

Possible role of hydrogen sulphide gas in self-heating of pyrrhotite-rich materials

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ABSTRACT

Self-heating of sulphides poses safety, environmental and economic concerns to the mining and metallurgical industries, especially when sulphide ores or concentrates have to be stored or transported. The first target of this investigation is the self-heating of pyrrhotite (Po), the most commonly suspected mineral to trigger the phenomenon because of its fast oxidation in moist air. Following a standard experimental protocol, self-heating was assessed on samples of Po mixed with sand as an inert material. With increasing Po content, self-heating rates progressively increased but the samples visually appeared less and less oxidized. A high Po content, it was hypothesized, may give a more reducing environment favouring formation of hydrogen sulphide (H₂S). The presence of this gas could be significant for self-heating for several reasons which are discussed. The hypothesis was tested by including copper pieces to detect the gas by forming copper sulphide, and adding copper sulphate in excess which suppressed self-heating, apparently by reacting with and removing the gas.

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1. Introduction

Self-heating of sulphide minerals is the result of oxidation reactions. The material self-heats when, without any external heat input, the rate of heat release by exothermic reactions exceeds that of heat loss. Self-heating of sulphides may give rise to dramatic consequences. An historical example is the sinking of the N.Y.K. liner S/S Boyko Maru in 1939, while transporting copper concentrate (Hikami, Katuyuki, 1942 cited by Kirshenbaum (1968)). Oxygen depletion and fires in mines have been reported at various times (Tally et al., 1917; Harrington et al., 1923; Rachilly and Butte, 1923; Lukaszewski, 1969; Farnsworth, 1977; Good, 1977). Based on 53 years of observation (from 1869 to 1923), Harrington et al. (1923) reported an average loss of 10 lives per year due to “metal-mine fires”. Self-heating of sulphides when transporting iron-copper ore was reported as early as 1871 (Stevens (1871) as quoted by Kirshenbaum (1968)). Good (1977) described streams of molten metal from draw holes and sulphide dust explosions in the Sullivan mine (British Columbia). A photograph of the incandescent sulphide ore was the cover page of the CIM Bulletin vol. 70/782, year 1977. Self-heating and smouldering of sulphides poses problems of air quality in and around mines (Brown and Miller, 1977) and contributes to acid mine drainage.

The reactions initiating self-heating at low temperature are not known (Good, 1977; Rosenblum et al., 1982; Rosenblum and Spira,

1995). Oxidation of sulphides by oxygen (air) (Lukaszewski, 1969; Good, 1977; Ninteman, 1978; Rosenblum and Spira, 1995), by dissolved Fe^{III} (Lukaszewski, 1969) or by nitrates (Lukaszewski, 1969) has been considered. Good (1977) enumerated 12 exothermic reactions, based on on-site observation of reaction products where self-heating occurred. These products included ferrous and ferric sulphates and hydroxysulphates, ferric oxides and hydroxides, sulphuric and sulphurous (SO₂ dissolved in water) acids and elemental sulphur. Incipient heat was attributed to reactions giving rise to elemental sulphur (Good, 1977; Rosenblum and Spira, 1993, 1995; Rosenblum et al., 2001).

Elemental sulphur is considered to result from reactions between ferric oxide and sulphuric acid or from the reaction between pyrrhotite (FeS) and ferric sulphate. Hydrolysis of iron species, formation of water soluble iron sulphate (Good, 1977; Steger, 1982) and heat of hydration were suggested (Rosenblum and Spira, 1995) as responsible for temperature increases up to 100 °C. Rosenblum and Spira (1993) monitored temperature increase from room temperature in self-heating tests. They showed that the weight gain measured at the end of experiments conducted at 40 °C, 50 °C and 70 °C was proportional to the S⁰ content. Goethite and iron sulphates were also reported as reaction products. However, synthetic mixtures of elemental sulphur and sand or hematite did not heat (Rosenblum and Spira, 1993, 1995).

Self-heating risk assessment methods were reviewed by Rosenblum and Spira (1981). Based on experience using column tests (Rosenblum et al., 1982), a self-heating assessment method was developed and applied to various sulphide-bearing materials (Rosenblum and Spira, 1993, 1995; Rosenblum et al., 2001). The

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second generation technique was based on automated calorimetric cells. A standard test comprises measuring heat output during a sequence of air injections for about one week at two temperatures, typically 70 °C (stage A) and 140 °C (stage B). By comparing heat output in stages A and B, a sample could be ranked for self-heating risk. Most nickel sulphide concentrates were classified with a high potential of self-heating, a response presumably due to their pyrrhotite content, while the reactivity of copper, lead and zinc sulphide concentrates was site specific (Rosenblum et al., 2001). The technology is now available to McGill researchers and was used for the present study.

The standard self-heating test is more direct although more complex than an alternative procedure that has been proposed based on measuring weight gain over a few weeks (e.g., Steger, 1976; Rosenblum and Spira, 1993; Wu and Li, 2005). It is more sophisticated than the standard risk assessment procedure adopted by the United Nations (1995) which is commonly applied for transport of dangerous goods.

The present work aims to better understand how self-heating is initiated as a step towards mitigation and control. Pyrrhotite (Po) was chosen as test mineral because it is commonly regarded as the most reactive among the common sulphides. The tests followed the protocol of Rosenblum and Spira (1995), using mixtures prepared with varying proportions of pyrrhotite and coarse quartz sand (Test series I). A wider range of controlled Po content was achieved in this manner compared to previous test work (Rosenblum and Spira, 1995). With increasing Po content, self-heating rates progressively increased but the samples visually appeared less and less oxidized. A high Po content, it was hypothesized, may give a more reducing environment favouring formation of hydrogen sulphide (H₂S). The procedure was then modified to test for hydrogen sulphide gas (H₂S) release (Test series II). Finally, the role of H₂S on self-heating was indirectly tested: it is shown that by capturing H₂S as a stable sulphide before it reacts with oxygen, self-heating was suppressed (Test series III). To our knowledge, this is the first time that a role of H₂S has been considered with regard to self-heating of sulphides. It introduces a potentially important avenue of investigation into self-heating mechanisms.

2. Experimental methods

2.1. Sulphide samples

The material in Tests series I and II were samples from the pyrrhotite tail (PoT) stream of the Falconbridge (now Xstrata Nickel) Strathcona mill (Sudbury, Canada). This stream runs ca. 70% Po with particle size 80% – 48 µm (Wells et al., 1997). There is a magnetic separation step and the Po in the samples is predominantly monoclinic. While questions of oxidation and contamination with flotation reagents can be raised the overwhelming advantage is the material is available in large quantities, an important consideration as several hundred grams at a time are used for a standard self-heating test.

The samples were collected by plant personnel and held under a water cover in a plastic container while transported to Montréal. Upon receiving, they were re-pulped and sub-sampled under wet conditions into 100 g and 500 g fractions. The sub-samples were pressure filtered with air (few minutes) and immediately frozen in double-plastic bags. The sub-samples were kept in a freezer below –45 °C under a vacuum better than 5 µm Hg until freeze-dried. No attempt was made to remove air from the voids after freeze-drying.

Materials used in Test series III and for estimation of reproducibility were a nickel concentrate (Ni-Con) from the Strathcona mill and a pyrrhotite magnetic concentrate from the Inco (now Vale-Inco) Clarabelle mill (Sudbury, Canada).

2.2. Test series I: pyrrhotite/sand mixtures

2.2.1. Sample preparation for standard self-heating test

The sulphide concentrates were mixed with coarse sand in various weight proportions (6–50 wt.%). The sand (90.9% >650 µm, Opta Mineral) was oven dried before use. The sand helped ensure a homogeneous gas flow and was considered a chemically inert matrix. Although quartz was the major mineral (>99.5 wt.% SiO₂), the sand did contain trace feldspars and carbonates. Samples (500 g of dry powder) were homogeneously moisturised immediately preceding a test by mixing in a sealed plastic bag with 30 g of distilled, deionised water to give the standard 6 wt.% moisture.

2.2.2. The self-heating apparatus (Fig. 1a)

The device consists of a specially designed glassware sample container surrounded by a heater, and covered by an insulating cylinder (the “cell”) as described in Rosenblum and Spira (1995). Five cells were used. The sample (530 g solids including water) was held in the middle of the glassware by a stainless steel screen. Diffusion of air was aided by a piece of porous plastic for the Test series I (Fig. 1a) and by a layer of coarse sand for the Test series II (Fig. 1b). Dry air preheated to the test temperature was injected at the bottom of the cell. Fluids (liquid in the pool at the bottom of the cell, gas/vapour evaporated from the heated sample) were flushed out as condensates into two collection vessels, at two times in the self-heating test. Excess gases/vapours were evacuated to a fume hood.

2.2.3. Standard self-heating test

The tests were performed following the protocol of Rosenblum and Spira (1995). A standard test consists of two stages, A and B, where the temperature and air flow rate are maintained at 70 °C and at 100 mL/min during stage A, and at 140 °C and at 250 mL/min during stage B. Stages A and B are a succession of periodic air injections (10 for each stage evenly spaced over a period of 62 h 30 min) commencing after a fixed period of 6 h 46 min where the temperature is brought to the base level. The duration of a full self-heating test is ca. 6 days. The air injection is over a 15 min period. The two stages are separated by a 9-h interval during which nitrogen is flushed through at 250 mL/min while the temperature is increased from 70 °C to 140 °C. After stage A a 30-s vacuum is applied to drive out the condensate collected in the bottom reservoir into a trap (the sample’s free water). Water evaporated while the sample is brought to 140 °C is flushed out by nitrogen into another flask. Some vapour is lost to the exhaust gas/vapour evacuation system. Any temperature response during stages A and B is automatically recorded.

The evolution of temperature as a function of time gives a thermogram (Fig. 2) with a base level of ca. 70 °C for stage A and ca. 140 °C for stage B. If the material is reactive, an abrupt exothermic peak is observed as soon as air is injected into the cell. Thermograms are interpreted in terms of heating rates through an in-house program. The calculation is based on a moving average.

2.2.4. Precision of self-heating test

One homogenized sample of nickel concentrate was subdivided into five fractions ($n = 5$) and tested the same way using five different cells of the self-heating facility to determine precision (Wong, 2005). The relative error, expressed as the standard deviation over the mean stage heating rate, is of order 15% and 18% for stages A and B, respectively.

2.3. Test series II: H₂S release

To test the hypothesis that H₂S was released during self-heating in stage A, a series of trials employed copper, both as metal and

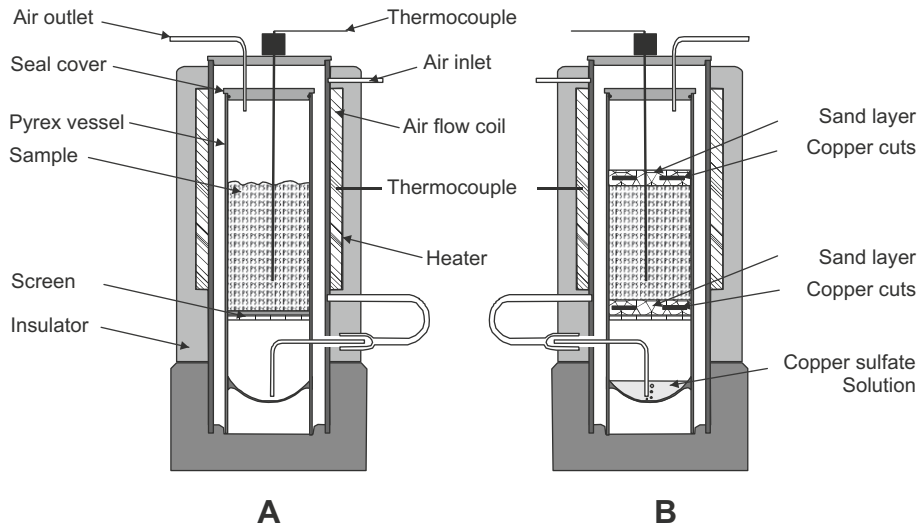


Fig. 1. Self-heating apparatus (a) for standard tests as developed by Rosenblum and Spira (1995) and (b) as used to test the release of hydrogen sulphide (redrawn from Rosenblum and Spira (1995)).

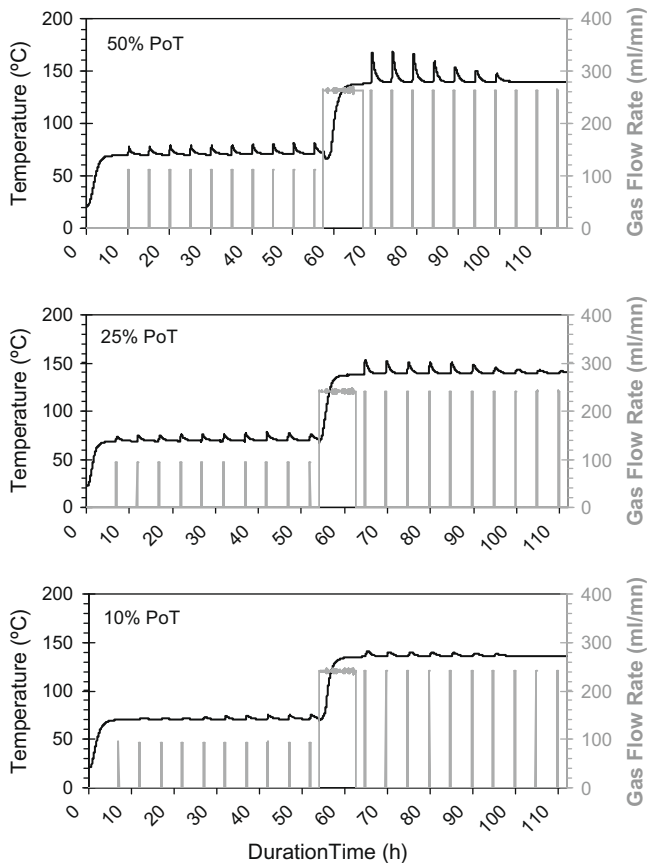


Fig. 2. Thermogram traces for samples: (a) 50% PoT in cell 1, (b) 25% PoT in cell 2, (c) 10% PoT in cell 4. Air injections are also reported (grey bars) with a 5 h interval in stage A (70 °C) and stage B (140 °C). Between stages A and B, nitrogen is blown for 9 h 32 min in 50% PoT, for 8 h 27 min in 25% PoT and for 9 h 01 min in 10% PoT.

sulphate solution, to detect H_2S by forming copper sulphides. Both tarnishing of copper pieces (Tran et al., 2005) and formation of black precipitates of copper sulphide in the solution would be good indicators of the release of H_2S gas.

The stage A (70 °C) standard test on a 50% PoT sample was modified to include the copper pieces and copper sulphate solution. The

copper sulphate solution was placed in the bottom pool of the self-heating cell (Fig. 1b) and the elemental copper pieces were laid below and on top of the samples, protected from direct contact by embedding in the coarse sand layer (Fig. 1b). The copper sulphate solution (0.1 M) was prepared from 99+ pure copper(II) sulphate pentahydrate powder ($CuSO_4 \cdot 5H_2O$ from Fisher Scientific) and deionised water. The presence of the solution was shown not to alter the self-heating response (Wong, 2005). The copper pieces (ca. 1 cm^2) were cut from commercial copper sheet (oxygen-free electronic grade, 99.99% pure from McMaster-Carr). The surface was roughened to promote contact with reactants and then cleaned with acetone to remove grease.

2.4. Test series III: suppressing self-heating by addition of copper sulphate

The aim of this series was to provide a side-reaction and remove H_2S by sulphidation of copper ions. Copper(II) sulphate powder ($CuSO_4 \cdot 5H_2O$ 99+ grade from Fisher Scientific) was added to two pyrrhotite-rich materials with high self-heating rates: the nickel concentrate (Ni-Con) and a 50% PoT sample (as in Test series I). A standard self-heating test was run on mixtures of 250 g moist sample, 125 g sand and 125 g copper sulphate. Two successive stage A tests were run on the Ni-Con sample before stage B. Self-heating response was compared to a 250 g moist sample with 250 g sand.

3. Results

3.1. Test series I: pyrrhotite/sand mixtures

In terms of risk assessment as described by Rosenblum and Spira (1995) and Rosenblum et al. (2001), all samples were in the high risk zone 5 ("Mitigation methods are required").

The thermograms (Fig. 2) illustrate a fast, exothermic response as soon as air is injected, except for the initial air injections on the 10% (and less, not shown) PoT samples. For these Po-poor samples, it seems there is an induction period. A slight (up to 4 °C) and progressive increase in heating rates and of the base temperature were noted in stage A for the 25% PoT samples and above.

Table 1
Self-heating rates ($^{\circ}\text{C}/\text{h}$) given by the standard self-heating method for each air injection for pyrrhotite tail samples (PoT) diluted with coarse sand.

	Number of air injection	04-S-15 50% PoT	04-S-16 25% PoT	04-S-18 10% PoT	04-S-18 8% PoT	04-S-18 6% PoT
Stage A	1	38 \pm 6	15 \pm 2	0	0	0
	2	42 \pm 6	26 \pm 4	2 \pm 1	2 \pm 1	1 \pm 1
	3	44 \pm 7	30 \pm 4	3 \pm 1	2 \pm 1	2 \pm 1
	4	44 \pm 7	31 \pm 5	4 \pm 1	4 \pm 1	3 \pm 1
	5	46 \pm 7	31 \pm 5	8 \pm 1	9 \pm 1	3 \pm 1
	6	47 \pm 7	33 \pm 5	15 \pm 2	16 \pm 2	5 \pm 1
	7	49 \pm 7	37 \pm 6	21 \pm 3	20 \pm 3	10 \pm 2
	8	51 \pm 8	42 \pm 6	24 \pm 4	20 \pm 3	10 \pm 2
	9	53 \pm 8	34 \pm 5	25 \pm 4	16 \pm 2	7 \pm 1
	10	57 \pm 9	20 \pm 3	25 \pm 4	10 \pm 1	5 \pm 1
Average		47 \pm 7	30 \pm 4	13 \pm 2	10 \pm 1	5 \pm 1
Stage B	1	138 \pm 25	61 \pm 11	24 \pm 4	18 \pm 3	12 \pm 2
	2	137 \pm 25	50 \pm 9	16 \pm 3	11 \pm 2	7 \pm 1
	3	118 \pm 21	46 \pm 8	13 \pm 2	9 \pm 2	5 \pm 1
	4	84 \pm 15	43 \pm 8	12 \pm 2	8 \pm 1	5 \pm 1
	5	56 \pm 10	46 \pm 8	11 \pm 2	7 \pm 1	4 \pm 1
	6	39 \pm 7	39 \pm 7	10 \pm 2	7 \pm 1	4 \pm 1
	7	28 \pm 5	22 \pm 4	9 \pm 2	6 \pm 1	3 \pm 1
	8	1 \pm 1	14 \pm 3	2 \pm 1	5 \pm 1	4 \pm 1
	9	0	10 \pm 2	0	6 \pm 1	6 \pm 1
	10	0	7 \pm 1	0	6 \pm 1	0
Average		60 \pm 10	34 \pm 6	10 \pm 2	8 \pm 1	5 \pm 1

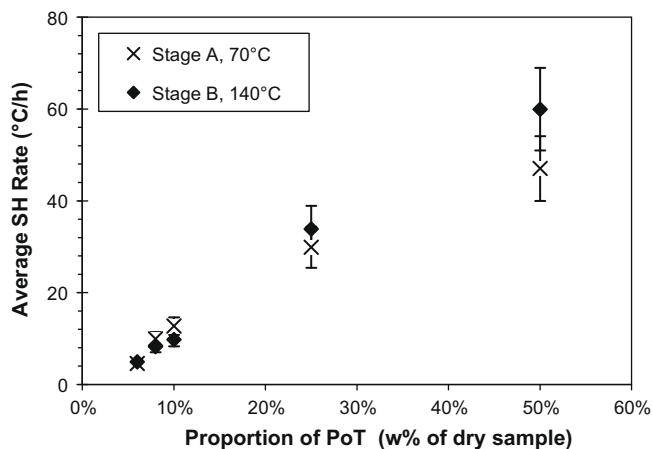


Fig. 3. Average self-heating (SH) rates for stages A and B (standard self-heating tests) versus the weight proportion of pyrrhotite sample (% PoT) mixed with silica sand.

The five mixtures (6%, 8%, 10%, 25% and 50% PoT) showed that as the proportion of sulphide increased the higher was the resulting average heating rate for both stages (Table 1; Fig. 3). Visually, however, the samples with lower Po content appeared to have reacted more: the 50% PoT sample remained grey after the self-heating test, became olive green for the 25% PoT sample and then progressively reddened as the PoT content decreased to 5%. This indicates production of iron oxide/oxyhydroxides, which was confirmed by mineralogical examination. It was this observation that suggested a reaction pathway other than direct oxidation of the sulphide was responsible for high self-heating rates.

3.2. Test series II: qualitative evidence of the presence of H_2S

The copper pieces were darkened (Fig. 4a) and a black precipitate of sulphide formed on the surface of the copper sulphate solution (Fig. 4b) indicating that H_2S was released during self-heating. This has been reproduced several times (Wang, 2007). On the copper pieces, dark indigo-blue metallic lustre crystals were identified as covellite (CuS). An XRD analysis also revealed some digenite (Cu_9S_5) and chalcocite (Cu_2S).

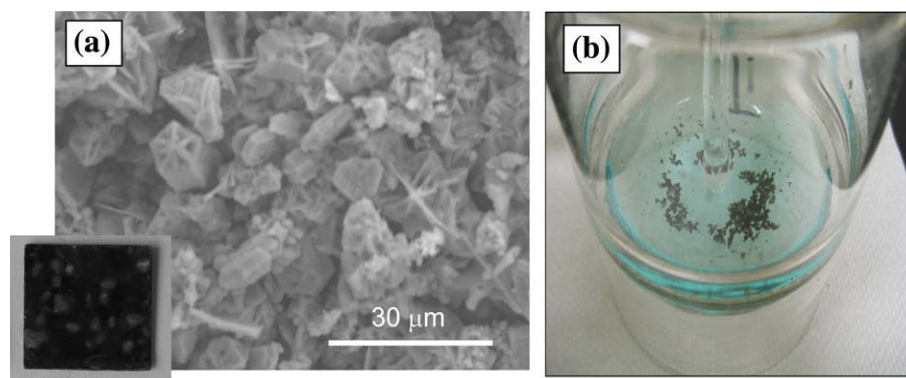


Fig. 4. Qualitative evidences of hydrogen sulphide release from 50% PoT sample during a stage A self-heating test: (a) 1 cm^2 copper pieces (bottom side) blackened by formation of copper sulphides and micrograph taken by SEM; (b) black amorphous copper sulphides formed on top of copper sulphate solution.

Table 2

Average self-heating rates (°C/h) obtained in stages A and B on nickel concentrates (Ni-Con) and on pyrrhotite tail (PoT) samples before and after treatment by copper sulphate powder.

	Stage A (70 °C)	Stage B (140 °C)
50% Ni-Con in sand	40 ± 6	18 ± 3
50% Ni-Con with 25% CuSO ₄ and 25% sand ^a	<1	3 ± 1
50% PoT in sand	31 ± 5	67 ± 12
50% PoT with 25% CuSO ₄ and 25% sand ^b	0	0

^a Two successive stages A were run, to try to 'force' a response. The first stage A response was null. The average is that for second stage A, which was followed by stage B.

^b Stage B was stopped after four air injections showing no heating.

3.3. Test series III: suppressing self-heating by addition of copper sulphate powder

Self-heating of both the Ni-Con and the 50% PoT samples was suppressed by the presence of copper sulphate powder (Table 2). It was verified by optical microscopy and by electron microprobe (WDS) analysis on polished sections of the sample that covellite had formed. Covellite was found as a coating at the surface of pyrrhotite (Drianov, 2007), and, in this work, as discrete crystals in the sample voids.

4. Discussion

The abrupt and fast response to air injection (Fig. 2) suggested exothermic reactions between air and a gas/vapour or a catalysed reaction (by mineral surfaces or by water), rather than liquid water-based reactions or direct gas (air)–solid reactions. Because the temperature returned quickly to the base level once air injection was stopped, and at about the same rate for all samples, this excluded a major contribution to self-heating from physical parameters (differences in heat conductivity) and of exothermic hydrogeochemical reactions such as the oxidation of sulphides by dissolved oxidants (dissolved oxygen or Fe^{III}) or hydration of reaction products (for example iron oxyhydroxides and sulphate compounds) for which reactions (and thus any heat evolution) would continue after air injection is stopped.

Samples which visually showed limited oxidation of iron released more heat than samples where the iron had oxidized further. For example, the 50% PoT sample heated 3.6 times faster than the 10% PoT sample in stage A. High concentrations of sulphides relative to oxygen availability provide a reducing environment. The two most concentrated elements in samples are iron and sulphur. Overall, results of the present study suggest a contribution to self-heating of reduced sulphur species oxidation rather than from ferrous iron species oxidation.

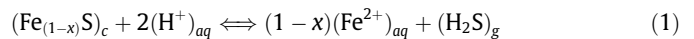
At this juncture the results led to the search for a potential gas that is readily and exothermically oxidized by air, which could be produced by sulphides and whose formation would be favoured under reducing conditions. These considerations suggested hydrogen sulphide. The gas is known to oxidize catalytically, even in dry air, at low temperature (Kovalenko et al., 1998, 2001), giving an exothermic reaction that may be fast (e.g., Wormald, 2003).

The presence of H₂S was qualitatively demonstrated by sulphidation of elemental copper and of copper sulphate solution; and illustrated by suppression of self-heating by addition of excess copper sulphate powder. An alternative reaction considered was copper reacting with the elemental sulphur (S⁰) known to form in standard self-heating tests. It is generally considered that elemental sulphur reacts with elemental copper only above the latter's melting point (Dutrizac and MacDonald, 1973; Blachnik and Mül-

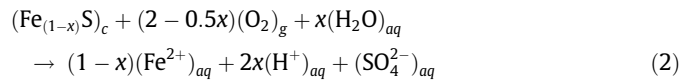
ler, 2000, 2001). A direct reaction of elemental sulphur with the copper sulphate solution (Cu²⁺·SO₄²⁻) is not possible. One way elemental sulphur may be distributed is via H₂S and its subsequent partial oxidation. Yellow sulphur deposits were sometimes seen on the instrument piping, for example. This introduces a sulphur mobilizing role of the gas adding to its potential importance in the self-heating process.

Release of H₂S by sulphides when acidified, especially pyrrhotite, has long been known. Berzelius (1819) reported that Stromeyer observed the release of H₂S and the formation of elemental sulphur after the dissolution of "magnetic pyrite" in dilute sulphuric acid. This led to the Kipp's apparatus widely used in the past to produce H₂S, in which pyrrhotite was preferred to other sulphides due to its fast reaction.

The reaction is generally represented by (Lowson, 1982):



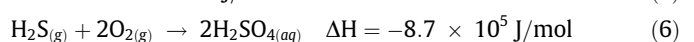
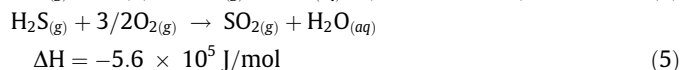
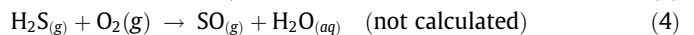
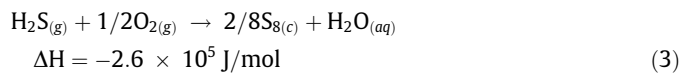
In the present context, the acidity is readily produced by pyrrhotite in the presence of moisture and air (Buckley and Woods, 1985), according to:



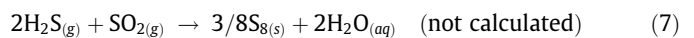
The H₂S hypothesis, therefore, also accounts for the fact that moisture is known to be an essential component in the self-heating process (Rosenblum and Spira, 1995).

Behind these simple representations, the mechanisms at the surface of pyrrhotite actually involve complex multiple steps (Thomas et al., 1998, 2000, 2001; Mikhlin et al., 2000, 2001, 2002; Mikhlin and Tomashevich, 2005; Skinner et al., 2004; Cruz et al., 2005; Chiriță and Descostes, 2006a,b).

Once released, H₂S may be oxidized partially or totally by oxygen depending upon the oxygen/H₂S ratio, among other physico-chemical parameters (e.g., temperature, water content, pressure, pH), according to, for example:



A further reaction which could contribute to high self-heating rates once SO₂ has formed could be (Pfeiffer, 1978),



as applied in the low temperature (i.e., between 200 °C and 310 °C), catalytic stage of the Claus process.

Enthalpies are calculated at 70 °C, 1 atmosphere for each reaction using FactSage. Calculations are based on Janaf Thermochemical Tables (Stull and Prophet, 1971; Chase, 1998). All the reactions are exothermic and thermodynamically possible. However, enthalpies of reactions do not explain directly the higher heat release under restricted oxygen/sulphide ratios as the higher the O₂/H₂S the higher the enthalpy of reaction. Thermodynamics helps in determining probable reactions, but in such a complex system (i.e., several probable concomitant reactions), self-heating rates will be dominated by the fastest reaction and probably limited by the release rate of H₂S from the mineral (i.e., self-heating rates are governed by kinetics as opposed to thermodynamics).

In kinetics, the first step is to define precisely the set of reactions. The above reactions were selected to the best of our current observations (i.e., characterization of reaction products in this set

of experiments). Release rates of H₂S by pyrrhotite under various conditions (temperature, moisture, mineral mixtures) remain unknown.

A control on self-heating may be exerted by fast competing side-reactions: this is the explanation offered for what is happening when copper ions (Cu²⁺) are introduced and suppress self-heating. This side-reaction may occur without specific addition of reactant (e.g., copper sulphate) if concentrates contain soluble copper (or lead, arsenic, mercury, silver: i.e., chalcophile metals able to form sulphides under low temperature conditions).

The understanding prompted by this work suggests self-heating could be mitigated by limiting rates of reactions of two kinds: that leading to H₂S release from the surface of sulphide minerals and that of H₂S oxidation by oxygen. While not practical at the quantities employed, the suppression by addition of copper sulphate is an example of control of the second kind. Future work will exploit the findings to design mitigation tests, as well as continuing to probe the reaction mechanisms from a physico-chemical standpoint.

5. Conclusion

Standard self-heating tests on pyrrhotite (Po)–sand mixtures showed increasing self-heating as Po content increased but less and less visual evidence of oxidation. It was hypothesized that high Po content produced conditions favouring hydrogen sulphide (H₂S) formation and that it was oxidation of H₂S which contributes to self-heating. A gas phase reaction is suggested by the abrupt and rapid response to air injection. Formation of H₂S also offers an explanation of the importance of moisture in self-heating. The hypothesis was supported by observing sulphidization of copper, and by adding sufficient copper (as copper sulphate) which suppressed self-heating by providing a competing reaction (formation of copper sulphide). The findings introduce a potentially important avenue into the investigation of self-heating mechanisms and open possible routes for mitigation.

Acknowledgments

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