Self-heating of Sulphide Ores, Transition from Stage A to B and Evaluating Reliability of UN Test Protocol

Sungjae Moon

Department of Mining and Materials Engineering
McGill University
Montreal, Canada

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Sungjae Moon
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ABSTRACT

Some materials when exposed to the atmosphere can exhibit a rise in temperature without requiring an external heat source. These materials are generally referred to as pyrophoric or self-heating substances. The handling, storage, and transportation of these products has been, and continues to be, a challenge.

Reliably assessing the self-heating potential of these products is an essential first step. Over the years, a number of test methodologies have been developed and successfully used to “raise a red flag” when a material exhibits self-heating properties. A widely accepted test method recommended by United Nations is routinely used to certify the safety of shipping pyrophoric goods. Test work conducted at McGill University has shown that the U.N. approved test and other single stage testing methods can yield diametrically opposed test results when evaluating the self-heating properties of sulphides. Depending on the degree of oxidation (weathering), an active sulphide can exhibit a level of self-heating values ranging from less than 5J/g to 50J/g. Under the currently accepted analysis, a sulphide concentrate could be tested and shown to be negative (exhibiting minimal heating) which would be considered safe for shipping. If, however, that concentrate is stored over an extended period of time in a weathering favorable environment, the concentrate could oxidize and present a handling, storage, or shipping problem. To make the U.N. and other single stage self-heating procedure more reliable when testing of sulphides, it is suggested that a pre-weathering step is incorporated with the self-heating testing.

The second study focuses on the transition of sulphide containing material from heating in Stage A (low temperature heating) to Stage B (mid-high temperature heating). With increasing sample temperature, sample moisture decreased leading to elimination of water which is a key reactant in stage A. Stage B reactions are independent from Stage A reactions and moisture is not required. It has been hypothesized that transition zone results from orthorhombic sulphur (stable below 95.3°C) transforming into monoclinic (beta) sulphur (stable from 95.3°C to 119.6°C). FR-test technique was used to determine this transition zone. Past studies by F. Rosenblum have shown that transition from Stage A to Stage B is unclear. A study was undertaken to examine the relationship between the Stage transition and various factors including weathering duration,

ambient temperature and initial element sulphur content of a sample. Results suggest that self-heating capacity measurements do not indicate whether a sample will progress to Stage B.

RÉSUMÉ

Lorsqu'ils sont exposés à l'atmosphère, certains matériaux peuvent présenter une élévation de température sans influence d'une source de chaleur externe. Ces substances sont généralement désignées sous le nom de substances pyrophoriques, ou auto-échauffantes. La manipulation, le stockage et le transport de ces matériaux constituent depuis de nombreuses années un défi qui se pose aujourd'hui encore.

Évaluer de façon fiable le potentiel d'auto-échauffement de ces produits représente une première étape essentielle. Au fil des ans, plusieurs méthodologies de test ont été élaborées et employées avec succès afin de « sonner l'alarme » lorsqu'un matériau présente des propriétés auto-échauffantes. Une méthode de test largement reconnue et recommandée par les Nations Unies est habituellement utilisée pour certifier que les produits pyrophoriques sont transportés en toute sécurité. Cependant, une série d'essais menée à l'Université McGill a montré que le test approuvé par l'ONU, tout comme d'autres méthodes de test en une seule étape, pouvaient produire des résultats diamétralement opposés lorsqu'on les appliquait pour déterminer les propriétés auto-échauffantes des sulfures. En fonction de son degré d'oxydation (ou altération), un sulfure actif peut présenter un pouvoir calorifique d'auto-échauffement allant de moins de 5 J/g à 50 J/g. D'après l'analyse actuellement reconnue, un concentré de sulfure peut être testé négatif (montrant un échauffement moindre) et son transport jugé sûr. Cependant, si ce concentré est stocké pendant une période prolongée dans un environnement favorisant son altération, il peut s'oxyder et présenter des problèmes de manipulation, stockage ou transport. Afin de rendre le test de l'ONU et les autres procédures d'auto-échauffement à une étape plus fiables lors de l'évaluation des sulfures, il est donc suggéré d'intégrer une étape de pré-altération dans le test d'auto-échauffement.

La seconde étude se penche sur la transition d'une substance contenant du sulfure de l'étape A (chauffage à basse température) à l'étape B (chauffage à moyenne température). L'augmentation de la température de l'échantillon provoque une réduction de son taux d'humidité conduisant à la disparition de l'eau, qui est un réactif-clé durant l'étape A. Les réactions intervenant durant l'étape B sont indépendantes de l'étape A et ne nécessitent pas d'eau. Il a été supposé que la zone de transition est causée par la transformation du soufre orthorhombique (stable en-dessous

de 95,3°C) en soufre monoclinique (ou soufre bêta, stable entre 95,3°C et 119,6°C). La technique de test FR a été utilisée pour déterminer cette zone de transition. Des études passées menées par F. Rosenblum ont montré que la transition de l'étape A à l'étape B est ambigüe. Une étude a été entreprise afin d'examiner la relation entre la transition d'une étape à l'autre et de nombreux facteurs tels que la durée d'altération, la température ambiante, et la quantité de soufre initialement présente dans l'échantillon. Les résultats suggèrent que la mesure de la capacité d'auto-échauffement ne permet pas de déterminer si un échantillon va progresser à l'étape B.

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TABLE OF CONTENTS

List of Figures

List of Tables

Chapter 1. Introduction

1.1. Introduction to Self-heating

Sulphide containing ores are one of the most predominant materials found when mining for valuable minerals such as copper, lead, nickel, zinc, and gold. A typical copper sulphide deposit contains 3~5% sulphide mineral and 0.5~1.0% copper sulphides (Chambers, D, 2006). Sulphide ores are reduced from large rocks by drilling and blasting processes at the mine site. These ores are then transported to the plant where valuables are liberated by particle size reduction (crushing and grinding). Valuables are further classified to concentrates through separation techniques such as flotation and extracted by smelting and refining processes. During mining and mineral processing, sulphide ores are exposed to various environments.

Past studies have shown that humidity of air and ambient temperature can promote in self-heating of sulphides. If self-heating is unsupervised, the increase in the temperature may lead to spontaneous combustion, which is particularly difficult to control. During mining, problems from self-heating of sulphides were seldom encountered with open pit mines whereas self-heating problems were periodically encountered within underground mines. In some cases, active ores that were left in underground mines for a prolonged duration oxidized rapidly and self-heated. A well-known incident occurred in Sullivan Mine in Kimberly, British Colombia (Good, 1977) where sulphide ores have been reported reaching smelting temperatures due to impeded external cooling (Hamilton and Woods, 1981). Another problem that occurs with self-heating is the depletion of oxygen. Since self-heating is an oxidation reaction, oxygen is consumed during the process. In an underground mine where oxygen is limited, the depletion of oxygen could lead to suffocation of the workers. Problems are also encountered during crushing and handling processes, where sulphide ores are commonly introduced to humid air and oxygen, promoting self-heating. In some cases, large pillars of fires have been noticed from the impact of particles during handling. Self-heating of sulphides were also periodically reported during storage and transportation. In Westminster BC, a sulphide containing copper concentrate that were stored in storage self-heated up to 150°C and released 16ppm of SO_2 (Hamilton and Woods, 1981). Past studies have also shown that toxic gases such as hydrogen disulphide (H_2S) and sulphur dioxide (SO_2) are produced as intermediate products during self-heating reaction (Ninteman, 1978;

Somot and Finch, 2010). These toxic gases endanger health and safety of workers and its exposure limits are strictly regulated worldwide. In Quebec, the exposure limit for hydrogen disulphide is 10 ppm and the exposure limit for Sulphur dioxide is 2 ppm (Ontario Ministry of Labour, 2015). This can make working conditions potentially dangerous as oxygen is consumed from the surrounding air and significant quantities of sulphur dioxide (SO_2) can be released (Ninteman, 1978).

Self-heating is an exothermic oxidation reaction. A material is self-heating when heat generated within the material, without external heat input, is greater than the heat being dissipated to the surroundings (Semenov, 1935). Iron sulphides, especially pyrrhotite, are predominantly associated with self-heating of sulphide ores (Rosenblum and Spira, 1995). Past studies have shown that the structure of pyrrhotite imposes a deficiency in metal ions. It is proposed that this deficiency causes pyrrhotite to be unstable and as a result very active to oxidation (Nicholson, and Scharer, 1994).

1.2. Thesis Objectives

The objectives of the thesis are:

1. To evaluate the reliability of the UN test protocol
2. To study the oxidation state of the sample which can bridge temperature transition from stage A to stage B

1.3. Thesis Structure

The Thesis is presented as a manuscript-based thesis. Chapter 1 is the introduction to self-heating of sulphide containing ores, a brief history of accidents associated with self-heating. Chapter 2 is a literature review. Chapter 3 is a manuscript which has been approved and will be published in IMPC 2016. Chapter 4 is on the temperature transition from stage A to B. Finally, Chapter 5 is the conclusion and recommendations.

1.4. Contribution of authors

The manuscript entitled “Evaluation of the U.N. Self-heating Test for Sulphides (Chapter 3) is co-authored by Prof. James A. Finch, my supervisor and Mr. F. Rosenblum in his capacity as research co-supervisor. Mr. J. E. Nesset and Prof. K. E. Waters assisted in proofreading the manuscript. Sungjae Moon carried out all the experiments.

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Chapter 2. Literature Review

2.1 Sulphide in Nature

Sulphides have been proposed to be the cause of self-heating since 1871 (Stevens, 1871; Kirshenbaum, 1968 & Good, 1977). Metal sulphides are a major group of ores and iron sulphides are the most common occurring sulphide mineral in nature (Vaughan & Lennie, 1991). Table 2.1 shows common or important metal sulphides, which contain one or more atoms of metal and sulphur (Klein and Hurlbut, 1986).

Table 2.1 - Common sulphide minerals found in nature.

Name	Chemical Formula
Acanthite	Ag_2S
Chalcocite	Cu_2S
Bornite	Cu_5FeS_4
Galena	PbS
Sphalerite	ZnS
Chalcopyrite	$CuFeS_2$
Pyrrhotite	$Fe_{1-x}S$
Milerite	NiS
Pentlandite	$(Fe,Ni)_9S_8$
Covellite	CuS
Cinnabar	HgS
Realgar	AsS
Orpiment	As_2S_3
Stibnite	Sb_2S_3
Pyrite	FeS_2
Marcasite	FeS_2
Molybdenite	MoS_2

Past studies have shown that the reactivity of sulphide materials are related to the sulphur to iron ratio (Ninteman, 1978). Pyrrhotite and pyrite have been reported as the most reactive and prone to self-heating out of other sulphide minerals due to the high iron-deficiency (Reimers and Hjelmsd, 1987; Rosenblum and Spira, 1995; Rosenblum, Nesset and Spira, 2001). This low iron to sulphur ratio leads to vacancies and defects in the structure, causing pyrrhotite to be very reactive (Vanyukov et al. 1972; Vaughan, D. J., & Lennie, A. R., 1991).

2.2. Self-heating Stages for sulphides

Self-heating of sulphides progress in three distinct stages: Stage A, Stage B, and Stage C (Rosenblum and Spira, 1995; Rosenblum et al, 2001). In each stage, heat is generated from distinctive exothermic oxidation reactions.

Stage A takes place from ambient temperature to temperature below 100°C and it is the only stage that requires moisture for the reactions to occur. In this stage, heat is generated by active sulphide minerals that oxidize to produce elemental sulphur, a key reactant in stage B reaction, and other byproducts such as H_2S and SO_2 (Somot and Finch, 2010). Therefore, Stage A is considered as a preceding stage for Stage B and is also known as the weathering stage. Reactions in Stage A are initiated by the formation of sulphuric acid and consequently the oxidation of sulphide materials. Under certain circumstances, Stage A reactions can be delayed by the presence of non-sulphide acid-buffering minerals formed on the particle surface.

Stage B takes place from roughly 100°C to 390°C depending on the type of minerals present (Rosenblum, Nesset and Finch, 2014). In Stage B, elemental sulphur formed in Stage A becomes a key reactant and oxidizes to generate more heat and SO_2 (Somot and Finch, 2010). Because the reactions are initiated at about the flash point of water, sulphides entering Stage B reactions are dry. The Stage B reactions will be largely impacted based on the preceding reactions occurred in Stage A.

Stage C, also known as the roasting or ignition stage, occurs at the sample’s ignition point, typically temperatures above 390°C depending on the type of materials present (Rosenblum, Spira and Konigsmann 1982). Past studies indicate that Stage C is independent of events occurred in Stage A and Stage B, as unreacted sulphur oxidizes and enters a spontaneous combustion. Figure 2.1 shows self-heating of sulphide progressing from Stage A to Stage C with temperature rise in a sample. Simplified major reaction is shown in each stage.

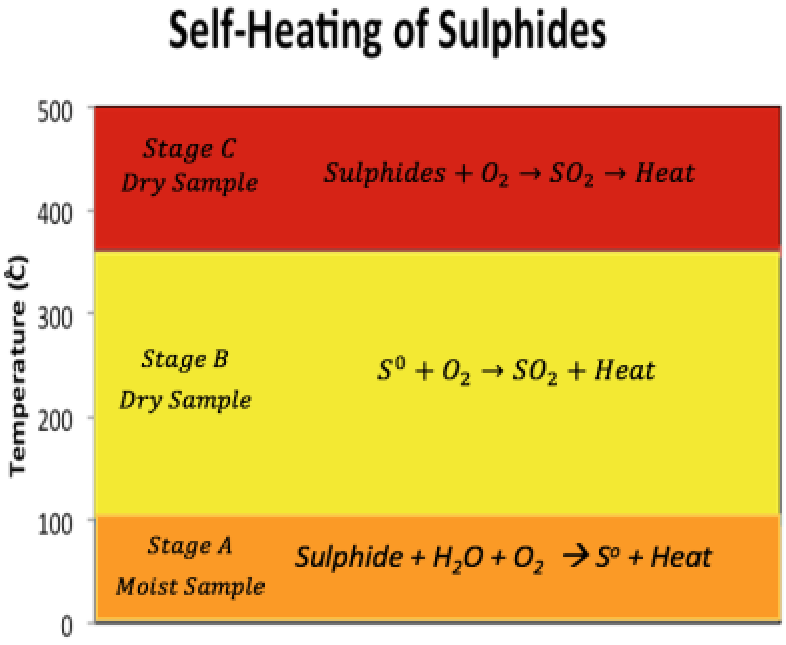

Figure 2.1. Self-heating Stage A, Stage B and to Stage C

2.3. Self-heating Methodologies

As mentioned in Chapter 1.1, it has become essential to have reliable test methodologies that can predict self-heating of various sulphides to prevent hazardous accidents from happening. Well-known conventional test methodologies list in Table 2.2 are reviewed. Throughout this paper, two methodologies: FR Test and U.N. Recommended Test are discussed.

Table 2.2 Well-known Self-Heating Test Methodologies

Self-Heating Test Methodology	Publications
FR Test	Rosenblum & Spira, 1982
U.N. Recommended Test	Bouffard & Senior, 2011
Basket Heating Methodology	Chen, 1999
Oxidation Kinetics Testing Methodolog	Wang et al, 2009
F-K Methodology	Zhang & You, 2013 Nugroho et al, 2000 Survey, 2003
Crossing Point Temperature Methodology (	Chen & Chong, 1998
Heat Release Methodology (HR)	Sen et al, 2009
Activation Energy Methodology	Wang et al., 2009 Ngabe, Edwin van der Spuy, & Finch, 2011
Differencial Thermal Analysis (DTA)	Gouws & Wade, 1989

2.3.1. FR Test

In 1982, Rosenblum et al. (1982) developed a self-heating apparatus (FR-2) designed specifically for sulphides at the Centre de Technologie Noranda. In 2003, the self-heating facility was relocated to the Department of Material & Mining at McGill university in Montreal, Canada.

The apparatus is a type of a calorimeter with a gas injection and exhaust system. It consists of a 2L Pyrex Vessel, constant-temperature coiled heater, metal mesh screen, concrete base and an insulator as shown in Figure 2.2. The apparatus is set to a desired temperature and once the temperature of sample inside reaches the set point temperature, gas (typically air) is routinely introduced at the bottom of the Pyrex vessel containing the sample. The gas flows through the sample and exits at the top through the exhaust. The temperature of the sample is logged every minute during the span of the experiment (Rosenblum et al., 2001). The self-heating rate is obtained from the rate at which the temperature increases during the gas injection (Rosenblum et al., 2001). Using the self-heating rates, the self-heating capacity (energy released per unit mass of sample) can be estimated.

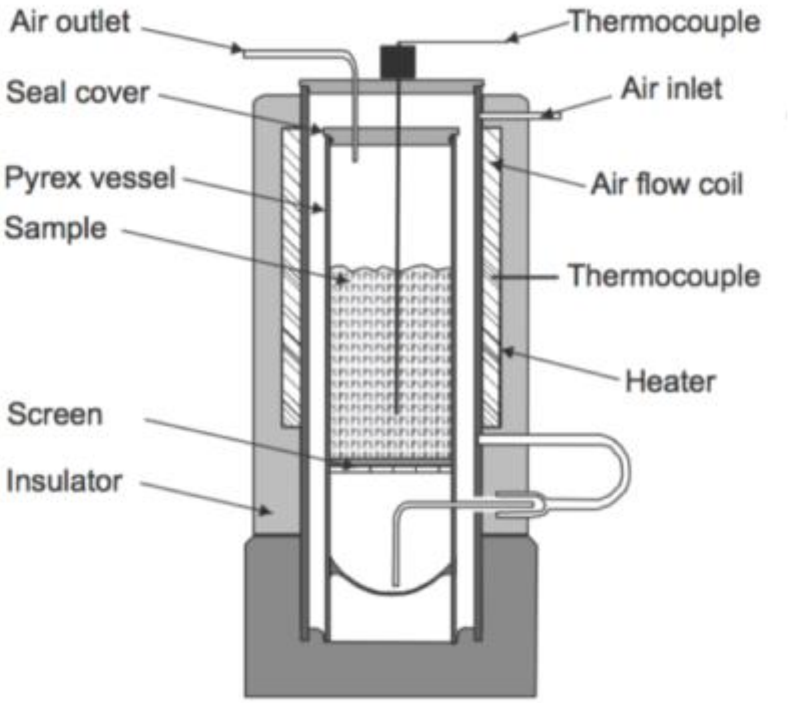

Figure 2.2. FR Test Apparatus (Somot & Finch, 2010)

2.3.2. United Nations (U.N.) Recommended Test

In 1956, United Nations published the first version of Recommendation on Transport of Dangerous Goods (ST/ECA/43-E/CN.2/170) to governments and to the international originations to provide international guidelines with regards to the safety in the transport of dangerous goods (U.N., 2015). Sulphide materials fall under Division 4.2 – Substances liable to spontaneous combustion. Materials that fall under this category is known to self-heat in the presence of air and moisture.

The U.N. Test protocol involves a type of a Cage test, which classifies material into discrete packing groups. Packing group I refers to substances presenting high danger; Packing group II refers to substances presenting medium danger and Packing group III refers to substances presenting low danger. In a cage test, a powdered sulphide sample is gently packed into a $100mm^3$ open-top metal mesh basket. The basket is held inside a convection oven, which supplies fresh oxygen by circulating air, and the thermocouples are place in the center of the sample and at the wall of the oven (Figure 2.3).

Figure 2.3. U.N. Recommended Test Apparatus in McGill University

The test initiates as the oven is set to 140°C for 24 hours. During the test period, the temperature of the sample and oven are logged in the DAQ system. If the temperature of the sample surpasses the temperature of the oven by 60°C within the 24 hour period, the sample obtains a positive result. A positive result indicates that the sample is liable to spontaneous combustion, which gets classified in Packing group I, II, or III. If a negative result is obtained, then the sample is not considered dangerous and does not get classified as Division 4.2. If a positive result is obtained, then the sample with identical characteristics gets tested inside a 25mm^3 metal mesh basket at 140°C for 24hours with a sample thermocouple configuration. During 24 hours, if the temperature of the sample increases beyond 60°C of the temperature of the oven, the sample will be classified to Packing Group II. If a negative result is obtained for 25mm^3 basket test, the sample is classified as Packing Group III. A schematic drawing of this process is shown below (Figure 2.4).

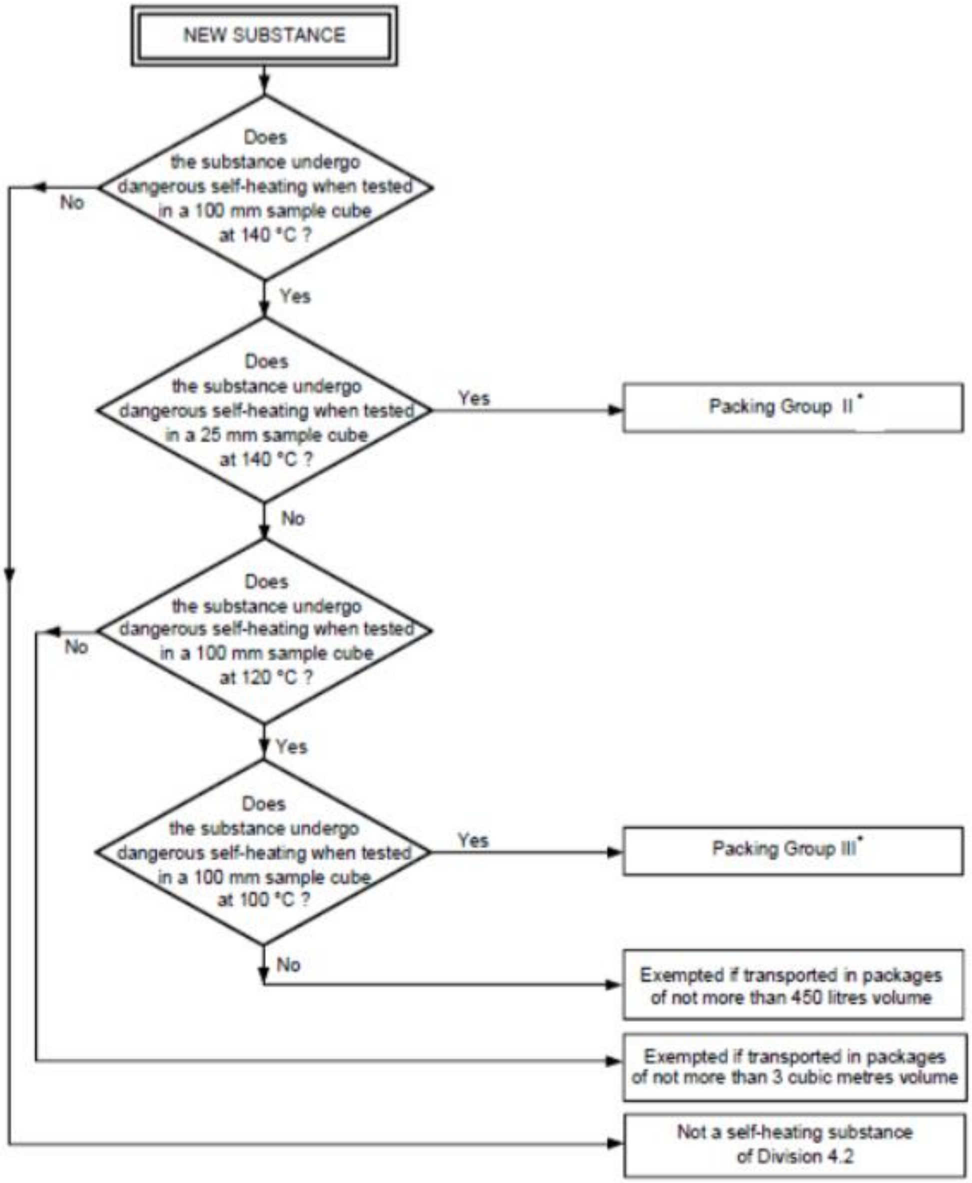

Figure 2.4. United Nations Schematic Diagram for Division 4.2

2.4. Self-heating Measurement (FR-Test)

Self-heating of sulphides are quantified and presented as the self-heating rate (SHR), the temperature rise within a sample per unit time (i.e. °C/h), and as the self-heating capacity (SHC), energy release per unit mass (i.e. J/g) (Somot and Finch, 2006).

The SHR is derived from the slope of the temperature curve during the time when the sulphide sample is in contact with air. When the heating response of a sample is detected, the slope of the temperature vs time graph is added and then averaged out throughout the 7 minutes while the self-heating of the sample has reached its optimum. SHR is computed automatically by the SH software (Rosenblum, Nesset and Spira, 2001). The temperature slope after certain period of self-heating minutes is not considered in the calculation due to rising temperature of the sample, which leads to increasing rate of heat being dissipated to the surroundings. The increasing rate of heat dissipation is known to reduce the actual self-heating rate leading to an under-evaluation of the self-heating behavior of the material.

The SHC is calculated from the sum of all the SHRs that occur in each stage of the self-heating (i.e. SHC_A from SHR_A and SHC_B from SHR_B). The SHC calculation is shown in Equation (2.1)

$$SHC_i = \Sigma SHR_i \cdot Cp \cdot t \qquad (2.1)$$

where:
SHC_i = Self-heating capacity of the corresponding stage
Cp = Specific heat of the sulphide mixture
t = Air injection period

The specific heat for sulphides found in nature ranges from 0.5 to 0.7 $\frac{\mathrm{J}}{\mathrm{g°C}}$ over the temperature range of 25°C to 500°C (Pankratz et al., 1984). Sulphides that are found in nature have compositions that vary from location to location. Due to the wide range of composition of sulphide mixtures, the specific heat have been chosen as the middle value of 0.6 $\frac{\mathrm{J}}{\mathrm{g°C}}$ to simplify the equation. The air injection period has been set to 15 minutes for each injection cycle as the standard test parameter. Equation 2.1 can be simplified to Equation 2.2:

$$SHC_i = 0.6\left(\frac{J}{g°C}\right) \cdot 0.25\mathrm{hr} \cdot \Sigma SHR_i = 0.15 \cdot \Sigma SHR_i \qquad (2.2)$$

Table 2.3 –Self-heating data Stage ASHR and SHC values for common sulphide concentrates (Rosenblum et al., 2001).

Concentrate	SHR_A (°C/h)	SHR_B (°C/h)	SHC_A (J/g)	SHC_B (J/g)
Cu-conc.	<0.3 - 17.3	<0.3 - 29	<0.1 - 21.9	<0.1 – 56.9
Ni-conc.	33.2 - 45.2	44.1 - 159.0	44.4 – 60.5	6.62 – 41.4
Pb-conc.	0.6 – 8.1	2.9 – 11.3	0.26 – 10.6	0.48 – 13.5
Zn-conc.	0.8 – 5.8	0.7 – 10.5	0.11 - 5.25	0.29 – 4.46

2.5. Weathering and Oxidation reactions

Conventional self-heating tests were mainly focused on materials such as coal, wood chip and powdered milk. However, it is essential to consider self-heating of sulphides independently from the other self-heating materials that have invariable self-heating behaviour. Sulphides have the tendency to increase in self-heating activity over time as they are constantly exposed to oxidization in nature (Ninteman, D. J.,1978). Environmental aspects such as humidity, moisture content, oxygen uptake rate and ambient temperature help the formation of elemental sulphur and affect the self-heating reactivity of sulphides over time (Rosenblum, Nesset & Finch, 2014). This process is also known as weathering (Somot and Finch, 2006).

2.5.1. Effect of weathering

Weathering process describes any incidence where a sulphides undergo an oxidation reaction from exposure to moisture, humidity, and oxygen. Ambient temperatures, and duration of exposure are other factors that are known to affect weathering of sulphides. Wang (2007) developed a weathering test by setting up weathering chamber. The chamber consists of polypropylene filter, copper piece, reaction vessel, and a rack as shown in Figure 2.5.

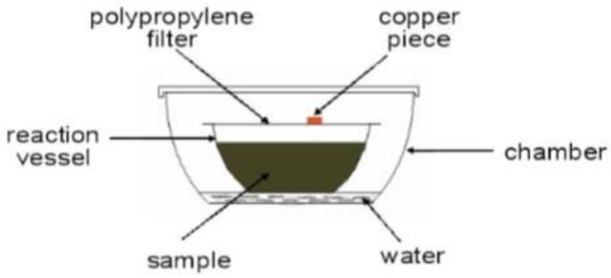

Figure 2.5. Weathering test setup developed by Wang at el. (2007)

Rosenblum and Spira (1995) designed the FR-Test apparatus such that the Stage A test can weather the samples by injecting air for 15 minutes periodically for a set point duration. Stage A is also known as a simulated weathering stage. Table 2.4 shows the standard weathering test conditions for the FR-Test Apparatus.

Table 2.4 – Weathering test parameter

Sample Mass (g)	500
Temperature (ºC)	70
Number of Air injection Cycles	10
Duration of air injection (min)	15
Rest period between each air injection (h)	5
Air Flowrate (mL/min)	100

Figure 2.6 shows an example of the changes in the elemental sulphur (S°) content of a pyrrhotite-rich tailing with progressive weathering in the FR-Apparatus at various temperatures (Park, 2013). The quantitative analysis shows that there is not a significant amount of elemental sulphur inside the sample at 10 cycles (<1 wt%). With 40 weathering cycles, the elemental sulphur content inside the sample increased by twofold (>1 wt%).

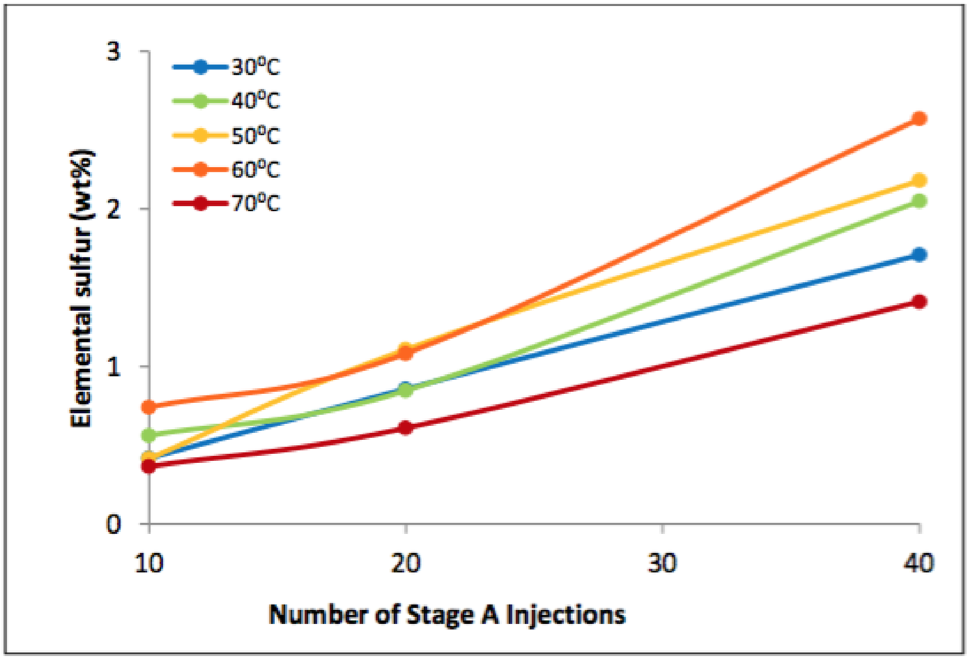

Figure 2.6. Elemental Sulphur Formation as a Function of Number of Stage A Injections, Sudbury Sample (Park, 2013)

Elemental sulphur produced from the weathering stage is known to react as a fuel in Stage B. Figure 2.7 shows elemental sulphur that was produced from weathering in FR-Apparatus for 10 cycles under standard test conditions.

Figure 2.7. Elemental sulphur build up after 10 weathering cycles

2.5.2. Self-Heating Reactions and Reaction Products

A number of exothermic reactions have been proposed for metal sulphides, mainly for FeS_2 and Fe_7S_8 (Rosenblum and Spira, 2001; Li, 2007; Wu & Meng, 1995; Gu & Li, 2006; Yang, Wu and Li, 2011).

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4;\ \Delta H = -2558.4\ KJ \tag{2.1}$$

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8H_2SO_4;\ \Delta H = -5092\ KJ \tag{2.2}$$

$$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + H_2SO_4; \Delta H = -5740.5KJ \tag{2.3}$$

$$2Fe_7S_8 + 31O_2 + 2H_2O \rightarrow 14FeSO_4 + 2H_2SO_4; \Delta H = -12590KJ \tag{2.4}$$

$$2FeS + 8H_2O + O_2 \rightarrow FeSO_4{\cdot}H_2O + FeSO_4{\cdot}7H_2O; \Delta H = -1771.3KJ \tag{2.5}$$

$$12FeSO_4 + 6H_2O + 3O_2 \rightarrow 4Fe_2(SO_4)_3 + 4Fe(OH)_3;\ \Delta H = -762KJ \tag{2.6}$$

The predominant reaction for Stage A is shown in Equation (2.7).

$$4FeS + 3O_2 + 2H_2O \rightarrow 4FeO{\cdot}OH + 4S \tag{2.7}$$

The predominant reaction for Stage B is shown in Equation (2.8).

$$S^0 + O_2 \rightarrow SO_2 \tag{2.8}$$

There is no predominant reaction for Stage C as it is a combustion stage where all the unreacted sulphide combusts.

However, even to this day, the reactions that initiate self-heating at low ambient temperatures are still not fully understood (Good, 1977; Rosenblum, Spira and Konigsmann 1982; Rosenblum and Spira, 1995). Past studies have shown that from on-site observations, self-heating products include: ferrous and ferric sulphates and hydroxysulphates, ferric oxides and hydroxides, sulphuric and sulphurous acids and elemental sulphur (Good, 1977). Other studies have proposed electrochemical reactions guiding self-heating of sulphides (Payant, Rosenblum, Nesset and Finch, 2012). Oxidation reactions of sulphides are known to be caused by oxidants such as dissolved oxygen and Fe^{3+} (Somot & Finch, 2010). In Stage A, the hydrolysis of iron species, formation of water soluble iron sulphate (Good, 1977; Steger, 1982) and heat of hydration

(Rosenblum and Spira, 1995) were proposed to be the cause of self-heating. Studies have also shown a strong relationship between self-heating activity and the formation of elemental sulphur (Good 1977; Rosenblum and Spira 1993, 1995; Rosenblum et al., 2001). Somot and Finch (2010) proposed that hydrogen disulphide, which is produced by the Stage A self-heating reactions, did not affect self-heating of sulphides directly. Products for pyrrhotite self-heating reactions were goethite, hematite and sulphur. Sulphur dioxide (SO_2) formation was noticed around 100°C and the evolution of SO_2 showed linear correlation with the self-heating rate (Rosenblum and Spira, 1995).

2.6. Factors contributing to Sulphide Self-Heating

Numerous factors account for sulphides to become self-heating in nature. Some of the major factors include: humidity of the atmosphere, moisture content, oxygen uptake, particle size, pyrrhotite content, ambient temperature and pH. Each factor contributing to self-heating is irrelevant from one and another and that is what makes the self-heating process very interesting and complex.

2.6.1. Humidity & Moisture content

Humidity and moisture content inside sulphide essential for the oxidization process, where water is a key reactant in the reaction below 100°C. However, these two factors must not be considered as one factor. Moisture content indicates how much water is initially contained per unit mass of the sample. The actual moisture content of the material continuously changes as H_2O is consumed in an oxidative environment as reactants and by evaporation from wind and heat. Certain levels of humidity are known to promote self-heating reaction of sulphides (Habashi, 1966; Tributsch and Gerischer, 1976). Humidity introduces water to sulphides in a vaporized form from the surroundings, allowing the sulphide to be moist even during a temperature increase, which tends to evaporate moisture inside the sample. Once the moisture inside the sample decreases to a certain level, humidity acts as a buffer to sustain the water content inside to a new equilibrium. Even when the sample temperature is elevated to near boiling point of water, humidity supplies water to the system allowing sulphides to self-heat. Past studies have shown that moisture content plays an important role during the first few hours of the test and then humidity of surrounding governs the drive force to sustain the oxidation reaction in stage A

(Jung, 2012).

Figure 2.8 shows the self-heating rate and O_2 consumption rate of the sample with respect to the weight % moisture of the sample ranging from 0 to 26%. Studies have shown that when sulphides are dry (0 wt% moisture content), the sample does not show any self-heating behaviour. As % moisture increases to 4%, self-heating reaches optimum condition and decreases linearly as moisture increase. Below moisture content of 3wt%, there is not enough water in the system from the oxidation reaction to occur effectively and moisture is a limiting factor in the reaction. At moisture content of 3 to 8 wt%, water is no longer a limiting factor and the maximum self-heating rate is observed. After this point, self-heating rate decreases even though %moisture increases as the moisture works as a buffer to take away the heat that is generated from the sample. In other words, the energy released is used to raise the temperature of the excess water in the system rather than raising the temperature of the sample. Therefore, the application of excess water can be used as a mitigation method also known as “water flooding” (Ninteman, 1978).

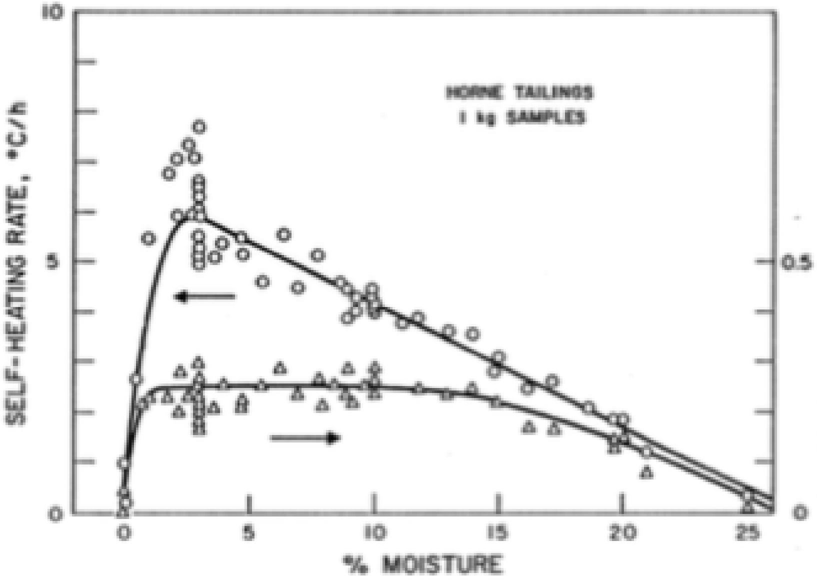

Figure 2.8. Self-heating rate and O2 Consumption rate with respect to % moisture content of sulphide mixture (Rosenblum and Spira, 1981)

2.6.2. Oxygen Uptake Rate

Self-heating oxidative reaction requires oxygen as a reactant. Figure 2.9 shows a linear correlation between self-heating rate with respect to oxygen uptake

Due to their linear relationship, the self-heating rate can be reduced by reducing the oxygen uptake rate to sulphides. However, oxygen is abundant in nature and it is often not a limiting factor in the reaction unless considering the sulphides inside underground mines.

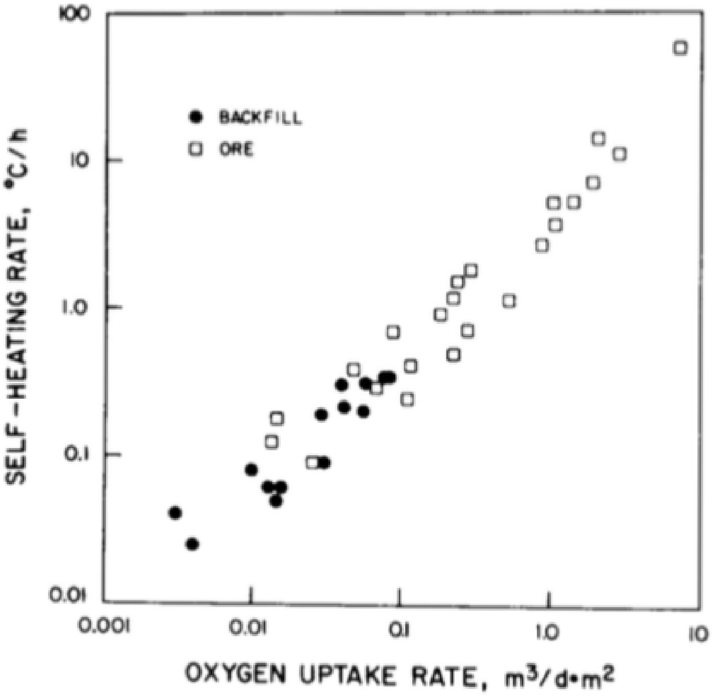

Figure 2.9. Correlation of self-heating rate with respect to oxygen uptake rate (Rosenblum & Spira, 1982)

2.6.3. Particle Size & Surface Area

It has been well documented that with finer particles, the total surface area increases in an equal mass of solid. Greater surface area indicates that there are more space for reactions to occur. Similarly, researchers have determined that the finer the sulphides, the more aggressive self-heating activities were observed (Good, 1977) and self-heating rates were observed to have a positive correlation with decreasing particle size. Figure 2.10 shows the effect of particles size on the self-heating rate (Rosenblum and Spira, 1995). Studies have shown that -44um particles exhibited self-heating rate of twofold strength compared to particles with +44um (Rosenblum and Spira, 1981).

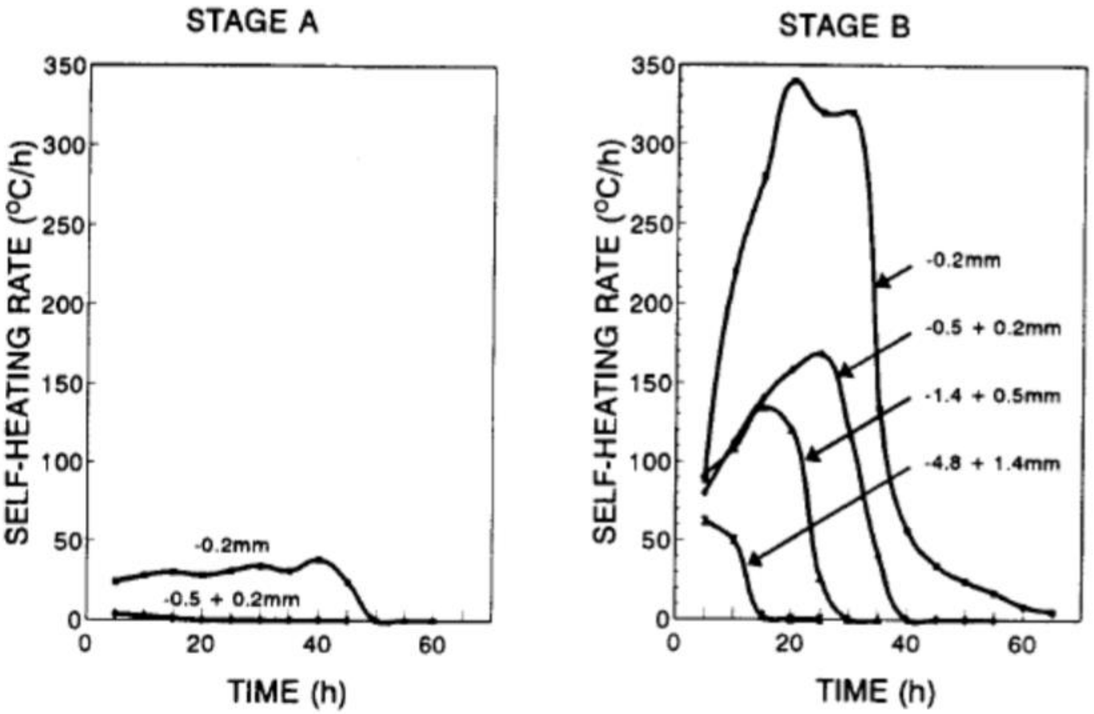

Figure 2.10. Self-heating rate with respect to various particle size (Rosenblum and Spira, 1995)

2.6.4. Pyrrhotite

High self-heating rates were observed for materials with the materials having pyrrhotite content of 10wt% or more. (Somot and Finch, 2010). Pyrrhotite containing mixture showed greater self-heating response due to decreased activation energy (Janzen, Nicholson and Scharer, 2000).

2.6.5. Elemental Sulphur

Researchers have shown that the amount of elemental sulphur correlated well with the self-heating in Stage B to a certain limit. Self-heating in Stage B was found to last until the elemental sulphur was fully exhausted. However, cumulative elemental sulphur content was directly proportional to the amount of heat released in the sample, especially with the samples that had been excessively weathered. Excessive weathering leads to the formation of impurities on the surface of the sulphide and reduces self-heating reactions, which are surface reactions.

It has been proposed that elemental sulphur is formed by reactions between ferric oxide and sulphuric acid or from the reaction between pyrrhotite and ferric sulphate (Steger, 1982; Janzen et al., 2000; Gunsinger et al., 2006). Steger and Dejardins (1978) showed pyrrhotite, at low temperatures oxidized to elemental sulphur, sulphate, thiosulphate and sulphur dioxide as shown in Equations 2.9 to 2.11 (Good, 1977; Gunsinger et al., 2006).

$$S + \frac{3}{2}O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \tag{2.9}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{2.10}$$

$$2SO_2 + 2H_2O + O_2 \rightarrow 2H_2SO_4 \tag{2.11}$$

In 2000, Janzen et al. suggested that 80 to 86% of the elemental sulphur was formed due to the oxidization of sulphur, especially due to oxidation involving ferric iron. Goethite and iron sulphates were also reported as byproducts of self-heating reaction.

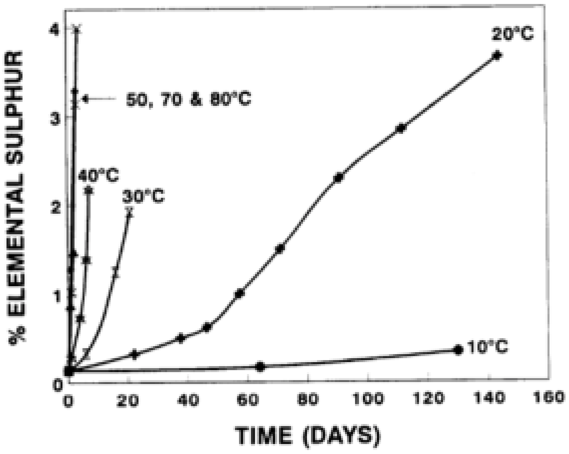

Figure 2.11. Elemental sulphur formation (wt%) versus weathering duration (Rosenblum & Spira, 1982)

2.6.6. Temperature

Researchers have shown that elevated temperatures promote self-heating reactions leading to higher self-heating rates (Rosenblum and Spira, 1995). Studies have shown that sulphide samples do not heat below standard room temperature. With increasing temperatures, the atoms collide with stronger impacts and therefore react. Increase in ambient temperatures also support oxygen diffusion and increase in humidity (Steger, 1982).

2.6.7. pH and Ionization

As discussed in section 2.5.2, self-heating reactions of sulphides are initiated by the ionization of Fe3+ and dissolved oxygen in presence of moisture. Studies have shown that Fe3+ acts as the primary oxidizing agent (Tributsch and Gerischer, 1976). An example of pyrrhotite reaction rate with respect to ferric iron concentration is as shown in Figure 2.12. Reaction rate correlated well with ferric iron concentration with R2 value of 0.9974.

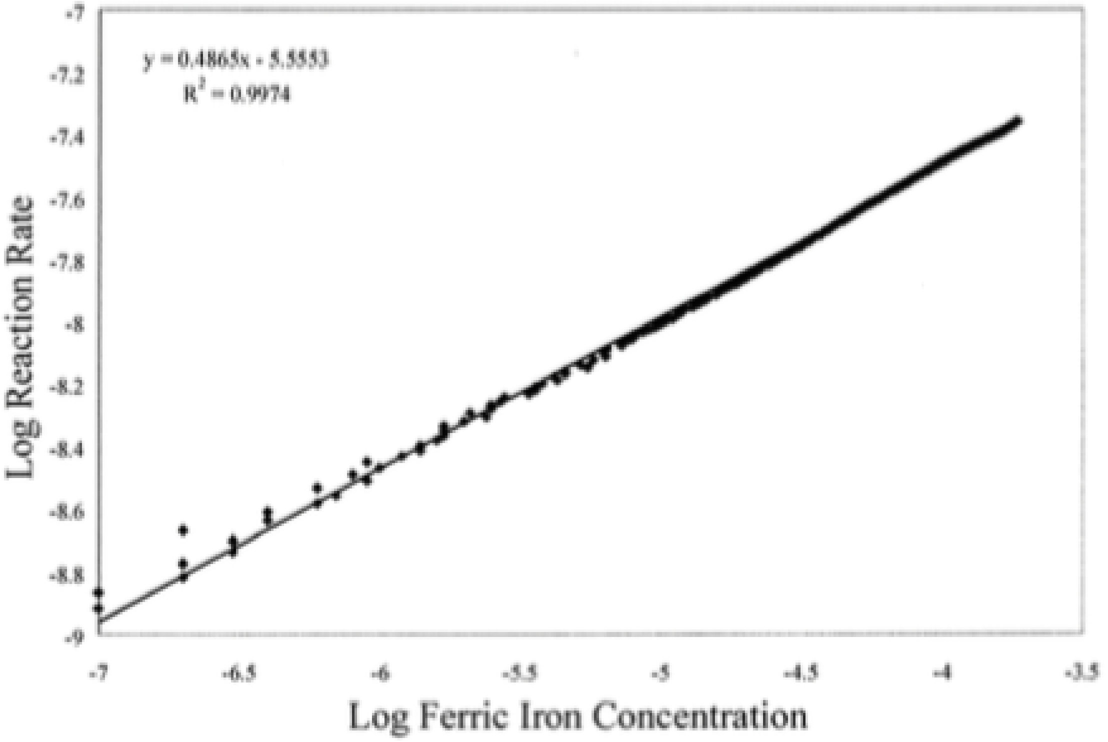

Figure 2.12. Pyrrhotite reaction rate versus ferric iron concentration (Rosenblum et al., 1982)

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Chapter 3. Evaluation of the U.N. Self-heating Test for Sulphides

3.1. Introduction

3.1.1. Self-heating

Self-heating occurs when exothermic reactions produce heat faster than can be dissipated to the surroundings. Numerous substances self-heat, ranging from wood chips and powdered milk to coal and sulphide minerals (Beever & Crowhurst, 1989; Hudak, 2002). Mixtures of sulphide minerals, most notably those containing the iron sulphide pyrrhotite ($Fe_{(1-x)}S$), commonly encountered in the extraction of base metals (e.g., copper, zinc, lead, and nickel), are particularly prone to self-heating (Rosenblum, Nesset and Spira, 2001; Payant, Rosenblum, Nesset and Finch, 2012). In the mining and subsequent processing stages, the minerals are progressively liberated and finely ground, then separated, usually by flotation, with the resulting concentrates stored and transported to smelters for metal extraction. At most of these stages the sulphides are exposed to both moisture and oxygen, conditions that promote partial sulphide oxidation and the formation of elemental sulphur. Studies have shown that pyrrhotite, in particular, readily oxidizes to form elemental sulphur (Bernier & Li, 2003; Belzile et al., 2004; Somot & Finch, 2010). The elemental sulphur becomes fuel for further self-heating as the temperature of the mineral mixture increases above 100 ^{o}C (Rosenblum & Spira, 1995; Somot & Finch, 2010). It is believed the propensity of pyrrhotite to self-heat is a result of its iron-deficient, and hence somewhat unstable structure. It is worth noting that pure metal sulphides (with the exception of pyrrhotite) do not exhibit appreciable self-heating. A mixture of minerals sufficiently different in their electrochemical rest potential is required to initiate self-heating at ambient temperatures (Payant, Rosenblum, Nesset and Finch, 2012).

The self-heating of sulphides leads to formation of "hot spots" (Rosenblum et al., 2001; Beamish, 2005) within storage piles. The initiation of these oxidation reactions at ambient conditions is not fully understood (Good 1977; Rosenblum et al. 1982; Somot & Finch, 2010). What is known is that continued exposure to moisture and oxygen (air) will change the reactivity of sulphide mixtures (Rosenblum & Spira, 1995). If uncontrolled and without sufficient heat dissipation, heating reactions may lead to such hazards as generation of toxic gases, notably dihydrogen sulphide (H_2S) and sulphur dioxide (SO_2), depletion of oxygen if in a contained environment, and even fires as temperatures rise (Farnsworth and Duties, 1977; Ninteman, 1978; Rosenblum et al., 1982; Rosenblum et al., 2001). Notable examples include sinking of the N.Y.K. liner Boyko Maru in 1939, attributed to self-heating of the copper concentrate being carried (Kirshenbaum, 1968), and in-situ "smelting" of lead ore at the Sullivan mine (O'Brien & Banks, 1926). Less dramatic outcomes are the degradation of the quality of the mineral concentrates (due to accumulated oxidation products) that can result in higher treatment costs and even the rejection of shipments by the smelter; detrimental impact of ore oxidation on flotation, and the unwanted oxidation of mine paste-fill made with sulphide tailings (Bernier & Li, 2003).

3.1.2 Self-heating tests

Several self-heating risk assessment methods have been developed, among them: the U.N (recommended) test (U.N., 2015), The Noranda FR-2 test (Rosenblum & Spira, 1995), Crossing Point test (Chen &Chong, 1995), Mahadevan – Ramlu Heat Release test (Nelson & Chen, 2007), and the Wits-Ehac test (Gouws, 1987). Most of these methods evaluate a sample based on the assumption that the material is invariant, that is, there is no effect of ageing on the reactivity of the sample, i.e. that a fresh sample will react the same way as a sample exposed to air and moisture for a period of time. This assumption can lead to errors, in particular false negatives, when evaluating un-oxidised (fresh) samples that do not represent the true reactivity of oxidized (weathered) materials.

The U.N. test (Bouffard & Senior, 2011; United Nations, 2015), which assumes no ageing effect, is widely applied to assess risk when transporting goods. It is important, therefore, to assess its applicability for the case of sulphide mixtures. The FR test, developed specifically for sulphides (Rosenblum et al., 1982; 1995) explicitly incorporates an ageing/oxidation stage in the test procedure. It measures heating rate (^oC/min) and self-heating capacity (SHC, J/g)in two stages over an extended period of time (~50 hours); Stage A is an accelerated weathering stage at 70^oC in the presence of both moisture and air, while Stage B is conducted at 140 ^oC and also measures the effect of the oxidation (weathering) produced in Stage A. Results are reported in terms of self-heating capacity (J/g) for Stages A and B and are plotted on a *risk assessment chart* of Stage A versus Stage B (Rosenblum et al., 2001).

This paper compares outcomes of the U.N. and FR tests for two cases of sulphide mixtures; a nickel (pentlandite, pyrrhotite) concentrate and a copper-lead-zinc (chalcopyrite, galena, sphalerite, pyrite) ore A previous publication (Rosenblum et al., 2014) reviewed the key role of sample oxidation for various testing methodologies, including the U.N. test.

3.2. Experimental Methodologies

3.2.1. Samples

Samples of a massive sulphide chalcopyrite-lead-zinc-pyrite ore (rod mill discharge, RMD) from Glencore's Brunswick Mine (New Brunswick, Canada), and a pentlandite-pyrrhotite nickel concentrate (Ni Con) from the Glencore Raglan Mine (Quebec, Canada) were used as test materials. The samples were ground at the mine site to ~75μm passing 80% and shipped wet to McGill University in airtight containers. Upon receipt, the samples were dewatered by pressure filtration and dried on flat trays in a convection oven for 5 hours at 40°C until bone-dry. The samples were well-mixed and divided by rotary splitter into 500g lots and stored in airtight poly bags and stored in a freezer. This procedure is the established protocol for minimizing sample oxidation.

3.2.2. Self-Heating Apparatus

U.N. Recommended Test

For the U.N. recommended test, also known as the *Self-Heating Substances Test*, the setup consists of (Figure 3.1): hot-air circulating convection oven with inner volume greater than 9L; 100mm x 100mm x 100mm open-topped stainless steel cubic mesh basket with mesh opening of 0.05mm; thermocouples; and data acquisition system (U.N. 2015). In this work, the cubic mesh basket was replaced by a cylindrical basket having equivalent volume. A cylindrical basket has the advantage of a uniform distance from the centre to the outer surface of the sample allowing the heat to dissipate evenly in the horizontal plane. This modification reduced temperature variations resulting from "cold spots" detected at the corners of the cubic basket. One thermocouple was placed in the centre of the sample and a second in the oven wall, exposed to the air but not touching the surface of the oven.

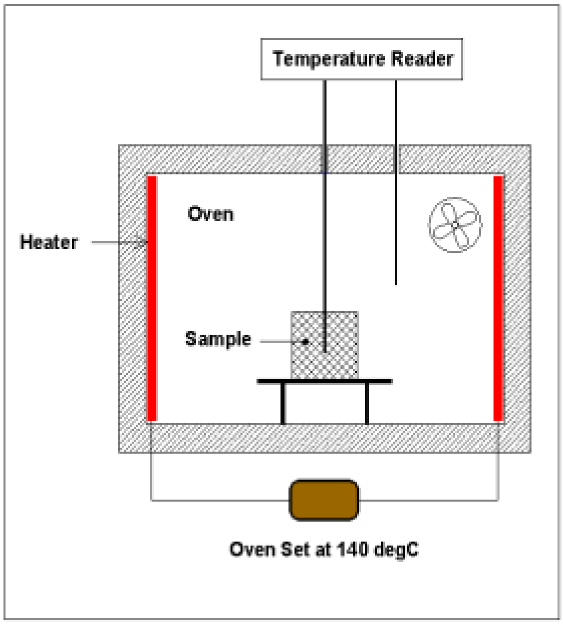

Figure 3.1. Apparatus for U.N. Recommended Self-heating test (Rosenblum et al., 2014).

<u>FR Test</u>

The FR setup (Figure 3.2) consists of: 2L Pyrex glass cell with screen to support the 500g powdered sample; an insulating cylinder; a coiled heater surrounding the cell; thermocouples; and gas inlet and exhaust systems (Rosenblum & Spira, 1995).

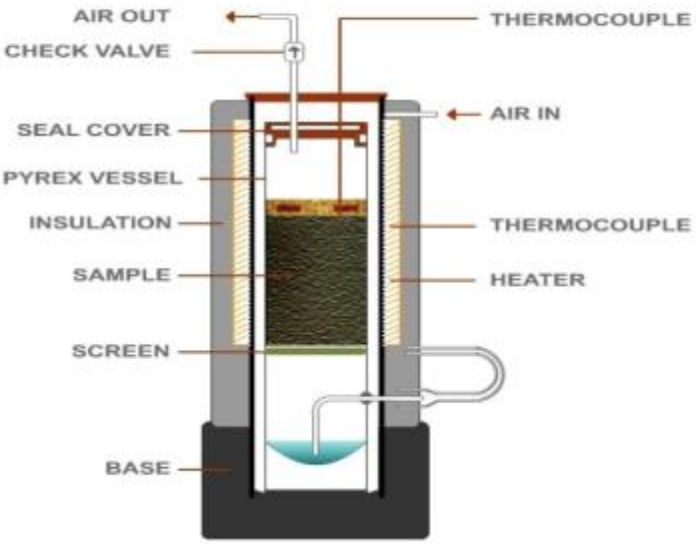

Figure 3.2. FR self-heating apparatus developed by Rosenblum and Spira (1995)

3.2.3. Standard Test Procedure and Data Interpretation

U.N. Test

The standard tests were performed according to the procedure described in the Manual of Tests and Criteria, Part III, sub-section 33.3.1.4, published by United Nations. A 1Kg powdered sample was places inside a 4in cylinder (5in high) mesh basket and placed in the oven set at 140°C for 24 hours. The temperature of the sample and the oven were continuously logged over this period and presented as a thermogram (temperature versus time). If the sample temperature exceeds the oven temperature by 60°C (i.e., exceeds 200°C) within the first 24 hours, the result is "positive", that is, the sample is judged to pose self-heating risk (Division 4.2 category from the U.N. manual).

FR Test

The standard test followed the procedure described by Rosenblum and Spira (1995). 500g of powdered dry sample was moistened to 6wt% with (reverse osmosis) purified water and placed on top of the stainless steel mesh screen in the Pyrex cell. The test consists of two stages. In Stage A, the sample temperature was controlled at 70°C, and 100 mL/min of air was injected through the cell for 15 minutes every 5 hours for a total of 10 cycles. (One air injection and rest period is referred to as a “cycle”.) At the end of Stage A, vacuum was applied for 30s to remove excess water (draining from the moist sample) from the bottom of the cell. To initiate Stage B, the temperature of the sample was first raised to 140°C while continuously passing nitrogen at 250mL/min through the cell (Note. The nitrogen prevents the sample from reacting with oxygen during temperature elevation and aids in further drying the sample). Once at temperature (140 ^{o}C), 250mL/min of air was injected for 15 minutes every 5 hours. The cycles were repeated until no more heating was observed. The sample temperature versus time response (thermogram) was logged for both low and high temperature cycles. Reactive samples will exhibit a temperature rise with air injections and from which self-heating rates (SHR, temperature rise per unit time) were determined at each air injection. From the sum o the SHR values a self-heating capacity (SHC) for each stage was calculated according to:

$$\mathrm{SHC} = \sum_{i=1}^{n} (\mathrm{SHR_i} \cdot \mathrm{Specific\ Heat_{sample}} \cdot \mathrm{Air\ injection\ time}) \qquad (1)$$

where *i* represents the individual air injection cycle and *n* represents the total number of cycles in a stage.

To assess risk the Stage A SHC is plotted versus Stage B SHC on a log-log basis, called the risk assessment chart (Figure 3.3). The chart classifies material into five regions: (1) safe, (2) will not heat beyond 100°C, (3) do not expose to a high heat source, (4) monitoring recommended, and (5) preventive action recommended. The regions of the chart were developed from field experience with a large number of sulphide materials (Rosenblum et al., 2001). Region 5 represents the highest potential risk for self-heating and occurs where Stage A SHC and Stage B SHC are both > 5 J/g.

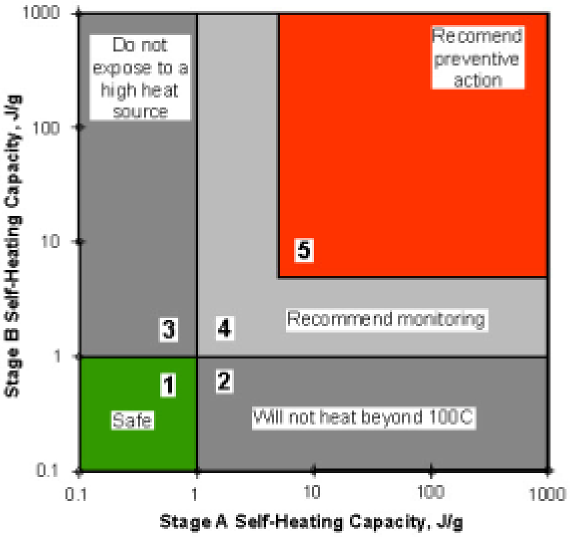

Figure 3.3. Risk Assessment Chart for plotting SHC in Stage A versus Stage B and showing five regions of risk (Rosenblum et al., 2001)

3.2.4. Weathered Sample Test

To simulate the effect of increasing amounts of weathering on self-heating reactivity, samples were subjected to Stage A conditions only (6% moisture and 70^{o}C) for 5, 10 and 15 cycles in the FR apparatus. The samples were then divided into 1.5kg and 500g lots for testing in the U.N and FR apparatus respectively.

3.2.5. Sulphur Determination

Using the carbon disulphide method of Steger (1976) for the determination of elemental sulphur, the amount of elemental sulphur generated from increased sample weathering (described above) was determined. Figure 3.4a clearly shows the elemental sulphur formed from a sample after one of these weathering test. Before the test, the samples are dried using a vacuum oven to prevent further oxidation. When samples are completely dry, 5 grams of representative samples are placed in 100mL beakers. The beakers are placed in a fume hood and 20mL of carbon disulphide is added to each beaker. After sitting the mixture for 15 minutes, the beakers are then placed in a vibrator and stirred for 10 minutes. The mixture is then filtered to a beaker while applying 2-3 mL of additional carbon disulphide to the funnel to dissolve the excess elemental sulphur residue.

Then the carbon disulphide is evaporated using a directed airflow. The remaining solids as shown in Figure 3.4b (elemental sulphur) are weighed and recorded. Elemental sulphur formation is believed to be the key reaction during sulphide weathering that result in the self-heating reactions which occur in Stage B (Somot & Finch, 2010)

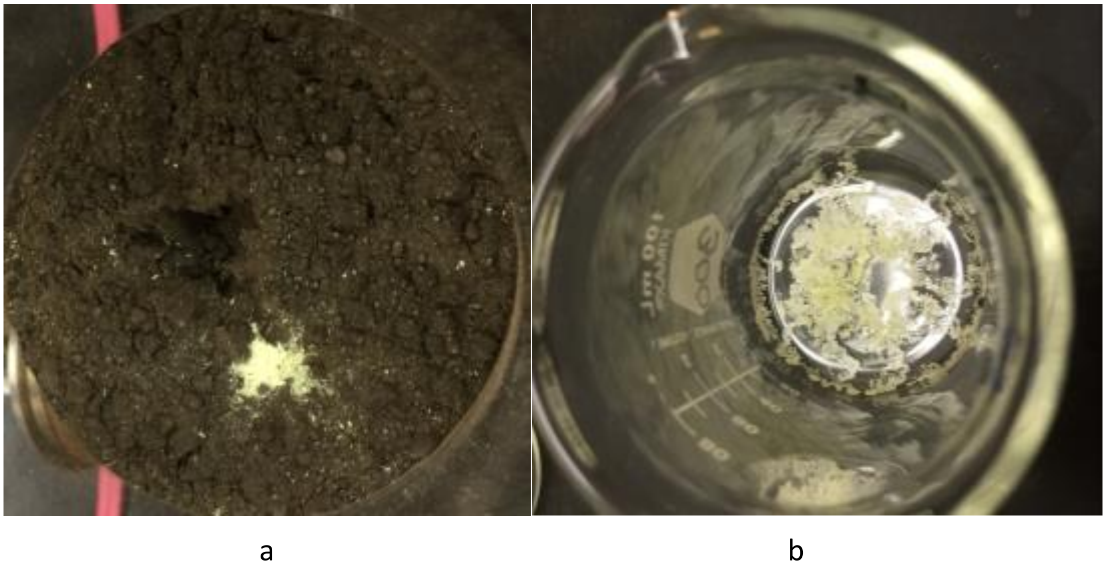

Figure 3.4. (a) Elemental sulphur formed after weathering RMD sample for 10 cycles (b) from sample analysis: remaining elemental sulphur from 5 grams of.

3.3 Results

3.3.1. Sample Thermograms

As-Received Samples

The U.N. test thermograms for the as received RMD and Ni Con samples are shown in Figure 3.5. The temperature of both samples increased beyond the ambient oven temperature of 140°C, indicating that the material self-heated to a limited extent. The maximum temperature, however, did not reach the threshold limit of 200°C. Based on this, the test results are negative and both samples would therefore be classified as *safe*, that is, materials that do not pose a hazardous self-heating risk.

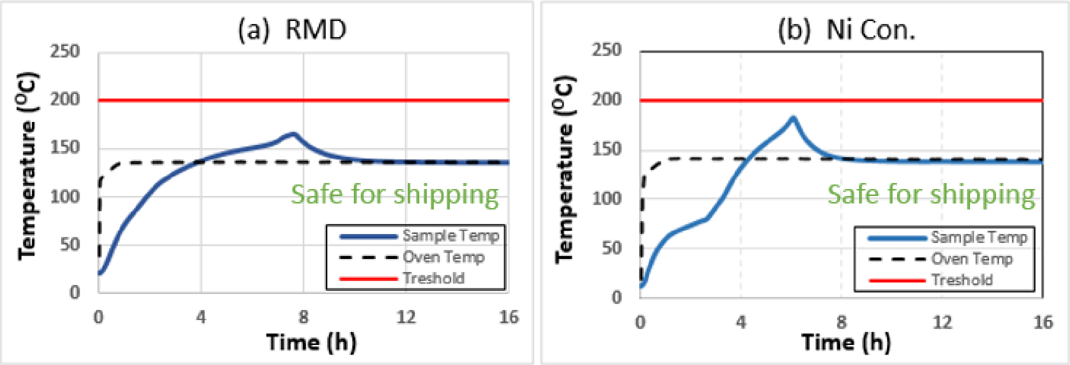

Figure 3.5. Thermograms for U.N. test for as-received samples: (a) RMD and (b) Ni Con

The standard self-heating test results for the as-received RMD and the Ni Con samples are presented in Figure 3.6. The Ni Con sample shows practically no self-heating in Stage A (0.4 J/g) however, it does exhibit extensive self-heating in Stage B (49.1 j/g). Based on the risk assessment chart, this material is classified as: *do not expose to high heat source* category. In contrast, the RMD sample exhibits high self-heating capacity in Stage A (51.4 J/g) and significant self-heating in Stage B (24.6 J/g). Based on the risk assessment chart this material falls in reagent 5 – *recommended preventive action* to mitigate the risk.

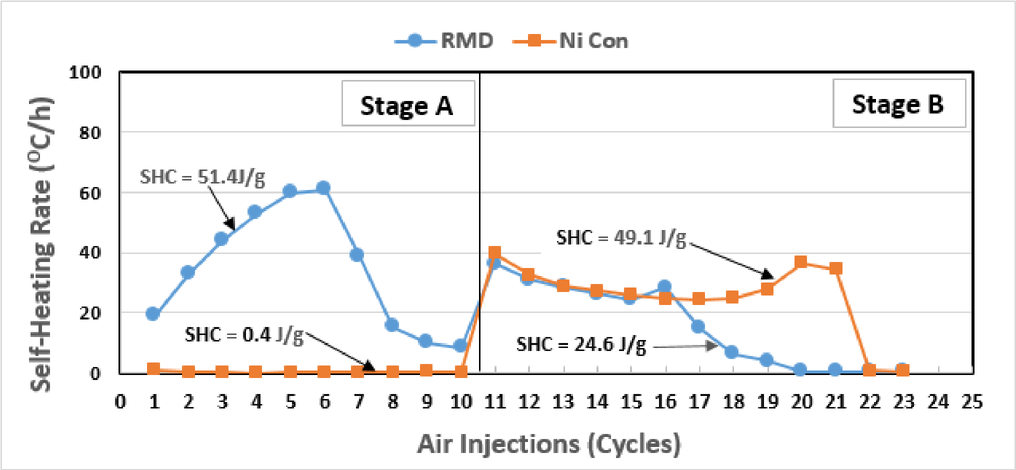

Figure 3.6. Standard test results for as-received samples of RMD and Cu Con, using the FR-2 apparatus

Weathered Samples

Figure 3.7 presents the U.N. test results for the as –received RMD sample, and after weathering for 5, 10 and 15 cycles. The sample weathered for 10 cycles (maximum temperature 229.2°C) and 15 (maximum temperature 227.3°C) cycles had temperature increases beyond the 200°C threshold, indicating this material would be classified as *positive*, that is, representing a significant self-heating risk. This contradicts the test finding for the un-weathered as-received sample (Figure 3.7a) of the same material.

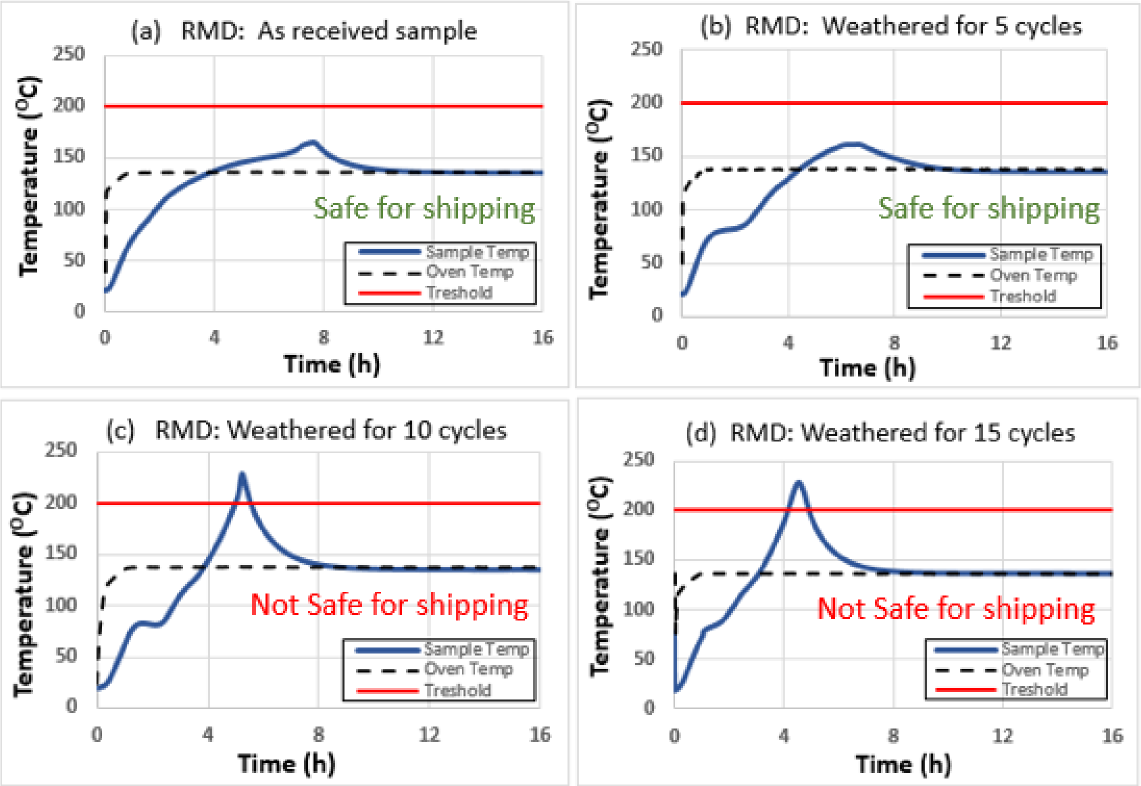

Figure 3.7. Thermograms for RMD for U.N. test: (a) As received, and weathered for (b) 5 cycles, (c) 10 cycles, and (d) 15 cycles.

The U.N. test results for Ni Con weathered for 5, 10 and 15 cycles compared to the as received sample are presented in Figure 3.8. With progressive weathering, the Ni Con showed increasing self-heating response (maximum temperature increased with increased cycles) and by 15 cycles, the material self-heating response became *positive* by exceeding the 200°C threshold (reaching maximum temperature 211.0°C). By increasing the amount of weathering the sample response changed to indicate a sample prone to self-heating and therefore a hazardous material.

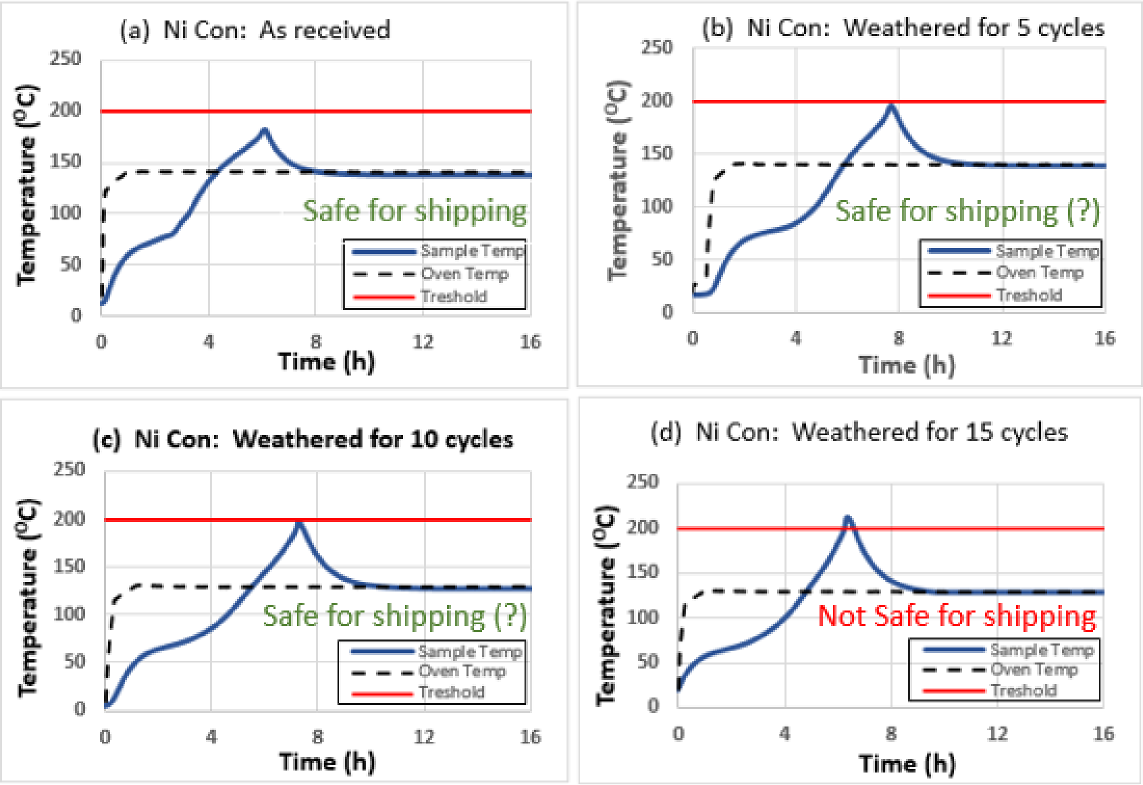

Figure 3.8. Thermograms for Ni Con for U.N. test: (a) tested as received, and weathered for (b) 5 cycles, (c) 10 cycles, and (d) 15 cycles.

The Stage B self-heating capacity (SHC) results for increased weathering (cycles) for RMD and Ni Con samples are presented in Figure 3.9. It is evident that increased weathering results in increased Stage B SHC for both the RMD and Ni Conc samples. Together, Figures 3.9 and 3.10 show the importance of accounting for weathering when testing the self-heating reactivity of sulphide materials.

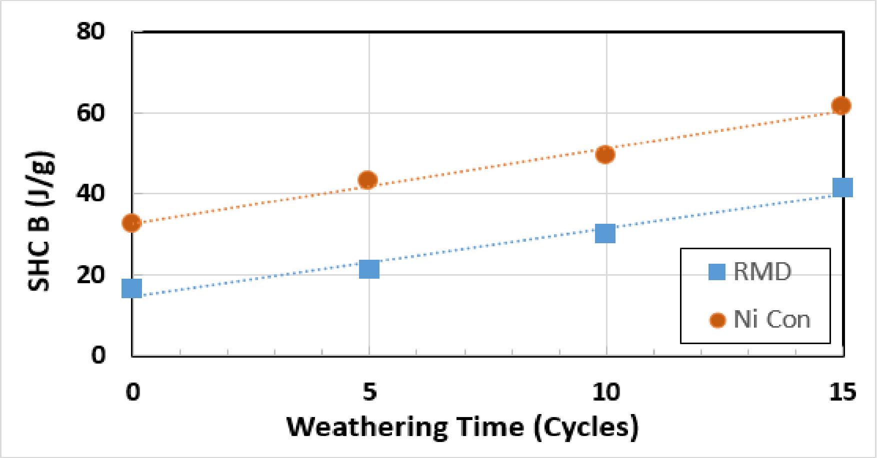

Figure 3.9. Self-heating capacity in Stage B (SHC B) for FR test as function of increasing number of weathering cycles

3.3.2. Elemental Sulphur

Elemental sulphur (S^o) analysis (Figure 3.11) showed that the as received Ni Conc contained a significant level of S^o (0.96wt %), while the RMD sample contained very little S^o (0.05w %). With progressive weathering (cycles) the amount of S^o increased for both; the RMD, increasing significantly reaching 1.80% S^o, and the Ni Conc more modestly, reaching 1.16% S^o. The increase in S^o with weathering also corresponds to the increase in maximum temperature (U.N. test) and Stage B SHC (FR test) as seen in Figure 3.9. The effect of increased weathering on S^o content and Stage B SHC has been noted in earlier publications (Rosenblum et al., 2014)

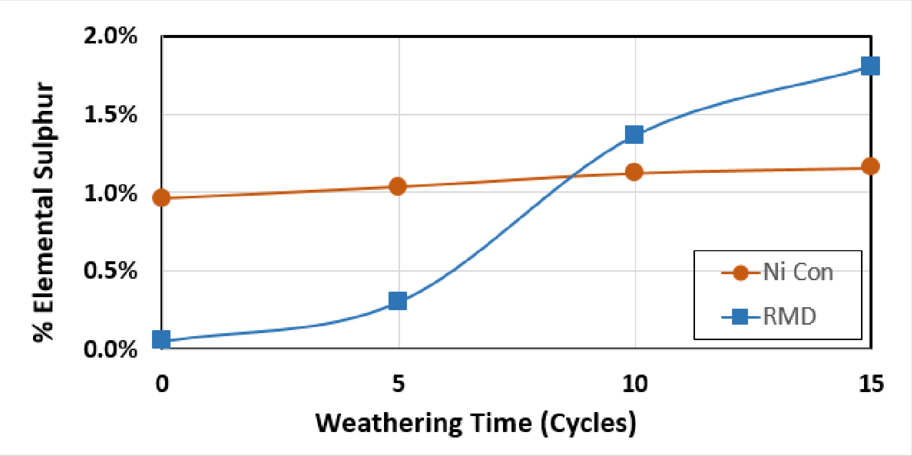

Figure 3.10. Elemental sulphur content with progressive weathering cycles: RMD, and Ni Con

3.4. Discussion

Both as received materials showed different responses for the standard U.N. test and the FR-2 test. The U.N. test resulted in a negative response (i.e., the samples were judged safe) whereas the FR-2 test, in contrast, suggested that both materials were potentially hazardous (recommending preventive action be taken). Clearly, the difference must lie in the test procedures. The U.N. test is a single stage test that does not allow for the effect of changes that may occur due to oxidation from ageing (i.e. weathering). On the other hand, the FR test is a two-stage test where the first stage (Stage A at 70ºC) is specifically designed to be an accelerated weathering stage, followed by a higher temperature stage (Stage B at 140ºC) that tests for the overall reactivity of the as received sample plus the weathering. In effect, the U.N. test only considers the Stage B equivalent of the FR test. This difference is clearly an important one as the U.N. test can result in *false negative* classification and incorrect conclusions concerning potential self-heating behaviour.

The samples tested here (RMD and Ni Con) have illustrated that some materials (in this case the RMD) may exhibit significant self-heating behaviour in both Stage A and Stage B; in other words, at both low temperature ambient conditions and at higher temperature (>100ºC) conditions. Such materials represent a higher risk for self-heating in the field since under the right conditions, heating can begin at low temperatures and progress to problems of heat and toxic gas evolution as temperatures exceed 100°C. The second sample (Ni Con) is representative of materials that pose little risk of temperature rise at ambient conditions, but that will self-heat aggressively if exposed to a high heat source such as an open flame, welding spark or overheated bearing. Since sulphides can be susceptible to oxidation, especially under conditions of extended storage/transportation times, high relative humidity and ambient temperatures exceeding 30°C, a test for self-heating must incorporate a procedure that reflects this behaviour.

The shortcoming of single stage tests such as the U.N. test, as highlighted by Figures 8 and 9, is that the resulting outcome can change depending on the previous history of the tested sample; in these examples the negative (safe) designation becomes a positive (hazardous) one depending on the number of weathering cycles (essentially the weathering time). The shortcoming of single stage testing for sulphides has been discussed at length in a previous publication evaluating test procedures (Rosenblum et al., 2014). Most available testing protocols were not designed specifically for sulphide materials, so the fault does not lie with the tests themselves but rather with their inappropriate application to sulphide mixtures.

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 dependent 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. The reactions are multiple and complex and a sequence of possible reactions leading to the formation of S^o have been proposed by Somot & Finch (2010). It is believed that the S^o formed during Stage A oxidation ultimately represents the "fuel" that reacts in the rapid heating and evolution of hazardous gases during Stage B. If a sample is progressively and increasingly oxidized under ambient conditions, its Stage A SHC may well decrease with the increased weathering while at the same time its Stage B SHC values increase as S^o increases. This has been observed with the shipment of nickel concentrate from Australia to North America, where samples were taken progressively over time during transportation. Ultimately, a fire in the shipped concentrate occurred in a storage shed near the end of the journey due to the increased level of S^o. A single stage test, like the U.N. test, on a fresh sample taken at the beginning of the journey would not have detected this risk and would have returned a safe classification, whereas a two stage test, like the FR test, would have rated the material as being hazardous allowing suitable precautions to have been taken.

3.5. Conclusions

It has been shown that the weathering of sulphide materials can intensify the self-heating response in standard test protocols such as the U.N. and FR test methods. Both the maximum temperature from the U.N. test and the Stage B SHC values from the FR test were increased by weathering for sulphide samples of ore (RMF) and nickel concentrate (Ni Con). The increased response of samples tested by both test methods correlates to an increase in concentration of elemental sulphur resulting from the increased weathering.

The shortcomings of the U.N. and similar single stage tests for assessing the self-heating risk of sulphide materials were demonstrated. This deficiency stems from the fact that a weathering (oxidation) stage is not incorporated into the test protocols, and as a consequence, such single stage tests can produce false negative results with respect to sample self-heating risk. It was shown that the two stage FR test does not suffer from this deficiency and is more appropriate for assessing the self-heating risk of sulphide materials.

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Chapter 4. Self-heating of Sulphides: Transition from stage A to Stage B

4.1. Introduction

4.1.1. Self-heating of Sulphide ores

Mixtures of sulphide minerals, most notably those containing the iron sulphide pyrrhotite ($Fe_{(1-x)}S$), commonly encountered in the extraction of base metals (e.g., copper, zinc, lead, and nickel), are particularly prone to self-heating (Rosenblum, Nesset and Spira, 2001; (Payant, Rosenblum, Nesset and Finch, 2012). Sulphides are exposed to oxidative conditions during mining and mineral processing. Natural oxidative conditions, such as moisture oxygen and elevated ambient temperature may potentially initiate exothermic oxidation reactions, which may lead to natural disasters (Good, 1977; Hamilton and Woods, 1981; Ninteman, 1978). Self-heating of sulphide occurs when exothermic reactions produce heat faster than can be dissipated to the surroundings (Semenov, 1935).

4.1.2. Background

The low temperature self-heating reactions in Stage A require oxygen and moisture in order to initiate the oxidation process (Ninteman, 1978; Rosenblum and Spira, 1995). Under specific conditions, sulphides transition into Stage B from A which is a dry reaction stage. The temperature transition from Stage A to B is uncertain; this experiment investigates the factors in which Stage A transition into Stage B.

As the temperature of sulphides approach the boiling temperature of water, the moisture inside the sample either evaporates or is consumed in the reaction (Jung, 2012). This lack of moisture inside the sample causes Stage A self-heating reactions to terminate before Stage B reactions start; however, it is apparent that Stage B and Stage C reactions naturally occur as shown in past self-heating accidents. The only way to reach Stage B and C is through self-heating of stage A, given that the ambient temperature is below 100°C.

Figure 4.1 illustrates a case where a sample transitions from Stage A to Stage B. On the boundary of Stage A and B, the heat being released is significantly reduced and temperature rise is minimized before Stage B reactions initiate.

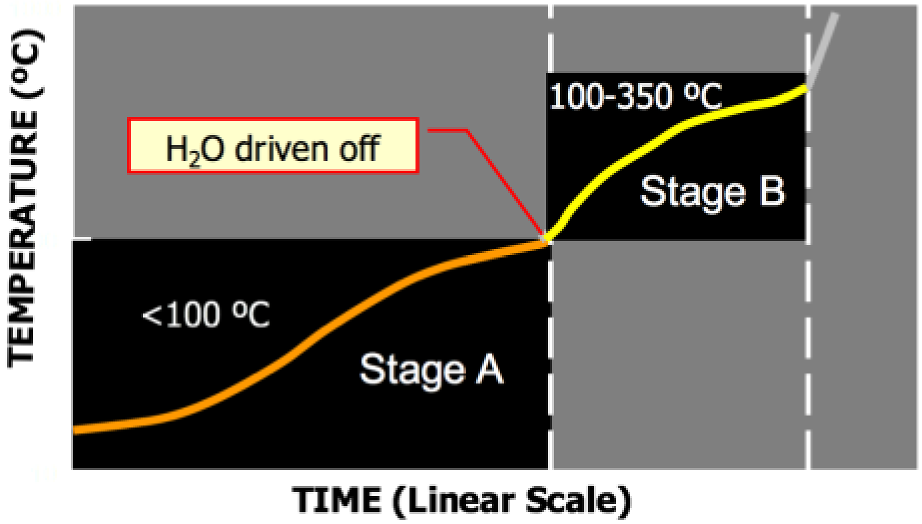


Figure 4.1. – Stage A to Stage B Transition

Rosenblum & Spira (1995) conducted series of self-heating test at different ambient temperature as shown in Figure 4.2. It has been confirmed that moist sulphide samples did not show any heating at temperature below 30°C. At 40°C, small self-heating rate was noticed and the rate of heating increase as temperature increased up to 70°C. After 70°C, the sample's self-heating rate decreased sharply and reached zero as temperature reached 95°C. With the sample with representatively identical sample, same set of tests were conducted with dry samples. With dry samples self-heating were observed after 100°C. This set of test confirmed that there is a transition zone where the self-heating rate is minimized as sulphides transition from Stage A to Stage B.

Past studies have only measured self-heating behavior of materials of sulphide at specific temperatures in Stage A and B separately. To this date, there is no study that investigates how Stage A progresses into Stage B.

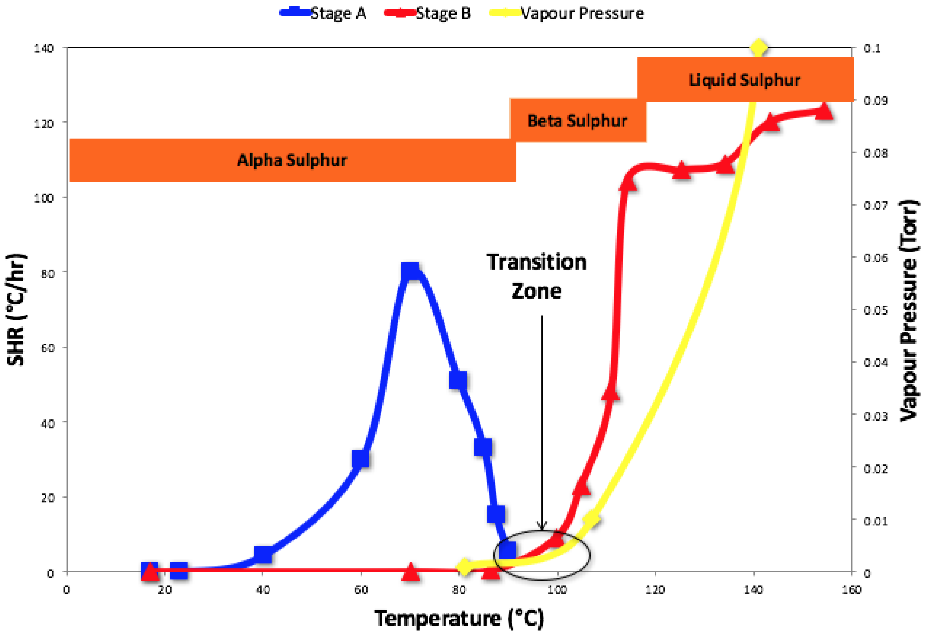
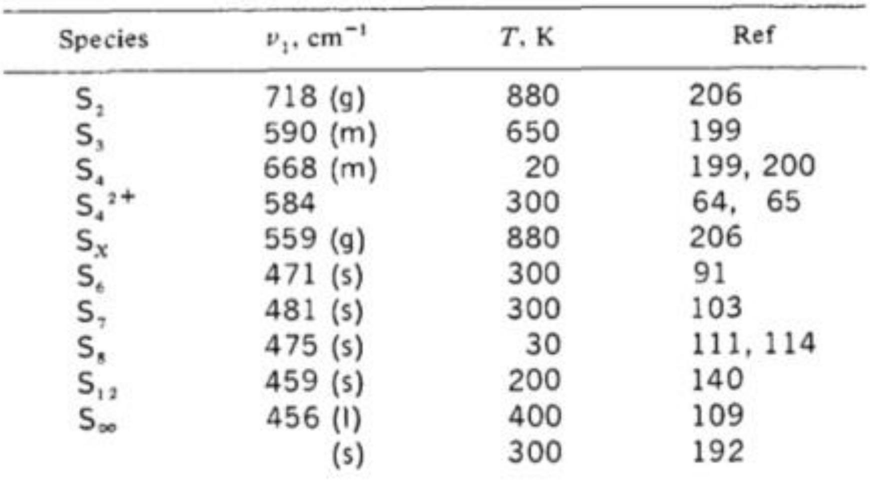


Figure 4.2. Graph of SHR and Vapour Pressure vs Sample Temperature indicating a transition zone.

It is hypothesized that there are two stable forms of elemental sulphur in nature, orthorhombic and monoclinic, at different temperatures that dictate stage A and stage B reactions. However, due to the complexity of reactions and the fact that millions of meta stable allotropes of sulphur exist in nature as seen in Table 4.1, true chemistry behind the reactions are not fully known to this date (Theilig, 1982; Park, 2013). Stages A and B are bridged as elemental sulphur undergoes structural changes from orthorhombic to monoclinic which results in a transition zone.

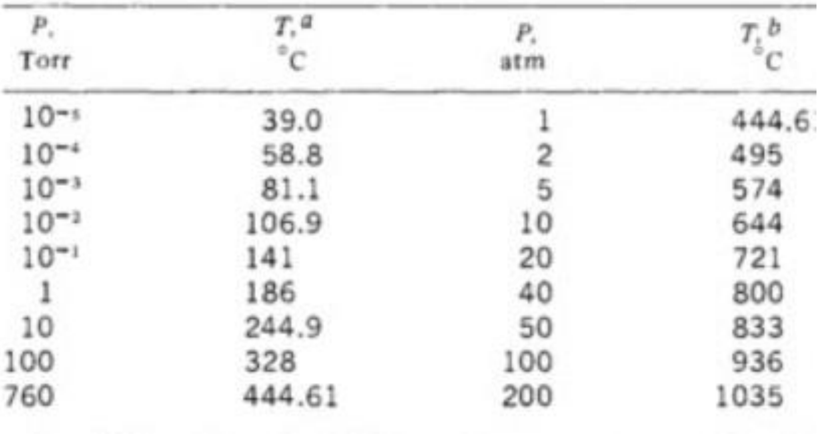
Table 4.1 – Sulphur Allotropes



Species	ν_1, cm^{-1}	T, K	Ref
S_2	718 (g)	880	206
S_3	590 (m)	650	199
S_4	668 (m)	20	199, 200
S_4^{2+}	584	300	64, 65
S_x	559 (g)	880	206
S_6	471 (s)	300	91
S_7	481 (s)	300	103
S_8	475 (s)	30	111, 114
S_{12}	459 (s)	200	140
S_∞	456 (l)	400	109
	(s)	300	192

Another hypothesis is that the elemental sulphur vapour pressure, as seen in Table 4.2, generated in weathered sulphide minerals may be one of the primary causes for self-heating in stage B. There are numerous statements that are in line with this hypothesis. For example: S_8 sulphur has a transition point at 95°C: (going from Alpha to Beta sulphur) which is just about the observed temperature at which the self-heating and the SO_2 are first observed. Figure 4.2 shows that Stage B, the off-gas and the vapour pressure all start at about 95°C and all have the about same curve shape. Past tests have shown self-heating and the SO_2 are observed at about 90°C which is very close to the transition zone (Bojes, Lerbscher, Wamburi and Dilley, 2010). It is also stated in literature that below 95°C the sulphur is stable while above that temperature the sulphur is "reactive" (Theilig, 1982).

Table 4.2 Vapor Pressure of Elemental Sulphur



P, Torr	T,^{a} °C	P, atm	T,^{b} °C
10^{-5}	39.0	1	444.6
10^{-4}	58.8	2	495
10^{-3}	81.1	5	574
10^{-2}	106.9	10	644
10^{-1}	141	20	721
1	186	40	800
10	244.9	50	833
100	328	100	936
760	444.61	200	1035

The purpose of this paper is to investigate how certain factors promote self-heating or not in the transition zone using the FR-Test, a self-heating methodology developed specifically for sulphides (Rosenblum and Nesset, 2001). The factors include: weathering duration, ambient temperature and initial element sulphur content of a sample.

4.2. Experimental

4.2.1 Samples

Rod mill discharge (RMD) from Glencore's Brunswick Mine and nickel concentrate (Ni Con) Glencore Raglan Mine were sampled and used. The samples were reduced to 75μm passing 80% at the mine, dewatered and sent to McGill University. The samples were dried at 40°C for 5 hours in a convectional oven and then representatively divided into 500g bags using a rotary splitter. The samples were then stored in a freezer to prevent oxidation.

4.2.2 Self-heating Apparatus

The FR setup (Figure 4.3) consists of: 2L Pyrex glass cell with screen to support the powdered sample; an insulating cylinder; a coiled heater surrounding the cell; thermocouples; and gas inlet and exhaust systems (Rosenblum & Spira, 1995). Gas inlet is connected to MEGS compressed air (specification: THC<0.1ppm, Oxygen< 20-22%, Water<2.0ppm, carbon monoxide< 1.0 ppm, and carbon dioxide <1.0ppm) and nitrogen (99.998% pure) cylinder. The gas flow was controlled by Sierra's Mass-Trak mass flow meters (Model 810; range: 0-10 SCCM to 0-100 SLPM; accuracy: ±1.5%; response time: 5 seconds to within 2% of set point).

Figure 4.3. FR self-heating apparatus developed by Rosenblum and Spira

4.2.3 Sample Weathering Test

Weathering test is a simulated oxidation test. Tests were conducted in Stage A conditions and samples were packed into 500g or 1000g according to the test required. For a standard weathering condition, the apparatus was set to 70^{o}C and the air injection rate is kept constant at 100mL/min for 15 minutes at 5-hour intervals for total of 10 cycles. This procedure is analogous to a sample being weathered during shipping and storage under ideal weathering conditions.

4.2.4 Standard Self-Heating Test

In the Pyrex cell, purified water is sprayed to 500g of powdered bone-dry samples until the moisture content reaches 6wt%. The Pyrex cell is place in the self-heating chamber and the metal insulator with integrated coiled heater is placed over the cell. A thermocouple is inserted to the centre of the sample and the seal cover is place on the top to lock the thermocouple. In Stage A, the apparatus temperature is set to 70°C and the gas flow meter regulates air injections at 100mL/min for 15 minutes every 5 hours. This air injection is done for 10 cycles. After completing 10 cycles, residing water is vacuumed out of the apparatus and the temperature of the apparatus is set to 140°C. In Stage B, the apparatus temperature is set to 140°C and the air injection is controlled at 250mL/min for 15 minutes every 5 hours. Stage B cycles continue until there is no more heat observed. Stage A and B temperature values are logged every minutes until the end of the test. Temperature vs time graphs can be generated from the logged data. From the slope of temperature rise during air injection cycles, Self-heating rate (SHR) is calculated. After all SHR of self-heating peaks are calculated, Equation 4.1 can be used to calculate Self-heating capacity (SHC) for each stage.

$$\mathrm{SHC} = \sum_{i=1}^{n}(\mathrm{SHR}_i \cdot \mathrm{Specific\ Heat}_{\mathrm{sample}} \cdot \mathrm{Air\ injection\ time}) \qquad (4.1)$$

where *i* represents the individual air injection cycle and *n* represents the total number of cycles in a stage.

Figure 4.4 shows risk assessment chart for self-heating materials containing sulphides (Rosenblum et al., 2001). Upon obtaining SHC of Stage A and B, the risk of a sample can be plotted into the chart as the assessment. There are five regions in the chart: (1) safe, (2) will not heat beyond 100°C, (3) do not expose to a high heat source, (4) monitoring recommended, and (5) preventive action recommended and (5) preventive action recommended.

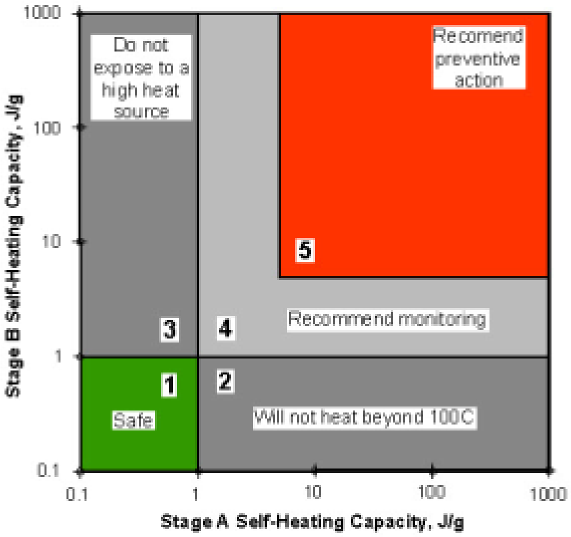


Figure 4.4. Risk Assessment Chart for plotting SHC in Stage A versus Stage B and showing five regions of risk (Rosenblum, Nesset and Spira, 2001)

4.2.5 Adiabatic Continuous Air Injection Test

Adiabatic continuous air injection test is carried out to observe the progress of the temperature rise in a self-heating sample under presence of oxygen from stage A to stage B through the transition zone. In the beginning of the test, the temperature of the apparatus is set to a desired temperature in stage A (i.e. 70^{o}C). Once the sample temperature reaches the set point, air is injected to the system at a continuous flow rate until there is no more heat generated by the sample. Pioneering tests were carried out on a conventional test setup with a fixed oven (ambient) temperature. This was assuming that conductional and convectional heat loss is negligible. However, with progressive self-heating, this temperature difference between the sample and the oven increased, and both conductional and convectional heat loss became significant, causing self-heating measurements (self-heating rate and self-heating capacity) to be under evaluated.

In attempt to minimize the heat loss of the self-heating sample, PID controller was modified. The fixed set point temperature of the oven was changed to follow the temperature of the sample. Figure 4.5 shows schematic set up for with the external set point PID controller.

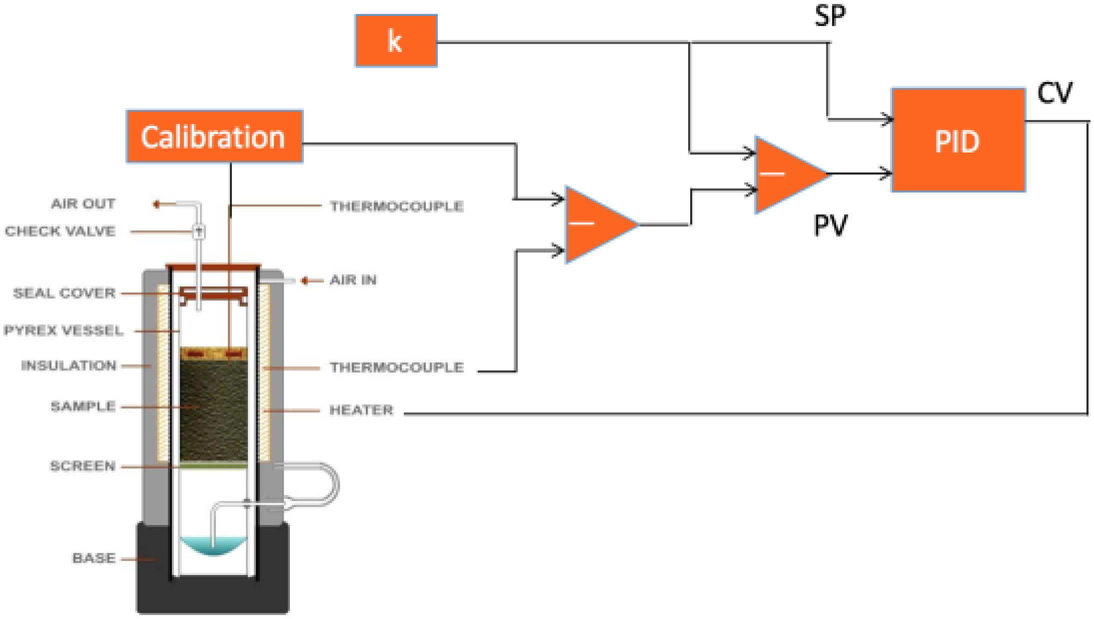


Figure 4.5. Schematic set up for the continuous air injection test

Sulphur Determination

Carbon Disulphide method (Steger, 1976) is used to determine elemental sulphur composition of the sample. 15 mL of Sigma-Aldrich 99.9% A.C.S regent grade carbon disulphide is well mixed with 5 grams of sample inside a 50mL beaker. The mixture is then placed in a vibrator for 10 minutes for mixing. Carbon disulphide dissolves elemental sulphur inside the sample and when the solution is filter in a 50mL flask, a clear solution is collected. The solution is then air dried inside a fume hood until carbon disulphide is completed evaporate. After evaporation, yellow elemental sulphur remains in the beaker. The elemental sulphur is weighed and the weight percentage of elemental sulphur is calculated from the initial sample mass. Figure 4.6 shows extracted elemental sulphur from 5 grams of a sample.

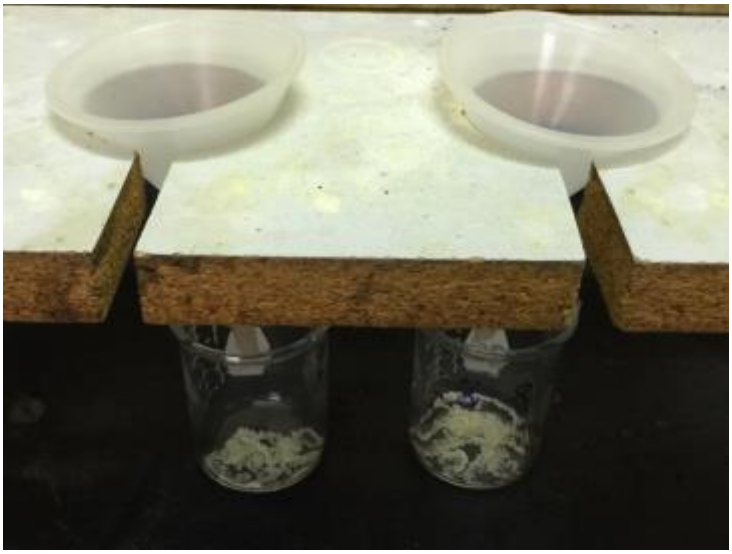


Figure 4.6. Elemental Sulphur Analysis: After extraction of elemental sulphur from 10g of weathered sulphide sample.

4.3 Results

Maximum sample temperature and self-heating capacity in Stage A and B were observed as response in order to observe self-heating activity of the sample during the transition zone.

Figure 4.7 shows the result from adiabatic continuous air injection test. At a standard Stage A temperature, air is continuously blown into the sample at a constant rate of 100mL/min.
Figure 4.7a shows a sample temperature sharply increasing from 70^{o}C to approx. 91^{o}C, then the temperature stays constant for almost one hour. Then heating increases, reaching its maximum SHR of 31.9^{o}C/hr at 17th hour and reaching maximum temperature of 165.7^{o}C.
Figure 4.7b shows a sample temperature increasing to 91.7^{o}C from 70^{o}C. Then the sample temperature stays constant for about one hour and then cools down slowly as self-heating activity is reduced. Results from figure 4.7a & b are completely different. Surprisingly the samples have the same composition.

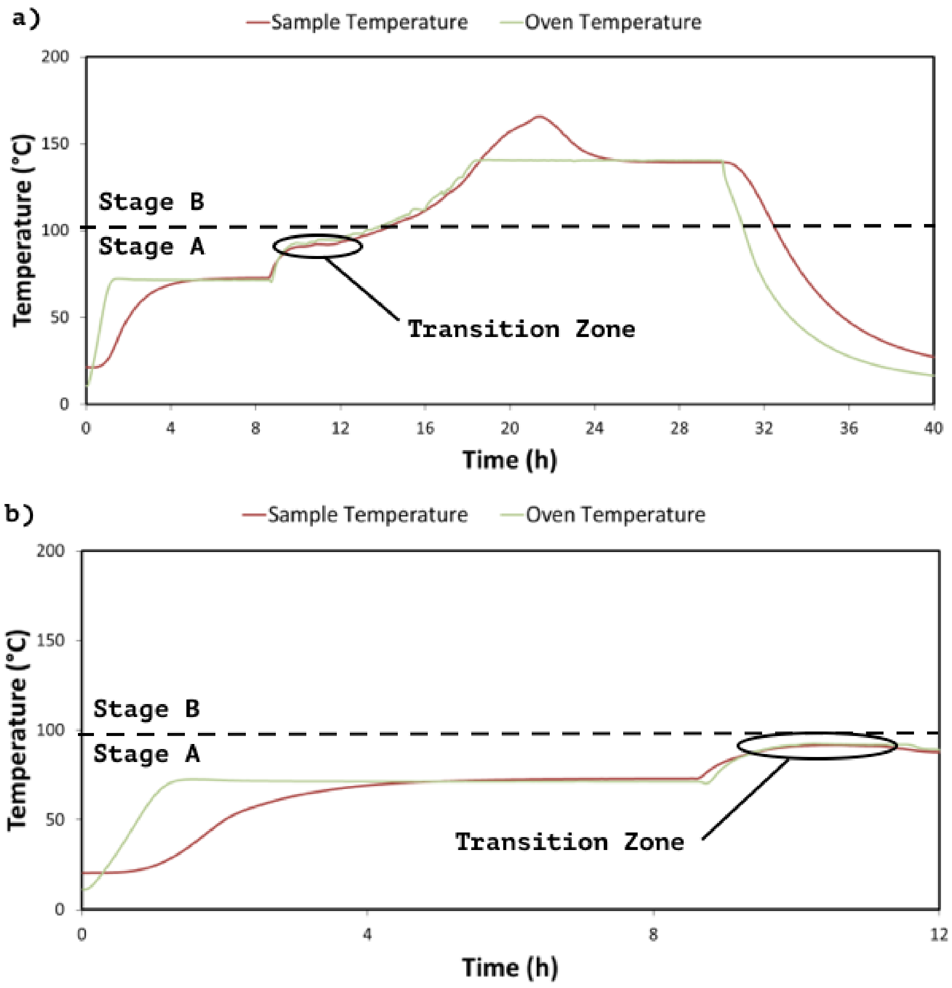


Figure 4.7. a & b – Example of adiabatic continuous air injection test showing a) the sample transitioning from stage A to Stage B & b) self-heating begin stopped in the transition zone

4.3.1 Weathering Duration (Stage A Test)

Table 4.3 and figure 4.8 shows the self-heating response data with varying weathering cycles of 0, 5, 10 and 15 where 0 weathering cycles indicate relatively fresh ground sample that has not been treated from the mine site. The initial starting temperature were all set to standard stage A temperature, 70°C. For samples with 0, 5 and 15 cycles, the maximum temperature reached were below 100°C indicating that the sample did not reach Stage B reaction.

Table 4.3 – Self-heating response data for weathering cycles: 0 ,5, 10 and 15

Stage A Cycles	Initial Temp (ºC)	Maximum Temp (ºC)	Temp Difference	Max SHR (ºC/hr)	Time to reach Maxium Temp (hr)	Elemental Sulphur (%)	SHC_B (J/g)
0	70.0	91.7	21.7	31.9	2.0	0.3%	16.3
5	70.0	97.9	27.9	28.3	8.4	0.3%	24.3
10	70.0	165.7	95.7	32.6	12.8	1.4%	30.0
15	70.0	89.2	19.2	31.8	4.2	1.8%	41.3

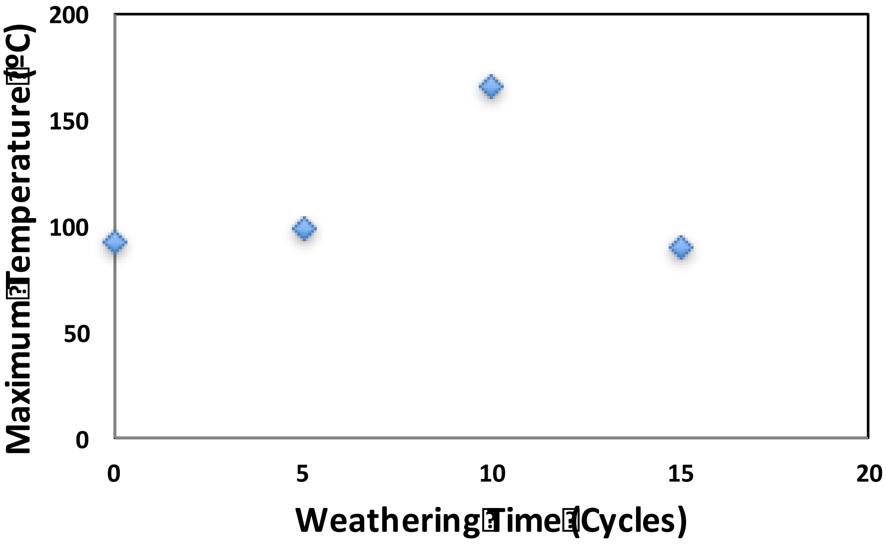


Figure 4.8. Maximum Temperature for RMD samples weathered 0, 5, 10 and 15 cycles

Only the sample that was weathered for 10 cycles indicated the sample proceeding into Stage B and reached exceptionally high sample temperature compared to the value of 165.7°C. The maximum self-heating rate (SHR) value was 31.9°C/hr (no weathering), 28.3°C/hr (5 weathering cycle), 32.6°C/hr (10 weathering cycle), and 31.8°C/hr (15 weathering cycle), showing no significant changes. The time it took to reach the maximum temperature value was 2.0 hr (no weathering), 8.4 hr (5 weathering cycle), 12.8 hr (10 weathering cycle), and 4.2 hr (15 weathering cycle). Initial elemental sulphur content produced during prior weathering stage showed an increase with increasing weathering cycle. Elemental sulphur content was 0.3wt% (no weathering), 0.3 wt% (5 weathering cycle), 1.4 wt% (10 weathering cycle), and 1.8 (15 weathering cycle). Self-heating capacity of the sample increased with increasing elemental sulphur content and weathering duration with 16.3 J/g (no weathering), 23.3 J/g (5 weathering cycle), 30.0 J/g (10 weathering cycle), and 41.3 J/g (15 weathering cycle) shown in Figure 4.9.

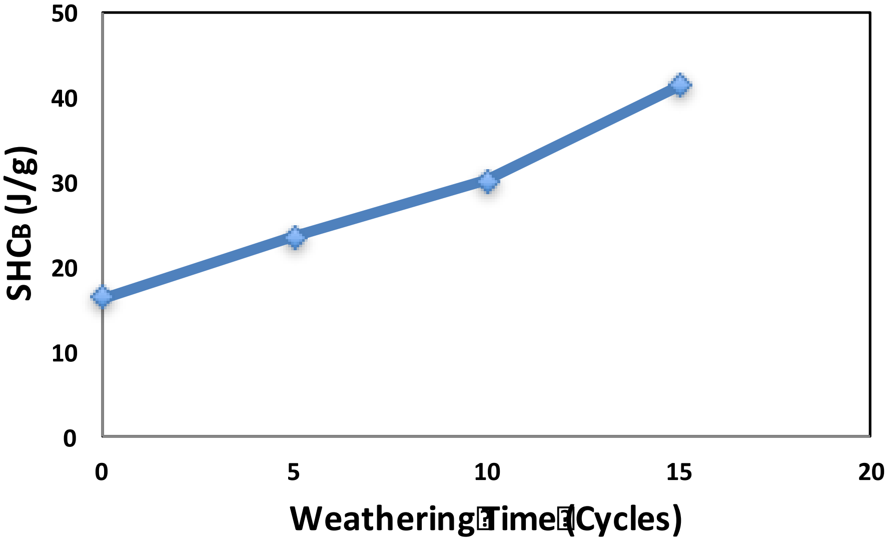


Figure 4.9. Self-heating capacity in Stage B for RMD samples weathered 0,5,10 and 15 cycles

Figure 4.10 shows combined data from multiple samples together. There was no absolute number of weathering cycles that promote sample transition from Stage A to Stage B.
It is interesting to observe that with the exception of one test, all the samples that did not reach stage B reached temperature of near 100ºC. Repeated tests show that samples easily reach the transition zone, the 90ºC-100ºC temperature zone, but have difficulty reaching Stage B.

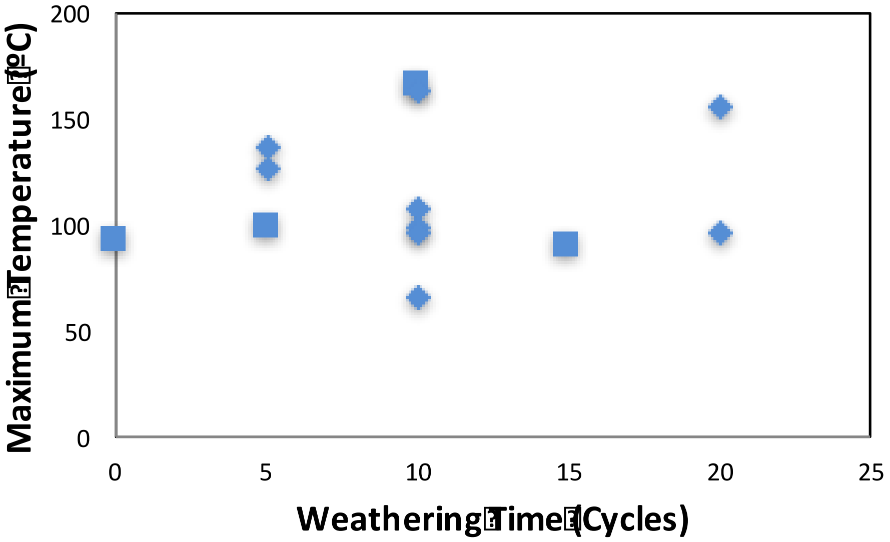


Figure 4.10. Self-heating capacity in Stage B for various samples weathered 0,5,10 and 15 cycles

4.3.2. Maximum Temperature vs SHC in Stage A

Figure 4.11 shows the maximum temperature reached for the samples during a continuous air injection test for the samples with different SHC in stage A. It has been hypothesized that self-heating capacity in stage A is directly linked to the sample's capability of transitioning to Stage B. Greater SHC indicates the sample generating more energy per mass, hence, greater driving force for the sample to reach stage B. The sample will be able to reach Stage B only if it generates enough heat to raise its own temperature up to Stage B region (>100°C). The test result shows that higher SHC does not necessarily indicate that the sample will reach Stage B.

4.3.3. Moisture content & Re-Moisturizing Test

Past studies have shown that moisture is a key reactant in stage A and sulphide samples would not self-heating without moisture (Rosenblum and Spira, 1981). Therefore, one could suggest that transition zone is simply caused by the moisture driving off from the sample as temperature reached the boiling point of water. For the tests where sample temperature stopped increasing in the transition zone, the samples were taken out and quickly re-applied with moisture of 2%. Re-moisturizing did not have any effect on self-heating near the transition zone.

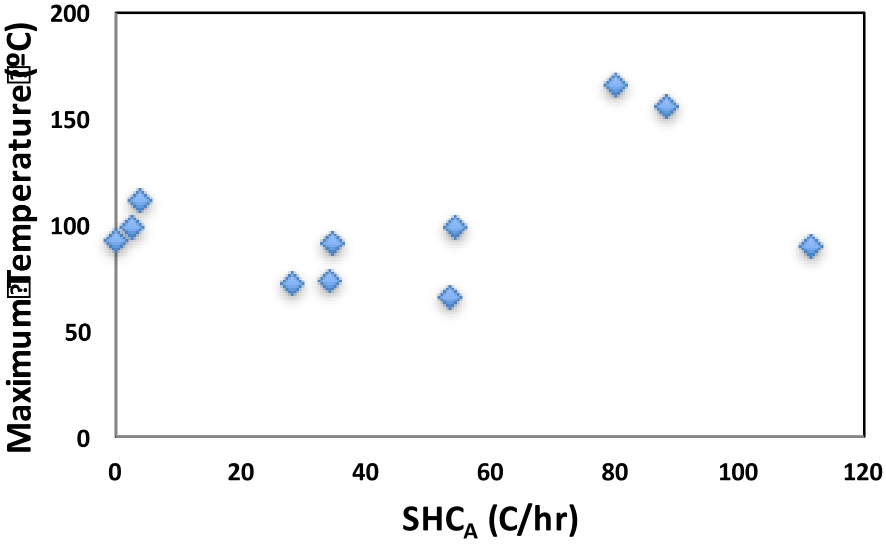


Figure 4.11 – Maximum Temperature reached for with respect to SHC in stage A

4.3.4. Initial Temperature

Figure 4.12 shows the maximum temperature reached for tailing sample at different initial temperatures. All the samples were weathered under a standard condition mentioned in Section 4.2. As initial temperature increased, the maximum temperature increased. For this specific sample, maximum temperature passed 100°C when initial temperature was greater than 70°C. However, repetitive tests showed only some samples reaching stage B. When the surrounding temperature is low, the majority heat generated is consumed to raise the temperature of sample instead of being able to use the energy to break through the transition zone.

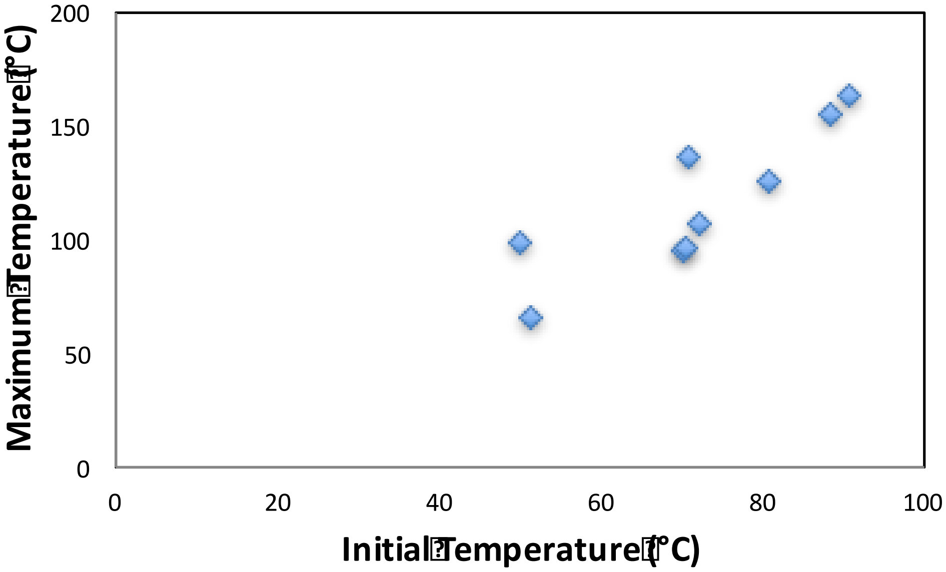


Figure 4.12 – Example of the effect of initial temperature on the maximum sample temperature reached

4.3.5. Elemental sulphur content

Figure 4.13 shows maximum temperature with respect to the elemental sulphur content inside the sample regardless of the weathering conditions. Increased elemental sulphur resulted in increased maximum temperature up to 1.5wt% initial elemental sulphur content. After this point, maximum temperature decreased with increased elemental sulphur content. Stage B reactions (sample temperature over 100°C) occurred for samples having elemental sulphur in the region of 1 to 2 wt%.

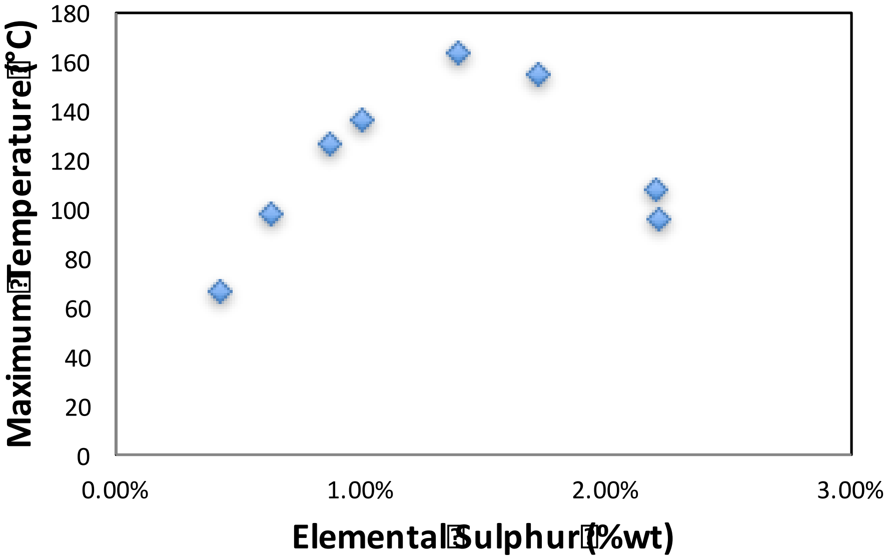


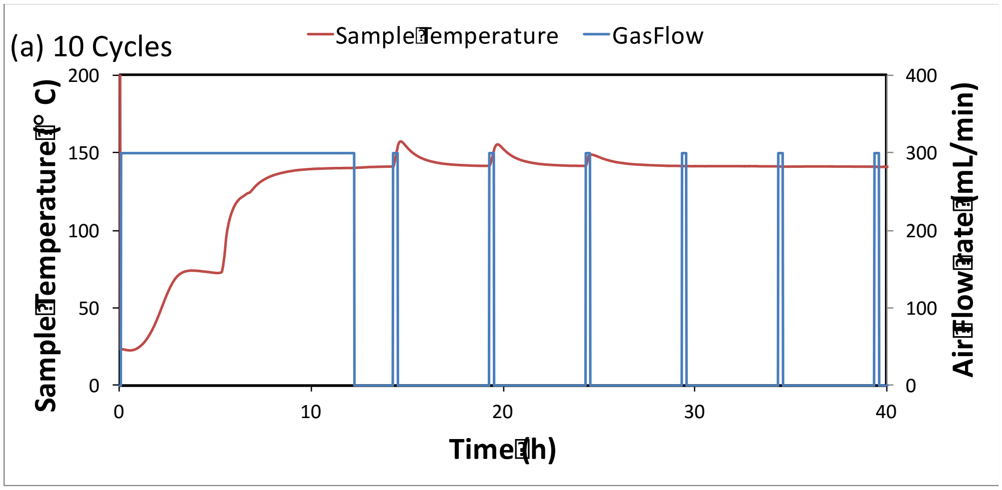
Figure 4.13 Example of the effect of elemental sulphur on the maximum temperature reached

4.4. Discussion

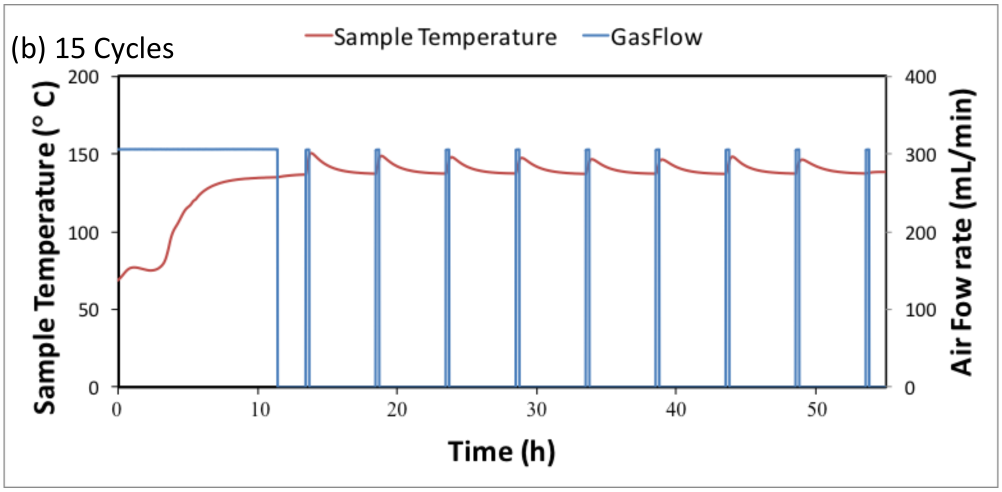
As proposed earlier, the self-heating transition from Stage A to stage B is affected by weathering duration. With progressive weathering from 0 to 15, the self-heating capacity in Stage B showed proportional increase with increasing weathering duration. Based on the standard self-heating test results, the sample with 15 weathered cycles had the largest SHC_B with the value of 41.3 J/g. When comparing the standard self-heating test with the transition test (adiabatic continuous air injection test), only the sample with 10 weathering cycles passed the transition zone and reached stage B reaction. All other samples stopped heating near 90°C-100°C. This result suggests that although SHC in Stage B suggest total self-heating potential of Stage B; it does not necessarily indicate whether the sample will be able to reach Stage B reactions.

Figure 4.14 shows an example of standard Stage B self-heating test for the RMD samples that are weathered for 10 and 15 cycles. For sample 4.14a, the number of self-heating peaks in Stage B occurred 3 times whereas for sample 4.14b, the number of peaks occurred 8 times. The SHC_B for sample 4.14a is 24.3J/g and SHC_B for sample 4.14b is 41.3J/g. Self-heating capacities generally increased with increasing weathering cycle. However, when considering an individual self-heating peak, sample 4.14a had peaks with greater SHR with 60.6°C/h for the 1st peak and

50.2°C/h for the 2nd peak than the sample 4.14b with SHR of 54.2°C/h for the first peak and 43.8°C/h for the second peak. SHC$_A$ cannot be applied to tests with varying weathering duration because the SHC$_A$ calculation is based on 10 set of the cycles. Unlike SHC$_B$, where the test cycles last until the sample cannot self-heat anymore, Stage A cycles can be elongated indefinitely. An attempt was made to adjust the SHC$_A$ based on the number of cycles. For example, if a sample was weathered for 7 cycles, a factor of $10/7$ would be applied to make the magnitude equivalent to 10 cycles. However, the adjustment would be biased because past researches have shown that sample compositions, induction periods, and its past history of weathering can postpone or amplify magnitude of certain peaks (Wu and Li, 2013; Janzen, Nicholson, and Scharer, 2000). For example, some samples may have an induction period of 5 cycles. If a 5 cycle test was conducted in Stage A, the material would have shown 0 SHC$_A$ when the actual SHC$_A$ is greater than 0. SHC for Stage A and B should not be used alone to predict whether sample will heat beyond Stage A.



Cycle	SHR$_B$ (°C/h)
1	60.6
2	50.2
3	52.1
4	0.0
5	0.0



Cycle	SHR $_B$ (°C/h)
1	54.2
2	43.8
3	39.2
4	36.5
5	33.6
6	32.6
7	39.4
8	46.6
9	3.3
10	0.0

Figure 4.14. Standard Stage B test for samples with weathering of a) 10 cycles & b) 15 Cycles

Past studies have shown that moisture is a key reactant in stage A and sulphide samples would not self-heat without moisture (Ninteman, 1978; Rosenblum, Spira, & Konigsmann, 1982; Wu & Li, 2013). Therefore, one could suggest that transition zone is simply caused by the moisture driving off from the sample as temperature reached boiling point of water. Samples with maximum temperature between 90^{o}C and 100^{o}C during the adiabatic tests were taken out, sprayed with 2wt% of water, mixed and placed back into the adiabatic test. Samples' temperatures did not progress into Stage B reaction and re-moisturizing did not have any effect on the self-heating near the transition zone. Water is not the primary reason why samples cannot transition into stage B reaction.

Increased ambient temperature leads to an increase in maximum temperature reached by the sample and shows increases chance of for materials to reach stage B. From our data, there appears to be a linear increasing trend in maximum temperature of the sample with increasing initial ambient temperature.

Elemental sulphur content of the sample shows parabolic correlation with the sample's self-heating response transitioning to Stage B as shown in Figure 4.15. The increase in the amount of elemental sulphur has increasing effect on the maximum temperature reached by the sample up to 1.5 wt%. However, the decrease in the maximum temperature after 1.5wt% can be explained by impurities formed during Stage A reactions. Samples with elemental sulphur greater than

1.5wt% were weathered for 15 or 20 cycles, with value of 1.72, 2.20 and 2.21 wt% of elemental sulphur. There are bi-products such as goethite produced from oxidation of sulphides, which are shown below:

$$4FeS + 3O_2 + 2H_2O \rightarrow 4FeOOH + 4S^0 \tag{4.2}$$

$$Fe^{3+} + 2H_2O \rightarrow \propto FeOOH + 3H^+ \tag{4.3}$$

Past studies have shown XRD results of goethite forming after weathering cycles, notably after 20 weathering cycles (Park, 2013).

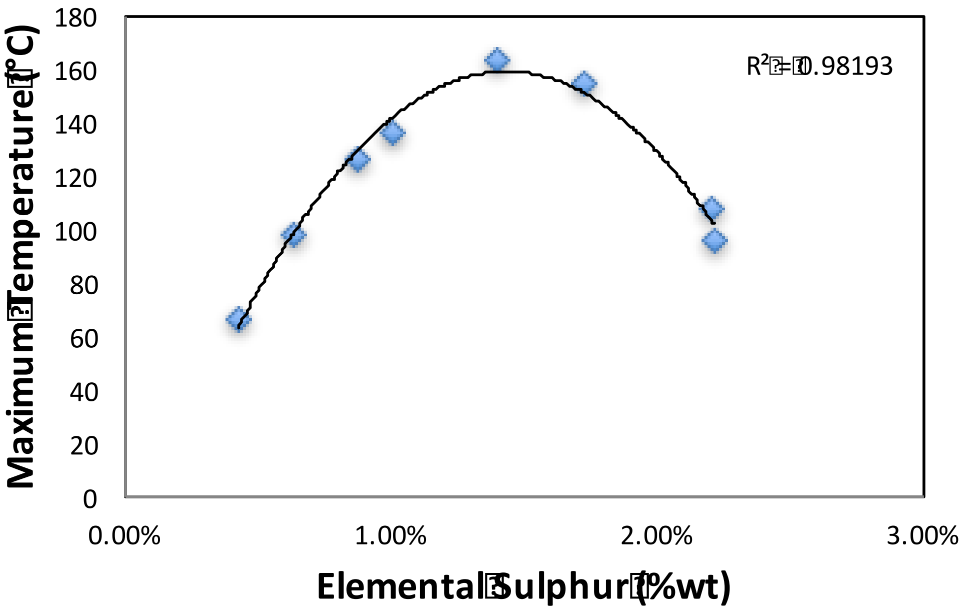


Figure 4.15. Maximum temperature of the sample as a function of elemental sulphur content

The U.N. evaluation test is used internationally and it remains the benchmark when evaluating the risk of self-heating. The FR Test, however, is increasingly used by companies aware that the potential for self-heating of sulphide materials may not be always be determined reliably by a single stage test. It will take time for the FR Test to be validated and accepted, but at this stage it seems the most promising method of assessing the self-heating risk potential of sulphides.

4.5. Conclusions

It has been shown that there are various factors that can affect sample transitioning from Stage A to Stage B. Transition zone has been confirmed to exist where the sample temperature rise is significantly reduced. Many samples easily reached transition zone temperature, however, they stopped heating beyond this level. At the higher ambient temperatures, samples showed a greater chance to transition into Stage B. Moisture content of the sample did not have an effect on the transition zone heating. Increased elemental sulphur content resulted in increasing maximum temperature and transition to Stage B. However, extensive weathering showed decrease in maximum temperature to a degree where sample will not transition to Stage B.

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Chapter 5. Conclusions and Future Work

5.1 Conclusions

The thesis addressed limitations to the self-heating test methods: U.N Recommended Test and FR-Test, recommendations to correctly measure self-heating risk of sulphides, the relationship between transition from Stage A to Stage B and the factors contributing the transition. The following conclusions are drawn from the studies:

- Weathering of sulphide materials can intensify the self-heating response in standard test protocols such as the U.N. and FR test methods.
- The maximum temperature from the U.N. test and the Stage B SHC values from the FR test were increased by weathering for sulphide samples of ore (RMF) and nickel concentrate (Ni Con).
- The increased response of samples tested by both test methods correlates to an increase in concentration of elemental sulphur resulting from the increased weathering.
- This deficiency of U.N recommended test stems from the lack of the (oxidation) stage in the test protocols. As a consequence, such single stage tests can produce false negative results with respect to sample self-heating risk.
- FR test does not suffer from this deficiency and is more appropriate for assessing the self-heating risk of sulphide materials.
- High ambient temperatures have positive effect on the transition from Stage A to B
- Elemental sulphur have positive effect and impurities cause by excessive weathering have negative effect on the transition from Stage A to B
- SHC for Stage A and B cannot be solely used to predict sample’s risk of reaching high temperature (Stage B).

5.2. Future Work

- Conduct more repeat tests using diverse samples.
- Suggest test weathering procedure that can be integrated in to U.N. Test
- Monitor and quantify the rate of H_2S and SO_2 off gas to estimate reactions that occur during weathering stages with various weathering factors.
- Investigate orthorhombic and monoclinic sulphur changes with increasing temperature