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## Effect of Additives on Pyrite Oxidation

By G. W. Reimers and D. F. Franke

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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### UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	$\mu\text{m}$	micrometer
$\text{cm}^3/\text{min}$	cubic centimeter per minute	mg	milligram
$^{\circ}\text{C}$	degree Celsius	mL	milliliter
$^{\circ}\text{C}/\text{min}$	degree Celsius per minute	min	minute
g	gram	mm	millimeter
h	hour	pct	percent
kcal/mol	kilocalorie per mole	wt pct	weight pct

# EFFECT OF ADDITIVES ON PYRITE OXIDATION

By G. W. Reimers<sup>1</sup> and D. F. Franke<sup>2</sup>

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## ABSTRACT

Exothermic oxidation reactions of sulfide minerals can produce self-heating situations in underground mines. If the self-heating is unchecked and the resulting heat is not sufficiently dissipated, the result can be spontaneous combustion fires. This U.S. Bureau of Mines report describes laboratory tests conducted to measure the reactivity of pyrite following treatment with additives to counter its self-heating tendencies. Thermal gravimetric analysis (TGA) and isothermal oxidation procedures were used to obtain information on pyrite ignition and the behavior of pyrite during low-temperature oxidation to ferrous sulfate.

The determination of treatment effectiveness was evaluated by adding 5 wt pct of the compound to the pyrite before milling. The resulting samples were then heated in moistened air and after 24 h, the amount of pyrite oxidation determined. Results of these tests indicated that several phosphate compounds reduced the oxidation of pyrite to sulfate to about 50 pct or less compared with the oxidation of untreated sample at 200° C. Cupric sulfate reduced oxidation to about 20 pct untreated sample at 200° C. Sodium, calcium, and potassium chloride reduced pyrite oxidation to levels of approximately 15 pct or less of the untreated sample. Using only 1 pct of sodium or calcium chloride was effective in slowing pyrite oxidation to less than 20 pct of the untreated sample.

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## INTRODUCTION

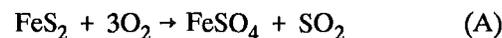
This report describes the results of laboratory experiments conducted by the U.S. Bureau of Mines to evaluate the effect additives have on the oxidation of pyrite. The ability to control oxidation of pyrite could find application in slowing self-heating or retarding ignition of the sulfide. These tests are part of a continuing research effort to develop technology that will suppress the oxidation of sulfide minerals in underground mines and thus reduce the possibility of spontaneous combustion mine fires.

Before beginning the current research effort, Ninteman (1)<sup>3</sup> conducted an extensive literature review of sulfide spontaneous combustion events. This review describes, on a wide scope, details of several mine fires that originated from sulfide self-heating. Since sulfide oxidation is exothermic, failure to dissipate the heat generated will cause the temperature in a mineral mass to rise. As the temperature rises, a thermal runaway situation may develop that will produce ignition of the sulfide and other nearby combustibles.

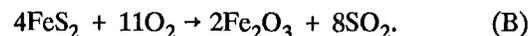
The early or incipient stages of self-heating often go unnoticed and this makes the resulting fire appear to be a spontaneous event. Also, these fires often start in abandoned, backfilled, and/or caved areas where access is difficult or impossible. These factors all contribute to make prediction, detection, and suppression difficult and therefore place a high priority on fire prevention. However, as the reactions and mechanisms that result in spontaneous combustion are not completely understood, efforts to control the problem, although well intended, are not always based on sound technical principles.

In previous Bureau research (2-3), the oxidation of several sulfides was studied, and the results indicated that several sulfides, including pyrite, could under certain conditions, oxidize to sulfate at temperatures below their ignition point. As this is an exothermic reaction, any inhibition could serve to slow the generation of heat and lessen the chance of ignition. Under certain conditions, the use of chemicals has been found to slow sulfide

oxidation. For example, when phosphates are added to pyrite, the resulting oxidation under aqueous conditions have been found to be reduced (4-5). Rosenblum (6) reported that conditioning a sulfide tailing with copper sulfate resulted in a reduced heating rate in their temperature-rise measurement apparatus. Likewise, the consolidation, due to oxidation of muck piles with a high concentration of pyrrhotite was reduced when the water used for dust control was replaced with a solution of copper sulfate (7). The effect of chemical additives on wet and dry oxidation of copper concentrates was studied by Pearse (8). The results of adding sodium hydroxide, lime, magnesium sulfate heptahydrate, and buffering agents had a mixed effect on the resulting oxidation of copper sulfides. Wet oxidation with hydrogen peroxide of a chalcopyrite concentrate (9) with additions of lime, a mixture of potassium dihydrogen phosphate and disodium hydrogen phosphate, or borax also produced mixed results. In this study, only the phosphate mixture decreased the oxidation with increased additive dosage. In a study of the oxidation of synthetic pyrite in dry air, Banergee (10) reports a promotion rather than an inhibition of the oxidation of sulfide to sulfate below 400° C when 10 and 30 pct silica was present as an additive. These studies indicate the potential for altering the behavior of sulfides under oxidizing conditions, and this report describes the effect several additives have on the exothermic oxidation of pyrite to ferrous sulfate according to the reaction



and to ferric oxide according to the reaction



These reactions result in the liberation of 252.7 and 199.4 kcal/mole FeS<sub>2</sub>, respectively.

## EQUIPMENT AND TEST PROCEDURES

Ignition points of treated pyrite samples were obtained using Perkin Elmer<sup>4</sup> TGA components. TGA tests were conducted on samples of approximately 40 mg using a heating rate of 25° C/min. A flow rate of 500 cm<sup>3</sup>/min was used for purging the system with nitrogen and for

supplying air during the oxidation tests. Moisture was added to the system by bubbling air into water contained in a flask and then routed to the TGA furnace. Tests were conducted by loading the sample into the balance pan and then purging the furnace assembly with nitrogen while preheating to 100° C. At this point, the nitrogen was replaced with the oxidizing gas, and the sample was heated until ignition as indicated by sample weight change. Additional details on this procedure are provided in an earlier Bureau report (2).

<sup>3</sup>Italic numbers in parentheses refer to items in the list of references at the end of this report.

<sup>4</sup>Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

Two systems were used to conduct isothermal oxidation experiments. The first used a National Appliance Co. model 5831 oven to run an experiment of 3 weeks duration at 50° C. A humid atmosphere was produced in the oven by bubbling air at 500 cm<sup>3</sup>/min into a glass dish set on the oven floor. Water was added to the dish as needed to saturate the oxidizing atmosphere. Samples of 1 g were loaded into four 67- by 9- by 9-mm porcelain boats that were placed into a glass petri dish that rested on a rack positioned in the center of the oven. The sample boats were then removed from the oven at selected intervals and the contents analyzed for water-soluble iron.

The second system, described in a previous Bureau report (3) was used to evaluate chemical treatments for slowing pyrite oxidation. In brief, these tests were run using Lindburg model 55035, horizontal-hinged, tube

furnaces having a bore of 2.5 cm and a length of 33 cm. A 5-g sample, unless indicated otherwise, was loaded into a porcelain boat that was positioned at the center of the furnace inside a Pyrex heat-resistant glass tube. Tests were conducted at 100° and 200° C, and the samples were oxidized in moist air at a flow rate of 500 cm<sup>3</sup>/min for 24 h. The air contained 60 pct water vapor for tests at 100° C and approximately 5 pct for tests at 200° C. The percent of pyrite oxidation for each test was determined by leaching the soluble iron sulfate from oxidized samples with 40 mL of water. Solutions were collected by filtration and then analyzed for their iron content. Knowing the iron content of the starting sample and the amount of soluble iron formed during an oxidation test allowed calculation of the degree of oxidation of the sulfide to sulfate.

## SAMPLE PREPARATION

The pyrite used in this investigation was a moisture free concentrate from a commercial mill containing 43.1 pct Fe, 46.9 pct S, and 2.2 pct Si. In addition, the pyrite also contained approximately 0.5 pct of Ca, Al, Zn, and Pb. The majority of the concentrate was in the size range of minus 48 plus 270 mesh, and further size reduction was done in a Bleuler mill by milling 20-g batches for 15 min. To decrease the possibility of oxidation during milling, the samples were milled along with 20 mL of heptane. The resulting slurry was dried in air at room temperature and then screened to breakup lumps producing the fine powder

used for testing. The average particle size of the pyrite after milling was 5 μm, which was similar to the size range of sulfides studied previously (2-3). All additives were tested by milling the chemical-pyrite mixture along with heptane. In addition, several additives were also tested by dissolving the treatment chemical in water and then mixing this solution with milled pyrite after evaporation of the heptane. The resulting paste contained 20 wt pct water and was in turn dried and then screened to provide powder for testing.

## RESULTS AND DISCUSSION

In this investigation, two methods were used to measure the effect chemical treatments have on the oxidation of pyrite. One of these methods used TGA to follow the weight change of samples during rapid heating in an oxidizing atmosphere. The other method involved isothermal heating of samples in moist air for test intervals of 24 h or more at lower temperatures and provides a measure of the type of oxidation that may contribute to the self-heating found in underground mines.

### THERMAL GRAVIMETRIC ANALYSIS

TGA was used to follow the oxidation of pyrite samples treated with several chemicals in atmospheres of dry air or air containing water vapor. Figure 1A illustrates the results of tests conducted on an untreated or blank pyrite sample. The Y-axis of the figure indicates the percentage of the original sample weight beginning at 100 pct, or the original weight prior to heating, and continuing over the

temperature range of the test as shown on the X-axis. The ignition point of the sample was taken as the point on the curve where rapid weight loss occurred. The most obvious weight change event that occurred during the test when the sample was oxidized in dry air was ignition at 390° C to ferric oxide. Heating the sample in moist air caused an increase in sample ignition point to 415° C. Oxidation in moist air also caused the sample to begin gaining weight about 320° C. This weight gain prior to ignition is typical when pyrite samples are oxidized in the presence of water vapor. Chemical and X-ray diffraction (XRD) analysis of pyrite samples that were oxidized in moist air for several hours at temperatures lower than the ignition point confirmed that the sulfide was partially converted to sulfate and its formation was responsible for the weight gain. Additional information on the formation of iron sulfate will be discussed in detail in the following section.

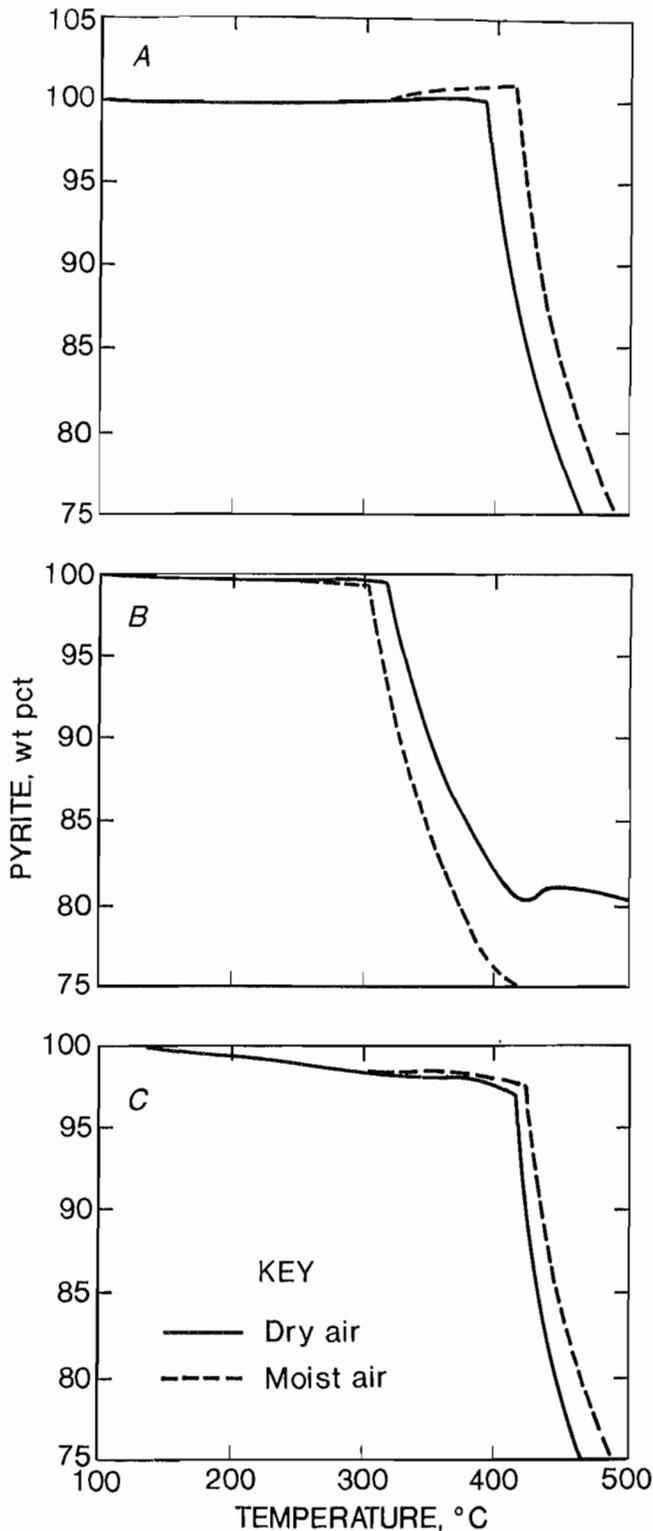


Figure 1.—Thermal gravimetric analysis of (A), untreated pyrite; (B), pyrite treated with sodium chloride; (C), pyrite treated with dibasic ammonium phosphate.

Figures 1B and 1C illustrate the results of TGA conducted on treated pyrite and illustrates that chemicals can alter the sample ignition point. The addition of 5 wt pct sodium chloride to pyrite (fig. 1B) before milling lowered the ignition point of the sample to 315° C in dry air and slightly lower to 305° C moist air. An increase in sample ignition point is shown in figure 1C when 5 wt pct dibasic ammonium phosphate was added to pyrite. This treatment increased the sample ignition to 415° and 425° C in dry and moist air, respectively. The treated pyrite samples shown in figures 1B and 1C did not undergo the gain in sample weight just prior to ignition that was indicated for the untreated pyrite in figure 1A. This absence of weight gain suggests that little iron sulfate was formed prior to ignition. The slight weight loss shown in figures 1B and 1C prior to ignition were likely the result of volatilization of sulfur from the pyrite and the volatilization or decomposition of the additive.

Table 1 summarizes TGA runs on pyrite treated with several chemicals that were candidates for slowing pyrite oxidation. These tests were run concurrently with the isothermal tests and results were obtained at the 5 wt pct additive level for the chemicals and at the 1 wt pct additive level for chemicals that were found to slow pyrite oxidation to iron sulfate. The ignition point of the blank sample and most of the treated samples was higher when water vapor was present in the oxidizing atmosphere. This suggests that the partial oxidation of pyrite to form ferrous sulfate on the sulfide surface is causing an increase in ignition point.

## ISOTHERMAL OXIDATION

### Analysis of Sulfate Formation

TGA of pyrite indicates a weight gain prior to ignition when the heating occurs with water vapor present in the oxidizing atmosphere. This weight gain could be caused by the formation of sulfates and it is hypothesized that this exothermic reaction, which occurs at relatively low temperature, could be the trigger that initiates spontaneous combustion fires. In a previous study (3), isothermal oxidation tests confirmed that the presence of moisture in the oxidizing atmosphere was necessary for significant oxidation of pyrite to iron sulfate. These results indicated that only about 5 pct of the pyrite was oxidized to iron sulfate in dry air, while about 80 pct oxidation occurred in moist air after 24 h at 200° C. To obtain additional information on this reaction, the composition of pyrite samples that were oxidized in a tube furnace at 100° and 200° C in moist air for 24 h were determined by XRD analysis.

Positive identification of ferrous sulfate was obtained from the analysis of the sample oxidized at 200° C. XRD analysis of samples oxidized at 100° C did not indicate the presence of ferrous sulfate. The absence of positive indication for sulfate was probably due to a low concentration or lack of good crystal formation at this relatively low test temperature. However, crystalline ferrous sulfate was recovered from these oxidized samples after they were leached with water, filtered, and the filtrate dried. The results of XRD analyses of the crystals confirmed the presence of melanterite, (a hydrous ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), a green-blue crystalline material resulting from the decomposition of pyrite or marcasite (11). While it is unlikely that melanterite was directly formed during oxidation, its recovery from pyrite oxidized at 100° C in moist air serves to illustrate that pyrite oxidation to ferrous sulfate can occur at a relatively low temperature.

**Table 1.—Ignition points of treated pyrite samples determined by TGA in dry and moist air**

Chemical additive	Additive, pct	Ignition point, °C	
		Dry air	Moist air
None . . . . .	NAP	390	415
Ammonium phosphate:			
Monobasic . . . . .	5	410	420
Dibasic . . . . .	5	415	425
Borax . . . . .	5	385	430
Calcium carbonate . . . . .	5	390	425
Calcium chloride . . . . .	1	350	375
. . . . .	5	340	335
Calcium oxide . . . . .	5	405	405
Calcium phosphate:			
Monobasic . . . . .	5	400	415
Dibasic . . . . .	5	390	425
Cupric sulfate . . . . .	1	385	395
. . . . .	5	380	385
Ferric sulfate . . . . .	5	375	410
Potassium bicarbonate . . . . .	5	375	410
Potassium chloride . . . . .	5	325	320
Potassium phosphate, monobasic . . . . .	5	415	415
Silica . . . . .	5	380	400
Sodium bicarbonate . . . . .	5	355	355
Sodium chloride . . . . .	1	345	360
. . . . .	5	315	305
Sodium phosphate:			
Monobasic . . . . .	1	390	405
. . . . .	5	410	410
Dibasic . . . . .	5	360	375
Tribasic . . . . .	5	380	395
Sodium silicate . . . . .	1	390	405
. . . . .	5	350	360

NAP Not applicable.

Figure 2 shows sample boats A and B that contain pyrite oxidized for 24 h in moist air at 100° and 200° C, respectively. The appearance of boat A changed little after oxidation, however, the pyrite in boat B was changed to a gray color, and the volume of the sample expanded to

spill from the boat. Chemical analysis of the contents of the boats indicate that about 26 pct of the pyrite heated to 100° C was oxidized to sulfate while at 200° C, conversion to sulfate was about 80 pct. Figure 3 illustrates the results of oxidation experiments conducted for 24 h at 100° and 200° C in moist air on untreated or blank pyrite samples. The bar graphs for samples A-D are duplicate runs while sample E illustrates that little change in oxidation occurred when the milled pyrite was moistened with water and then dried before testing.

The preceding experiments were conducted at fairly high temperatures and serve to demonstrate that the formation of ferrous sulfate can occur rather rapidly, and that the rate of formation increases as temperature rises. However, it is also highly significant that ferrous sulfate also forms at lower temperatures. This was evident from the results obtained when pyrite was oxidized in a humidity oven at 50° C. Several U.S. metal mines have encountered rock temperature in excess of 50° C, and as other mines proceed deeper, they too will encounter such temperatures (12).

Figure 4 illustrates the oxidation of pyrite to soluble iron (indicative of sulfate formation) during a 21-day test conducted at 50° C in an atmosphere of moist air. Slightly over 20 pct of the pyrite was oxidized to sulfate during this test. Oxidation proceeded slowly under these test conditions (isothermal). However, under adiabatic conditions (as would likely exist underground) the heat generated would not be dissipated and would cause the temperature of the sulfide to increase. As noted previously, the reaction is accelerated at higher temperatures. Thus, these results support the hypothesis that the thermal runaway conditions necessary to cause a spontaneous combustion fire could be initiated at low temperatures by the conversion of sulfide to sulfate.

### Analysis of Chemical Inhibitors

Experiments to evaluate chemicals to slow pyrite oxidation began with the use of phosphate compounds. Figure 5 illustrates the results of adding 5 wt pct monobasic, dibasic, and tribasic sodium phosphate to pyrite. These sodium phosphate compounds contain 69, 35, and 25 pct  $\text{P}_2\text{O}_5$ , respectively. Monobasic sodium phosphate with its higher phosphate content was the most effective of this group of chemicals in reducing the level of pyrite oxidation. The conversion to soluble iron was 8 and 43 pct at 100° and 200° C, after 24 h, compared with the blank samples values of 26 and 80 pct. The method used to add monobasic sodium phosphate to pyrite was also examined in this laboratory study. Figure 6 illustrates the results of oxidizing milled pyrite (A), milling phosphate with the pyrite (B), mixing phosphate with milled pyrite (C), and dissolving the phosphate in water, mixing the solution with

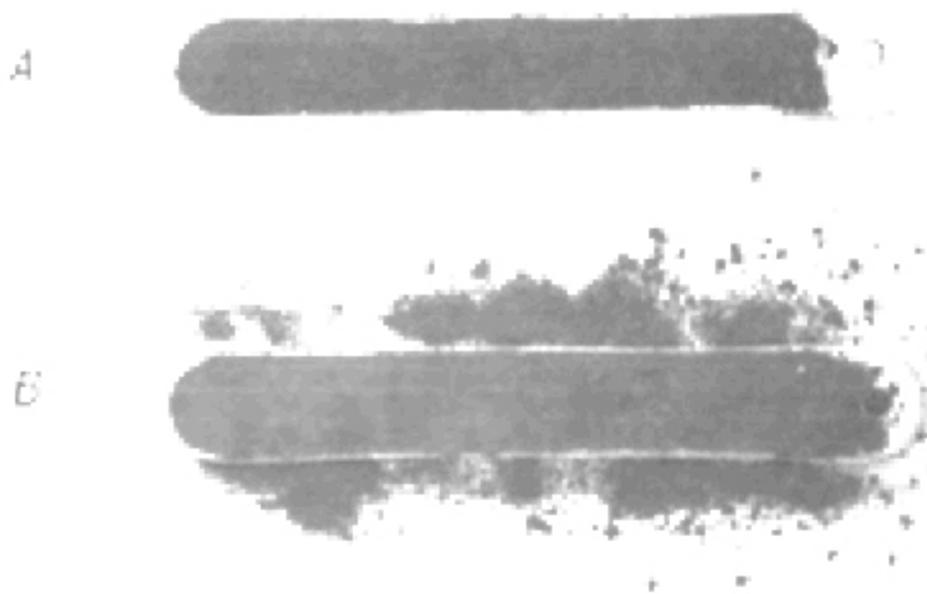


Figure 2.—Sample boats containing pyrite after oxidation at (A), 100° C; (B), 200° C.

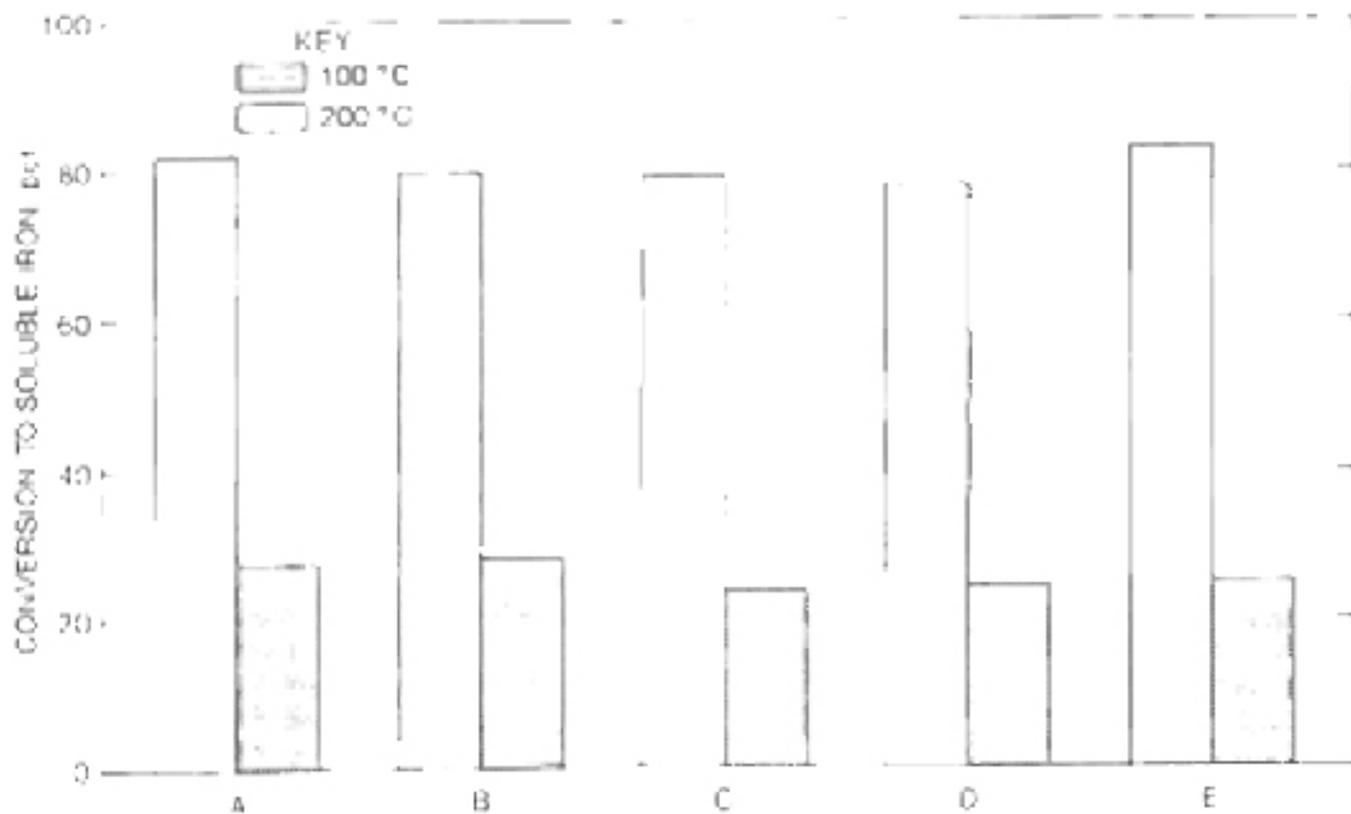


Figure 3. Isothermal oxidation of pyrite samples to soluble iron at 100° and 200° C (A-D), blank runs (E), moistened sample.

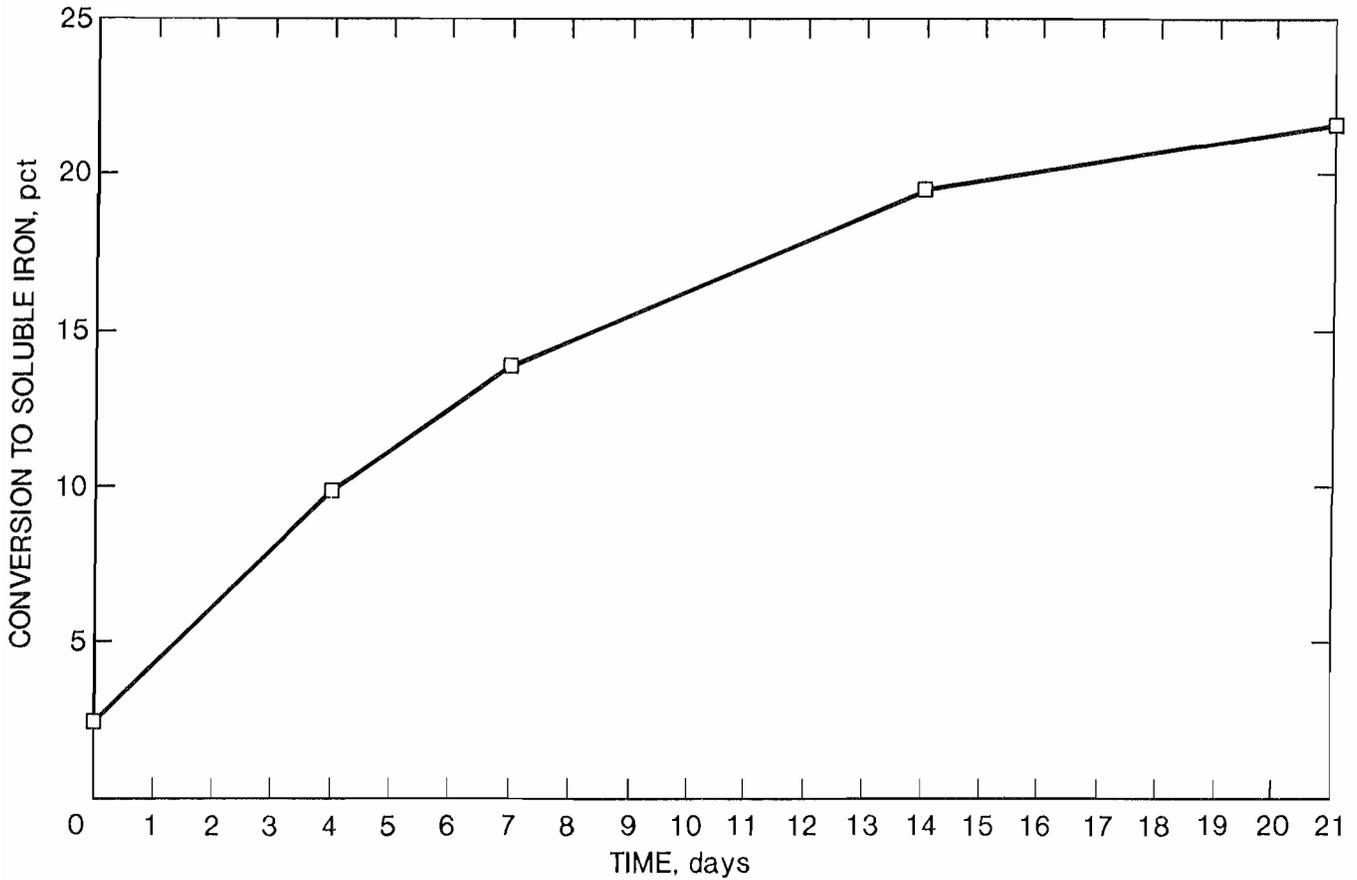


Figure 4.—Humidity oven oxidation of pyrite to soluble iron at 50° C.

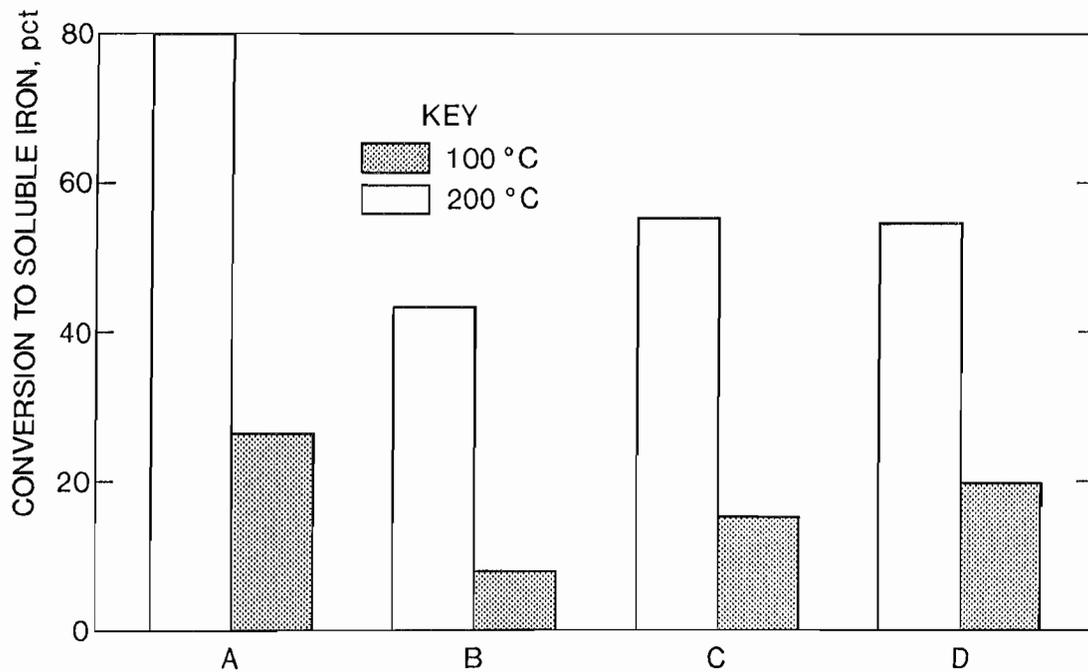


Figure 5.—Effect of (A), no treatment; (B), monobasic sodium phosphate; (C), dibasic sodium phosphate; (D), tribasic sodium phosphate additions on oxidation of pyrite to soluble iron.

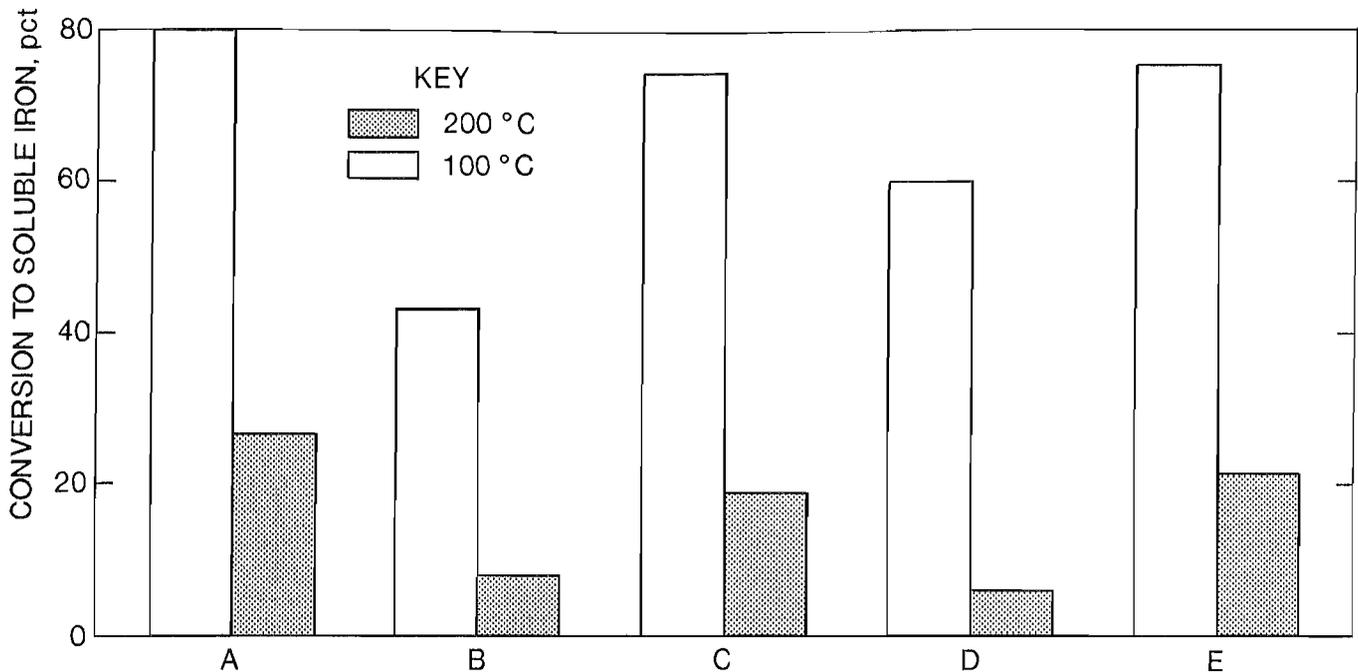


Figure 6.—Effect of method addition and concentration of monobasic sodium phosphate have on oxidation of pyrite to soluble iron. (A), No treatment; (B), adding 5 wt pct phosphate before milling; (C), adding 5 wt pct phosphate after milling; (D), adding 5 wt pct phosphate as a solution; (E), adding 1 wt pct phosphate before milling.

milled pyrite and then drying the sample before testing (D). Also included in Figure 6 are the results of adding 1 wt pct monobasic sodium phosphate to pyrite before milling (E). In examining these treatments, the intimate mixing of phosphate obtained through milling or as a solution additive provided the greatest reduction in oxidation. Simply mixing the phosphate with milled pyrite caused little reduction in oxidation as did reducing the treatment level to 1 wt pct.

Additional phosphate chemicals tested included monobasic and dibasic calcium phosphate, monobasic potassium phosphate, and monobasic and dibasic ammonium phosphate. Results of the oxidation tests are shown in figure 7 and indicate that monobasic calcium phosphate was more effective than dibasic calcium phosphate and reduced pyrite oxidation to about 65 pct of the blank test at 200° C. Monobasic ammonium phosphate slowed oxidation at 200° C to less than 50 pct of the blank, while at 100° C both the mono and dibasic ammonium phosphate and the monobasic potassium phosphate slowed oxidation to less than 50 pct of the blank.

Sodium silicate pentahydrate, borax, and fumed silica were also tested to measure their effect on pyrite oxidation to soluble sulfate. The results of these tests are given in figure 8. Sodium silicate was found to retard significantly oxidation at 200° C, while borax was less effective. The fumed silica had little or no effect. At the lower test

temperature, none of the additives appeared useful in slowing oxidation. Figure 8 also illustrates the effect of additions of calcium oxide, calcium carbonate, potassium bicarbonate, and sodium bicarbonate. In this group of additives, calcium oxide was the most effective and reduced oxidation at 100° and 200° C to about 50 and 60 pct, respectively, of the values measured for the blank samples. Calcium carbonate caused little change. Potassium bicarbonate reduced oxidation at the lower test temperature while sodium bicarbonate reduced oxidation at the higher temperature. Calcium carbonate is often the principal component of rock dust applied in coal mines and based on these results, its use would not be expected to accelerate oxidation in mines having high levels of pyrite.

Figure 9 illustrates the results of oxidation experiments when ferric sulfate and cupric sulfate were added to pyrite. Ferric sulfate is responsible for accelerating the oxidation of pyrite under aqueous conditions (5), however, without free water, it appears to have little effect based on the results of the isothermal tests. Adding cupric sulfate to pyrite resulted with a significant reduction of pyrite oxidation at both test temperatures. Adding cupric sulfate as a solution produced better results than when milling the chemical with the pyrite. As shown in figure 9, adding 5 wt pct cupric sulfate as a solution reduced the level of pyrite oxidation to less than 10 pct of the blank test at the higher test temperature. Lowering the cupric sulfate

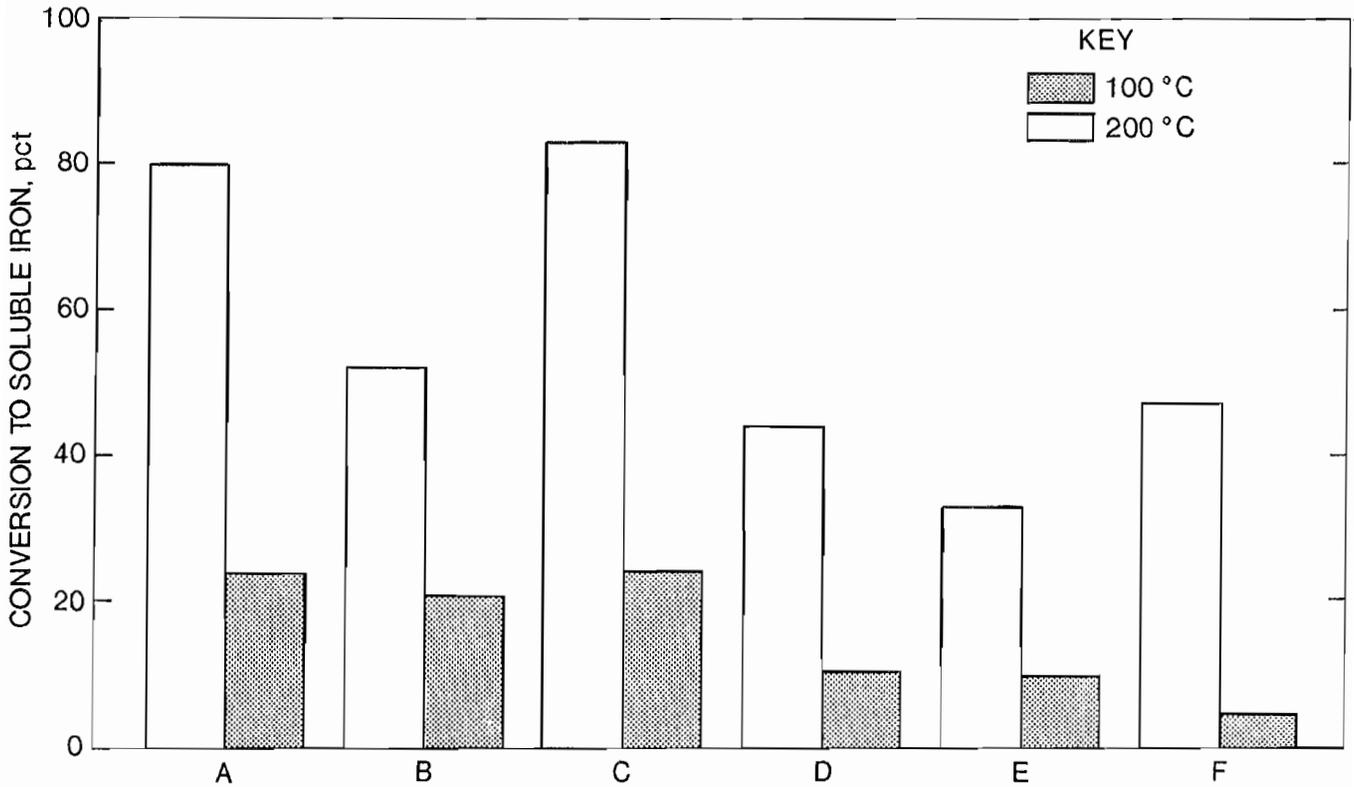


Figure 7.—Effect of (A), no treatment; (B), monobasic calcium phosphate; (C), dibasic calcium phosphate; (D), monobasic potassium phosphate; (E), monobasic ammonium phosphate; (F), dibasic ammonium phosphate on oxidation of pyrite to soluble iron.

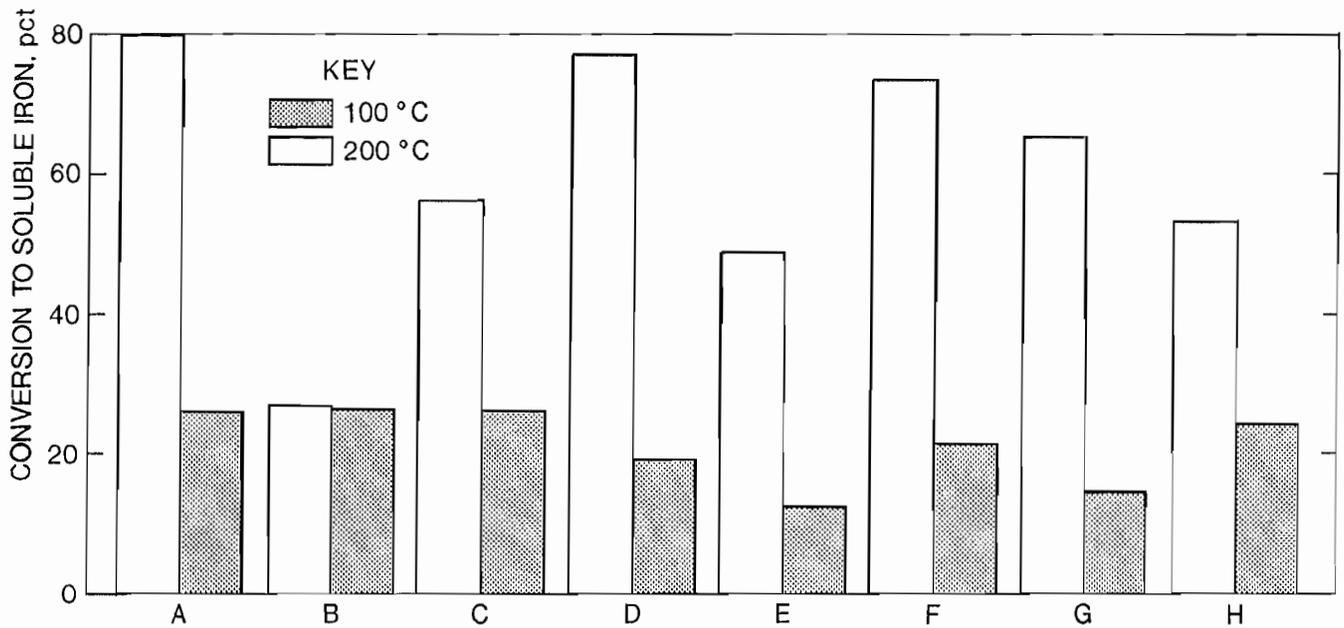


Figure 8.—Effect of (A), no treatment; (B) sodium silicate; (C) borax; (D), fumed silica; (E), calcium oxide; (F), calcium carbonate; (G), potassium bicarbonate; (H), sodium bicarbonate on oxidation of pyrite to soluble iron.

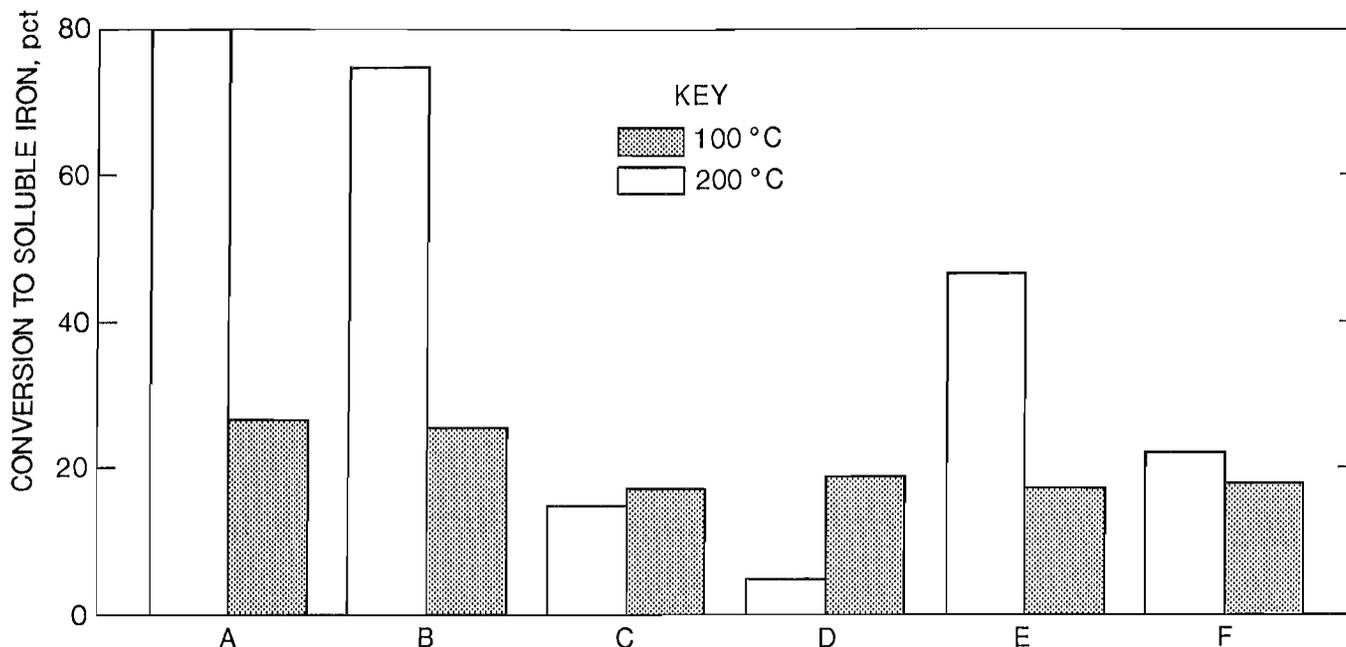


Figure 9.—Effect of method addition and concentration of ferric and cupric sulfate have on oxidation of pyrite to soluble iron. (A), No treatment; (B), adding 5 wt pct ferric sulfate before milling; (C), adding 5 wt pct cupric sulfate before milling; (D), adding 5 wt pct cupric sulfate as a solution; (E), adding 1 wt pct cupric sulfate before milling; (F), adding 1 wt pct cupric sulfate as a solution.

concentration to 1 wt pct also reduced oxidation and when added as a solution reduced oxidation to about 65 and 30 pct of the blank tests at 100° and 200° C.

The final treatments examined in this study involved the use of sodium chloride, calcium chloride dihydrate, and potassium chloride. Examination of the sample boats contents after the initial tests at 200° C indicated that ignition occurred. The samples tested at 100° C appeared normal and chemical analysis indicated that very little oxidation to sulfate had occurred. Ignition under these isothermal test conditions was about 150° C lower than was observed from the TGA tests. The observation of sulfide samples igniting at lower temperatures under isothermal conditions than is observed during TGA was also observed in an earlier study (2). The ignition of marcasite was found to be lower when measured by an isothermal procedure that kept the sample in an inert atmosphere until the test temperature was reached. During the TGA procedure, the samples are heated under an oxidizing atmosphere and this causes sulfate to form that in turn could raise the ignition point of the sample. If the presence of chloride salts impedes the formation of sulfate on pyrite surfaces, then the samples in this study may behave as though they were protected from oxidation by an inert atmosphere. A second possibility for the ignition observed in the ceramic boats at 200° C may have been related to the sample size. The TGA procedure used approximately 40 mg of sample while the additive study

used 5-g samples. The sample with the chloride additions may have undergone an exothermic behavior different from the untreated sample during testing and this may have taken the larger sample mass above the test temperature. As the TGA sample was much smaller, the heat from an exothermic reaction may have been dissipated from the sample pan keeping the sample closer to the programmed temperature. It is also possible that the presence of chloride salts lowered the ignition point of pyrite. In any case, when the sample amount was reduced to 3 g, ignition did not occur, and it was then possible to measure the degree of oxidation at 200° C. The cause of the apparent lowering of the pyrite ignition point will be addressed in future research.

The reduction of pyrite oxidation provided by these salts is illustrated in figure 10, and it is apparent that the sodium and calcium chloride additions have nearly eliminated the formation of ferrous sulfate. The results resemble those obtained when pyrite is tested in dry air (3). Although some oxidation occurs when potassium chloride was used as the treatment, it reduced the levels to values well below those recorded for the other nonchloride salt treatments.

The effectiveness of the sodium and calcium chloride additives in slowing pyrite oxidation prompted additional testing to measure the effect of lowering the salt concentration and to determine if adding salts to pyrite as solutions would also slow oxidation. Figure 11 indicates the

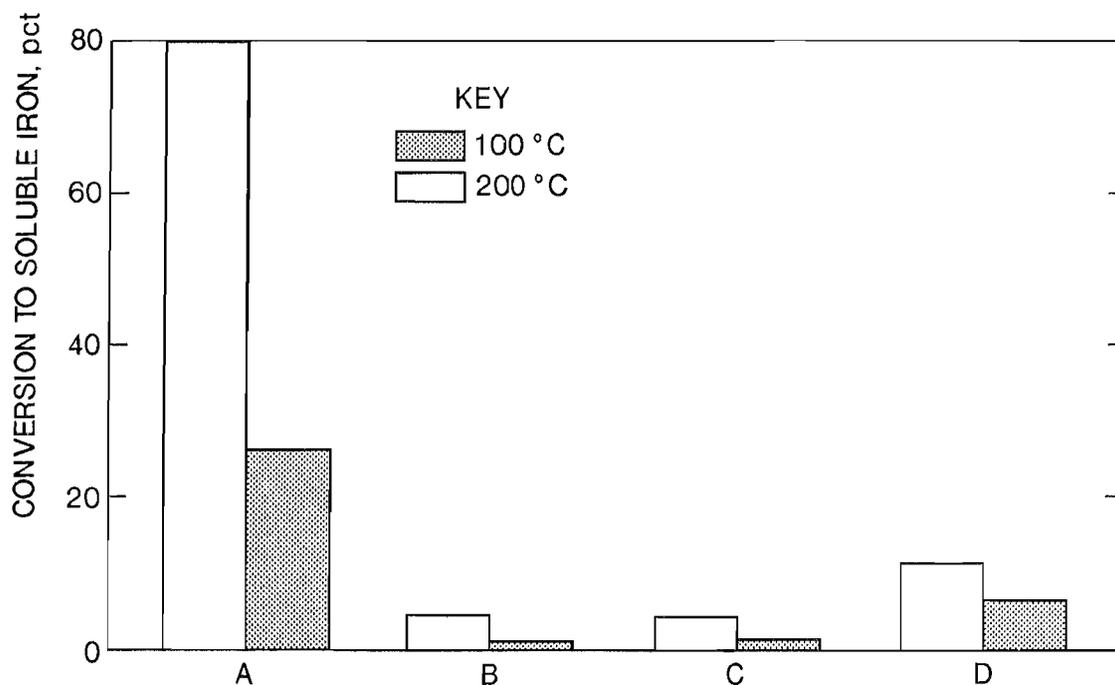


Figure 10.—Effect of (A), no treatment; (B), sodium chloride; (C), calcium chloride; (D), potassium chloride on oxidation of pyrite to soluble iron.

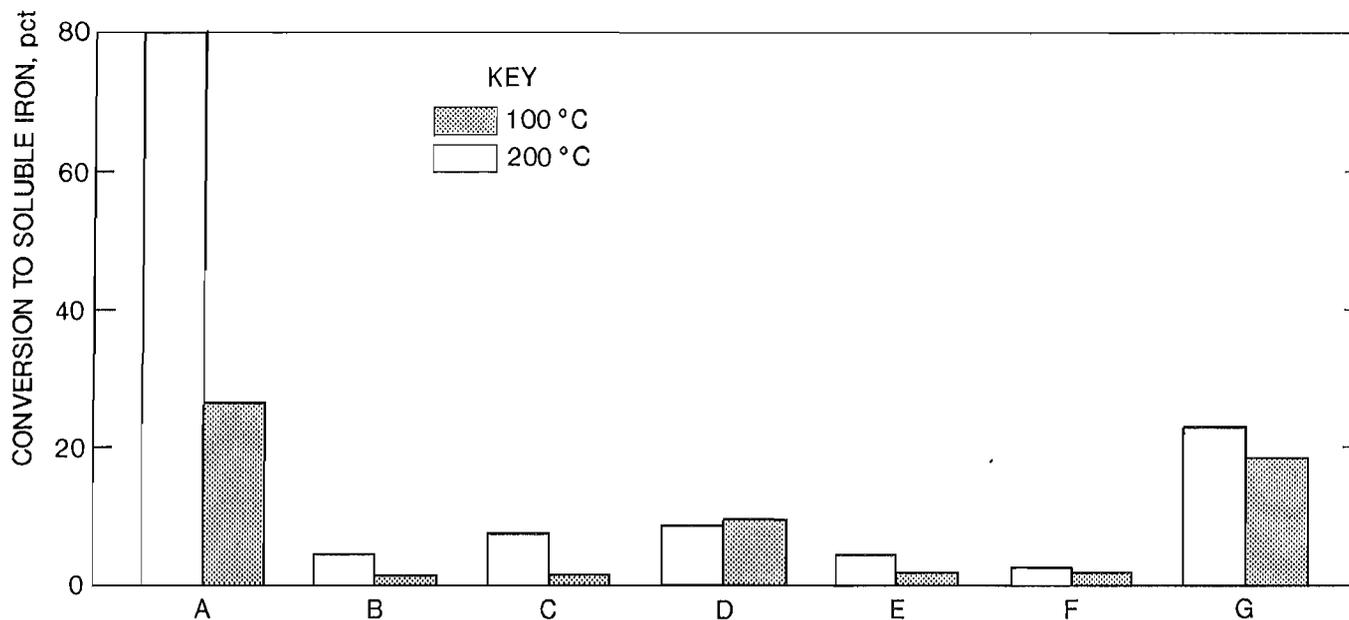


Figure 11.—Effect of method addition and concentration of sodium and calcium chloride have on oxidation of pyrite to soluble iron. (A), No treatment; (B), adding 5 wt pct sodium chloride before milling; (C), adding 5 wt pct sodium chloride as a solution; (D), adding 1 wt pct sodium chloride before milling; (E), adding 5 wt pct calcium chloride before milling; (F), adding 5 wt pct calcium chloride as a solution; (G), adding 1 wt pct calcium chloride before milling.

results when a sodium chloride solution was added to milled pyrite to provide a concentration of 5 pct after drying the sample. Included in this figure are the results when 1 wt pct sodium chloride was added to the pyrite before milling. Figure 11 also includes the results when

pyrite was treated in a similar manner with calcium chloride. These tests indicate that either salt could be applied as a solution and reduce oxidation. At the 1 pct treatment level, both salts remained effective in slowing oxidation with sodium chloride providing somewhat better results.

## SUMMARY AND CONCLUSIONS

Pyrite was milled with various chemical additives, to provide intimate mixing as a first step in evaluating the potential of the additives to reduce the potential for self-heating or to increase the ignition temperature of the sulfide. The effect of the additives was measured for change in the sample ignition point and in the degree of oxidation of sulfide to sulfate in a fixed interval at a set temperature. Additives that caused a reduction in the oxidation of pyrite to ferrous sulfate were then examined in more detail. In these additional experiments, additives were added at lower dosage and in some cases as solutions. Several of the additives were found to have an effect on the pyrite ignition point and/or the amount of conversion of sulfide to sulfate. The reason or mechanism for these effects was not studied, but will be addressed in future research.

In reviewing the results of the TGA determination of sample ignition to ferric oxide, many of the recorded values are higher when the samples were tested in moistened air. During the heating process, it is likely that sulfate is formed on the pyrite surface and, as a humid atmosphere tends to promote the formation of ferrous sulfate, this increased quantity appears to raise the temperature of ignition. At the higher dose levels, the chloride salts were found to cause a significant lowering of sample ignition points. As these same salts reduced sulfate formation in isothermal tests, the lower values obtained by TGA may represent a pyrite that has undergone little oxidation and has a surface that is nearly free of ferrous sulfate that would raise the ignition point. The remaining additives had less effect on pyrite ignition, with borax raising the ignition point about 15° C above the blank. Sodium bicarbonate and sodium silicate were found to lower the ignition point in moist air by 55° and 60° C, respectively, below the blank.

The results of lower temperature (50° C) isothermal oxidation tests indicate fine pyrite will undergo significant oxidation to soluble iron sulfate. A test with a duration of

21 days resulted in the conversion of 20 pct of the pyrite to sulfate. Increasing the test temperature causes an increase in conversion, with about 80 pct of the pyrite oxidized to sulfate after 24 h at 200° C. The use of XRD analysis confirmed that pyrite was converted to ferrous sulfate after oxidation for 24 h at 200° C. Similar examination of the pyrite oxidized at lower temperature failed to confirm the presence of sulfate and this may have been an effect of concentration or degree of crystal formation. Iron sulfate was subsequently identified when the oxidized pyrite was leached with water and the filtrate dried. The resulting crystals were identified as melanterite, a hydrous ferrous sulfate.

Reviewing the results of the isothermal oxidation tests, several of the additives were found to slow pyrite oxidation to sulfate and should undergo further evaluation in thermal tests to verify their effectiveness to slow self-heating. Among the various additives that slowed oxidation of pyrite at 200° C were the monobasic, dibasic, and tribasic forms of sodium phosphate, dibasic potassium phosphate, monobasic and dibasic ammonium phosphate, and cupric sulfate. Of this group, cupric sulfate was the most effective in reducing the oxidation of pyrite to sulfate to less than 10 pct of the blank test. Sodium silicate, calcium oxide, and sodium bicarbonate also had some effect in slowing oxidation at 200° C. Tests at 100° C indicated that monobasic and dibasic sodium phosphate, monobasic potassium phosphate, monobasic and dibasic ammonium phosphate, potassium bicarbonate, and calcium oxide all slowed oxidation. The largest effect in slowing oxidation at both test temperatures came from the use of calcium, potassium, and sodium chlorides. When used at the 5-pct level of addition, all were found to lower the amount of oxidation to 20 pct or less of the control test. Both calcium and sodium chloride at the 5-pct level were effective when added as a solution. Reducing the additive concentration to 1 pct also slowed oxidation.

## REFERENCES

1. Ninteman, D. J. Spontaneous Oxidation and Combustion of Sulfide Ores in Underground Mines. A Literature Survey. BuMines IC 8775, 1978, 36 pp.
2. Reimers, G. W., and K. E. Hjelmstad. Analysis of the Oxidation of Chalcopyrite, Chalcocite, Galena, Pyrrhotite, Marcasite, and Arsenopyrite. BuMines RI 9118, 1987, 16 pp.
3. Reimers, G. W., and W. H. Pomroy. Spontaneous Combustion Susceptibility of Sulfide Minerals-Recent Developments in Metal and Nonmetal Mine Fire Protection. Paper in Recent Developments in Metal and Nonmetal Mine Fire Protection. Proceedings: Bureau of Mines Technology Transfer Seminars, Denver, CO, October 18-19, Detroit, MI, October 20-21; Las Vegas, NV, November 1-2; and Spokane, WA, November 3-4, 1988. BuMines IC 9206, 1988, pp. 54-60.
4. Watkin, E. M., and J. Watkin. Inhibiting Pyrite Oxidation Can Lower Reclamation Costs. Can. Min. J., Dec. 1983, pp. 29, 31.
5. K. D. Hester & Associates. Practical Considerations of Pyrite Oxidation Control In Uranium Tailings (contract OSQ 83-00278). Rep. to Natl. Uranium Tailings Program, CANMET, Ontario, Canada, July 5, 1984, 279 pp.
6. Rosenblum, F., and P. Spira. Self-Heating of Sulfides. Paper in Proceedings: Symposium of Canadian Mineral Processors, January 1981, CANMET, 1981, pp. 34-51.
7. Kehinde-Phillips, O. O., O. T. Djamgouz, and S. Nikolic. Experimental Investigation of the Oxidation and Consolidation of Sulfide Aggregate and the Application to Underground Muck-Piles-Lockerby Mine, Sudbury, Ontario. CIM Bull., v. 77, No. 861, Jan. 1984, pp. 52-59.
8. Pearse, M. J. Chemical Study of Oxidation of Sulfide Concentrates. Inst. Min. and Metall., Trans., Sec. C, v. 89, 1980, pp. 26-36.
9. Guedes de Carvalho, R. A., C. G. González Beca, M. N. Sampaio, O. Neves, M. C. Sol Perira, and H. Sousa Vale. A Study of Transportation and Storage Characteristics of a Chalcopyrite Concentrate From Neves Corvo Mine, Alentejo, Portugal. CIM Bull., v. 82, No. 923, Mar. 1989, pp. 134-142.
10. Banerjee, A. C., P. Rangaswamy, and S. Sood. Mechanism of Oxidation of Iron Pyrite in Dynamic Air. Paper in Proceedings of the 6th International Conference on Thermal Analysis, ICTA 80, Beyreuth, W. Germany. Birkhaeuser, v. 2, 1980, pp. 241-246.
11. Thrush, P. W. (comp.) A Dictionary of Mining, Mineral, and Related Terms. BuMines Spec. Publ., 1968, p. 691.
12. Hartman, H. L. Mine Ventilation and Air Conditioning. Wiley, 2d ed., 1982, p. 566.