Physical Chemistry of Sulphide Self-Heating

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To my wife Josephine Ngabe,
my daughters,
Barnette Alma Ngabe,
Jessica Lucie Mango Ngabe
Rebecca, Benedicte Ngabe
and to all who are dear to me

My PhD work time has been very hard. During the same year 2011, my brother Dr. Denis NGabe who taught me the basic science and my mother Germaine Mango NGabe died. At this special moment I would like to recall that my thoughts are and will always accompany them and my father Gaston Ngabe, my brother Jacques Moundzila Ngabe and sister Monique Ngabe who died before.

En faisant mes doctorats, j'ai singulièrement voulu, de cette manière, inscrire ma modeste part dans l'héritage scientifique de l'humanité.

Barnabe Ngabe

ABSTRACT

A prerequisite step towards building a self-heating (SH) model for sulphide materials is the determination of physico-chemical parameters such as the specific heat capacity (C_p), and the energy of activation (E_a). The specific heat capacity of one copper and three nickel concentrates was determined over the temperature range 50 to 80^oC in the presence of 6% moisture using the self-heating (SH) apparatus and confirmed by Drop Calorimetry. The C_p values from both techniques were comparable. The C_p values were similar for all concentrates increasing from 0.4 to 1.4 $Jg^{-1}K^{-1}$ as temperature increased from 50 to 80^oC. From the C_p values, the enthalpy change (ΔH), the entropy change (ΔS) and the Gibbs free energy change (ΔG) for self-heating, were determined. The ΔG was negative, demonstrating that self-heating of the concentrates was spontaneous.

Using the self-heating apparatus the, activation energy (E_a) was determined for the Ni-and Cu-concentrates and for pairs of sulphide minerals. The E_a ranged from 22 to 30 $kJ.mol^{-1}$, implying a common reaction. Further support for a common reaction is the strong positive correlation between E_a and $\ln(QA/C_p)$ where Q ($J.kg^{-1}$) is the heat of reaction causing self-heating and A the Arrhenius pre-exponential factor (s^{-1}). Comparing to literature, the E_a values correspond to partial oxidation of hydrogen sulphide, supporting the contention that H_2S may be an intermediate product in the self-heating of sulphide minerals.

A positive relationship between E_a and the rest potential difference (ΔV) for the sulphide pairs and a negative relationship between C_p and ΔV were demonstrated which support a connection between self-heating and the galvanic effect.

RESUMÉ

La réalisation d'un modèle mathématique de l'auto-échauffement des concentrés sulfurés de nickel et de cuivre et des mélanges des minerais sulfurés, enjoint à la détermination des paramètres physico-chimiques tels que les capacités de chaleur spécifiques (C_p), et les énergies d'activation (E_a).

Les capacités de chaleur spécifiques d'un concentré de cuivre et de trois concentrés de nickel contenant 6% d'humidité, ont été déterminées par utilisation d'un instrument de mesure de vitesse d'auto – échauffement et validées par la calorimétrie de chute dans l'intervalle de températures allant de 50 à 80°C. Les C_p (0.4 à 1.4 $Jg^{-1}K^{-1}$) obtenues sont similaires pour tous les échantillons. A partir des valeurs des C_p, les variations de l'enthalpie (ΔH), l'entropie (ΔS) et de l'énergie libre de Gibbs (ΔG) de l'auto échauffement ont été déterminées. La valeur négative de ΔG confirme le caractère spontané de l'auto échauffement des minerais sulfurés.

Les énergies d'activation (E_a) pour l'auto-échauffement des concentrés de nickel et cuivre et des paires de minerais sulfurés étaient déterminées en faisant usage de l'appareil d'auto-échauffement. Les E_a ainsi obtenues oscillent entre 22 et 30 $kJ.mol^{-1}$: Ce qui est suggestif d'une rèaction chimique commune gouvernant l'auto-échauffement de ces matériaux. Ce fait est corroboré par la forte corrélation obtenue entre E_a et $\ln(QA/C_p)$ (Q ($J.kg^{-1}$) est la chaleur de la rèaction chimique responsable de l'auto-échauffement et A (s^{-1}) la constante d'Arrhenius).Ensuite celles-ci sont similaires à celle de l'oxydation partielle du H_2S. Il se pourrait, ce faisant, que H_2S soit un composé intermediaire lors de l'auto–échauffement des sulfures.

Enfin, la corrélation positive entre E_a et la difference de potential (ΔV) dans les paires de minerais sulfurés et celle negative entre C_p et ΔV sont une preuve qu'il existe bel et bien une connection entre l'auto-échauffement et l'effet galvanique.

Contributions of the authors

The manuscripts listed below were used in preparation of this thesis. All experiments were conducted by the candidate under the supervisions of Pr. James A. Finch and Pr. In-Ho Jung as research supervisors.

List of manuscripts

1. Barnabe Ngabe, James A. Finch. 2014. Determination of specific heat capacity of sulphide materials at temperature below 100°C in presence of moisture. 2014. Minerals Engineering, 58 (2014), 73-79.
2. Self-heating: The enthalpy, entropy and Gibbs free energy changes for sulphide concentrates.
3. Barnabe Ngabe, J. Edwin van der Spuy, James A. Finch. 2011. Estimating activation energy from a sulphide self-heating test. Minerals Engineering, 24, 1645-1650.
4. Barnabe Ngabe, James A. Finch. 2014. Activation energy and specific heat capacity of sulphide mixtures at low temperature. Minerals Engineering, 55, 154-161.

As a research supervisor, Professor Finch was a co-author in all manuscripts. Note in the third manuscript, Edwin van der Spuy, was a technician in Professor Finch group who helped in modify the SH apparatus for the establishment of the temperature uniformity in the center plane of the sample. Beyond the contributions of the authors mentioned here, all the work presented in this dissertation was done by the candidate under the supervision of Professor Finch and Professor In-Ho Jung.

Acknowledgements

I am grateful to professors Finch and In Ho Jung for their guidance. I would like to say special thanks to Professor Finch for financing this work. My thanks are also addressed to Frank Rosenblum for his help in building, fixing equipment and for his patience in technical discussions on self-heating, Raymond Langlois for his help in sample preparation, Dr. Stéphanie Somot and Dr. Mitra Mirnezami who received me in the group, Barbara Hanley who advised me on administrative matters and all my colleagues who helped as they could.

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Chapter 1 . Introduction

1.1 Self-heating: Definition

The expression self-heating (SH) refers to the material heating when there is no external source of heat. The SH of sulphide minerals originates in the exothermic reactions of the components. Self-heating occurs when the rate at which heat is generated within the material is higher than the rate at which heat is dissipated to the surroundings (Semenov, 1935; Frank-Kametskii, 1969; Carres and Saghafi, 1988; Poffet, 2007; Quintiere et al. 2012). The rate of heat loss (Q_l) is given by (Semenov, 1935; Poffet, 2007):

$$Q_l = hS(T-T_a)/V \qquad (1.1)$$

where T (K) is the temperature in the reacting system, T_a (K) the temperature of the surroundings, h ($W.m^{-2}.K^{-1}$) the overall heat transfer coefficient, S (m^2) the surface area through which heat is being lost and V(m^3) the volume in which the reaction is taking place. The rate of heat generation (Q_g) is (Frank-Kamenetsii, 1969; Cuzzillo and Pagni, 1999):

$$Q_g = \rho QAe^{(-Ea/RT)} \qquad (1.2)$$

where, ρ is the density of the material(kg m^{-3}), Q the heat of reaction (J kg^{-1}) A(s^{-1}) is the Arrhenius pre-exponential factor, E_a (J mol^{-1}) is the energy of activation of the reaction, and R is the gas constant. Thus self-heating refers to cases where $Q_g > Q_l$

1.2.The issue: Self-heating and mining of sulphide ores

It is known that sulphide minerals can self-heat. The phenomenon has been observed on occasions. Pearse (1980) reported SH of concentrates during storage and shipment. Explosions due to SH of sulphide dusts have been reported in mine development mining (Reimers and Hjelmsd, 1987). More recently, Yang et al. (2011) reported the occurrence of combustion at the Donguashan Copper Mine, China, when sulphide concentrates were stored for long times (Figure 1.1).

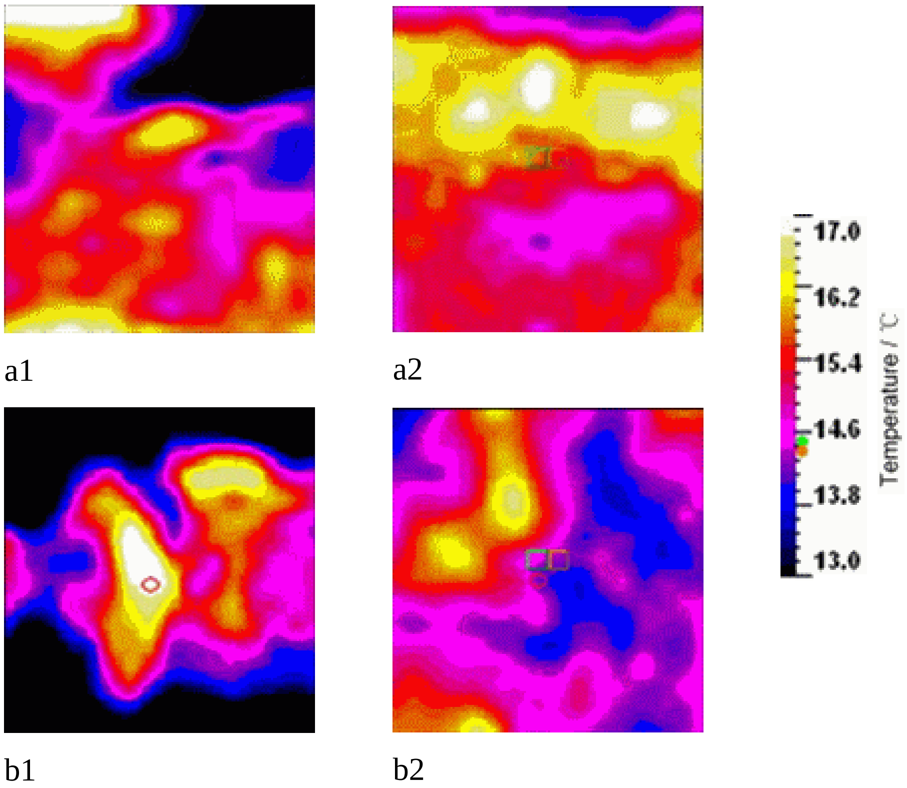

Figure 1.1 Thermal image pictures for sulphide concentrates in the storage yard of Dongguashan Copper Mine.: (a1, b1) in summer time; (a2, b2) in winter time (from Yang et al. 2011).

When SH is not controlled, it can lead to fires. Fires in underground mines, in concentrate storage sheds and during shipment and in tailings disposal areas have been reported (Ninteman, 1978; Harries and Ritchie, 1987; Rosenblum et al., 2001; Liu, 2002; Elberding, 2005; Wu and Li, 2005. Some specific examples are described. Self-heating of marcasite (an iron sulphide) evolved into a fire at a mine in the Joplin district of Missouri in 1914 (Rosenblum, 1982). At Mines de Poirier, a copper–zinc producing mine in Quebec SH provoked a fire (Rosenblum, 1982). At the Sullivan Mine, Kimberley, British Columbia, fires due to SH were reported underground (Figure 1.2) (Rosenblum, 1982). The same author reported temperatures exceeding 500^{o} C. It is significant that this event was reported in the CIM bulletin in 1977, about 50 years after the first mention by O'Brien and Banks (1926) in the CIM magazine (Figure 1.2). Underground at the Brunswick Mine (New Brunswick), fires lasted 25 years as a result of ignition of back-filled sulphide tailings. Cant (1963) also reported on SH from backfill causing a fire underground at the Horne mine. Above ground at a Pb-Zn mine, waste rock was observed to oxidize with the elemental sulphur formation and emission of SO_2 and steam (private communication, from Nesset, 2009). At the port of Montreal, the temperature of a stored Cu-concentrate reached 150° C and the SO_2 level of 16 ppm (private communication from Rosenblum, 2009) (Figure 1.2). Some of the described events are shown in Figure 1.2.

Figure 1.2 Some dramatic SH events

Sahu and Kpal, (1996) reported on the environmental damages due to mine fires. In particular, these authors observed a large variety of environmental problems (contamination of air, water and soils with chemicals generated by mine fires (e.g. SO_2), subsoils water loss (leading to strata destruction), lower dissolved oxygen, increasing of soil salinity, erodability of soil and leachage of nutrients. Blomqvist and Persson, (2008) showed that the emissions from self-heating bear toxic compounds which can generate health problems to humans. Effects of H_2S on aquatic fauna were reported by Picot and Grenouillet, (1992). Milby and Baselt, (1999) reported on H_2S poisoning among the oil field workers. Sulphur dioxide (SO_2) is one of the major pollutants registered as criteria pollutants by the American Protection Agency (EPA). Deliterious effects of sulfuric acid (H_2SO_4) on water ecosystems are known. For example, in Canada and in particular in the provinces that belong to the Canadian Precambrien Shield, (e.g. Ontario, Quebec, New Brunswick and Nova Scotia) where many waters and soils are deficient in natural alkanility and thus cannot neutralize acid naturally, acid deposition is a serious problem (Environment Canada, 2003).

Despite the obvious importance of SH, there is a lack of data on the physico-chemical parameters of sulphide SH. Such information would help produce a fundamental model of sulphide self-heating.

1.3. Objectives of the thesis

As steps toward building a model for SH based on physical chemical properties:

1. Determine specific heat capacity (C_p) for sulphide concentrates at temperatures $< 100^o$ C where SH starts, using the Rosenblum et al. (2001) SH apparatus and the Drop Calorimetry technique;
2. Determine the enthalpy change, the entropy change and the Gibbs free energy change of sulphide concentrates
3. Determine the energy of activation (E_a) of the reaction surmised to cause SH of sulphide concentrates in stage A using the SH apparatus and applying the transient model of self-heating;
4. Determine the C_p and E_a for mixtures of sulphides to relate to the galvanic effect reported by Payant et al. (2011).

1.4. Structure of the thesis

This thesis encompasses seven chapters. The first is the introduction which deals with the definition and problems associated with self-heating of sulphide materials. The second is the background which includes description of sulphide materials, self-heating instrumentation and measurement procedures, physico-chemical processes (oxidation reactions, H_2S hypothesis, galvanic effect). The transient model of SH for porous materials and examples of activation energy being used to identify reactions are also discussed.

The third chapter contains the determination of C_p for sulphide concentrates using the SH apparatus and Drop Calorimetry. The fourth chapter deals with the determination of the enthalpy, entropy and Gibbs free energy changes of self-heating using the self-heating apparatus and applying numerical physical chemistry methods. The fifth chapter reports activation energy of two nickel concentrates from Raglan and a copper concentrate from Voisey's Bay and mixtures of sphalerite and pyrite using the SH apparatus and applying the transient model.

The sixth expands the E_a of the reactions causing the self-heating of sulphide mixtures: pyrite and galena; chalcopyrite and galena; sphalerite and galena. Specific heat capacity of the mixtures is also included.

The seventh chapter presents the conclusions and enumerates the original contributions and suggested future work.

Given the manuscript style, descriptions of the SH apparatus and procedures are repeated in Chapter 2, 3, 4, 5, and 6 and the transient model is repeated in chapters 2, 5, and 6. Therefore, the reader is invited to skip the repeat portions.

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Chapter 2 . Background

2.1. Sulphide minerals

Sulphide minerals are the source of most base metals. Some sulphide minerals and their chemical formulae are shown in Table 2.1. These minerals contain one or more atoms of metal and sulphur. Pyrrhotite has been shown by a number of researchers to be more reactive and therefore more prone to SH than most other sulphides (Flann and Lukaszewski, 1970; Lukaszewski, 1970; Reimers and Hjelmsd, 1987; Rosenblum et al. 1995; 2001). The difference in reactivities of sulphides may be related to the iron to sulfur ratio (Ninteman, 1978), or to defects in the sulphide structure or to the thermodynamic properties of the sulphides (Vanyukov et al. 1972).

Table 2.1Some suphide minerals and their chemical formulas

Mineral	**Chemical formula**
Arsenopyrite	FeAsS
Chalcopyrite	$CuFeS_2$
Galena	PbS
Hauerite	MnS_2
Molybdenite	MoS_2
Orpiment	As_2S_3
Pentlandtite	$(Fe, Ni)_9S_8$
Pyrite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Realgar	As_4S_4
Sphalerite	Zn(Fe)S

The mining of sulphide ores can be underground or open pit and involves production of concentrates (saleable products) and tailings (waste products). The sulphides are invariably present as mixtures. Even concentrates dominated by one sulphide always contain other sulphides most commonly pyrite and pyrrhotite.

2.1.1. Stages in self-heating

Rosenblum et al.(2001) argued that self-heating progresses in 3 stages: Stage A which takes place from ambient to 100^{o} C and involves moisture in the reactions that appear to produce elemental sulphur; stage B from 100^{o} C - 350^{o} C which appears to involve oxidation of the sulphur produced in stage A and stage C at about 350^{o} C which the runaway stage B where the sulphides ignite (in essence smelting occurs).

2.2. SH apparatus and measurements

Rosenblum et al. (1982) assembled an instrument to measure the SH rates of sulphides under controlled conditions at the Centre de Recherche Noranda in 1976. The derivatives of this instrument now reside in the Department of Mining and Materials Engineering, McGill University (Figure 2.1).

The apparatus, which is basically a calorimeter (Somot and Finch, 2010), consists of the following major components (Figure 2.1): a Pyrex cell, a thermocouple, a gas inlet and exhaust system, a heater, insulation, a stainless steel screen, and a seal cover. The sample is placed in the middle of the Pyrex glass supported by the screen. Air is introduced from the bottom and exhausted, along with any other resulting gases, at the top of the cell. The heating response to a timed sequence of air injections is recorded, from which heating rates (SHRs) are computed.

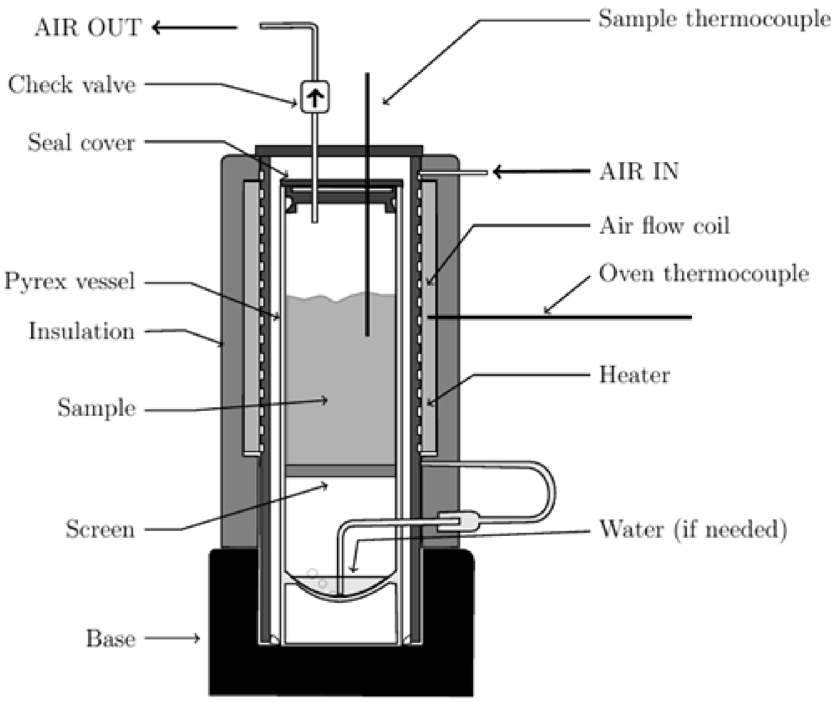

Figure 2.1 SH apparatus (adapted from Rosenblum)

The standard test encompasses two stages, A and B, with the following conditions:

- Number of cycles: 10;
- Duration of air injection for every cycle: 15 min;
- Time between injections: 5 hours (to return sample to the set temperature)
- Temperature (^{o}C): 70 (stage A), 140 (stage B)
- Air flow rate (ml.min^{-1}): 100 (stage A) and 250 (stage B).

An example of a SH test thermogram of a reactive material is shown in Figure 2.2.

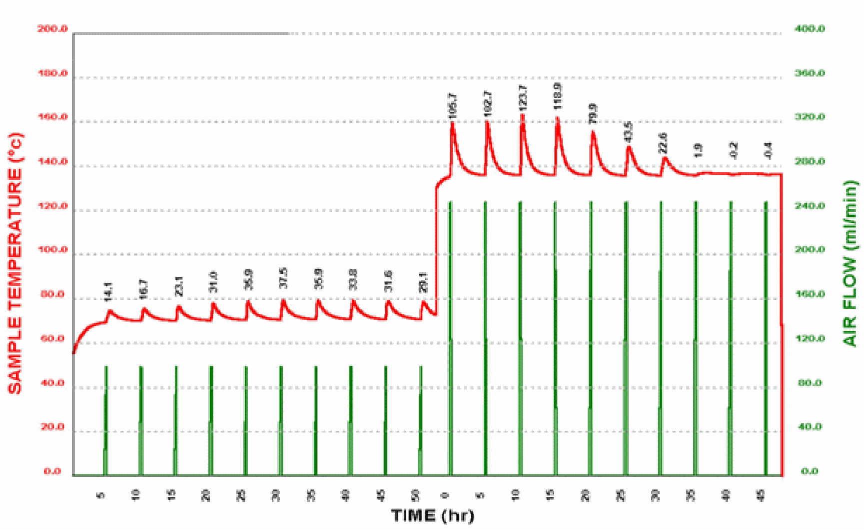

Figure 2.2 SH output: the upper area is the temperature, showing 'spikes' corresponding to the air injection, the lower area

Rosenblum et al. (2001) calculated a self-heating heat capacity (SHC) from the self-heating rates. This is the sum of the heating rates calculated multiplied by the specific heat capacity of the sulphide over the testing time multiplied by the air injection time.

SHC (stage A or B) = sum of self-heating rates(^{o} C/h) × $C_{p\times}$(0.6J.g^{-1} .^{o} C) × 0.25 h = (0.15J.g^{-1}) × (sum of heating rates)

The injection time was: 0.25 h and C_p was taken equal to: 0.6J.g^{-1}.^{o} C^{-1}. It is recognized that the calculation is only approximate (Rosenblum et al. 2001) as a single specific heat capacity (C_p) is used. Example SH rates and SHC are given in Table 2.2.

Table 2.2 Example of SH rates (^{o}C. hrs^{-1}) and SHC(J.g^{-1}) for sulphide concentrates (Rosenblum et al. 2001).

Concentrate	SHR(A)	SHR(B)	SHC(A)	SHC(B)
Cu-conc.	0.1–17.3	0.3–29.1	0.1–21.9	0.1–56.9
Ni-conc.	33.2–45.2	44.1–102	6.62–41.4	44.4–60.5
Pb-conc.	0.6–8.1	2.9–11.3	0.26–10.6	0.48–13.5
Zn-conc.	0.7–5.8	0.7–14.6	0.11–5.25	0.29–4.46

Rosenblum et al. (2001) compared the SHC of sulphide concentrates with the heat outputs from a DSC (Figure 2.3) for stage C.

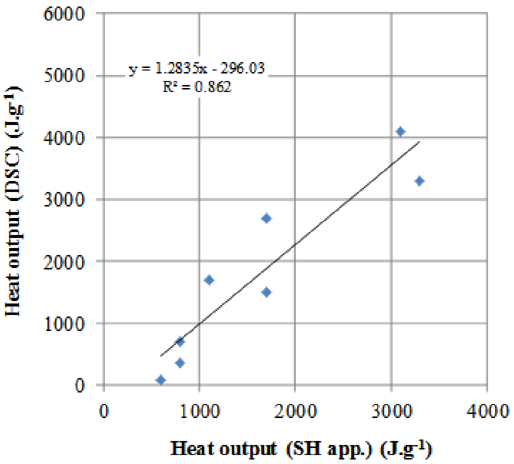

Figure 2.3 Heat output (stage C) from SH apparatus vs. heat output from DSC (plotted from Rosenblum, 2001)

The least square best fit was: y = 1.284x - 296 with an R^2 of 0.862. This shows that the SH apparatus is a type of DSC.

Other important findings reported by Rosenblum et al. (1982; 1995; 2001) are the effects of moisture and oxygen on SH rates. Experiments at ambient temperature, revealed that dry sulphide concentrates did not self-heat, but did in the presence of moisture (Rosenblum et al., 2001). As little as 0.5% moisture in a Ni-concentrate could enhance SHR (Rosenblum et al., 2001). The same authors also showed that a number of pyrrhotites have a high propensity to SH.

A number of exothermic reactions which cause SH have been proposed (Rosenblum and Spira, 2001; Li, 2007; Wu & Meng, 1995). (Gu & Li, 2006; Wu and Li, 2005; Wu, Li & Zhou, 2004; Yang et al. 2011); among them:

$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4$; ΔH = -2558.4 kJ (2.1)

$4\ FeS_2 + 15\ O_2 + 14\ H_2O = 4\ Fe(OH)_3 + 8\ H_2SO_4$; ΔH = -5092 kJ (2.2)

$4\ FeS_2 + 15\ O_2 + 8\ H_2O = 2\ Fe_2O_3 + H_2SO_4$; ΔH = -5740.5 kJ (2.3)

$2\ Fe_7S_8 + 31\ O_2 + 2\ H_2O = 14\ FeSO_4 + 2H_2SO_4$; ΔH = -12590 kJ (2.4)

$2\ FeS + 8\ H_2O + O_2 = FeSO_4.H_2O + FeSO_4.7H_2O$; ΔH = -1771.3 kJ (2.5)

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

2.3. H$_2$S Hypothesis

Somot and Finch (2010) pointed out that high SH rates observed for pyrrhotite rich samples from Xstrata Nickel's Strathcona mill (Sudbury) were not accompanied by visible signs of oxidation. These authors argued that a gaseous reaction was occurring rather than direct oxidation of the sulphides. They demonstrated that H_2S was released in stage A. They proposed that H_2S may be generated by the following reaction (Lowson, 1982; Thomas et al. 2001):

$Fe_{(1-x)}S + 2H^+ = (1-x)(Fe^{2+}) + H_2S$ (2.7)

Somot and Finch (2010) suggested that the acidity involved in reaction 2.7 is generated by reactions associated with the well-known phenomenon of acid generation such as (Buckley and Woods, 1985):

$Fe_{(1-x)}S + (2-0.5x)O_2 + xH_2O = (1-x)Fe^{2+} + 2xH^+ + SO_4^{2-}$ (2.8)

The H_2S may react with oxygen as follows (Somot and Finch, 2010):

$H_2S + {}^1/_2O_2 = S + H_2O;\ \ \Delta H = -2.6 \times 10^5\ J.mol^{-1}$ (2.9)

$H_2S + O_2 = SO + H_2O$ (2.10)

$H_2S + 3/2O_2 = SO_2 + H_2O;\ \Delta H = -5.6 \times 10^5\ J.mol^{-1}$ (2.11)

$H_2S + 2O_2 = 2H_2SO_4:\ \Delta H = -8.5 \times 10^5\ J.mol^{-1}$ (2.12)

H_2S may also react with SO_2 (Somot and Finch, 2010; Pfeiffer, 1978)

$2H_2S+SO_2=S+2H_2O$ (2.13)

A role of H_2S in a different context, ignition of crude oil, was reported by Hughes et al. (1974); Walker et al. (1986); Walker, (2000); Kostur et al. (1987) and Ping et al. (2005)

2.4. Galvanic interaction

A number of metal sulphides are semiconductors and as a result exhibit a rest potential (Kwong et al., 2003; Shuey, 1975; Sato, 1960; 1966; Peters, 1977; Osseo-Asare, 1992). The rest potential of some selected sulphides are shown in Table 2.3.

Table 2.3 Rest potentials for selected sulphides from literature

Mineral	Rest potential (V vs. SHE)	References
Pyrite	0.63	Biegler & Swift, 1979
		Mehta & Murr, 1983
	0.66	Kocabag, 1985
	0.69	Payant and Finch, 2010
Chalcopyrite	0.52	Warren, 1978
		Mehta & Murr, 1983
	0.56	Kocabag, 1985
	0.62	Payant and Finch, 2010
Galena	0.28	Mehta & Murr, 1983
		Kocabag, 1985
Sphalerite		Mehta & Murr, 1983
	0.46	Kocabag, 1985

In the presence of an electrolyte, two sulphides with different rest potential in contact form a galvanic cell. By convention, the cathode is the sulphide with higher rest potential and the anode the sulphide with lower rest potential (Kwong et al. 2003). In an oxidative milieu, the anodic reaction for a sulphide mineral containing a bivalent metal is (Kwong et al. 2003):

$$MS=M^{2+}+S+2e \quad (2.14)$$

and the cathodic reaction (Kwong et al., 2003) is:

$$^{1}/_{2}O_2+2H^{+}+2e=H_2O \quad (2.15)$$

giving the overall reaction:

$$MS+^{1}/_{2}O_2+2H^{+}=M^{2+}+S+H_2O \quad (2.16)$$

An alternative cathode reaction, as noted by Payant et al. (2001), is:

$$Fe^{3+} + e = Fe^{2+} \quad (2.17)$$

2.5. Galvanic effect in stage A

Payant et al. (2011) reported on the role of galvanic effects in SH of sulphide mixtures, and pointed out that sulphide mixtures with a rest potential difference (ΔV) higher than 0.2 V did SH whilst mixtures with $\Delta V < 0.1$ V did not self-heat.

The moisture present in stage A plays the role of electrolyte. Taking the mixture sphalerite and pyrite as an example, pyrite with higher rest potential acts as the cathode, whilst sphalerite with lower rest potential acts as the anode. The electrochemical process is represented by the following equations:

$ZnS = Zn^{2+} + S^{o} + 2e$ (2.18)

${}^{1}/_{2}O_2 + H_2O + 2e = 2OH^{-}$ (2.15)

$Fe^{3+} + e = Fe^{2+}$ (2.17)

It is the rest potential difference (ΔV) that is the driving force for the galvanic effect. The larger the ΔV, the greater the probability of galvanic interaction (Rao and Finch, 1988).

In a review of the electrometallurgy of sulphides, Wadsworth (1972) showed that the initial dissolution of ZnS resulted in the formation of H_2S. The apparition of H_2S during dissolution of sulphide minerals was also reported by Thomas et al. (2001) and Harmer et al. (2006) who proposed the following route:

$S_2^{2-} + 2Fe^{2+} + 2H^{+} = H_2S + S^{2-} + 2Fe^{3+}$ (2.19)

The formed H_2S is further oxidized conform (Wadsworth, 1972):

$H_2S + H_2SO_4 = H_2SO_3 + H_2O + S^{0}$ (2.20)

$2H_2S + O_2 = 2S^{0} + 2H_2O$ (2.21)

$H_2S + 2O_2 = SO_4^{2-} + 2H^{+}$ (2.22)

Wadsworth argued that Eq. 2.20 is predominant in high acid solutions whilst Eq. 2.22 is most important at high temperature and Eq. 2.21 which represents the partial oxidation of H_2S is slower and rate limiting.

Due to the ubiquity of the iron ions in sulphide minerals (Payant et al. 2012), Harmer et al. (2006) argued that when the concentration of Fe^{2+} ions in Eq. 2.19 increases, the Fe^{2+} ions may form an oxido-reduction cycle made of reaction 2.17 representing the galvanic effect and Eq. 2.19 representing the dissolution reaction leading to the formation of H_2S. As the concentration of Fe^{2+} in Eq. 2.19 increases, more H_2S and Fe^{3+} are formed conform Le Chatelier principle and because of the oxido-reduction cycle Fe^{3+} is reduced to Fe^{2+} and the cycle is repeated.

2.6. The transient model of SH

2.6.1. Theory

Models to describe SH for a reactive porous solid involve physico-chemical parameters (e.g., the specific heat capacity, the activation energy, the enthalpy of the reaction) (Semenov, 1928; Frank-Kametskii, 1969; Bowes, 1984; Chen & Chong, 1995; Chong et al., 1995; Cuzzillo & Pagni, 1998; Nugroho et al., 1998; Clothier & Pritchard, 2003; Yang et al., 2011). One is the transient self-heating model (Chen & Chong, 1995):

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho Q A e^{-E_a / RT} \tag{2.23}$$

where ρ is the density of the solid (kg.m^{-3}), C_p the specific heat capacity of the solid (J.kg^{-1}.K^{1}), T temperature (K), t time (s), λ the thermal conductivity of the solid (W.m^{-1}.K^{-1}), x distance (m), Q the heat of reaction (J.kg^{-1}), A the pre-exponential factor of the Arrhenius equation (s^{-1}), E_a the apparent activation energy (J mol^{-1}), and R the universal gas constant (J mol^{-1}.K^{-1}). The left hand side of the equation is the local rate of enthalpy change in the solid, i.e., the heat loss term. The first term on the right-hand side is the conduction term, and the last term is the heat gain due to the exothermic reaction. Yang et al. (2011); Chen & Chong (1995) and Chong et al. (1995) identified a uniform temperature profile in the center line of their samples in which case the conduction term becomes zero and equation (2.22) can be rewritten as:

$$\frac{\partial T}{\partial t} = SHR = \frac{QA}{C_p} e^{-E_a/RT} \tag{2.24}$$

or

$$\ln(SHR) = \ln(QA/C_p) - E_a/RT \tag{2.25}$$

where SHR is self-heating rate.

The cognizance of C_p may help assess self-heating risk, find application in the modeling of SH of sulphide materials and modify SH standard test. Knowledge of E_a has several potential uses: to identify reactions by comparison with literature data; to classify a material's tendency to SH; and to provide an essential component in building a model of sulphide self-heating. Since there is a correlation between activation energies and bond energies in molecules, determining E_a may help to trace the nature of the chemical reactions (Hirschfelder, 1941).

2.6.2. Examples of the use of E_a in determination of reaction mechanism

Vyazovkin and Linert, (1997); Vyazovkin and Lesnikovich, (1988); Chornet and Roy, (1980); Larsson and Mascetti, (1997) and Boudart and Mariadassou, (1984) found a linear relationship between the energy of activation (E_a) and the logarithm of the Arrhenius pre-exponential factor (A):

$\ln A = a + bE_a$ (2.26)

The slope b in Equation 2.25 is given by relation (Larsson and Mascetti, 1997; Vyazovkin and Linert, 1995):

$b = 1/RT_{iso}$ (2.27)

where T_{iso} is the isokinetic temperature. From the T_{iso}, the resonance vibrational frequency (ν_{iso}) is calculated from (Vyazovkin and Linert, 1995):

$\nu_{iso} = k_b T_{iso}/h$ (2.28)

where k_b and h are the Boltzman and Planck constants respectively. For example, Fairbridge et al. (1978) reported for pyrolysis of cellulose and a number of wood products, the following relation for the Arrhenius parameters (E_a and A):

$$\ln(A)(\mathrm{min}^{-1})=-1.86+0.2E_a\times(\mathrm{kJ\ mol}^{-1}) \tag{2.29}$$

The isokinetic temperature, T_{iso}, was 602 K and ν_{iso} = 418 cm^{-1}. This value of the resonance vibrational frequency corresponded to the far infrared (i.r) spectra of cellulose with a broad adsorption band at about 450 cm^{-1} (Vyazovkin and Linert, 1995). Park et al. (2009) found a strong positive relationship between ln(QA) and E_a. They concluded that QA (a reaction term) can be expressed by varying only the energy of activation. Hirschfelder (1941) showed that the E_a can be related to the bonding energy of the reactants. For the exothermic reaction: a + bc = ab + c, Hirschfelder derived the following relation between E_a and the energy of the bond bc:

$$E_a = 0.055D_{bc} \tag{2.30}$$

Michaelides, (2003) established a relationship between E_a and the enthalpy changes for dissociation reactions.

2.6.3. SH studies by Yang et al. (2011)

Sulphide SH studies were performed by Yang et al. (2011) using the so-called “basket method”, their apparatus made of a cylindrical wire mesh basket, 3 thermocouples, a data logger thermometer and a computer (Figure 2.4). The aim of their work was to measure the self-heating rates for sulphide minerals at the cross point temperature.

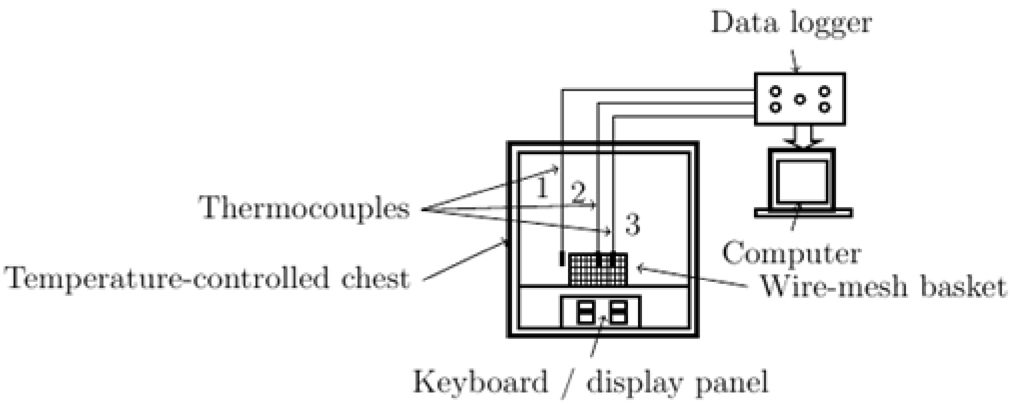

Figure 2.4 Self-heating instrumentation (basket method) (adapted from Yang et al. 2011)

The sample was placed into the basket which was introduced into a chamber with recirculating air to sustain a temperature up to 300° C. Two thermocouples were used to measure the temperature at the center of the sample and another at a point located 10 mm from the center. The third thermocouple was used to measure the ambient temperature. All thermocouples were connected to a data logger which was linked to a computer. Temperature vs. time curves for two samples at a constant temperature of 160° C resulting from the work by Yang et al. are shown in Figure (2.5).

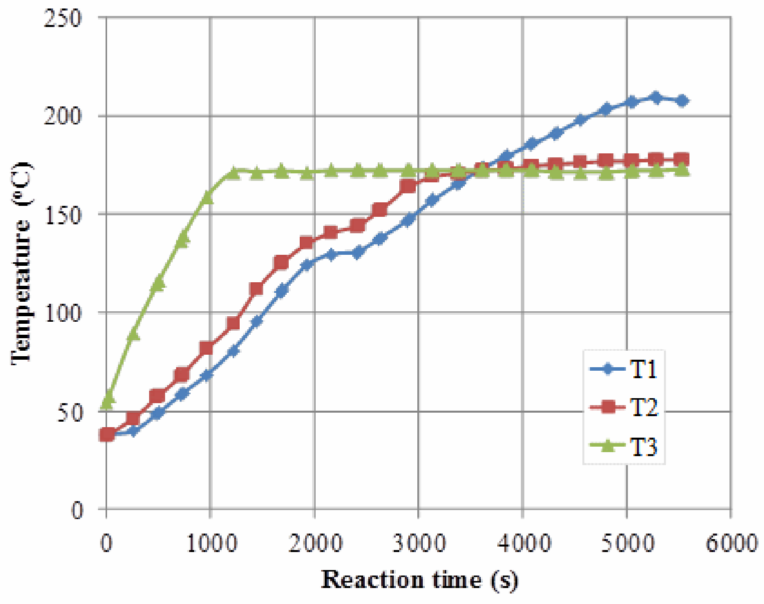

Figure 2.5 (adapted from Yang et al. 2011)

Samples were heated at constant ambient temperature till such time as the temperature at the center (T1) became higher than the temperature at 10 mm off the center (T2). The cross point temperature (To) was found at the intersection of the curves described by T1, T2 and the ambient temperature (T3). The crossing - points for sulfur rich and iron—rich sulfide concentrates were 176.1° C and 170.5° C respectively. The SHR were determined at the crossing point temperature. For the data analysis, Yang et al. (2011) used the transient model of self-heating. Plots of ln(dT/dt) vs. -1000/(RT_o) from Yang et al. 2011, are shown in Figure 2.6.

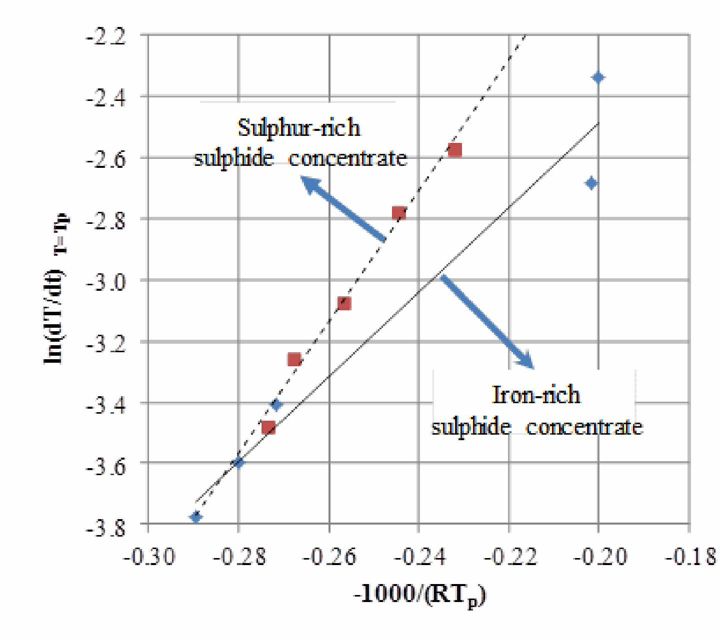

Figure 2.6 ln(dT/dt) vs. -1000/T (adapted from Yang et al. 2011)

From the slopes of these lines, the energy of activation was estimated, giving values: 21.38 $kJ.mol^{-1}$ and 13.76 $kJ.mol^{-1}$ for sulphur-rich and iron-rich sulphide concentrates respectively. Noting the difference, Yang et al. (2011) suggested that iron-rich sulphide concentrates are more reactive than the sulphur- rich sulphide concentrates.

From Figure 2.6, it is possible to obtain values of ln(QA/C_p), about 4 for the sulphur-rich sulphide concentrate and 3.7 for the iron-rich sulphide. The experiments of Yang et al. (2011) were conducted at temperatures which correspond to stage B of SH. Although it is important to obtain data on SH at high temperatures, knowledge of SH physico-chemical parameters at temperatures where SH begins, i.e. temperature < 100° C are essential for SH prediction.

2.7. Summary

1. Self-heating (SH) of sulphide concentrates is a serious issue which can lead to fires in mining operations, and in storage and transportation of concentrates and environmental damages;
2. Self-heating occurs in stages, A (from ambient to 100° C), B (from 140° C), C (350° C, the ignition point);
3. Sulphide mineral concentrates self-heat in presence of moisture in stage A;
4. Self-heating is enhanced with certain mixtures of sulphides, surmised to be a galvanic effect ;
5. Self-heating capacity (SHC) was calculated using heat capacities of sulphide minerals from literature. SHC is not a characteristic property of the material like the specific heat capacity;
6. The positive relationship between the heat outputs from SH apparatus and heat outputs from DSC in stage C demonstrates that the SH apparatus is a type of calorimeter;
7. Energy of activation for bone dry iron-rich and sulphur-rich concentrates have been determined using the basket method and applying the transient model of SH;
8. There is a lack on the data on physico-chemical properties (C_p, E_a, enthalpy change ΔH, entropy change ΔS and Gibbs free energy change ΔG) of SH of sulphide concentrates in the temperature range where SH begins, i.e. < 100° C.

In the next chapter (Chapter 3), the determination of the specific heat capacity of sulphide concentrates will be described.

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Chapter 3 : Self-heating: Determination of specific heat capacity of sulphide materials at temperatures below 100°C in presence of moisture

Abstract

The specific heat capacity (C_p) of one copper and three nickel concentrates was determined using the self-heating apparatus and by drop calorimetry over the temperature range 50 to 80° C in the presence of 6% moisture. The C_p values from both techniques were comparable and shown to be measuring the same property. The C_p values were similar for all four concentrates increasing from ca 0.4 to 1.4 $J.g^{-1}.K^{-1}$ as temperature increased from 50° to 80° C. Uses of C_p to identify self-heating risk and to modify the standard test are discussed.

3.1. INTRODUCTION

Substances possess characteristic properties that determine their physico-chemical behavior (Grenier et al., 1998: Marchenko, 2012). One of the principal properties that characterises heat transfer is the specific heat capacity. For example, Waples and Waples (2004) note the importance of specific heat capacity in modeling thermal history of rocks; and closer to the topic of this paper, Bunyan et al. (1988) argued that knowledge of the specific heat capacities of materials could permit prediction of self-heating. Models of self-heating contain the specific heat capacity term (Semenov, 1928; Frank-Kamenetskii, 1969; Bowes, 1984; Beever and Drysdale, 1992; Chen and Chong, 1995; Cuzzillo and Pagni, 1998; Nugroho et al. 1998; Miyake et al.2000; Clothier and Pritchard, 2003; Yang et al. 2011).

Self-heating of sulphide minerals is known to commence at temperatures < 100° C in presence of moisture (Rosenblum et al. 1995; 2001). Although specific heat capacities of synthetic minerals at low temperature are available (Anderson et al. 1932; 1937; Grønvold et al. 1959; Čermák and Rybach, 1982; Schön, 1983; Demensky and Teplov, 1987; Berezovskii et al. 2001), there is little data on specific heat capacities of natural materials at low temperature in the presence of moisture.

In this work, the specific heat capacity of one copper and three nickel concentrates is determined in the presence of moisture as a function of temperature below 100^{o} C using the self-heating apparatus of Rosenblum et al. (1995, 2001) and a standard technique, drop calorimetry.

3.2. THEORY

3.2.1. Specific heat capacity

The specific heat capacity at constant pressure (C_p) of a substance is the amount of heat needed to raise the temperature of one gram of the substance by 1K. The specific heat capacity is a physical characteristic of a material and is an intensive thermodynamic property, that is, independent of the size of the sample. The C_p can be estimated from the relation (Chang, 1981; Noggle, 1985; Cemič, 2005):

$$\Delta Q = mC_p\Delta T \tag{3.1}$$

where ΔQ (J) is the heat supplied, m (g) the mass of the substance, and ΔT (K) the temperature rise. The higher the C_p of a substance, the more difficult it is to heat up and the slower it is to cool down. Specific heat capacities for pure compounds can be estimated using the Maier and Kelly relation (Maier and Kelly, 1932) when the composition of the compound is known:

$$C_p = a + bT + cT^{-2} \tag{3.2}$$

where a, b, c are specific heat coefficients and T is temperature (K). Equation 3.2 was developed from standard calorimetric methods (Goranson, 1942). Values of a, b, c for some sulphides are summarized in Table 3.1.

Table 3.1 Values of a, b, c for some sulphides (Anderson and Crerar, 1993)

Sulphides	**Formula**	**a**	**b x 10^3**	**c x 10^{-5}**
Bornite	Cu_5FeS_4	0.414	0.292	0.0112
Chalcopyrite	$CuFeS_2$	0.472	0.291	0.0304
Pyrite	FeS_2	0.623	0.0459	0.106
Triolite	FeS	0.246	1.25	NR

N.B. Values of a, b, c are from Anderson and Crerar (1993) and converted from $cal.mol^{-1}.K^{-1}$ for a and $cal.mol^{-1}.K^{-2}$ for b and $cal.\ mol^{-1}.K$ for c. NR: not reported.

Table 3.2 shows specific heat capacities of several sulphide minerals measured at temperatures below 100^o C (Anderson et al., 1932; 1937; Grønvold et al. 1959; Lewis et al. 1961; Čermák and Rybach, 1982; Schön, 1983).

Table 3.2 Measured C_p ($J.g^{-1}.K^{-1}$) of some sulphide minerals at T < 100^o C

Sulphide mineral	**C_p**	**Reference**
Chalcopyrite	0.540	Čermák and Rybach (1982)
Galena	0.207	Čermák and Rybach (1982)
	0.205–0.206	Anderson (1932; 1937)
Pyrite	0.500–0.520	Schön (1983)
	0.502–0.515	Anderson (1932; 1937)
Pyrrhotite (FeS)	0.556–0.639	Grønvold, et al. (1959)
Pyrrhotite ($Fe_{0.887}S$)	0.594–0.652	
Sphalerite	0.450	Čermák and Rybach (1982)

Most sulphide materials encountered in mining are mixtures. Therefore Equation 3.2 is not strictly applicable and the C_p needs to be measured. Further, self-heating at low temperature (< 100^o C) is prompted by presence of moisture, which needs to be included in test work. The test procedure of Rosenblum et al., (2001) uses a standard addition of 6% moisture which is used in the present study. Since the C_p for water is relatively high, this must be taken into account when determining the C_p of the samples. To illustrate, Harries and Ritchie, (1987) reported C_p of 0.867 $J.g^{-1}.K^{-1}$ for an oxidized dry pyritic waste and a C_p of 1.350 $J.g^{-1}.K^{-1}$ for the same material containing 11% moisture. The C_p of water as a function of temperature is given by (Osborne et al. 1937; Marsh, 1987):

$$\frac{C_p(T^oC)}{C_p(15^oC)} = 0.996185 + 0.0002874 \times (\frac{T+100}{100})^{5.26} + 0.11160 \times 10^{-0036T} \quad (3.3)$$

where T is temperature (^{o} C). The reference to water at 15^o C was adopted by the International Committee for Weights and Measures, Paris 1950, following the suggestion of de Haas (Richarson, 2012). The C_p of water at 15^o C is 4.1855 $J.g^{-1}.K^{-1}$.

3.2.2. Measurement of C_p using Self-heating Apparatus

The procedure in the self-heating apparatus of Rosenblum et al. (2001) is to expose a sample to a series of air injections and record the temperature vs. time response. Provided that the reaction is close to or at completion and the temperature variation is small, the area under the temperature vs. time curve (referred to here as the 'heating curve') is related to the total heat generated by the reaction (s) in the system (Thomas and Bowes, 1961; Dosch, and Wendlant, 1970; Satava and Veprek, 1976; Zivkovic, 1979; Bunyan, 1988).

Bunyan (1988) proposed that if samples were run under the same conditions, then one with known C_p could be used to calculate C_p for a sample of unknown C_p as follows:

$$C_{pu} = \frac{m_k \times A_u \times C_{p_k}}{m_u \times A_k} \quad (3.4)$$

where m is mass in gram, A area under the heating curve and subscripts u and k refer to unknown and known, respectively.

Equation 3.4 is a consequence of the relationship between the sample mass and the enthalpy of the reaction (Eq. 3.5) (Satava and Veprek, 1976; Zivan and Zivkovic, 1979; Legendre et al. 2006):

$$m_s \Delta H_r = K(\gamma, \lambda) \times A \tag{3.5}$$

where m_s is the mass of the sample (g), ΔH_r the enthalpy of the reaction($J.K^{-1}$), $K(\gamma, \lambda)$ a calorimeter constant which is a function of γ, the geometry of the calorimeter, and λ, the thermal conductivity of the sample.

3.2.3. Measurement of C_p by Drop Calorimetry

Drop calorimetry is a technique in which the amount of heat given up by a substance is measured by cooling it from an initial temperature (T_i) to a final temperature (T_f) at constant pressure (Anderson et al., 1993). Commonly, a sample is heated in an oven to T_i and quenched in a Dewar containing water to T_f. The estimation of specific heat capacity ($J.g^{-1}.K^{-1}$) is as follows (Kukkonen and Lindberg, 1998):

$$C_{pu} = \frac{(C_{cal} + C_{pw}) \times (T_f - T_{wi}) \times m_w}{m_u \times (T_i - T_f)} \tag{3.6}$$

where C_{cal} is the heat capacity of the Dewar ($J.K^{-1}$), C_{pw} the specific heat capacity of water estimated using Equation 3.3, and T_{wi} the temperature of water in ^{o} C, immediately before introducing the sample.

3.3. EXPERIMENTAL

3.3.1. Materials

The samples were three Ni-concentrates, two from Raglan (Nunavik, Canada, Raglan 1 and Raglan 2) and one from Voisey’s Bay (Labrador, Canada), and a Cu-concentrate from Voisey’s Bay. As a substance of known C_p, Chalcopyrite (75%) from Xstrata Nickel’Strathcona Mine was used. The principal components of the samples are shown in Table 3.3. In the concentrates, note the presence of substantial pyrrhotite (Po), which is perhaps the most reactive self-heating sulphide (Rosenblum et al., 2001). As a test material of known specific heat capacity to verify the drop calorimeter method zinc (99.99%) purchased from Alfa Aesar, Ward Hill, MA was used.

Table 3.3 Major components of the samples (%)

Sample	Chalcopyrite	Pentlandite	Pyrrhotite
Ni-conc. (Voisey's Bay)	1.3	72	25
Ni-conc. (Raglan 1)	3.9	42	29
Ni-conc. (Raglan 2)	4.2	45	30
Cu-conc. (Voisey's Bay)	88	1.9	10
Chalcopyrite sample	75	NR	NR

NR: not reported

3.3.2. Self-heating apparatus technique

3.3.2.1. The setup

The SH apparatus and the experimental procedures are described in Rosenblum et al. (1995; 2001), and Somot and Finch (2010). The apparatus is shown in Figure 3.1. It consists of the following major components: a Pyrex cell, a thermocouple, a gas inlet and exhaust system, a heater, insulation, a stainless steel screen, and a seal cover. The sample is placed in the middle of the Pyrex cell supported by the screen. Air is introduced from the bottom and exhausted, along with any other resulting gases, at the top of the cell. The heating response to a timed sequence of air injections is recorded, from which the self-heating rate (SHR) is computed.

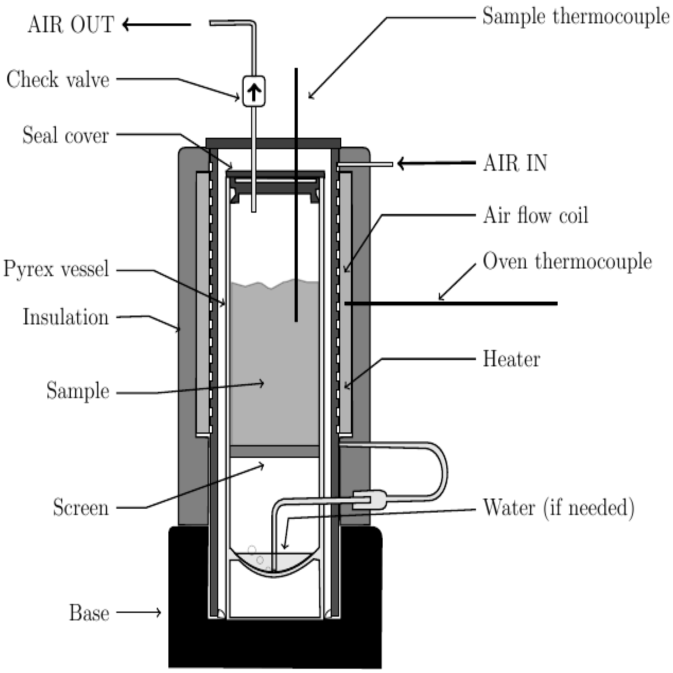

Figure 3.1 Schematic of the self-heating apparatus (adapted from Rosenblum et al. 2001)

3.3.2.2. Procedure

The procedure is based on the standard test of Rosenblum et al. (2001) (for discussion purposes referred to as ‘Rosenblum standard test’). Five hundred gram bone dry samples were mixed with 31 g water, introduced as a spray and the samples thoroughly homogenized by strongly shaking the mixture within the plastic bag, to give the standard 6% moisture. The samples were placed in the Pyrex cell. Three 80 mL.min^{-1} air injections each of 15 minutes duration were used spaced 5 hours to return to the set temperature. The test was performed at 50, 60, 65, 70 and 80^{o} C. At the set temperature, the average SHR was measured for the 3 air injections. An example heating curve is given in Figure 3.2. The number above the peak is the SHR, calculated as shown in the inset. The number below the peak is the area under the (heating) curve determined by the midpoint rectangular rule for use in Eq. 3.4.

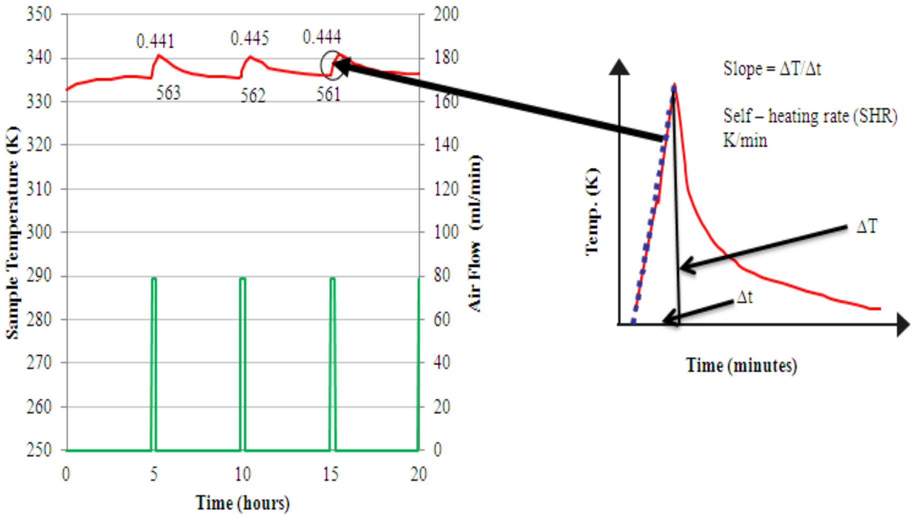

Figure 3.2 Example of self-heating curve (or thermogram) showing response to 3 air injections of 80 mL.min^{-1} (left); and method of calculating SHR (right) and area under the curve.

At the end of the test, after one hour the temperature was raised to the next temperature and the process repeated. Each condition was repeated three times and the mean and 95% confidence interval determined.

3.3.3. Drop calorimetry technique

3.3.3.1 Determination of the heat capacity of the calorimetry (C_{cal})

The calorimeter was a Dewar from Dilvac (UK) made of a double-walled glass chamber with a stainless steel cover. The specifications were: capacity; 1liter; outer diameter; 11.3 cm; overall height; 22.5 cm; internal diameter; 8.3 cm; and internal depth; 18 cm.

The heat capacity can be determined by measuring the temperature change when a known mass of water at elevated temperature is added to a known mass of water at lower temperature (Barlag et al. 2010; Misra, 2012). The heat lost is gained by the cold water and calorimeter, provided no heat leaks to the surroundings. In the present case the cold and hot water were used and mixed for about 5 minutes. The following equation was then used to calculate C_{cal} (Misra, 2012):

$$C_{pu} = \frac{C_{pw} \times m \times (\Delta T_h - \Delta T_c)}{\Delta T_c} \tag{3.7}$$

where m is the mass of cold (or hot) water , and

$$\Delta T_h = T_h - T_m \tag{3.8}$$

with T_h the temperature of hot water immediately before mixing, and T_m the temperature after mixing, and

$$\Delta T_c = T_m - T_c \tag{3.9}$$

with T_c the temperature of cold water just before mixing.

3.3.3.2. Procedure

A 150 g of sulphide sample homogenized with 9 g water to give 6% moisture was heated to a known temperature in an oven made in our laboratory. This had a metal chamber for heating. The heated sample at measured temperature T_r was immediately quenched in water of known mass (500 g) and temperature (T_{wi}) in the Dewar which was at ambient temperature. The sample was well mixed with the water using a spatula to achieve thermal equilibrium and the final temperature (T_f) was measured. Temperature was monitored using a thermocouple (TKJ model HH23, Omega) with a resolution of 0.1 K and Eq. 3.6 was solved to determine the specific heat capacity. A schematic of the procedure is shown in Figure 3.3. Each condition was tested three times and the mean and 95% confidence interval were estimated. To test validity, the specific capacity of zinc (mass = 200 g) was also determined 3 times.

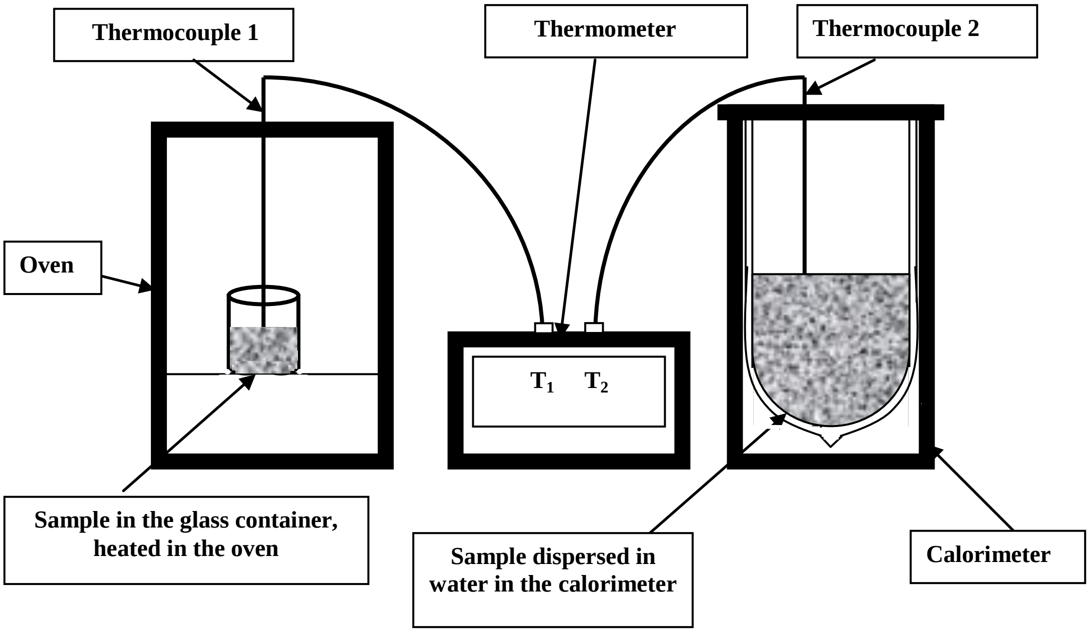

Figure 3.3 The schematic of procedure for drop calorimetry

3.3.4. Comparison of methods

Bland and Altman (1983; 1986; 1995) noted that two (or more) measurements could be correlated but not necessarily measuring the same property. They developed a test, the Bland-Altman plot, which is the difference between the two measurements against the average of the two measurements. The plot reveals any bias which can be tested for statistical significance. The plot is used in many fields including analytical chemistry and medical statistics (Dewitte et al. 2002).

3.4. RESULTS

3.4.1. C_p for the standard reference sample

The C_p for the standard reference Cu-concentrate sample with 6% moisture was determined by drop calorimetry at each temperature. The results are presented in Table 3.4.

Table 3.4 Specific heat capacities ($J.g^{-1}.K^{-1}$) (95% CI) for reference Chalcopyrite sample with 6% w/w water.

Temperature (K)	**$C_p(J.g^{-1}.K^{-1})$**
323	0.336 – 0.339
333	0.800 – 0.802
338	1.106 – 1.108
343	1.297 – 1.299
353	1.436 – 1.438

3.4.2. Self-heating apparatus technique

A specimen calculation of C_p is illustrated: At 70^o C (343 K), the area under the SH curve for Ni-concentrate Raglan 1was 566 K.min and for the reference sample the area was 570 K.min with corresponding C_{pk} of 1.298 $J.g^{-1}.K^{-1}$ (Table 3.4). Using Eq. 3.4, and taking the mass of the sample with known C_{pk} (m_k) equal to that of the sample with unknown C_{pu} (m_u), then,

$$C_{pu} = \frac{566K.\min \times 1.298J.g^{-1}.K^{-1}}{570K.\min} = 1.289J.g^{-1}.K^{-1} \qquad (3.10)$$

Repeating these calculations for all conditions, the 95% confidence interval (95% CI) for C_p for the concentrates as a function of temperature are shown in Table 3.5.

Table 3.5 C_p ($J.g^{-1}.K^{-1}$) (95% CI) for the concentrates determined using SH apparatus

Temperature (K)	**Ni-conc. Raglan 1**	**Ni-conc. Raglan 2**	**Ni-conc. Voisey's Bay**	**Cu-conc. Voisey's Bay**
323	0.545 – 0.563	0.346 – 0.530	0.442 – 0.468	0.332 – 0.368
333	1.189 – 1.217	1.088 – 1.102	0.876 – 0.978	0.773 – 0.778
338	1.255 – 1.299	1.383 – 1.403	1.216 – 1.228	1.192 – 1.193
343	1.288 – 1.290	1.409 – 1.426	1.226 – 1.244	1.316 – 1.318
353	1.559 – 1.581	1.537 – 1.539	1.263 – 1.491	1.437 – 1.438

3.4.3. Drop calorimetry technique

3.4.3.1. Heat capacity of calorimeter (C_{cal})

The heat capacity of the calorimeter was measured 3 times by setting the cold water temperature at 15.0 ^{o}C and the hot water temperature accurately at 45.0 ^{o}C. Using Equation 3.6, the mean C_{cal} was 77.4 ± 2.5 $J.K^{-1}$ (95% CI).

3.4.3.2. Validation: Specific heat capacity of zinc

The 95% CI for the C_p of zinc determined in this this work is shown to be comparable to the literature (Table 3.6).

Table 3.6 The C_p ($Jg^{-1}K^{-1}$) of zinc

This work		**Literature**		**Reference**
Temperature (K)	**C_p**	**Temperature (K)**	**C_p**	
366	0.317– 0.377	273 – 773	0.385 – 0.470	Marsh, 1987
		372 - 634	0.392 – 0.411	Jaeger and Bottema, 1933

3.4.3.3. The concentrates.

The specific heat capacities (95% CI) determined as a function of temperature using Eq. 3.10 are recorded in Table 3.7.

Table 3.7 C_p ($J.g^{-1}.K^{-1}$) (95% CI) for nickel- and copper concentrates using drop calorimetry

Temperature (K)	**Ni-conc. Raglan 1**	**Ni-conc. Raglan 2**	**Ni-conc. Voisey'Bay**	**Cu-conc. Voisey's Bay**
323	0.582 – 0.668	0.414 – 0.572	0.501 – 0.523	0.330 – 0.346
333	1.106 – 1.306	0.787 – 0.999	0.825 – 1.031	0.731 – 0.871
338	1.257 – 1.315	1.162 – 1.317	1.177 – 1.281	1.070 – 1.144
343	1.295 – 1.519	1.115 – 1.369	1.290 – 1.434	1.247 – 1.349
353	1.437 – 1.743	1.438 – 1.664	1.360 – 1.578	1.362 – 1.512

3.4.3.4. Comparison of methods

The precision of measurement was similar for both the SH and DC techniques, the pooled estimate of standard deviation being 0.168 and 0.155, respectively.

To assess whether the two methods are measuring the same property, the Bland-Altman plot was used (Figure 3.4). It is observed that a mean difference of -0.015, which lies well within the bounds of the the 95% upper and lower limits of agreement indicating that this is not significantly different from line (0). The evidence is that both methods are measuring the same property.

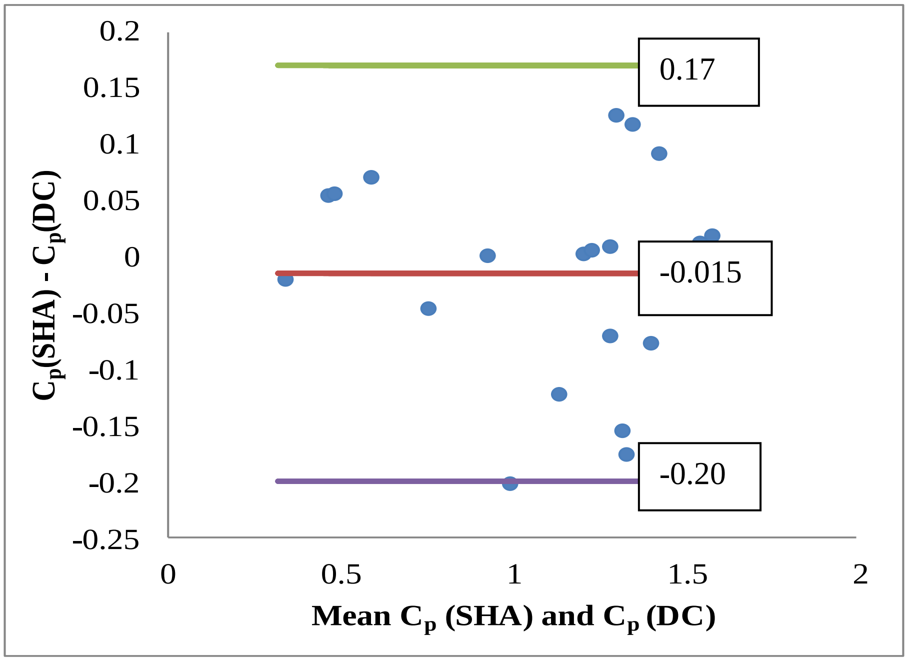

Figure 3.4 Bland-Altman plot of C_p data obtained from 20 paired samples using self-heating apparatus and drop calorimetry (mid line is average difference with upper and lower 95% confidence bounds).

3.4.3.5. C_p vs.Temperature from this work and literature

The C_p vs. temperature for the concentrates from this work and for synthetic sulphide minerals from literature is shown in Figure 3.5. The best fit line for the concentrates with an adjusted R^2 of 0.889 by both methods is:

$$C_p = -0.00095T^2 + 0.680T - 120 \qquad (3.11)$$

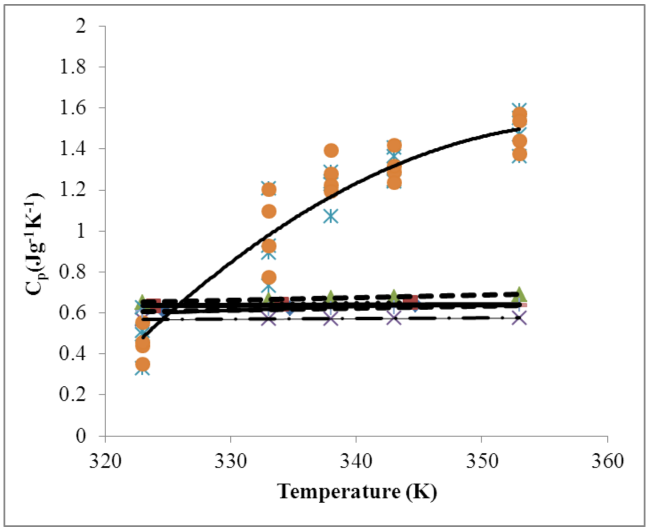

Figure 3.5 C_p vs. temperature for concentrates measured in this work (stars are by drop calorimetry and filled circles are by self-heating apparatus), and for indicated synthetic sulphide minerals from Grønvold, 1959 ($Fe_{1.000}S$, $Fe_{0.877}S$); Satava and Veprek, 1976 (FeS); Anderson and Crerar,1993 ($CuFeS_2$, FeS); and Berezovskii, 2001 ($Fe_{4.60}Ni_{4.54}S_8$).

3.5. DISCUSSION

The argument has been advanced that the self-heating apparatus of Rosenblum et al. can be treated as a calorimeter and thus can be used to measure physico-chemical properties related to self-heating (SH) (Rosenblum et al., 2001; Ngabe et al., 2011; Somot and Finch, 2011). This is attractive as the apparatus is designed to make measurements under the practical conditions of temperatures below 100^{o} C in presence of moisture. The present work supports this contention. The Bland-Altman plot indicates that the SH C_p results correspond with the independent measure using drop calorimetry (DC) which in turn was validated by showing the C_p for zinc was comparable to literature values. The equivalence between the SH and DC methods indicates that the source of heat, internal from oxidation reactions in the case of SH and external in the case of DC is immaterial, which is thermodynamically correct. The evidence is that the SH apparatus yields valid estimates of C_p.

The use of the SH apparatus may have advantages determining the C_p of materials that self-heat. The technique is straight forward but does take time (5 hours). Conventional calorimetric methods tend to be unsuitable for materials which self-heat because exothermic reactions may occur to affect the C_p measurement (Bunyan, 1988). This problem does not appear to be a factor in the present DC experiments according to the interpretation of Figure 3.5 and certainly there was no indication of chemical reactions (e.g. pH change, color change). The reason is likely to be the high water content in the DC experiment. Rosenblum et al. (2001) noted that self-heating was eliminated when moisture exceeded 10%(in the present case the water content in the DC case was 333%(150 g sample added to 500 g water). The C_p values for three Ni-concentrates do differ slightly. Since the samples are not identical in composition that is likely the source of the differences which lead variation in the intensity of atomic vibrations.

The concentrate C_p values are of the same magnitude as the synthetic mineral data (Table 3.2) but trend with temperature. Calculations showed that the difference is not due to the presence of moisture: mathematically adding 6% moisture to the synthetic mineral data increased C_p by about 20% but did not introduce the trend. The difference may be due to the mix of major components (e.g. pyrrhotite with pentlandite, and pyrrhotite with chalcopyrite) and the presence of impurities. Hogan, (1969) showed that even small concentrations of impurities in alloys can cause a large change in specific heat capacity. The contributions of the impurities to C_p of a number of substances have been reported by Mancini and Potter, (1987); Nadareishvili et al. (2003); and Okulov et al. (2011). Mojumdar et al. (2009) found at 30 – 200^o C, that the specific heat capacity of stored pyrite (6.58 – 9.13J.g^{-1}.K^{-1}) was 10 times higher than that of fresh grinded pyrite (0.56 – 0.65 J.g^{-1}K^{-1}). The difference in C_p between the concentrates and synthetic minerals seem to have several possible origins that would require further work; but, regardless, the difference implies it is best to measure C_p if possible. The present work has shown that measurement is feasible using the Rosenblum standard test technology.

The determination of C_p has a number of uses in the study of sulphide self-heating. Since most SH models include C_p, a measurement technique is required. In the Rosenblum standard test risk assessment involves the self-heating capacity (SHC) which is computed from the self-heating rate multiplied by C_p for which an average value is used for all sulphide materials. (The value is 0.6 $J.g^{-1}.K^{-1}$, as noted in Figure 5). The thermogram output from the standard test contains the heating curve used here to calculate C_p suggesting that an algorithm could be included to provide an estimate of C_p in the computation of SHC. What is required is a reference C_p material that self-heats.

The magnitude of C_p does indicate the tendency to heat up, so the value may be indicative of a sample's heating response to any self-heating reactions that are occurring. Thus including a C_p determination may help assess self-heating risk. Knowing C_p is a step towards computing the entropy and enthalpy of the SH process and hence the Gibbs free energy. This latter application of C_p will be explored in chapter 4.

3.6. CONCLUSIONS

The specific heat capacity (C_p) of three Ni- and one Cu-sulphide concentrates was determined under conditions where self-heating starts, i.e., temperatures $< 100^{o}$ C in presence of moisture, using the self-heating (SH) apparatus in an adaptation of the Rosenblum et al. test method and confirmed by drop calorimetry (DC). The measurement of C_p could be incorporated into the standard self-heating test of Rosenblum et al. (2001). The C_p of the concentrates was found to increase with temperature over the range 50-80^{o} C, different from the literature for synthetic sulphide minerals where C_p is largely independent of temperature over this range. This difference emphasizes the need to measure C_p. The measurement of C_p demonstrated in this work may help assess self-heating risk and find application in the modeling of self-heating of sulphide materials.

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Chapter 4 . Self-heating: Enthalpy, Entropy and Gibbs free energy changes for sulphide concentrates

Abstract

The enthalpy (ΔH) (J.g^{-1}) and entropy (ΔS) (J.k^{-1}.g^{-1}) changes for the self-heating (SH) of sulphide concentrates were determined at 50 – 80^{o} C. The enthalpy change was negative and the entropy change positive. The Gibbs free energy change (ΔG) (J.g^{-1}) determined at the mean temperature of 65^{o} C was negative. The values of ΔH and ΔG being negative, self-heating is exothermic and spontaneous. The value of ΔH determined in this work is similar to that for sulphide minerals self-heating found in literature.

4.1. INTRODUCTION

In the literature, self-heating (SH) of materials is referred to as spontaneous heating (Raemy and Lambelet, 1982). That it is spontaneous follows from ordinary experience, the heat flow which proceeds only in one direction is considered spontaneous (Noggle, 1985; Cemič, 2005). Spontaneous heating of sulphide concentrates has been widely reported (e.g. Rosenblum et al.2001; Somot and Finch, 2010; Yang et al. 2011). The spontaneity of a process is determined by thermodynamic functions (e.g. entropy, Gibbs free energy) (Noggle, 1985; Cemič, 2005, 1985) and thermodynamic stability occurs when the system is at its lowest energy state. The stability of sulphide materials subject to self-heating needs to be assessed.

The purpose of this chapter is to determine the enthalpy, entropy and Gibbs free energy changes due to self-heating of nickel and copper concentrates using self-heating apparatus and test methodology.

4.2 THEORY

4.2.1. Determination of the specific heat capacity C_p

The theory of C_p determination using the self-heating apparatus was outlined in Chapter 3. We recall here that the measurement procedure in the self-heating apparatus (Rosenblum et al. 2001; Somot and Finch, 2010) is to expose a sample to air injection and record the temperature vs. time response. Provided that the reaction(s) is close to or at completion and the temperature variation is small, the area under the temperature vs. time curve is related to the total heat generated by the reaction in the system (Thomas & Bowes, 1961; Dosch, and Wendlant, 1970; Satava and Veprek, 1976; Zivkovic, 1979; Bunyan, 1988). Bunyan (1988) argued that if samples were run under the same condition, then one with known C_p could be used to calculate C_p for a sample of unknown C_p as follows:

$$C_{pu} = \frac{m_k \times A_u \times C_{pk}}{m_u \times A_k} \tag{4.1}$$

where C_{pu} and C_{pk} are the specific heat capacities for samples of unknown and known heat capacity, m_k and m_u are the masses (g) of the samples of known and unknown specific heat capacity, A_k and A_u the areas under the heating curves for the samples of known and unknown specific heat, respectively.

Equation 4.1 is a consequence of the relationship between the sample mass and the enthalpy of the reaction (Equation 4.2) (Satava & Veprek, 1976; Zivan & Zivkovic, 1979; Legendre et al. 2006):

$$m\ \Delta H_r = K(\gamma, \lambda) \times A \tag{4.2}$$

where m is the mass of the sample, ΔH_r is the enthalpy of the reaction, K(g, λ) is a calorimeter constant which is a function of g, the geometry of the calorimeter, and λ, the thermal conductivity of the sample.

4.2.2. Enthalpy and Entropy change

The enthalpy change with temperature at constant pressure is described by the relations (Noggle, 1985):

$$dH = C_p dT \tag{4.3}$$

and:

$$dH = TdS \tag{4.4}$$

where dH is the enthalpy change, C_p ($\mathrm{Jmol^{-1}K^{-1}}$), the heat capacity, and T is temperature (K) and dS the entropy change ($\mathrm{JK^{-1}}$).

$$TdS = C_p dT \tag{4.5}$$

or:

$$dS = \frac{C_p dT}{T} \tag{4.6}$$

Therefore, the entropy change can be expressed as (Noggle, 1985):

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT \tag{4.7}$$

Since dT/T = d(lnT), the entropy change becomes:

$$\Delta S = \int_{\ln T_1}^{\ln T_2} C_p d(\ln T) \tag{4.8}$$

4.2.3. The Gibbs free energy change

Knowledge of ΔS is not sufficient to prove the spontaneity of a process, the change in Gibbs free energy (ΔG) must be known as well (Noggle, 1985). The Gibbs free energy function G is defined (Nash, 1970; 2005; Noggle, 1985):

$$G = H - TS \tag{4.9}$$

where G, H, S are the Gibbs free energy, enthalpy and entropy functions respectively. For a change at constant temperature and pressure (Noggle, 1985),

$$(dG)_{T,P} = dH - TdS \tag{4.10}$$

Integrating eq. 4.10, the change in Gibbs free energy is (Nash, 2005):

$$\Delta G = \Delta H - T\Delta S \tag{4.11}$$

The criterion for a spontaneous change at constant T and P is (Nash, 2005):

$$\Delta G = \Delta H - T\Delta S < 0 \tag{4.12}$$

The possible combinations (cases) for enthalpy, entropy and Gibbs free energy changes are summarized in Table 4.1 (Nash, 1970; 2005). A process can occur when ΔG is negative (Nash, 1970; 2005).

Table 4.1 Possible cases for ΔH, ΔS and ΔG

ΔH	**ΔS**	**ΔG**
-	+	- process always favored
+	-	process never favored
-	-	? process favored when temperature low
+	+	? process favored when temperature high

4.3. EXPERIMENTAL

4.3.1. Materials

The samples were three Ni-concentrates two from Raglan (Nunavik, Canada:, Raglan 1 and Raglan 2), and one from Voisey's Bay (Labrador), and a Cu-concentrate from Voisey's Bay. As a substance of known C_p, $CuFeS_2$ of high purity from Xstrata Nickel's Strathcona Mine was used. The main components of the samples are shown in Table 4.2. In the concentrates, note the presence of substantial pyrrhotite (Po), which is perhaps the most reactive self-heating sulphide (Rosenblum et al., 2001).

Table 4.2 Major components of the samples (%)

Sample	Chalcopyrite	Pentlandite	Pyrrhotite
Ni-conc. (Voisey's Bay)	1.3	72	25
Ni-conc. (Raglan 1)	3.9	42	29
Ni-conc. (Raglan 2)	4.2	45	30
Cu-conc. (Voisey's Bay)	88	1.9	10

4.3.2. Self-heating apparatus and technique

4.3.2.1. The setup

The SH apparatus and the experimental procedures are described in Rosenblum et al. (1995; 2001), and Somot and Finch (2010). The apparatus is shown in Figure 3.1. It consists of the following major components (Figure 3.1): a Pyrex cell, a thermocouple, a gas inlet and an exhaust system, a heater, insulation, a stainless steel screen and a seal cover. The sample is placed in the middle of the Pyrex glass supported by the screen. Air is introduced from the bottom and exhausted, along with any other resulting gases, at the top of the cell. The heating response to a timed sequence of air injections is recorded (thermogram), from which the self-heating rate (SHR) is computed.

4.3.2.2. Procedure

The procedure is based on the standard test (Rosenblum et al. 2001). In the present case three air injections each of 15 minutes duration and spaced 5 hours to return to the set temperature were used. The test was performed at 50, 60, 65, 70 and 80^{o} C. At the set temperature, the average SHR was measured for the 3 air injections. An example thermogram showing three temperature-time responses is given in Figure 3.2. The number below the peak is the area under the curve determined by the midpoint rectangular rule; and the enlarged view of the third peak illustrates how the SHR is determined.

After a one-hour cooling, period a third air injection, the temperature was raised to the next setting and SHR measured again.

The C_p for the standard reference chalcopyrite sample with 6% moisture (Table 4.3) was reported in Chapter 3.

Table 4.3 Specific heat capacities ($J.g^{-1}.K^{-1}$) (95% CI) for reference chalcopyrite sample with 6% w/w water.

Temperature (K)	$C_p(J.g^{-1}K^{-1})$
323	0.336 – 0.339
333	0.800 – 0.802
338	1.106 – 1.108
343	1.297 – 1.299
353	1.436 – 1.438

4.4. RESULTS AND DISCUSSION

4.4.1. Specific heat capacity

A specimen calculation of C_p is illustrated: At 70°C (343 K), the area under the SH curve for Ni-concentrate Raglan 1 was 566 K.min and for the reference sample the area was 570 K.min with corresponding C_{pk} of 1.298 $J.g^{-1}.K^{-1}$ (Chapter 3) and (Table 4.3). Using Eq. 4.1, and taking the mass of the sample with known C_{pk} (m_k) equal to that of the sample with unknown C_{pu} (m_u), then

$$C_{pu} = \frac{566K.\min \times 1.298 J.g^{-1}.K^{-1}}{570K\min} = 1.289 J.g^{-1}.K^{-1} \tag{4.14}$$

Repeating these calculations for all conditions, the 95% confidence interval (95% CI) for C_p for the concentrates as a function of temperature is shown in Table 4.4 and Figure 4.1.

Table 4.4 C_p values (95% CI) for Ni- and Cu-concentrates determined using SH apparatus

Temperature (K)	**Ni-conc. Raglan 1**	**Ni-conc. Raglan 2**	**Ni-conc. Voisey'Bay**	**Cu-conc. Voisey's Bay**
T_u(K)	**C_p($JK^{-1}g^{-1}$)**	**C_p($JK^{-1}g^{-1}$)**	**C_p($JK^{-1}g^{-1}$)**	**C_p($JK^{-1}g^{-1}$)**
323	0.545 – 0.563	0.346 – 0.530	0.442 – 0.468	0.332 – 0.368
333	1.189 – 1.217	1.088 – 1.102	0.876 – 0.978	0.773 – 0.778
338	1.255 – 1.299	1.383 – 1.403	1.216 – 1.228	1.192 – 1.193
343	1.288 – 1.290	1.409 – 1.426	1.226 – 1.244	1.316 – 1.318
353	1.559 – 1.581	1.537 – 1.539	1.263 – 1.491	1.437 – 1.438

4.4.2. Determination of ΔH, ΔS and ΔG

4.4.2.1. Determination of ΔH

A plot of C_p against temperature is shown in Figure 4.1. The best fit line with an adjusted R^2 = 0.889 is:

$$C_p = -0.00095T^2 + 0.680T - 120 \tag{4.15}$$

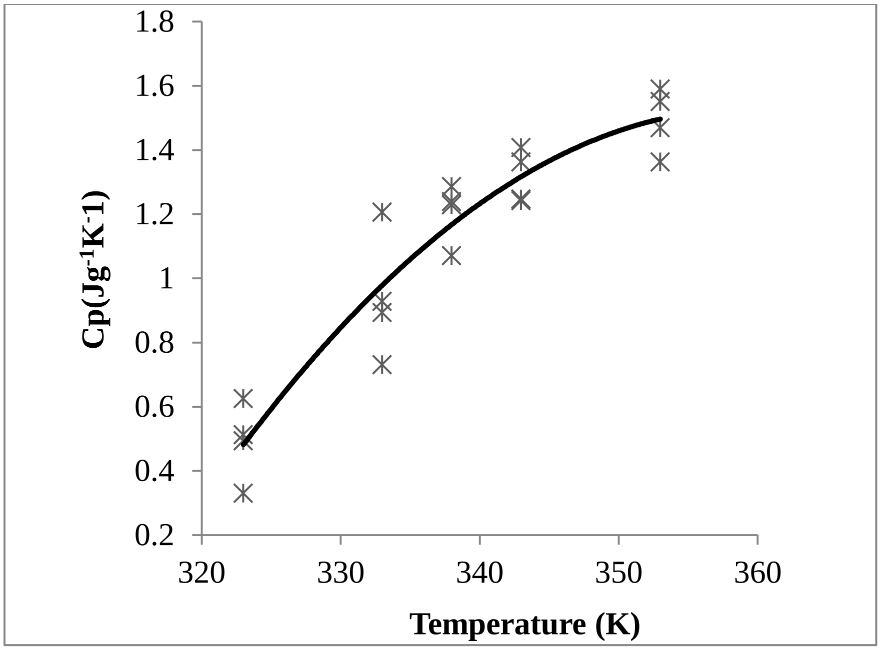

Figure 4.1 Specific heat capacity vs. temperature.

The enthalpy change ΔH was determined from the integration of eq. relation 4.15. The enthalpy change was equal to -134 $J.g^{-1}$. This value compares well the one case found in literature (Table 4.5).

Table 4.5 Values of enthalpy change from this work and literature

Sample	Temperature range (K)	Other conditions	$\Delta H (Jg^{-1})$	Source
Ni-and Cu-conc.	323 - 353	Heating due to Self-heating using self-heating apparatus in stage A	-134	This work
Sulphide minerals ores	423 - 523	Heating due to self-heating using DSC in stage B	-188.2 to -42.1	Iliyas et al. 2011

4.4.2.3. Determination of ΔS and ΔG

The plot of C_p vs. lnT is shown in Figure 4.2. The best fit line with an adjusted $R^2 = 0.910$ is:

$$C_p = -123.59(\ln T)^2 + 1450.6 \ln T - 4255.2 \qquad (4.16)$$

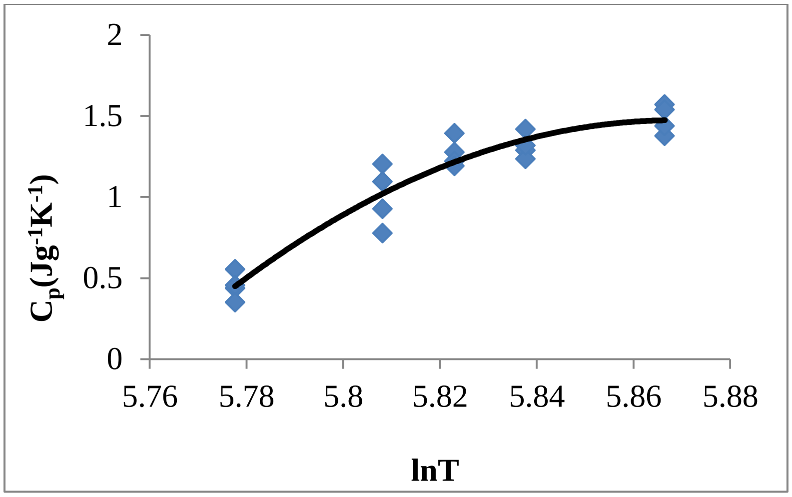

Figure 4.2 Specific heat capacity vs. ln T

The entropy change ΔS and the Gibbs free energy changes were calculated using Eq.4.16 and Eq. 4.12 respectively. Δ**S** was equal to 0.0839 $J.K^{-1}.g^{-1}$and ΔG at the mean temperature of 65^o C equal to -163 $J.g^{-1}$.

The enthalpy (ΔH) and the entropy (ΔS) changes were negative and positive respectively. The value for ΔG determined at the mean temperature of 65^o C was negative. The values of ΔH and ΔG being negative, self-heating of sulphide concentrates is exothermic and spontaneous. Since ΔH is negative and ΔS is positive, the self-heating process will always occur (Nash, 1970; 2005) (Table 4.1).

The physico-chemical parameters determined here are needed, along with the energy of activation of the reaction responsible for self-heating, in the modelling. Therefore, in the next chapter (chapter 5), the energy of activation for the reaction causing the self-heating of concentrates will be determined.

4.5. CONCLUSIONS

The enthalpy, entropy and Gibbs free energy changes for self-heating of Ni-and Cu-concentrates have been determined. The enthalpy change and the Gibbs free energy being negative, self-heating is exothermic and spontaneous.

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Chapter 5 . Self-heating: Estimating activation energy from a sulphide self-heating test

Abstract

Using a custom-designed self-heating apparatus and procedure, activation energy (E_a) was determined for four sulfide-bearing materials: two nickel concentrates, a copper concentrate and a sphalerite/pyrite mixture. The E_a ranged from 22-29 kJ.mol^{-1}, implying a common reaction. Comparing to literature, the E_a values correspond to partial oxidation of hydrogen sulfide, supporting the contention that H_2S may be an intermediate product in the self-heating of sulfide minerals.

5.1. INTRODUCTION

The extraction of mined resources can encounter spontaneous exothermic reactions that initiate spontaneous heating or self-heating (SH). One example is coal (Zarrouk & O'Sullivan, 2006) and others, the subject of concern here, are sulfide minerals. The SH of some sulfides poses a challenge in all stages of production: mining, concentrate storage and shipment, and tailings disposal (Ninteman, 1978; Harries and Ritchie, 1987; Rosenblum et al., 2001; Liu, 2002; Elberling, 2005; Wu & Li, 2005; Wang et al., 2009; Somot & Finch, 2010; Yang et al., 2011). The problem is attracting increasing study, particularly as the new IMSBC (International Maritime Solid Bulk Cargoes) code for safe handling of mineral concentrates, which now includes self-heating specifically, has come into effect since January 2011 (Laudal, 2010). Data on SH rates and capacities have been published by Rosenblum and co-workers (1995, 2001), Somot and Finch (2010), and Payant et al. (2011). Activation energies have been reported by Yang et al. (2011) in a study of spontaneous combustion of sulphide concentrates during storage and by Ilyas et al. (2010) in a study of thermal stability of sulphide minerals.

Self-heating of sulphides is considered to occur in stages (Rosenblum et al., 2001): stage A below 100^{o} C where moisture is critical (ca. 3 – 8% moisture accelerates SH); stage B (ca. 100 – 350^{o} C) where SH appears to be related to elemental sulfur generated in stage A reactions; and stage C, above 350^{o} C where ignition occurs (the process has runaway). Stage A, therefore initiates the SH process and the associated reactions (i.e., the mechanism) are a research focus. The purpose of this work is to determine the self-heating activation energy associated with stage A using the SH test apparatus and procedure of Rosenblum and co-workers (1995, 2001).

5.2. THEORY

Models to describe SH for a reactive porous solid involve physico-chemical parameters (e.g., the activation energy, the enthalpy of the reaction) (Semenov, 1928; Frank-Kametskii, 1969; Bowes, 1984; Chen & Chong, 1995; Chong et al., 1995; Cuzzillo & Pagni, 1998; Nugroho et al., 1998; Clothier & Pritchard, 2003; Yang et al., 2011). One is the transient self-heating model (Chen & Chong, 1995):

$$\rho C_p \frac{\partial T}{\partial t} = \lambda \frac{\partial^2 T}{\partial x^2} + \rho Q A e^{-E_a / RT} \tag{5.1}$$

where ρ is the density of the solid ($kg.m^{-3}$), C_p the specific heat capacity of the solid ($J.kg^{-1}.K^{1}$), T temperature (K), t time (s), λ the thermal conductivity of the solid ($W.m^{-1}.K^{-1}$), x distance (m), Q the heat of reaction ($J.kg^{-1}$), A the pre-exponential factor of the Arrhenius equation (s^{-1}), E_a the apparent activation energy ($J.mol^{-1}$), and R the universal gas constant ($J.mol^{-1}.K^{-1}$). The left hand side of the equation is the local rate of enthalpy change in the solid, the heat loss term. The first term on the right-hand side is the conduction term, and the last term is the heat gain due to the exothermic reaction, assuming no depletion of the sample. Chen & Chong (1995) and Chong et al. (1995) identified a uniform temperature profile in the center line of their samples in which case the conduction term becomes zero and equation (5.1) can be rewritten as:

$$\frac{\partial T}{\partial t} = SHR = \frac{QA}{C_p} e^{-E_a/RT} \tag{5.2}$$

or

$$\ln(SHR) = \ln(QA/C_p) - E_a/RT \tag{5.3}$$

where SHR is self-heating rate. This paper presents estimates of the energy of activation of self-heating of sulphide samples at < 100^{o} C using equation (5.2) by adapting the apparatus and test procedure of Rosenblum and co-workers (1995, 2001) to measure SHR as a function of temperature.

Knowledge of E_a has several potential uses: to identify reactions by comparison with literature data; to classify a material's tendency to SH; and to provide an essential component in building a model of sulfide mineral self-heating. Since there is a correlation between activation energies and bond energies in molecules, determining E_a may help to trace the nature of the chemical reactions (Hirschfelder, 1941).

5. 3. EXPERIMENTAL

5.3.1. Samples

The samples were two Ni-concentrates, one from Voisey's Bay (Labrador, Canada) and the second from Raglan (Nunavik, Canada), a Cu-concentrate from Voisey's Bay and a mixture of pyrite and sphalerite. The principal components of the samples are shown in Table 1. In the concentrates, note the presence of substantial pyrrhotite (Po), which is perhaps the most reactive sulphide (Rosenblum et al., 2001; Somot & Finch, 2010). As a material with no pyrrhotite, the mixture of sphalerite (Sp) and pyrite (Py), found to self-heat by Payant et al. 2011.

Table 5.1 Major components of the samples (%)

Sample	Chalcopyrite	Pentlandite	Pyrite	Pyrrhotite	Sphalerite
Ni-conc. (Voisey's Bay)	1.3	72		25	
Cu-conc. (Voisey's Bay)	88	1.9		10	
Ni-conc. (Raglan)	3.9	42		29	
Sphalerite / Pyrite			50		50

The concentrate samples were shipped as slurry in sealed containers. They were pressure filtered, placed in plastic bags, sealed and stored in a freezer. Prior to a test, 500g subsamples were cut, dried for 24 hours at 60^{o} C in a vacuum oven, ground to less than 53 µm to increase the surface area, and to each, 6% moisture was set by spraying and mixing in 31 g of water.

For the sphalerite / pyrite case, around 4 kg samples of pyrite from Zacatecas (Mexico), and sphalerite (Balmat, USA) were purchased from Wards Scientific. The materials were received as ~ 2 – 3 cm^3 chunks which were crushed using a Marcy jaw crusher and reduced to less than 53 µm in a ball mill with inert ceramic grinding media. A 50:50 500 g mixture was made and 30 g of water was added.

5.3.2. SELF-HEATING TEST

5.3.2.1. SH apparatus

Experiments were performed using a standard SH method (Rosenblum and co-workers, 1995; 2001; Somot & Finch, 2010).

The apparatus consists of the following major components (Figure 3.1): a Pyrex cell, a thermocouple, a gas inlet and an exhaust system, a heater, insulation, a stainless steel screen and a seal cover. The sample is placed in the middle of the Pyrex glass supported by the screen. Air is introduced from the bottom and exhausted, along with any other resulting gases, at the top of the cell. The heating response to a timed sequence of air injections is recorded, from which heating rates (SHRs) are computed. The standard test encompasses the two stages, A and B, with the following conditions:

1. Number of cycles: 10;
2. Duration of air injection for every cycle: 15 min;
3. Time between injections: 5 hours (to return sample to the set temperature)
4. Temperature (^{o}C): 70 (stage A), 140 ^{o}C (stage B)
5. Air flow rate (ml.min^{-1}): 100 (stage A) and 250 (stage B).

In this work, we are concerned only with stage A. The test was modified to have only 3 air injections and a range of set temperatures.

5.3.2.2. Test for temperature uniformity

An array of 9 calibrated thermocouples was inserted at the centre plane of the sample where the set temperature is recorded (Figure 5.1). This setup was designed to test conformity with equation (5.1).

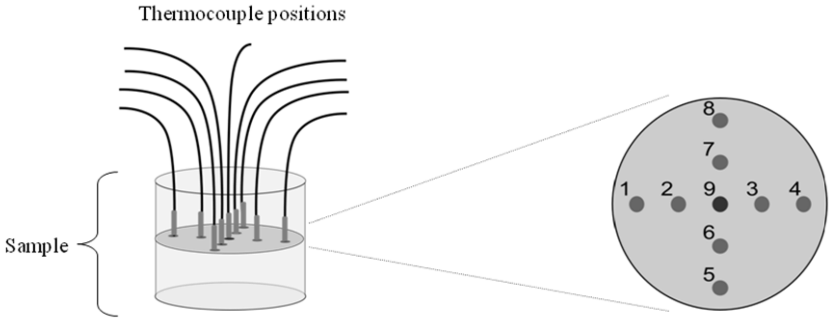

Figure 5.1 Setup to test temperature uniformity: array and numbering of thermocouples

5.3.2.3. Procedure

Samples were tested at 45 to 85^{o} C (318 to 358K) in 5^{o} C increments. At the set temperature, the self-heating rate was measured for 3 air injections (total time 15 hours). An example thermogram and estimation of SHR are illustrated in Figure 3.2. After cooling for one hour, the temperature was raised 5^o C and SHR measured again. This was repeated for 3 independent samples for the concentrates (i.e., 9 SHR values at each temperature) and twice for the less abundant Sp / Py mixture (i.e., 6 SHR values) from which the mean and ninety–five percent confidence interval (95% CI) were determined.

5.4. RESULTS

5.4.1. Temperature uniformity

An example illustrating the uniformity of the temperature (and SHR) at the centre plane is given in Table 5.2. This is judged to meet the requirement to employ Equation (5.2).

Table 5.2 Establishing uniformity of temperature and SHR at center plane of sample

Thermocouple no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Temperature (^{o}C)	70.3	70.1	70.2	70.2	70.3	70.2	70.2	70.3	70.2
SHR(^{o}C/hr)	26.5	26.7	26.6	26.2	26.5	26.5	26.6	26.5	26.6

5.4.2. Self-heating rate

The 95% CI for SHR (K.min^{-1}) (Table 5.3) demonstrates good repeatability. Self-heating rates were higher for the two Ni-concentrates than for the Cu-concentrate and the Sp / Py mixture.

Table 5.3 Self-heating rate (K.min^{-1}): 95% confidence interval

Temperature (K)	**Ni-Concentrate, Voisey's Bay (n = 9)**	**Ni-Concentrate, Raglan (n=9)**	**Cu-Concentrate, Voisey's Bay (n=9)**	**Sp / Py (n = 6)**
318	0.205 – 0.210	0.294 – 0.299	0.0810 – 0.0830	0.0991 - 0.0993
328	0.307 – 0.320	0.372 – 0.380	0.111 – 0.113	0.127 – 0.128
333	0.323 – 0.329	0.419 – 0.427	0.133 – 0.135	0.141 - 0.142
338	0.379 – 0.387	0.482 – 0.502	0.152 – 0.155	0.160 – 0.161
343	0.440 – 0.449	0.527 – 0.538	0.177 – 0.181	0.176 – 0.177
348	0.512 – 0.522	0.589 – 0.600	0.198 – 0.202	0.206 – 0.210
353	0.631 – 0.657	0.665 – 0.678	0.257 – 0.262	0.230 – 0.233
358	0.664 – 0.693	0.748 – 0.763	0.278 – 0.283	0.250 – 0.253

5.4.3. Determining E_a

Plots of ln(SHR) vs. 1/T resulted in linear negative relationships of Arrhenius type with R^2 ranging from 0.993 to 0.997 (Figure 5.2). The least squares best fits were: y = -2.636x + 7.0624 for Ni-concentrate from Raglan; y = -3.356x + 8.992 for Ni-concentrate from Voisey's Bay; y = -3.533x + 8.586 for Cu-concentrate from Voisey's Bay and y = -2.727x + 6.249 for the Sp/ Py mixture. From the slopes the E_a can be calculated (Table 5.4).

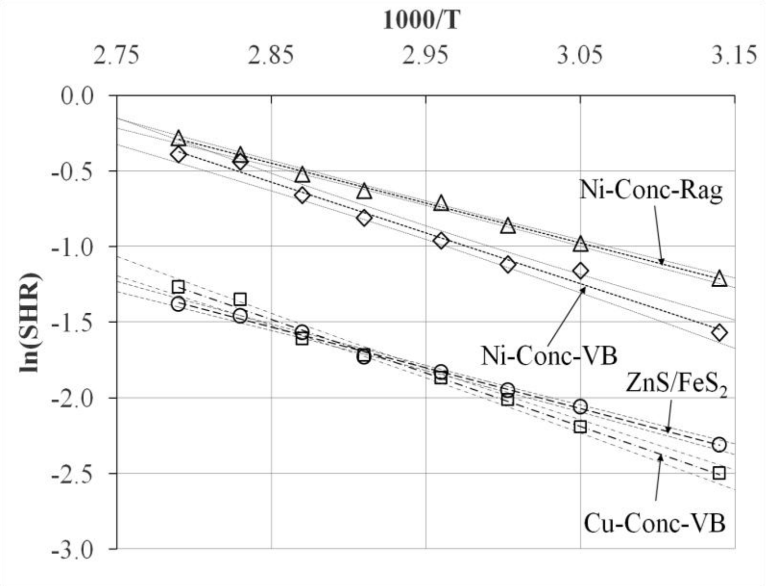

Figure 5.2 The ln(SHR) vs. 1000/T plots for the four samples

Table 5.4 Energy of activation for the reaction causing self-heating : 95% CI

Samples	**E_a(kJ.mol^{-1})**
Ni–conc. (Voisey's Bay)	26-29
Ni - conc. (Raglan)	22-23
Cu - conc. (Voisey's Bay)	28-30
Sp / Py	22-23

5.4.4. Comparison of SH E_a values with literature

A number of reactions have been surmised to cause SH of sulfide minerals. Some of these and the associated energies of activation are shown in Tables 5.5a and 5.5b.

Table 5.5 a. Energy of activation for oxidation of sulfide minerals

Reaction	**Temperature Range (^oC)**	**Other conditions**	**E_a (kJ.mol^{-1})**	**Source**
$FeS + O_2 + H_2O = 4Fe(OH)_2 + 4S^0$	25 – 45	pH: 2.5	47 – 63	Janzen et al., 2000
$FeS + O_2 = Fe_2O_3 + SO_2$	46 – 120	Oxidation with dry air $\Delta H = 22 – 34\ Jg^{-1}$	80 - 120	Iliyas et al., 2010
$FeS + 3/4O_2(aq) + 1/2H_2O = S(aq) + FeOOH\ (s)$	25	pH: 2.75 – 3.45	31 – 52	Chirița et al., 2008
$FeS_2 + O_2 + 1/2H_2O = Fe^{2+} + 2SO4^{2-} + 2H^+$	3 – 25	Carbonated buffered solution	88	Nicholson et al., 1988
$FeS_2 + O_2 + H_2O = Fe^{2+} + 2SO4^{2-} + 2H$	NR	pH: 2	49 - 64	Mckibben & Barnes, 1986
$CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2(g)$	330 - 440		222 - 282	Sokič, 2008

Table 5.5 b: Energy of activation E_a (kJ.mol^{-1}) for oxidation of H_2S

Reaction	**Temp. (^{o} C)**	**Other conditions**	**E_a**	**Source**
$H_2S + 1/2O_2 = H_2O + S$	NR	Direct catalytic oxidation on Mg-Cr	34	Konshenko et al., 2001
	8 -24	pH: 3-10, oxidation in sour waste water on activated carbon	21	Dalai et al., 1999
	30 - 80	Oxidation on activation carbon, relative humidity: 5 – 60%, $O_2/H_2S = 2$	30	Wang et al., 2006
	25 - 50	pH: 3.5 – 5, on $PW_{11}M(H_2O)O^{-5}_{39}$, (M=Fe, Co, Ni)	25	Kuznetsova & Yurchenko,, 1989
	< 120	γ-Al_2O_3 catalyst	33	Steijns et al., 1976
	120 - 240	Active charcoal	13 – 17	
	> 300	Al_2O_3	40	Steijns et al., 1976
	125 -200	Activated charcoal	24	Ghosh & Tollefson, 1986
$H_2S + 3/2O_2 = H_2O + SO_2$	>300	γ-Al2O3; Carbon molecular sieve (CMS); sugar as catalysts	68	Dupont et al., 2003

5.5. DISCUSSION

While the self-heating rates for two Ni-concentrates were higher than the other two samples (Table 5.3), the E_a values were similar for all samples (Table 5.4). This implies that the reaction is the same regardless whether the sample contains substantial pyrrhotite or not; i.e., it appears to be independent of the mineral type.

The range in E_a, 22-30 $kJ.mol^{-1}$ (Table 5.4), is generally lower than that reported for oxidation of iron and copper sulphide minerals at low temperature, 47-120 $kJ.mol^{-1}$ (Table 5.5a). Iliyas et al. (2010) even found that the oxidation of iron sulphides was endothermic at low temperature. It seems therefore that direct oxidation of sulphide minerals is not the cause of SH below 100^o C, at least in the present test setup. Somot and Finch (2010) raised the possibility that H_2S is an intermediate reaction product in stage A. Its subsequent partial oxidation (upper reaction in Table 5.5b) could be responsible for SH and for producing and mobilizing the sulfur that appears to be the fuel for stage B SH reactions. There have been several investigations of H_2S oxidation (Table 5.5b). While the conditions varied, the range in E_a reported for partial oxidation at low temperature, 21–33 $kJ.mol^{-1}$, is similar to that found here. At low temperature, it is expected that the incomplete oxidation of H_2S is more likely than complete oxidation to SO_2 (Steinjs et al., 1976).

Hirschfelder (1941) argued that the experimental activation energy may be related to the bonding energy and suggested that if the reaction A + BC = AB + C is exothermic then the energy of activation is equal to:

$$E_a = 0.055 D_{BC} \tag{5.4}$$

where D_{BC} is the bonding energy of reactant BC. For the partial oxidation (exothermic) reaction $1/2O_2 + H_2S = H_2O + S$, with average bonding energy for (H–S) being 368 $kJ.mol^{-1}$ (Chang, 1981), then the estimated E_a is: $0.055 * 368\ kJ.mol^{-1} \sim 20.2\ kJ.mol^{-1}$. For H_2S, the bonding energy for H-S is 376 $kJ.mol^{-1}$ (Chottard et al.1995) and E_a is 0.055*376kJ.mol-1~21.0. These values being close to the measurement here offers further support for the partial oxidation of H_2S being the origin of SH at low temperature (i.e., stage A). Yang et.al. (2011) reported E_a = 21 $kJ.mol^{-1}$ and 14 $kJmol^{-1}$ for the SH of sulfur-rich sulfide concentrates and iron-rich sulfide concentrates at 176 and 170^{o} C, respectively. Although the temperatures are higher, the E_a values again correspond to partial oxidation of H_2S, the values being close to E_a for the partial oxidation of H_2S at elevated temperature (120 – 240^{o} C) on an active charcoal catalyst (Table 5.5b). Yang et al. attributed their finding to spontaneous combustion of the sulfides themselves. While we can debate the reaction at elevated temperature (> 100^{o} C), as argued earlier the important exothermic reactions are probably at low temperature (< 100^{o} C) which initiate the self-heating process in practice.

The E_a data obtained here, therefore, are similar to the activation energies for H_2S partial oxidation determined in various sample matrices and as predicted based on Hirschfelder (1941). The presence of the H_2S is attributed to reaction between sulphide and moisture, either directly (Somot & Finch, 2010) or via polysulfides (Harmer et al., 2006; Payant et al., 2011). Moisture is known to be key in SH at low temperature (Rosenblum et al., 1982) and since all sulphides are capable of generating H_2S the type of sulphide would not be important in the stage A SH process, as found here. Pyrrhotite is perhaps the most prone of all the sulphides to forming H_2S (Belzile et al., 2004), which may contribute to its high SH reactivity. The presence of water has also been reported to enhance the rate of H_2S oxidation (Bagreev & Bandosz, 2001; Primavera et al., 1998); and the presence of various potential catalysts for H_2S oxidation in natural materials, like Ni, and Fe (Weres & Tsao, 1983; Avrahmi & Golding, 1968), may be another contributing factor enhancing SH.

In light of the above, it may be surmised that the SH of sulphide minerals at low temperature (<100^{o} C) is caused by the partial oxidation of H_2S as hypothesized by Somot & Finch (2010). As a historical precedent, Divers (1884) reported that H_2S generated in an alkali waste governed the oxidation; that is, a gas generated in bulk can play a major role in the process in which the bulk is not involved. Any mechanism of self-heating must include reactions at low temperature where the process starts. From the present investigation, H_2S appears to play a role.

However, the purpose of this work was the determination of the energy of activation for the reaction surmised to cause self-heating of sulphide materials. The energy of activation for the reaction causing self-heating of concentrates has been determined in Chapter 5. In Chapter 3, the specific heat capacity of concentrates was determined. In the next chapter (chapter 6), the energy of activation and the specific heat capacity for sulphide mixtures will be determined.

5.6. CONCLUSIONS

Activation energy (E_a) for self-heating (SH) of sulphides has been determined in the low temperature range (< 100^{o} C) in the presence of moisture by adapting the self-heating test procedure of Rosenblum and co-workers. The E_a values were similar for the four samples, two Ni concentrates, a Cu concentrate and a mixture of sphalerite / pyrite. The SH E_a were similar to the E_a reported for partial oxidation of H_2S, supporting the suspected role of this intermediate product in initiating self-heating of sulphides at temperatures below 100^{o} C.

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Chapter 6 . Self-heating activation energy and specific heat capacity of sulphide mixtures at low temperature

Abstract

Energy of activation (E_a) and specific heat capacity (C_p) for mixtures of sulphide minerals that on their own do not self-heat (SH), sphalerite / pyrite, pyrite / galena, chalcopyrite / galena and sphalerite / galena, were determined using a self-heating apparatus at temperatures below 100^o C in presence of moisture. The mixtures all gave E_a ranging from 22.0 to 27.8 $kJ.mol^{-1}$, similar to the range reported for Ni- and Cu-concentrates. The E_a is close to that for partial oxidation of H_2S which adds to the contention that the partial oxidation of H_2S contributes to SH of sulphides at low temperature. The C_p values ranged from 0.152 to1.071 $J.K^{-1}g^{-1}$ as temperature rose from 50^o C to 80^o C, similar to the reported findings on Ni- and Cu-concentrates. The role of galvanic interaction in promoting SH is tested by examining correlations with the rest potential difference of the sulphides in the mixture.

6.1. INTRODUCTION

The spontaneous or self-heating of sulphide minerals can pose a hazard anywhere along the extraction chain from mining to concentrate transport. There have been a number of studies of the phenomenon over the years (O'Brien and Banks, 1926; Kirshenbaum, 1968; Farnsworth, 1977; Ninteman, 1978; Johnson, 1981; Rosenblum and Spira, 1995; Wu and Meng, 1995; Rosenblum et al., 2001; Wu and Li, 2005; Wang, 2007; Li, 2007; Somot and Finch, 2010; Payant et al., 2010; 2011; Yang et al., 2011; Bouffard and Senior, 2011). Two conclusions are that self-heating commences at temperatures below 100^o C provided moisture is present, and that pyrrhotite is the sulphide most prone to self-heat (Rosenblum et al., 1995, 2001). Another finding is that many sulphide minerals alone do not self-heat (SH) but can become active in mixtures. Payant et al. (2010; 2011) found this to be the case for 50:50 weight mixtures of chalcopyrite and galena, pyrite and galena, and sphalerite and pyrite. They attributed the origin of the self-heating of the mixtures to galvanic interaction.

Galvanic interaction is driven by the rest potential difference between the components and is known to affect the reactivity of sulphides (Mielczarski & Mielczarski, 2005). For example, an increase in oxidation rate of a mixture of a number of sulphides with pyrite has been reported (Byerley & Sharer, 1992). The patented Galvanox process (Tshilombo, 2004; Dixon et al. 2007) attests to that observation.

To have a role in self-heating the galvanic effect must contribute to one or more of the reactions surmised to be the cause of self-heating. Somot and Finch (2006; 2010) proposed that formation and oxidation of H_2S were important reactions at low temperature ($< 100^o$ C) in the presence of moisture (the 'H_2S hypothesis'). Payant et al. (2011) attributed the self-heating of mixtures to galvanic interaction promoting the formation of H_2S based on the work of Thomas et al. (2001) and Harmer et al. (2006).

We are engaged in determining physico-chemical properties of sulphide self-heating with at least three aims: to provide parameters to assess risk, to model the phenomenon, and to devise options for mitigation. This work is facilitated by a unique self-heating test apparatus developed by Rosenblum et al. (2001) designed to include study of the process at temperatures below 100^o C in the presence of moisture. In Chapter 5, the activation energy of the reaction suspected to cause self-heating (E_a) at temperatures below 100^o C in presence of 6% by weight moisture was determined for Ni-and Cu-concentrates and for a 50:50 weight pyrite / sphalerite mixture using the self-heating apparatus and applying the transient heat model of Chen and Chong (1995). The E_a for all cases was in the range 22-29 $kJ.mol^{-1}$ implying a common reaction. Comparison with literature E_a values suggested the reaction may be the partial oxidation of H_2S which lent support to the role of H_2S in self-heating at low temperature.

The transient heat model also includes the specific heat capacity (C_p). Bunyan (1988) argued that to understand self-heating requires knowledge of C_p. For some synthesized (pure) sulphide minerals, values for C_p are available. However it is known that for solids the C_p is affected by the presence of impurities (Voronin and Kustsenok, 2013). Products from mined sulphides are always mixtures to some degree making it necessary to measure C_p rather than rely on literature estimates. In order to be relevant to self-heating the measurements need to be performed at temperatures below 100^{o} C in the presence of moisture. The self-heating test procedure of Rosenblum et al. (2001) was therefore adapted to extract C_p (Chapter 3). The technique was verified by comparing the C_p results with those from a standard technique, drop calorimetry. The C_p was modeled as function of temperature over the range $50\text{-}80^{o}$ C.

The purpose of this work is to determine the self-heating apparent activation energy and specific heat capacity for a range of sulphide mixtures to test correlations against the rest potential difference to assess the contribution of galvanic interaction to self-heating.

6.2. BACKGROUND

6.2.1. Measurement of activation energy, E_a

Application of the transient self-heating model to sulphide self-heating to determine activation energy was introduced in Chapter 5. Using an array of thermocouples temperature uniformity at the centre plane of the sample in the self-heating apparatus was established permitting the simplified transient heat model of Chen and Chong (1995) to be applied:

$$\frac{\partial T}{\partial t} = SHR = \frac{QA}{C_p} e^{-E_a/RT} \qquad (6.1)$$

Or

$$\ln(SHR) = \ln(QA/C_p) - E_a/RT \qquad (6.2)$$

where C_p is the specific heat capacity of the solid ($J.kg^{-1}.K^{-1}$), T temperature (K), t time (s), Q the heat of reaction ($J.kg^{-1}$), A the pre-exponential factor of the Arrhenius equation (s^{-1}), E_a the activation energy ($J.mol^{-1}$), R the universal gas constant ($J.mol^{-1}.K^{-1}$), and SHR ($K.min^{-1}$) the self-heating rate. The energy of activation E_a and $\ln(QA/C_p)$ are determined, respectively, from the slope and intercept of the plot of ln(SHR) vs. 1/T (Eq. 6.2). The full procedure is described in Chapter 5.

When chemical reactions are alike or suitable for comparison, a linear relationship between the energy of activation E_a and the logarithm of the Arrhenius pre-exponential factor ln(A) has been obtained (Poço et al. 2002; Chornet and Roy (1980), Logvinenko 1980;, Boudart and Mariadassou 1984, Vyazovkin and Lesnikovich, 1988, Vyazovkin and Linert 1997, and Larsson and Mascetti 1997), which suggests:

$$lnA = c + dE_a \tag{6.3}$$

where c and d are the intercept and slope, respectively. This relationship is tested here to determine if self-heating is due to a similar or comparable chemical reaction.

6.2.2. Measurement of specific heat capacity (C_p)

The measurement methodology is described in detail in Chapter 3. The basis is the comparative technique developed by Bunyan (1988) to determine the C_p of an unknown sample from the C_p of a known sample:

$$C_{pu} = \frac{m_k \times S_u \times C_{p_k}}{m_u \times S_k} \tag{6.4}$$

where m is the sample mass in gram, S the area under the heating curve in the output (thermogram) of the self-heating test, and subscripts u and k refer to samples of unknown and known C_p. The technique was validated by showing that the C_p determined using the self-heating appartus agreed with the C_p determined in a standard test, the drop calorimetric method (Chapter 3).

6.2.3. Galvanic effect and H_2S hypothesis

In the presence of an electrolyte, two or more sulphides with differing rest potential in contact form a galvanic cell. Rest potential values from literature for the sulphides studied here are shown in Table 6.1 (Warren, 1978; Biegler & Swift, 1979; Mehta & Murr, 1983; Kocabag, 1985; Payant and Finch, 2010).

Table 6.1 Reported rest potential values (Volts) from literature

Mineral	**Rest potential (V vs. SHE)**	**References**
Pyrite	0.63	Biegler & Swift, 1979
		Mehta & Murr, 1983
	0.66	Kocabag, 1985
	0.69	Payant and Finch, 2010
Chalcopyrite	0.52	Warren, 1978
		Mehta & Murr, 1983
	0.56	Kocabag, 1985
	0.62	Payant and Finch, 2010
Galena	0.28	Mehta & Murr, 1983
		Kocabag, 1985
Sphalerite		Mehta & Murr, 1983
	0.46	Kocabag, 1985

By convention, the cathode is the sulphide with higher rest potential and the anode the sulphide with lower rest potential (Kwong et al. 2003). In an oxidative milieu, the anodic reaction for a sulphide mineral containing a bivalent metal (Me) is

$$MeS = Me^{2+} + S + 2e \qquad (6.5)$$

coupled with the common cathodic reaction:

$$^{1}/_{2}O_2 + 2H^+ + 2e = H_2O \qquad (6.6)$$

giving the overall reaction:

$$MeS + {}^{1}/_{2}O_2 + 2H^+ = Me^{2+} + S + H_2O \qquad (6.7)$$

An alternative cathodic reaction which may be relevant in the context of sulphide self-heating, as noted by Payant et al. (2011), is:

$$Fe^{3+} + e = Fe^{2+} \quad (6.8)$$

giving the overall reaction:

$$MeS + 2Fe^{3+} = Me^{2+} + S + 2Fe^{2+} \quad (6.9)$$

Payant and Finch (2012) linked SH of sulphide mixtures to galvanic effects promoting the formation of H_2S. The partial oxidation of H_2S is among the various reactions suspected to cause SH (the 'H_2S hypothesis'). Somot and Finch (2010) detected H_2S in a sulphide self-heating test and suggested the following reaction:

$$S^{2-} + 2H^{+} = H_2S \quad (6.10)$$

Wadsworth (1972) had shown H_2S to form during dissolution of sulphide minerals, and, among others, proposed the following reaction:

$$S_2^{2-} + 2Fe^{2+} + 2H^{+} = H_2S + S^{2-} + 2Fe^{3+} \quad (6.11)$$

where S_2^{2-} represents one of the polysulphides known to be present on the surface of sulphides due to superficial oxidation in presence of moisture.

The H_2S can be subsequently oxidized by various routes to release heat including (Wadsworth, 1972):

$$2H_2S + O_2 = 2S^0 + 2H_2O \quad (6.12)$$

i.e., the partial oxidation of H_2S.

Noting the almost universal presence of iron ions in sulphide mineral systems, Harmer et al. (2006) argued they may form an oxido-reduction cycle comprising Eq. 6.9, representing the galvanic effect, and Eq. 6.11, the formation of H_2S. It was this oxido-reductive cycle that Payant et al. (2011) suspected in the self-heating of sulphide mixtures.

The energy of activation (E_a) and C_p are physico-chemical terms for the reaction causing SH, and for the material respectively and will be expected to correlate with the rest potential difference (ΔV) of the sulphides in a mixture if galvanic effects are at play.

6.2.4. Relating E_a and C_p to ΔV

The fundamental equation relating the rest potential difference or electromotive force to the Gibbs free energy ΔG is (Chang, 1981; Noggle, 1985):

$$\Delta G = -nF\Delta V \tag{6.13}$$

where n is the number of moles of electrons transferred and F (= 96491 $C.mol^{-1}$) is the Faraday constant (Skoog and West,1980). But,

$$\Delta G = \Delta H - T\Delta S \tag{6.14}$$

where ΔH is the enthalpy change, T the temperature and ΔS the entropy variation; thus we can write:

$$\Delta H = -nF\Delta V + T\Delta S \tag{6.15}$$

According to the Polany-Semenov equation (Levenspiel, 1972; Shestakov, 2003; Uryadov and Ofitserov, 2003; Galtier, 2007):

$$E_a = -\alpha(-\Delta H) + \beta \tag{6.16}$$

where α and ß are constant; therefore,

$$E_a = \alpha nF\Delta V - \alpha T\Delta S + \beta \tag{6.17}$$

Thus we anticipate that E_a will increase as ΔV increases.

To relate ΔV with C_p we note that the enthalpy change is given by (Chang, 1981):

$$\Delta H = mC_p\Delta T \tag{6.18}$$

where m is the mass of the sample and ΔT is the temperature variation. Therefore:

$$C_p = \frac{-nF\Delta V + T\Delta S}{m\Delta T} \tag{6.19}$$

Thus we anticipate that C_p will decrease as ΔV increases.

6.3. EXPERIMENTAL

6.3.1. Samples

Around 4 kg samples of pyrite (from Zacatecas, Mexico), sphalerite (Balmat, USA) and galena (Morocco) were purchased from Wards Scientific and a high-grade chalcopyrite sample was supplied from Xstrata Nickel's Strathcona Mine (Sudbury, Canada). The materials were received as ~ 2-3 cm^3 chunks which were crushed using a Marcy jaw crusher and reduced to less than 53 μm in a ball mill with inert grinding media. The following 50:50 500 g mixtures were made: sphalerite / pyrite (Sp/Py); pyrite / galena (Py/Ga); chalcopyrite / galena (Chp/Ga); sphalerite / galena (Sp/Ga). Water (31 g) was sprayed onto and mixed into each mixture to achieve the 6% w/w moisture of the standard SH test (Rosenblum et al. 2001).

6.3.2. Self-heating (SH) apparatus

The SH apparatus (Figure 3.1) (Chapter 3) has been described by Rosenblum and co-workers, (1995; 2001); Somot & Finch (2010). The sample is held in the middle of the glass container by a stainless steel screen. Air is circulated to reach the set temperature and injected at the bottom. Emanating gases are exhausted at the top or condensed in the lower reservoir.

The standard test conditions for stage A (i.e., below 100°C) of Rosenblum et al. (2001) are modified as follows:

- Number of air injections (cycles): 3;
- Duration of air injection for every cycle: 15 min;
- Time between injections: 5 hours (to return sample to the set temperature);
- Temperature: 45-85°C;

- Air flow rate: 100 $mL.min^{-1}$

6.3.3. Procedure to determine E_a and $\ln(QA/C_p)$

This requires plotting ln(SHR) vs. 1/T, i.e., Eq 6.2. At the set temperature, the self-heating rate (SHR) was measured for the 3 air injections (total time 15 hours). An example output (thermogram) and estimation of SHR (given above the heating curve) are illustrated in Figure 3.2 (Chapter 3). After cooling for one hour, the temperature was raised 5^o C and SHR measured again. This was repeated for 3 replicate samples for all the mixtures except for the less abundant Sp/Py case where there were only 2 replicates. The ninety–five percent confidence interval (95% CI) is reported.

6.3.4. Procedure to determine C_p

Determinations were made at 50, 60, 65, 70 and 80^o C. Under the heating curve in Figure 3.2 (Chapter 3) is an estimation of the area (S, K.min.) using the midpoint rectangle rule. After cooling for one hour, the temperature was raised to the next setting and the measurements repeated. This was done for each sample. The tests were replicated 3 times and 95% CI reported. As the standard reference material for C_{pu} determination in Eq. 6.4 the high purity chalcopyrite (75% $CuFeS_2$) with 6% moisture was used. The C_p had been determined previously (Chapter 3) using the drop calorimetry technique. The data for the reference chalcopyrite are presented in Table 6.2.

Table 6.2 Reported specific heat capacities ($J.K^{-1}g^{-1}$) for the chalcopyrite sample with 6% w/w water (Chapter 3)

Temperature (K)	Calculated C_p
323	0.330 – 0.346
333	0.731 – 0.871
338	1.070 – 1.144
343	1.247 – 1.349
353	1.362 – 1.512

6.4. RESULTS

6.4.1. Activation energy

6.4.1.1 Self–heating rate, SHR

The 95% CI for SHR (K.min^{-1}) (Table 6.3) establishes the precision of the method. Self-heating rates were similar for all mixtures.

Table 6.3 Self-heating rate (K.min^{-1}): 95% confidence interval

Temperature (K)	**Chp/Ga (n = 9)**	**Py/Ga (n = 9)**	**Sp/Py (n = 6)**	**Sp/Ga (n = 9)**
318	0.0795–0.0797	0.0706–0.0707	0.0991–0.0993	0.0880–0.0884
328	0.108–0.109	0.0897–0.0899	0.127–0.128	0.125–0.127
333	0.121–0.123	0.101–0.102	0.141–0.142	0.139–0.141
338	0.185–0.187	0.111–0.113	0.160–0.161	0.155–0.160
343	0.169–0.171	0.163–0.165	0.176–0.177	0.175–0.177
348	0.193–0.195	0.165–0.166	0.206–0.210	0.204–0.209
353	0.219–0.221	0.189–0.190	0.230–0.233	0.225–0.230
358	0.249–0.253	0.215–0.216	0.250–0.253	0.249–0.251

6.4.1.2. Determining E_a and $\ln(QA/C_p)$

Figure 6.1 reveals linear negative relationships of ln(SHR) vs. reciprocal time (1/T) with R^2 ranging from 0.950 to 0.997.

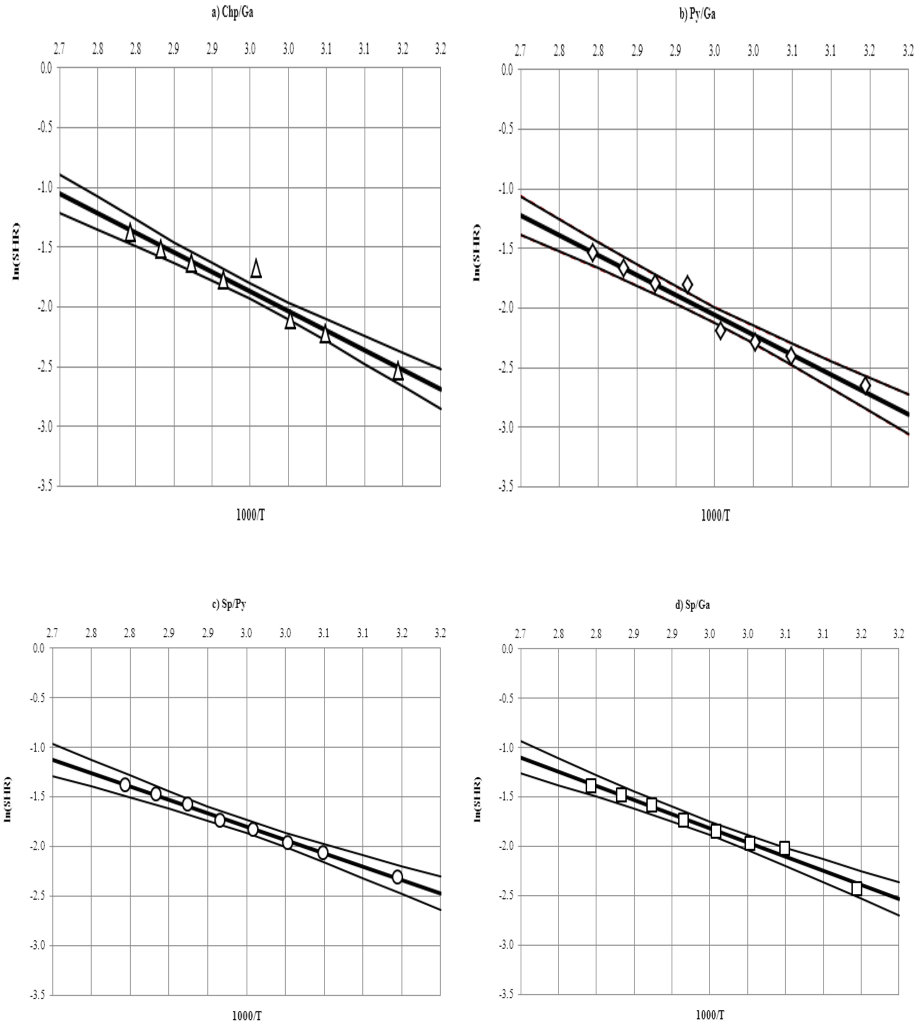

Figure 6.1 ln(SHR) vs. 1000/T for sulphide mixtures: a) Chp/Ga; b) Py/Ga; c) Sp/Py; d) Sp/Ga

The least squares best fits were: y = -3.338x + 7.791 for Py/Ga; y = -3.274x + 7.789 for Chp/Ga; y = -2.697x + 6.159 for Sp/Py; and y = -2.865x + 6.637 for Sp/Ga. From the slopes and intercepts the values of E_a and $\ln(QA/C_p)$ were calculated and the 95% CI are presented in Table 6.4.

Table 6.4 Values of E_a and $\ln(QA/C_p)$: 95% CI

Sample	E_a(kJmol^{-1})	$\ln(QA/C_p)$
Sphalerite / Pyrite	22.0 - 23.0	6.11 – 6.21
Pyrite / Galena	27.7 – 27.8	7.78 – 7.81
Chalcopyrite / Galena	27.1- 27.2	7.73 – 7.81
Sphalerite / Galena	24.1 – 24.2	6.74 – 7.77

6.4.1.3. Comparison of E_a with literature

Table 6.5 shows a comparison of E_a of the sulphide mixtures from this work and data for sulphides in the literature (excluding synthetics).

Table 6.5 Energy of activation for the sulphide mixtures and some literature data

Samples	E_a (kJ.mol^{-1})	References
Sp/Py	22.0–23.0	Ngabe et al. 2011
Py/Ga	27.7–27.8	This work
Chp/Ga	27.1–27.2	This work
Sp/Ga	24.1–24.2	This work
Ni-conc. (Voisey’s Bay)	26.0–29.0	Ngabe et al. 2011
Ni-conc. (Voisey”s Bay)	22–23	Ngabe et al. 2011
Sulfur and iron-rich sulphides	13.7–21.4	Yang et al. 2011
Cu-conc. (Voisey’s Bay)	28.0–30.0	Ngabe et al. 2011

6.4.1.4. Relationship between E_a and $\ln(QA/C_p)$

Figure 6.2 shows a positive relationship which supports Eq. 6.3. The least squares best fit is: $y = 0.324x - 1.131$ with $R^2 = 0.992$.

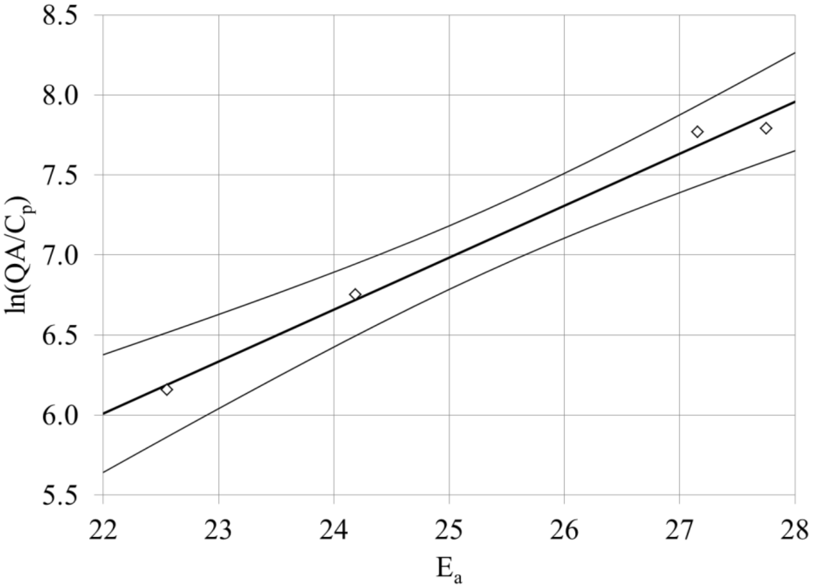

Figure 6.2 $\ln(QA/C_p)$ vs. E_a

6.4.1.5. Rest potential difference (ΔV) vs. $\ln(QA/C_p)$ and ΔV vs. E_a

6.4.1.5.1. Rest potential difference (ΔV) vs. E_a

The rest potential values are taken from Table 1.1, using the average of the range when applicable. Figure 6.3 shows a weak but positive correlation of E_a as a function of ΔV. The least square best fit was $y = 20.591x + 19.828$ with $R^2 = 0.754$.

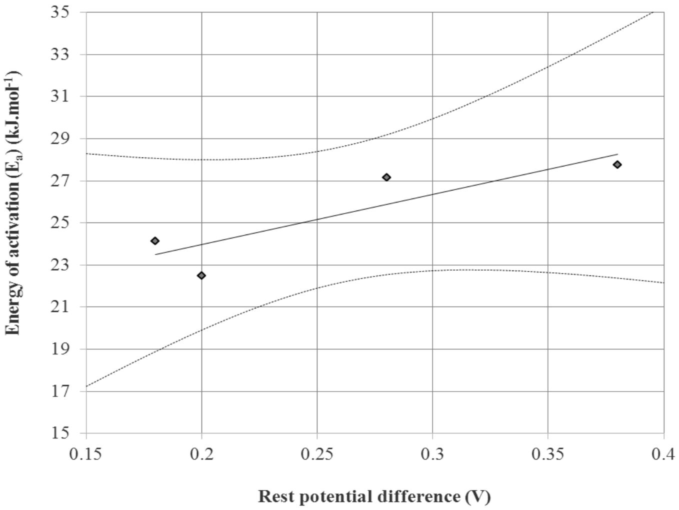

Figure 6.3 Energy of activation (E_a) vs, Rest potential difference

6.4.2. Specific heat capacity C_p

6.4.2.1. Estimates using Eq. 4

The procedure is illustrated by a specimen calculation for sphalerite / pyrite at 70^{o}C (343 K): the area under the heating curve for the mixture was 426 K.min; for the reference sample the area was 570 K.min with corresponding C_{pk} of 1.298 J.g^{-1}.K^{-1} (mean of the range in Table 6.3); using Eq. 6.4, and taking the mass of the sample (in gram) with known C_{pk} (m_k) equal to that of the sample with unknown C_{pu} (m_u), then:

$$C_{pu} = \frac{426K.\min \times 1.298J.g^{-1}K^{-1}}{570K.\min} = 0.970\ J.g^{-1} \quad (6.20)$$

Repeating for all cases, the 95% CI for C_p of the mixtures as a function of temperature is shown in Table 6.6 and Figure 6.6 (a, b, c, d). For comparison, the C_p of Ni- and Cu-concentrates (Chapter 3) is included in Table 6.6.

Table 6.6 C_p ($J.K^{-1}.g^{-1}$) (95% CI) for sulphide mixtures and concentrates from previous work

Temperature (K)	323	333	338	343	353
Samples					
Sp / Py	0.233 – 0.274	0.569 – 0.637	0.878 – 0.889	0.970 – 0.981	1.060 – 1.071
Py / Ga	0.160 – 0.175	0.373 – 0.379	0.575 – 0.577	0.636 – 0.641	0.690 – 0.694
Chp / Ga	0.152 – 0.167	0.374 – 0.375	0.548 – 0.550	0.607 – 0.609	0.659 – 0.661
Sp / Ga	0.182 – 0.203	0.444 – 0.446	0.655 – 0.657	0.726 – 0.728	0.787 – 0.789
Ni-conc. Raglan 1	0.545 – 0.563	1.189 – 1.217	1.255 – 1.299	1.288 – 1.290	1.559 – 1.581
Ni-conc. Raglan 2	0.346 – 0.530	1.088 – 1.102	1.383 – 1.403	1.409 – 1.426	1.537 – 1.539
Ni-conc. Voisey's Bay	0.442 – 0.468	0.876 – 0.978	1.216 – 1.228	1.226 – 1.244	1.263 – 1.491
Cu-conc. Voisey,s Bay	0.332 – 0.368	0.773 – 0.778	1.192 – 1.193	1.316 – 1.318	1.437 – 1.438

6.4.2.2. C_p vs. temperature

Figure 6.4 shows C_p as a function of temperature. The relationships are represented by second order polynomials (with adjusted R^2 ranging from 0.962 to 0.976):

$$C_p(\mathrm{Sp/Py}) = -0.0008T^2 + 0.5689T - 100.05 \tag{6.21}$$

$$C_p(\mathrm{Py/Ga}) = -0.0005T^2 + 0.3567T - 62.846 \tag{6.22}$$

$$C_p(\mathrm{Chp/Ga}) = -0.0005T^2 + 0.3554T - 62.469 \tag{6.23}$$

$$C_p(\mathrm{Sp/Ga}) = -0.0006T^2 + 0.4263T - 74.914 \tag{6.24}$$

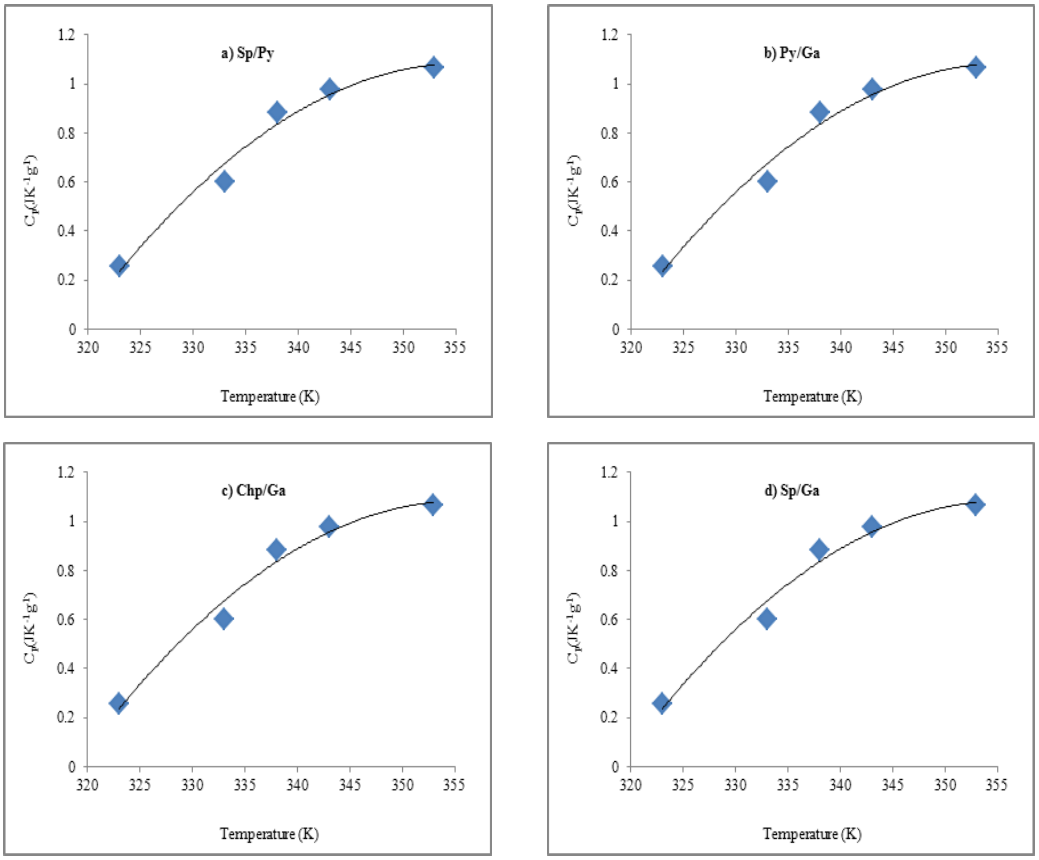

Figure 6.4 C_p vs. temperature for sulphide mixtures: a) Sp/Py; b) Py/Ga; c) Chp/Ga; d) Sp/Ga

6.4.2.3. Rest potential difference (ΔV) vs. C_p

A plot of C_p vs. ΔV at 65° C, chosen because it is the mean temperature of C_p determined in this work is shown in Figure 6.5. The trend corresponds to the expected (Eq. 6.20). The least squares best fit was $y = -1.025\ x + 0.933$ with $R^2 = 0.375$.

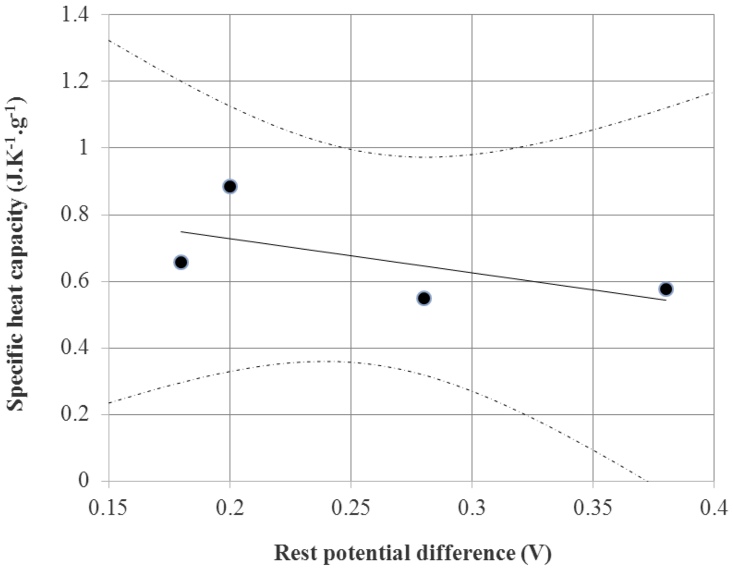

Figure 6.5 Specific heat capacity (at 65^{o} C) vs. rest potential difference

6.5. DISCUSSION

All the mixtures in this work self-heated. Payant et al. (2011) suggested that the critical rest potential difference for self-heating of mixtures driven by galvanic interaction was between $\Delta V = 0.1 – 0.2$, that mixtures with $\Delta V > 0.2$ tended to self-heat and that mixtures with $\Delta V < 0.1$ tended not to self-heat. The mixtures here respected that condition, the Sp/Ga with ΔV of 0.18 V being in the critical range but did self-heat. It is understood that the ΔV values are approximate.

The linear relationship for the Arrhenius type plot ln(SHR) vs. 1/T supports that there is a chemical reaction(s) (Carres and Saghafi, 1988) that is the cause of SH, as suggested by others (Rosenblum & Spira, 2001; Li, 2007; Wu & Meng, 1995; Gu & Li, 2006; Wu & Li, 2005; Wu et al. 2004; Yang et al. 2011); Somot & Finch, 2010; Yang et.al 2011). In a study of coal self-heating, Beamish and Arisoy (2008) reported a third order polynomial relation between the self-heating rate and the reverse of temperature and argued that self-heating was not only due to chemical reactions, but also to a number of competing physical processes occurring at the same time.

The E_a values for all the mixtures are in the same range (Table 6.5) which is similar to the range found for Ni-and Cu-concentrates (Chapter 3) and other iron- and sulphur-rich materials (Yang et al. 2011). This similarity supports that the SH reaction(s) are common to all sulphide systems. Further support for a common reaction(s) is the strong positive correlation between E_a and $\ln(QA/C_p)$ (Figure 6.2).

The range in E_a encompasses that for partial oxidation of H_2S which supports the H_2S hypothesis for SH at temperatures below 100^o C. This is not to rule out direct oxidation of sulphide minerals that has been suggested by others (Rosenblum & Spira, 2001; Li, 2007; Wu & Meng, 1995; Gu & Li, 2006; Wu & Li, 2005; Wu et al., 2004; Yang et al., 2011).

The specific heat capacities for the mixtures were also over a similar range and proved comparable with the values for Ni-and Cu-concentrates determined previously (Table 6). The C_p relationship with temperature followed the common second order polynomial (Figure 6.4) with R_{adj}^2 values indicating the models explain more than 75% of the variance of the data. The polynomial trend in C_p with T was also seen for the Ni-and Cu-concentrates, but, as noted in Chapter 3, the trend is not observed for synthetic (single) sulphide minerals.

In testing the role of galvanic interaction literature rest potential values were used to estimate ΔV. These values are approximations as our starting sulphides contained varying amounts of other sulphides. Some effects of sulphide impurities on sulphide reactivity are discussed by Cruz et al. (2005) and Madhuchhanda (2000). Beyond the presence of impurities, the rest potential values relevant to the conditions pertaining to self-heating, for example presence of 6% moisture, are not known and present a challenge to measure (Payant and Finch, 2010)**.** For now literature values at least offer a place to start. The positive relationship between E_a and ΔV (Figure 6.5) and the negative relationship between C_p and ΔV (Figure 6.5) support that there is a connection between self-heating and the galvanic effect.

6.6. CONCLUSIONS

The apparent activation energy E_a for the sulphide mixtures were in the range 22.0 to 27.8 kJ.mol^{-1}, similar to the E_a of Ni- and Cu-concentrates determined previously, and similar to E_a for partial oxidation of H_2S. This supports the contention that partial oxidation of H_2S may be the cause of SH of sulphides at temperatures below 100^o C in presence of moisture.

The specific heat capacity C_p of the sulphide mixtures were similar and ranged from 0.15 to 1.07 J.K^{-1}.g^{-1} as temperature rose from 50 to 80^o C which is comparable to the results for Ni- and Cu-concentrates determined previously. The C_p trends with temperature follow second order polynomial relationships, again resembling the trend for the Ni-and Cu-concentrates.

Relationships were found between rest potential difference ΔV and E_a and C_p which support a contribution of galvanic interaction to the reaction(s) surmised to cause SH.

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Chapter 7 . Conclusions, Contributions, claims to original research and suggested future work

7.1. Conclusions

The thesis presents results of a sulphide self-heating study to determine self-heating physico-chemical parameters in the presence of moisture at temperatures below 100^{o}C by adapting the self-heating technology of Rosenblum and co-workers. The main findings are summarized as follows:

1. The specific heat capacity C_p of concentrates and sulphide mixtures were determined and verified against a standard method, drop calorimetry.
2. Measuring the self-heating rate SHR, Arrhenius-type relationships between ln(SHR) and 1/T were found for sulphide concentrates and sulphide mixtures. The energy of activation E_a (from the slope) were similar and in the range of E_a for partial oxidation of H_2S supporting the contention that this reaction contributes to self-heating in the presence of moisture at temperatures below 100^{o}C
3. Positive linear relationships were found between (QA/C_p) (a reaction term) and the galvanic effect represented by the rest potential difference of sulphide pairs in sulphide mixtures.

4. The enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) of sulphide concentrate self-heating were determined. It is confirmed that self-heating of sulphide concentrates at temperature less than 100^oC is spontaneous, since $\Delta G < 0$. The Gibbs free energy values can be used as part of risk assessment.

5. The self-heating apparatus and methodology is versatile since in addition to risk assessment it can be used for the determination of self-heating physico-chemical parameters.

7.2. Contributions and Claims to original research

This work is significant and unique. It is significant since:

1. There is little data on the C_p of natural sulphide minerals and on the energy of activation (E_a) of the reaction causing self-heating of sulphide minerals at temperature < 100^oC, in presence of moisture.
2. The C_p and the E_a are needed in modeling as well in self-heating risk assessment.
3. The difference in the C_p vs. temperature trend for sulphide concentrates and synthetic minerals, suggests it is preferable to determine C_p, for example in the determination of self-heating capacity.
4. Knowledge of these physico-chemical parameters furthers our understanding of the sulphide self-heating phenomenon.

The work is unique for the following reasons:

1. The C_p of concentrates and mixtures of sulphides and the E_a of the reaction causing self-heating of concentrates and mixtures of sulphide minerals in presence of moisture at temperature < 100^oC have been determined using self-heating apparatus and adapting the test methodology.
2. Versatility of the self-heating apparatus to determine physico-chemical parameters in addition to assessing risk is established.
3. The spontaneity of self–heating of the sulphide concentrates and mixtures tested is thermodynamically proved whereas prior to this work, spontaneity was determined empirically.

4. A link is now made between the reaction causing self-heating and the galvanic effect in sulphide mixtures. Before this work, it was known that the galvanic effect causes self-heating of sulphide mixtures, but no relationship was established between the chemical reaction causing self-heating and galvanic effect.

7.3. Suggested future work

1. Understand the difference in trend with temperature for C_p of concentrates compared to synthetic minerals by mixing synthetic minerals, in particular mixing with pyrite and pyrrhotite.
2. Identify in situ the chemical reactions (primary, secondary ...) occurring during self-heating. This will require sensitive and sophisticated instrumentation.
3. Once the reaction is known, determine the concentrations of the reactants and products during self-heating.
4. Determine the heat transfer coefficients.
5. Use the parameters determined in this work, the concentrations of reactants and products, and heat transfer coefficient to build a sulphide self-heating model.
6. Investigate the levels of chemicals released from self-heating during storage and transportation to establish possible environmental impacts.