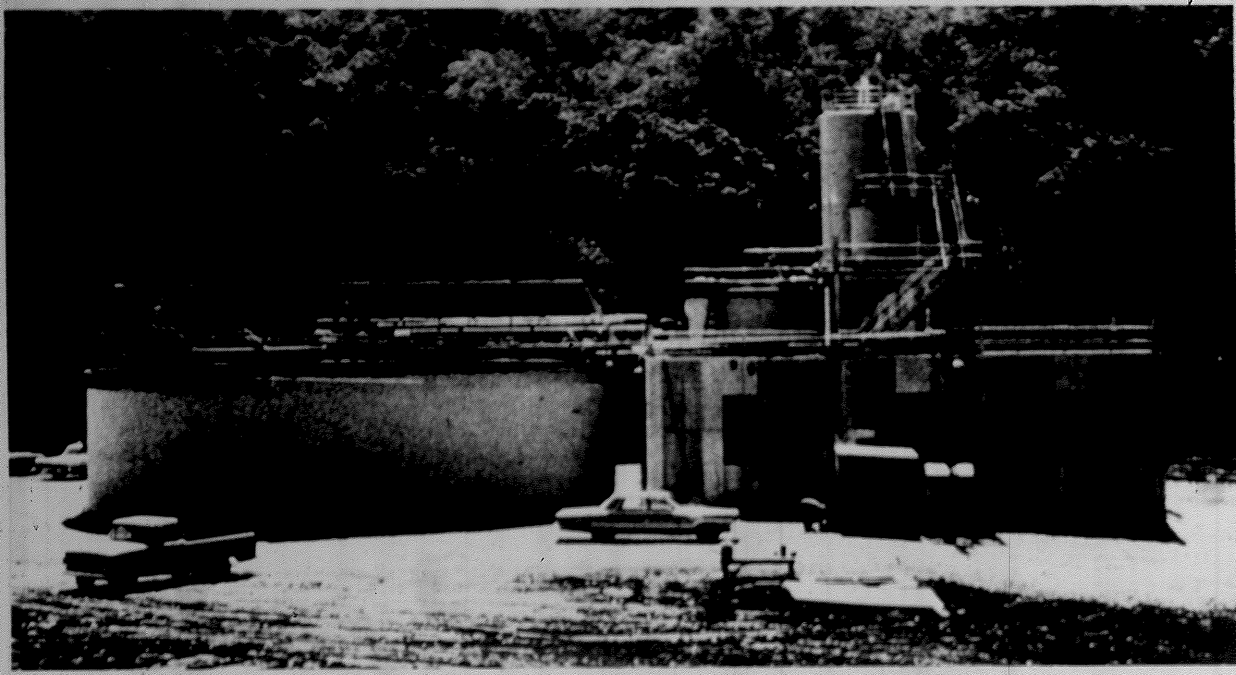

High-density sludge demonstration plant at Mine 32 tested process and developed optimum operating conditions.

High-density sludge treats acid

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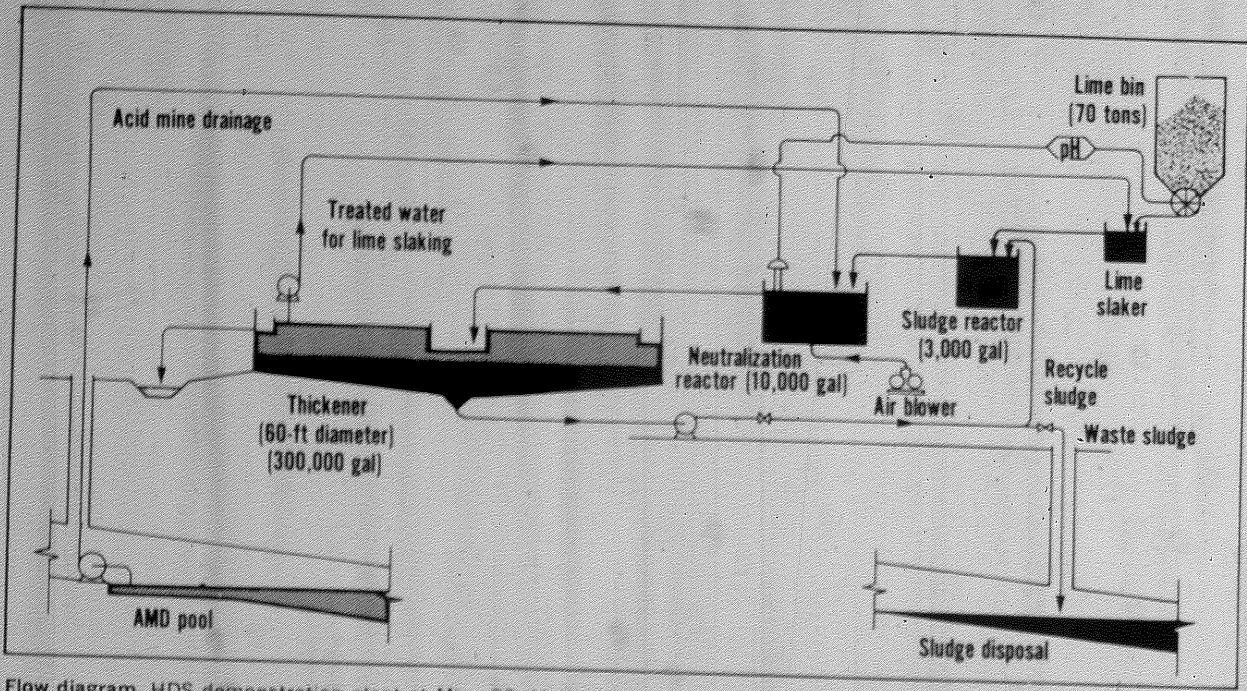
For the past several years the Bethlehem Steel Corp.'s research department and Bethlehem Mines Corp., a subsidiary of Bethlehem Steel, have cooperated in extensive test programs to find economical and technically feasible methods for treating the acid mine drainage (AMD) often associated with coal-mining operations. Particular emphasis was given to finding methods that could be applied successfully to the AMD discharges from coal mines at Bethlehem's Ellsworth and Cambria Divs. to meet Pennsylvania's effluent criteria for iron, pH, and acidity. These investigations of methods for treating acidic metal wastes covered a wide span of technology, ranging from conventional cold-lime neutralization to countercurrent continuous ion exchange. Among the other methods investigated were:

- Deep-well disposal
- Assimilation in a coal-cleaning circuit
- Neutralization and oxidation using reactors in series
- Moving-bed reactor
- Inhibition of pyrite oxidation by protective coatings
- Limestone neutralization
- Modified lime neutralization or high-density sludge

Since only the results from conventional lime neutralization are germane to the development of the high-density sludge process described, we need not discuss all the methods here. Because the moving-bed-reactor process offered a novel and possibly effective approach, it will be interesting to at least define its basic operating principles, as follows: Lime slurry and AMD are fed into a fluidized bed of inert material where neutralization occurs and where the cations are precipitated on the surfaces of the material. The physical characteristics of the precipitated solids are such that a thickener is not required to obtain solids-liquid separation, and rather than a watery sludge the result is waste solids having the consistency and draining qualities of wet sand. However, scale-up of this process has not been developed sufficiently to meet state deadlines for Beth-

Adapted from a paper presented at the Third Symposium on Coal Mine Drainage Research, Pittsburgh, Pa., May 19-20, 1970.



Flow diagram, HDS demonstration plant at Mine 32. Method involves recycling of part of settled sludge.

mine drainage

lehem's acid mine drainage discharges in Pennsylvania.

Both conventional lime neutralization and assimilation in a coal-cleaning circuit were successfully applied by Bethlehem in full-scale treatment of AMD from mines in the high-volatile Pittsburgh seam in the Ellsworth Div. in southwestern Pennsylvania. However, neither of these treatment methods was considered to be satisfactory for the AMD discharges from the low volatile Lower Kittanning seams at Bethlehem's mines in Cambria County, Pennsylvania (Nos. 31, 32, 33 and 77), where the total flow from three discharges is presently over 9 million gal per day (mgd). Conventional lime neutralization would have presented the formidable problem of storing or disposing of more than 700 acre-feet per year of sludge containing about 1% solids. Furthermore, since two of Cambria's mines are in a fairly early stage of development, the flow to be dealt with in the future may be even greater. As for assimilation in coal-cleaning circuits, the problem was not only the magnitude of the AMD flows from the Cambria mines but also the lack of sufficient alkalinity in the refuse to neutralize the acid water.

Although conventional lime neutralization is certainly adequate for many applications, our research efforts were directed toward improving both the settling characteristics of the neutralized slurries and the solids concentration of sludges normally obtained from the conventional process. The outgrowth of these efforts led to the development of a modified lime-neutralization process characterized by a high-density sludge that requires only a fraction of the storage space needed when the conventional process is used. For brevity, the modified process is known as the high-density sludge process.

Conventional lime neutralization, illustrated in the top half of Fig. 1, consists of:

Mixing high-calcium or dolomitic lime with water to produce a lime slurry;

Neutralizing the AMD with the lime slurry at ambient temperature in a stirred reaction tank, either with or without aeration;

Settling the solids precipitated from the AMD in a clarifier, thickener, or settling pond;

Disposing of the thickened residual sludge.

As the schematic in the bottom half of the figure shows, the HDS process differs from conventional lime neutralization in that provisions are made for:

Recycling a controlled volume of the settled sludge, and

Mixing the recycled sludge with lime slurry in a reaction tank prior to the neutralization and separation steps.

(*Continued*)

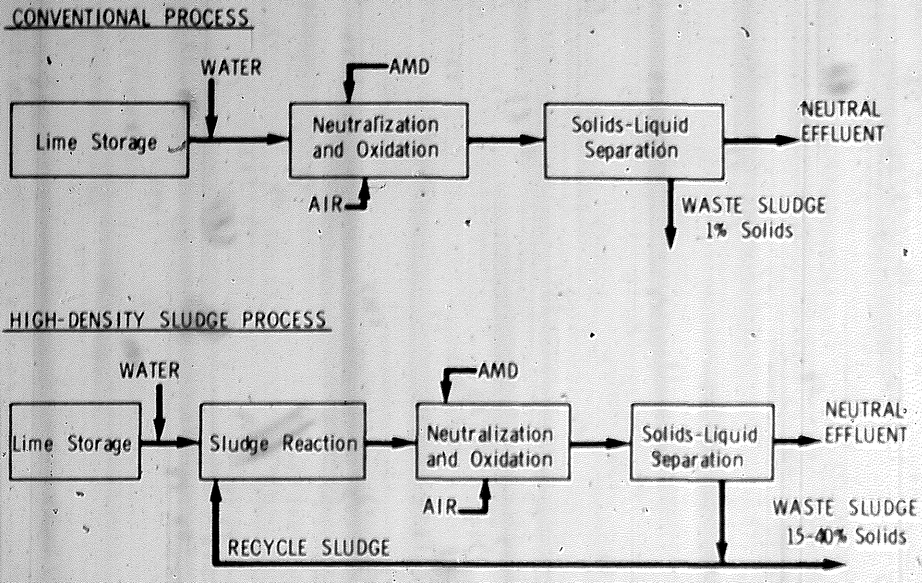


Fig. 1—Lime neutralization of acid mine drainage.

Researching the problem

Research efforts to develop an HDS process were initiated at Bethlehem's Homer Research Laboratories (HRL) in 1966 after it was demonstrated during pilot-plant testing that conventional lime neutralization of the AMD from the Cambria Div. mines resulted in settled sludges containing a maximum of 1% solids and thickener area requirements of 1,000-2,000 sq ft per ton of solids precipitated per day. Using bench-scale equipment, it was shown during exploratory testing of, the HDS process that neutralization of a synthetic AMD having nearly all of the contained iron in the ferrous state could result in settled sludges containing a minimum of 40% solids and a thickener area requirement of about 500 sq ft per ton of solids precipitated per day. To take one example, this would mean that the predicted settling area requirements could be reduced for the 4.2 million gal per day of AMD from the Mines 32 and 33 complex by a factor of four and that the volume of sludge requiring final disposal could be reduced from 210,000 gal per day to about 5,000 gal per day, or from 5% of the AMD flow to one-eighth of 1%.

On the basis of the laboratory results, we proceeded to on-site pilot-plant testing of a natural mine discharge to obtain design data for full-scale treatment plants, followed later by bench-scale testing to study the effects of mine water chemistry and operating parameters. The return to more fundamental studies in the laboratory was required after it was determined during the pilot-plant tests that a settled sludge containing 15% solids was the maximum that could be produced from an AMD discharge having an average of 30% of the contained iron in the ferrous state. These pilot-plant results indicated that the chemical differences of individual mine discharges would affect sludge quality and therefore present corresponding design problems.

Although the early laboratory and pilot-plant tests were not conclusive for some of the variables, particularly mine water chemistry, the data were useful for expediting the design and construction, in 1967, of an HDS demonstration plant at Mine 32 to test the process on a ferrous iron AMD and develop optimum operating conditions before proceeding with a full-scale installation. During the 2½-yr period of plant operations, more than one billion gallons of AMD was processed. Tests to determine the effects of operating parameters were conducted at processing rates ranging from 400 to 2,100 gpm, and settled sludges were produced that contained a maximum of 40% solids, with a normal range of 30 to 35% solids. The discharge of excess sludge via a borehole to an area adjacent to the underground mine-water pool proved to be a satisfactory disposal method. The construction of a full-scale HDS plant for treating the present and projected AMD flow from the Mines 32 and 33 complex is scheduled for 1970. Upon completion of this plant, underground disposal of sludge will be continued under present plans.

Later bench-scale tests designed to study the variables affecting the HDS process were conducted at the research laboratories both before and during the operation of the demonstration plant. These tests, detailed later in this article, were successful in:

- Defining variables having major and minor effects on the process.
- Providing operating guidelines and accurately predicting the results obtained in demonstration plant operations.
- Providing engineering design data for treatment plants at Mines 77 and 31, where most of the iron in the AMD is present in the ferric state. An HDS treatment plant for Mine 77 was completed in November, 1969, and a plant for Mine 31 is scheduled for 1970.

Process benefits

The successful development and application of a high-density sludge process to replace conventional lime neutralization for treating AMD has produced the following beneficial results:

- New technology has been developed that results in sludges denser than could be obtained previously by proven and practical processes. Depending mainly on the oxidation state of the iron in the mine water, the sludges contain 15 to 40% solids. Storage requirements for sludges are thus reduced by a factor of anywhere from 15 to 40.

- The higher solids concentrations make further dewatering via filtering or centrifuging a practical possibility if future developments should require these steps.
- The HDS process is inherently well-suited to treating AMD discharges with high ferrous to ferric iron ratios, previously considered the most difficult to treat.
- The effectiveness of the improved lime-neutralization process underscores the built-in advantage of inexpensive processing by lime and air, as contrasted with more sophisticated processes.

Table 1—Chemical analysis of AMD concentration, ppm

Component	Synthetic AMD (pH = 2.8-3.1)	Mine 32 Supply shaft AMD (pH = 2.8-2.9)
Fe^{+2}	300	60-120
Fe^{T}	300	200-320
Al_2O_3	200	170-330
CaO	250	230-270
MgO	50	10-120
Mn	—	7-9
SiO_2	—	40-70
$SO_4^{=}$	2,100	1,900-2,200

Laboratory and pilot-plant studies

The first AMD chosen for HDS studies was from a minor discharge at a supply shaft of Mine 32 for which design data had been developed previously for a conventional lime-neutralization system. For the initial, or exploratory, laboratory studies we used a synthetic mixture of the approximate composition of the mine water from the supply shaft of Mine 32 (Table 1). This was done to avoid the cumbersome and time-consuming problem of transporting daily samples from the mine to the research laboratories in Bethlehem. At this stage in the program no attempt was made to duplicate the ferrous to ferric iron ratio.

These initial laboratory tests of the HDS process in a bench-scale pilot unit showed that, without forced aeration, neutralization of the synthetic AMD to pH 8.0-8.3 with high-calcium hydrated lime could result in settled sludges containing 45% solids. When forced aeration was used to completely oxidize the iron in the neutralized slurry, a settled sludge containing 50% solids was produced at a neutralization pH of 7.0-7.2. The volume and area requirements for settling the neutral slurries and thickening the sludge were reduced by a minimum factor of four as compared with the results from the conventional lime neutralization of the same synthetic AMD.

To determine whether these results could be duplicated on a natural mine-water discharge, a pilot plant, shown in Fig. 2, was operated for about 20 days at the supply shaft at Mine 32. Scaled-down equipment based on this flow sheet was used for all bench-scale testing. With operating conditions comparable to those used in laboratory tests, the rate of density increase was much slower than the rates experienced using synthetic AMD, and the maximum settled solids concentration obtained was 15%. Changes in equipment and operating parameters had no apparent effect on either the rate of increase in density or the final concentration of the settled sludge. On-site bench-scale tests, conducted concurrently with the pilot-plant tests, confirmed the pilot-plant results and showed that the problems could not be attributed to scale-up considerations. The increase in solids concentrations as a function of operating time during these tests is shown in Fig. 3.

Although these initial tests of the HDS process could not provide a basis for complete design solutions at this stage of the program, the results did reveal the sludge densification possibilities of the process and, in particular, provided the following findings:

- A conventional lime neutralization system could be modified to an HDS process by the rather simple

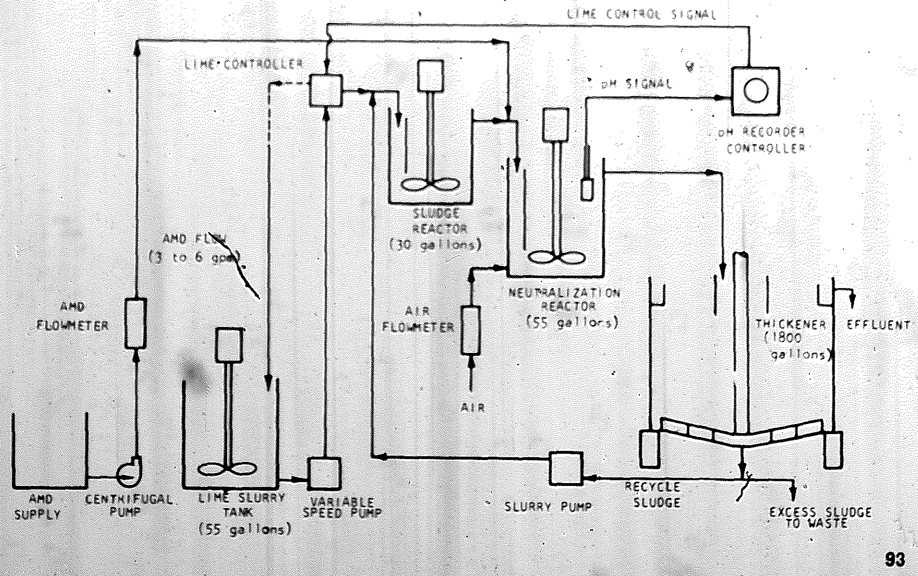


Fig. 2—Flow diagram for high-density sludge pilot plant at Mine 32 supply shaft.

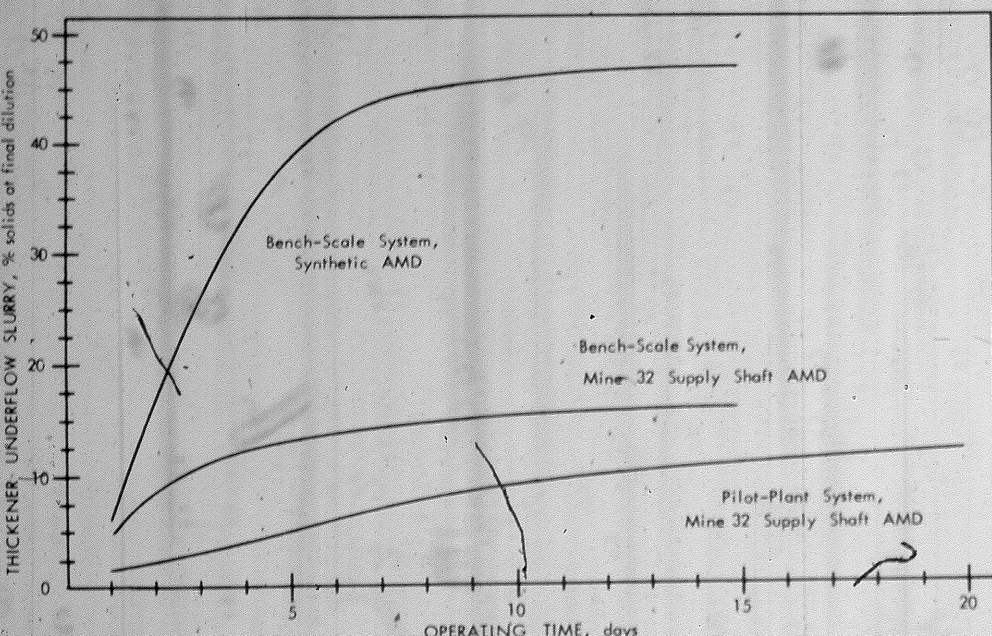


Fig. 3—High-density sludge tests, showing sludge density as a function of time.

Table 2—Flow rates and average chemical analysis of AMD from the Cambria Div. mines

	Mine 32 (Supply shaft)	Mine 31	Mines 32-33 (combined)	Mine 77
Flow, mgd	0.4	4.5	4.2	0.5
pH	2.9	3.0	3.2	3.2
Concentration, ppm				
Fe^{+2}	90	30	140	10
Fe^T	300	250	150	80
Al_2O_3	230	150	80	20
SiO_2	60	60	40	30
Mn	10	5	5	5
CaO	250	220	170	220
MgO	70	10	10	80
$SO_4^=$	2,100	2,000	1,400	1,200
Acidity ($CaCO_3$)	1,800	1,200	500	300

changes of adding a second reaction tank and a return system for thickener underflow slurry.

- The HDS process, when compared with conventional lime neutralization, would increase the solids concentration of settled sludges from 1% to a range of 15 to 50%.
- The maximum solids concentration obtainable was apparently related to the chemical composition.

Expanded program

These initial laboratory and pilot-plant findings furnished the basis for an expanded laboratory bench-scale program at the HRL. In this expanded program we made a more detailed study of the variables and operating parameters affecting sludge density. At the same time, to meet a mandated time schedule for implementing treatment facilities for the Mines 32 and 33 discharge, the data from testing the supply-shaft water were used to expedite the design and construction of a demonstration plant at Mine 32.

For the expanded program we first developed basic design data from Mines 32 and 33 water shipped in on a daily basis. This was done to minimize the possible effects of chemical changes and to eliminate errors that might be attributed to the use of synthetic mine-water mixtures. In the next phase of the expanded study we obtained design data for the HDS treatment of AMD from Mine 31, where the soluble iron in the mine water was more than 85% oxidized. Again, AMD samples were shipped from the mine on a daily schedule. However, even with the precaution of daily shipments of mine water from both sources, the oxidation of iron occurred to varying degrees and was found to affect sludge density, particularly in tests on AMD from Mines 32 and 33. That is, the ferrous to ferric ratio of the AMD emerged as an important factor to be taken into account in developing HDS design principles. Table 2 includes data on the AMD discharges used in the test, as well as data for Mine 77 where a full-scale HDS plant is in operation.

The results of the tests on AMD from Mines 31, 32 and 33, as well as pertinent data from the initial pilot-plant tests, tests on natural and synthetic steelplant wastes, and the demonstration plant, are summarized in the following sections on: ferrous to ferric iron ratios, ratio of solids recirculated to solids precipitated, point of alkalinity addition, neutralization pH, and detention time in reaction tanks.

Ferrous to ferric iron ratios

All test work showed that the ratio of ferrous to

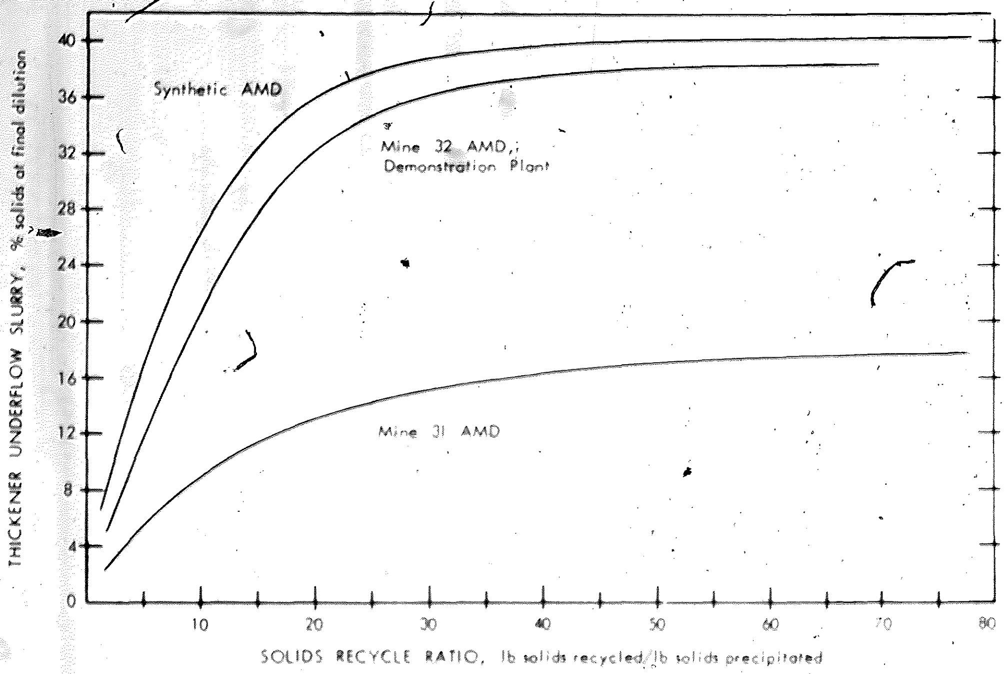


Fig. 4—High-density sludge treatment of AMD, solids concentration of settled sludges as a function of solids recycle ratios.

ferric iron in the wastes acted as an inherent control on the maximum concentration of settled solids that could be produced by HDS treatment. The effect of this ratio on the concentration of settled sludges is summarized in the following table:

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
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

These data show the strong effect of the iron ratios at the upper and lower limits. There is a general proportionality between increasing iron ratios and solids concentrations, with the curve undergoing a break as the highest ratios are approached. This conclusion is supported by the test data on Mines 32-33 AMD, which showed an approximately 100% increase in solids concentration when the percentage of ferrous iron increased from a nonequilibrium oxidation state averaging 70% ferrous iron (45 to 90% range) to a near-steady 90%. However, we have not conducted the precise and lengthy tests that would be required to precisely document the relationship throughout the full range from zero to 100% ferrous iron. Our test data do not indicate that the species or concentrations of anions or cations other than iron had any appreciable effects on sludge density.

Ratio of solids recirculated to solids precipitated

The ratio of solids recirculated within the system to the solids precipitated from the AMD by the neutralization reaction, which is a discretionary operating control and affects thickener sizes because of total solids loadings, was determined to be of primary importance in controlling sludge density. The effect of this ratio on the solids concentration of settled sludges for a synthetic AMD and for AMD from Mine 31 and from Mines 32 and 33 is shown in Fig. 4. The curves for synthetic AMD and Mine 31 AMD were drawn from averaged bench-scale test data at recirculation ratios from 20:1 to 80:1 and from the extrapolation of data at ratios below 20:1. The curve for Mines 32 and 33 AMD was drawn from demonstration plant operating data. The three curves show that the solids concentration increased rapidly as the recirculation ratio was increased to 20:1, the rate of increase in concentration decreased in the ratio range of about 20:1 to 30:1, and the percentage increase in concentration was relatively small in the ratio range of 30:1 to 80:1. The optimum range was 25:1 to 30:1, consistent with good process control, the production of near-maximum sludge densities, and minimum area requirements for sludge settling and thickening. It is of interest to note that this optimum ratio range was the same for both ferrous and ferric waters.

The combined effects of solids concentrations and recycle ratios on the size requirements for a thickener for Mine 31 AMD are shown in Fig. 5. These curves show that within the range of optimum recycle ratios the predicted thickener area requirement would be 2,100 sq ft per ton of solids precipitated per day, or about 20% higher than was determined for con-

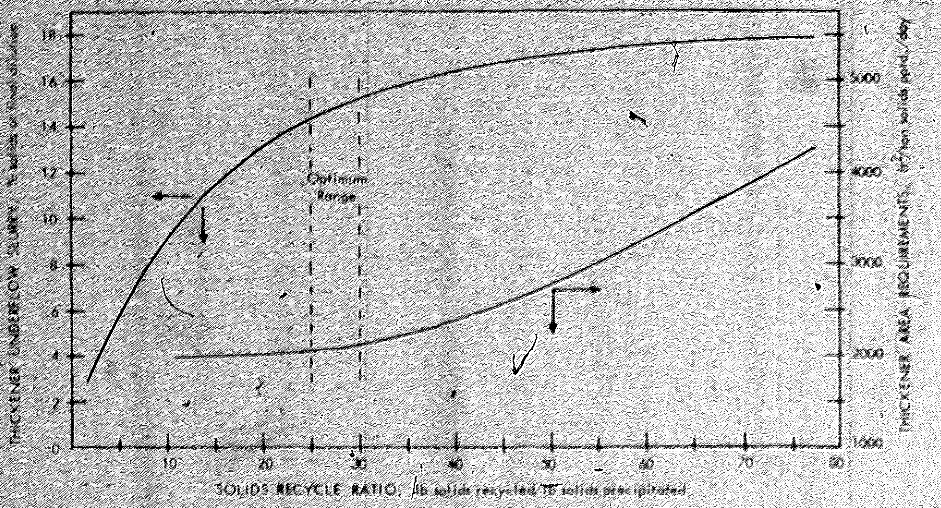


Fig. 5—High-density sludge treatment of Mine 31 AMD, solids concentration of settled sludges and thickener area requirements as a function of solids recycle ratios.

ventional lime neutralization of this AMD. The advantage of treating Mine 31 AMD by the HDS process would accordingly be predicated on a 15-fold increase in sludge concentration rather than on any reduction in thickener size.

Point of alkalinity addition

In the HDS process developed by Bethlehem, the ability to produce maximum-density sludges is based on the practice of mixing lime slurry with recycle slurry before reacting the high pH mixture with AMD. The effects of changing the point of alkalinity addition were determined in bench-scale tests and were later confirmed during demonstration plant operations. In a short-term test, it was shown that mixing lime slurry, recycle slurry, and AMD in a single reaction tank resulted in process failure, i.e., a 50% decrease in settled solids concentration and a 100% increase in thickener area requirements were experienced. Similarly poor results were obtained when the AMD and recycle slurry were mixed in the sludge reactor and the alkalinity was added to the mix in the neutralization reactor.

Neutralization pH

Bench-scale tests and tests at the demonstration plant showed that the neutralization pH had very significant effects on the physical characteristics of the neutralized slurry and on the thickener areas required for sludge settling. These effects are summarized as follows:

- The optimum pH range from overall process considerations was 7.2 to 7.7. Within this range, the oxidation rate of the ferrous iron was satisfactory, sludges of maximum density were produced, and thickener area requirements were at a minimum.
- A neutralization pH range of 6.0 to 6.5 reduced the alkalinity requirements, but the oxidation and precipitation rate of the iron was not satisfactory for practical consideration in sizing the neutralization reactor.
- An average neutralization pH of 8.5 reduced the turbidity of the clarified effluent but decreased the settled solids concentration from 35 to 20% and increased the thickener area requirements by a factor of 1.6.
- A pH range of 9.0 to 9.5 resulted in the production of a rubbery sludge that could not be pumped and that increased torque on the thickener rakes to the extent that the rakes became inoperative.

Detention time in reaction tanks

The HDS process utilizes separate reaction tanks for the sequential steps of mixing lime slurry with recycle slurry and for the combined reactions involving neutralization, oxidation of ferrous iron, and precipitation of cations. In considering reactor sizes for design purposes, it was recognized that the rates of reaction and precipitation are complex functions of numerous variables that can affect the detention times required for completing the chemical reactions. It was not considered necessary to devote detailed research studies to a rigorous or quantitative definition of these variables, since for design purposes it was sufficient to simply specify conservative detention times.

The effects of detention time on over-all process results were determined during laboratory testing of the HDS process. These tests showed that a detention time of 1 min in the sludge reaction tank was sufficient to produce and maintain sludges of maximum density and that a detention time of 10 min in the neutralization-oxidation tank ensured oxidation and precipitation of the ferrous iron at any pH value above 7.2. A maximum detention time of 1 min in the sludge reaction tank is considered to be a valid design number for an HDS system, but detention time in the neutralization tank would be a function of both the initial ferrous iron concentration and the neutralization pH.

Demonstration plant

Our findings about the effects of the above-described variables on the HDS process were incorporated into the operation of the demonstration plant which we had constructed in Mine 32 to treat the AMD from Mines 32 and 33. Before describing the design and operation of our demonstration plant it will be useful to briefly note some highlights of the steps preceding the construction of the plant.

In 1966 the Pennsylvania Sanitary Water Board approved a request by Bethlehem to construct and operate a demonstration plant at Mine 32, to test the HDS process, and to develop firm engineering design data before proceeding with full-scale treatment facilities at the Cambria Div. mines. This request was approved on the basis that the HDS process represented new and improved technology. At the same time, it was understood that the technology was still in the developmental stage and that our early laboratory and pilot-plant programs provided only primary guidance in terms of designing full-scale plants. The demonstration plant was approved by Bethlehem management in the fall of 1966, site preparation and construction were started in January, 1967, and a target startup date of early July was met. The capital cost of the plant, including equipment changes and plant modifications from 1966-69, was approximately $350,000.

Based on the results of the exploratory pilot-plant tests of the HDS process, a conservative estimate of the expected AMD processing rate was 300 gpm, and it was predicted that the settled sludge would contain at least 15% solids. This design flow was exceeded immediately after startup, and during the following 2½-yr period of plant operation the effects of operating parameters on process results were evaluated at flow rates ranging from 400 to 2,100 gpm. The solids concentrations of settled sludges were as high as 40% but ranged from 30 to 35% under operating conditions that were established for scale-up. An AMD rate of 800 gpm to the 60-ft-diameter thickener at the demonstration plant was established as a maximum design number for consistently meeting or bettering the state criterion of 7 ppm iron in the clarified effluent, while at the same time providing a 100% safety or efficiency factor for sludge settling and thickening—an efficiency factor of 100% is generally specified in conservative engineering design.

Plant operation at AMD rates up to about 1,400 gpm was satisfactory with respect to solids settling and thickening. However, the iron limit of 7 ppm could not be met because the higher hydraulic loadings and decreased detention times in the thickener resulted in an increase in the concentration of the very fine solids that accounted for nearly all of the iron in the clarified effluent. Test programs designed to find methods for improving clarification efficiency showed that either tube settlers installed in the thickener or a high-rate filter used for polishing the thickener effluent were effective in reducing the concentration of suspended solids. Methods found to be ineffective were secondary clarification in a settling pond and the use of flocculants. There are no present plans to implement the methods employing the tube settlers or a high-rate filter, because the capital cost to benefit ratio far exceeds that provided by the thickener capacity obtainable with conservative design for settling and thickening sludge.

Operation of the demonstration plant for a 2½-yr period proved the technical feasibility of the HDS process and provided firm design data for a full-scale AMD treatment plant for the Mines 32 and 33 complex. Utilizing the demonstration plant as a large-scale pilot unit over an extended period gave these benefits:

- Provided operating experience and solutions to problems associated with seasonal changes.
- Substantiated laboratory test data that had defined the effects of variables on the process.
- Resulted in modifications to the original plant design that simplified full-scale plant layout and reduced capital costs.
- Resulted in a discovery that reduced the costs for alkalinity for treating Mines 32 and 33 AMD.
- Proved the feasibility of disposing of thickened sludges in an abandoned area of the mine.

With reference to alkalinity costs, it was determined during early tests at the demonstration plant that the alkalinity requirements were substantially higher than was predicted from neutralization curves. This apparent anomaly was solved by Mines' personnel when it was determined that CO_2 in the mine water was responsible for the excessive lime demand and that the CO_2 could be readily stripped by aerating the AMD. Aeration of the mine water prior to introducing it into the neutralization reactor was incorporated as standard plant practice and resulted in reducing the lime demand by 25%.

Two of the bases used for choosing the site for the demonstration plant were that company-owned land was adjacent to the AMD boreholes and that discharging sludges directly underground from the plant to abandoned workings near the mine-water pool could be tested as a possible method for final disposal of thickened sludge. This sludge disposal method was found to be satisfactory during the entire period of plant operation. There was no evidence that sludge was either solubilized by contact with the acid water or short-circuited to the AMD pumps, and examination of the sludge underground showed further dewatering to 55% solids. Although it is expected that underground disposal will prove satisfactory for the foreseeable future, tests were conducted that showed that the sludge could be dewatered by either a filter or centrifuge to produce a cake suitable for handling and transport by truck.

Extensive and cooperative research conducted by Bethlehem Mines Corporation and Bethlehem Steel Corporation to develop practical processes for treating acid mine drainage (AMD) has covered the range from simple lime neutralization to sophisticated ion exchange. A modification of a conventional lime-neutralization process, referred to as a high-density sludge (HDS) process, which was developed in the laboratory and tested in a pilot plant, proved technically successful during a 2½-yr operating period of a 1-million-gal-per-day demonstration plant.

Compared with the 1% solids concentration of sludges obtained from conventional lime neutralization of three AMD discharges, the HDS process produced settled sludges containing 30 to 40% solids for a discharge having a high ferrous to ferric iron ratio and 15 to 18% solids for two discharges containing mainly ferric iron. A full-scale plant utilizing the HDS process was completed in 1969, and two plants are planned for 1970. Upon completion of these units, more than 9 million gal per day of AMD will be treated, the built-in design capacity being sufficient to handle expected increases. ■