BLASTING HAZARDS IN SULFIDE-BEARING ORE BODIES

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ABSTRACT

Two unplanned detonations occurred recently during surface blasting operations in sulfidebearing ores at a Nevada gold mine. Other premature detonations have also reportedly occurred at other Nevada, California

and Arizona gold mines within the past few years, with increasing frequency. Similar unplanned detonations have happened in copper mines, in a coal mine, and in a limestone mine which had oil shale bands containing pyrite interspersed in the limestone. The common denominators in all these events were (1) the presence of sulfide in the ores being mined and (2) the use of ammonium nitrate-fuel oil (ANFO) explosive in the blasting.

This report delineates the basic causes for these accidents. These are the exothermic oxidation of pyrite (FeS₂) and formation of ferrous sulfate (FeSO₄), the exothermic and energetic reaction of the resultant ferrous sulfate with ANFO-based explosives, and the associated elevated temperatures that can set off detonators and explosives in the boreholes.

Recommendations for safe operation for all mines containing sulfide ores include monitoring of temperatures in the blast holes, analyzing for sulfate and ferrous ions, and limiting the time between loading and firing in accordance with conditions in the blast holes.

INTRODUCTION

Two unplanned detonations occurred recently at a surface gold mine in Ne-

As a result of cutoffs, undetonated explosives can be present in the rubble, and can explode during mucking, thus presenting additional problems. Such unplanned events are believed to be caused by a series of steps.

vada (1)¹ These detonations have been attributed to hot boreholes in which temperatures higher than ambient were prevalent during, and following, the loading phase of the boreholes with explosives.

Another unplanned detonation was reported earlier for another gold mine (2). Additional hot boreholes have since been found at various active gold mines. Cutoffs in blasting trunklines and borehole downlines have also been reported, and are likewise a result of the elevated temperatures in the affected boreholes. As a result of cutoffs, undetonated explosives can be present in the rubble, and can explode during mucking, thus presenting additional problems. Such unplanned events are believed to be caused by a series of steps.

First, self-heating occurs in actively oxidizing pyrites commonly present in gold containing quartz (SiO₂) veins; concurrently ferrous sulfate (FeSO₄) is formed as an oxidation product. This is followed by the exothermic reaction between ammonium nitrate-fuel oil (ANFO) and the ferrous sulfate. Finally, the heat from these two sources leads to the explosion of the initiation devices used for setting off the ANFO charges, which, in turn, sets off the explosive charge in the borehole.

Such events are not unique to gold mines. Unplanned detonations and explosions have occurred over the years in other mines which contained pyrite and which used ANFO in their mining operations, more prominently copper mines (3) but also such mines as a limestone mine (4), a coal mine, and an iron mine. Explosions have also occurred in the road construc-

tion industry and in quarrying. Since unplanned detonations at gold mines are of current concern, the emphasis in this report will be on gold mines; however, the same basic information is as important and relevant to other operations mining sulfide-bearing ores.

Gold is present in the earth's crust to the extent of about 6 parts in 100 million. It is found in somewhat higher amounts in two main types of deposits, hydrothermal veins and placers (5). Hydrothermal veins are thin, sheetlike intrusions into crevices of mineral assemblages. Placers are hydrothermal veins which have undergone weathering and erosion and formed a mineral deposit. The mineral is usually a heavy metal such as gold. The gold, largely unaffected by the weathering process, is concentrated and separated from the other minerals in the placers. Most gold of hydrothermal origin is found in quartz (SiO₂) veins, commonly with pyrite, many other sulfides, and other miner-

Nearly all the gold is found in the metallic state. In addition, gold occurs as discrete grains, contained as inclusions in individual crystals of pyrite and arsenopyrite (FeS₂• FeAs₂). It may also be found in solid solution in the sulfides. The Mother Lode district of California contains all such forms of gold (6). Jean and Bancroft (7) suggest that gold chloride and cyanide species, found in the hydrothermal fluids, are

¹ Italic numbers in parentheses refer to items in the list of references at the end of this article.

adsorbed, and reduced by sulfide minerals to the metallic state. This explains the intimate contact between gold and the various sulfides.

Pyrite and the other sulfides easily weather/oxidize in the presence of air and moisture. Most of the metal sulfides form the corresponding sulfates upon oxidation; many of these also form sulfuric acid (H,SO) in the process. In addition to ferrous sulfate and sulfuric acid, ferric sulfate [Fe₂(SO₂),] also forms during the oxidation of pyrite, via oxidation of the ferrous sulfate. Bacterial activity promotes the oxidation. When a combination of sulfide minerals including pyrite is present, many reactions take place. Many of these reactions are highly exothermic and when the resultant heat is not dissipated, due to the poor thermal conductivity of the associated strata, the temperature of the strata rises. The increased temperatures pose a blasting hazard. When explosives are loaded into hot boreholes they can deteriorate if left in place for an extended time before they are set off. The exothermic reaction between ANFO and ferrous sulfate, which is initiated at a relatively low temperature, presents another danger, because it readily generates high temperatures. Heavy ANFO, or ANFO/emulsion blends, likewise undergo the same reaction with ferrous sulfate, probably at a similar low temperature. Sulfuric acid, one of the oxidation products, can react with the metal cases of blasting caps when these are used—and damage them. The explosives contained in the blasting caps are also sensitive to thermal stimuli and some of them explode at relatively low temperatures. Unplanned explosions and detonations are the undesirable end results.

OXIDATION AND SELF-HEATING OF SULFIDES

Gold deposits in silicified ores are found in close contact with many sulfides, such as pyrite, chalcopyrite (CuFeS₂), sphalerite (ZnS), galena (PbS), bismuthinite (Bi₂S₃), and famatinite [Cu₃(Sb,As)S₄], to mention a few (8). On oxidation, sulfate salts such as zinc sulfate (ZnSO₄) and lead sulfate (PbSO₄) result. Iron sulfides (pyrite and marcasite) undergo a series of reactions, as follows:

FeS₂ +
$$7/20_2$$
 + H₂0 \rightarrow FeSO₁ + H₂SO₁,
(Δ H = -303.57 Kcal or -3.87 cal/cm³ O₂
adsorbed) (A)

2FeSO₄ + I/2O₂ + H₂SO₄
$$\rightarrow$$
Fe₂(SO₄)₃ + 1/2H₂O, (ΔH = -87.03 Kcał) **(B)**

FeS₂ + 7Fe₂(SO₄)₃ + 8H₂0
$$\rightarrow$$
15FeSO₄ + 8H₂SO₄, (Δ H - +303.8 Kcal) (C)

forming ferrous sulfate, ferric sulfate and sulfuric acid in the process. Bacteria, such as *Thiobacillus ferrooxidans* act as catalysts and accelerate some of the reactions manyfold, especially when the temperature and acidity are in the range in which these microorganisms function well.

When copper sulfides, such as chalcocite (Cu₂S) and chalcopyrite are present, additional reactions occur. Further, when a mixture of many sulfides is found, a multitude of reactions is possible. Ferric sulfate, a strong oxidant, interacts with most of these sulfides, as for example (9),

Fe₂(SO₄)₃ + Cu₂S
$$\rightarrow$$
CuSO₄ + 2FeSO₄ + CuS, (ΔH 5 +36.0 Kcal). **(D)**

Fe₂(SO₄)₃ + PbS + 1-1/20₂ + H₂0
$$\rightarrow$$
PbS0₄
+ 2FeS0₄ + H₂S0₄, (Δ H = -109.9 Kcal) **(E)**

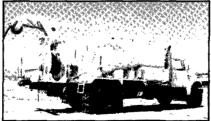
and.

$$2Fe_2(SO_4)_3 + CuFeS_2 \rightarrow CuSO_4 + 5FeSO_4 + 2S^{\circ}$$
. **(F)**

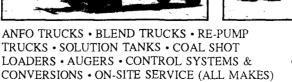
Iron sulfides, in addition to providing sulfuric acid and ferric sulfate to sustain the above reactions, promote the oxidation of lead, zinc, and copper sulfides as a result of electrolytic action due to contact with the iron sulfides (10). The sulfuric acid formed in these reactions will attack other minerals in the ore. The dissolved minerals and the highly acidic conditions will support bacterial growth and supply the necessary nutrients.

The sulfide minerals present in quartz veins are also able to support bacterial activity, as was shown by Duncan and Drummond (11) in laboratory tests. The Thiobacillus ferrooxidans which was used for these tests was grown on a chalcopyrite-zinc sulfide ore, so as to adapt it to this mixture of minerals. Preferential leaching was observed in the tests; chalcocite was completely consumed whereas chalcopyrite was not completely oxidized. The surfaces of the pyrite were observed in the scanning electron microscope and were seen to be etched with many pits, grooves and holes, none of which were observed on the surfaces of the pyrite prior to the tests. In another study (12), in which mixed cultures of Thiobacillus ferrooxidans were used to study the bacterial oxidation of a low-grade sulfide gold ore, positive results were obtained. The cultures were isolated from the ore, indicating that bacteria can be present in gold mines. As a matter of fact, biological oxidation is used in the

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Table 1—Explosion temperatures of various detonators¹

	Detonator			Average explosion temperature
* *	Description ²			°C ·
MANUFACTURER 1				· .
EPC No 6 alterior	0.000			160
Instantanoous EDC	Na 6	**************************************	ka mana ji ka ngangan ngangan jagan angan garan ina mana pigangan nga ngan nga ngan ngan ngan ngan	160
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Delay EDC, 300-11186	c delay linie, aldimiditi case	n Kanantan ya ya maya ya maya ya maya da maya na maya Maya na maya n	कुर सम्प्रको सुन्दा कुनेकुर महीत्र अस्तिक वे स्कारकारी किये के स्वापी किया सकता प्रमुखन कुन्दा प्रकार करती सकत स्वापी करते हैं कि सुनिवास के प्रकार किया है किया है कि सम्बद्धित है कि सम्बद्धित है कि सम्बद्धित है कि स्वापी	
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	ng cap. FBC - Fuse blasting cap			
 Detonators were h 	eated at a constant rate of 0.5° C	J per minute.		그 그들은 40

- Numbers in this column indicate the relative strength of the detonators
- ³ Decomposed active elements flowed out of fuse cavity.

APACHE

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processing of such ores, to enhance gold and silver recovery from refractory ores (13-16).

The oxidation of pyrite, and its attendant reactions, is, overall, an exothermic process. As shown earlier for equation A, approximately $4.0\,\mathrm{cal}$ are released by pyrite for each cm³ of $\mathrm{O_2}$ adsorbed. Additional heat is released by some of the other reactions, and when all the reactions are balanced, the net result is an exothermic process.

If this heat is not dissipated, the pyrite will self-heat, and might even ignite. Mining of sulfide ores is often accompanied by self-heating, spontaneous ignitions, and major fires. One example of the severe problems associated with mining sulfide ores is described for the

Sullivar Mine in British Columbia which contains sphalerite, galena, pyrrhotite (FeS), and pyrite (17-18). Another mine which encountered many complex problems during development and production was the 500 Copper Orebody at Mount Isa, Australia, which contains sulfides (3).

Gold is commonly found in close proximity to pyrite and other sulfides. Several mines in Nevada, which currently produces more gold than any other state in the Union (19), in both open pit and underground mines, have large amounts of sulfides. The possibilities for unplanned explosions exist; at these mines, and at similar operations, steps should be taken to minimize or eliminate these hazards

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REACTIVE PYRITES

It is a known fact that some pyrites oxidize and undergo physical changes within days, while others remain unchanged for years. The causes for this behavior are only partly understood. The source of the pyrite, its mode of

formation and, degree of acidity during its formation are partly responsible. The shape and the size of the crystals also influence reactivity, which in general increases with decreasing crystal size. Framboidal pyrite crystals, among the smallest known, are highly susceptible to oxidation.

Impurities in the pyrite, and especially metallic elements, act as catalysts and can affect its rate of oxidation or reactivity. Defects in the pyrite crystals are also thought to be preferred sites for attack by oxygen and water, and perhaps by the bacteria which attach themselves to specific sites on the surfaces of the crystals. The electrical properties of thesemiconductive pyrites, such as p-and

There is no simple and fast method to identify reactive and nonreactive pyrites and their proportions in a mine.

Consequently, the concentration of pyrite in the ore is not always a reliable indicator of the degree of hazard to be expected.

Nonetheless, in general, the higher the concentration of pyrite, the greater the probability for hazards.

n-types, have also been cited as determinants of reactivity by some workers in the field, while found to be insignificant by others (20).

Finally, the mineralogy of the ore can affect the oxidation of pyrite, as well as the rate of oxidation. The matrix in which the pyrite is embedded can also undergo weathering/oxidation processes. In many instances the matrix is also reactive and can function as a buffer, as an adsorbent, or as a binder of water, and in this manner affects the overall rate of reaction. For instance, aluminosilicates and silicates weather and release anions or form anionic adsorption sites which can bind iron. They may also form silica gels and obstruct

the flow of liquids, as described by Ehrlich and Fox (21), who also delineate the major parameters that are involved in oxidation and bacterial leaching of mineral sulfides. Finally, silver ions can also increase the rate of oxidation of pyrite and of chalcopyrite. In addition, due to

their close association with gold, silver ions can also affect the rate of oxidation of sulfides in gold ores (22).

One main problem facing coal mines, sulfide mines, gold mines, or other mines in which pyrite is present is the inability to easily assess the reactivity of the pyrite. There is no simple and fast method to identify reactive and nonreactive pyrites and their proportions in a mine. Consequently, the concentration of pyrite in the ore is not always a reliable indicator of the degree of hazard to be expected. Nonetheless, in general, the higher the concentration of pyrite, the greater the probability for hazards.

BLASTING HAZARDS REACTIONS OF ANFO WITH FERROUS SULFATE

ANFO explosives are commonly used at open pit gold mines. Bulk AN and/or bulk ANFO are delivered to the mines in 25- or 37-ton pneumatic tankers. When AN prills are used they are mixed with the fuel oil through an auger on the on-site mix truck. Bulk ANFO (94% AN - 6% fuel oil) is delivered premixed. The ANFO prills are pneumatically transferred to the boreholes; they may also be augered. Any drill cuttings remaining in the holes can come in contact with the ANFO prills. The effects of hot ground on the behavior of ANFO prills have been studied in detail, utilizing thermal analysis and other laboratory test methods (23-24). Similar studies were conducted by the U.S. Bureau of Mines (25), in which various sulfide ores were tested, and the effect of sulfuric acid was evaluated. Additional studies

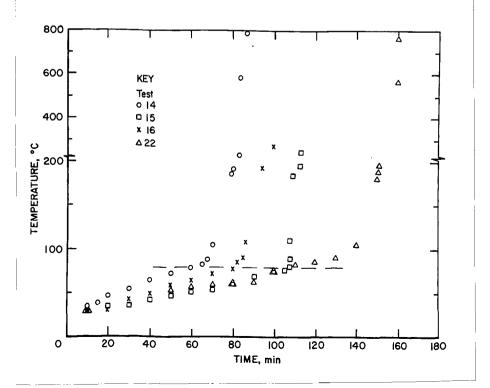


Figure 1. Temperature-time profiles for ANFO-ore-ferrous sulfate mixtures.

by the Bureau (26) have shown that the main reaction responsible for the initiation of exothermic behavior is that between oxidizing pyrite and ANFO, when in direct contact with one another, and specifically between the ferrous and nitrate ions in acidic media.

$$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO_1^+ + 2H_3^+0.$$
 (G)

The rate of this reaction depends on the relative quantities of ammonium nitrate and ferrous sulfate in addition to the amounts of pyrite and fuel oil present in the mixture, on the amount of sulfuric acid generated, and on the degree of mixing of these ingredients. It is reasonable to expect that ANFO/emulsion blends might react initially at a slower rate, because of

the lower concentration of ANFO in the explosive, but this has to be verified experimentally. Some of the results obtained in tests in which ANFO, pyrite ore (5 wt pct) and ferrous sulfate (5 wt pct) were premixed and slowly heated are shown in figure 1 (26). In the four tests depicted, the reaction takes off at about 75° C, as shown by the dashed line. With more reactive pyrites and with other proportions of the reactants, this runaway reaction can start at lower temperatures; likewise, at lower heating rates comparable to ones that might be found in hot boreholes, initiation can also occur at lower temperatures. The time to runaway reaction can be quite short, as seen in the figure. If permitted to continue, very high temperatures will be reached and an explosion or detonation will result.

Various inhibitors were evaluated in all these aforementioned studies, including phosphates, borates, oxides such as zinc oxide, and urea, with urea being among the better ones (27). Adding inhibitors to the ANFO prills complicates the preparation process and also increases the cost of the explosive. Urea adsorbs moisture even more easily than the hygroscopic ammonium nitrate, and thereby can reduce the stability of the prills. It also affects the flow of the prills into the boreholes. The

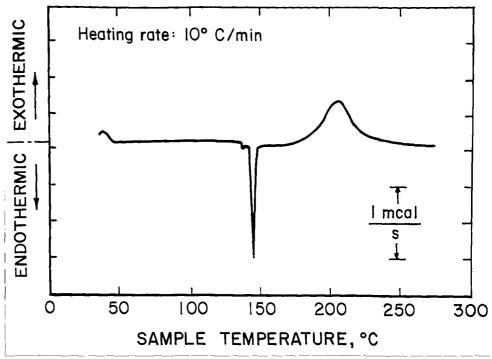


Figure 2. Differential scanning calorimeter thermogram for PETN.

addition of inhibitors may lower the sensitivity of the resultant ANFO blasting agent; as a result a large primer or a larger minimum diameter will be required. However, reports of misfires caused by using ANFO with inhibitors

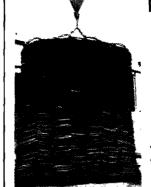
were not confirmed (28). Success with the use of either urea or zinc oxide as inhibitors in ANFO blasting agents has been reported by a coal company (29). Prior to the use of inhibitors, the coal mine had been plagued by surface fires when ANFO came in contact with borehole drill cuttings containing oxidized, pyriterich shale intermingled with the coal. The inhibitors eliminated the problem. Encasing the prills in plastic bags or liners will also increase the overall cost of the explosive, but contact between ANFO and ferrous sulfate will be prevented, thereby eliminating reaction G. However, the use of borehole liners will not eliminate all the hazards, as discussed in the next section.



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HAZARDS ASSOCIATED WITH INITIATION DEVICES

ANFO explosives are not cap-sensitive. They require high-velocity, high-energy primers, which are cap-sensitive and produce a high detonation pressure. The primers, in turn, can be

initiated by an electric or nonelectric detonator, by a 50-grain detonating cord, such as Primacord.2 or by shock tube detonators such as MS Primadet. E-Z det or Excel tube. Gold mines in Nevada use shock tube detonators to initiate the cast primers, which have a cup well and a tunnel well, into which a detonator is aluminum pan. A reference material of about the same weight, and consisting of inert glass beads, was likewise sealed.

Heating rate: IO° C/min

Imcal

Imca

ning calorimeter (DSC) at a heating rate

of 10° C/min, in an atmosphere of static

air. For a test, a small sample of the

order of 2 to 4 mg was sealed in an

Figure 3. Differential scanning calorimeter thermogram for RDX.

100

50

inserted and laced. The shock tube itself (such as Nonel) is a hollow plastic tube coated on the inside surface with the explosive material. The plastic tube deteriorates rapidly at about 65° to 71° C and misfires can result. Detonators have cylindrical metal shells containing several powder charges. The shells are constructed of either brass, copper, aluminum, or an aluminum alloy. These metals are prone to attack by sulfuric acid. For instance, copper will easily convert to copper sulfate, depending on acid strength. As a result, a crack or pinhole may develop in the shell, thus impairing the cap's performance.

The powders found inside the shells of the detonators include PETN {pentaerythritol tetranitrate, $[C(CH_2 ONO_2)_4]$ }, RDX [1,3,5-trinitrohexahydrostriazine, $(C_3H_6N_6O_6)$], and lead azide (PbN₆). PETN has a low melting point of 141° to 142° C. RDX has a melting point of 205.5° C, while lead azide melts at 245° to 250° C. PETN and RDX were tested in a differential scan-

The sample and reference were placed in the DSC and heated simultaneously. The resultant thermogram indicates the adsorption (endotherm) or release (exotherm) of heat by the sample, as a function of sample temperature. When heat is not exchanged, a straight baseline is recorded. A thermogram for PETN, presenting an exothermic decomposition process, is shown in figure 2, while figure 3 presents a thermogram for a sample of RDX. Both explosives show the initiation of exothermic behavior following melting, indicated by the endothoerms.

150

SAMPLE TEMPERATURE, °C

200

The thermal sensitivity of 19 commercial detonators was evaluated in a study conducted by the U.S. Bureau of Mines (30). Although these were electric detonators, they contain similar or identical combinations of powders to those found in nonelectric detonators, so that the results of the study are directly pertinent to either type of detonator. The detonators were placed in a sand-filled pipe, which was then heated

at 0.5° C/min, until an explosion occurred. The detonators, from seven manufacturers, contained various explosives, including PETN, lead azide, lead styphnate [lead 2,4,6 trinitroresorcinate, (C₆HN₃0₈P_b)], mannitol hexa-nitrate, [C₆H₄(NO₃)₆], and diazo-

dinitrophenol (NO,),C,H,N,0]. **Experimental** explosion temperatures (30)shown in table 1, correlate with the thermal properties of the explosive ingredients inside the detonators. Detonators containing mannitol hexanitrate exploded at the lowest temperatures (121°-130°C). Diazodinitrophenol, PETN, and lead azide re-

acted at successively higher temperatures. In similar tests with detonating fuses the fuses inside steel pipes filled with sand, exploded at 130° C (31).

300

250

These results indicate that when temperatures in the hot boreholes exceed 120° to 130° C, detonators are liable to explode and due consideration should be given to the heat sensitivity of detonators. Whenever possible, detonators which are more resistant to heat should be used. Since the reaction between ANFO and ferrous sulfate is initiated, and accelerates, at lower temperatures than those at which the detonators explode, depending on the relative concentrations, this reaction is the most hazardous. If liners are used to prevent direct contact between ANFO and ferrous sulfate, the possibility still exists for explosions to occur. This might happen if the amount of pyrite present is

² Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

relatively high, and it oxidizes at a fast rate, and the time from loading to firing is sufficient for temperatures in the borehole to rise above 120° or 130° C and initiate the detona-

MAJOR INDICATORS OF POTENTIAL **BLASTING HAZARDS**

The presence of sulfides, and especially of pyrite, is the first indicator of a possible hazard. The concentration and form of pyrite is the second hazard indicator. If sufficient amounts of fine crystalline pyrite are present, caution must be taken.

The temperatures in the boreholes and adjacent strata, the rate of temperature rise in these locations, and the acidity of the ore in these strata are also important indicators. Low pH values, on the order of 2.0 to 3.5, are indicative of active pyrite oxidation. However, in the presence of calcareous ore, neutralization of the acid is possible. The presence of various oxidation products, such as the soluble and insoluble iron sulfates, or insoluble hydrous iron oxides, is an important indicator of the stages of oxidation, and therefore can be quite helpful in assessing the degree of hazard. These indicators should be utilized as guidelines before setting blasting designs in the area.

PRECAUTIONARY MEASURES

To assure safe operations in mining in sulfide-bearing ores, precautionary measures are needed. In reference 1, emphasis is placed on the important factors that mine operators should be aware of, and on special treatments to be applied, as necessary. Recommendations are given with regard to monitoring the temperatures of the boreholes prior to loading. If the temperatures of the boreholes are between 32° and 38° C, it is recommended that loading-to-firing time should be limited to about 4 to 6 h, whereas, if the temperature is as high as 43°C, loadingto-firing time should be limited to 2 to 4 hunless special products are used. Similar procedures are recommended for mining in hot strata of coal and metal mines (32); they include limits on load-

The presence of sulfides, and especially of pyrite, is the first indicator of a possible hazard. The concentration and form of pyrite is the second hazard indicator. If sufficient amounts of fine crystalline pyrite are present, caution must be taken.

> ing-to-firing times, the monitoring of temperatures, and cooling of boreholes, whenever possible.

Based on first-hand experience, FMC Paradise Peak Corporation has prepared a safe operating procedure for blasting in their mine (33). This procedure includes instructions for measurements of borehole temperatures, for marking various boreholes according to their temperatures, and for communication of personnel, among other subjects. It is available to interested mines. It should be understood, though, that each mine has its own unique geology and mineralogy, and mining conditions that require blasting procedures tailored to their mine.

The use of inhibitors. such as zinc oxide and urea, has been shown work in a coal mine with a similar problem (29). One pct zinc oxide or 5 pct urea were enough to inhibit the reaction. Likewise, zinc oxide, magneu carbonate and aluminum oxide were evaluated as inhibitors for the iron mine, and zinc oxide, at 10 pct, performed best (34).Thus, inhibitors should be considered for precautionary measures. The choice of a specific inhibitor would depend, among other factors, on cost and how difficult the inhibitor would be to use in a humid atmosphere.

As more mines face this problem, a stan-

dard set of procedures will be adopted. General measures recommended by the U.S. Bureau of Mines for safe operating procedures include:

- · Geological and geochemical assessment of area to be mined.
- Analysis for sulfide content, wherever necessary.
- Analysis for the presence of sulfate, ferrous and ferric ions.
- Removal of drill cuttings from boreholes.
- Presence of water in borehole is undesirable. Water should be removed. or liners should be used.
- Temperature measurements in boreholes, as necessary.



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• Use of liners, when deemed necessary. Generation of static electricity during loading presents a problem; conductive liners would reduce the static hazard. The use of plastic liners would increase the amount of fumes produced somewhat,

The presence of various oxidation productsor insoluble hydrous iron oxides, is an important indicator of the stages of oxidation, and therefore can be quite helpful in assessing the degree of hazard. These indicators should be utilized as guidelines before setting blasting designs in the area.

because they would serve as additional fuel (25). This fact may be important in underground mines.

- Loading-to-firing times should be limited, based on borehole temperatures.
- Appropriate choice of initiation devices, as regards temperatures in boreholes, should be given consideration.
- Understanding of the self-heating process and its possible acceleration at higher temperatures.

SUMMARY

Many metal sulfides and especially pyrite are commonly present in close proximity to gold in gold-bearing veins. During mining, and exposure of the ore and veins to the ambient atmosphere, pyrite and the other sulfides can oxidize and self-heat. Pyrites are also found in other mines, and similarly oxidize, upon exposure to air. The main products of pyrite oxidation are ferrous sulfate and sulfuric acid. They react with ANFO and ANFO/emulsion blends exothermally. The heat from such a reaction can lead directly to explosions or can set off detonators. Blasting accidents are the end result. This report describes the oxidation of sulfides and pyrite, the reaction between ferrous sulfate and ANFO, and the resultant, increased probability for setting off detonations. Precautionary measures include the monitoring of temperatures of boreholes, analyzing for sulfate and ferrous ions and adjusting the loading-to-firing time as necessary. The use of inhibitors could also be considered.

REFERENCES

 Fischer, R. L. Investigation of Premature Detonations. Paradise Peak Mine, FMC Corporation, Gabb, Nevada. I.D. No. 26-01908. U.S. Department of Labor, MSHA Report No. D7431-S949, December 10, 1991, 9 pp.

Investigation of a Premature Detonation. Copper Canyon Mine. Battle Mountain Gold Company. Battle Mountain, Nevada. U.S. Department of Labor, MSHA Report No. D6681-S848, June 28, 1989, 6 pp.

3. Cox, D. M. The Use of Explosives in Hot Ground at Mount ISA Mines Limited. Paper in Eighth Commonwealth Mining and Metallurgy Congress. Gen. Pro. Publ., v. 6, 1967, pp. 339-348.

4. Mr. Stunmier, Holnam Inc., Fort Collins, CO. Personal communica-

5. Berry, L. G., and B. Mason. Mineralogy Concepts Descriptions Determinations. W. H. Freeman, 1959, pp. 279-287.

6. Heinen, H. J., G. E. McClelland, and R. E. Lindstrom. Recovery of Gold from Arsenopyrite Concentrates by Cyanidation-Carbon Adsorption. BuMines RI 8458, 1980, 10 pp.

7. Jean, G. E., and G. M. Bancroft. An XPS and SEM Study of Gold Decomposition at Low Temperatures on Sulphide Mineral Surfaces: Concentration of Gold by Adsorption/Reduction. Geochim. Cosmochim. Acta, v. 49, 1985, pp. 979-987.

8. Ashley, R. P., and J. P. Albers. Distribution of Gold and Other Ore-Related Elements Near Ore Bodies in the Oxidized Zone at Goldfield, Nevada. U.S. Geol. Surv. Prof. Pap. 843-A, 1975, 48 pp.

9. Lamey, C. A. Metallic and Industrial Mineral Deposits. McGraw-Hill,

1966, pp. 86-87.

10. Buehler, H. S., and V. H. Gottschalk. Oxidation of Sulphides. Econ. Geol., v. 7, 1912, pp. 15-

11. Duncan, D. W., and A. D. Drummond. Microbiological Leaching of Porphyry Copper Type Mineralization. Post-Leaching Observations. Can. J. Earth Sci., v. 10, 1973, pp 476-484.

12. Mihadov, B. V., and J. L Hendrix. Biooxidatio of a Sulfide Gold Orc Columns. Reno, NV).

dation To

Ores and

Pretreat-

Econom-

(Grant G1164132, Univ. of Nevada, Reno, Mackay Sch. Mine BuMines OFR 23-92, 1991, 15 pp.

13. Lawrence, R. W., and A. Bruynesteyn. Biological Pre Enhance Gold and Silver Recovery From Refractory Pyr-Concentrates. CIM Bull., v. 76, No. 857, Sept. 1983, pp. 10

14. Hutchins, S. R., J. A. Brierley, and C. L. Brierley. Micro ment of Refractory Sulfide and Carbonaceous Ores Improve

ics of Gold Recovery. Min. Eng., v. 40, Apr. 1988, pp. 249-25 15. Marchant, P. B., and R. W. Lawrence. Flowsheet De-1 Process Control and Operating Strategies in the Biooxidation of Ret ory Gold Ores. Paper in Proceedings of the Third Annual Generaeeting of Biominet, ed. by G. G. L. McCready, CANMET SP86-9, Canada. 36, pp. 39-

16. Torma, A. E. A Review of Gold Biohydrometallurg: Paper in Proceedings of the 8th International Biotechnology Symposium, ed. by G. Durand, L. Bobichon, and J. Florent. Soc. Fr. Microbiol., Paris (France), 17-22, July 1988, pp. 1158-1168.

17. Good, B. H. The Oxidation of Sulphide Minerals in the Sullivan Mine.

CIM Bull., v. 70, No. 782, June 1977, pp. 83-88.

18. Farnsworth, D. J. M. Introduction to and Background of Sulphide Fires in Pillar Mining at the Sullivan Mine. CIM Bull., v. 70, No. 782, June

19. Grabowski, R. B., R. G. Raney, and N. Wetzel. Behind Nevada's

Golden Renaissance. Miner. Today, Dec. 1991, pp. 14-19.

20. Springer, G. Observations on the Electrochemical Reactivity of Semiconducting Minerals. Trans. Inst. Min. Metall., v. 79, 1970, pp. Cll-C14.

21. Ehrlich, H. L., and S. I. Fox. Environmental Effects on Bacterial Copper Extraction from Low-Grade Copper Sulfide Ores. Biotechnol. and Bioeng., v. 9, 1967, pp. 471-485

22. Buckley, A. N., and H. J. Wouterlood. The Interaction of Pyrite with Solutions Containing Silver Ions. J. Appl. Electrochem., v. 19, 1989, pp. 744-

23. Lukaszewski, G. M. The Reaction of ANFO Explosives With Mineral Sulphides. Paper in Proceedings of the Australian Institute of Mining and Metallurgy, (Melbourne, Aust. Dec. 1968). Aust. Inst. Min. Metall., 1968, pp. 61-70.

. Natural Oxidation and the Reaction of AN-FO Explosives in Mineral Sulphides at Mount Isa Mines Limited, Australia. Paper in Proceedings of the 9th Commonwealth Mining and Metallurgy Congress. (CSIRO,

Div. of Miner. Chem., Melbourne, Australia), v. 1, 1969, pp. 803-819.25. Forshey, D. R., T. C. Ruhe, and C. M. Mason. The Reactivity of Ammonium Nitrate-Fuel Oil With Pyrite-Bearing Ores. BuMines RI 7187, Oct. 1968, 9 pp

26. Miron, Y., T. C. Ruhe, and R. W. Watson. Reactivity of AN-FO With Pyrite Containing Weathering Products. BuMines RI 8373, 1979, 24 pp.

27. Miron, Y., T. C. Ruhe and J. E. Hay. Reactivity of ANFO With Pyrite Containing Weathering Products-Evaluation of Additional Inhibitors. BuMines RI 8727, 1982, 14 pp.

28. Fischer, R. D. Private communication, 1992.

29. Wiram, V. P., and J. W. Brown. An Investigation Into the Physical/ Chemical Mechanisms Responsible for Spontaneous Combustion Reactions Between Admixtures of ANFO/Emulsion Blends and Rock Overburden. Inter. Co. Rep., Delta Mine, Amax Coal Co., Feb. 14, 1992, 23 pp.

30. Becker, K. R., J. C. Cooper, and R. W. Watson. Impact and Thermal Sensitivity of Commercial Detonators. BuMines RI 8085, 1975, 17 pp.

31. Nabiullah, M. D., R. NM. Gupta, B. Singh, and P. K. Gandopadhyay. A Study on Thermal Behavior of Some Commercial Explosives. Thermochem. Acta, v. 134, 1988, pp. 419-428.

32. Adhikari, G. R., R. N. Gupta, and R. B. Singh. Update on Open-Pit Coal Mine Blasting. J. Mines, Metals and Fuels, June 1987, pp. 219-222.

33. Reilly, M., and T. Hilderman. Precautionary Measures for Sulfide Blast Holes Hazard Recognition and Mitigation. FMC Paradise Peak Corp., FMC Gold Co., Dec. 3, 1991, 3 pp.

34. Harries, G., P. Bellairs, and J. S. Stewart. The Reaction of Ammonium Nitrate With Black Pyritic Shale at MT Whaleback. Paper in Proceedings of Australasian Institute of Mining and Metallurgy (Parkville, Aust. Oct. 1986). Australasian Inst. Min. Metall., 1986, pp. 141-146.