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Complexities in Heat Generation and Self-Heating of Mined Materials - a Review

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Acknowledgements

Many thanks go to Ms. Ann Lamontagne, Ph.D., of Lamont for bringing this issue to my attention, and showing me the urgency for better understanding of self-heating of mined materials.

Abstract

One issue that can arise at some mining operations is the self-heating of mined ore, waste rock, processing concentrates, and process tailings. In some cases, these geological materials can "catch fire" and "burn". Such events at an operating minesite can carry major risks to health, safety, the environment, and economics. Such expectations at a proposed minesite can lead to local opposition to the mining and to onerous operating conditions.

This review compiles, summarizes, and synthesizes worldwide information on self-heating of mined geologic materials that contain, as a minimum, sulphide minerals. The most common sulphide minerals include pyrrhotite ($Fe_{1-x}S$, x = 0 to 0.2) and pyrite (FeS_2).

The primary objective here is to clarify how a proposed or operating sulphidic minesite can predict or assess self-heating under full-scale site-specific conditions. As a result, any required site-specific control and remediation for heat generation can then be determined.

The first problem with understanding self-heating is in terminology. Many related terms like combustion and ignition have circular references. So this review explains the difference between self-heating and autoignition, where autoignition represents the typical expressions of "burning" and "catch fire". The autoignition temperatures of many sulphide minerals are above 300ºC, which is a temperature rarely reached by self-heating by sulphide oxidation.

In any case, self-heating (or lack thereof) under full-scale on-site conditions is dependent on a complex interplay of many physical and chemical factors. Some factors can add to the heating, and some can cool the mined materials. No single factor or test can determine this.

Nevertheless, self-heating tests have been designed and used, with the best-known one for sulphidic mined materials being Rosenblum et al. (2001). This test forces samples to 70ºC and then 140º C for days, and does not let the samples cool. Air is occasionally pumped into the sample to see if there is a significant spike in temperature, which indicates self-heating under these forced conditions.

Rosenblum et al. (2001) emphasized that this test procedure substantially accelerates self-heating relative to observed and measured self-heating under full-scale on-site conditions. In fact, Rosenblum et al. say, "most [sulphidic] concentrates show little or no propensity to self-heat". Where significant self-heating was detected, this was attributed to the formation of elemental

sulphur and not other potential causes like H_2S or SO_2 gas.

Another author emphasized, “It is worth reminding that the purpose of a standard [self-heating] test is only to assess the risk of self-heating occurring. Whether this will actually occur in the field is dependant [sic] on a large number of environmental and physical factors . . . ”

A review of compiled case studies of major self-heating at full-scale minesites, back to 1862, reveals that most cases of fire and combustion were caused by wood, timber, and coal being exposed to heat. In some cases, but not all, the cause of the heat that autoignited the organic carbon could be traced to sulphide-mineral oxidation. Other sources of heat included drilling and pouring of cement. There were no definitive full-scale examples of autoignition of sulphide minerals, but “red hot” sulphide minerals were occasionally reported.

No currently available models include all the important physical and chemical factors that need to be considered to predict whether self-heating will reach high temperatures under full-scale on-site conditions. Some simplified equations and a few more complex models are discussed.

1. INTRODUCTION

One issue that can arise at some mining operations is the self-heating of mined ore, waste rock, processing concentrates, and process tailings. In some cases, these geological materials can "catch fire" and "burn". Such events at an operating minesite can carry major risks to health, safety, the environment, and economics. Such expectations at a proposed minesite can lead to local opposition to the mining and to onerous operating conditions.

This review compiles, summarizes, and synthesizes worldwide information on self-heating of mined geologic materials that contain, as a minimum, sulphide minerals. The most common sulphide minerals include pyrrhotite ($Fe_{1-x}S$, $x = 0$ to 0.2) and pyrite (FeS_2).

The primary objective here is to clarify how a proposed or operating sulphidic minesite can predict or assess self-heating under site-specific conditions. As a result, any required site-specific control and remediation for heat generation can then be determined.

2. THE PROBLEM WITH TERMINOLOGY

A difficult task in this review is to clarify and reconcile terminology (see Appendix A). For example, here are some common definitions, and note the circular references:

- "combustion" is "the process of burning something"
- "to burn" is "to undergo combustion"
- "ignition" is "the action of setting something on fire or starting to burn"
- "fire" is "combustion or burning".

So what does it mean, in a precise and scientific manner, to say mined materials can burn or catch fire?

This review will look closely at that question, and the answer is not simple or generic. Many site-specific factors, some with positive and negative feedback loops, play a role in the answer.

Additionally, common methodologies for characterizing self-heating can force a geological sample to high temperatures that it might not otherwise attain. Then, sometimes, the temperature is forced even higher. The fact that materials burn under these "forced" conditions does not necessarily mean this would happen under ambient conditions. Self-heating under full-scale, realistic conditions is a complex interplay of many factors.

3. THEORY

In this review on heat generation, it is important to distinguish between (1) the heat supplied by an external source and (2) the heat generated internally by the geologic material ("self-heating"). This requires the clarification and usage of some terminology in Appendix A.

An obvious example of the first is placing a lit match into an open, aerated canister of gasoline (a "fuel"). It would likely "ignite", "combust", and "burn", quickly generating abundant heat.

However, it would not ignite spontaneously, without the match, below a temperature around 250-280ºC. This is gasoline's "autoignition temperature" under typical pressures and conditions. It is important to note that Wikipedia (2019) warns, "[Autoignition] Temperatures vary widely in the literature and should only be used as estimates."

Gasoline could be warmed carefully by a heat source completely below a temperature below 250ºC and it would not autoignite. In this case, it could well volatilize completely into the air before reaching its autoignition temperature. This is an example of "site-specific" conditions preventing ignition, that is, no gasoline remains in the container to autoignite.

In the second case, geological materials, like rock and tailings, are typically composed of combinations of minerals. In this case, certain minerals can act like the "match" for self-heating. Certain other minerals may then act like "fuel" when their mineral-specific autoignition temperatures are exceeded by the self-heated "match". In some cases, the match and the fuel can be the same or similar mineral, which is particularly relevant to processed concentrates composed of one or a few minerals.

The best known and best documented self-heating minerals are sulphide minerals, particularly the common iron-bearing ones of pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2). Heat generation is part of the classic equation for sulphide-mineral oxidation (Price, 2009) that also leads to acid rock drainage (ARD) and metal leaching (ML):

$$\textit{Certain sulphide minerals + oxygen + liquid/gaseous } H_2O \rightarrow \textit{heat + acidity + metals + sulphate} \qquad \textit{(Eq. 1)}$$

Notice in Equation 1 that all sulphide is assumed to oxidize to sulphate, which cannot oxidize any farther under surficial conditions. If some sulphur is not oxidized fully to sulphate, or if other forms of sulphur are present, then additional sulphur oxidation and heat generation can occur later. This point is critical to predictions and estimates of autoignition of reaction products like elemental sulphur, as discussed below in Section 4.

Based on Equation 1, exposing certain sulphide minerals to oxygen and moisture, such as by mining and processing, begins the self-heating of the geologic material. Because sulphide minerals generally have autoignition temperatures above 300ºC, as discussed below, rarely does Equation 1 lead to autoignition of the sulphide minerals (Figure 1).

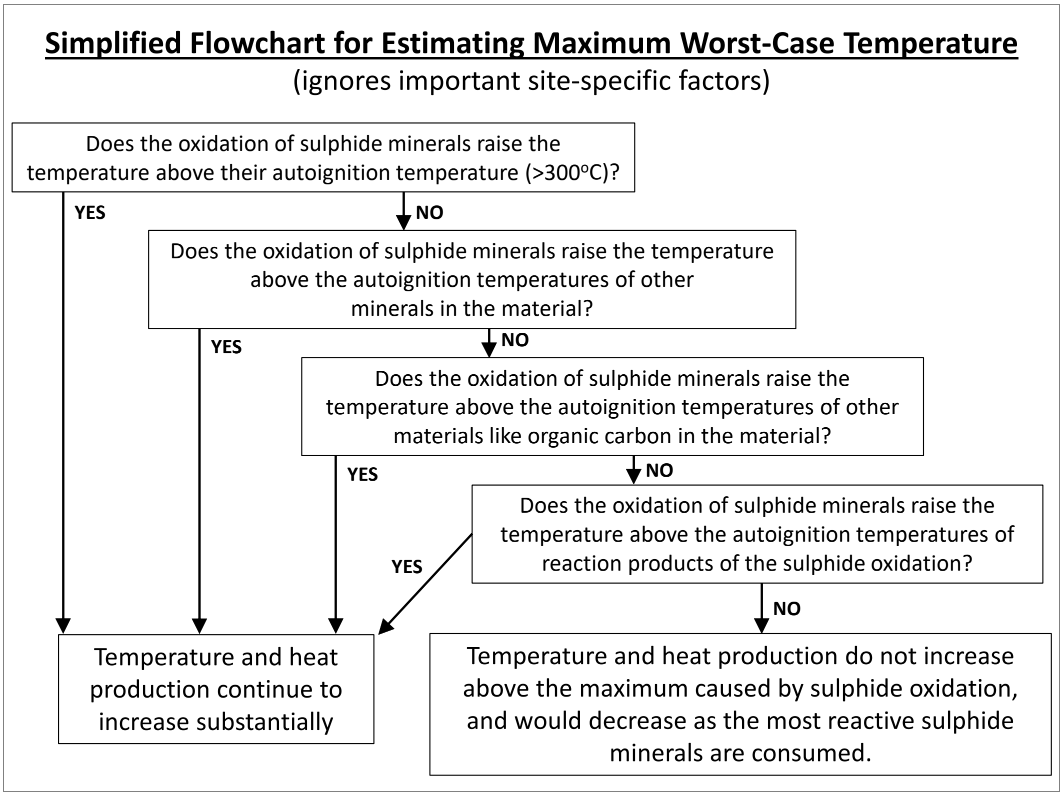

Figure 1. Simplified flowchart for estimating maximum worst-case temperature from sulphide-mineral oxidation (see also Figure 2).

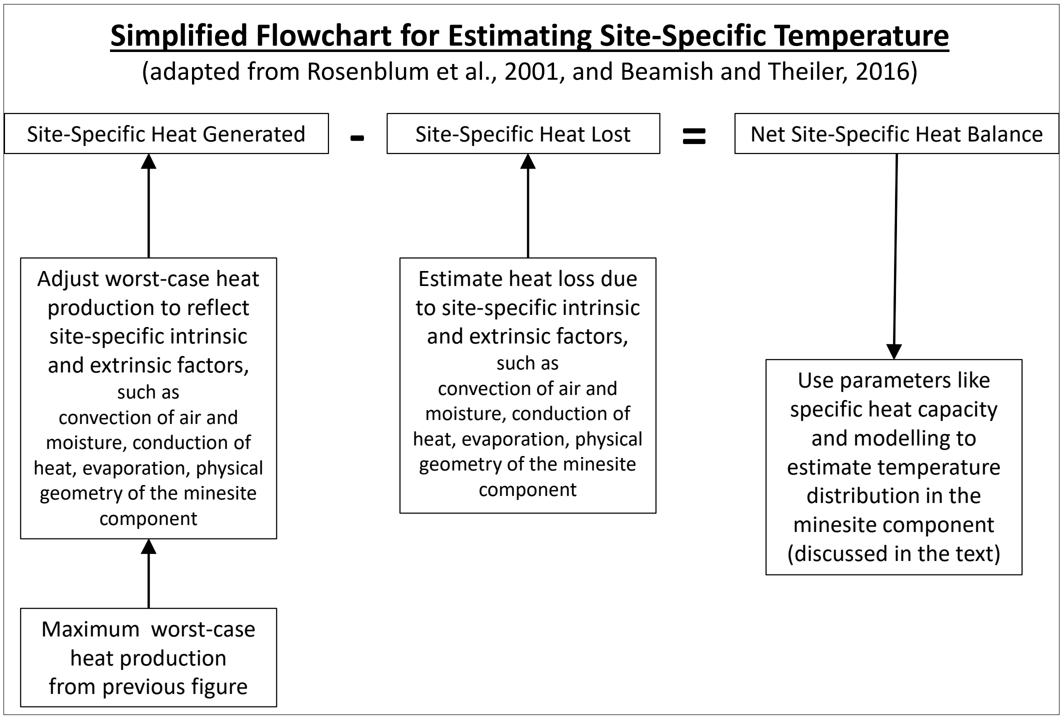

Figure 2. Simplified flowchart for estimating a reasonable site-specific temperature from sulphide-mineral oxidation.

However, the temperature in the geological material could rise high enough to exceed the autoignition temperature of other minerals and compounds. Section 5 discusses the particular case of coal and wood. Without this additional autoignition, there would be no additional heat generation and thus no further substantial increase in temperature.

A related issue is premature detonation of explosives in sulphidic-rock drillholes caused by self-heating above the explosives' autoignition temperature. Several case studies of such detonation are provided by Miron (1993) and Coaltech (2011).

Not all sulphide minerals have significant oxidation rates. As a result, the temperature and self-heating rate are strongly dependent on site-specific mineralogy.

The maximum heat production in Figure 1 is only one variable in the overall procedure to estimate site-specific heat production and temperature (Figure 2 and Table 1). This will be discussed in more detail in later sections.

Table 1. Some factors involved in self-heating of sulphidic mined materials (compiled from several references in this review; some factors overlap and are not exhaustive; references in this review show that one or a few factors can be dominant and that the dominant factors can change from site to site)

Primarily physical factors:

- size and dimensions of a pile or minesite component
- prior disturbance (such as blasting)
- particle size (with high-molar-volume secondary minerals causing expansion and decreasing size)
- reactive surface area
- internal temperature including spatial and temporal variations
- external temperature including spatial and temporal variations
- precipitation
- moisture content (water)
- humidity (vapour)
- conversion from water to/from vapour affecting heat balance and wetting/drying (evaporation and condensation)
- airflow (to supply oxygen and to remove heat predominantly by convection or diffusion or barometric variation or wind which is forced convection)
- water movement (to supply minimal oxygen and to remove heat)
- thermal conductivity, heat capacity, thermal diffusivity (thermal conductivity/volumetric heat capacity)
- porosity
- permeability
- subsurface temperature
- geothermal gradient

Primarily chemical factors:

- mineralogy (including forms and percentages of sulphide and combustible organic carbon)
- prior weathering
- oxidation rate
- rate of oxygen supply and heat removal
- reaction products of oxidation that can add to self-heating
- reaction products of oxidation that can limit self-heating (such as low-molar-volume mineral coatings)
- galvanic interactions

Other:

- temperature-dependent bacterial catalysis
- insolation
- barometric variation
- wind

4. COMMON METHODOLOGY FOR MEASURING SELF-HEATING

4.1 Rosenblum et al. (2001)

One of the most frequently referenced methods for measuring self-heating in sulphidic geological materials is Rosenblum et al. (2001). In that document, the authors studied processed concentrates of nearly pure sulphide minerals, based on prior work with mined ore and waste rock (Rosenblum and Spira, 1995). This method is sometimes called the FR-2 or Noranda method.

After 2001, extensive work examined some intrinsic and extrinsic factors (included in Table 1 and Figure 2) modifying the results and interpretations of this method. This subsequent work is discussed in more detail later in this section.

Even for nearly pure sulphide concentrates, Rosenblum et al. (2001) stated, “most concentrates show little or no propensity to self-heat”. This would be even more applicable to lower-sulphide tailings and waste rock.

Despite the general lack of significant self-heating of concentrates, Rosenblum et al. (2001) devised a test procedure, where temperatures in concentrates were externally forced to high levels, 70ºC and 140ºC. Rosenblum et al. then measured how much heat was generated at these temperatures as air was periodically pumped into the chamber and through the sample.

In reviewing past literature on self-heating, Rosenblum et al (2001) included the following statements.

- “the supply of oxygen by wind and the shape of the piles were the major factors in the development of hot spots”
- “In one of the earlier reported studies [on self-heating in waste rock], the authors did not detect any heating activity in concentrates tested in their self-heating apparatus.”

Thus, major self-heating of sulphide concentrates is reportedly rare, and is affected by site-specific conditions like wind and pile shape (Table 1 and Figure 2). None of these are considered by the test method, which forces sustained hot temperatures onto samples and is thus considered an accelerated weathering test (Rosenblum et al., 2018). To understand the results of this testing method accurately, it is first important to review the details of the testing.

Rosenblum et al. (2001) described “a complete self-heating episode”. Such an episode “rarely proceeds past the first or second stage”. As a result, sulphide autoignition, which the authors report as 300ºC to more than 600ºC, in Stage C is rare (Figure 3).

> *“This work has shown that a complete self-heating episode develops through a series of three stages. Stage A initiates under ambient conditions and ends at 100°C or when all moisture has evaporated. It is followed by an intermediate stage B, and at about 350°C — the so-called ignition point — by stage C which is highly exothermic and generates temperatures well over 500°C. This sequential process (Fig. 1) [Figure 3 in this review paper], however, rarely proceeds past the first or second stage, since in fact, most sulphide concentrates exhibit little or no activity.”*

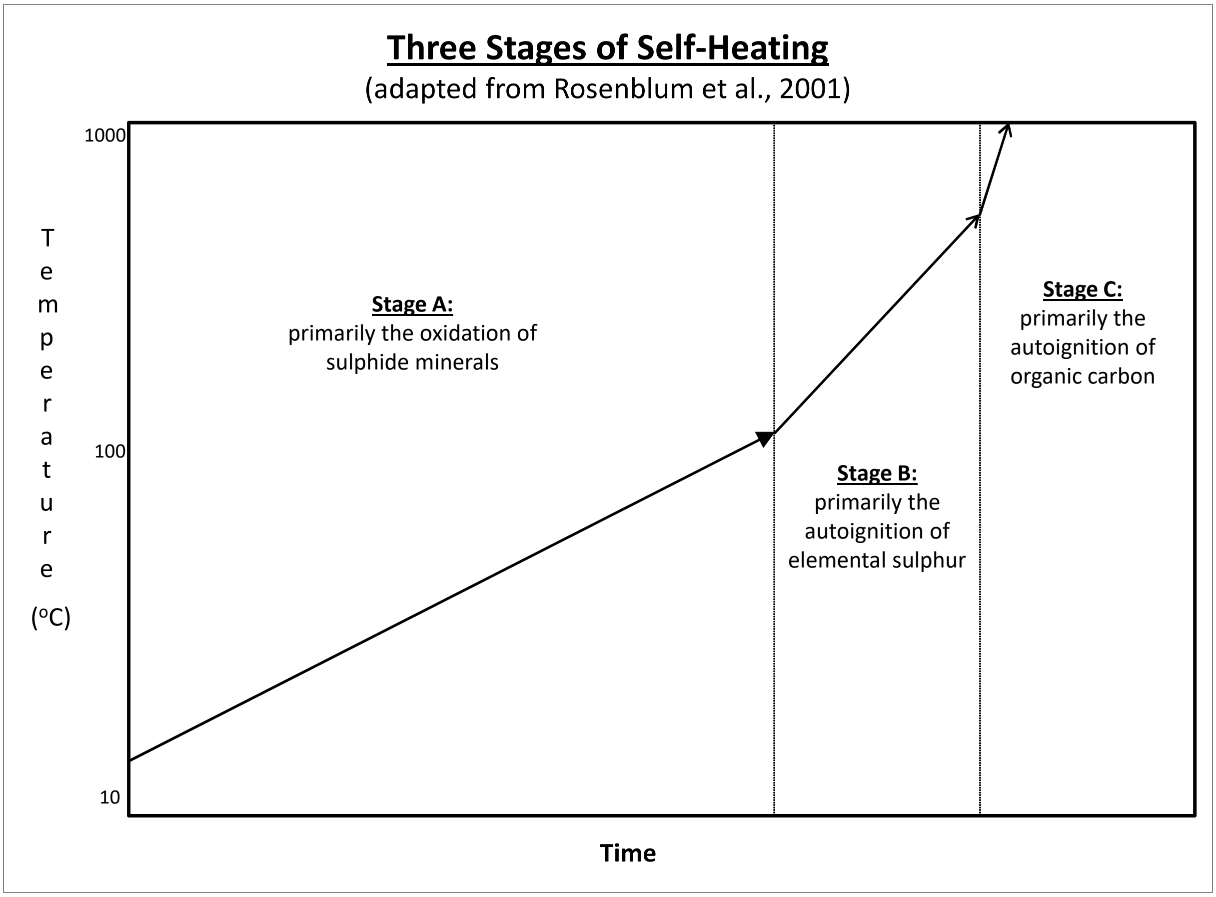

Figure 3. Three stages of a complete self-heating episode that rarely occurs (adapted from Rosenblum et al., 2001).

However, other authors have reported some sulphide autoignition as low as 200°C (e.g., Jendruś, 2016; Reimers and Hjelmstad, 1987).

Rosenblum et al. (2001) explained that Stage A is tested with an initially moist, finely-crushed sample forced to 70°C. This accelerates the self-heating of sulphides. Air is periodically pumped into the chamber, causing brief increases in temperature, which are mathematically converted to heat production.

Elemental sulphur is rarely reported as a reaction product in full-scale non-coal minesite components. Nevertheless, Rosenblum et al. found that elemental sulphur was the primary source of autoignition and of increased heat production in Stage B when temperature was forced to 140°C. Later work further supported this (Rosenblum et al., 2015). Without prior oxidation and creation of elemental sulphur, little heat would be generated in Stage B. Thus, in open-environment conditions with little elemental sulphur, the sample would instead cool as the most reactive sulphide was consumed in Stage A and the rates of oxidation and self-heating decreased.

Again, the autoignition with uncontrolled burning of nearly pure sulphide concentrate is “rare”, because Stage C is rarely reached under natural conditions. Thus, by implication, autoignition of lower-sulphide tailings and waste rock, at ambient temperatures and climatic conditions, must be even rarer. However, other minerals or compounds, like coal, in the mined materials could autoignite if the temperature produced by sulphide oxidation exceeds their autoignition temperatures (discussed in Section 5).

Rosenblum et al. (2001) clearly recognized the limitation of their self-heating method and the site-specific characteristics that could render the results meaningless (Table 1 and Figure 2). This is also true of any discussion of “ignition” and “catching on fire” in Stage C.

> *“[H]eating, which begins locally within a pile, proceeds from one stage to the next only if the net heating rate (heat generation minus heat loss) is high enough to raise the temperature of the hot spot to the threshold of the next stage. If stage A or B happen to be (essentially) inactive, as is often the case, self-heating either cannot begin (inactive or very low A) or will not proceed beyond 100°C (inactive or very low B). Similarly, the existence of an intense exothermic reaction in stage C is of no consequence (in the absence of external heating) if stage B or both A and B are (essentially) inactive. Hence, stage C testing does not provide any information on self-heating potential [and ignition] under ambient conditions.”*

Furthermore, field observations by those authors showed their method exaggerated the potential for realistic self-heating at lower temperatures.

> *“Based on the field observations of the authors, the actual rate inside a stockpile is on the order of one-tenth that seen in the testing apparatus. As indicated above, the Dewar test also gave a rate an order of magnitude lower than in the apparatus.”*

Rosenblum et al (2001) summarized three variables that affected self-heating, that is, variables that cause on-site, full-scale self-heating (Table 1 and Figure 2) to be much less than measured by their forced method. The three variables are as follow.

“1. The onset of self-heating at ambient conditions is contingent on a supply of oxygen and sufficient moisture. ‘Bone dry’ material will not heat nor will moist material in the absence of a supply of oxygen (air).” As an example, they add, “any initial heating [could] drive off the remaining moisture thereby stopping further reaction.”

“2. The rate of self-heating may be low or not measurable at ambient temperatures (e.g., below 30°C) but then increases rapidly as concentrate temperature rises. This behaviour can lead to the development of highly localized hot spots in storage piles, as illustrated in Figure 9 for chalcopyrite concentrate after about one month in storage.” The author’s Figure 9 shows a maximum measured temperature of 150ºC at the surface of a concentrate stockpile. However, after covering the concentrate, temperatures ranged from 37º to 72ºC at 30cm depth within a few days. This shows the methodology is an extreme condition, and relatively simple on-site controls can be effective for limiting self-heating.

“3. Some pyrrhotites (e.g., magnetic varieties) are highly prone to self-heating (Sudbury and Perkovitch, 1961) through a reaction in which oxidation in the presence of moisture produces elemental sulphur during stage A heating. The elemental sulphur then acts as a fuel in the subsequent stage B phase.” Here the authors were speculating on why some concentrates were more reactive than others, suspecting the physical contact of various sulphide minerals played a role in only partially oxidizing some sulphide to elemental sulphur. A later paper looked at this galvanic interaction more closely (Payant et al, 2012).

Rosenblum et al. (2001) listed relatively simple control measures for self-heating in stockpiles prone to or already heating (Figure 2).

- trimming the top to eliminate "peaked" pile geometry, which favours large surface area to volume and easy air ingress;
- covering tightly with plastic sheeting to isolate from air (edge and bottom seals are critical);
- removing the upper layer (typically 1 m) where heating has started, spreading on pad to cool, and remixing with the pile;
- compacting to minimize permeability to air; and
- spraying with chemical inhibitors (such as soaps) to coat the mineral surfaces.

Although Rosenblum et al. (2001) and Rosenblum and Spira (1995) remain the primary references for this self-heating method, subsequent work has focussed on the effects of various intrinsic and extrinsic factors (Table 1) that affect the test results. These factors have included particle size, pH, galvanic interaction, temperature, extent of prior weathering, H_2S gas production from pyrrhotite, formation of elemental sulphur, moisture and relative humidity, surface coatings to reduce self-heating, additives to reduce self-heating, and comparisons with other methods (e.g., Somot and Finch, 2010; Zarassi et al., 2011; Jung, 2012; Payant et al., 2012; Moon et al., 2016; Rosenblum et al., 2014a and 2014b, 2015, 2017, and 2018).

As Moon et al. (2016) emphasized,

> *"It is worth reminding that the purpose of a standard test is only to assess the risk of self-heating occurring. Whether this will actually occur in the field is dependant [sic] on a large number of environmental and physical factors; ambient temperature, moisture content, relative humidity, specific surface area, heat dissipation rate, oxygen availability, relative abundance of neutralizing minerals, and by no means less important, the time available for the mineral mixture to undergo oxidation (weathering) leading to the formation of elemental sulphur."*

Furthermore, Moon (2016) clarified that extensive weathering could actually preclude Stage B, and that self-heating values from 5 to 50 J/g did not indicate whether a sample will leave Stage A and enter Stage B.

Despite the substantial uncertainties, Rosenblum et al. (2018) summarize,

> *"Whether sulphides in the field will heat sufficiently to be of concern will depend on the amount of elemental sulphur created in Stage A and the balance between the rates of heat generation and heat dissipation."*

4.2 R70 Method for Coal (Humphreys, 1979)

The R_{70} self-heating method is attributed to Humphreys (1979). It is important to note this method, using dried samples, and later variations including moisture are designed for coal. The additional complexity of self-heating of mined materials containing organic carbon, like coal, is discussed below in Section 5.

The regular R_{70} test method uses a dry sample (Beamish et al., 2000). A sample of coal is crushed to a particle size less than 212 μm at 110°C under nitrogen for approximately 16 hours. The coal sample is then cooled to 40°C while maintaining the nitrogen atmosphere. The sample is then transferred to an adiabatic oven with a nitrogen flow. Once the temperature is stabilized at 40°C, pure oxygen is pumped through the sample at a rate of 50 mL/min and a data logger records any rise in temperature due to the self-heating of the coal sample. Upon reaching 70°C, the average self-heating rate, known as the R_{70} index, is expressed in units of °C/h. Luo and Wang (2012) assembled a mathematical and computer-based model to simulate this R_{70} method.

Due to concerns over the additional effects of moisture and sulphide oxidation, Beamish and Beamish (2011) describe a “moist coal adiabatic oven test” based on the R_{70} method. The primary differences with the normal R_{70} method are (1) testing the coal at its ambient moisture content and temperature, (2) an increased sample size, and (3) a lower oxygen flow rate of 10 mL/min. Beamish and Beamish report that the increased sample size provides a greater mass of coal to react, and that the lower oxygen flow reduces the cooling effect caused by moisture evaporation. “Effectively, these changes optimise the worst case scenario of developing a heating from as-mined coal.”

The inclusion of moisture in the modified R70 method allows sulphide minerals to self-heat. For one sample, Beamish and Beamish (2011) found:

> *“The accelerated self-heating of this sample compared to all of the others can only be attributable to the presence of the pyrite in the coal reacting with the oxygen and moisture. It is quite a dramatic effect and one that has not been documented so clearly in experimental work before.”*

Factors that can affect and modify R70 self-heating interpretations (Figure 2) include convection, moisture content, coal rank, and inorganic mineral matter. These and other factors are discussed in Beamish et al. (2005), Beamish and Arisoy (2008), Beamish and Theiler (2016), and Theiler and Beamish (2016). Beamish et al. (2005) warned that “… there are dangers of oversimplification of the coal self-heating processes when incorporating only small-scale data into the models.”

4.3 United Nations Test Method N.4 for Self-Heating Substances

The United Nations has included a test for self-heating (Method N.4) in its UN Manual of Tests and Criteria. This Manual has been revised several times over the years, and test procedures have evolved.

An older version of the procedure used a 1 kg powdered sample in a mesh basket placed in an oven at 140°C for 24 hours. Air was not intentionally driven into and through the sample, unlike the Rosenblum et al. (2001) method in Section 4.1.

The temperature of the sample and the oven were continuously logged over this 24-hour period, to measure any increase in temperature. If autoignition occurred or if the temperature increased by at least 60°C during the 24 hours, the result was “positive” and the sample was considered a self-heating risk.

Moon et al. (2016) explained that self-heating of geologic materials like rock and tailings is dependent the extent and intensity of prior oxidation and weathering (Stage A of Figure 3). Thus, the UN N.4 method could yield “false negatives” on fresh samples that would otherwise test "positive" after some weathering.

The Sixth Revised Edition of the UN Manual (United Nations, 2016) retains the previous version as the first step. As before, if there is autoignition or if the temperature increases by at least 60°C over 24 hours, the result is "positive" and considered a self-heating risk. If "positive", additional testing can be done at various temperatures and with various sample volumes for further classification.

4.4 Other Self-Heating Methods

There are dozens of other methods that can be used for measuring self-heating. Based on Figure 3, some methods are limited to only one of the three Stages, whereas other methods include two stages. The reviews by Rosenblum et al. (2014a and 2014b) summarize and illustrate many of these methods. Specifically for coal (see Section 5), Beamish et al. (2000) and Lester (?) describe additional methods. For sulphidic materials, additional methods include those of Wu et al., (2008), Iliyas et al. (2010), and Zhao et al. (2011).

The important point is that, no matter the method, the result of a standardized self-heating test is not a direct predictor of larger-scale and in-field self-heating of mined materials like rock and tailings. Figures 1 and 2 illustrate the additional steps needed to predict realistic on-site self-heating from the results of the standardized method, and Table 1 summarizes the factors involved.

This review will continue to refer back to Figures 1 and 2 and to Table 1 as more information is reviewed and discussed below.

5. SELF-HEATING OF MINED MATERIALS CONTAINING ORGANIC CARBON, SUCH AS COAL AND WOOD

This review focusses on self-heating through the oxidation of sulphide minerals in mined materials like rock and tailings. Nevertheless, there is a related issue that cannot be ignored and is thus reviewed in this section.

By far, the widest known problem with self-heating from mined geological materials is spontaneously generated fires at coal minesites. Literally, there are books written about this (e.g., Stracher, 2007; Coaltech, 2011; and Stracher et al., 2014).

At a glance, this appears anomalous, because the autoignition temperatures for various grades of coal including lignite are generally reported around 450 to 600°C. The autoignition temperature of wood is roughly 300°C. In many cases, these temperatures are not being reached by self-heating of sulphide minerals or organic carbon, or by bacterial degradation of organic carbon, yet smoke and fire can arise and persist at coal sites (Section 6).

The explanation for this lies in an adaptation of Figure 1 to wood and coal. The applicable question is whether self-heating by oxidation of sulphide minerals and/or organic carbon raises the temperature above the autoignition temperatures of reaction products of organic carbon. A succinct answer is provided by Thomas (1997):

> *"Ignition studies after WW2 concentrated on ignition by radiation and it was recognised that cellulosic materials ignited because they produced flammable decomposition products which could be ignited in air by an auxiliary ignition source e.g. a spark or a small flame. Such fuel could only be produced by thermal heating causing decomposition. The incident heat flux in effect raises the surface temperature by conventional heat transfer processes until the temperature is high enough for any chemical heating to cause thermal instability; subsequent chemical decomposition produces flammable gaseous products rapidly enough."*

Thus, sufficient self-heating of geological materials containing organic carbon could lead to formation ("pyrolysis"), release, and autoignition of the gaseous decomposition products. Other proposed self-heating processes have included absorption of oxygen to various carbon compounds like phenols (e.g., Jendruś, 2016). In any case, this "indirect burning" could then raise the temperature further until it exceeds the autoignition temperature of wood and sulphide minerals. Also, drilling or other friction of sulphidic coal can create sparks sufficient to ignite methane and other gases below their autoignition temperatures (Miron, 1993; Coaltech, 2011). As a result, many case studies show that sulphide minerals did not autoignite, but nearby wood, timber, or coal ignited and burned (Section 6).

Perhaps the consequences of predicting or assessing self-heating in coal would be easier if "coal" and "organic carbon" were a single chemical entity. Instead, in addition to variable amounts and types of inorganic minerals in coal that can affect self-heating (Beamish and Arisoy, 2008), coals and some shales consist of large ranges and combinations of many types of macerals and other organic-carbon compounds. As shown in Figures 1 and 2, and listed in Table 1, such intrinsic and extrinsic factors make self-heating of mined materials (1) site specific and (2) difficult to characterize and predict reliably.

Miron (1993) summarized many decades of research on self-heating in coal. Overall:

- Many results were contradictory on the importance of various factors like sulphide content.
- Some indicated self-heating was a catalytic combination of sulphide and carbon oxidation.
- Some considered the physical expansion and breakage of coal to create more particle surface area, due to the formation of larger-volume secondary minerals from sulphide-mineral oxidation, to be more important than the heat generated by sulphide oxidation itself.

In the words of Lester (?), “Self heating [of coal] is a complex set of mechanisms –both macro and micro”. The same can be true of sulphidic mined materials with little organic carbon, in the cases where sulphide oxidation specifically creates sufficient elemental sulphur and/or gases (H_2S or SO_2) that can autoignite at a lower temperature.

6. COMPILED CASE STUDIES OF SELF-HEATING OF MINED MATERIALS

6.1. Historical Case Studies of Ninteman (1978)

Based on a literature survey, Ninteman (1978) concluded,

> *"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."*

Ninteman (1978) explained that the spontaneous oxidation and combustion of sulphide ores had been known for centuries, with his earliest detailed example from 1862. However, some examples were not literally combustion, as in autoignition, but notable self-heating.

Ninteman (1978) discussed many factors that can affect self-heating, which are compiled with others in Table 1. For moisture content, Ninteman, like others, discusses an "optimum" value, between 3% and 8%, with rates of self-heating decreasing at higher and lower moisture contents. Below 2%, the minimal moisture evaporates and self-heating ends. Above 8%, evaporation is sufficiently high to be a "heat sink" and maintain lower temperatures. The rate of self-heating increased with increasing fluctuations between high and low moisture.

Like others, Ninteman (1978) also discussed site-specific optimum values of airflow. Where rates of self-heating are low or excessive, minimizing airflow can control self-heating. Where rates are intermediate and oxygen is readily available, maximizing airflow can provide cooling by removing heat. Although not discussed by Ninteman, in a spatial and temporal sense, variable rates of airflow can determine the location and movement of maximum temperature within a self-heating pile or minesite component (e.g., Schmal et al., 1985; Zhu et al., 2013; Taraba et al., 2014; Lin et al., 2017).

Based on many case studies of self-heating, Ninteman (1978) made the following observations.

> *"...the process [of sulphide oxidation] 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."*
>
> *"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."*
>
> *"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."*
>
> *"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."*

On general prevention and control of self-heating and fires, Ninteman (1978) explained,

> *"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, transportation, or storage."*

For prevention and control in underground mines in particular, "good housekeeping" was recommended, including removal of combustible materials and capacity for high rates of air circulation. For concentrates, minimization of water content and water entry was recommended, or the rapid addition of substantial water for cooling by evaporation. In some cases, the addition of lime could create a secondary-mineral coating that could slow self-heating, but the shift to alkaline pH reportedly increased the rate of self-heating. In general, Ninteman did not address surficial piles of rock or tailings, where case studies show that low-permeable covers such as clay can reduce self-heating and temperature (e.g., Carras et al., 2005).

Summaries of some detailed case studies follow, based on references in Ninteman (1978). Note that these are all in underground mines.

> Horne Mine, Quebec, Canada (1962): sulphide-dust explosions during blasting (76 fires) and self-heating of stopes and backfill (7 fires). Timbering contributed to the fires, and was replaced with steel. Cementation of backfill is an exothermic reaction, and may have contributed to the self-heating.
>
> Magma Copper Mine, Arizona, USA (1961): "The fires started [in a caved section of the underground workings] 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."
>
> United Verde Copper Co., Arizona, USA (1916): "The first fire of 1894 was caused by spontaneous combustion, following a cave-in… many fires [in the underground workings] started when red-hot dust dropped on the timbers from fractures in ground above".
>
> Pocahontas Mine, Missouri, USA (1914): "First serious mine fire … 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…."
>
> Minnie Healy Mine, Montana, USA (1922): "The heat resulting from the oxidation of the fine broken sulfide ore is sometimes sufficient to set fire to the timbers. [The 1906 fire] eventually was controlled by blocking it off and filling it with mill tailings."
>
> Sunshine Mining Co., Idaho, USA (1972): "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."
>
> Homestake Mining Co., South Dakota, USA (1965): "Origin of the fire was spontaneous combustion [of sulphide minerals in sand backfill] initiated by a sudden drop in ventilation."

6.2 Case Studes in China by Zhao et al. (2011)

Zhao et al. (2011) reported that "tens of mine fire cases have been mobilized by spontaneous combustion behavior of sulfide ores" in China. This included the Wushan Mine in Jiangxi Province, and the Xinqiao Mine and Xiangshan Mine in Anhui Province. Details of these mine fires were not provided or referenced.

7. ESTIMATING THE LOCAL NET HEAT BALANCE IN MINED MATERIALS

This section reviews and summarizes concepts, models, and equations of self-heating and cooling in mined materials. Models for coal self-heating are summarized first (Section 7.1), then models strictly for sulphide self-heating are reviewed (Section 7.2). As will be shown, there is extensive overlap among these models, due to their inclusions of various factors from Table 1 and from Figures 1 and 2. In all cases, the warning of Beamish et al. (2005) should be remembered:

> *"However, there are dangers of oversimplification of . . . self-heating processes when incorporating only small-scale data into the models."*

Furthermore, in their thorough review of coal self-heating, Carras and Young (1994) also warned:

> *"Predictions at the 2500 t test level [scale] for one particular model may not be valid at the 100,000 t level [scale]. The effect of scale-up on natural convection and other heat and mass transfer processes in the models remains to be investigated . . . . In view of the past record on simple predictive techniques for assessing the self-heating propensity . . . , it is clear that no single property can be employed to assess self-heating behaviour. The conditions under which that property is measured are normally too confining and fail to match the real world."*

7.1 Self-Heating Models Primarily for Coal

A popular modelling approach for self-heating and autoignition of coal involves singularity theory or bifurcation parameters, such as the Frank-Kamenetskii or simpler Semenov approaches (e.g., Nelson et al., 2003; Wang et al., 2017). This approach theoretically predicts "abrupt" transitions in heating and autoignition. For example, Nelson et al. (2003) simulated self-heating of compost piles with a Semenov model, and observed:

> *"Self-heating in compost piles can lead to one of three types of behaviour: negligible temperature increase; an elevated temperature increase without ignition; and ignition of cellulosic materials."*

However, many coal self-heating models are not as "abrupt". In these models, the dependence of oxidation rate on temperature is often modelled as the Arrhenius Equation without singularities or bifurcations (discussed further in Section 7.2 and Equation 4). Activation Energy, as part of the Arrhenius Equation, is estimated in many papers that include self-heating measurements, and its value varies widely. For example, Activation Energies for some Australian coals were reported at 63-69 kJ/mole (Carras and Young, 1994), and one Chinese coal yielded an Activation Energy of roughly 139 kJ/mol with a calorific value of 14,380 kJ/kg (Wang et al., 2017).

For coal oxidation and self-heating, the Arrhenius Equation is sometimes combined with an equation describing a decreasing rate as time increases. This decay equation in some cases is called the "Elovich Equation" (e.g., Carras and Young, 1994; Zhang et al., 2016a).

Elaborate models for coal self-heating and combustion, including many factors listed in Table 1, have been developed over many decades. More recent approaches and models include Fierro et al. (2001), Wang et al. (2003), Ejlali et al. (2011), Zhu et al. (2013), Hooman and Maas (2014), Taraba et al. (2014), Zhang et al. (2016a), Zhang et al., (2016b), Wang et al. (2017).

Coal “stockpiles” of various small heights (2.5 to 100 cm heights) were tested under laboratory conditions and then modelled (Wang et al., 2017). The volume of the experimental pile, up to 100 m^3, was the most important factor in self-heating. Increasing volume corresponded to increasing probability of spontaneous combustion, but also to increasing lag time before such combustion occurred.

Larger experimental coal piles of 2000-3000 tonnes were constructed and monitored by Fierro et al. (2001). This composited coal was mixed low-grade lignite from the Teruel basins of Spain, containing 3.60%S pyrite and 0.39%S pre-oxidized sulphate. Based on previous one-dimensional models (e.g., Nordon, 1979; Schmal et al., 1985; Brooks and Glasser, 1986), the input of 20 values for various physical and chemical factors led to reasonable “order of magnitude” matches of simulated and measured one-dimensional data for temperature, oxygen, and moisture. Porosity, allowing convection, was the primary variable controlling the extent of self-heating. Self-heating was experimentally reduced by several methods, with a surficial cover of ash being the most economical.

7.2 Self-Heating Models Primarily for Sulphide Minerals

In Section 3 above, Equation 1 for oxidation of some sulphide minerals produces heat, acidity, metals, sulphate. The latter three are characteristics of acid rock drainage (ARD) which can result in substantial adverse environmental effects. Because of this, most models of sulphide oxidation focus on the resulting ARD, and few focus specifically on heat.

ARD models are discussed in many conference proceedings such as the periodic International Conference on Acid Rock Drainage (ICARD), at online websites like the Global Acid Rock Drainage (GARD) Guide (www.gardguide.com), and in many publications and documents (e.g., Morth et al., 1972; Morin and Hutt, 1997 and 2001; and Price, 2009).

Implicitly, all sulphide-oxidation models can include all reaction products including heat. However, for this review, emphasis is on models that integrate heat generation. Furthermore, sulphide oxidation on an atomic basis can be complex (Murphy and Strongin, 2009), but this review focusses on larger-scale, more macroscopic models.

In its simplest form, the equation, or “model”, for the local heat balance (Q) and temperature (T) of a small sample, pile, or minesite component over a short period of time is the combination of Equations 2 and 3.

$$\Delta Q_{stored} = Q_{self\text{-}heating} + Q_{in} - Q_{out} \qquad \textit{(Eq. 2)}$$

Changes in temperature can be related to ΔQ_{stored} by Equation 3.

$$\Delta T = \Delta Q_{stored} / (c\ m) \qquad \textit{(Eq. 3)}$$

where c = specific heat capacity

m = mass

Equations 2 and 3 form a simple and easy-to-understand model. However, their application to the real world can be impressively complex, as illustrated in Figures 1 and 2 and in Table 1, and as explained in the previous sections of this review.

Similar to many self-heating coal models (Section 7.1), the dependence of sulphide-oxidation rate (part of $Q_{\text{self-heating}}$) on local temperature variations (Equation 3) is often modelled with the Arrhenius Equation (one variation is given in Equation 4).

$$k = A\, e^{(-Ea/RT)} \qquad \text{(Eq. 4)}$$

where k = rate constant
T = absolute temperature (kelvin)
A = pre-exponential factor
E_a = activation energy
R = universal gas constant

This creates a feedback loop and an autocatalytic effect to accelerate $Q_{\text{self-heating}}$ as T rises. However, T would not rise if Q_{out} in Equation 2 were greater.

There are many issues and concerns with the Arrhenius Equation (e.g., Logan, 1982; Peleg et al., 2012). As one of many examples, optimum temperatures of any microbial catalysis would not be included. Also, the applicable temperature in Equation 4 would be in the microenvironment around the sulphide minerals, which could be different from the measurable temperature in the pore spaces. Additionally, minesite drainages contain mixtures of exothermic and endothermic aqueous and solid-liquid reactions, so that the application of Equation 4 to a single reaction in the mixture is questionable. There are so many limitations to the Arrhenius Equations that Logan summarized:

> *"Thus, it is now widely accepted that . . . [the Arrhenius Equation] is not in general obeyed, even by elementary chemical reactions, in the sense that unique constants A and E_a do not exist for each reaction. Thus, it is now widely recognized that even when the Arrhenius plot is apparently linear, E_a is best regarded as an empirical or a phenomenological quantity . . . ."*

Thus, Activation Energy (E_a), as part of the Arrhenius Equation (Equation 4), may have limited meaning or applicability. Nevertheless, E_a has been determined for sulphide oxidation as a constant in many papers, but Iliyas et al. (2010) pointed out that their average E_a value of 75±5 kJ/mole changed as self-heating progressed.

The preceding basic models do not include many factors in Figures 1 and 2 and Table 1. Nevertheless, there are many more elaborate models and software, ranging from flowcharts to linked partial differential equations. For example, Chao (1995) created a fault tree analysis, including AND and OR logic gates, with 17 key factors. Based on this, Chao recommended that a more detailed mathematical model be based on heat transfer and diffusion theory. Wu et al. (2008) used ANSYS and FLUENT software to model self-heating of underground high-sulphide broken-rock piles, with later work including heat generation for specific sulphide minerals and various reaction products (Yang et al., 2011).

National Research Council Canada (NRC) created and applied a two-dimensional, axisymmetric, vertical-plane model to simulate movement of water and solutes, pore-gas movement, evolution of aqueous chemistry, and heat generation and transport (Liu et al., 2017; Ma et al., 2018 and 2019).

Pore-gas convection was not initially included, but has been added to the model along with coarse-grained internal preferential channels (Ma et al., in prep).

Self-heating by sulphide minerals was an integral part of the NRC model and was mathematically coupled with all other parts. This model was applied and calibrated to a relatively warm, full-scale waste-rock pile with a maximum internal temperature of 54°C. It showed heat generation affected and was also affected by the other parts of the model.

These coupled effects were altered by the installation of a fine-grained cover over the waste rock. Prior to covering, air inflow was focussed around the outer toe (base) of the waste rock, with pore-gas outflow focussed on the upper surfaces, primarily reflecting thermal conduction from self-heating. After covering, the pore-gas recirculated within the waste rock, leading to generally lower oxygen levels, and exited at the toe adjacent to the fresh-air inflow.

8. CONCLUSION

This review compiled, summarized, and synthesized worldwide information on self-heating of mined geologic materials that contain, as a minimum, sulphide minerals. The most common sulphide minerals include pyrrhotite ($Fe_{1-x}S$, x = 0 to 0.2) and pyrite (FeS_2).

The primary objective here was to clarify how a proposed or operating sulphidic minesite can predict or assess self-heating under full-scale site-specific conditions. As a result, any required site-specific control and remediation for heat generation can then be determined.

The first problem with understanding self-heating was in terminology. So this review explained the difference between self-heating and autoignition, where autoignition represents the typical expressions of "burning" and "catch fire". The autoignition temperatures of many sulphide minerals are above 300ºC, which is a temperature rarely reached by self-heating by sulphide oxidation.

In any case, self-heating (or lack thereof) under full-scale on-site conditions was shown to be dependent on a complex interplay of many physical and chemical factors. Some factors can add to the heating, and some can cool the mined materials. No single factor or test can determine this.

This review showed that the best known self-heating test for sulphidic mined materials is Rosenblum et al. (2001). This test forces samples to 70ºC and then 140º C for days, and does not let the samples cool. Air is occasionally pumped into the sample to see if there is a significant spike in temperature, which indicates self-heating under these forced conditions.

Rosenblum et al. (2001) emphasized that this test procedure substantially accelerates self-heating relative to observed and measured self-heating under full-scale on-site conditions. In fact, Rosenblum et al. say, "most [sulphidic] concentrates show little or no propensity to self-heat". Where significant self-heating was detected, this was attributed to the formation of elemental sulphur and not other potential causes like H_2S or SO_2 gas.

Another author emphasized, "It is worth reminding that the purpose of a standard [self-heating] test is only to assess the risk of self-heating occurring. Whether this will actually occur in the field is dependant [sic] on a large number of environmental and physical factors . . . "

A review of compiled case studies of major self-heating at full-scale minesites, back to 1862, revealed that most cases of fire and combustion were caused by wood, timber, and coal being exposed to heat. In some cases, but not all, the cause of the heat that autoignited the organic carbon could be traced to sulphide-mineral oxidation. Other sources of heat included drilling and pouring of cement. There were no definitive full-scale examples of autoignition of sulphide minerals, but "red hot" sulphide minerals were occasionally reported.

No currently available models include all the important physical and chemical factors that need to be considered to predict whether self-heating will reach high temperatures under full-scale on-site conditions. Some simplified equations and a few more complex models were discussed.

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APPENDIX A: Relevant Terminology Obtained from Internet Searches and the United Nations Globally Harmonized System (GHS) of Classification and Labelling of Chemicals

Autoignition temperature: the lowest temperature at which a substance will spontaneously ignite in normal atmosphere without an external source of ignition, such as a flame or spark (e.g., 247-280ºC for gasoline and 1315ºC for iron); the temperature at or above which a material will spontaneously ignite (catch fire) without an external spark or flame; Wikipedia (2019) warns, "Temperatures vary widely in the literature and should only be used as estimates"; see also ignition point/temperature.

Combustion: the process of burning something; rapid chemical combination of a substance with oxygen, involving the production of heat and light; in a combustion process, when a flame is produced it is referred to as burning; see also spontaneous combustion.

To Burn: to undergo combustion; flame or glow while consuming a material such as coal or wood.

Exothermic: accompanied by the release of heat; characterized by or formed with evolution of heat.

Fire: combustion or burning, in which substances combine chemically with oxygen from the air and typically give out bright light, heat, and smoke; the phenomenon of combustion manifested in light, flame, and heat; fire is burning, which is combustion, and combustion is a type of oxidation reaction.

Flame: a hot glowing body of ignited gas that is generated by something on fire; a state of blazing combustion.

Fuel: material such as coal, gas, or oil that is burned to produce heat or power; a material used to produce heat or power by burning.

Heat: the condition or quality of being hot; a form of energy that is transferred between two substances at different temperatures without the transfer of matter; the SI unit of heat is the joule (J).

Ignition: the action of setting something on fire or starting to burn; starting a fire; see also ignition point/temperature.

Ignition point/temperature: the lowest temperature at which a combustible substance in air will ignite and continue to burn; the lowest temperature at which a volatile material will be vaporised into a gas which ignites without the help of any external flame or ignition source; see also autoignition temperature.

Incendive: able to ignite or cause ignition.

Pyrophoric substances: sometimes also called spontaneously combusting substances; those solids or liquids that even in small quantities are liable to ignite within five minutes after coming into contact with air (from the United Nations Globally Harmonized System of Classification and Labelling of Chemicals; ignition was not defined)

Readily combustible solid: powdered, granular, or pasty substance or mixture which is dangerous if it can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly (from the United Nations Globally Harmonized System of Classification and Labelling of Chemicals; ignition was not defined)

Self-heating: a self-heating solid or liquid, other than a pyrophoric substance, is one which, by reaction with air and without energy supply, are liable to self-heat (from the United Nations Globally Harmonized System of Classification and Labelling of Chemicals)

Spontaneous combustion: autoignition of combustible material through chemical action (such as oxidation) of its constituents; the ignition of organic matter (e.g., hay or coal) without apparent cause, typically through heat generated internally by rapid oxidation; see also combustion.

Temperature: the degree or intensity of heat present in a substance or object, expressed on a comparative scale and shown by a thermometer or perceived by touch; a measure of the warmth or coldness of an object or substance with reference to some standard value; a physical quantity expressing hot and cold.