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Determination of specific heat capacity of sulphide materials at temperatures below 100 °C in presence of moisture

Barnabe Ngabe *, James A. Finch

Department of Mining and Materials Engineering, McGill University, Montreal, Quebec H3A 2B2, Canada

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The specific heat capacity (C_p) of one copper and three nickel concentrates was determined using a 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 Rosenblum standard test are discussed.

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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 (1988) argue 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 (Frank-Kamenetskii, 1969; Beever and Drysdale, 1992; Chen, 1998; Nugroho et al., 1998; Miyake et al., 2000; Yang et al. 2011).

Self-heating of sulphide minerals is known to commence at temperatures <100 °C in the presence of moisture (2001). Although specific heat capacities of synthetic minerals at low temperature are available (Anderson, 1931, 1937; Grønvold et al., 1959; Čermák and Rybach, 1982; Schön, 1983; Demensky and Teplov, 1987; Berezovkii et al., 2001), there is little 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 °C using the self-heating apparatus of Rosenblum et al. (2001) and verified against a standard technique, drop calorimetry.

2. Theory

2.1. Specific heat capacity

There are two ways of expressing the specific heat capacity of materials. One is the heat capacity at constant volume (C_v) and another is the specific heat capacity at constant pressure (C_p). For practical reasons, it is measured almost exclusively at constant pressure (Cemič, 2005). The specific heat capacity (C_p) of a substance is the amount of heat needed to raise the temperature of one gram of the substance by 1 K. 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 following equation (Chang, 1981; Noggle, 1985; Cemič, 2005):

$$\Delta Q = mC_p\Delta T \tag{1}$$

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 equation (Maier and Kelly, 1932) when the composition of the compound is known:

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

where a, b, c are specific heat coefficients and T is temperature (K). Values of a, b, c for some sulphides are summarized in Table 1. The increase of C_p with temperature is explained by quantum

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* Corresponding author. Tel.: +1 514 354 9546.
E-mail address: barnabe.ngabe@mail.mcgill.ca (B. Ngabe).

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mechanical theory and is due to the excitation of atomic vibrations (Cemič, 2005).

Table 2 shows specific heat capacities of several sulphide minerals measured at temperatures below 100 °C (Anderson, 1931, 1937; Grønvold et al., 1959; Lewis et al., 1961; Čermák and Rybach, 1982; Schön, 1983).

Most sulphide materials encountered in mining are mixtures. Therefore Eq. (2) is not strictly applicable and C_p needs to be measured. Further, self-heating of sulphides at low temperature (< 100 °C) is prompted by presence of moisture, which needs to be allowed for 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 samples. To illustrate, Harries and Ritchie, 1987 reported C_p 0.867 $\mathrm{J\,g^{-1}\,K^{-1}}$ for an oxidized dry pyritic waste and C_p 1.350 $\mathrm{J\,g^{-1}\,K^{-1}}$ for the same material containing 11% moisture. The C_p of water as a function of temperature is given by (Marsh, 1987):

$$\frac{C_p(K)}{C_p(288K)} = 0.996185 + 0.0002874 \times \left(\frac{T+100}{100}\right)^{5.26} + 0.11160 \times 10^{-0036T} \tag{3}$$

where T is temperature (K). The reference to C_p at 288 K 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 °C is 4.1855 $\mathrm{J\,g^{-1}\,K^{-1}}$.

2.2. Measurement of C_p using self-heating apparatus

The procedure using 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:

$$C_{pu} = \frac{m_k \times A_u \times C_{pk}}{m_u \times A_k} \tag{4}$$

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

Eq. (4) is a consequence of the relationship between the sample mass and the enthalpy of the reaction (Satava and Veprek, 1976; Zivkovic, 1979; Legendre et al., 2006):

$$M_s \Delta H_r = K(\gamma, \lambda) \times A \tag{5}$$

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

Table 1
Values of a, b, c for some sulphides (Anderson and Crerar, 1993).

Sulphides	Formula	a	$b \times 10^3$	$c \times 10^5$
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 $\mathrm{cal\,mol^{-1}\,K^{-1}}$ for a, $\mathrm{cal\,mol^{-1}\,K^{-2}}$ for b, and $\mathrm{cal\,mol^{-1}\,K}$ for c. NR: not reported.

Table 2
Measured C_p ($\mathrm{J\,g^{-1}\,K^{-1}}$) of some sulphide minerals at T < 100 °C.

Sulphide mineral	C_p	Reference
Chalcopyrite	0.540	Čermák and Rybach (1982)
Galena	0.207 0.205–0.206	Čermák and Rybach (1982) Anderson (1931, 1937)
Pyrite	0.500–0.520 0.502–0.515	Schön (1983) Anderson (1931, 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)

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 and Crerar, 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 ($\mathrm{J\,g^{-1}\,K^{-1}}$) is then as follows (Kukkonen and Lindberg, 1998):

$$C_{pu} = \frac{(C_{cal} + C_{pw}) \times (T_f - T_{wi}) \times m_w}{m_u \times (T_i - T_f)} \tag{6}$$

where C_{cal} is the heat capacity of the Dewar ($\mathrm{J\,K^{-1}}$), C_{pw} the specific heat capacity of water estimated using Eq. (3), and T_{wi} the temperature of water immediately before introducing the sample.

3. Experimental

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, chalcopyrite from Xstrata Nickel's Strathcona Mine was used. The principal components of the samples are shown in Table 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.

3.2. Self-heating apparatus technique

3.2.1. The setup

The self-heating (SH) apparatus and the experimental procedures are described in Rosenblum et al. (2001), Somot and Finch (2010) and Ngabe et al. (2011). The apparatus is shown in Fig. 1. It consists of the following major components: a Pyrex cell, a

Table 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.

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