Microwave assisted alkaline roasting-water leaching for the valorisation of goethite sludge from zinc refining process

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Abstract

Microwave (MW) alkaline roasting followed by water leaching was studied to selectively extract valuable (Zn, Pb) and hazardous (As) elements for the decontamination of the goethite sludge. During alkaline roasting stable $ZnFe_2O_4$ was decomposed to ZnO. The influence of alkali source (KOH, NaOH) and the heating source (conventional *vs.* microwave) were systematically investigated. Generally, $ZnFe_2O_4$ decomposed better upon increasing roasting temperatures.

For the water leaching step, different liquid-to-solid ratios (L:S= 10, 3, 2) and addition of alkaline agents (KOH, NaOH) were tested to enhance Zn extraction. NaOH addition to the leaching solution (60 °C, 30 min, L:S=10) gave the best extractions for Zn and Pb for both MW KOH roasted (84.3±0.4% Zn and 38±3% Pb) and MW NaOH roasted (83±1% Zn and 36.3±0.3% Pb extraction) materials (400 °C, 60 min). Alternatively, decreasing the L:S of water leaching to 2 gave a similar Zn extraction (83±1%) and reduced alkali consumption. By increasing the set MW roasting temperature to 450 °C, Zn leachability was 87±3% (NaOH roasting, water leaching L:S = 2, 60 °C, 30 min). Additionally, As removal in the studied system was 98-100%. Interestingly, roasting with KOH increased the Mn solubility as (per)manganate and decreased Zn leachability by consuming OH^- for disproportionation reactions of manganate. The leachability of matrix elements Ca and Fe was negligible.

Keywords: goethite sludge; goethite decontamination; selective Zn recovery; microwave alkaline roasting-water leaching; franklinite decomposition.

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1. Introduction

A considerable economic and environmental issue for the metallurgical industry is the management of secondary waste streams, including topsoil, waste-rock and process tailings. Metallurgical residues from ore extraction and processing are one of the largest waste streams in Europe and can be classified as inert, non-hazardous or hazardous (*e.g.* heavy metals-bearing materials that could generate pollution by weathering), depending on their composition (European Commission, 2018).

This is also the case of a waste stream generated during zinc production, goethite sludge which still contains an attractive amount of profitable base metal (*e.g.* Zn and Pb), as well as hazardous heavy metals, such as Sb and As. Nowadays, goethite is landfilled. Recently, Di Maria and Van Acker (2018) proposed that in order to valorise this waste material the metals (valuable and hazardous) should be removed and the remaining iron-rich residue should be recycled as *e.g.* a construction material (Di Maria and Van Acker, 2018).

Goethite is produced by precipitation of iron from pregnant leach solutions during hydrometallurgical refining of metallic zinc. The typical zinc content in the goethite residue varies from 5 to 10% by weight. Consequently, this part of the zinc is lost in these tailings that are for considerable extent landfilled, stockpiled or deposited in ponds. Aside from Zn, the goethite also captures other elements, such as Pb, In and As, through coprecipitation. Thus Fe-precipitation leads to the generation of a secondary solid stream, which may represent a secondary source of valuable elements and of an iron-rich mineral resource on the condition that hazardous elements can be safely removed.

Much research has been undertaken in terms of valorisation of zinc plant residues ZPRs from both pyro- and hydrometallurgical plants. Generally, the strategy used for Zn recovery is related to the speciation of zinc in the host material. Despite zinc can be profitably extracted from low-grade ore containing Zn as smithsonite ($ZnCO_3$) (Seyed Ghasemi and Azizi, 2018) by alkaline leaching, the same technique does not dissolve franklinite spinel ($ZnFe_2O_4$) even with microwave caustic leaching (Xia and Pickles, 2000). Goethite is known to contain Zn as ZnO and $ZnFe_2O_4$, particularly when zinc calcine is used as neutralizing agent (Han et al., 2014).

Franklinite is a very stable spinel structure that requires other routes than those above mentioned to liberate Zn for dissolution. Those may include several methods to decompose the franklinite structure or to reduce the iron and the zinc present in the spinel, as illustrated in Table 1 (Güler et al., 2011; Havlik et al., 2004; Kazemi and Sichen, 2016; Kukurugya et al., 2015; Omran et al., 2017; Santos et al., 2015; Turan et al., 2004; Zhao Youcai and Stanforth, 2000a, 2000b; Zang et al., 2016).

Amongst these techniques, an effective and selective combination of thermal and hydrometallurgical treatments, composed of preliminary hydrolysis- NaOH roasting- NaOH leaching, was explored by Youcai *et al.* to quantitatively extract zinc from franklinite-bearing EAF dusts (Zhao Youcai and Stanforth, 2000b, 2000a). This hydrolysis-roasting procedure was further optimised by Lenz *et al.* who used simple water leaching, decreasing the liquid-to-solid ratio to 4, to achieve the same Zn recovery.

The use of microwaves (MWs) as heating source to assist extractive processes has several advantages (*e.g.* fast, volumetric and selective heating, reduced energy consumption, elevated reproducibility, ease of control) (Jones et al., 2002). For example, the selectivity of heating in a MW field was successfully applied for the dechlorination of zinc leaching residue (Ai-Yuan et al., 2017). MW heating has also been applied by Wang *et al.* (Wang et al., 2018) to perform NaOH roasting experiments followed by water leaching for germanium extraction from ZnO dust. Response surface methodology RSM was applied to optimize the experimental parameters, achieving 93% of Ge recovery in optimized conditions (alkali to dust weight ratio of 1; 6-days ageing; roasting: T = 397 °C, 10 min; autoclave leaching: 67 °C, 60 min, L:S=6). Gao *et al.* (Gao et al., 2017) applied MW calcification (CaO) roasting to extract Cr and V from a chromium-vanadium-rich slag followed by sulfuric acid leaching (alkali to slag 0.95; roasting: 850 °C, 1.5 h; 20% wt. H_2SO_4 leaching: 95 °C 2 h, L:S=10) to extract selectively 98% of V.

Table 1: Methods for Zn recovery from franklinite-bearing materials

Reference	Material	Investigated methods	Outcomes
(Kukurugya et al., 2015)	EAF dust	**Sulfuric acid leaching** (H_2SO_4= 0.05-1 M, T= 20-95 °C, L:S= 10, 20, 50)	- Zn recovery up to 87% - Coextraction of Fe -Selectivity increased at low conc. of sulfuric acid
(Havlik et al., 2004)	EAF dust	**Pressure (sulfuric acid) leaching** (H_2SO_4= 0.4 M, T= 100-250 °C P= 1-41 bar, L:S= 0.4-1.2)	- Zn recovery > 80% - Dissolved iron precipitates at high P, T, and low L:S (Fe< 5%)
(Güler et al., 2011)	ZPR (Zn plant residue, Leach residue)	**Sulfating roasting + Water leaching** *+ HCl leach for Pb removal* (Roasting: H_2SO_4/ZPR=0.5-4, T= 100-700 °C Leaching: (water) 20% solid ratio T= RT)	- Appreciable Zn recoveries (≈80%) roasting below 600°C - Coextraction of Fe in water leaching (≈0-60%)
(Turan et al., 2004)	ZPR (Cake from Waelz kiln)	**Sulfating roasting +Water leaching** *+ HCl leach for Pb removal* Roasting: H_2SO_4/ZPR=0-3, T= 50-800 °C Leaching: (water) 20% solid ratio, T= 25-80 °C	- Zn recovery up to 86% - Coextraction of Fe in water leaching (≈0-50%)
(Zhao Youcai and Stanforth, 2000a, 2000b)	EAF dust	**Hydrolysis-NaOH roasting-NaOH leaching** (Hydrolysis: L:S= 0.5-3.3, t=4-48 h Roasting: NaOH/EAF=1.27, T=350 °C, t=1 h Leaching: NaOH 5 M, t= 20-60 h, L:S= 6.6-10)	- Zn recovery 100% selectively from Fe
(Kazemi and Sichen, 2016)	$ZnFe_2O_4$	**1) Carbothermic reduction** (2 g $ZnFe_2O_4$ + 0.3 g graphite T= 700, 750, 800 °C, Ar atmosphere) **2) H_2 reduction** (2 g $ZnFe_2O_4$ flushing H_2 up to 1 atm)	1) At 800°C, $ZnFe_2O_4$ is reduced to Zn vapor and FeO + C 2) At 600°C and short processing time (30 min), $ZnFe_2O_4$ is only obtained as ZnO
(Omran et al., 2017)	$ZnFe_2O_4$	**MW assisted carbothermic reduction** (N_2 atmosphere, $ZnFe_2O_4$: graphite= 1:1, 1:2, 1:3 according to reduction stoichiometry of $ZnFe_2O_4$ to ZnO, Fe and/or Fe_2O_3, MW power 700 W, time= 1-12 min)	- 99% $ZnFe_2O_4$ converted using two-fold the stoichiometric carbon, but some Zn is lost as vapor. - 48% $ZnFe_2O_4$ is converted, mainly to ZnO, FeO and C, using stoichiometric carbon
(Santos et al., 2015)	EAF dust	**1) Chlorination by Cl_2** (T= 800 °C, t=30 min) **2) Chlorination by $HCl_{(g)}$** (T= 700 °C, t=15 min) **3) Reducing by Cl_2 and C** (T= 800 °C, t=30 min C=6.1% of total wt.) **4) $CaCl_2$ roasting with C and O_2** (T=1000 °C, t=20 min)	1) 99.73% Zn and 40.32 % Fe as volatile chlorides 2) >95% Zn, ≈60% Fe 3) 100% Zn, 97% Fe 4) ≈50% Zn, 15% Fe
(Zang et al., 2016)	$ZnFe_2O_4$	**Mechanochemical reduction + alkaline leaching** (Fe (0): $ZnFe_2O_4$=0-5, t=0-6 h, 6 M NaOH, T=90 °C)	- Zn recovery ≈70%

However, MW assisted alkaline roasting of goethite sludge has not been investigated.

In this work, the benefits of microwave heating and the effectiveness of alkaline roasting were combined, aiming at decontaminating the gypsum and iron phases and simultaneously recovering valuable (Zn, Pb) and hazardous (As, Pb, Cr) elements in a subsequent water (alkaline) leaching step with a minimal dissolution of matrix materials (Fe and Ca).

2. Experimental

2.1 Materials

A representative sample of goethite sludge was provided by Nyrstar from their production plant situated in Balen (Belgium). The as received material was initially dried at 40 °C until constant weight was reached. The moisture content was 34.8% of the total weight. The dried goethite material was used as starting material in all described experiments. NaOH pellets for analysis EMSURE® (*Merck*) and KOH powder for synthesis (*Merck*) were used as alkali source for roasting and leaching experiments. Milli-Q water was used for all experiments that required water as a solvent.

2.2 Analytical methods

The particle size distribution of the goethite material was measured by laser diffraction analysis (*Microtrac S3500*). The elemental composition of goethite was obtained by XRF analyser (*Niton XL3t GOLDD+)* and ICP-OES (*Perkin Elmer, Optima 3000 DV*) after microwave acid digestion, according to the EN 13656 procedure, using HBF_4 rather than HF. Liquids were analysed with ICP-OES (*Perkin Elmer, AVIO 500*). In addition, the mineralogical composition of the solid materials was determined by XRD, using a *PANalytical EMPYREAN* system, with a cobalt anode (Co Kα) and equipped with a BBHD (Bragg Brentano High Definition) and a 3D detector (*PIXcel 3D*). *High-Score Plus* software was used for phase identification and Rietveld quantification. The latter used an external standard (TiO_2, *Kronos International*) as reference measurement.

A high-temperature chamber (HTK N16, *PANalytical*) was used for in-situ X-ray powder diffraction measurements at various temperatures of goethite sludge. The sample was placed on a platinum strip and heated at a rate of 120 °C/h to the set temperatures, with a 30-minute dwelling time before acquiring the spectra at each temperature.

Scanning electron microscopy (SEM) analysis was carried out by a *FEI NOVA NANOSEM 450* with EDX analyser *BRUKER QUANTAX 200* with SDD detector to observe the morphology and determine the elemental composition of particles within the goethite sample. Prior to SEM-EDX analyses goethite samples were imbedded in an epoxy resin, which was further polished while residues were Pt-coated.

2.3 Experimental methods

2.3.1 Microwave (MW) and conventional (CF) alkaline roasting

Alkaline roasting of goethite sludge was performed through either conventional heating in a muffle furnace (L/H 30/13, *Nabertherm*) or MW heating in a *Milestone PYRO* advanced microwave muffle furnace. All experiments were carried out in air atmosphere.

The goethite sludge was roasted in the presence of either NaOH (melting temperature, T_m= 318 °C) or KOH (melting temperature, T_m= 360 °C). All roasting tests have been performed using 50 mL ceramic crucibles (*VWR* 459-0212 DIN, 45x56 mm). In a typical experiment goethite is carefully weighted (2 or 5 g) and then mixed in a 1:1 weight ratio with alkali powders. Potassium hydroxide powder was directly mixed with the goethite sludge. Instead sodium hydroxide pellets were first ground, using mortar and pestle, and then dried at 40 °C to constant weight, before blending with the goethite material.

For conventional furnace (CF) alkaline roasting, samples were heated at a rate of 120 °C/h from room temperature to the set temperature (385 to 660 °C) at which they were held for 60 min. Cooling to room temperature occurred spontaneous after switching off the heating. Therefore, the total roasting process, excluded cooling, lasted for between 240 and 380 min. The temperature was measured with a thermocouple situated just above the crucibles.

For the MW assisted roasting, the heating program was composed of a 30-minute ramp up from room temperature to the set temperature (350 and 400 °C) and 60 min dwelling time. While, to reach 450 °C the ramp up time lasted 35 min and thus the dwelling time at 450 °C was reduced to 55 min in order to maintain an overall roasting time, excluding cooling, of 90 min. The *Milestone PYRO* advanced microwave muffle furnace was connected to a suction-scrubber system for off-gas treatment. In this work, the heating inside the MW furnace was supplied by a combination of direct MW absorption of samples and indirect conductive heat. This latter is promoted by a silicon carbide plate present at the top of the MW cavity, which strongly absorbs in the MW region and release heat by convection. In the PYRO furnace the temperature is measured by a ceramic coated thermocouple, placed in the muffle close to the crucibles.

The goethite-alkali mixtures were weighed before and after roasting to determine weight losses.

2.3.2 Water and alkaline leaching after alkaline roasting

The sample weight after roasting was used to calculate the liquid-to-solid (L:S) ratio for the subsequent leaching step. The required amount of Milli-Q water was partially poured directly in the crucibles used for roasting in order to quantitatively recover the contained mixture and transfer it to 100 ml high density polyethylene (HD-PE) containers. Next, the remaining DI water was added, and the containers were placed in a linear shaking thermostatic bath (*GRANT GLS 400*) at 60 °C and a shaking rate of 250 strokes/min for 30 min. Different L:S ratios (10, 3, 2) were tested. Room temperature leaching at an L:S = 2 was performed by placing the HD-PE reaction vessel on a magnetic stirrer (700 rpm) for 30 min.

Furthermore, leaching with addition of supplementary NaOH and KOH was also investigated. In these cases, the samples roasted with NaOH at 400 °C and with KOH were mixed with DI water at L:S=10, then solid NaOH (6.5 g) to pH 14.1 or KOH (6 g) to pH 14.3 were added, respectively. Magnetic stirring (700 rpm) was applied for 30 min at room temperature. All the obtained slurries after leaching were vacuum filtered over filter paper (*Whatman* 589/3). The obtained liquids were filtered a second time before analyses, using 0.45 µm syringe filtration.

The leaching efficiencies for each single metal were calculated as follows:

$$\% = \frac{mass\ of\ solubilized\ metal}{mass\ of\ metal\ in\ goethite} \times 100$$

where mass of solubilized metal was obtained by multiplying the measured metal concentration in the leachate by the total volume of the leachate.

In the case of manganese, due to post precipitation of manganese oxide, the leachability was calculated through the following equation:

$$\% = \frac{mass\ of\ Mn\ in\ goethite -\ mass\ of\ Mn\ in\ the\ residues}{mass\ of\ Mn\ in\ goethite} \times 100$$

where mass of Mn in the residues was derived from the measured Mn concentration in the residue multiplied by the total residue mass.

3. Results and discussion

3.1 Characterization of goethite sludge

Goethite sludge is an iron-bearing, fine-grained material with an average particle size (d_{50}) of about 7 µm and d_{99} = 79 µm. The mineralogy of the material is characterized by an abundant amorphous

phase (64%), which is rich in Fe-phases, such as iron oxyhydroxide (FeOOH) and iron (II) and iron (II-III) oxides/hydroxides.

Identified crystalline iron phases in the XRD diffractogram (Figure 1) were jarosite ($KFe_3(SO_4)_2(OH)_6$, 9.3%) and franklinite ($ZnFe_2O_4$, 9.3%).
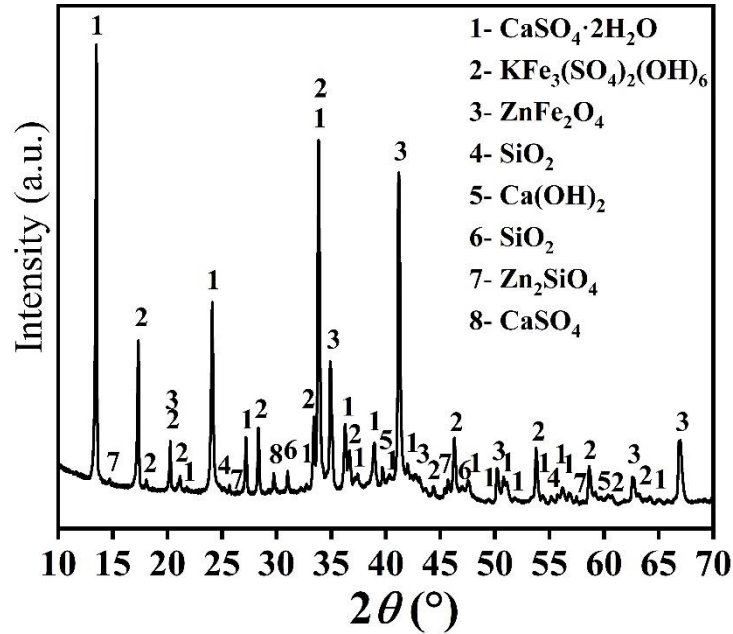

Figure 1: XRD pattern of dried goethite sludge.

Zinc was also present as willemite ($ZnSiO_4$, 0.4%). However, the mass balance of zinc suggests that zinc is occurring in additional mineral forms that could not be observed by XRD. In fact, it is likely that Zn is also present as sulfate ($ZnSO_4$), from H_2SO_4 leaching pregnant solution, and potentially as zincite (ZnO) (Han et al., 2014) or other complex compounds in the amorphous phase.

The main elemental content of goethite sludge is reported in Table 2. The material contains 1.8 wt% of Pb and SEM/EDX analyses (Fig. I, SI) suggest that Pb is mainly present as $PbSO_4$.

Table 2: Elemental composition of goethite sludge

Element	Content (wt%)
Fe	24.1
S	9.2
Ca	5.9
Zn	5.9
Pb	1.8
Si	1.3
Al	0.9
Cu	0.4
Mn	0.4
As	0.3
Ba	0.1
Element	Content (mg/kg)
Sn	455
Cr	475
Mo	82
V	75

3.2 Microwave (MW) and conventional (CF) alkaline roasting

The thermal behaviour of goethite was studied by in-situ XRD upon heating to 700 °C under an air atmosphere (Fig. II, SI). It was observed that franklinite is stable within the studied temperature range. Upon heating gypsum dehydrated from 100 °C onward to produce hexagonal calcium sulphate, which further converted to orthorhombic anhydrite ($CaSO_4$) from 300 up to 700 °C. At 300 °C, jarosite peaks disappeared, while between 300 and 400 °C hematite (Fe_2O_3) peaks started to appear.
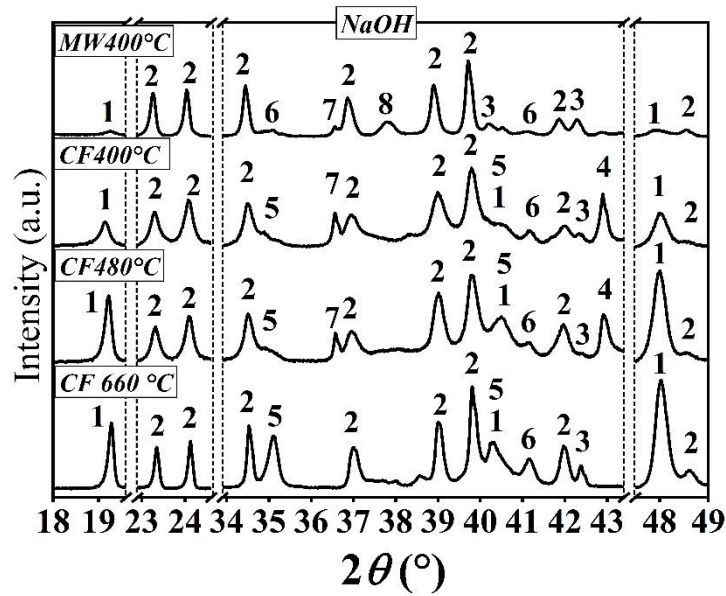
Figure 2: XRD patterns of the goethite after roasting with NaOH (goethite: NaOH = 1: 1 wt.) at 400 °C using MW at 400 °C and CF at 400 °C, 480 °C, 660°C. **1- Sodium ferrite (rhombohedral), α-NaFeO$_2$. 2- Sodium ferrite (orthorhombic), β-NaFeO$_2$. 3- Zincite, ZnO. 4- Andradite, Ca$_3$Fe$_2$(SiO$_4$)$_3$. 5- Natrite, Na$_2$CO$_3$. 6 – Franklinite, ZnFe$_2$O$_4$. 7- Anhydrite, CaSO$_4$. 8- Calcium oxide, CaO.**

Hematite could form by the thermal conversion of either goethite (eq.1) and/or by jarosite decomposition. In fact, jarosite thermally decomposes via dehydroxylation (eq. 2) and desulfation reactions (eq. 3) (Chen, 2018).

(1) $2FeOOH \rightleftharpoons Fe_2O_3 + H_2O$

(2) $KFe_3(SO_4)_2(OH)_6 \rightleftharpoons KFe(SO_4)_2 + Fe_2O_3 + 3H_2O$

(3) $2KFe(SO_4)_2 \rightleftharpoons K_2SO_4 + Fe_2O_3 + 3SO_3$
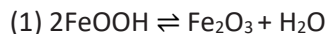
Alkaline roasting of goethite was tested by both conventional heating and MW heating. Figure 2 and Figure 3 show the XRD patterns of goethite tailing samples after roasting in the presence of NaOH and KOH, respectively. Samples were roasted at 400 °C in a microwave furnace or at 400, 480, 660 °C in a conventional muffle furnace.
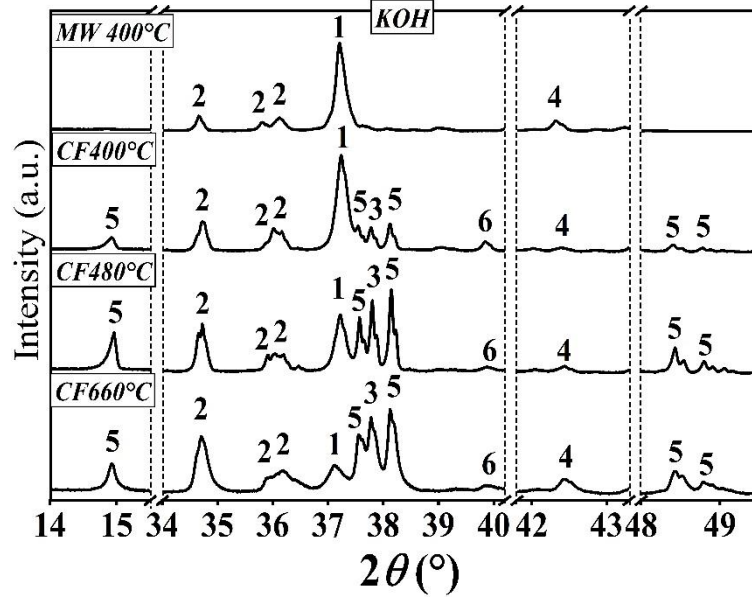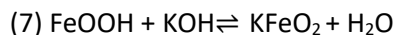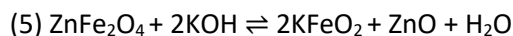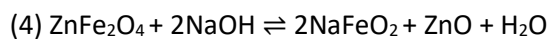
Figure 3: XRD patterns of the goethite after roasting with KOH (goethite: KOH = 1: 1 wt.) using MW at 400°C and CF at 400°C, 480°C, 660°C. **1- Potassium ferrite (orthorhombic), $KFeO_2$. 2- Potassium sulfate, K_2SO_4. 3- Calcium oxide, CaO. 4- Zincite, ZnO. 5- Potassium carbonate hydrate, $K_2(CO_3)(H_2O)_{1.5}$. 6- Portlandite, $Ca(OH)_2$.**

In comparison to untreated goethite sludge (Figure 1), all alkaline roasted samples show the absence of gypsum and jarosite, while franklinite peak intensities were significant lower. Furthermore, roasted samples contained zincite (ZnO) and ferrite of sodium ($NaFeO_2$) or potassium ($KFeO_2$), depending on the alkaline source used. These latter compounds could originate from franklinite decomposition in the presence of an alkali salt (eq. 4-5). However, thermodynamic calculations evidenced that also goethite can spontaneously react with alkali sources to ferrite compounds (eq. 6-7) in the investigated temperature range (Fig. III-IV, SI).

(4) $ZnFe_2O_4 + 2NaOH \rightleftharpoons 2NaFeO_2 + ZnO + H_2O$

(5) $ZnFe_2O_4 + 2KOH \rightleftharpoons 2KFeO_2 + ZnO + H_2O$

(6) $FeOOH + NaOH \rightleftharpoons NaFeO_2 + H_2O$

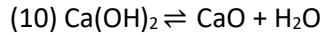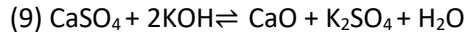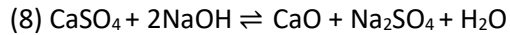(7) $FeOOH + KOH \rightleftharpoons KFeO_2 + H_2O$

Some striking differences were noted between the mineralogy of the MW and CF roasted samples. CF roasted materials contained more carbonated products, such as natrite, Na_2CO_3, and potassium carbonate hydrate, $K_2(CO_3)(H_2O)_{1.5}$. This was seemingly related to atmospheric CO_2 adsorption, mainly at the expense of alkali ferrite formation, due to the different heating method (*e.g.* heating/cooling rate and time, aeration of the ovens, volumetric heating of goethite by MW absorption, etc.) (Yanase et al., 2018).

Remarkably, MW NaOH roasting yielded sodium ferrite in its orthorhombic β-polymorph, while both the β- and the α-polymorphs (rhombohedral) were obtained by conventional roasting. The nature of precursors as well as the synthetic conditions (*e.g.* temperature and time of heat treatments) may affect the polymorphism of sodium ferrite (Takeda et al., 1980; Yanase et al., 2018).

The formation of CaO during KOH roasting was more pronounced for CF roasting, and increased with temperature. While in the case of NaOH roasting, more CaO was detected in the MW roasted products. Direct thermal degradation of calcium sulfate to CaO could be excluded since it occurs at temperature above 1000 °C, according to in-situ XRD (Fig. I, SI), thermodynamics (Fig. V, SI) and literature data (Bollen, 1954). Upon increasing roasting temperatures more CaO and K_2SO_4 formed in the KOH-goethite system (Figure 3), that could indicate that anhydrite reacts with KOH (eq. 9).

Additionally, $Ca(OH)_2$ could dehydrate (eq. 10), which reaction generally occurs in the temperature range of 300-600 °C (Irabien et al., 1990).

(8) $CaSO_4 + 2NaOH \rightleftharpoons CaO + Na_2SO_4 + H_2O$

(9) $CaSO_4 + 2KOH \rightleftharpoons CaO + K_2SO_4 + H_2O$

(10) $Ca(OH)_2 \rightleftharpoons CaO + H_2O$

In the case of NaOH roasting, no Na_2SO_4 was observed, although the $CaSO_4$ decomposition reaction in the presence of NaOH is thermodynamically favourable (eq. 8, 9, 10, Fig. VI, SI). Thus, calcium resulted highly mobile and reactive in the molten phase and in the case of NaOH roasting at 400 and 480 °C in CF, it could be found associated with silicates and iron (oxyhydro-) oxides in andradite form, $Ca_3Fe_2(SiO_4)_3$. Teylor and Juhn (Teylor and Juhn, 1978) described the formation of andradite through a naturally occurring reaction in geological siliceous sediments of calcium carbonate with iron oxide/oxyhydroxide and silicates (eq. 11), which is energetically favourable above 200 °C (Fig. VII, SI).

(11) $Fe_2O_3 + 3SiO_2 + 3CaCO_3 \rightleftharpoons Ca_3Fe_2(SiO_4)_3 + 3CO_2$

3.3 Leaching tests

3.3.1 Water leaching (L:S=10) of microwave (MW) and conventionally (CF) roasted samples with NaOH and KOH at different temperatures

The alkali CF and MW roasted samples were leached with Milli-Q water at L:S = 10 and 60 °C, the leachabilities of Al, As, Cr, Mo, Pb, Sn, V and Zn are reported in Figure 4.

Zn leachability was generally low (3.6-7.8% KOH; 14.7-28.9% NaOH), as well as Pb (0.8-10%) and Sn (0-26%) leaching. While, for other amphoteric metals considerable dissolution took place: Al (34-67%), As (50-88%), Cr (67-94%), Mo (58-93%), V (15-60%). The solubilization of both calcium and iron was below 300 μg/L. Cu leachability was below reporting limit (<100-200 ppb).

XRD diffractograms of the leaching residues clearly show the appearance of zincite (ZnO) and disappearance of franklinite ($ZnFe_2O_4$) upon increasing roasting temperatures (Figure 5). This confirms the decomposition of the stable spinel franklinite into zincite and ferrite. Notwithstanding the decomposition of stable franklinite, the Zn solubility remained low, because ZnO requires a high pH to dissolve (Fig. VIII, SI, eq. 12), which is not reached by water leaching at L:S = 10 of the roasted samples (pH = 13.5-13.6) .

(12) $ZnO + 2OH^- \rightleftharpoons ZnO_2^{2-} + H_2O$
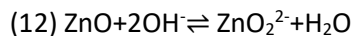
Zn extraction was lower for goethite-KOH than for goethite-NaOH roasted materials, due to the lower OH^- concentration, because both KOH and NaOH were used according to a 1 to 1 weight ratio with goethite (*i.e.* $[OH^-]_{NaOH} / [OH^-]_{KOH}$ = 1.39).
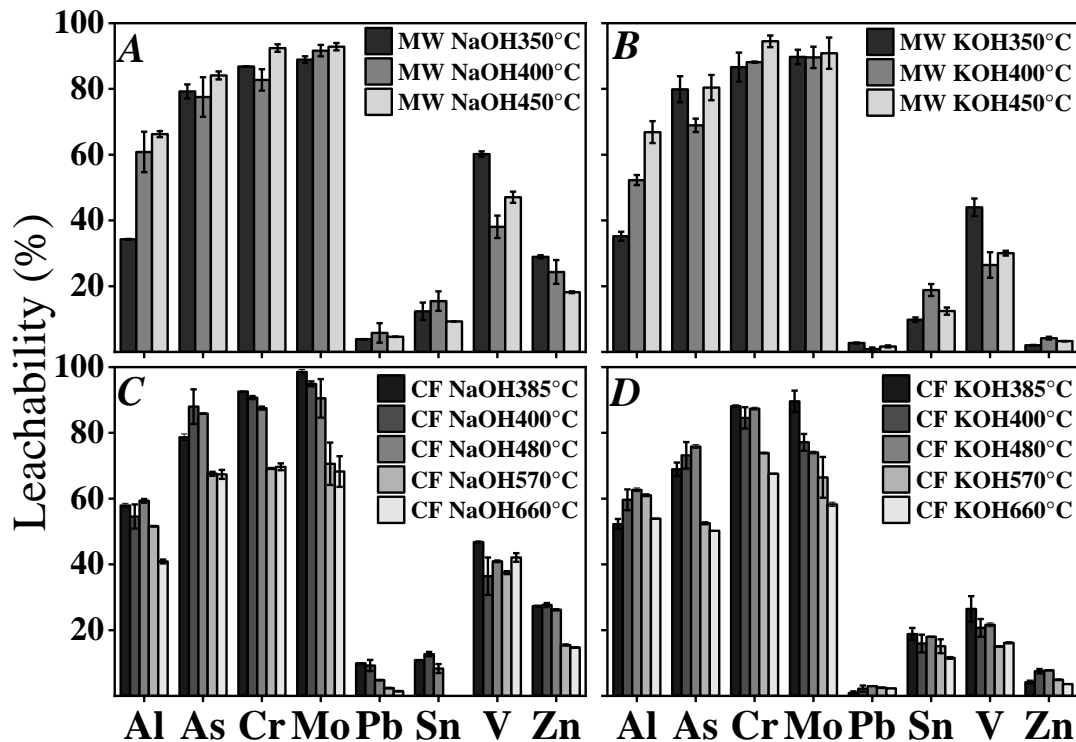
Figure 4: Leachability of goethite elements after roasting (alkali: goethite= 1 wt.) and water leaching (60°C, 30 min, L:S=10): A) NaOH in MW furnace at 350, 400, 450°C; B) KOH in MW furnace at 350, 400, 450°C; C) NaOH in CF at 385, 400, 480, 570, 660°C; D) KOH in CF at 385, 400, 480, 570, 660°C.

Increasing the set temperature during MW NaOH and KOH roasting from 350 to 450 °C led to similar or slightly enhanced extraction yields in water at L/S = 10 for Al, As, Cr, Mo, Pb, while V showed a decreasing trend (Figure 4). It must be noted that the set MW roasting temperature represents the temperature inside the muffle but does not necessary represents the sample temperature during roasting as the material can additionally heat through absorbing MW energy.

It should be considered that the concentrations of minor elements (Cr, Mo, Sn, V) in the goethite was low, and heterogeneity of metal distribution as well as experimental error might have affected the slight differences observed during MW roasting for such elements.

Whereas for CF roasting, at higher roasting temperatures the leaching efficiencies of Zn, Cr, Mo, As and Al decreased with 20-30%, going from 480 to 570 °C. This could be partially ascribed to the formation of calcium lead hydroxide, $CaPb(OH)_6$ (Inagaki, 1986), which consumed substantial OH^- moles during roasting and leaching.

Moreover, XRD analyses (Figure 2) showed that by CF NaOH roasting the relative amount of α-sodium ferrite (α-$NaFeO_2$) increased by increasing the roasting temperature. This compound was formed through reaction of franklinite and goethite with NaOH according to eq. (4) and (6), respectively. These reactions decreased the availability of OH^- in the leaching solution, with a negative effect on the leachability of amphoteric elements, accordingly.

A similar effect occurred for CF KOH roasting wherein more potassium carbonate hydrate, $K_2(CO_3)(H_2O)_{1.5}$, was produced at higher temperatures (Figure 3). It is believed that the formation of potassium carbonate hydrate can be likely associated to the reactions presented in eq. (5) and (6) followed by CO_2/H_2O adsorption. This also led to a lowering of pH and decreased leaching efficiency at higher CF roasting temperature (from 570°C onwards), in concomitance with the formation of $CaPb(OH)_6$, as previously mentioned.

For the materials roasted at lower temperatures, the metal leaching behaviour in water was similar, independent of the used roasting method or alkaline agent.
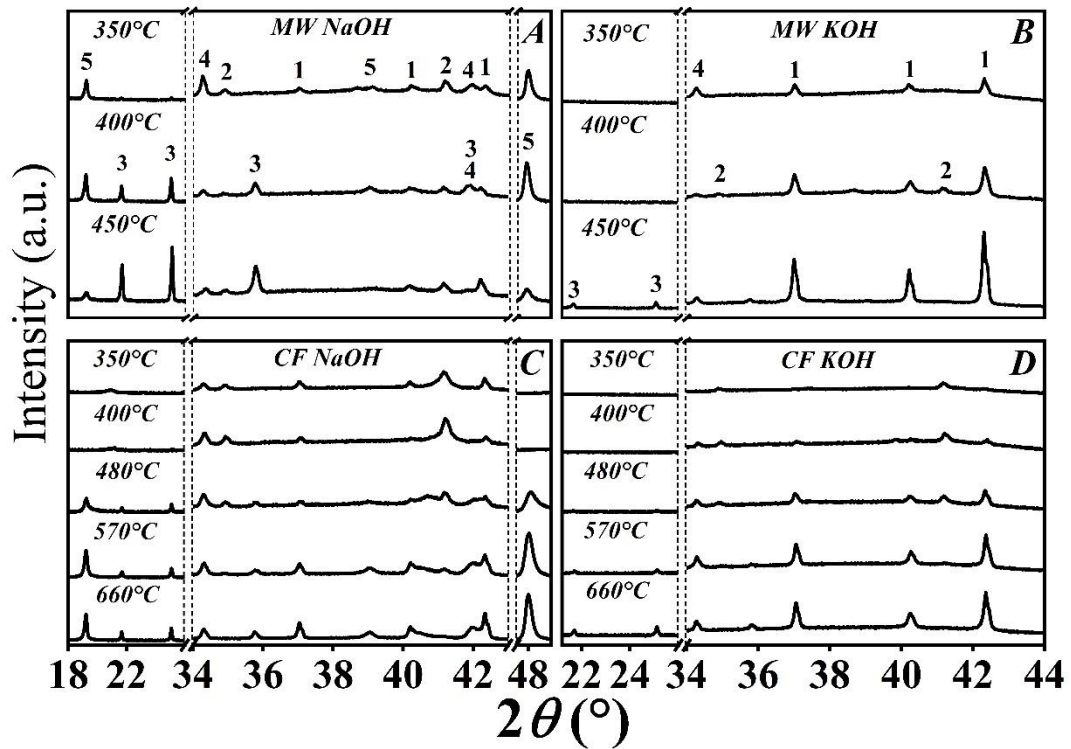
Figure 5: XRD patterns of residues after roasting (alkali: goethite= 1 wt.) and water leaching (60°C, 30 min, L:S=10): A) NaOH in MW furnace at 350, 400, 450°C; B) KOH in MW furnace at 350, 400, 450°C; C) NaOH in CF at 385, 400, 480, 570, 660°C; D) KOH in CF at 385, 400, 480, 570, 660°C. **1- Zincite, ZnO. 2- Franklinite, ZnFe₂O₄. 3- Calcium lead hydroxide, CaPb(OH)₆. 4- Calcite (rhombohedral), CaCO₃. 5- Sodium ferrite (rhombohedral), α-NaFeO₂.**

As stated above, the individual sample temperature during MW roasting could not be precisely determined, whereas the sample temperature during CF roasting was fixed. Thus, by comparing the leaching residue mineralogy and weight loss of identical samples treated by CF roasting at known temperatures with those treated by MW roasting, the roasting temperature of the MW samples could be estimated. For instance, the mineral composition of the residue obtained by NaOH MW roasting at 400 °C is similar to CF NaOH roasted samples between 480 and 570 °C. Similarly, the residues' mineralogy of MW KOH 400 °C and CF KOH 480-570°C; MW NaOH 450 °C and CF NaOH 570-660 °C; and so forth are correlated. This observation supports the hypothesis that the sample temperatures during MW assisted alkaline roasting were higher than those measured by the thermocouple place in the MW muffle due to absorption of MWs by the samples. Clearly, MW heating was faster than conventional heating for the studied samples.

Both MW and CF roasted leaching residues contained α-NaFeO₂ (Figure 5 A and C) which did not dissolve during leaching, contrarily to β-NaFeO₂ that completely dissolved. A similar behaviour was noticed by Yanase *et al.*, which describe the formation of α-Na$_{(1-x)}$FeO₂ and γ-Fe₂O₃ by a slight Na⁺ release in water, while β-NaFeO₂ decomposed completely to α- Fe₂O₃ (Yanase et al., 2018).

In conclusion, the ZnO formed from franklinite during roasting, did not dissolve when water leaching at L/S=10 was applied. Also Pb leachability was limited. A higher pH is required to dissolve Zn and Pb after roasting.

The MW hybrid heating was able to heat the goethite-alkali mixture faster than conventional heating. Thus, processing time and energy consumption were decreased (1.8-2.6 kwh for MW heating and ventilation, according to the mass loaded: max. load= 80 g- 40 g goethite + 40 g alkali).

3.3.2 Water leaching (L: S = 10) of MW roasted samples with NaOH and KOH at 400 °C

In order to increase the dissolution of ZnO, the pH of the leaching mixture was raised to >14 through addition of either solid NaOH or KOH. Leaching reactions were performed with MW alkali roasted goethite samples (400 °C, 60 min, 1:1 wt. ratio goethite: NaOH or KOH) in Milli-Q water (L:S=10). Four experimental conditions were investigated wherein the alkali salt added to the leaching (NaOH, KOH) was either the same or different than the one used for roasting (NaOH, KOH) (Figure 6).
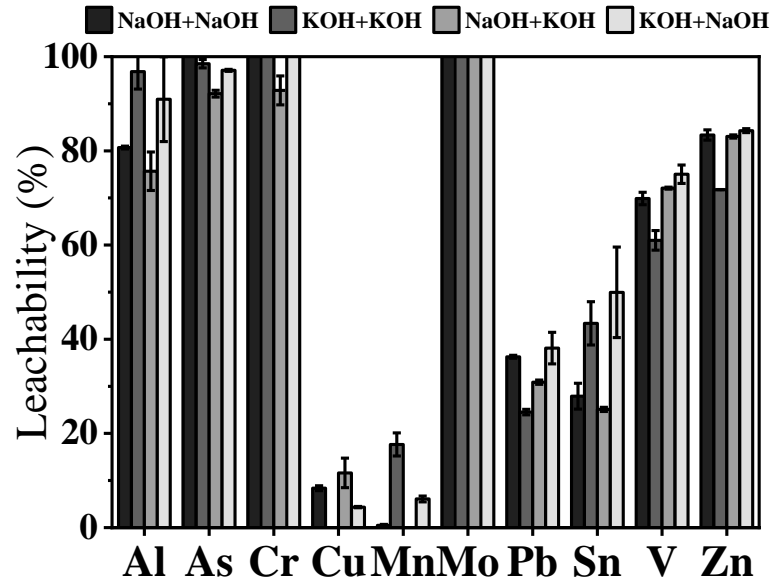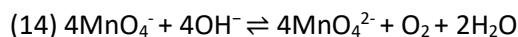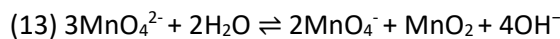

Figure 6: Leachability of goethite elements after MW assisted roasting (goethite: KOH/NaOH ratio=1:1 wt.) at 400 °C and subsequent alkaline leaching (60 °C, 30 min, L:S=10) in linearly-shaken thermostatic bath: NaOH MW roasting + NaOH leaching , KOH MW roasting + KOH leaching, NaOH MW roasting + KOH leaching and KOH MW roasting + NaOH leaching.

Through addition of an alkali to the leaching mixture to obtain a pH $\geq$ 14, the zinc extraction substantially improved to about 83-84% for KOH+NaOH, NaOH+NaOH, NaOH+KOH and 72% for KOH+KOH (Figure 6) systems. Pb recoveries were also ameliorated from 0.5-10% to respectively 38, 36, 31 and 25%. As, Cr and Mo reached quantitative extraction in the most favourable cases and >90% extraction in all four conditions (Figure 6). Al was leached for about 80% when samples were roasted with NaOH and >90% with KOH roasting. The V leachability varied from 61% (KOH+KOH) to 75% (KOH+NaOH) following a similar trend as Zn. Sn extraction ranged between 25-27% when NaOH roasted and 43-50% after KOH roasting.

Furthermore, NaOH roasted samples leached Cu (8% for NaOH+NaOH and 11% for NaOH+KOH), while KOH roasting promoted Mn leaching (17% for KOH+KOH and 6% for KOH+NaOH). It is believed that Na$^+$ better stabilizes soluble copper species (Cu(OH)$_3^-$, Cu(OH)$_4^{2-}$, CuO$_2^{2-}$. Fig. IX, SI) and K$^+$ those of manganese (MnO$_4^-$, MnO$_4^{2-}$. Fig. X, SI) in the leachates.

The formation of manganate (VI), MnO$_4^{2-}$, was evident from the green colour of the samples after the roasting (both for KOH and NaOH). Furthermore, in the leaching step after KOH roasting potassium permanganate, KMnO$_4$, was observed giving to the leaching solution an initial purple colour. KMnO$_4$ was rapidly formed in solution due to the disproportionation/hydrolysis reaction of manganate (eq. 13). Whereas, upon time the solution turned green again to more stable manganate (graphical visualization in SI, Fig. XI), according to self-decomposition/deoxidation (eq. 14) (Posselt, 1972).

(13) $3MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_4^- + MnO_2 + 4OH^-$

(14) $4MnO_4^- + 4OH^- \rightleftharpoons 4MnO_4^{2-} + O_2 + 2H_2O$

Subsequently, manganate in solution is further reduced and slowly precipitates over a period of 1-6 days as a fine brown solid, which can be ascribed to amorphous MnO_2 (eq. 15). The small amount of precipitates could be collected on a filter. The Mn content of these precipitates was about 20% and 4%, after KOH and NaOH leaching, respectively. Furthermore, XRF and XRD analyses of the precipitates revealed potassium (K_2SO_4 and $KHCO_3$) or sodium (Na_2CO_3, $Na_2CO_3 \cdot H_2O$ and $Na_6CO_3(SO_4)_2$) salts to be the main components (Fig. XII, SI). Also trace amounts of Zn and Pb were detected, which are negligible in terms of leachability.

(15) $2MnO_4^{2-} + 2H_2O \rightleftharpoons 2MnO_2 + 4OH^- + O_2$
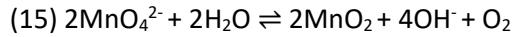
Thus, the MW leachability of Mn, which is calculated based on its concentration in the leachate, is underestimated. In fact, the Mn leachability based on XRF analyses of the solid residues indicated that the NaOH-NaOH system yielded 4±1%, NaOH-KOH 51.9±0.4%, KOH+KOH 94.2±0.2% and KOH-NaOH 98±2%. The higher dissolution of Mn and its reduction to MnO_2, promoted by KOH in the KOH+KOH process, was a cofactor causing consumption of OH^- and consequently decreasing Zn extraction (71.8%), the lowest among the four tested conditions.

XRD analyses of the residues after alkaline leaching (Figure XI, SI) confirmed the complete dissolution of ZnO. Besides, the main crystalline phase in the residues was hydro-andradite, $Ca_3Fe_2Si_{1.15}O_{4.6}(OH)_{7.4}$, presumably favoured by the insertion of hydroxyl anions within the $Ca_3Fe_2(SiO_4)_3$ lattice by substitution of the tetrahedral silicon (*i.e.* $(O_4H_4)^{4-} \rightleftharpoons (SiO_4)^{4-}$) (Amthauer and Rossman, 1998) during leaching.

Rietveld refinement of goethite residue output of MW NaOH roasting at 400 °C and leaching with extra NaOH (L:S=10) quantified that 84.5% of franklinite decomposed (from 9.3 to 2.0%) and that hydro-andradite (15.0%), non-leached α-$NaFeO_2$ (5.7%) and amorphous phase (76.4%) accounted for the remainder of phases in the residue (Fig. XIII, SI). It is noteworthy that the total alkali (KOH or NaOH) addition with respect to goethite is 4:1 in weight ratio when alkali is added to both the roasting and leaching step in order to recover a maximum amount of Zn. Whereas, the roasting step alone requires a 1:1 weight ratio.

MW alkali roasting at 400 °C followed by alkaline leaching achieved satisfactory Zn recoveries, however the required amount of additional alkaline agents will be uneconomical for larger scale application.

3.3.3 Water leaching at low L:S (= 2, 3) of microwave roasted samples in presence of NaOH and KOH at 400 and 450 °C

Water leaching at low L:S ratio after alkali roasting was applied to obtain a sufficiently high pH to dissolve Zn without having to add extra alkali during the leaching step.

Initially, water leaching experiments at L:S ratios of 2 and 3 were performed in a thermostatic shaking bath at 60 °C on MW alkali roasted goethite (NaOH or KOH, 400 °C, 60 min). The pH of all leachates was close to pH=14. At L:S=2 the leaching efficiencies for Zn and Pb were low, reaching 30±10 and 40±1% for Zn and 4±1 and 2.4±0.1% for Pb for NaOH and KOH, respectively (Figure XIV, SI). While, at L:S=3 the leachability of Zn significantly improved to 73±2% (Pb, 9±2%) for the NaOH system. At L:S=3 the leachabilities of Zn (32±3%) and Pb (4.5±0.5%) for KOH roasted goethite were less efficient.

The higher viscosity at low L:S impeded sufficient mixing in the linear shaking system and caused reduced diffusion with a consequential lower metal leachability (Figure XIV, SI) than for leaching at L:S = 10 with additional alkali sources (Figure 6).
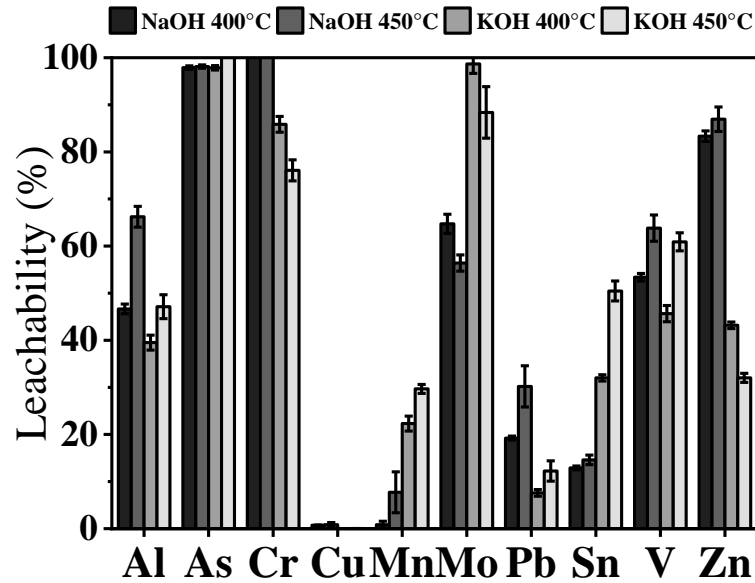
Figure 7: Leachability of goethite elements after MW assisted roasting (goethite: KOH/NaOH ratio=1:1) and subsequent water leaching L:S=2 (RT, 30 min, L:S=2) with magnetic stirring at 700 rpm. NaOH MW roasting at 400 °C, KOH MW roasting at 400 °C, NaOH MW roasting at 450 °C and KOH MW roasting at 450 °C.

Therefore, magnetic stirring (700 rpm) was applied to enhance the fluid dynamics. Besides, the leaching temperature was lowered to room temperature. Both parameters were tested for samples roasted at 400 and 450 °C in the presence of NaOH and KOH and leached with water at an L:S=2.

For samples roasted at 400 °C, Zn and Pb extractions (Figure 7) were similar to the leachability with extra source of alkali at L:S=10 (Figure 6). Nevertheless, the leachability of other elements was reduced to some degree (such as Pb- only 19% - Al, Mo, V, Sn, Cu) or kept constant (As, Cr). The goethite roasting with KOH at 400 °C and leaching at L:S=2 lost efficiency in terms of Zn and Pb extraction in favour of Mn leachability (22%).

To further improve the Zn leachability through better decomposition of franklinite, the MW roasting temperature was increased to 450 °C and the residue subsequently leached in Milli-Q water at L:S=2. The higher roasting temperature improved the Zn leachability to 87%, as well as Pb leaching (30%) for NaOH roasted goethite (Figure 7). KOH roasting at 450 °C (Figure 7) showed once again the predisposition to extract more Mn (30%) at the expense of Zn extraction (32%), which remained behind in the residue as ZnO.

XRD diffractograms of leaching residues of NaOH roasted samples showed a clear trend whereby upon increasing roasting temperature the intensity of $ZnFe_2O_4$ peaks decrease, while those of α-$NaFeO_2$ increase (Figure 5 A, Figure 8 a, b). Whereas, the XRD of KOH roasted samples (Figure 8 c, d) show that K_2SO_4, a product of gypsum and jarosite decomposition, did not completely dissolve at L:S=2. In general, matrix elements are not leached (Fe and Ca <300 µg/L) and the best results in terms of Zn and Pb leachability were obtained by NaOH roasting and water leaching at L:S=2. By working at low L:S, the overall alkali consumption is decreased to a goethite to alkali weight ratio of 1:1, without a drastic drop in performance if compared to leaching with extra source of NaOH.

The Mn leachability was calculated based on the chemical analyses of the leach residue, the MnO_2 post-filtration precipitate (see above). The leaching yields of Mn were 31 and 46% for NaOH at 400 and 450 °C respectively, while Mn leaching was favoured by KOH MW roasting giving 81% at 400 °C and 88% at450 °C.

Additionally, XRF analyses on leach residues (Table III, SI) confirmed the observed leaching trends which were measured by ICP-AES analyses of the leachates as described above.

The MW NaOH roasting, both at 400 and 450 °C, followed by water leaching at L/S 2 were so far the best tested conditions for the leaching of Zn (84 and 87%, respectively), equalizing or increasing the performances obtained for MW roasting followed by alkaline leaching, but substantially reducing the amount of hydroxide used (about 75%).

In the case of MW KOH roasting, the leaching at L/S 2 was limited for Zn, but an elevated Mn removal was obtained.

Recovery of Zn from the alkaline leachate can possibly be achieve cost effectively through electrowinning (Zhao Youcai and Stanforth, 2000a) after purification of the leachate that might be performed by selective precipitation (Lenz and Martins, 2007; Youcai and Stanforth, 2001).
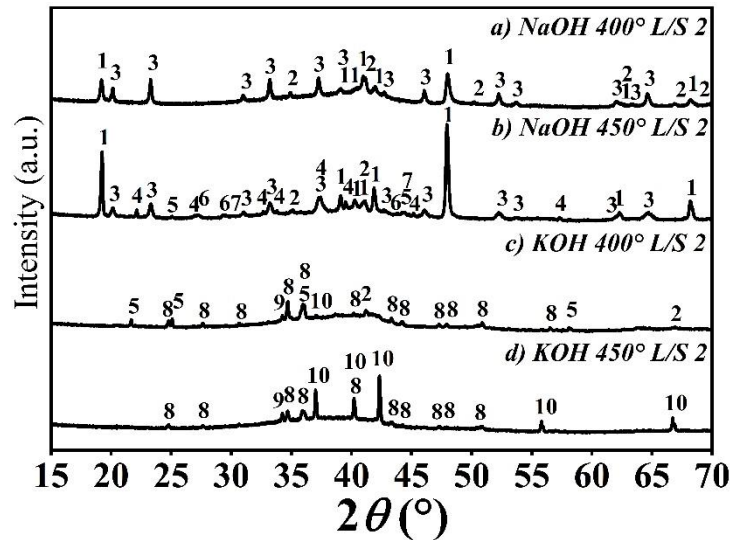

Figure 8: XRD patterns of residues after MW assisted roasting (goethite: KOH/NaOH ratio=1:1) at 400 °C and 450 °C and subsequent water leaching (RT, 30 min, L:S=2) with magnetic stirring at 700 rpm. NaOH MW roasting at 400 °C (a), KOH MW roasting at 400 °C (b), NaOH MW roasting at 450 °C (c) and KOH MW roasting at 450 °C (d). **1- α-Sodium ferrate(III) (rhombohedral), α-NaFeO₂. 2- Franklinite, ZnFe₂O₄. 3- Hydro-andradite, Ca₃Fe₂Si₁.₁₅O₄.₆(OH)₇.₄. 4- Thenardite, Na₂SO₄. 5- Calcium lead hydroxide CaPb(OH)₆. 6-PbS (?). 7-Na₂CO₃. 8- K₂SO₄. 9- Calcite (rhombohedral), CaCO₃. 10- Zincite, ZnO.**

4. Conclusions

In this study MW assisted alkaline roasting followed by water (alkaline) leaching was studied for the extraction of valuable and hazardous elements from goethite sludge.

First, we showed through comparing the mineralogy of CF roasted samples at different temperatures with MW roasted samples that samples absorb MWs during MW roasting and heat to a higher temperature than the temperature measured inside the muffle.

Roasting with both NaOH and KOH promoted the decomposition of franklinite to ZnO and NaFeO₂ and KFeO₂, respectively. However, using MW hybrid technology, the processing time and associated energy consumption can be significantly decreased.

Applying 400 °C MW NaOH roasting a franklinite conversion of about 84% was reached. Franklinite decomposition further improved upon increasing the MW roasting temperature to 450 °C.

It was shown that ZnO dissolution in water from the roasted material required a high pH≈14, which was not reached when leached with Milli-Q water at L:S = 10. However addition of extra alkali salt to the leaching solution at L:S=10 or decreasing of the L:S to 2 upon vigorous stirring allowed for complete ZnO dissolution. The latter method consumes less alkali, *i.e.* an alkali salt to goethite weight ratio of 1:1.

Sodium hydroxide gave better leaching performances for Zn and Pb than potassium hydroxide. We showed that KOH roasting promotes the formation of soluble manganate and subsequent precipitation of MnO_2 in the leachate, which consumes OH^- anions and consequently lowers the leachability of Zn and Pb. Zn was most efficiently leached (87±3%) from goethite sludge after NaOH MW roasting at 450 °C followed by water leaching (L:S=2, RT, 30 min).

The developed alkaline leaching system inhibits the dissolution of the main matrix elements of goethite, Ca and Fe. However, a considerable amount of Fe and Ca compounds are converted to (hydro-)andradite during the process. Arsenic could be extracted quantitatively, but the optimal Pb (best 38%) and Cd (<200 ppb) extractions are not satisfactory and need further study to completely valorise the goethite mineral fraction.

The main bottleneck of the studied system is the high alkali to goethite material ratio equal to one, which is too elevated for an economic application on large scale. This drawback necessitates a study into further process optimisation and an efficient metal recovery process from the leachate, such as electrowinning, and subsequent re-use of the alkaline source.

5. Acknowledgements

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