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Leaching of niobium- and REE-bearing iron ores: Significant reduction of H_2SO_4 consumption using SO_2 and activated carbon

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ABSTRACT

An innovative process was developed for the leaching of niobium- and rare earth elements-bearing pyrochlores ores and the subsequent separation of Nb from the REE. Compared to the conventional Nb hydrometallurgical methods, the proposed leaching process is based on a triphasic system: $\text{H}_2\text{SO}_{4(\text{aq})}$ - $\text{SO}_{2(\text{g})}$ -activated carbon/ore. The implementation of this leaching step allows the selective dissolution of the non-valuable phases while significantly reducing the H_2SO_4 consumption. The results obtained in continuous operation, at the pilot scale, show a reduction of the sulfur consumption by 48% when compared to the classical H_2SO_4 pasting-roasting process. The presence of activated carbon, at concentration as low as 0.4% (w/w), was found to considerably fasten the dissolution reactions and allows optimizing the SO_2 utilization to a nearly quantitative rate. The triphasic leaching also affords concentrating the Nb stream which decreases the energy consumption of the down-stream operations and especially for the subsequent Nb-REE-bearing pyrochlores roasting step. The process was optimized at the laboratory scale and then tested in continuous operation for 15 days at a flow of 15 kg h^{-1} of dry equivalent of non-magnetic Nb-REE pyrochlore ore from the Gabonese *Mabounié* deposit and the equivalent of 8.25 kg h^{-1} of H_2SO_4 and 0.15 kg h^{-1} of activated carbon.

1. Introduction

Although not well known to the general public, niobium (Nb, $Z = 41$) has become essential to several Today's applications. Indeed, 90% of the Nb world-production is used to make low-doped niobium alloys, known as HSLA steels (*high-strength low-alloy* steels), that are key ingredients for gas pipelines, automobile structures and buildings or bridges backbones [1,2]. In a lesser extend (about 10% of the market), high-purity Nb compounds are also critical for the electronic industry, for jet engines manufacturers and for various supraconducting magnets applications such as the medical *Magnetic Resonance Imaging* instruments and also the research nuclear fusion reactors or particles accelerators like ITER [3–6]. About 99% of the Nb produced worldwide is extracted from pyrochlores-type minerals that are refractory rocks of general formula $\text{A}_{1 \leq x \leq 2}\text{B}_2\text{O}_6(\text{O}, \text{OH}, \text{F}) \cdot n\text{H}_2\text{O}$ (with $\text{A} = \text{REE}, \text{Ba}, \text{Bi}, \text{Ca}, \text{Cs}, \text{K}, \text{Na}, \text{Pb}, \text{Sb}, \text{Sn}, \text{Sr}, \text{Th}, \text{U}, \text{Y}, \text{Zr}$ and $\text{B} = \text{Fe}, \text{Nb}, \text{Sn}, \text{Ta}, \text{Ti}, \text{W}$) [7,8]. Consequently, most of the Nb ores currently exploited contain other valuable elements and, in particular, rare earth elements (REE) and tantalum. Like niobium, REE are also strategic elements for producing most of the critical items for the industry including, among others, permanent magnets, display phosphorous, oil refining catalysts,

optic and electronic components, etc. [9,10]. Thanks to the increasing use of electronic devices, the development of REE-based LED and the growing demand for renewal energy production based on solar panels and wind turbines, the REE markets has been expanding year after year and particularly for Nd, Eu, Tb, Dy and Y [10–12].

Besides the presence of several valuable elements, the Nb-bearing ores also contain a large amount of impurities, among which iron plays a central role. The currently exploited niobium raw ores typically contain 5–18 kg of Nb per ton of ore [8]. As a consequence, hydrometallurgical or pyrometallurgical processes are necessary to extract and purify the valuable elements from this type of raw materials. Current industrial processes for producing HSLA products (~90% of the Nb market) consist of two main parts. The first part of the process is a physicochemical enrichment of the natural ores using magnetic separations [13], flotation techniques and diluted HCl leachings. This first part allows obtaining primary concentrates containing typically 35% (w/w) of Nb. The second part of the process then consists of pyrometallurgical steps, usually aluminothermic reductions, which yield iron-niobium alloys [8,14]. These alloys, called ferrometallurgical, contain 60–70% (w/w) of Nb and can be directly sold on the market for the production of the final HSLA steels and their derivatives. The

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production of high-purity Nb compounds (~10% of the market) is currently achieved by hydrometallurgical processes using fluoride-based concentrated solutions [15]. A primary Nb concentrate is usually dissolved in a mixture of concentrated HF and H₂SO₄ or NH₄ and H₂SO₄ and then refined by solvent extraction using methylisobutyl ketone (MIBK) or octanol derivatives. The fluoride media have been investigated since the beginning of the development of the Nb industry because Nb is sparingly soluble in conventional mineral acids (HNO₃, HCl, H₂SO₄, etc.) and because separation from tantalum, which has almost identical chemical properties, can be obtained by liquid-liquid extraction processes based on fluoride complexes [16,17]. Nonetheless, the high toxicity of the fluoride solutions has pushed industrial companies and academic researchers to develop cleaner processes for the purification of Nb. The alkaline-based media currently represent one of the rare industry-relevant alternatives for the purification of Nb concentrates as we have recently reported [18]. For the REE, the extraction-purification processes are operated in milder conditions than the Nb valorization processes. The decomposition of natural REE ores or concentrates can be achieved in either acidic or basic media. The separation of the REE is then classically achieved in HCl or HNO₃ media by liquid-liquid extraction techniques [19]. The main industrial example of REE extraction process is the Chinese Bayan-Obo deposit. This world-class mine also contains a non-negligible amount of Nb but unfortunately this element is currently not recovered [20]. So far, there is no industrial process that can extract and purify both Nb and the REE from a natural deposit at the same time.

In this regard, the Gabonese deposit called *Mabounié* has caught growing attention for the past few years since it is a world-class niobium deposit which also contains a significant amount of REE (Table 1) [21]. The *Mabounié* deposit also contains other valuable elements like uranium, tantalum and scandium that can potentially be recovered as by-products [22–24]. A hydrometallurgical process has therefore been developed for the recovery and purification of Nb and the REE from the *Mabounié* ore. The down-stream part of the process, in which high-purity Nb₂O₅ is obtained from a niobium raw concentrate, has recently been described [18,25,26]. The development and optimization of the up-stream part of the process, which yields the recovery of the REE and the production of Nb raw concentrate from the *Mabounié* ore, are detailed in the present work.

The original flowsheet of the up-stream part of the hydrometallurgical process developed for the recovery of Nb and the REE from the *Mabounié* ore is given in Fig. 1. The first step of the process consists of reacting the non-magnetic ore with 96% H₂SO₄ and then roasting the resulting paste at 250–300 °C. This step aims at decomposing the refractory mineral pyrochlores that bear Nb and also the REE, Ta and U. The resulting calcinate is then leached with water so that Nb, REE, Ta and U are solubilized. Finally the third step selectively precipitates Nb and Ta from the REE and U by thermal precipitation. This critical step yields two main streams: (i) a low grade Nb solid which is then purified by caustic conversion and (ii) an acidic solution containing the REE and U which is further processed by liquid-liquid extraction or selective REE double-salt precipitation [18,25,27,28]. On the one hand, the main advantage of this hydrometallurgical process is that it does not require any fluorinated reagent and can be applied to both natural ores and Nb raw concentrates. On the other hand, the process requires a high amount sulfuric acid (about 1600 kg of H₂SO₄ per ton of ore). Another drawback of the process is that the pyrochlores roasting step has to be performed on the primary stream. This

Fig. 1. Simplified original flowsheet for the recovery of Nb, REE and U from the *Mabounié* ore [26].

negatively impacts the energy consumption of the process and dramatically increases the size of the roaster. Additionally, since the ratio H₂SO₄/ore required to decompose the pyrochlores is high, the acidity of the leaching solution, which contains U and the REE, can be as high as 3 mol L⁻¹, which hinders the subsequent recovery and purification of these valuable elements [29].

In the present paper, we report a significant improvement of the process by developing a leaching step based on a triphasic system: H₂SO_{4(aq)}-SO_{2(g)}-activated carbon (AC)/ore. This leaching step, implemented prior to the roasting step, allows reducing drastically the acid and energy consumption of the process and makes it economically and technically viable. Moreover, the strategy developed for the *Mabounié* deposit could be extended to other iron-niobium-REE minerals.

2. Experimental

2.1. Materials and methods

The composition of the non-magnetic ore used during this study is given in Table 1. The non-magnetic fraction was obtained after ore pretreatment consisting in ore crushing, gravimetric and magnetic separation and sieving. Concentrated H₂SO₄ solutions (96.0%; Sigma Aldrich), I₂ solutions (0.5 mol L⁻¹, Sigma-Aldrich), KI (99%, Sigma-Aldrich), Na₂S₂O₃ (99%, Sigma-Aldrich), NaOH (5 mol L⁻¹, VWR), Fe₂(SO₄)₃ (97%; Sigma-Aldrich), REE₂(SO₄)₃·xH₂O (Sigma Aldrich) were used without further purification. SO₂ (99.9%) was purchased from Air Liquid (France). Activated carbon (Ecosorb SP23) was supplied by JACOBI CARBONS (Sweden). This active carbon was wet 12 h in distilled water before being used in experiments.

Powder XRD spectra were collected using Cu K_{α1} radiation with a wavelength of 1.54053 Å. Diffraction patterns were obtained using a Panalytical X'Pert Pro diffractometer and identified with the software HighScore (Panalytical). Microprobe analyses were performed at

Table 1

Typical composition of the *Mabounié* non-magnetic ore. The niobium and total rare earth contents are highlighted in bold.

Element	Fe	Al	Ti	P	S	Nb	Ta	U	Σ REE	Sc	Nd	Eu	Tb	Dy	Y
Content	35 w/w	6.1 w/w	1.3 w/w	2.7 w/w	0.2 w/w	1.2 w/w	300 ppm	300 ppm	1.4 w/w	120 ppm	0.27 w/w	100 ppm	40 ppm	140 ppm	550 ppm

ERAMET Research using a Cameca SX100. Operating conditions were fixed at 15 kV and 20 nA. QEMSCAN® analyses were carried out at the ERAMET Research mineralogical service (France), using a FEI Quanta 650F SEM (Scanning Electron Microscope) platform with two BrukerXflash 30 mm silicon drift energy dispersive X-ray detectors. The software's used included iMeasure v. 5.2 for the data acquisition and iDiscover v. 5.2 for the spectral interpretation and data processing. The FieldImage measurement mode was used to collect X-ray data every 2.5 µm across the polished sample surfaces, with X-rays acquired at 10,000 total X-ray counts per spectrum. Qemscan database was calibrated using microprobe measurements for elemental deportment, and XRD identifications for mineral names. All the mineralogical results are joined to this work as [supporting information](#).

Al, Fe, P, S, Ce, La, Nd, Gd, Pr, Y and Nb concentrations were determined by ICP-OES using an iCAP 6000 series spectrometer (Thermo Scientific). Others REE (Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu), Sc and U were determined by ICP-MS using an Aurora M90 spectrometer (Brucker). Liquid samples were diluted in 2% HNO₃ for analysis. Solid samples were treated by peroxide fusion following by leaching with 25% w/w HCl. Quantitative analysis were performed at 308.215 nm, 238.204 nm, 177.434 nm, 180.669 nm, 446.021 nm, 333.749 nm, 410.945 nm, 336.224 nm, 371.029 nm and 313.078 nm spectral emission lines for Al, Fe, P, S, Ce, La, Nd, Gd, Y and Nb, respectively. The limits of quantification of our method were 0.5 mg/L in the initial aqueous sample and 20 ppm in the initial solid samples.

Iron(III) concentrations were determined according to the UV–Vis spectrophotometric method described by Afeworki and Chandravanshi [30]. Iron(II) concentrations were determined using a classical potassium dichromate potentiometric titration method. The free acidity, corresponding to the quantity of H⁺_(aq) available in the solution after reaction, was measured by classical NaOH titration after complexation of the metal ions with oxalate or EDTA. ORP measurements were performed with an ENDRESS-HAUSER rH 225 electrode (CPS12D, Ag/AgCl lead with Advanced Gel 3 mol·L⁻¹ KCl, AgCl free). The quantity of carbon in solid was measured by using carbon/sulfur analyzer (Horiba EMIA-320 V).

2.2. Experimental procedures

2.2.1. Determination of the SO₂ utilization

The experimental setup used for the determination of the SO₂ utilization is described in Fig. 2. A 2 L reactor was equipped with a titanium distributor allowing SO₂ bubbling. SO₂ feeding was performed with dedicated gas lines maintained above 25 °C to avoid liquefaction. A Fe³⁺_(aq) solution (100 g L⁻¹) was pumped into the reactor and the activated carbon was directly added at the beginning of the experiment. The reaction mixture was heated at 90 °C with a heating plate and stirred with an agitator consisting in a Rushton-type impeller, four

stirring blades forming a 45° angle with the bottom of the reactor and baffles in order to optimize the diffusion of the gas during the reaction. Fumes were condensed in a water-condenser and the excess of SO₂ was collected with a pump in a succession of two traps containing an I₂-KI caustic solution (0.1 mol L⁻¹ I₂, 0.1 mol L⁻¹ KI and 1 mol L⁻¹ NaOH). SO₂ was solubilized as HSO₃⁻ species in basic solution (Eq. (1)), which reacted with I₃⁻ to form SO₄²⁻ and I⁻ (Eq. (3)). The excess of iodine (I₂) was then measured by ORP titration using sodium thiosulfate reagent according to Eq. (4). The reactions occurring during the procedure are summarized as follows.

2.2.2. Ore acidic leaching

Typically, 200 g of non-magnetic ore and 0.08–8 g of activated carbon were introduced in a 2 L reactor and were mixed with water (510–830 mL). Sulfuric acid (100 to 170 g) was then slowly added under stirring in order to obtain a liquid to solid ratio of 3 or 4.6 mL g⁻¹. Once the targeted temperature (95 °C) was reached, SO₂ bubbling was turned on to get an ORP value of 200 mV with activated carbon. 20 mL aliquots were taken for further analyses. Samples and the slurry at the end of the test were centrifuged at 3000 rpm during 15 min. The solid was then washed three times with deionized water using a liquid/solid ratio of 10 mL g⁻¹ and centrifugation. The mass and the density of the filtrates and the solid were measured and a sample was kept for elemental analysis and Fe(III)/Fe(II) analysis.

2.2.3. Iron reduction

50 g of activated carbon were added to 500 mL of a 0.5 mol·L⁻¹ H₂SO₄ solution and heated at 95 °C. A 100 g L⁻¹ ferric sulfate solution was then added at a 3 mL min⁻¹ flow rate. Simultaneously, SO₂ bubbling was turned on (3.9 NL h⁻¹) as well as the pump to create vacuum and gas trapping. Samples from the main reactors and the two SO₂ traps were regularly collected for Fe(II), Fe(III), and S analyses.

2.2.4. Pasting, roasting and water leaching

300 g of ore or leached concentrate were slowly mixed with 500 g of sulfuric acid (1600 kg per ton of solid) using a spatula until the mixture became solid. The pasted solid was then roasting at 300 °C for 3 h in an oven. After roasting the solid was leached with water using a 1:1 ratio at 90 °C. After 2 h, the solid and the liquid were separated using the same procedure that of the ore acidic leaching. The solid was then

Fig. 2. Experimental setup used for the determination of SO₂ utilization.

washed three times with deionized water (liquid to solid ratio of 10 mL g⁻¹) and then centrifuged. The mass and the density of the filtrates and the solid were measured and a sample was kept for elemental analysis.

2.3. Calculation methods

2.3.1. Recovery yield

Recovery yields were calculated using liquid and solid analyses and according to the following formula:

$$\eta_M = \frac{m_{\text{solid after reaction}} * \%M}{m_{\text{solid after reaction}} * \%M + V_{\text{filtrate}} * [M]_{\text{filtrate}} + V_{\text{washing}} * [M]_{\text{washing}}} \quad (5)$$

With

$m_{\text{solid after reaction}}$: mass of dried solid obtained after reaction and washing,

$\%M$: the content of element M in the dried solid,

V_{filtrate} : the volume of filtrate obtained after reaction,

$[M]_{\text{filtrate}}$: the concentration of the element M in the filtrate,

V_{washing} : the total volume recovered from the three washes

$[M]_{\text{washing}}$: the average concentration of the element M present in the washing solution.

2.3.2. Mass loss determination

$$\text{Mass loss} = 1 - \frac{m_{\text{solid after reaction}}}{m_{\text{solid before reaction}}} \quad (6)$$

2.3.3. Dissolved iron reduction rate

$$\text{Fe}_{\text{rr}}(t) = \frac{[\text{Fe}^{2+}](t)}{[\text{Fe}^{2+}](t) + [\text{Fe}^{3+}](t)} \quad (7)$$

$[\text{Fe}^{2+}](t)$ and $[\text{Fe}^{3+}](t)$ refer to the concentrations of iron(II) and iron(III) in the filtrates at a time t , respectively. Fe_{rr} stands for the iron reduction rate, i.e. the percentage of iron present as iron(II) in the filtrates.

2.3.4. SO₂ utilization rate

2.3.4.1. For iron reduction tests.

$$\text{SO}_{2\text{utilization rate}}(t) = \text{Fe}_{\text{rr}}(t) \frac{2 * n_{\text{Fe}^{3+}}^{\text{added}}(t)}{n_{\text{SO}_2}(t)} \quad (8)$$

where

$\text{SO}_{2\text{utilization rate}}(t)$ stands for the percentage of SO₂ introduced in the reactor used to reduce iron(III) into iron(II) at a time t .

$n_{\text{SO}_2}(t)$ refers to the quantity (mole) of SO₂ introduced in the reactor at a time t . $n_{\text{Fe}^{3+}}^{\text{added}}(t)$ denotes the quantity (mole) of iron(III) introduced in the reactor from the mother liquor at a time t .

2.3.4.2. For ore leaching tests.

$$\text{SO}_{2\text{utilization rate}}(t) = \frac{2 * [\text{Fe}^{2+}](t) * V(t)}{n_{\text{SO}_2}(t)} \quad (9)$$

where

$V(t)$ refers to the volume of the solution at a time t determined using the following equation:

$$V(t) = \frac{m_{\text{total sample}}(t) - m_{\text{washed and dried solid sample}}(t)}{\rho_{\text{liquor sample}}(t)} * \frac{m_{\text{total}}(t_0)}{m_{\text{total sample}}(t)} \quad (10)$$

in which

$m_{\text{total}}(t_0)$ and $m_{\text{total sample}}(t)$ refers to the total mass of reagents introduced in the reactor at the beginning of the experiment and to the mass of the sample collected at a time t for analyses, respectively.

$m_{\text{washed and dried solid sample}}(t)$ denotes the mass of solid obtained after solid liquid separation of the sample and washing and drying of this solid.

$\rho_{\text{liquor sample}}(t)$ refers to the bulk density of the filtrate obtained after solid liquid separation of the sample.

3. Results and discussion

3.1. Effect of activated carbon

In order to reduce the acid and energy consumption of the pyrochlores roasting step, and of the global process in general (Fig. 1), a leaching step was developed. The simplest way to reach these goals is obviously to limit the quantity of material entering the pyrochlores roaster. This can be achieved if the minerals that do not bear the valuable elements (Nb and REE) are leached before the roasting step. In addition to the valuable Nb-REE pyrochlores, the main mineral phase contained in the *Mabounié* ore is goethite FeOOH [31–33] (supporting information), associated with other iron hydroxides (ferrihydrite). To simplify mineralogical descriptions, iron hydroxides will collectively be name as goethite, which is the only one that can be seen on XRD measurements (see supporting information). Taking into account the speciation of Fe(III) in sulfate media (Fig. S1), the pKa values of H_2SO_4 and the high acidity of the proposed leaching step, the decomposition of goethite follows Eqs. (11) and (12):

Combining Eqs. (5) and (6), the dissolution of goethite can be summarized as follows.

Though converting FeOOH into $\text{Fe}_2(\text{SO}_4)_3$ by reaction with H_2SO_4 consumes lot of acid (Eq. (13)), and seems counter-intuitive for reducing the acid consumption of the process, this solution was selected. Indeed, once converted into $\text{Fe}_2(\text{SO}_4)_3$, H_2SO_4 can be partially regenerated *in situ* by adding sulfur dioxide in the system (Eq. (14)). The addition of gaseous SO₂ triggers, after its solubilization, the reduction of iron(III) into iron(II) and regenerates one acid molecule for each iron atom.

The balanced equation for Eqs. (13) and (14) is given by Eq. (15). The addition of SO₂ and consequent reduction of Fe(III) can theoretically decrease by 33% the consumption of sulfur due to iron phases leaching, as shown by the difference between Eq. (13) and Eq. (15). Moreover, SO₂ is an intermediate product of the generation of H_2SO_4 and its industrial production is usually inexpensive [34]. The other advantage for a reducing-leaching of the iron phases in the case of Nb and REE ores is that these elements only exhibit the oxidation states V and +III in aqueous solution (also +IV for cerium), respectively, and cannot be reduced by SO₂ [10,15]. The leaching concentrate is consequently enriched in Nb and REE. The equations given above also suggest that two parameters can be used to follow the dissolution of the goethite grains. The first parameter is the weight loss of the ore and it is also a good indicator of the quantity of solid material that has to be processed in the down-stream steps i.e. it is a direct indicator of the energy consumption of the whole process. The second parameter is the reduction rate of Fe(III) which is also an indicator of the quantity of acid regenerated *in situ*.

Fig. 3. Influence of the leaching duration on the reduction rate of iron (solidlines) and on the ore weight loss (dotted lines). $T = 95^\circ\text{C}$. Liquid to solid ratio: 4.6 L kg^{-1} of ore. Activated carbon (AC): 4 kg ton^{-1} of ore (circles) or 0 (squares). Sulfuric acid: 850 kg/ton of ore. $\text{SO}_{2(g)}$ bubbling to reach an ORP of 200 mV vs Ag/AgCl in the presence of AC. In the absence of AC, the ORP of the solution was only about 400 mV .

Fig. 3 gives the ore weight loss and the reduction rate of Fe(III) as a function of time for a diphasic leaching $\text{H}_2\text{SO}_4\text{-SO}_2$ and for a triphasic leaching $\text{H}_2\text{SO}_4\text{-SO}_2\text{-activated carbon}$. Whether adding the catalyzer or not in the system, the ore weight loss reaches 55–65% for a leaching duration of 24 h. Hence, this represents a significant decrease in the energy consumption for the down-stream steps and especially for the roasting of the Nb- and REE-bearing phases. Under the conditions given in Fig. 3, the concentration of Nb measured in the filtrates was lower than 16 mg L^{-1} which corresponds to a loss of less than 2%. Moreover, it was observed that the addition of AC in the system has a tremendous effect on the kinetics of the reactions. The maximum ore weight loss was reached within 6 h in the presence of AC compared to more than 24 h without catalyzer. Additionally, the Fe(III) reduction rate reaches 100% in less than 2 h, in other words, the theoretical maxima for the H_2SO_4 regeneration can be reached when AC is added to the system, and more importantly, the leaching reactions occurs in a time scale that is compatible with large industrial operations.

The influence of the concentration of AC catalyzer, used for the leaching step, on the iron reduction rate was then studied (Fig. 4). The addition of AC was found to have a significant impact even for a concentration as low as 400 g per ton of ore (400 ppm). The results depicted in Fig. 4 clearly show the advantage of using a catalyzer for this type of leaching process. The main gain, in terms of iron(III) reduction, was observed for a concentration of 4 kg of AC per ton of ore. Higher concentrations of catalyzer did not yield any improvement, in terms of iron(III) reduction kinetic, which suggests that beyond this threshold

the reduction was primarily limited by the diffusion of SO_2 . This is thought to be due to the experimental setup used at this laboratory scale. It should also be noted that no significant difference was observed when using wood (CECA) or coconut activated carbon which are two main types of AC catalyzer available in bulk quantity (Fig. 5) [35–37].

3.2. Effect of the initial sulfuric acid concentration

Besides the ore weight loss, which is directly linked to the energy consumption of the process, the other important parameter is the acidity of the pregnant leach solution. Indeed, in the case of the process developed here, the pregnant leach solution (PLS) does not contain the elements of interest (Nb and REE) since the refractory pyrochlores, which bear the valuable elements, are only attacked during the following roasting step. Nonetheless, as detailed below (Fig. 9), a recycling loop can be implemented to use a sulfuric acid solution that contains the REE (after separation from Nb); and in that particular case, the PLS contains the REE and needs to be further processed. Whether considering the H_2SO_4 recycling loop or not, the PLS has to be either neutralized or purified by liquid-liquid extraction and in both scenarios a lower acidity is beneficial.

Fig. 6 gives the ore weight loss and the free acidity of the PLS for three different initial H_2SO_4 concentrations and for different reaction times. As expected, the higher the initial H_2SO_4 concentration, the higher the ore weight loss due to the better attack of the goethite minerals (Eq. (13)). Although counter-intuitive, the use of a higher

Fig. 4. Influence of the concentration of carbon active used during the leaching on the reduction rate of Fe(III). Concentration of AC as indicated on the graphic. $T = 95^\circ\text{C}$. Liquid to solid ratio: 4.6 L kg^{-1} of ore. Sulfuric acid: 750 kg t^{-1} of ore. $\text{SO}_{2(g)}$ bubbling to reach an ORP of 200 mV vs Ag/AgCl . In the absence of AC, the ORP of the solution was about 400 mV .

Fig. 5. Influence of the nature of the activated carbon used during the leaching on the reduction rate of Fe(III). Activated carbon (AC): 4 kg ton⁻¹ of ore. AC from coconut (green) or wood (black). T = 95 °C. Liquid to solid ratio: 4.6 L kg⁻¹ of ore. Sulfuric acid: 750 kg ton⁻¹ of ore. SO_{2(g)} bubbling to reach an ORP of 200 mV vs Ag/AgCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

H₂SO₄/ore ratio does not necessarily yield a higher acidity for the PLS. In fact, as explained above, the combination of the goethite dissolution reaction and the reduction of Fe(III) (Eq. (9)) consumes H₂SO₄. Hence, the acidity of the resulting PLS is a balance between the initial quantity of acid, the dissolution yield of FeOOH and the reduction rate of Fe(III). The results given in Fig. 6 highlight that the use of 850 kg of H₂SO₄ per ton of ore affords a fast iron(III) reaction kinetic and a high ore weight loss while keeping the acidity of the PLS relatively low which facilitates its processing, in the downstream steps, to recover the REE that it may contain.

3.3. Optimization of the SO₂ utilization rate

In order to evaluate the effect of AC on the SO₂ consumption, experiments were performed on synthetic solutions of sulfuric acid containing iron(III). All gaseous vapors were collected and analyzed using an alkali-iodine trap in order to determine the gas mass balance. The SO₂ utilization rate was calculated according to the formula given in Section 2.3. Fig. 7 gives the SO₂ utilization as a function of the AC concentration in the system. Whereas less than 50% of the initial gas quantity is used for reducing Fe(III) when using a biphasic system H₂SO₄-SO₂, the addition of activated carbon at concentration of 10–25 kg t⁻¹ of ore increases the SO₂ utilization rate to about 90%. The data obtained on synthetic solutions also corroborate that obtained with real industrial solutions (Fig. 7). These results clearly show the

advantage of using activated carbon as a higher SO₂ utilization rate allows down-sizing the leaching unit.

The influence of the SO₂ flowrate on its utilization rate was also studied (Fig. 8). As observed above, the use of a triphasic system H₂SO₄-SO₂-AC more than doubles the SO₂ utilization rate when compared to a biphasic system without activated carbon. More importantly, a very high gas utilization rate was obtained over a large SO₂ flowrates range.

It is worth mentioning that the SO₂ flowrates range tested on synthetic solutions (Fig. 8) largely exceed the typical SO₂ flowrates used at the industrial scale. Since the SO₂ utilization rate decreases as the SO₂ flowrate increases, a SO₂ utilization rate higher than 90% could be expected after scaling up the leaching step to its industrial size. The results depicted in Figs. 7 and 8 therefore confirm the advantages of this type of triphasic systems for the leaching of iron ores.

3.4. Proposal of a catalytic mechanism

Before considering a catalytic mechanism, it must be proved that the activated carbon serves as a catalyzer and not a reductant. This was achieved using two different points. Firstly, during ore acid leaching tests, the activated carbon was mixed with ore in acidic conditions and the mixture was heated up to 95 °C. At this time and before starting the SO₂ injection, a sample was taken and revealed that the iron leaching has started (typically [Fe³⁺] = 25 g L⁻¹) but not the reduction ([Fe²⁺] < 0.5 g L⁻¹). Thus, the reduction seems requiring the

Fig. 6. Influence of the initial concentration of H₂SO₄ (kg t⁻¹ of ore; as indicated on the graphic) used for the leaching on the free acidity of the filtrates (solid lines) and on the ore weight loss (dotted lines) for different reaction times. T = 95 °C. Liquid to solid ratio: 4.6 L kg⁻¹ of ore. Activated carbon: 4 kg t⁻¹ of ore. SO₂ bubbling to reach an ORP of 200 mV.

Fig. 7. SO₂ utilization rate as a function of the concentration of activated carbon (AC). Synthetic solution (diamonds) or industrial solution (square). Initial synthetic solution at $[\text{Fe}] = 100 \text{ g L}^{-1}$, $t = 5 \text{ h}$ and $T = 90^\circ \text{C}$. $t = 12 \text{ h}$ for the industrial solution. The AC concentration was converted from kg t^{-1} of iron into kg t^{-1} of ore using the iron content of the *Maboumié* ore (35% w/w).

Fig. 8. SO₂ utilization rate as a function of the gas flowrate and in the presence (squares) or absence (diamonds) of activated carbon catalyst. Initial synthetic solution at $[\text{Fe}^{3+}] = 100 \text{ g L}^{-1}$, $t = 5 \text{ h}$ and $T = 90^\circ \text{C}$.

Fig. 9. Simplified flowsheet proposed for the recovery of Nb, REE and U from the *Maboumié* ore. The entire process was tested at the pilot scale. The recycling of the U and REE solution into the leaching step is depicted with dotted lines.

Table 2

Carbon mass balance of test presented on Fig. 4 for 4 kg of AC per ton of non mag ore.

	AC	Non mag ore	Leaching concentrate	Mass balance ^a
Quantity (g)	0.80	200.0	121.2	/
% of C	86.0%	< 0.01%	0.61	/
Quantity of C (mg)	688	< 20	744	105%

^a Output/entry.

injection of SO₂. To confirm that the activated carbon was not consumed during the tests, the activated carbon was recovered at the end of the ore acid leaching test (4 kg of AC per ton of non mag ore, Fig. 4) together with the leaching concentrate. A carbon mass balance was performed revealing that the carbon was not consumed during the experience (Table 2) and so CA was a catalyzer.

Once the role of catalyzer confirmed for the activated carbon, it was possible to propose a mechanism. It can be supposed that the dissolved HSO₃[−] according reaction (Eq. (1)) was adsorbed on activated carbon according to Eq. (16), where the reduction of iron according Eq. (17) took place.

where W and $\dot{W}$ refers to a free active site and to an occupied active site of activated carbon, respectively.

3.5. Validation at the pilot scale

In order to validate the leaching process developed at the laboratory scale, a continuous running test was performed at the pilot scale. Due to the presence of uranium in the ore, the pilot test was performed at AREVA Mines' facility located at Bessines sur Gartempe (FRANCE). The process was operated for 15 days under steady-state conditions using an feed flow rate of 37.5 kg h^{−1} of non-magnetic *Mabounié* ore at 40% w/w in water (15 kg h^{−1} of dry equivalent non-magnetic ore), further diluted with 10 kg h^{−1} of water, for a total primary flow of 47.5 kg h^{−1}. The leaching step was performed in five reactors of 80 L at 95 °C, at atmospheric pressure and using a residence time of 10 h. The non-magnetic ore, the highly concentrated sulfuric acid solution (96%) and solid activated carbon were added in the first reactor in order to obtain the equivalent of 550 kg of H₂SO₄ and 10 kg of activated carbon per ton of non-magnetic ore. Gaseous SO₂ was bubbled and dispersed in the slurry

Fig. 10. Average values of iron, iron(III), acidity and reduction rate measured during the pilot campaign without recycling in the three reactors used for the leaching step.

Table 3

Dissolution yields and composition of the pregnant leach solution (PLS) with and without implementing the recycling of the filtrates coming from the thermal precipitation step. See Fig. 9 for the corresponding process flowsheet. The dissolution yields obtained with the developed process are highlighted in bold.

Element	Fe	Al	P	Nb	U	REE	[H ⁺]
Non-magnetic ore (% w/w)	35	6.1	2.7	1.2	0.030	1.4	/
Element/Nb in ore (g g ^{−1})	29.4	5.1	2.3	/	0.025	1.2	/
<i>Without recycling of the thermal precipitation filtrates</i>							
Leaching concentrate (% w/w)	18.5	5.6	3.7	1.9	0.023	1.9	/
Element/Nb in concentrate (g g ^{−1})	9.8	2.9	1.9	/	0.016	1.0	/
Separation factor relative to Nb	3.0	1.7	1.2	/	1.6	1.2	/
PLS (g L ^{−1})	68	11	4	0.050	0.078	0.240	0.4
Dissolution yield (%)	65	40	25	< 1	55	10	/
<i>With recycling of the thermal precipitation filtrates</i>							
PLS (g L ^{−1})	64	16	6	0.100	0.081	2.60	0.4

Table 4

Sulfur consumption (as H₂SO₄ or SO₂) for the different parts of the process designed for the recovery of Nb, REE and U from the *Mabounié* ore. Direct roasting: as in Fig. 1.

Configuration	Direct roasting ^a	Tri-phasic leaching without recycling ^b	Tri-phasic leaching with recycling ^b
S consumption (kg t ^{−1} of non-magnetic ore)			
Leaching (H ₂ SO ₄)	/	180	50
Leaching (SO ₂)	/	65	65
Pasting (H ₂ SO ₄)	520	160	160
Total S consumption	520	405	275
Energy needs comparison			
Mass of pasted material per ton of ore (kg t ^{−1})	2600	1200	1200
Comparison of the roasting energy needs ^c	100%	46%	46%

^a Process described in Fig. 1.^b Process described in Fig. 9.^c Estimated.

using Rushton blades in the three reactors to maintain an ORP of 200 mV (vs Ag/AgCl). The leach solid concentrate was then washed three times with 1 mol·L^{−1} H₂SO₄ solution using a liquid to solid ratio of 4 L kg^{−1} to ensure the complete removal impregnated solution. The flowsheet of the entire process tested during the pilot campaign is given

in Fig. 9.

During the first 5 days of the campaign, the recycling loop (dotted lines in Fig. 9) was not operated so that a nominal flow of 550 kg of H_2SO_4 per ton of non-magnetic ore was introduced at the leaching step. Since the acidity of the filtrates coming from the Nb thermal precipitation (down-stream step, see Fig. 9) step was comprised between 3.5 and 4.0 mol L^{-1} and such filtrate contained up to 5.5 g L^{-1} of REE, a recycling loop was implemented after 5 days of continuous running test. The filtrates coming from the thermal precipitation of Nb were re-injected in the first reactor of the leaching step. This recycling loop corresponds to 450 kg of H_2SO_4 per ton of non-magnetic ore so that the nominal consumption of H_2SO_4 was decreased to 100 kg per ton of non-magnetic ore. Moreover, the recycling loop allows enriching the PLS in REE, U and Sc since these elements do not precipitate under the conditions used for the thermal precipitation of Nb [18,38].

The Fe(III) reduction rate reached 100 (± 2)% throughout the 15 days of pilot test. Fig. 10 gives the average Fe(III) reduction rate measured in the three consecutive reactors of the leaching step without recycling. The acidity was maximum in the first reactor due to the introduction of sulfuric acid reagent where 30% of the iron of the non-mag ore was solubilized. The acidity decreased in the other two reactors to reach equilibrium at 0.4 mol L^{-1} because of the solubilization of iron (Eq. (13)). Reduction rate was already higher than 94% in the second reactor of the unit.

The average dissolution yields and composition of the leaching concentrate obtained during the pilot campaign are given in Table 3. Similar dissolution yields and leaching concentrate composition were obtained in both studied operating conditions. The average ore weight loss measured varied from 35 to 40% with an average of 37 (± 3)%, which is slightly lower than the results obtained in batch experiments at a smaller scale (Fig. 6). However, the results confirmed the significant ore weight loss that can be achieved when implementing the triphasic leaching step prior to the roasting of the Nb- and REE-bearing pyrochlores. The solid phase recovered after the leaching step was depleted in impurities (Fe, Al, P and U) and enriched niobium and REE, with the highest separation factor relative to niobium measured for iron. The loss of valuable elements in the PLS was limited to less than 1% for Nb and the dissolution rate for the REE was 10% due to inclusion of REE in the goethite phases (see supporting information). This apparent loss can actually be recovered if the filtrates recycling loop is implemented, as detailed in Fig. 9. The acidity of the REE and uranium PLS was 0.4 mol L^{-1} whether the recycling loop was implemented or not. The PLS acidity measured during the pilot campaign was lower than the results obtained at the laboratory scale (Fig. 6). This is thought to be due to a better mixing and solubilization of $\text{SO}_{2(g)}$ at the pilot scale when compared to the laboratory scale experiments. Processes for the recovery and purification of the REE and U from this type of sulfate solutions have been proposed elsewhere [24,25]. Similarly, an innovative hydrometallurgical route has been recently proposed for the purification of niobium from the intermediate solid concentrate obtained after the thermal precipitation step depicted in Fig. 9 [18].

4. Conclusions

A triphasic leaching step was developed for the selective dissolution of the iron phases of Pyrochlore ores containing niobium and rare earth elements. The leaching step, based on the use of concentrated H_2SO_4 , gaseous SO_2 and activated carbon, allows dissolving the iron hydroxide phases (mainly goethite) selectively from the Nb- and REE-bearing pyrochlores. The selective dissolution of the non-valuable phase reduces the amount of material entering in the down-stream steps (especially the roasting of the pyrochlores) and ultimately decreases the energy consumption of the whole process. The addition of $\text{SO}_{2(g)}$ in the system reduces the dissolved Fe(III) species into Fe(II) and affords the partial *in situ* regeneration of H_2SO_4 . A summary of the H_2SO_4 and SO_2 consumptions of the new process is given in Table 4. The introduction

of the triphasic leaching steps decreases the total sulfur consumption from 522 to 275 kg t^{-1} of ore. Moreover, the presence of activated carbon catalyzer at a concentration of 10 kg t^{-1} of non-magnetic ore drastically improves the kinetic of the Fe(III) reduction affording an industry relevant system compared to the original process using a bi-phasic leaching system. The triphasic leaching step was successfully tested in continuous operation and at a pilot scale on the *Mabounié* Gabonese ore. Considering the energy requirements for the roasting, they are in first order proportional to the amount of pasted material that needs to be roasted (ore or leach concentrate + acid). A comparison of the mass of pasted material revealed a decreased of more than 50% of the mass to be roasted that can be converted in a decreased in the energy consumption of the same order of magnitude.

A flowsheet for the selective recovery of niobium and the REE from the *Mabounié* deposit is proposed in Fig. 9 and represents a significant simplification compared to the initial *Mabounié* process (Fig. 1). The hydrometallurgical process described in this work, combined with the down-stream parts already published [18,25], offers an innovative route for the recovery and purification of Nb-REE from pyrochlore ores, and so, without using any fluorinated reagent.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2017.07.073>.

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