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Characterization of elemental sulfur in chalcopyrite leach residues using simultaneous thermal analysis

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Abstract: A key component in the atmospheric leaching of metal sulfides is the oxidation of sulfide to either elemental sulfur or **hexavalent sulfur**. The final oxidation state of sulfur significantly influences the economic viability of a leaching process because of its effects on oxygen consumption, acid generation, and surface passivation. Thus, in the process of developing new leaching technologies, it is important to both characterize and quantify the sulfur oxidation products. In this work, a new method based on Simultaneous Thermal Analysis (STA) is established for the quantification and thermal characterization of elemental sulfur in chalcopyrite leach residues. The STA method refers to the simultaneous application of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The DSC measurements yield information on phase transformation, which can be used to identify the sulfur allotropes. The linear relationship between the melting enthalpy of β -sulfur determined by DSC and the sulfur content determined by TGA is expediently used to quantify the unknown sulfur content in leach residues.

Keywords: Chalcopyrite leach residue; Elemental sulfur; Allotrope; Quantification; STA.

1. Introduction

As an alternative to pyrometallurgical processes, hydrometallurgical extraction of copper from chalcopyrite (CuFeS_2) has the advantages of less environmental pollution and greater ability to treat low-grade ores, especially those containing a significant amount of detrimental elements, such as arsenic, bismuth, zinc and lead (Berezowsky and Trytten, 2002; Braithwaite and Wadsworth, 1976). Among the various hydrometallurgical extraction processes to treat chalcopyrite, acidic ferric ion leaching is believed to be a promising and low-cost route to produce pure copper (Córdoba et al., 2008; Dutrizac, 1982; Javier, 2009). However, the leaching process is difficult to carry out under atmospheric pressure because of the unique electronic structure of chalcopyrite and the complexity of the reaction pathways (Crundwell, 2015; Osseo-Asare, 1992). It has been found that as the acidic ferric ion leaching reaction proceeds (indicated by Eq. 1 and Eq. 2), a passivation layer is formed on the surface of the chalcopyrite particles. This results in slow kinetics and poor copper recoveries due to the formation of a diffusion barrier between the solution and chalcopyrite grains (Ghahremaninezhad et al., 2010; Ghahremaninezhad et al., 2012; Olvera et al., 2016; Rivera-Vasquez et al., 2015; Wang et al., 2016). Although there is still some controversy about the exact composition of this passivation layer, elemental sulfur or polysulfides are observed consistently and considered as systemic products in the acidic ferric ion dissolution of chalcopyrite (Córdoba et al., 2008; Córdoba et al., 2009; Klauber, 2008).

In the most simple and widespread model for passivation by sulfur products, these products are not released into solution at room temperature, but form an electrically non-conductive layer at the surface of the particles. Hence, the overall reaction rate is decreased by inhibiting the electron transfer through the surface sulfur, eventually leading to passivation of the leaching process (Nazari et al., 2012; Pradhan et al., 2008). Wan et al. (1984) found that only 40% copper was extracted from chalcopyrite due to the produced sulfur, and the leaching rate was regained after the elimination of sulfur layer by distillation under a nitrogen atmosphere, proving the inhibition effect of elemental sulfur. Havlik and Kammel (1995) found that when chalcopyrite was oxidized in the presence of carbon tetrachloride, copper extraction was significantly increased.

To address the passivation problem, global engineering company FLSmidth® has developed a mechanochemical approach, i.e., the FLSmidth® Rapid Oxidative Leach (ROL) process for atmospheric leaching of chalcopyrite in acidic ferric sulfate. The process can provide more than 97% copper recovery in 6 h or less. The ROL process includes a chemical activation step as pretreatment and a downstream mechanochemically assisted leaching step that fractures partially leached particles and mitigates the passivation processes (Chaiko et al., 2015a, 2015b; Karcz et al., 2017; Eyzaguirre et al., 2015). In the ROL process, some of the chalcopyrite sulfide is advantageously oxidized to sulfuric acid, as shown in Eq. 3, which is an economic and operational benefit. This is because the produced sulfuric acid can replenish the acidity required for the leaching process, as shown in Eq. 2 (Dutrizac and MacDonald, 1974; Gómez et al., 1996). However, the final sulfur species in the leach product is not well understood. As the sulfur products can have significant impact on oxygen consumption, acid generation, and surface passivation of the leaching process, it is important to establish a method to characterize and identify the sulfur species in the leach product (McDonald and Muir, 2007; Sahu and Asselin, 2011).

In this paper, a method based on Simultaneous Thermal Analysis (STA) is developed and tested to analyze the elemental sulfur in the residue obtained from the FLSmidth® ROL process. The STA method employs the simultaneous application of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The combined DSC and TGA signals can provide qualitative information about the sulfur allotropes present in the sample. By using model compounds containing elemental sulfur, quartz, and chalcopyrite, a method for quantifying the amount of elemental sulfur in the leach residue is established and validated.

2 Materials and Methods

2.1 Materials

The chalcopyrite leach residue used in the present work was obtained from the FLSmidth® ROL process (Chaiko et al., 2015a; Chaiko et al., 2015b; Eyzaguirre et al., 2015). The feed copper concentrate with 24 wt. % Cu (shown in Table S1) was slurry split. The primary crystalline phases present in the feed material (according to the XRD analysis in Figure S1) were chalcopyrite, pyrite, and quartz. The feed material was leached in acidic ferric sulfate media at 80 °C with an initial iron concentration of 20 g/L, in accordance with the FLSmidth® ROL procedure described in detail in Chaiko et al. (2015a). At the end of the leach experiment, the residue was filtered and dried, and the dry sample was then shipped from FLSmidth USA Inc. to DTU in Denmark. The leach residue was

characterized by the methods described in Section 2.2. Elemental sulfur (α -sulfur, powder, > 99.98% trace metals basis) and quartz powder were purchased from Sigma-Aldrich. Pure chalcopyrite mineral was purchased from Alfa Aesar and was ground to 100% < 74 μm with an agate mortar and pestle. Toluene of anhydrous grade and assay $\geq 99.8\%$ was purchased from Sigma-Aldrich.

2.2 Analytical methods

The elemental composition of the leach residue was analyzed by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). The sample was dried overnight to remove moisture. A sample of 0.050 g was mixed with 2 mL H_2O_2 , 7.5 mL HNO_3 and 1.7 mL HF (48%) and digested in a high-pressure reactor, which was heated to 210 $^\circ\text{C}$ within 10 min and kept at this temperature for 15 min. Then, the solution was cooled and neutralized with 20 mL H_3BO_3 (4% w/v) and diluted to 100 mL with ultrapure water prior to ICP-OES analysis based on the standard DS/EN ISO 11885.

The X-Ray Diffraction (XRD) analysis of crystalline phases in the leach residue was carried out on a Panalytical X'Pert PRO system using $\text{Cu-K}\alpha$ radiation in the diffraction angle (2θ) range of 3° - 100° . The crystalline phases were identified by Crystallgraphica Search Match software to reference the relevant peaks to the standard diffraction database (PDF-2 2004 from ICDD).

The compositions of the leach residue and mixed pure mineral standards were characterized using a field emission Scanning Electron Microscope (SEM, JEOL 2100F), equipped with an Energy Dispersive Spectrometer (EDS). Samples of 1 - 2 g were embedded within resin and curing agent for 12 hours. Then, the cured sample was polished on SiC pads of 200-mesh, 800-mesh, 1200-mesh, and 2000-mesh in preparation for measurement by SEM-EDS.

The thermal behavior of minerals in the residue was evaluated by STA using a Netzsch STA 449F1 instrument. During the experiments, the sample was placed in an alumina crucible, with an empty crucible alongside as a reference. Unless otherwise stated, the furnace was heated from 25 $^\circ\text{C}$ to 400 $^\circ\text{C}$ for all experiments. Different heating rates and heating programs (heating-cooling cycles) were applied for the establishment of the STA characterization method. The relevant details for the different experiments are provided in the Results and Discussion (Section 3). Nitrogen purge gas with a purity of 99.9% was used as the protective gas with a flow of 100 mL/min. All STA data were baseline-corrected using a scan of an empty crucible. The analyses of DSC and TGA curves were done using NETZSCH Proteus Thermal Analysis software. As illustrated in Figure 1, the derivatives of the DSC and TGA curves were used to identify the onset and endpoint of the mass or heat changes when calculating the mass loss or the reaction enthalpy (Chiu, 1963; Gill et al., 2010; Munther et al., 2010). In this paper, all the enthalpy and mass change calculations were based on the

method above. In order to simplify the presentation, the derivative curves for the DSC and TGA data were omitted in each figure.

Figure 1. Schematic diagram for the calculation of DSC (a) and TGA (b).

The mass fraction of elemental sulfur in the leach residue can be determined gravimetrically by toluene extraction. Extraction of sulfur by organic solutions, such as carbon disulfide and carbon tetrachloride, is often used to quantify the amount of sulfur (Meyer et al., 1971; Sciamanna and Lynn, 1988). However, the potentially carcinogenic nature of these solvents makes their use undesirable. Sulfur is also soluble in solvents such as toluene, cyclohexane, octane, and dry methanol (Jay et al., 2009). In this experiment, toluene was chosen as the solvent based on the high elemental sulfur solubility. Approximate 3 g **sub-sample of leach residue** was added to toluene at 60 °C. The mixture was stirred for 15 - 20 min at 600 rpm after which the slurry was filtered and the solids were washed with warm toluene. The residual solid was dried in an oven at 50 °C to constant weight. The percentage of elemental sulfur was calculated by Eq. 4.

$$\text{wt.\% of sulfur} = \frac{\text{initial sample mass} - \text{residual sample mass}}{\text{initial sample mass}} \times 100\% \quad (4)$$

3. Results and discussion

3.1 Elemental composition and mineral phases in the leach residue

114 The **elemental** composition of the leach residue is shown in Table 1. From Table 1, we can see
 115 that S is the predominant element, which consists of 65.0 wt.%. The content of Si is high (8.7 wt.%),
 116 and together with Al, K, and Mg, they may constitute the gangue minerals. There are also 2.6% of
 117 Cu and 2.4% of Fe in the residue. Other elements such as Ca, Na, and P are present in minor
 118 amounts of less than 0.1 wt.%. The XRD pattern in Figure 2 shows that the primary crystalline
 119 phases detected are elemental sulfur (S^0), quartz (SiO_2), and chalcopyrite ($CuFeS_2$). The pattern for
 120 sulfur is very sharp and strong, which is consistent with the large content of elemental sulfur
 121 detected by ICP-OES. Other elements were not detected as their host minerals by XRD (which may
 122 be due to their low contents).

123 Figure 3 shows the morphology and EDS point analysis of the leach residue. It seems that most
 124 of the sample particles adhere to each other, possibly because of the large amount of sulfur. The
 125 EDS results show that the bright points contain mostly S, Fe, and Cu (see Figure 3e Spectrum 3 and
 126 Figure 3f Spectrum 1), indicating the presence of chalcopyrite. Figure 3e Spectrum 1 contains
 127 mainly S, Co, and Cu, indicating the possibility of carrollite ($CuCo_2S_4$). The gray point (see Figure
 128 3f Spectrum 2) contains Mg, Al, Si, and S, indicating that it is mostly composed of silicate and/or
 129 muscovite. The further gray points (see Figure 3e Spectrum 2 and Figure 3f Spectrum 3) contain
 130 abundant sulfur. It appears that sulfur is poriferous. The particle size distribution (PSD) of the leach
 131 residue (see Figure S2 in supplementary materials) reveals a fine-mode peak in the interval from
 132 0.40 μm to 20 μm . The PSD in terms of volume distribution (D_v) values for the leach residue was:
 133 $D_v(10)=1.11 \mu m$, $D_v(50)=3.83 \mu m$, $D_v(90)=9.36 \mu m$. About 10% of the leach residue is $> 9.36 \mu m$,
 134 which may be due to the unreacted minerals in chalcopyrite concentrate.

135 Table 1. Elemental composition of the leach residue (wt.%) as determined by ICP-OES.

Element	S	Si	Cu	Fe	Al	Co
w/%	65.0	8.7	2.6	2.4	2.1	1.3
Element	K	Mg	Ti	Ca	Na	P
w/%	0.86	0.45	0.18	<0.1	<0.1	<0.1

Figure 2. XRD analysis of the leach residue.

Figure 3. Morphology and composition of leach residue as determined by SEM-EDS. (Spectra in (e) and (f) correspond to the points labeled in (c) and (d), respectively.)

3.2 STA analysis of leach residue

As previously stated, STA is a combined technique of DSC and TGA, which can be used to analyze the elemental sulfur thermal properties. Elemental sulfur can exist as a number of different allotropes. Table S2 (see supplementary materials) compiles data for different sulfur phase transitions at different temperatures. In view of these phase transition data, it is possible to use STA to identify the phases of elemental sulfur in chalcopyrite leach residue. The STA of the leach residue is shown in Figure 4, with the cycle heating program as follows (heating/cooling rates of 2 °C /min, N₂ flow of 100 mL/min, samples mass of 10 mg):

First stage (1st stage): Heating from 25 °C to 130 °C;

Second stage (2nd stage): Cooling from 130 °C to 25 °C;

Third stage (3rd stage): Heating from 25 °C to 150 °C;

Fourth stage (4th stage): Continuous heating from 150 °C to 400 °C.

Figure 4. STA of leach residue with cycle heating program.

3.2.1 The DSC curve

3.2.1.1 First stage

At this stage, the sample is heated from 25 °C to 130 °C. Figure 4 shows two distinct endothermic peaks at 108.2 °C and 119.0 °C for the leach residue. From similar STA analyses of pure mineral samples (Figure S3-S6 in supplementary materials), it can be seen that there are no

162 endothermic peaks or exothermic peaks for quartz, chalcopyrite, or pyrite below 130 °C shown by
163 DSC, while there are two clear endothermic peaks at 108.7 °C and 123.1 °C for pure sulfur. Except
164 for the slight shift in peak temperatures, the appearances of the DSC curves for the leach residue
165 (Figure 4) and pure sulfur are quite consistent. Assuming that the shifts in peak temperatures reflect
166 that the leach residue contains impurities as compared to the pure sulfur sample (which is further
167 evidenced in Section 4.1, Figure 5, and Table S2), the results strongly indicate that the two
168 endothermic peaks of the 1st stage are caused by the transformation of elemental sulfur.

169 According to Table S2, the small endothermic peak at 108.2 °C indicates either the depressed
170 melting point of orthorhombic sulfur (α -sulfur), or the solid-solid transformation of α -sulfur into
171 monoclinic sulfur (β -sulfur). In the work of Ficara and Moreira, there are two endothermic peaks at
172 108.25 °C and 119.50 °C for the DSC of standard sulfur, which represent the α -sulfur to β -sulfur
173 transition and the melting of sulfur, respectively (Ficara and Moreira, 1988). Their measurement
174 conditions are very close to this study; thus, the first peak at 108.2 °C could be assigned to the
175 transformation of α -sulfur into β -sulfur (Laitinen and Niinisto, 1978; Miller, 1971; Thackray, 1970).
176 Meanwhile, the peak at 119.0 °C is most probably due to the melting of β -sulfur. Different melting
177 points have been reported for β -sulfur. “Natural” β -sulfur should melt at 114.6 °C, while melting
178 temperatures of 119.6 °C and 120.4 °C have been reported for regular and microcrystalline β -sulfur,
179 respectively (Koningsberger and De Neef, 1972; Meyer, 1964; Meyer 1976; Thackray, 1970).

180 The integrated DSC peak area can be used to determine the enthalpy of phase transition, and
181 thus, a peak area analysis of the DSC scans can be used to support the above conclusions regarding
182 sulfur allotropes present in the leach residue. The area of the first endothermic peak at 108.2 °C
183 suggests an endothermic enthalpy of 5.73 J/g, which is about 1/4 of the heat absorption of the second
184 peak at 119.0 °C (22.08 J/g). According to the thermal data for phase transitions of sulfur, the
185 enthalpy for the α - β sulfur transition is 12.56 J/g, while it is 50.25 J/g for the melting of β -sulfur
186 (the value differences lie in various samples), which corresponds to a ratio of about 1:4 (Meyer,
187 1964; Meyer, 1976; Hemingway, 1999). Hence, it is plausible to conclude that the two peaks in the
188 1st stage represent the α - β sulfur transition and the melting of β -sulfur, respectively. The good
189 quantitative agreement (the 1:4 ratio) also suggests that the only sulfur allotrope present at the
190 beginning of the analysis is the stable α -sulfur allotrope.

191

192 3.2.1.2 Second stage

During this stage, the sample is cooled from 130 °C to 25 °C. A distinct exothermic peak is present at 85.6 °C, and this peak is most likely attributed to the recrystallization of β -sulfur. A temperature of around 50 °C for recrystallization of β -sulfur has been reported elsewhere (Perrenot and Widmann, 1994). The much higher phase change temperature in our case can be ascribed to the content of other minerals (impurities) in the leach residue sample, and this is further discussed in Section 4.1.

3.2.1.3 Third stage

In this stage, the sample is heated from 25 °C to 150 °C. The distinct endothermic peak at 118.3°C is probably the re-melting of β -sulfur as compared with the melting of β -sulfur in the 1st stage, indicating the sole presence of β -sulfur in the residue after heat treatment. In support of this, additional DSC investigations of the re-melting of sulfur allotropes in leach residue are presented in Figure S7 of the supplementary materials. The heat flux of the single endothermic peak at 118.3 °C gives a value of 21.27 J/g, which is approximately equivalent to the 1st stage, further evidencing that the peak belongs to the melting of β -sulfur.

3.2.1.4 Fourth stage

The sample is heated from 150 °C to 400 °C. At this stage, there is a distinct mass loss after a small endothermic peak at around 165.0 °C. According to Miller (1964, 1971), the melted β -sulfur can transform into the lambda form of sulfur (λ -sulfur), which can polymerize to form catena-sulfur (Meyer, 1964; Meyer, 1976). With the increase of temperature, the catena-sulfur begins to vaporize at around 233.3 °C and leads to the obvious mass loss.

3.2.2 The TGA curve

The TGA curve is also plotted in Figure 4. The result reveals a small mass loss of 1.92% during the 130 °C isothermal stage. As shown in Figure S3, there is a slight mass loss for pure sulfur before 130 °C, while in Figure S4 – S6, the mass losses for quartz, chalcopyrite, and pyrite between 25 °C - 130 °C are 0.18%, 0.34%, and 0.29%, respectively, which may be due to other labile substance in these samples. Thus, it is concluded that the 1.92% mass loss is probably due to the slight sulfur loss during the isothermal stage. During the fourth stage, there is a distinct mass loss of 58.28%, which can be explained by the vaporization of sulfur.

4. Quantification of the leach residue

4.1 Establishment of quantification method by STA

Based on the characterization of the leach residue in Section 3.1, we identified the main mineral phases in the leach residue as sulfur, quartz, and chalcopryrite (with the contents of other compositions being below 4 wt.%). Synthetic samples consisting of pure elemental sulfur (S^0), pure chalcopryrite ($CuFeS_2$), and pure quartz (SiO_2) in different ratios were prepared and measured by STA in order to verify the STA measurement method and formulate a melting enthalpy-based standard curve for the measurement of leach residues. Different amounts of pure elemental sulfur, chalcopryrite, and quartz were weighed using an electronic balance with 0.01 mg accuracy to produce ratios for S^0 : $CuFeS_2$: SiO_2 of 2.7:1:3, 4.8:1:3, 15.3:1:3, 1:0:0, which were given the sample identities J1, J2, J3, and J4, respectively. The mixed mineral samples were then ground in an agate mortar to < 200 mesh. The STA measurements of the synthetic samples with different sulfur contents are shown in Figure 5 and Table 2. The conditions are the same as the cycle heating of the leach residue in Section 3.2. With regard to the synthetic samples, the STA analysis was also divided into four stages, which are interpreted next.

Figure 5. STA of synthetic samples with different sulfur contents.

Table 2. Peak temperatures for different synthetic samples according to STA analysis.

Sample	S:CuFeS ₂ :SiO ₂ ratios	First stage		Second stage	Third stage	Fourth stage	
		T ₁ (°C)	T ₂ (°C)	T ₃ (°C)	T ₄ (°C)	T ₅ (°C)	T ₆ (°C)
J1	2.7:1:3	115.5	120.6	71.4	120.4	162.6	222.9
J2	4.8:1:3	114.6	121.2	81.0	115.4	164.4	232.0
J3	15.3:1:3	110.0	121.6	78.4	93.9/ 120.7	165.7	242.2
J4	1:0:0	106.0	121.8	54.9	108.9	167.2	255.3

4.1.1 First stage

At this stage, there are two distinct endothermic peaks at around 110.0 °C and 121.0 °C for the four samples. Table 2 shows that the temperature of peak **T1** is reduced with the increase of the sulfur content in the synthetic samples, indicating that the conversion of sulfur proceeds slowly near the transformation temperature, which can be again assigned to the α -sulfur to β -sulfur transformation (Donohue, 1974; Sands, 1965). It has been reported that the transformation time is influenced by the purity of the sample (Steudel, 1984). The peak **T2** at around 120.0 °C is likely the melting of β -sulfur, which typically occurs at around 119 °C (Meyer, 1964). It is noticeable that the β -sulfur melting temperature changes little with the increase of sulfur content.

4.1.2 Second stage

During this stage, the samples are cooled from 130 °C to 25 °C. A distinct exothermic peak **T3** is present at 54.9 °C, 78.4 °C, 81.0 °C, and 71.4 °C for different synthetic samples, respectively. Similarly, the exothermic peak in synthetic samples may also be attributed to the recrystallization of β -sulfur (or a mixture of β -sulfur and other cyclic molecules) (Perrenot and Widmann, 1994). The increased recrystallization temperature of mixed mineral samples as compared to the pure sulfur sample (J4) may be explained by the presence of other minerals (such as quartz) in the sample, which can “seed” the crystallization of sulfur.

4.1.3 Third stage

In this stage, the samples are heated from 25 °C to 150 °C. The distinct endothermic peak **T4** position at 108.9 °C, 120.7 °C, 115.4 °C, and 120.4 °C for the four samples, respectively. As compared to the melting point of what is supposed to be monoclinic β -sulfur during the first stage

heating (around 120.3 °C), the positions of the peak for samples J2 and J4 are shifted significantly toward lower temperatures. This indicates that the re-crystallized sulfur formed during the second stage is another (metastable) allotrope of sulfur instead of monoclinic β -sulfur or the mixture of sulfur allotropes. Meyer (1964) suggests that it is probably the melting of monoclinic γ -sulfur (m.p. 106.8 °C). This allotrope of sulfur can be obtained from a solution of cyclo-S₈ and from its melt (which would be the case here).

4.1.4 Fourth stage

At this stage, the samples are heated from 150 °C to 400 °C. There are also small endothermic peaks at around 165.0 °C for the four samples, which could be assigned to the production of λ -sulfur. With the increase of temperature, the λ -sulfur evaporates within one hour (Currell and Williams, 1974; Steudel and Eckert, 2003).

4.1.5 The TGA curves

Examination of the TGA curves indicates the performance of the four synthetic samples are almost the same as the leach residue, with small mass losses of 1.62% during the 130 °C isothermal stage and large mass losses above 150 °C, as shown in Table 3. There are total mass losses of 41.82%, 59.31%, 82.62%, and 98.13% for J1, J2, J3 and J4, respectively, which are all close to the theoretical sulfur contents using toluene extraction method in samples given the high purity of the sulfur used, as verified in Table S3.

Figure 6. Melting enthalpy of β -sulfur for synthetic samples with various sulfur contents.

Table 3. Correspondence between TGA and DSC data.

Sample	Mass loss by TGA (%)	Melting enthalpy of β -sulfur (ΔH , J/g*)
J1	41.82	14.40
J2	59.31	24.76
J3	82.62	34.20
J4	98.13	42.73

*Note: The value is based on the Joules per gram of residue.

Based on the melting enthalpy of elemental sulfur, the quantification of sulfur can be performed from STA measurements. In the above analysis, the second peak during the 1st stage was assumed to be caused by the melting of β -sulfur, both for the synthetic samples and the leach residue. Additionally, the melting of β -sulfur occurs at a stable temperature around 120 °C, suggesting that no other changes affect the melting enthalpy of β -sulfur. Thus, the melting of β -sulfur is used for the quantification of sulfur. The related function is calculated from a plot of sulfur melting enthalpy versus mass change, based on the DSC and TGA data in Table 3. The linear function-fitting plot is shown in Figure 7, with the equation interpreted as follows:

$$\Delta H = 0.4364 x - 1.3858 (R^2 = 0.9882) \dots \dots \dots (5)$$

Here, the variable x refers to the percentage of elemental sulfur mass lost; R^2 refers to the coefficient of determination. Based on this equation, the sulfur content can be easily determined as long as the melting enthalpy is supplied.

Figure 7. The linear fitting of TGA-based mass loss and DSC-based enthalpy.

4.2 STA of leach residue with different sample masses

To determine the influence of sample mass on the STA measurement, various sample masses were analyzed with a heating rate of 2 °C/min. The results are shown in Figure 8 and Table 4.

Figure 8. STA of the leach residue with various sample masses.

As evidenced by TGA, the mass losses from the leach residue with samples masses of 6.31 mg, 8.90 mg and 10.00 mg were 57.11%, 58.30% and 60.42%, respectively, with an average mass loss of 58.61%. In the DSC curve, the curve shape is similar for the samples with various masses. The two endothermic peaks at around 108.6 °C and 119.1 °C are in agreement with the transformation of α -sulfur to β -sulfur and the melting of β -sulfur, respectively. The melting enthalpy (marked as area under the curves in Figure 8) of β -sulfur below 150 °C (when there is no mass loss) was used to calculate the percentage of sulfur in the residue by referring to the function in Eq. 5. The calculation results are shown in Table 4.

It was observed that the TGA-based sulfur content (average 58.61%) is in accordance with DSC-based sulfur content (average 58.32%), illustrating the reliability of STA quantification methods. There is a slight increase of sulfur content with the increase of sample mass, as shown in Table 4. This can be explained by the existence of other components, such as chalcopyrite and quartz, in the leach residue, which may have a negative effect on the endothermic change rate of elemental sulfur and lead to the difference of sulfur content values (also see Section 4.3).

Table 4. Sulfur percentage of leach residue with various sample masses.

Sample mass(mg)	TGA-based sulfur content (%)	Average by TGA (%)	DSC-based sulfur content (%)	Average by DSC (%)
6.31	57.11		56.13	
8.90	58.30	58.61 $\pm$ 1.37	58.88	58.32 $\pm$ 1.60
10.00	60.42		59.94	

4.3 STA of leach residue with different heating rate

To determine the influence of heating rate on the STA measurement, the STA of leach residue with a mass of 10.00 mg was analyzed, as shown in Figure 9 and Table 5.

Figure 9. STA of leach residue with various heating rates.

Figure 9 shows the STA of the leach residue with different heating rates from 2 °C/min to 10 °C/min. For the TGA curves, when the temperature is increased to above 150°C, the mass begins to decrease. There is an average mass loss of 60.26% for the various heating rates of 2 °C/min, 5 °C/min, and 10 °C/min, which is attributed to the volatilization of elemental sulfur. From the DSC curve data, the melting enthalpies were calculated to increase slightly from 24.72 J/g to 26.42 J/g with heating rates increasing from 2 °C/min to 10 °C/min. The corresponding sulfur percentage based on Eq. 5 is listed in Table 5. It was concluded that the heating rate affects the calculation of sulfur percentage by DSC with an average of 61.70%, which is 1.44% higher than the sulfur content by TGA. The DSC calculated sulfur contents seem to be positively correlated with the heating rate, which may be due to the overlap between the two peaks at around 110°C and 120°C. The overlap between the two peaks is less for the heating rate of 2 °C/min; therefore, the area of the higher temperature peak is more accurately estimated. Hence, 2 °C/min was identified to be the appropriate heating rate for the leach residue.

Table 5. Sulfur percentage of leach residue with various heating rates.

Heating rate (°C/min)	TGA-based sulfur content (%)	Average by TGA (%)	DSC-based sulfur content (%)	Average by DSC (%)
2	60.15	60.26 ± 0.10	59.82	61.70 ± 1.59
5	60.25		61.56	
10	60.39		63.72	

348 **4.4 The analysis of STA-treated ash**

349 After the leach residue was treated by STA with a sample mass of 10.00 mg and heating rate of
350 2 °C/min, the ash was collected and subjected to XRD analysis. From the XRD data, it can be seen
351 that the remaining components are quartz, chalcopyrite, pyrite, and muscovite. The elemental sulfur
352 level was below detection limit, confirming that evaporation of elemental sulfur was complete.
353 According to semi-quantitative analysis of XRD, the amount of chalcopyrite is greater than 45%,
354 indicating that the leach residue could be recycled to recover the chalcopyrite.

355
356 Figure 10. X-ray diffraction pattern of STA-treated ash.

357 **4.5 Validation by toluene extraction**

358 After extraction of sulfur by toluene for 15 to 20 minutes, it was assumed that the elemental
359 sulfur was completely dissolved in toluene. The results are shown in Table 6. The toluene
360 extraction of elemental sulfur confirms that the elemental sulfur content in the leach residue is
361 $61.14 \pm 0.15\%$.

362 Table 6. Extraction of sulfur from leach residue by toluene.

Group	Initial sample mass (g)	Volume of toluene (mL)	Time (min)	Residual sample mass(g)	Sulfur content (%)	Average sulfur content (%)
1	3.00230	150	15	1.16701	61.13	61.14 $\pm$ 0.15
2	3.00150	150	20	1.17369	60.90	
3	3.00091	200	15	1.16348	61.23	
4	2.86188	150	20	1.10800	61.28	

364 As comparison with the result of toluene extraction, the sulfur content determined by DSC and
365 TGA methods (using 10.00 mg sample and 2 °C/min heating rate), both of which are around 60%,
366 is consistent with 61.14%, indicating the usage of STA as a promising method for the qualitative
367 and quantitative **characterization** of leach residues. DSC can also be used to determine the enthalpy
368 change of the sample, giving information on the element allotropes and thermal changes of
369 elemental sulfur. The TGA measurement is comparatively stable and accurate for the samples tested.
370 Thus, STA provides a comprehensive method for samples of the kind investigated in this study.

371 **5 Conclusions**

372 In this work, an STA-based method for quantification and thermal characterization of the
373 sulfur in the residue from a chalcopyrite leaching process was developed and evaluated. It was
374 found that STA, which refers to the simultaneous application of thermogravimetric analysis (TGA)
375 and differential scanning calorimetry (DSC) in a single instrument, can be conveniently used for the
376 quantification and thermal characterization of sulfur in leach residues from the FLSmidth® ROL
377 process.

378 The STA-based method on pure mineral assemblages using a known content of sulfur was
379 used to establish the function to estimate sulfur content and verify the reliability of the method. The
380 sulfur percentage was readily calculated **from the sulfur melting enthalpy** and mass loss.

381 For the leach residue sample, the only volatile component was elemental sulfur, which was
382 readily evaporated in N₂ at 400 °C. A TGA-determined mass loss of around 60% for the leach
383 residue was dominated by the evaporation of sulfur. Endothermic peaks at around 112°C in the
384 DSC curve suggest that there is a sulfur phase change from α -sulfur to β -sulfur, which melts at
385 around 120 °C. Furthermore, DSC not only indicates the sulfur phase changes, but it also allows the
386 percentage of each phase to be calculated. Taking advantage of the enthalpy changes in DSC and
387 the corresponding mass loss in TGA, the amount of elemental sulfur present in the sample can be
388 determined from a pre-established linear function. The results that were verified by toluene
389 extraction show there is a good consistency with both the DSC sulfur quantification method and the
390 TGA quantification. In summary, STA is recommended as a comprehensive quantification and
391 characterization method for chalcopyrite leach residues containing elemental sulfur.

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