

# MINE WATER RESEARCH

## Neutralization

By Maurice Deul and E. A. Mihok

\* \* \* \* \* report of investigations 6987



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## PREFACE

This is the first report on a series of studies currently underway by the Bureau on treatment of mine drainage, and is concerned mainly with neutralization of mine waters. Treatment alone is not a solution to stream pollution by mine waters; rather, all phases of the problem--collection, treatment, liquid-solid separation, and solids disposal--must be considered. Collection of mine waters for treatment and disposal of the resultant solids are being studied as a part of the Bureau's broad research program on environmental control in mining operations.

The contributing factors to the most effective means of neutralizing acid mine waters which are being investigated include ratio of raw water to limestone, size and composition of limestone, residence time, temperature effects, degree of agitation and abrasion, and the establishment of an effective air-liquid-solid interfacial area. Only when these factors are known will it be possible to develop the design criteria for a continuous limestone neutralization reactor, with and without second stage lime treatment.

Several methods of liquid-solids separation have been and are being investigated. In addition to the vacuum precoat filter tests conducted under a cooperative agreement with the Johns-Manville Company, exploratory tests have been conducted on cyclone separation, centrifugal concentration, froth flotation, and the use of selected flocculants for solids concentration. Samples from these tests now are being analyzed and the data are being evaluated.

The most difficult technical aspect of mine water treatment is the removal of soluble ferrous iron. The mechanism of ferrous iron oxidation is being studied to establish the best means of accelerating the formation of insoluble iron compounds. These investigations must be conducted under controlled laboratory conditions because ferrous iron is extremely sensitive to changes in such environmental conditions as temperature, pH, Eh (oxidation potential), and oxygen concentration.

## CONTENTS

	<u>Page</u>
Preface.....	i
Abstract.....	1
Conclusions and recommendations.....	2
Introduction.....	2
Acknowledgments.....	2
Waters tested.....	3
Test program.....	3
Procedure.....	3
Reactor.....	4
Neutralizing agents.....	4
Analytical methods.....	4
Limestone neutralization.....	6
Lime neutralization.....	7
Limestone-lime neutralization.....	7
Continuous limestone neutralization.....	8
Test results.....	8
pH increase with limestone treatment.....	8
Ferrous iron depletion with limestone treatment.....	8
Ferrous iron depletion with limestone-lime treatment.....	13
Sludge settling rates and sludge volumes.....	13
Summary of batch test results.....	22
Continuous treatment with limestone and ferrous iron depletion....	22
Discussion.....	24

## ILLUSTRATIONS

Fig.

1. Photograph of reactor.....	5
2. Limestone neutralization of A-1 and A-2 mine waters.....	9
3. Limestone neutralization of B-1, B-2, and B-3 mine waters.....	9
4. Limestone neutralization of B-2 mine water with 250 lb limestone..	10
5. Limestone neutralization of C-1 mine water.....	10
6. Limestone neutralization of D-1 mine water.....	11
7. Limestone neutralization of E-1 and E-2 mine waters.....	11
8. Ferrous iron depletion with limestone treatment of various mine waters.....	12
9. Ferrous iron depletion with limestone-lime mixed treatment.....	13
10. Settling rate of sludges from A-1 treated water.....	14
11. Settling rate of sludge from A-2 treated water.....	15
12. Settling rate of sludges from B-1 treated water.....	16
13. Settling rate of sludges from B-2 treated water.....	17
14. Settling rate of sludges from B-3 treated water.....	18
15. Settling rate of sludges from C-1 treated water.....	19
16. Settling rate of sludges from D-1 treated water.....	20
17. Settling rate of sludges from E-1 treated water.....	21
18. Settling rate of sludges from E-2 treated water.....	22

## TABLES

	<u>Page</u>
1. Analysis of mine waters collected during reconnaissance.....	3
2. Analysis of neutralizing agents.....	4
3. Composition of waters treated, batch test results, and volume and weight of solids after 1 hour settling.....	23

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by

Maurice Deul<sup>1</sup> and E. A. Mihok<sup>2</sup>

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### ABSTRACT

A special short-term research project was initiated to develop plant design parameters for treating mine waters to yield an effluent acceptable for discharge into streams and a sludge amenable to effective and economic disposal.

Neutralization was investigated to provide simple and direct treatment of ferruginous acid waters using lime, coarse limestone, and limestone followed by lime. Limestone treatment was accomplished using a small cement mixer as a simple reactor to provide abrasive agitation of limestone and mine water. Results from tests with nine mine waters encompassing a wide range of iron and acid concentrations showed that coarse limestone, one of the cheapest neutralizing agents known, is potentially useful for treating mine water discharges. However, process variables must be defined more completely before the practical applications and limitations of the process can be fully established.

In all the tests a pH of  $>7.2$  was obtained ultimately with limestone. Reaction time to reduce the iron content below 7 ppm in the water was dependent on the original ferrous iron concentration. For waters with high ferrous iron content, treatment with limestone followed by lime rapidly produced an acceptable treated water. Sludges with good settling and handling characteristics resulted when limestone was used for neutralization either alone or with subsequent treatment.

Reaction rates are expressed graphically as pH change and iron depletion curves; characteristic solids settling curves are shown. The temperature dependency of ferrous iron oxidation was verified.

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<sup>1</sup>Geologist, Pittsburgh Mining Research Center, Bureau of Mines, Pittsburgh, Pa.

<sup>2</sup>Chemical research engineer, Pittsburgh Mining Research Center, Bureau of Mines, Pittsburgh, Pa.

## CONCLUSIONS AND RECOMMENDATIONS

Coarse limestone in a dynamic state with mine water and air has been demonstrated to provide sufficient sustained action to neutralize acid and to remove iron. For mine waters containing low to moderate concentrations of iron, the treated water had a pH of 7 to 8 and an iron concentration of less than 7 ppm; the precipitated solids compacted well. Mine waters high in ferrous iron required long reaction times (>15 min) with coarse limestone, and the treatment had to be supplemented with lime in a second stage to produce acceptable waters in a short reaction time. Nine mine waters of widely ranging acid and iron concentrations were treated by one or more of these methods for comparison with lime neutralization. These exploratory investigations show that coarse limestone, one of the cheapest neutralizing agents known, is potentially useful for treating mine water discharges.

It is recommended that investigations of neutralization processes should continue to (1) study the effect of contributing factors to the overall reaction such as size distribution and composition of limestone, residence time, temperature, degree of agitation and abrasion, and air-liquid-solid interfacial area; (2) design an efficient reactor to treat large volumes; and (3) develop plant design criteria for neutralization of acid mine waters.

## INTRODUCTION

The Bureau of Mines, as a special adjunct to its comprehensive research program on the chemistry of mine waters, recently undertook a short-term project to define quickly and clearly the investigative effort that would be required to develop practical plant-design parameters for treating acid mine water. This project was initiated by the Bureau's Director, at the request of a group of coal mine operators, with the long-range goal of yielding an effluent acceptable for discharge into streams and a sludge amenable to effective and economic disposal.

A research program was outlined and implemented, encompassing an extensive field of investigation including neutralization, oxidation, settling characteristics, and sludge dewatering techniques. It was generally agreed that water treatment testing should consist of neutralization with lime, with limestone, and with limestone followed by lime. The emphasis on the use of limestone as a neutralization agent was due mainly to its low cost and easy availability.

## ACKNOWLEDGMENTS

The cooperation of many representatives of the coal mining industry is gratefully acknowledged. These included Rochester & Pittsburgh Coal Company; Pittsburgh Coal Company, Division of Consolidation Coal Company; Bethlehem Steel Company; Powell Coal Company; and Jones & Laughlin Steel Corporation. Without their assistance and personal guidance in site selection, their making available temporary field laboratory space, and free access to their records of water analyses, progress of the work would have been much slower. The free exchange of information is exemplified by the disclosure by Rochester &

Pittsburgh Coal Company officials that they had been investigating a promising limestone neutralization process.

We are grateful for their demonstrated concern for maintenance of safe working conditions in crowded and potentially hazardous locations.

We also acknowledge the efforts of C. E. Chamberlain, chemist, and K. D. Curley and Fred Pichi, technicians, for their high efficiency throughout a difficult and arduous field program.

#### WATERS TESTED

A reconnaissance survey and sampling of mine waters representing a wide range of composition were conducted on sites of the cooperating coal mining companies. Nine mine water discharges were selected. Typical analyses of these waters are presented in table 1.

TABLE 1. - Analysis of mine waters collected during reconnaissance

Mine water.....	A-1	A-2	B-1	B-2	B-3	C-1	D-1	E-1	E-2
pH.....	2.80	3.65	2.85	4.20	3.20	3.10	6.70	2.70	6.10
Total acidity <sup>1</sup> .....ppm	1,215	685	775	1,720	1,380	1,050	5	4,530	55
Dissolved solids.....ppm	3,180	( <sup>2</sup> )	2,520	5,330	3,490	3,310	2,090	( <sup>2</sup> )	7,680
Total sulfates (as SO <sub>4</sub> ).....ppm	2,150	( <sup>2</sup> )	1,660	3,350	2,180	2,175	1,150	( <sup>2</sup> )	4,440
Total iron.....ppm	294	168	154	713	406	425	42	1,176	56
Ferrous iron, Fe <sup>++</sup> ...ppm	98	162	0	699	70	( <sup>2</sup> )	35	577	42
Calcium, Ca <sup>++</sup> .....ppm	148	( <sup>2</sup> )	220	360	188	249	172	( <sup>2</sup> )	392
Magnesium, Mg <sup>++</sup> .....ppm	( <sup>2</sup> )	( <sup>2</sup> )	83	117	95	109	41	( <sup>2</sup> )	107
Eh (oxidation potential) .....mv	675	( <sup>2</sup> )	800	435	600	615	165	( <sup>2</sup> )	260
Conductivity.....mmho	2,900	( <sup>2</sup> )	2,430	4,040	2,800	2,811	2,420	( <sup>2</sup> )	8,300

<sup>1</sup>End point = pH 8.20 at 60° C.

<sup>2</sup>Not determined.

The composition of any mine water discharge is variable and subject to almost daily fluctuation. The waters used in the field tests were taken 1 to 2 months after the reconnaissance sampling. The composition of the mine waters actually tested and the test results are given in the section describing the test results.

#### TEST PROGRAM

##### Procedure

The characteristics of mine water change with time; consequently, it was necessary to conduct experimental work at the point of discharge. The field equipment consisted of laboratory analysis facilities and neutralization, settling, and filtration equipment. Samples of mine water were taken from the discharge for analysis and neutralization. The reaction was monitored for pH and for ferrous iron concentrations. In most cases, the initial test was run

beyond the point of complete iron removal to obtain a pH trend in the neutralization process. When that point was determined, additional batches of neutralized water were made to provide sufficient volume for settling and filtration tests. Samples for detailed analysis at the Bureau of Mines laboratories were withdrawn at various stages of treatment. This procedure was substantially the same for all water treated.

### Reactor

A modified cement mixer, 1/4-cubic-yard capacity, was used as a reactor (fig. 1). Except for continuous tests, all neutralization tests were conducted on a batch basis, keeping the reactor conditions constant. Rather than design a reactor in the short time allotted this project, it was decided that a cement mixer could impart the necessary interaction between mine water, limestone, and air. The mixer was driven by a gasoline engine at constant speed of 22 rpm. The mixer was held at a set angle of tilt about 20° from the horizontal for all tests to insure containment of the limestone and prevent loss of water by overflow and splashing. The inside surface of the mixer was coated with an inert epoxy resin to prevent contamination of the waters by extraneous iron that might be dissolved by the acid water.

### Neutralizing Agents

The neutralizing agents used for the tests were high-calcium, double-screened (1- by 1/2-inch and 1/2- by 1/4-inch) limestones and commercial hydrated lime. The analysis of the reagents is shown in table 2. The limestones were obtained locally from lime and stone companies as standard commercial products.

TABLE 2. - Analysis of neutralizing agents, pct

Composition	Limestone		Composition	Lime
	(1- by 1/2-inch)	(1/2- by 1/4-inch)		
CaCO <sub>3</sub> .....	94.27	98.81	CaO.....	73.17
MgCO <sub>3</sub> .....	.21	.58	MgO.....	1.03
Silica.....	4.07	( <sup>1</sup> )	Iron.....	.22
Iron.....	.29	.06		

<sup>1</sup>Not determined.

### Analytical Methods

Methods of analysis used in the field are as follows:

1. pH. Determined by electrometric measurement by means of the glass electrode.

2. Acidity. Sample was oxidized and boiled to hydrolyze all iron salts and remove CO<sub>2</sub>, then titrated with standard sodium hydroxide to an electrometric pH of 8.2 at 60° C.

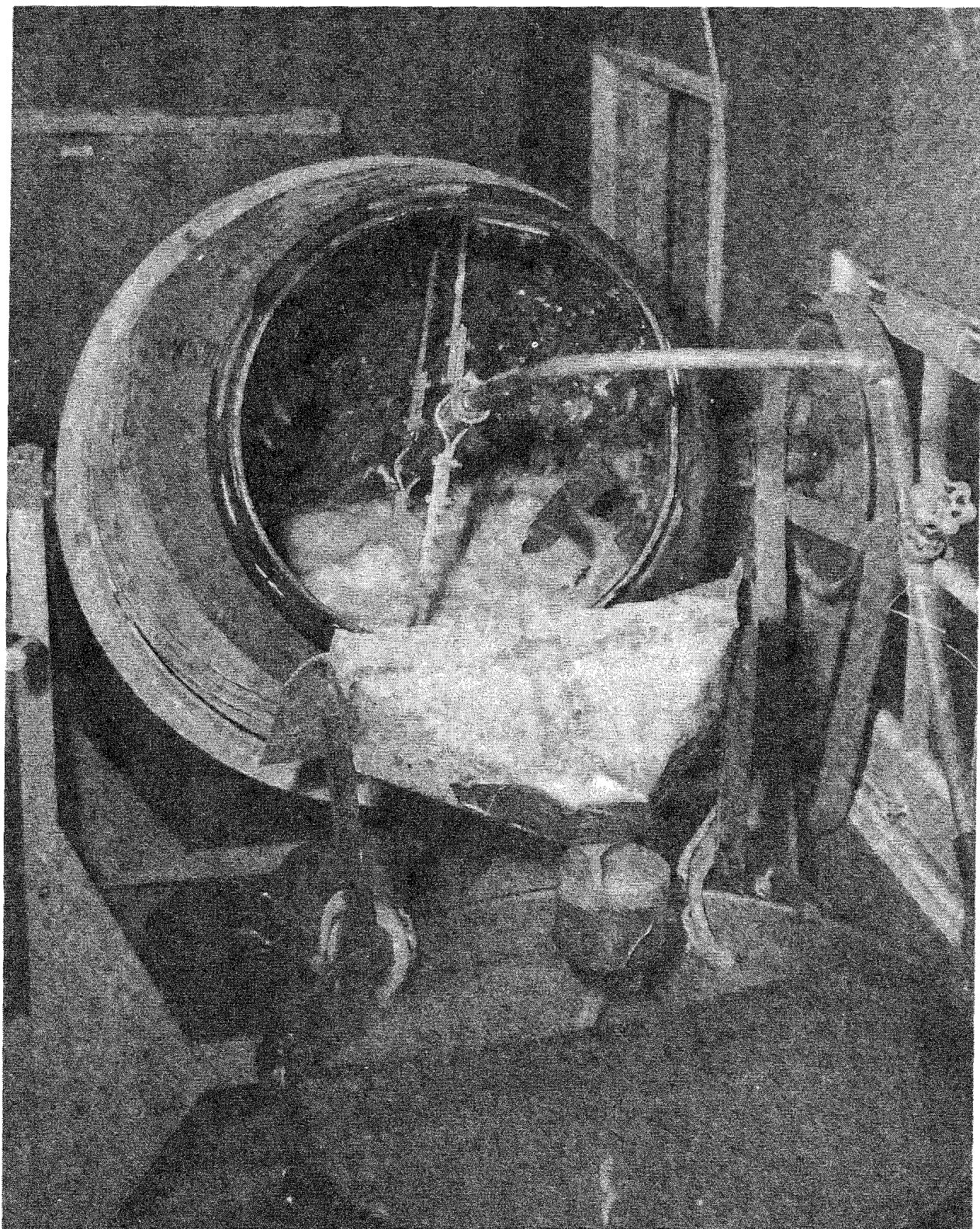


FIGURE 1. - Photograph of Reactor.

3. Iron, ferrous. Sulfuric acid-phosphoric acid mixture and sodium salt of diphenylamine sulfonate indicator were added to the sample and titrated with standard potassium dichromate.

4. Iron, total. Sample was oxidized with bromine water, iron precipitated with ammonium hydroxide, filtered and redissolved with hydrochloric acid, reduced with stannous chloride, and titrated with standard potassium dichromate.

Other determinations were made in the laboratory as follows:

1. Carbon dioxide. Evolved by acid and absorbed in ascarite.

2. Sulfate. Precipitated as barium sulfate and weighed as such.

3. Calcium. Precipitated as calcium oxalate, ignited, and weighed as calcium oxide.

4. Magnesium. Precipitated as magnesium ammonium phosphate, ignited, and weighed as magnesium pyrophosphate.

5. Silica. Hydrochloric acid insoluble material was ignited and weighed; then evaporated with hydrofluoric acid to expel  $\text{SiO}_2$ . Difference in weight is  $\text{SiO}_2$ .

6. Water. Sample air dried at  $85^\circ \text{F}$ , then dried to constant weight at  $105^\circ \text{C}$ .

7. Solids, weight-percent. Net weight of sample obtained by weighing sample plus bottle, and subtracting weight of bottle. Filtered by gravity on weighed filter paper. Paper and contents dried at  $105^\circ \text{C}$  to constant weight.

8. Eh (oxidation potential). Electrometric measurement of oxidation potential by means of an electrode pair consisting of an inert (platinum) electrode and a reference (calomel) electrode.

#### Limestone Neutralization

The literature and laboratory tests on the use of limestone--coarse, powdered, and granular--as an acid neutralizing agent indicate that the terminal pH is usually in the range of 6.0 to 6.5. This pH, however, is not maintained on a continuing basis. The limestone reactivity steadily decreases; this is due in part to the deposition of reaction solids on the surface of limestone particles. Failure to remove carbon dioxide from the solution, resulting in the formation of carbonic acid, also inhibits the neutralizing action.

Exploratory tests in the laboratory using acid mine water with coarse (1- by 1/2-inch) limestone in a small cement mixer, which can be construed to be a tilted revolving chamber with baffles and lifter plates, resulted in a terminal pH above 8. The inordinately high alkalinity obtained gave immediate impetus to reinvestigate this reaction. The present explanation is that this

high pH is achieved by vigorous cascading agitation to provide (1) abrasion to eliminate coating of limestone particles with precipitated solids and continual renewal of reactive surface; (2) large aeration surface for oxidation of ferrous iron; and (3) removal of  $\text{CO}_2$  from the solution.

Prior efforts to utilize limestone<sup>3</sup> as an alkaline agent were concerned with stoichiometric proportions or a small excess of limestone. Theoretically, smaller particles should contribute to greater activity. However, this is not the basis to maintain sustained high activity. A great excess of limestone is needed to provide a constantly renewed reactive surface. For most of the batch neutralization tests, the ratio was approximately 1 part water to 2 parts limestone, or 10 gal (83 lb) of water to 150 lb of limestone.

#### Lime Neutralization

Most industrial acid waste liquors are neutralized with lime. The lime used in the form of a quicklime, or hydrate, usually provides a cheap source of alkalinity. The reactivity of commercial lime is great enough to neutralize economically the acid and precipitate the high iron concentrations normally encountered in industrial waste liquors.<sup>4</sup> Since acid mine drainage, at worst, contains only a fraction of the acid and iron found in industrial acid waste liquors, the use of lime supplies a ready solution. The disadvantages in the use of lime as a treatment of mine waters are (1) the high cost of alkalinity and (2) that the precipitated solids occupy large volumes which must be disposed of with difficulty. The technology of lime treatment of acid wastes is highly advanced so that estimates of treatment costs can be obtained readily.

#### Limestone-Lime Neutralization

Another method of treating mine waters was investigated using primary treatment with limestone followed by secondary lime treatment. In most cases, the mine water was allowed to mix with the coarse limestone in the reactor for at least 1 min and then the lime was added in small increments until the pH of the solution reached 8 to 9.

Using limestone, long reaction periods were needed to treat mine waters high in ferrous iron. With lime, the same waters were rapidly neutralized, but larger amounts of reagent were required to precipitate all the iron. Therefore, a dual treatment using the two alkaline agents would produce an effect combining the best of both reactions.

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<sup>3</sup>Boynton, Robert S. Chemistry and Technology of Lime and Limestone. Interscience Publishers, New York, 1966, pp. 370-372.

<sup>4</sup>Hoak, Richard D., Clifford J. Lewis, Charles J. Sindlinger, and Bernice Klein. Lime Treatment of Waste Pickle Liquor. Ind. and Eng. Chem., v. 39, No. 2, 1947, pp. 131-135.

### Continuous Limestone Neutralization

The limestone reactor was converted from batch neutralization to continuous operation. A raw water feed line was introduced into the reactor with the discharge outlet submerged in the coarse limestone. A discharge well was provided near the opening of the reactor for insertion of pH electrodes to continuously monitor the treated water discharge. Settling containers also were provided to collect concentrated solids and clarified effluent.

Piping difficulties imposed limitations on the raw feed supply. As a result, a flow rate of only 1 to 1-1/4 gpm was obtained. The first test was conducted with 150 lb of 1- by 1/2-inch limestone. The continuous operation was conducted for about 4-1/2 hours on the first day and for about 5-1/2 hours on the following day. Approximately 700 gal of raw water, pH 5.8 and ferrous iron content of 70 ppm, at a temperature of 12° to 13° C was treated. The equilibrium pH varied from 7.80 to 7.55. The ferrous iron concentration of the reactor discharge in the settling basin and the clarified effluent was determined at intervals throughout the test. Ferrous iron concentration in the treated water did not exceed 3 ppm.

The second test was conducted with 150 lb of 1/2- by 1/4-inch limestone at an initial raw water feed rate of 2.5 gpm, with pH of 5.6 and ferrous iron content of 90 ppm. A pH of 7.15 was obtained in the reactor and 7.35 in the settling basin. An additional 117 lb was added to the reactor. The pH rose slightly to 7.40, but considerable ferrous iron, about 50 ppm, was still present. The test was run for approximately 30 min. The temperature of the raw water in this test was 6° C (43° F).

The third test consisted of 300 lb of 1/2- by 1/4-inch limestone with a raw water feed rate of 2-3/4 gpm. After 30 min of operation, the pH steadied at 7.6. The ferrous iron content in the treated water was 22 to 28 ppm. The raw water feed was reduced to 2 gpm with a resulting pH of 7.8, but the iron content remained at 22 ppm. The temperature of this water was 6° C (43° F).

### TEST RESULTS

#### pH Increase With Limestone Treatment

Figures 2 through 7 show the change in pH with time as the reaction progressed for all waters tested. The points on the curve indicate the time a sample of the water was withdrawn from the reactor and the pH determined electrometrically. The total reaction time was arbitrarily set at 20 min, with several tests prolonged beyond that.

#### Ferrous Iron Depletion With Limestone Treatment

Figure 8 shows the concentrations of dissolved ferrous iron ( $\text{Fe}^{++}$ ) as the reaction progressed. The ferrous iron determination was made from the same sample that was withdrawn for pH measurement. Relatively few ferrous iron determinations were obtained. The ferrous iron concentration is dependent on

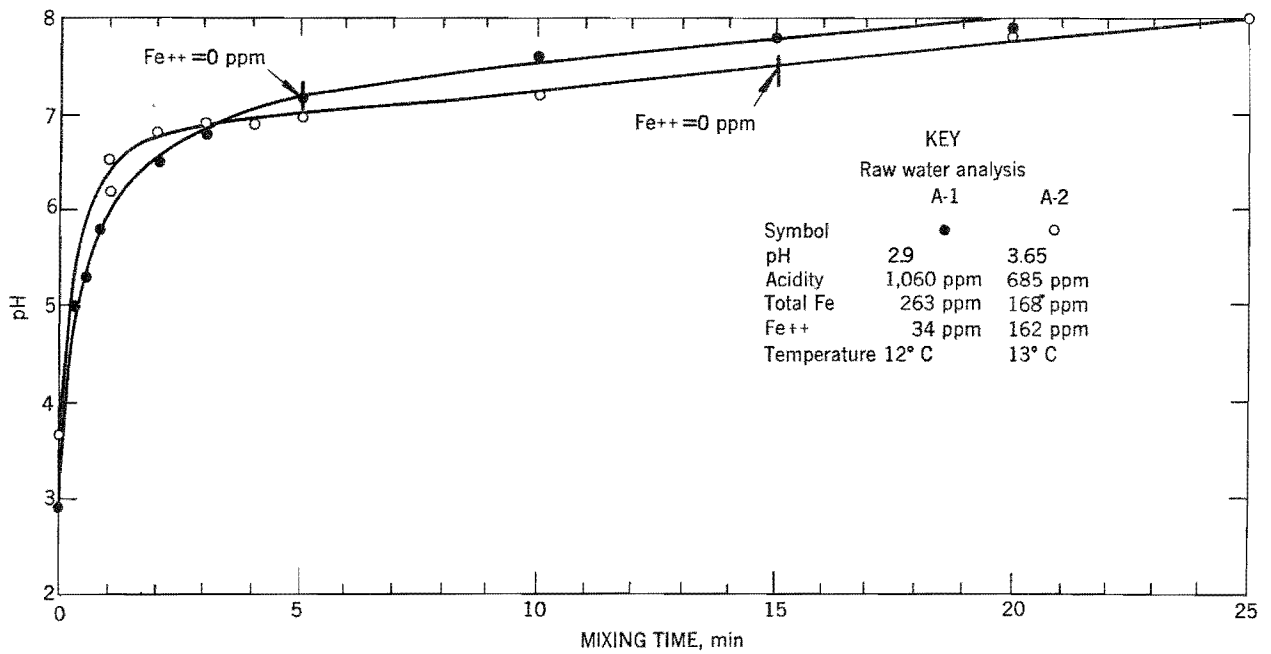


FIGURE 2. - Limestone Neutralization of A-1 and A-2 Mine Waters.

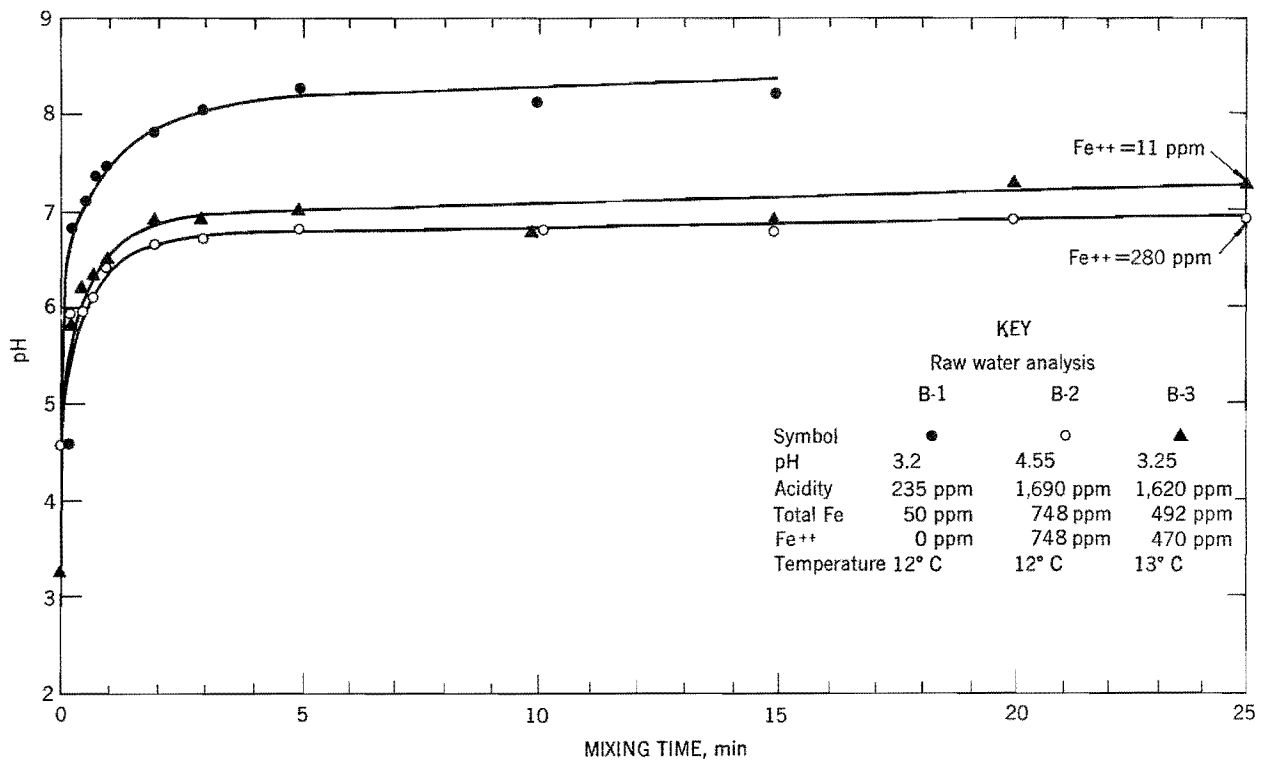


FIGURE 3. - Limestone Neutralization of B-1, B-2, and B-3 Mine Waters.

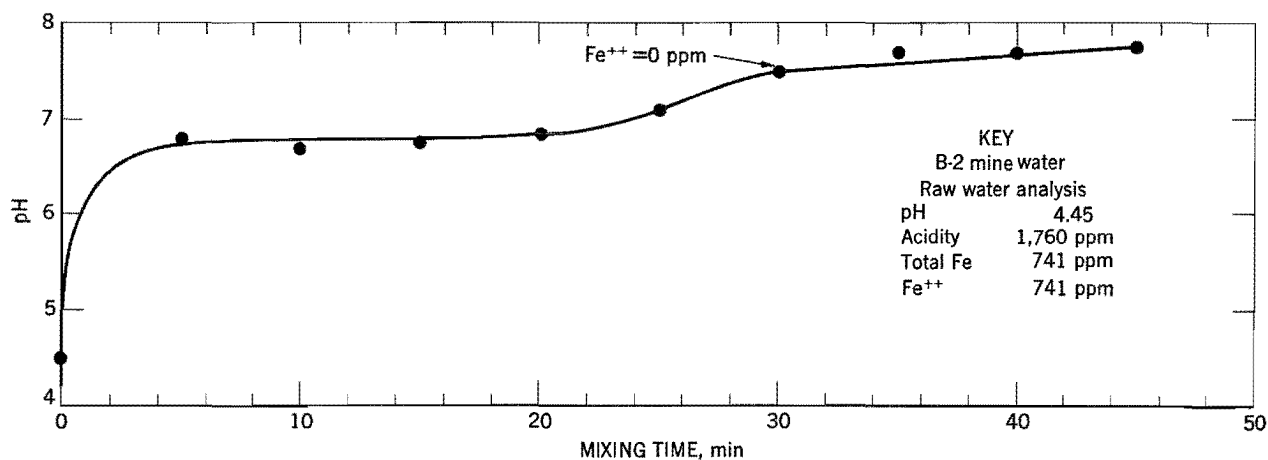


FIGURE 4. - Limestone Neutralization of B-2 Mine Water With 250 lb Limestone.

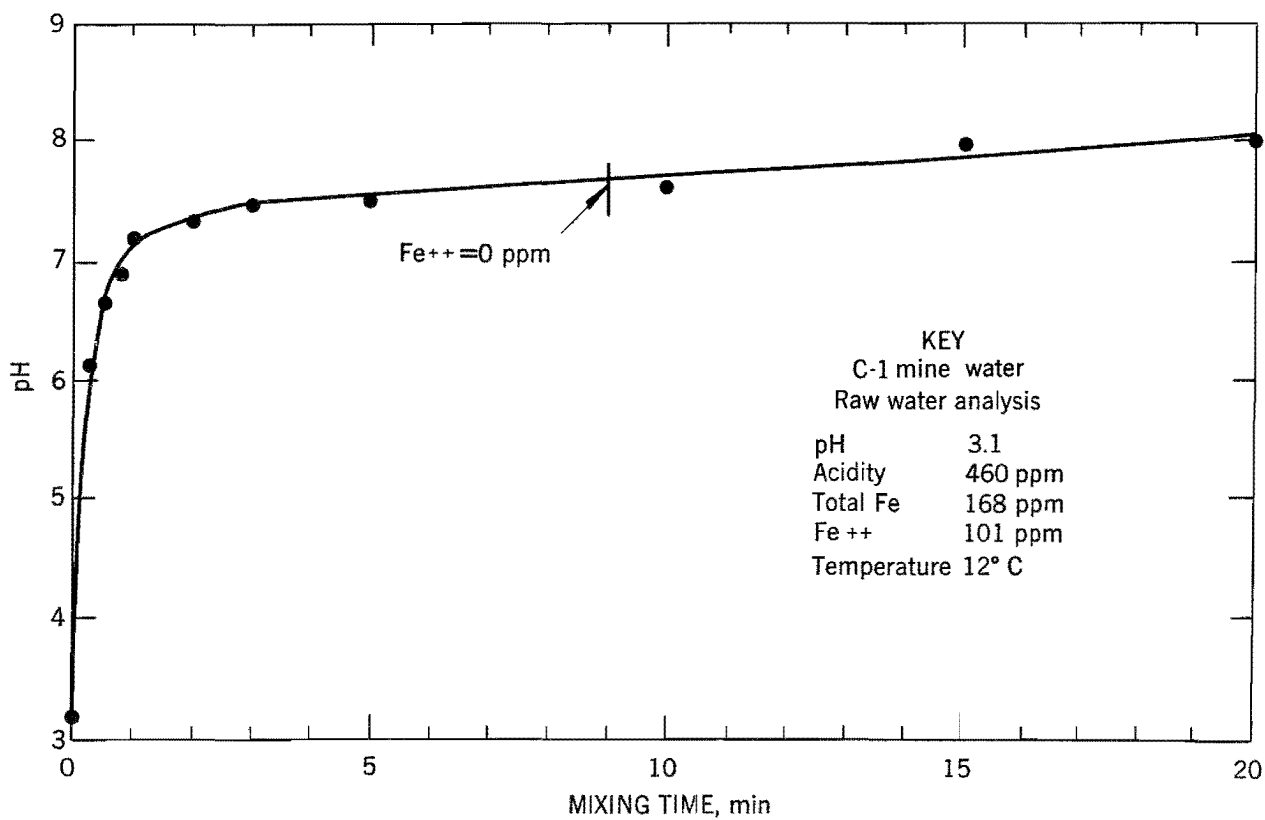


FIGURE 5. - Limestone Neutralization of C-1 Mine Water.

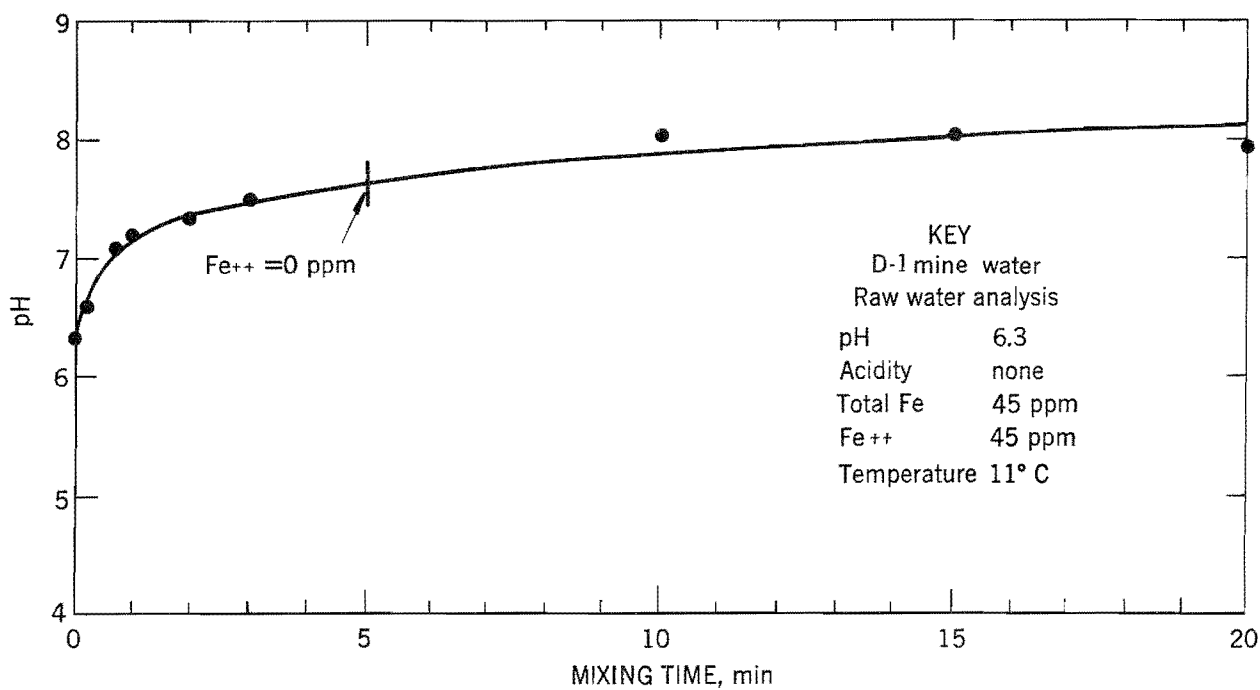


FIGURE 6. - Limestone Neutralization of D-1 Mine Water.

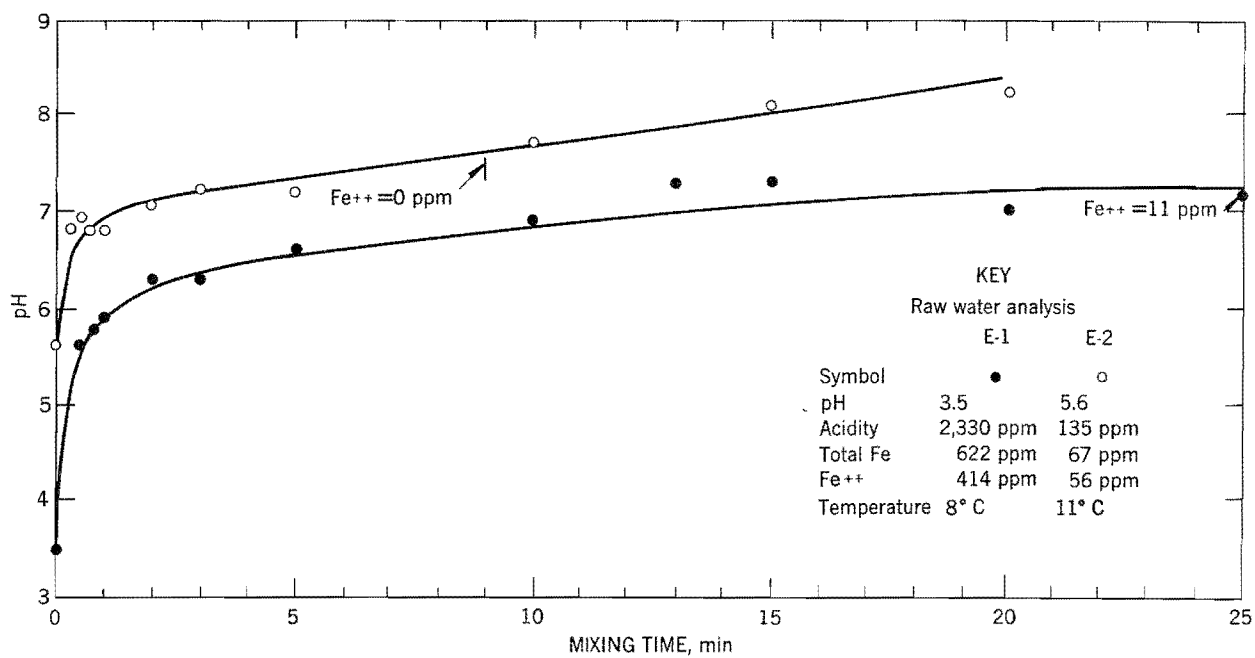


FIGURE 7. - Limestone Neutralization of E-1 and E-2 Mine Waters.

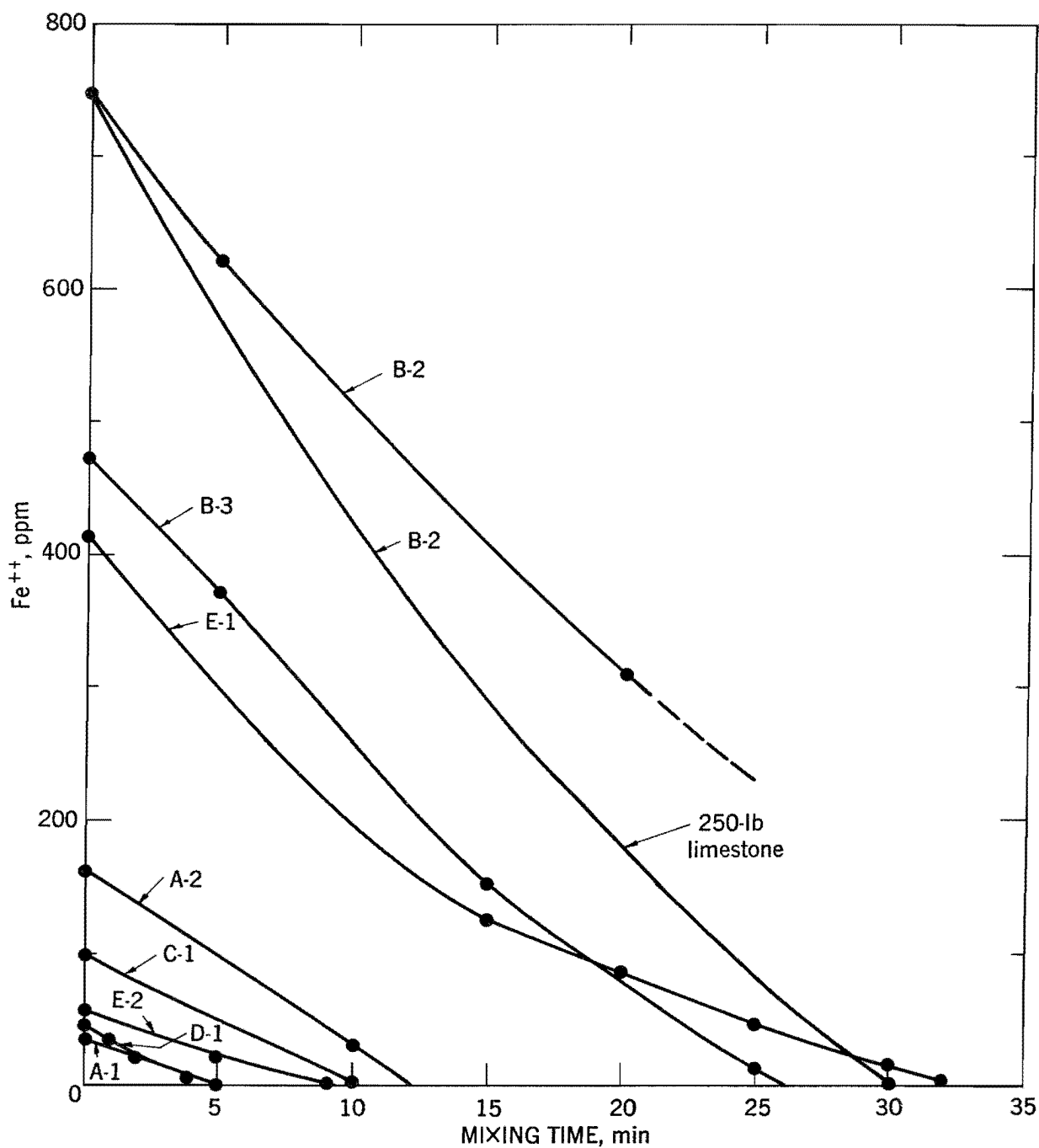


FIGURE 8. - Ferrous Iron Depletion With Limestone Treatment of Various Mine Waters.

reaction time, but the determination itself is time consuming; therefore, reactor samples could not be saved for later analysis.

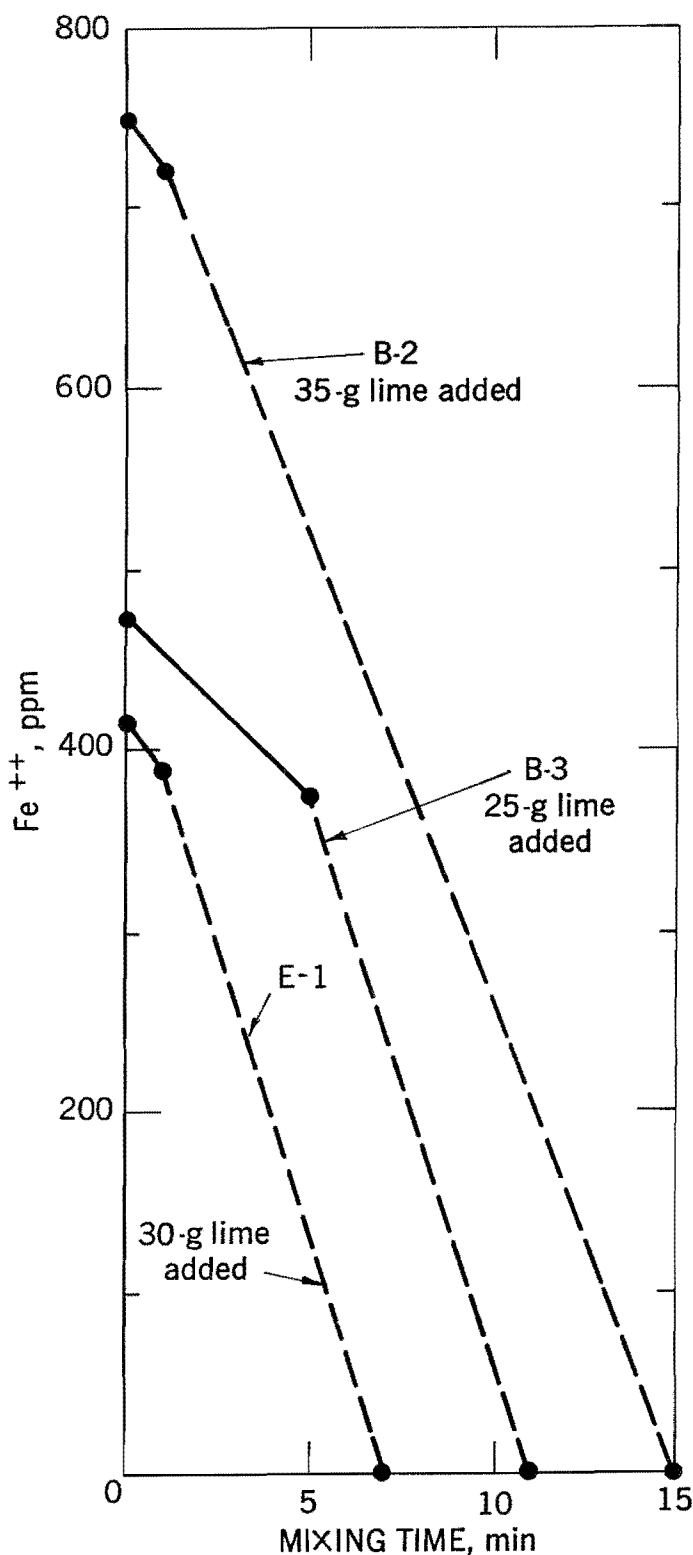


FIGURE 9. - Ferrous Iron Depletion With Limestone-Lime Mixed Treatment.

#### Ferrous Iron Depletion With Limestone-Lime Treatment

Figure 9 shows the ferrous iron depletion trend of several mine waters high in ferrous iron with a primary limestone treatment of 1 to 5 min, and with indicated amounts of hydrated lime added and mixed for the remaining time.

#### Sludge Settling Rates and Sludge Volumes

As soon as the neutralization process was completed, portions of the treated water were placed in 1-liter graduated cylinders for settling rate and sludge volume determinations. The results of these tests are shown in figures 10 through 18. Well-defined interfaces between settled solids and supernate were observed where there were high solids concentrations; dilute solids concentrations, especially those formed with lime, showed poorly defined interfaces in the early stages of settling.

These settling rate curves show that wherever limestone is used for neutralization treatment, either alone or with lime, the settling rates and volumes of compacted solids indicate more favorable conditions for solids-liquid separation than when lime alone is used.

It is obvious that the more rapid settling rates and high degree of compaction for limestone-treated water are due, in part, to the excess limestone abraded during the mixing action. This, of course, can be minimized but it is expected that the favorable influence of limestone on settling and

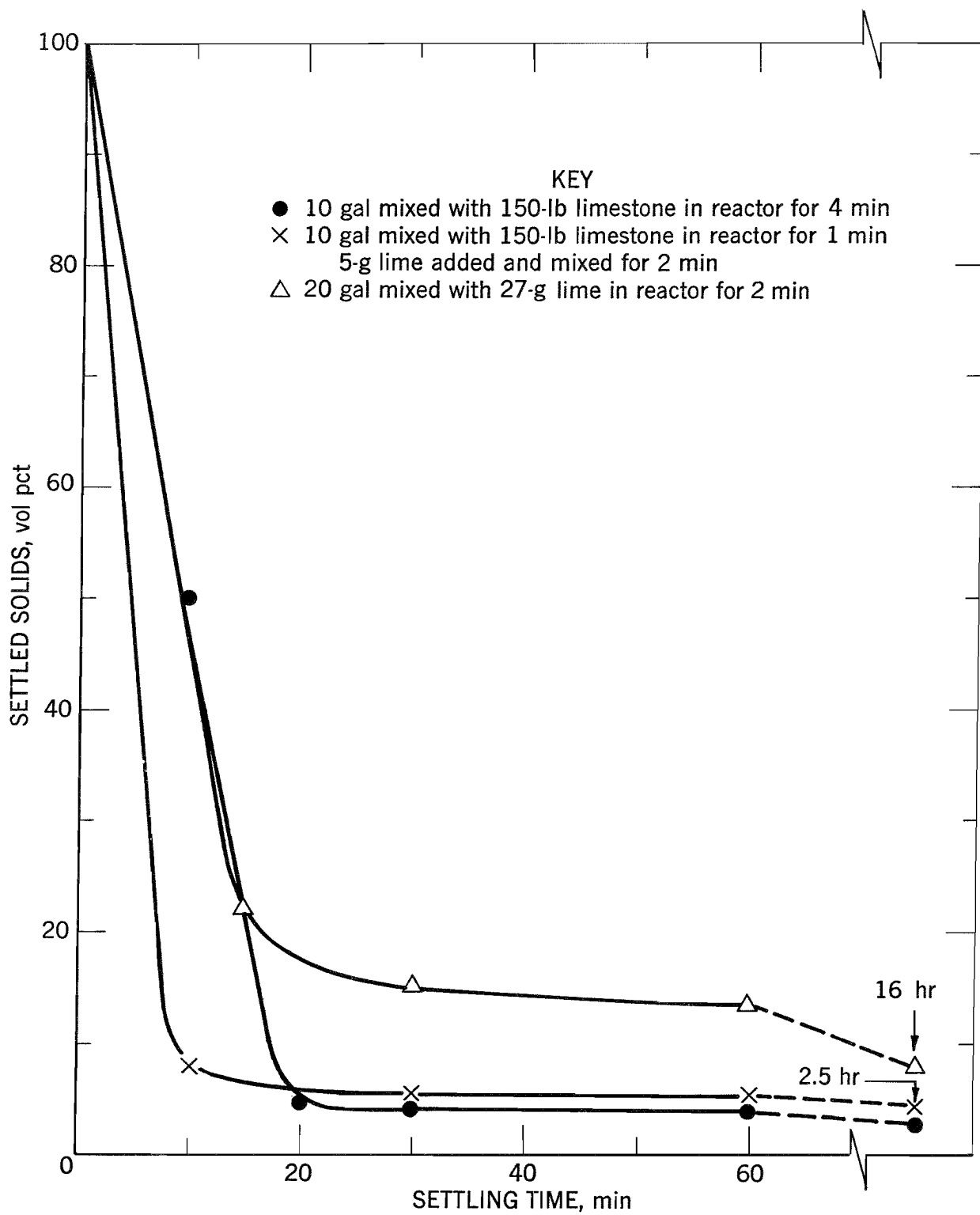


FIGURE 10. - Settling Rate of Sludges From A-1 Treated Water.

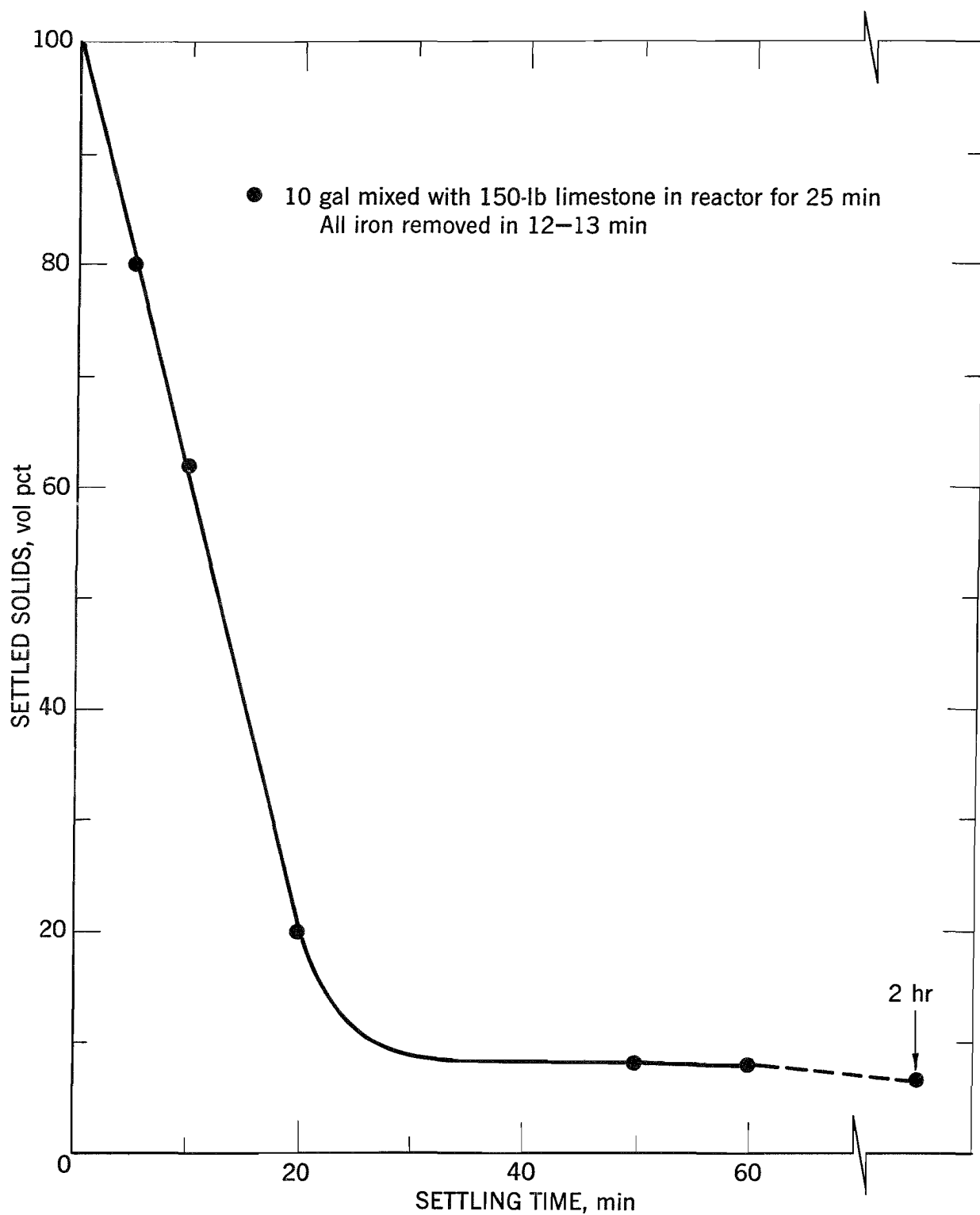


FIGURE 11. - Settling Rate of Sludge From A-2 Treated Water.

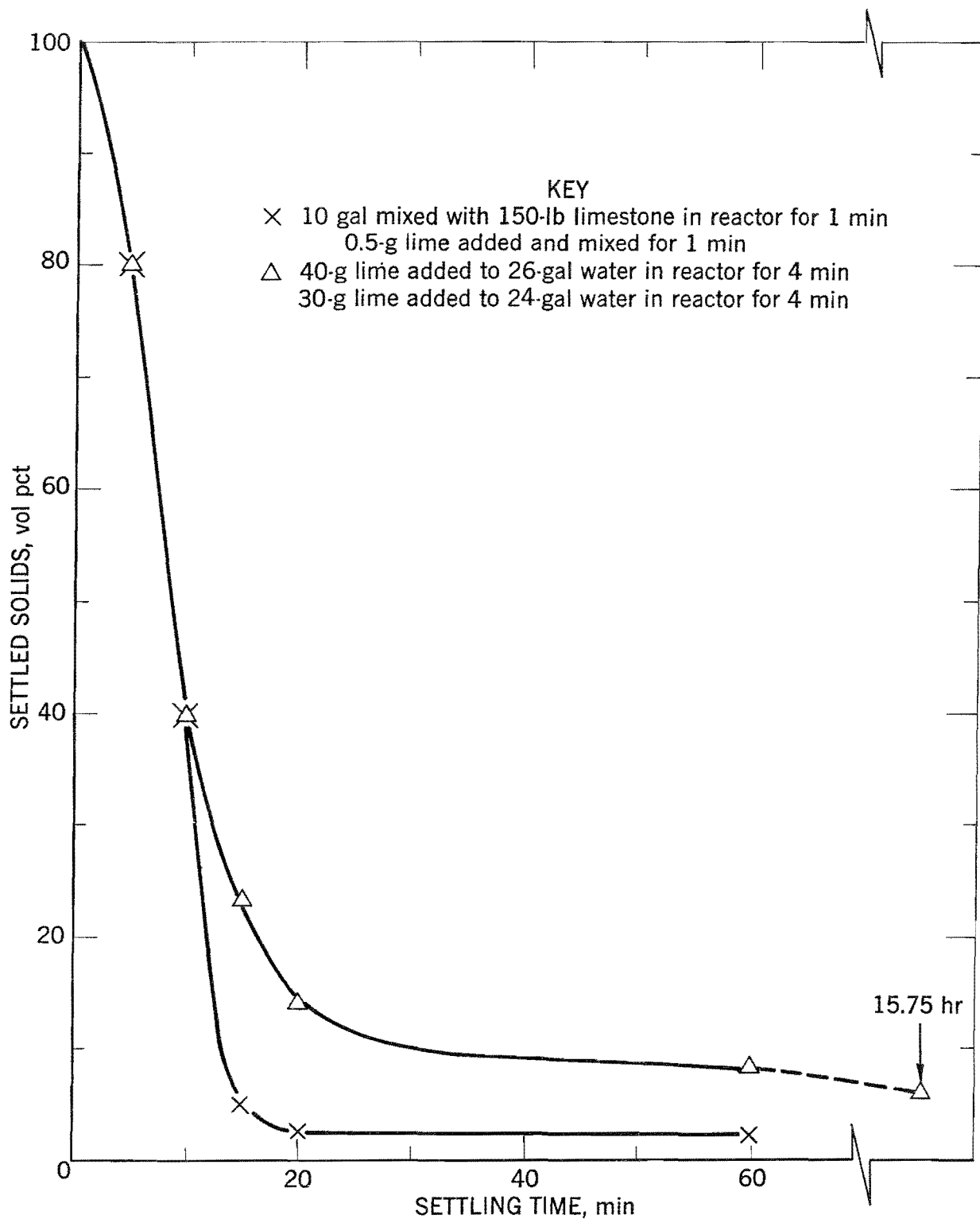


FIGURE 12. - Settling Rate of Sludges From B-1 Treated Water.

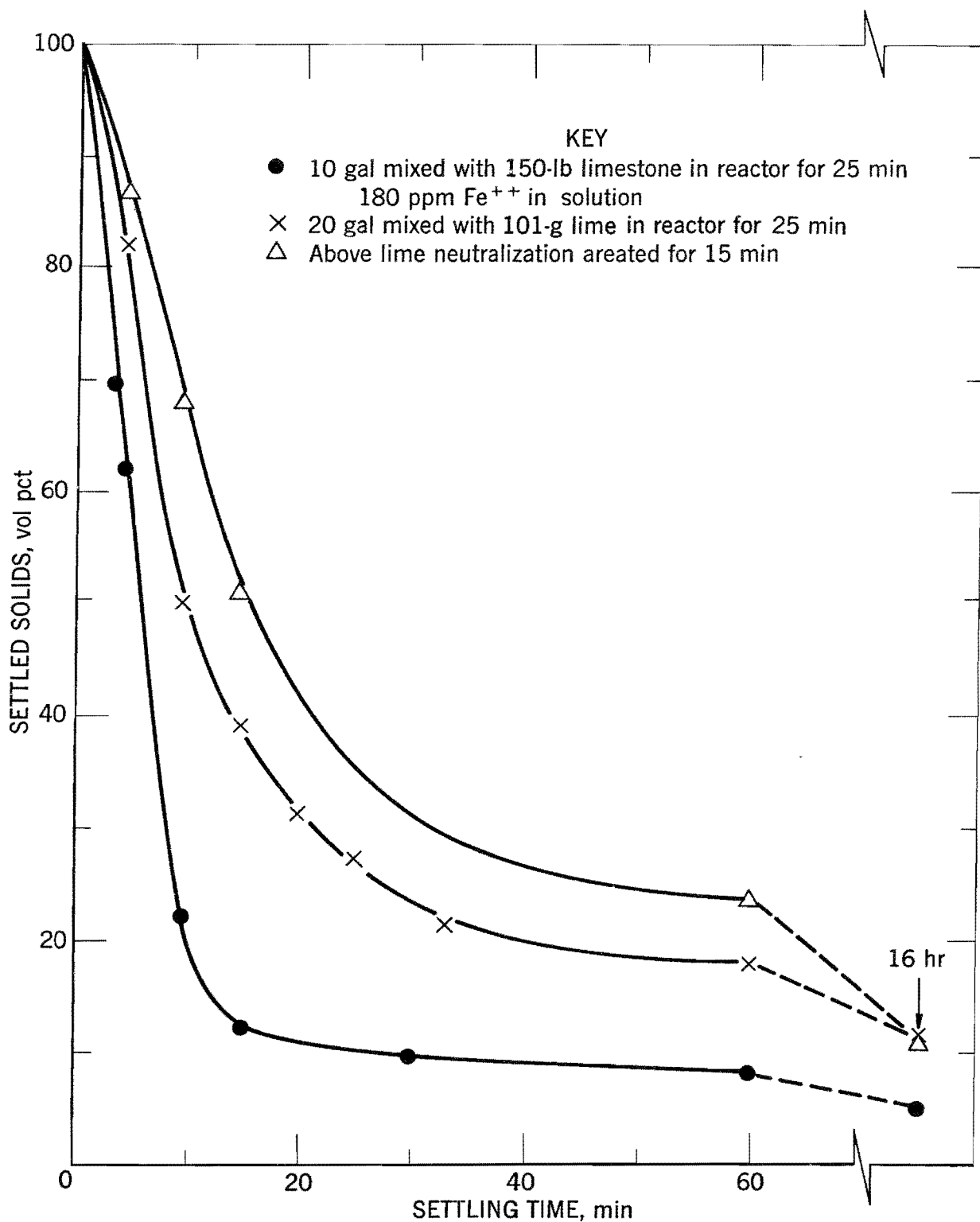


FIGURE 13. - Settling Rate of Sludges From B-2 Treated Water.

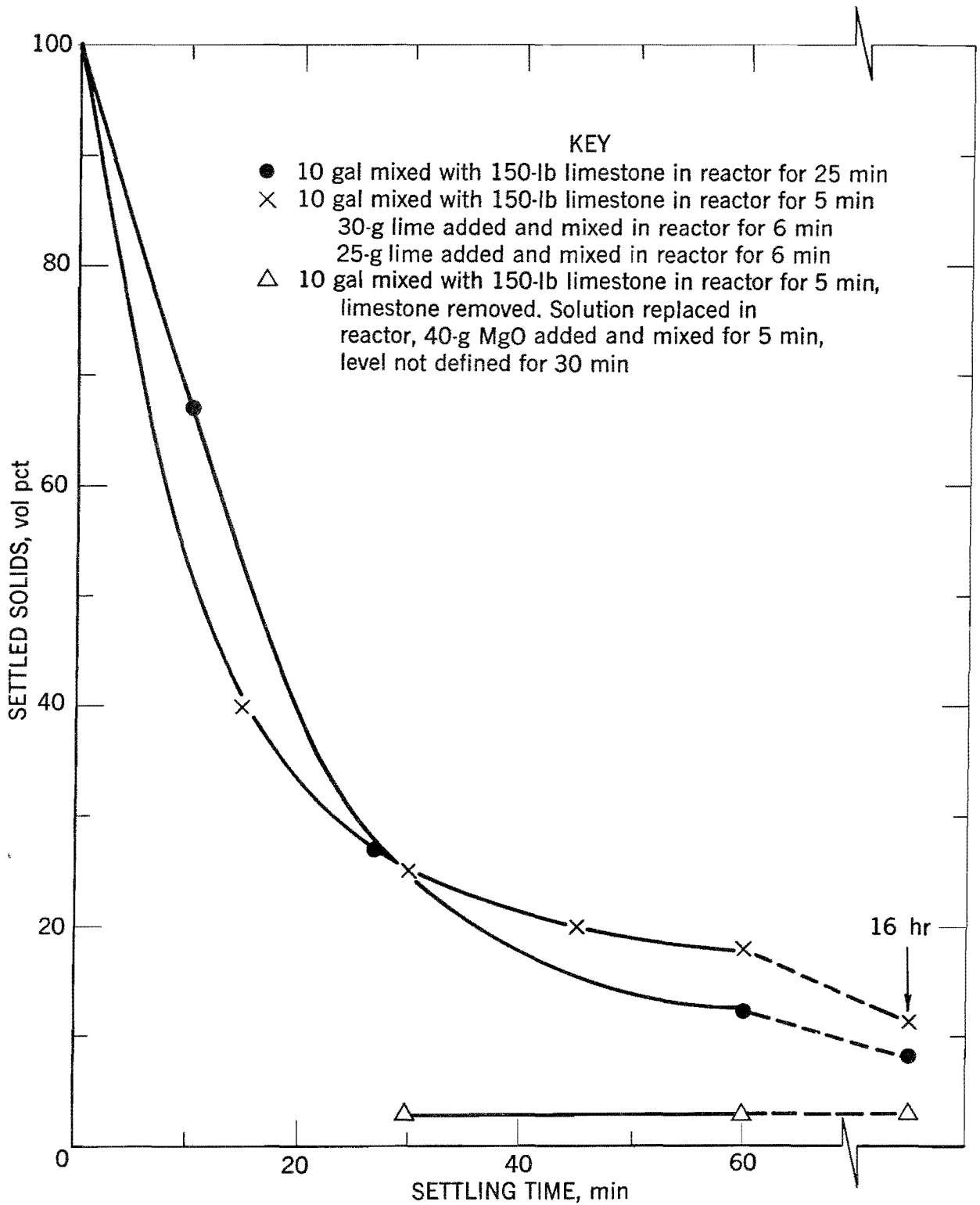


FIGURE 14. - Settling Rate of Sludges From B-3 Treated Water.

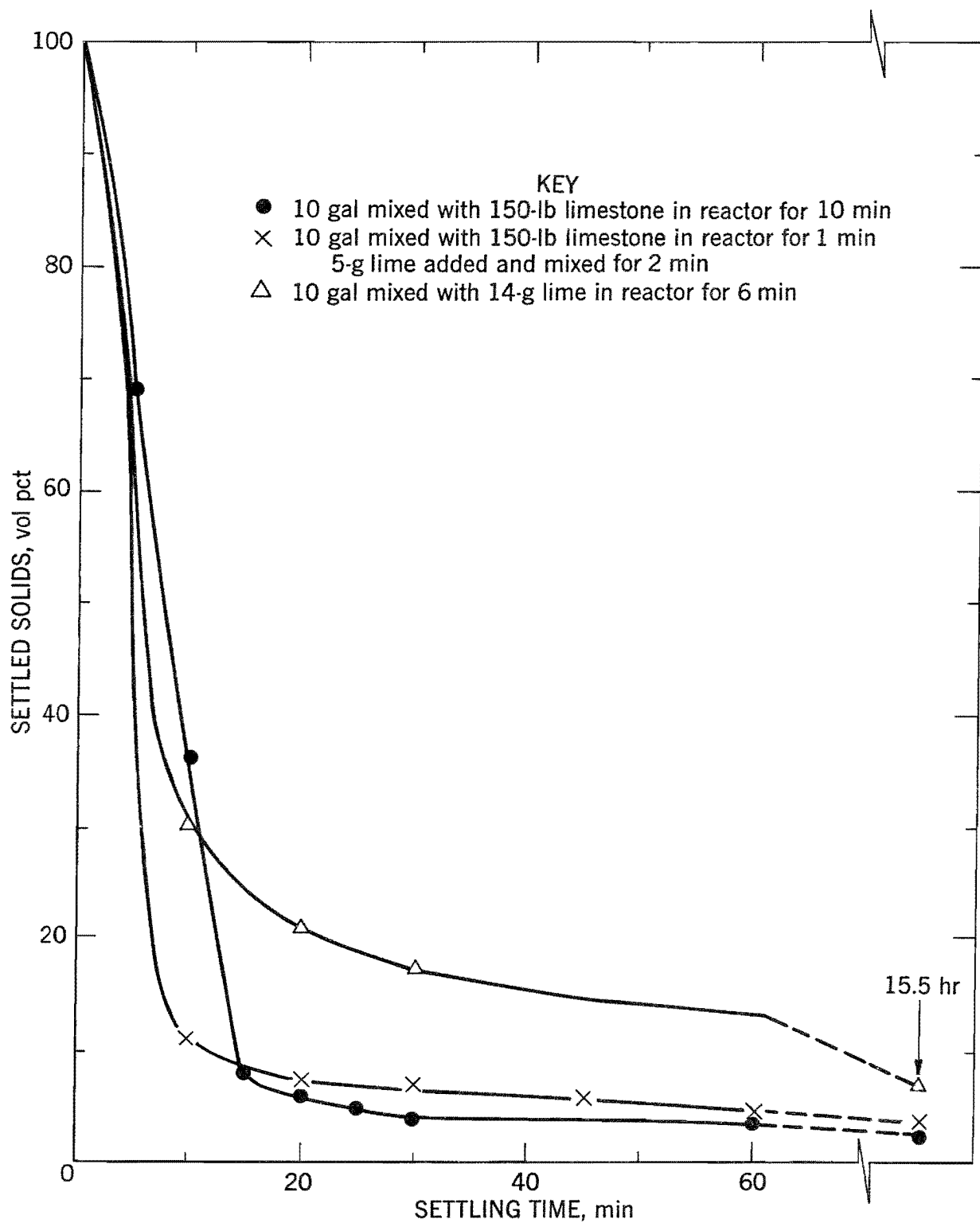


FIGURE 15. - Settling Rate of Sludges From C-1 Treated Water.

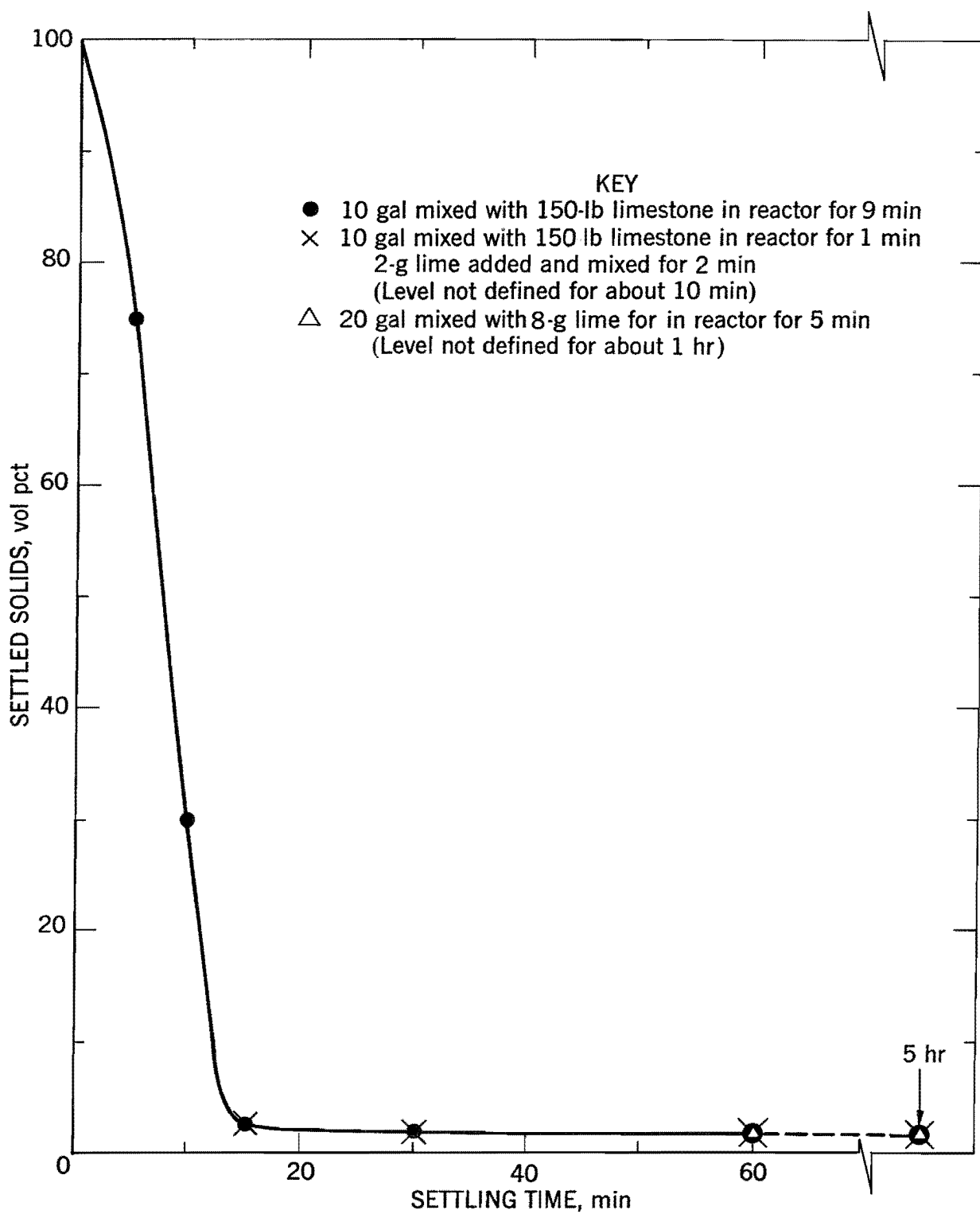


FIGURE 16. Settling Rate of Sludges From D-1 Treated Water.

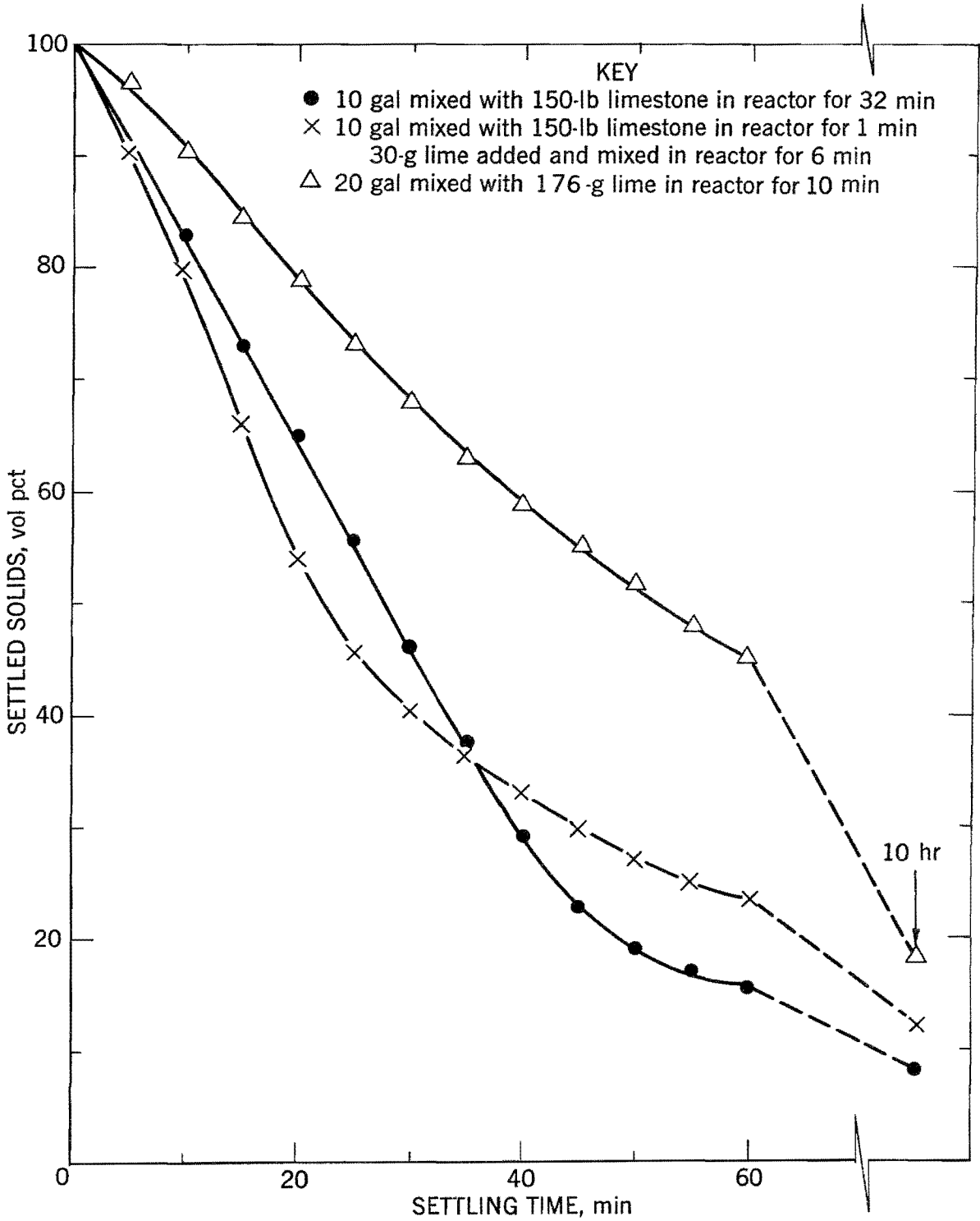


FIGURE 17. - Settling Rate of Sludges From E-1 Treated Water.

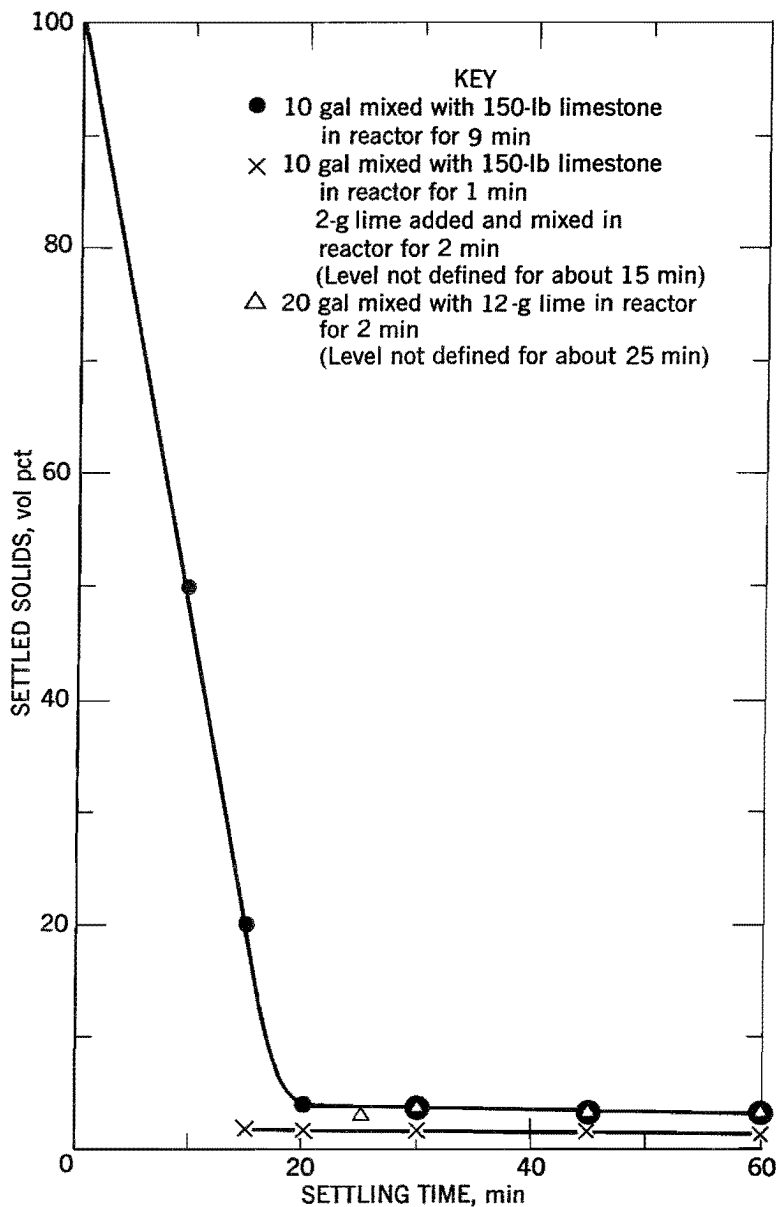


FIGURE 18. - Settling Rate of Sludges From E-2 Treated Water.

compaction characteristics will remain. The discussion of this effect will be deferred to a later report.

#### Summary of Batch Test Results

The analyses of the waters treated in the field and the results of all the batch neutralization tests are summarized in table 3. Also included are the volumes and weights of settled solids from the batch tests.

#### Continuous Treatment With Limestone and Ferrous Iron Depletion

Continuous limestone neutralization tests were conducted on the E-2 mine water using 1/2- by 1-inch and 1/4- by 1/2-inch limestones.

With low flow rates of about 1 gpm, the reactor operated satisfactorily; however, with higher flow rates, an effluent quality meeting minimum standards could not be attained. Thus, it appears that the reactor, as used for batch neutralization, was operating efficiently. The reactor functions as both a neutralizer and oxidizer;

consequently, it was not possible to separate the reactions for rate studies of each separate process. Continuous neutralization could not be studied effectively at the flow rates used and under variable temperature conditions.

TABLE 3. - Composition of waters treated, batch test results, and volume and weight of solids after 1 hour settling

Mine water	Raw water analysis					Mine water treatment											Volume and weight of solids, 1 hour settling, pct					
	Temperature, °C	pH	Acidity (as CaCO <sub>3</sub> ), ppm	Total Fe, ppm	Fe <sup>++</sup> , ppm	Limestone <sup>1</sup>			Limestone-lime <sup>2</sup>				Lime <sup>3</sup>				Limestone		Limestone-lime		Lime	
						Final pH	Time, min	Fe <sup>++</sup> , ppm	Final pH	Time, min	Fe, ppm	Lime, g	Final pH	Time, min	Fe <sup>++</sup> , ppm	Lime, g	Vol	Wt	Vol	Wt	Vol	Wt
A-1	12	2.90	1,060	263	34	7.35	5	0	7.00	3	6	5	8.20	2	0	27	5.5	-	10.0	-	13.0	-
A-2	13	3.65	-	168	162	7.70	15	0	-	-	-	-	-	-	-	-	8.0	-	-	-	-	-
B-1	12	3.20	235	50	0	8.05	3	0	8.60	2	0	.5	8.50	4	0	14	-	-	2.0	-	8.0	-
B-2	12	4.50	1,725	748	748	6.85	20	280	7.80	15	0	35	9.10	25	0	101	7.5	-	17.5	-	20.0	-
B-2 <sup>4</sup>	-	4.45	1,760	741	741	7.50	30	40	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B-3	13	3.25	1,620	492	470	7.20	25	11	8.60	6	0	25	-	-	-	-	-	-	-	-	-	-
C-1	12	3.15	460	168	101	7.30	10	0	8.50	3	0	5	9.15	6	0	28	3.5	1.43	5.0	0.38	13.5	0.06
D-1	11	6.30	-	45	45	7.60	5	0	7.75	3	0	2	7.55	5	0	8	1.5	.72	1.5	.26	1.5	.01
E-1	8	3.50	2,330	622	414	7.70	32	6	7.85	7	0	30	9.05	10	0	176	15.5	2.59	23.5	.86	45.0	.62
E-2	11	5.60	135	67	56	7.70	9	0	7.80	3	0	2	9.15	2	0	12	3.0	.80	1.0	.30	3.0	.04

<sup>1</sup>10 gal of mine water added to 150 lb of limestone (1- by 1/2-inch) in reactor at 22 rpm.<sup>2</sup>10 gal of mine water added to 150 lb of limestone, after 1 min in reactor, lime added and mixed.<sup>3</sup>20 gal of mine water; lime added and mixed in reactor at 22 rpm.<sup>4</sup>10 gal of mine water added to 250 lb limestone (1- by 1/2-inch) in reactor at 22 rpm.

## DISCUSSION

As mentioned in the Introduction, the use of limestone as a neutralizing agent in the treatment of mine water promises several important advantages. Lime is the most commonly used acid neutralizing agent and iron precipitant; consequently, the technology of lime neutralization is highly developed in water treatment and neutralization of pickle liquor from steel processing plants. Although there have been many attempts at using limestone for pickle liquor neutralization, none have been successful. Results of experiments described in this report indicate that the benefits to be derived from the use of limestone are greater than merely from the use of a cheaper reagent.

Mine waters have a much lower iron and acid sulfate concentration than pickle liquor, but the volume of water that may require treatment is many times greater and it must be recognized that, despite the general similarities, the differences are large.

Lime neutralization of acid mine waters yields a highly flocculent iron hydrate precipitate which does not compact well. In contrast, limestone neutralized mine waters do not yield a hydrophilic floc; the precipitated material is crystalline gypsum with coprecipitated iron oxide. A complete study of these contrasting reactions is being conducted as part of the continuing long range research program of the Bureau on the chemistry of mine waters.

The use of coarse limestone, with abrasive agitation, to provide a large surface of air-water-limestone interfaces appears to be the key to making limestone neutralization work. Fixed bed, coarse limestone and finely pulverized limestone reactions have failed in the past because surface coatings of neutralization products have hindered further reaction. Only in a dynamic system are reactive surfaces continuously renewed.

The oxidation of ferrous iron is highly temperature dependent.<sup>5</sup> This was demonstrated in limestone neutralization tests where a temperature drop of 5° C resulted in high ferrous iron concentration remaining in treated waters at a pH of about 7.5, in contrast with ferrous iron concentration less than 7 ppm achieved at pH 7.5 at 11° C.

For very high ferrous iron concentrations, the reaction time with limestone alone may be excessive. Yet with lime alone, the precipitated sludge would be extremely difficult to concentrate to a high solids concentration. The best effects of both reactions can be achieved by first neutralizing with limestone to a pH near 7, and using lime to complete the precipitation of the remaining iron. This is especially significant because the rate of lime neutralization of highly ferruginous acid waters is not well established. This too is being investigated as part of our long-range program.

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<sup>5</sup>Barthauer, G. L. Mine Drainage Treatment: Fact and Fiction. Coal Age, June 1966, pp. 79-82.