Sulfidic mine tailings and marl waste rock as compatible resources in a microwave-assisted roasting process

Maarten Everaert[a,b]*, Vincent Lemmens[a], Thomas Abo Atia[a,b], Jeroen Spooren[a,b]

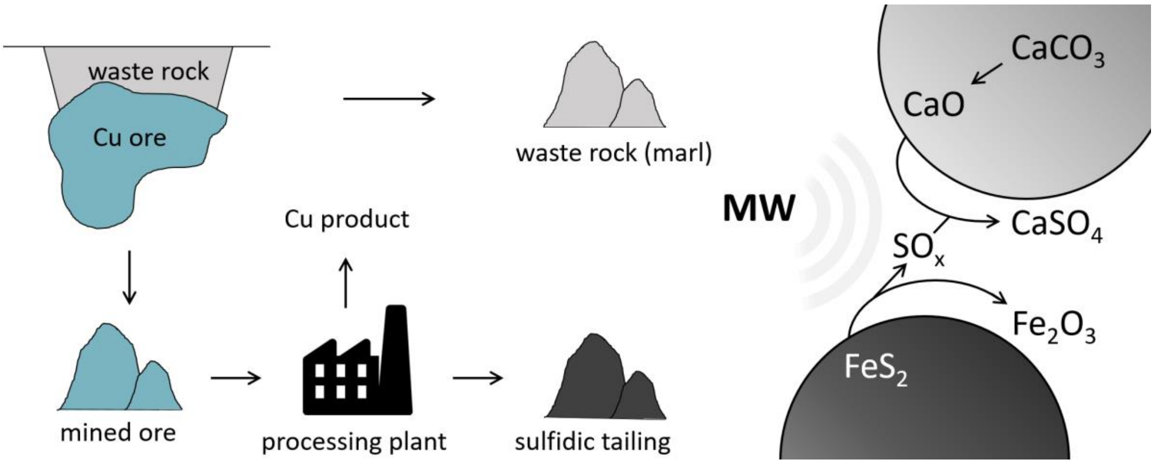
[a] Flemish Institute for Technological Research (VITO), Unit Sustainable Materials Management, Boeretang 200, 2400 Mol, Belgium

[b] SIM vzw, Technologiepark 48, 9052 Zwijnaarde, Belgium

* Corresponding author: maarten.everaert@vito.be, tel.: + 32 14 33 53 48

Abstract

Copper (Cu) is a popular commodity metal, and novel technologies are being developed to extract Cu from low-grade sources, such as sulfidic tailings. Roasting of tailings allows efficient Cu extraction and reduces environmental risks associated with tailing storage. However, conventional roasting is energy-intensive and releases harmful sulfur oxide gas (SO_x). This study combines two mining wastes, sulfidic tailing and carbonate-rich waste rock (marl), in an energy-efficient microwave-assisted roasting step to simultaneously oxidize sulfide minerals and fixate formed SO_x gas as sulfates. The roasting procedure was first optimized via conventional roasting (varying temperature, mixing ratio) by characterizing roasted materials (XRD/Rietveld, SEM-EDX, XRF, TGA-MS). Later, these optimized conditions were tested with microwave-assisted roasting. Subsequently, the influence of roasting treatments on Cu extraction was examined via ammoniacal leaching. Results showed that sulfate formation (SO_x fixation) was highest for roasting at 500 °C via conventional roasting and increases with increasing marl content. Microwave-assisted roasting at 500 °C performs slightly below conventional roasting, as FeS_2 was not fully oxidized. Marl addition negatively affects Cu extraction, likely because it limits the formation of water-soluble $CuSO_4$. This study demonstrates the potential of mixing marl with tailings to control SO_x emissions during roasting, but also shows limitations in terms of Cu extraction.



1. Introduction

Copper (Cu) is one of the most popular commodity metals, and demand for Cu is expected to increase substantially during the next few decades (Elshkaki et al., 2016). Development of novel technology is required to allow the extraction of Cu from low-grade sources, thereby also diminishing the environmental impact. Recently, also the extraction of Cu from secondary sources, such as sulfidic mine tailings, became of interest (Li et al., 2014).

Sulfidic tailings are a waste material remaining after ore processing, yet often these materials still contain considerable amounts of valuable metals. The storage of sulfidic tailing raises environmental concerns, as this can result in acid mine drainage (Kefeni et al., 2017). In order to mitigate this problem, alkaline amendments (*e.g.* $CaCO_3$ or CaO) are added, which can prevent acidification and help to immobilize harmful metals for a short period of time (Catalan and Yin, 2003; Davis et al., 1999). As a long-term solution, the roasting of sulfidic tailings has been proposed to i) minimize the environmental risk related to acid mine drainage (Lindsay et al., 2015) and ii) facilitate the extraction of remaining valuable metals, *e.g.* Cu (Nyamjargal et al., 2018). After the removal of valuable metals and harmful elements (Zn, Pb, As), the remaining matrix can be valorized as, for instance, an alternative building material(Park et al., 2019). In the roasting process of sulfidic tailings, two general mechanisms of roasting have been identified: i) oxidative roasting, which converts metal sulfide to metal oxide, thereby also forming SO_x (SO_2 or SO_3) gas, and ii) sulfation roasting, which converts metal sulfide and O_2 gas to metal sulfate. In reality, however, the roasting process of a heterogeneous material, such as tailing, is complex and advanced characterization techniques are required to identify the phase transitions that a specific material undergoes during roasting (Shamsuddin, 2016).

Conventional roasting can offer a long-term solution for acid mine drainage, yet this technology is linked to a few major drawbacks. Firstly, roasting in conventional furnaces is a very energy demanding process. Therefore, recent developments in roasting technology are focusing on the use of microwave-assisted heating to improve the energy efficiency of the roasting process of sulfidic tailings (Al-Harahsheh and Kingman, 2004; Liu et al., 2015; Moravvej et al., 2018). Sulfidic tailings contain pyrite and Cu/Pb/Zn-bearing sulfidic minerals, which can very efficiently absorb microwave energy and thus heat fast to high temperatures (Kingman and Rowson, 1998). A second issue related to the roasting of sulfidic tailing is that, during oxidative roasting, most sulfide is converted to SO_x, a harmful and toxic gas, which is released into the atmosphere (Smith et al., 2001). Gas treatment technology based on alkali chemical materials allows the desulfurization of the flue gas and the absorbed S can be released from the sorbent with a regeneration treatment, yielding *e.g.* sulfuric acid. Yet, often the spent sorbent is disposed of as waste (Rezvanipour et al., 2018). Recently, a new roasting technology for sulfidic tailings was proposed to reduce these SO_x emissions. Roasting the tailing in a mixture with a SO_x capturing agent, such as $CaCO_3$ or CaO, results in the fixation of SO_x due to the formation of sulfate compounds. In this reaction, the SO_2 gas, formed in the oxidizing conditions of a roasting treatment, is converted to sulfate (Tullin and Ljungström, 1989).

$$CaCO_3(s) + SO_2(g) + 0.5\ O_2(g) \leftrightarrow CaSO_4(s) + CO_2(g) \qquad (1)$$

Based on this technology, Barlett *et al.* used conventional roasting of pellets prepared from a mix of Cu sulfide concentrate and CaO to capture up to 95% of S in the form of $CaSO_4$. Similar S retention was obtained by Riveros *et al*. and Hua *et al*., using microwave-assisted roasting of pellets prepared from a mix of Cu-Fe sulfide concentrate and $CaCO_3$. This microwave-based technology can still be further improved, as i) pelletizing a mixture of tailing and $CaCO_3$/CaO is not achievable on industrial scale, so testing of this technology is required for powder mixtures of these materials, and ii) using pure $CaCO_3$ or CaO is not an economically viable option to treat tailings, which shift the attention towards carbonate-rich waste streams.

In this work, the aim was to treat sulfidic tailings to simultaneously oxidize sulfide minerals and fixate the formed SO_2 gas and, in a subsequent step, to extract Cu from the roasted materials. With microwave-assisted roasting, a sustainable recycling option is proposed to utilize two waste streams obtained from a single mining site: i) a low-grade sulfidic Cu tailing and ii) a carbonate-rich waste material (marl). The latter material, a common residue in mining practices (Oggeri et al., 2019), can serve as secondary source of $CaCO_3$ to use during the roasting of the tailing (Figure 1). First, mixtures of tailing and marl with varying mixing ratios were prepared. Using conventional roasting, a range of roasting conditions were assessed based on Rietveld-characterization of the obtained materials. The most promising roasting conditions were transferred to a microwave-roasting system. Finally, the extraction of Cu from the obtained roasted materials was assessed via ammoniacal leaching.

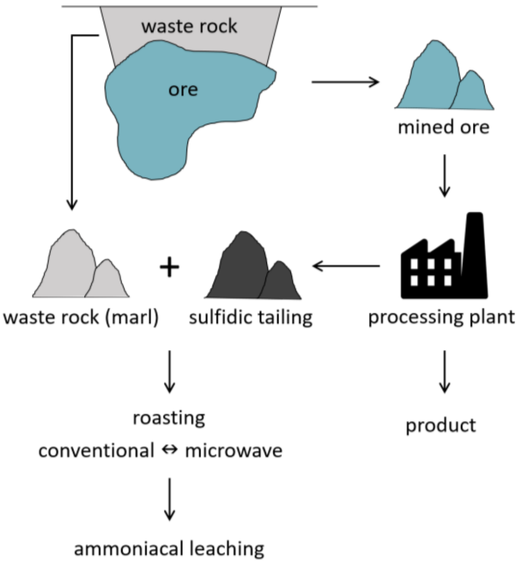


Figure 1. *Overview of the procedure proposed in this study, in which a secondary raw material (marl) is used as additive to sulfidic tailing in the roasting step.*

2. Materials and methods

2.1. Materials

The selected sulfidic tailing and the marl material (waste rock) originate from the Cobre Las Cruces mine, located in Spain. The sulfidic tailing was dried at 40°C after sampling, while the marl was dried at 105°C until constant weight. Subsequently, the marl was ground using a disc mill (*Retsch*® Disc Mill DM 200), and sieved over a 1 mm sieve. The chemical composition of both materials was determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES, *Perkin Elmer Avio 500* with *Elemental Scientific prepFAST* autosampler) after microwave digestion in $HCl/HNO_3/HBF_4$ for 2 hours at 105°C. The crystallographic characteristics of the materials were investigated using X-ray diffraction (XRD, *PANalytical Empyrean Diffractometer*). The diffractometer operated at 40 kV and 45 mA, with cobalt anode material and equipped with a BBHD and a 3D detector (*PIXcel 3D*) with an active scanning length of 3.347° 2θ. Continuous mode scans with a scanning speed of 0.06° s^{-1} and step size of 0.013° were performed within a 2θ range of 5-120° 2θ. The obtained diffractograms were qualitatively and quantitatively analyzed with the aid of HighScore Plus software. Quantitative analyses by Rietveld refinement used an external standard (TiO_2, *Kronos International*) as reference measurement. Using mass spectroscopy coupled thermogravimetric analysis (TGA-MS, *Netzsch STA449 C Jupiter*), the thermal behavior of the sulfidic tailing and the marl was determined. Approximately 50 mg of powders was placed in a Alumina crucible and heated from 30°C to 1050°C with a heating rate of 10°C min^{-1} under air flow of 50 mL min^{-1}. The setup had an integrated quadrupole mass spectrometer (*Netzsch TGA/STA-QMS 403 D Aëolos*) to simultaneously follow the evolved gasses as the powder is heated, which allowed us to relate the weight loss obtained from TGA curve to various phases decomposition. Morphological observations were carried out by a SEM microscope FEI NOVA NANOSEM 450 with EDX analyzer BRUKER QUANTAX 200 with SDD detector.

2.2. Conventional roasting

The roasting with a conventional furnace (*Nabertherm LH 60/14*) was performed on the pure tailing, the pure marl and a range of tailing/marl mixtures prepared at five different tailing/marl ratios: 80%, 60%, 50%, 35% or 20% tailing, always complemented with marl and respectively referred to as 80T/20M, 60T/40M, 50T/50M, 35T/65M and 20T/80M. The tailing and the marl were weighed separately, added together and mixed thoroughly using mortar and pestle, thereby obtaining a fine, homogeneous powder. The actual sample mass added to the crucibles was 10 g for mixed samples and 5 g for reference samples, *i.e.* pure tailing and pure marl. A selection of these mixed samples were characterized with TGA-MS. For the conventional roasting, the samples (prepared in duplicate) were roasted at either 400°C, 500°C, 600°C, 700°C or 800°C (ramp 100°C h^{-1}, 60 min dwell time). After reaching room temperature, the crucibles were weighed to determine the weight loss of each sample. The obtained roasted materials were characterized by X-ray fluorescence (XRF, *Niton XL3T GOLDD+*) and XRD. For a selection of samples, also Rietveld refinement and SEM-EDX was used.

2.3. Microwave-assisted roasting

Microwave-assisted roasting was performed using a PYRO advanced microwave furnace (*Milestone*). The microwave was equipped with a silicon carbide (SiC) plate at the top of the heating chamber. This plate was installed to ensure the temperature inside the chamber stayed at the set temperature, as the exact temperature of the samples was unknown. The plate introduces the effect of a conventional furnace, by heating up under microwave irradiation and releasing heat to the sample chamber by convection and thermal radiation. The microwave-assisted roasting was performed on a pure tailing sample, a pure marl sample and a mixed sample prepared with a tailing/marl ratio of 50% (50T/50M), always using duplicates. These samples were roasted at either 300°C, 400°C or 500°C in the microwave furnace (30 min ramp time, 60 min dwell time, 1200 W maximum power). Additionally, the microwave-assisted roasting at 500°C was also performed using a dwell time of 15 min and 30 min, instead of 60 min dwell. After reaching room temperature, the crucibles were weighed to determine the weight loss of each sample. The obtained roasted samples were characterized by XRF and XRD.

2.4. Leaching

The original sulfidic tailing, the marl and all roasted samples were leached in a solution of 3.5 M NH_3 and 3 M $(NH_4)_2CO_3$ (L:S ratio of 10), according to the method of Hua *et al*. The samples were placed in a linear shaking water bath (*Grant GLS 400*) at 60°C for 4 hours. Preliminary experiments confirmed that after 4 hours reaction time, maximum Cu extraction was obtained. After this treatment, the leachate was carefully sampled and filtered (*chromafil® RC-45/25* – 0.45 µm). The filtered samples were measured by ICP-OES to determine the leaching of Cu.

3. Results and discussion

3.1. Material characterization

The chemical composition of the tailing and the marl material (Table 1) is in line with the mineral phases determined with XRD and Rietveld refinement (Figure S1 and Table 2). The sulfidic tailing is rich in pyrite (56.3%) and quartz (27.9%). Minor S-containing minerals in the tailing are calcium sulfate hydrate, anhydrate, gypsum, rhomboclase, szomolnokite and elemental sulfur. The main mineral phases present in the marl material include calcite (33.0%), quartz (14.1%) and aluminium silicates, such as muscovite-2M1, dickite and microcline.

Table 1. Elemental composition of the sulfidic tailing and the marl material.

	Tailing *mg kg^{-1} dm*	Marl *mg kg^{-1} dm*
Ag	32	0.53
Al	3640	44800
As	2270	4.4
Au	<2	<0.1
Ba	49	486
Be	<0.5	2.2
Bi	238	0.42
Ca	8380	99400
Cd	2.9	<0.5
Co	323	13
Cr	17	107
Cu	4370	25
Fe	305000	33900
Ga	2.3	17
Ge	3.5	1.2
K	763	18300
Mg	290	15100
Mn	102	418
Mo	8.3	<2
Na	318	6740
Ni	17	45
Pb	6700	16
S	348000	4370
Sb	316	<4
Sc	1.6	3.5
Se	15	<4
Sn	58	<4
Sr	25	679
Th	1.8	7.6
Ti	1380	2190
Tl	19	<4
U	1.5	4.2
V	12	144
Zn	1120	89

Table 2. Mineral phase composition of the sulfidic tailing and the marl material.

Name mineral phase	Composition mineral phase	Phase composition tailing %	Phase composition marl %
Albite	$NaAlSi_3O_8$	0.0	1.6
Anhydrate	$CaSO_4$	1.2	0.0
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	0.0	1.0
Calcium sulphate hydrate	$CaSO_4 \cdot H_2O$	5.6	0.0
Calcite	$CaCO_3$	0.2	33.0
Dickite	$Al_2Si_2O_5(OH)_4$	0.0	11.3
Gypsum	$CaSO_4 \cdot 2H_2O$	3.3	0.0
Microcline	$KAlSi_3O_8$	0.0	1.4
Muscovite-2M1	$KAl_2(AlSi_3O_{10})(F,OH)_2$	0.0	37.5
Pyrite	FeS_2	56.3	0.0
Quartz	SiO_2	27.9	14.1
Rhomboclase	$HFe(SO_4)_2 \cdot 4H_2O$	1.5	0.0
Sulfur	S	2.2	0.0
Szomolnokite	$FeSO_4 \cdot H_2O$	1.9	0.0
Total composition		100.1	99.9

The speciation of Cu in the tailing material could not be determined using XRD, due to the relative low Cu content (0.44%). Generally, the Cu speciation in ores is a sulfidic Cu form, such as chalcocite or chalcopyrite (Prasad and Pandey, 2002, 1998). Using SEM-EDX, associations between Cu and other common elements in the sulfidic tailing were investigated (Figure 2). Strong associations were observed between the appearance of Cu, Fe and S in the sample, which indeed suggests Cu to be present in sulfidic form. Furthermore, the elemental mapping revealed a clear association between Si and O, which confirmed the Rietveld phase quantification that identified SiO_2 as the most prominent O-containing phase in the sulfidic tailing. Also an association between S and O is shown and, to lesser extend with Fe, which could point towards the rhomboclase and szomolnokite phases, also identified with XRD.

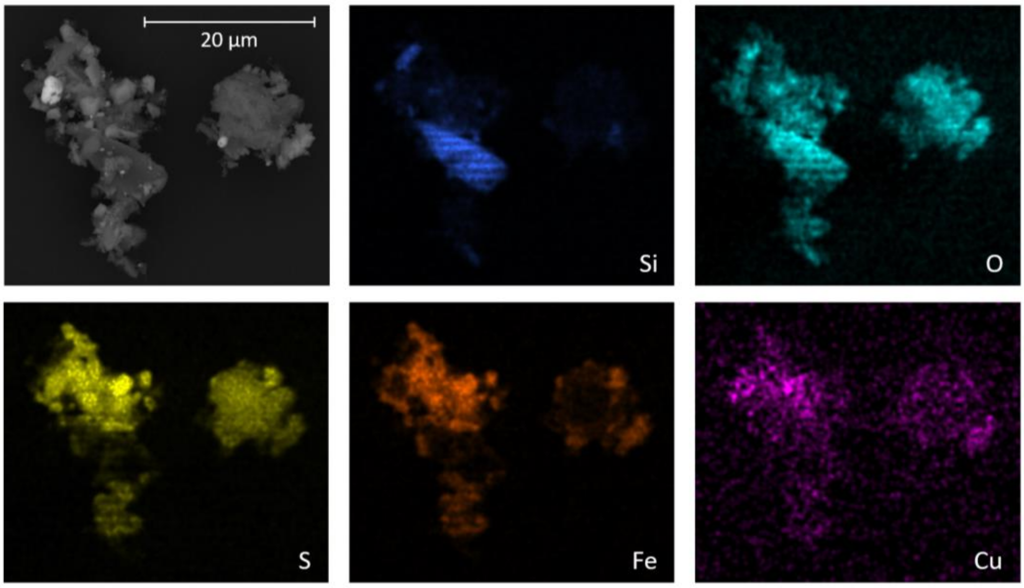


***Figure 2.** SEM micrograph and EDX elemental maps (Si, O, S, Fe, Cu) of particles of the sulfidic tailing.*

The thermal behavior of the tailing and the marl, examined by TGA-MS, is presented in Figure 3. For the sulfidic tailing, the weight loss occurring in the temperature range of 370-530°C was linked to the oxidation of sulfide, which resulted in SO_2 gas formation (Ozer et al., 2017). The thermal behavior of the marl sample was linked to the decomposition of $CaCO_3$, which resulted in the release of CO_2 gas. This decomposition reaction starts from 400°C, but is most pronounced at 755°C (Dollimore et al., 1996). Also, for a selection of tailing/marl mixtures, TGA-MS measurement was performed. The MS signals of the mixtures show that the release of SO_2 was always accompanied by a release of CO_2. This was promising, as this suggested that the reaction of eq. 1 took place. The ratio of the intensity of the CO_2 signal over that of the SO_2 signal increased with increasing marl content, indicating that SO_2 fixation might have been more pronounced at higher marl content. Also, from the MS signals of the mixtures (especially of 80T/20M and 50T/50M) two peaks in SO_2 and CO_2 release were present, likely the result of two distinct mechanisms of SO_2 formation. It was suggested that following reactions occurred in the first region:

$$FeS_2(s) + O_2(g) \leftrightarrow FeS(s) + SO_2(g) \qquad (2)$$

$$3\ FeS(s) + 5\ O_2(g) \leftrightarrow Fe_3O_4(s) + 3\ SO_2(g) \qquad (3)$$

$$FeS(s) + 2\ O_2(g) \leftrightarrow FeSO_4(s) \qquad (4)$$

After the formation of FeS (eq. 2), FeS could either further decompose to Fe_3O_4 (eq. 3), thereby releasing SO_2, or make the transition to $FeSO_4$ (eq. 4). It could be noted that direct oxidation of FeS_2 (cubic crystal) would first results in the formation of Fe_3O_4 (cubic crystal), which later relaxes into Fe_2O_3 (rhombohedral crystal). The reaction that took place in the second region is the decomposition of $FeSO_4$, which results in Fe_2O_3 formation and SO_x release:

$$FeSO_4(s) \leftrightarrow Fe_2O_3(s) + SO_2(g) + SO_3(g) \qquad (5)$$

The decomposition of $FeSO_4$ (rhombohedral crystal) would result directly in Fe_2O_3 (rhombohedral crystal) (Music et al., 1992). In mixtures with low marl content (e.g. 80T/20M), reactions in the first region were responsible for most of the SO_2 release (eq. 2 and 3), while for mixtures with high marl content (e.g. 35T/65M) the SO_2 release was mainly attributed to decomposition of $FeSO_4$ (eq. 5). The release of CO_2 indicated the fixation of SO_2 as sulfate, which was likely present in the form of $CaSO_4$. After formation the $CaSO_4$ phase remained stable in the whole temperature region presented here.

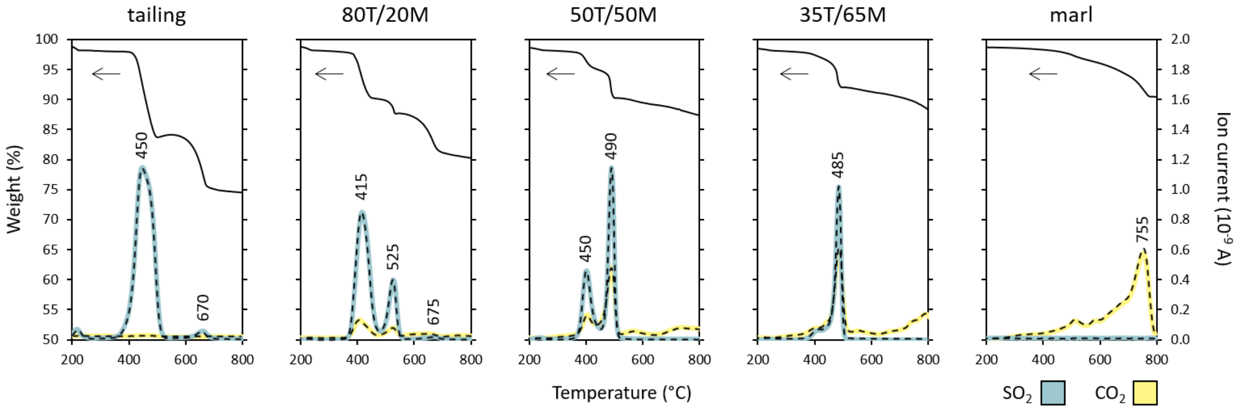


Figure 3. *TGA-MS curves of the sulfidic tailing, the marl and three selected mixtures of tailing and marl.*

3.2. Conventional roasting

3.2.1. Weight loss during roasting

During the conventional roasting treatment, all samples exhibited a weight loss (Figure 4, a). Generally, weight loss from sulfide/carbonate based materials can be attributed to characteristic reactions, including i) the conversion of sulfides to SO_2 gas, which is lost to the atmosphere (eq. 2 and 3), ii) the conversion of sulfate to SO_2 gas (eq. 5) and iii) the conversion of carbonate to CO_2. However, the weight loss caused by previous reactions can be partly counteracted by the (indirect) conversion reaction of sulfide to sulfate (eq. 4), from which a material gains weight. Figure 4 (a) shows that the weight loss of the samples increased with increasing roasting temperature. The weight loss of the pure tailing increased from 11.1% at 400°C to 26.1% at 800°C. With a high pyrite content and an almost negligible content of $CaCO_3$, the main reaction affecting the weight loss of the pure tailing was the conversion of sulfide to SO_x. The weight loss of the pure marl increased from 2.2% at 400°C to 17.2% at 800°C. The marl material is rich in carbonate and low in S, so weight losses of the pure marl was likely attributed to conversion of carbonate to CO_2. The weight loss of the tailing/marl mixtures during roasting are more complex to describe, as these mixtures likely were subjected to a combination of reactions affecting sample weight. Therefore, the effect of the initial marl content and the roasting temperature on the weight loss from these mixtures during conventional roasting is discussed later.

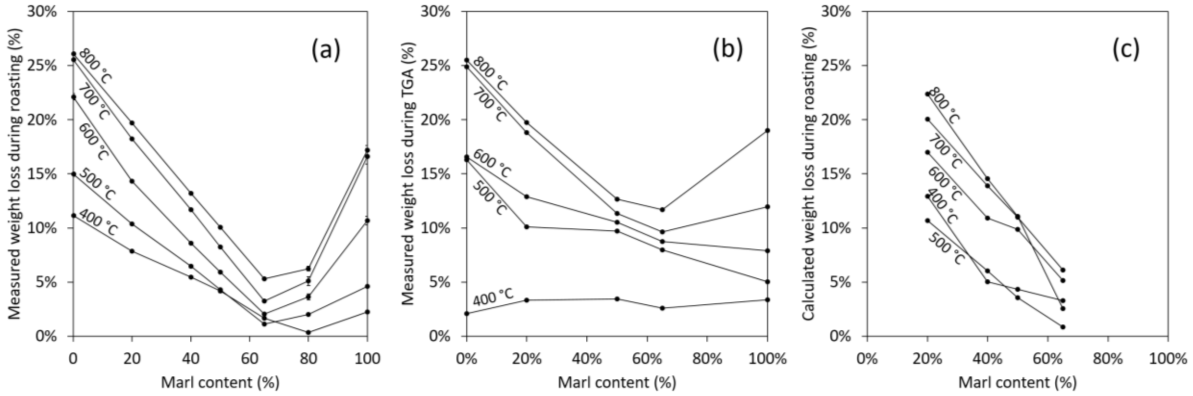


Figure 4. *The measured weight loss during conventional roasting (a), the measured weight loss during TGA-MS measurement (b) and the weight loss calculated from the sulfide, sulfate and carbonate content of the roasted samples, determined with Rietveld refinement (c) of the samples treated by conventional roasting at different temperatures, presented as a function of the initial marl content of the tailing/marl mixture. Error bars (only in Figure 4, a) represent standard deviation (n=2).*

The weight loss of the samples in the conventional oven (Figure 4, a) could also be compared to the weight loss observed during the TGA-MS measurement (Figure 4, b). Generally, some deviations could be expected due to i) the large difference in sample volume used in both roasting tests and, ii) roasting conditions in a furnace being less accurately controlled compared to in the TGA furnace. Yet, for the pure tailing an the pure marl, differences in weight loss between the roasting experiment and the TGA-MS measurement remained limited, with exception of the roasting of the tailing at 400°C. For mixtures high in tailing, the weight loss at 400°C in the TGA furnace was underestimated in comparison with the conventional oven. However, the most interesting comparison was obtained for the 35T/65M mixture (50T/50M to a less extend) treated at 500°C, 600°C, 700°C and 800°C, as the weight loss in the TGA strongly exceeded the weight loss obtained in the conventional oven. This suggested that the formation of sulfate during roasting in the TGA furnace was more limited compared to roasting in the conventional oven. This could be attributed to the fact that for TGA measurement only a very limited amount of sample was used (± 50 mg) in a very well aerated roasting atmosphere. In this environment, the formed SO_x gas easily escaped from the powder mixture and would therefore be lost for sulfate formation.

3.2.2. Mineral phase transitions during roasting

Roasting of materials can cause minerals to decompose and transform. For 80T/20M, 60T/40M, 50T/50M and 35T/65M samples, the transformation of the mineral composition as a function of the roasting temperature is presented in Figure 5 (a)**Figure 5** (more detailed in Table S1, SI). First of all, differences between the roasted samples of different initial tailing/marl mixtures were expected, as the mineral and elemental composition varies with the mixing ratio. Secondly, for all four investigated mixtures, the contribution of pyrite (FeS_2) diminished with increasing temperature. For 80T/20M and 60T/40M, FeS_2 is completely decomposed at 600°C, while for 50T/50M and 35T/65M this occurs at 500°C. Thirdly, the contribution of hematite (Fe_2O_3) strongly increased with increasing temperature. The contribution of Fe_2O_3 was more pronounced in the samples obtained from the mixtures with high tailing content, which was related to the high Fe content of these mixtures. Finally, the relative contribution of $CaSO_4$ increased with increasing marl content, while the effect of temperature was ambiguous. It is clear that, next to the anhydrate phase, also other sulfate-bearing phases were present in the roasted samples: mikasaite $Fe_2(SO_4)_3$, perkovaite $CaMg_2(SO_4)_3$ and angesite $PbSO_4$. Therefore, in order to evaluate SO_x capturing in varying conditions (roasting temperature, mixing ratio), all sulfate-bearing phases should be taken into account.

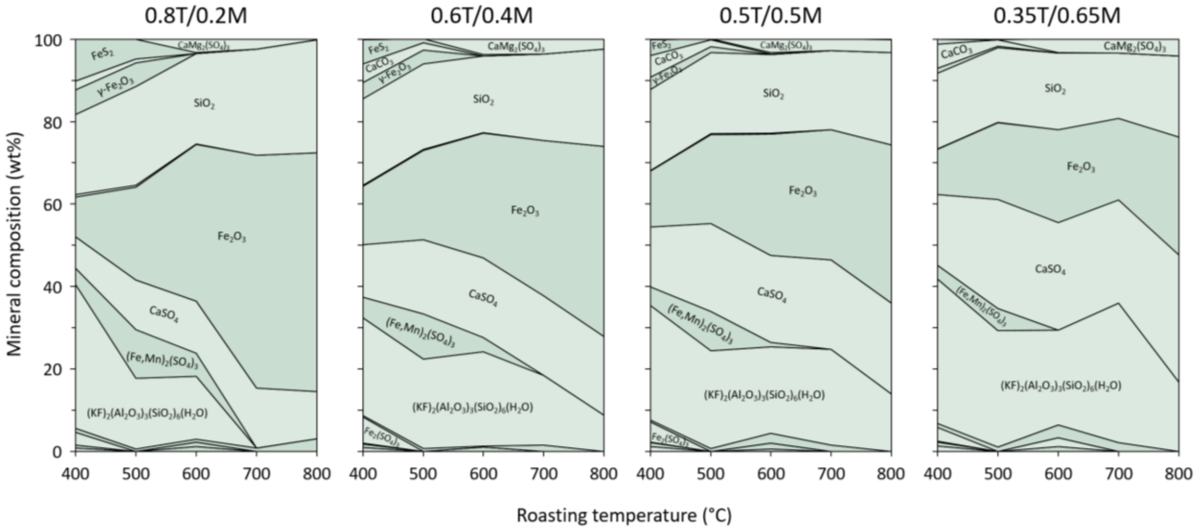


Figure 5. *The mineral phase composition of 80T/20M, 60T/40M, 50T/50M and 35MT/65M samples after conventional roasting at varying temperature.*

3.2.3. Stoichiometry of sulfate formation and sulfide/carbonate consumption

The relative weight contribution of each phase in the roasted samples, as presented in Figure 5, was suitable to derive the trends in phase transitions within one specific tailing/marl mixture. However, in order to calculate the amount of sulfate formed and the amount of sulfide and carbonate consumed, the weight-based Rietveld-derived phase contribution needed to be transformed to a mole-based phase contribution. Using the molar weights of FeS_2, $CaCO_3$, $CaSO_4$, $Fe_2(SO_4)_3$, $CaMg_2(SO_4)_3$ and $PbSO_4$ and the amount of sulfide, carbonate and sulfate within each mineral formula, the relative molar contribution of sulfide, carbonate and sulfate (mmol g^{-1} material) could be calculated for the roasted materials (Figure 6, left). The relative molar contribution of sulfide, carbonate and sulfate in the pre-roasting mixture of tailing/marl could be derived from the contribution of the latter phases in the pure tailing and the pure marl, corrected with the mixing ratio of a specific tailing/marl mixture. This representation confirmed that FeS_2 fully decomposed at 600°C in 80T/20M and 60T/40M, and at 500°C in 50T/50M and 35T/65M. Furthermore, it shows that, at roasting temperatures above 500°C, no carbonate phases remained.

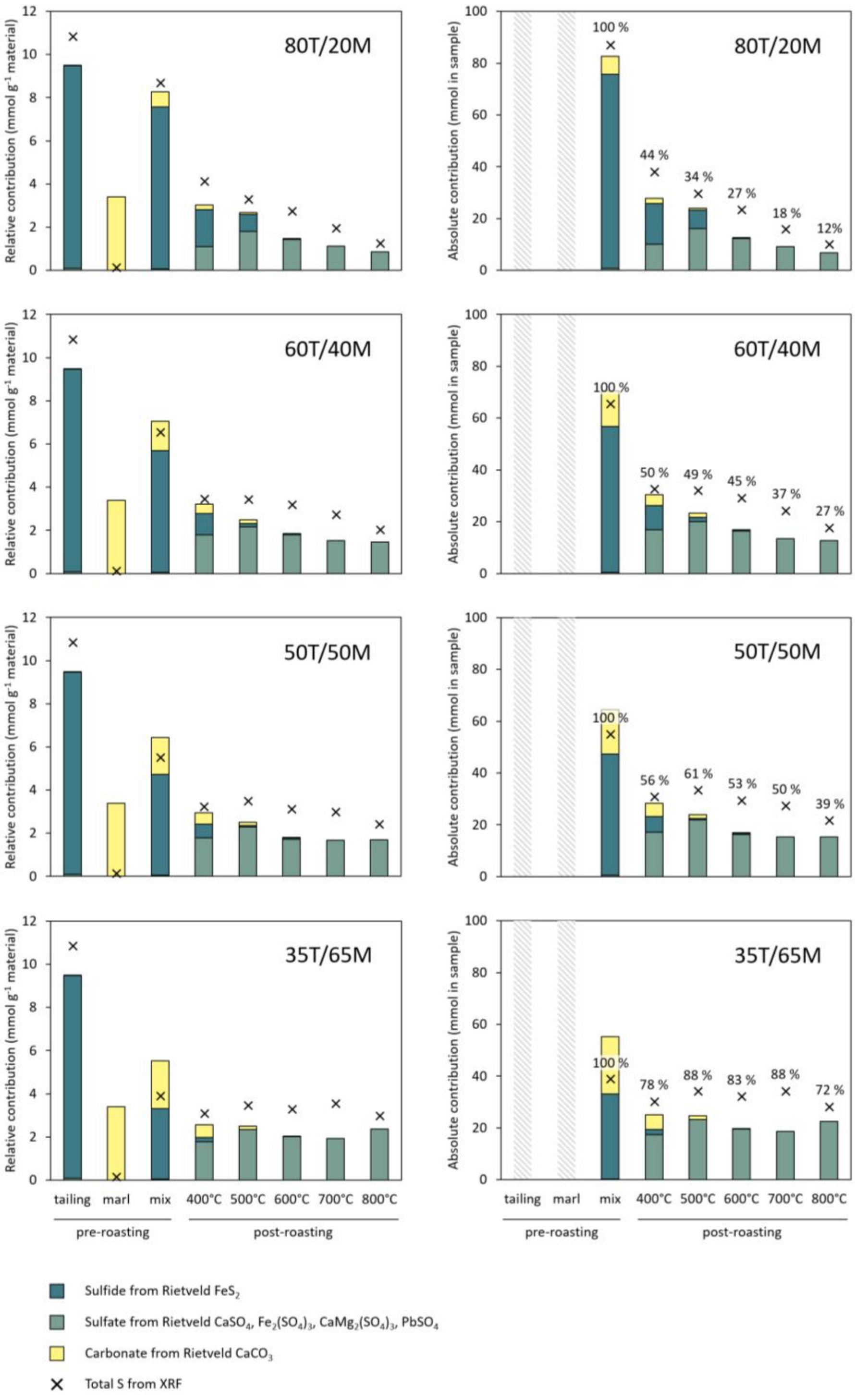


Figure 6. *The relative molar contribution (left figures) and absolute molar contribution (right figures) of sulfide, sulfate and carbonate in the pre-roasted (tailing, marl and mixtures 80T/20M, 60T/40M, 50T/50M and 35T/65M) and post-roasted samples after conventional roasting at varying temperature. Next to the Rietveld derived results, also the total S (measured with XRF) of each sample is presented.*

In Figure 6 (left), the sum of the relative molar contribution of sulfide and sulfate could be interpreted as the Rietveld-derived value for the total S content (mmol g^{-1}). This value could be compared to the total S content as measured by XRF. The absolute values for total S deviated slightly for both measurement techniques, as could be expected from the accuracy of the techniques. Nevertheless, both techniques confirmed the unique trends for each tailing/marl mixture in terms of the total S as a function of the roasting temperature. On the one hand, the pre-roast mixture with high tailing content (*e.g.* 80T/20M) showed the highest initial S content, since here only small amounts of marl were added to the S-rich tailing. However, after roasting these materials showed a strong decrease in the total S content, and the S content further decreased with increasing roasting temperature. This trend was also obtained for the roasting various sulfidic Fe/Cu minerals, such as chalcocite, pyrite, iron sulfide and chalcopyrite, without the presence of S-capturing agents (Mitovski et al., 2015; Ozer et al., 2017; Prasad and Pandey, 2002, 1998; Zivkovic et al., 1996). The presence of sulfate-bearing minerals diminished with increasing roasting temperature and from 800°C onward all Fe species were completely converted to oxide forms. On the other hand, the low S content in the pre-roast mixture with high marl content (*e.g.* 35T/65M) was well maintained in the solid during roasting, indicating the effectiveness of the SO_x capturing mechanism of the marl material.

From the weight loss results and the relative molar contribution of sulfide, carbonate and sulfate in the pre-roasted and post-roasted materials, the absolute molar contribution (mmol) was calculated (Figure 5, right). The comparison between the amount of sulfide, carbonate and sulfate in the pre-roasted mixture and that in the post-roasted materials allows the visual presentation of how an amount of sulfide and carbonate minerals resulted in the formation of a certain amount of sulfate. Also in this representation, both the Rietveld-derived results and the XRF results confirmed that the SO_x capturing capacity of a tailing/marl mixture increased with the increase of the marl content. For example, with the roasting of 35T/65M at 500°C, 88% of S was maintained in the material, whereas this was only 34% for the 80T/20M at the same temperature. Proof of the favored convention of sulfide to sulfate in the presence of marl could be found in the contribution of Fe-containing phases from samples with varying initial marl content, roasted at the same temperature (presented for 500°C in Figure S2, a). With higher marl content, less maghemite was formed, which suggested that the sulfate formation reaction in eq. 4 was favored over the SO_x formation reaction in eq. 3.

3.2.4. S fixing capacity affected by roasting temperature and mixing ratio

The molar amount of sulfate formed during roasting reached for all roasted samples a maximum at a roasting temperature of 500°C (Figure 5, right). This effect was more clearly presented in Figure 7 (a). The amount of sulfate formed at a roasting temperature of 400°C was well below that at 500°C, likely because at 400°C still much of the S remained in sulfidic form. Also roasting temperatures above 500°C resulted in less sulfate in the obtained roasted sample, because the Fe sulfate, that formed around 400-500°C during the heating stage, decomposed to SO_x at higher temperatures. These results did, however, not yet prove that 500°C was the preferred roasting temperature to efficiently convert sulfide to sulfate in the tailing/marl mixtures. This was because the yield of sulfate in each condition was not only determined by the amount of sulfate that was formed, but also by the amounts of consumed sulfide and carbonate, which could be considered as reagents in the formation reaction of sulfate. This issue was addressed by calculating i) the molar ratio of sulfate formed over sulfide consumed (Figure 7, b) and ii) the molar ratio of sulfate formed over calcite consumed (Figure 7**Figure 7**, c). For this, the molar amount of consumed sulfide and consumed carbonate were calculated from the results in Figure 6, right. As mentioned before, the weight loss from tailing/marl mixtures during roasting was more complex to describe in comparison with the weight loss from pure tailing and pure marl, due to the fact that the contribution of individual reactions involving sulfide, sulfate and carbonate needed to be quantified. By combining the molar amount of formed sulfate, consumed sulfide and consumed carbonate, the weight loss due to roasting was reconstructed from the Rietveld results (Figure 4, c). From the comparison between the measured and the calculated weight losses it could be concluded that the performed Rietveld-based analysis on the sulfide, sulfate and carbonate chemistry was indeed accurate and, therefore, could contribute to a better understanding of the stoichiometry of SO_x capturing in varying experimental conditions. The contribution of hydrate water losses during roasting was neglected in this analysis.

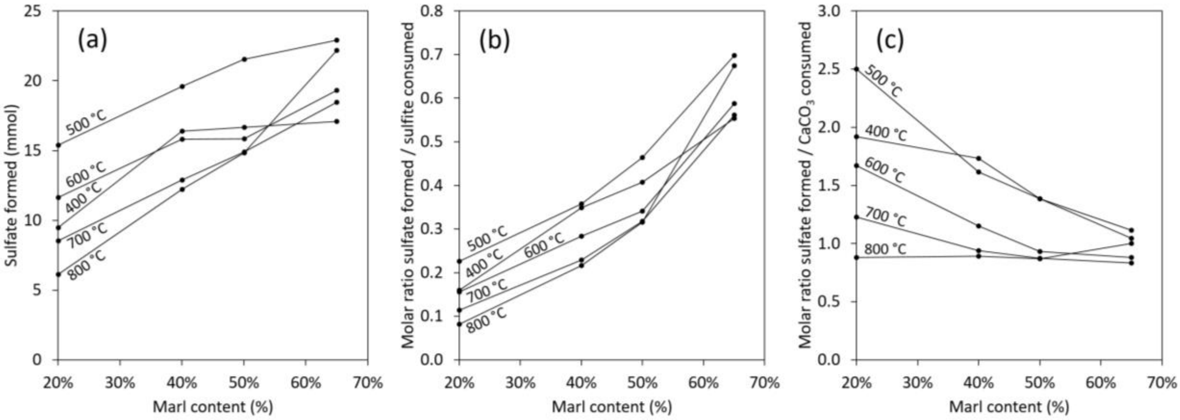


Figure 7. *The molar amount of sulfate formed in each sample (a), the molar ratio of sulfate formed and sulfide consumed (b) and the molar ratio of sulfate formed and $CaCO_3$ consumed (c), all presented as a function of the initial marl content of the tailing/marl mixture.*

The molar ratio of sulfate formed over sulfide consumed was maximized at a roasting temperature of 500°C over the whole range of marl contents (Figure 7, b). It was clear that, for all roasting temperatures, the molar ratio of sulfate formation over sulfide consumption strongly increased with increasing marl content. Absolute values for SO_x fixation, either derived from XRF and presented in % S maintained relative to the initial tailing/marl mixture (Figure 6, right), or derived from Rietveld and presented as the molar ratio between the amount of sulfate formed and the amount of sulfide consumed (Figure 7, b), slightly varied but showed these very similar trends.

The molar ratio of sulfate formed and $CaCO_3$ consumed represented the efficiency of the $CaCO_3$ consumption to the benefit of sulfate formation for each condition (Figure 7, c). Again for this conversion, 500°C was the most optimal roasting temperature. For materials with a lower initial marl content, a large temperature-dependency was shown. This was associated to the fact that, at 500°C carbonate was consumed merely only to the benefit of sulfate formation, whereas higher roasting temperatures (*e.g.* 800°C) resulted in the complete decomposition of carbonate. For materials with a higher initial marl content, the molar ratio of sulfate formed and $CaCO_3$ consumed converged towards a value of 1 for all roasting temperatures.

It could be concluded that 500°C was indeed the most efficient roasting temperature for the formation of sulfate, with respect to the amount of sulfide and $CaCO_3$ consumed (Figure 7, c). Defining the most efficient mixing ratio for tailing and marl to efficiently convert sulfide to sulfate in the tailing/marl mixtures was, however, less straightforward. For roasting at 500°C (or at any other roasting temperature), no maximum value was obtained for SO_x capturing: the sulfate formation and SO_x capturing always further increased with increasing marl content (Figure 6, right; Figure 7, b). From the perspective of using marl material as additive for SO_x fixation during roasting treatment of sulfidic tailings, low tailing/marl mixing ratios were less preferred because of i) the high energy demand required to roast a certain amount of tailing and ii) the extra lixiviant required for metal extraction. Therefore, an industrially relevant mixing ratio of 50T/50M was selected to continue further testing with microwave-assisted roasting.

3.3. Microwave-assisted roasting

3.3.1. Weight loss during microwave-assisted roasting

During microwave-assisted roasting, weight loss was recorded for all samples (Figure 8). For the pure tailing, microwave-assisted roasting at 400°C and 500°C yielded slightly lower weight losses in comparison with the conventional roasting at the same temperatures (Figure 4, a), while microwave-assisted roasting of the tailing at 300°C (not tested with conventional roasting) resulted in very low weight loss. For the pure marl, microwave-assisted and conventional roasting at 400°C and 500°C resulted in very comparable limited weight losses. For the 50T/50M mixture, the weight losses obtained with microwave-assisted roasting at 400°C and 500°C were slightly higher than those obtained with conventional roasting.

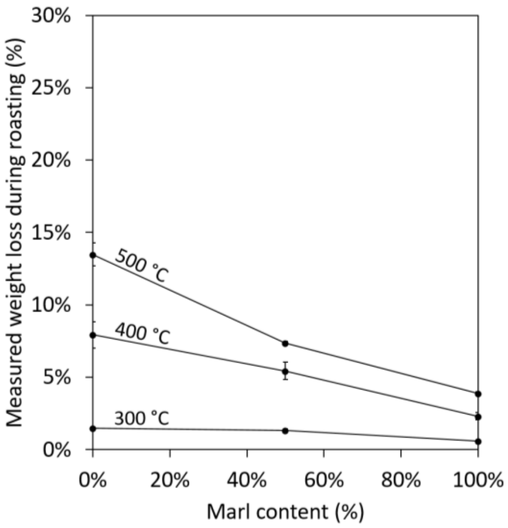


Figure 8. *The measured weight loss of the samples treated by microwave-assisted roasting at different temperatures, presented as a function of the initial marl content of the tailing/marl mixture. Error bars represent standard deviation (n=2).*

Comparing the results from the conventional and microwave-assisted roasting was not very straightforward. This was due to the fact that i) in this study, the ramp period in the conventional roasting treatment was longer than that of the microwave-assisted treatment (ramp rate of 100°C h^{-1} for conventional roasting versus ramp period of 30 min for microwave-assisted roasting), ii) heating in a conventional furnace via conduction/convection processes is non-selective towards the chemistry of a sample, while during microwave-assisted treatment selective heating of the sample can occur, as some mineral phases (*e.g.* FeS_2) more strongly interact with microwave radiation than others (*e.g.* $CaCO_3$), and iii) other furnace specific properties may have varied apart from the heating process, such as the ventilation in the heating chamber. Taken together, this means that in the conventional furnace the actual temperature of the samples would likely have closely approached the set temperature, while in the microwave furnace the actual temperature of the samples could still strongly deviate from the set temperature, depending *e.g.* on microwave-specific coupling. Naturally, this had implications for the reactions that place, which are discussed later.

3.3.2. Sulfate formation during microwave-assisted roasting

Analogue to the analysis previously discussed for conventional roasting, the conversion of sulfide to sulfate and the consumption of carbonate were determined for the 50T/50M sample treated in the microwave furnace at 500°C (Table S2), and compared to those obtained from conventional roasting at the same temperature (Figure 9). Firstly, this showed that conventional roasting resulted in almost 50% more sulfate formation compared to microwave-assisted roasting. Secondly, after roasting in the microwave furnace, still 9% of the sulfide initially present in the sample remained, while this was only 1% for the conventional roasting. Thirdly, 22% of the initially present carbonate remained in the sample treated in the microwave furnace, while this was only 9% for the conventional roasting. Finally, XRF suggested that the S retention was slightly better with the conventional roasting (61%) than with the microwave-assisted roasting (49%). These trends could be explained by a different heating time, but likely also by selective heating that occurred during microwave-heating. The FeS_2 phase more strongly interacted with microwave radiation than $CaCO_3$. Therefore, FeS_2 rich particles would have had a higher local temperature than $CaCO_3$ rich particles. As a result, the ratio between sulfide decomposition and carbonate decomposition would be higher for the microwave-assisted roasting than for the conventional roasting and, therefore, less S will be fixed as sulfate in the microwave treatment. The contribution of the different Fe phases in the samples obtained from either conventional or microwave-assisted roasting at 500°C revealed that indeed more FeS_2 was present in the microwave-assisted roasted sample compared to the conventional roasted sample, but also that more maghemite was formed, which caused additional SO_x release (Figure S2, b). This could mean that, in the microwave furnace, reaction in eq. 3 was favored above reaction in eq. 4, what also contributed to the lower S content after microwave-assisted roasting. This analysis was also in line with the higher weight loss that is obtained for the 50T/50M sample during microwave treatment relative to that during the conventional roasting (Figure 8 and Figure 4, a).

The SO_x fixation during this microwave-assisted roasting, using a mix of both powdered tailing and marl, was below the SO_x fixation values obtained in previous studies using pressed pellets of tailing and $CaCO_3$ (Hua et al., 2006; Riveros et al., 2004). This was likely related to the fact that, in a pressed pellet, diffusion of formed SO_x gas is hindered and contact with CaO is more likely to take place, leading to a better formation of $CaSO_4$, whereas a powder mixture in a well-flushed heating chamber might be much more exposed to losses of SO_x to the atmosphere.

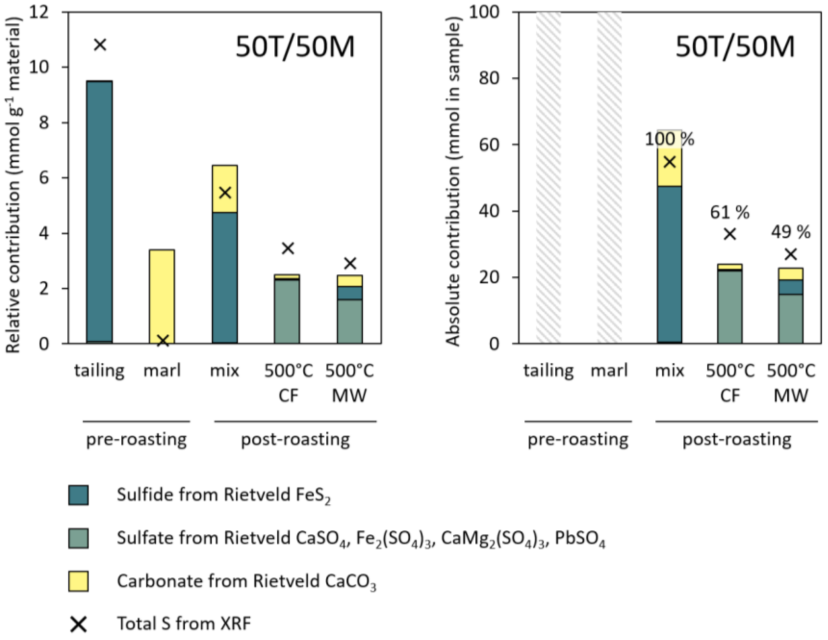


Figure 9. *The relative molar contribution (left figure) and absolute molar contribution (right figure) of sulfide, sulfate and carbonate in the pre-roasted (tailing, marl and mixture 50T/50M) and post-roasted samples after roasting at 500°C in a conventional furnace (CF) or microwave oven (MW). Next to the Rietveld derived results, also the total S (measured with XRF) of each sample is presented.*

3.4. Leaching

The extraction of Cu from the materials obtained after conventional or microwave-assisted roasting was assessed via ammoniacal leaching (Figure 10). For comparison, also untreated tailing was leached. Only 2% of Cu was extracted from untreated tailing material, which can be ascribed to Cu being present in the tailing as stable sulfide phases (Al-Harahsheh and Kingman, 2004).

3.4.1.Leaching from conventionally roasted materials

With conventional roasting without marl addition, maximum Cu extraction was obtained for roasting temperatures of 500°C (93%) and 600°C (88%) (Figure 10, a). Low roasting temperatures (400°C) resulted in lower Cu extraction, which was the result of the fact that Cu was still partly present in sulfidic form. Roasting temperatures exceeding 600°C also resulted in lower Cu extraction, with the tailing treated at 800°C showing the lowest Cu extraction of all roasted tailing materials. The low extraction of Cu after roasting at high temperatures was related to the formation of cuprous ferrite ($CuO \cdot Fe_2O_3$), which occurred above 700°C (Prasad and Pandey, 1999). The cuprous ferrite phase is a stable spinel phase with a very low solubility, resulting in low Cu extraction (Zhang and Reddy, 2012). With the addition of marl material to the tailing/marl mixes, the Cu extraction very clearly changed. For the mixes treated at 500°C, 600°C and 700°C, the Cu extraction strongly decreases with marl addition, while for the mixtures treated at 400°C and with marl content up to 50%, the Cu extraction slightly increased with increasing marl content. The pH values of the leachates after reaction were all close to pH 10 and not significantly different. Therefore, differences in Cu extraction for the mixed samples were likely not related to pH-dependent solubility, but to the speciation of Cu in the roasted materials. The low Cu content of the roasted materials did not allow spectroscopic identification of the Cu speciation. Yet, the Cu speciation was likely affected by the addition of marl, or more specifically, by the $CaCO_3$ phase within the marl material. The $CaCO_3$ phase did not directly participate in the fixation of SO_x, as depicted by eq. 1 (Tullin and Ljungström, 1989). From roasting temperatures around 400°C and onwards (Figure 3), $CaCO_3$ was first converted to CaO:

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g) \qquad (6)$$

Only after the formation of CaO, SO_2 reacted to form $CaSO_4$:

$$CaO(s) + SO_2(g) + 0.5\ O_2(g) \leftrightarrow CaSO_4(s) \qquad (7)$$

The initial Cu speciation was likely a sulfidic form, such as Cu_2S (Zivkovic et al., 1996). Under increased oxidative conditions and increased SO_2 pressure, this phase converted to $CuSO_4$:

$$Cu_2S(s) + SO_2(g) + 3\ O_2(g) \leftrightarrow 2\ CuSO_4(s) \qquad (8)$$

Yet, even at relative low roasting temperatures around 450°C, $CuSO_4$ could convert to CuO:

$$2\ CuSO_4(s) \leftrightarrow 2\ CuO(s) + SO_2(g) + 0.5\ O_2(g) \qquad (9)$$

From eq. 8 and eq. 9, it is clear that SO_2, or more specifically the local SO_2 pressure, had a significant effect on the contribution of these reactions, and thus the speciation of Cu. The main source of SO_2 in the samples was the oxidation of FeS_2, which is present in high amounts in the sulfidic tailing (Table 2). Roasting the pure tailings at 500°C - 600°C thus resulted in a relative high SO_2 pressure, which promoted the formation of the water soluble $CuSO_4$ (eq. 8). The Cu speciation of $CuSO_4$ explained the high Cu extraction for these roasted samples. For the materials with a low initial marl content (*e.g.* 20%), the decrease in Cu extraction was relatively limited, while for those with a high initial marl content (*e.g.* 80 %), the Cu extraction dropped down to 10-25%. Here it was hypothesized that, with increasing marl content, the contribution of the $CuSO_4$ relative to the total Cu in the roasted samples would decrease. This was the result of the lower total sulfide content in pre-roasted sample, which resulted in less SO_2 formation, but especially followed from the fact that, at roasting temperatures exceeding 400°C, the formed CaO would compete with the Cu phases for sulfation (eq. 7 and eq. 9). With a higher content of CaO in the sample during roasting, an increasing amount of SO_2 was captured by CaO and fixed as $CaSO_4$, resulting in a shift in Cu speciation from readily soluble $CuSO_4$ to poorly soluble CuO. At a roasting temperature of 400°C, the CaO formation was only very limited and is, therefore, not negatively affecting the Cu extraction. This hypothesis was supported by the SEM-EDX measurements performed on pure tailing (Figure S3, a), 60T/40M (Figure S3, b) and 20T/80M (Figure S3, c) after conventional roasting at 600°C. The elemental maps of the pure tailing after roasting showed clear association between Cu and S, which was in line with Cu being present in a $CuSO_4$ rather than in CuO. The association between Fe and S was almost completely absent in this mapping, confirming Fe_2O_3 to be the main Fe phase after roasting. Also the association between S and Ca was present, yet to a lesser extend compared to Cu. This trend was reversed for 60T/40M roasted at 600°C, where the association between S and Ca was clearly more pronounced in comparison with the association with Cu. Finally, for 20T/80M roasted at 600°C, association between S and Cu was rather poor, which was in line with the assumption that Cu in this roasted material was mainly present as CuO, causing poor extraction via leaching.

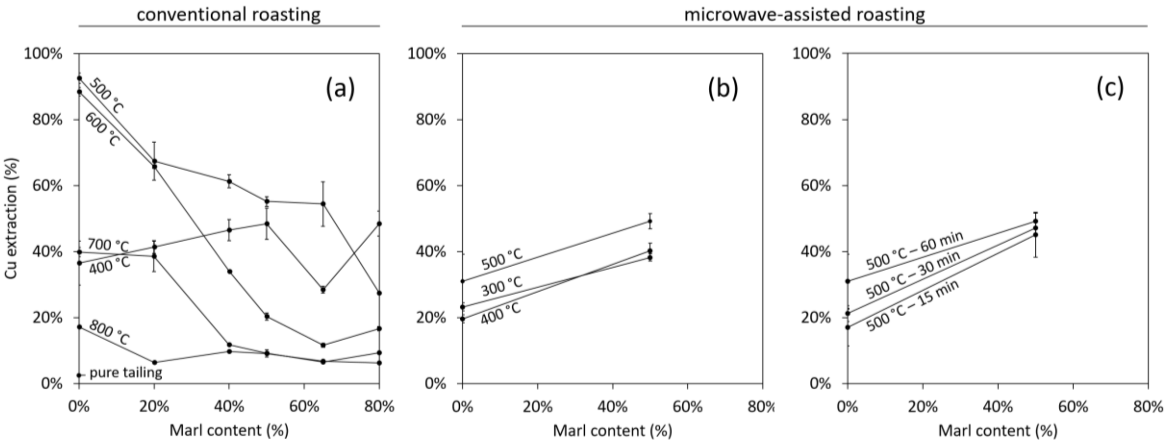


Figure 10. *The extraction of Cu from the roasted samples, obtained from conventional roasting (a) and microwave-assisted roasting (b and c), as function of the initial marl content of the tailing/marl mixture. Error bars represent standard deviation (n=2).*

3.4.2.Leaching from microwave-assisted roasted materials

Using microwave-assisted roasting up to 500°C, high Cu extraction as for conventional roasting at 500°C was not obtained (Figure 10, b). The absolute values of Cu extraction, as well as the slightly positive trend in Cu extraction as a function of the marl content, were comparable to those from materials conventionally roasted at 400°C. Increasing the operating temperature of the microwave roasting from 300°C to 500°C increased the Cu extraction slightly (Figure 10, b), as well as increasing the roasting time of a 500°C microwave treatment from 15 min to 60 min (Figure 10, c). Both trends indicated that sulfide phases were still present in the materials, which also explains the positive effect of marl addition on Cu extraction in the same way it did for the conventional roasting at 400°C.

4. Conclusions

This study examined the potential of microwave-assisted roasting of a tailing/marl mixture for SO_x fixation and Cu extraction purposes. Marl addition strongly increased the SO_x fixation (sulfate formation) proving it has a strong ability to reduce harmful SO_x emissions. Yet, for high SO_x fixation (*e.g.* >70%) also a relative high content of 65% marl was required. Using conventional roasting, an optimal roasting temperature of 500°C was obtained for sulfate formation. In comparison with conventional roasting, no advantage in the use of microwave-assisted roasting was obtained, as the sulfate formation at 500°C for microwave-assisted roasting slightly below that for conventional roasting. From the perspective of Cu extraction during post-roasting ammoniacal leaching, the addition of marl to the roasting mixture had a substantial negative effect. This effect is attributed to the fact that, with increasing marl content, the marl-derived CaO phase during roasting more strongly competes with Cu species for sulfation, thereby preventing the formation of water-soluble $CuSO_4$. For these results, it can be concluded that further optimization of this roasting system can be obtained by physically separating the tailing and the marl during roasting in such a way that the marl would merely serve as a gas filter material.

Acknowledgement

This work was supported by the Strategic Initiative Materials in Flanders (SIM), in the context of the Strategic Basic Research (SBO) program: SBO-SMART: Sustainable Metal Extraction from Tailings [grant number HBC.2016.0456]. Also the authors would like to thank Myrjam Mertens for the XRD/Rietveld analysis and Warre Van Dun for the ICP-OES measurements.

References

Al-Harahsheh, M., Kingman, S.W., 2004. Microwave-assisted leaching - A review. Hydrometallurgy 73, 189–203. https://doi.org/10.1016/j.hydromet.2003.10.006

Bartlett, R.W., Haung, H.H., 1973. The lime-concentrate-pellet roast process for treating copper. J. Met. 28–34.

Catalan, L.J.J., Yin, G., 2003. Comparison of calcite to quicklime for amending partially oxidized sulfidic mine tailings before flooding. Environ. Sci. Technol. 37, 1408–1413. https://doi.org/10.1021/es020781z

Davis, A., Eary, L.E., Helgen, S., 1999. Assessing the efficacy of lime amendment to geochemically stabilize mine tailings. Environ. Sci. Technol. 33, 2626–2632. https://doi.org/10.1021/es9810078

Dollimore, D., Tong, P., Alexander, K.S., 1996. The kinetic interpretation of the decomposition of calcium carbonate by use of relationships other than the Arrhenius equation. Thermochim. Acta 282–283, 13–27.

https://doi.org/10.1016/0040-6031(95)02810-2

Elshkaki, A., Graedel, T.E., Ciacci, L., Reck, B., 2016. Copper demand, supply, and associated energy use to 2050. Glob. Environ. Chang. 39, 305–315. https://doi.org/10.1016/j.gloenvcha.2016.06.006

Hua, Y., Cai, C., Cui, Y., 2006. Microwave-enhanced roasting of copper sulfide concentrate in the presence of CaCO3. Sep. Purif. Technol. 50, 22–29. https://doi.org/10.1016/j.seppur.2005.11.003

Kefeni, K.K., Msagati, T.A.M., Mamba, B.B., 2017. Acid mine drainage: Prevention, treatment options, and resource recovery: A review. J. Clean. Prod. 151, 475–493. https://doi.org/10.1016/j.jclepro.2017.03.082

Kingman, S.W., Rowson, N.A., 1998. Microwave Treatment of Minerals - A Review 11, 1081–1087.

Li, X., Li, B., Deng, J., Lu, T., Wang, S., Li, J., Chen, D., Liu, Y., Wang, S., 2014. Environmental-friendly process for recovering copper and nickel from Jinchuan tailings by silica-based selective adsorbents. Ind. Eng. Chem. Res. 53, 11137–11144. https://doi.org/10.1021/ie501527r

Lindsay, M.B.J., Moncur, M.C., Bain, J.G., Jambor, J.L., Ptacek, C.J., Blowes, D.W., 2015. Geochemical and mineralogical aspects of sulfide mine tailings. Appl. Geochemistry 57, 157–177. https://doi.org/10.1016/j.apgeochem.2015.01.009

Liu, Z., Lei, H., Bai, T., Wang, W., Chen, K., Chen, J., Hu, Q., 2015. Microwave-assisted arsenic removal and the magnetic effects of typical arsenopyrite-bearing mine tailings. Chem. Eng. J. 272, 1–11. https://doi.org/10.1016/j.cej.2015.02.084

Mitovski, A., Strbac, N., Manasijevic, D., Sokic, M., Dakovic, A., Zivkovic, D., Balanovic, L., 2015. Chalcopyrite-Pyrite Concentrate Oxidation Process. Metalurgija 54, 311–314.

Moravvej, Z., Mohebbi, A., Daneshpajouh, S., 2018. The microwave irradiation effect on copper leaching from sulfide/oxide ores. Mater. Manuf. Process. 33, 1–6. https://doi.org/10.1080/10426914.2016.1244850

Music, S., Popovic, S., Ristic, M., 1992. Thermal decomposition of pyrite. J. Radioanal. Nucl. Chem. 162, 217–226.

Nyamjargal, L., Batdemberel, G., Burmaa, G., Burmaa, D., 2018. Effect of Roasting Temperature for Copper Leaching of Sulfide Concentrate by Combined Methods. Open J. Appl. Sci. 8, 545–553. https://doi.org/10.4236/ojapps.2018.812044

Oggeri, C., Maria, T., Godio, A., Vinai, R., 2019. Overburden management in open pits: options and limits in large limestone quarries. Int. J. Min. Sci. Technol. 29, 217–228. https://doi.org/10.1016/j.ijmst.2018.06.011

Ozer, M., Acma, E., Atesok, G., 2017. Sulfation roasting characteristics of copper-bearing materials. Asia-Pacific J. Chem. Eng. 12, 365–373. https://doi.org/10.1002/apj

Park, I., Tabelin, C.B., Jeon, S., Li, X., Seno, K., Ito, M., Hiroyoshi, N., 2019. A review of recent strategies for acid mine drainage prevention and mine tailings recycling. Chemosphere 219, 588–606. https://doi.org/10.1016/j.chemosphere.2018.11.053

Prasad, S., Pandey, B.D., 2002. Alternative processes for treatment of chalcopyrite - A review. Miner. Eng. 11, 763–781. https://doi.org/10.1016/s0892-6875(98)00061-2

Prasad, S., Pandey, B.D., 1999. Thermoanalytical studies on copper-iron sulphides. J. Therm. Anal. Calorim. 58, 625–637. https://doi.org/https://doi.org/10.1023/A:1010108729034

Prasad, S., Pandey, B.D., 1998. Thermoanalytical Studies on Copper-Iron Sulphides. J. Therm. Anal. Calorim. 58, 625–637. https://doi.org/10.1023/A

Rezvanipour, H., Mostafavi, A., Ahmadi, A., Karimimobarakabadi, M., Khezri, M., 2018. Desulfurization of Iron Ores : Processes and Challenges 1700568, 1–14. https://doi.org/10.1002/srin.201700568

Riveros, G., Mar, T., Puga, C., 2004. Lime-concentrate roasting studies - effect of activated limestone 17, 469–471. https://doi.org/10.1016/j.mineng.2003.11.001

Shamsuddin, M., 2016. Physical Chemistry of Metallurgical Processes. Phys. Chem. Metall. Process. 1–592. https://doi.org/10.1002/9781119078326

Smith, S.J., Pitchera, H., Wigley, T.M.L., 2001. Global and regional anthropogenic sulfur dioxide emissions. Glob. Planet. Change 29, 99–119. https://doi.org/10.1016/S0921-8181(00)00057-6

Tullin, C., Ljungström, E., 1989. Reaction between Calcium Carbonate and Sulfur Dioxide. Energy and Fuels 3, 284–287. https://doi.org/10.1021/ef00015a003

Zhang, Z., Reddy, R.G., 2012. Experimental Studies on Flash Oxidation of Chalcopyrite, in: Young, C.A., Luttrel, G.. (Eds.), Separation Technologies for Minerals, Coal, and Earth Resources. Englewood, Colorado, USA, pp. 325–331.

Zivkovic, Z.D., Mitevska, N., Savovii, V., 1996. Kinetics and mechanism of the chalcopyrite-pyrite concentrate oxidation process. Thermochim. Acta 283, 121–130.

Supporting information

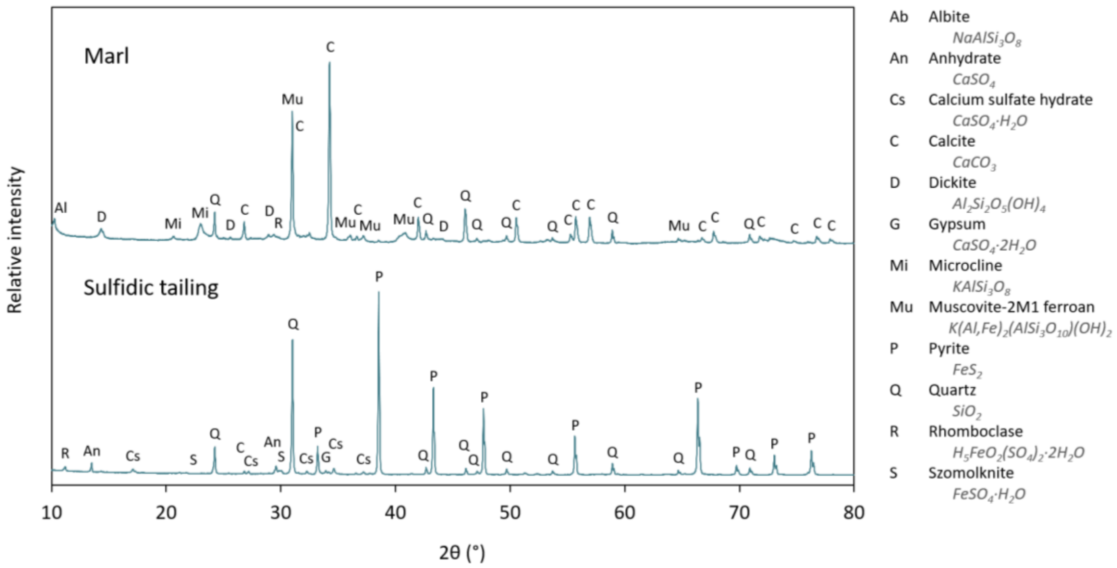


Figure S1. *XRD patterns of the sulfidic tailing and the marl material.*

Table S1. *The mineral phase composition of the initial tailing and marl material and the 80%8/0.2M, the 60%T/40%M, the 50%T/50%M and the 35%T/65%M materials obtained after conventional roasting at varying temperature.*

		Pre-roast		Post-roast 80%T/20%M					Post-roast 60%T/40%M					Post-roast 50%T/50%M					Post-roast 35%T/65%M				
Mineral	Composition	Tailing	Marl	400°C	500°C	600°C	700°C	800°C	400°C	500°C	600°C	700°C	800°C	400°C	500°C	600°C	700°C	800°C	400°C	500°C	600°C	700°C	800°C
Albite	$NaAlSi_3O_8$		1.6	0.2		1.1			0.8					1.0		0.6			1.0		1.1		
Anglesite	$PbSO_4$			0.2	0.5	0.1			0.3	0.3	0.1			0.2	0.3	0.2			0.1	0.1			
Anhydrite	$CaSO_4$	1.2		7.6	12.1	12.6	14.5	11.5	12.7	18.0	19.3	19.4	19.1	14.5	21.4	21.1	21.7	22.0	17.2	26.4	26.1	25.1	30.8
Anorthite	$CaAl_2Si_2O_8$					1.1			0.3		1.0			0.1		1.4			0.2		2.2		
Calcite	$CaCO_3$	0.2	34.0	2.7	0.9				4.5	1.7				5.3	1.6	0.1			5.9	1.6	0.2		
Calciumsulfate hydrate	$CaSO_4{\cdot}H_2O$	5.6																					
Dickite	$Al_2Si_2O_5(OH)_4$		11.3	1.1					0.9					1.1					1.2				
Gypsum	$CaSO_4{\cdot}2H_2O$	3.3																					
Hematite	Fe_2O_3			11.8	22.5	38.1	56.5	57.9	14.2	21.7	30.3	37.6	46.1	13.6	21.5	29.5	31.7	38.4	11.0	18.6	22.5	19.8	28.6
Iron sulfate	$FeSO_4$			4.0					6.3					4.9					3.4				
Maghemite	Fe_2O_3			8.3	5.8				3.9	3.4				3.0	1.4				1.2	0.3			
Microcline	$KAlSi_3O_8$		1.4	2.9	0.5	0.7	0.8	3.0	0.3	0.7	0.3	1.5		0.5	0.7	2.4	1.5		1.0	1.0	3.1	2.1	
Mikasaite	$Fe_2(SO_4)_3$			4.7	11.8	5.6			5.0	10.9	3.5			4.6	9.5	1.1			3.3	5.4			
Muscovite-2M1	$K(Al,Fe)_2AlSi_3O_{10}(OH)_2$		37.5	18.8	17.2	15.3			23.8	21.7	22.8	16.9	8.8	27.7	23.7	20.9	23.2	13.9	35.0	28.3	23.0	33.8	16.8
Perkovaite	$CaMg_2(SO_4)_3$					3.3	2.4	0.2			3.9	3.6	2.4			3.4	2.9	3.1			3.3	3.5	4.2
Pyrite	FeS_2	56.3		12.5	4.8	0.2			5.9	1.0	0.4			3.8	0.3	0.3			1.2				
Quartz	SiO_2	27.9	14.1	24.1	23.9	21.9	25.8	27.4	21.0	20.7	18.6	21.0	23.6	19.6	19.7	19.1	19.1	22.5	18.3	18.2	18.6	15.8	19.7
Rhomboclase	$H_5FeO_2(SO_4)_2{\cdot}2H_2O$	1.5																					
Sulfur	S	2.2																					
Szomolknite	$FeSO_4{\cdot}H_2O$	1.9																					
Total		100.1	99.9	100.1	100.0	100.0	100.0	100.0	99.9	100.1	100.2	100.0	100.0	99.9	100.1	100.1	100.1	99.9	100.0	99.9	100.1	100.1	100.1

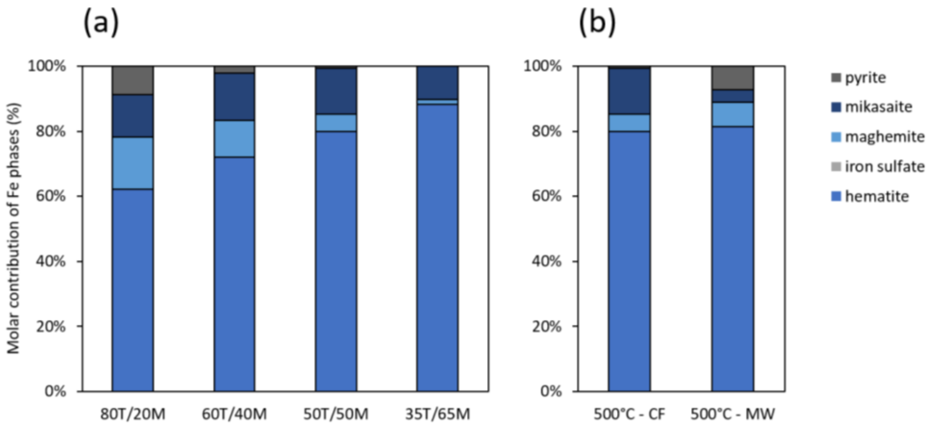


Figure S2. *Relative molar content of Fe-containing phases in the samples with varying marl content obtained after conventional roasting at 500°C (a) and the 50T/50M samples obtained after conventional roasting and microwave-assisted roasting (b).*

Table S2. *The mineral phase composition of the initial tailing and marl material, and the 50%T/50%M material after roasting at 500°C in a conventional furnace (CF) or in a microwave furnace (MW).*

		pre-roast		post-roast 50%T/50%M	
Mineral	Mineral composition	Tailing	Marl	500°C CF	500°C MW
Albite	$NaAlSi_3O_8$		1.6		
Anglesite	$PbSO_4$			0.3	
Anhydrite	$CaSO_4$	1.2		21.4	19.2
Anorthite	$CaAl_2Si_2O_8$				
Calcite	$CaCO_3$	0.2	34.0	1.6	4.0
Calciumsulfate hydrate	$CaSO_4 \cdot H_2O$	5.6			
Dickite	$Al_2Si_2O_5(OH)_4$		11.3		
Gypsum	$CaSO_4 \cdot 2H_2O$	3.3			
Hematite	Fe_2O_3			21.5	20.8
Iron sulfate	$FeSO_4$				
Maghemite	Fe_2O_3			1.4	1.9
Microcline	$KAlSi_3O_8$		1.4	0.7	0.8
Mikasaite	$Fe_2(SO_4)_3$			9.5	2.5
Muscovite-2M1	$K(Al,Fe)_2AlSi_3O_{10}(OH)_2$		37.5	23.7	26.6
Perkovaite	$CaMg_2(SO_4)_3$				
Pyrite	FeS_2	56.3		0.3	2.8
Quartz	SiO_2	27.9	14.1	19.7	21.4
Rhomboclase	$H_5FeO_2(SO_4)_2 \cdot 2H_2O$	1.5			
Sulfur	S	2.2			
Szomolknite	$FeSO_4 \cdot H_2O$	1.9			
Total		100.1	99.9	100.1	100.0

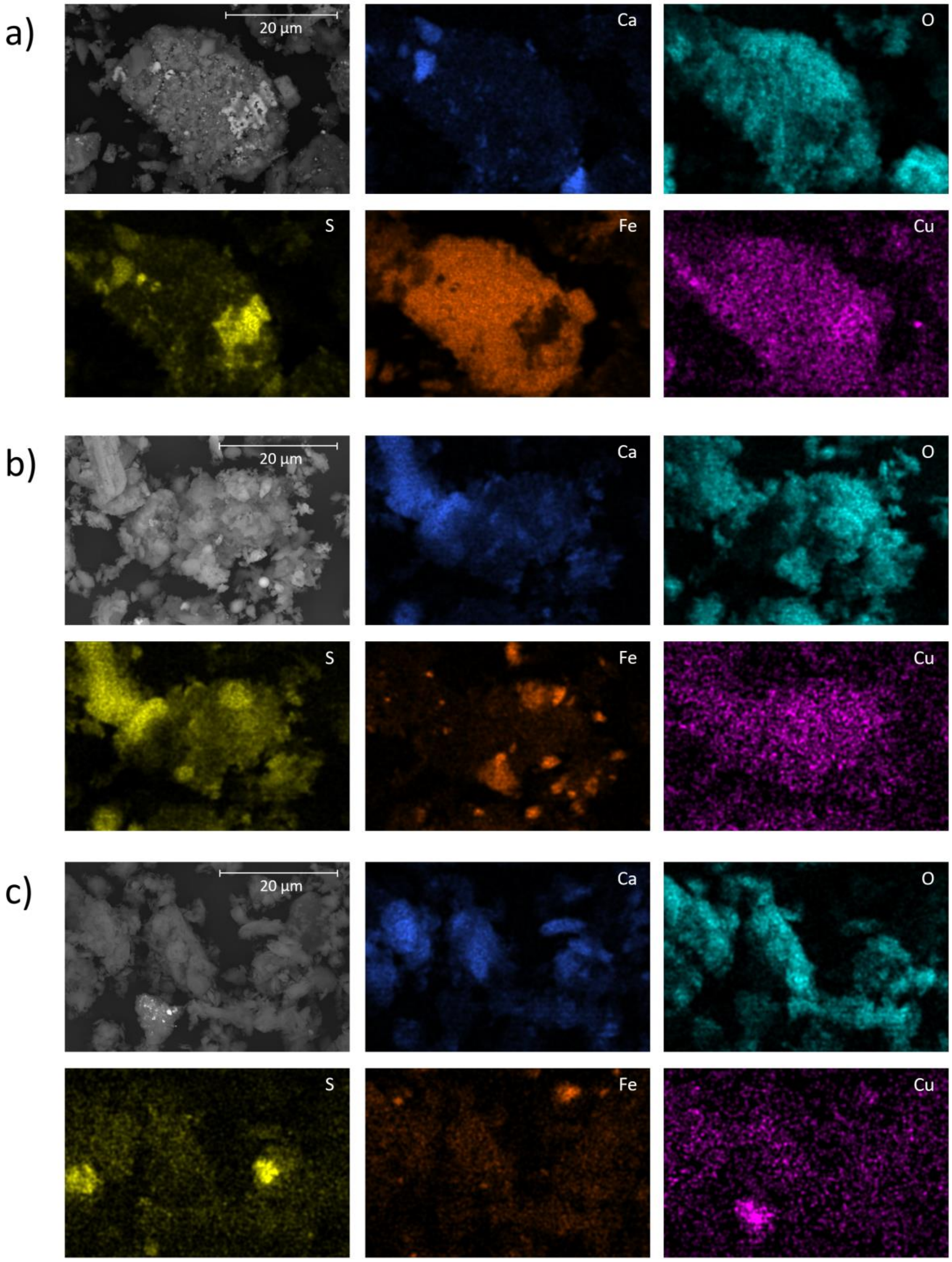


Figure S3. *SEM micrographs and EDX elemental maps (Ca, O, S, Fe, Cu) of particles of the pure tailing (a), the 60%T/40%M mixture (b) and the 20%T/80%M mixture (c) after conventional roasting at 600°C.*