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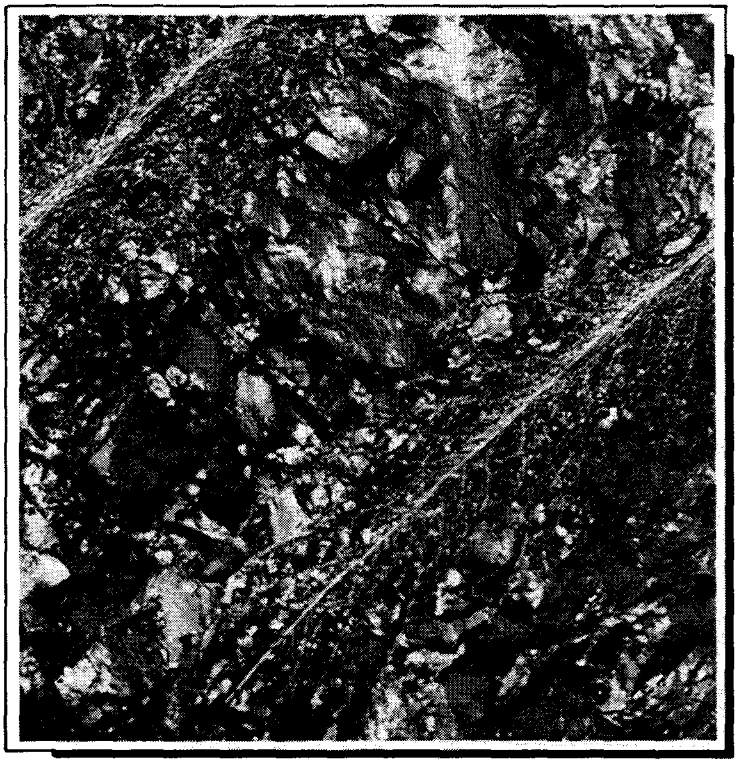
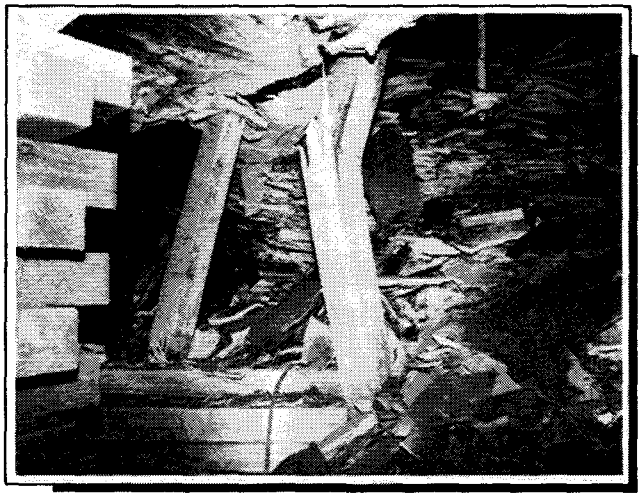
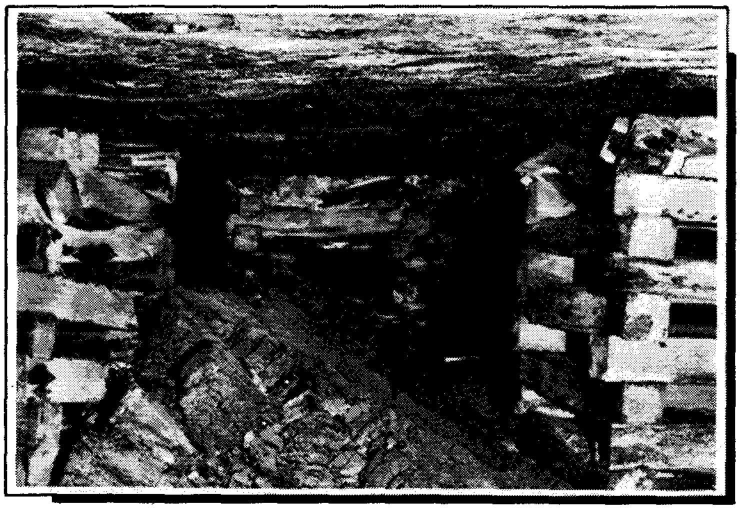


Pyrite Problems in the Coal Mining Industry

By Yael Miron





United States Department of the Interior

Bureau of Mines

***Cover Photographs:** Top, Pyrite in Pittsburgh Seam coal, Bruceton Mine (Photograph by Sidney Pollack, Department of Energy, Pittsburgh, PA); Middle, Galatia Mine roof fall (Photograph by Frank Chase, U.S. Bureau of Mines, Pittsburgh, PA); Bottom, Floor upheaval on the Maple Meadow pillar line (Photograph by Frank Chase, U.S. Bureau of Mines, Pittsburgh, PA).*

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UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES

Library of Congress Cataloging in Publication Data:

Miron, Yael.
Pyrite problems in the coal mining industry / by Yael Miron.

p. cm. — (Information circular; 9381)

Includes bibliographical references (p. 11).

Supt. of Docs. no.: I 28.27:9381.

1. Coal mines and mining—Safety measures. 2. Coal—Mineral inclusions. 3. Pyrites—Oxidation—Environmental aspects. I. Title. II. Series: Information circular (United States. Bureau of Mines); 9381.

TN295.U4 [622'.82] 622 s—dc20 93-39734 CIP

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	h	hour
cal	calorie	kg	kilogram
cm^3	cubic centimeter	kPa	kilopascal
cm^3/min	cubic centimeter per minute	m	meter
ft	foot	pct	percent
g	gram	wt pct	weight percent

PYRITE PROBLEMS IN THE COAL MINING INDUSTRY

By Yael Miron[1]

ABSTRACT

The presence of pyrite (FeS_2) in coal can cause or contribute to several problems for the coal mining industry. These problems, which include spontaneous combustion, roof falls, floor heave, and accidental explosions in coal surface mining when ammonium nitrate-fuel oil (ANFO) explosives are used, result from pyrite oxidation.

Pyrite oxidizes exothermically in the presence of air and moisture to form a large variety of products, including hydrated ferrous and ferric sulfates, and sulfuric acid. Some of the products are reactive chemicals and strong oxidants. The volume of many of these oxidation products exceeds the original volume of the pyrite; as a result, the adjacent coal disintegrates and its surface increases, rendering it more susceptible to oxidation. The heat from pyrite oxidation raises the temperature of the adjacent coal, accelerating the oxidation and self-heating rates of the coal. These combined chemical, physical, and thermal effects are the cause of the aforementioned problems. When ANFO is used in surface coal mines and contacts ferrous sulfate, a highly exothermic reaction ensues. Additional hazards are fires or explosions caused by the frictional ignition of methane when the pyrite in the coal is struck by a cutting bit during mining.

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INTRODUCTION

Pyrite (FeS_2), the most abundant of the iron sulfides, is widely distributed and occurs in rocks of all kinds. Deposits of economic importance occur as masses of great size, and are presently mined in Spain, Portugal, and elsewhere for their sulfur content (*1*).[2] Pyrite is not mined currently in the United States, other than by a few individuals for specialty uses.[3] Pyrite is present in most coals in the United States; large coal resources in other countries also contain pyrite. Marcasite, a polymorph of pyrite, occurs in mineral veins as crystals, in some lead-zinc ores, and in clay and coal (*2*). However, it is not identified as marcasite in a typical coal analysis; instead, it is included with the pyrite. Pyrrhotite, a monosulfide (FeS, though it actually ranges from Fe_3S_4 to $Fe_{16}S_{17}$) is not usually present in coal, nor is it specifically shown in the analysis. If present, it is included with the organic sulfur in analysis results. The main emphasis of this review paper is on pyrite in coal and some of the problems that it can create under certain conditions, especially conditions suitable for its oxidation.

The coal resources of the United States are divided into six provinces as follows: Eastern, Interior, Rocky Mountains, Northern Great Plains, Gulf, and the Pacific Coast. Of these, high-sulfur coals are mostly found in the Interior province. Low-sulfur to medium-sulfur coals are found in the Pacific Coast province, whereas the sulfur contents of the coals from the Eastern province (Appalachian Basin) vary widely (*3*). The other three provinces contain mostly low-sulfur coals. These terms of high sulfur or low sulfur are relative ones, not only to the coal basins but even within a coalbed. In general, if sulfur content, on an as-received basis, is 1 pct or less, the coal is classified as low-sulfur coal; if sulfur content is 3 pct or more, the coal is a high-sulfur coal; whereas it is a medium-sulfur coal for concentrations higher than 1 pct and lower than 3 pct. To show the range of pyrite concentration in various coals, some averaged sulfur values for U.S. coals are presented in table 1, and sulfur contents for a few specific U.S. coals, as measured by X-ray absorption fine structure spectroscopy, are shown in table 2. Similar variations in sulfur content are found in coals throughout the world.

Table 1.—Sulfur values in U.S. coals[1]

Province and region	States	Age	Sulfur (dry basis), wt pct, mean: Total	Pyrite	Organic	Number of samples
Eastern:						
Appalachian	AL, Eastern KY, OH, PA, TN	Pennsylvanian	2.3	1.4	0.8	163
Anthracite	PA	..do.	2.2	1.3	.8	175
			.9	.3	.6	12
Interior:						
Eastern	IL, IN, Western KY	..do.	3.9	2.2	1.5	48
Western	AR, IA, KS, MO, OK	..do.	4.3	2.3	1.6	43
Gulf	LA, TX	Paleocene-Eocene	1.3	.3	1.0	11
Northern Great Plains	CO, MT, ND, NM, WY	Upper Cretaceous-Eocene	.6	.2	.5	22
Rocky Mountains	AZ, CO, NM, UT, WY	..do.	.7	.2	.5	53
Pacific	WA	Eocene	.9	.3	.6	3

[1] Davis, A. Sulfur in Coal. Earth and Mineral Sciences, v. 51, No. 2, 1982, pp. 1, 18-21.

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

[3] Information from D. A. Buckingham, Minerals Availability Field Office, U.S. Bureau of Mines, Denver, CO.

Table 2.—The sulfur content of a few U.S. coals[1]

Coal sample		Total sulfur, wt pct
Seam	State	
Beulah-Zap	ND	0.80
Illinois No. 6	IL	4.83
Pittsburgh No. 8	PA	2.19
Pocahontas No. 3	PA	.66
Upper Freeport	PA	2.32

[1] Huffman, G. P., S. Mitra, F. E. Huggins, N. Shah, S. Vaidya, and F. Lu. Quantitative Analysis of All Major Forms of Sulfur in Coal by X-ray Absorption Fine Structure Spectroscopy. Energy and Fuels, v. 5, 1991, pp. 574-581.

The major forms of sulfur in coal are pyritic, organic, and sulfatic, with the first two forming the bulk of the sulfur in coal. Pyrite is the major inorganic sulfide mineral in coal, and it occurs in several forms including nodules and partings, veins, balls, thin plates in cleats, and also in disseminated forms. The abundance and forms of sulfur in coal differ in the various geologic environments, and depend to a large extent on the sedimentary environment during peat deposition, following peat accumulation, and during peat compaction and coalification. Levels of pyrite in peats from fresh water are an order of magnitude lower than those in the marine-associated peats (*4-6*). Likewise, coals that formed in the presence of fresh water contain less sulfur than coals that were overlain by seawater or formed in a marine environment (*7-9*). Thus, coal with a marine-type roof above the bed usually has a higher sulfur content, whereas, when the roof is a nonmarine gray shale, the sulfur content of the coal is usually lower. These relationships as to roof type and depositional environment have been identified in major coal fields in Europe, China, and the United States.

There are several safety hazards associated with the mining of coals that contain relatively large amounts of pyrite. These hazards, which include spontaneous combustion, roof falls, floor heave, and unplanned explosions, are due to (1) the oxidation and self-heating of pyrite and the resultant heating of the associated coal; (2) the increased volume of the oxidation products of pyrite causing expansion and breakage of the associated strata, in turn leading to accelerated oxidation and self-heating of the coal as well as to roof falls and floor heave; and (3) the exothermic reactions between ANFO explosives used in surface mines and the weathering-oxidation products of pyrite. Another safety hazard, associated directly with pyrite but not with its oxidation or oxidation products, is the frictional ignition of methane, which can result when pyrite is struck by cutting bits on an operating mining machine. A detailed description of these hazards and their causes is presented in this review paper.

The main emphasis will be on the hazards associated with the coal mining process. Acid mine drainage, primarily a post-mining problem, and the various approaches to alleviate its effects, are discussed in great detail elsewhere in the literature and will not be addressed in this review.

OXIDATION OF PYRITE AND THE PRODUCTS OF ITS OXIDATION

Oxidation of pyrite has been studied extensively and many review papers on the aqueous oxidation of pyrite at ambient temperature are available (*10-14*). Pyrite reacts with oxygen and water to form sulfates of iron and sulfuric acid. The overall process is usually described by the following reactions;

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

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

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

However, pyrite oxidation is a complicated process that involves a variety of reactions and steps, including chemical and microbial oxidation, hydrolysis, dissolution, and precipitation, and is not yet completely understood (*12*). Among the intermediate sulfur species are sulfites (SO_3^{2-}), thiosulfates ($S_2O_3^{2-}$), tetrathionates ($S_4O_6^{2-}$), polythionates (such as $S_3O_6^{2-}$ and $S_5O_6^{2-}$), and sulfur (S^0). Also, oxygen is not the only oxidant capable of oxidizing pyrite. Ferric ion also can act as a strong oxidizer. As its concentration increases, and as higher acidity prevails, ferric ion becomes the major oxidizing agent, as in reaction C.

Many factors can affect the oxidation of pyrite, among them temperature, surface area and morphology of the pyrite, the presence of impurities, and the partial pressure of oxygen. Different rates of reaction and different activation energies were determined and reported by various researchers for the aqueous oxidation of pyrite. One explanation for the discrepancies in these values is incomplete cleaning of test specimens; oxidation products, such as soluble sulfates and insoluble iron oxides, remain on the surface. These products influence the oxidation process, and hence the results (*15*). Another explanation was given by McKibben and Barnes (*16*) who evaluated the preparation procedures of their pyrite samples for oxidation tests. They viewed the cleaned samples in a scanning electron microscope (SEM) and saw intragranular variations in the surface structure. Fractures, inclusion pits, defects, grain edges, and cleavages were identified by them, and by many other workers in the field, as the reactive surface sites where oxidation occurs. Such sites form during mineral formation and during sample preparation. The defects vary from grain to grain, and the variable experimental results are, therefore, not surprising. When the samples were viewed in the SEM after the oxidation tests, the reactive sites appeared more etched and contained new pits and edges, while the other areas appeared smooth and untouched. In almost all studies of pyrite oxidation, very fine particles are used to obtain measurable reaction rates. Extensive grinding is required to prepare such particles. The mechanical grinding action and the heat generated during grinding also contribute to the formation of damaged and strained areas on the surfaces of the particles (*16*). Another cause for the discrepancies between various experimental results is the surface area of the particles. Surface areas are estimated by a variety of techniques and vary from geometric overall surface areas to highly detailed areas, which include fractures, pits, and other defects. The actual area of reactive sites is somewhere between these two, and is seldom known accurately.

In addition to the inorganic, or chemical, oxidation of pyrite, microbial oxidation also takes place. Sulfur-oxidizing microorganisms, the *Thiobacilli*, utilize sulfur as an energy source and carbon dioxide for carbon. One species of this group, *Thiobacillus ferrooxidans*, can oxidize pyrite, ferrous iron, and sulfur. These bacteria act optimally at low pH values, but can survive at neutral pH values, and contribute to acid formation and pyrite oxidation even at a pH level of 6 (*17*). These bacteria catalyze the rate of oxidation of ferrous to ferric ions by a few orders of magnitude; the resultant ferric ions then oxidize the pyrite (reaction C). Other acidophilic bacteria that can oxidize ferrous iron are known (*18*). Fungi, yeast, and molds also have been identified in acid mine drainage at different localities, and might be involved in oxidation (*19*). Among the fungi are acid-producing species (*20*), which also can contribute to the reduction in pH. The fungi can derive their nutrients from cellular components of other dead microorganisms as well as from extracellular organic matter synthesized by living microorganisms such as algae or cyanobacteria. Thus, there is evidence for close association and interdependence among many varied microorganisms.

Laboratory measurements of pyrite oxidation rates are conducted mostly in aqueous solutions. In sulfide and coal mines, pyrites and other sulfide minerals usually are not exposed to aqueous solutions; rather, they are exposed to cycles of dry or moist air. For an understanding of pyrite behavior in these conditions, Pahlman and Reimers (*21*) made use of thermogravimetric analysis. They heated their pyrite samples at a constant heating rate, and determined temperatures at which their samples ignited. Additional results, showing increased rates of oxidation due to humidity, at 50° C, are presented by Reimers and Franke (*22*). In a similar manner, Fuller (*23*) observed samples of pyrite-bearing coals obtained from freshly opened mine faces at various controlled relative humidities, and found that gypsum ($CaSO_4 \cdot 2H_2O$) crystals formed on the coal surfaces after a short while. The gypsum crystals were not detected at low relative humidities (<20 pct), nor were they detected at high relative humidities (60 to 90 pct), in the absence of air. According to Fuller, sufficient water is imbibed by the coal, at high humidity, to transfer soluble entities of the pyrite oxidation products from inside the coal to the surface where they precipitate; the imbibed water serves as a transport medium. At lower relative humidities, the amount of water inside the coal is retained strongly and does not act as a transport medium.

In similar studies, Baltrus and Diehl (*24*) evaluated the effects of relative humidity and oxygen partial pressure on the relative rates of surface oxidation of pyrite derived from various coal seams, including Illinois No. 6, Pittsburgh, and Tuscarora seams. In general, their results indicated that the relative humidity had a greater influence on the extent and rate of surface oxidation than did oxygen. White needles, composed primarily of gypsum with traces of jarosite [$KFe_3(SO_4)_2 \cdot (OH)_6$], were formed immediately upon initiation of oxidation on the surface of the pyrite sample derived from the Pittsburgh Seam coal, and severe changes in surface morphology were observed. Gypsum crystals are the major contributors to volume expansion of the oxidation products, and therefore can accelerate floor heave, roof falls, and the disintegration of coal.

Pyrite oxidation studies conducted in the laboratory cannot duplicate field conditions, which are impacted by additional parameters such as the geology of the strata, hydrology, and climate. Therefore, the complete nature of the complex process in the field is not yet known. Some aspects of direct impact on the hazards associated with pyrite in coal are the exothermicity of pyrite oxidation and the many oxidation products. These products can further interact with the associated strata, including coal, shale, clays, and the other aluminosilicates, and cause additional undesirable changes. According to Winmill (*25*), approximately 4.3 cal are released by pyrite for each cubic centimeter of adsorbed oxygen; for the same amount of oxygen adsorbed, coal releases about half that number of calories. The reactions of some of the pyrite oxidation products with the strata also can be exothermic. With increased temperature, the rate of oxidation increases and self-heating accelerates. Under "optimal" conditions, the reaction can reach runaway proportions.

Sulfuric acid (H_2SO_4), one of the products of pyrite oxidation, attacks clays and liberates various ions, including sodium, calcium, magnesium, aluminum, silicon, and iron. Some of these ions hydrolyze as follows,

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+, \qquad (D)$$

and

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+, \qquad (E)$$

and in turn increase the acidity even more (*26*). The increased acidity optimizes the bacterial activity.

Other pyrite oxidation products include a large number of hydrous salts, among them water soluble iron sulfate hydrates and insoluble and less-soluble iron oxides and sulfates of calcium, barium, and magnesium. The more common iron sulfates are $FeSO_4 \cdot 7H_2O$ (melanterite), $FeSO_4 \cdot 4H_2O$ (rozenite), $FeSO_4 \cdot H_2O$ (szomolnokite), and $Fe_2(SO_4)_3 \cdot 9H_2O$ (coquimbite), while $FeSO_4 \cdot 5H_2O$ (siderotil) and $FeSO_4 \cdot 6H_2O$ are less common. Among the insoluble sulfate salts, $KFe_3(SO_4)_2 \cdot (OH)_6$, $Fe^{2+} \cdot Fe_4^{3+}(SO_4)_6 \cdot (OH)_2 \cdot 20H_2O$ (copiapite) and $CaSO_4 \cdot 2H_2O$ are the most prevalent, while the iron oxides include α-FeOOH (goethite), $Fe_2O_3 \cdot XH_2O$ (limonite or brown hematite), and $Fe(OH)_3$ (ferric hydroxide or ferrihydrite) (*12*). The soluble sulfates can be transported by water to other areas, leaving behind mostly the insoluble sulfates jarosite and gypsum, and the oxides. Thus, the relative amounts of these products can serve as indicators of the relative extent of pyrite oxidation.

The large number of pyrite oxidation products, the highly reactive nature of some of the products, the overall exothermic nature of the oxidation process, and the pressure exerted by the products on the associated strata combine under certain conditions to cause or contribute to major problems in some coal mines.

PYRITE AS A CAUSE OF SPONTANEOUS COMBUSTION

Prior to evaluating the effects of pyrite on the spontaneous combustion of coal, it is beneficial to review the process for spontaneous combustion of pyrite itself. When favorable conditions exist, pyrite can oxidize and attain high enough temperatures to ignite spontaneously. Due to the high exothermicity of pyrite oxidation, sulfide ore mines are often faced with problems of self-heating, spontaneous ignition, and fires. The concentrations of sulfides in these ores are much higher than those found in coals, and the associated problems are also much greater. Thus, examples of the major problems that some sulfide mines have undergone, and the dangers confronted in the mines, portend the possibility of similar dangers to coal mines that extract coal with pyrite contents greater than 3 pct. One example of the severe problems encountered during the mining in sulfide ore is described for the Sullivan Mine in Kimberly, southeastern British Columbia, Canada (*27*). This mine contains galena (PbS), sphalerite (ZnS), pyrrhotite (FeS), and pyrite as the major sulfide constituents. In the late 1960's this mine produced ore from pillars remaining in the ore body from previous mining operations. The pillars, located anywhere from 100 to 2,000 ft below the surface, sustained high pressures, resulting in deteriorating ground conditions. To alleviate these conditions, broken masses of ore were left as additional support between the other pillars. As a result, large surface areas of the sulfide minerals were exposed to air. Initially, heatings developed in a few localized areas associated with a major water course. Some time later, fires developed in the broken ore masses. These fires could not be extinguished except by removing the burning ore from the mine. Mining methods had to be changed and redesigned, and operating procedures were modified to minimize the many hazards associated with the mining of the hot ore (*28*). Hazards included sulfur dioxide emissions, low oxygen levels, hot dust (superheated fines), acid mist, radiant heat, and clinkering (formation of clinkers by sintering of the hot ore).

Loading and blasting of the explosive charges in the hot ground also posed major problems in the Sullivan Mine in British Columbia (*29*). Special loading and blasting procedures had to be developed, and special mining and mucking methods were utilized. Additional strategies to deal with these situations included high production rates immediately following a blast to remove the broken ore from the mine. Fire fighting procedures also were tailored to specific mine sites. Other mines that experienced identical problems include the Horne Mine in Noranda, Quebec, Canada (*30*), and Mount Isa in Australia (*31-33*). Ninteman presents various case histories of spontaneous combustion in sulfide mines (*34*).

PYRITE AS A FACTOR IN THE SPONTANEOUS COMBUSTION OF COAL

Since the early days of spontaneous combustion events in coal mines, pyrite has been cited as a main cause. The theory that pyrite oxidation was the principal cause of the spontaneous combustion of coal was accepted until, in 1875, John Percy (in his book *Metallurgy*; quoted by Thacker (*35*)) pointed out the fact that the highly susceptible coal from South Stafford, United Kingdom contained only small amounts of pyrite (*35*). Subsequent experiments to prove or disprove the role of pyrite in the development of spontaneous combustion in coal have not been always conclusive.

Parr and Kressman (*36*) evaluated the effects of increased amounts of pyrite on the self-heating of a coal from Williamson County, Illinois. This coal contained about 1.65 wt pct pyrite. To increase the content of pyrite in the coal, lumps of pyrite from a coal from Vermillion County, Illinois were utilized. These lumps of pyrite (just as they occurred in the coal measures) were ground to pass through a 20-mesh sieve. Increasing the pyrite content in the Williamson coal sample to 3 and 5 wt pct increased the self-heating of the coal, especially of the finer fractions, in each case. Large amounts of coal (approximately 20 kg) were used in these tests, which were conducted in large ovens. In another set of experiments, Li and Parr (*37*) used four coals, all from Illinois, with varying amounts of pyrite. Small samples, 5 g each, were used in tests at 25° and 100° C. Results indicated that under suitable conditions the pyrite in the coal oxidized rapidly and might be a dominating and determining factor in the self-heating of coal. Dry air or oxygen did not promote pyrite oxidation but, in the presence of high moisture in the coal sample, pyrite oxidized readily and rapidly. The results from these two studies (*36-37*) indicate that both autochthonous and extraneously added pyrite can contribute to increased self-heating of coal samples containing pyrite.

In small scale tests to assess the effect of pyrite on coal, Ghosh added increasing amounts of pyrite powder to five coals of variable susceptibility to spontaneous combustion (*38*). Peroxy indices of the coals, which are a measure of the extent of the surface oxidation of a coal, were measured and found to increase almost linearly with increasing pyrite content for all five coals. Such results suggest that pyrite is an active factor in the process of coal oxidation. Winmill (*25*) also assessed the role of pyrite in the spontaneous combustion of coal in coal mines. He exposed samples of pyrite from two coal seams, the North Staffordshire Seam and the Barnsley Seam (both in the United Kingdom), to oxygen and measured the amounts of sulfate formed as well as the rise in temperature in the samples. Winmill suggested that although atmospheric oxidation of coal itself was quite sufficient to cause gob fires, it was possible that pyrite might be a contributory factor to the initial heating. Based on additional measurements of the rate of reaction of the pyrite with oxygen as a function of temperature and of partial pressure of oxygen, he concluded that finely divided pyrite in considerable proportions in coal might be the chief factor in causing combustion. Graham (*39*) conducted similar tests, with samples of pyrite, marcasite, and pyrrhotite, and noticed that as soon as all the moisture was used up, the adsorption of oxygen practically ceased. In test samples from a South Wales coalbed that contained pyrite, Graham found that most of the oxygen was consumed by the pyrite; the coal substance adsorbed little oxygen in comparison.

A fire in the gob of a coal mine, which was probably initiated by the presence of pyrite, was reported by Newton (*40*). The material placed in the gob came from the layers above the coal and contained as much as 14.5 wt pct pyrite. The pyrite was very fine and so well mixed with the coal that it could not be identified by a visual examination.

Early descriptions of microscopic examinations of coals were presented by Lomax (*41*). He tested coals from seams known to have problems with gob fires and from those not susceptible to spontaneous ignition. These seams in the United Kingdom included the Doe Seam from the Bolton District, and the Bullhurst Seam and Cockshead Seam from North Staffordshire. He identified various forms of pyrite and tried to correlate the formation of alteration products on the freshly exposed surfaces with spontaneous combustion. Drakeley (*42*) conducted experiments in which various amounts of pyrite, ferrous sulfate, or sulfuric acid were added to coal and the amounts of air adsorbed by the various mixtures, as well as by individual ingredients, were observed as a function of time. The amount of air adsorbed by the mixture of coal and pyrite was somewhat larger than the sum of the amounts of air adsorbed by the coal and the pyrite separately. Drakeley concluded that pyrite had a small effect on the spontaneous combustion of coal, but that it was not entirely negligible and could not be disregarded. Haldane and Meachem (*43*) describe in detail various measurements of temperatures and results of analyses of gas samples taken in Hamstead Colliery (South Staffordshire, United Kingdom). Based on these results and on various calculations, these authors concluded that oxidation of pyrite contributed to the liberation of heat in the mine. The actual ratios of oxygen to carbon dioxide in the mine atmosphere, and as calculated from the following reactions,

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4, \qquad (F)$$

and $$8H_2SO_4 + 8CaCO_3 \rightarrow 8CO_2 + 8CaSO_4 + 8H_2O, \qquad (G)$$

were used as a basis for their conclusions.

MacPherson, Simpkin, and Wild (*44*) measured the oxidation rates of various pyrite samples from the Ravine Seam (Lancashire Coalfield, United Kingdom) by exposing them to moist air in open dishes at ambient temperature. They found a relationship between the samples that oxidized at the highest rate and the amounts of encrustations (oxidation products) at the locations in the mine from which the samples were obtained in situ. They analyzed the encrustations, which varied in color (white, yellow, pink, and green), and found them to be chiefly iron sulfates in varying states of oxidation and hydration. They recognized the importance of ferric ions, but did not understand the reason for it. They also pointed out that in the presence of carbonaceous matter, the ferric salts were reduced to ferrous salts. In a later publication (*45*), the same authors described the results of analyses of the various sections of the complete Ravine Seam, and related the amounts of pyrite and the oxidation of pyrite to the disintegration observed in the mine, in the gob areas, and the hazards of self-heating due to the disintegration of the coal.

Teichmann (*46*) reviewed some of the literature on the effect of pyrite on the spontaneous combustion of coal and agreed that results of previous experiments were so conflicting that no meaningful conclusions could be drawn. His own laboratory investigations with South African coals, with pyrite separated from these coals and with mixtures of the two, led him to the conclusion that the rate of oxidation of the mixtures was in most cases faster than the rate obtained by calculation from the constituent parts. Some other important observations of his were that (1) in coal lumps with visible particles of pyrite, the oxidation of the pyrite was greatest at its contact point with the coal, probably due to the availability of moisture and adsorbed oxygen at the coal surface; and (2) the pyritic coal was far more oxidized in the underground mine, possibly because of the lower rate of heat dissipation there.

Downs (*47*) presented a list of references on the oxidation of pyrite in coal, and also on its relation to spontaneous combustion. Then, Burke and Downs (*48*) conducted laboratory studies in order to understand the mechanism of pyrite oxidation under the conditions of its occurrence in bituminous coal mines. In their experiments they used highly reactive "sulfur balls" obtained from the coal strata. They were concerned with the detrimental effects of pyrite oxidation on coal mining, including spontaneous combustion in the mine and in storage, roof falls, and floor heave due to the breakage and shattering of the coal structure by the oxidation products of pyrite, and acid mine drainage. This breakage of the coal and the resultant availability of larger coal surfaces for oxidation is thought by some investigators (*49*) to be pyrite's only contribution to the spontaneous combustion process of coal. These investigators consider coal breakage to be a more important factor in roof falls and floor upheavals.

The fact that pyrite in coal is much more susceptible to oxidation than pyrite from other sources has been recognized by many of the researchers in the field. For example, Shyu, Vishnava, and Montano (*50*) used Mössbauer spectroscopy to assess the behavior of mineral pyrite and pyrite in coal in an oxygen atmosphere at various temperatures. They found that only about 7 pct of the mineral pyrite samples oxidized when heated up from ambient temperature to 400° C, as compared to 100 pct of the pyrite in coal. Esposito, Chander, and Aplan (*51*) studied seven pyrite samples from coal sources and one pyrite sample from an ore source and found that the apparent specific gravities of the pyrites from bituminous coal sources were substantially lower than the corresponding values of the ore pyrite and the pyrite from an anthracite coal. The samples with the lower specific gravity values were more porous and sponge-like. Wiese, Powell, and Fyfe (*52*) also observed samples of pyrite-bearing and marcasite-bearing coal and noted that the porous, spongy-textured sulfides were more prone to atmospheric oxidation than the well crystallized pyrite. The lower density of the pyrite crystals in the coal could be due to incorporation of carbonaceous material during the formation of the pyrite.

In another study in which the relative reactivities of pyrite from coal and mineral sources were analyzed, Lai, Diehl, Hammack, and Khan (*53*), utilized cyclic voltammetry, X-ray photoelectron spectroscopy, and flotation response. They reported differences in the behavior of the pyrites from the different sources, which they attributed to the semiconductive nature of the pyrite. The coal pyrite behaved as a n-type semiconductor, whereas the mineral pyrite behaved as a p-type semiconductor. In similar flotation-response tests for comparing ore-pyrite and coal-pyrite, Chernosky and Lyon (*54*) also found that the pyrite samples from the different sources were chemically and physically different. The pyrite from the coal contained carbonaceous matter and was more porous and less dense. Occasional fossil imprints also were noted in some of the grains. As a result, the response to flotation varied. The semiconductive type of the specimens was not considered in this work. When Biegler and Swift (*55*) evaluated the behavior of pyrite samples with conventional electrochemical techniques, they concluded that the type of semiconductivity of the mineral pyrite specimens that they tested did not affect the kinetics of anode processes.

In addition to the presence of carbonaceous material in the pyrite from coal, the presence of clay and other aluminosilicate compounds in the coal also has a bearing on the oxidation of coal pyrite. Wiese, Powell, and Fyfe (*52*) found that samples of pyrite from Ohio and Utah coals were more susceptible to oxidation when clay was present in association with the coal and sulfide. According to them, the clay plays a part in the formation of hydrated sulfates. The clays are hygroscopic and retain water for extended periods of time. Kaolinite, a clay, can take part in the following reaction,

$$Al_2Si_2O_5(OH)_4 + 2FeS_2 + 19H_2O + 7O_2 + 2H^+ \rightarrow FeAl_2(SO_4)_4 \cdot 22H_2O + 2SiO_2 + Fe^{2+}, \qquad (H)$$

forming halotrichite. The hydrated sulfate salts, such as halotrichite, which contain large amounts of water of hydration, are much larger in volume than the original, unoxidized minerals. They exert great pressure on the associated neighboring strata and break them open. When the coal breaks apart, its exposed surface area increases and, as a result, both the oxidation rate and the resultant heat of oxidation increase. A few other highly hydrated sulfates that were identified near or at coalbeds containing pyrite were $MgAl_2(SO_4)_4 \cdot 22H_2O$ (pickeringite), $Fe^{2+} \cdot Fe_4^{3+}(SO_4)_6 \cdot (OH)_2 \cdot 20H_2O$ (copiapite), $MgSO_4 \cdot 7H_2O$ (epsomite), and $Na_2SO_4 \cdot 10H_2O$ (mirabilite) (*56*). These products also can exert high pressure and break apart the associated coal and render it more susceptible to oxidation.

The involvement of clay in the oxidation of pyrite in coal was also observed in Mössbauer spectroscopic studies conducted by Huggins, Huffman, and Lin (*57*), although they could not identify the exact interaction. Geidel and Caruccio (*58*) likewise noted the role of clay minerals in the overall oxidation process. Kerr and Kulp (*59*) characterized clay minerals by differential thermal analysis techniques and determined that grinding of the minerals introduced disorder in the lattice, and that water was adsorbed between the lattice layers if the extent of disorder was large. This water would promote pyrite oxidation. Watzlaf and Hammack (*60*) leached pyritic shale, which was hand picked from a sample of Pittsburgh coal, in large columns. Both fresh and weathered samples were leached. Comparison of leachates from fresh and weathered material showed similar release rates of sulfate, iron, and aluminum for each type of sample. Their results indicate that a relationship exists between the pyrite oxidation processes and the solubilization of aluminum, probably from clay in the shale.

In an effort to establish a risk index of coal to be used in estimating the spontaneous-combustion liability potential of a coal, for the purposes of mine design and planning, Singh and Demirbilek (*61*) tested 47 coals in an adiabatic oxidation test. They attempted to find a correlation between the sulfur and iron content of the sample and its rate of oxidation but found none. In their test, 100-g samples of vacuum dried coal (-75 mesh) were exposed to a flow of 200 cm^3/min of dry air for 8 h; initial temperature of the samples was 40° C. The rate of temperature increase was monitored, and the initial rate of temperature increase was used for comparison. Not surprisingly, Singh and Demirbilek did not find a relationship between the sulfur and iron content of the coals and their oxidation potential. Since pyrite does not oxidize at low temperatures in dry air to any perceptible extent, any pyrite in the sample would not undergo oxidation during such a test and thus would not influence the coal oxidation.

It is of interest that among 16 papers presented at a symposium on actual occurrences of spontaneous combustion in many British coal mines, only one paper (*62*) pointed out that the two seams being mined contained a fair amount of pyrite, and only one additional paper (*63*) indicated that the coals in question contained over 6 wt pct of sulfur. These latter seams contained high-rank coal of low-volatile content, and in general were not considered liable to spontaneous heating. Thus, the occurrence of spontaneous combustion in such mines underscores the influence of parameters such as the presence of relatively large amounts of pyrite, geologic conditions, and mining procedures, among others, on the overall process of spontaneous combustion. In these two cases (*62-63*), no attempt was made to identify the role of pyrite in the spontaneous combustion events.

Many self-heating events have occurred in the last few years in one U.S. coal mine where a high-rank bituminous coal is being mined. Relatively large amounts of finely disseminated pyrite were identified in samples from some of the zones beneath the floor, which was also subject to heaving. The self-heating events in this deep underground mine, in a section of the mine separated by a fault line, were attributed to the presence of this pyrite in the floor of the mine (*64*).

High-rank coals are not generally susceptible to self-heating or spontaneous ignition, and therefore, it is specifically in coal mines with high-rank coal that the contribution of pyrite to the spontaneous combustion of carbonaceous material can be discerned most easily. Mining procedures, geological conditions, and ventilation cannot be discounted as causes of spontaneous combustion, but certainly pyrite can contribute in at least two ways, namely, via self-heating and increasing the temperature of the surrounding strata, and by aiding in the disintegration of the coal.

All the studies cited here clearly indicate that pyrite can play an important role in the spontaneous combustion of coal in mines when present in concentrations higher than 3 to 5 pct. In addition to parameters such as particle size, surface area, oxygen availability, and temperature, the nature of pyrite in coal and its association with other minerals in the coal render it highly susceptible to oxidation and to spontaneous ignition, and in turn, increases the likelihood of coal to ignite spontaneously.

HEAVING AND ROOF FALLS—THE RESULTS OF INCREASED VOLUME OF PYRITE OXIDATION PRODUCTS

The ability of the oxidation products of pyrite to exert pressure has been cited previously in this text and elsewhere (*48-49*). Both roof falls and floor heaves can result from this pressure.

The occurrences of floor heave in construction due to the oxidation of pyrite in shale have been documented, (*65-66*). The Billings Formation in Canada, where floor heaves were found, is a black shale that contains pyrite in certain locations. The rocks in this formation are cut by two major faults and by numerous minor faults, which facilitate the entry of air needed for the oxidation of pyrite and for the *Thiobacillus* bacteria. Pyritic sulfur content in the unheaved areas, adjacent to the heaved area, was about 1.3 to 1.6 pct. The amount of pyrite in the heaved shale was small, but considerable amounts of oxidation products, including jarosite and gypsum, were found in it. The increase in molar volume from pyrite to jarosite is 115 pct and from calcite ($CaCO_3$) to hemihydrate ($CaSO_4 \cdot 1/2H_2O$), a precursor of gypsum, is 189 pct (*65*).

Hydration-pressure relations in heaving shale were analyzed by Power, Towle, and Plaza (*67*). According to them, pressures of considerable magnitude can result if the expanding materials are confined. Pressures on the order of 10,000 psi were quoted for crystals of gypsum growing in shale (*68*). Quigley, Zajic, McKyes, and Yong (*69*) have carefully studied the shale involved in heave occurrences in Ottawa, Canada. Special attention was given to the alteration products in the pyritic shale. In their opinion, the crystals of gypsum formed in the shale were responsible for the heaving, while the jarosite and natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] may have only a secondary effect on the generation of heave pressures.

Dougherty and Barsotti (*70*) analyzed the causes of heave in Ohio and Pennsylvania and came to a similar conclusion about the role of gypsum crystals in the heave process. They studied in detail the effects of parameters such as sulfide concentration and various environmental conditions. In a related study, Fasiska, Wagenblast, and Dougherty (*71*) identified additional sulfates, such as aluminum sulfates [$Al_2(SO_4)_3$ and $Al_2(SO_4)_3 \cdot 16H_2O$] and titanium sulfate [$Ti(SO_4)_2$], among crystals in the alteration products of black shale from six heaving sites. The shale was composed primarily of silts and clays containing some carbonaceous matter and the aluminum and titanium leached from the oxidized clays.

Finally, Hawkins and Pinches (*72*) investigated a ground floor heave of a hospital complex at Cardiff, United Kingdom. After detailed and careful inspections and surveys, and many laboratory analyses, they concluded that the gypsum crystals that formed in the calcareous mudstones of the Upper Triassic rocks on which the hospital was built were responsible for the heave. The hospital was built parallel to the trend of the Penorth Fault, on the outcrop of the Triassic Penorth Group. The mudstone contained pyrite that oxidized, and the resultant sulfuric acid interacted with the calcite to form the gypsum. The presence of fault zones near areas that undergo heave is a clear indication of the importance of air and/or water ingress to the oxidation of pyrite in various rock strata.

In coal mines, floor heave and roof falls are caused by various mechanisms not related specifically to pyrite oxidation. Stress relief as a cause of roof instability is discussed by Sames and Moebs (*73*) in some detail. Roof falls also are caused by the weathering of carbonaceous shale. The clay minerals in the shale adsorb moisture from the ventilation air, and then swell and disintegrate, or slake (*74-75*). Pyrite is not necessary to this process, but when it is present, it can be a primary cause, as described in some detail by Holland (*76*). Floor heave in coal mines also can be due to factors other than pyrite oxidation, especially in deep mines subject to high pressures (*77*). Pillar "punching" into the floor due to overburden pressure will cause floor heave (*78*). However, when the floor material in such a mine contains finely disseminated, reactive pyrite, the floor heave will provide entry of moist air and accelerate pyrite oxidation. Its oxidation products could then, in turn, contribute to the overall heave phenomenon. From these examples we see that pyrite, via its oxidation, can be an important factor in both floor heave and roof falls, but because there are other causes to these events, the influence of pyrite may be, and usually is, neglected or overlooked.

REACTIONS OF ANFO CHARGES WITH PYRITE AND ITS OXIDATION PRODUCTS

ANFO explosives are used in mining and in construction worldwide. They are either prepared on location and pumped directly into the boreholes or mixed in a plant and encased in plastic bags for shipment to work sites. Over the years many premature explosions or deflagrations of ANFO charges have occurred, especially at elevated ambient temperatures. Although the main problems have been encountered in metal sulfide mines, ANFO-induced fires and explosions have also happened in surface coal mines, and in other mines.

The behavior of ANFO explosives in "hot" ground was studied intensely because of the many problems encountered during development and production in the 500 Copper Ore Body at Mount Isa, Australia (*31-33*). An extensive system of cross faulting in the ore body allowed entry of meteoric waters and percolation of acidic waters from nearby surface oxidation zones. The geology of the ore body also created problems in ground support, ventilation, and blasting procedures. For example, the required high ventilation rates accelerated the oxidation of the sulfide minerals comprising the ore, and increased the concomitant heat generation of increased sulfide oxidation. Ground temperatures reached 100° C in some locations. ANFO charges in contact with moisture and sulfides at these temperatures underwent deterioration, degradation, direct reaction with the sulfides, combustion, and explosion. Thermal analysis methods were used to evaluate the reactivity of ANFO with the ore ingredients, as well as to assess potential inhibitors (*79*), including urea and a few phosphates and borates. The Sullivan Mine in British Columbia faced similar problems (*29*) when using ANFO charges. Following laboratory tests and evaluations of a variety of explosives, the mine company formulated its own brand of slurry explosives. But even with the newly formulated explosives, special procedures were required when temperatures in the boreholes exceeded 65° C, including the use of asbestos sleeves as sheaths for the explosive charges.

The effect of sulfuric acid on the reactivity of ANFO with pyrite-bearing ores was evaluated by Forshey, Ruhe, and Mason (*80*). Miron, Ruhe, and Watson (*81*) and Miron, Ruhe, and Hay (*82*) have shown that the main reaction between ANFO and pyrite ores is the following,

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

in which the nitrate reacts in an acidic medium with the ferrous ions formed in the pyrite oxidation-weathering process. Urea was found to be a very good inhibitor of the reaction because it complexes with hydrated ferrous salts and also decreases the acidity of the solution. Magnesium oxide was found to be a good inhibitor, but less effective than urea (*81, 82*).

Although the problems associated with the use of ANFO explosive charges are most prevalent in sulfide mines, similar problems are encountered in construction areas, when sulfide minerals, and specifically pyrite, are present in concentrations of at least a few weight percent (*83*). Likewise, surface coal mines containing pyrite might face the same problems when ANFO charges are used in various phases of the mining process (*84*). Detonations of ammonium nitrate charges also occurred in black pyritic shale (*85*), and in a limestone mine that contained pyrite (*86*). Without question, the presence of pyrite in surface coal mines, and in other mines, poses a serious problem for the users of ANFO explosives. If the presence of pyrite is known, appropriate and careful procedures for the use and handling of ANFO should be instituted to prevent fires and premature detonations.

IGNITION OF METHANE BY STRIKING PYRITE WITH COAL CUTTING BITS

Methane ignitions due to frictional heating during coal mining have been studied for many years. Frictional ignitions in U.S. coal mines almost always involve metal bits cutting into sandstone (*87*), and forming a luminous hot streak on the sandstone surface. The few exceptions are some frictional ignitions that appear to have been caused by a bit cutting into pyritic matter. The ability of pyrite, when present in the rock, to heat up and in turn ignite methane has been suggested by some researchers and refuted by others. Allsop and Wheeler (*88*) succeeded in igniting methane-air mixtures in a laboratory setting when they used worn picks in a coal cutter machine. When the picks rubbed against pyrite nodules in the rock, the gas mixture ignited easily. They deduced that the pyrite nodules reached temperatures of 200° to 300° C, at which time they easily oxidized to form some elemental sulfur. The sulfur burned and the sulfur flame ignited the methane mixture. Ignitions were not produced under the same test conditions when sharp picks were used (*89*). Other publications and reviews on the subject of ignition of flammable gases by friction (*90-92*) also report that ignitions were produced only with dull picks. To prevent ignitions, diluting the gas mixture with large amounts of carbon dioxide (25 pct of the whole) was required, which was not a practical solution. Unlike ignitions by rubbing of pyrite nodules or inclusions, much higher temperatures on the order of 1,450° C or more are required for ignitions by hot streaks (*93*). In addition to the temperature, other necessary parameters are the areas and the lifetimes of the hot streaks.

A recent publication by Ward, Cohen, Panich, Crouch, Schaller, and Dutta (*94*) describes a test method for determining the potential of different rocks to ignite methane atmospheres, which is based on rock-on-rock friction behavior in a rotating-wheel test rig. Statistical analysis of their results has shown that high frictional ignition potential is associated with large amounts of quartz and, to a lesser extent, with feldspar grains in the rocks tested, whereas carbonates, mica, and clay minerals lower the ignition potential. Unfortunately, the presence of pyrite in the sandstone, or in the coal and its effect on the ignition potential was not looked for or evaluated in the statistical analysis. When pyrite is present in a gassy coal mine, the potential for methane ignitions exists and additional precautionary measures should be taken to guard against such events. Worn bits should not be used, and water sprays should be used at all times.

SUMMARY

This review paper describes in some detail the problems that can be associated with the mining of pyrite-bearing coal. These problems include spontaneous combustion, roof falls, and floor upheaval. Other problems include the reactions of ANFO explosive charges with pyrite oxidation products in surface coal mines and the ignition of a flammable methane atmosphere by sulfur flames produced by coal cutting bits striking pyrite.

Pyrite oxidation products, which include various iron sulfates and oxides, as well as sulfuric acid and the heat generated in the oxidation process are the main causes in almost all of these problems. Since the prevention of pyrite oxidation is not accomplished easily, especially under mining conditions, it is of paramount importance to ascertain the presence or absence of pyrite in coal seams slated for extraction and to plan for encountering pyrite and the probable consequences of its presence.

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