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Dewatering of Mine Drainage Sludge



U.S. ENVIRONMENTAL PROTECTION AGENCY

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Dewatering of Mine Drainage Sludge

by

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for the

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ABSTRACT

This report is a literature review on thickening and dewatering of sludge resulting from lime or limestone neutralization of coal mine drainage.

The effects of mine water constituents and methods of treatment on the physical and chemical characteristics of the resulting sludge are described. Such current practices as aeration, recirculation and neutralization are discussed. Additional techniques at various stages of development, such as thickening, conditioning, and dewatering are evaluated for use in coal mine drainage treatment.

The most promising coal mine sludge dewatering technique appears to be vacuum filtration. Other methods such as sand bed filtration, pressure filtration and centrifugation may also be applicable.

Recommendations are made as to the areas in coal mine drainage treatment and sludge densification that need further research.

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CONCLUSIONS

The major conclusions that can be drawn from this review are:

1. Coal mine water constituents and treatment methods strongly affect the resulting sludge characteristics. The most important sludge characteristics affected are volume, density, and the ability to flow, settle and dewater.
2. New coal mine drainage treatment methods, such as the Densator[®] Process and High Density Sludge Process, are available that produce sludges with high concentrations of solids. However, these new treatment methods are not applicable to the full spectrum of coal mine waters.
3. Where applicable, limestone neutralization produces a sludge that generally settles faster, and settles to a smaller volume with a higher density, as compared to conventional lime neutralization methods.
4. From the research reported to date, vacuum filtration alone or used in conjunction with a precoat appears to be the most feasible method of dewatering coal mine sludge. Other processes such as sand bed filtration, centrifugation and pressure filtration may also be applicable.
5. Mine drainage sludge can be slightly densified by the use of a clarifier thickener or Hydraulic Rake[®]. Rapid settling of the sludge solids can be achieved by chemical conditioning with organic polyelectrolytes. Sludge conditioning by artificial freezing has been attempted on other sludges with reasonable success. Further application of freezing to mine drainage sludge could be possible if the cost of the freezing process were reduced.
6. When land is available, lagooning is the method most commonly used in the treatment of water for clarification and sludge disposal. However, plain lagooning does not allow the sludge to undergo significant concentration.
7. When feasible, treatment plant operators are disposing sludge to inactive, deep coal mines. This disposal method allows for the construction of smaller clarification basins which leads to reduced construction costs. The ecological effects of deep mine disposal have not been determined.
8. There is currently no practical use for coal mine sludge nor is there any practical method for the recovery of by-products.

RECOMMENDATIONS

More research is needed to:

1. Develop a better understanding of the effects of raw water chemistry and treatment methods on sludge characteristics. Raw water chemistry is so variable that the resultant sludge can change from day to day. It is recommended, therefore, that research be directed toward studying the effects of different treatment methods and the raw water chemistry variability on the resultant sludge.
2. Emulate, with coal mine sludge, the initial success achieved with the dewatering and volumetric reduction of sewage and water treatment sludge using freezing and thawing techniques.
3. Determine the feasibility of using organic polyelectrolytes on coal mine drainage sludge to aid vacuum filtration and to increase the rate of water clarification. Similar applications of organic polyelectrolytes to waste treatment processes have proven highly successful.
4. Further enhance the advantages of sludge recirculation combined with limestone and lime neutralization processes. These processes increase the percent solids, reduce sludge volume, and increase treatment efficiency.
5. Amplify the potential of tube settling which appears to be a feasible clarification technique for certain mine waters.
6. Study the dissolution of coal mine sludge in underground mines.
7. Evaluate pressure filtration and centrifuging which seem to have been prematurely disregarded as feasible methods for dewatering coal mine sludges.
8. Realize by-product recovery or direct utilization of coal mine sludge.

INTRODUCTION

The coal mining industry, under severe pressure from states such as the Commonwealth of Pennsylvania, has in some cases adopted effective measures in dealing with the drainage resulting from active coal mines. Currently, acid mine drainage treatment employs the use of lime or limestone as neutralizing agents. While being effective in mine drainage treatment, these neutralizing agents contribute to the production of substantial quantities of sludge or insoluble precipitates. In some cases as much as 33 percent of the treatment plant inflow can remain as sludge.(1)

This precipitated sludge may be composed of over 99 percent water which compounds handling and disposal problems. In West Virginia alone, enough sludge is currently produced to require an estimated 400 acres of land a year on which to construct storage ponds. Further, this creates a situation where large land areas in northern West Virginia and other sections of the State are put to inefficient use.(2)

Sludge is one of the products of an expensive water treatment process and must be handled by the coal mine operators. Since sludge is valueless, it is desirable to dispose of this waste product in the cheapest manner possible. Currently, sludge is either perpetually stored in ponds, pumped underground into mined-out workings, trucked to abandoned mines for disposal, or dumped into drying lagoons.

This situation may be altered in the future. Land areas for storage lagoons may be too expensive or not available and underground disposal may be undesirable. Coupled with this, the national alarm over ecological disturbances due to waste disposal has motivated industry, the Federal and State governments, and universities to make an indepth review of the coal mine sludge question.

To this end, this report reviews the current status of coal mine sludge densification and dewatering as a means of obtaining a better understanding of the coal mine drainage treatment system and methods of improvement.

THE FORMATION AND CHARACTERISTICS OF MINE WATER SLUDGE

General Characteristics

Physical-Chemical

There are two effluents from the mine drainage neutralization process: (1) treated water and (2) sludge.

Sludge formed from the neutralization process is generally affected first, by the mine water composition and second, by the neutralization method.

The chemical composition of acid mine drainage sludge is highly variable and non-uniform in nature. Lovell⁽³⁾ reports that sludge is generally composed of hydrated ferrous or ferric oxides, gypsum, hydrated aluminum oxide, varying amounts of sulfates, calcium, carbonates, bicarbonates, and trace amounts of silica, phosphate, manganese, titanium, copper and zinc. A typical sludge analysis is shown in Table 1.

Table 1

Thompson Shaft Borehole Sludge Analysis - Hydrated Lime Treatment

Calcium Sulfate	CaSO ₄ -- 40%
Magnesium Sulfate	MgSO ₄ -- 5%
Free Lime	CaO -- 3%
Magnesia	MgO -- 1%
Ferric Oxide	Fe ₂ O ₃ -- 15%
Manganese Oxide	Mn ₂ O ₃ -- 4%
Silica	SiO ₂ -- 20%
Aluminum Oxide	Al ₂ O ₃ -- 12%

After Young and Steinman⁽⁴⁾

As mine drainage typically contains high iron concentrations, the precipitation of ferric hydroxide ($\text{Fe}(\text{OH})_3$) or "yellow boy", accounts for the generally high concentrations of this compound that occur in coal mine sludge. Because of the captured water within this iron compound, much of the sludge settleability and final volume will be influenced by ferric hydroxide as opposed to the other hydrous oxides present within the sludge. The formation of ferric hydroxide occurs by the oxidation of the ferrous iron to the ferric state followed by hydrolysis or by the formation of the ferrous hydroxide followed by oxidation to the ferric state. Iron III, (ferric iron) in the presence of most alkaline agents, begins to precipitate at approximately pH 4 and approaches residual concentrations at pH values between 6 and 7.⁽³⁾

Ferrous hydroxide ($\text{Fe}(\text{OH})_2$) also exhibits control over sludge properties. Being similar in nature to its ferric counterpart, ferrous hydroxide "binds" considerable amounts of water and also affects sludge settling and final volume.

The sulfate concentration in sludge varies with the amount of sulfate present in the parent acid mine water. When high concentrations of lime or limestone are needed to neutralize highly acidic waters, the solubility limit of calcium sulfate (approximately 2000 mg/l) may be exceeded and precipitation would then occur. The precipitation of calcium sulfate not only changes sludge properties, but creates problems by formation of scale on sludge withdrawal ports, overflow pipes and channels.

Sludge physical and chemical properties are affected by both mine water chemistry and process parameters which include the sequence of unit operations, reaction rates, completeness of the reactions, temperatures, agitation, catalytic effects, and bacteriological influences.⁽³⁾

The more important physical sludge properties are settleability, density, "dewaterability", particle characteristics, particle surface properties, and sludge flow properties such as viscosity.⁽³⁾

The general term "sludge settleability" now seems to have the connotation of combining into one term the aspects of sludge settling rate and final sludge volume formed from a given amount of treated water. Results from a study by Sanmarful⁽⁵⁾ on the effects of different neutralizing agents (using synthetic acid mine drainage) on sludge settling rates, densities and compaction levels showed that carbonates yield a granular, dense sludge as compared to the semi-gelatinous form resulting from hydroxide neutralizing agents.

Sludge density is another physical property of interest. Sludge densities are generally reported as percent solids by weight. Densities ranging from 0.9 to 4.98 percent from clarifier underflows when using hydrated lime as the neutralizing agent have been reported by Charmbury and Maneval⁽⁶⁾. Wilmoth and Hill⁽⁷⁾ conducted limestone neutralization studies and found sludge solids as high as 9.5 percent.

Properties of coal mine drainage sludge such as viscosity have not been reported in any depth in the literature. The ability of sludge to flow is of considerable importance since sludge is frequently pumped or otherwise moved from one location to another. Viscosity, therefore, is important in treatment plant design.

Surface properties, particularly electrostatic charge, influence the coagulation of sludge flocs. The ability of sludge flocs to aggregate affects the sludge settling rate which in turn is related to sedimentation basin size. Use of coagulating aids to reduce the zeta potential can greatly enhance settling rate.

Sludge particle size, like electrostatic charge, is a physical property that influences coagulation and sedimentation processes. Factors that affect floc size and the relative importance of floc size are discussed in later sections of this report.

Sludge "dewaterability" connotes the ability of sludge to be concentrated into a more manageable form. The success of coal mine sludge concentration, as will be shown later in this report, depends upon the method of concentration and the type of sludge being studied.

Chemical Analyses of Coal Mine Drainage and Sludge

The concentrations of cations such as ferrous iron, ferric iron, calcium, magnesium, aluminum, manganese and the sulfate anion as well as pH, acidity and alkalinity properties are commonly analyzed in coal mine drainage. Alkalinity refers to the concentrations of hydroxide, carbonate and bicarbonate anions present in solution, while acidity is derived from a combination of the free acidity normally resulting from the hydrolysis of iron sulfate plus acidity due to cation oxidation as, for example, the oxidation of ferrous iron. Acidity and ferrous iron determinations can be used to predetermine the quantity of alkaline agent and aeration, respectively, which would be required to neutralize the mine water.

Water characterization is generally carried out by chemical analytical techniques specifically designed for acid mine water analysis or adapted from other water analysis methods. Analytical kits produced by Hach Chemical Company and others can be used for chemical analysis of mine water in the field. Laboratory techniques, using both wet chemical and instrumental methods, have been published which may be directly used or adapted for coal mine drainage analysis. (8,9,10)

Coal mine sludge analysis has traditionally involved determination of percent solids, settled volume and settling rate. Very little work is being done in the area of chemical analysis of sludge. However, some of the conventional chemical analysis techniques such as atomic absorption spectroscopy can be readily adapted to coal mine sludge analysis. Some of the more important elements in coal mine sludge that can be determined by absorption spectroscopy are iron, calcium, silicon, magnesium and aluminum.

Comparison With Other Sludges

Acid wastewaters have been discharged in large quantities for many years. Some of these acidic wastes have been treated with various neutralizing agents. Since lime and limestone are relatively cheap neutralizing agents their use has been extensive. However, their use creates problems due to the production of substantial amounts of sludge.

A number of sludges produced from lime or limestone treatment are reviewed in this section with the intention of presenting an overview of sludges and their properties. This overview will illustrate the variability of sludges and sludge properties and describe other waste sludges which often undergo some comparable form of treatment which could be applicable to coal mine drainage sludge.

Pickle Liquor

Steel fabrication processes produce a surface scale that must be removed prior to finishing operations. The most common method of scale removal is by immersing (pickling) the steel product in a dilute sulfuric acid solution (15-25 percent by weight). After immersion in the pickling solution the steel is rinsed in clean water for removal of sulfuric acid. The pickling solution, after repeated usage, will contain large amounts of ferrous sulfate resulting from reaction of iron oxide and the sulfuric acid. As the

ferrous sulfate content is increased, the cleaning action is decreased to the point of ineffectiveness and the pickling solution must be discarded. Water used to rinse the steel following the pickling operation eventually becomes acidic and must be replaced. This rinse water represents another waste that must be dealt with. A comparative analysis of coal mine drainage, pickle liquor and rinse water is illustrated in Table 2.

Table 2

Comparative Analysis of Coal Mine Drainage,
Pickle Liquor and Rinse Water

Comparative Analyses mg/l or ppm				
	Mine Drainage (Maneval 1966)		"Typical" Steel Mill Pickle Liquors (FWPCA 1968)	
	Morea (strip pit)	Marianna (bore hole)	Rinse Water	Strong Liquor
Acidity as CaCO ₃ or H ₂ SO ₄	190	4,040	3,000	38,000
Fe	6	815	4,100	52,000
SO ₄	290	10,000	10,800	125,000
pH	3.2	2.6	less than 2.0	

(11)

After Dean

Although the compositions of the rinse water used on pickled steel and of coal mine drainage are similar, the volume of drainage from coal mines is much greater than the acid rinse produced from pickling operations.

Numerous treatment methods have evolved from the research on pickle liquor. Various alkaline neutralizing agents have been studied with high calcium quicklime or hydrate emerging as the most successful. Use of lime as the neutralizing agent in pickle liquor treatment creates voluminous amounts of sludges that are similar to the sludge from coal mine drainage treatment.

A comparison between the chemical composition of mine drainage, rinse water and strong pickle liquor presented in Table 2 illustrates that the resulting sludges contain similar chemical constituents. Mine drainage, however, can contain various amounts of magnesium, manganese, silica and aluminum, which are usually precipitated during the neutralization process and end up in the sludge.

The effects of these additional elements on mine drainage sludge are not completely known due to the variability of raw mine waters. Aluminum alone in the hydrous form can add to total sludge volume.

Parsons⁽¹²⁾ summarized the results of research on sludges produced from acid wastes. The following factors were found to affect sludge volume and characteristics:

1. Alkaline agent
2. Acid concentration
3. Degree of neutralization
4. Temperature
5. Oxidation state
6. Seed nuclei

The volume of sludge formed from the treatment process represents the amount of material to be handled; therefore, if an alkaline agent produces an insoluble product, the ultimate sludge volume can be directly influenced by that neutralizing agent.

The relationship between acid concentration and sludge volume exhibits two interesting but contradictory phenomena. First, as acid concentration of the wastes increases, the percent solids or density of the sludge tends to increase. Second, when sulfuric acid wastes are diluted with water they become less concentrated. When this diluted waste is neutralized with calcium based alkalies, the solubility product of calcium sulfate is not exceeded. This dilution process decreases the calcium sulfate precipitate which, in turn, reduces the total sludge volume. The implication is that if a minimum sludge volume is desired there are two opposing alternatives that can produce similar ends - namely lower sludge volumes.⁽¹²⁾

The oxidation state of iron influences sludge density which in turn affects the resulting sludge volume and settling rates. As illustrated in Figure 1, the completely oxidized sludge settles quickly, but compacts to only about 57 percent of the original volume. The un-oxidized sludge settles slowly, but compacts to a final volume of 30 percent of the original. The sludge that is 65 percent oxidized exhibits both high compaction and rapid settling.

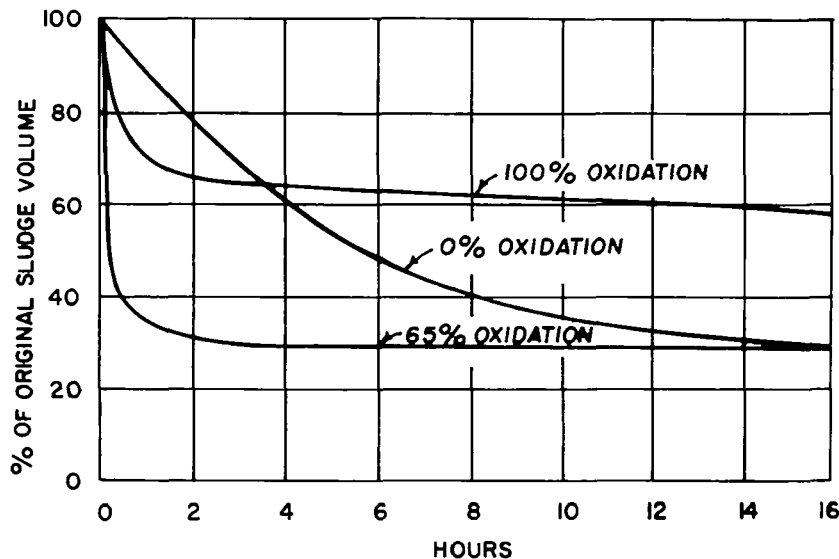


Figure 1 - Influence of Iron Oxidation on Pickle Liquor Sludge. After Levine and Rudolfs (13)

The hydrogen ion concentration (pH) or degree of neutralization is another major factor to be considered in the neutralization of pickle liquor. A pH of 8.5 is generally required for the precipitation of ferrous iron, but this does not necessarily mean the optimum sludge volume is achieved. The pH effects on sludge volume are presented in Figure 2. A slight increase of pH from 8.5 to 9.5 reduces the final sludge volume 30 percent, although increasing the pH to 11.0 increases the sludge volume. (13)

The amount of neutralizing agent added, therefore, is critical in the effective treatment of the acid waste and the concurrent production of a minimum sludge volume.

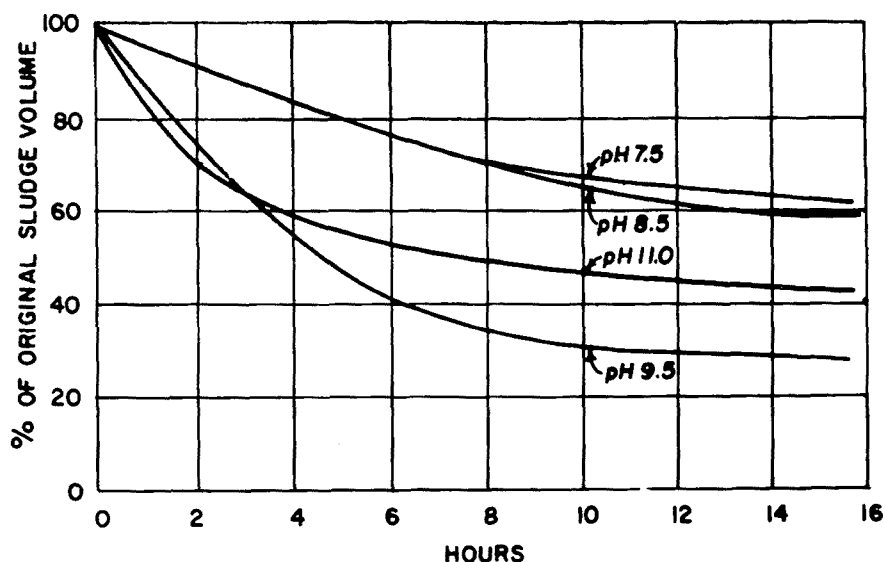


Figure 2 - Influence of Treatment pH on Pickle Liquor Sludge. After Levine and Rudolfs⁽¹³⁾

Temperature effects on sludge characteristics can be expected due to changes in viscosity and density of the solutions. Hoak and Sindlinger⁽¹⁴⁾ have reported pickle liquor studies where the reaction temperature was kept at 75°C or above and substantial improvement in the sludge settling rate was observed.

The problem of dilute acid solutions resulting in high sludge volumes, has induced research into seed nucleation. Faust, et al.^(15,16,17,18) found that calcium sulfate could be induced to precipitate on gypsum crystals which had been previously precipitated or intentionally added as ground rock gypsum. The addition of either ground rock gypsum or previously precipitated gypsum dramatically increased the suspended solids concentration with a corresponding reduction in sludge volume. Superior sludge properties resulted from the addition of ground rock gypsum. However, the most practical method to provide previously precipitated gypsum was by the use of sludge recirculation.

Pickle liquor sludge was initially thought to be dewaterable only by pressure filtration.⁽¹⁹⁾ As dewatering technology advanced other techniques such as centrifugation were studied.⁽²⁰⁾ Levine and Rudolfs⁽¹³⁾ studied vacuum filtration of pickle liquor sludges and found that neutralization with either dolomitic lime or high calcium lime produces a sludge that could be acceptably dewatered.

A quicklime pickle liquor treatment process developed by Wing⁽²¹⁾ produced a sludge that exhibited exceptional filtration properties. The sludge cake from a rotary vacuum filter averaged about 58 percent moisture.

It must be understood that the chemical composition of coal mine drainage is highly variable as compared to the reasonably constant composition of waste pickle liquor and rinse water. Due to pickle liquor's extreme concentration of acidity, iron, and sulfates, direct comparison to the "average" coal mine drainage may not be entirely valid. However, research performed with lime and limestone neutralization of pickle liquors has laid much of the ground work for neutralization studies of coal mine drainage and much of the work has direct application in coal mine drainage neutralization. Moreover, the dewatering studies conducted on pickle liquor sludge have also contributed to densification studies on coal mine drainage sludge.

Municipal Waste and Water Treatment

Municipal sludges have characteristics which are largely determined by the waste treatment process. Being organic in nature, sewage sludge is completely different in character from inorganic coal mine drainage sludge.

Since the concentration process primarily thickens sludge and the dewatering process removes or reduces the water content, the use of gravity filtration, vacuum filtration and other concentrating and dewatering techniques has established technology and general cost data which serve as a guide in coal mine drainage sludge dewatering. Cost data will be discussed in section X.

Plating Waste

Wastes from the plating industry are many and varied depending upon the plating operation. In most cases wastewaters result from the rinsing operations after the various plating processes. The treatment of these waters is generally accomplished by precipitation, thickening, and disposal. Lime slurry is a common neutralizer and precipitating agent. The resulting sludge can contain various amounts of copper,

nickel, chromium, zinc, aluminum, iron and other impurities depending on the plating process. (22)

In most cases the quantity of sludge produced from plating waste treatment is small compared to the sludge produced from coal mine drainage treatment. Small and Graulich (22) reported that a moderate sized plating operation creates about 1000 gallons of sludge per day containing four percent solids. This sludge usually constitutes one percent or less of the original volume of acid waste.

Dewatering of plating waste sludge is frequently accomplished by a continuous vacuum filter. Thin filter cloths are used to eliminate cloth blinding and a strong discharge system is used to remove the dewatered cake.

In actual practice filtration rates have varied from 1.5 lb to 30 lb of dry solids per hour per square foot of filter area. (22) The wide variance in filtration rates clearly indicates the need for pilot plant experimentation prior to construction of an operational vacuum filtration system.

The problems experienced in treating plating waste sludges, particularly the judgments as to filter size and type of cloth, are the same problems a coal mine drainage treatment plant operator would encounter if he were to construct a vacuum filtration dewatering system.

THE EFFECT OF RAW WATER CHEMISTRY ON SLUDGE FORMATION AND CHARACTERISTICS

Hill⁽²³⁾ and Barthauer⁽²⁴⁾ found that coal mine drainage can be separated into distinct types or classes according to chemical characteristics. Three general classifications have been reported and the chemical constituents within these classifications can contribute to sludge formation and characteristics. It must be remembered, however, that other factors such as treatment method affect sludge characteristics and that an attempt has been made to discount these factors and dwell specifically on the raw water chemistry effects.

The first type of mine drainage usually has a pH of 6.5 to 7.5 or greater, very little or no acidity, and contains iron, usually in the ferrous state, that varies from less than 60 mg/l up to 1000 mg/l. Barthauer⁽²⁴⁾ reported that a sludge from this type of water was light and fluffy in character and settled to 0.5 percent of the original treated volume.

Mine waters of this type need not necessarily be neutralized due to the lack of present acidity; however, when there are large amounts of ferrous iron present, lime may be needed to raise the pH to handle potential acidity resulting from the oxidation of ferrous iron. If the water does not need lime addition, the volume of the sludge is totally dependent upon the iron content and other possible precipitable elements present in the water.

A second type of mine drainage is partially oxidized water that can have a pH in the range of 3.5 to 6.5, acidity values that range from 0 to 1000 mg/l, iron in both the ferric and ferrous state and small amounts of aluminum. This type of water can contain both acidity and alkalinity and the relative amounts of ferric and ferrous iron depend upon the pH.⁽²³⁾

Sludges from this second type of water can vary depending upon the raw water constituents. Iron content will be a major contributor to the sludge volume, but when considering this type of water, neutralization processes have to be introduced which drastically change sludge properties.

Raw mine waters of the second type frequently contain bicarbonate which can lead to a unique sludge problem. Lombardo⁽²⁵⁾ reported on one such water that was very close to alkaline with a pH ranging from 5 - 6.5, but contained a large amount of ferrous iron and varying concentrations of bicarbonate. When this water was treated with lime and

aerated, the relatively tight floc formation that normally occurs did not develop and extended retention time was required for complete sedimentation. This problem was solved by eliminating the aeration step and allowing the iron to remain in the unoxidized ferrous hydroxide form. Lime consumption increased in this treatment process due to the higher pH (8.8 - 9.3) required to properly remove ferrous iron as ferrous hydroxide. In this case the bicarbonate content of the raw water played a deciding role in affecting the sludge settling characteristics.

Another water reported by Wilmoth and Hill⁽⁷⁾ falls into this second classification. This water is characterized by a low pH (2.8), a low aluminum content (31 mg/l) and a low iron content (93 mg/l), which was primarily in the ferric state. The low iron and aluminum content of the water would normally produce a small volume of sludge. In this case the water was treated with three different kinds of neutralizers and each neutralizing agent had a different effect on the sludge settling rate and final settled volume.

The third type of water is highly acidic. This water frequently contains large amounts of acidity (1000 - 15,000 mg/l), large amounts of iron (500 - 10,000 mg/l), mostly in the ferrous state, and aluminum (0 - 2000 mg/l).⁽²³⁾

The volume of sludge formed from this water is generally high. The high iron content will naturally contribute to the sludge volume, but in this case the presence of aluminum in the form of hydrous oxide adds to the sludge volume. The fact that aluminum III reaches residual concentrations at approximately pH 4-4.5, and then resolubilizes above pH 8.0 has been well documented.⁽²³⁾ The total effect of aluminum on the sludge volume will, therefore, be dependent upon the treatment pH.

Girard and Kaplan⁽²⁶⁾ found that silica present with alumina aided sludge sedimentation due to the formation of large flocs which in turn aided the coagulation of the iron hydroxide.

Lovell⁽³⁾ reported that calcium sulfate precipitate can change sludge properties. The exact nature of this change is not reported, but calcium sulfate is known to contribute to scaling on sludge withdrawal ports and other equipment.

To summarize, coal mine drainage can generally be classified into three types depending upon chemical characteristics. In addition, the resulting sludges can also vary as the raw water and treatment methods change. Generally iron, aluminum, sulfates, bicarbonates, silicon, calcium, and acidity are the major chemical constituents in coal mine drainage that affect sludge properties.

THE EFFECT OF TREATMENT PROCESSES ON SLUDGE FORMATION AND CHARACTERISTICS

The chemical constituents of raw mine water greatly influence sludge formation and characteristics; however, unit operations and type of neutralizing agent used during treatment exert the greatest influence on sludge properties.

Lime Neutralization

Conventional

Calcium hydrate (Ca(OH)_2) is the most widely used neutralizing agent in the treatment of coal mine drainage. In some cases, such as Jones and Laughlin's Shannopin Airshaft Number 1 Treatment Plant, quicklime (CaO) is used instead of calcium hydrate. Steinman⁽²⁷⁾ reported an economic advantage from the slaking of the quicklime; however, treatment operators have generally depended upon the hydrated form due to the high cost of the slaking equipment required with quicklime as well as handling problems.

In a report on hydrated versus quicklime, Bisceglia⁽²⁸⁾ stated that most quicklime manufacturers leave a small amount (2-3 percent) of unburned limestone or "core" in the quicklime. This "core" is generally removed from hydrated lime. Thus considerably less sludge is produced from hydrated lime neutralization as compared to quicklime treatment.

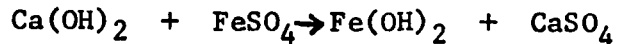
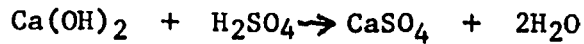
Sanmarful⁽⁵⁾ studied sludge characteristics resulting from a synthetic mine water using various alkaline agents. Examining Ca(OH)_2 as the neutralizing agent, the sludges produced were light, gelatinous in nature and were very voluminous as compared to sludge formed by the use of CaCO_3 , Na_2CO_3 and NaOH neutralizing agents.

Dolomitic lime has been extensively studied in the treatment of waste pickle liquor. Reactivity of the magnesia component of dolomitic lime is required in the presence of pickle liquor. Therefore, more lime is required for complete neutralization. As more lime is added, the unreacted magnesium oxide and calcium sulfate add to the normal sludge production. Depending upon the reactivity of the dolomitic lime the sludge volume and solids content can be appreciably higher as compared to high calcium lime neutralization.⁽¹³⁾

Non-Aeration

The basic chemical reactions related to lime treatment of coal mine

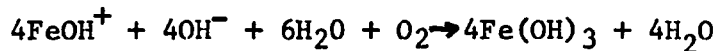
drainage are as follows:



One of the more important aspects of the above equations is that without additional oxygen, ferrous sulfate reacts with lime to form ferrous hydroxide. Non-aerated ferrous hydroxide sludges have considerably different sludge properties compared to sludges that contain iron in the ferric state. Settling curves in Figure 3 illustrate that non-aerated sludge settles slightly faster than aerated sludge, but produces a larger settled volume. However, in order to remove ferrous iron from mine drainage the pH must be increased to a much higher level (approximately pH 9) than is required for ferric iron removal (pH 5).

Mechanical Aeration

Mechanical aeration is the most common method employed to oxidize ferrous hydroxide to ferric hydroxide in the treatment of coal mine drainage. The following equation represents the approximate chemical reaction that takes place:



Research was conducted at West Virginia University⁽¹⁾ on the aeration of lime neutralized coal mine drainage and the following conclusions were drawn:

1. When iron is in the ferric state, the volume of settled sludge is less than that for ferrous iron.
2. A savings in lime costs can be realized due to the lower treatment pH required if the iron is in the ferric state.

Different methods of aeration and aeration devices were also studied and the smallest possible air bubbles were found to be the most desirable for aeration due to increased bubble surface area. Bubble size was dependent upon the type of dispersion device used.

Lagoon Aeration

The use of a lagoon or a large pond to complete the iron oxidation is applicable in some cases. Factors affecting lagoon oxidation

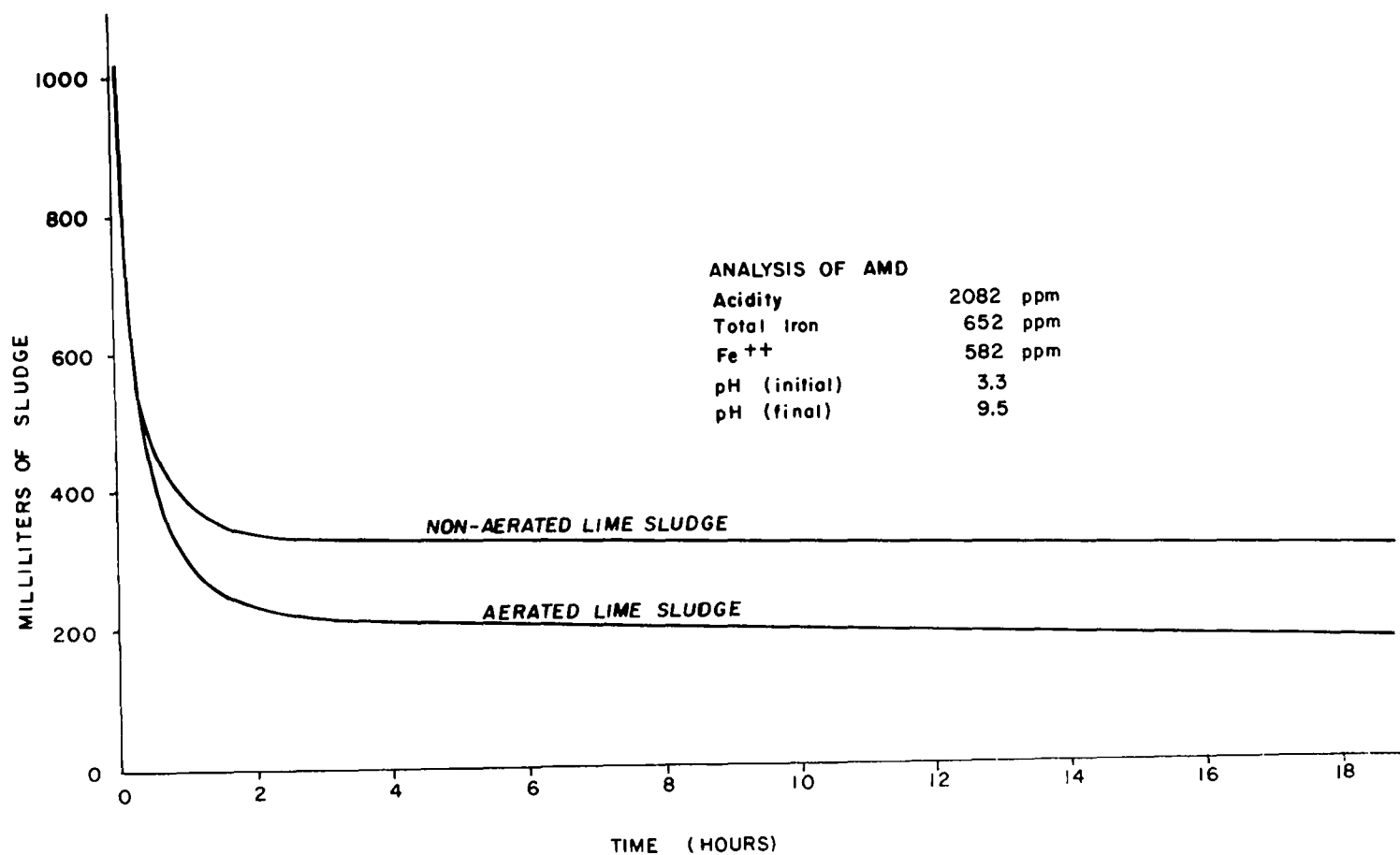


Figure 3 - Influence of Aeration on Sludge Volume and Settling Characteristics. After Pudlo (29)

have been reported by Barthauer⁽²⁴⁾ to be temperature, rate of oxygen diffusion and pH of the discharge.

The influence of temperature on oxidation rate of ferrous iron is illustrated in Figure 4. As the water temperature varies from 73°F to 40°F, the time required to oxidize the ferrous iron ranges from 4.5 days to more than 14 days.

Water temperature of an underground mine discharge is reasonably constant (approximately 54°F) and would generally not approach the lower temperatures indicated in Figure 4. Under certain conditions, however, evaporative cooling takes place and affects the oxidation rate. A mine water holding pond is a case where cold, windy winter weather can drastically reduce the iron oxidation rate. Another example would be a treatment plant that is located some distance from the discharge point and water which is exposed to the prevailing atmospheric conditions while traveling to the treatment plant.

Another factor found to be important in this study of aeration by lagooning was the rate of oxygen diffusion into the pond. The relationship between oxygen diffusion and pond depth is presented in Figure 5. Even under ideal conditions, the diffusion rate of oxygen into the pond is very slow.

The pH of the discharge was the last factor mentioned by Barthauer that affects oxidation rate. Stumm and Lee⁽³¹⁾ have found that the oxidation rate of ferrous iron is strongly influenced by pH as illustrated in Figure 6.

The use of the lagoon as the sole means of aeration is practical only with certain types of coal mine waters, generally alkaline waters having a low ferrous iron content. Sludges produced under these conditions are generally slow settling and settle to a small final volume.

Barthauer neglected to mention the importance of another factor, natural bacteriological oxidation of iron. This phenomenon is important and cannot be dismissed when discussing lagoon oxidation.

pH

Pudlo⁽²⁹⁾ studied the effects of treatment pH on sludge volume and found that with certain mine waters a higher treatment pH resulted in a larger sludge volume. A mine water with an analysis of 1041 mg/l acidity, 326 mg/l total iron, 291 mg/l ferrous iron was treated

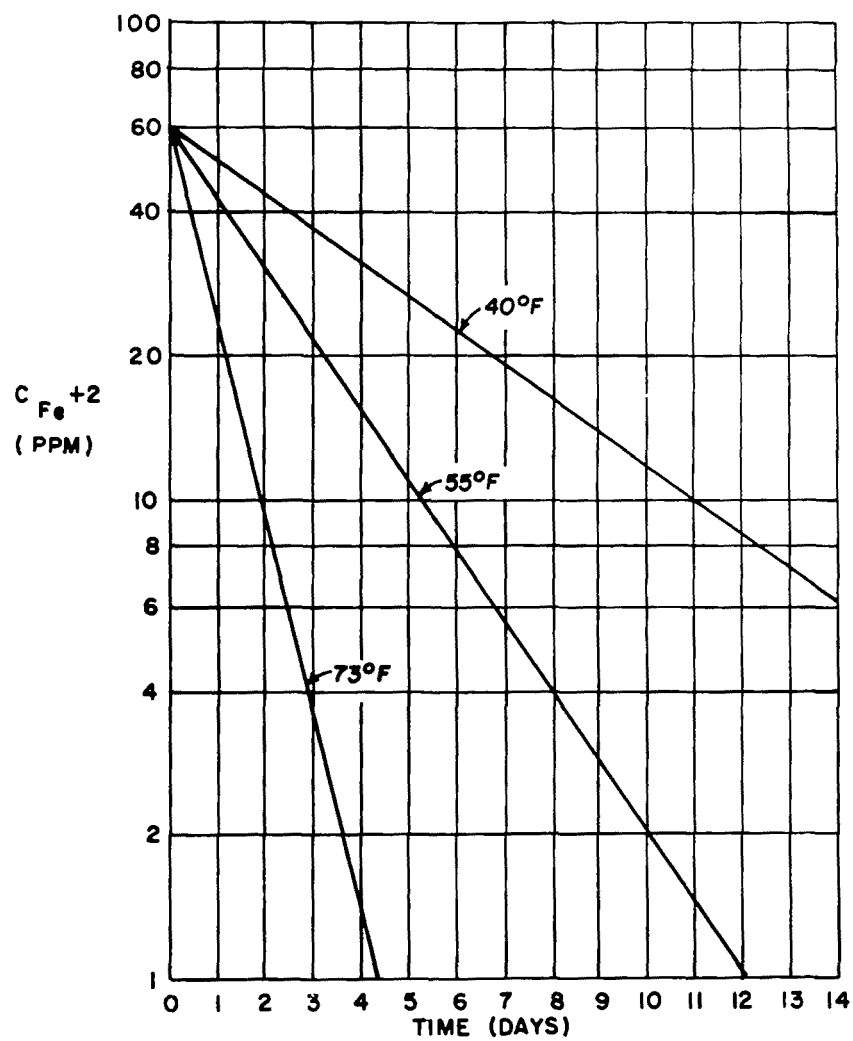


Figure 4 - Influence of Temperature on Iron Oxidation Rate. After Barthauer (24)

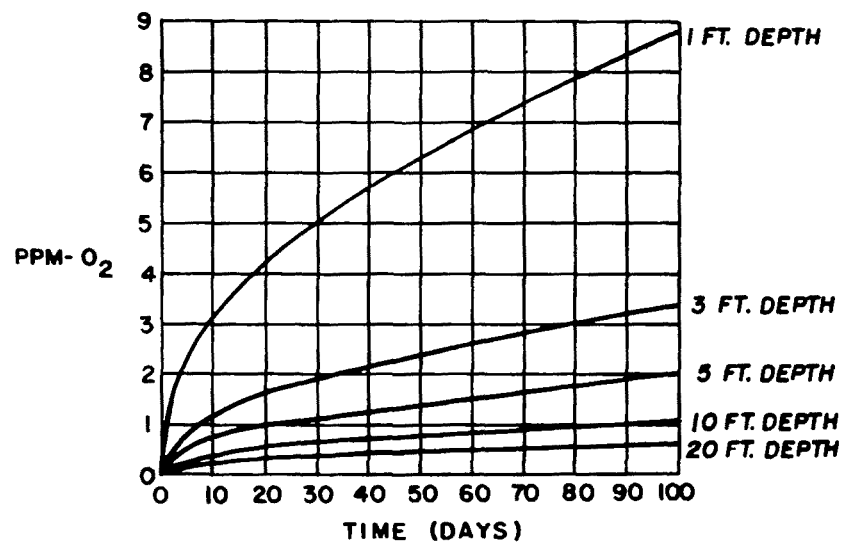


Figure 5 - Oxygen Diffusion into a Still Pond at 60°F.
After Phelps (30)

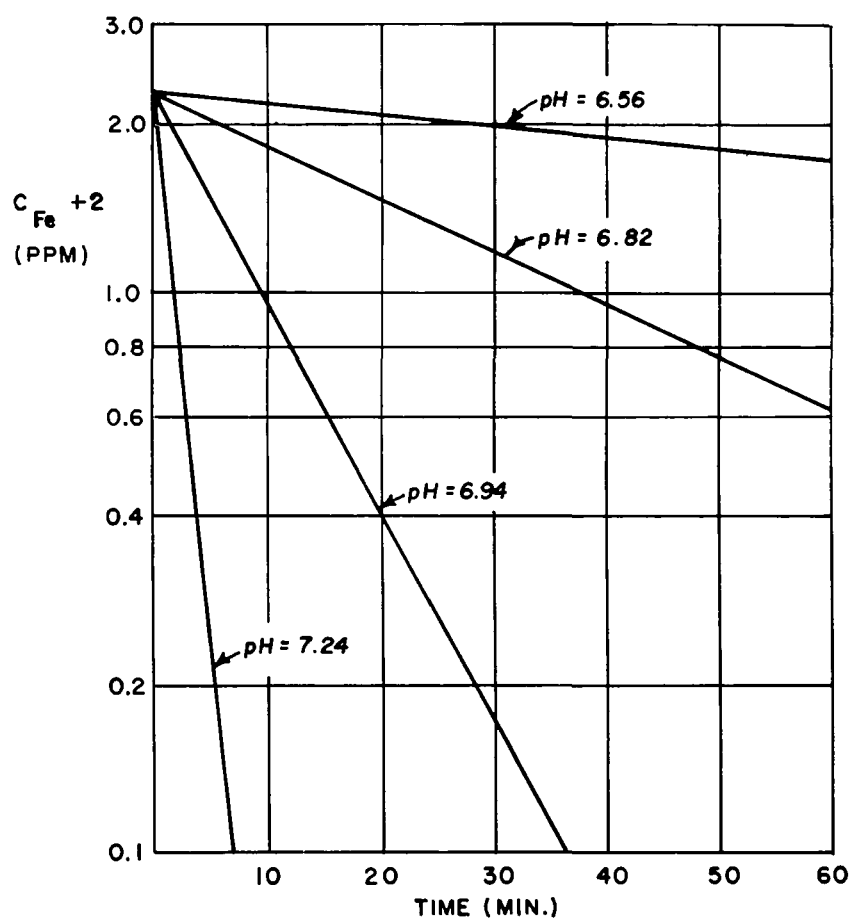


Figure 6 - Influence of pH on Iron Oxidation Rate.
After Stumm and Lee⁽³¹⁾

at pH 9.5, 10.0 and 10.8. Increasing the treatment pH from 9.5 to 10.0 resulted in a 20.5 percent greater sludge volume. When the pH was increased from 9.5 to 10.8 a 50 percent increase in sludge volume was observed. Treating the water below pH 9.5 did not adequately precipitate the ferrous iron. This effect of pH on sludge volume is shown in Figure 7.

This study was extended using two more mine waters. The second mine water contained 2082 mg/l acidity, 652 mg/l total iron, 585 mg/l ferrous iron. When treated to a pH of 10.0 and 10.5 and compared to the initial treatment pH of 9.5, the sludge volume increased 25 and 30 percent respectively. The third water was the strongest of the three waters examined (6500 mg/l acidity, 2386 mg/l total iron, 1500 mg/l ferrous iron.) Treating this water at pH 9.5, 10.0 and 10.75 resulted in no significant differences in sludge volume.

Pudlc(29) explained that at higher treatment pH values the abundant hydroxyl ions may attach themselves to the flocs causing the flocs to be negatively charged and repellent to each other. This repellent action may be the cause of the increased sludge volumes at higher pH values.

Sludge Recirculation

Sludge recirculation is a concept that has been applied in the past to waste pickle liquor treated with lime. Recently sludge recirculation has referred to the treatment of coal mine drainage where a portion of the precipitated sludge is returned to the beginning of the treatment process for the purpose of reducing sludge volume and increasing sedimentation rates.

The mechanism that controls the sludge characteristics during recirculation is not exactly understood. However, most authors agree that the returned sludge acts as a nucleation site for further growth and sedimentation.

Lovell(32) reported that sludge recirculation studies were initially conducted at Pennsylvania State University on a lime treated mine water containing 2060 mg/l iron (mostly in the ferrous state) and 6800 mg/l acidity. After approximately 85 recirculation cycles, the final sludge volume was reduced from the 20 percent originally obtained to 7.2 percent. From this and other pilot plant studies the following recirculation process parameters were observed: iron oxidation state, water composition, reaction time, reaction steps, neutralization levels, sludge recycle rates, and sludge blow down frequencies and levels. Lovell later found that suspended solids level in the reactor vessel is important and should be kept near 3000 mg/l.

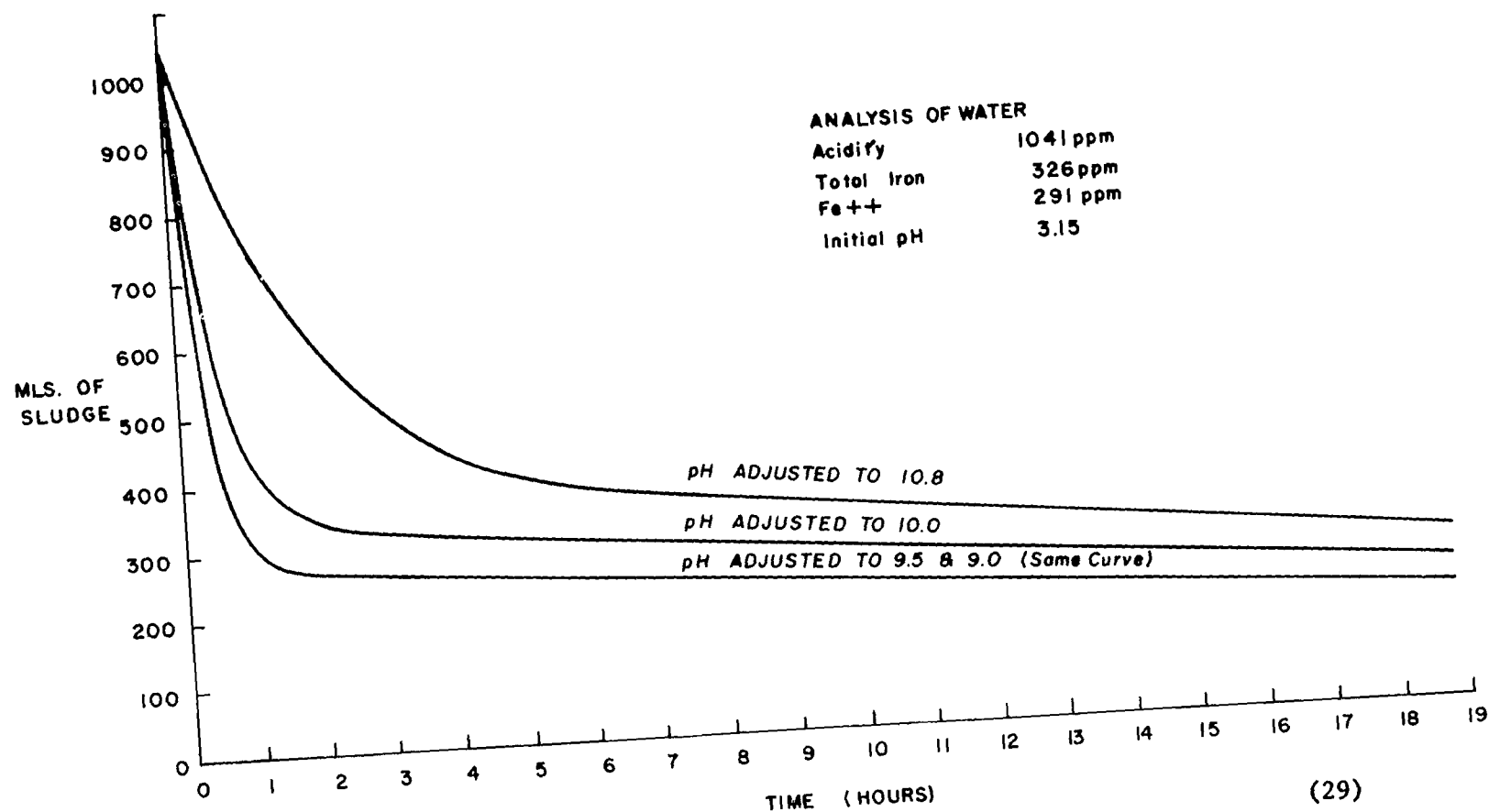


Figure 7 - Influence of Treatment pH on Sludge Volume. After Pudlo (29)

Initial sludge recirculation attempts reported by Lombardo⁽²⁵⁾ were very successful in increasing the solids content from a clarifier underflow. Under normal conditions, the solids content from the clarifier underflow was about 0.6 percent. After recirculation was introduced into the system the solids content increased to 4 - 4.5 percent. Prior to sludge recirculation, sludge was being discarded from the clarifier at the rate of 50 gallons per minute, but after recirculation the sludge discharge rate was reduced to seven gallons per minute. Lombardo also mentioned that another benefit from sludge recirculation was the utilization of some of the alkalinity in the sludge, resulting in a reduction of lime demands.

Sludge recirculation is being utilized in mine drainage treatment on a limited scale probably due to a lack of understanding of the process or because adequate land is available and a dense sludge is not needed. An illustration of how sludge recirculation is currently being used in mine drainage treatment is presented in Figure 8.

The research conducted on sludge recirculation has led to the discovery of unique treatment methods that show promise in total treatment of coal mine drainage. A discussion of these treatment methods follows.

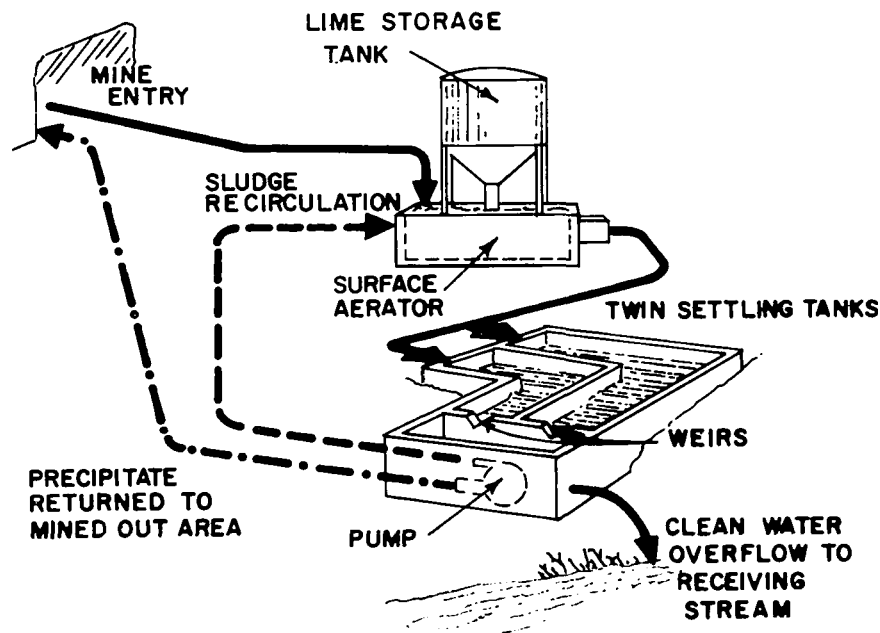


Figure 8 - Mine Drainage Treatment Plant Utilizing Sludge Recirculation. After Goddard⁽³³⁾

High Density Sludge Process

The technology related to sludge recirculation and acid mine drainage has been recently enhanced by research reported by Bethlehem Steel Corporation and Bethlehem Mines Corporation.(34)

The "High Density Sludge Process" combines conventional acid mine drainage treatment with sludge recirculation. However, the treatment process is unique in that recirculated sludge is mixed with the lime slurry prior to the neutralization process.

A conventional process and the high density sludge process are compared in Figure 9.

The following advantages are reported to result from the high density sludge process: a dense sludge containing 15 to 40 percent solids; reduced sludge storage requirements; easier sludge dewatering by filtering or centrifuging resulting from high sludge solids concentrations; applicability to high ferrous iron waters which are the most difficult to treat; and inexpensive processing with lime and air oxidation due to the simplicity of the process.(34)

Experimentation on the high density sludge process has shown that the ferrous to ferric iron ratio has a limiting affect on the maximum concentration of settled solids that can be produced. The current findings on the relationship of ferrous iron content to the concentration of settled solids is listed in Table 3.

Table 3

Influence of Ferrous Iron Content on Sludge Settled Solids

Water Source	Ferrous iron, Avg. % of total iron	Maximum Concentration of settled solids, %
Mines 32-33 AMD (source discharge)	90	40
Synthetic AMD	95	50
Synthetic steel plant waste	95	45
Steel plant waste	95	45

Table 3 (Continued)

Influence of Ferrous Iron Content on Sludge Settled Solids

Water Source	Ferrous iron, Avg. % of total iron	Maximum Concentration of settled solids, %
Mines 32-33 AMD (shipped samples)	70 (range 45-90)	22
Mine 32, supply- shaft AMD	30	15
Mine 31 AMD (shipped samples)	2	18

After Haines and Kostenbader⁽³⁴⁾

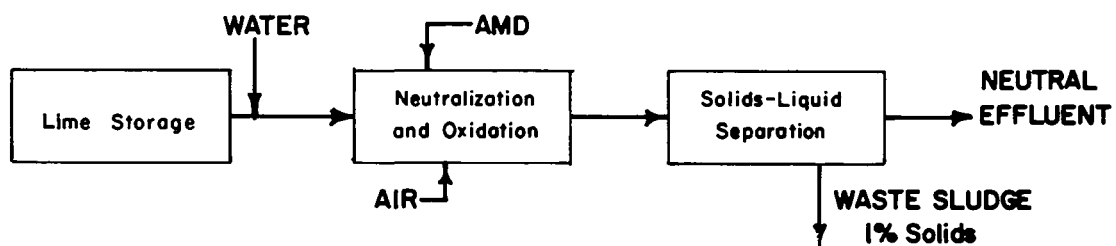
The ratio of solids recirculated to solids precipitated also had a limiting affect on both sludge density and thickener size requirements.

The chemistry involved in production of high density sludge by this process is largely unknown. However, the sequence of unit operations has been found to be the key to the effectiveness of the operation. Mixing the lime slurry, recycle slurry and acid mine drainage in the same tank was found to decrease settled solids concentration by 50 percent and increase thickener area requirements by 100 percent. The only way the higher sludge solids content could be realized was by mixing the lime slurry and recycle slurry prior to the neutralization step.

Densator[®] Process

Sludge recirculation is also a key step in a proprietary apparatus called the Infilco Densator[®] (35). This treatment device contains a primary reaction zone, a secondary reaction zone, a sludge zone, and a sludge storage zone all within a single tank. The major advantage of this process, other than the single tank operation, is that the sludge created is very dense and can be easily dewatered.

CONVENTIONAL PROCESS



HIGH-DENSITY SLUDGE PROCESS

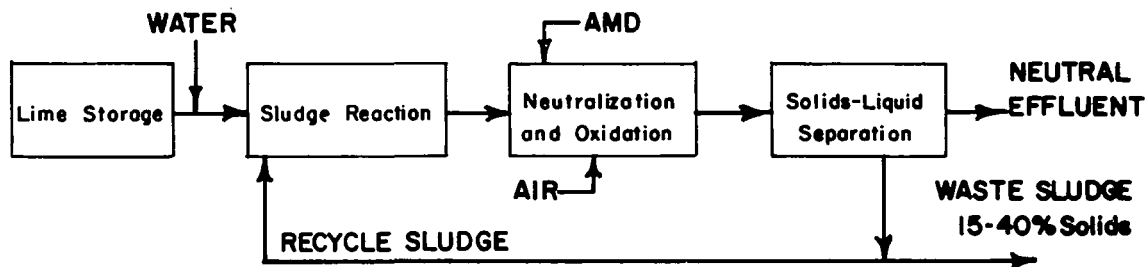


Figure 9 - High Density Sludge Process vs. Conventional Process.
After Haines and Kostenbader⁽³⁴⁾

Laboratory studies were conducted applying this process to waste pickle liquor with lime being used as the neutralizing agent. Evans reported that sludge from the Densator[®] contained 90 to 110 grams of dry solids per liter which was approximately 10 times the concentration obtained in high rate solids contact units.⁽³⁶⁾

The report further explained that the reaction involved in production of dense ferrous hydroxide is one of cation exchange. In the primary reaction zone, hydrogen and ferrous ions from the pickle liquor displace calcium ions from recirculated sludge. In the secondary reaction zone calcium ions provided from lime displace hydrogen ions from the sludge to form water. The ferrous hydroxide acts as a cation exchange material and precipitation of additional ferrous hydroxide from the pickle liquor takes place as a result of ion exchange, rather than by direct neutralization.

Filter leaf tests on Densator[®] sludge indicated that a vacuum filter rate of 25 pounds of dry solids per hour per square foot of filter area could be obtained with a cake containing approximately 37 percent solids.

A Densator[®] unit used in the treatment of coal mine drainage is being studied by Pennsylvania State University at Hollywood, Pennsylvania, but data is not available at this time (See Figure 10).

The Infilco Densator[®] and Bethlehem's High Density Sludge Process are similar due to the sludge recirculation step differing only at the point where the recirculated sludge enters the treatment process. Recirculated sludge from the Densator[®] Plant is mixed with the raw mine water prior to the addition of the lime feed. Recirculated sludge from Bethlehem's High Density Sludge Process is mixed with the lime slurry prior to the addition of the raw mine water.

The Infilco Densator[®] and the Bethlehem's High Density Sludge Process contradict each other particularly in the sequence of unit operations. Further research will have to be conducted on both processes to find their optimum usage in the treatment of coal mine drainage.

Elpo Treatment Process

The "Elpo I Treatment Process" is a proprietary method of treating coal mine drainage involving the addition of a cationic polyelectrolyte to aerated coal mine drainage followed by the addition of a neutralizing agent and a final step of adding an anionic polyelectrolyte.⁽³⁷⁾

Investigators conducting pilot plant operations on the "Elpo" process demonstrated that there was a marked increase in the rate of treated

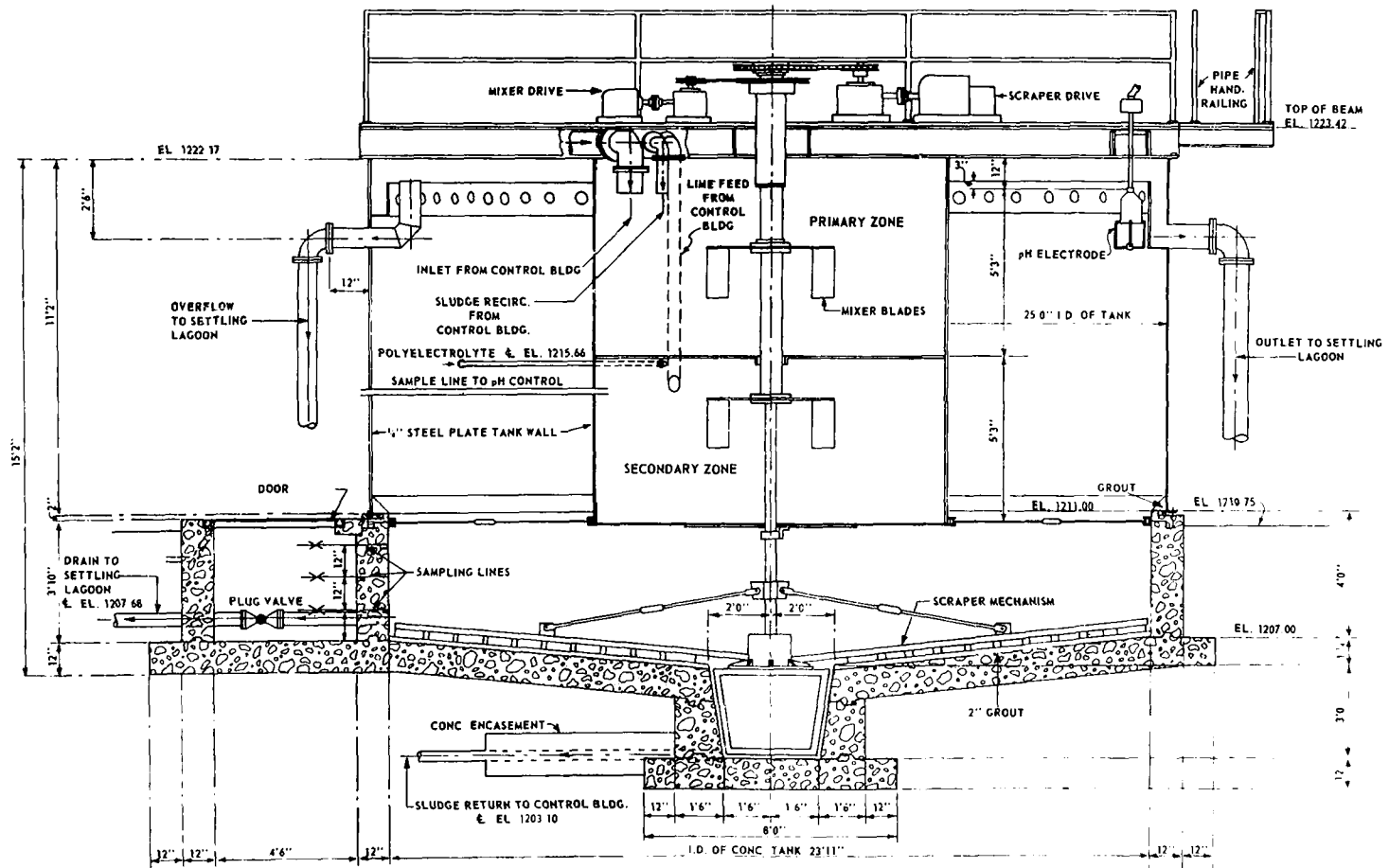


Figure 10 - Densator® Treatment Plant. Compliments of The Pennsylvania State University.

water clarification and "the resulting sludge was more easily handled than sludges generated by neutralization alone."⁽³⁸⁾ Data is currently not available from the early pilot plant investigations.

The "Elpo II Treatment Process," a modified version of the "Elpo I" process that utilizes sludge recirculation, is currently being studied at L. R. Kimball, Consulting Engineers, Ebensburg, Pennsylvania. Attempts are being made to define the reaction mechanisms and process parameters involved in this treatment process.⁽³⁸⁾

Magnetic Sludge

Bituminous Coal Research⁽³⁹⁾ studied synthetic and natural coal mine water in an attempt to form magnetic sludge. A magnetic sludge could then be treated using commercially available wet or dry magnetic separators to remove the solids from the mine drainage treatment system. The first tests were run with a synthetic mine water treated with sodium hydroxide or lime. In both cases a black magnetic precipitate was achieved at pH 10.0. Gentle aeration noticeably increased the rate of conversion of the alkaline suspension to the magnetic product.

Later attempts to produce a magnetic sludge from natural coal mine waters were unsuccessful. However, in further studies it was found that under the proper conditions of pH, reaction temperature, and low aluminum and magnesium concentrations a magnetic sludge could be produced that exhibited a five-fold reduction in settled volume as compared to conventional precipitates formed from lime neutralization.

Sludge thickening was attempted prior to the conversion to a magnetic form by gravity settling with the addition of two coagulant aids. The sludge thickening step was found to be advantageous in the magnetic conversion process.

Additional sludge thickening was investigated with a centrifuge. The solids content of gravity settled ferrous hydroxide sludges increased from about two to nine percent by weight following centrifuging. This increase in sludge concentration aided the subsequent magnetic formation step. Centrifugation of the sludge prior to the magnetic formation step also exhibited residual effects on the final settled sludge volume and solids content. An example of this effect was noted when a centrifuged sludge sample settled to 0.17 percent of original treated volume and had a solids content of 17.7 percent by weight. Similarly, a magnetic sludge sample prepared in the same manner was allowed to gravity settle without the centrifugation step. This sludge settled to a higher volume (0.54 percent of the original volume) and had a solids content of 12.1 percent by weight.

The practical application of magnetic sludge treatment has not been established, but further research is being conducted and an evaluation as to its practicality will be made in the future.

Limestone Neutralization

Limestone (CaCO_3) shows promise in the treatment of certain types of mine drainages and has definite advantages, particularly in the area of sludge control.

Conventional (Coarse Size Stone)

The feasibility of limestone treatment of coal mine drainage was established by Tracy as early as 1913.⁽⁴⁰⁾ As time passed limestone was studied in hopes of replacing or being used in conjunction with conventional lime neutralization of waste pickle liquor and other acid wastes.^(41,42,43,44) Later Braley⁽⁴⁵⁾ studied limestone neutralization by passing the mine water through a flume containing five tons of one to two inch limestone. This research presented a problem that has plagued investigators from the beginning of limestone neutralization research, the loss of limestone reactivity due to the coating of limestone by the precipitation products iron and calcium sulfate.

Zurbuch⁽⁴⁶⁾ solved the problem of limestone coating by placing the limestone in a drum and placing the drum in a stream bed. The flow of the stream caused the drum to turn like a water wheel and the surface of the limestone was kept reactive due to the abrasive action between the limestone particles.

Deul and Mihok⁽⁴⁷⁾ conducted research into limestone neutralization of coal mine drainage using a modified cement mixer as the reactor. Exploratory tests were run on a batch and continuous basis using high calcium, double screened (1-by 1/2-inch and 1/2-by 1/4-inch) limestone. The raw mine water was fed into the reactor that contained the coarse limestone and the treated water was monitored for pH and ferrous iron concentrations. The researchers found that mine waters containing low to moderate concentrations of iron (less than 100 mg/l) could be treated with limestone to produce a water that had a pH of 7 to 8 and an iron concentration of less than 7 mg/l. Mine waters containing high ferrous iron concentrations required longer reaction times with limestone and ultimately had to be supplemented with lime to reach acceptable water quality in a short reaction time.

Sludge settling rates and volumes of settled solids were also studied for limestone, lime, and a combination limestone-lime treatments. In every case where limestone was used for neutralization, either in combination with lime or alone, the sludge settling rates and volume of compacted solids were more favorable than where lime alone was used. Figure 11 illustrates the favorable settling characteristics of a limestone treated mine water.

Aeration

The use of mechanical aeration in limestone treatment has been studied^(7,39,48) in an attempt to maximize the treatment efficiency, but little work has been done on the effects of aeration on the resulting sludge properties. As more research is conducted into limestone neutralization further light may be shed on the effects of aeration on limestone sludge properties.

Sludge Recirculation

Bituminous Coal Research⁽³⁹⁾ briefly attempted sludge recirculation with two natural mine waters and found that recirculated sludge aided reducing the iron content in the raw water to a satisfactory level. Optimum treatment results were obtained when sludge was introduced with untreated mine water in the limestone reaction tank.

Other authors⁽⁷⁾ reported that sludge recirculation may aid the treatment process by taking advantage of the alkalinity within the sludge and further research is needed to confirm this possible aid to treatment efficiency.

Biochemical Oxidation

The inability of limestone to effectively treat coal mine drainages containing large quantities of ferrous iron has led to the discovery of a promising treatment process. Glover⁽⁴⁹⁾ reported on a biochemical oxidation process that first converts the ferrous iron to the ferric state. After the iron is oxidized the mine water is pumped upward through a limestone reactor to neutralize the acid. The treated water then flows into a clarifier where the ferric hydroxide and calcium sulfate sludge precipitates. Upon completion of clarification, the treated water is removed and the settled sludge is pumped to a vacuum filtration unit for dewatering. Glover found that the sludge created from this process exhibited poor initial settling characteristics, but finally settled to a volume of about one percent of the original volume treated and had a solids content of 9 - 12 percent by weight. Sludge from lime treatment of the same mine drainage had a

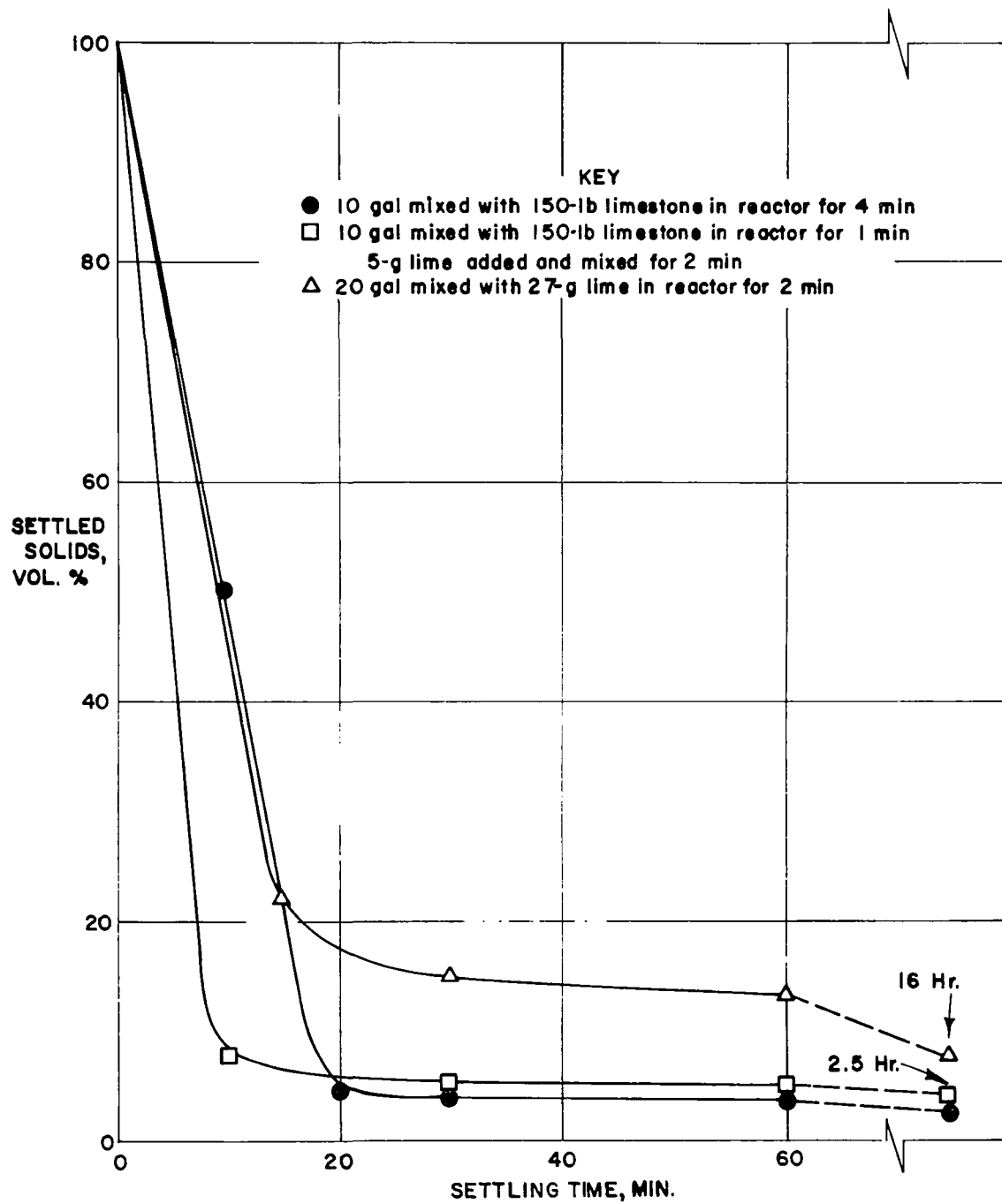


Figure 11 - Settling Rate of Sludges From Limestone, Limestone and Lime, and Lime Treated Mine Water. After Deul and Mihok(47)

relative volume of about 10 percent of the original treated mine water and had a solids content of about 1.2 percent. A flow diagram of the biological oxidation and limestone neutralization process is presented in Figure 12.

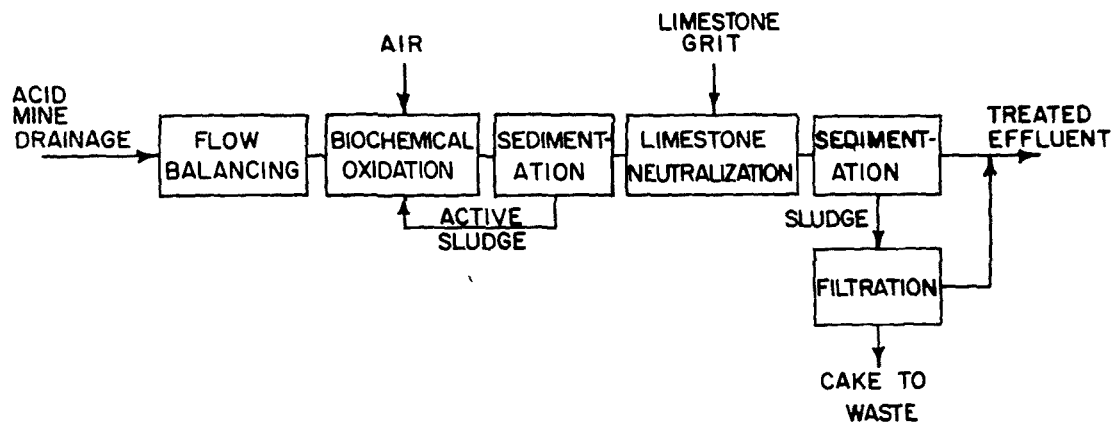


Figure 12 - Flow Diagram of Complete Biochemical Oxidation and Limestone Neutralization Process. After Glover⁽⁴⁹⁾

Rotating Drum

After early studies by Tracy⁽⁴⁰⁾, Braley⁽⁴⁵⁾, Zurbuch⁽⁴⁶⁾ and later studies by Birch⁽⁵⁰⁾ and Calhoun⁽⁵¹⁾, the Bureau of Mines continued research into rotating drum limestone treatment. Preliminary work and pilot plant studies found that vigorous agitation of the limestone in a drum present with the mine water provided substantial abrasion to eliminate limestone coating and removed CO₂ from solution.⁽⁵²⁾

Settling and compaction of precipitated solids was one of the main investigations undertaken during this study. Mine water containing a pH of 2.8, 36 mg/l ferrous iron, 360 mg/l total iron and 1700 mg/l acidity was treated to the same end conditions (pH 6.9) using limestone and lime as separate neutralizing agents. The treated slurry was allowed to settle in separate cylinders each having a capacity of 4.9 liters. After 24 hours the limestone treated sludge settled to approximately 2.5 percent of the original volume of treated water while the lime sludge settled to only 12 percent. The settling test was continued for 43 days with the limestone sludge settling to less than two percent compared to the lime sludge that settled to approximately 6.5 percent.⁽⁵²⁾ Results from this settling test are shown in Figure 13.

In the same study, an attempt was also made to determine the compaction of both lime and limestone sludges. Equal volumes of lime and limestone sludges were prepared in separate glass cylinders and the supernatant liquid was decanted. The authors reported that absolute sludge compaction properties were not established; however, results from the data indicated that there was no compaction for the lime neutralized sludge and only slight compaction for the limestone neutralized sludge.⁽⁵²⁾

A full scale rotary drum limestone treatment plant has been built by Rochester and Pittsburgh Coal Company⁽⁵³⁾ utilizing a drum three feet in diameter and 30 feet long with four one inch rods welded to the inside to provide lift for the limestone. The volume of sludge from this installation was 25 percent of the volume of precipitates produced from treatment with hydrated lime. Further sludge properties such as percent solids were not reported.

Ground Limestone

Results of studies by Jacobs⁽⁴⁴⁾, Hoak, et al.⁽⁴²⁾, and Ford⁽⁵⁴⁾ have shown that neutralization reaction rates are affected by the

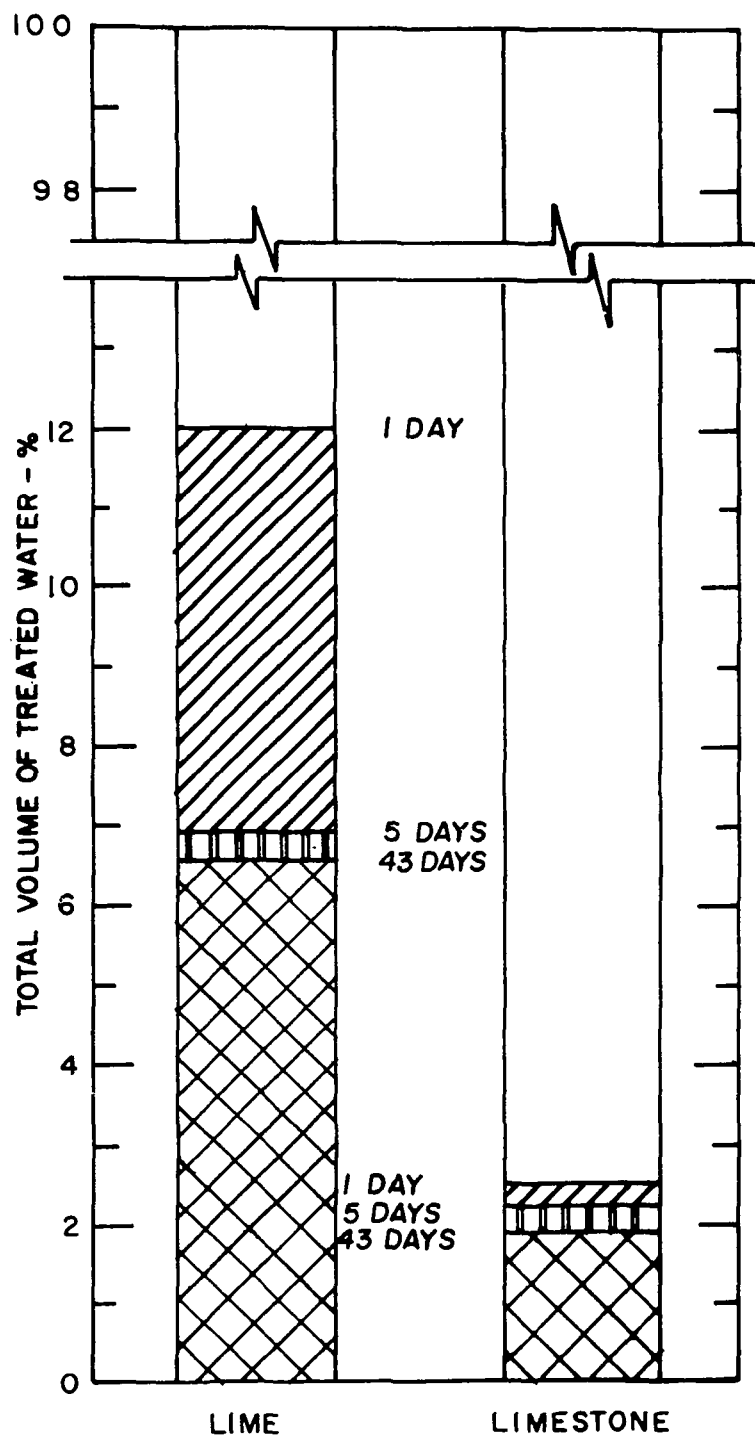


Figure 13 - Heights of Precipitated Sludge From Lime and Limestone Neutralized Water. After Mihok, et al. (52)

fineness of the limestone used in the treatment of acid wastes and coal mine drainage.

Wilmoth and Hill⁽⁷⁾ studied the treatment of high ferric iron (mean value total iron 93 mg/l, 80 percent in ferric state) mine water using lime, limestone "rock dust" and soda ash as neutralizing agents. Both batch and continuous flow tests were conducted and it was found that all three neutralizing agents were suitable for treating the mine water under investigation.

Comparative tests were also conducted on the settling rates of the sludges produced from the various neutralization agents. The lime sludge exhibiting the fastest initial settling rate followed by the soda ash and the limestone sludges. Limestone sludge settled to the smallest volume while lime and soda ash sludges settled to higher final volumes as illustrated in Figure 14.

Percent solids of the lime, limestone and soda ash sludges were compared using the same water and treated to approximately the same pH (pH 6.5 for lime and soda ash and pH 6.2 for limestone). After 24 hours settling the limestone sludge had a solids content of 9.5 percent as compared to 1.5 percent for lime and 0.7 percent for soda ash. Table 4 presents the results from this test.⁽⁷⁾

Table 4

Percent Solids of Lime, Limestone and Soda Ash Sludges^{*}

Neutralizing Agent	Supernatant pH	Percent Solids of Sludge
Lime	pH 6.5	1.5
Limestone	pH 6.2	9.5
Soda Ash	pH 6.5	0.7

^{*}

After 24 hours of undisturbed settling. After Wilmoth and Hill⁽⁷⁾

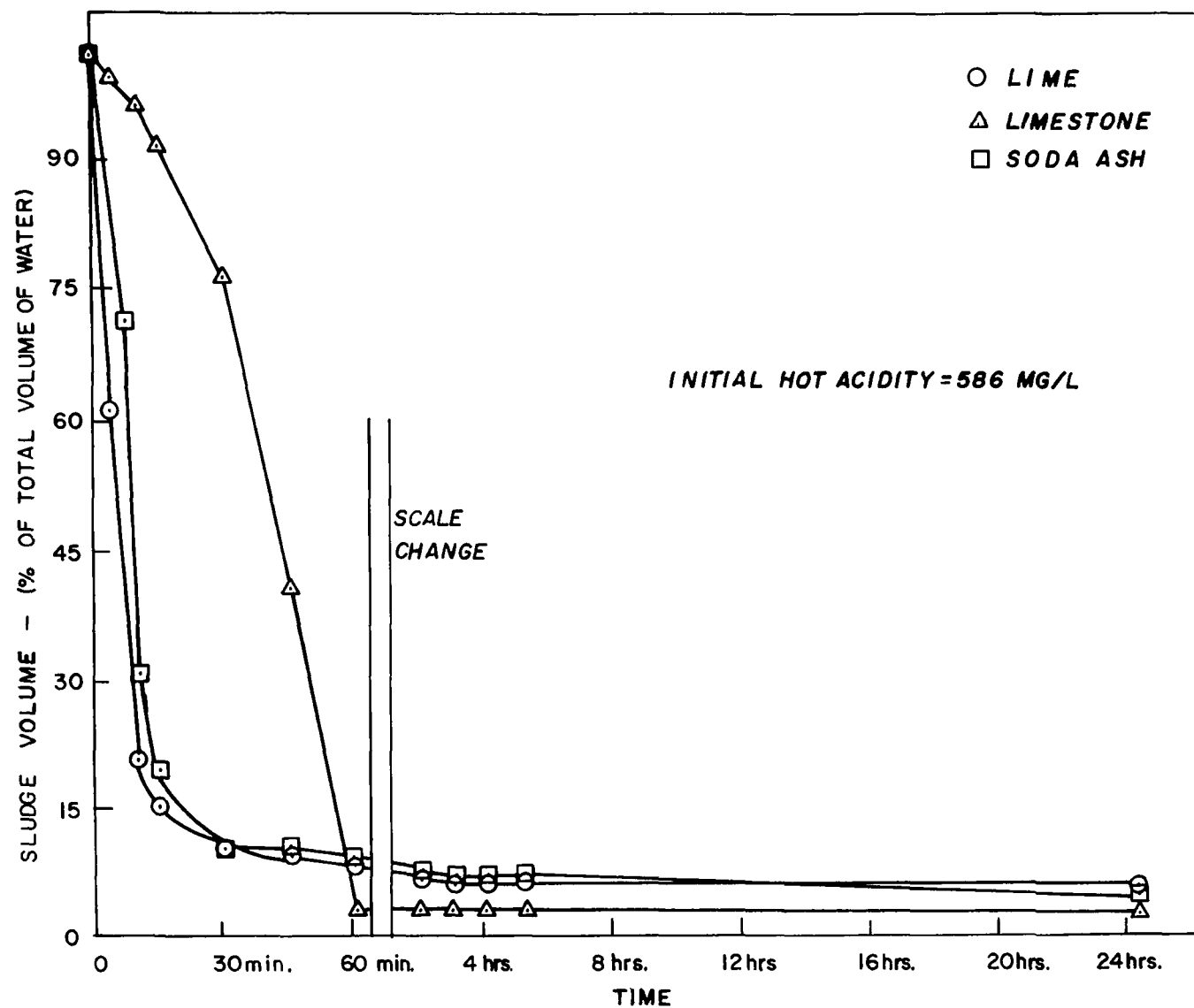


Figure 14 - Comparison of Settling Rate for Lime, Limestone and Soda Ash Sludges.
After Wilmoth and Hill(7)

Holland, et al.⁽⁴⁸⁾ also conducted neutralization studies using lime, limestone "rockdust" and limestone chips and observed the resulting sludges. Sludge settling data was not presented. However, the authors did indicate that considerably less sludge was produced from limestone neutralizing agents as compared to similar treatments with lime. The authors went on to point out that the apparent advantage of small sludge volumes may not be meaningful, because under similar drying conditions in sludge ponds both lime and limestone sludges could arrive at about the same final volume.

Limestone-Lime Neutralization

The inefficient limestone treatment of mine drainage containing large amounts of ferrous iron (above 100 mg/l) has, in part, induced studies of a treatment method that combines limestone and lime into a split treatment system.^(47,48) Limestone is used to raise the pH of the mine water to about 5.0 and then lime is added to raise the pH to the required treatment level. The efficiency of operation is high when the neutralizing agents are utilized in these pH ranges. It is hoped the resultant combination treatment will produce superior treatment results and reduced costs.

Results of preliminary studies on split treatment of coal mine drainage have shown that the proper combination of limestone and lime produces a good effluent and superior sludge properties.^(47,48)

Current research on split treatment is being conducted by Wilmoth at EPA's Norton Mine Drainage Treatment Plant. Preliminary results indicate that raw material cost reductions in excess of 20 percent can be achieved with split treatment as compared to lime or limestone when operating at pH 6.5.⁽⁵⁵⁾

A study is being conducted by Peabody Coal Company at Carrier Mills, Illinois under a grant from the Environmental Protection Agency (Grant No. 14010 DAX) that provides for the construction of a full scale limestone-lime demonstration plant. Results from this study may reveal the most economic combination which will utilize the desirable characteristics of lime (high pH) and limestone (low sludge volume).

SLUDGE SETTLING

Treatment of coal mine drainage, like the treatment of many acidic industrial wastes, is one of purification by chemical addition. The acid is neutralized and specific polluttional material is removed by the formation of insoluble products. Insoluble materials or precipitated products are usually separated from their water environment by sedimentation.

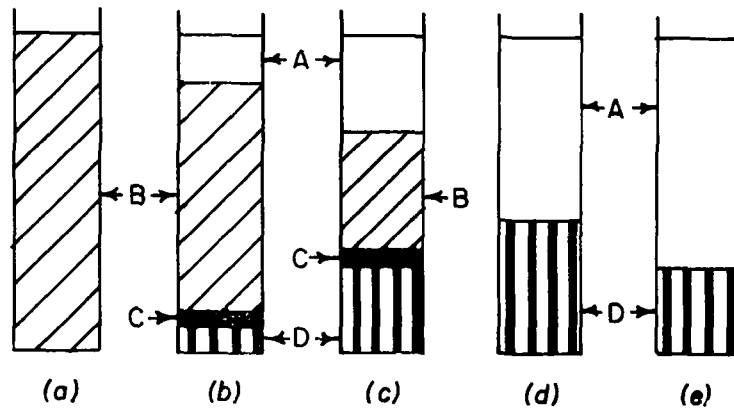
Sedimentation

Sedimentation of coal mine drainage sludge has been described by Lovell⁽³⁾ as having three phases: free settling and floc growth, a transition zone, and compression. Different phases that can occur in the general sedimentation process are illustrated in Figure 15. Early floc formation in the liquid ready for settling is shown in Figure 15(a). Solids first appear in Zone D which consists of layers of flocs as in Figure 15(b). Immediately above Zone D is Zone C, commonly called the transition layer, which has a solids composition that varies between Zone D and the original slurry. Zone B is the original slurry and Zone A is the clear liquid. As further settling occurs, all of the solids settle to Zone D as can be seen in Figure 15(e). When all the solids are settled into Zone D, compaction begins to occur. The transition from settling to compaction is called the critical point. In compaction, part of the liquid that was entrapped by the solids is forced out when the weight of the deposit breaks down the structure of the flocs. Equilibrium finally occurs when the weight of the solids equals the strength of the flocs. At this point, settling stabilizes since the height of the sludge is fixed.⁽⁵⁶⁾

A plot of sludge height versus settling time is shown in Figure 16. The curve is reasonably straight during early settling, but at some point in time the critical point (Point C) is reached and compaction occurs.

The amount of water soluble constituents affects, to a degree, the settling rate and the density of the sludge.⁽³⁾ This is due to the quantity and floc size of minerals that precipitate out of solution. Similarly, a sludge with a higher solids concentration exhibits a definite interface between the clear supernatant liquid and the settled solids, while in the case of a sludge with a lower solids content, the interface is cloudy and not well defined.⁽⁴⁷⁾

The type of neutralizing agent used also affects sludge settling. In one settling study using synthetic coal mine water with limestone, a well defined interface never formed between the clarified water and the precipitate during the settling period. Rather, a continuous



A-Clear liquid
 B-Original slurry
 C-Transition layer
 D-Settled solids

Figure 15 - Batch Sedimentation. After McCabe and Smith⁽⁵⁶⁾

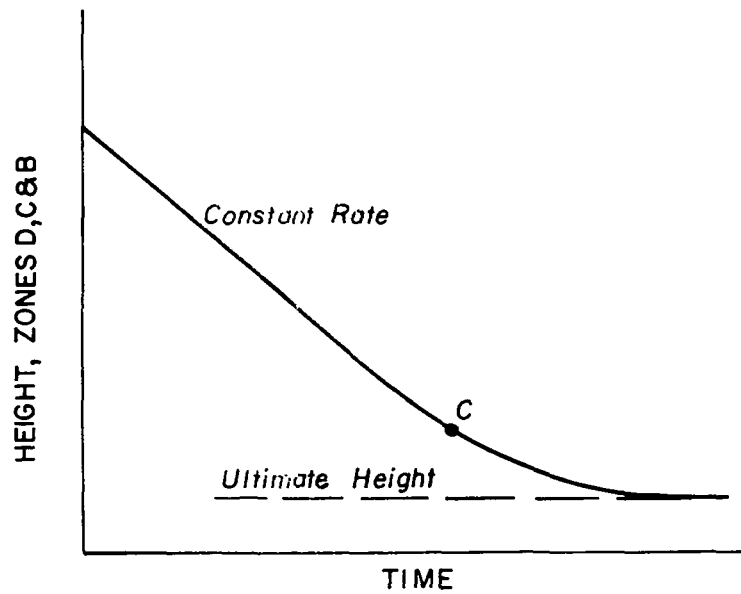


Figure 16 - Settling Curve. After McCabe and Smith⁽⁵⁶⁾

cloudy gradient was apparent until complete settling had occurred.⁽⁵⁾

Flocculation characteristics (agglomeration or sticking together of solid particles) of lime neutralized coal mine sludge are not well understood. One characteristic of flocculated particles is the loose structure of the flocs.⁽⁵⁶⁾ The bond between the particles is weak and they retain water within their structure while they settle. The second characteristic is that the flocculated particle settling mechanism is complicated and settling takes place in phases as illustrated in Figure 15.

The precipitate from limestone neutralization exhibits a completely different structure as compared to the lime precipitate. Limestone neutralized solids are not hydrophilic (water holding) like a lime sludge, but are actually crystalline gypsum with co-precipitated iron oxide.⁽⁴⁷⁾ Sedimentation characteristics of solids from limestone neutralized mine water are attributable to the attachment of $\text{Fe}(\text{OH})_3$ to the gypsum formed on the surfaces of CaCO_3 particles. This resulting structure cuts off the hydrophilic structural formation normally exhibited by $\text{Fe}(\text{OH})_3$.⁽⁵⁷⁾

The importance of temperature on solid-fluid separation has been recognized,⁽⁵⁸⁾ but has not been extensively studied with coal mine drainage sludge. Stoke's formula for settling velocity includes a factor representing the coefficient of viscosity of the fluid.⁽⁵⁹⁾ The coefficient of viscosity is temperature dependent, which under normal conditions would allow settling to proceed faster as the temperature increases. However, the temperature effect on settling of coal mine drainage solids is not well understood.

Sedimentation Basin Design

The removal of solids from coal mine drainage by sedimentation requires collection of the solids as they settle. Examples of sedimentation basins used in coal mine drainage treatment are settling tanks, lagoons and thickeners.

Settling tanks have been constructed for wastewater sedimentation in a great variety of designs depending partly upon the size, density and flocculation properties of the solids. Some of the common settling tank shapes are circular, square, or rectangular with either horizontal or vertical flow patterns.

The earthen lagoon is the most commonly used sedimentation device

in coal mine drainage treatment. The dimensions or design of lagoons are not as critical as for settling tanks and generally lagoon construction is dictated by the contour of the available land. Old strip pits have often served as lagoons. When strip pits or land is not available for lagoon construction, settling tanks or clarifier thickeners with sludge withdrawal systems are employed.

Optimum dimensions for settling tanks at times seem to be ignored especially when detention time is the major consideration rather than performance needs. Of all tank shapes, the long narrow rectangular model performs the best. Other tank designs perform inefficiently for two reasons: (a) effective settling zone is reduced because the inlet and outlet zones occupy too great a part of the total flow path and (b) short circuiting and instability of flow prevail in short tanks.⁽⁶⁰⁾

Recently, wastewater gravity separation techniques have advanced with the use of small diameter tubes as settling devices. The tubes placed horizontally or at a steep inclination provide for efficient clarification at substantially lower detention times as compared to conventional clarifiers. In the horizontal designed tube system, settled solids in the tubes can be removed by backwashing. In the inclined tube design, the solids do not accumulate but continuously slide down the tubes, countercurrent to the slurry flow.⁽⁶¹⁾

SLUDGE CONDITIONING

Conditioning of sludge traditionally has been used to enhance the sludge dewatering rate. Sludge conditioning processes can be broken down into two groups: (a) chemical conditioning and (b) physical conditioning. Most of the sludge conditioning operations for coal mine drainage sludge have evolved from the treatment of sewage and industrial sludges.

Thickening

Sludge thickening has been defined as the process of removing water from sludge after initial separation from the wastewater.⁽⁶²⁾ The objective of thickening or concentrating sludge is to reduce the volume of liquid sludge to be handled. The simplest, least expensive and probably the oldest method of thickening is by gravity. Gravity thickening and sedimentation are terms erroneously used interchangeably by some authors. Although the mechanism of settling is the same in both cases, the objectives are different. Sedimentation implies water clarification, whereas thickening requires a reduction in total sludge volume (increase in solids content).

Lagooning is an example of gravity thickening which is currently being extensively used in the treatment of coal mine drainage sludge. In most cases sludge is perpetually stored in large lagoons where some compaction occurs. However, settling tanks and mechanical thickeners are also being used in continuous operations where lagooning is not feasible.

The mechanical thickener is a large, fairly shallow tank with slow moving radial rakes driven from a central shaft. The treated slurry usually flows down an inclined trough or is pumped from a centrally located discharge pipe into the center of the thickener where the slurry moves radially allowing the solids to settle to the bottom of the tank and the clear water to overflow around the perimeter. The rake arms rotate slowly and move the settled sludge to the center of the tank, where the sludge flows through an opening to the inlet of a sludge pump.⁽⁵⁶⁾

The mechanical thickener allows for both settling and thickening. The settling zones of a continuous thickener are not the same as the settling zones established in batch settling. Basically two zones are established, a free settling zone and a compression zone. Movement of the rakes in the compression zone aids the compaction of the settling particles by breaking up the floc and

thus producing a more concentrated underflow than can be achieved by simple settling.(56)

A new thickener system called the Hydraulic Rake[®] Static Underflow System is finding increased usage in coal mine drainage treatment.(63) This thickening system consists of a grid network on the floor of a settling basin. The grid network is a series of parallel pipes containing orifices through which the sludge is pumped. Each pipe is brought independently outside of the thickener to a valve which is operated pneumatically or electrically and connected to a timing device. Each pipe is operated separately so that a limited area of the bottom surface is being pumped. When the sludge has been pumped from one area along the bottom, the first pipe is shut off and the next one begins operation. This sequence produces what is described as a "hydraulic rake". The manufacturer claims the Hydraulic Rake[®] can be applied to all settling tank designs and, since settling is unimpeded, more efficient thickening results.

Chemical

Chemical treatment or chemical coagulation has been defined as the addition of chemicals (coagulants) for the purpose of de-stabilization and aggregation of dispersed materials, followed by separation of the aggregated material from the suspending liquid.(12) The principal objective of the chemical coagulation process is to promote the aggregation of the non-settleable or slow settling solids into aggregates more amenable to sedimentation or filtration.

Recently the term "coagulant aid" has been applied to agents that are used by themselves, or in addition to conventional coagulant chemicals, to assist in the de-stabilization, flocculation, or sedimentation phases of the coagulation process.(12) Organic polyelectrolytes, also known as flocculants, fall into this classification of chemical agents.

Polyelectrolyte coagulant aids are synthetic compounds that have a very high molecular weight. These compounds can be characterized according to their ionized form as cationic, anionic or nonionic. Dorr-Oliver conducted bench-scale studies using polyelectrolytes on the aerator overflow from different coal mine waters. Polyelectrolytes improved the settling rate of the solids and at the same time reduced the iron concentration of the treated water but did not increase the solids concentration of the thickener underflow. Some flocculants were pH sensitive making precise pH control necessary for effective polyelectrolyte usage. Centrifugation and filtration tests were

conducted on polyelectrolyte conditioned sludge with limited success. Sludge pumping disturbed the conditioned sludge and the floc formation never returned to the more desirable well flocculated form. Conclusions drawn from this research were that even though improved settling could be achieved no real benefits could be gained from flocculation in further mechanical dewatering steps.⁽⁶⁴⁾

Bituminous Coal Research⁽³⁹⁾ studied sludge conditioning using anionic polyelectrolytes, anionic electrolytes and inert solids. The effect of the coagulant aids on the electrostatic charge of particles in suspension was investigated using both ferrous and ferric hydroxide sludges. Forces of mutual repulsion of suspended particles were minimized at or near the isoelectric point (point of minimum zeta potential) with the addition of proper coagulant aids. Reducing the repulsive forces allowed the suspended particles to coagulate and facilitated faster setting. The results from tests run using the various coagulant aids on $\text{Fe}(\text{OH})_2$ are presented in Table 5.

In the same study the effect of adding both an inert solid (flyash) and a polyelectrolyte (Calgon 240) to ferrous hydroxide particles was observed. The addition of 500 mg/l of flyash 30 seconds prior to the polyelectrolyte addition reduced the amount of polyelectrolyte required to achieve the isoelectric point by one mg/l. The flyash-Calgon 240 combination appreciably increased the settling rate and final settled sludge volume as illustrated in Figure 17.⁽³⁹⁾

Finally, studies were conducted on the effects of coagulant aids on the zeta potential of freshly prepared ferric hydroxide particles formed by limestone neutralization of synthetic coal mine water. Generally, the amount of coagulant required to reach the isoelectric point with ferric hydroxide sludges is much less than that required with ferrous hydroxide. The reason for better coagulant performance with ferric hydroxide sludges is not reported by the authors, probably due to the complicated nature of the problem. The coagulant aids used and their respective concentrations at the isoelectric point for both ferrous and ferric sludge are listed in Table 6.⁽³⁹⁾

A flocculant feed system has been installed in a full scale mine drainage treatment plant for the purpose of aiding settling.⁽³³⁾ The flocculant (.25 mg/l) was injected into the discharge from the aeration tank prior to entry into the settling tanks. Reports on this sludge conditioning attempt have yet to be published.

Freezing

Sludge freezing is an unusual method of sludge conditioning that

Table 5

Effect of Coagulant Aids on $\text{Fe}(\text{OH})_2$			Concentration at Isoelectric Point, ppm Added to $\text{Fe}(\text{OH})_2$
Additive	Source	Description	
Ludox HS-40	E. I. duPont de Nemours & Co.	Sodium stabilized colloidal silica	*
Ludox AS	E. I. duPont de Nemours & Co.	Ammonia stabilized colloidal silica	*
Solution No. 24	Philadelphia Quartz Co.	Activated silica sol	100
$\text{Na}_4\text{P}_2\text{O}_7$	Fisher Scientific Co.	Anionic electrolyte	100
Calgon C-55	Calgon Corporation	Anionic mixture	75
Calgon 37	Calgon Corporation	Clay-anionic polyelectrolyte mixture	35
Lomar D	Diamond Shamrock Chemical Co. Nopco Chemical Division	Naphthalene sulfonate polymer	19
Primaflow A-10	Rohm and Haas Co.	Anionic polyelectrolyte	15
Purifloc A-21	Dow Chemical Co.	Anionic polyelectrolyte	9
Calgon 240	Calgon Corporation	Anionic polyelectrolyte	5
Poly-Floc 1130	Betz Laboratories, Inc.	Anionic polyelectrolyte	1
M and D Clay	Kentucky-Tennessee Clay Co., Inc.	Ball clay, minus 400 mesh	*
"Red Dog"	Sewickley Township Westmoreland County, Pennsylvania	Similar to (completely burned) coal ash, minus 200 mesh	*
Fly Ash	Colfax Power Station Duquesne Light Co.	Similar to coal ash but not completely burned, minus 400 mesh	500

*

Isoelectric point never achieved - remained electropositive. After Bituminous Coal Research⁽³⁹⁾

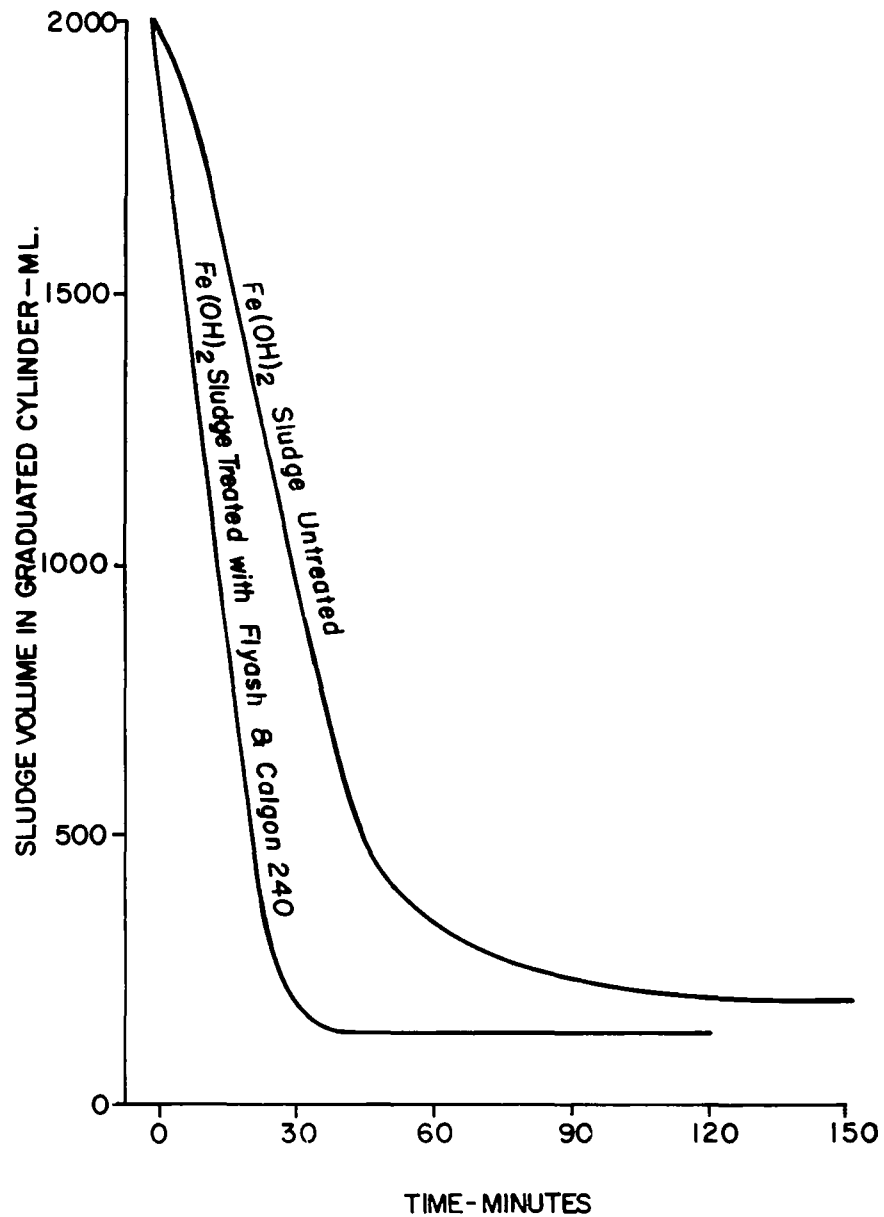


Figure 17 - Effect of Treatment with Flyash and Calgon 240 on Settling of $\text{Fe}(\text{OH})_2$ Sludge. After Bituminous Coal Research⁽³⁹⁾

Table 6

Effect of Coagulant Aids on Fe(OH)_2 and Fe(OH)_3

Name	Source	Concentration at Iso- electric Point, ppm Added to Fe(OH)_2	Concentration at Iso- electric Point, ppm Added to Fe(OH)_3
Poly-Floc 1130	Betz Laboratories, Inc.	1	0.1
Calgon 240	Calgon Corp.	5	0.4
Purifloc A-21	Dow Chemical Co.	9	0.4
Calgon C-55	Calgon Corp.	75	0.8
54 Ludox AS	E. I. duPont de Nemours, Inc.	*	1.1
Primaflow A-10	Rohm and Haas Co.	15	1.2
Ludox HS-40	E. I. duPont de Nemours, Inc.	*	1.5
Lomar D	Diamond Shamrock Chemical Co.	19	1.5
Calgon 37	Calgon Corp.	35	1.8
Solution 24	Philadelphia Quartz Co.	100	1.8
$\text{Na}_4\text{P}_2\text{O}_7$	Fisher Scientific Co.	100	6.0

* Isoelectric point never achieved - remained electropositive. After Bituminous Coal Research⁽³⁹⁾

has found application in sewage and municipal water treatment. The concept of sludge freezing has evolved from observations made on sludge frozen by nature and later thawed resulting in improved sludge dewatering characteristics. Early work on sewage sludge freezing led observers to believe that freezing disrupted the cell walls retaining the internal moisture in sludge, thereby allowing water release and drainage.⁽⁶²⁾

Early research on sludge freezing and dewatering was conducted in Great Britain with mixed success. Clements, et al.⁽⁶⁵⁾ reported initial success in sludge freezing prior to vacuum filtration while Bruce, et al.⁽⁶⁶⁾ reported negative results. Later Doe⁽⁶⁷⁾ undertook preliminary freezing studies on washwater sludge and found that after freezing and thawing the sludge had lost its gelatinous consistency and sludge particle size was approximately 0.1 to 1.0 mm. The freeze conditioned sludge also settled quickly. A 100 gram sample of freeze conditioned sludge was filtered in a conventional filter funnel in a few minutes compared to 36 hours for the same quantity of unfrozen sludge. This work led to the construction of a sludge freezing plant at Lancashire, England to condition 8500 gallons of washwater sludge per day.⁽⁶⁸⁾ However, high cost forced the plant to be abandoned.

Further freezing studies by Katz and Mason⁽⁶⁹⁾ were conducted in the U.S.A. on activated sewage sludge. The investigators concluded that freeze conditioned sludge can be dewatered by gravity draining using wire screen cloth (40-80 mesh) and that the filtrate and filter cake quality are equivalent or better than that produced by conventional vacuum filtration.

Freeze conditioning of coal mine sludge has been attempted by the Scientific Control Group of the National Coal Board, but data on the effects on sludge solids and settled volume is not yet available.⁽⁷⁰⁾ Rummel⁽⁷¹⁾ reported success in coal mine sludge concentration (.6 percent solids to 7.5 percent solids) by sludge freezing, but did not follow up the research again due to the apparent high cost.

Ultrasonic

Ultra high-frequency sound was proposed as an aid in the coagulation of the hydrous iron (III) oxide formed by oxidation.⁽⁷²⁾ This proposal was later investigated by Rozelle.⁽⁷³⁾ Results were disappointing because a fixed frequency (80 kc/sec) was found to create a dispersion effect rather than coagulation. The project personnel concluded that further research would not be warranted unless a

multiple-frequency generator was used. Rummel⁽⁷¹⁾ also investigated sludge conditioning by ultrasonics (50 c/sec) without success.

Heating

Sludge heating is another less common sludge conditioning method that has been applied to sewage treatment sludges. When sewage sludge is exposed to heat and pressure, the cell structure is destroyed, and the solids coagulate reducing the hydrophilic nature of the solids.⁽⁶²⁾

Rummel⁽⁷¹⁾ attempted coal mine sludge heat conditioning, but did not observe any apparent sludge dehydration which could have resulted in improved sludge characteristics.

Artificial Seeding

Artificial seeding involves the introduction of a material which acts as a nucleation site upon which the precipitate can grow. As previously mentioned, considerable research has been conducted on this subject using spent pickle liquor wastes. This research eventually included sludge recirculation as discussed earlier in this report.

Other

Solvent extraction, electrical treatment and bacteria treatment are conditioning processes that have been attempted with sewage sludge and found impracticable. Rummel⁽⁷¹⁾ attempted to concentrate coal mine sludge by electrophoretic and magnetic treatment. Both attempts did not in any way affect the sludge structure. No recorded attempts at coal mine sludge conditioning with either bacteria or solvent extraction were found and due to the unsuccessful attempts with sewage, the application of these conditioning processes to coal mine sludge seems remote.

Summary of Sludge Conditioning

Several steps can be taken to precondition coal mine sludge for further dewatering. Sludge thickening, either by stirring with the conventional clarifier thickener or by the use of the Hydraulic Rake[®],

can be achieved.

Chemical treatment with coagulants such as organic polyelectrolytes can dramatically improve the sludge settling rate, but does not necessarily increase the solids content of the settled sludge. Unsuccessful attempts have been made in the use of coagulants as sludge conditioners prior to dewatering by centrifugation and vacuum filtration. However, new flocculants are now available that may be applicable.

Sludge conditioning by artificial freezing has not been extensively studied with coal mine sludge. However, the initial success with other sludges indicates that application to coal mine sludges may be feasible.

SLUDGE DEWATERING

The primary objective of any dewatering operation is to reduce the moisture content (increase solids content) in the sludge to minimize disposed volume. In terms of the operations that may be performed on sludge, sludge dewatering follows the steps of liquid-solid separation and sludge conditioning.

Figure 18 is a flow chart of unit operations (neutralization, clarification, sludge conditioning, sludge dewatering) that could be used in a future mine drainage treatment plant. Neutralization and clarification are two operations currently employed in all coal mine drainage treatment. Sludge conditioning operations such as polyelectrolyte addition and/or freezing may be conventional practices in the future. However, they are not absolutely required in current sludge dewatering technology.

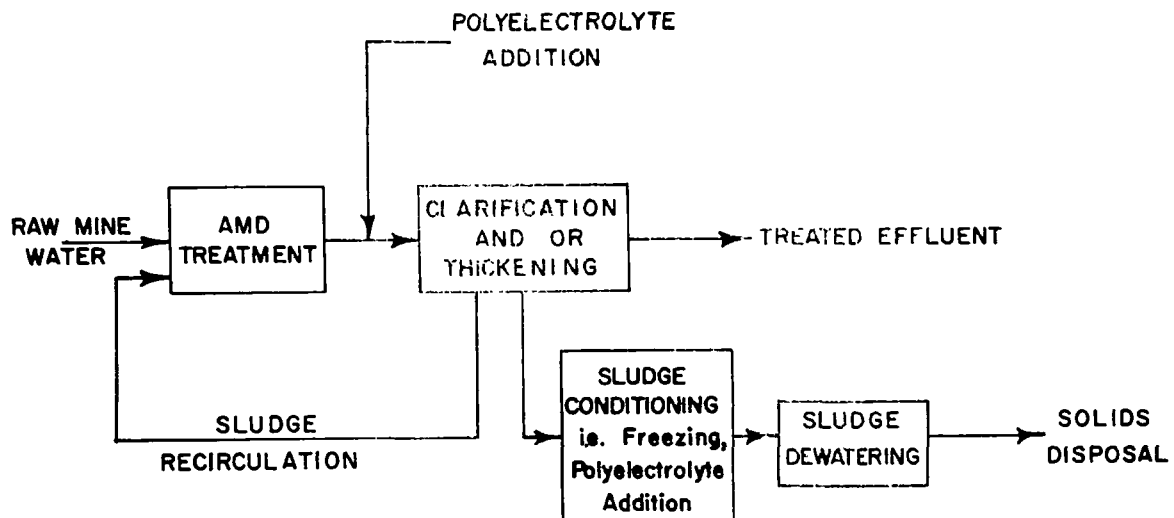


Figure 18 - Flow Chart of Future AMD Treatment System.

Vacuum Filtration

The revolving-drum is the most commonly used type of vacuum filter and is characterized by a series of vacuum cells that run the length of the drum. The drum turns at a slow peripheral speed (one rpm or less) and passes through a reservoir containing the sludge to be dewatered (See Figure 19). As the drum passes through the sludge a vacuum of 12 to 26 inches of mercury is applied to the submerged cells drawing a sludge cake to the surface of the filter media. As the cell emerges from the sludge reservoir it is partially dried by the vacuum and is then removed from the drum by a scraper, a blast of air, or coiled springs. The sludge is then carried away for further drying or disposal.⁽⁷⁴⁾

Mechanical dewatering by vacuum filtration has been applied to almost all types of sewage sludge and many industrial waste water sludges. The ability to dewater a sludge is affected by many variables, some of which are listed below:⁽⁶²⁾

Sludge Variables

1. Concentration of solids
2. Age and temperature
3. Viscosity
4. Compressibility
5. Chemical composition
6. Nature of solids

Operating Variables

1. Vacuum
2. Amount of drum submergence
3. Drum speed
4. Degree of agitation
5. Filter media
6. Conditioning of sludge prior to filtration

One of the first attempts to dewater lime treated coal mine drainage sludge by vacuum filtration was conducted by Rummel⁽⁷¹⁾ on an experimental basis in Germany. A method to dewater the sludge was desired in the recovery of the iron (III) - oxyhydrate which was used as purification material for gas, as a color pigment or as smelting feed. The filtration tests were run on a unit that had a 3.2 square meter filter surface area. Optimum conditions were obtained with a special nylon filter cloth and a drum speed that corresponded to a 20 second drying time with a vacuum of .6 atmos-

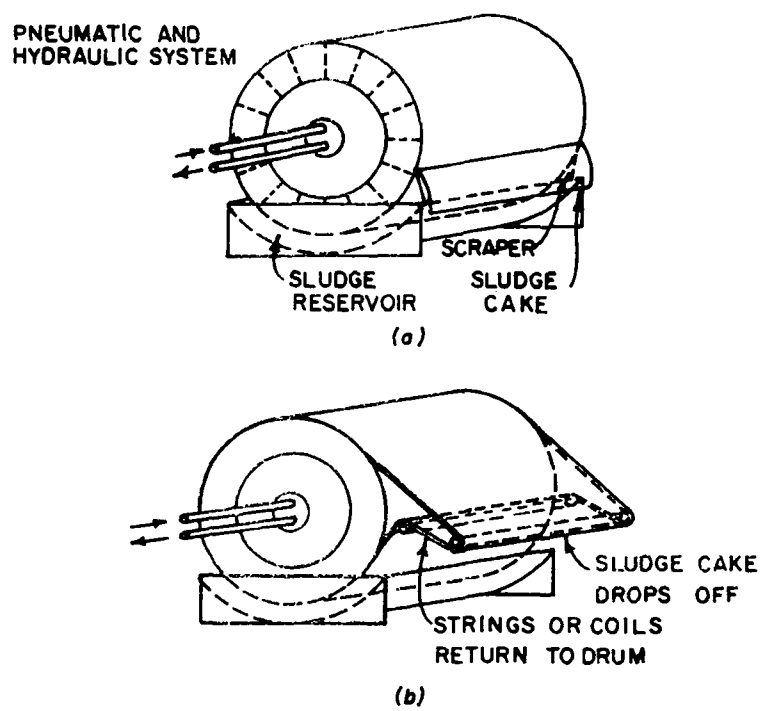


Figure 19 - Sketches of Drum Vacuum Filters.
After Fair, et al.⁽⁷⁴⁾

pheres at immersion. The test apparatus had an output of .085 gpm/ft² and produced a filter cake that averaged approximately 23 percent solids as compared to an original .6 percent solids.

"Operation Yellowboy" studies included filtration tests on coal mine sludge thickener underflow from numerous hydrated lime treated mine waters. A 0.1 square foot filter leaf to simulate the conditions of drum and disc filter operations was employed using a relatively tight nylon cloth as the filter media. Filter cakes were formed with solids contents as high as 29.8 percent. Little advantage was gained from the filtration of a thickener underflow that had been conditioned with a flocculating agent.⁽⁶⁴⁾ A rotary vacuum filter was incorporated as the dewatering unit in the scale-up design.

Sludge from biochemical oxidation and limestone neutralization treatment has very good vacuum filtration possibilities. This sludge was dewatered on a one square foot model rotary vacuum drum filter. The filter cake had a thickness of 3/32 inch with a 45 percent solids content and exhibited good discharge and handling characteristics. Glover⁽⁴⁹⁾ calculated that vacuum filters with 250 square feet of filtration area operating 10 hours/day, 7 days/week could dewater the sludge created from the treatment of 1,000,000 gallons/day of coal mine drainage containing approximately 300 mg/l of dissolved iron.

Vacuum Filtration and Filter Aids

At times certain sludges which are slimy or contain very fine solids form a dense, impermeable cake that "blinds" the filter medium and hinders the flow of liquid through the filter. To combat this situation filter aids are used to increase the porosity of the cake so the filtrate can flow at a reasonable rate.⁽⁵⁶⁾

Filter aids have two different applications, as an addition (admix) to the sludge slurry or as a precoating to the filter surface.⁽⁵⁶⁾ Depending upon the use of the filter cake, the filter aid may be separated from the cake or if the solids have no value, the total mixture may be discarded.

Bituminous coal used as an admix filter aid to coal mine sludge has been studied with mixed success. Test results indicated that the addition of coal aided the filtration slightly, but at the same time filter area requirements increased.⁽⁶⁴⁾

Successful laboratory and pilot plant studies by Brown, et al. (75) have been conducted using diatomaceous earth as the precoat for rotary vacuum filtration of coal mine drainage sludge produced from various mine waters and treatment methods. Filter cake from hydrated lime, limestone-lime and limestone treated mine waters averaged 22, 45 and 63 percent solids respectively. A Water Quality Office, Environmental Protection Agency, Report 14010 DII presents these results in detail.

Another investigation into precoat vacuum filtration of coal mine drainage sludge is currently being conducted using a full scale vacuum filtration unit at the EPA - Penn State Experimental Mine Drainage Treatment Plant located at Hollywood, Pennsylvania. This unit has 113 square feet of filtering area which is precoatd with either diatomaceous earth or fine coal.(76) Results from this investigations will be published when available.

Porous Bed Drying

The use of a porous bed for sludge dewatering is common and the literature is abundant with theory and applications.(62,74,77) Various types of granular filtering materials have been used for porous bed drying some of which are natural silica sand, crushed anthracite, crushed magnetite and garnet sands. The most common application of porous beds is in municipal and industrial treatment where the sludge or slurry is passed through sized sand and gravel to remove suspended solids.

Dewatering occurs in porous beds by drainage and evaporation. Some of the parameters that affect the design and usage of porous beds are listed below:(62)

1. Weather conditions
2. Land values and proximity of residences
3. Sludge characteristics
4. Use of sludge conditioning aids
5. Subsoil permeability

Weather is the most important and to a certain degree uncontrollable parameter to be considered in porous bed drying. Some of the weather factors are rate and amount of precipitation, percentage of sunshine, air temperature, relative humidity and wind velocity.

Various design modifications have been attempted in porous bed drying, most of which relate to the use of the sand bed. Some of

the design modifications are as follows.⁽⁶²⁾

1. Covering the drying bed in some manner to protect the sludge from adverse weather conditions.
2. Covering the bottom of the bed with asphalt or concrete to facilitate removal of the dried sludge.
3. Heating the drying beds.
4. Conditioning the sludges with materials such as organic flocculants, polymeric flocculants, sawdust, anthracite or activated carbon.

The sludge drying process is affected by the nature and moisture content of the discharged sludge. Vogler and Rudolfs⁽⁷⁸⁾ studied paper mill white-water sludge in the laboratory. They found that as the initial sludge solids content decreased the final cake moisture decreased and the cake was easier to handle.

The solids content at which various sludges are "liftable" (condition of sludge when removal is possible) differs considerably. Burd⁽⁶²⁾ in a review of sand bed drying stated that some sludges are considered lifttable at 55 percent solids while other sludges can be lifted at 16 percent solids.

Rummel⁽⁷¹⁾ considered drying beds as a method of coal mine sludge enrichment, but decided that the idea was not feasible due to the large amount of sludge to be treated and the unfavorable weather conditions in the area.

Yeh and Jenkins⁽⁷⁹⁾ conducted laboratory sand bed drying tests on a coal mine sludge (one percent solids) that was being discharged into a lagoon at the rate of 800 gpm. Results from calculations showed that the filter area requirements for one day of sludge production (sludge depth 1 foot) would be 1.8 acres. Drying time was approximated to be 10 days assuming similar laboratory weather conditions.

A coal mine sludge drying basin is currently being studied at Hollywood, Pennsylvania which was designed to achieve dewatering by combined percolation, evaporation and freezing. A drainage tile system for discharge of the percolate is constructed on a base of compacted clay. The tile is covered with 24 inches of well-burnt red dog and topped with two inches of sand. The drying basin is divided into three sections separated by concrete walls. One section is open to the sun, the next is covered with plastic supported

by an aluminum frame and open at the ends and the third section has a close-fitting plastic cover, which simulates a solar still.⁽³⁾ Data has yet to be published from this research.

Lovell found that during sludge removal attempts, a rubber wheeled vehicle could not negotiate well in the basin due to the presence of the red dog. The vehicle also compacted the red dog which impeded the flow of the filtrate to the drain tiles. Lovell plans to replace the red dog with graded limestone.⁽⁸⁰⁾

Pressure Filtration

Pressure filtration, like vacuum filtration, operates on the principle of a pressure differential across the filter media. In pressure filtration the material to be filtered is forced under pressure against a filter media that catches the solids while the liquid passes through. Among the common enclosed pressure filtration systems are shell-and-leaf filters and plate and frame presses. The shell-and-leaf filters are characterized by filter leaves suspended inside a shell into which the material to be filtered is charged under pressure. The plate and frame press utilizes filter media such as cloth, screens or paper held between a metal, wood, or rubber plate and a frame assembly to form a frame unit. The material to be filtered is placed within the frame under pressure.⁽⁵⁹⁾

Pressure filtration of waste sludge has not been widely accepted in the United States due to the inherent batch operations involving high labor and maintenance costs.⁽⁶²⁾ However, pressure filtration is finding increased usage in England and other European countries.

Lime, aluminum chloride, aluminum chlorohydrate and ferric salts have been used overseas as sludge conditioning agents prior to pressure filtration.⁽⁶²⁾ Polyelectrolytes and flyash were among the conditioning agents studied by Gerlich⁽⁸¹⁾ during sewage sludge dewatering investigations. The addition of flyash, used both as an admix and precoat during pressure filtration, helped produce a filter cake which contained 50 percent solids.

Pressure filtration of coal mine drainage sludge was investigated by Rummel.⁽⁷¹⁾ The sludge was aged 14 days in a large basin where it thickened to 1.2 percent solids prior to filtering. The solids content of the filter cake ranged between 20 to 30 percent after filtering. The output varied from operation to operation with the Kelly Filter being the most successful unit. Filtration rate was 50 liters of sludge per square meter of filter surface per hour

(.061 gpm/ft²). It was concluded that filter output was not sufficient to handle large quantities of sludge.

Cycloning

The likelihood of sludge dewatering with a cyclone is doubtful due to the similar specific gravities of coal mine drainage sludge and water. Rummel⁽⁷¹⁾ discussed the possibility of sludge dewatering with a hydrocyclone and concluded that the density of the sludge (1.003) was too close to water for practical liquid-solid separation.

Centrifugation

Centrifuges separate solids from liquid by sedimentation and centrifugal force. Sludge enters the centrifuge through a feed tube located in the center of the machine. The sludge is accelerated and distributed to the periphery of the bowl or basket where the solids are compacted by centrifugal force against the walls of the bowl. The separated liquid is discharged at one end while the solids are pushed out the other end by a screw conveyor or are cut away with a knife mechanism. Various centrifuge models are available for dewatering waste sludge, the most effective model being the horizontal, cylindrical-conical, solid bowl machine.⁽⁶²⁾

Rummel⁽⁷¹⁾ considered centrifuging but concluded that high speed centrifuges would fail to separate the low density coal mine sludge.

Centrifuge tests were also conducted during "Operation Yellowboy" studies using a Merco Z-1-L solid bowl model on coal mine drainage sludge thickener underflow. The centrifuge cake averaged 30 percent solids or greater and the suspended solids recovery was virtually 100 percent. However, the desired feed rate could not be achieved and power costs were high. The centrifuge was therefore eliminated in the scale-up design.⁽⁶⁴⁾

Centrifugation as a method of dewatering coal mine sludge has not received a thorough investigation. The conclusions drawn from the early attempts at centrifugation seem to have been premature.

Thermal Drying

Thermal drying of sludges is accomplished by the introduction of hot gases to rapidly remove moisture from the solids. Thermal

drying has been applied to sewage sludges. In most sewage sludge thermal drying applications the dried product is sold as fertilizer to offset a portion of the operating costs. The basic advantages of thermal drying are the reduction of harmful pathogenic micro-organisms, odor destruction, and massive reduction in sludge volume.⁽⁶²⁾

The following types of thermal dryers are applicable to sludge drying: (1) flash, (2) multiple hearth, (3) rotary drum and (4) atomizing spray dryers. All of these units use hot gases for drying and possess the capability to dry wastewater sludges to less than 10 percent moisture.⁽⁶²⁾

Due to high fuel requirements, thermal drying of coal mine sludge is economically unattractive. If waste heat were available or if the dried product had some economic value, thermal drying might be practical. No attempts to dewater coal mine sludge by thermal drying techniques were found in the literature.

Screening

Screening is used to dewater sludge by applying the basic principles of gravity filtration. The material to be dewatered is applied to a fine mesh screen that catches the solids and allows the liquid phase to pass through.

Dewatering of sludge by screening, particularly with vibrating screens, has been successfully applied on a pilot plant basis to sewage sludge. This operation consists of a series of three screens. First, a coarse stationary screen (8 x 24 mm) removes the large solids. Next, a sonic screen (1.2 - 2 mm) and three sonic filters (varying between 0.1 - 0.5 mm) remove the small solids. The last screen and filters are vibrated by electromagnetic vibrators. With the introduction of a roll press in the system, sewage sludge was dewatered to 35-40 percent solids.⁽⁸²⁾

The application of screening to coal mine sludge dewatering seems remote due to the inability of the screens to catch fine solids. However, if large, firm flocs could be produced from a sludge conditioning process, screening may become feasible.

Flotation

The use of sludge flotation has been applied to thickening or clarification operations. Solids are separated from the water by the

attachment of minute air bubbles which drag the solids along as they move to the top of the flotation cell.

Flotation experiments have been attempted on coal mine drainage sludge using various flotation agents. Insignificant solids removal was reported with the conclusion that, under the conditions examined, the flotation separation of solids from the sludge slurry was unsatisfactory.⁽³⁹⁾

Lagooning

The lagoon serves three purposes in the treatment of coal mine drainage: as a clarification basin, as a sludge dewatering area, and finally as a sludge storage area.

When a single lagoon performs all three functions the sludge dewatering function is served the least effectively. In a single lagoon, only slight compaction occurs. The presence of surface water undergoing clarification does not allow the sludge to be exposed to the beneficial effects of evaporation and natural freezing. Thus, the single lagoon cannot be considered an effective sludge dewatering device.

Another type of lagooning system that is receiving increased attention is the series system. Kosowski and Henderson⁽⁸³⁾ designed a series system in which the first lagoon catches most of the sludge as it precipitates and settles. The second lagoon "polishes" the treated water allowing for complete sedimentation. The designers report that the system was built to minimize sludge "plugging", to allow visual observation of the flow and to reduce sludge short circuiting. The series lagoon system has the same disadvantage as the single lagoon due to the presence of water.

Lagooning operations at times take advantage of evaporation and natural freezing brought about through atmospheric conditions.⁽⁸⁴⁾ Where land is available the construction of two lagoons each having sufficient retention time to handle the entire flow appears advantageous. This dual or parallel system allows for the alternate use of lagoons so that sludge in the inactive lagoon can dewater, compact and dry. However, to take full advantage of the dual lagoon system the inactive, drying lagoon must be decanted of surface water. A covering of water will not allow the sludge to be fully exposed to the drying effects of the sun, wind, and freezing conditions.

A variation of the dual lagoon system has been reported by Holland, et al.⁽¹⁾ on an experimental mine drainage treatment plant. Sludge was pumped from the inactive lagoon to a separate sludge drying lagoon. While in the drying lagoon, sludge was allowed to undergo evaporation, freezing and compaction. Holland found that if the sludge was left undisturbed the percent solids may increase by as much as 12 to 20 percent over a three week period.

Pudlo⁽²⁹⁾ extended this work by quantifying the effect of evaporation on sludge volume. He first simulated a normal single lagoon by determining the percent solids and the cubic feet per pound of dry solids of sludge samples settled in a 1000 ml graduated cylinder. Samples were then taken from Holland's sludge drying lagoon and analyzed in the same manner. By comparing the samples taken from the drying lagoon to the samples from the graduated cylinder, Pudlo found that evaporation reduced the volume of the sludge 90 percent as compared to normal single lagoon conditions. Data from this study is presented in Table 7.

Table 7

Effect of Evaporation on Sludge Volume

Cubic feet per pound of dry solids from sludge in 1000 ml graduate		Cubic feet per pound of dry solids from sludge in pond	
Sample No.		Sample No.	
1	0.44	1	0.047
2	0.40	2	0.047
3	0.35	3	0.052
4	0.36	4	0.049
		5	0.042
		6	0.035

After Pudlo⁽²⁹⁾

In summary lagoon drying can substantially reduce sludge volume, but requires large land areas. If land is unavailable, other dewatering techniques may be required to handle the sludge.

Summary of Sludge Dewatering

The most promising method of mechanically dewatering coal mine sludge is by vacuum filtration. Lime and limestone coal mine sludges have been successfully dewatered using both conventional rotary vacuum filtration and precoat rotary vacuum filtration.

Sand bed filtration appears to be a feasible dewatering technique. However, data is not available from the research currently being conducted on this process and a critical analysis cannot be made.

Pressure filtration of coal mine sludge has been studied on a limited scale. Initial results were reasonably successful, but the inherent disadvantages of the batch dewatering process plus the lack of high filter output favored vacuum filtration. The initial study on pressure filtration was conducted almost 15 years ago suggesting that pressure filtration research should be updated.

Centrifugation studies conducted on coal mine sludge used the solid bowl model throughout the investigation. Other models such as the basket type centrifuge may be applicable to coal mine sludge. Therefore, centrifugation should receive further study.

A summary of mine drainage sludge dewatering methods and results is presented in Table 8.

Table 8

Coal Mine Sludge Dewatering Attempts

<u>Dewatering Method</u>	<u>Percent Solids of Cake</u>
Vacuum Filtration	23-45
Precoat Vacuum Filtration	22-63
Sand Bed Drying*	12-33
Pressure Filtration	20-30
Centrifugation	30 average
Single Lagoon	.5-4.5
Drying Lagoon	12-20

★

No data available, results projected by author.
Percent solids of input sludge (.5 - 9.5 percent).

COST COMPARISON BETWEEN METHODS FOR DEWATERING

Sludge dewatering costs as related specifically to coal mine drainage have not been reported in any depth. This is due to the almost universal use of lagooning which frequently serves both dewatering and disposal functions.

Since data is generally not available for various coal mine drainage dewatering schemes, a study into other sludges and their dewatering economics is in order. It must be understood that average cost figures from one type of sludge cannot be directly compared to coal mine drainage sludge.

A general review has been made on economic data related to the average sludge handling and disposal costs of sewage sludge.⁽⁶²⁾ Table 9 presents the capital and operating costs of various sludge handling systems as they relate to sewage sludge. The costs in this table do not include any conditioning costs or costs for ultimate disposal.

As can be expected lagooning is the least expensive treatment method. Heat drying is the most expensive and the costs of other dewatering techniques falls between the two extremes.

Table 9

Costs of Sludge Handling System For Sewage Sludge

Sludge Handling System	Capital and Operating Costs (\$/ Dry Ton)	
	<u>Average</u>	<u>Range</u>
Lagooning	2	1-5
Sand Bed Drying	-	3-20
Centrifugation	12	5-35
Vacuum Filtration	15	8-50
Heat Drying	35	25-40

After Burd⁽⁶²⁾

METHODS OF SLUDGE DISPOSAL

The quantity of sludge created by the lime or limestone neutralization process is large. When suitable land is available, lagooning is the normal disposal method. Holland, et al.⁽¹⁾ aptly described the land requirements for sludge disposal in a report related to an experimental treatment plant. This plant treated water at the rate of 200 gpm, 16 hours per day, 5 days per week (approximately 52,000,000 gallons per year) and if kept in continuous operation would have produced 4 acre feet/year of settled sludge.

The indiscriminate disposal of sludge created from the treatment of coal mine drainage could result in a pollution problem as serious in some cases as the original problem caused by mine drainage. Besides the adverse environmental effects of sludge dumpings, there is the possible danger of slippage or subsidence caused by the storage of sludges above grade in residential areas.

Lagooning for the purpose of water clarification and sludge thickening is almost universally practiced. The natural extension of this practice is to leave the sludge in the lagoon for long periods of time. This is in fact the most common disposal method currently in use. Problems can evolve from this practice, especially when the sludge starts to occupy a large portion of the lagoon volume. If the occupied volume becomes large enough to reduce required retention time, short circuiting may introduce solids into local streams.

It is possible to alleviate this problem by pumping the settled sludge into a separate lagoon for further dewatering and drying. In this case the sludge can be exposed to evaporation and freezing conditions which can substantially increase the solids content. The sludge can then be periodically removed to landfill operations, however no record of this practice has been found.

Disposal of coal mine sludge to abandoned deep mines is being used when conditions warrant.^(27,33) Like other disposal methods, underground disposal can lead to other problems. When factors such as the geological and legal environment permit and underground disposal is feasible, the cost savings for this method can be substantial.

REGULATIONS CONCERNING SLUDGE DISPOSAL

Disposal problems of coal mine drainage sludge have been recognized by state agencies, particularly in the Commonwealth of Pennsylvania. The Sanitary Water Board, Pennsylvania Department of Health, has established guidelines for the underground disposal of sludge from coal mine drainage treatment.⁽⁸⁵⁾ The main criteria for underground sludge disposal is that the sludge must have a pH of 7.0 or above and that all the iron present must be in the ferric state. Other factors that have to be considered are the location of disposal, mine hydrology, quality of the water in the mine where the sludge is to be disposed, sludge characteristics, and geology.

A major concern with underground disposal is the possibility of the sludge redissolving. Lovell⁽³⁾ reported that work has been done on sludge dissolution but that further study is needed. To alleviate this problem the Commonwealth of Pennsylvania requires the mine operator to supply data to show that the disposed sludges will not affect present or future discharges from the mine pool.

In addition to underground disposal data, Pennsylvania requires detailed information on sludge lagooning such as lagoon depth, capacity, expected life and geologic data. A description must also be submitted on proposed methods of removal and disposal of the contents of the lagoon during and after its expected life.

When sludge is to be dispersed on land, indepth data must be prepared on the type of waste, location, bedrock, solids and ground water of the disposal site. If the site is also used for sanitary landfill operations, the landfill must be approved by the Pennsylvania Department of Health.

The recent public concern over pollution will probably lead to further regulations of sludge disposal on both the state and Federal level.

USES FOR SLUDGE

One of the first commercial applications of coal mine drainage sludge was found when coal mine drainage treatment was still in its infancy. Sludge underflow from a thickener was dried on a steam heated rotary drum, and the dried material was sold as a component for a gas purification sponge used to remove hydrogen sulfide from gas generated during the combustion of bituminous coal. Studies were also made using the same sludge as a soil conditioning agent. It was found that fifteen to twenty pounds per acre of dried precipitate could increase crop yield by up to 75 percent. However, quantities in excess of that amount were toxic. Plans were also made for construction of a calcining plant to convert the sludge precipitate into paint pigment, but were never implemented.⁽³³⁾

Jeh and Jenkins⁽⁷⁹⁾ attempted greenhouse experiments using mine drainage sludge. They found that a mixture of mine drainage sludge, sewage sludge and mine spoil (approximately 25% - 30% - 45% respectively) substantially increased plant growth. The authors suggest that this mixture could be used in revegetation of areas disturbed by surface mining.

Other investigations have been made into the utilization of coal mine drainage sludge in four areas: additives used in the building materials industry; recovery of iron; the application of gypsum technology to the sulfate portion of the sludge; and separation of the major chemical components.⁽⁸⁶⁾ These investigations were generally technical feasibility studies and did not include economic consideration.

Osman, et al.⁽⁸⁶⁾ concluded that small amounts of sludge (1-2%) could be added in some cases to clay to induce color or texture changes in structural brick. The use of sludge in cement manufacture and in concrete was not attractive.

Sludge was also successfully pelletized and used as a component of blast furnace feed.⁽⁸⁶⁾

Due to the fact that the calcium sulfate in the sludge is not cementitious, the application of elementary gypsum technology to form plaster of paris was unsuccessful. Other processes such as the Merseburg reaction and the OSW process appear attractive but will require considerable process development before they can be applied to coal mine sludge.⁽⁸⁶⁾

Wet sieving was reported to be a feasible method for separating sludge into its iron and sulfate constituents. Even more effective separation could occur if prior nucleation (crystal growth) was introduced in the mine drainage treatment system.(86)

The authors also felt that raw sludge from thickeners could be used in soil engineering as pond wall sealant or drilling mud.(86)

To summarize, there is no known major practical use for coal mine sludge. If a use could be found, an economic payback could be realized which might offset, at least in part, the substantial costs of treating coal mine drainage. Therefore, it is recommended that further research be conducted into the use of, or by-product recovery from coal mine sludge.

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* * *

A significant objective of this project was to investigate practical means of abating mine drainage pollution. Such research projects, intended to assist in the prevention of pollution of water by industry, are required by Section 6 b of the Water Pollution Control Act, as amended. This project of EPA was conducted under the direction of the Pollution Control Analysis Section, Ernst P. Hall, Chief, Dr. James M. Shackelford, Project Manager, and Roger C. Wilmoth, Project Officer.

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GLOSSARY OF TERMS

Admix - Particulate materials that are added to sludge which tend to form a porous, permeable and rigid lattice structure. This structure helps retain solids but allows passage of liquid during filtration.

Clarifier Underflow - Settled sludge that is pumped or otherwise removed from the bottom of a clarifier.

Decantation - Removal of clarified water from sedimentation basin.

Diatomaceous Earth - Skeletal remains of single cell plant life (fossil silica) that can be used as a sludge admix or precoat during filtration.

FPM - Feet per minute.

Flocculation - Agglomeration or tying up of finely suspended material in large masses that settle quickly.

Flocs - Suspended particles that are joined together to form a larger mass.

Flyash - Unburned fine inorganic residue resulting from the combustion of coal used in power generation.

GPD - Gallons per day.

Mg/l - Milligrams per liter or parts per million.

Mine Spoil - The overburden material removed in gaining access to the mineral material in surface mining.

Organic Polyelectrolytes - Synthetic compounds that aid the agglomeration of finely suspended material during water clarification processes.

pH - Measurement of the negative log of the immediate hydrogen ion concentration in moles per liter.

Rock Dust - Limestone that is crushed so that 65-80 percent will pass through a 200 mesh screen.

Roll Press - Dewatering apparatus that removes water from sewage sludge by passing the sludge through a series of rolls rotating in opposite directions.

Short Circuiting - Inflow to settling basin reaches outlet in less than the theoretical detention period.

Slaking - Quicklime (CaO) is converted to a hydrate form (putty, slurry or milk-of-lime).

Synthetic Coal Mine Drainage - Man-made mixture of the major constituents of coal mine drainage.

Zeta Potential - A measure of electrostatic charge on particles in suspension.

