CRYSTAL SEEDING FOR THE CONTROL OF SLUDGE PROPERTIES

by

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I. INTRODUCTION AND OBJECTIVES

Numerous industrial processes, including steel manufacture, munitions industries, chemical industries, and oil refineries, utilize acid solutions in various steps of their manufacturing processes. As these solutions are recycled through the process they acquire foreign materials which interfere with the intended action of the acids. When this occurs it becomes necessary to replace the contaminated acid with a fresh solution. Since it is often uneconomical to recover the contaminates or the acid it becomes necessary to discharge the solution as waste. The majority of acids used for these processes are either hydrochloric, nitric or sulfuric acid with sulfuric composing about 90 percent of all acids so used.

The discharge of unneutralized acid waste to sewers, rivers or streams is undesirable because of the harmful effects which the acid has upon the chemical and biological characteristics of the receiving waters. These effects include such things as killing of fish and other aquatic life in streams and rivers; corrosion of sewers, bridges and boats; and interference with biological sewage treatment processes.

There are many acceptable methods for neutralizing acid waste; however, the use of lime, since it is readily available,

relatively inexpensive and highly effective, is the most common method. A disadvantage in using lime for sulfuric acid neutralization is the precipitation of calcium sulfate which creates a sludge disposal problem. Current methods of collecting and dewatering this sludge include sedimentation, vacuum filtration and lagooning. The increasing amount of waste being discharged from industrial plants and the increasing shortage of land area have made sedimentation and lagooning less attractive as treatment methods. However, vacuum filtration, since it can be designed in compact units to handle large volumes of waste, appears to be gaining in popularity. Since disposal of the sludge, in the form of filter cake, following vacuum filtration is a major expense, a method of reducing the final sludge volume would be a great improvement for this operation. Recent developments in waste treatment (10)(11) have produced processes which reduce sludge volumes following neutralization. However, these processes cannot be applied to the treatment of high volume, metal free sulfuric acid wastes for several reasons: a) the temperatures at which these processes must be operated prohibit their use for high volume wastes, b) the methods compact the sludge by modifying the physical structure of certain iron oxides present in the waste. Since little or no iron would be present in certain sulfuric acid wastes, this approach to compact the sludge would not be effective.

Recent work (6)(7)(8)(9) has been directed at exploring a sludge compaction method which appears to solve the problems associated with the previously mentioned processes, while affecting a high degree of sludge compaction. This method, crystal seeding, consists of addition of precipitation nuclei to sulfuric acid waste prior to neutralization. The addition of these seed crystals results in reduced volumes and improved compaction and handling properties of the resulting sludges. The process can be carried out at room temperature and its operation is not dependent on the presence of foreign ions.

Very limited data is available from the literature on the filterability of calcium sulfate sludges resulting from lime neutralization of sulfuric acid wastes. This can be attributed to the lack of a simple laboratory method capable of measuring the relative filterability of different sludges. Coackley and Jones (5) appear to have solved this problem by adapting the method of specific resistance to measure the relative filterability of various sewage sludges. Such a concept makes it possible to examine the filterability of sludges from various waste treatment processes and determine which process yields the most filterable sludge.

The objective of this thesis is to investigate, by the concept of specific resistance, the effect of certain variables on the filterability of calcium sulfate sludges

resulting from lime neutralization of return sludge seeded, sulfuric acid samples. The variables to be investigated will determine what effect, if any, such variation might have on the operation of a waste treatment process. It is hoped that this information, when made available, will lead to improved sludge dewatering practices based upon optimization of the overall process.

II. LITERATURE REVIEW

Since lime, in one form or another, has been widely used for the treatment of acid waste, there is a certain amount of data available in the literature regarding its effectiveness and use. The process of crystal seeding, addition of precipitation nuclei, has not, however, received extensive study and as a result limited data are available from the literature on this subject. Information on the filterability of calcium sulfate sludge, as measured by the concept of specific resistance, is only available as the result of one preliminary study on the subject.

Heise and Johnson (10) discuss a continuous flow lime neutralization process employed to treat steel pickle liquor waste containing two to five per cent sulfuric acid and 25 per cent ferrous sulfate. The lime used for this process consisted of a waste calcium hydroxide sludge produced at a nearby acetylene industry. This lime was slurried in a water-tight building and pumped into the bottom of the reaction tank. Waste pickle liquor was likewise pumped into the bottom of the tank and the two materials were mechanically agitated. After a five to fifteen minute reaction time the slurry was drawn off the top of the reaction tank and pumped to a rotary vacuum filter for dewatering. The filter cake, consisting of $Fe(OH)_2$, $Fe(OH)_3$ and $CaSO_4$, was discharged to a truck and hauled away. This filter cake proved

to be quite good when used as a secondary fill material and
was found to be of some value when used as a soil conditioner.
The neutralized filtrate was either returned to lime slurring
operations or discharged to the municipal sewer.

Initial operation of this system was not a complete
success since the neutral precipitate was very slimy and
clogged the filter media. It was discovered that rate of
agitation affected filter cake thickness and that different
shaped agitator blades affected particle size. A double set
of flat, three bladed, turbine impellers rotating at 70 rpm
was finally selected for use. The placing of a compressed
air line under the impellers to oxidize the ferrous hydroxide
to ferric hydroxide was found to improve the filterability.
Complete oxidation was not attained, since it was found that
when from two to five per cent of the ferrous ion was oxidized
to the ferric state the best filter rates were obtained.

Hoak and Sindlinger (11) describe a process utilizing
controlled oxidation and neutralization to treat waste pickle
liquor. The fundamental principle of this process was the
controlled oxidation which oxidizes the ferrous hydrate pre-
sent in the waste to ferrosoferric oxide, a more settleable
and filterable form. In order for ferrosoferric oxide to
form, however, it was necessary that a reactor temperature
above 75°C be maintained.

In operating this process eight liters of fresh pickle liquor waste were neutralized in the presence of approximately eight liters of slurry retained from the previous neutralization. Agitation was provided by three shrouded impellers mounted equidistant on a shaft and operating at a peripheral speed of 700 feet per minute. It was noted that the characteristics of the sludge produced in succeeding cycles were affected to some extent by the quality of the slurry carried over from the previous run, but this effect was described as being small even for extreme changes in the variables.

The performance of three different alkalies, magnesia, high calcium quicklime and dolomitic quicklime, were studied using this process. Results indicated that any of these agents could be used with good results as long as the ferric to ferrous ratio was maintained in the range of two to five. When this ratio was maintained, increased sludge settling rates and improved filtration for the resulting sludges was noted.

The authors describe a controlled oxidation process that produces a 20 fold increase in filtration rates for pickle liquor wastes neutralized with high calcium quicklime. They cite two factors as being responsible for the increased performance: a) iron is precipitated as a finely divided, nongelatinous, hydrated ferrosoferric oxide, b) the calcium sulfate is distributed through the slurry as needle shaped crystals that act as filter aids.

The fundamental principle of this process is the controlled oxidation of ferrous hydrate to ferrosoferric oxide which is a finely divided, nongelatinous compound that settles rapidly and dewaters easily. The authors state that an optimum ratio of ferric to ferrous should be in the range of 2.5 to 3.5 in order to obtain the best results and that the temperature should be above 75°C, preferably above 80°C. The results indicated that an optimum ferric to ferrous ratio, obtained at a lower temperature, did not filter as well as a less than optimum ratio for a sample tested at a higher temperature. This would indicate that the temperature was actually a more important variable in the improved filtration rates than the ferric to ferrous ratio. While the authors noted the effect of temperature on filtration rates they gave no explanation for these effects other than stating that a high temperature was necessary to promote the formation of ferrosoferric oxide. It seems reasonable to assume that the factors which would yield increased filtration rates of the magnitude noted in this article could only result from a change in composition of a major portion of the sludge. Since calcium sulfate constituted a major portion of the sludge formed in this process it is conceivable that the effect of temperature on filterability concerned a modification of the calcium sulfate crystals in the sludge.

A study of the phase diagram for calcium sulfate reveals
that the transition from the dihydrate to the hemihydrate
form occurs at a temperature of approximately 110°C. The
presence of salts in the solution (formed as reaction pro-
ducts) could possibly cause this transition, and therefore
the formation of the hemihydrate, to occur at a lower tempera-
ture by lowering the vapor pressure of the solution. The
crystal habit of the dihydrate could perhaps best be de-
scribed as prismatic while the crystal habit for the hemi-
hydrate is longer and more slender and can best be described
as needle shaped. The slender, needle shaped crystals of the
hemihydrate might form a more open filter cake, and therefore
a more rapid filtering cake, than the prismatic dihydrate
crystals. The authors noted the presence of needle shaped
crystals of calcium sulfate in the slurry and stated that
these crystals served as a filter aid.

It is thought that the crystal habit modification de-
scribed above may have occurred in the process described by
Hoak and Sindlinger and was a major factor in the high fil-
tration rates obtained.

Faust et al (9) used three types of seed crystals in
their investigation of crystal seeding as a means of con-
centrating sludges from lime neutralization of sulfuric acid
wastes. The three types of seed crystals used were native
gypsum powder, return sludge initially seeded with gypsum
and return of unseeded sludge.

It was found that the addition of native gypsum powder to a sulfuric acid sample prior to neutralization served to compact the resulting sludge. It was also noted that there existed a seed dosage which resulted in maximum sludge volume reduction and additional seed dosage above this amount was unnecessary. This optimum dosage was found to increase linearly for increased acid concentration and was less for dolomitic lime systems than for high calcium lime systems. The presence of such materials as iron, aluminum, and organic acids did not interfere with the action of the gypsum seed crystals.

The authors felt that a return sludge process, whereby the sludge from one neutralization was returned to the next acid sample would be more satisfactory for commercial application than would a process involving the continuous addition of gypsum. Experiments to investigate the effectiveness of return sludge as a seed material were started by neutralizing two samples of sulfuric acid, one seeded with native gypsum prior to neutralization and the other unseeded. The sludge from these samples was added to the acid sample of a subsequent neutralization. It was found that for one recycle the seeded sludge was more effective in compacting sludges than the unseeded sludge.

The authors found that on an equivalent weight basis gypsum powder was more effective in reducing sludge volume than was the returned sludge. The authors concluded that freshly precipitated gypsum offered a poor crystal seed surface for additional calcium sulfate deposition, and therefore a large seed dosage was required to receive the reaction products. It was shown experimentally that a sludge seeded with 30,000 p.p.m. of gypsum acquired a solids concentration of 25 per cent whereas the same sludge seeded with 125,000 p.p.m. of freshly precipitated calcium sulfate acquired a solids concentration of only 14 per cent.

From the various return sludge experiments it was concluded that an optimum return sludge dosage existed, beyond which sludge solids concentration did not increase. The experimental data indicated that the optimum dosage appeared to range from one to three times the weight of calcium sulfate formed on neutralization, depending on the properties of the seed crystals employed.

Faust and Orford (8) used microscopic examination to investigate the mechanisms responsible for sludge compaction following crystal seeding. Examination of recycled sludge particles, obtained from neutralization of a sulfuric acid sample initially seeded with native gypsum powder, revealed an increase in particle size which proved that the deposition

of reaction products on the seed materials had in fact occurred as suggested by previous studies (9). The authors felt that this increase in mean particle size was not the only factor involved with improved sedimentation and suggested that crystal habit of the seed material was also a factor. The settling characteristics of native gypsum powder and precipitated gypsum were compared and it was observed that the spherical particles of native gypsum compacted to a denser sludge than did the prismatic particles of precipitated gypsum. A comparison of the seeding properties of these two materials revealed that seeding with native gypsum effected a much greater concentration of the sludge resulting from neutralization than did seeding with precipitated gypsum. Microscopic examination revealed an absence of prismatic crystals in the sludge seeded with native gypsum and a predominance of spherical particles, indicating that the reaction products had been deposited on the seed. A similar examination of the sludge seeded with precipitated gypsum revealed that the sludge particles were primarily prismatic and that little, if any, of the reaction products had been deposited. The authors reasoned that native gypsum is more effective, "because of a more perfect crystal orientation acquired through an infinite aging period." The lack of aging, and subsequent lack of perfection of crystalling structure served to explain the ineffective seeding properties of precipitated gypsum.

Faust (7) stated that information from the literature suggested that acid concentration and type of lime are factors affecting sludge characteristics resulting from lime neutralization of sulfuric acid solutions. However, no data was offered to support these observations. He conducted experiments to obtain this information using high calcium and dolomitic quicklime neutralization of sulfuric acid solutions ranging from one to 10 per cent sulfuric acid by weight.

High calcium quicklime neutralization produced larger sludge volumes with denser sludges than dolomitic quicklime neutralization at equivalent acid concentrations. An increase in acid concentration increased the sludge volumes and dry solids concentration for both lime systems.

An arbitrary definition was chosen to distinguish the sedimentation phase of the calcium sulfate sludge from its compaction phase. Fifteen minutes to one hour was chosen as the sedimentation period and any change in sludge volume or dry solids concentration occurring after one hour was defined as compaction. It was noted that high calcium quicklime sludges settled faster than dolomitic quicklime sludges and that as the acid concentrations increased the settling rates decreased for both types of lime.

It was observed that compaction of these sludges, decrease in sludge volume and increase in sludge dry solids occurring after the one hour sedimentation phase, was poor.

This fact was attributed to the needle-like shape of the calcium sulfate crystal. The use of returned sludge or native gypsum powder as seed crystals has been shown (9) to improve the compaction properties of calcium sulfate sludges but no data has been given regarding the effect of acid concentration or type of lime on the crystal seeding process. When native gypsum seed dosages were added to the various sulfuric acid samples it was noted that an increase of acid concentration decreased the degree of compaction within a given system and that dolomitic lime sludges showed a higher degree of compaction than high calcium lime sludges at equivalent acid concentrations.

The effect of degree of neutralization on sludge characteristics was investigated and it was observed that under-neutralization or over-neutralization had no effect on sludge volume or sludge density resulting from high calcium quicklime neutralization of one and two per cent acid waste. Degree of neutralization did, however, effect sludge characteristics resulting from dolomitic quicklime neutralization due to the precipitation of magnesium hydroxide at pH values above pH 10.

Coackley and Jones (5) in search of a parameter to be used in comparing the resistance to filtration of different sewage sludges, analyzed the various theories of filtration.

Their analysis revealed that the simplest and most applicable theory was the concept of specific resistance developed by Carman (2, 3, 4). Specific resistance is defined as, "the resistance of a unit weight of cake per unit area at a given pressure," and is calculated by the equation:

$$r = \frac{2\ PA^2b}{uc}$$

where:

r = specific resistance (sec^2/gm)

P = suction pressure in gm/sq.cm.

A = filtering area in sq. cm.

b = the slope of a line obtained by plotting the ratio of time to filtrate volume versus filtrate volume. (sec/ml^2)

u = viscosity of filtrate in poises (gm/sec.cm.)

c = solids content of the filtrate in (gm/ml)

Laboratory experiments, conducted to establish the accuracy of specific resistance in describing the results of filtration tests, confirmed the applicability of Carman's theory. Specific resistance remained practically constant when the solids content of the filtrate was varied over the range from 8.5 per cent to 1.5 per cent but showed a significant decrease as the solids content was lowered from 13.5 per cent to 8.5 per cent. This decrease was felt to be due to a

variation in the state of peptization of the particles and
was not considered as disproving Carman's theory which as-
sumes that specific resistance is independent of solids con-
tent at a given suction pressure.

Additional experiments, conducted with sludges which
had received various types and degrees of prefiltration
treatment, found that specific resistance, as a measure of
filterability, was a suitable parameter to use as a means of
comparing the effectiveness of the various methods of
treatment.

A complete mathematical analysis of specific resistance
is given in Appendix A.

Faust (6) employed the concept of specific resistance
in filtration studies of calcium sulfate sludges resulting
from high calcium quicklime neutralization of sulfuric acid
waste following crystal seeding with precipitated gypsum.
He reported that calcium sulfate sludges have specific re-
sistance values in the order of 10^6 sec^2/gram.

III. METHODS AND MATERIALS

The purpose of the research conducted in connection with this thesis was to investigate the effect of certain variables on the filterability of calcium sulfate sludges resulting from lime neutralization of sulfuric acid waste. The method of specific resistance, first conceived by Carman (2, 3, 4) and later adapted by Coackley (5), was utilized as a means of comparison of the various samples tested. The process of crystal seeding, addition of precipitation nuclei, was employed to improve the filterability of the waste and the handling properties of the resulting sludges. Crystal seeding was accomplished by addition to the acid solution of a calcium sulfate sludge formed by high calcium hydrated lime neutralization of a two per cent (0.408 N) sulfuric acid solution.

The following is a description of the manner in which the experiments were conducted.

A stock sulfuric acid solution, ten per cent sulfuric acid by weight (2.04 N), was prepared by mixing concentrated sulfuric acid and distilled water. A standard sodium hydroxide solution, prepared in accordance with the procedure contained in "Standard Methods for the Examination of Water and Wastewater," was used to standardize the stock solution. The samples to be investigated were prepared to the desired concentrations by diluting the stock solution with distilled

water. The desired amounts of return sludge, obtained as stated previously, were added to the acid samples prior to neutralization of the sample. A ten per cent by weight slurry of chemical grade high calcium hydrated lime was used to neutralize the samples. This lime was obtained from the U.S. Gypsum Company in Kimballton, Virginia.

Experiments were conducted with 1000 ml slurries of the acid solution and return sludge. The slurries were mixed in 1500 ml beakers which were equipped with baffles to assure uniform mixing. Mixing was accomplished with a variable speed mixer equipped with a six bladed propeller which had the dimensions and shape shown in Figure 1. The samples were mixed for 20 minutes at a speed of 400 rpm with the proper amount of lime slurry being added to bring the sample to the desired pH. The pH of the sample was continuously measured during the mixing period by an electronic pH meter. After mixing, the samples were poured into graduated cylinders and allowed to settle for 45 minutes. A 25 ml portion of the sample was withdrawn, filtered through a tared Gooch crucible, and dried for three days at $103^{\circ}C$ to determine the dry solids content of the slurry. Both the mixing and settling operations were conducted at a temperature held at $28^{\circ}C \pm 1^{\circ}C$ by use of a water bath. After settling for 45 minutes the amount of settled sludge was noted and the sample was filtered.
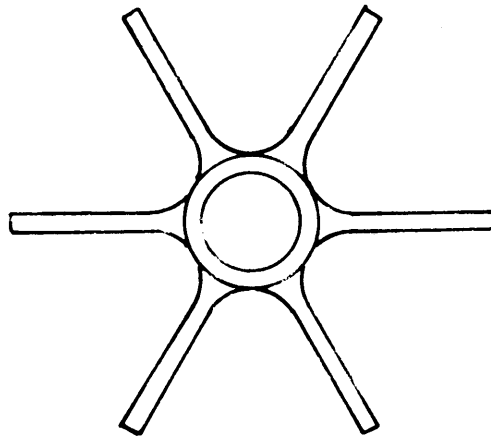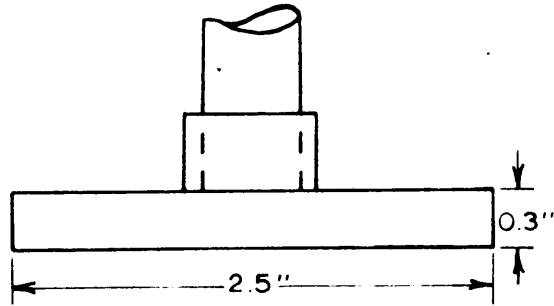
FIGURE 1 MIXING PROPELLER

Vacuum filtration was conducted in a 4.6 centimeter deep and 9.1 centimeter diameter Buchner funnel. The funnel volume was increased by a section of plexiglas pipe, 10.15 centimeters in diameter and 10.15 centimeters in height which was attached to the top of the Buchner funnel by means of a 1.5 inch wide rubber band. The funnel assembly was attached to a 1000 ml graduated cylinder which served to measure the filtrate volume. A rubber stopper was placed in the top of the cylinder and a 1.5 centimeter glass tube was passed through the stopper. The Buchner funnel was attached to the glass tube by means of a section of rubber hose equipped with a screw clamp which served to cut off suction to the filter while allowing it to build up in the graduated cylinder. A manometer connected in parallel with the vacuum pump was used to measure the vacuum in the cylinder. A bleed-off valve regulated the pressure in the cylinder. A sketch of the Buchner funnel modification is shown in Figure 2.

Two moistened pieces of #4 Whatman filter paper were placed in the funnel and vacuum was applied to assure a firm contact of the paper. The vacuum was then discontinued in the funnel but allowed to build up in the cylinder to the desired pressure of 5 inches of mercury. The slurry of calcium sulfate was poured into the funnel, allowed to stand for ten seconds to permit initial formation of a filter cake, and vacuum was then applied. Filtrate volume readings were
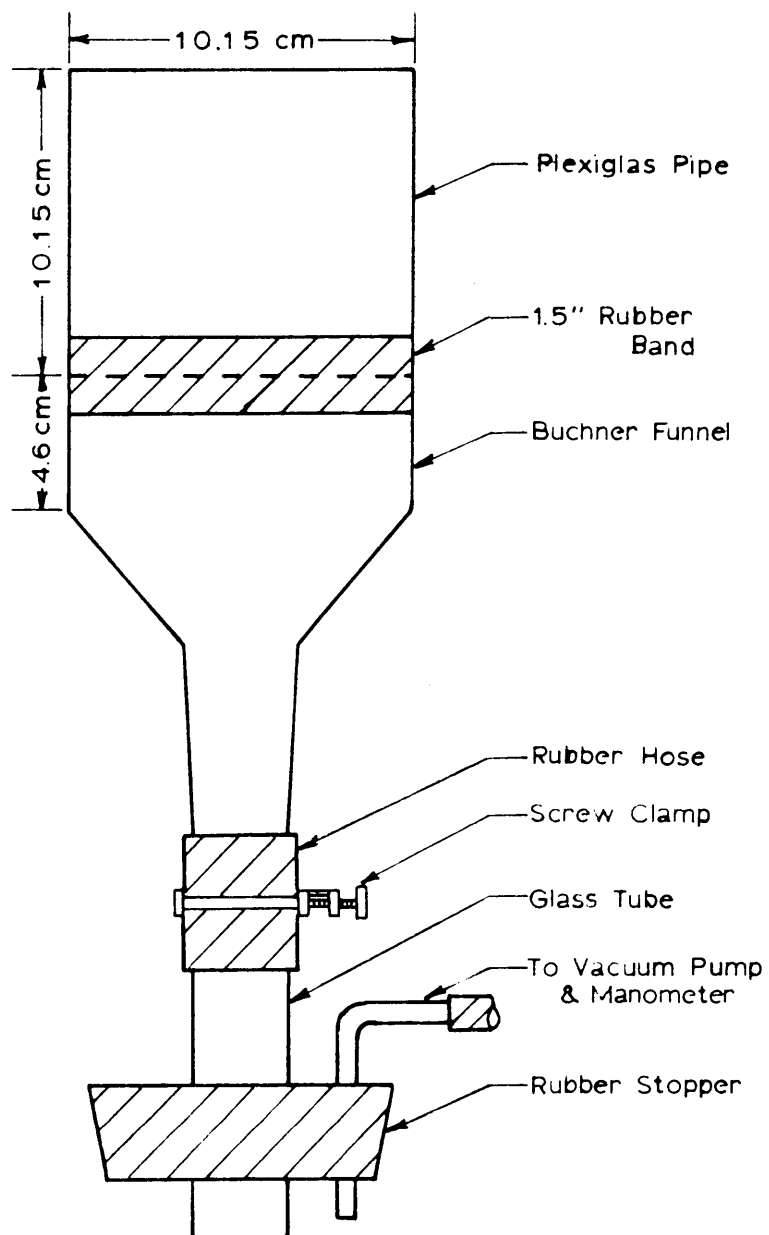
FIGURE 2 BUCHNER FUNNEL APPARATUS

taken every 15 or 30 seconds depending upon the apparent rate at which the sample was filtering. The vacuum was maintained on the filter until a constant volume of filtrate was obtained or until the filter cake cracked.

A portion of the filter cake was placed in a tared crucible and weighed before and after drying at 103°C for three days. Cake moisture was determined by loss of weight procedure.

Table 1. Typical Analysis of High Calcium Hydrated Lime

Component	Per Cent
$Ca(OH)_2$	73.59
$SiO_2 + X$	1.43
MgO	1.11
Al_2O_3	0.32
Fe_2O_3	0.15
SO_3	0.04
Loss on ignition	23.32
Free moisture	0.20

IV. EXPERIMENTAL RESULTS

a) Determination of Optimum Mixing Rates and Lime Addition Rates.

It was of interest to determine the effect of mixing rates and lime addition rates on the filterability and dewatering properties of the calcium sulfate sludges. Rapid and slow mixing and rapid and slow lime addition were the variables investigated. These variables are defined as follows:

Rapid Mixing - Mixing at 400 rpm with the propeller shown in Figure 1.

Slow Mixing - Mixing at 100 rpm with the propeller shown in Figure 1.

Rapid Lime Addition - Pouring the necessary amount of lime slurry into the sulfuric acid sample without hesitation.

Slow Lime Addition - Pipetting 5 ml of lime slurry into the sulfuric acid sample at one minute intervals.

Return sludge samples were prepared with all possible combinations of mixing and lime addition rates described above. Each return sludge was used to seed four sulfuric acid samples. Each of these samples was then neutralized using all possible combinations of mixing and lime addition. The object of this procedure was to determine the effect of varying the rates of mixing and lime addition on samples seeded with the same return sludge. It was desired to evaluate the effect the different return sludges would have on samples

mixed and neutralized in the same manner. It was hoped that the data acquired would indicate the combination of mixing and lime addition for both the return sludge and sample that would yield the optimum sludge, in terms of ease of filtering and dewatering.

Results

A complete set of data is given in Tables 2, 3, 4 and 5 for all possible combinations of mixing and lime addition for both the return sludge and the sample. These data are condensed in Table 6 and these figures will be used for the purpose of comparing the results. It can be seen from Table 6 that the samples seeded with the return sludge, obtained using slow mixing and slow lime addition, have the lowest specific resistance of all samples tested. The other return sludges, in the order of decreasing effectiveness, are rapid mixing - slow lime addition, slow mixing - rapid lime addition, and rapid mixing - rapid lime addition. Table 6 also indicates that for a given type of return sludge the samples neutralized using slow mixing and slow lime addition have the lowest specific resistances. The other rates of mixing and lime addition are, in order of increasing specific resistance, slow mixing - rapid lime addition, rapid mixing - rapid lime addition, and rapid mixing - slow lime addition.

The data given in Table 6 indicate that the lowest filter cake moisture values were obtained when rapid mixing and slow lime addition were employed for both the return sludge and the sample.

Table 2. Filter Test Results for Various Samples Seeded With Return Sludge Obtained Using Slow Mixing and Rapid Lime Addition.

Return Sludge		Sample						
Mixing Rate	Lime Add. Rate	Mixing Rate	Lime Add. Rate	Acid Conc.%	Final pH	Return sludge-ml	Final sludge-ml	Slurry Dry Solids gm/ml
Slow	Rapid	Slow	Slow	1	10.9	400	420	0.0221
Slow	Rapid	Slow	Slow	1	10.8	400	430	0.0217
Slow	Rapid	Slow	Rapid	1	11.85	400	390	0.0237
Slow	Rapid	Slow	Rapid	1	11.80	400	380	0.0243
Slow	Rapid	Rapid	Rapid	1	11.90	400	420	0.0219
Slow	Rapid	Rapid	Rapid	1	11.05	400	475	0.0245
Slow	Rapid	Rapid	Slow	1	10.8	400	450	0.0219
Slow	Rapid	Rapid	Slow	1	11.02	400	500	0.0218

Table 2. (Continued)

Sample							
Filtrate Volume—ml*					Slope b x 10-4	Specific Resistance r x 106 +	Cake Moisture
30 sec.	60 sec.	90 sec.	120 sec.	150 sec.			
170	320	500	640	770	0.435	0.329	85.2%
200	380	550	700	770	0.450	0.347	85.5
175	320	460	580	695	0.730	0.515	85.2
175	320	460	600	720	0.535	0.369	85.9
210	360	515	650	770	0.697	0.533	83.6
190	320	450	575	690	0.764	0.521	84.0
230	405	560	700	810	0.914	0.697	85.2
220	405	570	700	810	0.820	0.631	85.9

* Filtrate volume readings stopped when it was apparent that straight line relationship had been lost.

+ Values obtained using #1 Whatman filter paper.

Table 3. Filter Test Results for Various Samples Seeded With Return Sludge Obtained Using Rapid Mixing and Rapid Lime Addition.

Return Sludge		Sample						
Mixing Rate	Lime Add. Rate	Mixing Rate	Lime Add. Rate	Acid Conc.%	Final pH	Return Sludge-ml	Final Sludge-ml	Slurry Dry Solids gm/ml
Rapid	Rapid	Slow	Slow	1	11.25	400	375	0.0169
Rapid	Rapid	Slow	Slow	1	11.0	400	385	0.0169
Rapid	Rapid	Slow	Rapid	1	11.65	400	350	0.0169
Rapid	Rapid	Slow	Rapid	1	11.95	400	340	0.0181
Rapid	Rapid	Rapid	Rapid	1	11.90	400	330	0.0177
Rapid	Rapid	Rapid	Rapid	1	11.90	400	370	0.0173
Rapid	Rapid	Rapid	Slow	1	10.90	400	310	0.01655
Rapid	Rapid	Rapid	Slow	1	10.85	400	420	0.0175

Table 3. (Continued)

Sample	Filtrate Volume-ml*					Slope b x 10-4	Specific Resistance r x 10-6 +	Cake Moisture
	30 sec.	60 sec.	90 sec.	120 sec.	150 sec.			
	210	380	555	710	850	0.40	0.396	84.3%
	200	370	535	695	840	0.378	0.374	83.2
	205	375	525	670	800	0.652	0.646	79.6
	170	330	460	600	720	0.634	0.595	82.2
	150	300	450	590	705	0.800	0.756	84.2
	180	330	465	600	710	0.825	0.800	-
	160	310	430	550	660	0.746	0.756	82.0
	150	280	400	520	635	0.639	0.639	82.5

* Filtrate volume readings stopped when it was apparent that straight line relationship had been lost.

+ Values obtained using #1 Whatman filter paper.

Table 4. Filter Test Results for Various Samples Seeded with Return Sludge Obtained Using Slow Mixing and Slow Lime Addition.

| Return sludge | | Sample | | | | | | |
Mixing Rate	Lime Add. Rate	Mixing Rate	Lime Add. Rate	Acid Conc.%	Final pH	Return sludge-ml	Final sludge-ml	Slurry Dry Solids gm/ml
Slow	Slow	Slow	Slow	1	10.90	400	360	0.0226
Slow	Slow	Slow	Slow	1	10.85	400	360	0.0220
Slow	Slow	Slow	Rapid	1	11.80	400	370	0.0197
Slow	Slow	Slow	Rapid	1	11.40	400	370	0.0209
Slow	Slow	Rapid	Rapid	1	12.1	400	335	0.0209
Slow	Slow	Rapid	Rapid	1	11.0	400	300	0.0207
Slow	Slow	Rapid	Slow	1	11.2	400	315	0.0187
Slow	Slow	Rapid	Slow	1	11.0	400	290	0.0161

Table 4. (Continued)

Sample

Filtrate Volume-ml*				Slope $b \times 10^{-4}$	Specific Resistance $r \times 10^{6}$ +	Cake Moisture
20 sec.	**40 sec.**	**60 sec.**	**80 sec.**			
150	310	450	585	0.273	0.202	85.2%
150	300	440	580	0.206	0.157	–
30 sec.	**60 sec.**	**90 sec.**				
250	480	690		0.226	0.192	87.2
265	505	735		0.167	0.136	87.5
30 sec.	**60 sec.**	**90 sec.**	**120 sec.**	**150 sec.**		
190	350	500	645	785	0.461	0.369	85.7
225	415	590	760	–	0.395	0.320	83.7
30 sec.	**60 sec.**	**90 sec.**	**120 sec.**	**150 sec.**		
255	475	665	–	–	0.469	0.419	85.9
190	365	525	680	–	0.419	0.436	84.9

* Filtrate volume readings were stopped when it was apparent that straight line relationship had been lost.

+ Values obtained using #1 Whatman filter paper.

Table 5. Filter Test Results for Various Samples Seeded With Return Sludge Obtained Using Rapid Mixing and Slow Lime Addition.

Return Sludge				Sample				
Mixing Rate	Lime Add. Rate	Mixing Rate	Lime Add. Rate	Acid Conc.%	Final pH	Return Sludge-ml	Final Sludge-ml	Slurry Dry Solids gm/ml
Rapid	Slow	Slow	Slow	1	10.95	400	420	0.0236
Rapid	Slow	Slow	Slow	1	10.35	400	410	0.0229
Rapid	Slow	Slow	Rapid	1	11.75	400	385	0.0239
Rapid	Slow	Slow	Rapid	1	12.05	400	390	0.0256
Rapid	Slow	Rapid	Rapid	1	11.65	400	365	0.0239
Rapid	Slow	Rapid	Rapid	1	11.40	400	465	0.0287
Rapid	Slow	Rapid	Slow	1	11.35	400	340	0.0192
Rapid	Slow	Rapid	Slow	1	10.95	400	340	0.028

Table 5. (Continued)

Sample	Filtrate Volume—ml*					Slope b x 10-4	Specific Resistance r x 10⁶ +	Cake Moisture
	30 sec.	60 sec.	90 sec.	120 sec.	150 sec.			
	240	455	645	-	-	0.445	0.316	82.5
	230	440	640	805	-	0.383	0.280	84.5
	225	415	585	745	830	0.629	0.440	81.7
	205	375	530	670	-	0.666	0.436	84.7
	210	380	550	690	810	0.577	0.404	82.1
	200	355	500	620	735	0.913	0.534	83.3
	220	390	550	700	820	0.66	0.576	75.0
	260	420	570	705	825	1.00	0.598	71.7

* Filtrate volume readings stopped when it was apparent that straight line relationship had been lost.

+ Values obtained using #1 Whatman filter paper.

Table 6. Affect of Varying Mixing Rates and Lime Addition Rates on Specific Resistance and Cake Moisture.

Return Sludge		Sample			
		Slow Mixing-Slow Lime Add.		Slow Mixing-Rapid Lime Add.	
Mixing Rate	Lime Addition Rate	Specific Resistance (r x 10⁶)	Cake Moist. %	Specific Resistance (r x 10⁶)	Cake Moist. %
Slow	Slow	0.179	85.2	0.164	87.3
Rapid	Slow	0.298	83.5	0.438	83.2
Slow	Rapid	0.338	85.3	0.495	85.5
Rapid	Rapid	0.385	83.7	0.620	80.9

All tests conducted using #1 Whatman filter paper.

Table 6. (Continued)

	Sample			
Rapid Mixing - Rapid Lime Addition		Rapid Mixing - Slow Lime Addition		
Specific Resistance(r x 10⁶)	Cake Moist.%	Specific Resistance(r x 10⁶)	Cake Moist.%	
0.345	84.7	0.427	85.4	
0.469	82.7	0.587	73.2	
0.526	83.8	0.664	85.1	
0.778	84.2	0.696	82.2	

Discussion

When particles of the same material and same relative shape are allowed to settle, the ones with the largest size will settle fastest. In terms of filterability, large sludge particles would filter more easily than smaller particles, of the same relative shape, since a larger void space would be present between the particles. A measure of the settleability of a material is the dry solids concentration of the settled sludge. The average dry solids concentrations for return sludge samples, prepared as indicated, is shown in Table 7.

Table 7. Return Sludge Dry Solids Concentration

Mixing Rate	Lime Addition Rate	Sludge Dry Solids Concentration - gm/ml
Slow	Slow	0.0479
Rapid	Slow	0.0475
Slow	Rapid	0.0425
Rapid	Rapid	0.0289

These data reveal that the sludge produced by slow mixing and slow lime addition settles to the highest dry solids concentration and conceivably is composed of the largest sludge particles. Therefore, this return sludge should be

the most effective seed material in terms of producing the
most filterable sludges since deposition of the reaction pro-
duct would serve to further increase the particle size. The
other types of return sludge should decrease in effectiveness
with decreasing dry solids concentration. This interpreta-
tion is supported by the data given in Table 6 which shows
the order of decreasing effectiveness of the return sludge to
be the same as the order of decreasing dry solids concentra-
tion. The data in Table 7 indicate that slow lime addition
produces sludges which settle to higher dry solids concentra-
tion, presumably due to larger sludge particles, than rapid
lime addition regardless of the type mixing employed. A
probable explanation for this is that slow lime addition
would result in a slow buildup of calcium sulfate supersatura-
tion as opposed to rapid lime addition, in which case the
supersaturation would be instantaneous. The slower buildup
in supersaturation would result in the formation of large
calcium sulfate crystals once supersaturation is reached,
while an instantaneous buildup would result in the formation
of smaller crystals. It was observed that an extremely low
dry solids concentration was obtained for the return sludge
samples prepared using rapid mixing and rapid lime addition.

In terms of sample mixing and lime addition rates the
order of decreasing effectiveness was not the same as for

the return sludge studies. It was thought that this order should be the same since the process which apparently resulted in the largest return sludge particles would also produce the largest particles when used for sample neutralization. It appears that slow mixing is more effective in producing a rapid filtering sludge than rapid mixing and this is probably because rapid mixing tended to make the lime slurry go into solution more rapidly thereby increasing the rate of super-saturation buildup and resulted in smaller particle size. The author is unable to give a satisfactory explanation for the order of effectiveness demonstrated by the various combinations of rates of mixing and lime addition utilized for sample neutralization.

It can be seen from Table 6 that the samples which exhibited the best filterability did not have the lowest cake moisture content. In a commercial operation no advantage would be gained from using a process which filtered rapidly if the resulting filter cake created sludge disposal problems. Therefore it was decided that the procedure which yielded the lowest filter cake moisture would be the most desirable method to use in continuing this investigation. This procedure appeared to be rapid mixing and slow lime addition for both the return sludge and the sample since it resulted in much lower filter cake moistures than the other processes.

This series of experiments was conducted using #1 Whatman filter paper instead of the #4 Whatman filter paper used for the remaining experiments. During the early stages of a filtration test the major resistance to the flow of filtrate is offered by the filter paper since only a small amount of filter cake has been deposited. The resistance of the filter paper continues to influence the filter test until such time as a cake capable of masking the filter paper resistance is deposited. The effect of this filter paper interference is to increase the experimental values of specific resistance. Since #1 filter paper is less porous than #4 filter paper it offers more resistance to filtration and has greater effect on the specific resistance values obtained. Therefore the specific resistance values for this set of experiments, obtained using #1 filter paper, should not be compared with values given in other sections of this thesis in which #4 filter paper was used.

b) <u>Effect</u> <u>of</u> <u>Varying</u> <u>the</u> <u>Degree</u> <u>of</u> <u>Neutralization</u> <u>of</u> <u>the</u> <u>Sample</u>.

This series of experiments was conducted to determine the effect the final pH of the sample would have on the filterability of the sludge (precipitated gypsum). The adverse effects which acid wastes have on aquatic life, hydraulic structures and biological sewage treatment plants are overcome when the acidity of the waste is neutralized.

The extent to which the neutralization must be carried prior to the discharge of the waste to a watercourse varies depending upon the characteristics and uses of the water; therefore, the effect of degree of neutralization on the filterability of sludge is of interest in this investigation.

Results

A complete set of filter test data is shown in Table 8 for sulfuric acid samples neutralized to final pH values in the range of 4.35, 8.70, and 11.15 with high calcium hydrated lime. The average of these values, shown in Table 9, was taken to consolidate the data and these figures will be used for the purpose of comparing the results. It is evident that the final sludge volumes resulting from neutralization to pH values of 8.70 and 4.35 were slightly lower than that obtained for neutralization to pH 11.15. The dry solids content of the samples was essentially constant for all pH values. The specific resistance of the samples decreased as the final pH of the sample decreased. The magnitude of this variation was small, however, and therefore it can be said the degree of neutralization to which a sulfuric acid sample is taken has only a minor effect on the filterability of the sludge. The cake moisture content remained constant for the samples neutralized to the pH values of 11.15 and 8.70 but showed a significant decrease for the sample neutralized to pH 4.35.

Table 8. Filter Test Results for Samples With Varying Degrees of Neutralization

Sample No.	Acid Conc.%	Final pH	Return sludge-ml	Final sludge-ml	Dry solids-g/ml	Filtrate Volume-ml.		
						30 sec.	45 sec.	60 sec.
1	1	11.15	400	390	0.0207	305	-	550
2	1	11.15	400	370	0.0245	355	490	615
3	1	11.35	400	390	0.0245	355	490	610
4	1	8.45	400	340	0.01985	385	535	655
5	1	8.80	400	350	0.0215	400	-	655
6	1	8.90	400	335	0.0219	420	-	695
7	1	4.35	400	345	0.0223	395	-	675
8	1	4.35	400	345	0.0252	430	595	720
9	1	4.45	400	330	0.0211	430	590	710

Table 8. (Continued)

Filtrate Volume-ml *				Slope b x 10-4	Specific Resistance + r x 10^6	Cake Moisture %
75 sec.	90 sec.	105 sec.	120 sec.			
-	750	-	870	0.542	0.439	79.0
710	800	835	850	0.631	0.431	77.1
710	800	835	845	0.625	0.426	80.5
775	855	-	-	0.484	0.407	79.0
780	855	-	-	0.590	0.459	78.6
815	865	-	-	0.500	0.382	78.5
795	840	-	-	0.461	0.346	72.5
830	-	-	-	0.467	0.311	73.7
825	-	-	-	0.535	0.424	74.9

* Filtrate volume readings taken every 15 or 30 seconds depending on the rate at which the sample was filtering.

Filtrate volume readings were stopped when it was apparent that straight line relationship had been lost.

+ Values obtained using #4 filter paper.

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Table 9. Average Filter Test Results for Samples with Varying Degrees of Neutralization.*

Acid Concentration % H2SO4	Final pH	Final Sludge—ml**	Dry Solids gm/ml	Slope b x 10^{-4}	Specific Resistance*** r x 10^6	Cake Moisture %
1	11.20	383	0.0233	0.599	0.432	78.8
1	8.70	342	0.0210	0.525	0.416	78.8
1	4.38	340	0.0229	0.489	0.361	73.7

* Average values of three tests conducted for each degree of neutralization as shown in Table 8.

** Initially seeded with 400 ml. of return sludge.

*** Values obtained using #4 filter paper.

Discussion

A typical analysis of high calcium hydrated lime, shown
in Table 1, reveals that the oxides of iron, aluminum and
magnesium are present in small percentages. An investigation
of the solubility of the reaction products formed when these
compounds react with the sulfuric acid sample reveals a
possible answer to the differences in sludge volume, cake
moisture and specific resistance obtained for the different
degrees of neutralization. The salts of aluminum, magnesium
and iron formed from these reactions are quite soluble for
all pH values and would be dissolved into solution. The
hydroxides of iron and aluminum are, however, quite insolu-
ble for high pH values, with the solubility increasing as
the pH of the solution decreases. Therefore at high pH
values these compounds will precipitate in the form of addi-
tional sludge with the amount precipitating decreasing with
decreasing pH. Magnesium hydroxide is insoluble, however,
above pH 10. Therefore, it would only precipitate at pH
values above this point. The carbon dioxide present in the
lime combines with water to form carbonic acid, H_2CO_3. When
this carbonic acid is neutralized with lime two possible
reaction products exist, calcium bicarbonate, which is solu-
ble, or calcium carbonate which is insoluble. At low values
of pH there is negligible carbonate present and the oxidized

carbon is present as carbonic acid or soluble calcium bicarbonate. At high values of pH carbonate is more prevalent than bicarbonate and the insoluble calcium carbonate is formed which precipitates as sludge. These effects of pH on solubility are thought to be a probable explanation for the sludge volume variations noted.

The minor variations in filterability obtained with varying pH are thought to be caused by these same factors. The presence of the gelatinous hydroxide precipitates in a sludge would tend to clog the pores of the sludge and the filter paper and thus decrease the rate of flow of the filtrate. Since the amount of these compounds increases with increased pH it is reasonable that the specific resistance would also increase. That the specific resistance does increase with increased pH can be seen in Table 9.

The decrease in cake moisture noted for the sample neutralized to pH 4.35 cannot be explained by the author.

c) Effect of Varying the Return Sludge Dosage of the Sample.

This series of experiments was conducted to determine what effect varying the return sludge dosage would have on the filterability of the sample. It has been noted (7)(9) that return sludge dosage affects the settling and compactive properties of calcium sulfate sludges. Therefore the effect of return sludge dosage on the filterability of the sludge was of interest in this investigation.

Results

A complete set of filter test data is shown in Table 10 for one per cent sulfuric acid samples receiving 300, 400 and 500 milliliters of return sludge prior to neutralization with high calcium hydrated lime. The average of these values, shown in Table 11, was taken to consolidate the data and these figures will be used for the purpose of comparing the results. It can be seen from Table 11 that the specific resistance of the samples increased with increased return sludge dosage. The magnitude of this variation was small, however, and therefore it can be said that the range of return sludge dosages investigated had only a minor effect on the filterability of the sludge. The filter cake moisture content did not show a significant variation for the range of return sludge dosages investigated. However the dry solids concentration of the mixture showed a definite increase with increased return sludge dosage.

Table 10. Filter Test Results for Samples with Varying Return Sludge Dosage.

Sample No.	Acid Conc.%	Final pH	Return sludge-ml	Final sludge-ml	Dry solids-gm/ml	Filtrate Volume - ml		
						30 sec.	45 sec.	60 sec.
1	1	11.05	300	270	0.01995	400	560	695
2	1	11.10	300	305	0.0190	380	525	650
3	1	11.00	300	260	0.0193	420	580	710
4	1	11.15	400	390	0.0207	305	-	550
5	1	11.15	400	370	0.0245	355	490	615
6	1	11.35	400	390	0.0245	355	490	610
7	1	10.95	500	550	0.0273	360	490	595
8	1	11.20	500	530	0.0283	350	475	580
9	1	11.20	500	525	0.0243	370	500	605

Table 10. (Continued)

| Filtrate Volume-ml* | | | | Slope b x 10-4 | Specific Resistance*** r x 106 | Cake Moisture % |
75 sec.	90 sec.	105 sec.**	120 sec.			
810	-	-	-	0.416	0.349	82.5
770	-	-	-	0.466	0.411	81.1
835	-	-	-	0.477	0.414	85.0
-	750	-	870	0.542	0.439	79.0
710	800	835	850	0.631	0.431	77.1
710	800	835	845	0.625	0.426	80.5
690	780	-	-	0.742	0.455	77.9
680	755	-	-	0.775	0.459	79.8
-	800	-	-	0.735	0.506	80.2

* Filtrate volume readings taken every 15 or 30 seconds depending on the
  rate at which the sample was filtering.

** Filtrate volume readings were stopped when it was apparent that straight
   line relationship had been lost.

*** Values obtained using #4 filter paper.

Table 11. Average Filter Test Results for Samples With Varying Return sludge
           Dosage.*

Acid Conc. % H2SO4	Return sludge-ml	Final pH	Final Sludge-ml**	Dry Solids gm/ml	Slope b x 10⁻⁴	Specific Resistance** r x 10⁶	Cake Moisture %
1	300	11.05	278	0.0194	0.453	0.392	83.0
1	400	11.15	383	0.0233	0.599	0.432	78.8
1	500	11.10	535	0.0266	0.750	0.473	79.3

* Average values of three tests conducted for each return sludge dosage
  as shown in Table 10.

** Obtained using #4 filter paper.

Table 12. Return Sludge Dosage

Return Sludge Dosage—ml	Dry Weight of Sludge Added—gm	Grams of Sludge Added per Liter Acid*	Volumetric Sludge Return %**	Dry Weight of Sludge Added*** / Dry Weight of Sludge Formed
300	13.2	18.9	42.9	2.48
400	18.5	30.8	66.7	4.06
500	22.3	44.6	100	5.89

* Based on 500, 600, 700 ml acid samples.

** Expressed as per cent of acid volume.

*** Neutralization of 600 ml of acid produced 4.55 grams of dry sludge.

Discussion

When precipitated gypsum seed crystals are present in a sulfuric acid sample prior to neutralization with lime, a portion of the calcium sulfate which is formed is deposited upon the surface of the seed crystals. The result is a calcium sulfate particle of a larger size and with improved settling and compacting properties. Faust et al (9) report that there exists an optimum return sludge dosage for a given acid-lime system which results in maximum solids concentration for that system. A return sludge dosage smaller or larger than the optimum would result in a lesser degree of compaction of the resulting sludge. The explanation for this lies in the fact that a return sludge dosage smaller than the optimum would not provide sufficient crystal surfaces to accomodate the deposition of all of the reaction products. This would result in the presence of virgin microcrystals of calcium sulfate in the mixture. These crystals would be smaller than the seed crystals which had attracted calcium sulfate and would settle and compact to a lesser extent. The same reasoning would apply to an overdose of return sludge in which case there would be seed crystals in excess of the amount necessary to accomodate the reaction products. These crystals would maintain their small size since less than optimum reaction product would be available for deposition on their surface. The presence of these smaller crystals in a sludge would decrease the

filterability of the sludge by filling the voids between the larger particles. The greater the percentage of smaller crystals the greater would be the impairment of the filterability of the sludge.

Previous work (9) has suggested that the optimum return sludge dosage was, "from one to three times the weight of calcium sulfate formed on neutralization, depending on the properties of the seed crystals employed." Faust (7) estimates optimum loadings for native gypsum seeded return sludge in high calcium quicklime-acid systems. He suggests a volumetric sludge return of 20 to 25 per cent of the acid volume neutralized, amounting to 25 to 35 grams of dry sludge per liter of acid, would be optimum in terms of sludge compaction. The return sludge dosages used in these experiments, when expressed in terms of volumetric sludge return and percentage of reaction products formed are as shown in Table 12. These data indicate the 300 ml return sludge dosage provides a seed dosage closest to the optimum values given in the literature in terms of volumetric return and ratio of sludge added to reaction product formed. The 400 ml return sludge dosage shows a significant increase over these optimum values while the 500 ml dosage shows an even greater increase.

It is probable that all the return sludge dosages employed in these experiments were in excess of the optimum dosage for this acid-lime system. As this excess of sludge

was increased the percentage of small crystals in the mixture increased and therefore the specific resistance of the sludge increased. An optimum return sludge dosage for a given acid-lime system would result in a minimum number of microcrystals present in the slurry and should therefore produce the most filterable sludge. No attempt was made in these experiments to obtain the optimum return sludge loading and therefore the values of specific resistance obtained for the range of dosages investigated cannot be considered a complete evaluation of this variable.

d) Effect of Varying the Acid Concentration of the Sample.

This series of experiments was conducted to determine what effect varying acid concentrations would have on the filterability of calcium sulfate sludges. Since the acid concentration of industrial wastes vary from factory to factory, it was of interest to determine what effect this variation would have on the filterability of the resulting sludges.

Results

A complete set of filter test data is shown in Table 13 for samples containing one, two and five per cent sulfuric acid. The average of these values, shown in Table 14, was taken to consolidate the data and these figures will be used for the purpose of comparing the results. It can be seen,

from Table 14, that as the acid concentration of the sample increased the amount of sludge formed upon neutralization increased, as did the dry solids content of the mixture. The specific resistance decreased slightly with increased acid concentration. Cake moisture increased slightly with increased acid concentration, but the difference was too small to be considered significant.

Table 13. Filter Test Results for Samples With Varying Acid Concentrations.

Sample No.	Acid Conc.%	Final pH	Return sludge-ml	Final sludge-ml	Dry Solids g/ml	Filtrate Volume-ml				
						30 sec.	45 sec.	60 sec.	75 sec.	
1	1	11.15	400	390	0.0207	305	-	550	-	
2	1	11.15	400	370	0.0245	355	490	615	710	
3	1	11.35	400	390	0.0245	355	490	610	710	
4	2	11.00	400	465	0.0305	340	-	565	-	
5	2	11.05	400	445	0.0299	335	-	565	-	
6	2	11.15	400	405	0.0289	370	500	610	710	
7	5	11.55	400	550	0.0468	290	-	485	-	
8	5	11.60	400	650	0.0466	305	-	515	-	
9	5	11.30	400	670	0.0517	315	-	505	580	

Table 13. (Continued)

| Filtrate Volume—ml* | | | Slope b x 10-4 | Specific Resistance *** r x 106 | Cake Moisture % |
90 sec.	105 sec.**	120 sec.**			
750	–	870	0.542	0.439	79.0
800	835	850	0.631	0.431	77.1
800	835	845	0.625	0.426	80.5
750	–	820	0.770	0.423	79.9
760	–	–	0.720	0.404	78.6
790	–	–	0.750	0.434	81.0
655	700	–	0.935	0.355	82.4
685	–	–	0.865	0.311	81.6
660	–	–	1.140	0.368	82.0

* Filtrate volume readings taken every 15 or 30 seconds depending on the rate at which the sample was filtering.

** Filtrate volume readings were stopped when it was apparent that straight line relationship had been lost.

*** Values obtained using #4 filter paper.

Table 14. Average Filter Test Results For Samples With Varying Acid
           Concentrations.*

Acid Concentration % H2SO4	Final pH	Final Sludge—ml**	Dry Solids gm/ml	Slope b x 10-4	Specific Resistance*** r x 106	Cake Moisture %
1	11.15	383	0.0233	0.599	0.432	78.8
2	11.05	438	0.0297	0.746	0.420	79.7
5	11.50	624	0.0484	0.771	0.345	82.0

* Average values of three tests conducted for each acid concentration
  as shown in Table 13.

** Initially seeded with 400 ml of return sludge.

*** Values obtained using #4 filter paper.

Discussion

When sulfuric acid samples are neutralized to the same extent with lime an increase in sample acid concentration would result in an increased amount of lime required to complete the neutralization. It follows, from quantitative chemical calculations, that if the weight of the reactants is increased the weight of the product, in this case calcium sulfate, would also increase. This accounts for the increased sludge volumes and dry solids concentrations obtained with increased sulfuric acid concentrations of the samples.

According to the theory of specific resistance as developed by Carman (2, 3, 4), the specific resistance of a sludge is independent of solids concentration at a given pressure since it is a measure of the flow of filtrate through a unit weight of cake per unit area. At equal suction pressures the characteristics of a unit weight of cake per unit area do not change and therefore the resistance to the flow of filtrate per unit volume of filter cake does not change. Since increased acid concentration serves mainly to increase the solids concentration of the slurry it follows that increased acid concentration should not affect the specific resistance of the sludge.

It will be observed in Table 14 that as the acid concentration of the samples increased, and likewise the dry solids

concentration, the specific resistance decreased slightly.
Faust (6) noted a similar decrease in specific resistance for
calcium sulfate sludges with increased dry solids concentra-
tion. An explanation for this variation is thought to lie
in the resistance to filtration offered by the filter paper
used in the experiments. Carman (3), in establishing the
theory of specific resistance, noted that in order to mask
the resistance of the filtering media it was necessary to
initially deposit a thickness of filter cake equal in resist-
ance to the filter media being used. Carmon delayed taking
time and filtrate readings until the necessary amount of cake
had been deposited and in this manner was able to minimize
the interference from filter cloth resistance. Coackley and
Jones (5), in filtering sewage sludges, employed the same
methods in their work. It was not practical to use this
technique in these experiments conducted on the rapid filter-
ing calcium sulfate sludges. Preliminary calculations reveal
that for a typical one per cent sulfuric acid sample, neutra-
lized to pH 11.00, 500 milliliters of slurry would have to
pass through the filter paper before sufficient material had
been deposited to overcome the resistance of the paper. Since
only one liter samples were used this would, in most cases,
result in an insufficient number of time-filtrate volume
readings remaining to yield a satisfactory plot. Therefore

no attempt was made to mask the resistance of the filter paper
and the values of specific resistance given in this thesis are
necessarily influenced by this factor. It will be noted, how-
ever, that in all cases, except the experiments on varying
acid concentration, the dry solids content of the slurry did
not vary appreciably. For samples with similar dry solids
concentrations, approximately the same amount of the slurry
of each sample would be required to pass through the filter
paper before the resistance of the paper was overcome. There-
fore, although the values of specific resistance are not pure-
ly measures of the resistance of the calcium sulfate, it is
thought that the trends indicated by these values are valid
since each would be affected approximately the same by the
resistance of the filter paper. However, for samples which
did not contain similar dry solids concentrations, the amount
of slurry necessary to mask the resistance of the filter paper
would vary. The result would be that the samples which con-
tained the highest dry solids concentration would be less in-
fluenced by the resistance of the filter paper, since they
would overcome this resistance at an earlier stage in the
filtration process and would therefore yield the lowest values
of specific resistance.

An investigation of Table 14 reveals that the dry solids
concentration of the two per cent sample was slightly larger

than the one per cent sample while the dry solids concentra-
tion for the five per cent sample was significantly increased.
It can also be seen from Table 14 that the specific resistance
for the two per cent sulfuric acid sample was slightly lower
than for the one per cent sample while the five per cent sam-
ple showed a significant decrease over the one per cent sample.
This variation in specific resistance was thought to be due
to the factors stated above. That is, as the acid concentra-
tion, and likewise the dry solids concentration, of the sample
was increased the effect of filter paper resistance on the
sample decreased and therefore the specific resistance of the
sample decreased. The variations noted in these experiments
therefore are thought to be caused by variations in the ef-
fect of filter paper resistance rather than by variations in
sludge filterability.

V. DISCUSSION OF RESULTS

The concept of specific resistance was used to investigate the affect of certain variables on the filterability of calcium sulfate sludge resulting from high calcium hydrated lime neutralization of return sludge seeded, sulfuric acid samples. Mixing rate, lime addition rate, degree of neutralization, return sludge dosage and acid concentrations were the variables investigated.

Heise and Johnson (10), in describing a continuous flow acid waste treatment process, noted that different shaped propeller blades affected particle size and that each blade required a different speed to produce a sludge with maximum filterability. The data obtained in this investigation indicated that mixing rate and lime rate were factors affecting the filterability of calcium sulfate sludge. In the return sludge studies, lime addition rate appeared to have more effect on sludge characteristics than did mixing rate with the return sludge obtained using slow lime addition being a more effective seed material than that obtained using rapid lime addition. This was thought to be because slow lime addition produced a slow buildup in supersaturation resulting in the formation of large sludge particles once supersaturation was reached. Mixing rate, rather than lime addition rate, appeared to be the factor controlling the filterability of

sludges obtained from neutralization of return sludge seeded, sulfuric acid samples. For a given return sludge-sulfuric acid system, slow mixing produced a more filterable sludge than did rapid mixing regardless of the lime addition rate employed. However, slow mixing and slow lime addition produced the most rapidly filtering sludge. It was thought that rapid mixing was less effective than slow mixing because it tended to increase the rate at which the lime slurry went into solution and thereby increased the rate of supersaturation buildup, resulting in a smaller particle size. It was noted that samples which exhibited the highest filtration rates did not dewater most completely.

The degree of neutralization to which a sulfuric acid sample was extended appeared to have only a minor effect on the filterability of the resulting sludge. This effect was in the form of a slight decrease in the filterability of the sludge as the final pH of the sample was increased. An explanation for this decreased filterability with increased pH is thought to lie in the solubility of the reaction products formed upon lime neutralization of the sulfuric acid samples. Small percentages of iron and aluminum are present in the neutralizing lime and, upon reacting with the sulfuric acid, the hydroxides of these substances are formed. These hydroxides, gelatinous in texture, are soluble at low values of pH but become increasingly insoluble with increased pH. Therefore as the final pH of the sample is increased the percentage

of these compounds contained in the sludge is increased. The
presence of these gelatinous compounds in the sludge tends to
clog the pores of the sludge and the filter paper and thus
decrease the rate of flow of filtrates. This interference,
and likewise the specific resistance, is increased with in-
creased pH since larger amounts of the hydroxides would be
precipitated to hinder the flow of filtrate. The fact that
underneutralization to pH 4.35 produced a significant decrease
in filter cake moisture was noted, but no explanation for
this observation could be given.

It was observed that the filterability of the calcium
sulfate sludge decreased with increased return sludge dosage;
however, the variation was minor for the range of dosages
investigated. The optimum return sludge loading for a given
acid-lime system would produce the most filterable sludge
for that system since a minimum number of virgin micro-
crystals would be present in the slurry. No attempt was
made in these experiments to obtain the optimum return sludge
loadings; therefore, the complete significance of this vari-
able was not evaluated.

The values of specific resistance obtained in these
experiments were not solely a measure of the resistance of
the calcium sulfate sludge but were affected by the resist-
ance of the filter paper. During the early stages of a fil-
tration test, prior to buildup of a filter cake, the major
resistance to the flow of filtrate would be offered by the

filter paper. As the filter cake builds up, however, the effect of the filter paper would decrease since the flow of filtrate would become more and more affected by the resistance of the filter cake. For samples with similar dry solids concentrations the influence of the filter paper on the filtration test results would be similar since the time required for build up of the necessary filter cake would be approximately the same. Therefore, although the values of specific resistance would be increased by the filter paper resistance, the trend exhibited by the values would be valid. However, for samples with widely varying dry solids concentrations the influence of the filter paper would not be the same. As the solids concentration of the samples increased, the length of time required to deposit a filter cake of a given thickness would decrease. Therefore samples with high dry solids concentrations would overcome the resistance of the filter paper more rapidly than would samples with a lower dry solids concentration. The result would be that samples with high dry solids concentration, since they would be less affected by the filter paper resistance, would have lower specific resistance values. Theoretically, solids concentration has no affect on specific resistance; however, this is only true when the filtration is conducted in such a way that the resistance of the filter paper is negligible for the entire period of the test.

For samples with varying acid concentrations it was observed that the specific resistance decreased slightly with increased acid concentration. It was also observed that the dry solids concentration of the samples increased with increased acid concentration and an explanation for the variations in specific resistance obtained is thought to lie in this fact. Based on the above discussion, samples with high dry solids concentrations are less influenced by filter paper resistance than are samples with lower dry solids concentrations. Therefore as the acid concentration of the sample increased, and likewise the solids concentration, the effect of the filter paper on the specific resistance values obtained would decrease. This would result in the values of specific resistance decreasing with increased sample acid concentration, as was the case in these experiments.

The studies conducted in connection with this thesis were carried out using samples containing only sulfuric acid and distilled water. Actual industrial wastes, however, contain impurities in the form of metal ions, organic compounds and inorganic acids other than sulfuric. The reaction products which these compounds form, upon lime neutralization, coprecipitate in the sludge and interfere with the filtration of these wastes. Therefore this investigation should be extended to actual industrial wastes before a complete evaluation of the effect of these same variables on a commercial process can be evaluated.

VI. CONCLUSIONS

This preliminary investigation had led to the following conclusions:

1) Mixing rates and lime addition rates are factors which affect the characteristics and filterability of calcium sulfate sludge. Slow lime addition produced a more effective return sludge than did rapid lime addition regardless of the mixing rate employed. Slow sample mixing produced a more filterable sludge than did rapid mixing for a given lime addition rate, with slow mixing and slow lime addition producing the most filterable sludge.

2) The degree of neutralization to which a sulfuric acid sample is extended effects only minor variations in the filterability of the resulting calcium sulfate sludge.

3) The return sludge loadings used in these experiments effected only minor variations in the filterability of the samples tested. Further tests should be conducted to determine the optimum return sludge loading for this acid lime system before the complete significance of return sludge loading can be made.

4) A decrease in specific resistance was observed with increased acid concentration. This variation was thought to be due to varying amounts of filter paper resistance influencing the tests rather than a modification of sludge filterability with varying acid concentration.

VII. SUMMARY

The object of this investigation was to determine, by the concept of specific resistance, the effect of certain variables on the filterability of calcium sulfate sludge resulting from lime neutralization of synthetic, return sludge seeded, sulfuric acid samples. The variables investigated were rate of mixing, rate of lime addition, degree of neutralization, return sludge loadings and acid concentration.

Mixing rates and lime addition rates are factors which affect the characteristics and filterability of calcium sulfate sludge. Slow lime addition produced a more effective return sludge than did rapid lime addition regardless of the mixing rate employed. Slow sample mixing produced a more filterable sludge than did rapid mixing for a given lime addition rate, with slow mixing and slow lime addition producing the most filterable sludge.

The degree of neutralization to which a sulfuric acid sample was extended and the amount of return sludge added to the sample prior to neutralization appeared to have only a minor effect on the filterability of the samples tested.

The values of specific resistance obtained in these experiments were not solely a measure of the resistance of the calcium sulfate sludge but were affected by the resistance of the filter paper. It was thought that this effect was

approximately the same for samples containing similar dry solids concentrations and therefore, in such cases, did not affect the trends of the results. As the dry solids concentration of the samples increased, however, the effect of filter paper resistance would decrease and therefore the specific resistance of the sample would decrease.

A decrease in specific resistance was observed with increased acid concentration. This variation was thought to be caused by variations in filter paper resistance influencing the results rather than variations in sludge filterability.

The values of specific resistance obtained in these experiments were of the same order of magnitude as those contained in the literature.

VIII. ACKNOWLEDGMENTS

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XI. APPENDICES

APPENDIX A

Mathematical Theory of the Specific Resistance Filtration Method. (From Faust (6))

Coackley developed the "specific resistance" method for determination of the filterability of sewage sludge from numerous sources. The term "specific resistance" was conceived by Carman (1, 2, 3). He found that $dv/d\theta$, the rate of flow of liquid through a filter cake was equal to:

1) $\dfrac{dv}{d\theta} = \dfrac{pA^2}{u(rcV + R_mA)}$

where:

P = suction pressure

r = specific resistance

V = volume of filtrate

Rm = initial resistance of one sq. cm. of filtering surface

A = area of filtering surface

u = viscosity of filtrate (assumed to be that of water at 28°C)

c = weight of dry solids per unit volume of liquid before filtration.

In order to determine r, Equation 1) must be integrated to:

2) $\theta = \dfrac{urc}{2PA^2}(v)^2 + \dfrac{uRm}{PA}(v)$

Then,

3) $\dfrac{\theta}{V} = \dfrac{urc}{2PA^2} \cdot V + \dfrac{uRm}{PA}$

or,

4) $\dfrac{\theta}{V} = bV + a$

where:

$b = \dfrac{urc}{2PA^2}$

If θ/V is plotted against V a straight line with a slope of b is obtained. Specific resistance is then calculated from the equation:

5) $r = \dfrac{2bPA^2}{uc}$

Units of expression for the variables in Equation 5) are as follows:

P = suction pressure in gm/sq.cm

A = area in sq. cm.

u = viscosity in poises (gm/sec.cm.)

c = solids content in gm/ml

r is expressed as sec^2/gm.

These equations do not completely express the rate of filtration in the case of compressible cake unless r is regarded as a function of the pressure. A satisfactory equation relating specific resistance and pressure was found to be:

6) $r = r^1 p^s$

where

r^1 = a constant if filter cake were ideal

s = a constant, the coefficient of compressibility

The coefficient of compressibility, s, is characteristic for a given filter cake. A positive value of s indicates a compressible cake and is determined from r values at different pressures. A plot of log r versus log p gives a straight line with slope s.

APPENDIX B

Sample Calculation of Specific Resistance

The following is a sample calculation of the specific resistance of a neutralized slurry of a one per cent sulfuric acid solution. Filtrate volume readings, shown in Table 15, were taken every 15 seconds until a constant volume of 860 ml was obtained. A plot of the ratio of time to filtrate volume versus filtrate volume to obtain the slope "b" is shown in Figure 3. After determination of the slope, the specific resistance can be calculated from equation 5) as follows:

$$5) \quad r = \frac{2bPA^2}{uc}$$

where:

b = slope of line = 0.0000631

P = suction pressure = 5.0 inches of Hg or 172.66 gm/sq.cm

A = filter area = 63.62 sq. cm.

u = filtrate viscosity at $28^{\circ}C$ = 0.008360 poises

c = solids content = 0.0245 gm/ml.

Then:

$$r = \frac{2 \times 172.66 \times (63.62)^2 \times 0.0000631}{0.008360 \times 0.0245}$$

$$r = 0.431 \times 10^6 \ sec^2/gm$$

TABLE 15 FILTER TEST DATA

Θ-sec	V-ml	$\frac{Θ}{V}$
0	0	—
30	355	0.084
45	490	0.092
60	615	0.098
75	710	0.106
90	800	0.113
105	835	0.126
120	850	0.141
135	855	0.158
150	860	0.175
165	860	0.192

Suction pressure = 5.0 inches Hg or 172.66 gm/sq cm

Filtrate viscosity at 28 °C = 0.008360 poises

Filter area = 63.62 sq cm

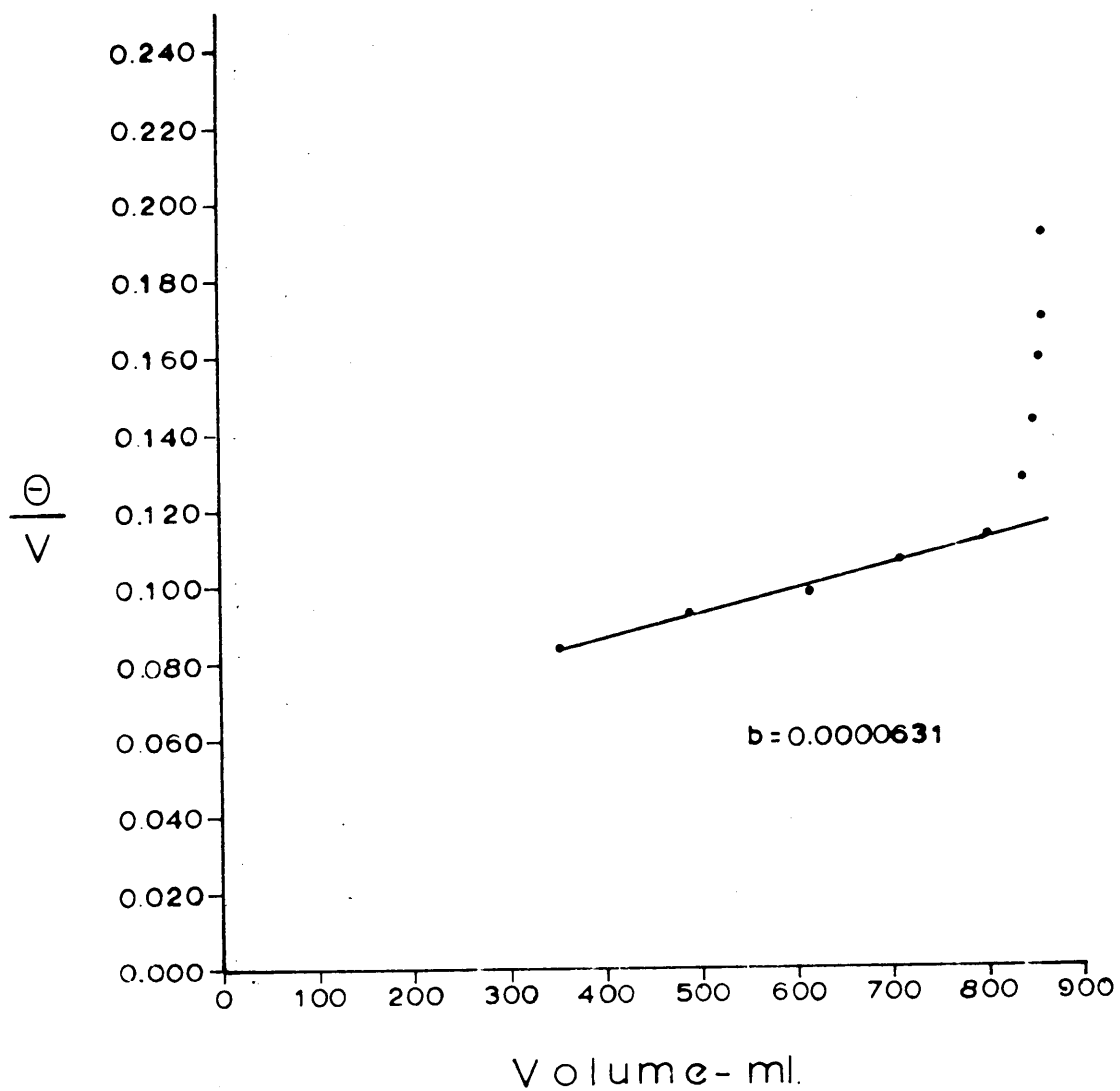Slope, b = 0.0000631 sec/cm^6

Solid content = 0.0245 gm/ml

FIGURE 3 DETERMINATION OF SLOPE "b"

APPENDIX C

A Review of Crystallization Theory

The first theory of crystal growth which gained serious
consideration was that of Curie developed in 1885. This
theory was based primarily on surface energy considerations
and stated, "that a crystal will adopt such an end form as
will be consistent with its possessing a minimum sum total
of surface energies." If, for example, a crystalling body
were limited by faces whose surface areas were S, S_1, S_2,
S_3, . . . and whose corresponding capillary constants (the
energy required to be expended on increasing the surface by
a unit of area) were A, A_1, A_2, A_3, . . . then the final form
of the growing crystal would be such that $A \cdot S + A_1 \cdot S_1 +
A_2 \cdot S_2 + $ . . . has a minimum value. Curie's theory was
accepted for some time after it appeared and was extended
by other workers. However Berthoud and Valeton showed that
one of the implications of Curie's theory was that the great-
er the supersaturation of a solution the more rapid is the
growth and in consequence, the crystal habit ought to become
more complex. The reverse seems to be true, however, as "a
crystal becomes simpler, the more rapid the growth, usually
until one single form predominates to the practical exclusion
of all others."

Having showed the limitations of the theory of Curie,
Berthoud and Valeton, turned to developing a theory concern-
ing the diffusion of crystal material through a thin layer of
quiescent solution. These "diffusion theories", developed
from a publication by Noyes and Whitney in 1897, were popular
for a number of years after the shortcomings of Curie's sur-
face energy theory had led to a decrease in its popularity.
The "diffusion theories" assumed that dissolution (and
growth) was practically a diffusion phenomen and was defined
by the equation:

$$dx = \frac{DS}{L} (C_0 - C_2)\, dt$$

where:

dx = the amount detached from the surface of the
crystal

dt = the length of time taken in the process of
detaching the amount dx

D = coefficient of diffusion

S = surface of the crystal exposed

C_0 = concentration of the solution at saturation

C_2 = concentration actually prevailing (C_2 is under-
saturation during dissolution and, if applied to
growth, supersaturation)

L = the thickness of layer through which diffusion
is taking place.

The "diffusion theory" implied that dissolution and growth
occurred at the same rate and also that the rate of growth or

dissolution of all the faces of a crystal are equal. Later work proved that these facts are not true and led to criticism of the diffusion theories.

Of the recent theories of crystal growth one of the more popular ones appeared to be that of Kossel. His theory of equivalent or repeatable step was, "the first to explain a view of crystal growth which emphasizes the atomistic rather than the thermodynamic side of surface relationship." Kossel proposes that crystal growth occurs in a layerwise fashion with the growth of one layer being completed before a new layer is begun. This is because the energy yield of the repeatable step, continued addition of ions in the latice of a growing layer, is greater than that of starting a new layer. The point at which the crystal growth begins depends on the type of crystal. For heteropolar (ionic) crystals the preferred building sites are the corners, edges and faces of the crystals while for homopolar crystals the order is reversed.

Any factor that interferes with the uniform flow of material to all parts of a growing crystal may lead to malformations of the standard crystal habit. Such things as proximity to another crystal or the walls of the containing vessel, or the maintenance of a degree of supersaturation to one side of the crystal are factors which may cause malformations. Apart from such obvious environmental differences

there are two important factors that influence the shapes of
the crystals of a particular substance:

    a) Rate of growth - rapid growth often leads to such
          extremes of development as thin needles or
          plates, while slow growth produces more
          compact crystals.

    b) Effect of solvent or added impurity - the action
          of solvents and impurities present in solu-
          tion tend to modify crystal habit by in-
          hibiting the growth of certain faces of
          the crystal.

Crystal shape is very important in processes which in-
volve the filtration of solutions containing crystals. There-
fore an effort should be made in such processes to provide
conditions that will insure both constancy of habit in dif-
ferent batches and suitability of crystal shape.

Abstract

CRYSTAL SEEDING FOR THE CONTROL OF SLUDGE PROPERTIES

The object of this investigation was to determine, by the concept of specific resistance, the effect of certain variables on the filterability of calcium sulfate sludge resulting from lime neutralization of synthetic, return sludge seeded, sulfuric acid samples. The variables investigated were rate of mixing, rate of lime addition, degree of neutralization, return sludge loadings and acid concentration.

Mixing rate and lime addition rate are factors affecting the characteristics and filterability of calcium sulfate sludge. Slow lime addition provided a more effective return sludge than did rapid lime addition. Slow sample mixing produced a more filterable sludge than did rapid mixing for a given lime addition rate.

The degree of sample neutralization appeared to have only a minor effect on the filterability of the sludge, with the filterability improving as the final pH of the sample decreased.

The sample return sludge dosage appeared to have only a minor effect on the filterability of the resulting sludge with filterability decreasing as return sludge loadings increased. A complete evaluation of the effect of return sludge loading cannot be made, however, until these studies are expanded to include the optimum return sludge loading for the given acid-lime system.

The values of specific resistance obtained were influenced by the resistance of the filter paper. For samples with similar dry solids concentration the effect is approximately the same; however, the amount of filter paper interference decreases with increased sample dry solids concentration.

For varying acid concentrations there was a minor decrease in specific resistance as the acid concentration, and dry solids concentration, of the samples increased. This decrease was thought to be due to decreasing amounts of filter paper interference rather than improved sludge filterability.