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# Role of Elemental Sulphur in Stage B Self-Heating of Sulphide Minerals, and the Potential Role of Polysulphides

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**Abstract:** Sulphide minerals undergo numerous stages of mineral processing to extract the desired metal. When they are exposed to certain environmental conditions, some sulphide minerals can spontaneously heat up, a process called self-heating (SH), which, if left unchecked, can be a major hazard. Self-heating occurs in three distinct temperature stages, termed Stage A (temperature below 100 °C), Stage B (temperature range of 100 °C–350 °C), and Stage C (above 350 °C). Historically, it was understood that elemental sulphur generated in Stage A fuels Stage B reactions; however, the full extent of this behaviour is still unknown. The aim of this study is to understand the role of elemental sulphur in Stage B reactions. The results have demonstrated that elemental sulphur is incapable of fueling Stage B self-heating on its own, and it needs to interact with sulphide minerals in ambient temperatures in the presence of moisture and air. This interaction seems to be unique to pyrrhotite, as it failed to demonstrate stage B self-heating with other sulphide minerals. Previous works in surface chemistry suggest that this interaction leads to the formation of polysulphides.

**Keywords:** self-heating; elemental sulphur; rock-forming sulphides

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## 1. Introduction

Millions of tons of sulphide minerals are mined, processed, and stockpiled annually, as they are the source of numerous industrial metals, such as copper, nickel, lead, and zinc [1]. When they are exposed to the environment, especially moisture, sulphides have shown a propensity to oxidize and generate heat without an external heat source (i.e., self-heating) [2]. The detrimental effects of self-heating range from a minor impact on flotation to major disruptions, including the loss of equipment and fatalities [3,4]. Since the hazards were first documented by Good [4], relatively minimal work has been published on the sulphide self-heating of ores and concentrates, with the exception of [2,5–14]. The majority of the research on self-heating has been on the coal [15–17] and wood industries [18].

Among the Rock-Forming sulphides (pyrite, pyrrhotite, chalcopyrite, sphalerite, and galena), pyrrhotite has exhibited the highest self-heating potential on its own [5]. However, a variety of sulphide mineral mixtures with sufficient differences in their electrochemical potentials can undergo self-heating as well [5].

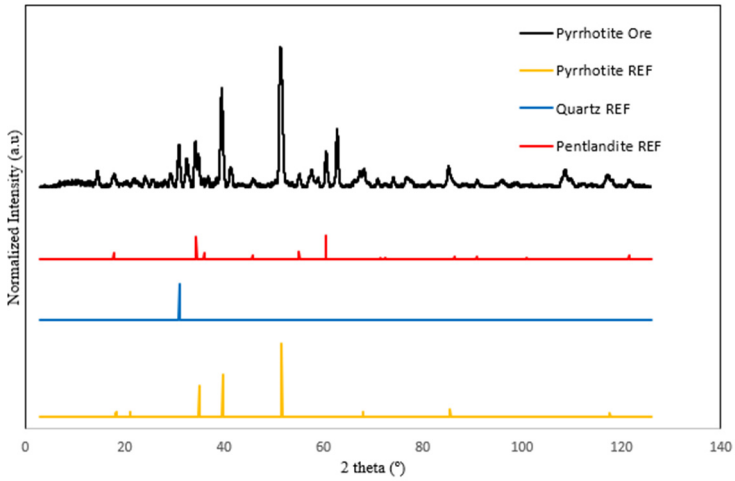
Self-heating occurs in three distinct stages, termed Stage A, Stage B, and Stage C. The role of elemental sulphur during different stages of self-heating reactions has been studied in the past [19]. It has been theorized that elemental sulphur generated during Stage A (from an ambient temperature to 100 °C) fuels Stage B self-heating reactions (from 100 °C to 350 °C) [19]. This theory was further solidified when it was shown that the sulphur content increased from practically 0 wt.% to over 3 wt.% during Stage A (50 h at 70 °C) and decreased from 3 wt.% to 0 wt.% in Stage B (50 h at 140 °C) [19]. However, the mechanism of how elemental sulphur promotes Stage B self-heating is still not yet fully understood.

The aim of this study is to investigate whether the addition of elemental sulphur will induce self-heating in Stage B for pure minerals and pyrrhotite-containing ore.

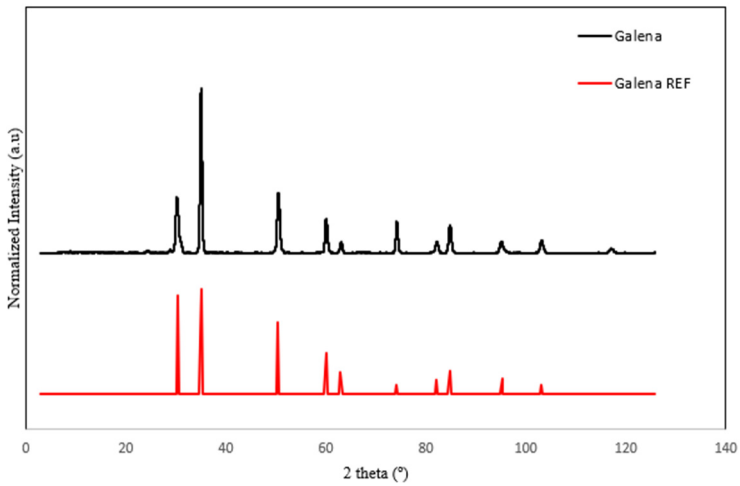
## 2. Materials and Methods

### *2.1. Samples*

Samples of a massive sulphide ore mostly composed of magnetic pyrrhotite were taken from a mine in Northern Quebec, Canada. The samples were dried at the mine and shipped in airtight conditions. The purities of the sulphide minerals and the elemental sulphur used in this experiment pyrrhotite ore were verified via X-ray diffraction (XRD) (Bruker D8 Discover, Billerica, Massachusetts, USA). Figure 1 below shows that except for the received ore that contained quartz and pentlandite as minor impurities, the other minerals were of a high grade. The patterns were analyzed using DIFFRAC.EVA software (Bruker, Billerica, Massachusetts, USA), and reference data were collected from the International Centre for Diffraction Data (ICDD, 2022).

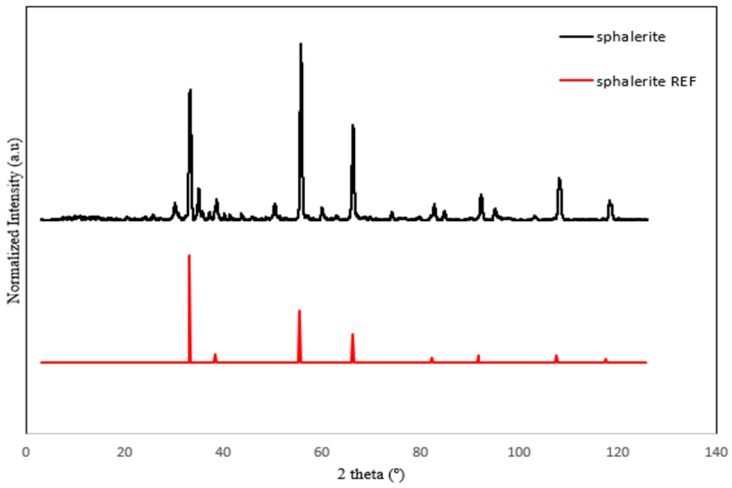



(**a**)




(**b**)

**Figure 1.** *Cont.*

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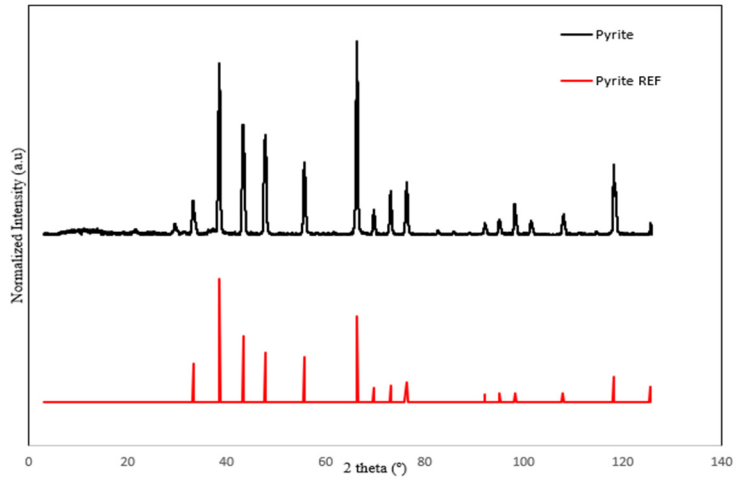


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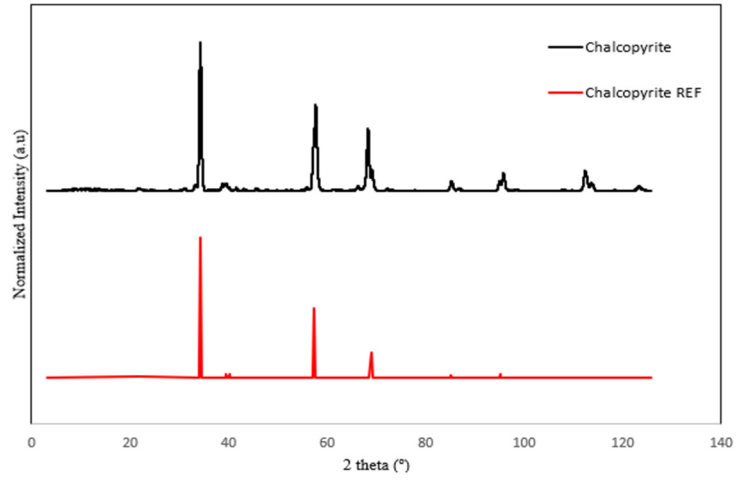


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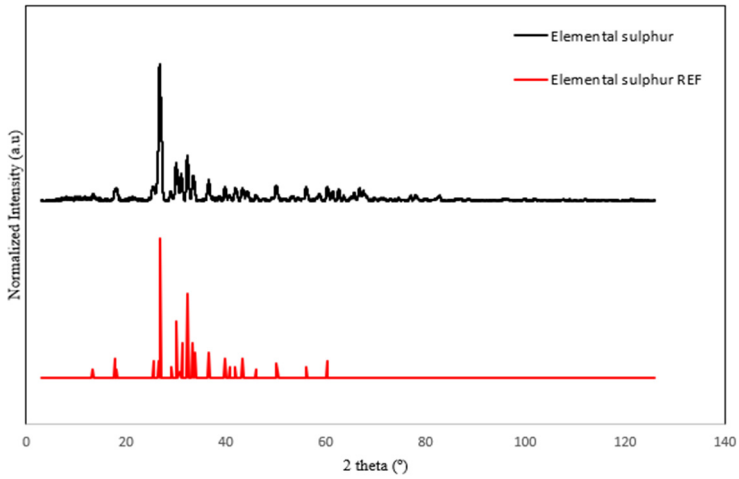
**Figure 1.** *Cont.*




(**f**)

**Figure 1.** XRD patterns of (**a**) pyrrhotite ore, pyrite REF (PDF 00-042-1340), pyrrhotite REF (PDF 04-021-2764), and quartz REF (PDF 00-046-1045), (**b**) galena and galena REF (PDF 04-004-4329), (**c**) sphalerite and sphalerite REF (PDF 01-071-5976), (**d**) pyrite and pyrite REF (PDF 00-042-1340), (**e**) chalcopyrite and chalcopyrite REF (PDF 00-037-0471), elemental sulphur, and (**f**) elemental sulphur REF (PDF 00-008-0248).

Once received, the samples were finely ground using the Siebtechnik pulveriser type T100. The resulting material was split with a rotary splitter (Dickie & Stockler, Johannesburg, South Africa), and each portion weighed approximately 250 g. The ground samples were then kept at room temperature in sealed plastic bags. Other Rock-Forming mineral samples (pyrite, sphalerite, chalcopyrite, and galena) were purchased from Wards Science Plus (Rochester, New York, USA) and pulverized in the same manner as the pyrrhotite ore samples were. The 80% passing size ($X_{80}$) of the sulphide minerals used in this research are shown in Table 1 below.

**Table 1.** Particle size distribution of sulphide samples.

| Sample | $X_{80}$ (μm) |
|---|---|
| Pyrrhotite ore | 150 |
| Pyrite | 233 |
| Galena | 240 |
| Sphalerite | 323 |
| Chalcopyrite | 203 |

Elemental sulphur powder was purchased from Alfa Aesar (Haverhill, MA, USA), with a 100% passing size ($X_{100}$) of 44 μm. Elemental sulphur powder was kept at room temperature in its original packaging.

Silica sand powder ($SiO_2$) was purchased from Sigma-Aldrich (St. Louis, MO, USA), with a 100% passing size ($X_{100}$) of 44 μm. Silica sand powder was kept at room temperature in its original packaging.

### *2.2. FR-2 Self-Heating Testing Apparatus*

All tests for this study were conducted using the FR-2 self-heating apparatus. The apparatus consists of 5 major components, a 2L Pyrex Vessel, a constant-temperature coiled heater, a metal mesh screen, a concrete base, and an insulator. The schematic of this apparatus is shown in Figure 2 below, adapted from [2].

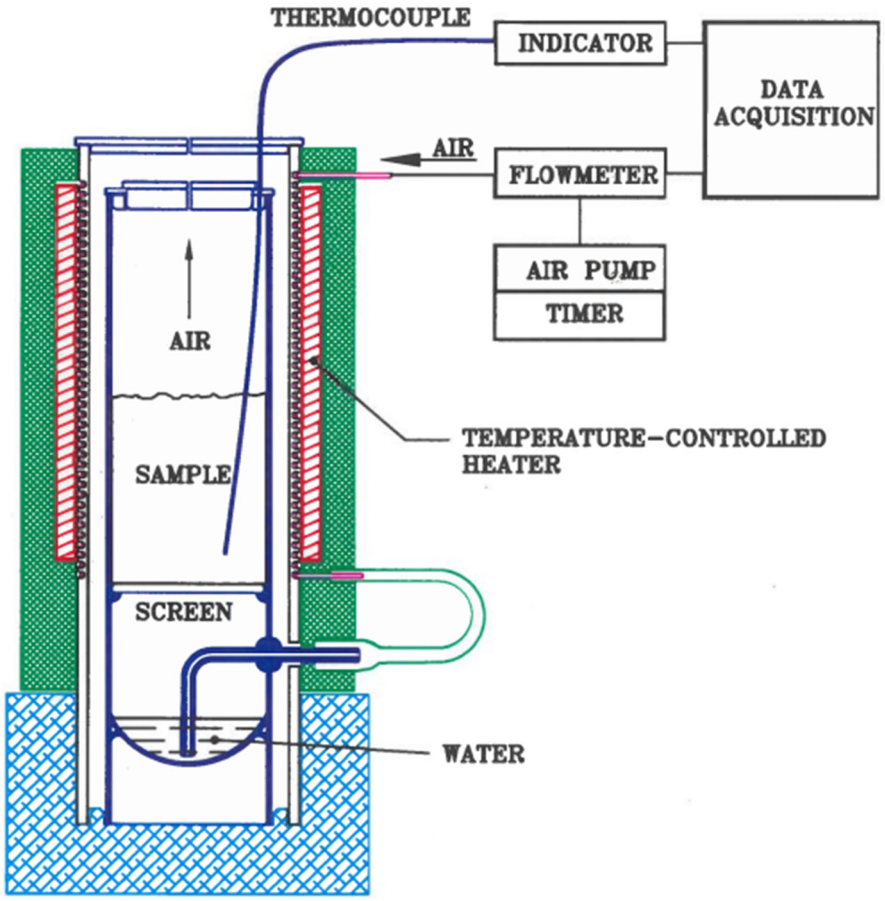



**Figure 2.** FR-2 test apparatus.

Once the sample was placed in the 2L Pyrex Vessel, the temperature was raised in nitrogen (140 °C for Stage B) for each test. Once the equilibrium temperature was reached, 100 mL/min of air was injected for 15 min every 5 h for a total of 10 cycles [2]. The thermocouple was connected to a data logger to graph the temperature change over time, which recorded the sample temperature every minute. A reactive sample demonstrates a temperature increase with air injections, whereas a non-reactive sample shows the equilibrium temperature throughout the cycles.

For reactive samples, the Self-Heating Capacities (*SHC*) of the reactive samples were calculated using the following equation (Equation (1)).

$$SHC_{\,i} = \sum SHR\left(\frac{^{\circ}C}{hr}\right)_{i} * Cp\left(\frac{J}{g^{\circ}C}\right) * 0.25hr = \left(\frac{J}{g}\right) \quad (1)$$

where:

*SHC* = Self-Heating Capacity;
*SHR* = self-heating rate;
*Cp* = specific heat capacity;
*T* = Time.

The slopes of the temperature peak coincide with the self-heating rate (*SHR*) at the time of each of the 10 air injections. A single value of 0.6 J/g °C was used as specific heat capacity for all sulphide *SHC* calculations; it was found that nearly all the sulphides relevant to this work fell into the range from 0.5 J/g °C to 0.7 J/g °C, which is over the relevant temperature range (from 25 °C to 500 °C) [19]. As the oxygen exposure time was capped at 15 min, the time (*T*) value was substituted with 0.25.

Therefore, Equation (1) was rewritten as:

$$SHC_{\,i} = \sum SHR_{\,i} * 0.6\left(\frac{J}{g^{\circ}C}\right) * 0.25hr \quad (2)$$

Simplified to:

$$SHC_{\,i} = \sum SHR_{\,i} * 0.15 \quad (3)$$

### *2.3. Surface Chemistry Analysis—XPS*

The elemental sulphur–sulphide chemical interface was analyzed via X-ray Photoelectron Spectroscopy (XPS) (Thermo Fisher Scientific, Waltham, MA, USA, Model K-Alpha). Experiments were carried out under the conditions of 50 eV pass energy, 200 µm X-ray size, and a chamber pressure of $10^{-7}$ Pa. Data collection and analysis were conducted using Avantage software (Thermo Fisher Scientific, Waltham, MA, USA, version 5.9931).

### *2.4. Sample Preparation and Experimental Procedure*

To determine whether the mixture of elemental sulphur and silica sand (chemically inert) could exhibit Stage B self-heating, 15 g (6 wt.%) of elemental sulphur was added to 250 g of silica sand, and then subjected to the Stage B test.

To address whether pyrrhotite ore simply in contact with elemental sulphur could exhibit Stage B self-heating, a 250 g pyrrhotite ore sample was mixed with 6 wt.% elemental sulphur, and then subjected to the Stage B test.

For the context of this study, the term conditioning refers to a phase where moistened sulphide samples are mixed with elemental sulphur, and then exposed to the ambient environment for a given time while continuously blowing air. To address whether conditioned pyrrhotite ore could exhibit Stage B self-heating, 250 g of pyrrhotite ore sample and 6 wt.% elemental sulphur were mixed with 5 wt.% moisture and rested for 8 h at 80 °C with a constant supply of air (100 mL/min). The conditioned sample was then subjected to the Stage B test.

Lastly, 250 g of pyrite, galena, sphalerite, and Chalcopyrite samples were mixed with 6 wt.% elemental sulphur and conditioned the same way before being subjected to the Stage B test.

## 3. Results and Discussion

### *3.1. Stage B Thermographs*

#### 3.1.1. Elemental Sulphur

The Stage B thermograph of a mixture of silica sand and elemental sulphur is shown in Figure 3 below. The sample showed very little reactivity with each of the 10 air injections, and the total Self-Heating Capacity (*SHC*) of the sample remained at approximately 1.2 J/g. Based on this test result, it is evident that elemental sulphur alone does not pose the threat of Stage B self-heating. This implies that elemental sulphur needs to interact with sulphide minerals to pose the threat of self-heating.

#### 3.1.2. Unconditioned Mixture of Elemental Sulphur and Pyrrhotite Ore

A Stage B thermograph of the unconditioned mixture of pyrrhotite ore and elemental sulphur is shown in Figure 4 below. The sample again showed very little reactivity with air, and the total *SHC* was 2.5 J/g. Based on this test result, it can be observed that elemental sulphur simply in contact with pyrrhotite ore does not experience any Stage B self-heating. This result implies that for Stage B self-heating to occur, a previous step is needed in Stage A.

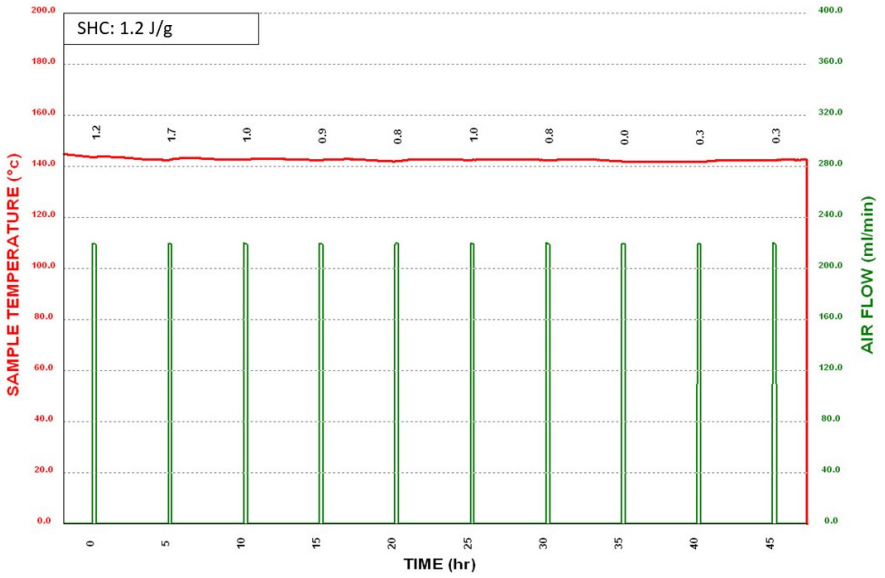



**Figure 3.** Thermograph of elemental sulphur + silica sand.

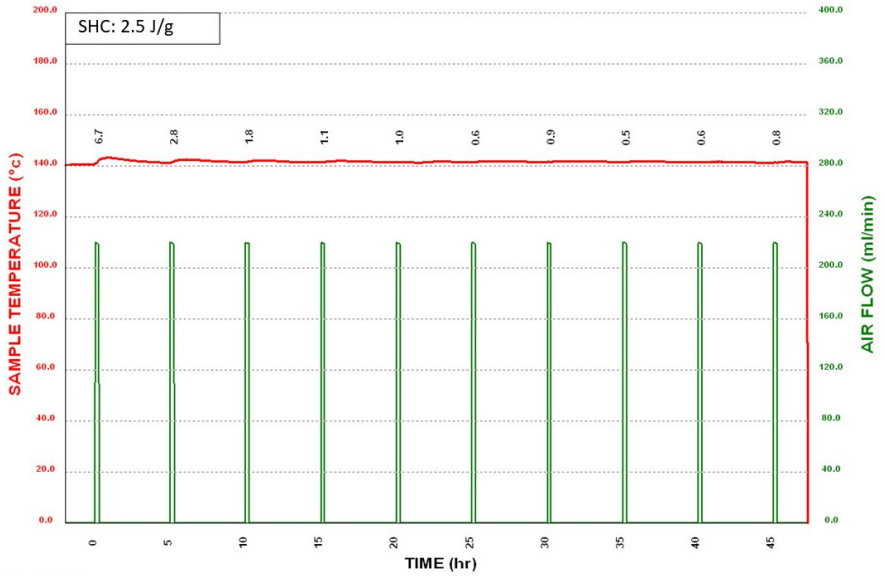



**Figure 4.** Thermograph of unconditioned pyrrhotite ore + elemental sulphur.

### 3.1.3. Conditioned Mixture of Elemental Sulphur and Pyrrhotite Ore

A Stage B thermograph of the conditioned mixture of pyrrhotite ore and elemental sulphur is shown in Figure 5 below. The conditioned sample showed a very high propensity for Stage B self-heating. Based on this test result, it can be observed that elemental sulphur reacting with pyrrhotite ore in ambient conditions in the presence of air and moisture is a critical step, which then leads to Stage B self-heating.

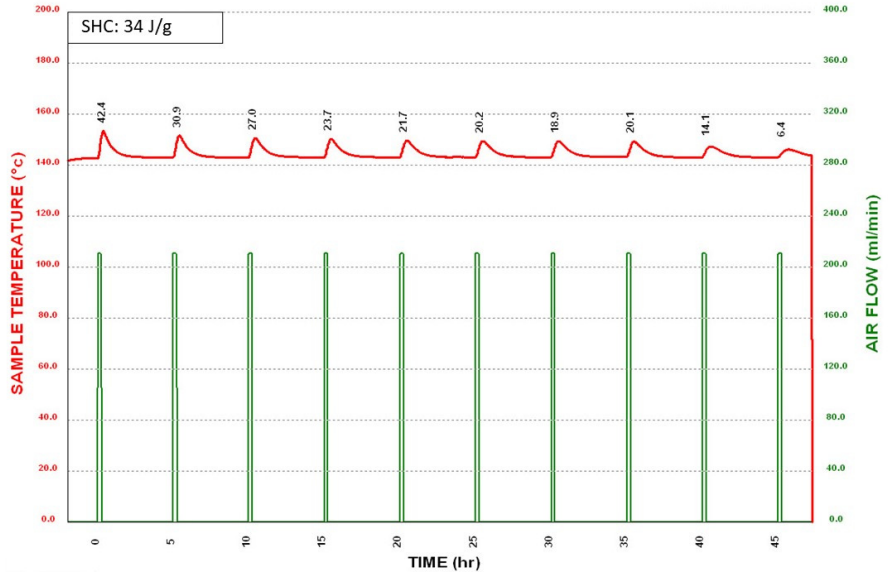



**Figure 5.** Thermograph of conditioned pyrrhotite ore + elemental sulphur.

#### 3.1.4. Generated Elemental Sulphur vs. Added Elemental Sulphur

Since the conditioning phase is similar to Stage A, a distinction was drawn between the heat generated from artificially added elemental sulphur and the heat generated by elemental sulphur created during the conditioning phase. The result shows that although both samples demonstrated self-heating, the conditioned sample with added elemental sulphur had an *SHC* of 34 J/g (Figure 5), a value much higher than that of the sample without any sulphur added (Figure 6). It was highlighted in previous works that the self-heating rate in Stage B dropped to zero as the elemental sulphur content also dropped to zero [19]. This phenomenon can be observed in Figure 6, where after the first air injection, the peaks continuously decrease until becoming flat. This shows that the elemental sulphur that was generated during the conditioning phase depleted. However, when elemental sulphur was added artificially and conditioned (Figure 5), the sample was highly reactive until the 8th air injection, before gradually diminishing.

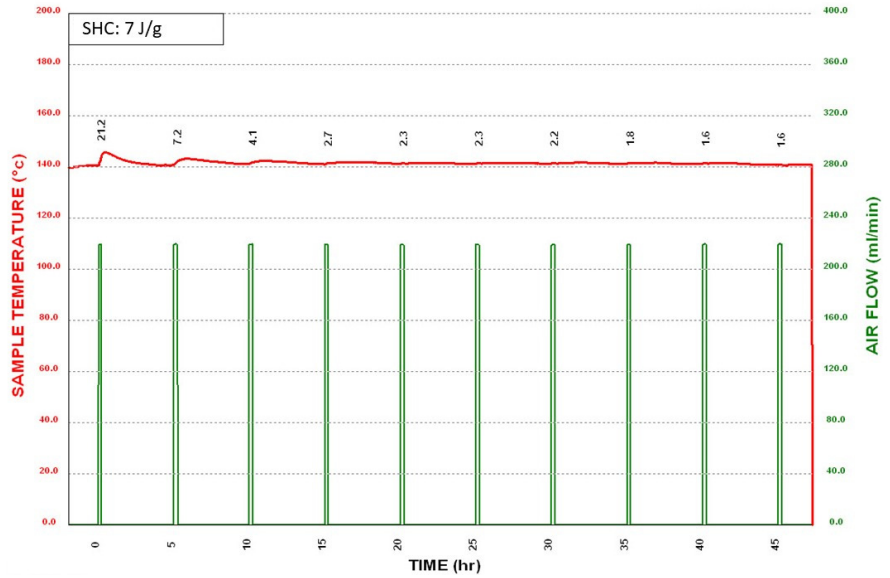



**Figure 6.** Thermograph of conditioned pyrrhotite ore.

This shows that the source of the contribution of elemental sulphur to Stage B self-heating is irrelevant if it is given enough time to react with the pyrrhotite ore under Stage A conditions. This result strongly implies the formation of a chemical reaction between elemental sulphur and pyrrhotite ore in Stage A conditions.

#### 3.1.5. Conditioned Mixture of Elemental Sulphur and Other Sulphide Minerals

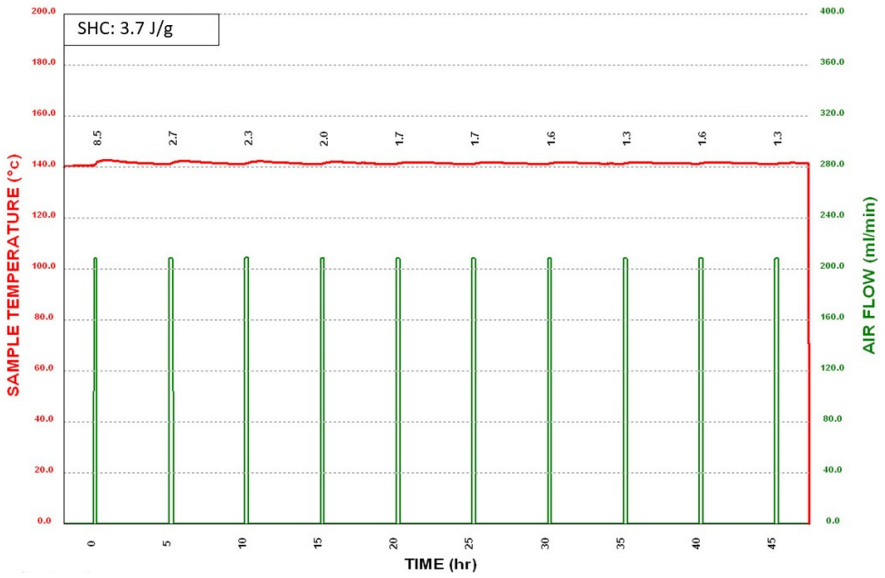
Thermographs of conditioned mixtures of pyrite, chalcopyrite, sphalerite, and galena with elemental sulphur are shown in Figure 7 below. None of the conditioned samples were reactive with incoming oxygen, showing *SHCs* of 3.7, 2.4, 0.2, and 2 J/g for pyrite, chalcopyrite, sphalerite, and galena, respectively. Based on these test results, it can be observed that with the exception of pyrrhotite ore, conditioned mixtures of sulphide minerals and elemental sulphur do not experience Stage B self-heating.

### *3.2. XPS Results*

The change in chemical composition between the unconditioned and conditioned mixtures of elemental sulphur and pyrrhotite ore was investigated using XPS. The results are shown below in Figures 8 and 9. The unconditioned sample only has two distinct visible peaks, which correspond to elemental sulphur and pyrrhotite, respectively. However, the conditioned sample has three distinct peaks, which correspond to elemental sulphur, pyrrhotite, and polysulphide, respectively. The only notable difference is the presence of polysulphide, and it forms the basis of potential future studies. A summary of the peaks is shown in Table 2 below.

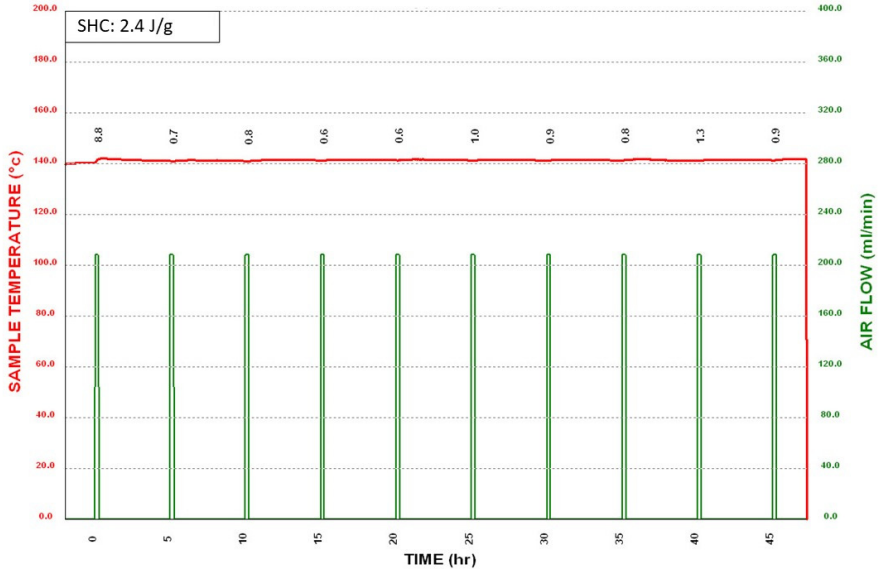
**Table 2.** Binding energy.

| Mineral Compound | Binding Energy | Reference |
|---|---|---|
| Pyrrhotite | 163 | [20] |
| Disulphide ($S_2^{2-}$) | 162 | [20] |
| Elemental sulphur ($S^o$) | 164.5 | [20] |
| Polysulfides ($S_n^{2-}$) | 164 | [20] |




(**a**)

**Figure 7.** *Cont.*

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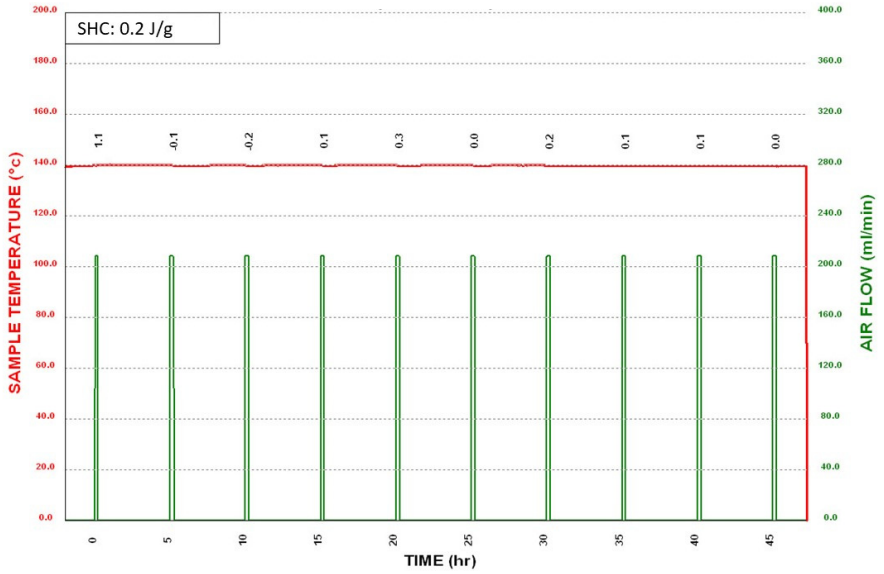
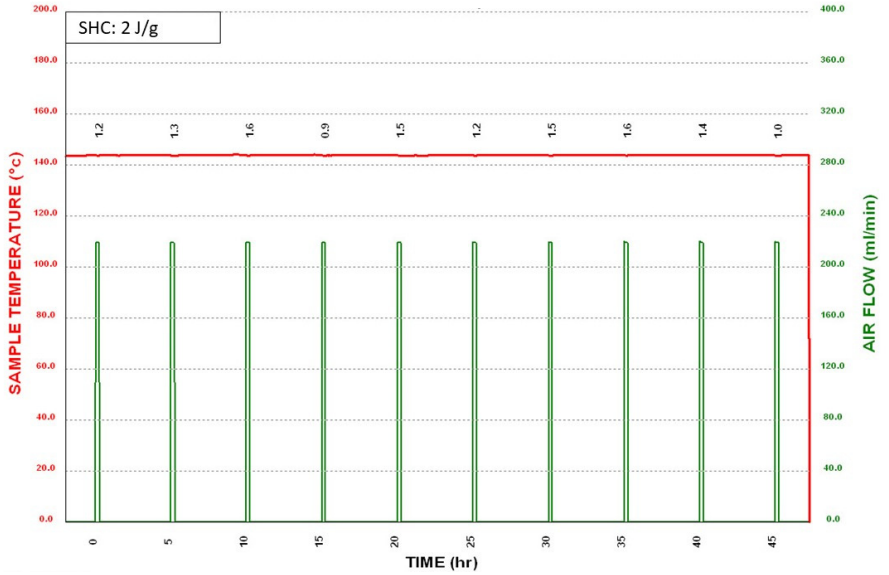



(**c**)

**Figure 7.** *Cont*.




(**d**)

**Figure 7.** Thermographs of (**a**) conditioned pyrite + elemental sulphur; (**b**) chalcopyrite + elemental sulphur; (**c**) sphalerite + elemental sulphur; (**d**) galena + elemental sulphur.

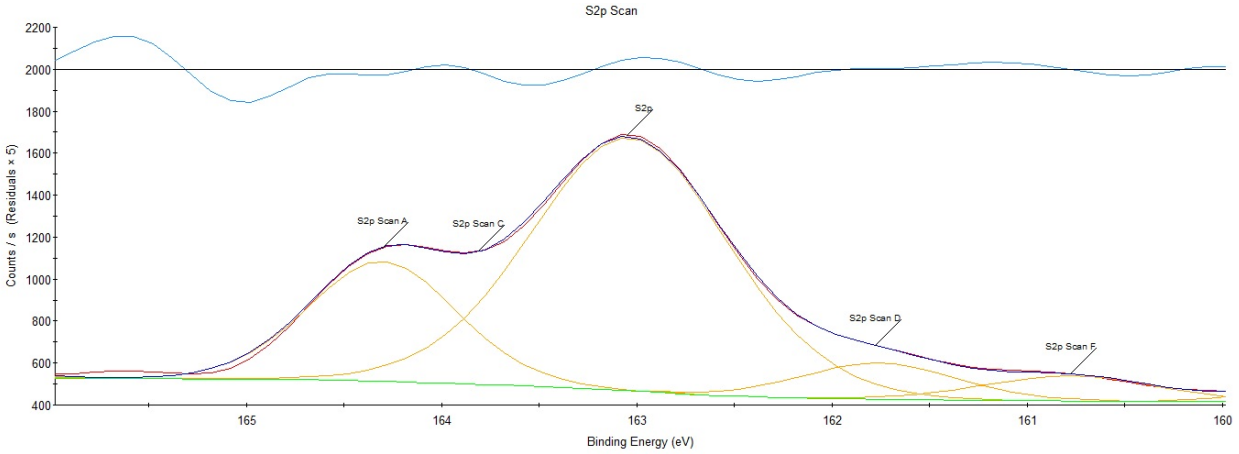



**Figure 8.** XPS of the unconditioned mixture of pyrrhotite ore and elemental sulphur.

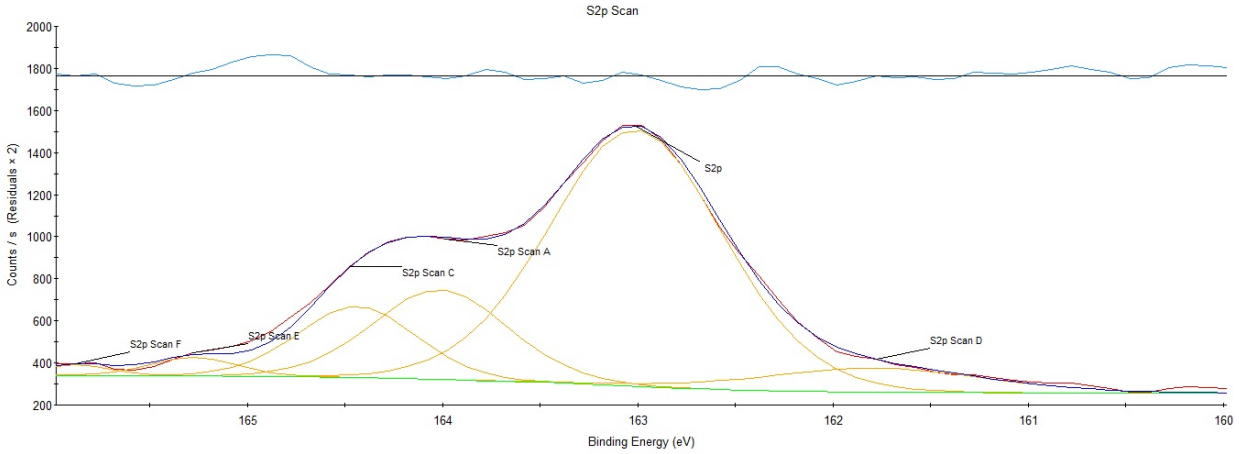



**Figure 9.** XPS of the conditioned mixture of pyrrhotite ore and elemental sulphur.

## 4. Conclusions and Future Studies

This study demonstrated that elemental sulphur on its own is incapable of influencing Stage B self-heating. Additionally, this study found that Stage B self-heating does not occur if elemental sulphur fails to form a necessary chemical connection with a sulphide mineral under ambient conditions. This chemical connection seems to be uniquely formed between pyrrhotite ore and elemental sulphur, as other Rock-Forming sulphide samples failed to demonstrate Stage B self-heating even after being conditioned.

Previous works on surface chemistry analysis suggest the possibility that Stage B self-heating is driven by polysulphides. However, more research is required.

Although this study showed that the elemental sulphur generated during the conditioning phase impacted the *SHC* minimally, future studies are required to clarify its impact on the overall reaction.

**Author Contributions:** Conceptualization, F.R., O.K. and K.W.; methodology, H.K. and F.R.; validation, F.R. and O.K.; formal analysis, H.K., F.R. and O.K.; investigation, H.K. and O.K.; Resources, K.W.; data curation, H.K.; writing—original draft, H.K.; writing—review and editing, F.R., O.K. and K.W.; supervision, K.W.; project administration, K.W.; funding acquisition, K.W. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The experimental data used to support the conclusions of this study are included within the article.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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