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Limestone Treatment of Rinse Waters from Hydrochloric Acid Pickling of Steel

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LIMESTONE TREATMENT OF RINSE WATERS FROM HYDROCHLORIC ACID PICKLING OF STEEL

by

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for the

Water Quality Office

Environmental Protection Agency

PROJECT 12010 DUL

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ABSTRACT

Two hydrochloric acid picklers for cleaning steel strip at Armco Steel Corporation's Middletown, Ohio, Works produce up to 1,500 gpm of acid rinse waters which contain up to 0.5 g/l free hydrochloric acid and up to 0.87 g/l ferrous chloride. A facility for disposal of these rinse waters was designed, based on a process developed at bench scale by Armco research scientists. This process utilizes limestone for neutralization plus aeration and sludge recirculation to oxidize ferrous iron and form soluble calcium chloride. This report describes the investigation of process variables at pilot scale and the optimization and demonstration of the process at full scale.

Pilot studies indicated that a 25 percent excess of limestone was normally required, sludge recirculation was very beneficial, and temperatures above 120°F led to higher sludge filtration rates and system capacities. Operation at lower temperatures required larger limestone excesses, higher aeration rates, higher sludge recirculation rates, and limestone of smaller particle sizes.

The full scale facility provided 100 percent neutralization of free acid and over 99 percent removal of iron using a 50 percent excess of limestone. A very dense, easily filtered sludge was produced. Although influent temperatures as low as 59°F were encountered, game fish populations were maintained in the treated water. Capital costs for a facility to treat 1,500 gpm acid rinse water were $1,360,000. Operating costs were 24.0¢/1,000 gal. or 4.38¢/ton of steel pickled.

This report was submitted in fulfillment of Project 12010 DUL under the partial sponsorship of the Environmental Protection Agency.

Key Words: Acid rinse water, aeration, clarification, ferric hydroxide, ferrous iron, flocculation, limestone, neutralization, pickle rinse water, sludge recirculation.

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SECTION I

CONCLUSIONS

This process clearly demonstrated an ability to effectively, efficiently, and economically treat large volumes of hydrochloric acid rinse waters. The conclusions stated in this section have been derived from pilot scale and full scale studies.

1. The treatment facility described in this report provided 100 percent neutralization of free acid and over 99 percent removal of iron from the acid rinse waters. Temperatures were normally above 95°F (35°C). Temperatures as low as 59°F were encountered briefly; while the process was still effective, the reaction rate was appreciably reduced. Typical data are found in Tables III and IV (p. 18, 19).

2. The process produced a very dense, easily filtered sludge. The sludge was typically filtered at a rate of 80 lb wet cake/sq ft/hr with a moisture content of 30 percent and a cake thickness of about 3/4 in. (p. 24).

3. With 90,000 gal. surge capacity ahead of the aeration-mix tank, the treatment facility was operated satisfactorily by one man using manual control; however, automatic control would probably improve efficiency substantially by precisely regulating limestone dosage and might reduce the surge capacity requirements (p. 21).

4. Typical treatment costs were 24.0¢/1,000 gal. or 4.38¢/ton of steel pickled (p. 19).

5. The facility was designed to handle 6,900 lb iron/day. The normal load, however, was only about 2,500 lb/day. The plant capacity was determined experimentally to be in the range of 7,000 to 9,000 lb/day, depending on temperature, when using one 250 SCFM blower. Using two blowers, the capacity was increased about 25 to 50 percent (p. 11).

6. Game fish populations were maintained in the treated effluent water (p. 25).

7. A minimum amount of recirculated sludge was needed to improve floc quality. Exceeding this minimum amount of sludge did not affect floc quality (p. 16).

8. Practically all the iron in the acid rinse water was present in the ferrous form (p. 9). This led to higher filtration rates than anticipated, and the filter capacity provided was more than required (p. 24).

9. A minimum pH of 6.6 in the effluent from the aeration-mix tank was required for complete oxidation of the iron; this is a prime indicator of proper plant operation (p. 12).

10. The sludge was too heavy to be handled with conventional A-frame flocculators. This problem was solved by substitution of turbine-type mixers (p. 23).

11. Higher filtration rates were achieved at higher temperatures (p. 8).

12. The amount of air required for oxidation decreased noticeably with increasing temperature (p. 7).

13. The aeration-mix tank was adequately sized. Both the temperature and the flow rate were less than anticipated. The 45 to 50 min retention time available was sufficient at the temperatures experienced; pilot studies indicated 30 min to be sufficient only above 120°F (p. 15).

14. The flocculation tank was designed for 30 min retention time at 1,500 gpm. This appeared to be excessive, since the floc formed quickly and was very dense (p. 23).

15. The clarifier was designed with a rise rate of 0.8 gpm/sq ft at 1,500 gpm. This proved to be of sufficient size (p. 23).

SECTION II

RECOMMENDATIONS

1. The aeration-mix tank should be sized with the operating temperature in mind. Additional retention time is required at lower temperatures.

2. A flocculator - clarifier should be evaluated as a substitute for separate flocculation and clarification.

3. If a separate flocculation tank is used, variable-speed turbine-type flocculators are recommended.

4. Automatic monitoring of the plant influent for total acid is recommended. Automatic control of limestone addition should be considered. Manual monitoring and control require sufficient surge capacity ahead of the aeration-mix tank to prevent upset of the plant between tests. Automatic control of flow rate might also be considered.

5. Vacuum filter capacity should be based on the ferric/ferrous ratio of the iron in the acid rinse water. The presence of ferric iron in the waste substantially reduces the filtration rate of the sludge.

6. The clarifier effluent normally had a pH of about 6.9 and contained less than 5 mg/l total iron. However, a small lagoon is recommended as a back-up for the facility.

SECTION III

INTRODUCTION

Ferrous metals develop an oxide coating in the course of manufacture. This coating is customarily removed from low carbon steels by pickling in acid and rinsing with water. Two different waste streams result: spent acid from the pickling baths, and once-through rinse water. Two new hydrochloric acid pickling lines were constructed at Armco Steel Corporation's Middletown, Ohio, Works. Disposal of the spent pickling acid was provided, but a facility to dispose of the acid rinse water was needed.

Armco research scientists had developed at bench scale a hydrochloric acid pickling rinse water treatment process that was believed to be economical and controllable. This process is unique in that it utilizes limestone neutralization along with aeration and sludge recirculation to oxidize ferrous iron and produce a readily filterable precipitate. The reactions for this process are:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$$

$$4FeCl_2 + 4\ CaCO_3 + 6H_2O + O_2 \rightarrow 4CaCl_2 + 4Fe(OH)_3 + 4CO_2$$

A facility for this type process was needed immediately, so plant design was based only on bench level information. Several of the design criteria were based on experience gained in the design of previous similar structures. Pilot scale tests were carried out concurrently with construction so that, upon completion of the facility, the pilot level information would be available for use at the treatment facility.

On May 16, 1968, Armco Steel Corporation received an Environmental Protection Agency grant to: develop at pilot scale the process to convert large volumes of hydrochloric acid rinse waters into good quality water and an easily handled sludge; design and construct a full scale installation to demonstrate the process developed in the laboratory; develop and determine a simple, economical, efficient, and controllable method of operation of the process; and, demonstrate the efficiency, economy, and controllability of the process.

SECTION IV

PILOT STUDIES

EXPERIMENTAL

The pilot plant was designed for a maximum flow rate of 0.5 gpm. A schematic diagram of the plant is shown in Fig. I. A brief description of equipment and operating practice follows:

Acid Rinse Water

The acid rinse water (ARW) to be treated was programmed to contain about 1.0 g/l of total hydrochloric acid (0.5 g/l of hydrochloric acid plus 0.87 g/l of ferrous chloride[1]). The decision was made to prepare a more concentrated solution of ARW and meter it into the pilot facility. With this approach, reaction temperatures could be controlled more easily by dilution of the ARW stock solution with heated tap water.

A stock solution of ARW was synthesized by dissolving a specified weight of powdered iron in a known amount of hydrochloric acid. The solution was then diluted to 55 gal. with water, and samples were taken to be analyzed for total acid and ferrous iron.[2]

The ARW stock solution was metered into the system by means of a variable-flow tubing pump which could be precisely controlled to deliver 0 to 940 ml/min.

Limestone Slurry

Prior to a run, 20 gal. of limestone slurry were prepared. Limestone concentration in the slurry was determined by oven-drying a sample overnight. The value

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[1] 0.87 g/l of ferrous chloride is equivalent to 0.5 g/l of hydrochloric acid.

[2] Samples of this solution were analyzed for both ferrous and ferric iron during the first experimental runs. Despite exposure to the atmosphere over a period of several weeks at room temperature, ferrous chloride remained unoxidized.

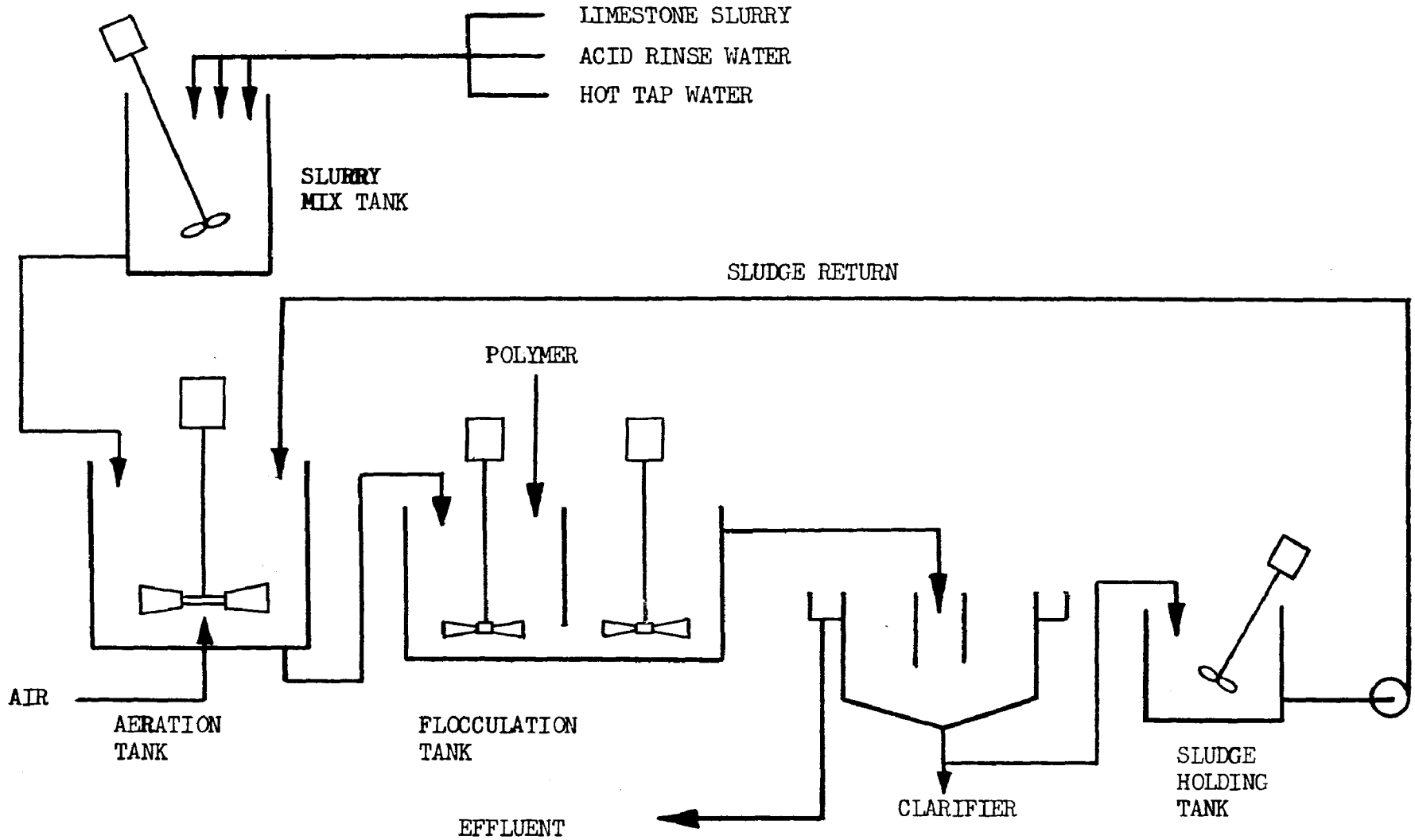

FIGURE I.

SCHEMATIC OF PILOT PLANT

obtained determined the rate at which the slurry was pumped. The slurry was metered into the process by means of a variable-flow tubing pump, also having 0 to 940 ml/min capability.

Air

Air was supplied to the process by means of a 3 SCFM blower. Air flow rate was indicated by one of two rotameters having ranges of 0 to 3 and 0 to 13 l/min.

Equipment

The pilot plant consisted of five tanks. The first tank, the slurry mix tank, was used to blend the ARW stock solution and heated tap water with the limestone slurry. Retention time in this tank was normally 30 sec, but a 90-sec retention time was also possible.

The ARW-limestone-water mixture flowed from the slurry mix tank into the aeration-mix tank. This tank was 22 in. in diameter and was baffled with four steel plates (each 12 in. high by 2 in. wide) set against the outside wall of the tank 90 deg apart. The reaction mixture was agitated by a 4-in. diameter flat-blade turbine set 2 in. above the center of the bottom of the tank. The turbine had six blades and was powered by a 1/4 hp variable-speed (0 to 350 rpm) motor. Normal operating speed was 350 rpm. Air was introduced into the tank at a point directly below the turbine. Retention time of the tank was 30 min.

From the aeration-mix tank, the treated ARW flowed by gravity into the flocculation tank. An organic flocculating aid was added at this point. The tank itself was divided into two chambers, each having a 15-min retention time. The contents of each chamber were mixed with a 4 by 1½ in. paddle. Tip speeds were 6 ft/sec in the first chamber and 2 ft/sec in the second chamber.

The reaction products passed from the flocculation tank to the center well of the clarifier by means of an overflow weir and a siphon which was secured 3 in. below the liquid level in the second chamber of the flocculation tank.

The clarifier was a cylindrical polymethylmethacrylate tank with an effective height of 4 ft and an inside

diameter of 9½ in. The center well was a polymethylmethacrylate tube 2 ft long and 4 in. I.D. At a flow rate of 0.5 gpm, the clarifier had a rise rate of 0.155 ft/min (1.15 gpm/sq ft). The clarified effluent overflowed a peripheral weir and was directed to a drain. Settled sludge was removed from the bottom of the clarifier daily. Part of this sludge was stored in a holding tank from which it was recirculated back into the aeration-mix tank with a variable-flow tubing pump.

Operation

At the full scale facility, the variables which are controllable are type and dosage of limestone and the sludge recirculation rate. Variables such as flow rate, temperature, and acid concentration depend upon pickler operation.

At the time the pilot scale studies were commenced, ARW temperatures in the range 150° to 170°F were expected. No bench scale work had been carried out at temperatures above 120°F, and temperature effects had been explored only briefly. Therefore, investigation of temperature effects was incorporated into the pilot scale studies.

Significant differences in filtration rates were expected when varying the temperature, limestone type, limestone excess, and sludge recirculation rate. The effect of these variables must be known to be able to establish optimum treatment plant operating procedures. A designed experiment was set up to evaluate these four parameters. The schedule called for 24 runs to include the following conditions:

A. Temperature: 120°, 135°, and 150°F (49°, 57°, 66°C)
B. Limestone:
   1. YA Grade[3] - 25 and 100 percent excess of theoretical
   2. #2 LS Grade[4] - 25 and 100 percent excess of theoretical
C. Sludge Recirculation Rate: 5 and 15 g solids/min

Table I summarizes the results of these runs.

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[3] 84 to 87% through 200 mesh; 65 to 70% through 300 mesh
[4] 99.6% through 200 mesh; 99.0% through 300 mesh

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DISCUSSION

The principal functions of this waste treatment process are to remove iron and neutralize the acid originating in pickling rinse waters. A proposed criterion for effluent quality is that the treated rinse waters shall not contain more than 5 mg/l of ferric hydroxide or approximately 3 mg/l of iron. Further, turbidity other than that originating from the ferric hydroxide should be negligible.

Limestone Dosage

The filtration tests and the completeness of the treatment (as evidenced by the amount of iron in the effluent), indicate there is little to be gained by using a 100 percent excess of limestone instead of a 25 percent excess at the temperatures investigated.

If the concentration of total acid in the waste to be treated varies only slightly, a 25 percent excess of limestone should be a sufficient quantity. Highly variable concentrations of total acid should be treated by a somewhat larger excess to accommodate sudden acid peaks.

Aeration Rate

Generally, as the temperature of the ARW was increased, smaller quantities of air were required to completely oxidize the ferrous iron.

The values given for the aeration rate actually represent about a 50 percent excess over the minimum amount required as determined by trial and error. In no way are they meant to show the amount of air required for oxidation. The full scale plant should have an adequate air supply under the same conditions.

Sludge Recirculation Rate

The return of sludge to the aeration tank is known to decrease sludge volumes (3,6,7). The process in this case consists of the addition of precipitation nuclei in the form of ferric hydroxide (and excess limestone) from the clarifier underflow to the aeration-mix tank.

The ratio of precipitation sites to the amount of precipitating material might affect particle growth. Variation of recirculation rate is the only means of controlling this variable at pilot plant and full scale.

The necessity of sludge recirculation in this process has been demonstrated on bench scale (Appendix A). The quantity of recirculation could not be determined from a batch operation. Therefore, one of the functions of the pilot plant was to ascertain the effects of varying recirculation rates. The rates 5 and 15 g sludge/min were selected for the designed experiments in anticipation that significantly different filtration test values would result.

As can be seen from the data in Table I, a rate of 5 g sludge/min was a satisfactory recirculation rate in itself, and increasing the rate to 15 g/min did not measurably affect the filtration rate.

The filtration rate was influenced markedly by the absence of sludge recirculation. Two one-week pilot runs were carried out; these runs were identical, except that during the first week no sludge was recirculated. Conditions were: Temperature - 150°F; limestone - 175 percent of theoretical, YA type; air - 6 l/min; recirculation rates - 0 and 3 g/min. As is shown in Table I, sludge recirculation improved the wet filtration rate by more than 17 percent and the dry rate by over 30 percent while lowering the cake moisture almost 12 percent. Material balance calculations indicate that a sludge return rate of 3 g/min would increase the solids concentration in the aeration tank 90 percent (from 1.77 g/l to 3.36 g/l).

Optimum sludge return rates were not determined during the course of the pilot plant experiments. However, observation of many pilot plant experiments suggested the optimum recirculation rate to be less than 3 g/min.

Temperature

The comparison of filtration tests (Table I) obtained from runs at 120°, 135°, and 150°F indicated that higher temperatures produced higher filtration rates. Another apparent advantage is that a smaller excess of air is required.

At temperatures above 120°F (49°C), the pilot process satisfactorily removed iron and produced a filterable sludge using YA grade limestone. At 120°F, the #2LS grade limestone (finer, therefore more surface area) was required, together with a higher limestone dosage and/or a higher sludge recirculation rate.

Ferric/Ferrous Ratio

The full scale facility was started up several weeks before the studies described above were completed. As was the case with the synthetic ARW used for pilot investigations, the ferric iron concentration in the treatment plant influent was found to be negligible. The ferric/ferrous ratio could, then, no longer be considered a variable in this plant and was not investigated at pilot scale.

SECTION V

FIELD STUDIES

A facility was designed and constructed (Appendix B) to apply the limestone-aeration process to the rinse waters from the hydrochloric acid pickle lines at the Middletown, Ohio, Works. The optimization and demonstration of the facility are described below.

Capacity of Plant

The treatment plant was programmed to handle a 1,500 gpm flow of acid rinse water (ARW) containing 1.0 g/l total hydrochloric acid at temperatures in excess of 150°F (66°C). About half of the total acid was expected to be in the form of ferrous chloride (0.87 g/l ferrous chloride or 0.38 g/l iron, or 0.5 g/l hydrochloric acid). This gives a plant design load of 6,900 lb Fe/day.

Since start-up in May 1969, flow rates have seldom exceeded 1,100 gpm. The temperature of the ARW has never reached that which was expected; generally, temperatures are in the range 104 to 113°F (45 to 50°C). The quantity of iron the plant could handle under these conditions was determined in order to ascertain whether design modifications were necessary.

By injecting spent pickling acid into the ARW, the concentration of ferrous iron in the ARW could be controlled at high levels for the purpose of determining plant capacity. The temperature of the ARW was not controllable but remained constant during the course of any given test. Flow rates were adjustable, but higher rates were available for a limited time only.

The capacity of the plant was determined for various flows and temperatures by metering spent pickling acid into the ARW until ferrous iron was detected in the effluent from the aeration-mix tank. The presence of 3 mg/l ferrous iron at this point was taken as evidence that the capacity of the system for oxidizing iron had been reached. A limestone dosage of 60 lb/min was used for all tests; at no time was this less than a 50 percent excess.

Table II presents the empirically determined plant capacities for various flow rates, temperatures, and aeration rates.

Table II

CAPACITY OF PLANT UNDER VARIOUS CONDITIONS*

Test No.	Flow (gpm)	Temp (°F)	Influent Fe,(mg/l)	Air (SCFM)	Oxygen Transfer Eff. (%)	Plant Capacity (lb Fe/day)
1	470	113	1,700	230	27.6	9,600
2	800	113	950	230	27.8	9,100
3	1,200	113	800	230	30.2	11,500
4	800	113	1,400	470	18.9	13,400
5	1,200	113	1,000	470	20.2	14,400
6	850	102	700	230	20.6	7,100
7	850	102	900	470	12.8	9,200
Design	1,500	150-170	380	230	20.5	6,900

*Limestone dosage - 60 lb/min

As these experiments indicate, the capacity of the plant to oxidize ferrous iron increased 30 to 45 percent with an 11-deg increase in temperature. Doubling the aeration rate resulted in only a 25 to 50 percent increase in plant capacity.

Limestone Requirements

The limestone used for this process is produced by Armco's Piqua Quarries in Piqua, Ohio, under the designation "YA Stone Dust". This limestone contains 84 to 87 percent calcium carbonate and 11 to 14 percent magnesium carbonate. The available alkalinity averages 55.5 percent as calcium oxide.

Screening specifications are:

99 to 99.5% through a 100 mesh screen
84 to 87% through 200 mesh
65 to 70% through 300 mesh

Bench scale studies (Appendix A) had previously shown that an excess of limestone is necessary to raise the pH in the aeration tank sufficiently high to bring about oxidation of ferrous iron.

Full scale studies were carried out between September and December 1969 to determine the minimum pH at which the process should be maintained. This was done by monitoring the pH and ferrous iron concentration in the flocculation tank. Ferrous iron concentrations above 3 mg/l at this point resulted in both a turbid clarifier and more than 5 mg/l total iron in the clarifier effluent.

Figure II shows the median and maximum ferrous iron values in the flocculation tank at various pH values during the period. Figure III shows the percentage of the period that the ferrous iron concentration in the flocculation tank was 3 mg/l or less. To determine the minimum pH to be maintained, these two figures should be used together. At a pH value of 6.8, the ferrous iron concentration in the flocculation tank is maintained at 3 mg/l or less for 97 percent of the time; if the pH were to drop to 6.6, the iron concentration would remain satisfactory 80 percent of the time.

Due to the variable nature of the ARW a limestone excess of 50 percent was chosen. Using this excess, minor increases in the acid concentration could be easily handled. If the acid concentration suddenly decreased without detection, the quantity of limestone added above the 50 percent excess would not adversely affect the process; the filter cake would contain less moisture and iron.

Air Requirements

The treatment plant is equipped with two identical blowers capable of delivering 470 SCFM of air when combined in parallel. This quantity of air is theoretically able to oxidize 52 lb Fe/min. The plant design calls for the capability of oxidizing 4.7 lb Fe/min (1,500 gpm at 380 mg/l iron).

The effect of temperature on the air requirements for the plant is threefold. Higher temperatures decrease the solubility of oxygen in water, thus decreasing the driving force in the system (the difference between

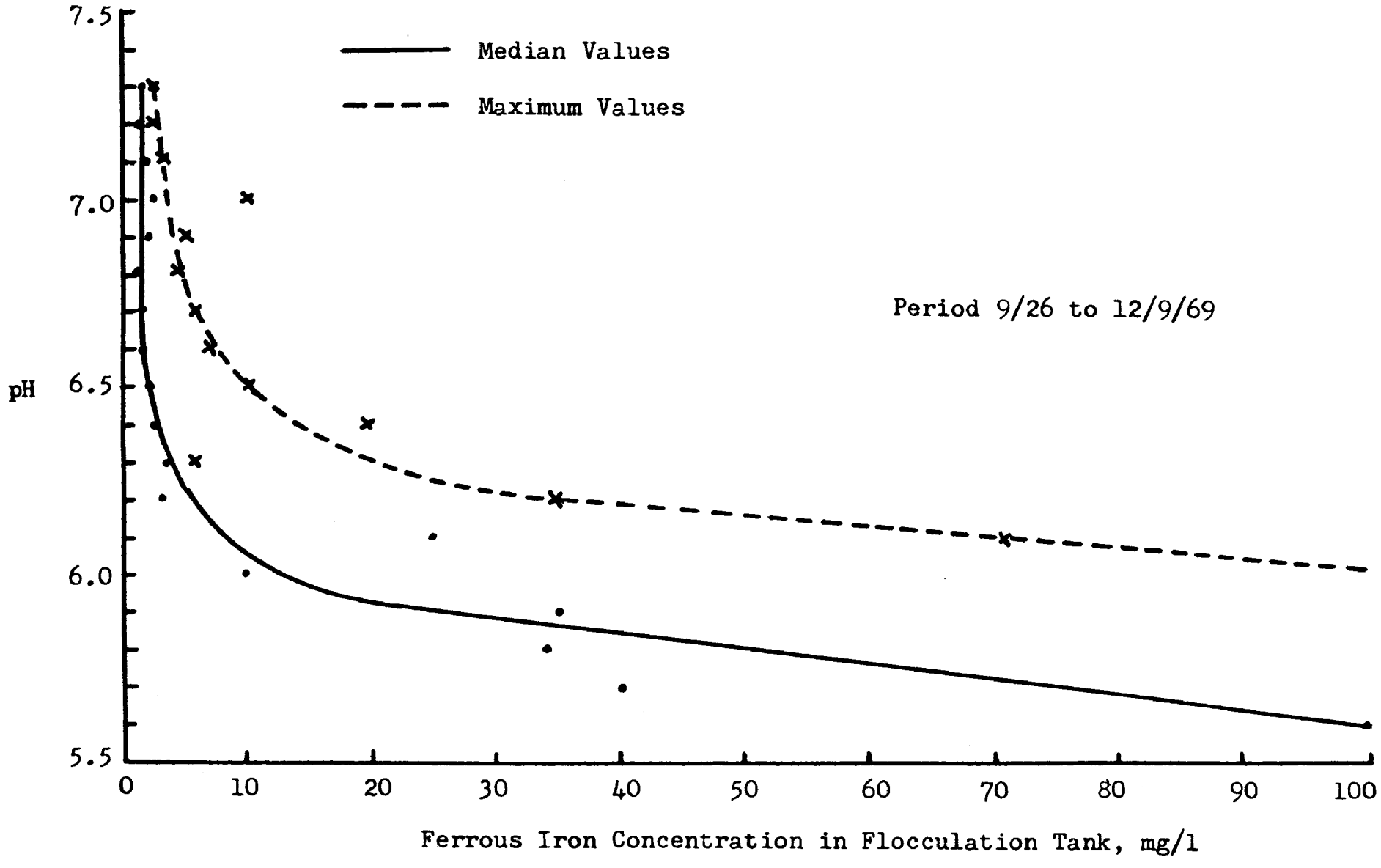

FIGURE II

EFFECT OF pH ON FERROUS IRON CONCENTRATION IN FLOCCULATION TANK

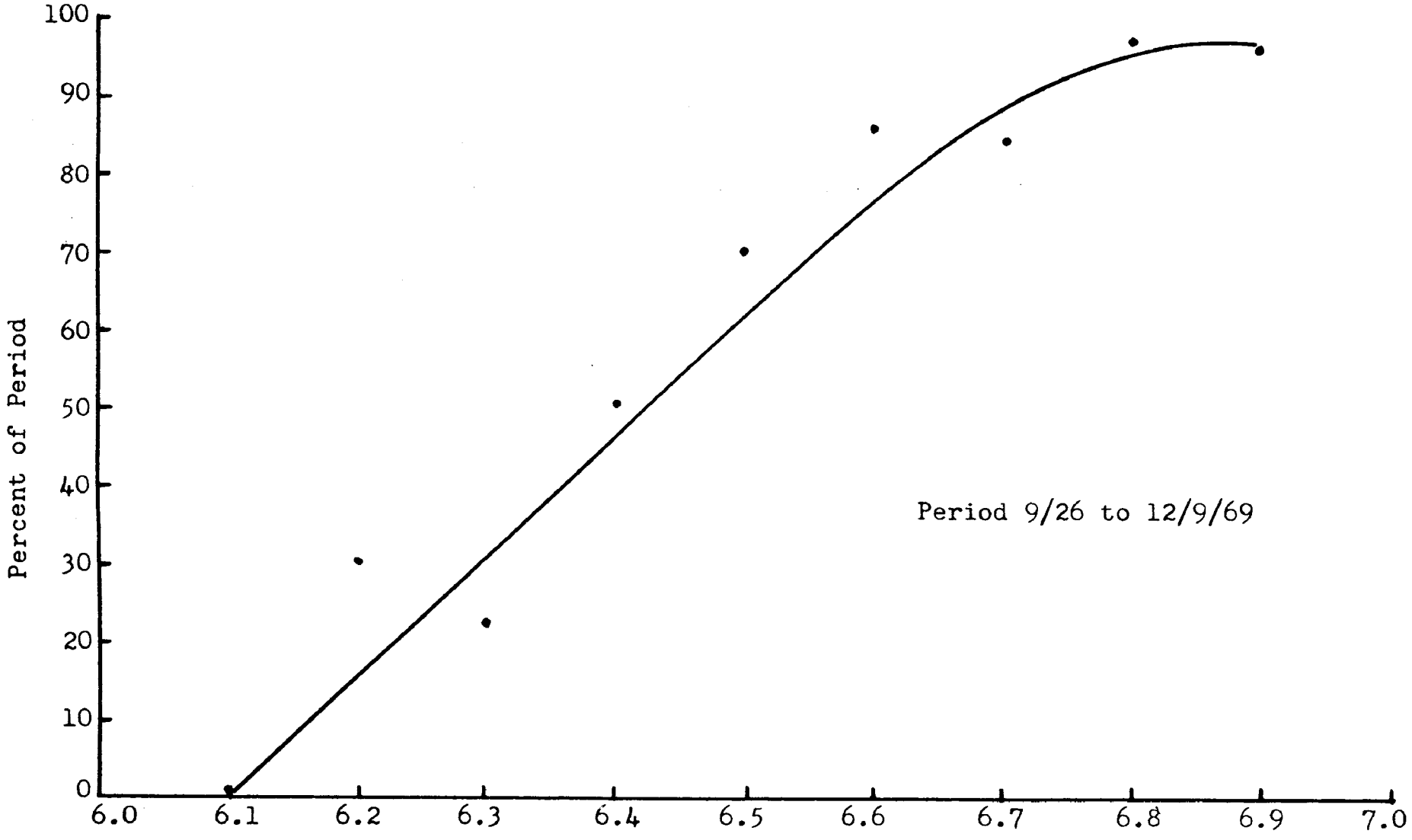

FIGURE III

PERCENT OF PERIOD FERROUS IRON CONCENTRATION IN FLOCCULATION TANK 3 mg/l OR LESS VS. pH

the saturation value of oxygen in the waste and the actual dissolved oxygen). However, higher temperatures increase the ability of oxygen to pass through the liquid film from the atmosphere. The net result of these two effects is a general increase in oxygen transfer with an increase in temperature. Finally, higher temperatures increase the reaction rate, thereby decreasing the dissolved oxygen concentration and increasing the driving force.

At higher temperatures, e.g. 150°F, the oxidation of ferrous iron would probably progress toward completion in less than the design aeration time of 30 min. Since start-up, the treatment plant has never encountered a waste temperature higher than 122°F (50°C). The normal range is 104° to 113°F. Pilot scale experience with a very similar process indicates a definite "trade-off" between temperature and aeration time. Apparently, the full scale facility successfully handled wastes at lower temperatures because higher aeration tank retention times were experienced.

During periods of sub-freezing weather, ARW temperatures as low as 59°F (15°C) were recorded. Fortunately, these low temperatures lasted only 6 to 12 hours at a time and were accompanied by low flow rates and iron concentrations; there was no apparent effect on the process.

Effect of Sludge Recirculation

The advantages of returning sludge to the aeration-mix tank have been discussed (Section IV and Appendix A). Others (3,6,7) have commented on the effectiveness of recirculation on improving sludge settleability and filterability.

An attempt was made to quantify the amount of sludge recirculated by running at a selected rate for one week followed by one week during which no sludge was recirculated. Variations in the solids concentration in the clarifier underflow, which can be directed either to the aeration-mix tank or to the filters, made it difficult to operate at a specific rate; these concentrations have been observed to vary from 120 - 800 g/l over a three-day period. The solids concentration in the aeration-mix tank did not exceed 2 g/l without recirculation, and was never less than 3 g/l (average 7 g/l) with recirculation.

Observations made over the sixteen month period indicate three important benefits from recirculating sludge:

a. There was a noticeable red color, due to finely divided ferric hydroxide, in the clarifier effluent each time recirculation was halted. On restoration of sludge recirculation, the red color disappeared.

b. Sludge recirculation improved sludge settleability. When recirculation was stopped the flocculator tip speed required to keep the sludge suspended was reduced by about 25 percent.

c. During the period when the total acid concentration in the ARW far exceeded the capacity of the facility, the alkalinity values in the recirculated sludge (from the excess limestone) contributed towards neutralizing the acid.

Sludge recirculation has no effect on the final pH when the facility is operating within the design limits.

Flocculator Operation & Polymer Practice

The original A-frame flocculators did not provide sufficient agitation to keep the floc particles in suspension (p. 23). Turbine-type flocculators were substituted for the A-frames; when these mixers were operated at their maximum tip speed of 8.1 ft/sec (24 rpm), excellent agitation was obtained. As little as a 4 rpm decrease resulted in the formation of a sludge layer several feet below the surface of the tank. While this sludge layer was still being kept in motion by the mixers, the flow from the bottom discharge pipe was impaired by the increase in the solids concentration. Restoring the maximum mixer setting lifted the sludge layer.

To aid in flocculation of the precipitated iron and excess limestone, facilities were incorporated for the preparation and dispensing of a water-soluble organic polymer to the flocculation tank. The polymer, or flocculating aid, is prepared in one of two 2,400 gal. tanks at a concentration not exceeding 0.1 percent. Positive displacement pumps transfer the solution to any of three distribution points: across the top of either flocculation chamber or into the discharge from the aeration tank. Normal practice during a period of low

flow rate, (less than 700 gpm) is to add the polymer to the last chamber of the tank. This minimizes the disintegration of the floc particles that results at this low flow rate from extended contact with the turbine mixers. At higher flow rates, addition of the polymer into the aeration-mix tank discharge has been satisfactory.

During the bench-scale investigation, a nonionic polyacrylamide was found to be the most efficient flocculating aid. At pilot scale the nature of the precipitate was apparently different and an anionic polyacrylamide was superior to the one previously used. At the conclusion of the pilot plant investigation, after approximately fifty polymers had been evaluated, "Polymer A", a highly anionic polyacrylamide derivative, was selected for full-scale trial. Despite poor agitation in the flocculating tank, performance was good; a 1.5 to 2.0 mg/l dosage was required for good flocculation.

After the breakdown of the flocculators and the subsequent replacement of same with turbine mixers, a higher dosage, (8 to 10 mg/l) of polymer was required for flocculation. Jar testing at the site suggested a change in polymer be made. "Polymer B", also an anionic polyacrylamide derivative but having a lower charge density than "Polymer A", was chosen. The optimum dosage rate for "Polymer B" was found to be about 3.0 to 3.5 mg/l.

Demonstration

This process clearly demonstrated an ability to effectively, efficiently, and economically treat large volumes of hydrochloric acid rinse waters. The sludge produced was easily de-watered and readily handled. Operating results for one typical month during the demonstration period are presented in Tables III and IV. Except during periods of plant upset, the water produced by this process consistently had a total iron concentration less than 5 mg/l, a turbidity less than 15 J.T.U. and a pH of 6.8 to 7.1. The average amount of chlorides and hardness added to the waste stream by the picklers and treatment plant can be calculated from the data in Tables III and IV. These calculated values indicate that the picklers add 475 mg/l chlorides to the process water which contains 55 mg/l chlorides. The treatment plant adds 670 mg/l hardness as $CaCO_3$ to the 200 mg/l hardness of the influent river water used at the picklers. The game fish, such as large-mouth bass, channel catfish, and bluegill, that have been thriving in the waste treatment lagoon are further evidence of the quality of the effluent.

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Table IV

TYPICAL TREATMENT PLANT OPERATING DATA (APRIL 1970)[1]

Influent		Effluent	
Avg. Flow	- 730 gpm	Avg. Total Iron	- 4.0 mg/l
Avg. pH	- 2.5	Avg. pH	- 6.9
Avg. Temperature	- 102° F	Avg. Turbidity	- 10 JTU
Avg. Total Acid	- 490 mg/l		

Process Requirements		Sludge Characteristics	
Limestone @ 50% Excess	- 4.5 tons/day	Quantity	- 4.6 tons/day (wet)
Air	- 250 SCFM	Moisture	- 31%
Flocculating Aid @ 3.5 mg/l	- 30.7 lb/day	Iron	- 27% (dry)
Sludge Recirculation[2]	- 60 gpm		

The treatment facility was easily operated by one man. The primary functions of the operator included: periodic tests of influent and effluent concentrations, limestone feeder adjustment, flocculating aid make-up, and sludge filtration. A regular inspection of the mechanical equipment, general clean-up, and preventive maintenance items were also included. Maintenance personnel were required only when equipment trouble developed.

The cost data presented in the following paragraphs are based on the facility in Middletown. Costs will vary for other installations depending on several factors, such as geographical location and the volumes and characteristics of the rinse waters.

Using the data given in Table IV, operating costs for the demonstration period, excluding supervision and sludge disposal are calculated to be $7,530/mo (Table V). This is equivalent to 4.38¢/ton of steel pickled or 24.0¢/1,000 gal. ARW.

---

1 Pickling Rate 240 tons/hour

2 Solids concentration varied between 10 and 75%

Table V

TYPICAL TREATMENT PLANT OPERATING COSTS

Limestone, 135 tons @ $5.52/ton (delivered)	$ 750
Flocculating aid, 920 lb @ $1.38/lb	1,270
Operating personnel, one man @ 4.50/hr (21 turns/wk)	3,200
Maintenance personnel, 185 hr/mo @ $6.94/hr	1,280
Repair material	400
Supplies	350
Utilities	280
Total operating costs/mo	$ 7,530

Table VI presents the capital costs required to construct this treatment plant at the Middletown Works during the period of November 1967 through May 1969.

Table VI

TREATMENT PLANT CAPITAL COSTS

Yard Work	$ 15,000
Structures	124,000
Equipment (Installed):	
Collection Tanks & Pumps	30,400
Surge Tanks	70,400
Aeration-Mix Tank & Mixer	30,700
Flocculation Tank & Mixers	26,700
Clarifier	89,400
Limestone Feed Equipment	33,300
Vacuum Filters	41,300
Misc. Equipment	74,800
Instrumentation	105,000
Final Lagoon	142,000
Piping	190,000
Electrical & Lighting	144,000
Indirect Costs	243,000
Total Capital Costs	1,360,000

Changes, such as reducing the size of the back-up lagoon, could reduce capital costs. The relative location of the treatment facility to the waste source could also affect piping costs significantly. Variations in construction labor rates may also affect capital costs.

SECTION VI

EQUIPMENT DESIGN EVALUATION

Since construction of the treatment plant was begun directly from bench level information, many of the design criteria were made empirically. During the field studies and demonstration period, some design errors became apparent. The basic units of the existing facility have been evaluated in the following sections.

Surge Capacity

The ARW is transferred to the treatment plant with one or both of two 750-gpm pumps. Therefore, the flow rate to the plant is either zero, 750, or 1,500 gpm. To give some equalization of flow, and acid concentration as well, 90,000 gal. of surge capacity were provided to receive the ARW prior to treatment. This consists of two 45,000-gal. reinforced fiberglass tanks arranged in parallel.

In practice, the ARW level in the surge tanks was maintained in the intermediate range by means of a throttling valve downstream from the tanks. Adjustment of this valve was rarely necessary. Although hour-to-hour variations in flow through the treatment plant did occur (Fig. 4), these changes were relatively gradual. In this plant, influent conditions were checked periodically and chemical additions manually adjusted. The effluent iron concentrations remained satisfactory (also shown in Fig. 4), so additional surge capacity is apparently unnecessary.

Aeration-Mix Tank

The aeration-mix tank is the reaction zone for the process. Limestone is added here to neutralize free acid and raise the pH to the appropriate level; air is mixed in to oxidize ferrous to ferric iron. Research data from bench level studies (Appendix A) indicated a 30-min retention time was necessary for this tank. A square 45,000-gal. aeration-mix tank was installed. Following equipment manufacturer's recommendations, the aeration-mix tank was equipped with a 30-hp submerged turbine type aerator and a blower rated at 250 SCFM.

The tank was apparently sized correctly for 1,500 gpm at 150°F. The temperature of the ARW actually received was

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considerably less than 150°F; fortunately, the flow was considerably less than 1,500 gpm, and the 45,000-gal. tank proved sufficient. (See Section V.)

Flocculation Tank

This tank is designed to promote flocculation of the ferric hydroxide particles with the addition of an organic polyelectrolyte. The tank is rectangular with a 45,000-gal. capacity and 30-min retention time. A baffle was mounted mid-way across the width of the tank to prevent short-circuiting or stratification. It originally had two A-frame oscillating flocculators, one in each chamber, with a maximum tip speed of 1.6 ft/sec. Although bench scale investigations (Appendix A) utilized a flocculation time of 15 min, previous experience in water clarification indicated a period of 30 min would be more favorable.

Upon start-up of the treatment facility, immediate problems were encountered in the flocculation tank. Sludge settled in the bottom of the tank, impeding and eventually stopping the movement of the flocculators. Air lances were used to break up the sludge formations; however, this damaged the floc particles, resulting in a turbid effluent due to high iron carryover. Attempts were made to alleviate the problem by using a finer grade limestone and reinforcing the A-frame, but excessive settling continued. Eventually one of the A-frames broke at an axle weld.

The A-frame flocculators were replaced with turbine-type flocculators. The turbine blades were 78 in. in diameter with a 45 deg pitch, and could be driven from 6 to 24 rpm by means of a 5 hp variable-speed motor.

A flocculation time of 30 min was much greater than actually necessary. The floc has proven to form quickly and to be very dense. A flocculator-clarifier would seem to be applicable here.

Clarifier

The 50-ft diameter clarifier was designed with a rise rate of 0.8 gpm/sq ft at 1,500 gpm. This rise rate was chosen by previous experience in water clarification.

If the rise rate were too high, iron floc particles would be carried over in the clarifier effluent. Over a 10-day period, the flow and total iron concentrations in the

effluent were observed. The results are shown in Fig. IV. During this period the flow varied between 400 and 1,200 gpm, and the total iron in the effluent was less than 5 mg/l for 95% of the time; it exceeded 7 mg/l only once, and then only for one hour. This indicates that the clarifier is large enough for the maximum flow achieved during the period. Due to the difficulty in obtaining large flows for extended periods, the maximum flow that this clarifier will handle is unresolved.

Sludge Filters

The filters were sized from bench scale data; assuming an ARW temperature of 120°F and a maximum ferric/ferrous ratio of 1/3, a filtration rate of 18 lb dry cake/sq ft/hr was anticipated (Table A-II, experiment no. 7). Material balance calculations indicate at design flow and acid concentration, and assuming the use of a 50 percent excess of limestone, a sludge accumulation rate of 12.8 tons dry cake/day, or 1,060 lb/hr. Therefore, a minimum of 60 sq ft of filter area would be needed if the filters were run continuously; a minimum of 180 sq ft would be needed if the filters were run only one turn daily. Two belt-type rotary vacuum filters were installed. Each filter has a 6-ft diameter and a 6-ft wide face with approximately 113 sq ft of filtration area. A vacuum of 5 SCFM/sq ft at 20 in. Hg is required.

Initially, sludge buildup on the belt due to inadequate washing resulted in a tracking problem. This was eliminated by the installation of spray headers to provide a thorough wash on both edges of the belt.

The sludge accumulation rate experienced at the full-scale facility was about 4 tons dry cake/day. The actual filtration rate achieved was about 80 lb wet cake/sq ft/hr with an average of 30 percent moisture; the difference between the 56 lb dry cake/sq ft/hr experienced and the 18 lb value expected is explained by the practical absence of ferric iron in the ARW. The operation of one filter a few hours at a time several times per week was sufficient to handle the sludge from this facility. The filter cake density was approximately 100 lb/cu ft, so removal of the cake from the plant site required about one gondola car (1775 cu ft) per week.

By varying filter belt speed, cake thicknesses of 1/2 in. to 2 in. were produced. If a filter cake thickness of 2 in. were maintained, however, undue stresses were added to the belt and tracking problems resulted. A thickness

of 3/4 in. appeared to be the optimum based on moisture content and ease of operation.

Polypropylene belts were normally used on these filters; nylon also performed satisfactorily, but is less resistant to low pH values. Failure of the belt generally occurred at the seam, probably due to the abrasiveness of the limestone in the sludge.

Final Lagoon

The 16-acre 30 million gal. final lagoon was originally proposed as a back-up for the treatment facility in anticipation that some water not suitable for direct discharge to a public waterway might be produced during the testing program.

During the demonstration period it became apparent that the final lagoon was unnecessary for the process. Armco research scientists determined that stocking the final lagoon with game fish would be feasible. Largemouth basses, bluegills, and channel catfishes were obtained from the Federal hatchery at Hebron, Ohio, or purchased privately by Armco. Stocking of the final lagoon, which contains only treated acid rinse water, has proven to be a highlight of the demonstration phase of this project.

Automatic Acidity Analyzer

To insure efficient operation of the process, the limestone feed rate must be proportional to both the ARW flow rate and to the total acidity. An automatic acidity analyzer was originally provided for control of the limestone feed rate. The analyzer receives a constant sample flow of ARW and automatically and continuously titrates this sample to a selected pH value with a caustic (sodium hydroxide) solution. A ratio setter is provided to compensate for variations in caustic concentration. The amount of caustic flow is measured and electronically converted to a signal which is sent to a multiplier. A signal from a magnetic flow meter measuring ARW flow is also sent to the multiplier. The multiplier combines these two signals and in turn sends a signal to the limestone feeders which is proportional to limestone demand.

Since a continuous acidity analyzer for this particular application was not commercially available, a custom-designed instrument was built. It proved to be a highly

sophisticated instrument, too delicate for plant operations. Frequent adjustment and cleaning were needed. Instead, the operator determined ARW conditions and manually adjusted the feeders.

An acidity analyzer could be worthwhile if it were built simply enough to allow inexperienced personnel to handle the instrument.

SECTION VII

ACKNOWLEDGMENTS

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SECTION VIII

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SECTION IX

GLOSSARY

LIST OF TERMS

Acid Rinse Waters - Low acid and iron mixtures resulting from rinsing of steel strip after hydrochloric acid pickling; and fume scrubber water.

Oxygen Transfer Efficiency - The ratio expressed as a percentage, of oxygen consumed to oxygen supplied.

Sludge - Precipitated ferric hydroxide and excess limestone.

LIST OF ABBREVIATIONS

ARW - acid rinse waters

cps - centipoises

gpm - gallons per minute

hp - horsepower

in. Hg - inches of mercury

SCFM - standard cubic feet per minute

TDH - total dynamic head

SECTION X

APPENDIXES

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APPENDIX A - BENCH SCALE RESEARCH & DEVELOPMENT WORK

Introduction

Because hydrochloric acid pickling is a relatively new process, methods for a practical chemical treatment of the wastes were not known. A considerable number of treatment processes have been proposed for the disposal of spent sulfuric acid. Though most of these do not appear to be economically feasible, the initial approach employed for our investigations into the disposal of iron chloride wastes was a modification of previously proposed methods. These methods treat acid waste with lime. Free acid is neutralized, and dissolved metal salts are precipitated. The resulting sludge may be separated by filtration or by settling, and the effluent discharged into a public waterway.

A plant has been in operation at Armco's Works at Butler, Pa., for seven years for treatment of nitric acid-hydrofluoric acid spent pickle liquor resulting from pickling of stainless steel. During development of this treatment process, various alkaline reagents had been tested. Some of these, such as sodium hydroxide, ammonium hydroxide, ammonium carbonate, high-calcium lime, and magnesium oxide, precipitated the metals but did not produce a filterable sludge. Others, such as dolomitic lime and limestone, produced a filterable sludge. Limestone was discarded because complete precipitation of metals was impossible. Dolomitic lime is now used in this process.

For treatment of sulfuric acid spent pickle liquors, two methods (5,9) use lime to neutralize the free acid and precipitate the iron with controlled aeration of the mixture at elevated temperatures. This converts the ferrous iron to precipitated ferroso-feric oxide, $FeO \cdot Fe_2O_3$. Optimum efficiency is claimed when a ferric/ferrous ratio between 2 and 5 is maintained.

Description of Problem

Rinse waters from full-scale pickling operations were expected to contain 1.07 grams of hydrochloric acid equivalent per liter, half as free acid and half as iron chlorides. Further, the wastes were expected to enter the treatment plant at about 100°F. The temperature range of 75°F to 120°F was therefore used in this investigation.

Investigation of Treatment with Dolomitic Lime

To determine the ferric/ferrous ratio at which ferroso-ferric oxide is formed from hydrochloric acid solutions, waste waters containing ferric/ferrous ratios of 1/0, 3/1, 2/1, and 1/1 were treated with 120 percent of the theoretical amount of dolomitic lime (alkalinity 92.5 percent as CaO). Two solutions, one ferric and the other ferrous chloride, were prepared such that any combination of the two, totaling 50 ml and diluted to one liter, would be equivalent to the free acid and iron chloride expected in the waste water.

This investigation was carried out on a relatively small scale, in beakers, by batchwise addition of neutralizing chemical to the simulated waste. The procedure was as follows:

> Fifteen hundred milliliters of tap water at the desired temperature were added to each of four beakers. A 500 ml buret was positioned above each beaker; each was filled with 100 ml of concentrated acid-iron chloride solution and 400 ml of tap water at slightly above the desired temperature. As the burets were emptied into the beakers, a slurry of neutralizing chemical was added in greater than stoichiometric amounts. The contents of the beakers were stirred at 120 rpm (tip speed 2 ft/sec) during the additions.
>
> After 15 min reaction time, 1.5 mg/l flocculating aid was added. This was followed by mixing at 120 rpm for one min and at 60 rpm for 15 min. The mixer was then shut off and the sludges permitted to settle.
>
> After siphoning off the supernatant solutions, the sludges were combined and accumulated by repeating the above procedures.
>
> Variation in this procedure consisted of running each neutralization in the presence of "seed" sludge from previous batches.

A test leaf filter having an effective area of 0.1 sq ft was used with a nylon filter cloth. Filtration tests were made when sufficient sludge was collected. Data obtained were: total solids in the accumulated sludge before filtration, weight of wet and dry filter

cake, water in the wet cake, iron in the dry cake, thickness of cake and volume of filtrate.

Sludge produced by lime treatment of Butler waste pickle liquor was used as a control. The results obtained for both the hydrochloric acid and control solutions are given in Table A-I. The data indicate that, at best, only one-third as much dry filter cake is produced with chloride wastes as with the control sample. Apparently, weak hydrochloric acid waste did not react in the same manner and another approach was necessary.

In no case was a ferroso-ferric oxide observed.

The size and density of the precipitated metal compounds affect both settling rates and filtering rates. The high activity of lime apparently results in the formation of many small particles of ferrous hydroxide when chloride wastes are treated. This suggests that the best filtering characteristics might be produced when the hydroxyl ion is introduced slowly, resulting in slower precipitation and agglomeration of the metal compounds. Limestone, because of its slower reaction rate, might serve this purpose. Subsequent tests were carried out using limestone.

Investigation of Treatment with Limestone

Limestone alone does not convert ferrous iron into insoluble $Fe(OH)_2$. However, by passing air through the solution while carrying out the treatment with limestone, iron can be oxidized and quantitatively precipitated from the solution as ferric hydroxide. Consequently, the test procedure described previously was modified as follows:

1. Air was bubbled into the solution through gas dispersion tubes during a 30 min neutralizing and precipitating period. When the iron was initially present in the ferric form, no air was used and a 15 min reaction time allowed. Then aeration was discontinued and flocculating aid was added.

2. Initial and final pH of the solution were measured.

3. A test leaf filter having an effective area of 0.0256 sq ft was substituted for the 0.1 sq ft filter.

The alkalinity of the limestone was 55.5 percent (as CaO); the chemical analysis was 87.5 percent $CaCO_3$, 10.2 percent $MgCO_3$, 1.3 percent SiO_2, and 0.45 percent Al_2O_3.

Ideally, the limestone requirement would be that required to just neutralize an acid solution. In practice, the physical combination of magnesium carbonate in the limestone matrix affects its reactivity, and greater than stoichiometric quantities are required. A limestone excess of 50 percent was necessary for solutions containing ferrous iron, whereas a 20 percent excess appeared suitable for wastes with all of the iron in the ferric form.

All iron in the acid rinse water should initially be in the ferrous form. However, through exposure to atmosphere a portion of the ferrous iron might be converted to ferric iron. The ratio of ferric to ferrous iron at the time of treatment was not known until full-scale pickling operations were begun. Consequently, this variable was included in the laboratory studies.

Values obtained were for waste waters having ferric/ferrous ratios of 0/1, 1/3, and 1/0. Accumulating sufficient amounts of sludge for filtration tests was tedious because the sludge produced with limestone was more dense and occupied less volume than that produced with lime. This problem was ameliorated by substituting a 0.0256 sq ft test leaf filter for the 0.1 sq ft filter.

Various chemicals to aid in the flocculation of the precipitated iron were evaluated. Nonionic polymers were found to be satisfactory when used at a concentration of 1.5 mg/l.

The best sludge was produced from the solution containing no ferric iron. The specific gravity of this sludge after standing 16 hr was 1.5 g/ml at 21°C. The viscosity at 21°C, using a Brookfield Model RVF-100 viscometer with the no. 4 spindle, was 2,200 cps at 20 rpm and 1,700 cps at 50 rpm. The settling rate of this sludge was too high to measure. This sludge yielded filtration rates as high as 114 lbs dry cake/sq ft/hr and 30 lbs iron/sq ft/hr (Table A-II).

When a solution having a ferric/ferrous ratio of 1/3 was treated, the filtration rate values dropped dramatically. The waste having no ferrous iron gave the lowest values; this sludge also exhibited the poorest settling rate, about 3 in/min.

To oxidize ferrous iron to ferric with molecular oxygen and precipitate the iron as ferric hydroxide, a pH in excess of 5.7 is critical. The first few batches of all experiments involving ferrous iron failed to achieve this critical pH. When enough excess limestone had been accumulated from preceding batches to push the pH above 5.7, the ferrous iron was oxidized and precipitated. The total iron in the supernatant solution then dropped to less than 1.0 mg/l.

Studies of temperature effects were carried out on waste waters having ferric/ferrous ratios of 0/1 and 1/3 at 100° and 120°F. At a ferric/ferrous ratio of 1/3, a 25 percent reduction in the filtration rate was experienced when the temperature was increased from 100° to 120°F. The temperature effect was quite different at a ferric/ferrous ratio of 0/1, however. The sludge prepared at 120°F was exhausted after only 30 sec filtration, one-half of the usual filtration time. Had sufficient sludge been available for a one min filtration, the yield probably would have been higher than that produced when the same solution was treated at 100°F.

Normally, the runs were made with limestone containing particles of which 92 percent were less than 115 mesh and 74 percent were less than 200 mesh. A coarser grade of limestone, one with particles less than 100 mesh and larger than 200 mesh, was used to neutralize solutions having ferric/ferrous ratios of 1/3 and 1/0. At a ferric/ferrous ratio of 1/3, it was difficult to get the pH up to 5.7 in order to oxidize the ferrous iron. A waste water solution having all ferric iron was successfully treated. Switching from the finer to the coarser limestone produced a 60 percent increase in filtration rate.

Summary

Laboratory experiments have been made to determine the parameters necessary to precipitate iron from a dilute hydrochloric acid pickling waste so as to obtain both a filterable sludge and water of acceptable quality.

In terms of filterability, the sludge produced by limestone treatment of dilute hydrochloric acid wastes is obviously superior to that produced by lime. The best sludge results from treatment of wastes containing no ferric iron; the difference is more dramatic in the case of limestone than with lime.

Conclusions

1. Limestone, in amounts up to 150 percent of the stoichiometric amount required, has been successfully used to produce a filterable sludge. Lime completely precipitates the iron but yields a sludge generally unsuitable for filtering.

2. Aeration and a minimum pH of 5.7 is necessary to oxidize ferrous iron and precipitate it as ferric hydroxide.

3. Optimum filtering characteristics are obtained if all of the iron is initially present as ferrous iron. This sludge has a specific gravity of 1.5 g/ml (21°C) and a viscosity of 2,200 cps at 20 rpm and 1,700 cps at 50 rpm. The settling rate is too fast to measure. Filtering rates of 114 lbs dry cake/sq ft/hr or 30 lbs iron/sq ft/hr have been achieved on a laboratory scale.

4. Minimum filtering rates are obtained if all of the iron is initially present as ferric iron.

5. The recirculation of sludge is necessary to produce an acceptable filtration rate.

6. A nonionic organic polymer at a concentration of about 1.5 mg/l is required as a flocculating aid.

7. A better sludge was produced at 100°F than at 120°F only when the iron was present in the ferric form.

8. A larger limestone particle size increases the rate of filtration only if all of the iron is initially present as ferric iron.

9. Total iron in the treated waste was less than 1.0 l/min.

Basis for Plant Design

Based on this investigation the following operations will be necessary for the treatment plant:

1. Aeration-Mix Tank - Dilute waste acid will enter the plant at this point, where it is reacted with a limestone slurry and previously precipitated ferric hydroxide in the form of settled sludge. Molecular oxygen is continuously introduced into the solution in the form of air. Retention time in this tank should be not less than 30 min.

2. Flocculating Tank - The mixture will flow to a second tank where flocculation takes place. Flocculating aid will be added at this point. Retention time should be at least 15 min, and slow mixing will be necessary.

3. Clarifier - The precipitate from the flocculating process will be permitted to settle in a clarifier. Means for returning a portion of the settled sludge to the aeration-mix tank will be provided.

4. Vacuum Filter - After settling, the sludge will be de-watered by filtration.

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APPENDIX B - DETAILED ENGINEERING REPORT & DRAWINGS

Introduction

The terminal treatment plant is designed to prevent stream pollution due to contaminated rinse waters from two new hydrochloric acid picklers.

The facility is designed to neutralize free acid, oxidize ferrous iron, then flocculate the resulting ferric hydroxide and separate it from the water in a clarifier. The process neutralizes 100 percent of the free acid and oxidizes essentially 100 percent of the ferrous iron, which is collected as ferric hydroxide sludge. This effectively solves the problem normally associated with hydrochloric acid rinse water (ARW).

General Description

ARW, including fume scrubber water, received at a maximum of 1,500 gpm (750 gpm per pickle line) is collected in one of two 12,000-gal. tanks, one adjacent to each pickle line. The tanks are interconnected to pumps which transfer the rinse waters through an overhead pipeline, approximately 1,300 ft long, to two 45,000-gal. surge tanks. These surge tanks are elevated to provide gravity flow through the treatment facilities.

The ARW then flows to an aeration-mix tank where limestone is added and air is blown through to effect oxidation. This neutralizes the free acid and reacts with the ferrous chloride which forms insoluble ferric hydroxide, when oxidized, and soluble calcium chloride. The ferric hydroxide and the insoluble limestone solids are then flocculated with turbine type flocculators and, with the addition of a flocculating aid, are agglomerated into a readily settleable mass which is subsequently separated in a clarifier.

The clarifier effluent flows to a 16-acre, 30-million gal. final lagoon which discharges to a public waterway. The ferric hydroxide sludge collected in the clarifier is pumped to rotary vacuum filters for de-watering. The filter cake is collected in gondola cars and is hauled away for storage. Clarifier sludge is also recirculated to the aeration-mix tank.

Two 230-SCFM air blowers, two cylindrical limestone storage bins with 60 deg conical bottoms, and two

flocculating aid dilution tanks with 2,400 gal. capacity each are required to support the above operation. Each flocculating aid dilution tank has suitable mixing equipment for dissolving the chemicals in water.

A storage area for a 30-day supply of flocculating aid is also provided.

Control

The influent line to the aeration-mix tank has a magnetic flow meter that measures the flow which is recorded in the control room. Influent pickle rinse water acid and iron tests are normally conducted each hour, and the chemical feeders are adjusted manually by the operator. Clarifier sludge rakes have a torque meter which indicates amount of sludge in the clarifier. ARW surge tanks, flocculating aid dilution tanks and limestone storage bins have level gauges.

All pumps are controlled manually. This includes the clarifier sludge recirculation pump and clarifier sludge pump to the vacuum filters.

Enclosure

The enclosure for the terminal treatment plant is 80 ft long and 70 ft wide. The enclosure contains the limestone storage and feed bins, flocculating aid dilution tanks, dry storage area, air blowers, and rotary vacuum filters.

MAJOR EQUIPMENT

Pickler Storage Tanks

One 12,000 gal. reinforced fiberglass storage tank is located at each of the two HCl picklers. Two 750-gpm pumps transfer the ARW from these storage tanks 1,300 ft in an overhead line to the surge tanks located at the terminal treatment plant.

Surge Tanks

Two 45,000-gal. reinforced fiberglass tanks provide equalization and surge capacity for the treatment plant. These tanks are elevated to provide gravity flow for the remainder of the system. These tanks are interconnected and have a manually operated valve so that flow through the plant may be regulated. They provide

a one-hour minimum retention time. Effluent from the surge tanks flows by gravity to the aeration-mix tank.

Aeration-Mix Tank

The aeration-mix tank is a 23 ft square by 15 ft high concrete walled tank with a 30-min minimum retention time. The aeration-mix tank has a 30-hp turbine-type aeration mixer designed to mix limestone and recirculated sludge into the waste water and maintain the suspension. Air is blown to the aeration mixer by a 25-hp blower capable of 230 SCFM to oxidize the iron from ferrous to ferric. Sludge is recirculated to the aeration-mix tank from the clarifier by an air-operated diaphragm-type pump capable of pumping 60 gpm. Effluent from the aeration-mix tank flows by gravity to the flocculation tank.

Limestone Storage Bins

The limestone is stored in one of two 75-ton capacity bins equipped with screw operated dry feed mechanisms. Each bin is 13 ft in diameter with 9-ft straight sides and a 60 deg conical bottom. Bins are filled by pneumatic piping from an outdoor truck loading station. The bins are equipped with a dust collector. The limestone is dry fed into a trough in which it is slurried with water from recirculated clarifier water. The slurry is then fed to the aeration-mix tank.

Flocculation Tank

The flocculation tank is 30 ft long, 16 ft wide, and 14 ft deep. It is concrete walled and has a design minimum retention time of 30 min. The tank is divided into two sections by a baffle in the middle of the tank. This extends from the surface down to 7 ft from the bottom of the tank and is designed to prevent stratification and short-circuiting in the flocculation tank. Two 5-hp, variable-speed turbine-type flocculators keep the floc particles in suspension.

Flocculating aid is added in the flocculation tank at the surface of the first half or the second half, or both halves of the tank. The flocculating aid is mixed in one of two 2,400-gal. steel solution tanks equipped with dispersion funnels and mixers. The flocculating aid is then fed to the flocculation tank by a 1-hp proportioning pump capable of 225 gal./hr.

Clarifier

The clarifier is a steel shell with sludge rake assembly. It has a diameter of 50 ft and a side water depth of 15 ft. At 1,500 gpm the rise rate is 0.8 gpm/sq ft. The clarified water flows to a final lagoon. The sludge is periodically filtered. Clarifier effluent water is provided to the terminal treatment plant as process water.

Vacuum Filters

Some of the sludge which settles in the clarifier is constantly recirculated to the aeration-mix tank. When necessary to filter sludge, it is pumped to one of two rotary vacuum belt-type filters by means of an air-operated diaphragm sludge pump capable of about 60 gpm. The filters are 6 ft in diameter and 6 ft long with filtrate receivers, filtrate pumps, and vacuum pumps with 30-hp motors. The filter cake drops into gondola cars and is hauled away for storage. The gondola cars can be moved limited distances within the immediate terminal treatment plant area by a car puller driven by a 10-hp motor.

Major Equipment

Three (3) transfer pumps for pumping ARW from the pickle lines to surge tanks, 750 gpm @ 100 feet TDH, 60-hp motor

Three (3) sump pumps, 75 gpm @ 40 feet TDH, 5-hp motor, at pickle line collection areas

Two (2) sump pumps, 75 gpm @ 70 feet TDH, 15-hp motors at terminal treatment plant

Two (2) ARW collection tanks, 12,000 gal. each, rubber-lined steel, at pickle line

Two (2) influent surge tanks, 45,000 gal. each, reinforced fiberglass, at terminal treatment plant

Two (2) limestone storage bins, 3-day supply (75 tons) each, 13 ft diameter with 9 ft straight sides and 60 deg cone bottom, with pneumatic piping from outdoor truck loading station

Two (2) limestone feeders, dry volumetric, 60 cu ft/hr

One (1) aeration mixer with gear reducer and 25-hp motor

Two (2) flocculators, turbine type, 5-hp motor

One (1) clarifier, 50 ft diameter by 15 ft side water depth, steel shell with sludge rake assembly, rated @ 0.8 gpm/sq ft for 1,500 gpm

Two (2) sludge pumps, air-operated diaphragm type, 60 gpm

Two (2) sludge filters, rotary vacuum belt-type, 6 ft diameter by 6 ft long drums, with filtrate receivers, filtrate pumps, and vacuum pumps with 30-hp motors

One (1) flocculating aid proportioning pump, 225 gal./hr, with 1-hp motor

Two (2) flocculating aid solution tanks, 2,400 gal. steel with agitators

Two (2) clarified water pumps, horizontal centrifugal, 200 gpm @ 200 feet TDH

One (1) car puller, with rope guides and return sheaves, with 10-hp motor

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