Information Circular 8775

Spontaneous Oxidation and Combustion of Sulfide Ores in Underground Mines

A Literature Survey

By Donald J. Ninteman

UNITED STATES DEPARTMENT OF THE INTERIOR
Cecil D. Andrus, Secretary

BUREAU OF MINES

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A Literature Survey

by

Donald J. Nineman[1]

ABSTRACT

This Bureau of Mines publication is a literature study of the problem of spontaneous oxidation and combustion of sulfides in underground mines. It summarizes the present-day hazards, process mechanisms, and prevention and control techniques of this growing problem in underground mines.

The iron sulfides generally have the greatest tendency to oxidize, particularly pyrrhotite. The presence of moisture and oxygen is essential for the oxidation reaction. Highly fractured sulfides, when found with timber or combustible refuse in slowly circulating air, pose the most serious fire hazard. Quenching with water is effective in quickly dealing with local hot spots, but ventilation at high flow rates is the most effective and economical means for long-term prevention and control.

INTRODUCTION

> "In 1966, during production from the highly leached region of the orebody at 900 feet, incandescent ore appeared in the northern extraction cross-cuts of the mine. Ore temperatures in excess of 1000° F were recorded and large volumes of sulfur dioxide gas were produced" (27).[2]

Although the occurrence of spontaneous oxidation and combustion of sulfide ores has been known and documented for centuries, the incident quoted (concerning Mount Isa Mines Ltd., Australia) typifies some of the spontaneous oxidation hazards in today's modern underground metal and nonmetal mines. The 19th century witnessed some extreme cases of the dangers of spontaneous combustion of sulfide ore as noted by Kirshenbaum (22): "a ship carrying Chilean copper ore was entirely consumed by fire in 1862." Reports from Spain's Huelva pyrite mines in 1922 showed that underground fires from the spontaneous combustion of the high-sulfide ores occurred regularly several weeks after a

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[2]Underlined numbers in parentheses refer to items in the bibliography at the end of this report.

fall of ore in the cut-and-fill mining environment. Even today, Lukaszewski (27) notes that despite improved ore handling controls and safeguards in mining operations, the problems relating to natural oxidation and spontaneous heating have persisted with the increase in pace and scope of world mining operations.

The previous examples concern mines abroad; however, the problem is equally significant in the United States and Canada:

> "Measurements in the Tintic district, Utah, and at Superior, Ariz., show that pyrite sulfide veins commonly are marked by thermal highs from 10° to 40° F above the normal rock temperature, with horizontal gradients of several degrees per 100 feet near them. During the field investigation of the San Manuel mine at San Manuel, Ariz., the author (Lovering) noted that as the chutes were pulled in some grizzlie drifts on the 2015 level the muck ran quite hot (134°); whereas, at other draw points there was no apparent increase in muck temperature. The sulfide content (of the muck) was less in areas of the mine that did not experience the hot muck. The ventilation engineer at the Creighton mine at Sudbury, Ontario, stated that in the winter it was quite evident that considerable heat was being liberated from a large pile of ore on surface" (8).

As underground metal mines in this country sink deeper for new, richer ore bodies, heat and oxidation problems become more severe and will require more careful attention and definite action. This literature survey is a first step by the Bureau of Mines to establish background information from which research can be planned that will help solve this problem.

PROBLEMS AND HAZARDS

The effects of sulfide oxidation are far-reaching, ranging from fire hazards and dust explosions to mine fill complications and loss of ore. A brief listing is presented here.

Fire Hazard

When the heat generated from spontaneous oxidation of sulfides is not dissipated and temperatures exceed the boiling point of water (after all moisture present has vaporized), combustion can occur. This is "roasting" and is not only highly exothermic, but also produces sulfur dioxide gas. A chain reaction can occur; timber, more sulfide, as well as extraneous matter in the mine may also combust as a result of the heat or flame propagation. It is this spontaneity that makes these fires extremely difficult to control.

Heat

Heat generation from sulfide oxidation not only constitutes a fire hazard by acting as a catalyst for spontaneous combustion, but also by itself poses serious mining hazards. At working faces, where broken sulfide ore may oxidize readily, air can become very hot; in the Huelva mine in Spain, face

temperatures ranging from 122° to 131° F (50° to 55° C) made working conditions extremely difficult. The exact amount of heat generated by sulfide oxidation is impossible to determine; where severe heating does occur, increased ventilation, air-conditioning, or some other form of heat removal must be used.

Fumes

Combating the heating of sulfide ore is made still more difficult due to the noxious fumes that are emitted. The direct decomposition of sulfides to oxides will evolve significant quantities of sulfur dioxide (SO_2) gas at mineral temperatures above about 125° C, and very large volumes have been recorded at ore temperatures above 1,000° F (538° C) (3, 40). In extreme cases moist, hot, sulfurous acid gas (H_2SO_3) is produced, requiring the use of artificial breathing apparatus. If timber is present in a heated zone where there is not sufficient air to permit combustion, toxic carbon monoxide (CO) gas may be given off. The most common product of oxidation, however, is carbon dioxide (CO_2) and although not toxic by itself, it presents serious breathing problems when it replaces oxygen (consumed during the oxidation process) in slowly circulating mine air.

Dusts

Decreasing the particle size of sulfide minerals will increase their reactivity by enlarging the surface area exposed to air. Sulfide dust explosions, particularly where elemental sulfur is present, have occurred in various metal mines as a result of the ignition and quick chain-reaction flame propagation of sulfide particles suspended in air. A dust cloud is created and may be ignited in stopes by the blasting of sulfide ore. Such explosions have resulted in severe loss of life and widespread injury to men who inhaled the hot, sulfur dioxide gas in the quickly advancing envelope of flame (1, 5). Such explosions often touch off fires.

Handling and Storage

Storing reactive sulfides in the open may cause a bulk volume increase of up to 20 pct as a result of oxide formation. When prolonged oxidation takes place, agglomeration occurs as the oxide products coat the minerals and fill the void spaces within the broken material (10). A hard, immovable composite may be produced (fig. 8), creating numerous handling and storage problems.

Effect on Explosives

Much literature has been written on the effect of sulfide oxidation on explosives; the topic will only be mentioned here (8, 12, 27-28). In reactive ore, the oxidation heat directly increases the instability of explosives used in underground mining. The heat and reaction products of natural oxidation may decompose explosives, such as AN-FO, and cause deterioration, misfires, premature detonation, and direct reactions between the explosive charge and ore. Sulfide-explosive reactions will produce heat and sulfur dioxide gas,

and do not require water as a catalyst (water is necessary for natural spontaneous oxidation, as will be pointed out later).

Mine Fill

Mine fill, commonly a mixture of mill tailings and cement, provides low-cost support for stope walls, a very safe working floor or ceiling, and a good source for the disposal of flotation tailings. If the fill contains a large quantity of reactive sulfides and the proper moisture content, accelerated oxidation may result in heat and sulfur dioxide fumes, acid mine drainage, and the reduction of the oxygen supply in stopes. All cements oxidize during the curing process to give off heat; sulfide material may spontaneously oxidize also, depending on the sulfide reactivity, the fineness and proportion of sulfide cementing agents present, as well as the balance between the heat liberated and the heat dissipated during oxidation (29). Reactive pyrrhotite ($Fe_{0.8-1.0}S$) poses the greatest oxidation problem in mine fill. Although these problems have occurred in self-cementing fill containing 3 to 10 pct by weight sulfides, Bureau of Mines testing in Pittsburgh, Pa., on backfill samples of from 2 to 4 pct sulfide from the Homestake gold mine in South Dakota "indicate that the samples are not capable of self-heating" (25). Further study of the oxidation mechanism of mine fill would be beneficial.

Ore Alteration and Loss

The irreversible chemical changes resulting from sulfide mineral oxidation may produce resistant oxide coatings, adversely affecting the recovery of values and reagent consumption in the subsequent flotation processes (34). When sulfide fires cannot be extinguished, extensive areas of the mine must be sealed off, resulting in the loss of large amounts of often high-grade ore.

Underground Coal

The frequent occurrence of spontaneous combustion of coal in underground mines will not be covered in this paper. However, much of the following material is applicable to underground coal mining since it is believed that oxidation of pyrite can initiate coal combustion (16, 39).

MECHANISM AND REACTIVITIES

The probable sequence of events leading up to spontaneous combustion is described by Brown (3) in the following report from the Huelva pyrite mines:

> "The mineral is broken up a great deal (as after blasting), and consequently considerable more surface is exposed. Air naturally fills the spaces (between the pieces), and slight oxidation and heating take place. There is, however, no flow of air to take away the heat generated; consequently, it accumulates and the chemical action increases. As the air becomes heated, it expands, and there is a small air flow set up through the broken mineral. This is sufficient to renew the air and bring all the oxygen required to continue the chemical reaction, but not sufficient to take away the

heat generated....If no timber is present, the temperature will gradually increase until sulfur dioxide is given off; and the fire will steadily increase and spread unless something is done to stop it. If, however, timber is present, (it will ignite much sooner at a lower combustion temperature)."

This sequence of events hinges on sulfide oxidation. The oxidation process may depend largely on physical factors, such as the reduction of particle size as a result of mining or caving. In other cases, such as in the presence of acid mine water, oxidation will be more largely due to chemical factors. Chemical factors are related to the electrode potential relations at mineral interfaces; therefore, electrical effects need to be considered. Although all these effects interdependently combine in the oxidation process, they will be discussed separately here as chemical, physical, and electrochemical effects.

Chemical Effects

The oxidation of sulfide ore in underground mining environments is nearly identical chemically to the natural oxidation of near-surface sulfide ores. Much of today's data on the chemical mechanism of sulfide oxidation is based on geological studies concerning the formation of oxide ore bodies from weathering sulfides. In both cases, the process is extremely complex and dynamic, depending upon the interrelationship of several controlling factors in an environment that provides almost infinite scope for variation in these factors. A variety of chemical equations exists for each set of physical and chemical conditions, and all these equations only approximate the complex oxidation processes (24).

Chemical Mechanism

As mentioned earlier, the oxidation of sulfides proceeds in stages. The first step is to release the metal atom from the sulfide into solution as an ion. Thus, slightly acidic solutions must be present (sulfides are essentially insoluble in pure, neutral water). This step is the critical, rate determining step, since it involves breaking the strong, predominantly ionic, bonds within the crystal lattice of the sulfide.

The moving of the metal cation into solution causes an increase in the sulfur-to-metal ratio in the solid phase. With only sulfide ions remaining on the local surface of the mineral, and hydrogen ions remaining close by, step 2 occurs as sulfur ions are released into solution. These ions quickly oxidize (step 3) to form sulfate ion. Sufficient oxygen must be dissolved in the solution to permit this critical oxidation of sulfur. With sulfur removed from the surface of the mineral, a fresh sulfide surface is exposed and more metal (and then more sulfur) can be dissolved. This process continues until the liquid can no longer accept more ions (saturation). The generation of sulfate ions necessitates the formation of H^+ ions from water. As a result, the oxidation process yields relatively acidic solutions.

Finally, in the fourth step, which may or may not occur, the metal ion combines with oxygen to form insoluble metal oxide or metal sulfate [MSO_4], carbonate [MCO_3], hydroxide [$M(OH)_2$], and chromate [$M(Cr_2O_4)$]. The precipitate that forms will generally depend on the relative concentrations of the complexing ions in the solution. The resultant oxide products may remain to coat the surface of the mineral, or they may pass into solution. These products may become hydrated to form compounds such as $PbSO_4 \cdot H_2O$. Figure 1 shows all four steps for the oxidation of galena (PbS); in this case, sulfate ions will precipitate lead ions (step 4) to form lead sulfate and lower pH solutions.

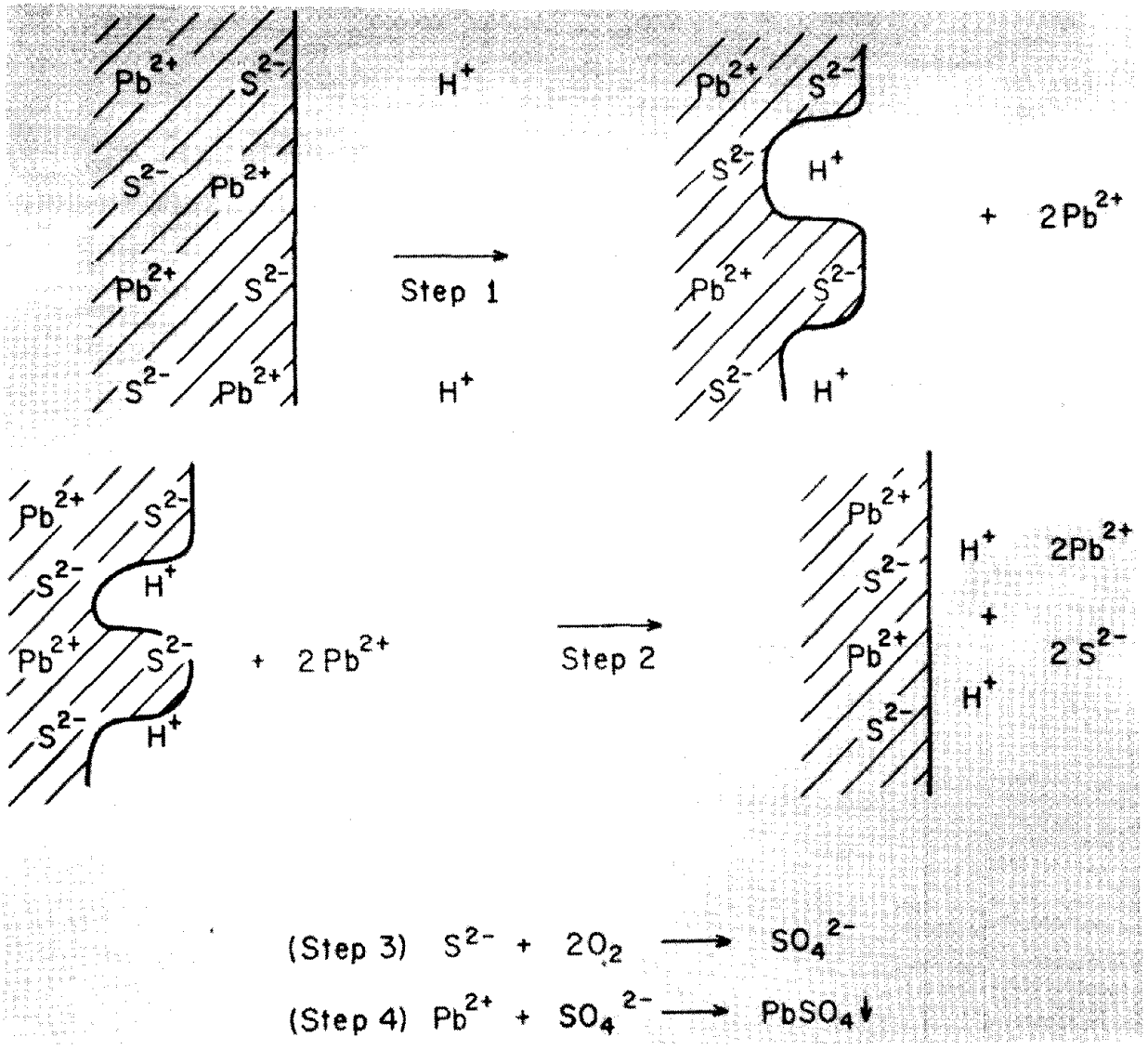

FIGURE 1. - Chemical steps in the oxidation of galena.

These steps will all occur at the same time in a dynamic equilibrium process. The oxidation reactions and the hydrolysis of the metal oxide are exothermic and the heat evolved tends to increase the reaction rate as less reactive sulfides may be triggered to oxidize. The entire mechanism proceeds very rapidly; noticeable oxidation can occur in a fraction of a second. As shown in figure 2, initially temperature will increase rapidly (A), then steadily rise at a slower rate (B) until it reaches a peak (C), and finally declines (D) when oxygen becomes depleted or when the oxide coating on the mineral blocks the reaction (40, p. C245).

The speed of the oxidation reaction will determine how severe it will affect the mining environment. For instance, extremely fast generation of heat could cause combustion, that is, direct oxidation at elevated temperatures. On the other hand, slow, steady oxidation may be tolerable in the mine if temperatures do not become too high. To predict the reaction rate, some of the many interdependent chemical factors that influence it must be examined in detail.

Chemical Factors Affecting Oxidation

Mineralogical Composition Effects

Because no two ore bodies are ever the same, considerable variations in chemical behavior or reactivity are to be expected from sulfide ores of differing origin and between sulfide zones of the same ore body. Reactivity, the tendency to oxidize, is a complex function of mineral composition. Variables

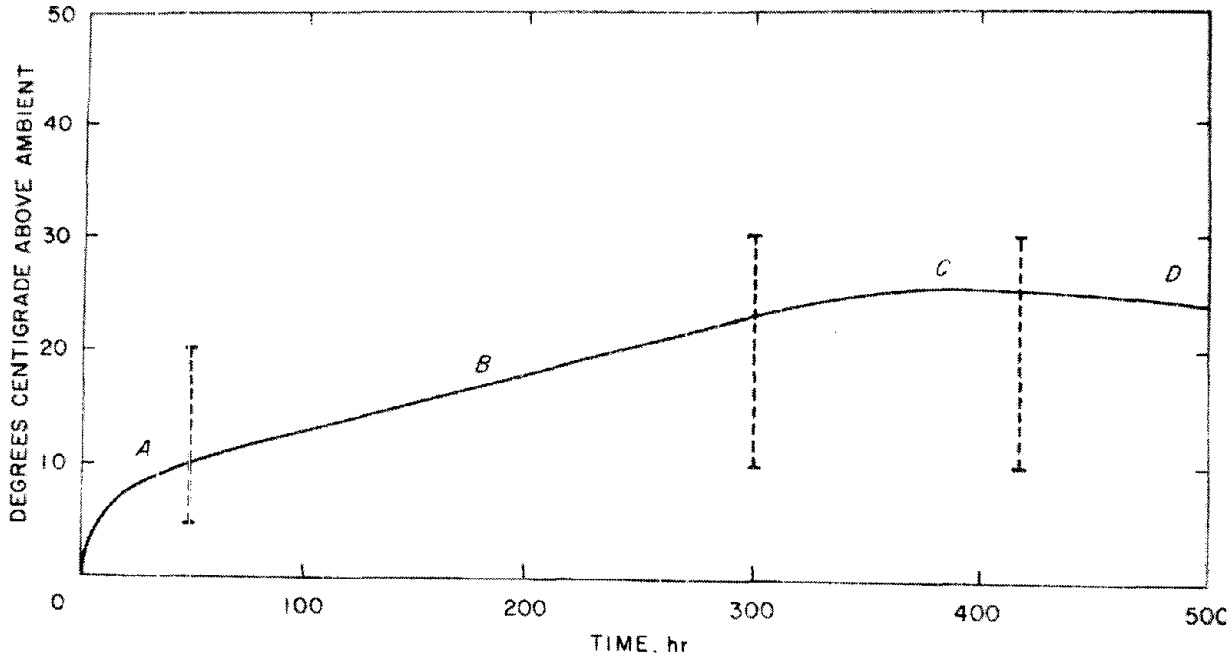

FIGURE 2. - Typical temperature-time profile for oxidizing conical-shaped dumps of sulfide concentrates (40).

include (1) sulfide type, (2) the number of sulfides present, (3) the percent of sulfides, and (4) the type of gangue mineral(s). Exposed surface area, related to grain size and the ore structure, is another important factor that will be discussed later.

Sulfide Type

It is generally agreed that during the spontaneous oxidation of sulfides, the iron sulfides, especially pyrrhotite, are the most serious offenders. Russian research has indicated that at higher temperatures the iron sulfides oxidize almost 10 times faster than the sulfides of copper, nickel, or cobalt. However, all sources do not exactly agree on the relative reactivities.

Klassen (23) lists these sulfides in a diminishing tendency to oxidize: arsenopyrite > pyrite > chalcopyrite > sphalerite > galena > chalcocite. Flann and Lukaszewski state that pyrrhotite is by far the most reactive in environments where the amount of moisture present is highly variable; they rate reactivities in decreasing order as pyrrhotite >> pyrite-arsenopyrite > chalcopyrite > sphalerite > galena.

It is important to note that the mineralogical composition, rather than the chemical assay, of a sulfide ore is critical. Within the iron sulfide group, for example, small changes in the iron-to-sulfur ratio will determine which mineral species, with its own unique physical and chemical properties, will be present. Although pyrite, FeS_2, and pyrrhotite, $Fe_{0.8-1.0}S$, have nearly identical chemical formulas, the slight variation in Fe:S ratio make the latter much more reactive. Thus, two ores with identical iron assays may oxidize at completely different rates depending on the relative amounts of each iron sulfide present.

Mixtures of Different Sulfides

Because of electrical effects, mixtures of two or more sulfides in an ore can markedly increase reactivity. Experimentally, Anderson found that in the presence of equal amounts of pyrite, samples of galena, sphalerite, covellite, and enargite were found to oxidize from 8 to 20 times faster than when allowed to oxidize alone.

Sulfide Content

When the sulfide level is significant in the ore, widespread oxidation may generate heat faster than it can be carried away. The heat catalyzes further oxidation and possible combustion. At the Mount Isa mines in Australia, some areas contain ore in excess of 50 pct sulfides. Hewett found that high-rate oxidation has been restricted to areas with well-above-average sulfide content. Obviously, heat production potential is determined by the amount of sulfide present.

Although severe heating may result from high sulfide content, considerable oxidation may occur in ore of much lower percent sulfides. At the

San Manuel mine near San Manuel, Ariz., a temperature of 134° F (57° C) was recorded in fine muck with a sulfide content of only about 5 pct.

The effect of increased sulfide content on spontaneous oxidation was closely examined in the laboratory. The results of thermal tests of pyrrhotite content in 500-gram sulfide concentrate samples show the effect (fig. 3).

Gangue Minerals

Certain nonsulfide minerals in the ore will affect the sulfide oxidation rate. Elemental sulfur may form under natural oxidation conditions and typically may constitute 1 to 2 pct of the ore by weight. This elemental sulfur will increase the reactivity of various sulfide ores and lower the ignition temperature. The high reactivity of pyrrhotite, which contains varying amounts of free sulfur, may be attributed to this. Carbon has been known to have a similar effect; when it forms a fine grained impurity in pyrite or copper sulfides, reactivity is much higher. The control of the combustion of carbonaceous shale containing iron sulfides is very difficult and expensive. Lukaszewski summarizes by stating that the total heat liberated is determined by the heat contributions from constituent sulfides and combustible gangue constituents such as sulfur or carbon. On the other hand, some minerals (for example dolomite) will decompose endothermically at high temperatures, and reduce the rate of oxidation or combustion.

Moisture Content Effects

There are widely conflicting views concerning the role and importance of moisture content on the oxidation of sulfides. However, the chemical mechanism involving water is based on a large amount of chemical evidence indicating that at normal environmental temperatures, water does play a critical role in sulfide oxidation. This will become more apparent later.

Role of Water

A sample of galena will indefinitely retain a lustrous, metallic appearance in the presence of air, but it will readily tarnish when moistened. This

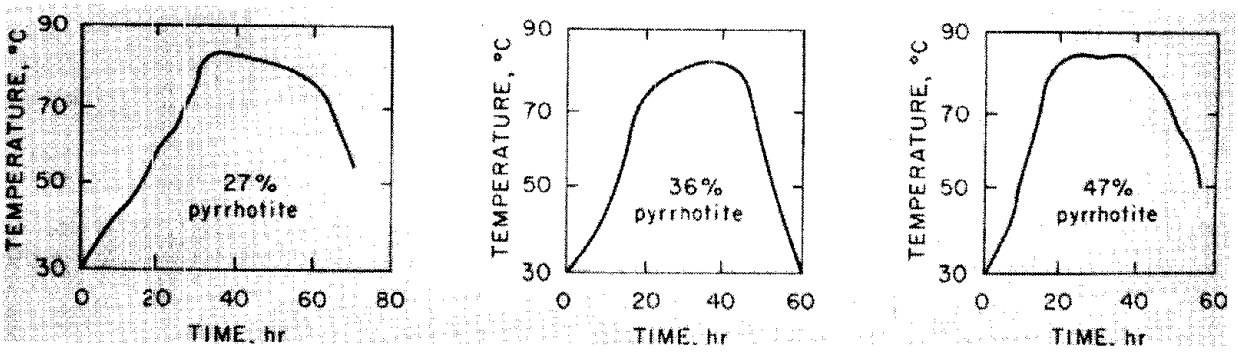

FIGURE 3. - Increase in initial heating rate with pyrrhotite content in sulfide concentrates, 500-gram samples (41).

observation is true of other sulfides and various theories have been proposed to explain the apparently critical role of water. Kirshenbaum noted that water provides a solvent in which reaction products can be removed from the surface of the mineral undergoing oxidation. This provides newly exposed sulfide with the opportunity to react, and it increases the overall reaction rate. A theory proposed by Sato (37) in 1960 suggested that hydrogen peroxide (H_2O_2) (present in very small amounts in water) is the agent responsible for the diffusional transporting of oxygen from the air through the water to then oxidize metal ions in solution. Much theoretical and experimental evidence tends to verify the peroxide theory (32). Water also acts as a solvent for other oxidizing agents such as the ferric ion (Fe^{3+}), which catalyze many oxidation reactions.

Only at temperatures above the boiling point will sulfides oxidize without the presence of water. This spontaneous combustion involves the same mechanism that occurs during roasting of sulfide concentrates. Roasting is highly exothermic and always generates sulfur dioxide gas.

Water Content

The critical water content is defined by Flann and Lukaszewski as the immediate requirement for the principal oxidation reaction relative to the mass of reactive sulfide over the available material surface. Unfortunately, little is known about the critical water content of ore or muck as found in the underground mining environment. Most of the information on this topic is concerned with sulfide mineral concentrates, where spontaneous heating during prolonged transport creates serious hazards.

Kirshenbaum compiled an excellent summary concerning the percent of water in sulfide concentrates during transport in ocean vessels. Although the critical moisture range depends on factors such as the type of concentrate, mesh size, etc., it was generally found that a moisture content of from 3 to 8 pct creates the most ideal conditions for spontaneous heating and combustion. Below about 2 pct, the little water available quickly evaporates as oxidation starts and thus heat generation is checked. Kirshenbaum points out that it is probable that "bone dry" concentrates might not heat up. Above 8 pct, sufficient water exists to absorb energy by evaporation and to act as a heat sink to prevent any areas of the concentrate load from becoming too hot. Water is often sprayed on the concentrates for cooling during long journeys and to prevent generation of sulfur dioxide gas. Laboratory experiments by Sudbury and Petkovich (41) on 500-gram samples have shown that approximately 3 to 9 pct moisture produces greatest heating in concentrates (fig. 4).

Fluctuating Moisture Content

Lukaszewski points out that oxidation processes are markedly accelerated by fluctuations in the proportions of water and air constituents, such as during weathering or changing underground environments. Alternately wetting and drying sulfide muck tends to dissolve oxide products, so reactions may continue. This also insures the replacement of reactant oxygen at the sulfide surface through increased capillary action. The reaction rate increases with

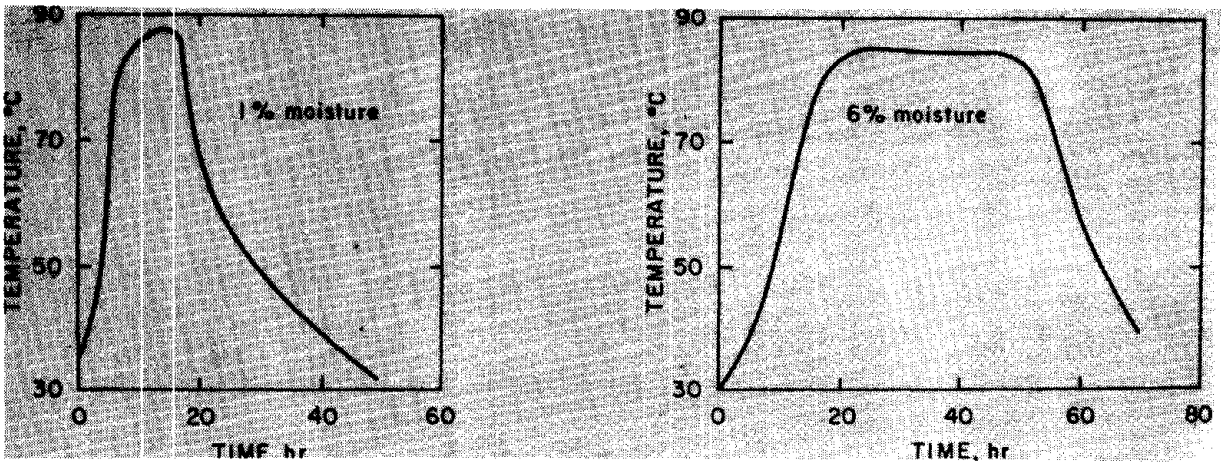

FIGURE 4. - Increase in duration of heating of oxidizing concentrates, 500-gram samples, with initial moisture content (41).

increased frequency of fluctuation. Laboratory tests by Sudbury and Petkovich on sulfide concentrate samples have shown the effect of the accumulation of oxide products (fig. 5) on successive oxidations, and also of how the removal of the soluble oxide, by water leaching, affects successive heating periods (fig. 6).

Ventilation Effects

The effect of ventilation on sulfide oxidation in many ways parallels that of water. Like water, oxygen is a vital constituent in the spontaneous oxidation of sulfides. Yet controlling ventilation to retard oxidation, as with controlling moisture content, has produced apparently contradictory effects. Looking separately at two important effects of ventilation, namely the change in oxygen availability and the cooling rate, shows that the combined net effect of ventilation will depend on the magnitudes of each factor.

Oxygen Availability

A fire can be extinguished by smothering the flame, thus preventing the oxygen-containing air from reacting with the combustible material. Oxygen availability is of critical importance during combustion and oxidation. Simpson made a computer simulation study on the effects of ventilation and wind on piles of sulfide concentrates, assuming that the reaction (oxidation) rate was proportional to the partial pressure of oxygen in the gas phase. The results of the study, based on this assumption, were then later verified by onsite temperature measurements of stockpiles of oxidizing lead-zinc sulfide concentrates. Further evidence of the role of oxygen availability was reported by Lukaszewski from the Mount Isa mine, Australia, where artificial ventilation, accompanying production, accelerated the oxidative processes of the previously undisturbed ore. Oxidation thus became more extensive causing ambient temperatures in the mine to rise by heat transfer. In these cases, increasing ventilation increases oxygen availability and so accelerates

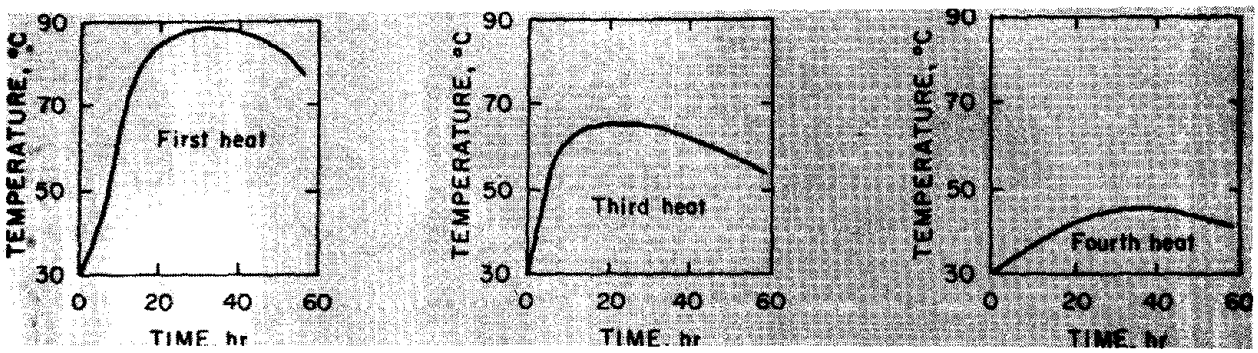

FIGURE 5. - Buildup of reaction products retards spontaneous heating of 500-gram concentrate samples (41).

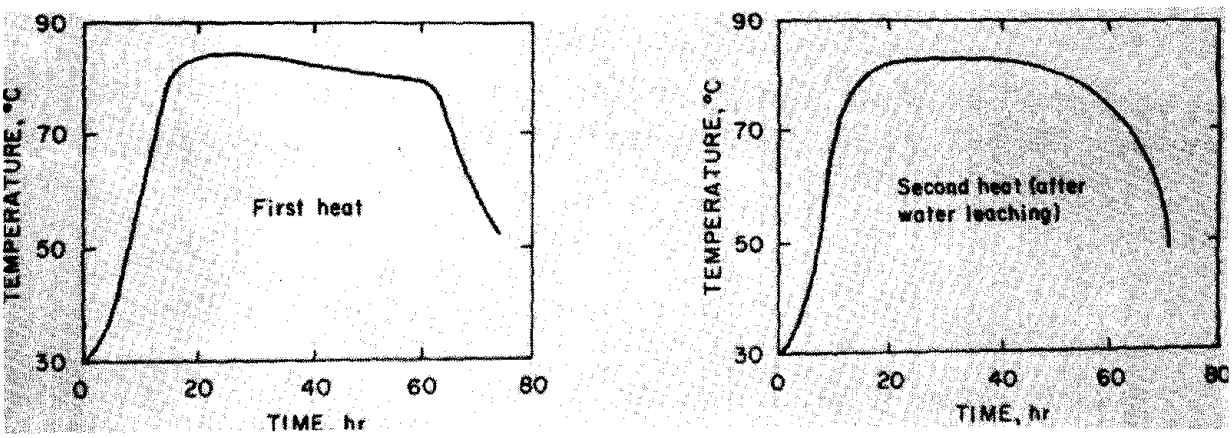

FIGURE 6. - Removing soluble reaction products restores spontaneous heating capacity of 500-gram concentrate samples (41).

oxidation. It should also be noted that oxygen availability depends on the porosity of a muck or concentrate pile, a factor which will be taken up later.

Cooling Rate

The previous observations, however, seem to be inconsistent with an experience at the Lady Jane mine at Mt. Garnet, Australia, giving evidence to the second ventilation effect--cooling. Denmead of the Geological Survey of Queensland is quoted by Hewett (19) as follows:

> "The Lady Jane Mine at Mt. Garnet on the Chillagoe Field was visited in its dying stages by my former colleague, C. C. Moreton. Moreton was one of the last men underground, and in fact it was so late in the history of the mine that the ventilation fan went off while he was there and he had to get out in a hurry. But before he did so, he noted that with dramatic suddenness the sulfides began to heat up. Before he left the mine there were spots where the ore was too hot to touch and in fact some of it had started fuming."

In this example, the cooling effect of the moving air carrying heat away was suddenly removed, thus allowing the temperature to rise and increase the oxidation rate. Although oxygen availability was decreased, the oxidation rate in this case increased. A cooling effect is responsible for this apparent contradiction. The ventilation draft carried away the built-up heat sufficiently so that, when removed, the less reactive sulfides began heating immediately.

Combined Net Effect

Table 1 summarizes the net effect of oxygen availability and cooling on the spontaneous oxidation and combustion of sulfide ores in reactive areas of underground mines.

TABLE 1. - Effect of ventilation on the oxidation of sulfide ores

	No oxidation	Some oxidation	Excessive oxidation and combustion
Critical effect.	Oxygen availability.	Cooling.....	Oxygen availability
Suggested ventilation action.	Minimum ventilation.	Maximum ventilation.	Minimum ventilation

Table 1, which is based on reports similar to Denmead's, shows that when there is no sulfide oxidation, oxygen availability is the most critical effect and must be controlled most carefully. In the development phase of underground mining, oxygen from ventilation comes into contact with sulfides that were previously in an undisturbed, oxygen-free environment. This contact greatly promotes oxidation and it explains the drastic acceleration in oxidation caused by artificial ventilation at the Mount Isa mine, quoted by Denmead. Although impractical, ventilation theoretically should otherwise be minimized during development.

Table 1 also shows that the cooling effect of ventilation dominates once oxidation has started. If some oxidation is occurring, as was the case at the Lady Jane mine, high ventilation rates are best since the resulting cooling effect is more significant than the increased oxygen availability. The conclusion is supported by Hewett who states that within the controllable range of airflow and oxygen content, the cooling effect of an airflow had a greater effect on reaction rate than the concurrent boosting effect of increased oxygen supply. This is likewise consistent with Simpson's simulation study and also with a considerable amount of his field data.

Finally, table 1 shows that when the oxidation rate is excessive, or when fire has broken out, the oxygen availability is most critical so no ventilation is recommended. Kirshenbaum makes the same conclusion concerning the heating of sulfide concentrates; that is, ventilation is not recommended once the concentrates have heated markedly, as the additional oxygen in the cooling air can increase the rate of oxidation. Thus, sealing off a burning area of a mine is a final resort if the combustion cannot be stopped by other means.

Effect of Extraneous Materials

Any combustible, foreign material present with fine sulfide ore in an underground mine is a potential source of oxidative heat. Materials such as oily or greasy waste, timber, empty boxes, sawdust, as well as discarded clothing, hay, and manure all can, like sulfide ore, spontaneously combust and readily spread fire (18). Timber, especially when decayed or rotted, is by far the most dangerous and widespread of these combustibles. It transmits fire very quickly and produces considerable quantities of poisonous carbon monoxide gas. Large quantities of crushed, decaying timber mixed in with fine sulfide muck or backfill form a very reactive combination.

Temperature Effects

For sulfide oxidation, as with most chemical reactions, an increase in temperature increases the rate of oxidation providing that enough water and oxygen are available. Laboratory experiments by Enderlin showed that in the temperature range of 30° to 60° C, the rate of oxidation of pyrite doubled for each 10° C rise in temperature. Sulfides in the presence of high background temperatures, as in very deep mines, make conditions favorable for spontaneous oxidation.

Other Effects

Various thermophilic bacteria accelerate sulfide oxidation. Certain strains catalyze leaching operations and may be responsible for excessive oxidation in some mines. The acidity of mine waters also affects oxidation; this will be discussed further in another section of this report. For sulfide concentrates above ground, the ambient temperature only slightly affects the rate of oxidation.

Physical Effects

Physical Mechanism

Whereas the chemical mechanism described the oxidation process on an atomic scale, the physical mechanism is the macrooxidation effect, the composite of all the microchemical reactions going on between atoms and molecules. The quotation cited at the beginning of this section concerning the Huelva pyrite mines describes the general physical mechanism for spontaneous oxidation and combustion. Although the listing of steps in table 2 is somewhat arbitrary, it does contain the essential ingredients. It is assumed in table 2 that some mechanism of removing the oxide products is maintained throughout oxidation.

TABLE 2. - Steps of the physical mechanism of sulfide oxidation

Step	Procedure
1.....	A large surface area of sulfide ore is required, which is usually accomplished by breaking ore during mining or caving.
2.....	Air is allowed to contact this large surface area and commence oxidation.
3.....	The heat produced is physically entrapped, but at the same time the oxygen supply is maintained to continue oxidation.
4.....	The temperature increases to ignite any elemental sulfur present.
5.....	The temperature increases to ignite fine, reactive sulfides.

Physical Factors Affecting Oxidation

The mechanism just described will help illustrate what and how certain physical factors affect the oxidation rate of sulfides.

Ore Fineness and Surface Area (Step 1)

For sufficient heat generation, many sulfide particles must oxidize concurrently; this will depend upon the amount of sulfide surface exposed to the air. Since surface area per unit mass is inversely proportional to particle diameter, only finely divided sulfides will spontaneously combust; Harrington found that massive sulfide ore rarely burns in place. Experiments by Enderlin showed that the rate of oxidation of pyrite is proportional to the pyrite surface exposed, or that it is inversely proportional to the particle diameter.

Hewett states the size of individual sulfide particles is perhaps the most important single factor influencing ore reactivity, and he has numerous observations at the Mount Isa mine to support his claim. Laboratory tests show that ignition temperature decreases with decreasing particle size. However, a critical particle size, the sulfide ore size needed for combustion, could not readily be specified. Too many other variables enter in, such as the sulfide involved, its crystal form, and whether or not individual grains are composite or pure. Furthermore, the presence or absence of other sulfide species as well as the history of the particles (freshly formed or tarnished surfaces) need to be known. The breaking up of crystals themselves also is important; it is known that crystals, so long as they remain complete, resist oxidation and other disintegrating forces, but if broken they begin to oxidize at once.

Spontaneous combustion is often triggered by the breaking up of lump sulfides during blasting and during shrinkage stoping and caving; this fragmentation completes step 1.

Porosity and Permeability (Step 2)

This second step in the physical mechanism is critical also, since air must be able to contact the newly exposed sulfide surfaces. Both porosity and permeability of the sulfide ore determine how much of the sulfide will be oxidized.

Increasing porosity of the sulfide, like increasing the fineness, increases surface area available for oxidation. The porosity of ore is greatly increased as a result of mining, evidenced by swell factor measurements. Thus muck piles, sulfide ore backfill, and broken ore in stopes all have porosity levels which could cause oxidation problems. At the Mount Isa mine, the ore being mined is a leached material in which much of the carbonate originally present has been dissolved and carried away (average density of unleached area is 270 lb/ft^3 (4.32 g/cm^3) compared with 125 lb/ft^3 (2.00 g/cm^3) in leached ground). This increased porosity of the sulfide increases both reactivity and friability, the latter causing the formation of fine sulfide pieces when broken.

Whereas porosity is a static property of a material, permeability is dynamic and may be defined as the ease with which fluids move through a substance. Permeability directly affects the second step, that is, the ease with which air is able to contact all internal sulfide surfaces. Obviously permeability depends to a large degree on porosity. Porosity is not the only determinant; experiments by Simpson on sulfide concentrate piles showed that moisture content also contributes to air penetration. Computer simulation in the same study showed that stockpile heating from oxidation depended on the ventilation rate through the stockpile which was determined by two factors--dump permeability and exposure of the dump to draft. Exposure to draft also has a cooling effect through the stockpile.

Electrochemical Effects

Many researchers believe that the oxidation of sulfide ores is an electrochemical mechanism (15, 17, 32). Most information on this subject comes from carefully controlled laboratory experiments and from studies of the weathering of sulfides in nature. A very brief summary of this topic, stressing only concepts, is presented here.

For any reaction to proceed, it must be both kinetically and thermodynamically favored. The kinetic factors have been investigated--the physical mechanism described macroeffects such as airflow through broken sulfides, and the chemical mechanism investigated the transport of reactants and products to and from the reaction site on the atomic scale. Both mechanisms influence the overall reaction rate. However, a reaction can never proceed without satisfying thermodynamic requirements.

The Nernst equation is the governing thermodynamic equation for any chemical reaction. When the Gibb's Free Energy change ΔG is less than zero or equivalently when the electrode potential Eh is greater than zero, the reaction will go thermodynamically. Standard electrode potentials and Free

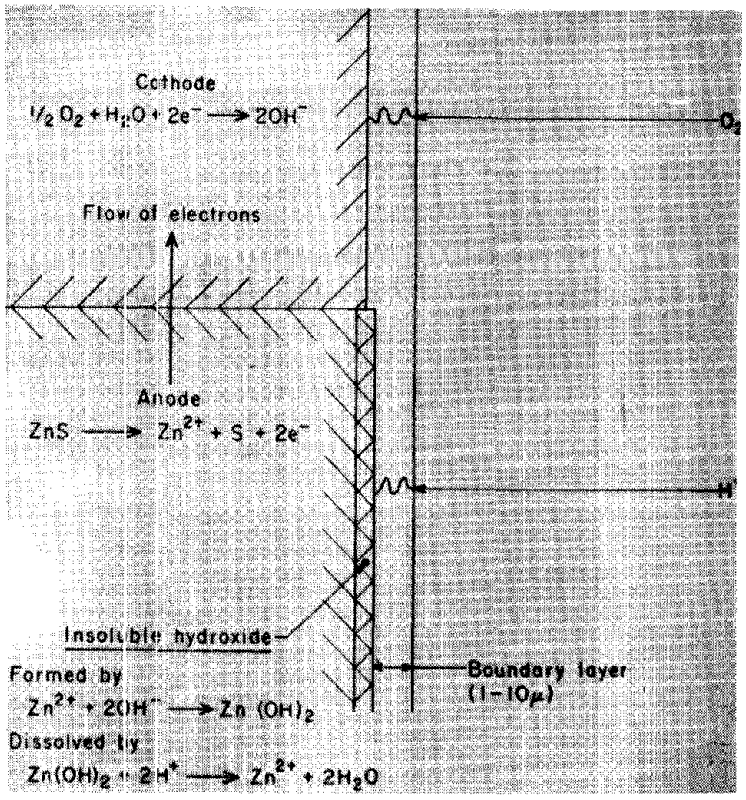

FIGURE 7. - Electrochemical mechanism for the oxidation of sulfides in solutions (17).

Energies of Formation of many compounds have been tabulated in other literature (26). Eh-pH diagrams for many oxidation systems have been constructed from these data. These diagrams can be used to determine which species is thermodynamically stable in a system under certain conditions of temperature, pH, and metal ion activity. The most complete source of Eh-pH data for elements and simple compounds is given by Pourbaix (35). Garrels and Christ is the best reference for electrochemical data of mineral-solution equilibria systems.

An electrochemical mechanism was proposed by Habashi which is based on the corrosion process of metals. His experimental data show considerable kinetic similarity between the two processes. At certain sites on the sulfide surface, called electrode sites, small electric cells are set up due to some imperfection of the sulfide crystal lattice (such as dislocations, interstitial and lattice substitution, small cracks, etc.). This anisotropic area divides into two zones: an anodic region where electrons are liberated and an adjacent cathodic region to which electrons flow and where oxygen is reduced. The half cell reactions of sphalerite, ZnS, for example, would be

$$\text{anode} = ZnS \longrightarrow Zn^{2+} + S^{o} + 2e^{-},$$

and

$$\text{cathode} = \tfrac{1}{2}O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-}.$$

Figure 7 shows the general electrochemical mechanism of sulfides using sphalerite as an example.

The hydroxide ion produced at the cathode will combine with the metal ion at the anode to form an insoluble metal hydroxide on the anode surface. This solid hydroxide coating will insulate the anode region from the solution and it will stop the reaction if not removed. Hydrogen ion, however, will dissolve the hydroxide; thus, acidic solutions are necessary for significant continued oxidation. Rates of reaction will also depend on the surface areas of

the cathodic and anodic zones, the concentration and diffusion coefficients of the ions present, and the partial pressure of oxygen.

Eh-pH diagrams for sulfide-water systems effectively summarize the mechanism for many different metal sulfides at room temperature. These diagrams show that the oxidation of sulfides by oxygen is thermodynamically favored at low pH. Superimposing diagrams will show that other oxidizing ions in solutions will further promote oxidation.

Majima used the electrochemical mechanism to explain the increase in oxidation of sulfide minerals associated with pyrite. When any two different sulfides are in contact and both are electrochemically connected by a solution, a current is generated which flows from the mineral of the higher electrochemical potential to the ore with the lower electrochemical potential. This results in the lower potential mineral greatly increasing its rate of oxidation. Majima reasoned that since pyrite has the highest rest potential of all the sulfide minerals, sulfide reactions of other sulfide minerals would be accelerated in the presence of pyrite. Experiments by both Peters and Majima (33) have confirmed this belief. Thus, mixtures of sulfide minerals, especially with pyrite, will thermodynamically oxidize faster than sulfides found alone.

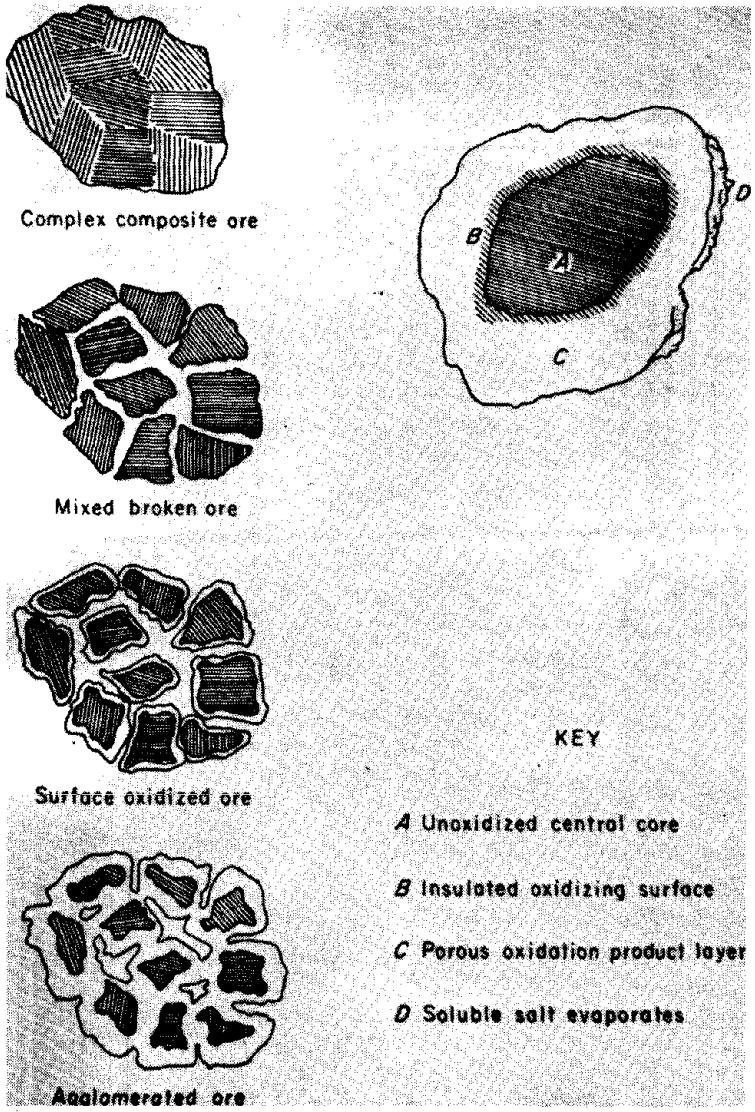

FIGURE 8. - Surface oxidation and agglomeration of sulfide ores containing pyrrhotite (10).

Oxidation Products

What occurs in the mine is a result of the composite effect of all the mechanisms and effects discussed thus far. The oxidizing process and succeeding reactions depend not only on the factors mentioned earlier but also on the extent of oxide product accumulation. For example, residual grains and nodules of galena very commonly occur in the oxidized outcroppings of ore bodies,

not because galena is resistant to the attack of oxidizing agents, but because the insoluble coating of sulfate or carbonate that is formed protects the sulfide. Thus, oxidation may be choked off by the formation of a sulfate, or carbonate crust, if no mechanism is present for oxide product removal. Figure 8, adapted from Flann and Lukaszewski, shows the steps involved.

The oxidation of various sulfide concentrates has been observed closely and demonstrates oxide product formation on a more concentrated scale. Stockpiles of pelletized lead-zinc concentrates were observed to form very hard, relatively impermeable sulfate layers on the agglomerated sulfides as a result of spontaneous oxidation and heating. X-ray analysis by Simpson showed that the white products, produced at pile areas where ventilation was low, were composed of $ZnSO_4 \cdot 7H_2O$[v] and $PbSO_4$. Other areas of more severe ventilation formed a red-brown material analyzed to be ZnO, $ZnO \cdot Fe_2O_3$, $PbSO_4$, and $2ZnO \cdot 3ZnSO_4$.

SULFIDE MINERALS

Reaction Equations

The oxidation of sulfide ores within mines is believed to be chemically identical to the natural oxidation of sulfides exposed to weathering. The process is highly complex and is described by a variety of equations which are at best only approximations. In this and the following sections the iron sulfides will be used as the basis of the analysis. The iron sulfides are typical sulfides but, because of their higher reactivities, they are the most important sulfides with respect to oxidation.

Pyrrhotite appears to be the most reactive sulfide. Under moist conditions, when it is the principal constituent of the sulfide mineral, rapid oxidation arises due to reaction 1:

$$4FeS + 3O_2 + 2H_2O \longrightarrow 4FeO \cdot OH + 4S. \qquad (1)$$

Pyrrhotite, $Fe_{0.8-1.0}S$ is represented here as FeS. Hydrated ferrous sulfate may also be formed at low temperatures when the sulfate ion is present in the solution.

$$FeS + 2O_2 + 7H_2O \longrightarrow FeSO_4 \cdot 7H_2O. \qquad (2)$$

As the proportion of pyrite in the mineral increases, the following acid producing reaction dominates as shown in equation 3.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4. \qquad (3)$$

The presence of basic magnesium- and calcium-containing minerals enhances the formation of sulfate and increases the oxidation rate. Basic minerals react with acid to decrease H_2SO_4 concentration, thus driving the later reaction to the right to form more and more $FeSO_4$.

Although not as reactive as pyrrhotite, pyrite is very important as an oxidizing sulfide since it is the most common sulfide mineral; few sulfide ore deposits lack this compound. In addition to the previous equation, pyrite may also oxidize to form hematite by reaction 4.

$$4FeS_2 + 15\ O_2 + 8H_2O \longrightarrow 2Fe_2O_3 + 8SO_4^{2-} + 16H^+. \quad (4)$$

In waters rich in oxygen (larger $\frac{O_2}{H_2O}$ ratio) pyrite may oxidize to ferric sulfate, $Fe_2(SO_4)_3$, instead of to ferrous sulfate, $FeSO_4$ (see equation 3).

$$4FeS_2 + 15\ O_2 + 2H_2O \longrightarrow 2Fe_2(SO_4)_3 + 2SO_4^{2-} + 4H^+. \quad (5)$$

Still another equation describes pyrite oxidation in neutral or basic solutions as follows:

$$FeS_2 + 3H_2O \longrightarrow Fe(OH)_3 + S_2 + 3H^+ + 3e^-. \quad (6)$$

This discussion has shown some useful chemical principles, such as the production of acidic solutions and the effect of basic gangue minerals. Also demonstrated is the complexity of the oxidation process in that a different oxidation equation applies for each set of conditions and many reactions can occur simultaneously. Thus, aside from the basic chemical principles, not much can be gained quantitatively from the detailed examination of chemical equations that will be helpful in this study.

Heat Output

Although the theoretical heat output for all the stoichiometric reactions mentioned may be computed from heats of formation data, the actual heat output from oxidizing sulfides in underground mines is almost impossible to calculate. For pyrite, complete oxidation of 1 gram yields 2,864 calories. But owing to many variables such as oxygen availability, heat of reaction, and thermal diffusivity, the intensity of oxidative heating cannot be predicted. Physical measurements of the conditions in each particular mining environment will probably give the best information on the net effects.

Critical Temperatures

Although recommendations have been made, at this time there are no standard critical temperatures indicating when oxidation is a serious problem or when it will cause combustion. Concerning sulfide concentrates, it has been suggested to avoid the building up of temperatures beyond 150° F (65° C) (13). Kirshenbaum points out that the heating of concentrates aboard ships causes serious concern when concentrates reach temperatures of about 340° F (170° C). Simpson showed that some sulfide systems spontaneously oxidize at temperatures as low as 122° F (50° C). The establishment of standard critical temperatures for various categories of mining environments would be extremely beneficial in reducing the hazards of spontaneous oxidation and combustion.

PREVENTION AND CONTROL

This paper has examined some of the chemical and physical processes upon which the oxidation of sulfides depends. For prevention and control of sulfide oxidation and combustion, action must be taken to counteract these processes. The measures used must be both control-effective and cost-effective.

There is no one universal method of effectively treating oxidizing sulfides. Each mining situation will require its own specific set of prevention and control measures. Flann and Lukaszewski suggest that prior to the adoption of any protective or safety measure, a chemical study of the mineral involved should be made to determine its stability and behavior in relation to proposed conditions of handling, transportion, or storage.

Prevention

Mining

A thorough assessment of a potentially reactive ore body should be carried out prior to mine development. Important areas include the ground structure, the composition of ground waters, and the chemical behavior of the sulfide minerals.

Preventative methods in mining and in development, given by Flann and Lukaszewski, are quoted as follows:

> "Premature drainage, dewatering and ventilation of excesssively large regions of porous ground containing sulfides should be avoided to lessen the risk of hot ground. If reactive sulfides are associated with the orebody, initial problems are likely to arise in proximity to faulted or brecciated zones. Periodic analysis of rock strata gases and mine waters will provide forewarning of underground oxidation as indicated by low oxygen and high carbon dioxide contents and the presence of increased quantities of soluble solids from carbonates, iron and metal values."

Good housekeeping, by removing various types of rubbish and combustible waste from mine workings, must always be practiced as should other standard underground fire prevention techniques. The mine should be designed for large-volume circulation of air since air should not be stagnant in slowly oxidizing areas.

Transportation and Handling

Complete exclusion of air and water from reactive sulfides in underground mines can never be achieved. However, coarse muck can be kept dry under conditions of low humidity and good ventilation, and thus retard oxidation. Excluding air from the sulfide surface can be accomplished with water when the moisture content of the muck is raised above about 10 pct; however, wet, sticky ore is often difficult to handle and the additional water required is

an added cost. Packaging of ore in the mine, unless ore is extremely valuable, is uneconomical.

During transport of reactive ore, changing ambient conditions should be avoided. Moisture content should not be made to fluctuate because this can accelerate oxidation. Unnecessary vibration and movement of ore acts to create fresh reactive surfaces, to generate friction, and to help remove oxide products, and should be avoided if oxidation is to be prevented. Air-conditioned ore storage and crushing areas may be effective.

Ventilation

Control of ventilation appears today to be the most economical and effective means of preventing and controlling oxidation of sulfide ores underground. Some preventive ventilation techniques in dealing with the heat problem at the Mount Isa mine are directed towards minimizing the increase in the temperature of the air in its passage to the workplace by (1) reducing the area of exposed rock (shorter circuits), (2) reducing heat transfer from rock by having dry airways, (3) increasing volume circulation, and (4) decreasing energy loss by smoothing airways.

Control

Water Spraying and Flooding

Water may be an inexpensive, readily available means of effective treatment. Water represses oxidation in two ways: by acting as heat sink, absorbing thermal energy and evening out temperature levels (temperatures above 100° C cannot be reached if water is present), and by filling pore spaces to prevent oxygen access directly by air. The necessity of water for oxidation has been mentioned earlier; it is somewhat ironic that a constituent required for oxidation is used to retard it. Thus, how and when water is applied is crucial. The use of water as a coolant for already hot sulfides should be avoided unless chemical combustion inhibitors are introduced or rapid inundation can be achieved. The application of insufficient water will accelerate oxidation, mobilize soluble products and sulfur, and consequently increase steam and sulfur dioxide formation.

Although spray application of water is commonly used in controlling rapid oxidation of sulfides in underground mines, its effect is relatively small and short lived. At Mount Isa, the temporary effect of water is used only to quickly resume normal operations. Spray water treatment is effective in dealing quickly with isolated hotspots in the mine; however, unless flooding is used, water is relatively ineffective in dealing with more extensive, long-term oxidizing areas.

Brown found that in using water it is better to put on a large volume for a short time rather than a small volume for a longer time. In severe cases of spontaneous combustion, the fire spreads so rapidly and so extensively that flooding of the area becomes necessary. The excessive damage done to the mine as a result of flooding (ruined workings, cavings, mud, as well as lost

production) make this a last resort technique. Even after the floodwater has been drained and ventilation reestablished, oxidation and combustion may break out again.

Chemical Additives

Lime is commonly added to water in treating reactive sulfides. At Mount Isa, a calcium hydroxide suspension in water is applied to coat the reactive sulfides with limonite, thereby restricting rapid oxidation. However, the lime neutralizes the acid solutions produced during oxidation and thus drives the reaction forward, promoting heating. As was the case with air and water, two opposing effects are present. Further studies of the lime effect would be useful. For pyrrhotite ores, various types of metallic corrosion inhibitors, including compounds containing dichromate, benzoate, and quinolate, have been effective in reducing reactivity. Chemical treatment has been used very restrictively underground; widespread application in mines would be difficult and the overall effectiveness during the mining operation would be marginal.

Worker Protection

High temperatures, large quantities of sulfur dioxide and carbon monoxide, desiccated dust, and depleted oxygen levels present serious hazards to persons working in an oxidizing area. In some reported cases, death from pneumonia has been attributed to these conditions. Working under these adverse conditions may increase the pulse rate and cause headaches. Brown found that excessive inhaling of sulfide dust may cause fits of severe sneezing and coughing. Many publications are available on the detrimental effects of mine gases on worker health (44).

Ventilation

Reactive ore should be mined out as soon as possible, but until the ore is removed, cooling by means of introducing large volumes of low-pressure air is advised. The object is to cool the reacting area so that appreciable oxidation cannot occur. At the same time, the increased ventilation is needed to carry away the large quantities of gases produced. This is accomplished if sufficient air can be passed; if considerably less than this critical amount of air is passed through the area, the rate of heating or combustion will often increase instead of decrease.

Basic control techniques using ventilation are listed by Mathews and North (31) in seven design criteria used at the Mount Isa mine as follows:

1. "Prepare the mine for large volume circulation of unconditioned air.

2. "Apply regional cooling to areas where increased volume circulation is not economical or practical.

3. "Design the ventilation system to transport air in dry airways for the shortest possible distance to point of use.

4. "Prepare main airways for moving air at the highest practical velocity.

5. "Divert air that has traversed an open stope directly to the return airway.

6. "Recirculate air by means of auxiliary fans and ducting if the volume required at the working place is too small.

7. "Pipe chilled water to cooling coils located near the working area where air cooling is required."

Air-conditioning is applied only when all other ventilation techniques of decreasing air temperature have been investigated and tried.

Without air-conditioning, volumes of air greatly above the normal design levels must be circulated to keep the oxidizing areas cool. At Mount Isa, estimated volume requirements for each particular mining method were increased because of hot, oxidized ground. Table 3, given by Davies (6), lists current circulation rates.

TABLE 3. - Air-circulation for mining methods at Mount Isa mine, Australia (6)

Mining method	Air-circulation per ton of ore per day	
	Ft^3/min	M^3/min
Sublevel open stoping.....	62	1.8
Narrow shrink stoping.....	83	2.4
Mechanized cut-and-fill stoping.....	80	2.3
Sublevel caving.....	100-120	2.8-3.4

Additional allowances were made for service areas, crushers, and ore passes, as well as for deeper mining in the future.

Today, control and cost-effectiveness make ventilation the most widely used strategy for controlling sulfide oxidation in large areas underground. Unfortunately, little data exists which quantify ventilation requirements in relation to particular mining environments. The establishment of exact engineering statistics and formulas giving the ventilation requirement as a function of the pertinent mine variables (for example, wall temperature, mining method, and humidity) would not only be helpful in control, but also in establishing standards for evaluating the safety of underground mines. Accordingly, disastrous and costly fires can be avoided in today's mines and in the even deeper mines of the future.

CASE STUDIES

Many instances of spontaneous oxidation and combustion of sulfides underground have been documented. Partial texts of a few of these follow.

Noranda Mines Ltd., Horne Mine, Canada, 1962 (4)[3]

"A major underground fire between the 9th and 3rd levels of the Horne mine commenced on or around the 6th of October, 1962.

Geology.--"The main orebody occurs as a massive sulfide replacement deposit in rhyolite flows and breccias, roughly 400 feet N-S by 800 feet E-W, (extending) down to about 3,100 feet below the surface. The mineralization consists of pyrite, pyrrhotite, magnetite, chalcopyrite, sphalerite, gold, and various tellurides.

Mining Methods.--"Early mining was done by open stoping. The completed open stopes subsequently were filled with cementing fill. Over 90 pct of present production is obtained by mining the pillars.

Causes of Fires.--"The chief causes were given as (1) dust explosions and (2) heat from oxidation of backfill. Since February 1949, 89 fires occurred underground at the Horne mine. Seventy-six of these were caused by (sulfide) dust explosions, seven by oxidation of backfill.

Fire Prevention.--"A record of the stope blasting is kept in the "Blasting Book!" This book is accessible at all times, being left in the Shift Boss's office. Its importance cannot be too highly emphasized. It was from the records kept in this book and from knowledge of the mine that the location of the fire was pin-pointed so quickly. (Dust explosions and sulfide oxidation often occur after blasts increase reactive surface area by fracturing lump sulfide).

Fighting the Fire.--"On Monday (October 8) one of the smelter employees noticed heavy smoke coming from the No. 3 shaft headframe. The location and extent of the fire (was determined to be) on the 909S millhole and it could also be seen that the east 4 x 7 foot flat timered manway had caught fire. The heat, smoke, and SO_2 were so intense that it was not possible to get near the fire area (direct sulfide oxidation (combustion) always produces SO_2 gas).

"The use of water as the prime weapon to fight the fire, and prevent its spread, caused problems. Water overflowed the ditches and the shaft drainage systems and, cascading down the shafts bypassed the normal dewatering system of the upper levels to overload the pumping installation on the 33rd level.

"Efforts after the fourth and fifth days consisted mainly of wetting down timber adjacent to the fire area, extinguishing live fires, cooling hot rock and gases, controlling the flow of water, and even trying to make inroads into the burnt out and/or burning areas.

"After the fire had died considerably, debris at a millhole producing large quantities of SO_2 gas was cleaned up. Much of the ore had slagged. Red

[3]Except for headings, the following passages are direct quotations from the indicated studies.

hot muck had to be drilled and blasted. The extent of the cleanup effort required 469 manshifts to clean up 8,220 tons of material.

Important Points.--"This type of fire starts slowly and is normally preceded by a charred smell or a small amount of smoke. Thus, it is usually detected and extinguished before it can assume major proportions.

"The regular fire inspection procedure which followed blasting operations, had not been extended to the particular workings where fire originated.

"The crew had noted small, but significant changes. The crew did not report these changes to the shift boss."

Bent (2) provided the following comment:

"Under certain conditions, broken ore high in pyrrhotite content will oxidize quite rapidly, and the heat generated may be high enough to char timber left in the ore (Total sulfide content was very high in this massive deposit and the presence of pyrite, and more so pyrrhotite, made the deposit even more reactive)."

Cant continues in his description:

"During the cementation of the backfill, the heat developed by the oxidation, unless removed by good ventilation, is occasionally intense enough to cause the outbreak of fire in timber left in or against the backfill (Sulfide backfill in mined out stopes presents an excellent opportunity for oxidation: the sulfides are highly fractured, ventilation is low so the cooling effect is small, and timbers and other combustible debris may well be present in or near the backfill).

Improving Prevention.--

"Weekend inspections instituted."

"Substitution of steel drift sets for timber drift sets in mined out areas."

"Removal of timber sets no longer needed."

"No piling of supplies at the top of the fill raise on the lower level above."

"More thorough wetting down."

"Filling of millholes when mining is finished."

"Cementing in place of wood."

"Installation of sprinklers at top of each stope."

Sprinkler systems for underground metal mine shafts have been developed by the Bureau of Mines Twin Cities (Minn.) Mining Research Center (11).

The pyrite dust produced during blasting at the Horne mine occasionally explodes violently in large stopes, sometimes blowing out ventilation doors in the immediate area. Such explosions produce a red oxide dust and large quantities of sulfur dioxide gas. An explosion may produce temperatures up to 3,000° F (1,650° C), causing spontaneous ignition on any timber or combustible matter present.

Magma Copper Co., Magma Mine, Arizona, 1961 (38)

"Spontaneous combustion in a caved section started a troublesome fire that stopped production for 2 months.

Geology and Mining Methods.--"The east section of the Magma mine where the fire occurred is a replacement type orebody in a bed of limestone that dips 30° to the east. The mined area is caved as mining proceeds down dip.

Cause of the Fire.--"The fire started in a caved section of the mine on December 2, 1961. The section had been mined out and in 1957 was sealed with brattices. The fires started by combustion when drill holes from a new drift admitted air into the sealed section. The fire was confined to the mine timber. The sulfide minerals did not burn.

Fighting the Fire.--"The fire advanced 250 feet overnight. Carbon monoxide concentration in the exhaust air soon reached 2 pct. (A CO concentration of .05 pct can cause death in 3 hours). Temporary brattices were planned to be built first and then these were to be followed with concrete block bulkheads later. Most crews were required to have oxygen breathing apparatus with them. Brattices were gunited.

"Water sprays were installed behind all brattices. These were designed to wet the back side of the brattices as well as the first few feet of timber beyond them. "Peekholes" that were cut in the brattices were opened each time the brattice was inspected to make a visual inspection for any sign of fire. The following observations were made:

"1. Condition of the water spray

"2. Pressure on the bulkhead as indicated on a water guage

"3. Carbon monoxide reading

"4. General conditions of the brattice (e.g., leaks, cracks)

"Sealing the fire required eight concrete bulkheads, four concrete block bulkheads, 70 feet of concrete drift, and concreting 60 feet of a three-compartment service raise. Current analysis of air inside the sealed area is 2.4 pct oxygen, 14 pct carbon dioxide, and 0.2 pct carbon monoxide."

Note that no sulfur dioxide gas is produced when sulfides do not burn. Again, caved, highly fractured areas cause oxidation which increases temperature to the point where timber combusts. The effect of oxygen availability is demonstrated when drill holes admitted air to the sealed area.

United Verde Copper Co., Jerome, Ariz., 1916 (42)

"Underground fires have been common in the mines of the United Verde Copper Co., for the past 22 years. The first fire started in the 300 Hampton stope in the fall of 1894, following a cave in that orebody. The soft and highly pyritic nature of the ores is responsible for most of these fires.

Geology.--"The ores are mostly chalcopyrite. The largest and most important of these reserves are in a pyrite gangue.

Mining Methods.--"Cut-and-fill, shrinkage and millhole systems have been largely employed. But 15 pct of the total tonnage now extracted is from timbered stopes. Most of this is from the upper levels where the ore is soft, heavy, and more or less broken to the surface.

History of Fires.--"The first fire of 1894 was caused by spontaneous combustion, following a cave-in. It was not extinguished and the district was bulkheaded from the remainder of the mine cutting off a large productive area of high grade ore. (Attempts to use water, steam, and carbon dioxide to extinguish the fire failed due to the fractures to the surface and underground workings outside the fire district which constantly provided fresh oxygen to the hot ground. A special ventilation system proved to be the solution, the cooling effect making possible the recovery of many rich areas previously bulkheaded and burning uncontrollably.)

Causes of the Fire.--"Probably 90 pct of all underground fires in pyrite or heavy sulfide ores are caused by spontaneous combustion."

In the fire district of this mine, many fires started when red-hot dust dropped on the timbers from fractures in ground above. Some fires were caused from friction due to caving.

"Fires from spontaneous combustion usually occur in the interior of a gob or filled stope and are due to the oxidation of fine sulfides in contact with timber. Very small amounts of air are necessary for spontaneous combustion and this air works its way through the filling along the line of bulkheads, timber or walls, where it comes into contact with sulfide dust. In the process of oxidization this produces sufficient heat to start a fire. This theory has been proven here by experiments. Considerable fine sulfide ore is lost in the fire stopes."

Prevention of Mines Fires.--"Main hoisting shafts in such properties should be constructed of concrete or other fireproof material. Where timber is used, a sprinkling system should be installed.

"Mine methods should be developed in which timber will be eliminated as far as possible.

"Heavy sulfide material should not be used for filling in the timbered stopes. In these places fine waste should be used and sprinkled so that it will pack and make conditions unfavorable for fire.

"In fire stopes or stopes adjacent to the fire district, the timber next to the walls or ends should be removed.

"Careful attention should be directed toward ventilation so that the temperature will be unfavorable for fires to start.

"In hot places the timber should be kept damp by sprinkling with water. Water should never be put on red-hot or burning ground, as this will invariably cause an explosion, one of the great dangers in handling mine fires.

"Watchmen should inspect the air outlets often and regularly in order to detect smoke as soon as possible.

"Iron fire doors should be erected in connections near all timbered stopes, so that in case a fire gets beyond control the doors can be closed and the district quickly sealed up, in order to protect the remainder of the mine."

Pocahontas Mine, Joplin District, Missouri, 1914 (9)

"First serious mine fire in the Joplin district was recently experienced when through the decomposition of marcasite (FeS_2) sufficient heat was generated to set timbering on fire in a badly caved portion of the Pocahontas ground. Due to the quick spreading of the fire it was decided to take out whatever machinery was near the shaft and abandon the mine and let the water rise. The closing of this mine and waiting for the water to rise puts out of commission two adjoining properties, both of which were heavy producers of ore up until the last few months. The fire started in an extensive cave-in which cut off the air between two shafts. This caving ground was filled with timbers over which lay some heavy deposits of marcasite, shale and mud."

Again, iron sulfides seem particularly reactive, and oxidation often occurs after a cave-in. Also, timber present with oxidizing sulfides is an especially serious hazard.

Anaconda Copper Mining Co., Butte District, Montana, 1922 (36)

"Spontaneous combustion has been the cause of most of the large fires here. The heat resulting from the oxidation of the fine broken sulfide ore is sometimes sufficient to set fire to the timbers."

This article describes a 1906 fire at the Minnie Healy mine which eventually was controlled by blocking it off and filling it with mill tailings. The fire area spread to a block "1000 ft by 1200 ft and from the 600 ft to the 2200 ft level. This block was composed largely of a series of parallel

northwest-southeast nearly vertical veins and stringers that form a large orebody, (badly fractured and faulted) with walls." The broken nature of the ground made it difficult to seal the fire effectively.

Tally described the following preventive measures adopted by the Anaconda Co.: "All underground fan stations, transformer and switch rooms and electrical apparatus have been made fire proof; a firebug (or watchman) goes through each shift boss' run in all mines after each shift; metal receptacles are used for oil waste and refuse and are in safe places; signs denoting directions to other mines and mainshafts are posted on all levels; mining methods are being adopted to eliminate as much timber as possible. Working shafts are usually downcast so that in case of fire, ordinarily men can come to the shaft and be hoisted without danger of suffocation."

Bisbee, Ariz., 1916 (42)

"All of our fires have been spontaneous, as far as we know, and they have all occurred in the centers of filled and abandoned stopes. I think they are undoubtedly caused by the heating of sulfides in stopes where they are loose and granular, and where there is little ventilation."

Sunshine Mining Co., Kellogg, Idaho, 1972 (20)

Investigations on the Sunshine disaster found evidence that the fire started in an abandoned area and burned through a bulkhead. The Bureau of Mines concluded that spontaneous combustion of refuse near scrap timber was probable cause of the fire. Although the vein material being mined contained less than 10 pct sulfide minerals and the Bureau of Mines found no instance of fire igniting spontaneously from sulfide minerals in the Coeur d'Alene Mining District, the final report did not rule out the possibility that sulfide oxidation in the abandoned area may have generated sufficient heat to ignite refuse or scrap timber.

The following notes are from an unpublished report by Waxvik (43).

Homestake Mining Co., Lead, S. Dak., February 13, 1965--"Spontaneous fire in sulfide minerals in sand backfill." May 9, 1975--Origin of the fire was spontaneous combustion initiated by a sudden drop in ventilation (7).

Cordero Mining Co., Humbolt County, Nev., September 24, 1965--Fire in abandoned stope; probably spontaneous combustion in sulfide ore.

Eagle mine, the New Jersey Zinc Co., Gillman, Colo., June 9, 1971--"Spontaneous fire in sulfide minerals; discovered when two stope miners became ill."

Dragon mine, Filtrol Corp., Eureka, Utah, September 9, 1971--"Probable cause: spontaneous combustion of sulfide minerals used as backfill."

Eagle mine, the New Jersey Zinc Co., Gillman, Colo., May 1973--"Spontaneous combustion in area above or behind present stopes."

SUMMARY

In today's underground metal mines, ores rarely spontaneously ignite. Oxidizing sulfides, particularly in combination with combustibles such as timber, pose a real problem to the health and safety of workers and to the efficient production of ore. Hazards such as increased temperatures, sulfur dioxide and carbon monoxide generation, depleted oxygen supply, dust explosions, lost ore and production, and fire in oxidizing underground metal mines will probably increase with the increasing depths of tomorrow's mines.

Although the exact oxidizing mechanism of sulfides is highly complex, the qualitative effects of the most important variables are known. The iron sulfides are the most reactive, and reactivity is increased when more than one type of sulfide is present. The greater the percent of sulfides, the greater the heat production will be. Water is necessary for oxidation, although too much water acts to cool the sulfides and reduce the reaction rate. Oxygen, too, is required for oxidation and is generally present in airflow. Moving air, however, also has a cooling effect so that the same level of ventilation in an oxidizing mine can cause very different effects in different situations. Highly fractured or porous rock allows air to bring oxygen to more sulfide surfaces; thus, the structure of the ore is critical also. The presence of any combustible material, such as timber or refuse, in contact with oxidizing sulfides seriously increases the danger of fire due to the much lower ignition temperatures of these materials.

Many sound prevention and control measures have been mentioned. The use of water to control sulfide oxidation is effective as a quick, although temporary, means of control in small, isolated areas. For long-term prevention and treatment of large oxidizing areas, effective ventilation at large flow rates is today's most reliable and economical method. Standard mine firefighting techniques and precautions should be applied whenever oxidation leads to combustion.

The most serious cases of spontaneous oxidation and combustion of sulfides occur when combustible organic material ignites due to the heat of sulfide oxidation. This will often happen in abandoned areas of a mine where there is little ventilation to carry away the heat being generated. Old stopes containing highly fractured backfill with a large sulfide content present ideal conditions for oxidation and combustion. Accelerated oxidation and fire often follow blasting or cave-ins as the sulfide ore fractures to expose more reactive surface. Highly fractured or faulted ore bodies with iron sulfides present serious problems when mined underground. Exploding sulfide dust is another danger especially during and after blasting.

CONCLUSIONS

Based on the information outlined in this paper, many underground metal mines in the United States have potential, if not existing, sulfide oxidation problems. Examples in Arizona, Montana, and Missouri were presented. By examining the geology, mining methods, and the general mining environment underground in other mining districts, susceptible mines can be pinpointed to

some extent. However, further studies and investigations are required to more fully understand when oxidation hazards exist and how to prevent and control their effects.

Many recommendations for research have already been made. Further study of the mechanisms and factors examined in this report and their interrelationships is critically needed. Once an overall model, using mathematical expressions to quantify these relationships, is established, the application of modern technology would be natural. Underground sensing and remote control have already proved to be very beneficial in metal mines. Applying this instrumentation to the model, possibly with computers to quickly handle the numerous calculations and accountings for different areas in the mine, the underground environment could be simulated above ground and dangerous situations could be predicted before they occur. It is believed that such efforts will be highly beneficial in maintaining safe working environments as well as high recoveries and productivities in today's undergound metal mines.

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