LABORATORY SCALE EVALUATION OF POTENTIAL LIME SUBSTITUTES FOR AMD TREATMENT

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ABSTRACT

A laboratory method to evaluate AMD treatment materials is presented. Hydrated lime, limestone, dolomite and lime-rich wastes are evaluated by this technique. Reagent particle size is an important parameter for neutralization and iron oxidation. Some lime-rich wastes may be cost competitive with hydrated lime as AMD neutralization reagents.

INTRODUCTION

The combination of hydrated lime neutralization, aeration, and settling is the most frequently used treatment for large volumes of iron-rich acid mine drainage (AMD). A diagram of a typical AMD treatment plant is shown in Figure 1. Hydrated lime is added to the AMD to neutralize the acidity and to increase the pH of the water so that favorable ferrous iron oxidation rates can be obtained. This oxidation step usually involves the use of mechanical aeration. After neutralization and iron oxidation, the AMD is transferred to a settling pond to allow precipitation of ferric hydroxides, and oxyhydroxides, gypsum ($CaSO_4$), calcium carbonate, etc. The alkaline, iron-rich sludge is often disposed in a deep mine, although permanent retention in the pond, on-site burial, and disposal at active coal refuse areas are also used.

OBJECTIVE

The objective of this work was to evaluate potential lime substitutes for the treatment of AMD to determine if a less expensive material could be used in place of hydrated lime. This required development of a laboratory-scale procedure to compare the AMD treatment efficiency of hydrated lime with that of other materials.

EXPERIMENTAL

APPARATUS AND CONDITIONS

A diagram of the apparatus used in the experiments is shown in Figure 2. A Neslab Cryobath CB-60 containing a water/methanol mixture was used to maintain the temperature of the

AMD at 13 ± 1^0C, typical of water being pumped from an underground mine. Temperature control is important since the iron oxidation rate increases with temperature.

A 1500 mL beaker containing 1 L of raw mine water was placed in the controlled temperature bath. The water was aerated at 4 SCFH through a fritted tube. Temperature and pH probes were positioned as shown in Figure 2.

Fresh raw mine water was collected in a collapsible bag every three days and stored in a refrigerator at 4^0C. Very little iron oxidation or pH change occurred during storage. Some degassing Of CO_2 occurred but was minimized by the low storage temperature and use of a gas-free collapsible storage container. The raw mine water was quickly warmed to 13^0C before beginning each experiment.

PROCEDURE

The procedure for the experiments is as follows:

1. Weigh desired quantity of test reagent.

2. Transfer I L of 130C raw mine water to the beaker and place in temperature bath.

3. Measure pH and [Fe^{2+}] concentration of raw mine water
4. Insert all probes.
5. Add test reagent, aeration tube, and start timer.
6. Continuously monitor pH and periodically remove samples for Fe^{2+} measurement (typically every 10 minutes).
7. After [Fe^{2+}] decreases to <3 mg/L, transfer treated mine water to a I L graduated cylinder for settling tests.

The raw mine water was aerated for 15 minutes prior to introduction of reagent in some of the experiments to reduce the dissolved CO_2 content.

ANALYTICAL PROCEDURES

Dichromate titration, utilizing diphenylamine sulfonic acid as an indicator was used to determine the Fe^{2+} concentration.

The pH was measured by a calibrated Fisher glass pH electrode and a Corning Model 610A portable pH meter.

The surface area measurements were performed using the N_2 gas adsorption technique of Brunauer, Emmett, and Teller (BET) with a commercial surface area analyzer (Quanta Chrome, Monosorb).

An inductively coupled plasma-atomic emission spectrometer (ICP-AES) was used for elemental analysis of the supernatants from the settling tests.

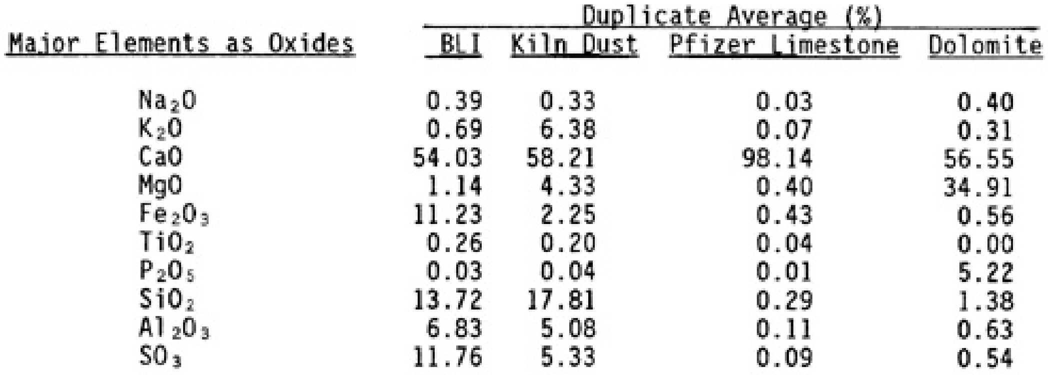
The active CaO in the reagents was determined by thermogravimetric analysis (TGA).

RESULTS AND DISCUSSION

Figure 3 shows the fraction of ferrous iron remaining vs. time for raw mine water aerated with and without neutralization by hydrated lime and limestone. The results obtained with no neutralization serve as a control. The quantity of hydrated lime used in this experiment (22.3 mM/L $Ca(OH)_2$) was based on the water quality and operating parameters of one particular AMD treatment plant at the time these experiments were performed. This quantity of hydrated lime (Figure 3) provides enough base to neutralize the acidity present in the raw mine water and to increase the pH of the mine water so that a reasonable iron oxidation rate can be obtained. The additional acidity produced by ferric iron hydrolysis is also neutralized. At the end of one hour the ferrous iron concentration was <3 mg/L. The one hour aeration time (oxidation) was more than sufficient to treat the AMD based on the flow rates and pond volumes at this particular AMD treatment plant. For experimental standardization purposes, later experiments were performed using quantities of materials stoichiometrically equivalent to 22.3 mM/L hydrated lime.

Results obtained when treating the AMD with 22.2 mM/L Pfizer limestone are also shown in Figure 3. This limestone was a very fine commercial grind obtained from the Pfizer Chemical Company. An elemental analysis of the material is shown below. Excellent experimental reproducibility is shown by the duplicate limestone experiments conducted -2 weeks apart. The time required for treatment of the AMD with this limestone was long (-6 hours). Doubling the amount of limestone significantly decreased the required treatment time (Figure 4).

	Duplicate Average (%)			
Major Elements as Oxides	BLI	Kiln Dust	Pfizer Limestone	Dolomite
Na_2O	0.39	0.33	0.03	0.40
K_2O	0.69	6.38	0.07	0.31
CaO	54.03	58.21	98.14	56.55
MgO	1.14	4.33	0.40	34.91
Fe_2O_3	11.23	2.25	0.43	0.56
TiO_2	0.26	0.20	0.04	0.00
P_2O_5	0.03	0.04	0.01	5.22
SiO_2	13.72	17.81	0.29	1.38
$A1_2O_3$	6.83	5.08	0.11	0.63
SO_3	11.76	5.33	0.09	0.54



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Dolomite, ($MgCO_3$.-$CaCO_3$), $MgCO_3$, and precipitated chalk ($CaCO_3$)were tested at stoichiometric quantities equivalent to 22 mM of hydrated lime (Ca basis) per liter of mine water. The dolomitic equivalent was calculated on a combined Mg and Ca basis. The results of these experiments are shown in Figure 5. The $MgCO_3$ is nearly equivalent to lime in AMD treatment capacity. However, precipitated chalk required almost twice as much treatment time as hydrated lime. Since both of these materials cost more than hydrated lime there is no incentive to use either for AMD treatment. The experiment using dolomite was ended after 2 hours since no appreciable iron oxidation occurred.

Lime-rich waste materials (elemental analyses shown earlier) were examined next since they may be available in large quantities at attractive prices. If the use of boiler limestone injection (BLI) sulfur abatement technology is adopted by utilities, disposal of large quantities of this calcium oxide rich waste would be required. Both BLI ash and cement kiln dust could be available for shipping costs alone.

Thermogravimetric analyses (TGA) of the BLI ash showed an available CaO content of 22.0% (~9% as $Ca(OH)_2$ and 13% as CaO) while the kiln dust contained about 25% available CaO (~9% $Ca(OH)_2$ plus ~16% anhydrous lime).

The results of the BLI and kiln dust (15.7 and 14.7 mM/L $Ca(OH)_2$ equivalent, respectively) experiments are shown in Figure 6. Al though the quantity of material used was based on total calcium content rather than the available CaO equivalent, complete iron oxidation was achieved. The data show an initially rapid iron oxidation rate which slows as the reaction proceeds. Three to four hours were required to reduce the Fe 2+ concentration to <3 mg/L. These data are plotted with the hydrated lime data for comparison.

The pH of the treated AMD during the BLI ash experiment remained relatively low (~6.6) until the ferrous iron concentration decreased to <25 mg/L (0.032 fraction remaining). The pH then rapidly increased to 9.0. The pH of the AMD treated with cement kiln dust remained at about 9.2. In both cases, the use of smaller concentrations of material may be necessary to maintain the pH of the discharge water within regulatory limits.

PREAERATION TESTS

The raw mine water used contains high levels of dissolved carbon dioxide which, if not removed prior to lime addition, must also be neutralized, increasing the hydrated lime requirements. Several experiments were performed in which the raw mine water was aerated for 15 minutes to evolve CO_2 before adding any basic material. From these experiments it was determined that after CO_2 removal, 8.8 mM of hydrated lime per liter of mine water would provide neutralization and sufficient iron oxidation to adequately treat the raw water in 30-35 minutes. The hydrated lime requirement without Preaeration was 13.5 mM/L. Another cement industry product, PozzalimeTM (lime index about 44%), was included in these studies.

Figures 7 and 8 show the results of experiments performed using 8.8, 10.0, 8 9 and 10.5 mM/L hydrated lime, BLI ash, cement kiln dust, and PozzalimeTM, respectively. Each water sample was aerated for 15 minutes prior to addition of neutralization material. The curves shown in Figures 7 and 8 indicate an initially rapid iron oxidation rate which significantly decreases with time. Again, as in experiments without pre-aeration, only the AMD treated with hydrated lime reaches iron concentrations below 3 mg/L within one hour.

Typical pH values for the treated AMD during the iron oxidation phase for the BLI ash, kiln dust, and PozzalimeTM experiments were 6.3, 10.1, and 6.6, respectively. The pH for the kiln dust treated AMD remained high throughout the experiment. When the ferrous iron concentration of the PozzalimeTM treated water reached about 100 mg/L (40 minutes), the pH rapidly increased to 10.0. The pH of the hydrated lime treated water increased to 7.4 upon addition of base and slowly decreased to 7.1 at which time the iron oxidation phase was complete (30 minutes). The pH then slowly increased to 7.7.

Calculations using the solubility product constant, Ksp, at 250C show the equilibrium concentration of ferrous hydroxide ($Fe(OH)_2$) in water to decrease from -500 mg/L at a pH of 7.5 to -50 mg/L at a pH of 8.0.

This indicates that a pH 0.5 is necessary to maintain ferrous iron in solution without precipitation as a hydroxide. If smaller quantities of kiln dust or PozzalimeTM were used in the above experiments, higher iron oxidation rates would be expected since higher pH values result in the precipitation of ferrous hydroxide. This agrees with the experimental observations discussed below.

Figure 9 shows the effect on iron oxidation when 8.1, 5.8 and 5.0, and 7.9 mM/L hydrated lime, cement kiln dust, and PozzalimeTM were used for treatment of the AMD. Typical pH values during the iron oxidation phase of each experiment were 7.4, 7.8, 7.0, and 6.4, respectively. The pH of the treated water for all the materials increased upon completion of the iron oxidation.

The AMD treated with 5 mM/L cement kiln required only a few more minutes for ferrous iron oxidation than was required for hydrated lime. However, this required about twice as much cement kiln dust, on a weight basis, as hydrated lime. This is because of the relatively low lime index of the kiln dust. The time required for AMD treatment increased to 70 minutes when a higher concentration (5.8 mM/L) of cement kiln dust was used.

The ferrous iron oxidation rate in aqueous solution increases with increasing pH. However, ferrous hydroxide will precipitate at pH values of about 7.5 and above for the ferrous iron concentration used in this study and the oxidation rate slows down due to the change from a homogeneous to a heterogeneous reaction. This is because the suspended solid ferrous hydroxide must first redissolve before oxidation can occur. Therefore, it is desirable to use enough material to maintain the pH of the treated water as high as possible without exceeding 7.5.

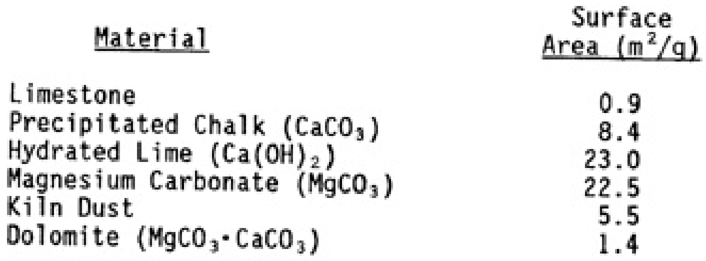
Of the waste materials studied, the cement kiln dust and PozzalimeTM appear to be the most promising potential lime substitutes. However, the chemistry of AMD treatment with these materials is quite complex. Because pH control of treated water is necessary for efficient utilization of reagent, using waste products of variable composition could cause problems.

If higher pH's are required, for example for manganese precipitation, small amounts of lime could be added after iron removal for pH adjustment.

CHARACTERISTICS OF MATERIALS STUDIED

Since physical parameters have a major impact on neutralization and iron oxidation rate, the surface areas (BET gas adsorption method) of the materials were measured. The results of the surface area measurements, shown below, suggest a relationship between surface area and reactivity.

Material	Surface Area (M2/q)
Limestone	**0.9**
Precipitated Chalk ($CaCO_3$)	**8.4**
Hydrated Lime ($Ca(OH)_2$)	**23.0**
Magnesium Carbonate ($MgCO_3$)	**22.5**
Kiln Dust	**5.5**
Dolomite ($MgCO_3$ ' $CaCO_3$)	**1.4**



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Kiln Dust	5.5
Dolomite ($MgCO_3 \cdot CaCO_3$)	1.4

The materials associated with high neutralization capacity and rapid iron oxidation tend to have large specific surface areas compared to the low neutralization capacity materials. The kiln dust, however, has a relatively low surface area yet the kiln dust resulted in fast iron oxidation. The distribution of available CaO throughout the heterogeneous kiln dust is not known and it is possible that it is enriched in the fines, in higher surface area particles, or on the surface of the particles.

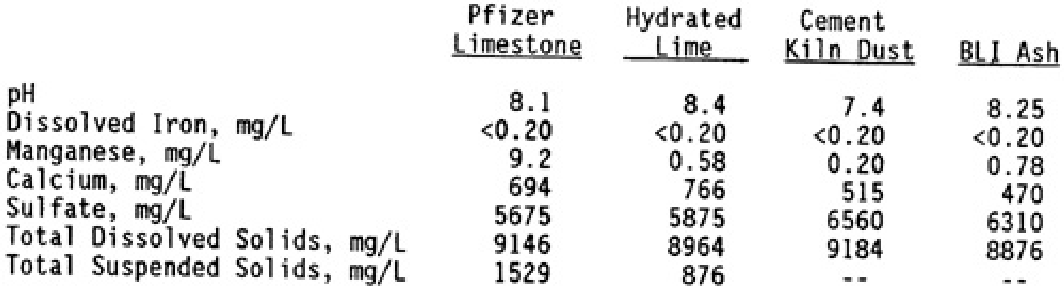
Grinding the materials to smaller particle sizes may significantly increase the neutralization capacity and oxidation rates. The cost of grinding these materials to sufficiently small particle sizes, however, may be prohibitive. $CaSO_4$ and/or $CaCO_3$ "coating" of particles occurs which reduces the neutralization capacity of all the materials studied, including hydrated lime. The removal of the carbonate precursor, dissolved CO_2, by preaeration appears to decrease the "coating" effect, and leading to better hydrated lime utilization.

SLUDGE SETTLING TESTS

Table 1 shows the results of the settling tests performed on the mine water samples after they had been treated with various materials. Preaeration was not used in any of these experiments. The normalized 24 hour value listed for each settling test was calculated on the basis of a uniform initial volume of 1000 mL. Comparison of these values indicates that the limestone, magnesium carbonate, and the BLI ash had the smallest sludge volumes. The hydrated lime and kiln dust sludge volumes were comparable to each other but were considerably larger than the sludge volumes obtained for the other materials. Smaller sludge volumes can result in a cost savings at AMD treatment plants if the sludge must be periodically removed from the settling basin.

Analyses performed on the supernatants of the settling tests after 24 hours, shown below, indicate the concentration levels expected to be present in the water discharged from the treatment plant. Only the water treated with the limestone (22.2 mM/L) would be out of compliance with Federal or State water quality standards due to the relatively high concentration of manganese (~9.2 ppm). All of the other materials studied here produced supernatant water characterized by Fe^{2+} <3.5 ppm, (Mn^{2+}) <2.0 ppm, and with a pH between 6.0 and 9.0 which are all within discharge water quality guidelines.

	Pfizer Limestone	Hydrated Lime	Cement Kiln Dust	BLI Ash
pH	8.1	8.4	7.4	8.25
Dissolved Iron, mg/L	<0.20	<0.20	<0.20	<0.20
Manganese, mg/L	9.2	0.58	0.20	0.78
Calcium, mg/L	694	766	515	470
Sulfate, mg/L	5675	5875	6560	6310
Total Dissolved Solids, mg/L	9146	8964	9184	8876
Total Suspended Solids, mg/L	1529	876		



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CONCLUSIONS

1. A laboratory scale procedure was developed which can be used to compare the neutralization and iron oxidation capacity of potential lime substitutes or AMD treatment materials.

2. Hydrated lime is the most effective reagent tested for use in an AMD treatment process involving neutralization, aeration, and settling.

3. Waste products such as BLI ash, cement kiln dust, and PozzalimeTM may be used for the treatment of AMD. However, due to the necessity of handling larger quantities of solid material, enlarged aeration basins (to increase residence time), etc., the long-term availability and delivered price will ultimately decide the usefulness of these materials for AMD treatment. Variability in composition of these waste products and their complex aqueous chemistry might hinder their application to AMD treatment.

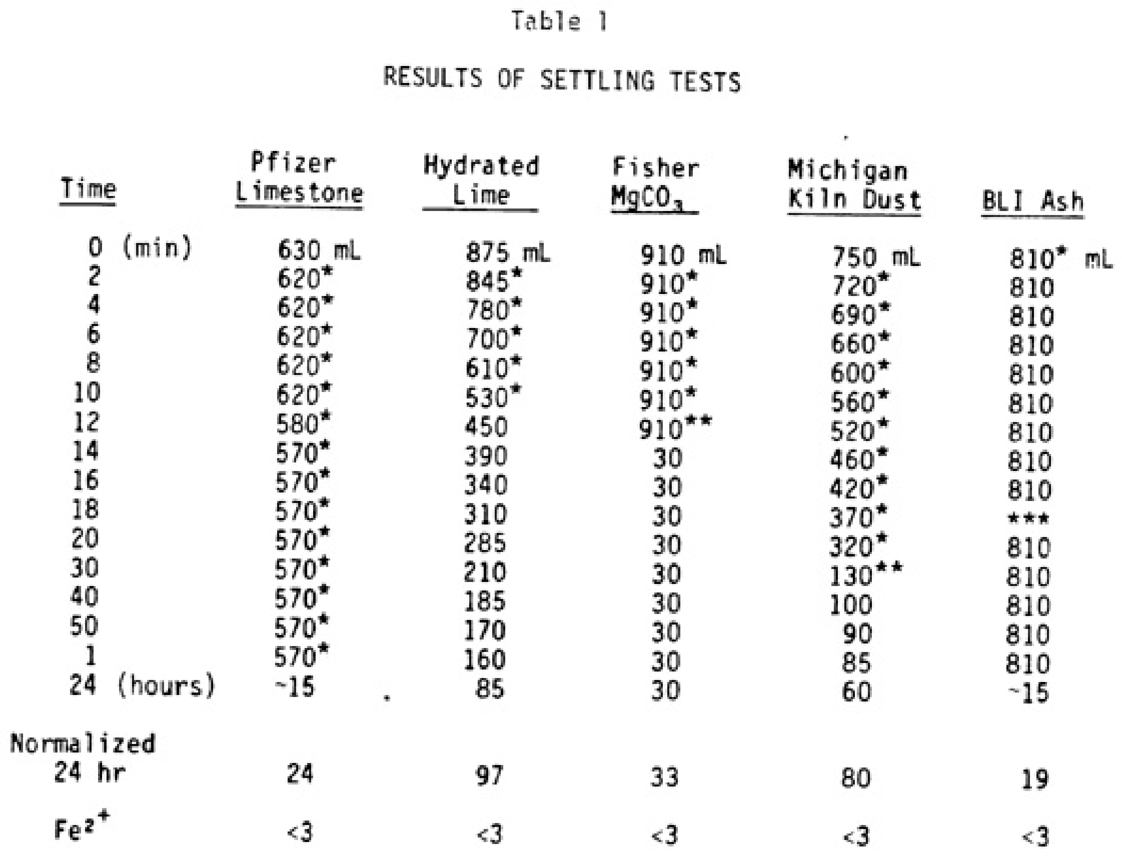
4. Discharge water from AMD treated with BLI ash or cement kiln dust is within State and Federal water quality guidelines for pH and trace metal content.

5. The iron oxidation rate is greatest at an initial pH value of about 7.5 for the iron concentrations used in this study. As the iron concentration decreases (<50 mg/L) the pH can increase to about 8.0 without ferrous hydroxide precipitation.

6. Specific surface area appears to play an important role in reagent activity.

Table 1

RESULTS OF SETTLING TESTS



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RESULTS OF SETTLING TESTS

Time	Pfizer Limestone	Hydrated Lime	Fisher $MgCO_3$	Michigan Kiln Dust	BLI Ash
0 (min)	630 mL	875 mL	910 mL	750 mL	810* mL
2	620*	845*	910*	720*	810
4	620*	780*	910*	690*	810
6	620*	700*	910*	660*	810
8	620*	610*	910*	600*	810
10	620*	530*	910*	560*	810
12	580*	450	910**	520*	810
14	570*	390	30	460*	810
16	570*	340	30	420*	810
18	570*	310	30	370*	***
20	570*	285	30	320*	810
30	570*	210	30	130**	810
40	570*	185	30	100	810
50	570*	170	30	90	810
1	570*	160	30	85	810
24 (hours)	~15	85	30	60	~15
Normalized 24 hr	24	97	33	80	19
Fe^{2+}	<3	<3	<3	<3	<3

* Cloudy and very difficult to distinguish interface between supernatant and solids.

** Interface is now clearly visible.

***Most of the solids are at the bottom but the supernatant contains a suspension of fine particles.

A Control Room
B Hydrated Lime Silo
C Lime Feed
D Open Channel (mine water brought to surface)
E First Aeration Basin (one 25 HP aerator)
F Second Aeration Basin (two 60 HP aerators)
G Sedimentation Pond
H Discharge

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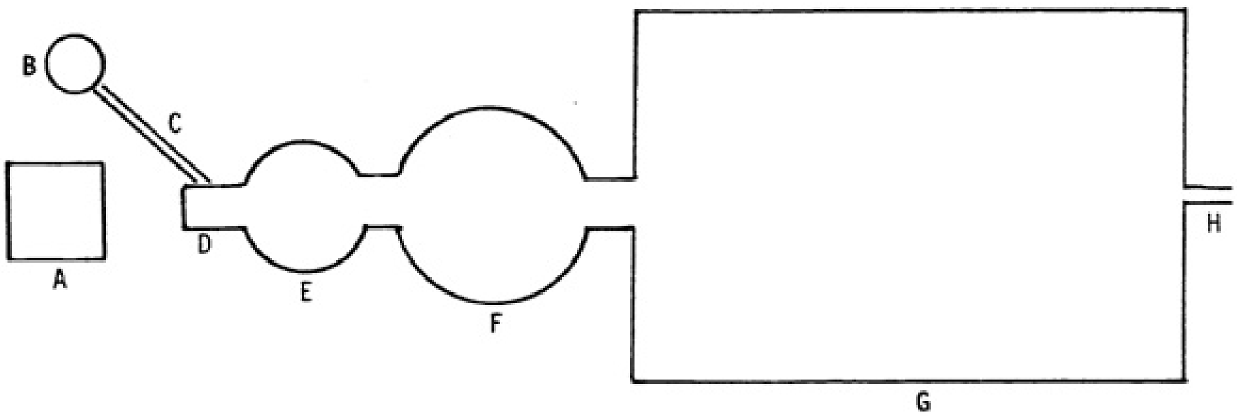

Figure 1. DIAGRAM OF A TYPICAL ACID MINE DRAINAGE TREATMENT FACILITY

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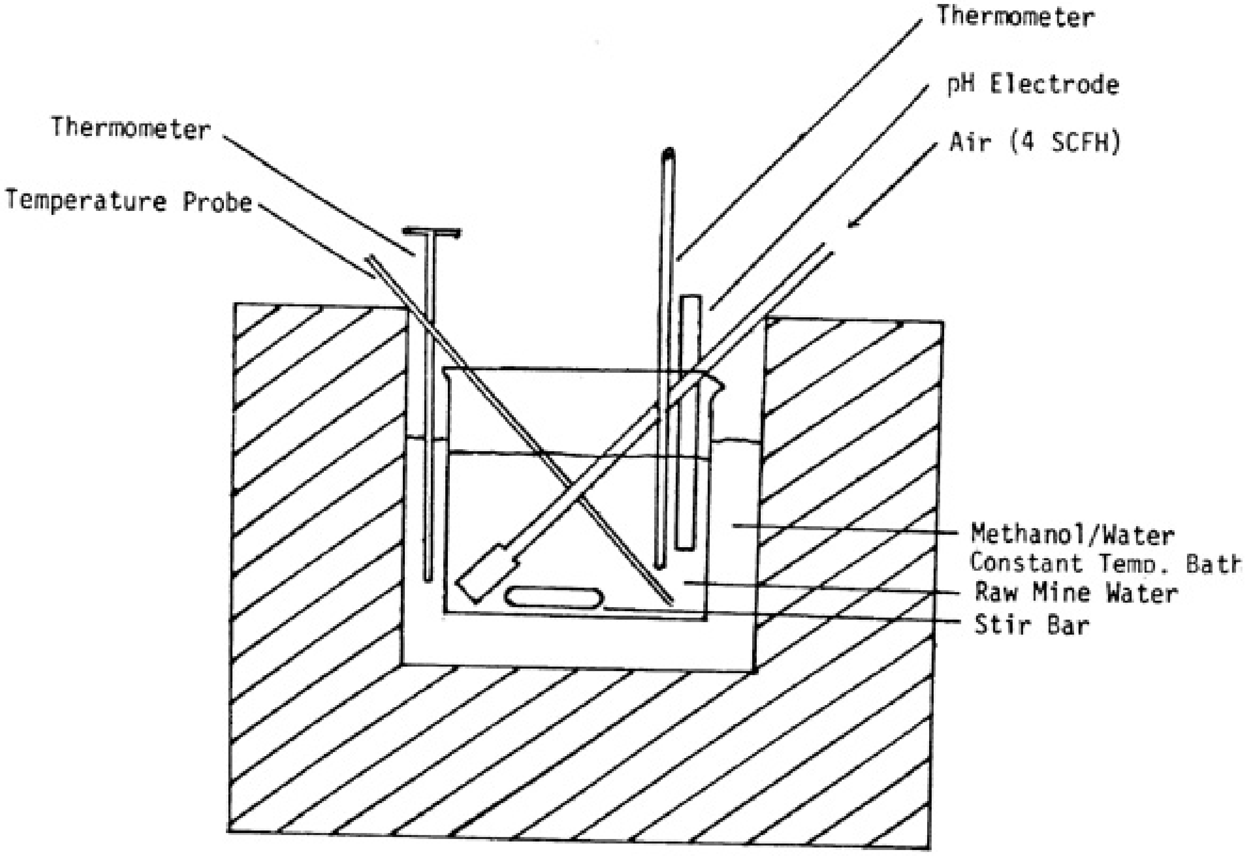

Figure 2. APPARATUS FOR BATCH AMD TREATMENT STUDIES

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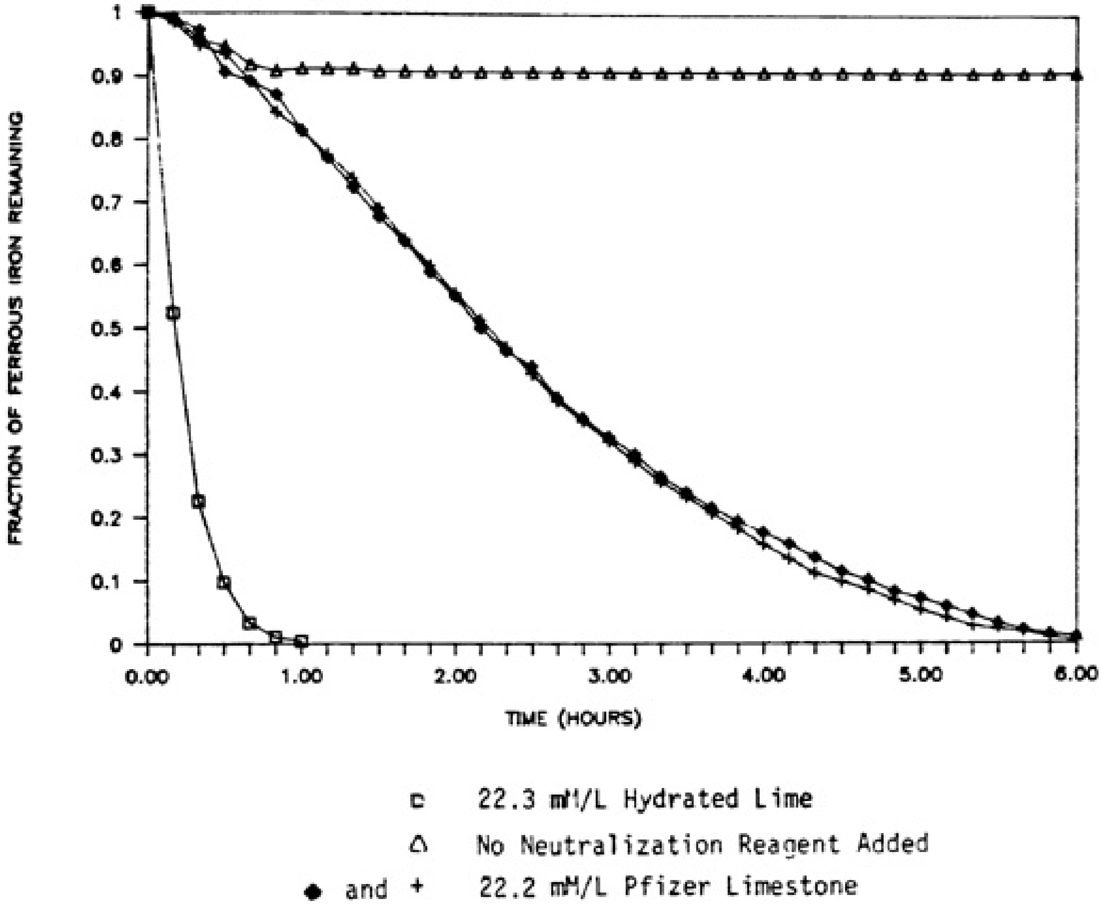

Figure 3. IRON OXIDATION RATES IN AMD TREATED WITH HYDRATED LIME AND LIMESTONE

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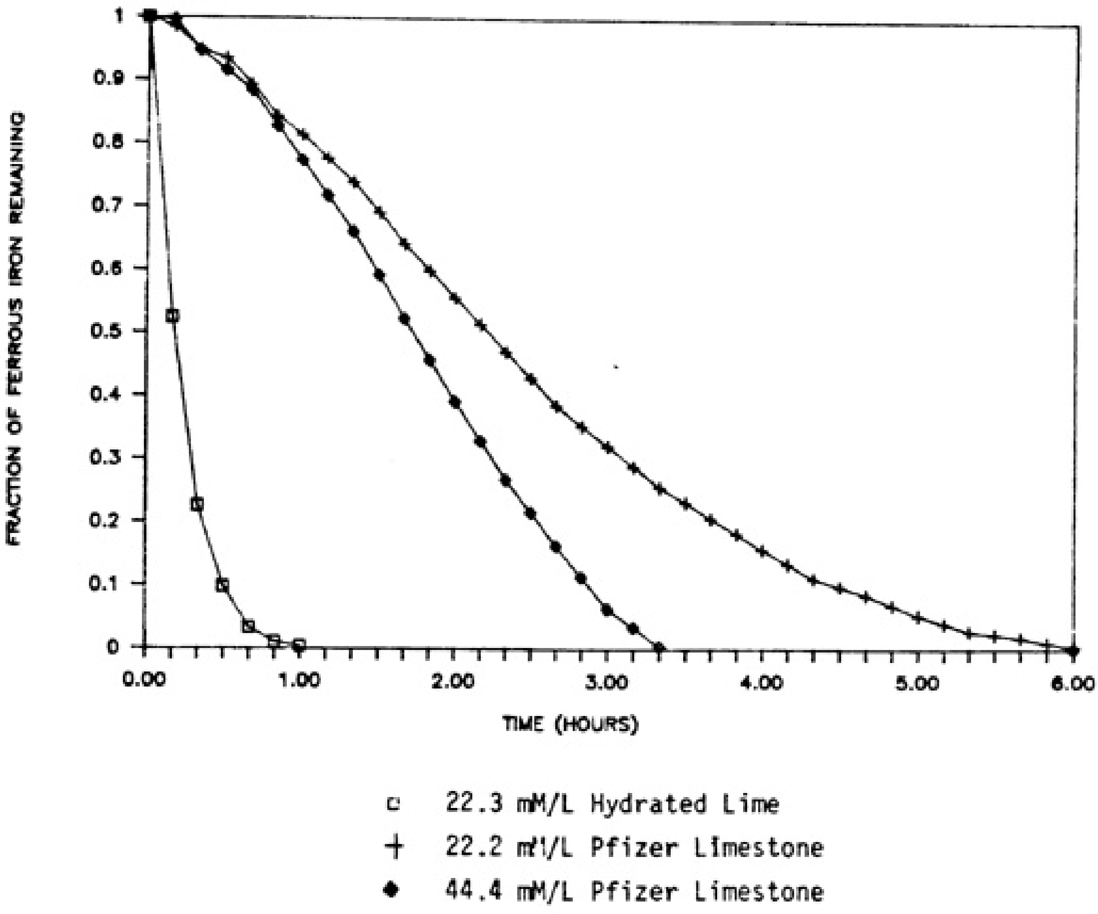

Figure 4. IRON OXIDATION RATE OF AMD TREATED WITH HYDRATED LIME AND LIMESTONE

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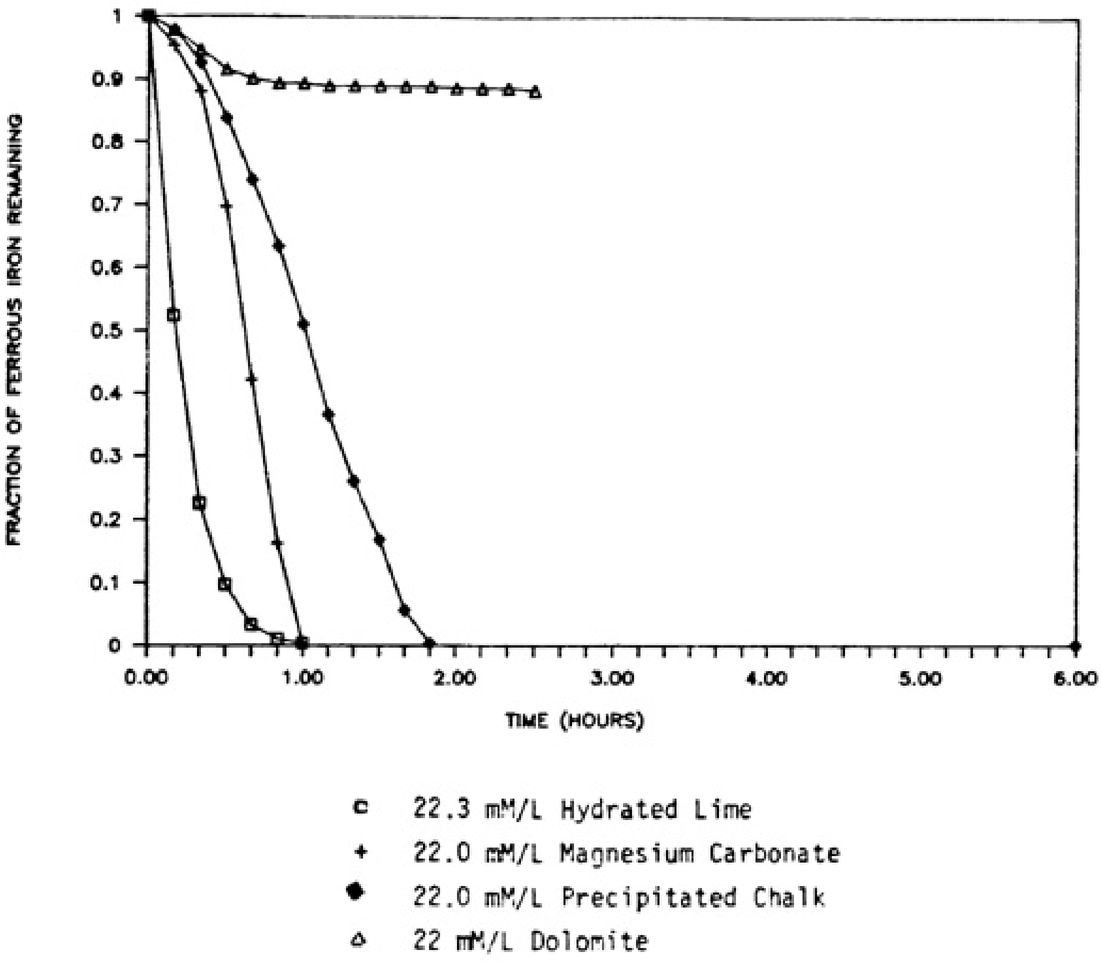

Figure 5. IRON OXIDATION RATE OF AMD TREATED WITH HYDRATED LIME, DOLOMITE, MAGNESIUM CARBONATE, AND PRECIPITATED CHALK

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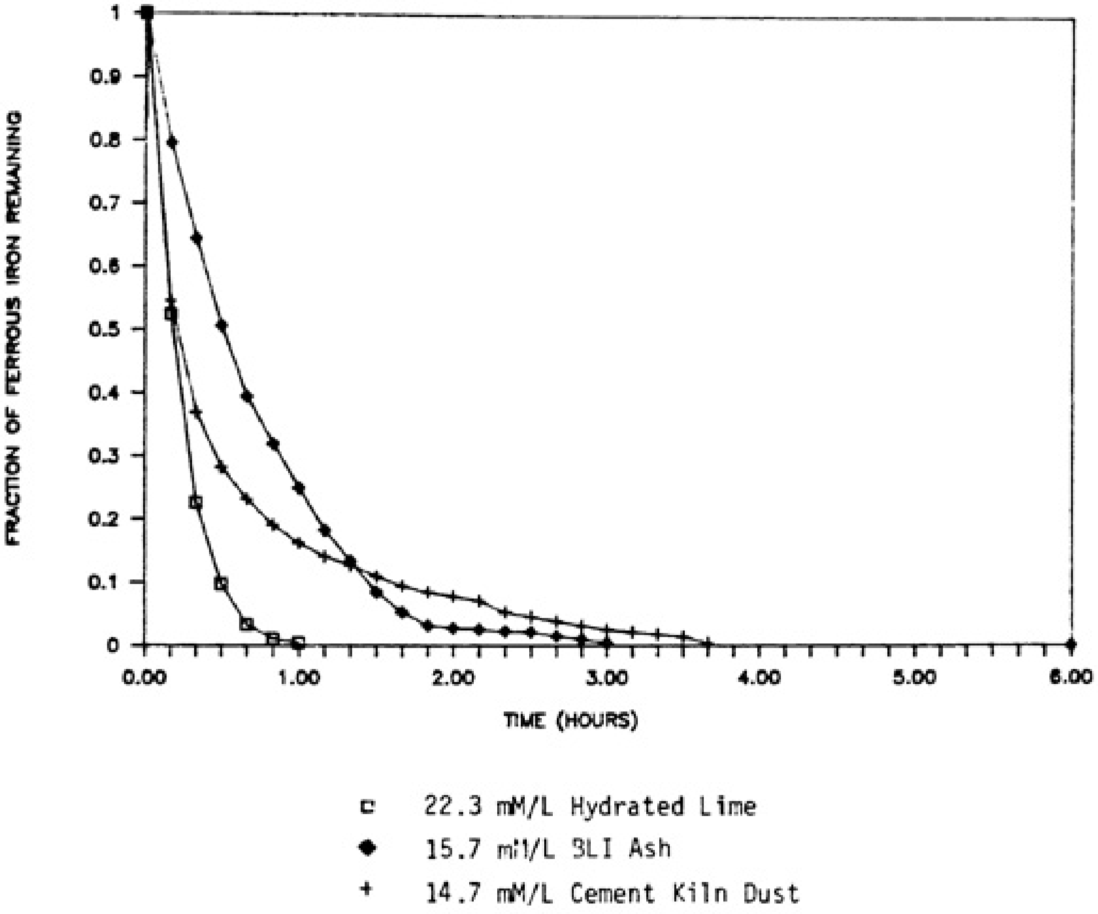

Figure 6. IRON OXIDATION RATE OF AMD TREATED WITH HYDRATED LIME, BLI ASH, AND CEMENT KILN DUST

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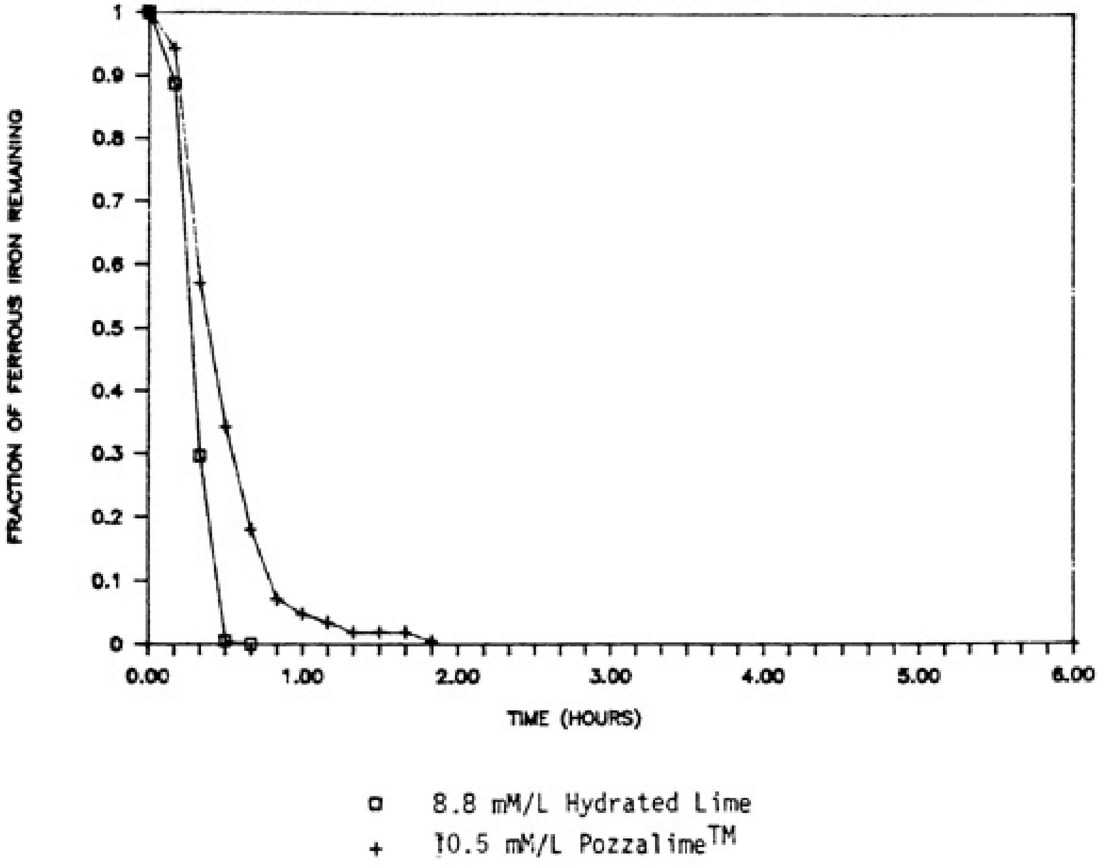

Figure 7. IRON OXIDATION RATE OF AMD TREATED WITH HYDRATED LIME AND POZZALIMETM AFTER FIFTEEN MINUTES OF PREAERATION

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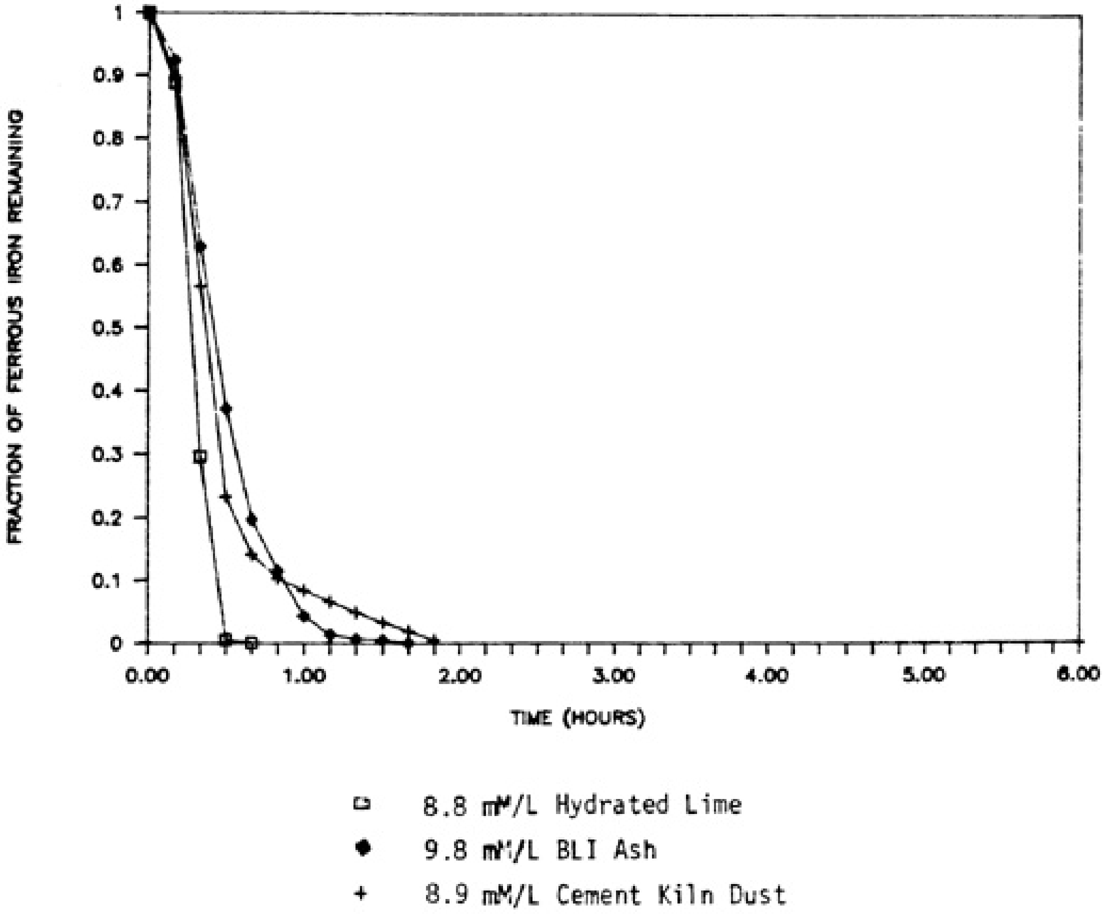

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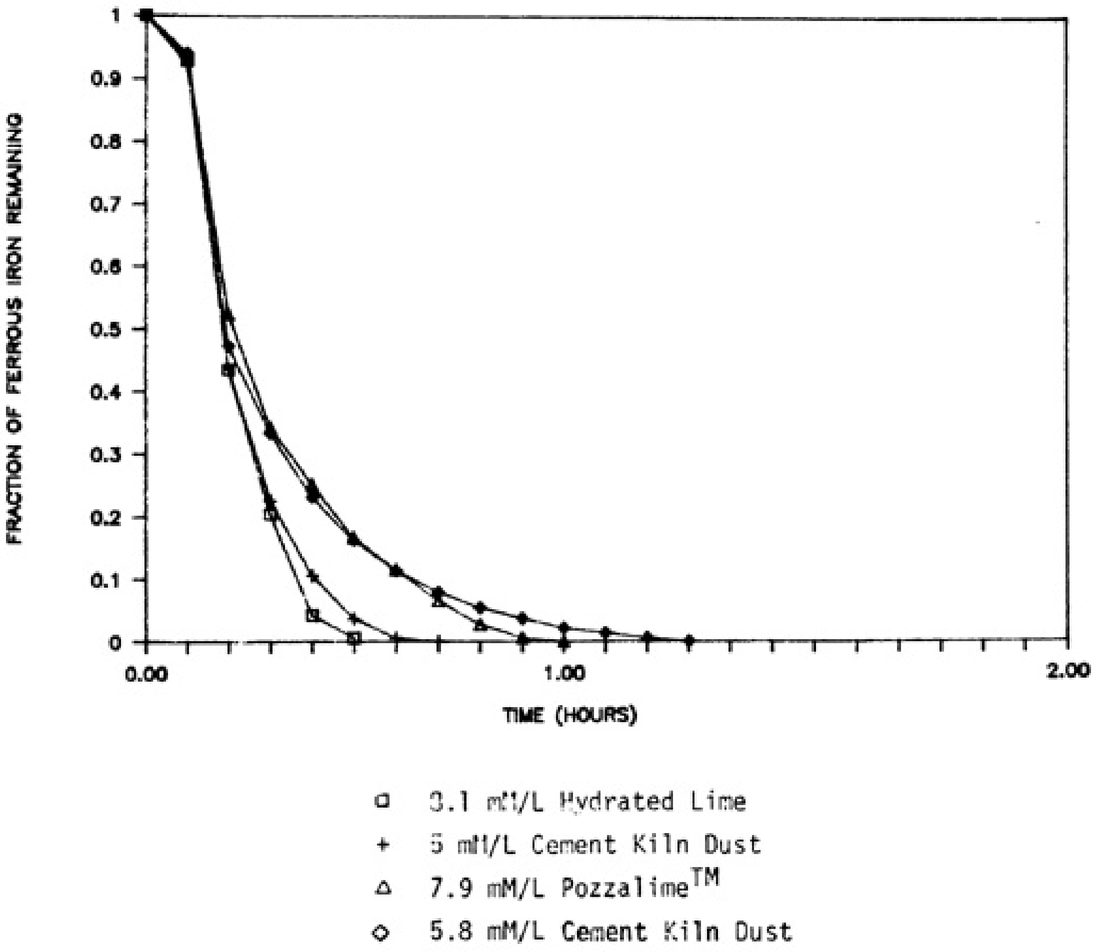

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