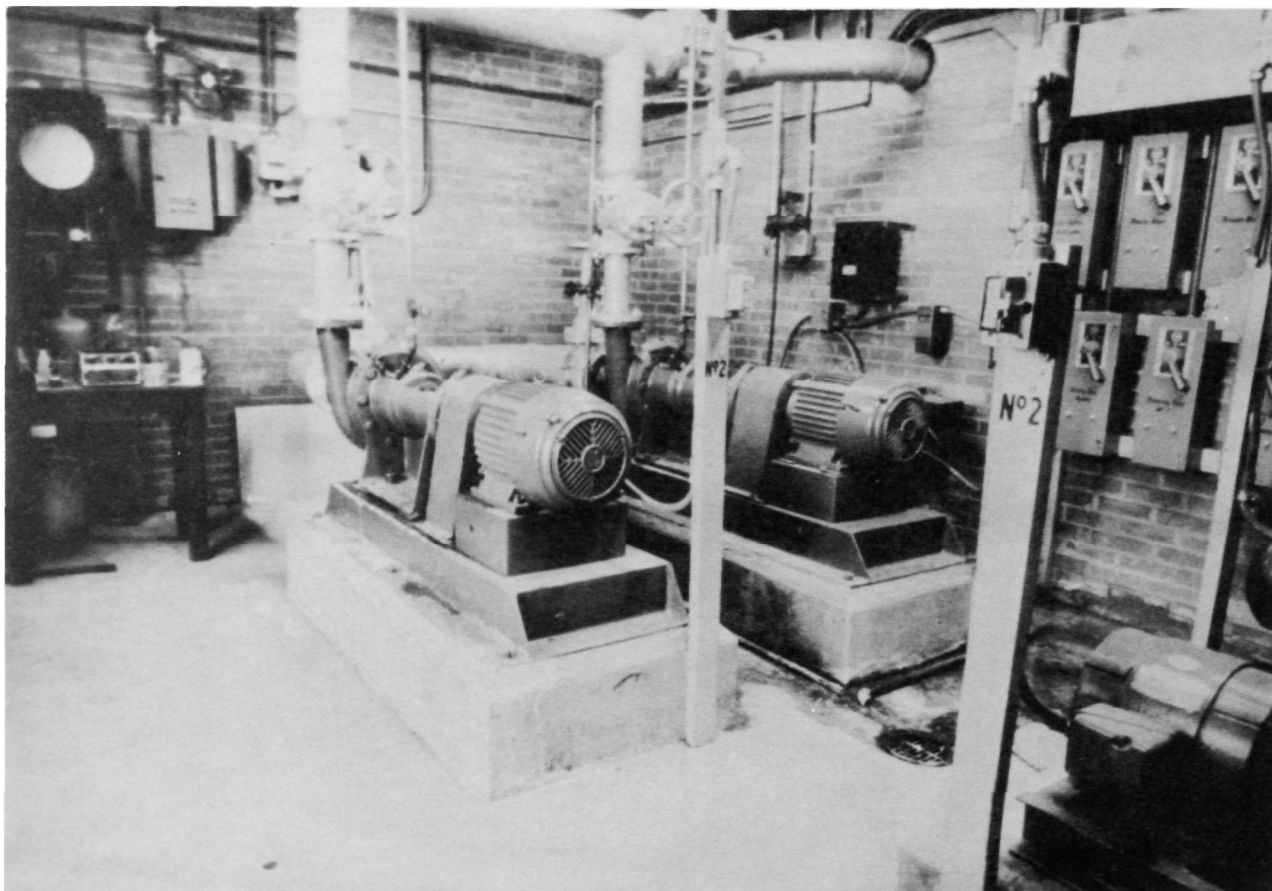


Figure 30: Interior of Pumphouse. The two sludge recirculating pumps (Item 9) in the center.

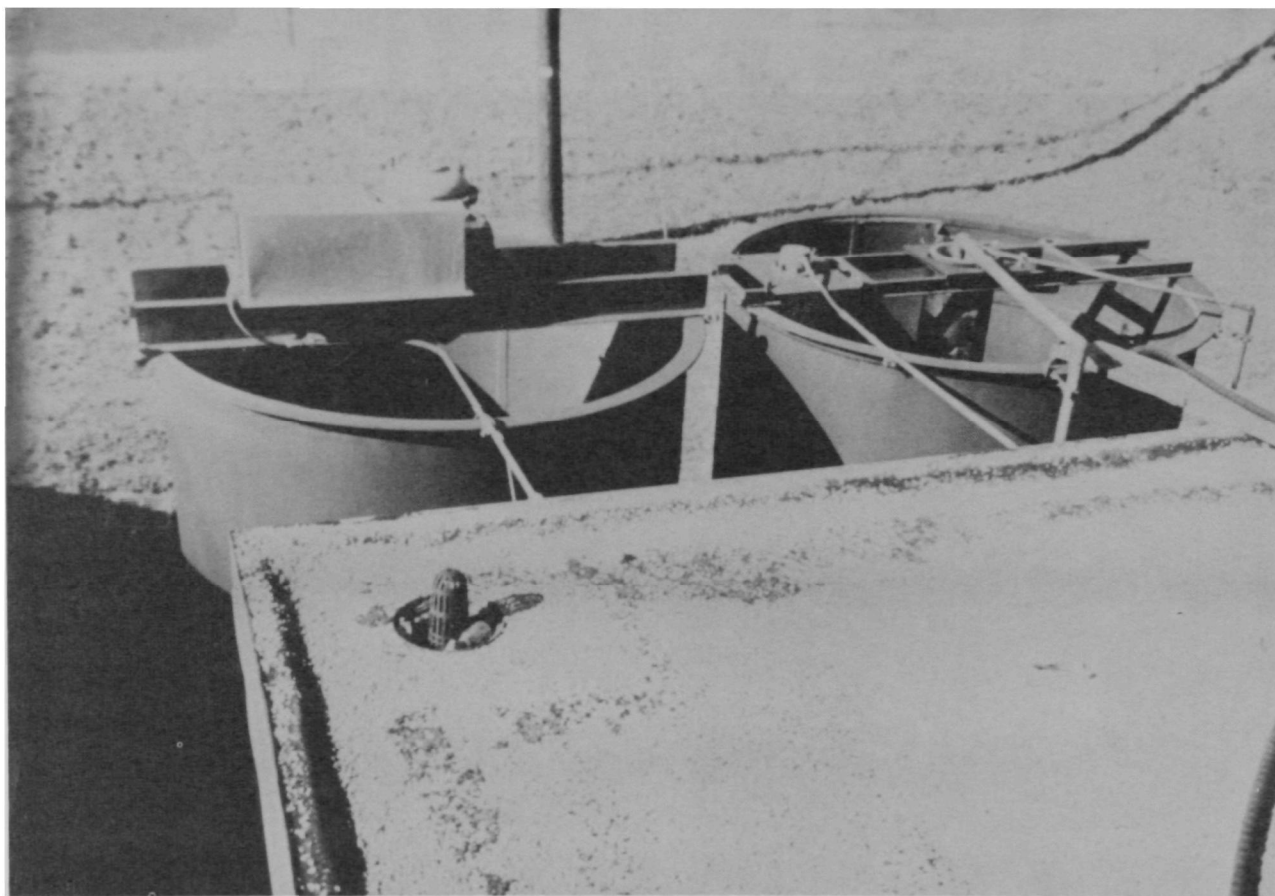


Figure 31: The Sludge Settling Tank (Item 10) at the left, and the sludge dissolving tank (Item 11) at the right, as viewed from the roof of the Pumphouse.

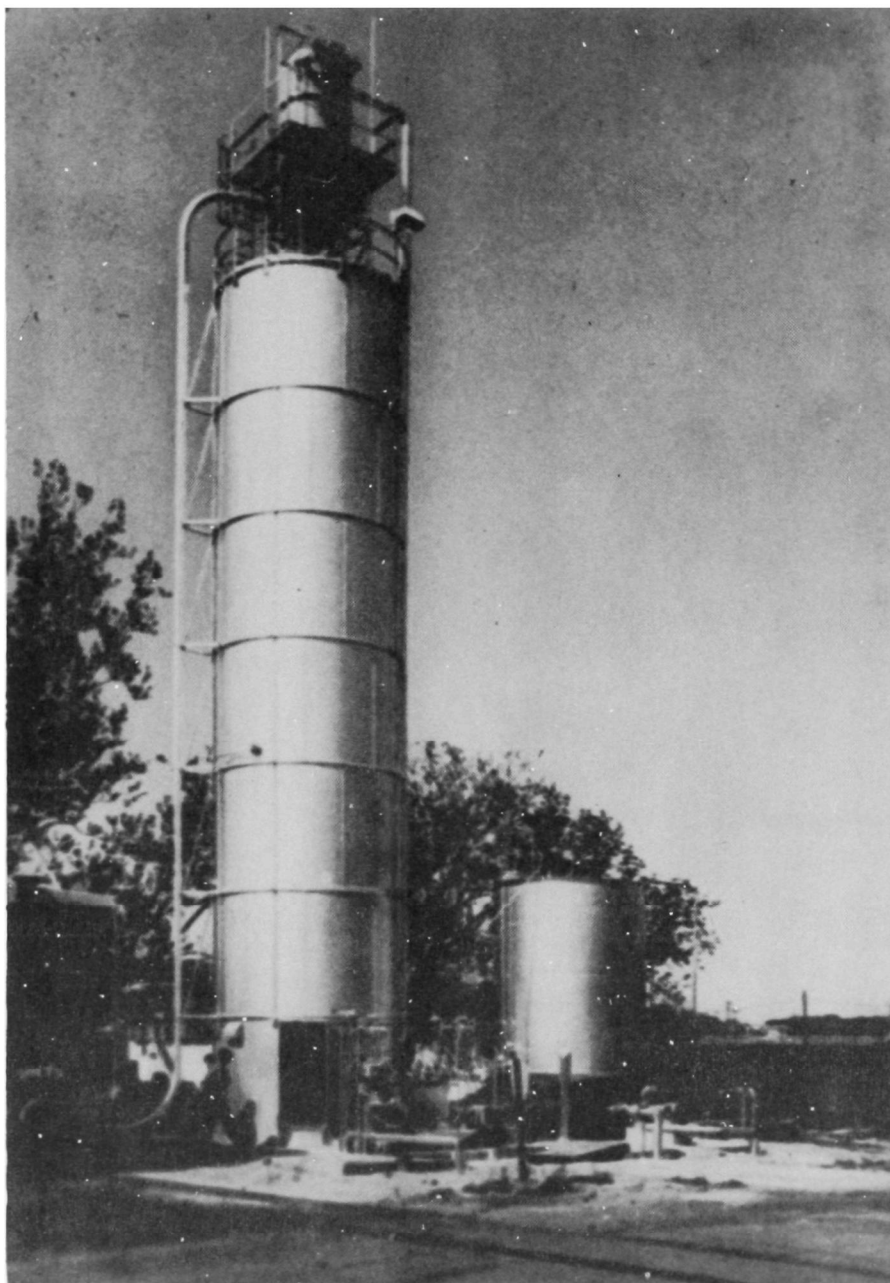


Figure 32: View of Quicklime Handling and Storage Equipment (Item 19), Slaker (Item 20) and Slurry Storage Tank (Item 22).

SUBJECT:

PROCEDURE FOR THE DETERMINATION OF ACID, ZINC, AND MAGNESIUM IN WASTE WATER

NUMBER:

028.3

DATE:

January 25, 1971

ACID:

Measure 100 ml. of sample into a 250 ml. Erlenmeyer flask, add 3 or 4 drops of 35% hydrogen peroxide, and let stand for 3 or 4 minutes. Add 2 or 3 drops of Methyl Red indicator, and titrate with N/10 NaOH.

Calculation: $\frac{\text{Titration} \times 0.1 \times 0.049 \times 100}{100} = \% \text{H}_2\text{SO}_4.$

ZINC:

Add 10 ml. of maleic acid - sodium maleate buffer solution (pH 6.8), and 4 to 8 drops of Eriochrome Black T indicator to the titrated solution used for acid determination. Titrate with 0.02 disodium versenate solution to a color change from purple-red to purple-blue.

Calculation: $\text{Titration} \times 6.5 = \text{p.p.m. as Zn.}$

MAGNESIUM:

Add 15 ml. of ammonia - ammonium chloride buffer solution (pH 10.0) to the titrated solution from the acid and zinc determinations. Titrate with 0.02 N disodium versenate solution to approximately 80% of the expected titration. Add 2 to 4 drops of Eriochrome Black T indicator and continue the titration to a sky-blue color

Calculation: $\text{Titration} \times 2.4 = \text{p.p.m. as Mg.}$

BY:

CHEMICAL-MICROSCOPICAL LABORATORY

B. V. Hill:jbd

COPIES:

5

Density of Milk of Lime Solution

Degrees Baumé	Specific gravity at 20 deg. C.	1 liter contains grams CaO	Per cent by weight CaO	1 liter contains grams Ca(OH) ₂	Per cent by weight Ca(OH) ₂
1.23	1.0085	10	0.99	13.2	1.31
2.43	1.017	20	1.96	26.4	2.59
3.47	1.0245	30	2.93	39.6	3.87
4.43	1.0315	40	3.88	52.8	5.13
5.44	1.039	50	4.81	66.1	6.36
6.375	1.046	60	5.74	79.3	7.58
7.36	1.0535	70	6.65	92.5	8.79
8.275	1.0605	80	7.54	105.7	9.96
9.17	1.0675	90	8.43	118.9	11.14
10.11	1.075	100	9.30	132.1	12.29
11.05	1.0825	110	10.16	145.3	13.43
11.91	1.0895	120	11.01	158.6	14.55
12.76	1.0965	130	11.86	171.8	15.67
13.66	1.104	140	12.68	185.0	16.76
14.5	1.111	150	13.50	198.2	17.84
15.36	1.1185	160	14.30	211.4	18.90
16.17	1.1255	170	15.10	224.6	19.95
16.97	1.1325	180	15.89	237.9	21.00
17.81	1.140	190	16.67	251.1	22.03
18.63	1.1475	200	17.43	264.3	23.03
19.40	1.1545	210	18.19	277.5	24.04
20.16	1.1615	220	18.94	290.7	25.03
20.91	1.1685	230	19.68	303.9	26.01
21.70	1.176	240	20.41	317.1	26.96
22.48	1.1835	250	21.12	330.4	27.91
23.20	1.1905	260	21.84	343.6	28.86
23.91	1.1975	270	22.55	356.8	29.80
24.67	1.205	280	23.24	370.0	30.71
25.41	1.2125	290	23.92	383.2	31.61
26.10	1.2195	300	24.60	396.4	32.51

Note: To convert grams per liter to pounds per cubic foot multiply by .06243
To convert grams per liter to pounds per Imperial gallon multiply by .01
To convert grams per liter to pounds per U. S. gallon multiply by .008345

1	Accession Number	2	Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
	W		05D	

5	Organization	American Enka Company Central Engineering Department
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6	Title	Zinc Precipitation and Recovery from Viscose Rayon Waste Water
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10	Author(s)	16	Project Designation
			EPA, WQO, Grant 12090 ESG
	Rock, David M. Allman, Grady	21	Note

22	Citation	
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23	Descriptors (Starred First)	
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25	Identifiers (Starred First)	Industrial wastes, heavy metals, textile fibers flocculation, chemical precipitation
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27	Abstract	<p>In May 1968, the Industrial Pollution Control Branch of the Water Quality Office/Environmental Protection Agency, initiated a research and development grant with American Enka Company to perfect an improved process for the precipitation and recovery of soluble zinc in rayon manufacturing wastewaters. In the production of viscose rayon, zinc sulfate is used as a component of the acid spinning bath. Zinc is lost in a dilute form when the acid spun yarns are washed with water and at various points in the spinning bath system. The novel zinc recovery system involves the initial neutralization of the waste stream to pH 6.0 sedimentation of insolubles, the crystallization of zinc hydroxide in a high pH environment, the sedimentation of zinc hydroxide and the solubilization of the zinc with sulfuric acid. This novel recovery system was operated at a 600-1000 gpm rate with 70-120 mg/l of Zn in the feedwater. The system can maintain an effluent concentration of Zn less than 1 mg/l, which corresponds to 98-99% removal efficiency. The unique zinc hydroxide sludge is easily concentrated to 5-7% solids by sedimentation and to 10% solids by centrifugation. The sludge particles obtained by this process are spheroids of 4-8 microns average diameter. A recovery of 2,000 pounds of zinc daily assures recovery of the 12.5 to 14.0 cents/lb. of Zn operating and maintenance costs. The cost of zinc oxide purchased by Enka amounts to 15.6 cents/lb. of equivalent Zn. This report was submitted in fulfillment of Grant Project 12090 ESG between the Water Quality Office/Environmental Protection Agency and American Enka Company.</p>
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Abstractor	David M. Rock	Institution	American Enka Company
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