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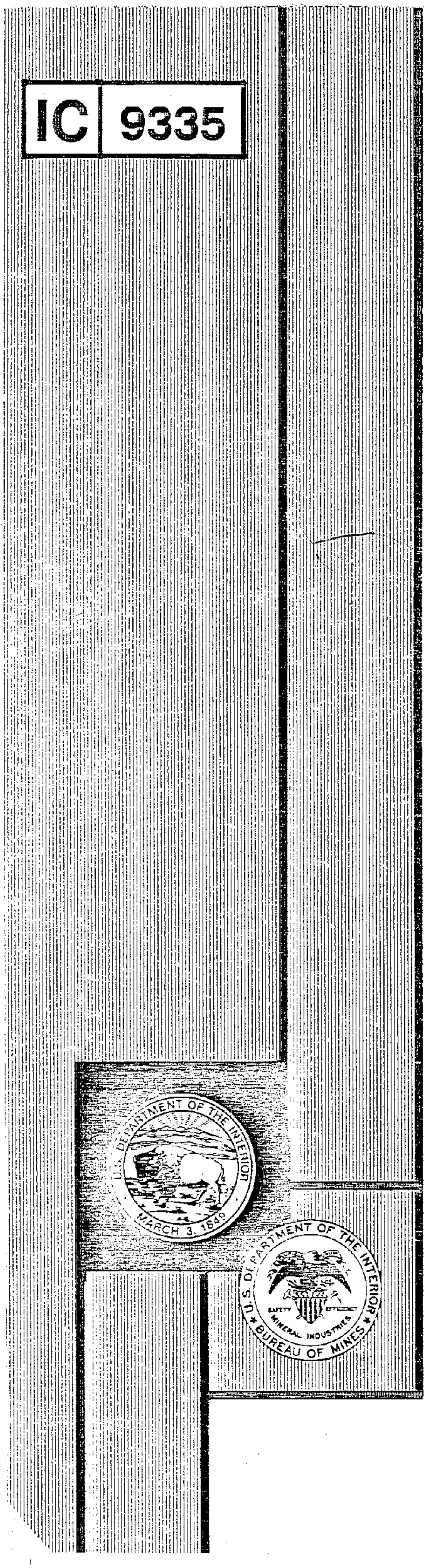

BUREAU OF MINES
INFORMATION CIRCULAR/1992

Blasting Hazards of Gold Mining in Sulfide-Bearing Ore Bodies

By Yael Miron

UNITED STATES DEPARTMENT OF THE INTERIOR

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Two recent unplanned detonations occurred during blasting operations in sulfide-bearing ores in a Nevada gold mine. Other premature detonations have also reportedly occurred at other Nevada, California and Arizona operations within the past few years, at increasing frequency. Unplanned or premature detonations can be extremely hazardous to life and can cause extensive property damage. A miner was injured in one of these occurences.

This report, by the U.S. Bureau of Mines, is intended to acquaint personnel involved in such mining activties with the basic causes for these accidents. These involve the exothermic oxidation of pyrite (FeS_2) and formation of ferrous sulfate ($FeSO_4$), the exothermic and energetic reaction of the ferrous sulfate with ammonium nitrate-fuel oil (ANFO) based explosives, and the associated elevated temperatures which can set off detonators and explosives in the boreholes.

Recommendations for safe operation, by MSHA, by the mine involved with the recent incidents, and by the Bureau of Mines include monitoring of temperatures in the blastholes, analyzing for sulfate and ferrous ions, and limiting loading to firing time accordingly. Other procedures, for safe operations, should fit specific conditions in the mines.

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UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary

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CONTENTS

Page

Abstract 1
Introduction 2
Acknowledgments 3
Oxidation and self-heating of sulfides 3
Reactive pyrites 4
Blasting hazards 4
  Reactions of ANFO with ferrous sulfate 4
  Hazards associated with initiation devices 6
Major indicators of potential blasting hazards 8
Precautionary measures 8
Summary 9
References 9

ILLUSTRATIONS

1. Temperature-time profiles for ANFO-ore-ferrous sulfate mixtures 5
2. Differential scanning calorimeter thermogram for PETN 6
3. Differential scanning calorimeter thermogram for RDX 7
4. Differential scanning calorimeter thermogram for RDX using increased sample weight 7

TABLES

1. Explosion temperatures of various detonators 7

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg	milligram
°C/min	degree Celsius per minute	min	minute
cal	calorie	ms	millisecond
°F	degree Fahrenheit	pct	percent
h	hour	s	second
mcal/s	millicalorie per second	wt pct	weight percent

BLASTING HAZARDS OF GOLD MINING IN SULFIDE-BEARING ORE BODIES

By Yael Miron[1]

ABSTRACT

Two recent unplanned detonations occurred during blasting operations in sulfide-bearing ores in a Nevada gold mine. Other premature detonations have also reportedly occurred at other Nevada, California, and Arizona operations within the past few years, with increasing frequency. Unplanned or premature detonations can be extremely hazardous to life and can cause extensive property damage. A miner was injured in one of these occurrences.

This report, by the U.S. Bureau of Mines, is intended to acquaint personnel involved in such mining activities with the basic causes for these accidents. These causes include the exothermic oxidation of pyrite (FeS_2) and formation of ferrous sulfate ($FeSO_4$), the exothermic and energetic reaction of the ferrous sulfate with ammonium nitrate-fuel oil (ANFO)-based explosives, and the associated elevated temperatures that can set off detonators and explosives in the boreholes.

Recommendations for safe operation by the Mine Safety and Health Administration, the Bureau, and the mine involved with the recent incidents include monitoring 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. Other procedures for safe operations should fit specific conditions in the mines.

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[1] Chemical engineer, Pittsburgh Research Center, U.S. Bureau of Mines, Pittsburgh, PA.

INTRODUCTION

Two unplanned detonations occurred recently at a surface gold mine in Nevada (*1*).[2] 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. Additional hot boreholes have been since found in this mine and at other active gold mines. Another unplanned detonation was reported earlier for another gold mine (*2*). 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 potential problems. Such unplanned events are believed to be caused by a series of events. First, self-heating occurs in actively oxidizing pyrites commonly present in gold-containing quartz (SiO_2) veins. Ferrous sulfate ($FeSO_4$) forms concurrently. This is followed by the reaction between ammonium nitrate-fuel oil (ANFO) and the ferrous sulfate formed. Finally, the heat from these two contributions causes the explosion of the initiation devices used for setting off the ANFO charges, which, in turn, sets off the explosive charge in the borehole.

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 (*3*). Hydrothermal veins are thin, sheetlike intrusions into crevices of mineral assemblages. The minerals form by precipitation from hydrothermal (hot water) solutions in channels of flow, as these solutions ascend toward the surface and cool in the process. The solutions interact with the wall rock of the channels, or veins, and alteration of wall material results.[3] Placers are hydrothermal veins that have undergone weathering and erosion (by mechanical agents such as alluvial, marine, lacustrine, or glacial processes) 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 veins, commonly with pyrite (FeS_2), many other sulfides, gold-silver tellurides, and other minerals. Nearly all the gold is found in the metallic (native) state. In addition, gold occurs as discrete grains, contained as inclusions in individual crystals of pyrite and arsenopyrite ($FeS_2 \cdot FeAs_2$). It may also be found in solid solution in the sulfides. The Mother Lode district of California contains all such forms of gold (*4*). Jean and Bancroft (*5*) suggest that gold chloride and cyanide species, found in the hydrothermal fluids, are adsorbed and reduced by sulfide minerals to the metallic state. This explains the intimate contact between gold and the various sulfides. Other ideas about associations between gold and host minerals are presented by other authors (*6-7*).

The presence of pyrite and of other sulfides in gold deposits can cause problems during blasting, because of the relative ease with which most of these sulfides weather and oxidize at ambient conditions, in the presence of air and moisture. Most of the metal sulfides form the corresponding sulfates upon oxidation; some of these also form sulfuric acid (H_2SO_4) in the process. Iron sulfides are unique in that, in addition to ferrous sulfate and sulfuric acid, ferric sulfate [$Fe_2(SO_4)_3$] is another oxidation product, resulting from the oxidation of ferrous sulfate. Bacterial activity promotes the oxidation. When a combination of sulfide minerals that includes pyrite is present, many reactions take place. Most of these reactions are highly exothermic, and when the resultant heat is not dissipated, because of the poor thermal conductivity of the associated strata, the strata heat up. 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 easily accelerates to 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 the blasting caps—when these are used—and damage them. The explosives contained in the blasting caps are also sensitive to thermal stimuli. Unplanned explosions and detonations are the undesirable end results.

This U.S. Bureau of Mines report was written to increase awareness of these potential hazards. Awareness of these hazards will lead to more careful planning and institution of safer mining procedures and hence will reduce the number of accidents.

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[2] Italic numbers in parentheses refer to items in the list of references at the end of this report.

[3] More detailed information on hydrothermal veins can be found in texts of geochemistry (such as "Physical Geochemistry" by F. G. Smith, Addison-Wesley, 1963).

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OXIDATION AND SELF-HEATING OF SULFIDES

Gold deposits in unoxidized silicified ores are found in close contact with many sulfides, such as pyrite, chalcopyrite ($CuFeS_2$), sphalerite (ZnS), galena (PbS), bismuthinite (Bi_2S_3), famatinite [$Cu_3(Sb,As)S_4$], tennanite [$(Cu,Fe)_{12}(Sb,As)_4S_{13}$], and goldfieldite [$Cu_3(Te,Sb,As)S_4$], to mention a few (*8*). On oxidation, sulfate salts such as zinc sulfate ($ZnSO_4$) and lead sulfate ($PbSO_4$) result. Iron sulfides (pyrite and marcasite) undergo a series of reactions, as follows:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{-2} + 2H^+ \quad \text{(A)}$$

(formation of ferrous sulfate and sulfuric acid),

$$Fe^{+2} + 1/4O_2 + H^+ \rightarrow Fe^{+3} + 1/2H_2O \quad \text{(B)}$$

(oxidation of ferrous ions to ferric ions in acidic media), and

$$FeS_2 + 14Fe^{+3} + 8H_2O \rightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \quad \text{(C)}$$

(oxidation of pyrite by ferric ions and formation of additional ferrous ions and sulfuric acid).

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 (Cu_2S) 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, for example (*9*),

$$Fe_2(SO_4)_3 + Cu_2S \rightarrow CuSO_4 + 2FeSO_4 + CuS, \quad \text{(D)}$$

$$Fe_2(SO_4)_3 + CuS + 1\text{-}1/2O_2 + H_2O \rightarrow CuSO_4 + 2FeSO_4 + H_2SO_4, \quad \text{(E)}$$

$$Fe_2(SO_4)_3 + PbS + 1\text{-}1/2O_2 + H_2O \rightarrow PbSO_4 + 2FeSO_4 + H_2SO_4, \quad \text{(F)}$$

$$Fe_2(SO_4)_3 + ZnS + 1\text{-}1/2O_2 + H_2O \rightarrow ZnSO_4 + 2FeSO_4 + H_2SO_4, \quad \text{(G)}$$

and finally,

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

The sulfur subsequently changes to sulfuric acid or sulfur dioxide (SO_2) under oxidizing conditions. 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 bacteria with necessary nutrients.

Duncan and Drummond (*11*) observed microbial leaching of a saussuritized (foliated and regionally metamorphosed) quartz diorite (a group of rocks formed at considerable depth by crystallization of magma or by chemical alteration, and intermediate in composition between acidic and basic), from the Gibraltar-Polyanna porphyry-copper-molybdenum deposit near McLeese Lake, B.C., Canada. The rock there is composed of quartz, plagioclase [general formula, $(Na,Ca)Al(Si,Al)Si_2O_8$], chlorite [$H_4(Mg,Fe)_6Si_8O_{24}$], and disseminated magnetite (Fe_3O_4). Mineralized veins in the rock contain quartz, pyrite, chalcopyrite, molybdenite (MoS_2), and magnetite and resemble in composition the quartz veins in which gold is generally found. Samples taken from the mineralized zone of the veins were used in tests in long-term leaching columns and in petri dishes to which only pyrite, separated from the same original samples, was added. The *Thiobacillus ferrooxidans* that was used for these tests was grown on a chalcopyrite-zinc sulfide ore, to adapt it to this mixture of minerals.

Preferential leaching was observed in the tests; molybdenite and magnetite were not oxidized. 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, jagged edges, and holes, none of which were observed on the surfaces of the pyrite prior to the tests. In the absence of bacteria, pyrite samples in the petri dishes were not pitted or etched, only slightly tarnished. These results suggest that indeed some of the various sulfides in the mineralized silicified veins in which gold is present can likewise oxidize, partially or completely, especially in the presence of bacteria, and that they can support bacterial growth.

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

As mentioned previously, the oxidation of pyrite, and its attendant reactions, is a highly exothermic process. Approximately 4.3 cal are released by pyrite for each cubic centimeter of oxygen adsorbed (*17*). Additional heat is released by the other reactions. 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 Sullivan Mine in British Columbia, which contains sphalerite, galena, pyrrhotite (FeS), and pyrite (*18-19*). Another mine that encountered many complex problems during development and production was the 500 Copper Orebody at Mount Isa, Australia, which contains sulfides (*20*).

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 (*21*), 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 possibilities.

REACTIVE PYRITES

It is a known fact that some pyrites oxidize at a fast rate 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 the 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.

The presence of impurities in the pyrite can affect its rate of oxidation or reactivity, because the impurities and especially metallic elements act as catalysts. Defects in the pyrite crystals are also thought to be preferred sites for attack by oxygen and water, and perhaps by the bacteria that attach themselves to specific sites on the surfaces of the crystals. The electrical properties of the semiconductive pyrites, such as p- and n-types, have also been cited as determinants of reactivity by some workers in the field, but have been found insignificant by others (*22*).

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 and 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 that can bind iron. They may also form silica gels and obstruct the flow of liquids, as described by Ehrlich and Fox (*23*), 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, and because of their close association with gold, can affect the rate of oxidation of sulfides in gold ores (*24*).

One main problem facing coal mines, sulfide mines, and gold mines in which pyrite is present is the inability to easily assess the reactivity of the pyrite. There is not a 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 hazard.

BLASTING HAZARDS

REACTIONS OF ANFO WITH FERROUS SULFATE

ANFO explosives are commonly used at open pit gold mines. Bulk ammonium nitrate and/or bulk ANFO are delivered to the mines in 25- or 37-ton pneumatic tankers. When ammonium nitrate prills are used they are mixed with the fuel oil through an auger on the on-site mix truck. Bulk ANFO (94 pct ammonium nitrate—6 pct 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 (*25-26*). Similar studies were conducted by the Bureau (*27*), in which many sulfide ores were tested, and the effect of sulfuric acid was evaluated. Additional studies by the Bureau (*28*) 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:

$$3Fe^{2+} + NO_3^- + 4H^+ \rightarrow 3Fe^{3+} + NO\uparrow + 2H_2O. \quad (I)$$

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 all 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 (*28*). 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 with 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, this reaction will reach very high temperatures, and an unplanned explosion or detonation will result.

Various inhibitors were evaluated in all these aforementioned studies, including phosphates, borates, oxides such as zinc oxide (ZnO), and urea $[CO(HN_2)_2]$, with urea being among the most effective (*29*). Adding inhibitors to the ANFO prills complicates the preparation process and also increases the cost of the explosive. Urea adsorbs

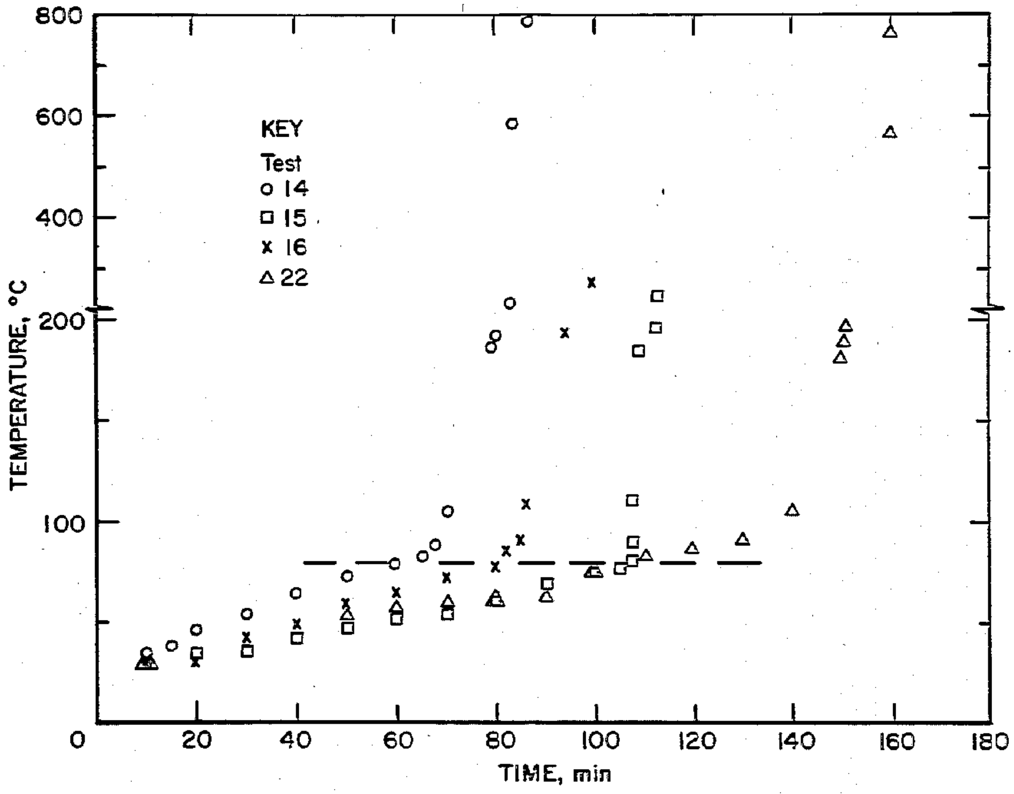

Figure 1.—Temperature-time profiles for ANFO-ore-ferrous sulfate mixtures. Dashed line indicates temperature at which reaction accelerates.

moisture even more easily than the hygroscopic ammonium nitrate, and thus can reduce the stability of the prills. It also affects the flow of the prills into the boreholes. The addition of inhibitors may affect the sensitivity of the resultant ANFO blasting agent, causing a need for a large primer or larger minimum diameter. However, reports of misfires caused by using ANFO with inhibitors were not confirmed (*30*). Success with the use of either urea or zinc oxide as inhibitors in ANFO blasting agents has been reported by a coal company (*31*). 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, pyrite-rich 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 I. However, the use of borehole liners will not eliminate all the hazards, as discussed in the next section.

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,[4] 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 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 60° to 65° C (150° to 160° F) and misfires can result. Detonators have cylindrical metal shells containing several powder charges. The shells are constructed of 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 ($CuSO_4$), 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 [$C(CH_2ONO_2)_4$]), RDX (1,3,5-trinitro-hexahydro-s-triazine [$C_3H_6N_6O_6$]), and lead azide (PbN_6). 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 du Pont 990 differential scanning 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 5 mg was sealed in an aluminum pan. A reference material of about the same weight, and consisting of inert glass beads, was likewise sealed. 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 is shown in figure 2, while figures 3 and 4 present thermograms for RDX. Milligram-size samples of PETN and RDX were used in each test; however, the sample used to obtain the thermogram in figure 4 was slightly larger than the sample used to record the thermogram in figure 3. As can be seen, the thermogram in figure 4 resembles an explosive-like behavior rather than a thermal decomposition process. The PETN undergoes exothermic decomposition once it melts. Had a slightly larger sample been tested, a similar, more violent behavior would also have been seen, immediately following melting, at about 145° C.

The thermal sensitivity of 19 commercial detonators was evaluated in a study conducted by the Bureau (*32*). Although they 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 [$C_6HN_3O_8Pb$]), mannitol hexanitrate [$C_6H_8(ONO_2)_6$], and diazodinitrophenol [$(NO_2)_2C_6H_2N_2O$]. Experimental explosion temperatures (*32*), shown in table 1, correlate with the thermal

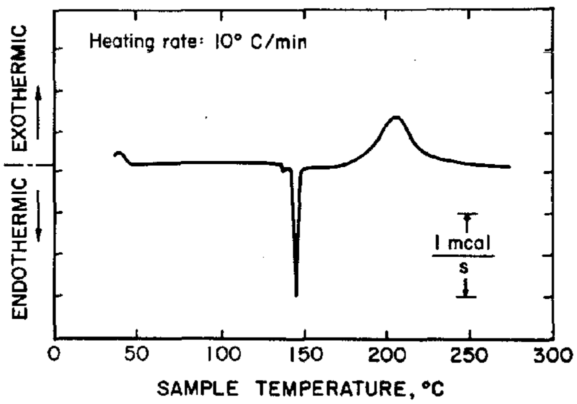

Figure 2.—Differential scanning calorimeter thermogram for PETN.

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[4] Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

properties of the explosive ingredients inside the detonators. Detonators containing mannitol hexanitrate exploded at the lowest temperatures (121° to 130° C). Diazodinitrophenol, PETN, and lead azide reacted at successively higher temperatures.

Table 1.—Explosion temperatures of various detonators[1]

Detonator description[2]	*Average explosion temperature, °C*
Manufacturer 1:	
FBC, No. 6, aluminum case	160
Instantaneous EBC, No. 6	150
Instantaneous EBC, No. 8	150
Delay EBC, 100-ms delay time	143
Delay EBC, 500-ms delay time, aluminum case	151
Manufacturer 2:	
FBC, No. 6	136
Instantaneous EBC, No. 6	133
Delay EBC, 100-ms delay time, No. 8	134
Delay EBC, 500-ms delay time, No. 8	134
Delay EBC, 2.9-s delay time, No. 8	137
Manufacturer 3:	
FBC, No. 6	([3])
Instantaneous EBC	121
Delay EBC, 175-ms delay time	122
Delay EBC, 500-ms delay time	130
Manufacturer 4:	
Instantaneous EBC, No. 6, plastic case	139
Delay EBC, No. 6, period 4 delay time, aluminum case	188
Manufacturer 5:	
FBC, No. 6, obsolete	132
Manufacturer 6:	
Instantaneous EBC, aluminum case, military item	149
Manufacturer 7:	
Instantaneous EBC, No. 6, foreign product	156
Delay EBC, 80-ms delay time, foreign product	151

EBC Electric blasting cap.
FBC Fuse blasting cap.

[1] Detonators were heated at constant rate of 0.5° C/min.

[2] Numbers in this column indicate the relative strength of the detonators.

[3] No explosion up to 240° C. Decomposed active elements flowed out of fuse cavity.

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 that 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 concentrations, the heat from the reaction will lead to detonator initiation, if sufficient time is allowed. The rate of self-heating of sulfides in a borehole depends on concentration of sulfides; availability of air, moisture, and bacteria; and strata temperature. It is thought to be a slower reaction than the one between ANFO and ferrous sulfate. If liners are used to prevent direct contact between ANFO and ferrous sulfate, the possibility still exists for explosions to occur. An explosion might happen if the amount of pyrite present is relatively high and it oxidizes at a fast rate, and if the time from loading to firing is sufficient for temperatures in the borehole to rise above 120° or 130° C and initiate the detonators.

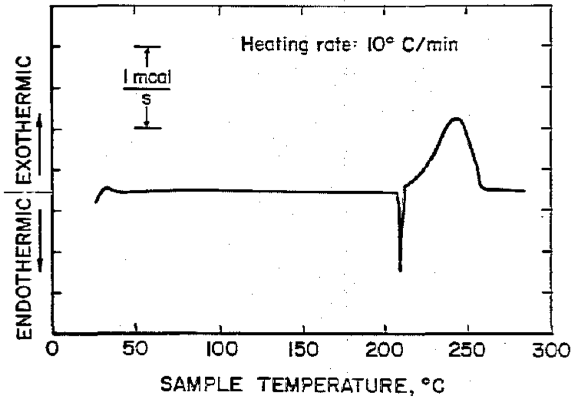

Figure 3.—Differential scanning calorimeter thermogram for RDX.

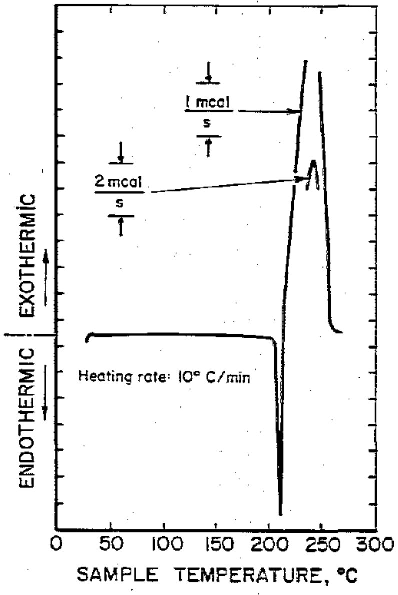

Figure 4.—Differential scanning calorimeter thermogram for RDX using increased sample weight.

MAJOR INDICATORS OF POTENTIAL BLASTING HAZARDS

Both oxidized and unoxidized ore is found in gold mines. The unoxidized ore contains various sulfides, tellurides, and arsenides in proximity with the gold (*8*). In the oxidized ore, the associated metal values are present mostly as oxides or sulfates.

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, note 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 iron sulfates or the insoluble jarosite $[K_2Fe_6(OH)_{12}(SO_4)_4]$ and hydrous iron oxides $(Fe_2O_3 \cdot XH_2O)$, 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 ensure safe operations in mining gold in sulfide-bearing ores, precautionary measures are needed. In a report by the Mine Safety and Health Administration (*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 (90° and 100° F) it is recommended that loading-to-firing time be limited to about 4 to 6 h; whereas, if temperature is 43° C (110° F), loading-to-firing time should be limited to 2 to 4 h unless special products are used.

Based on first-hand experience, FMC Paradise Peak Corp. has prepared a safe operating procedure for blasting in its mine (*33*). This procedure includes instructions for measurements of borehole temperatures, for marking various boreholes according to their temperatures, and for communication of personnel, amoung 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 the mine.

The use of inhibitors, such as zinc oxide and urea, has been shown to work in a coal mine with a similar problem (*31*). One percent zinc oxide or 5 pct urea were found sufficient to inhibit the reaction. Thus, inhibitors should be considered for precautionary measures. Choice of specific inhibitor would depend, among other factors, on cost and difficulty of use in a humid atmosphere.

As more mines face and address this problem, a standard set of procedures will be adopted. General measures recommended by the Bureau for safe operating procedures include the following:

- 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.
- Removal of water from boreholes or use of liners.
- Temperature measurements in boreholes, as necessary.
- 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, because they would serve as additional fuel (*27*). This fact may be important in underground mines.
- Limiting loading-to-firing time, based on borehole temperatures.
- Appropriate choice of initiation devices, based on borehole temperatures.
- 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. 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 and/or the heat released by pyrite oxidation can set off detonators. In addition, the energy produced by the abovementioned reaction is itself sufficiently violent to cause damage. 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 monitoring 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.

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