

BARIUM CARBONATE TREATMENT OF  
SULFURIC ACID WASTEWATER

by

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## I. INTRODUCTION

The broad interpretation and stringent enforcement by the Federal Government of the Refuse Act of 1899 (33 U.S.C. 407) has placed new emphasis on the treatment of industrial wastewaters. Industry is being forced to seek new technology for reducing the concentrations in wastewater effluents of substances heretofore considered capable of exerting only minor degradational influences on the quality of natural waters. One such constituent of many industrial wastewaters which has received little attention during the continuous evaluation and upgrading of waste treatment processes is the sulfate ion ( $\text{SO}_4^{=}$ ).

Sulfates may be discharged in the wastewaters of any industrial concern which uses sulfate bearing chemical compounds in its manufacturing process. By far the most universal sulfate bearing compound used in industry is sulfuric acid ( $\text{H}_2\text{SO}_4$ ). Carson (1) points this fact out by considering that "the consumption of sulfuric acid can still be taken, in general, as a barometer of industrial health, since it is indispensable in many industries."

The magnitude of sulfuric acid utilization in industry may best be appreciated by considering two of the most prestigious industries, the steel mill industry and the textile industry. A typical integrated steel mill uses approximately 45 lbs of sulfuric acid in pickling one ton of steel. This figure is significant when it is realized that an average typical integrated steel mill



produces 1,500,000 ingot tons per year, at least 50% of which is pickled using sulfuric acid (2). A second example of sulfuric acid utilization is in the textile industry where 10 lbs of sulfuric acid is used in finishing 1,000 lbs of cotton goods (3). A medium sized textile plant finishes, on an average 40,000 lbs per day of cotton cloth (4). Sulfuric acid is also used in battery manufacturing, as a catalyst in the alkylation process during petroleum refining, in the production of cellophane in the plastics industry and in numerous other industrial processes. Production of sulfuric acid (100 percent  $H_2SO_4$ ) totaled 29,536,914 short tons in 1969. Of this value approximately 28 million short tons were consumed by the producing plant or shipped to other users (5).

Large quantities of the sulfuric acid used in any manufacturing process usually end up in the waste effluent discharged from that process. For the integrated steel mill example mentioned above, waste sulfuric acid loads from the pickling operation consist of 12,350 lbs per day in the strong waste liquor and 2,180 lbs per day in the rinse-water and may vary from these figures by 35% or more (2). Logan (6) gives figures of 100,000 and 5,100 lbs of sulfuric acid as waste in the production of 100,000 lbs of smokeless powder and 100,000 lbs of nitroglycerine, respectively, in the munitions industry.

Proper treatment of waste effluents containing sulfuric acid is necessary before discharging the wastewater into natural bodies of water or into municipal sewerage systems. Treatment prior to discharge is necessary due to the adverse effects on the aquatic

environment and the deterioration of concrete and steel pipes and hydraulic structures caused by untreated sulfuric acid wastewater. Adequate treatment of mineral acidity is accomplished in industry in various ways among which are:

- (1) recovery of the sulfuric acid for:
  - a. reuse
  - b. for sale to other industries
- (2) neutralization by:
  - a. using inplant waste alkali
  - b. addition of commercial alkali
- (3) deep well disposal
- (4) barging to sea (controlled rate subsurface discharge)

Although recovery processes, deep well disposal and barging to sea are being practiced by some industrial concerns, neutralization, for economic reasons, is by far the most widely used method for treating sulfuric acid wastewaters.

Neutralization, or the adjustment of pH to a value approximating neutrality or pH 7, is accomplished in the case of sulfuric acid by the addition of an alkaline material. The alkali, in the proper amount to effect a desired pH change, is added to the acidic wastewater in either a batch or continuous flow system with subsequent settling of any precipitant formed during the reaction and discharge of the effluent into the receiving stream.

There are numerous alkaline chemicals available commercially which are suitable for neutralizing sulfuric acid wastewaters. A partial listing of applicable chemicals is presented in Table I.

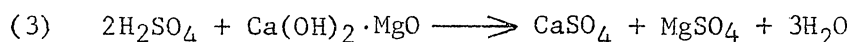
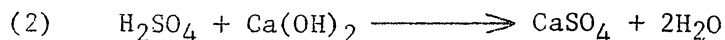
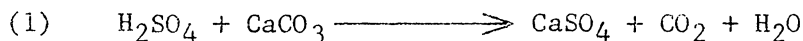
TABLE I

NEUTRALIZATION COST AND REACTION PRODUCT SOLUBILITY DATA FOR VARIOUS ALKALINE CHEMICALS (10,29)

ALKALI	CHEMICAL FORMULA	NEUT. COST (\$/100 lb H <sub>2</sub> SO <sub>4</sub> )	REACTION PRODUCT CONTAINING SO <sub>4</sub> <sup>=</sup>	SOLUBILITY (gm/100 ml H <sub>2</sub> O at 20°C)
Dolomitic Limestone	CaCO <sub>3</sub> ·MgCO <sub>3</sub>	0.19	CaSO <sub>4</sub> , MgSO <sub>4</sub>	0.21 , 25.2
High Calcium Limestone	CaCO <sub>3</sub>	0.21	CaSO <sub>4</sub>	0.21
Dolomitic Lime (unslaked)	CaO·MgO	0.27	CaSO <sub>4</sub> , MgSO <sub>4</sub>	0.21 , 25.2
High Calcium Lime (unslaked)	CaO	0.30	CaSO <sub>4</sub>	0.21
Dolomitic Lime (hydrated)	Ca(OH) <sub>2</sub> ·MgO	0.39	CaSO <sub>4</sub> , MgSO <sub>4</sub>	0.21 25.2
High Calcium Lime (hydrated)	Ca(OH) <sub>2</sub>	0.48	CaSO <sub>4</sub>	0.21
Anhydrous Ammonia (liquid)	NH <sub>3</sub>	1.37	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	75.4
Soda Ash	Na <sub>2</sub> CO <sub>3</sub>	1.64	Na <sub>2</sub> SO <sub>4</sub>	19.5
Aqua Ammonia (liquid)	NH <sub>4</sub> OH 26°Be	3.88*	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	75.4
Caustic Soda (liquid)	NaOH 50%	4.08	Na <sub>2</sub> SO <sub>4</sub>	19.5
Caustic Potash (liquid)	KOH	4.77*	K <sub>2</sub> SO <sub>4</sub>	10.6
Caustic Soda Flake	NaOH	5.71	Na <sub>2</sub> SO <sub>4</sub>	19.5

\* Based on price as quoted in Chemical Marketing Reporter (7)

All of the alkalies listed react with sulfuric acid to form sulfated salts through one of the three fundamental neutralization reactions illustrated by the following examples:



As shown by the last column of Table I, the reaction products formed during sulfuric acid neutralization are all soluble to some degree, the sodium, sodium-magnesium, potassium, and ammonium salts more so than the calcium salts. Solubility values are often higher than those presented in Table I due to supersaturation or the neutralization of wastewaters at higher temperatures. Figures 1 and 2 have been prepared by the author to illustrate the importance of temperature on solubility.

Sodium, sodium-magnesium or ammonium alkalies have often been chosen as neutralizing agents due to their high solubilities, thereby eliminating expensive sludge handling facilities. Garvie and Waite (10) list the increased solubility of ammonium salts as a benefit in their evaluation of using aqua ammonia in neutralizing the sulfuric acid used in regenerating a deionizer. Gurnham (11) notes that even though caustic soda and sodium carbonate are more convenient than lime, calcium base alkalies are cheaper and therefore are more widely used.

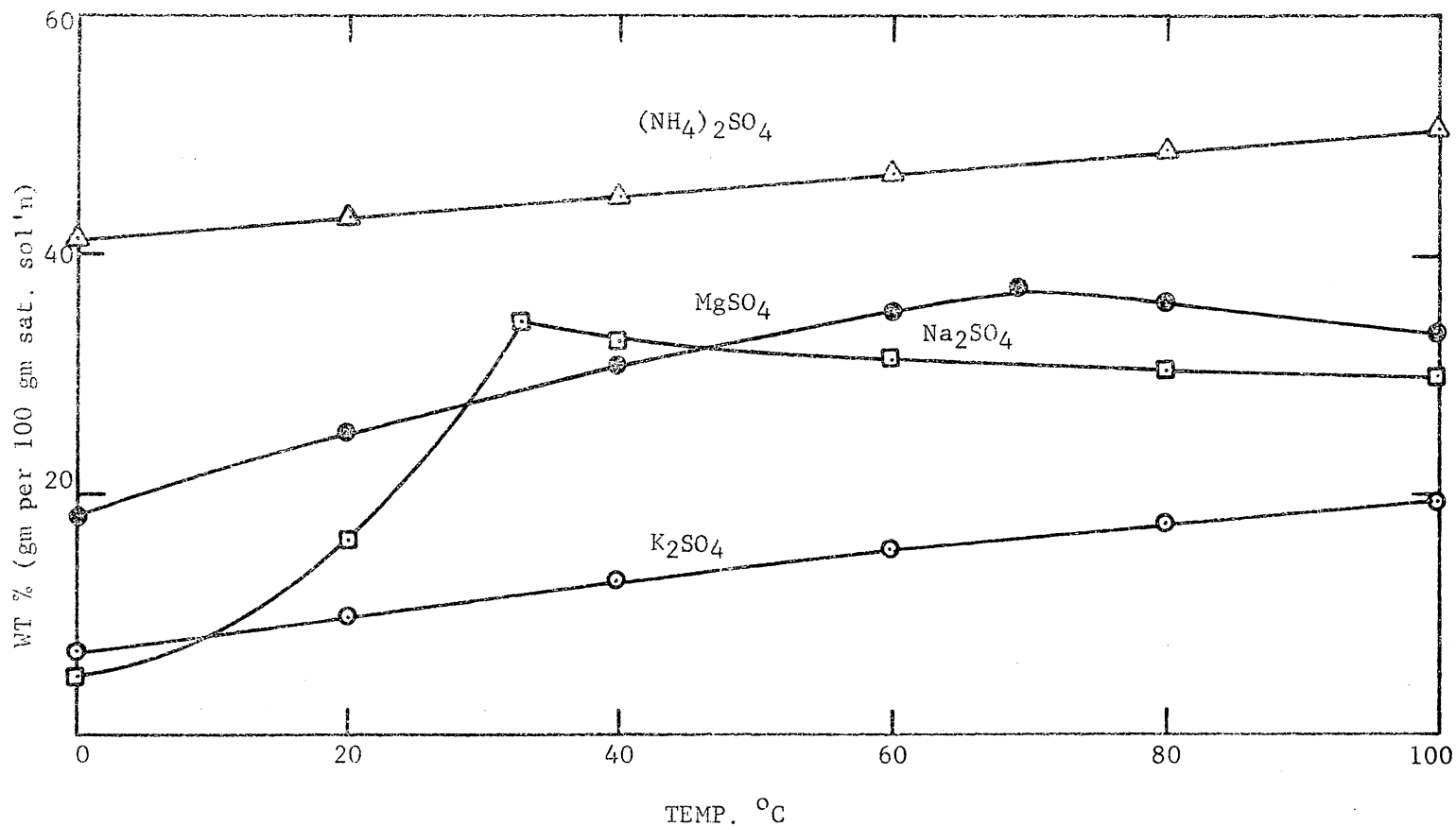


FIGURE 1. SOLUBILITY-TEMPERATURE RELATIONSHIP FOR THE REACTION PRODUCTS RESULTING FROM SULFURIC ACID NEUTRALIZATION BY COMMON ALKALIES (3)

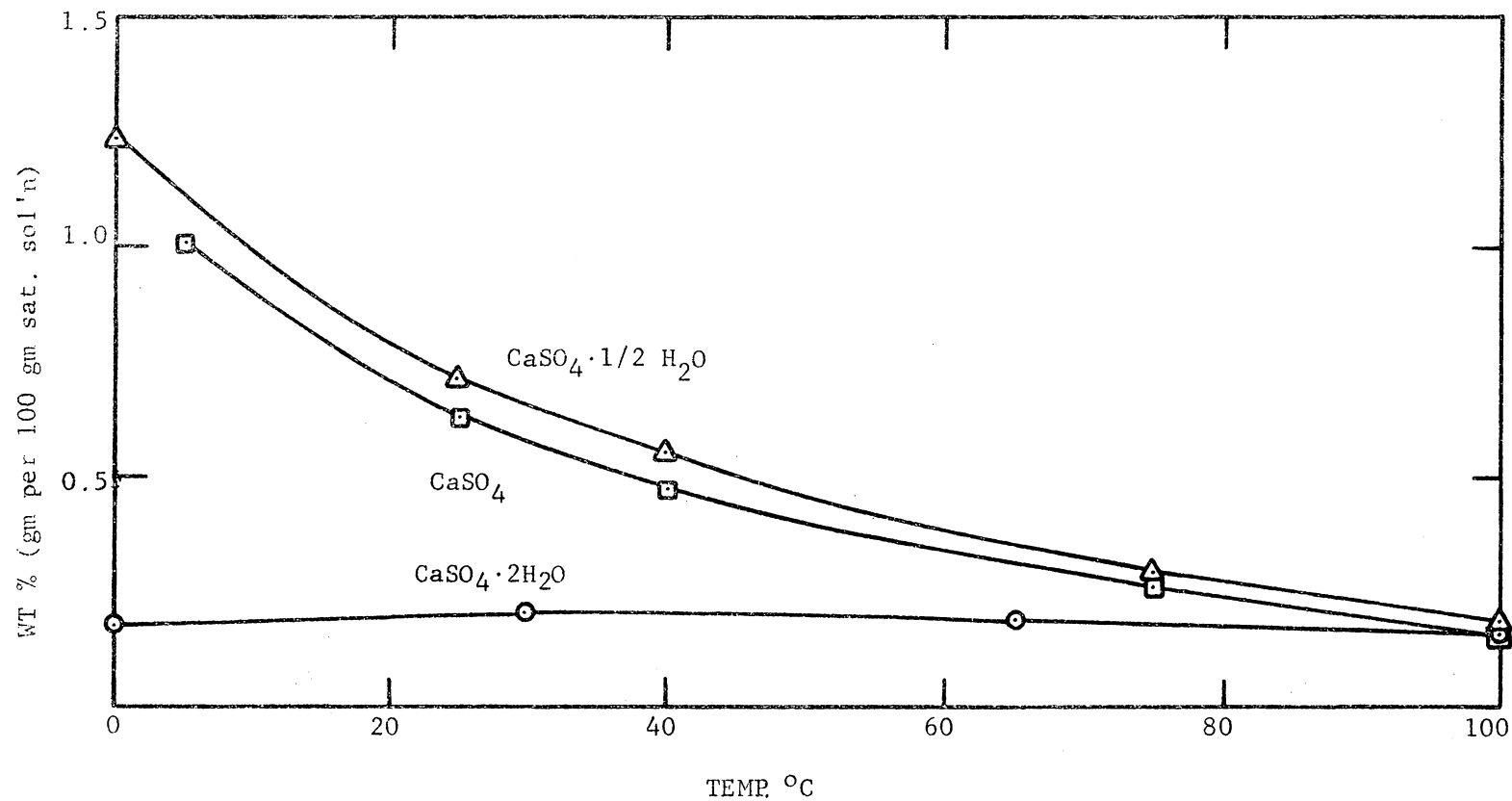


FIGURE 2. SOLUBILITY-TEMPERATURE RELATIONSHIP FOR DIHYDRATE, HEMIHYDRATE AND ANHYDRITE CALCIUM SULFATE (9)

Although lime is one of the less costly alkalies available commercially, lime neutralization of sulfuric acid wastes does present a sludge handling problem. Sludge conditioning, dewatering, and disposal are usually the major cost considerations when designing neutralization facilities utilizing lime. The calcium sulfate sludge formed during the neutralization reaction settles rapidly but exhibits poor compaction characteristics, therefore forming large sludge volumes.

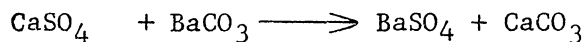
Regardless of the alkali used at the present time in neutralizing sulfuric acid wastewaters, considerable concentrations of soluble sulfates may be found in the treated effluents being discharged from typical sulfuric acid neutralization facilities. Considering the federal, state, and local governments' stand on total non-degradation of receiving streams by waste effluents, the sulfate concentrations imparted to natural waters due to the solubility of the reaction products resulting from using any of the alkalies listed in Table I is undesirable.

The investigation presented herein explored the possibility of solving the soluble sulfate problem encountered during sulfuric acid neutralization, by introducing barium carbonate into the neutralization reaction in order to form the very insoluble barium sulfate. Barium carbonate addition and subsequent formation of barium sulfate was effected in the following ways:

- (1) direct neutralization and subsequent precipitation



(2) precipitation from neutralized solution



Stoichiometric calculations show that considerable quantities of barium carbonate, depending on the acid concentration, are required for completion of either reaction (1) or (2). Considering that precipitated barium carbonate in carlot quantities costs \$140.00 per ton, the solution as presented above to the soluble sulfate problem would have been considered as late as two years ago as non-feasible due to cost considerations. Sanitary and environmental engineers, however, can no longer shelve waste treatment ideas due to undesirably high costs. Governmental and public awareness of the water pollution situation and their concern towards immediate action in improving the environment justify this study or any study which may be either directly applied to waste treatment or form the basis for further research in the water pollution control field.



## II. LITERATURE REVIEW

In order to gain insight into the effectiveness of using barium carbonate as a precipitating agent in removing sulfate ions from solution, numerous and varied subjects must be investigated. Proper mixing conditions, the precipitation mechanism, solubilities of the reactants and dewaterability of the resulting chemical sludge are but a few of the important areas which must be considered. The literature pertaining to the above mentioned areas and other important aspects of the subject study is presented in this review.

### Sulfuric Acid Neutralization

Generalities concerning the materials, methods and mechanisms involved in sulfuric acid neutralization have been mentioned briefly in the introduction. There are few industries, however, where sulfuric acid is the lone constituent of the wastewater to be treated. Waste components such as metals, organics, other waste acids, or inert materials may be found in almost all sulfuric acid wastewaters depending on the nature of the process in which sulfuric acid is utilized. One of the obvious exceptions is the wastewater accumulated during the manufacture of sulfuric acid (12). Further elaboration on the neutralization process or a review of the literature dealing with specific industries and the composition and treatment of their associated acidic wastewaters is beyond the scope of this study.

Numerous articles (12-23) presented in the literature of the past twenty-five years dealing with the neutralization of wastewaters containing sulfuric acid were studied to ascertain whether any recognition of a soluble sulfate problem was mentioned. Several indications of such recognition were noted, but none were very strongly expressed. Besselievre (16) mentions one instance in which a state health department was adverse to the use of dolomitic lime because of the possible increase in hardness of the receiving stream, which would impose a burden on the potable water users downstream. Besselievre believes that a study should be effected to ascertain situations during which it is justifiable to place the burden of extra expenditures for waste treatment on industry so as not to let downstream municipalities worry about the extra cost of softening.

After stating that precipitation during neutralization is undesirable, Parsons (21) adds that "in certain instances the discharge of effluents high in dissolved salt may also be detrimental to receiving streams". Neas (18) in reporting on the neutralization of viscose rayon wastes describes the substitution of dolomitic lime for hydrated lime when the acid concentration of the waste exceeds 1500 mg/l. The use of dolomitic limestone was found to prevent gypsum precipitation and to effect the redissolving of deposits of gypsum already present. Neas mentions, however, that the use of dolomitic lime is limited whenever it is necessary to prevent an increase of hardness in the receiving stream. Mudrack (22) advocates utilizing the temporary hardness of large receiving streams to

neutralize a portion of the acid waste from nitro-cellulose production. Mudrack points out that when the waste is neutralized completely in the plant, the permanent hardness of the waste is added to the hardness of the receiving water.

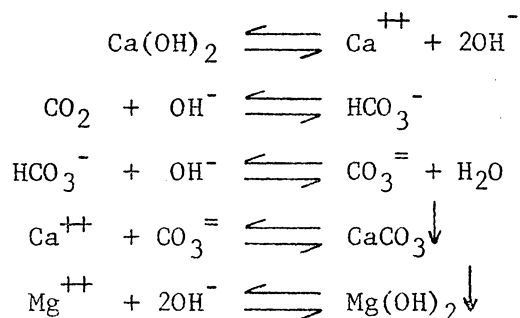
The general theme of the articles studied appeared to be the affirmation of lime treatment as both a cheap and effective method of neutralizing wastewaters containing sulfuric acid. In several articles, as presented above, mention was made of the realization that the discharge of the soluble portion of the reaction product of lime neutralization of sulfuric acid wastes increased the permanent hardness of the receiving stream.

#### Chemical Precipitation

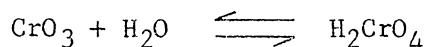
Chemical precipitation, a water purification and waste treatment process, is effected by the addition of suitable reagents to react with soluble pollutants whereby insoluble reaction products are formed. The precipitant is subsequently removed from the purified aqueous solution by sedimentation, centrifugation, filtration or flotation. Chemical precipitation should not be confused with chemical coagulation which involves the precipitation of chemicals purposely added to wastewater to form a precipitant which during agglomeration and settling enmeshes and subsequently removes suspended particles (11, 21).

The principles of chemical precipitation have been employed in the water purification field for many years in the deferrization,

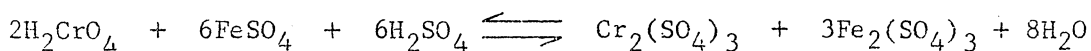
demanganization, and softening of public drinking water. In the removal of calcium and magnesium by the lime-soda process the following reactions occur (24):



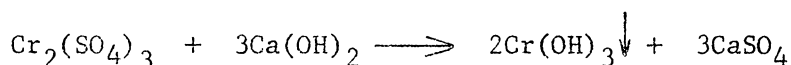
Wide use is made of chemical precipitation in industry for the removal from wastewater effluents of trace metals such as copper, chromium, iron, and zinc for either profitable recovery or water pollution control. In removing metallic ions an oxidation-reduction reaction may sometimes precede the chemical precipitation process. The classic example is the precipitation of hexavalent chromium after being reduced to the trivalent state by the ferrous ion as follows (25):



oxidation-reduction



precipitation



Chemical precipitation is also applicable in removing numerous other soluble pollutants from wastewater effluents. Parsons et al. (26) describe the removal of phosphates from digester supernatant liquor by using high calcium hydrate lime to form a precipitant of what is thought by the authors to be calcium hydroxyapatite  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ . Chemical precipitation of soluble phosphates using Fe(III) and Al(III) is described by Leckie and Stumm (27). Fluorides and aluminates are also susceptible to removal by chemical precipitation (11, 28, 29).

The mechanisms, kinetics and general characteristics of chemical precipitation are covered in detail by Walton (30). Design parameters for chemical precipitation processes are presented by Parsons (21) and include chemical dosage, reaction times, mixing rates, sludge settleability, sludge dewaterability and effluent quality. The effects of pH variation on the precipitation reaction should also be investigated. The precipitation process may be accomplished in either a batch or continuous flow system depending on waste flow rate, reaction period and frequency of waste discharge. In either operation, efficient and effective mixing of the reactants is of utmost importance.

Mixing, through the formation of velocity gradients by a rotating agitator, hastens molecular diffusion within liquids thereby producing a degree of homogenation (31). The art of mixing, long considered important in the chemical processing industry, has received relatively little mention in the literature of the water and wastewater treatment fields.

In the design of flocculators, devices in which increased particle contact is effected by hydraulic or mechanical means, the mean temporal velocity gradient is used as an indication of expected flocculator performance. The derivation of the theoretical mathematical relationship used in determining the mean temporal velocity gradient is presented elsewhere (24). The relationship for mechanical mixers utilizing flat paddles is:

$$G = \sqrt{C_D A U / 2 \nu V}$$

where

$G$  = mean temporal velocity gradient, fps/ft

$C_D$  = coefficient of drag for flat plates moving face on to the fluid

$A$  = area of the paddles, ft<sup>2</sup>

$U$  = velocity of the paddles relative to that of the fluid, ft/sec

$\nu$  = kinematic viscosity of the fluid, ft<sup>2</sup>/sec

$V$  = volume of the flocculator, ft<sup>3</sup>

This relationship shows that the mean temporal velocity gradient is a function of the power input, the volume of the vessel and the viscosity of the fluid.

The relationship presented above, however, is difficult to apply to mixing equipment other than flocculators, such as stirred tank reactors, where variables such as agitator type, size and location and vessel geometry become important. In fact,  $G$  has recently been found inadequate for predicting aggregation as pertains to a given chemical dosage during rapid mixing (32).

Consideration of the numerous variables which affect the efficiency of batch reactors, continuous flow stirred tank reactors (CFSTR's) and semi-batch stirred tank reactors are presented by Holland and Chapman (31). A diagram illustrating terms used in describing tank configuration and geometry by the chemical industry is presented in Figure 3 for future reference.

An extensive study of various types of impellers and their performance under varying conditions is available in the literature (33). In a comprehensive treatment of mixing, Rushton and Oldshue (34) state "that a mixer properly engineered for a particular chemical reaction or other operation will provide the desired ratio between mass flow on the macroscopic scale and turbulence on the microscopic scale to give the desired amount of forced convection to satisfy the demand of the particular system and the desired result".

Sterbacek and Tausk (35) in an excellent book concerning mixing in the chemical industry describe the influence of mixing on three chemical processes, dissolution, reaction and crystallization, which are common to the chemical precipitation process. The purpose of mixing when dissolving solids as explained by Sterbacek is three-fold:

- (1) "to reduce the thickness of the diffusion film at the surface of the solid particles by the streaming liquid.
- (2) to disperse the solid particles as uniformly as possible throughout the entire vessel by circulation and eddying of the liquid.
- (3) to distribute the dissolved molecules of the solid after

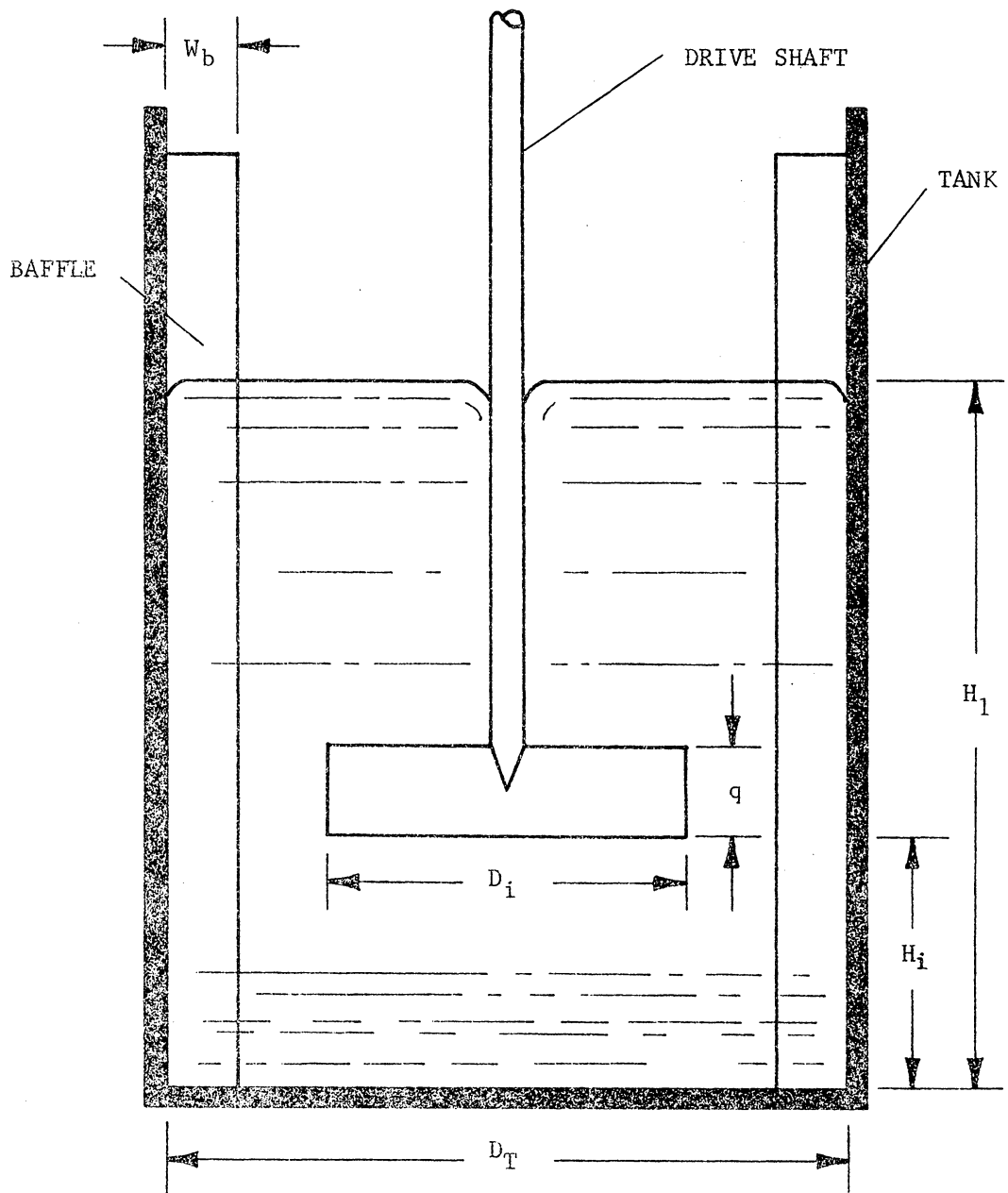


FIGURE 3. REFERENCE TANK CONFIGURATION (31)



their passage through the diffusion film uniformly and within the shortest time in the entire vessel".

Crystallization, the reverse of dissolution, involves the transfer of mass from the solution to the solid phase. Mixing, by reducing interfering thermal and diffusion films, accelerates both heat and mass transfer upon which crystallization is dependent.

In a heterogeneous reaction such as that between a solid and liquid phase, the over-all rate of reaction is governed by the slowest process, be it either the chemical reaction or mass transfer. If the chemical reaction is the slowest process and therefore governs the over-all rate of reaction, proper mixing to keep the concentration of the reactants uniform in the reactor should be employed. If mass transfer is the limiting process, it is necessary to provide efficient mixing which will reduce the thickness of the diffusion film and permit the dispersal of the diffused molecules.

#### Sulfates as Pollutants

Sulfates are pollutants, and their introduction into an aquatic environment such as a stream, river, lake or artificial impoundment causes a degradation of the quality of the life supporting aqueous medium, disrupts the biotope and creates difficulties for other water users. Turbidity, taste, odor and corrosion are but a few of the objectionable physical and chemical pollutional effects attributed to the presence of large concentrations of sulfates in natural waters.

Excessive turbidity and sludge formation problems may exist in streams or bodies of water that receive effluents from sulfuric acid neutralization facilities which utilize calcium-base alkalies. This situation, which is called "after precipitation" and is caused by the uncontrolled formation of a supersaturated solution of calcium sulfate, may persist for several days after completion of the neutralization process. Parsons (26) treats this subject extensively, further stating that at a given temperature the maximum supersaturation which may occur is represented by the difference between the solubility relation for hemihydrate ( $\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). This value has been shown to decrease with an increase in temperature (26).

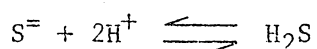
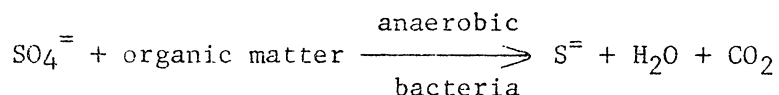
The turbidity associated with the delayed precipitation of calcium sulfate is undesirable not only due to its adverse aesthetic qualities but also because turbidity affects the depth of water to which sunlight penetrates thereby limiting phototrophic activity. Settling of the calcium sulfate precipitant over long periods of time may result in extensive sludge deposits which smother benthic organisms and cause destruction of plant and animal life which are natural food supplies for fish (36).

McKee and Wolf (37) present a quite complete bibliography in descriptive form of the literature concerning the effects of sulfates on domestic and industrial water supplies, irrigation, stock and wildlife watering, and fish and other aquatic life. In each of the categories mentioned above at least one reference is given which advocates defining either a limiting or a threshold concentration of

sulfates above which ill effects may occur. The taste threshold of calcium sulfate is given as 250 - 900 mg/l. Scofield, as quoted by McKee and Wolf, states that the permissible limit of sulfates for irrigation waters to be considered of excellent quality is 192 mg/l and that water containing concentrations exceeding 960 mg/l are unsuitable for irrigation. Of special interest, however, is that one article is reviewed that indicates through experimentation that algae require concentrations of sulfates in excess of 0.5 mg/l for adequate growth. This fact should be of interest to those environmentalists concerned with eutrophication.

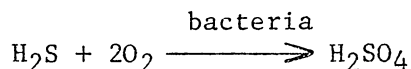
The toxicity of sulfates to mammals is presented in tabular form in a water quality report prepared for the U. S. Environmental Protection Agency by Arthur D. Little, Inc. (38). Sulfate concentrations of 3,590 and 2,104 mg/l are given as causing the weakening and death of cattle in Minnesota. 600 to 1,000 mg/l of sulfates have caused diarrhea in infants.

Odor and sewer corrosion are considered by Sawyer and McCarty (39) as two of the major problems associated with the presence of sulfates in wastewater. Both problems result from the reduction of sulfates to hydrogen sulfide by anaerobic bacteria, as illustrated by the following equations (39):



Odor problems occur at pH values below pH 8 with the formation of un-ionized  $\text{H}_2\text{S}$  completed at pH 5.

When  $\text{H}_2\text{S}$  escapes from wastewater in sewers, it rises to the crown of the sewer, dissolves in the moisture collected there and becomes available for conversion by sulfur-oxidizing bacteria such as Thiobacillus to sulfuric acid in the following manner (39, 40):



The sulfuric acid then reacts with the lime in the concrete to form calcium sulfate which weakens the structural strength of the sewer pipe. This process only occurs in sewers which are not properly ventilated and in which aerobic conditions exist above the level of wastewater flow. 300-1000 ppm of sulfates as  $\text{SO}_3^{=}$  has been presented as causing moderately severe deterioration of lean concretes cast in situ., (36). Deterioration of Portland cement concretes does not occur unless the  $\text{SO}_3^{=}$  concentration exceeds 1,000 mg/l for a considerable period of time.

Sulfates in natural waters also impart a non-carbonate or permanent hardness to the waters which increases costs of treatment when withdrawn for public or industrial use. Calcium and magnesium are considered among the principal hardness-causing cations. Hardness is undesirable in water supplies because it raises the soap-consuming capacity of the water thus lowering optimum cleansing conditions and also produces scale in pipes, boilers, and heaters.

#### Barium Carbonate, the Precipitating Agent

Barium carbonate is an inorganic chemical salt which not only occurs naturally as the mineral witherite, but may also be prepared

commercially in the precipitated form. The mineral witherite occurs as orthorhombic crystals isomorphous with aragonite and strontianite (41). Witherite is a yellowish to white ore with a specific gravity of 4.3 and a Mohs hardness between 3.00 and 3.75. Due to the limited amounts of naturally occurring barium carbonate available in the United States, almost all commercial users of barium carbonate limit themselves to using the precipitated form.

The physical appearance of precipitated barium carbonate varies from a fine, white powder with particle sizes ranging from 0.1 to 10 $\mu$ , depending on the grade, to calcined granules (41, 42). Precipitated barium carbonate has an absolute density of 4.25, a bulk density of from 41 to 150 lb/ft<sup>3</sup>, an index of refraction of 1.6 and a Mohs hardness of from 3.00 to 3.75 (41).

Precipitated barium carbonate is produced commercially by either of two methods, both of which use barium sulfide (black ash), produced from burning coal with barytes, as the source of the alkaline earth element Ba as illustrated (41, 43):



Method (1), although the simpler of the two methods, provides the purer BaCO<sub>3</sub>, but requires the larger investment in process equipment.

Barium carbonate is available commercially in several grades, i.e. natural (witherite), precipitated (98 to 99 per cent), sulfur-free, c. p. and technical and is shipped to the consumer in bags (50,80,100 lbs), drums or barrels depending on the grade and quantity

desired (43). Cost figures for barium carbonate vary with the grade, quantity and shipping distance, but range from \$140 to \$200 per ton (42, 44-46).

Barium carbonate is considered as the most important of the manufactured barium chemicals, being second in tonnage produced to barite, an impure form of barium sulfate found in nature (43). Barium carbonate is used in industry in numerous ways among which are (41):

(1) as a raw material for the production of other barium compounds such as  $\text{BaO}$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{BaTiO}_3$ .

(2) as a flux in ceramics.

(3) as a carbon carrier in case hardening baths.

Barium carbonate is also used, quite widely, as a purification medium for the removal of sulfates from aqueous solutions. Edwards (47) describes the use of barium carbonate as an additive to drilling muds used for drilling through gypsum formations. Barium carbonate prevents the formation of the anhydrite on the drilling bit when due to heat the transition point of the gypsum is surpassed. The addition of barium carbonate to tender drying clays used in the production of bricks is described by Wild (48). The control of sulfate ion content through the formation of very insoluble barium sulfate produces a reduction in the plasticity of the clay thereby aiding the drying process and reducing shrinkage.

There are numerous references (49 - 51) in the literature published prior to 1930 describing the use of barium carbonate to soften boiler feedwater by removing soluble sulfates through the precipitation of  $\text{BaSO}_4$ . In fact, a patented process for feedwater

softening using barium carbonate and lime was marketed by the Reisert Automatic Water Purifying Company of New York during the early 1900's (49).

The cold lime-barium process mentioned above has been described as having a very limited application, probably due to the high cost in procuring barium carbonate and its poisonous nature (52). Although the use of barium carbonate in softening hard waters has declined drastically since the early 1900's due to increased use of the lime-soda process, the cold lime-barium process is occasionally used in situations where extremely high sulfate concentrations exist and it is desirable not to use sodium salts (52).

Observations and research concerning the reaction rates, kinetics, and variables involved in the removal of soluble sulfates from solution by barium carbonate may be found in literature, originating primarily in the water softening and ceramics fields. Mehring (49) in a detailed description of the Reisert lime-barium water softening plant points out that the system is capable of precipitating all impurities causing permanent hardness in waters, including  $\text{H}_2\text{SO}_4$ .

A batch process for softening boiler feedwater using lime and witherite is explained by Edquist (51). Unslaked lime and finely pulverized witherite are added to the water contained in 20 ft diameter by 8 ft deep vats and agitated with stirrers for about twelve hours. Then the agitators are stopped and the precipitants ( $\text{BaCO}_3$ ,  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ ) allowed to settle. Edquist states that

the precipitants settle quickly leaving the supernatant "crystal-clear". Problems such as long reaction times, chloride build-up and large amounts of magnesium hydrate, calcium oxide and barium carbonate remaining in the treated water are mentioned. Possible solutions for the long reaction times encountered are given as insuring that calcium chloride is available during the reaction, providing a "hot" system, using a more finely ground witherite or substituting precipitated barium carbonate for witherite. All four of these suggestions involve increasing the solubility of barium carbonate.

The reactivity of barium carbonate as influenced by the particle size and deflocculation has been studied by Moody (53). Electron microscopic studies and reactivity tests on seven different commercially prepared types of barium carbonate showed that reactivity was greatest for deflocculated and small grain-sized barium carbonates.

Rodman (50) points out one important observation noted during the operation of a Reisert Lime-Barium Softener. He states that NaCl content should be kept up to at least one grain per gallon (14.3 mg/l) in order to provide an electrolyte which is sufficiently ionized to force the precipitation of barium sulfate and put it into a more readily filterable form.

#### Barium Sulfate, an Insoluble Product

The utilization of barium carbonate is so appealing in the removal of soluble sulfates by chemical precipitation because of the



insolubility of the reaction product, barium sulfate. The solubility of barium sulfate at 25°C is 2.5 mg/l and shows very little variation with temperature as illustrated in Figure 4. Due to its insolubility, barium sulfate is used in gravimetric analysis in the determination of sulfur and sulfates, in the uranium processing industry for absorbing and removing radioactivity from plant waste streams (54), in radiology (1) and as mentioned in a previous section, as the resulting precipitant in removing soluble sulfates from solution.

There are numerous references in the literature which treat the theoretical concepts and reaction kinetics pertaining to the precipitation of barium sulfate by various methods. The use of soluble barium salts such as  $\text{BaCl}_2$ ,  $\text{BaNO}_3$  and  $\text{Ba(OH)}_2$  as sources of barium ions in almost all experimental situations was noted. The fact that the initial supersaturation ratio of the precipitating substance has a large effect on the precipitation reaction rate might be the reason that slightly soluble barium carbonate was not used.

Among the numerous factors considered by Walton (30) as affecting precipitation kinetics are the presence of impurities, catalysis by active sites on container walls, electrodes, etc., methods of mixing, rate of stirring, and temperature. Almost all precipitation from aqueous solutions, especially those reactions effected by direct mixing, are heterogeneous in nature at least in the early stages due to the presence of impurities. A homogeneous process in contrast depends only on the solution supersaturation (55).

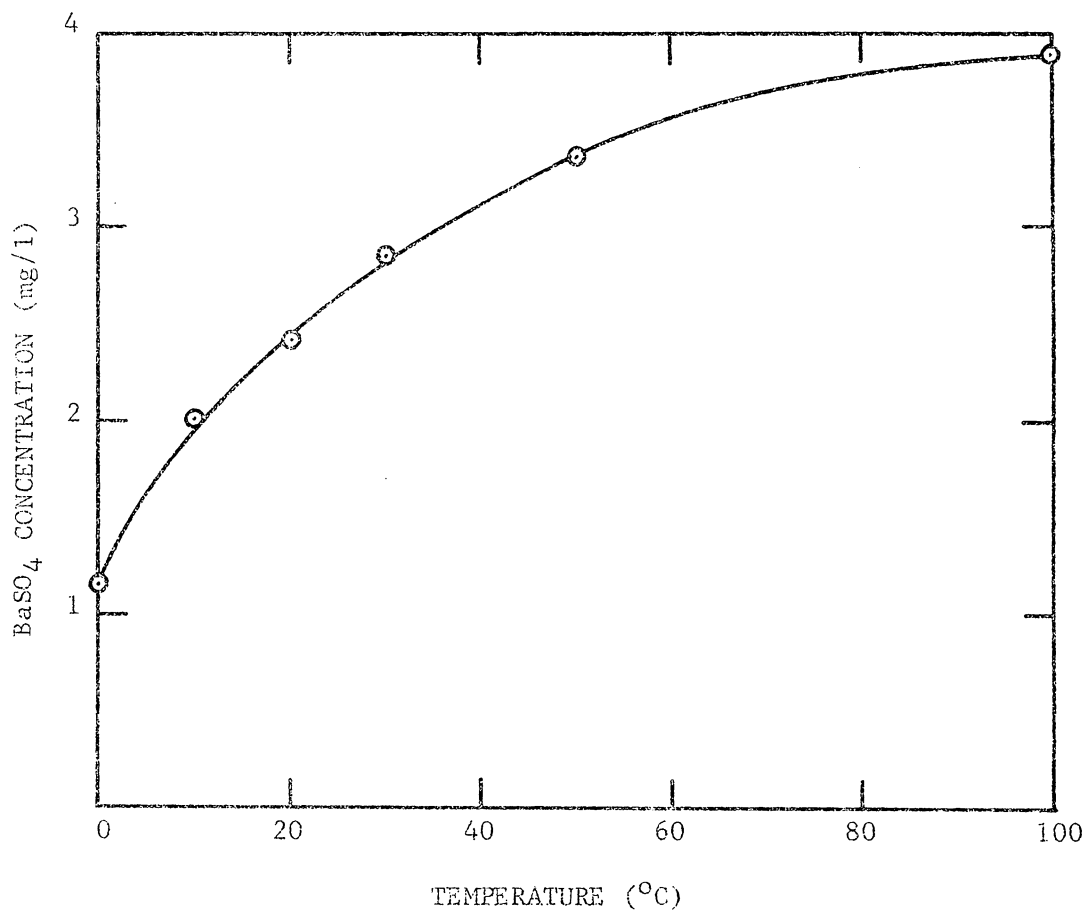


FIGURE 4. SOLUBILITY-TEMPERATURE RELATIONSHIP FOR BARIUM SULFATE IN AQUEOUS SOLUTION (8)

A sometimes undesirable characteristic of barium sulfate precipitation is that barium sulfate is susceptible to contamination during precipitation. This situation is called coprecipitation and is discussed quite extensively by Kolthoff et al., (56). Numerous foreign substances may be occluded and removed by the barium sulfate precipitant. Common substances which may coprecipitate with barium sulfate are presented in Table II. The coprecipitation of foreign substances by barium sulfate might be considered as another advantage of barium sulfate precipitation and might prove to be of assistance in treating wastewaters.

#### Coagulation Using Polymers

Due to the wide use of synthetic organic polyelectrolytes in improving solid-liquid separations in the wastewater treatment field and their possible application in this study, an overview of the mechanisms and available literature concerning polymeric coagulation is presented.

Burke and Dajani (57) believe the stability of suspended solids comprised of colloidal material to be due to one or more of three factors:

- (1) the presence of an electrical double-layer.
- (2) short-range hydration repulsion due to adsorbed water molecules on the particles.
- (3) a protective colloid phenomenon where surface-active molecules are adsorbed by the particles.

Coagulation is considered to be the process of destabilizing the particles so that aggregation and subsequent settling may occur.

TABLE II

VARIOUS SUBSTANCES OCCLUDED BY BARIUM SULFATE (56)

<u>SUBSTANCE</u>	<u>COPRECIPATED AS:</u>
FOREIGN ANIONS	
$\text{NO}_3^-$ , $\text{NO}_2^-$ , $\text{ClO}_3^-$ , $\text{Fe}(\text{CN})_6^{3-}$ , $\text{Fe}(\text{CN})_6^{4-}$ , $\text{MnO}_4^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{CN}^-$ , $\text{CNS}^-$ , $\text{I}^-$ , $\text{PO}_4^{=}$	BARIUM SALTS
FOREIGN CATIONS	
$\text{Cd}^{++}$ , $\text{Mn}^{++}$ , $\text{Cu}^{++}$ , $\text{Zn}^{++}$ , $\text{Al}^{3+}$ , $\text{Fe}^{++}$ , $\text{K}^+$ , $\text{Ni}^{++}$ , $\text{Na}^+$ , $\text{Li}^+$ , $\text{Mg}^{++}$ , $\text{Fe}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Ca}^{++}$	SULFATES BISULFATES
WATER	
SULFURIC ACID	

O'Melia (58) believes coagulation to result from both particle transport and particle destabilization while other authors (24, 40) apply the connotation, flocculation, to particle transport.

Jorden (59) in an excellent article on the aggregation of colloids explains quite clearly the four mechanisms, i.e., double layer repression, bridging, adsorption, and entrapment, by which destabilization of colloids may be effected. He differentiates between destabilization by double layer repression and by adsorption by pointing out that the charge on the particle does not go below zero in double-layer repression whereas in adsorption the particle charge may be reversed. This fact may be noted in Figure 5 which is adapted from Jorden and illustrates relationships between coagulant dosage and two important parameters, degree of destabilization and particle charge.

Synthetic organic polyelectrolytes are used as coagulants in the wastewater treatment field for the removal of turbidity and in the conditioning of sludge for final dewatering. Polyelectrolytes are water-soluble high molecular weight polymers which dissociate readily in water (39). How they dissociate in water determines whether they are considered as cationic, anionic or nonionic polymers.

Cationic polymers may be used as destabilizing agents by bridge formation, charge neutralization or both. Destabilization of colloids by anionic or nonionic polymers is essentially by bridge formation, and there is a minimum size of polymers required. O'Melia (58) presents a detailed explanation of all aspects concerning the

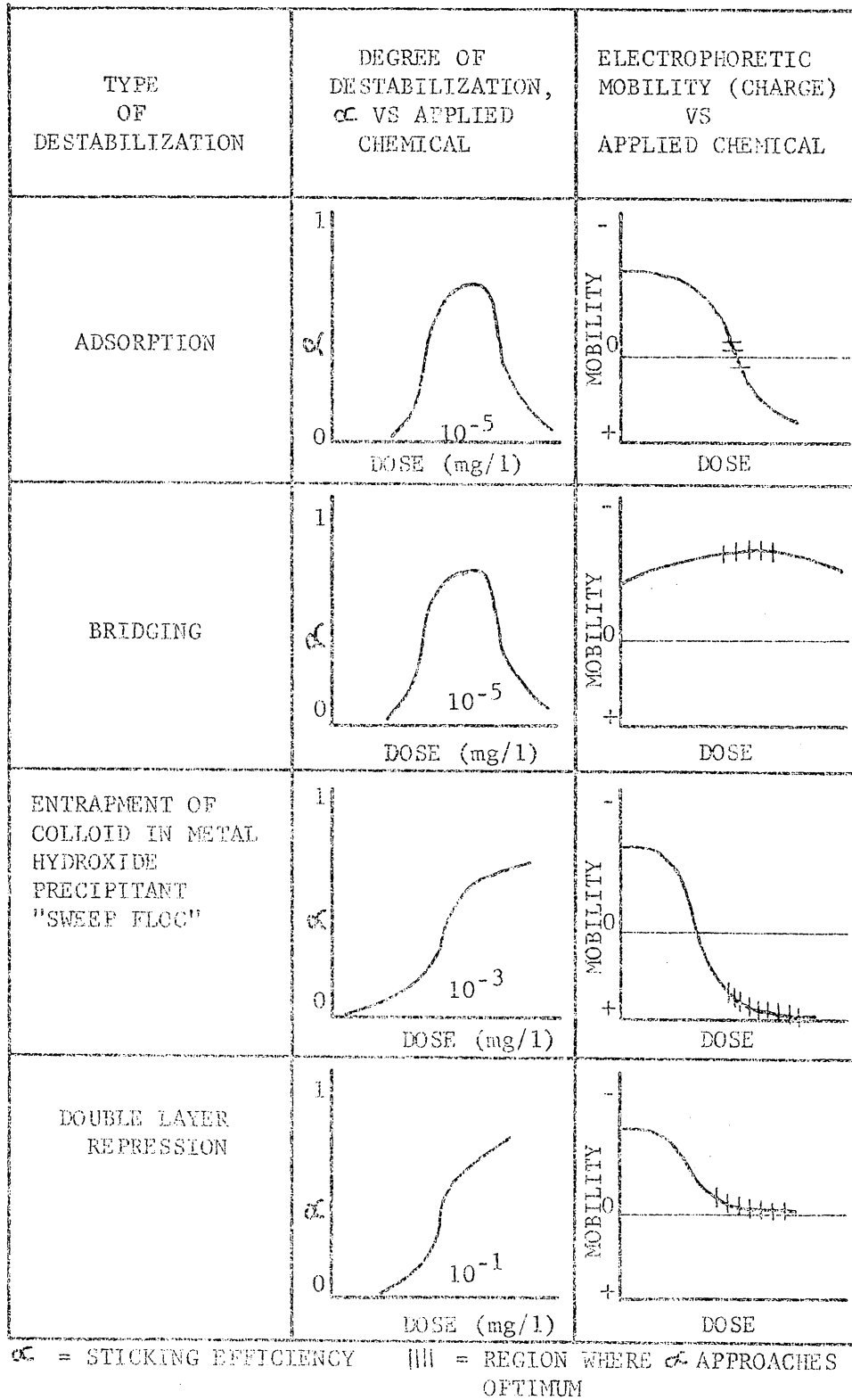


FIGURE 5: CHARACTERISTICS OF DESTABILIZATION (56)

mechanisms by which colloids are destabilized by polyelectrolytes. Descriptions concerning research on, and the uses of, destabilization of colloids by polyelectrolytes is available in the literature (57, 60, 61).

### Sludge Conditioning, Dewatering and Disposal

The treatment of industrial wastewaters by chemical precipitation requires the handling and disposal of chemical sludges which are characteristically large in volume but low in solids content. Oftentimes adjustment of the variables involved in chemical treatment such as the addition of seed nuclei, rate of addition of reagents, pH, temperature, and rate of agitation leads to the formation of precipitants which settle to more compact volumes and release water readily during dewatering processes (21). The addition of gypsum or return sludge to sulfuric acid before neutralization has been shown to effect a reduction in sludge volume after sulfuric acid neutralization (62). If process adjustment does not effect satisfactory results then sludge conditioning may be employed.

The major purpose of sludge conditioning is to improve the dewatering characteristics of the sludge by lowering its resistance to filtration. Satisfactory methods of sludge conditioning include elutriation (21), the addition of chemical conditioners such as ferric chloride, lime, aluminum sulfate, or organic polyelectrolytes, using filter aids or using physical conditioners such as fibrous materials (63). Flyash has been used as a filter aid in the conditioning and

dewatering of a sludge which consists primarily of lamp black, clays, vinyl and ferric sulfate (64).

Of special interest in the present study is the use of polyelectrolytes in conditioning sludges. A description of the mechanisms on which the usage of polyelectrolytes is based was presented in the preceding section. Bugg et al., (65) discovered that anionic polymers were superior to cationic and nonionic polymers in conditioning alum sludges from water treatment plants. The authors concluded, therefore, that the conditioning process was attributed to molecular bridging and that zeta potential was not an important control parameter. King et al., (66) in studying polyelectrolyte conditioning of ferric sulfate sludges found that sludge solids, and system pH definitely affected the polymer conditioning process.

Stirring speed and mix time were pointed out by Hilson (67) as influencing the polyelectrolyte conditioning of washwater from a pressure filter plant. Sludge was mixed with anionic polymer by a 13 cm propeller-type stirrer at 960 rpm for 5 seconds. A longer mix time was found to destroy the floc build-up and was undesirable.

In order to economically handle waste sludges, they are usually dewatered prior to ultimate disposal. Thickeners or flotation equipment may be utilized ahead of final dewatering processes so as to provide economical loadings. Atmospheric dewatering (sand beds or lagoons), vacuum filtration and centrifugation are the usual methods employed for final dewatering of sludges.

Atmospheric or gravity drainage of sludge, being one of the oldest used and most economical of the dewatering processes, has



been the basis of numerous studies, only one of which will be mentioned here. Jennett and Santry (68) in describing studies of the air drying of digested organic solids state that among the numerous variables involved in designing open sludge drying beds, the following variables are the most important:

- (1) climatic and atmospheric conditions
- (2) depth of sludge application
- (3) presence or absence of coagulants
- (4) sludge moisture content
- (5) source and type of sludge
- (6) extent of sludge digestion
- (7) sludge age
- (8) sludge composition
- (9) sludge concentration when applied
- (10) sludge bed construction

The authors point out that the use of polymers in conditioning sludges improves their drainage properties on open-air beds. Furthermore, they add that the use of sand provides optimum drainage conditions as pertains to sludge bed construction.

Where large land areas are unavailable for use in dewatering sludges, alternate methods such as centrifugation or vacuum filtration must be used. Discussions of the mechanisms, associated equipment and uses of the two processes are available in the literature (69 - 71) and the only mention of centrifugation and vacuum filtration to be made here will be limited to the fact that after

numerous years of use in the chemicals and mining industries, they are finally finding gradual acceptance in the pollution control field (40).

Ultimate disposal of sludge after dewatering has been the subject of numerous controversies (72). The basic methods available for disposal of dewatered sludge consists of ocean dumping, incineration, deep well burial, landfill, or use as animal feed supplements or fertilizers. Ewing and Dick (73), and Hilson (67) believe that there is great potential in the returning of sludges to the land, but all agree that further research is necessary before actually doing so.

### Summary

As can be seen from the literature, although large concentrations of sulfates can be detrimental to the quality of natural waters, little interest has been shown in the removal of sulfates from one of the prominent sources, sulfuric acid neutralization. The necessity for research in the removal of soluble sulfates is evident. Barium sulfate precipitation is used in numerous industrial fields for the removal of soluble sulfates and might also be of use in the wastewater treatment field for the same objective. The purpose of this research is to explore the possibilities of using barium sulfate precipitation to remove soluble sulfates from wastewater effluents containing sulfuric acid. Suspended solids removal and sludge conditioning and dewatering are inevitable in such a treatment

study, but the literature points out numerous treatment methods for application in these situations.

### III. EXPERIMENTAL PROCEDURE

The objective of any waste treatment study is the development of economical methods of treating a specified waste such that disposal of the resultant product may be accomplished in an acceptable manner. In the treatment of wastewaters there are usually two products, the treated effluent and a semifluid fraction normally termed sludge. There are numerous parameters depending on the original wastewater constituents which may be monitored during a treatment study in order to obtain optimum and satisfactory results.

In this study, two methods of treating sulfuric acid wastewater utilizing barium carbonate were investigated. The first method, hereafter designated Method I, consisted of utilizing the neutralization capacity of barium carbonate in directly neutralizing sulfuric acid wastewater. The second method, hereafter referred to as Method II, differed from Method I in that barium carbonate was added to the sulfuric acid wastewater after it had been neutralized with high calcium hydrate lime. In both methods, however, an effluent containing less than 250 mg/l sulfates and 1.0 mg/l barium was sought. These concentrations have recently been proposed as permissible levels by the National Technical Advisory Committee on Water Quality Criteria (74), and are also the maximum concentrations allowed in public drinking water under the jurisdiction of the U.S. Public Health Service (75).

The experimental procedures and analytical methods used in this treatment study are presented in the following sections.

### General Procedures

There is no standard pattern for accomplishing a waste treatment study. Some experimental procedures are devised during the study, while the majority are adapted from similar studies presented in the literature. The choice of each successive experiment to be performed is usually based on the results of the preceding experiment.

The treatment pattern which finally evolved from preliminary studies consisted of initially treating a 15 liter batch of synthetic sulfuric acid wastewater using the optimum dosage of barium carbonate found during tests as discussed in the next two sections. Mixing of the reactants was accomplished in an 18 liter circular glass container using aeration and a paddle mixing assembly, which was inclined due to the lack of vertical baffles.

After treatment had ceased as denoted by a stable alkaline pH in the case of Method I or maximum soluble sulfate removal in the case of Method II, the treated mixture was allowed to settle for one hour. At the end of the settling period, the supernatant was siphoned off to a point where the sludge began entering the siphon. If necessary, further treatment of the supernatant was investigated. Samples of the sludge remaining in the reaction vessel were removed for Buchner funnel tests. The sludge left in the reaction vessel was then diluted 1:3 for use in the gravity dewatering test.

The sulfuric acid waste used throughout this waste treatment study was prepared in the laboratory by diluting 5 ml of 36 N  $\text{H}_2\text{SO}_4$ , reagent grade, to 1 liter with laboratory distilled water. The

normality and sulfate concentration of this solution was calculated as 0.18 and 8,800 mg/l, respectively. The distilled water was found to contain approximately 4 mg/l  $\text{SO}_4^{--}$ . Batch solutions of 15 liters were prepared and utilized for all sets of experiments so that test solutions would be homogeneous.

The barium carbonate used in this study was a Certified, A.C.S. grade procured from Fisher Scientific Company, Fair Lawn, New Jersey. The barium carbonate was the precipitated type and usage was limited to one chemical lot, 714584. Weighing of chemical dosages was accomplished using a Harvard trip balance.

Method I In order to optimize the neutralization of the sulfuric acid waste by barium carbonate, a series of test runs involving combinations of mixing conditions and barium carbonate dosages was performed. Two types of mixing, aeration and mechanical stirring, were utilized. The time for neutralization to occur was chosen as the governing parameter with an elapsed time of less than one hour desired.

Air mixing was accomplished in a Nalgene 1/2 gal wide-mouth polyethylene container using a 1" long 7/8" diameter aloxite stone diffuser which was inserted into one end of a length of rubber tubing the other end of which was attached to the laboratory air supply. Air flow was regulated using a Gelman metering device. One liter of synthetic sulfuric acid wastewater was placed inside the container, the diffuser inserted, the desired dosage of barium carbonate added and the timer started. Values of pH were taken and recorded each

5 minutes until neutrality (pH 7) was reached. In an attempt to compare the efficiencies of air mixing and paddle mixing, values of  $G$ , the mean temporal velocity gradient, were calculated for air mixing using the following relationship presented by Fair and Geyer (24):

$$G = 9.0 \sqrt{Q_a \log [(H + 34)/34] / \mu V}$$

where  $G$  = mean temporal velocity gradient, fps/ft

$Q_a$  = free air flow, ft<sup>3</sup>/min

$H$  = depth of diffuser, ft

$\mu$  = absolute viscosity, lb-sec/ft<sup>2</sup>

$V$  = volume of aerated solution, ft<sup>3</sup>

Paddle mixing tests were carried out in a glass reaction vessel, 4" square and 7 1/2" deep. The use of a square tank eliminated the need for baffles, as the corners of a square tank create approximately the same flow patterns as result from using vertical baffles (31). A universal electric motor, a product of Mamco Corporation of Racine, Wisconsin, fitted with a stainless steel shaft and single paddle was used to agitate hence mix the test mixtures. Constant geometric parameters for the paddle mixing tests were as follows (see Figure 3):  $D_i = 6.4$  cm,  $q = 2.5$  cm,  $H_i = 2.5$  cm,  $H_1 = 12.1$  cm,  $D_T = 9.4$  cm,  $W_b = 1.7$  cm. The tank diameter was considered as the distance between two of the opposite walls with the additional distance of the corners taken as the baffle width. Motor speed was controlled using a powerstat-variable autotransformer, a product of Superior Electric Company of Bristol, Connecticut. Shaft rpm's were set using a General Radio Company strobotac, type 1531-A.

One liter of synthetic waste was placed inside the reaction vessel, the agitator inserted and started, the desired dosage of barium carbonate added and the timer started. Values of pH were taken and recorded every 5 minutes until neutrality (pH 7) was reached. A desired reaction completion time of 1 hour was sought. Values of G were calculated according to the relationship given previously in the literature review.

Method II One liter of sulfuric acid wastewater was neutralized to an approximate pH of 8.0 using Certified, A.C.S. grade high calcium hydrate lime,  $\text{Ca}(\text{OH})_2$ . An initial sulfate determination was made, the desired dosage of barium carbonate added and the timer started. The parameter chosen for study in this method was sulfate concentration. Sulfate concentration determinations were performed every 15 minutes for two hours or until the sulfate concentration of the reaction mixture was negligible, whichever occurred first. A sulfate concentration of less than 250 mg/l remaining at the end of one hour of reaction time was desired. Geometric parameters which remained constant during Method II mixing evaluation studies were as follows (see Figure 3):  $D_i = 5.1$  cm,  $q = 2.5$  cm,  $H_i = 2.7$  cm,  $H_l = 12.1$  cm,  $D_T = 9.4$  cm,  $W_b = 1.7$  cm.

### Analytical Procedures

Barium Carbonate Reactivity A simple reactivity test outlined by Moody (53) was performed on four samples of barium carbonate after it was discovered that of the two chemical lots being utilized in the study, one lot was of higher reactivity than the other lot. The test



consisted of preparing an 80% saturated solution of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , adding a theoretical amount of  $\text{BaCO}_3$  to effect a complete reaction to 250 ml of this solution and boiling the mixture for an hour. The test was conducted using 0.4440 gm of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and 0.4914 gm of  $\text{BaCO}_3$ . After boiling for an hour the solutions were filtered through Gooch crucibles and the unfilterable portions, after drying in a  $103^\circ\text{C}$  oven, weighed. Reactivity was calculated from solid residue weight gain.

Residue Determinations Total residue and nonfilterable residue (total suspended matter) were determined in accordance with the procedures as outlined in Standard Methods for the Examination of Water and Wastewater (76). After evaporating total residue samples to dryness, evaporating dishes were placed in a  $103^\circ\text{C}$  oven for 24 hours before final weighing. In determining total suspended matter a sample volume, depending on the consistency of the test mixture under investigation, was filtered through a tared 25 ml porcelain Gooch crucible containing a 2.1 cm glass fiber filter. Gooch crucibles containing nonfilterable residue were also dried for 24 hours in a  $103^\circ\text{C}$  oven before final weighing. All weighings were performed on a Mettler 410 single-pan automatic balance.

Settling Characteristics The settling characteristics of the mixed liquor resulting from the initial treatment of the sulfuric acid wastewater by either Method I or Method II were obtained using batch settling analyses described by Eckenfelder and Ford (77). The mixed liquor was poured into a 1 liter graduated cylinder, completely mixed and then allowed to settle. Raking action was not simulated.

The position of the sludge interface was recorded every 5 minutes for the first hour and then at the 8, 16, and 24 hour mark. Total suspended matter was determined for mixed liquor before settling had begun and for clarified supernatant after 1 hour of settling.

Zone settling velocities were determined by calculating the slope of the settling profile in the hindered zone. The time required for compression zone formation was found by projecting tangents from the settling profile within the hindered zone and the ultimate settling zone. The point at which a line that bisected the angle formed by the tangents intersected the settling curve was considered the point of compression (77).

pH Values of pH were determined using a Leeds and Northrup meter and Leeds and Northrup glass-calomel electrodes. Temperature was manually set at 26°C and the meter standardized against known pH solutions.

Sulfate Determinations Sulfate concentrations were determined in accordance with the turbidimetric method presented in Standard Methods for the Examination of Water and Wastewater (76). Each analysis was conducted in the following manner:

- 1) A 10 ml sample was filtered through a Millipore filter assembly containing a 0.45 µm filter. The filtrate was received in a 125 ml filtering flask which had been rinsed thoroughly with demineralized water, dried in a 103°C oven and cooled to room temperature.
- 2) A portion of the filtered sample depending on the desired concentration range was diluted with demineralized water to a volume of 100 ml in a volumetric flask.

3) The diluted sample was transferred to a 250 ml erlenmeyer flask, 5 ml of conditioning reagent added and a magnetic stirrer started.

4) A spoonful of barium chloride ( $\text{BaCl}_2$ ) crystals was added to the sample, a laboratory timer started and the solution stirred at a constant rate for one minute.

5) At the end of one minute of constant stirring the solution was transferred to an absorption cell and placed in a Klett-Summerson photoelectric colorimeter, Model 9003. Using a filter having maximum transmittance near 420 m $\mu$  and providing a light path of 4 cm, Klett values which are proportional to optical density were recorded every 30 seconds for four minutes. The highest value recorded during the four minutes was taken as the final recorded value. Readings appeared to be more stable in the 80 to 200 Klett range. Therefore, whenever possible, dilutions were made so that sulfate concentrations would lie in this range.

6) Using the Klett value, the sulfate concentration was obtained from a standard curve prepared beforehand.

Turbidity A Hach DR 6798B, DC operated colorimeter was used for measuring turbidity. The colorimeter was of the precalibrated type having a replaceable meter scale and filter. Precalibration for turbidity had been based on a formazin standard with the meter scale calibrated to read directly in Jackson Turbidity Units (JTU). Although not a precision analytical instrument, the colorimeter was easy to use, eliminated preparing a standard curve and provided adequate data for the treatment processes under investigation.

Nonsettleable Solids Composition      The chemical composition of the matter remaining in suspension after one hour of settling Method I mixed liquor was found by first determining the chemical composition of the settled sludge and then calculating the weight of chemicals not settling. The chemical composition of the sludge was determined by reacting a sludge sample of known weight with 150% of the theoretical amount of  $\text{H}_2\text{SO}_4$  necessary to completely react with an amount of  $\text{BaCO}_3$  equal to the sample weight. The sample of known weight along with 200 ml of  $\text{H}_2\text{SO}_4$  at the required concentration was boiled for ten minutes, after which the mixture was filtered through tared Gooch crucibles. The non-filtrable matter was then dried in an  $103^\circ\text{C}$  oven for 24 hours, at the end of which time the Gooches were reweighed and the total weight of non-filtrable matter determined.

Since the original sample was considered as consisting of both  $\text{BaCO}_3$  and  $\text{BaSO}_4$ , the following weight relationship was apparent:

$$(1) \quad W_i = S_i + C$$

where  $W_i$  = initial sample weight, gm

$S_i$  = weight of  $\text{BaSO}_4$  in initial sample, gm

$C$  = weight of  $\text{BaCO}_3$  in initial sample, gm

The weight of the dry non-filtrable matter remaining after the complete reaction of  $\text{BaCO}_3$  with  $\text{H}_2\text{SO}_4$  should equal the combined weights of the initial  $\text{BaSO}_4$  and any  $\text{BaSO}_4$  formed during the reaction as illustrated below:

$$(2) \quad W_f = S_i + S_f$$

where  $W_f$  = weight of non-filtrable matter after reaction, gm

$S_f$  = weight of  $BaSO_4$  resulting from the reaction of C gm  
of  $BaCO_3$  with excess  $H_2SO_4$ , gm

The relationship,  $S_f = 1.18 C$ , was developed by considering the stoichiometry of the chemical reaction between  $BaCO_3$  and  $H_2SO_4$ . After subtracting equation (2) from equation (1) and substituting  $1.18 C$  for  $S_f$ , the following relationships remained:

$$C = \frac{W_f - W_i}{0.18}$$

$$S_i = W_i - C$$

Using  $W_i$ , C and  $S_i$ , composition percentages of  $BaCO_3$  and  $BaSO_4$  were calculated and applied to a sludge solids determination. By considering the chemical equation for the reaction between  $BaCO_3$  and  $H_2SO_4$  and knowing the  $BaCO_3$  dosage, the amounts of  $BaCO_3$  and  $BaSO_4$  not found in the sludge were determined.

Coagulation Tests Preliminary coagulation tests were performed in 250 ml beakers using 200 ml samples. Each of the three electrolytes considered for application in this study and described in Table III was separately stirred into the sample in ever-increasing dosages until a noticeable floc was formed. Final coagulation tests were conducted on a standard six position jar test apparatus, a product of Phipps and Bird of Richmond, Virginia, using 1 liter samples. Various dosages of the selected polymer, varying in concentration from 50% to 200% of the floc-forming concentration found in

TABLE III  
POLYELECTROLYTE DATA

<u>POLYMER</u>	MAGNIFLOC 837A	MAGNIFLOC 900N	MAGNIFLOC 575C
Charge	anionic	nonionic	cationic
Physical form	white granular solid	white granular solid	dark viscous liquid
Viscosity or bulk density	40-45 lb/ft <sup>3</sup>	40-45 lb/ft <sup>3</sup>	25-50 cps at 25°C
Molecular weight	1,000,000 <sup>+</sup>	1,000,000 <sup>+</sup>	150,000 <sup>-</sup>

NOTE: Magnifloc polymers are a product of the  
American Cynamid Company, Wayne, New  
Jersey

the preliminary tests, were applied. Minimum turbidity remaining in the supernatant after a 30 minute settling period was chosen as the governing parameter in selecting the best polymer dosage.

Sludge Dewaterability Two methods of dewatering chemical sludges were investigated, vacuum filtration and gravity dewatering. Polyelectrolyte conditioning of the sludges was not investigated as it was considered that recovery of the unused  $\text{BaCO}_3$  and/or  $\text{BaSO}_4$  reaction product would follow treatment.

The parameter chosen for studying the filterability of the sludges on vacuum filters was specific resistance, a numerical value based on the results of a Buchner funnel filtration test. The mathematical relationship for specific resistance, theoretically developed by Ruth and Carman in 1933 and later modified to the present form by Coackley and Jones (78), is as follows:

$$r = \frac{2 P A^2}{\mu c} b$$

where  $r$  = specific resistance of sludge,  $\text{sec}^2/\text{gm}$

$P$  = pressure applied,  $\text{gm}/\text{cm}^2$

$A$  = filter area,  $\text{cm}^2$

$b$  = slope of the plot of  $T/V$  versus  $V$ ,  $\text{sec}/\text{cm}^6$

where  $T$  = time, sec

$V$  = volume of filtrate collected in time  $T$ , ml

$\mu$  = absolute viscosity of filtrate,  $\text{gm-mass}/\text{cm-sec}$

$c$  = ratio of grams dry cake solids per grams of liquid  
in the sludge before filtration,  $\text{gm}/\text{cm}^3$

Coakley and Jones (78), and Eckenfelder and Ford (77) agree that specific resistance is a useful parameter for expressing filtration results and comparing filtration characteristics of different sludges. Although the Buchner funnel test has been shown to have limited application in the scale-up of vacuum filters (79), this technique was considered to be adequate for comparing the sludges obtained during this treatment study.

The procedure and equipment, initially described by Coakley and Jones (78), was later modified by Rivera-Cordero (80). The modified Buchner funnel apparatus is shown in Figure 6. A 4.25 cm Buchner funnel with a plexiglass extension providing a filter area of 3.50 cm was used throughout the study. A thin layer of petroleum jelly was applied before each run to the end of the plexiglass extension which projected into the Buchner funnel in order to create a leak-proof juncture between the extension and the filter paper.

An initial nonfiltrable solids determination was performed on the sludge under investigation. The vacuum pump was started and through the adjusting of the vacuum adjusting clamp (see Figure 6) the pressure was set at the desired value as indicated by the mercury manometer. A sample volume of 100 ml was then applied to the Buchner funnel which contained a Whatman number 1 filter paper and the plexiglass extension. A hose clamp between the vacuum adjusting clamp and the Buchner funnel was released, the timer started and readings of elapsed time versus filtrate volume taken. Values of time versus filtrate volume for slow filtering samples were taken every 30 seconds for the first two minutes, every minute for five minutes and then



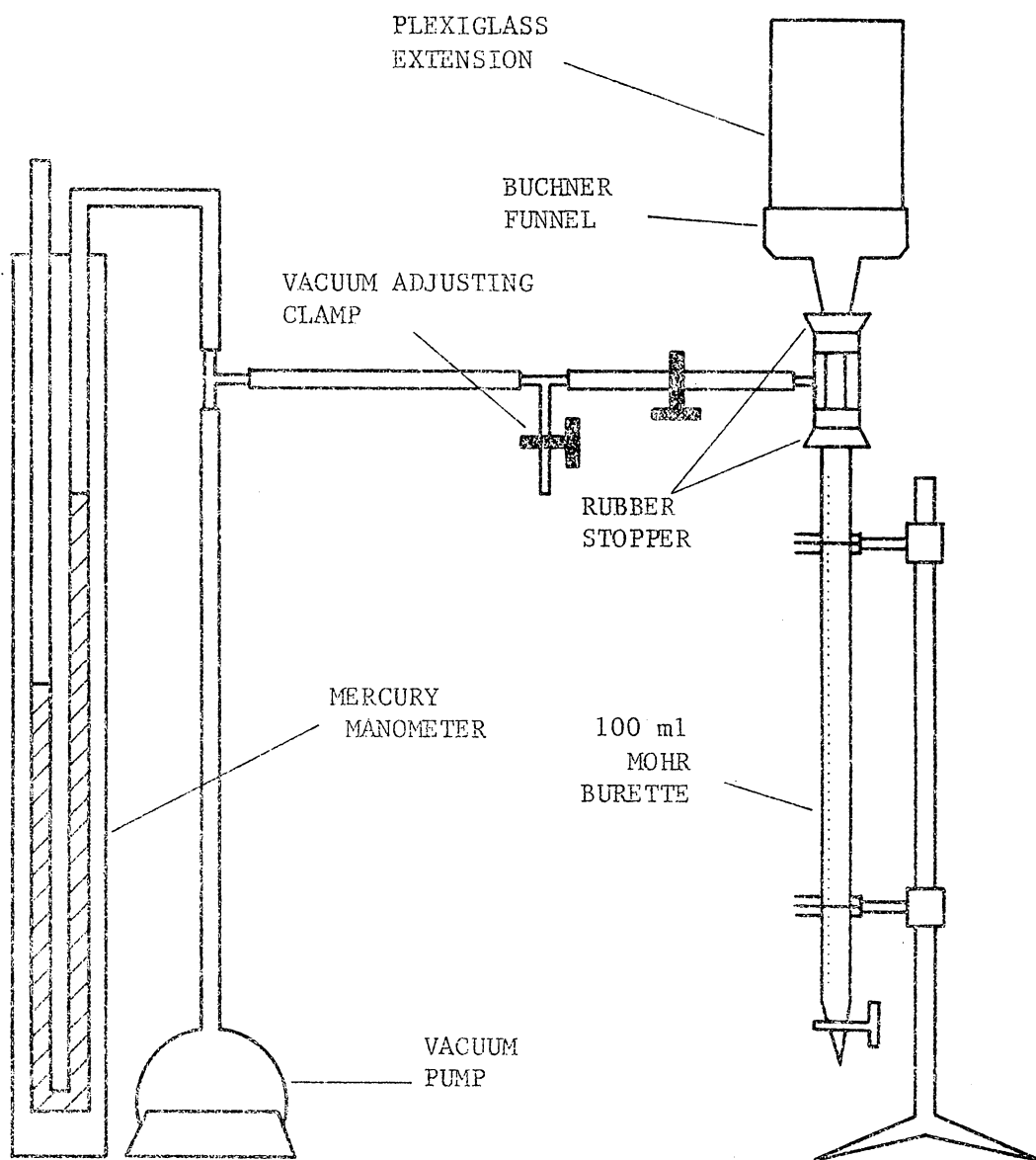


FIGURE 6. BUCHNER FUNNEL ASSEMBLY

every 2 minutes until the filter cake cracked or the filtrate volume became constant with time. Readings for fast filtering samples were recorded every 20 seconds.

A coefficient of compressibility was determined for each sludge investigated by using an empirical equation developed by Carman and verified experimentally as applicable in characterizing sludges by Coackley and Jones (78). The mathematical relationship is as follows:

$$r = r_i p^s$$

where  $r$  = specific resistance determined experimentally,  $\text{sec}^2/\text{gm}$

$r_i$  = specific resistance at reference head,  $\text{sec}^2/\text{gm}$

$P$  = applied pressure,  $\text{gm}/\text{cm}^2$

$s$  = coefficient of compressibility

The coefficient of compressibility was found by determining the specific resistance of samples of the same sludge at various applied pressures. By plotting  $\log_{10}$  (pressure) versus  $\log_{10}$  (specific resistance), the coefficient of compressibility was calculated as the slope of the straight line of best fit.

Gravity dewatering characteristics of the sludges produced during this study were investigated using a 30 cm long plexiglass tube with a 9.5 cm inside diameter. The tube contained a filter medium composed of a 4.5 cm layer of coarse sand which was retained on a number 10 soil sieve covered by 10 cm of light-weight Weblite aggregate sand with an effective size ( $D_{10}$ ) of 0.32 mm and a uniformity coefficient of 3.53. The filter medium was supported in the tube by a fine-mesh wire screen. A plastic funnel located at the

bottom of the tube directed the filtrate into a measuring device.

One liter of sludge, either conditioned or unconditioned, at a desired solids content was applied to the bed. The filtrate volume was determined at various times during the drainage process until the sludge was considered liftable. During gravity drainage cake moisture content was determined in the following manner:

$$M = 100 - \frac{(S_a)(V_a)}{V_a - V_f}$$

where M = cake moisture content at time T, %

$S_a$  = applied sludge solids, %

$V_a$  = applied sludge volume, ml

$V_f$  = filtrate volume at time T, ml

#### IV. EXPERIMENTAL RESULTS

Numerous variables pertinent to the optimization of the proposed methods of treating sulfuric acid wastewater with barium carbonate were investigated during this study. The results of these experiments and also of experiments dealing with characterizing the resulting reaction products are now presented.

##### Barium Carbonate Reactivity

In any study concerning the reaction properties of a specified chemical, it is imperative that the physical and chemical properties of the subject chemical remain unchanged throughout the study. Barium carbonate has been shown to vary in reactivity due to numerous properties controlled by manufacturers (53). Of the four chemical lots of barium carbonate chosen for testing during this study, one specific lot was found to be at least 9% more reactive than the remaining lots. Data for the reactivity test is given in Table IV. From the results of this test, lot 714584, as previously mentioned, was chosen for use in the treatment study.

##### Effect of Mixing Conditions and Barium Carbonate Dosage on the Neutralization of Sulfuric Acid Wastewater

Due to the evolution of carbon dioxide ( $\text{CO}_2$ ) as a reaction product during the neutralization of sulfuric acid by barium carbonate, aeration was chosen as a basis for the first series of

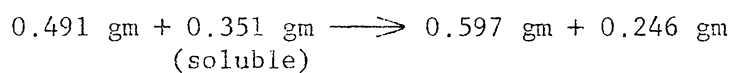
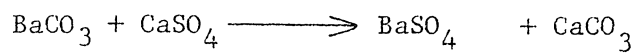
TABLE IV

## RESULTS OF THE BARIUM CARBONATE REACTIVITY TEST

<u>SAMPLE</u>	<u>WT. GAIN (gm)*</u>	<u>% REACTIVE**</u>
Lot 714584	0.273	78
Lot 702854	0.231	66
Lot 785781	0.242	69
Lot 1.3051	0.243	69

\* Based on an initial weight of 0.491 gm

\*\* Based on a final weight gain of 0.352 gm calculated from the following relationship:



mixing tests in which treatment Method I was employed. In the first set of experiments involving air mixing, the air flow rate into each of four reactors was maintained at 0.3 cfm while the barium carbonate dosage was varied in 10 gm increments from 15 gm to 45 gm. The results of this run are presented in Figure 7. The plots of the observed data give a family of curves not unlike those curves depicting the titration of a strong acid with a strong base. At the air flow rate of 0.3 cfm, or a G value of 373 fps/ft, a  $\text{BaCO}_3$  dosage of 35 gm/l was found to neutralize the wastewater satisfactorily within one hour. The final neutralization pH values approximating pH 8.0 indicated that carbon dioxide removal was being effected.

In a second set of experiments involving air mixing and treatment Method I, the air flow rate was varied while the barium carbonate dosage applied to each of three reactors was the same, 35 gm/l of wastewater. Air flow rate was set at 0.1, 0.3, and 0.6 cfm, which provided G values of 215, 373, and 527 fps/ft, respectively. The results of this experiment, which are plotted in Figure 8, point out that there is a value of G or a degree of agitation above which the neutralization reaction is disrupted. This test combined with the results of the previous test clearly points out that if aeration is used as the sole means of providing an agitated system for the reaction between barium carbonate and the subject wastewater, that an air flow of 0.3 cfm and a barium carbonate addition of 35 gm/l provide optimum conditions under the time criterion established.

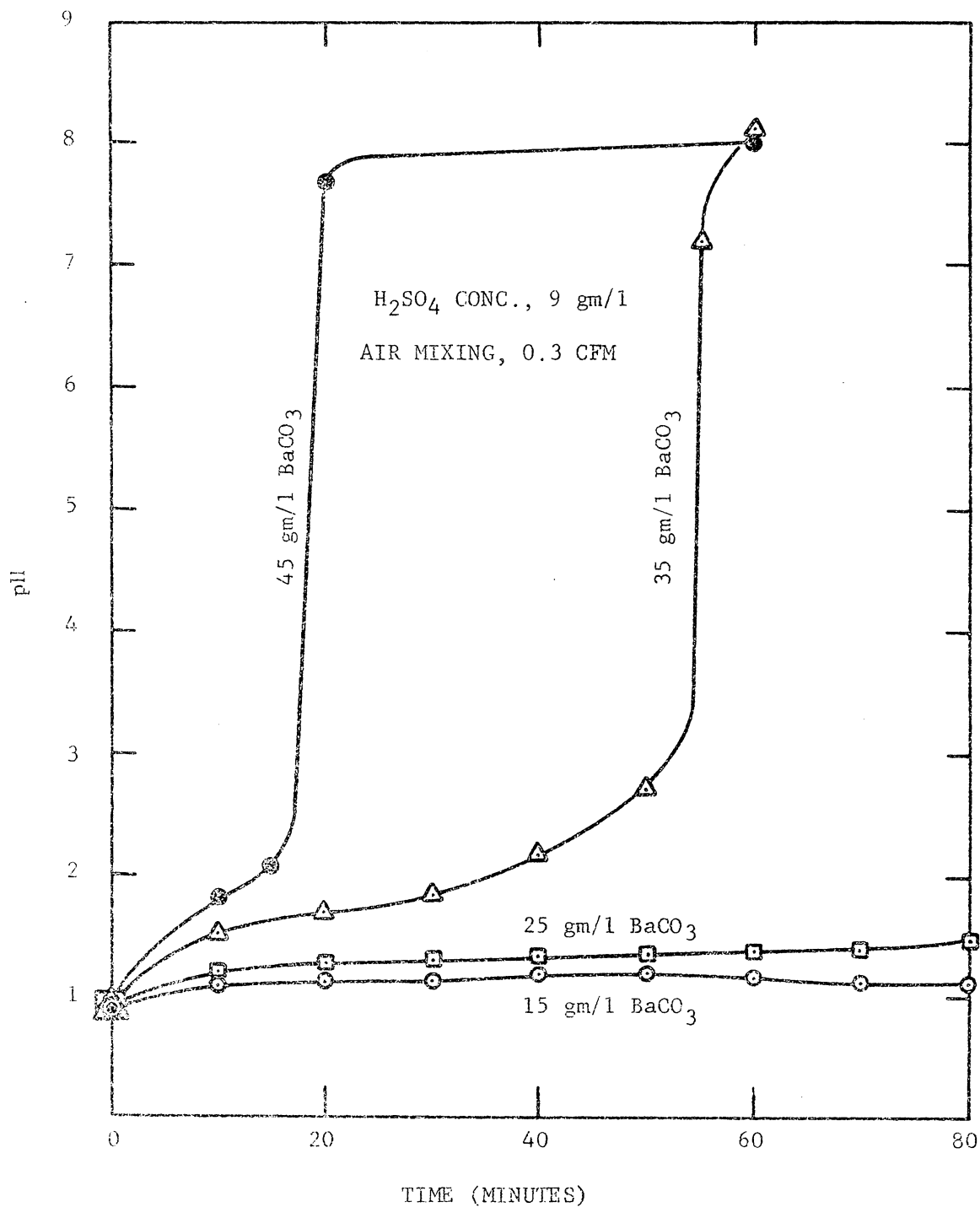


FIGURE 7. EFFECT OF  $\text{BaCO}_3$  DOSAGE ON THE TIME REQUIRED TO NEUTRALIZE SULFURIC ACID WASTEWATER AT CONSTANT AERATION

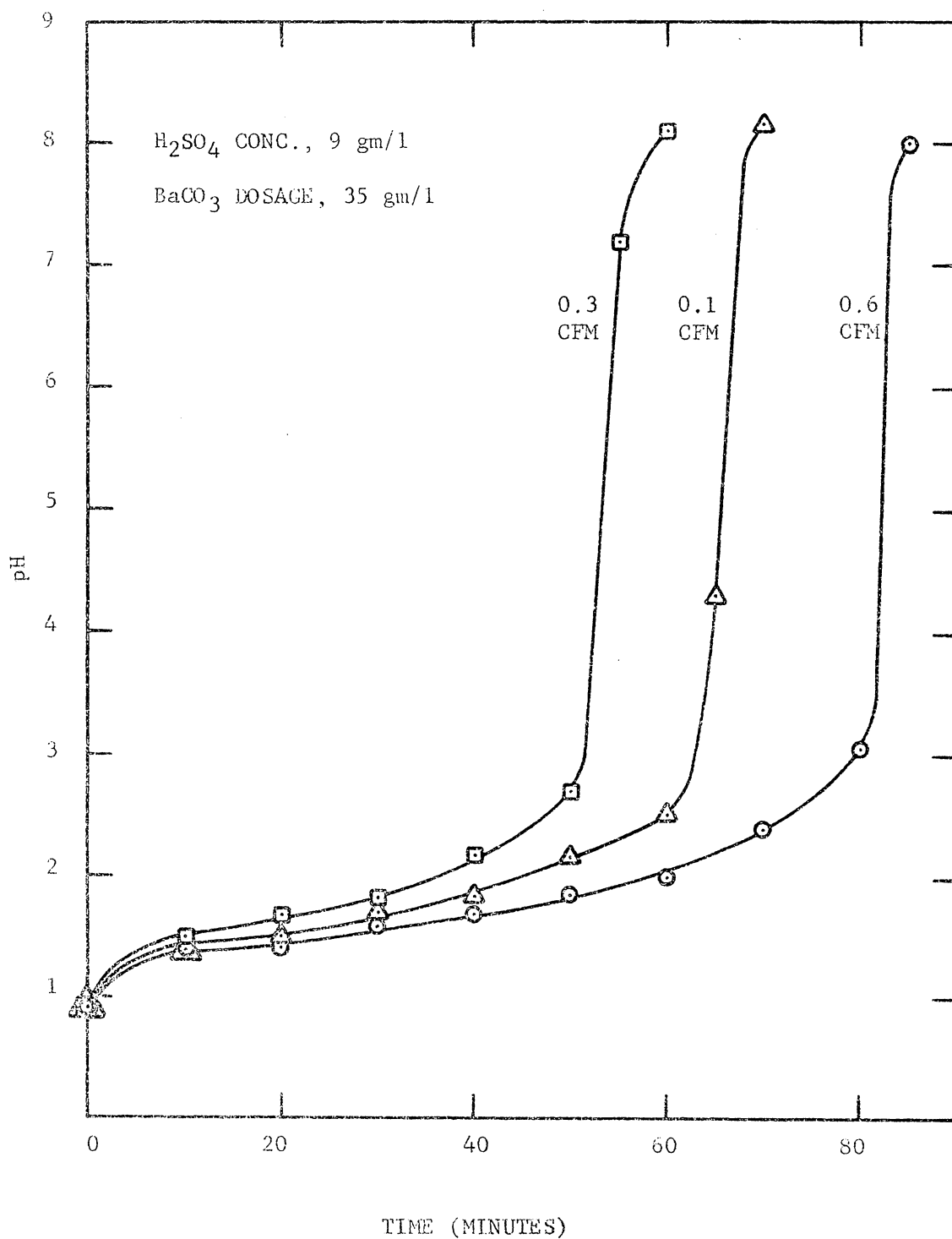


FIGURE 8. EFFECT OF AIR FLOW RATE ON THE TIME REQUIRED TO NEUTRALIZE SULFURIC ACID WASTEWATER AT CONSTANT  $\text{BaCO}_3$  DOSAGE.



In a second series of mixing tests, paddle mixing effects on the treatment Method I system were investigated. To study the effects of barium carbonate dosage, a stirrer assembly was maintained at a constant mixing speed of 250 rpm giving a G of 223 fps/ft while barium carbonate dosages were increased 5 gm for each run starting with a 25 gm/l dosage and ending with a 40 gm/l dosage. From the plot of the observed data which is presented in Figure 9, it is apparent that an optimum dosage less than 35 gm/l but above 30 gm/l might exist under the test conditions. The inability of the mixing conditions imposed on this system during the test to effectively aerate the mixture is supported by the low final pH values obtained. However, the use of paddle mixing did decrease the reaction time 20 minutes from that time required during air mixing for the same dosage of barium carbonate, 35 gm/l.

To find out whether or not an increase in paddle mixing speed might improve the reaction time, thereby lowering the barium carbonate dosage, a run was made at 500 rpm using a dosage of 35 gm/l. A G of 632 fps/ft was imposed on the system. Figure 10, which shows the results of this test along with a replot of the data observed during the previous test for a  $\text{BaCO}_3$  dosage of 35 gm/l at 250 rpm, points out that even though better  $\text{CO}_2$  removal was achieved at the higher mix speed, little change in reaction time occurred.

Frothing was observed accompanying the completion of the neutralization reaction during both aeration and mechanical mixing tests. This observation was not considered unusual as frothing is considered a problem associated with the release of carbon dioxide as a reaction product.

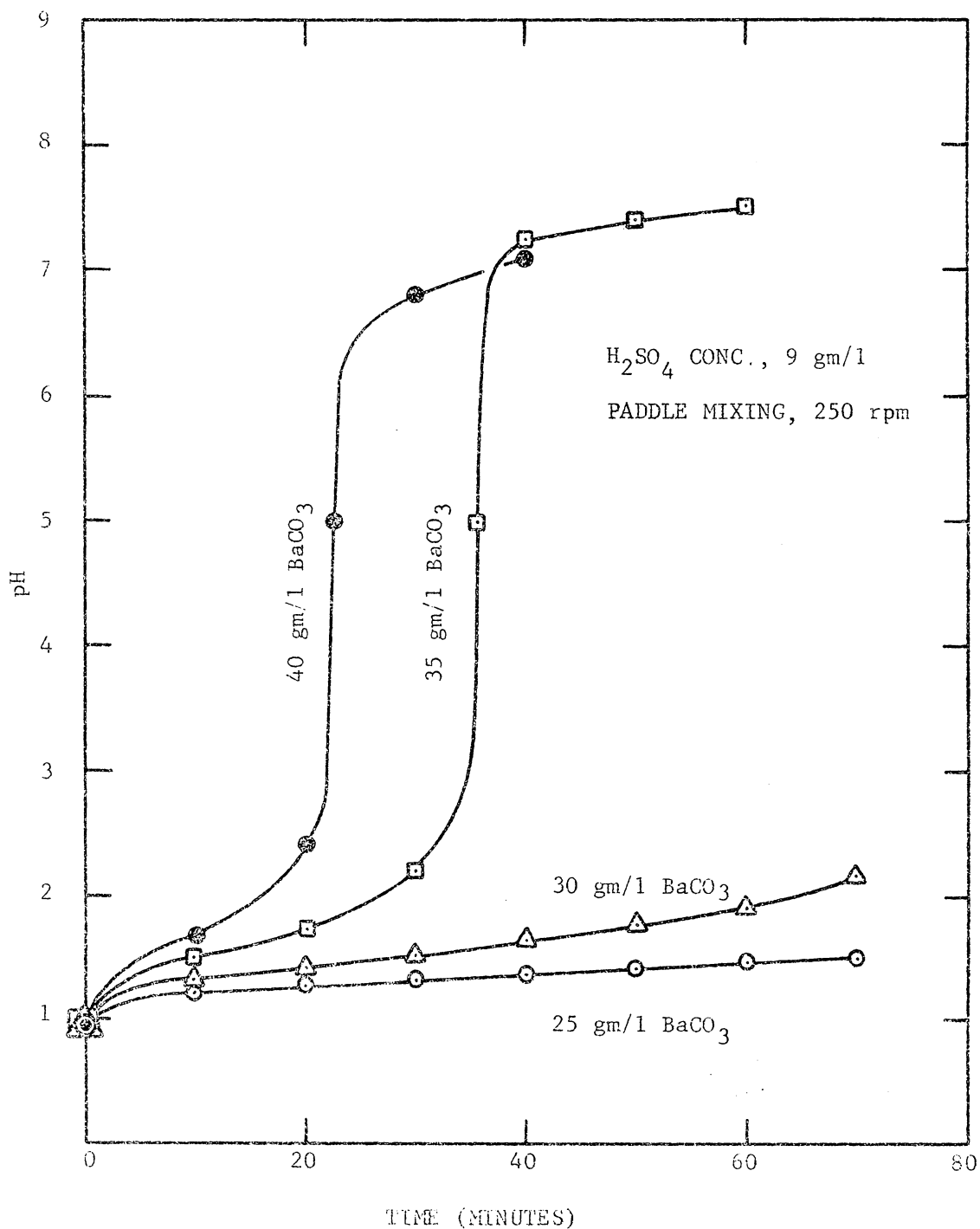


FIGURE 9. EFFECT OF  $\text{BaCO}_3$  DOSAGE ON THE TIME REQUIRED TO NEUTRALIZE SULFURIC ACID WASTEWATER AT CONSTANT PADDLE SPEED

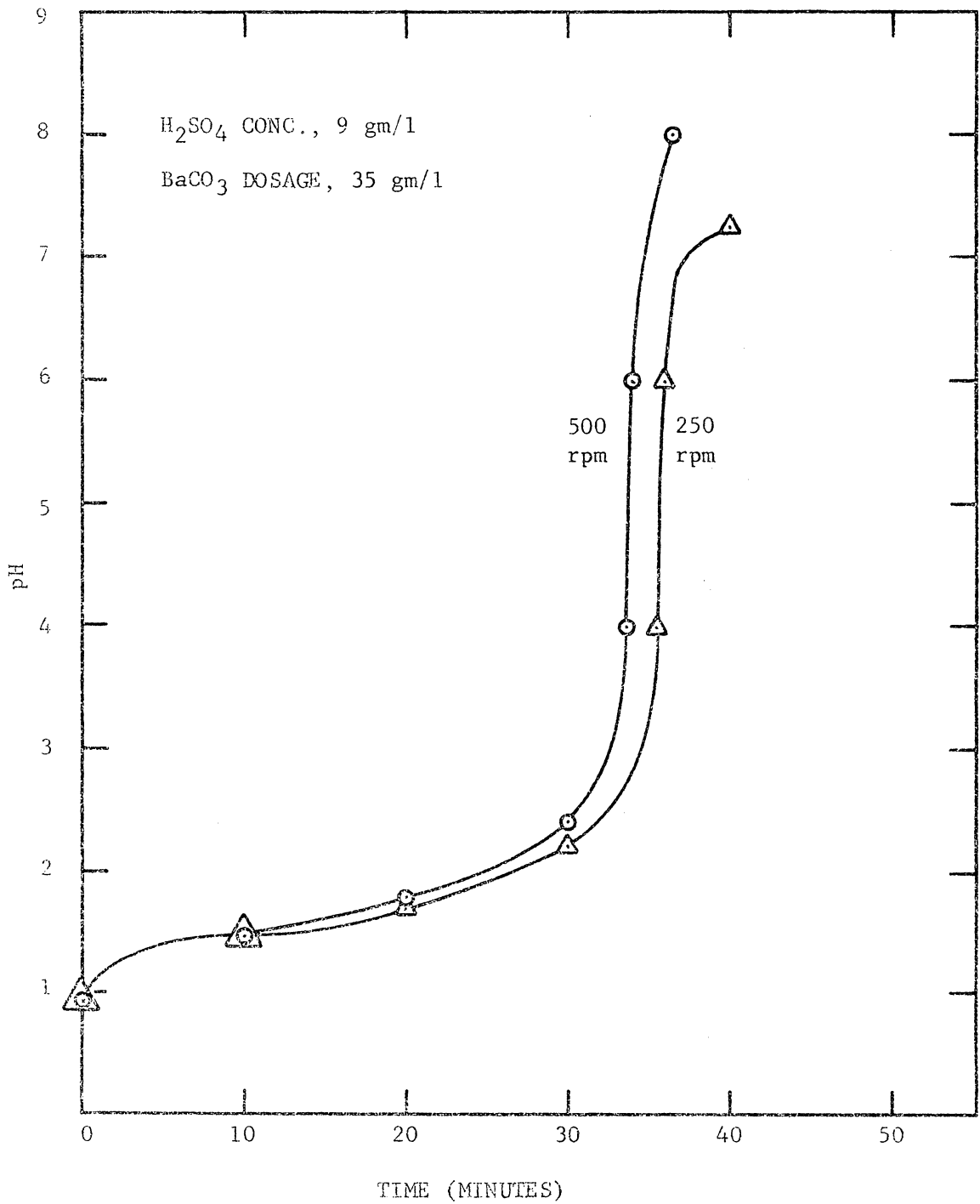


FIGURE 10. EFFECT OF PADDLE SPEED ON THE TIME REQUIRED TO NEUTRALIZE SULFURIC ACID WASTEWATER AT CONSTANT  $\text{BaCO}_3$  DOSAGE

Effect of Mixing Conditions and Barium Carbonate  
Dosage on the Removal of Sulfates from  
Neutralized Sulfuric Acid Wastewater

In optimizing the conditions necessary for satisfactory completion of the Method II treatment process, a procedural pattern, similar to that pattern developed in studying the Method I treatment process, was followed. Air mixing was not studied, however, because aeration was not required. Soluble sulfate concentration was monitored instead of pH as the sulfuric acid wastewater was neutralized prior to the addition of  $\text{BaCO}_3$  and removal of sulfates by precipitation.

Mixing at a paddle speed of 250 rpm, or a G of 142 fps/ft, was employed in the first series of tests aimed at developing an optimum mixing rate and barium carbonate dosage. Experimental runs were carried out at barium carbonate dosages of 15, 18, 20 and 25 gm/l of synthetic wastewater previously neutralized by lime addition to approximately pH 8.0. Initial and final conditions of the test mixtures are given in Table V. Results are plotted in Figure 11. A  $\text{BaCO}_3$  dosage of 25 gm/l was found to decrease the soluble sulfate concentration below 250 mg/l in the hour allotted for treatment. Precipitation or the removal of the sulfates in solution is shown by the data plotted in Figure 11 to proceed at a constant rate until a soluble surface concentration of 1400 to 1500 mg/l is reached. At that point the rate approaches zero for a period of time depending on the initial  $\text{BaCO}_3$  dosage. Thereafter the rate of removal of soluble sulfates is dependent on the initial  $\text{BaCO}_3$  dosage, with the larger dosages providing the faster rate of removal.

TABLE V

## METHOD II MIXING AND DOSAGE TEST DATA

TEST RUN	H <sub>2</sub> SO <sub>4</sub> CONC. (gm/l)	Ca(OH) <sub>2</sub> ADD. (gm)	NEUTRALIZED pH	INITIAL SO <sub>4</sub> <sup>=</sup> CONC. (mg/l)	BaCO <sub>3</sub> ADD. (gm)	MIX SPEED (rpm)	FINAL pH	FINAL SO <sub>4</sub> <sup>=</sup> CONC. (mg/l)
1	9	7.1	8.4	1901	15	250	8.1	1067
2	9	7.1	8.5	1851	18	250	9.3	47
3	9	7.1	8.6	1845	20	250	9.8	12
4	9	7.1	8.3	1902	25	250	9.8	5
5	9	7.1	8.7	1988	18*	250	9.4	6
6	9	7.1	8.9	1759	18	500	9.3	11

\* Filtered neutralized sulfuric acid wastewater

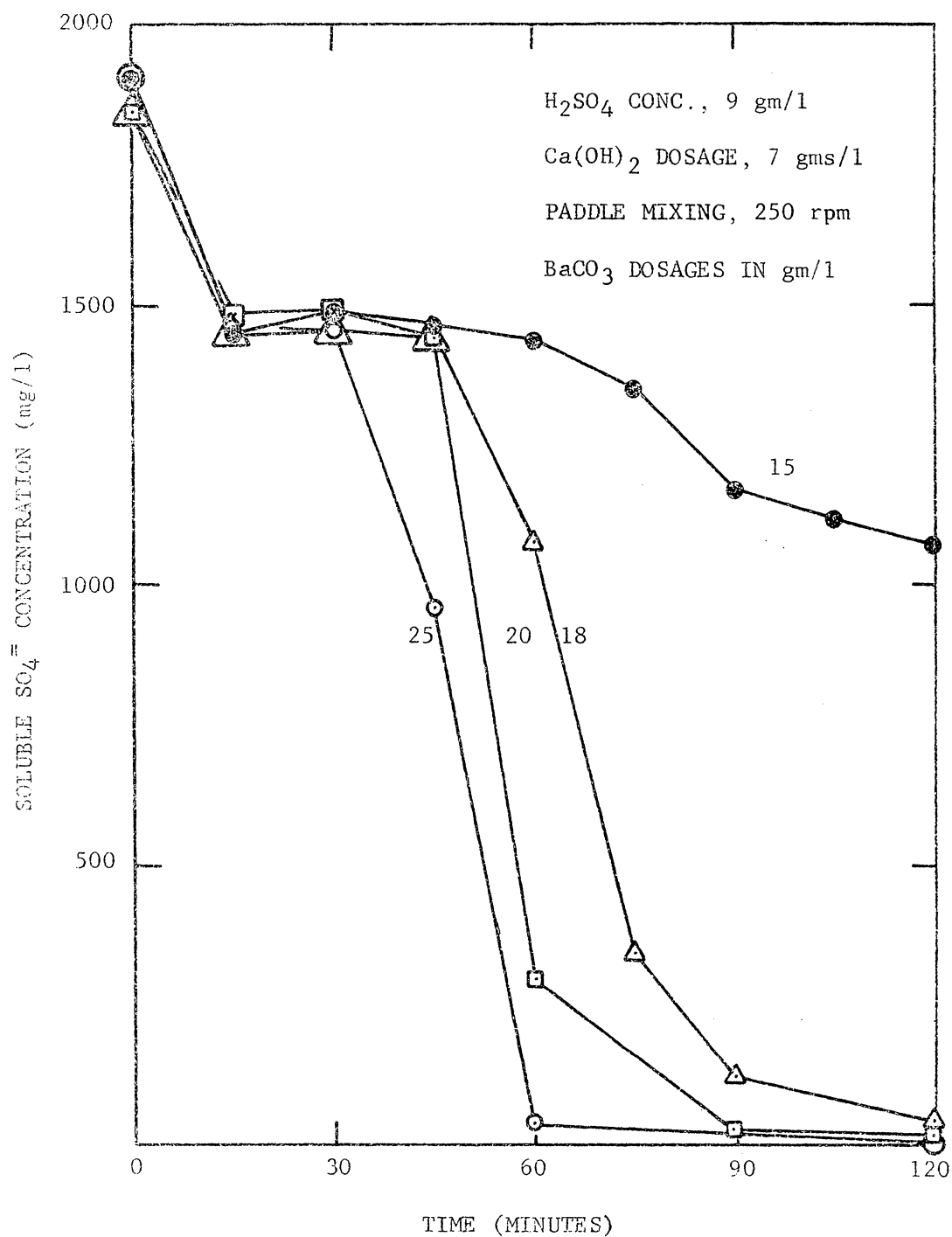


FIGURE 11. EFFECT OF  $\text{BaCO}_3$  DOSAGE ON THE TIME REQUIRED TO REMOVE SOLUBLE SULFATES FROM NEUTRALIZED SULFURIC ACID WASTEWATER AT CONSTANT PADDLE SPEED

To ascertain what effects an increase in mix speed might have on the  $\text{BaCO}_3$ - $\text{CaSO}_4$  reaction, one run at 500 rpm, representing a G value of 404 fps/ft, using a barium carbonate dosage of 18 gm/l was performed. Figure 12 shows that the results of this experiment were comparable to the results obtained at 250 rpm using 18 gm/l  $\text{BaCO}_3$  in that a zero sulfate removal rate occurred at a soluble sulfate concentration of 1400 to 1500 mg/l. Thereafter, the 500 rpm mix decreased the time required for completion of the reaction as compared with the 250 rpm mix speed replotted in Figure 12. Combining the results of this test and the dosage tests presented above, optimum conditions within the limits of this study occurred at a mixing speed of 500 rpm and a  $\text{BaCO}_3$  dosage of 18 gm/l when Method II was used for the removal of sulfates from the sulfuric acid wastewater.

The analytical method used in this study for determining sulfate concentration only provided soluble sulfate concentrations, therefore it was difficult to ascertain from the two tests presented above whether or not the  $\text{CaSO}_4$  precipitant was going into solution and being removed by means of  $\text{BaSO}_4$  precipitation. In order to resolve this question, 1 liter of wastewater was neutralized with  $\text{Ca(OH)}_2$  to an approximate pH of 8.0 and then filtered through a Millipore filter apparatus. This filtration removed the  $\text{CaSO}_4$  precipitant formed during the neutralization process. The filtrate was then dosed with 18 gm of  $\text{BaCO}_3$  and mixed at 250 rpm for 2 hours during which time the soluble sulfate concentration was monitored. The results of this experiment are presented in graphical form in Figure 12 and show a

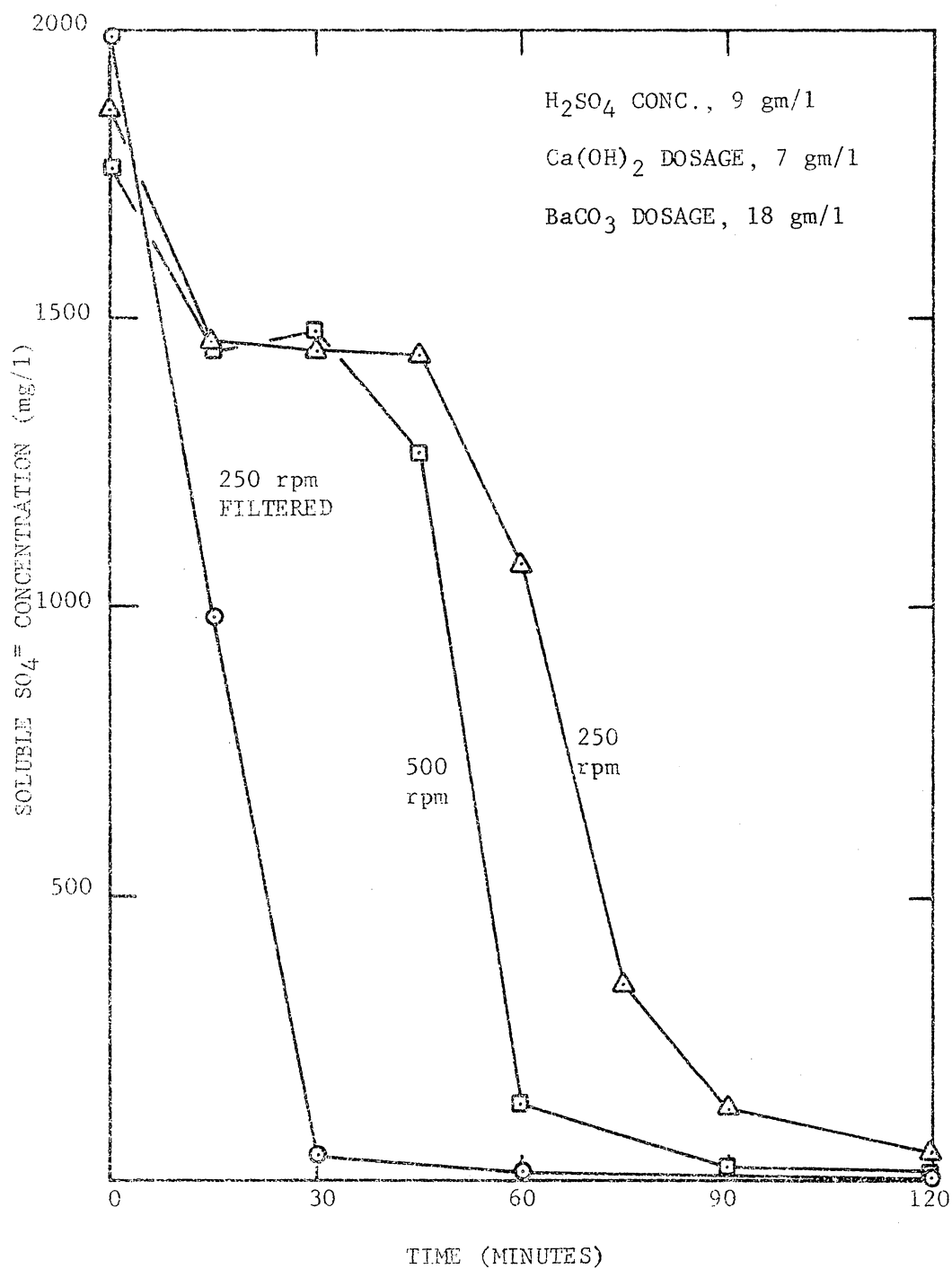


FIGURE 12. EFFECT OF PADDLE SPEED ON THE TIME REQUIRED TO REMOVE SOLUBLE SULFATES FROM NEUTRALIZED SULFURIC ACID WASTEWATER AT CONSTANT  $\text{BaCO}_3$  DOSAGE



constant rate of soluble sulfate removal which levels off after 30 minutes of reaction time.

Settleability of Sludges Resulting from Barium  
Carbonate Treatment of Sulfuric  
Acid Wastewater

Both methods of treating the sulfuric acid wastewater with barium carbonate produced chemical sludges which settled much more readily and to smaller volumes than the precipitant formed by merely neutralizing the sulfuric acid wastewater with  $\text{Ca}(\text{OH})_2$ . Sludge settling comparisons may be made by referring to Figure 13. While both Method I and Method II sludges displayed similar settling characteristics, the quality of their supernatants after one hour of settling were quite different. Table VI gives initial and final data taken during the settleability study and shows that Method I sludge after one hour of settling left a supernatant with 0.8% suspended solids creating a turbidity of approximately 2000 JTU. Method II supernatant contained negligible suspended solids and gave a turbidity reading of 15 JTU on the Hach colorimeter.

After approximately 18 hours of settling the Method I sludge, a secondary sludge interface formed and began to slowly settle. This interface was not monitored, but its formation pointed out that the turbid conditions of the supernatant might be improved by long term settling.

Removal of Turbidity from Method I Supernatant

As mentioned in the previous section, the supernatant resulting

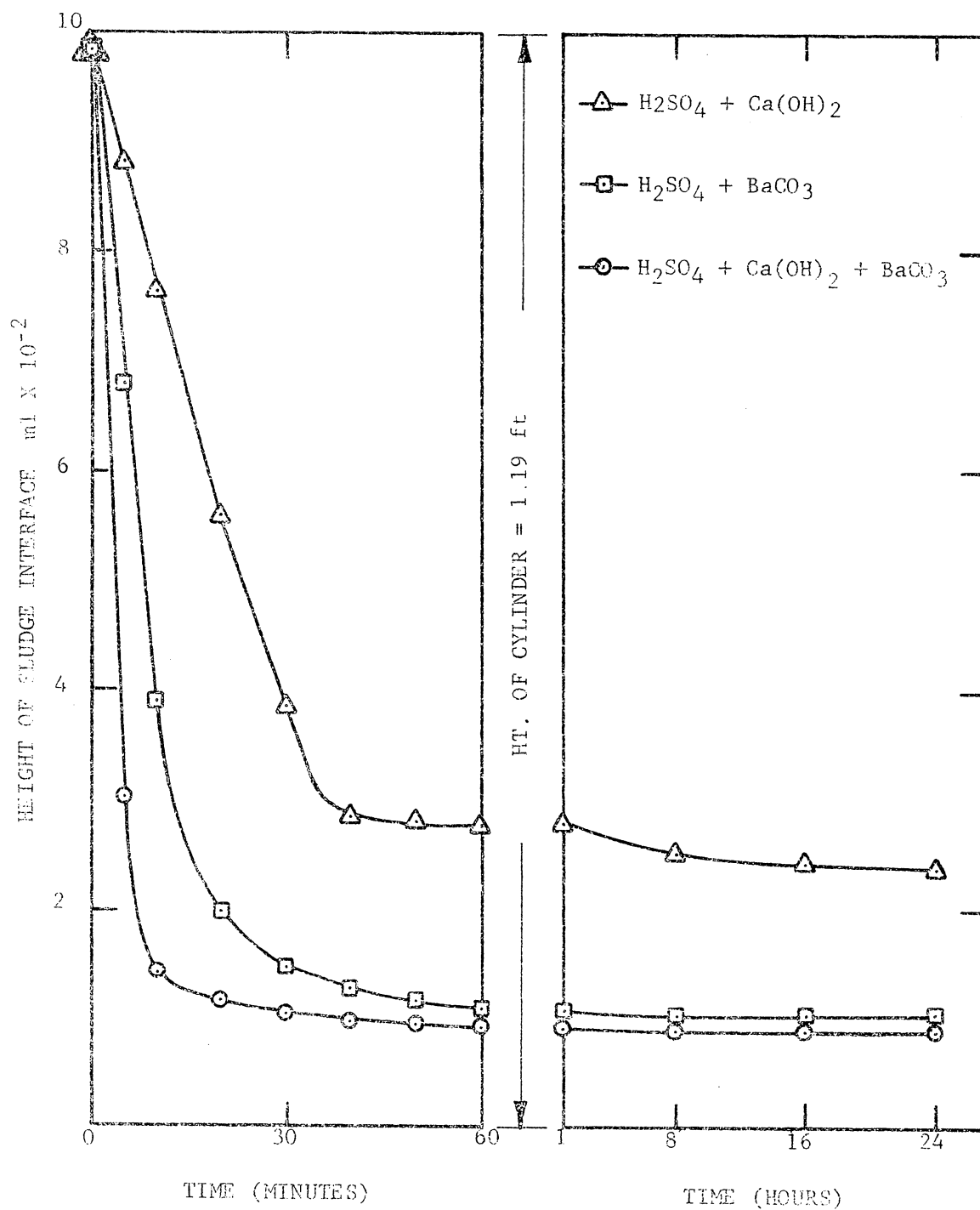


FIGURE 13. SETTLING CURVES FOR METHOD I, METHOD II AND  $\text{CaSO}_4$  SLUDGES

TABLE VI  
SETTLEABILITY TEST DATA

	$\text{H}_2\text{SO}_4$ + $\text{Ca(OH)}_2$ (control)	$\text{H}_2\text{SO}_4$ + $\text{BaCO}_3$ (method I)	$\text{H}_2\text{SO}_4$ + $\text{Ca(OH)}_2$ + $\text{BaCO}_3$ (method II)
$\text{H}_2\text{SO}_4$ concentration (gm/l)	9	9	9
initial pH	0.92	0.94	0.95
$\text{Ca(OH)}_2$ dosage (gm/l)	7.16	-----	7.15
neutralization pH	8.70	7.60	8.72
$\text{BaCO}_3$ dosage (gm/l)	-----	35	18
paddle mix rpm	250	250	500
mix time (min)	15	60	120
initial SS (%)	0.98	3.92	2.61
final SS (%) at one hour	-----	0.80	-----
turbidity of supernatant at one hour (JTU)	10	2000	15
zone settling velocity (ft/hr)	1.6	4.2	10.0
time to point of compression (min)	48	33	20
sludge height at point of compression (ml)	280	140	115

from a one hour settling of the mixed liquor from the Method II treatment process had only 15 JTU of turbidity, therefore this supernatant was considered satisfactory and no further treatment was attempted. However, the supernatant resulting from the one hour settling of the mixture remaining after treatment by Method I contained approximately 2000 JTU of turbidity and was considered unsuitable and needing further treatment.

A chemical analysis of the non-settleable solids forming the turbidity found in the Method I supernatant was performed and very surprising results were discovered. Of a 3 gm sludge sample, 1.03 gm (34%) was found to be  $\text{BaCO}_3$  with the remaining 1.97 gm (66%) being  $\text{BaSO}_4$ . Using the weight relationships expressed by the theoretical reaction equation for the reaction between  $\text{BaCO}_3$  and  $\text{H}_2\text{SO}_4$  in combination with the percentages of  $\text{BaCO}_3$  and  $\text{BaSO}_4$  mentioned above and a sludge solids determination, the non-settleable solids in the Method I supernatant was found to be composed of 80%  $\text{BaCO}_3$  and 20%  $\text{BaSO}_4$ , by weight. The calculated total weight of  $\text{BaCO}_3$  and  $\text{BaSO}_4$  in the supernatant was found to closely agree with a non-settleable solids determination.

Of the three polyelectrolytes chosen for study in the coagulation and removal of the turbidity from the Method I supernatant, Magnifloc 837A, an anionic polymer, was found in preliminary tests to be far superior to the nonionic and cationic polymers. Coagulation tests, as described previously using various dosages of Magnifloc 837A, were performed on a standard jar test apparatus. The supernatant resulting from a one hour settling of the mixed liquor from a

15 liter batch of sulfuric acid wastewater treated by the Method I process and containing 2080 JTU of turbidity was the coagulated medium. The results of the coagulation test, as illustrated in Figure 14, show that the turbidity can be successfully decreased to a value approximating 18 JTU by using a polymer dosage in the range, 5 to 7.5 mg/l.

#### Specific Resistance Analyses

The resistance to filtration of the Method II sludge during the Buchner funnel test was found to be much less than that resistance offered by the Method I sludge. This characteristic of the Method II sludge was noted from higher filtration rates as compared to the filtration rates of the Method I sludge. The specific resistance of the Method II sludge was found, as calculated, to be lower at all test pressures than those values for the Method I sludge. Using a pressure of filtration of  $415 \text{ gm/cm}^2$  or 12 inches of Hg for comparison, the specific resistance of Method I sludge was calculated from experimental data as  $1.086 \times 10^7 \text{ sec}^2/\text{gm}$ , while the specific resistance for Method II sludge was found to be  $1.649 \times 10^6 \text{ sec}^2/\text{gm}$ . The values of specific resistance for both sludges increased with an increase in filtration pressure.

By using the volume of filtrate indicated by that point on the graph of  $T/V$  versus  $V$  where the experimental data deviated from the straight line relationship, percent cake moisture was determined for each run utilizing the equation presented previously for gravity

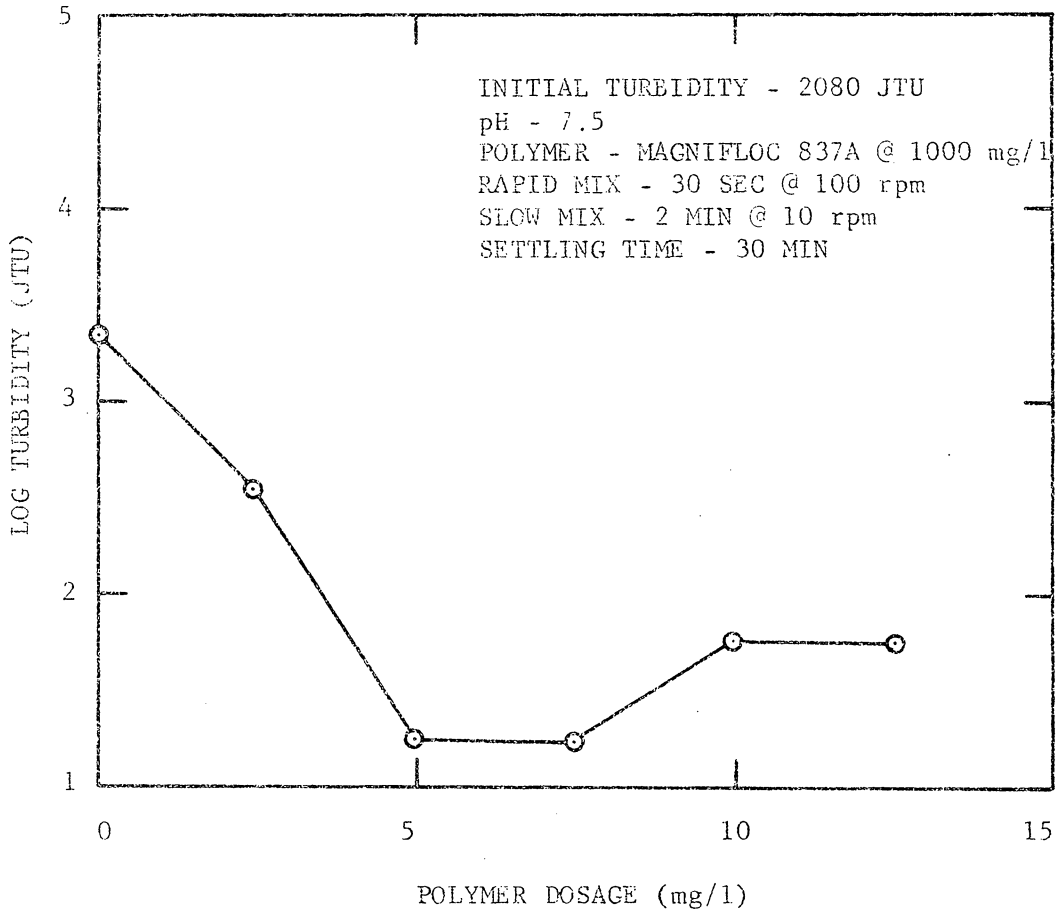


FIGURE 14. EFFECT OF POLYMER DOSAGE ON THE REMOVAL OF TURBIDITY FROM METHOD I SUPERNATANT

dewatering. At 6 inches of Hg or  $207 \text{ gm/cm}^2$  filtration pressure, the Method I sludge, initially containing 68.5% moisture, formed a cake having a final moisture content of 37%. At the same filtration pressure the Method II sludge, initially containing 72.7% moisture formed a cake having a final moisture content of 41.3%. Six inches of Hg was the only pressure at which the cake formed by the Method I sludge had a lower final moisture content than the cake formed by the Method II sludge. At 12 and 18 inches of Hg, the Method I sludge cakes cracked at moisture contents of 40.6% and 41.1%, respectively, while the Method II sludge cakes cracked at moisture contents of 36.5% and 38%, respectively.

Figure 15 is a presentation of the graph used in determining the coefficients of compressibility for the two sludges produced in this study. As shown, the coefficients of compressibility for Method I and Method II sludges, 0.58 and 0.67, respectively, were very similar.

#### Gravity Dewatering Tests

Both sludges, as illustrated in Figure 16, were rapidly dewatered by gravity, the filtration of water through the filter medium ceasing prior to an elapsed time of three hours for the Method I sludge and 20 minutes for the Method II sludge. The cake moisture versus elapsed time relationships for both sludges were developed using the initial solids content of the applied sludges. However, in the early stages of gravity dewatering of both sludges, solids escaped through the filter medium and were found with the filtrate in

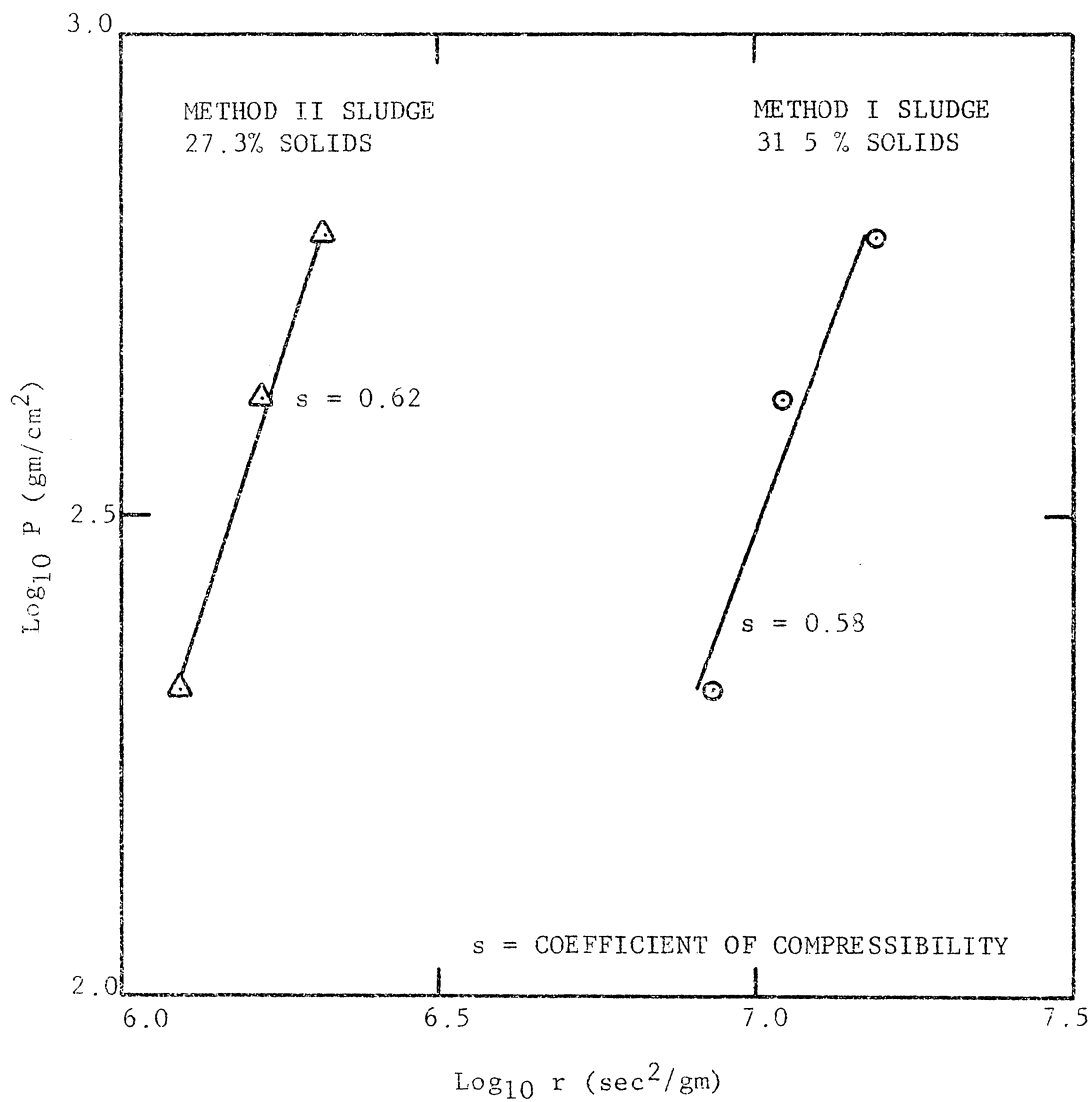


FIGURE 15. VARIATION OF SPECIFIC RESISTANCE WITH APPLIED PRESSURE FOR METHODS I AND II SLUDGES



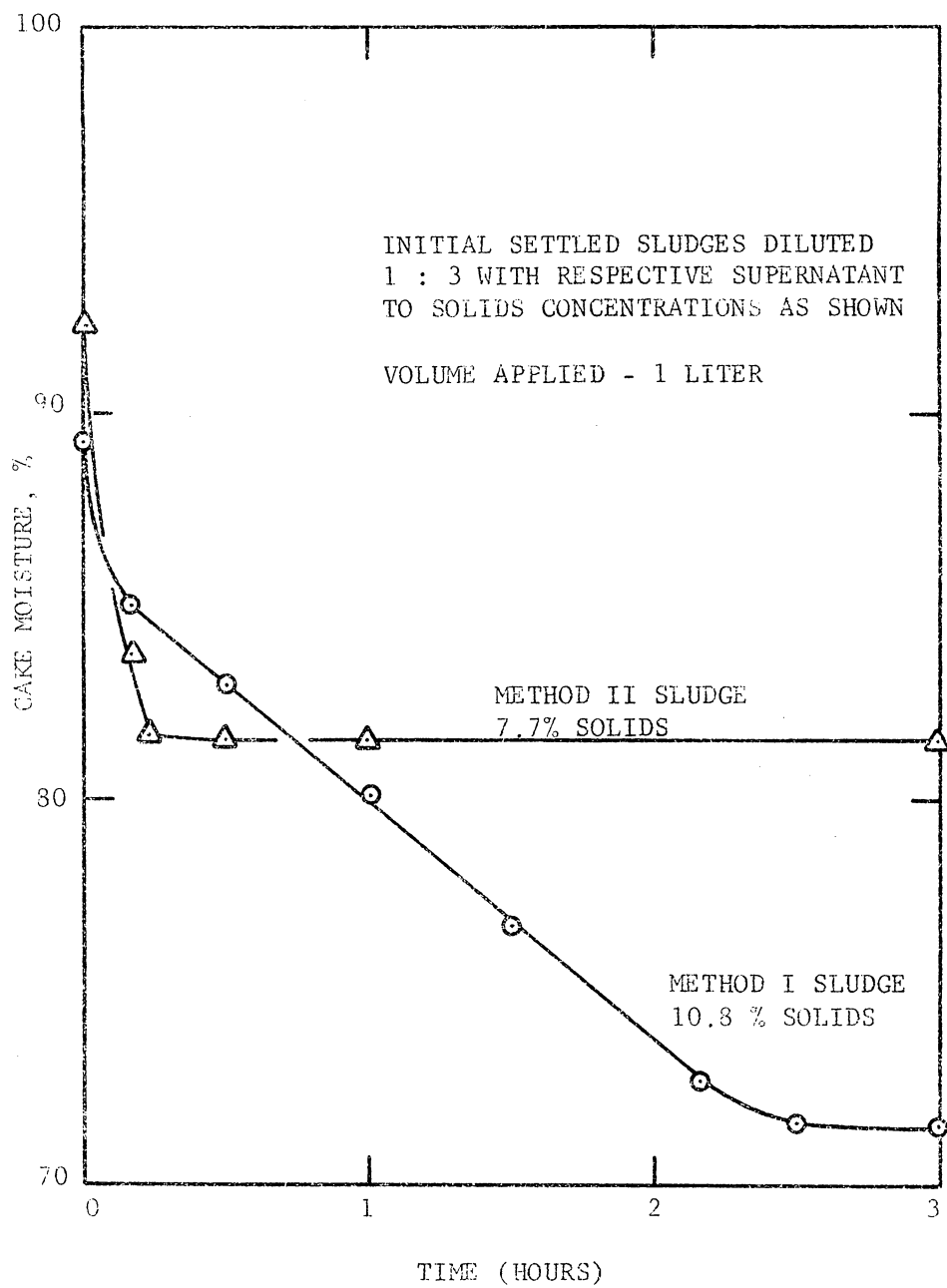


FIGURE 16. DEWATERING OF METHODS I AND II  
SLUDGES BY GRAVITY DRAINAGE

the measuring device. In fact, 16.5% of the initial solids of the Method II sludge escaped the filter medium in the first two minutes of gravity dewatering. After this initial breakthrough, the filter cake began to form and the filtrate became clearer in appearance.

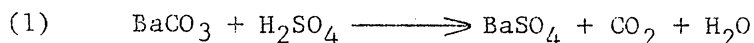
The Method I filtrate contained a very small amount of solids in comparison with the Method II filtrate. On the test beds used in these analyses, gravity dewatering was found to result in a filter cake containing a final moisture content of 71.5% for the Method I sludge and 81.5% for the Method II sludge. Further reduction of moisture content by air drying was not investigated.

## V. DISCUSSION OF RESULTS

The results of this study are significant in that they provide some insight into the mechanisms by which soluble sulfates are precipitated from solution through the formation of insoluble barium sulfate. More important, however, from a sanitary engineering viewpoint is that experimentation was accomplished on a "cold" system and on a macro-level thereby providing a feasible direction in which further studies may proceed. Also, not unlike other treatment studies, optimization of the principle treatment process was accomplished prior to investigating methods of disposal of the products resulting from treatment. The important results of this treatment study are discussed in the following sections.

### Method I - Barium Carbonate Neutralization of Sulfuric Acid Wastewater

Chemical Reaction Considerations    The chemical equation for the reaction between barium carbonate and sulfuric acid,



shows that 1 gram molecular weight of  $\text{BaCO}_3$  (197 grams) reacts with 1 gram molecular weight of  $\text{H}_2\text{SO}_4$  (98 grams) to form 1 gram molecular weight of  $\text{BaSO}_4$  (233 grams). Theoretically, 9 gm of pure  $\text{H}_2\text{SO}_4$ , the quantity of  $\text{H}_2\text{SO}_4$  in 1 liter of the test wastewater, should require only 18 gm of  $\text{BaCO}_3$  to effect neutralization. No indication of the

rate at which the chemical reaction proceeds, however, is afforded by the equation as presented above.

Experimentally the reaction rate was found, as illustrated in Figures 7 and 9, to be very slow even at  $\text{BaCO}_3$  dosages in excess of the theoretical amount required for completion of the reaction. Due to the slow reaction rate, a maximum reaction time of one hour was set as the criterion for optimizing the  $\text{BaCO}_3$  dosage and mixing conditions for use in evaluating the complete treatment process. The one hour reaction time was considered by the author as the maximum allowable time for use under actual batch or fill and draw treatment conditions.

Among the factors which influence the rate of chemical reaction are catalysis, the nature of the reactants, the concentration of the reactants and temperature (81). Effects of temperature on the rate of reaction were not considered as all experiments were performed at room temperature. The most reactive lot of barium carbonate in the laboratory was chosen for experimental use from the results of a barium carbonate reactivity test. The sulfuric acid concentration in the wastewater was preset. The only variables remaining were  $\text{BaCO}_3$  concentration and, due to the phase difference of the reactants, effective agitation of the system.

The reaction rate is controlled in part by the number of surface sites available or the area of contact between the solid ( $\text{BaCO}_3$ ) and liquid ( $\text{H}_2\text{SO}_4$ ) phases as illustrated by the experimental data plotted in Figure 9, where an increase in  $\text{BaCO}_3$  concentration was shown to

cause a decrease in reaction time. If the reaction rate had been controlled primarily by the reaction between the soluble portion of the  $\text{BaCO}_3$  and the  $\text{H}_2\text{SO}_4$  in the solution, then an increase in  $\text{BaCO}_3$  dosage would have provided no change in the reaction rate. The rate determining step, be it either transfer of the ions from the solution to the surface sites or removal of the reaction products from the surface sites, appeared from the test results plotted in Figure 8 to be best affected by an air flow rate of 0.6 cfm or a G value of 527 fps/ft. That a limiting mean temporal velocity gradient existed was not supported by the results of the same test performed using paddle mixing at 500 rpm or a higher G of 632 fps/ft (see Figure 10). This inconsistency may be accounted for partially by the inherent differences in mixing conditions provided by paddle mixing and air mixing but not reflected in their respective calculated G values.

The fact that paddle mixing provided a better agitated system than air mixing and that this is not reflected in the calculation of respective G values may be noted by comparing Figures 7 and 9. The plots of experimental data show that paddle mixing at a G of 223 fps/ft and a  $\text{BaCO}_3$  dosage of 35 gm/l provided a reaction time of 35 minutes whereas air mixing at a higher calculated G of 374 fps/ft provided a situation where 55 minutes of reaction time was required utilizing the same  $\text{BaCO}_3$  dosage. Although additional heat provided by the rotation of the paddle blade could have accounted for this difference in reaction time, it is believed that paddle mixing provided the more completely mixed system and that this was the major

factor. The fact still remains, however, that consideration of G values alone when characterizing mixing conditions is inadequate.

Considering the time necessary for completion of the reaction between  $\text{BaCO}_3$  and  $\text{H}_2\text{SO}_4$ , all further discussion of this method and Method II will be limited to treatment characteristics as they pertain to the successful operation of batch or fill and draw treatment processes. A continuous-flow process is believed to be largely inapplicable to the treatment of sulfuric acid wastewater by  $\text{BaCO}_3$ , because of the inherent difficulties in providing positive process control.

Sludge Separation Characteristics      The mixed liquor resulting from Method I treatment (35 gm/l  $\text{BaCO}_3$ ) of 1 liter of waste acid was found to contain a non-filtrable solids concentration of 7.6 gm/l which, from reaction (3), consisted of precipitated  $\text{BaSO}_4$  and unused  $\text{BaCO}_3$ . This sludge exhibited zone settling characteristics when settled in a graduated cylinder for 24 hours (see Figure 13). Hindered settling and the transition into compression were completed in approximately 33 minutes. This elapsed time for optimum settling of the sludge becomes significant when considering "scale-up" settling times, waste flows and sizing of reaction basins. Another advantage which may be attributed to the  $\text{BaCO}_3$  neutralization of sulfuric acid wastewater besides the precipitation and removal of soluble sulfates is the small volume of sludge which must be handled after sedimentation. This fact is quite evident in Figure 13 where a comparison between the sludge volumes remaining after various

settling times for a  $\text{CaSO}_4$  sludge and the Method I sludge may be made. This difference in sludge volumes is probably attributed to size, shape and weight differences of the particles which make up the non-filtrable solids content of each sludge. Calcium sulfate sludge has been shown to exhibit poor compaction characteristics due to the acicular shape of the calcium sulfate crystal formed during the neutralization reaction (82).

Vacuum filtration was investigated as a method of dewatering the sludge resulting from the reaction process and remaining after sedimentation. The determination of specific resistance in evaluating sludge filterability on vacuum filters was significant in that specific resistance is numerically equal to the pressure difference required to produce a unit rate of filtrate flow of unit viscosity through a unit weight of cake (77). Therefore, under the same test conditions, the filterability of different sludges may be compared. The values of specific resistance determined for Method I sludge at the test pressures approximate the range of values exhibited by sludge resulting from the neutralization of sulfuric acid using lime slurry (77). The coefficient of compressibility for Method I sludge was found to be 0.58 indicating that this sludge was almost incompressible. Sludge compressibility is one of the numerous factors which must be considered when determining loadings for vacuum filters.

Gravity dewatering was investigated as an alternate method to vacuum filtration in concentrating the solids in the Method I sludge. The sludge dewatered quickly as Figure 16 indicates. This result was

anticipated after observing the filtration rate during the Buchner funnel test. However, after determining that gravity dewatering produced a cake which contained 28.5% solids after 3 hours of filtration as compared to the 82% solids concentration of the cake remaining after 26 minutes of vacuum filtration at 12" of Hg, vacuum filtration was chosen as the optimum method for dewatering Method I sludge.

Treatment of Supernatant One very important disadvantage of the Method I treatment process was found to be the large amount of turbidity caused by suspended particles which remained in the supernatant even after 24 hours of gravity sedimentation. This turbidity, which was caused by non-settleable  $\text{BaCO}_3$  and  $\text{BaSO}_4$ , was such that the supernatant was opaque and milky in appearance. The turbidity was removed easily, however, through coagulation using an anionic polyelectrolyte. The occurrence of a relationship between turbidity and polymer dosage as shown in Figure 14 is characteristic of the destabilization of suspensions by either adsorption or bridging. This fact is illustrated in Figure 5 where  $\alpha$  may be considered as  $1/\text{turbidity}$ . Electrophoretic mobility or particle charge was not monitored; therefore, the actual mechanism by which the suspension in the Method I supernatant was destabilized could not be determined.

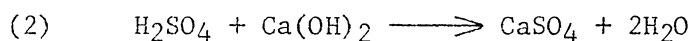
#### Method II - Barium Carbonate Removal of Soluble Sulfates from Neutralized Sulfuric Acid Wastewater

Chemical Reaction Considerations Waste treatment Method II differed from Method I in that the sulfuric acid wastewater was neu-



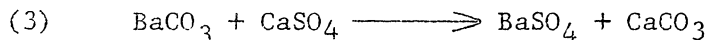
tralized prior to the addition of barium carbonate. This neutralization step accomplished before barium carbonate treatment complicated theoretical chemical reaction considerations but was found, as discussed in later sections, to provide an excellent system in which barium sulfate precipitation could be effected.

The chemical equation for the neutralization of sulfuric acid by calcium hydroxide,



shows that 1 gram molecular weight of  $\text{H}_2\text{SO}_4$  (98 grams) reacts with 1 gram molecular weight of  $\text{Ca}(\text{OH})_2$  (74 grams) to form 1 molecular weight of  $\text{CaSO}_4$  (136 grams). Although the anhydrite form of  $\text{CaSO}_4$  is shown in the above equation, the equilibrium solubility for  $\text{CaSO}_4$  is best represented by the relation for gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (21). Considering equation (1), 9 gm of pure  $\text{H}_2\text{SO}_4$  should require 6.8 gm  $\text{Ca}(\text{OH})_2$  to form 12.5 gm of  $\text{CaSO}_4$ .

If  $\text{BaCO}_3$  is added to the neutralized wastewater system, the following reaction should take place:



Considering the weight relationships presented in the above equation, 12.5 gm of  $\text{CaSO}_4$  should react with 18.1 gm of  $\text{BaCO}_3$  to form 21.4 gm of  $\text{BaSO}_4$  and 9.2 gm of  $\text{CaCO}_3$ . These figures hold true only in the absence of underneutralization. The solubility product constants ( $K_{s.p.}$ ) at 25°C for  $\text{BaSO}_4$  and  $\text{CaCO}_3$  are  $1.0 \times 10^{-10}$  and  $4.7 \times 10^{-9}$ ,

respectively (83). Therefore the reaction products of equation (3) would appear as precipitants.

The wastewater after neutralization theoretically contained approximately 2000 mg/l  $\text{CaSO}_4$  (see Figure 2) in solution and 10.5 gm  $\text{CaSO}_4$  in the precipitated state. As shown in Table V, the  $\text{SO}_4^{=}$  concentrations under experimental conditions were found to exceed that value for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  at  $30^\circ$  (1116 mg/l as  $\text{SO}_4^{=}$ ), ranging from 1759 to 1988 mg/l. This supersaturation could have been caused by numerous factors such as agitation during the neutralization process, temperature variations, or analytical errors inherent in the sulfate analysis.

Figures 11 and 12 show that at the experimental dosages of  $\text{BaCO}_3$  and mix speeds used in studying the Method II reaction process, four distinct regions of sulfate removal were found. A labeled graph of the four regions is presented in Figure 17 for discussion purposes. The initial rate of sulfate removal represented by section A of the graph was probably greater than any of those rates shown in Figures 11 and 12 for non-filtered wastewater. There was an initial demand placed on the system by the  $\text{BaCO}_3$  and this demand resulted in a constant rate of sulfate removal. This conclusion is supported by the results of the treatment of a wastewater sample which was filtered after neutralization, prior to  $\text{BaCO}_3$  dosing. The results of this experiment are shown in Figure 12. The dependence of this initial reaction rate on  $\text{BaCO}_3$  concentration could not be verified due to the lack of data points.

Section B of the graph is theorized as representing the formation of an equilibrium between the rate of removal of the soluble sulfates

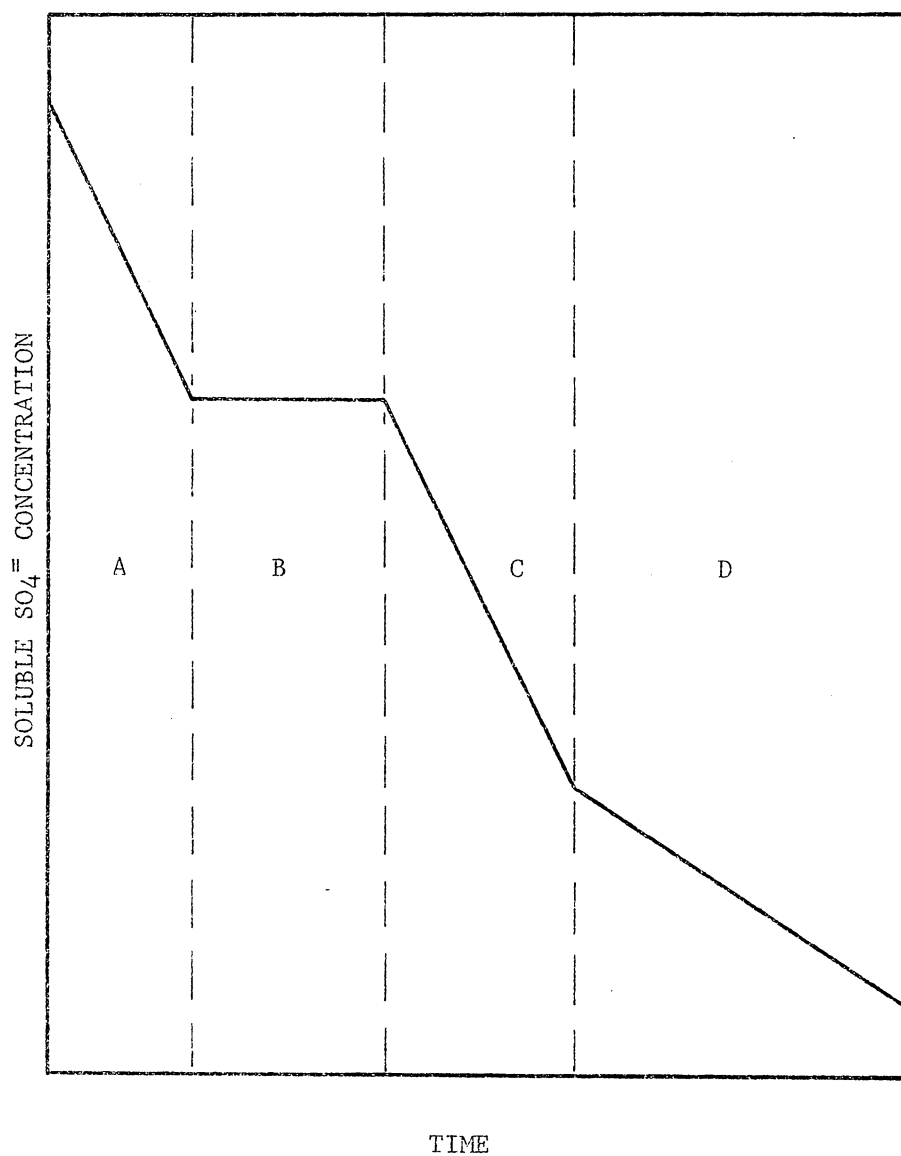


FIGURE 17. THEORETICAL RATE RELATION FOR SOLUBLE SULFATE REMOVAL BY THE METHOD II PROCESS

by barium sulfate precipitation and the rate of dissolution of the  $\text{CaSO}_4$  precipitant. The equilibrium was found to occur in all experiments at a point where 1400 to 1500 mg/l  $\text{SO}_4^{=}$  remained in solution.  $\text{BaCO}_3$  dosage and mix speed had no effect on the  $\text{SO}_4^{=}$  concentration remaining in solution at which this equilibrium occurred, but did affect the period of time over which the equilibrium lasted. Both an increase in  $\text{BaCO}_3$  dosage or mix speed caused an increase in the rate of soluble removal, as shown in Figures 11 and 12. This observation indicates that the rate of reaction between  $\text{BaCO}_3$  and  $\text{CaSO}_4$  depended in part on the amount of  $\text{BaCO}_3$  surface area available on which reactions could take place.

The point on the sulfate removal graph at which section C begins is believed to be the point at which all calcium sulfate has gone into solution thus disrupting the equilibrium relationship. The rate of soluble sulfate removal then proceeds at a constant rate approximating that rate indicated in section A. This rate is almost identical to the reaction rate for sulfate removal from filtered wastewater as shown in Figure 12. The rate of reaction represented by section C is little affected by initial  $\text{BaCO}_3$  dosage or mix speed, at least for the dosages and mix speeds used in this study. The decrease in reaction rate illustrated by section D is due to the decrease in the concentrations of reactants and is shown by the data plotted in Figures 11 and 12 to be affected not only by initial  $\text{BaCO}_3$  dosage but more so by mix speed.

After considering the experimental results as discussed above, a  $\text{BaCO}_3$  dosage of 13 gm/l and a mix speed of 500 rpm were found,

within the limitations of the experiments, to be optimum for Method II treatment of the subject wastewater.

Sludge Separation Characteristics Due to the solids content of the mixed liquor after treatment by the Method II process, sedimentation was envisioned as being required before the wastewater could be considered adequately treated. The sludge settling characteristics were found to be excellent, much better than those characteristics displayed by the Method I sludge (see Figure 13). The time to the point of compression of 20 minutes for Method II sludge indicated the optimum time necessary for settling in a batch or fill and draw reactor before removing the clarified effluent. A solids concentration of 222 gm/l was calculated for the sludge resulting from 20 minutes of settling. The sludge was easily movable even after 60 minutes of settling as was discovered during the settling of a 15 l batch of treated wastewater. The zone settling velocity of 10 ft/hr could probably be improved through the use of larger diameter settling columns.

A major difference between Method I sludge settling and Method II sludge settling was the condition of the respective supernatants remaining after 60 minutes of settling. Whereas Method I supernatant contained turbidity exceeding 2000 JTU, Method II supernatant contained an unappreciable turbidity of 15 JTU. This small value of turbidity meant that Method II supernatant, not considering barium content, could be discharged directly without further treatment, thus eliminating the costs associated with the removal of turbidity.

Due to the rapid filtering rate exhibited by the Method II sludge during the Buchner funnel filtration test, the calculated values of specific resistance were found at all pressures to be significantly lower than those values calculated for Method I sludge. This fact, in conjunction with the discovery that the coefficients of compressibility for both sludges were approximately the same, showed that Method II sludge could be filtered more readily and at higher loadings on vacuum filters than could Method I sludge. The difference in the values of specific resistance for the two sludges could probably be attributed to size and gradation differences of the particles forming the two sludges although this was not investigated and confirmed during this study.

The theory advanced in the previous statement was supported by the results of the gravity dewatering test of Method II sludge. Whereas the Method I sludge formed a good cake and developed a constant rate of dewatering, solids escape and filter medium blinding occurred during Method II sludge dewatering (see Figure 16). Considering that the filter medium was the same for both sludge dewatering tests, particle size and gradation differences between the two sludges were inferred.

#### Barium Ion Concentration

As mentioned previously, one of the criteria for this study was that the barium ion content of the treated effluent must not exceed 1 mg/l. Although barium ion ( $Ba^{++}$ ) concentrations of the treated

effluents developed during this study were not determined analytically, certain theoretical considerations may be advanced.

If  $\text{BaCO}_3$  is added in excess of the theoretical requirement for reaction completion to a sulfuric acid solution as was done in the Method I process, than at equilibrium both of the following expressions apply:

$$[\text{Ba}^{++}] [\text{CO}_3^{=}] = K_{s.p.}(\text{BaCO}_3)$$

$$[\text{Ba}^{++}] [\text{SO}_4^{=}] = K_{s.p.}(\text{BaSO}_4)$$

where [ ] = molar concentration of bracketed ion

$K_{s.p.}$  = solubility product where:

$$K_{s.p.}(\text{BaCO}_3) = 5.1 \times 10^{-9} \text{ at } 25^\circ\text{C (83)}$$

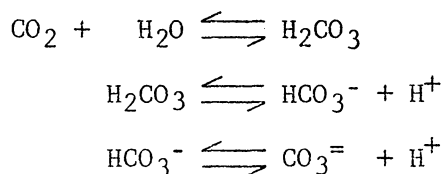
$$K_{s.p.}(\text{BaSO}_4) = 1.0 \times 10^{-10} \text{ at } 25^\circ\text{C (83)}$$

Dividing the equation for  $K_{s.p.}(\text{BaCO}_3)$  by the equation for  $K_{s.p.}(\text{BaSO}_4)$ , the  $[\text{Ba}^{++}]$  cancels, resulting in the following solubility product ratio:

$$\frac{[\text{CO}_3^{=}]}{[\text{SO}_4^{=}]} = \frac{K_{s.p.}(\text{BaCO}_3)}{K_{s.p.}(\text{BaSO}_4)} = \frac{10^{-8.29}}{10^{-10}} = 10^{+1.71}$$

The above relationship indicates that  $\text{BaCO}_3$  will not precipitate until the ion ratio of  $\text{CO}_3^{=}$  to  $\text{SO}_4^{=}$  is greater than the solubility product ratio which equals  $10^{+1.71}$ . This relationship also shows that the solubility of  $\text{BaCO}_3$  will have a greater effect on the  $\text{Ba}^{++}$  ion concentration at equilibrium than will the solubility of  $\text{BaSO}_4$ .

The solubility of  $\text{BaCO}_3$  varies with pH due to the dissociation of  $\text{H}_2\text{CO}_3$  formed by the release of  $\text{CO}_2$  during the neutralization reaction. When  $\text{CO}_2$  is dissolved in water the following equilibria are established:



Assuming an equilibrium pH of 8.0, the solubility of  $\text{BaCO}_3$  may be found using the following relationships:

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad ; \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{=}] }{[\text{HCO}_3^-]}$$

$$\text{H}_2\text{CO}_3 = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{=}]$$

where:  $K_1$  = first dissociation constant of carbonic acid,  
 $4.43 \times 10^{-7}$  at  $25^\circ\text{C}$  (83)

$K_2$  = second dissociation constant of carbonic acid,  
 $4.69 \times 10^{-11}$  at  $25^\circ\text{C}$  (83)

$\text{H}_2\text{CO}_3$  = molar concentration of carbonic acid (total)

$[\text{H}_2\text{CO}_3]$  = molar concentration of free (non-ionized) carbonic acid

By rearranging the expressions for the dissociation constants and substituting in the expression for the total concentration of carbonic acid, the following equation is developed:



$$\frac{H_2CO_3}{[CO_3^{=}] } = \frac{[H^+]^2 + K_1[H^+] + K_1K_2}{K_1K_2}$$

Inverting the above equation and solving for  $[CO_3^{=}] / H_2CO_3$  results in a value of  $10^{-5.44}$  for the fraction of the solubility attributed to the  $CO_3^{=}$ . Since the solubility of  $BaCO_3$  is given by:

$$K_{s.p.} = [Ba^{++}] [CO_3^{=}]$$

then 
$$K_{s.p.} = (S) \times 10^{-5.44} (S)$$

where: S = the solubility of  $BaCO_3$

then solving for S

$$S = 5.24 \times 10^{-3} \text{ moles/l}$$

Therefore, assuming a system temperature of  $25^{\circ}C$ , that the dissolved  $BaCO_3$  is present in solution entirely as ions and that no complex species are formed by the barium ion, the barium ion concentration at equilibrium is 0.72 gm/l. This barium ion concentration is extremely higher than the 1 mg/l criterion for the treatment process.

In treatment Method II, only the theoretical amount of  $Ba^{++}$  necessary to react with the available  $SO_4^{=}$  was required for completion of the reaction within the one hour criterion. At equilibrium in this case, making the same assumptions as above, the  $Ba^{++}$  concentration in solution should be dependent only on the relationship for  $K_{s.p.}(BaSO_4)$  and therefore equal  $1.0 \times 10^{-5}$  M or 1.37 mg/l. In actuality this concentration could be lowered by slightly decreasing

the  $\text{BaCO}_3$  dosage thereby leaving a soluble  $\text{SO}_4^{=}$  residual in the wastewater. A soluble  $\text{SO}_4^{=}$  residual anywhere in the range 3 mg/l to 250 mg/l would keep the  $\text{Ba}^{++}$  concentration below 0.5 mg/l and satisfy the criterion. Of course, temperature and the ionic strength of the solution have not been considered in the above calculations.

Another method for decreasing the  $\text{Ba}^{++}$  concentration in the treated effluent would be through dilution with another treated effluent. Using the theoretical  $\text{Ba}^{++}$  concentration calculated above, a dilution of 1 : 1.5 would decrease the  $\text{Ba}^{++}$  concentration to 0.9 mg/l.

#### Description of Selected Treatment Process

From the results of the treatment study as discussed in the above sections, Method II was selected as the more feasible of the two methods studied for  $\text{BaCO}_3$  treatment of sulfuric acid wastewater. This selection especially became evident after considering the additional costs of  $\text{BaCO}_3$ , polyelectrolytes and sludge dewatering associated with the Method II treatment process. If sludge return for particle nucleation had been investigated during Method I testing, perhaps the initial  $\text{BaCO}_3$  dosage could have been decreased.

A diagram of the selected Method II treatment process as proposed by the author is presented in Figure 18. As shown, neutralization,  $\text{BaCO}_3$  treatment and sedimentation would be performed in the same treatment tank or batch reactor. The sludge would be pumped to vacuum filters where further dewatering would take place. The fil-

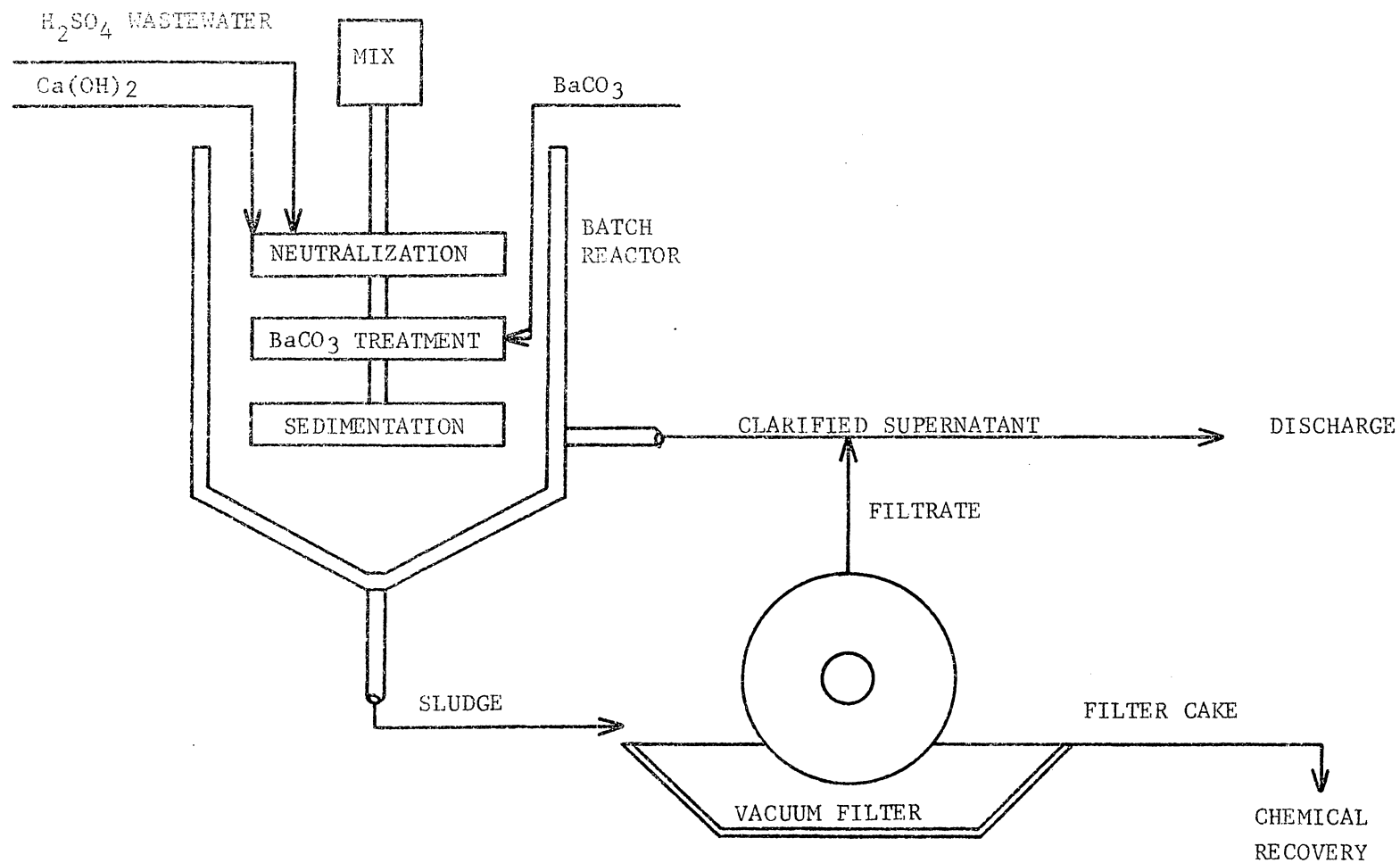


FIGURE 18. PROPOSED FLOW DIAGRAM FOR BARIUM CARBONATE TREATMENT OF SULFURIC ACID WASTEWATER

trate would be combined with the supernatant from the batch reactor and discharged. The most advantageous way of handling disposal of the filter cake would be through the separation and recovery of  $\text{BaSO}_4$  and  $\text{CaCO}_3$ . Both of these chemicals could be sold commercially or returned to the treatment process. Through the application of heat,  $\text{CaCO}_3$  can be converted to  $\text{CaO}$  and  $\text{CO}_2$ . The  $\text{CaO}$  could then be slaked and returned to the neutralization process as  $\text{Ca(OH)}_2$ . The  $\text{BaSO}_4$  could be heated with coal and reduced to  $\text{BaS}$  which, through a reaction with the  $\text{CO}_2$  formed during the decomposition of  $\text{CaCO}_3$ , could be converted to  $\text{BaCO}_3$ . This  $\text{BaCO}_3$  would be returned to the waste treatment process as makeup for the  $\text{BaCO}_3$  treatment step.

Considering the stoichiometry of the reaction between  $\text{BaCO}_3$  and  $\text{CaSO}_4$ , it would be more advantageous to sell the reaction product,  $\text{BaSO}_4$  than to attempt to convert  $\text{BaSO}_4$  to  $\text{BaCO}_3$ . Since blanc fixe (precipitated  $\text{BaSO}_4$ ) sells in bags in carlot quantities for \$192/ton while precipitated  $\text{BaCO}_3$  sells, on the same basis, for \$151/ton, the sale of the  $\text{BaSO}_4$  would pay for the  $\text{BaCO}_3$  used in the treatment process (7). Of course this depends on the degree of purity of  $\text{BaSO}_4$  achieved during the recovery process.

## VI. CONCLUSIONS

From the study of two different methods of utilizing barium carbonate in removing soluble sulfates from a synthetic sulfuric acid wastewater through the formation of a barium sulfate precipitant, the following conclusions have been drawn:

1. The rate of chemical reaction between barium carbonate and the sulfuric acid wastewater was slow and was dependent on mixing conditions and barium carbonate dosage.
2. Barium carbonate neutralization of the sulfuric acid wastewater resulted, after settling, in a highly turbid supernatant. The suspension, which was found to consist of insoluble particles of both  $\text{BaCO}_3$  and  $\text{BaSO}_4$ , was easily destabilized through coagulation using an anionic polyelectrolyte.
3. The rate of chemical reaction between barium carbonate and the calcium sulfate resulting from the neutralization of the sulfuric acid wastewater with calcium hydroxide was slow and was dependent on mixing conditions and barium carbonate dosage.
4. Unlike the reaction between  $\text{BaCO}_3$  and  $\text{H}_2\text{SO}_4$  which required almost twice the theoretical amount of  $\text{BaCO}_3$  for completion within an hour, the reaction between  $\text{BaCO}_3$  and  $\text{CaSO}_4$  only required approximately 10% in excess of the theoretical amount of  $\text{BaCO}_3$  in accomplishing the same results.

5. Optimization of mixing conditions resulted in decreasing the  $\text{BaCO}_3$  dosage such that the theoretical amount of  $\text{BaCO}_3$  would react completely with the  $\text{CaSO}_4$  within an hour.
6. Consideration of calculated values of the mean temporal velocity gradient or  $G$  alone when characterizing mixing efficiencies was found to be inadequate.
7. Although the  $\text{BaCO}_3$ - $\text{BaSO}_4$  sludges were dewatered quickly during the Buchner funnel filtration test, optimum vacuum filtration characteristics were exhibited by the  $\text{BaSO}_4$ - $\text{CaCO}_3$  sludges.
8. Gravity dewatering of  $\text{BaCO}_3$ - $\text{BaSO}_4$  sludge proceeded at a constant rate, whereas gravity dewatering of  $\text{BaSO}_4$ - $\text{CaCO}_3$  sludge proved unsatisfactory due to filter blinding by sludge particles.
9. Optimum sulfate removal from a sulfuric acid wastewater is accomplished by a process utilizing neutralization with lime and precipitation of sulfate by the addition of barium carbonate.

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BARIUM CARBONATE TREATMENT OF SULFURIC  
ACID WASTEWATER

by

Lowell Robert Norris, III

(ABSTRACT)

Two methods of removing sulfates from sulfuric acid wastewater through the addition of barium carbonate and the formation of a barium sulfate precipitant were investigated. Optimization of barium carbonate dosage, reaction time and mixing conditions was accomplished for each method prior to evaluating the treatability of the reaction products. A synthetic wastewater consisting of 9 gm/l  $H_2SO_4$  was treated. A soluble sulfate content of 250 mg/l or less remaining after one hour of reaction time was the criterion for the optimization tests.

The first method of sulfate removal consisted of utilizing barium carbonate in directly neutralizing sulfuric acid wastewater. Almost twice the theoretical amount of barium carbonate was required at a paddle mix speed of 250 rpm for completion of the reaction within an hour. The supernatant remaining after settling was highly turbid. This turbidity was easily removed by coagulation using an anionic 150 polyelectrolyte. The sludge was dewatered efficiently by both vacuum filtration and gravity drainage.

Optimum sulfate removal was accomplished by the second method which consisted of adding barium carbonate to the wastewater after

neutralization with high calcium hydrate lime. Only the theoretical amount of barium carbonate was required at a paddle mix speed of 500 rpm for completion of the  $\text{BaCO}_3$  -  $\text{CaSO}_4$  reaction within an hour. The supernatant after settling was acceptable. Experimental values of specific resistance for this sludge were found to be much lower than those values determined for the sludge from the first method. This sludge, however, blinded the sand bed during gravity dewatering.