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DEVELOPMENT OF THE MAGNESIA PROCESS FOR THE
TREATMENT OF HIGHLY ALKALINE TEXTILE WASTES

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TREATMENT OF HIGHLY ALKALINE TEXTILE WASTES

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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	iv
LIST OF ILLUSTRATIONS	v
SUMMARY	vi
Chapter	
I. INTRODUCTION	1
II. LABORATORY INVESTIGATIONS	4
III. FIELD INVESTIGATIONS	10
IV. PILOT PLANT OPERATION AND MODIFICATION	20
V. CONCLUSIONS	34
VI. RECOMMENDATIONS	36
BIBLIOGRAPHY	37

LIST OF ILLUSTRATIONS

Figure	Page
1. Settling and Compacting of Sample of Coagulated Waste	6
2. Picture of the Pilot Plant	11
3. Flow Diagram of the Pilot Plant	12
4. Picture of Tank No. 3	13
5. Flow Diagram of the Pilot Plant After Modifications	24
6. Rapid Mixing Chamber	26
7. Pictures of Sedimentation Tank Before and After Modifications	28

LIST OF TABLES

Table	Page
1. Sludge Concentration	9
2. Lagoon Influent Temperatures	15
3. pH and Temperature Study of Lagoon Effluent	17
4. Temperatures Inside Sedimentation Tank During Continuous Operation	19
5. Clarification of Waste During Continuous Run	33

SUMMARY

Waste treatment has long been a problem to the textile industry. The main disadvantages of chemical methods of treating highly alkaline textile wastes are both the large amounts of coagulating chemicals required (and therefore the high costs of chemicals) and the large volumes of sludge formed that present a costly disposal problem.

The main purpose of this study is the development of an improved chemical process to treat highly alkaline textile wastes that allow reclamation of the coagulating chemical and produces a low volume of sludge for disposal.

Investigation of the use of magnesium chloride for the clarification of highly alkaline textile wastes was begun by O. E. Morgan (1) in the Spring of 1958, at Georgia Institute of Technology in Atlanta, and Dundee Mills in Griffin, Georgia. Because of the onset of freezing weather in the fall of 1958, studies were discontinued by Morgan, and the investigations were resumed by the author beginning in the spring of 1959.

In this process, a solution of magnesium chloride is added to the waste to form magnesium hydroxide floc. The floc which forms also contains the suspended solids or turbidity of the original waste. Most of the original suspended matter is starch. After sedimentation, a clarified supernatant forms the effluent of the treatment process.

The remainder of the process consists in reclaiming the magnesium ion for reuse as coagulating chemical. The settled floc sludge is removed to a separate tank where it is concentrated. After this, it is pumped to a reaction vessel where acid is added and the sludge solution

is brought to pH 6.6 - 7.0. The acid redissolves the magnesium ion in the sludge. The mixture is then settled and the magnesium bearing supernatant can be drawn off and reused; the original suspended solids settle out and are wasted. The cycle is completed.

Morgan reported considerable difficulty with the magnesium hydroxide floc rising to the surface of the sedimentation basin of the pilot plant and leaving with the effluent. Finding a solution to this problem, and adapting the process to continuous pilot plant operation were the objectives strived for in this research.

The results show that the process is adaptable to continuous pilot plant operation. The cost of chemicals for treatment was found to be \$50.00 per million gallons and the volume of final sludge produced for disposal was only 0.5 per cent of the total volume of waste treated.

The clarification of the waste obtained with the pilot plant was as follows: 27 per cent reduction in the Biochemical Oxygen Demand (BOD); 95 per cent turbidity removal; and 50 per cent color removal.

It is believed that by using sound engineering judgment, the results of this study may be projected into the design of a full size treatment unit.

CHAPTER I

INTRODUCTION

Out of the industrial expansion that has occurred during the past one hundred years has arisen the problem of obnoxious industrial wastes. In the early years of this expansion all liquid wastes were emptied into some convenient water course and little thought was given to the effect which these wastes might have upon the stream. As growth continued, new and varied uses of natural water courses developed, pollution increased, litigation arose, and the problem of treatment or purification of wastes was born (2).

The textile industry, like many other industries today, recognizes the importance of the proper use of water. This means having a good supply of pure water, using it, and returning it to the receiving stream in good condition for others to use in turn.

Some of the outstanding research on textile waste treatment was carried out by The Textile Foundation in the late 1920's. Some of the treatment methods that evolved include neutralization, coagulation and precipitation, equalization, and both chemical and biological oxidation. This work has not been surpassed in its basic concept for treating textile wastes, although the study did not investigate the treatment of highly alkaline textile wastes without pH adjustment (3).

The work that is presented in this study deals specifically with an economical chemical method for treating highly alkaline textile wastes without pH adjustment.

Costs of chemicals for chemical treatment of mixed textile mill wastes are reported by Souther and Alspough as \$390.00 per million gallons of waste treated using combinations of copperas and lime or alum and acid (4). One of the principal reasons for discontinuing chemical methods of treating textile wastes has been the high cost of chemicals. Morgan, however, reports that the cost of chemicals for treating bleachery wastes is \$30.00 per million gallons (5). Thus \$30.00 per million gallons of waste treated is only one-tenth of the cost of chemicals used earlier and is a reasonable cost for chemicals.

Another difficulty with chemical treatment of textile wastes is the large volume of sludge that is produced. The cost of sludge disposal is directly proportional to the volume produced. Present chemical textile waste treatment processes produce a sludge volume of about four per cent of the initial volume of waste treated (6). However, treatment using magnesium chloride produces a final sludge volume of only 0.5 per cent of the initial volume treated or one-eighth of the volume mentioned above.

A follow up of the investigations made by Morgan was undertaken by the author and is reported here.

The main difficulty encountered by Morgan was the problem of rising floc in the sedimentation chamber (7). He attributed the rising floc to poor design of the baffling system inside the main sedimentation tank and reasoned that this caused breaking up of the floc, allowing it to rise and flow out the effluent pipe. This reduced the treatment efficiency.

Investigation of this phenomenon, and striving for a solution to correct it, which would pave the way for adoption of the process to

continuous treatment methods, was the object of the work which was done in the laboratory and at the pilot plant site.

CHAPTER II

LABORATORY INVESTIGATIONS

Since the main problem with the process was that of rising floc in the sedimentation tank, laboratory investigations were carried out to learn more about the characteristics of the floc.

The floc that is formed upon the addition of magnesium chloride to the alkaline waste is primarily magnesium hydroxide. Calcium carbonate and magnesium hydroxide are also formed in the excess-lime treatment process for water softening. Calcium carbonate crystals are small, settle in tiny clusters, contain about 75 per cent water and have a net density of about 1.2. Magnesium hydroxide, $Mg(OH)_2$, forms a voluminous, flocculent, precipitate which contains water much like alum floc. Hence, when the excess-lime process is used the density of the floc mass will be less as the relative content of magnesium hydroxide is increased (8). Therefore, with a sludge that is primarily magnesium hydroxide floc the settling is poor.

Camp describes hindered settling thus: "The particles are so close together and so flocculent that they appear to settle as a blanket, all going down at about the same velocity at the start and leaving a clear supernatant above the top of the sludge blanket," and sludge compacting with, "The weight of the sludge accumulating above distorts and compresses the supporting particles, slowly squeezing the liquid out of the sludge in an upward direction" (9). These are exact descriptions of the conditions that prevail when magnesium chloride is added to the

alkaline waste forming magnesium hydroxide floc.

A sample of the waste was brought into the laboratory for settling observations. The sample of the waste was poured into a 12 liter carboy and precipitated with magnesium. The total depth of the liquid was 31 centimeters and the depth of the settling sludge blanket was measured over a period of three hours. The results of this investigation are shown in Figure 1. The first, straight portion of the curve represents the hindered settling rate which is 0.00093 feet per second (fps). The lower portion of the curve illustrates the sludge compaction rate. The sludge was stirred slightly at time equal to 40, 45, 60 and 75 minutes to simulate sludge collectors that would be a part of a full size treatment device.

The specific gravity of the sludge was determined by finding the optimum dosage of 20 per cent magnesium chloride for a sample of the waste using a standard jar test apparatus (10) and this optimum dosage was used to coagulate several liters of waste to produce a sufficient volume of sludge to perform the specific gravity test. The specific gravity was determined by comparing the weight of equal volumes of the sludge and distilled water. The specific gravity was found to be 1.002 (11). This compares with a specific gravity of 1.005 for activated sludge having a suspended solids content of 2000 parts per million, (ppm), (12).

It was believed that perhaps using mixtures of calcium chloride with magnesium chloride, or ferric chloride with magnesium chloride to coagulate the waste, would help weigh down the floc and increase the rate of settling. Along with the usual 20 per cent magnesium chloride solution

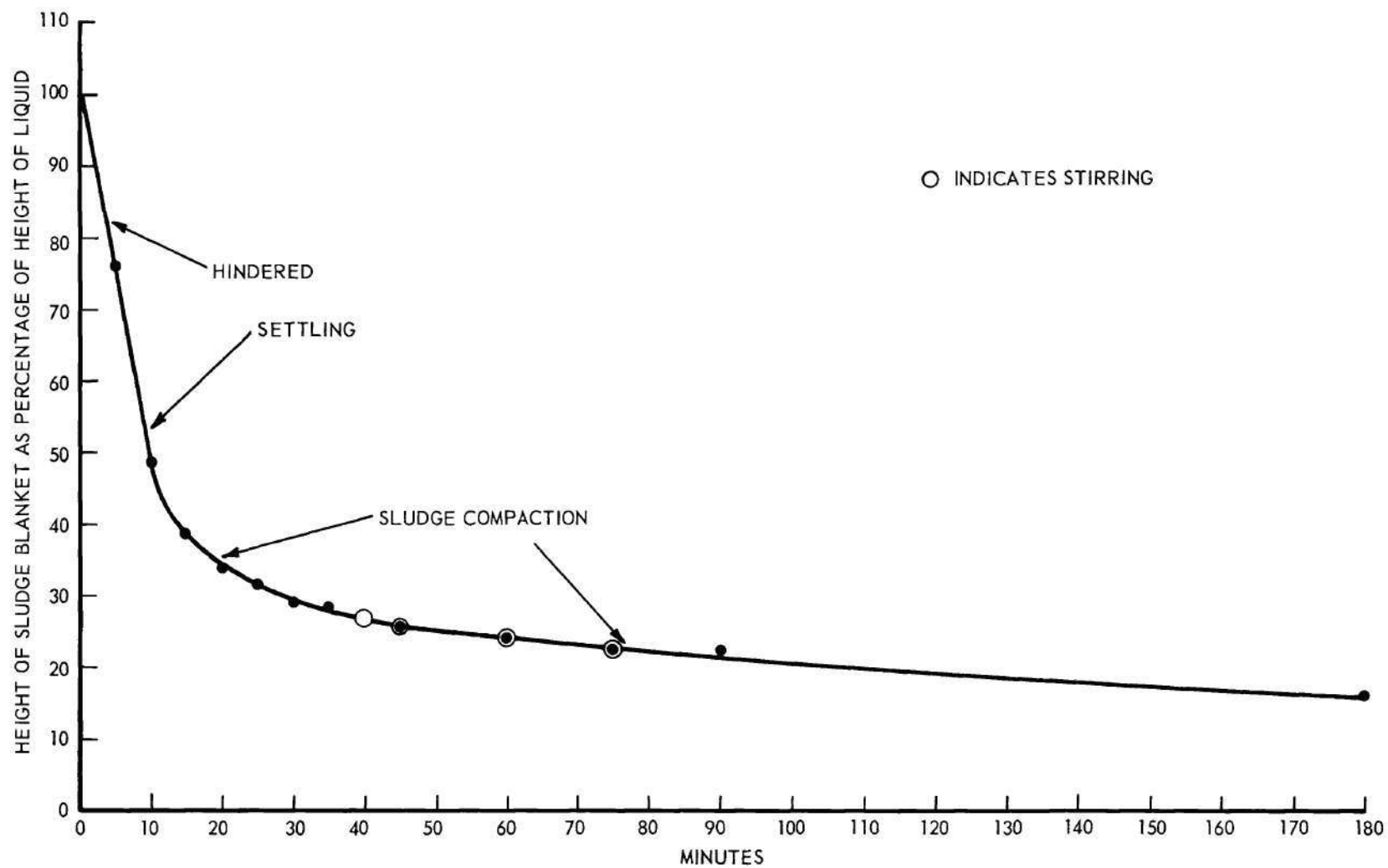


Figure 1. Settling and Compacting of Sample of Coagulated Waste.

that is used to treat the waste, enough 20 per cent calcium chloride solution was added to the original magnesium chloride solution to make up 20 per cent by volume of 20 per cent calcium chloride. It was hoped that the calcium chloride would react with the carbonates present in the waste, forming calcium carbonate in sufficient quantities to yield a higher density to the floc. Two liter graduates were filled with waste and one was dosed with magnesium chloride while the other was dosed with the mixture of magnesium and calcium chloride. No difference in the settling rates of the coagulated waste was noted in the two cylinders. Next, enough 20 per cent ferric chloride solution was added to the original magnesium chloride solution to make up 10 per cent by volume of ferric chloride, FeCl_3 . The procedure was repeated as above, and again, no difference in the settling rate was noticed between the two cylinders.

As a final laboratory investigation, the possibility of increasing settling and sludge thickening was investigated by using two commercial flocculating agents, Nalcolyte 110 and Separan 2610. These agents are described by the manufacturers as "synthetic organic water-soluble high molecular weight polymers for flocculating solids to improve settling and sludge thickening." If the rate of settling and/or sludge thickening could be increased by the addition of these agents, the resulting savings in size and cost of treatment units, and in acid required to neutralize the sludge could possibly compensate for the cost of the polymers.

A standard jar test apparatus was used to determine if the flocculating agents would be beneficial when added with magnesium chloride

to the raw waste. The optimum dose of magnesium chloride was added to each of the beakers; Nalcolyte 110 was added in concentrations of 1, 3 and 5 parts per million to three of the beakers; Separan 2610 was added in concentrations of 0.01, 0.08 and 0.15 parts per million to three more beakers, which left one beaker with only the magnesium dose for comparison as a blank. The samples were rapidly mixed for 5 minutes, slow mixed for 10 minutes and allowed to settle. No difference in the settling rates in the beakers containing either polyelectrolyte could be noticed from that of the blank.

Next, five liters of sludge were obtained by precipitating approximately 20 liters of waste with magnesium; allowing the sludge mass to settle and compact for one-half hour, and siphoning off the supernatant. One liter of this sludge was poured into each of five one-liter graduated cylinders. The first liter of sludge was retained for a blank and to each of the remaining four liters of sludge was added 2 parts per million and 5 parts per million Nalcolyte, 0.08 parts per million and 0.15 parts per million Separan, respectively. The samples were stirred at 1, 3 and 3.5 hours after the test was begun to simulate agitation that would be received in a treatment plant. The results of this investigation are reported in Table 1, and show a 12 per cent reduction in sludge volume after four hours. Due to limited time, an exhaustive study was not possible, but the use of flocculating agents for sludge concentration does show some promise and should be further investigated.

Table 1. Sludge Concentration Results

Dose	Milliliters Sludge Remaining				
	Blank	Nalcolyte		Separan	
		2 (ppm)	5 (ppm)	0.08 (ppm)	0.15 (ppm)
Time (hrs)					
0	1000	1000	1000	1000	1000
3	750	730	660	680	660
4	650	600	570	580	570
24	310	300	290	300	290

CHAPTER III

FIELD INVESTIGATIONS

The textile waste that is discharged from Dundee Mills in Griffin, Georgia, is piped to a lagoon at the rear of the mill. This waste enters the lagoon at about 45 degrees centigrade. The waste is very turbid and highly colored, the color varying as different batches of dye are dumped. The influent to the lagoon has an average BOD of 900 ppm, pH of 10.8 - 11.0, and total solids 2000 - 3000 ppm.

The waste is pumped from the lagoon to the pilot plant and enters the pilot plant at Tank No. 1 (Figure 3). The waste enters the center tube, the mixing zone, and is mixed with a solution of dissolved magnesium that is pumped from Tank No. 5 (Figure 3) by one side of a dual chemical feed pump. The magnesium solution and the raw waste is thoroughly mixed by the rotation of the mixing shaft and blades. After mixing and flocculation, the magnesium-sludge floc settles in the outer compartment of Tank No. 1 and the clarified waste discharges out the overflow pipe.

The magnesium-sludge floc is withdrawn from Tank No. 1 into Tank No. 2 by means of a quick-opening valve. The sludge is allowed to concentrate in Tank No. 2. The concentrated sludge is pumped from the bottom of Tank No. 2 to Tank No. 3 through a constant head orifice that discharges at a rate of 1.0 - 1.5 gallons per minute. This constant head orifice is shown in Figure 4.

Sulfuric acid is fed to the sludge in Tank No. 3 by the other side of the dual chemical feed pump. The acid and sludge are thoroughly mixed

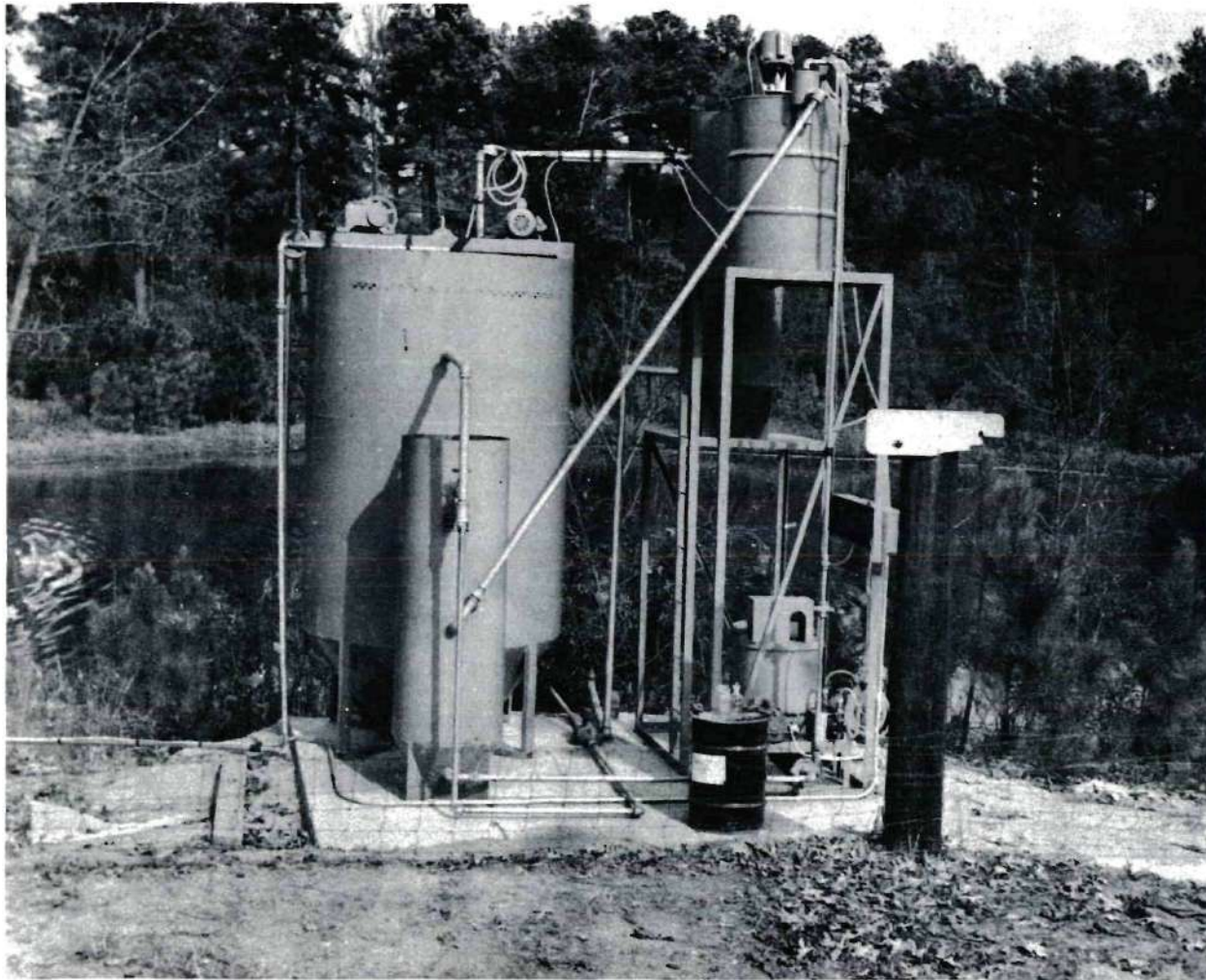


Figure 2. Picture of the Pilot Plant.

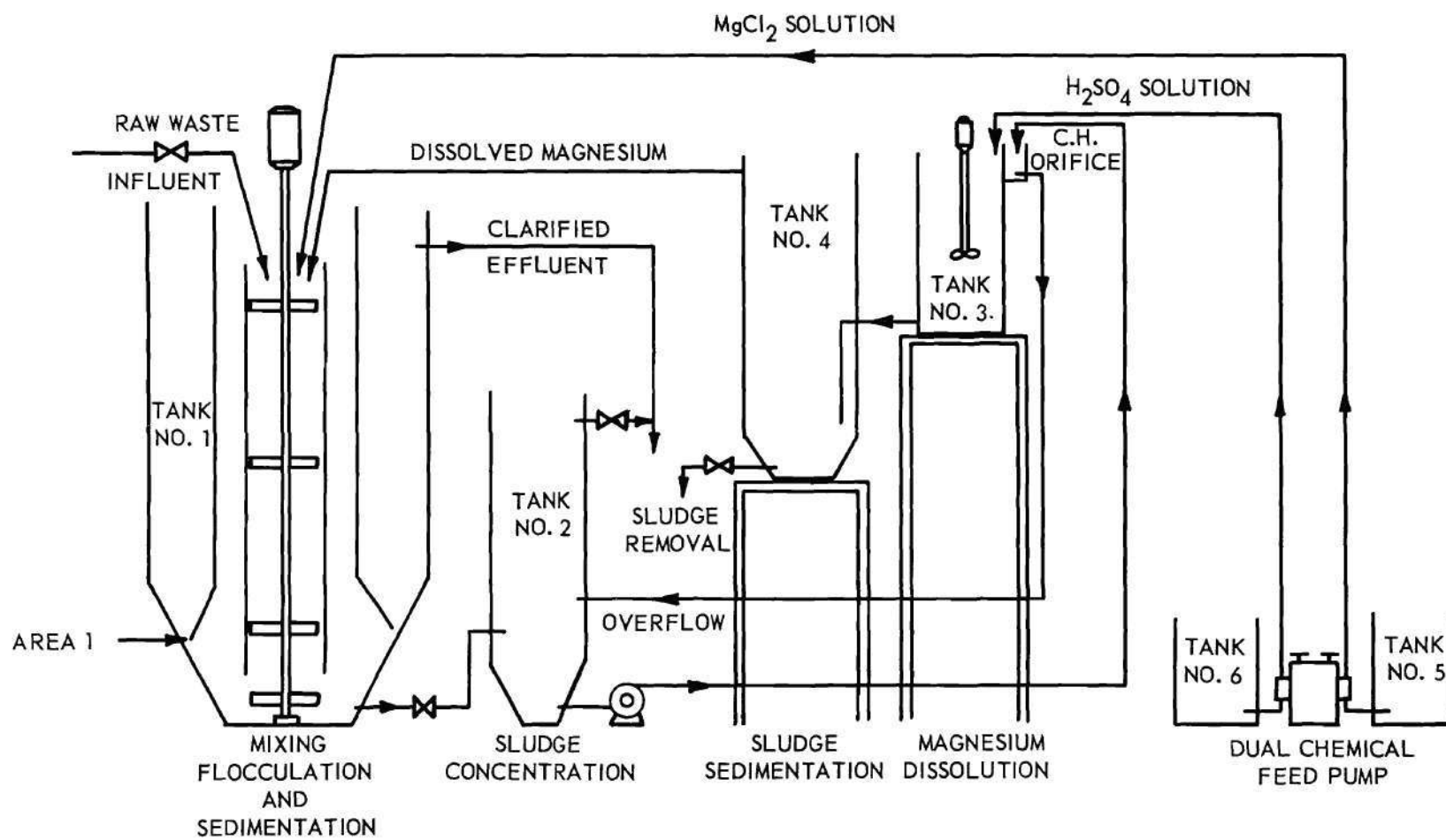


Figure 3. Flow Diagram of the Pilot Plant.

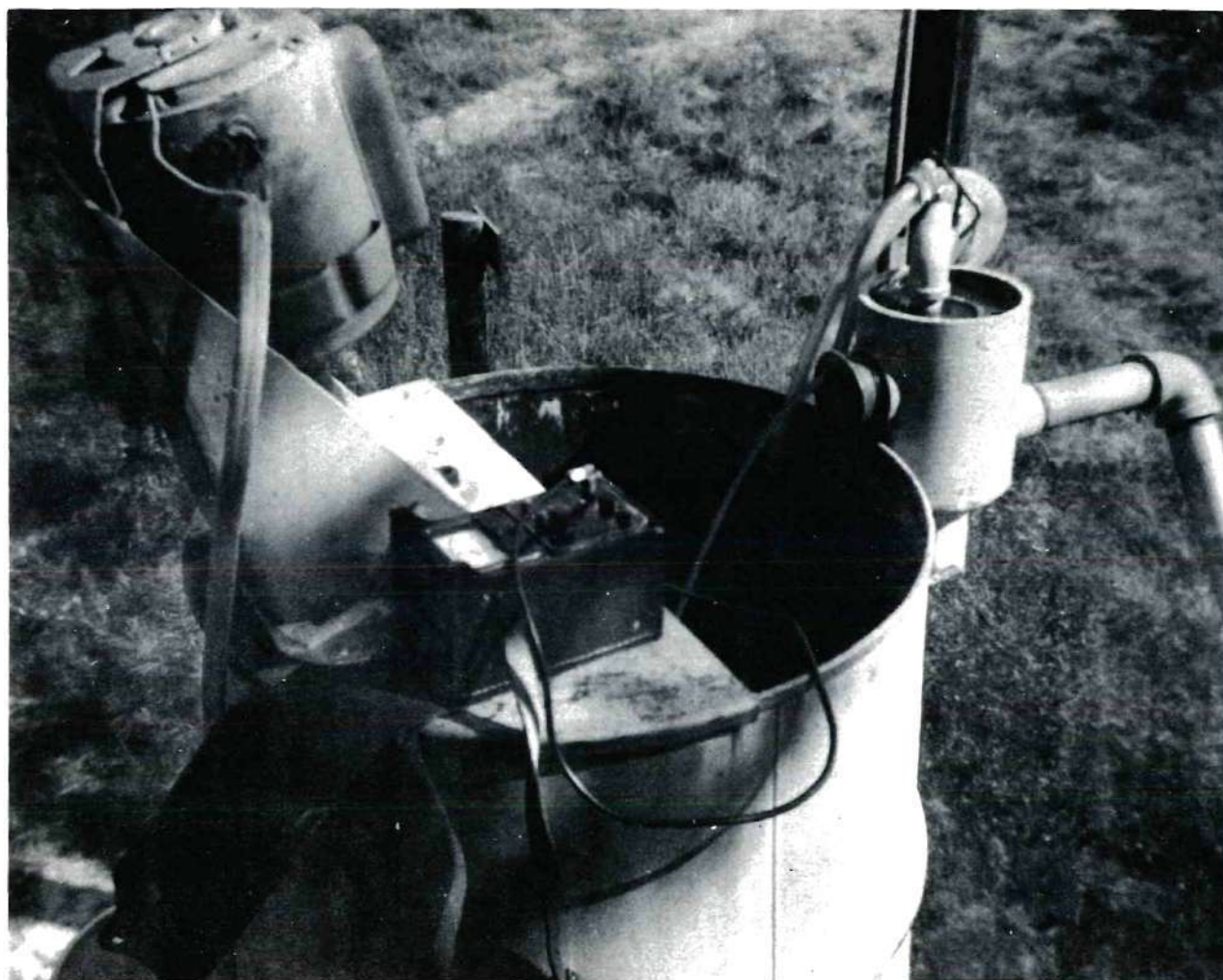


Figure 4. Picture of Tank No. 3.

by a stirrer which dissolves the magnesium hydroxide out of the sludge and leaves the insoluble material that was removed from the original waste. The resulting mixture of dissolved magnesium and insoluble material flows by gravity into Tank No. 4 (Figure 3).

In Tank No. 4 the magnesium bearing supernatant and the insoluble material are separated by sedimentation. The magnesium bearing supernatant flows by gravity back to Tank No. 1 (Figure 3) and precipitates more incoming alkaline waste and thus the cycle is completed. The insoluble material that settles in Tank No. 4 forms the final sludge of the process.

It was decided that perhaps temperature differences, and therefore density differences, could be the disturbing element in the sedimentation tank that was witnessed by Morgan (13). If a liquid of high temperature (low density) enters a tank of liquid at low temperature (high density) the warmer liquid will rise to the surface of the tank due to the differences in density of the two liquids, thereby causing short-circuiting and sludge rising.

The influent pump for the pilot plant was located at the point where the mill wastes enter the lagoon. Any sharp differences in the temperature of the waste entering the lagoon would be picked up by the influent pump and delivered to the pilot plant. A brief temperature survey of the waste entering the lagoon was made, the results of which are given in Table 2. A maximum of 5.7 degrees centigrade difference was recorded; the temperature of the waste being 42.2 degrees centigrade at 2:40 PM and rising to 47.9 degrees centigrade at 3:17 PM. This represents

Table 2. Lagoon Influent Temperatures

<u>Time</u>	<u>Temperature (°C)</u>
2:05	42.5
2:10	42.8
2:15	42.7
2:18	44.0
2:20	44.2
2:23	43.5
2:25	44.0
2:30	43.7
2:33	43.1
2:35	42.8
2:40	42.2
2:43	43.1
2:45	43.9
2:50	44.2
2:53	44.8
2:55	45.1
3:00	45.1
3:02	45.8
3:03	46.0
3:05	46.0
3:10	46.0
3:14	46.5
3:15	47.0
3:17	47.9
3:20	47.5
3:22	47.0
3:25	46.1
3:28	45.5
3:30	45.5
3:35	45.3

approximately a 0.25 per cent change in density which is considered sufficient to interfere with sedimentation and perhaps cause the floc to rise.

A new location for the pilot plant influent pump was sought and a position near the lagoon effluent structure seemed to be a logical place for the pump.

A temperature survey was conducted at the lagoon effluent structure to determine the changes of temperature with time at that point. First, the temperature was studied inside the effluent structure which draws waste from the bottom of the lagoon. The temperature of the effluent was fairly constant (Table 3) with a maximum difference observed of 0.5 degrees centigrade; however, the temperature of the lagoon effluent was about 15 degrees centigrade lower than the lagoon influent, with a slightly lower pH. The pH of the lagoon influent averages 10.8 whereas the lagoon effluent averages pH 10.4. This sampling was done on a Monday of the week and it is known that later on in the week the pH and temperature of the lagoon effluent do rise considerably.

The temperature and pH study was also made over the side of the lagoon effluent structure on the surface of the lagoon. The results in Table 3 show a maximum temperature difference of 0.3 degrees centigrade for the one hour observation period.

It was then believed that moving the pilot plant influent pump nearer the lagoon effluent structure would be especially beneficial to the operation and efficiency of the treatment process. With the help of personnel from the mill, the pump was moved to a location near the lagoon effluent structure.

Table 3. pH and Temperature Study of Lagoon Effluent

<u>Time</u>	<u>Temperature</u> (°C)	<u>pH</u>
12:30	32.2	10.4
12:35	30.2	
12:40	30.3	10.4
12:45	30.4	
12:50	30.5	10.5
12:55	30.6	
1:00	30.6	10.5
1:05	30.7	
1:15	30.6	
1:20	30.6	10.4
1:25	30.6	
1:30	30.5	10.5
1:35	30.6	
1:40	30.5	10.5
1:45	30.5	
1:50	30.5	10.5
1:55	30.5	
2:00	30.5	10.4
2:05	30.6	
2:10	30.7	10.5
2:15	30.6	
2:20	30.7	10.5
Above results obtained inside effluent structure. Below, over the side of effluent structure on the surface of the lagoon.		
2:30	42.0	11.0
2:35	41.8	
2:40	41.8	10.8
2:45	41.9	
2:50	42.0	10.8
2:55	42.1	
3:00	42.1	10.8
3:05	42.0	
3:10	42.0	10.8
3:15	42.0	
3:20	41.9	10.8
3:25	41.9	
3:30	41.8	10.8

Next, a temperature survey was made of the actual temperatures inside the sedimentation tank with the pump delivering from its new location. The pump was started up and the flow was adjusted to ten gallons per minute and allowed to run all night. Upon arrival the next morning, it was found that the flow had subsided to about one gallon per minute due to partial clogging of the unattended influent line valve. The flow was readjusted to five gallons per minute, magnesium chloride was fed at 750 parts per million, and sludge was withdrawn continuously using the sludge concentration tank as a secondary sedimentation basin. After about four hours of continuous operation floc was rising in the sedimentation tank. At this time, temperatures were taken inside the sedimentation zone and the mixing zone, using a Tele-thermometer with a 10 foot lead, and are reported in Table 4.

From Table 4 it can be seen that no significant differences in temperature were found and those recorded calculate to only 0.046 per cent maximum density difference. Therefore, with the pilot plant influent pump located in its position near the lagoon effluent, temperature differences could be ruled out as a major cause of sludge rising during continuous operation.

Table 4. Temperatures Inside Sedimentation Tank
During Continuous Operation

Settling Zone Temperatures		Mixing Zone Temperatures	
<u>Depth (ft)</u>	<u>°C</u>	<u>Depth (ft)</u>	<u>°C</u>
surface	38.7	surface	39.9(infl.)
1	38.8	1	39.6
2	38.8	2	39.6
3	38.8	3	39.6
4	38.8	4	39.6
5	38.8	5	39.5
6	39.2	6	39.3
7	39.3	7	39.3
bottom	38.7	bottom	39.2

CHAPTER IV

PILOT PLANT OPERATION AND MODIFICATION

The pilot plant operation was begun for the primary purpose of determining and correcting the cause of the rising floc and to attempt to adapt the process to continuous treatment.

Upon study of the plan of the sedimentation tank, it was noticed that the mixer had a blade on the bottom of the shaft that would tend to disturb and break up the settling sludge if the mixer were used while the pilot plant was in operation. (See Figure 3) The reason for the bottom blade in the first place was as follows: the pilot plant sedimentation tank was originally designed to operate as a high rate water softening and clarification treatment unit, but because of the troubles encountered with rising floc and the extreme lightness of the floc, the unit was operated as a straight sedimentation device for our purposes.

The pilot plant was started up at five gallons per minute and the mixer was used without the bottom blade attached. Sludge was withdrawn continuously using the sludge concentration tank as a secondary sedimentation basin, and the clarified effluent from both tanks was allowed to flow out the effluent pipe. The dosage used was 700 parts per million of magnesium chloride. This dosage was determined from a jar test performed in the field prior to starting the unit.

In about one-half hour floc began to rise in the sedimentation zone of Tank No. 1, Figure 3. The unit was left in operation in hopes that an equilibrium would be reached and the floc would subside, but floc continued to rise. A fair degree of clarification was achieved and could be

readily noticed when samples of the effluent from the pilot plant were compared with samples of the influent.

Clouds of rising floc appeared in the supernatant zone. Thus, a heavier concentration of floc was noticed in different places in the sedimentation zone from time to time. This caused a marked deterioration in the quality of the effluent.

Construction of a constant head device with an orifice discharge was used to regulate the influent to the pilot plant at low rates of flow (two gallons per minute). It was reasoned that if the process would work on a batch basis, as found by Morgan, perhaps there must be some minimum flow at which continuous operation would be successful.

The head box was installed and the pilot plant was started up from an empty condition at 2.6 gallons per minute at 11:30 AM. As soon as the liquid was visible, rising in the sedimentation zone, the author climbed down into the treatment unit for a close observation of the floc. The floc was voluminous and present throughout the liquid rising in the sedimentation zone. The floc particles were constantly on the move, slowly moving up, down, and sideways throughout the surrounding clarified liquid. As the liquid rose higher in the sedimentation zone the floc particles became smaller and less concentrated in the clarified liquid.

The theoretical detention period at 2.6 gallons per minute is 7.5 hours. Periodic sludge withdrawal was used to reduce the total volume of sludge in the unit. After 9:00 PM the unit had filled, good clarification was observed, but again a small amount of floc was distributed throughout the sedimentation zone and passed out with the effluent of the pilot plant.

The unit was shut down but the tanks were not drained. Upon arrival the next morning, all the floc had settled and the bottom of the tank with its accumulation of sludge was clearly visible through six feet of clarified waste.

Another alternative method of operation of the pilot plant was tried. The unit was started up from an empty condition and allowed to run all night at three gallons per minute without withdrawing any sludge. The sludge was allowed to build up purposely in an effort to use the accumulated sludge as a filter for the incoming coagulated, flocculated waste. Upon arrival the next morning, the sedimentation zone had filled with sludge just below the half-way mark and the floc was rising as usual. As the sludge built up higher and higher, the floc became more concentrated in the effluent, and this method of treatment was considered ineffective as a solution to the problem of rising floc.

Next, all the tanks of the pilot plant were drained and the unit was started at five gallons per minute, feeding 750 parts per million magnesium chloride. Sludge was continuously withdrawn at 1.5 gallons per minute, and allowed to go to waste without returning any sludge to the sludge concentration tank.

As the liquid level rose in the sedimentation zone, very little rising floc was observed. After about five hours the sedimentation tank had filled and very little floc was lost with the effluent. Operation was continued for another hour. An insignificant amount of floc was noticed in the effluent. It is believed that this successful run occurred because temperature differences inside the sedimentation tank were

minimized by starting the run with the sedimentation tank empty. Thus, only hot wastes were present in the tank during this operation. A minimum volume of sludge in the sedimentation tank was maintained in the sedimentation zone by the constant withdrawal of the sludge. This prevented the sludge from accumulating above the cone shaped baffle in the sedimentation tank (Figure 3). When the sludge was allowed to accumulate beyond this baffle, all incoming waste had to flow through this layer in order to reach the effluent pipe. This caused the light, magnesium hydroxide floc to be carried upward to the effluent discharge.

At this time it was decided that several major modifications should be made in the structure of the pilot plant to increase the efficiency of operation. The entire outer cone shaped baffle was removed from Tank No. 1 to eliminate the dead space occupied by this baffle (Figure 3). The bottom 18 inches of the inner baffle was cut off. From Figure 5 it can be seen that with the outer baffle removed no zone of high velocity can occur beyond the discharge of the inner flocculating tube. With throughput equal to five gallons per minute, the rising velocity at Area 1, Figure 3, was 0.00374 feet per second. This velocity is four times the hindered settling rate for the floc of 0.00093 feet per second. The rising velocity at Area 2, as shown in Figure 5, at five gallons per minute flow will be 0.00066 feet per second, which is lower than the hindered settling rate. Therefore, with the above modifications, velocities were decreased to an extent that allowed more effective sedimentation.

Next, the mixing shaft was removed and the three pitched blades on the shaft were replaced by two vertical paddles to reduce their contribution to disturbance of the sludge layer. The pitched blades induced

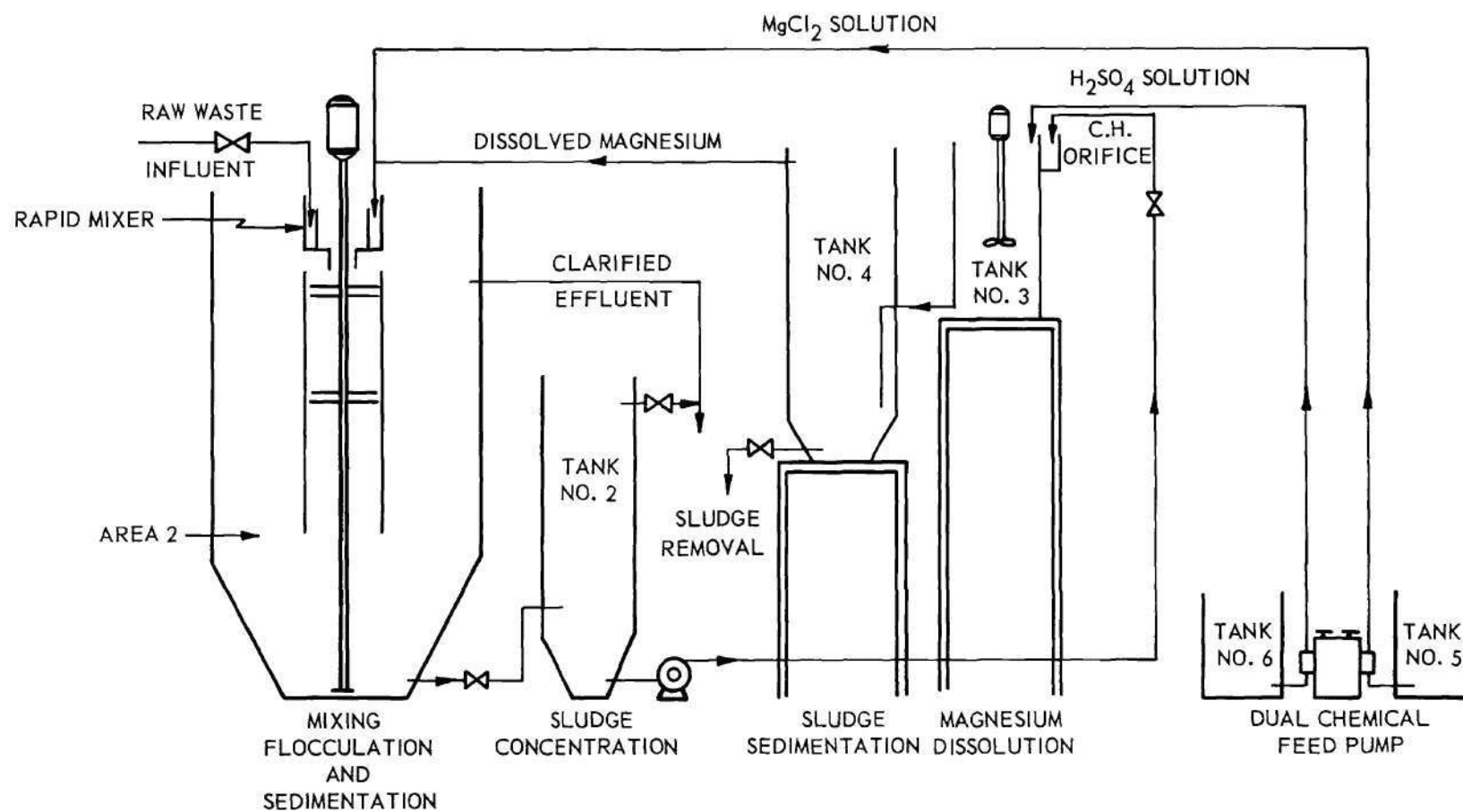


Figure 5. Flow Diagram of the Pilot Plant After Modifications.

either an updraft or a downdraft in the mixing zone, according to the direction of rotation. The speed of the mixing shaft was reduced to seven revolutions per minute to give a gentle mixing and flocculation action in the center draft tube.

Because of the reduced agitation in the center tube a rapid mixing chamber was purchased (Figure 6). The orifice on the raw waste discharge line imparts circular motion to the liquid in the mixer, thereby providing the mixing action. The rapid mixer provides for complete chemical reaction. The waste would then flow into the mixing chamber for slow stirring and flocculation, as discussed above. (Figure 5).

Finally, a valve was installed between the sludge return pump and the constant head orifice; a plug was placed in the sludge return line to prevent the return of the excess sludge from the constant head orifice to the sludge concentration tank. The valve adjusted the flow into the constant head orifice to the rate of discharge from the constant head orifice. Quiescent conditions in the sludge concentration tank are essential for its proper functioning. The flow diagram of the pilot plant after modifications is shown in Figure 5.

With the above modifications complete the pilot plant was placed in continuous operation. The first step was calibration of the orifice on the raw waste influent line (Figure 6). During the calibration, a sample of the rapid mix effluent was caught in a quart jar and allowed to stand for observation. The floc rose to the surface of the liquid instead of settling as expected. The extremely high velocity of the jet from the orifice caused such agitation that foaming developed because

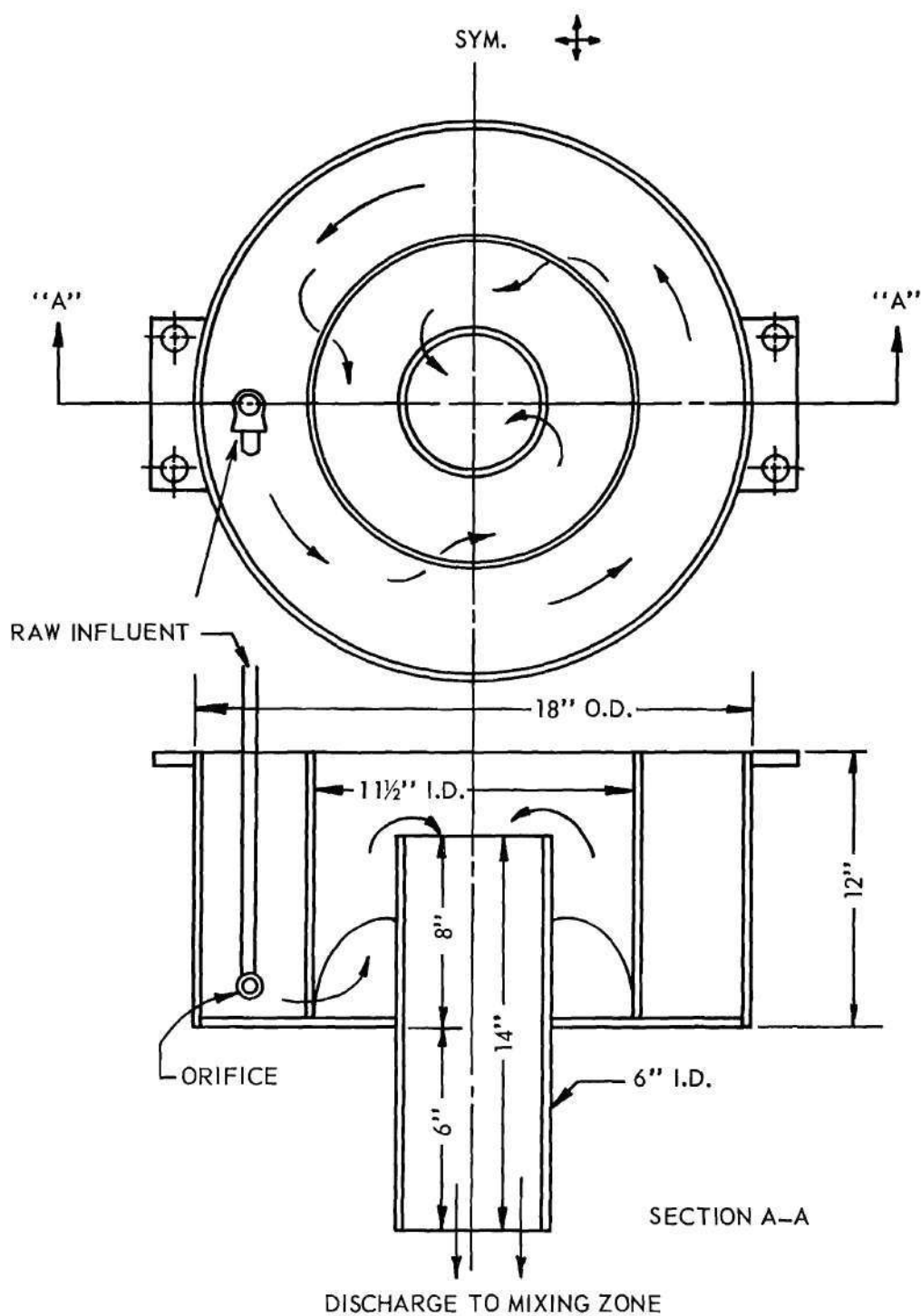
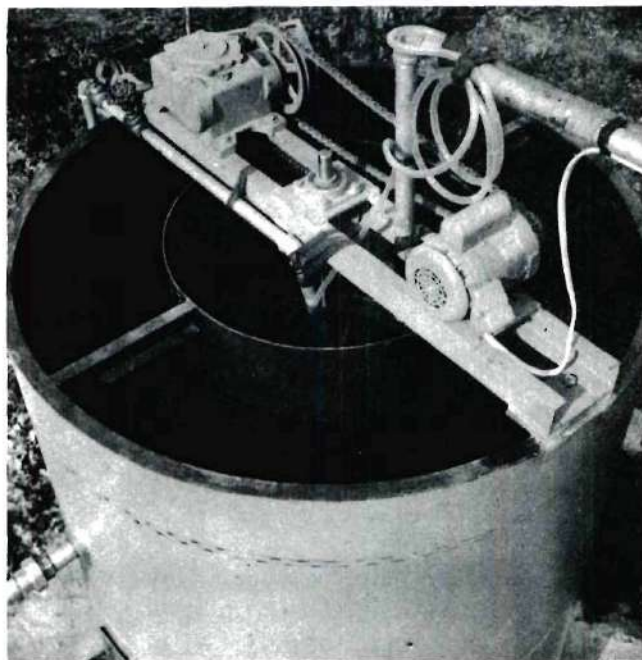


Figure 6. Rapid Mixing Chamber.

of the detergents in the waste. The floc was buoyed by the formation of air bubbles. This phenomenon of sludge flotation was highly undesirable because there was no means of handling floating sludge. The orifice was replaced by a piece of garden hose that was narrowed down at the tip to about three-eighths of an inch diameter. This "orifice" provided adequate circular motion in the mixing chamber but did not produce sludge flotation.

The pilot plant was started at a rate of five gallons per minute feeding 750 parts per million magnesium chloride in order to build up enough sludge to pump to the acid neutralization tank. After enough sludge had built up, the sludge was pumped to the acid neutralization tank, and acid was fed to bring the pH of the sludge to pH 7.0. The effluent from this operation flowed into Tank No. 4, Figure 5, where the final sludge was separated from the magnesium bearing supernatant. The process of filling all tanks in preparation for continuous full cycle treatment of the waste took two days because of the time required to build up sludge, shut down to allow sludge to concentrate, pump sludge to the acid neutralization tank, and fill Tank No. 4 to the level that would return magnesium bearing supernatant.

When all tanks had been filled, the pilot plant was placed in continuous operation at five gallons per minute. The makeup magnesium was adjusted to feed 125 parts per million magnesium chloride and sludge was withdrawn at 1.0 gallons per minute to provide the balance of needed magnesium by reclamation. After one-half hour, sludge began to rise and the pilot plant had to be shut down. At this point it looked as though



BEFORE



AFTER

Figure 7. Pictures of Sedimentation Tank Before and After Modifications.

all modifications had been made in vain and the process could be workable only on a batch operated basis. But it was remembered that it took two days to fill all tanks in preparation for continuous treatment and subsequently all the liquid in the sedimentation tank had cooled to the ambient air temperature. The incoming coagulated waste was relatively hot and as this liquid passed through the mixing zone and was discharged into the surrounding cool liquid in the sedimentation zone, density differences buoyed the floc to the surface of the tank. It was undesirable to drain the sedimentation tank because much of the accumulated magnesium hydroxide sludge would be lost, and loss of this sludge would interfere with the determination of cost of treatment because of the accompanying loss of returnable magnesium ion. The cool, clarified waste in the sedimentation tank was siphoned off overnight, using a long piece of garden hose, to a point just above the accumulated sludge level. The next morning the pilot plant was again started at five gallons per minute. Temperature differences were kept to a minimum because only hot coagulated waste was entering the sedimentation tank and the cooler sludge that was left after siphoning, was withdrawn as soon as possible.

Again the pilot plant was operated at five gallons per minute, feeding 125 parts per million make-up magnesium chloride and withdrawing 1.5 gallons per minute sludge for recycling. As the liquid level rose in the sedimentation basin rising floc was not visible. After three and one-half hours the sedimentation tank had filled and still no rising floc was visible. Sludge was continuously withdrawn at 1.5 gallons per minute and recycled.

Because it was hoped that this continuous run would be successful, as it was, careful records were kept with regard to total number of gallons of waste treated and amount of chemicals used so that a chemical cost estimate could be developed.

After about six hours of continuous treatment only a very insignificant amount of floc could be observed rising in the sedimentation zone. The pilot plant was shut down and the run was considered successful. A total of 3,157 gallons of waste were treated in the run. The average make-up magnesium chloride dose was 125 parts per million and the average acid dose was 290 parts per million for the run. From this information the cost of chemicals was computed. The prices of the chemicals were taken from Chemical News, June, 1959 edition and are F.O.B. place of manufacture. For magnesium chloride, at an average dose of 125 parts per million, the cost is \$26.00 per million gallons and for sulfuric acid, at an average dose of 290 parts per million, the cost is \$24.30 per million gallons, for a total chemical cost of about \$50.00 per million gallons. This cost is only slightly higher than the \$30.00 per million gallons previously reported by Morgan (14).

At this point, a discussion of the performance of each individual unit during the successful run would be useful and appropriate.

With temperature differences kept to a minimum, the sedimentation tank performed satisfactorily. The detention time in the rapid mixer was about one minute with five gallons per minute raw waste plus 1.5 gallons per minute return magnesium as the influent flow, and proved to be adequate. The detention time in the flocculation zone was 15 minutes under the above

conditions, while the total detention time in the sedimentation tank was four hours. The surface loading approximates 420 gallons per day per square foot of tank surface. This surface loading is low, when compared to some recommended values of 1200 gallons per day per square foot of tank surface for activated sludge, which has similar settling characteristics to magnesium chloride floc (15). In a full size treatment plant a carefully designed longitudinal flow sedimentation basin would be more suitable for the conditions of hindered settling and high temperatures which prevail with this waste.

The theoretical detention time in Tank No. 2, the sludge concentration tank, was 52 minutes at 1.5 gallons per minute flow. (The rate at which sludge was continuously withdrawn.) However, this detention time was never achieved because of the poor design of the tank. The influent pipe was located too near the effluent pipe of the tank and as a result the influent flow caused turbulence and short circuiting to the effluent pipe. Actual detention time was practically zero.

Figure 4 is a picture of Tank No. 3 showing the constant head orifice, mixer motor and portable pH meter used to check the pH of the acid-sludge mixture. This tank functioned well except for the fact that the pH was difficult to control. The amount of acid required to neutralize the sludge depends upon the concentration of the sludge which varied considerably during operation. In a full size treatment plant automatic pH control would eliminate this difficulty.

Tank No. 4, with a theoretical detention time of 52 minutes at 1.5 gallons per minute flow, did not operate as efficiently as was desired.

During continuous operation, particles of starch were observed returning along with the magnesium bearing supernatant that was to be mixed with the raw waste. This again was caused by the poor design of Tank No. 4. The effluent from Tank No. 3 entered the lower part of Tank No. 4 and caused sufficient turbulence to put the small light particles of starch in suspension. A grab sample of the supernatant was obtained and allowed to stand. The starch particles settled completely in about one hour; this proves that the particles will settle under suitable conditions. During the 3,157 gallon run, 15 gallons of final sludge was withdrawn from Tank No. 4 to waste. This means that about 0.5 per cent of the volume of waste treated ends up as waste sludge that must be disposed of by anaerobic biological digestion or some other suitable method.

During the continuous run, several samples were taken of the influent to the pilot plant and the effluent from the plant. The amount of clarification of the waste was obtained by determining the Biochemical Oxygen Demand removal, turbidity removal and color reduction. These results are reported in Table 5.

The biochemical Oxygen Demand of the raw waste was previously reported by Morgan as averaging about 900 parts per million but it must be remembered that at that time the influent pump to the pilot plant (from which the raw samples were taken) was located at the point where the mill wastes enter the lagoon (16). The pilot plant influent pump had since been moved to a point near the lagoon effluent structure. The analyses of the raw waste samples, which were taken from this new position are the ones that appear in Table 5. Therefore, there are indications that considerable Biochemical Oxygen Demand reduction is obtained by the lagoon itself from the time the waste enters the lagoon until it leaves the lagoon.

Table 5. Clarification of Waste During Continuous Run

<u>Test</u>	<u>Raw Influent</u> (PPM)	<u>Treated Effluent</u> (PPM)	<u>Reduction</u> (%)	<u>Average Reduction</u> (%)
BOD	240	180	25	
BOD	250	200	20	
BOD	270	168	37	
BOD	230	170	26	27
Turbidity Removal (Relative)				95
Color Removal (Relative)				50

CHAPTER V

CONCLUSIONS

Due to limited time, only one successful run was made with the pilot plant. However, the author feels that the experience gained from this run and the preceding unsuccessful runs, is sound enough basis for the following conclusions:

1. The magnesia process is an economical chemical method of treating highly alkaline textile wastes with a cost of \$30.00 - \$50.00 per million gallons.

2. Consideration must be given to the lightness of the floc, the characteristic hindered settling of the floc, and the high temperature of the waste in a full size treatment plant design.

3. The magnesium hydroxide floc that is formed in the process is light and voluminous, and has settling characteristics similar to activated sludge.

4. Mixtures of ferric chloride and magnesium chloride, calcium chloride and magnesium chloride and commercial flocculating agents and magnesium chloride did not aid the settling rates of primary sedimentation.

5. Limited tests indicate that commercial flocculating agents are beneficial to sludge compaction rates. Intermittant stirring is also helpful.

6. Successful continuous treatment with the pilot plant depended upon minimizing temperature differences, maintaining a quiescent sludge zone and keeping a low sludge volume in the sedimentation tank.

7. The sludge blanket filtration principle did not improve efficiency of operation in the pilot plant.

8. The magnesia process may well be an excellent method of reducing the high organic load contained in the mill waste and preparing this waste for disposal to a river.

CHAPTER VI

RECOMMENDATIONS

Investigations should be carried further with regard to the following recommendations:

1. Model studies should be made using a horizontal flow settling tank to determine optimum design dimensions and if sufficient sludge compaction can be achieved to eliminate the necessity of a sludge concentration tank.
2. Further studies should be made with commercial flocculating agents to evaluate their usefulness in sludge compaction.
3. An alternate method of magnesium reclamation should be studied. This method would consist of subjecting the compacted magnesium hydroxide-sludge mixture to biological total oxidation by using the activated sludge process. In the total oxidation activated sludge tank, the organics in the sludge would be oxidized to carbon dioxide and water; the carbon dioxide formed would neutralize the influent sludge to pH 7.0 redissolving the magnesium ion.
4. If flue gas is available the possibility of its use should be investigated in the design of a full size treatment plant to minimize acid costs.

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