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Original scientific paper

Electrolytic iron production from alkaline suspensions of solid oxides: compared cases of hematite, iron ore and iron-rich Bayer process residues

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Abstract
Iron can be produced by the direct electrochemical reduction of hematite particles suspended in hot, concentrated NaOH solutions. Because various other iron sources can be considered, the present work was aimed at investigating the electrolytic treatment of the "red mud" generated by the Bayer process for alumina preparation from bauxite. Such sources contain very high amounts of impurities, in particular silicon and aluminium oxide-based minerals, in addition to other mineral phases. Electrolytic reductive treatment of the industrial red mud sample was shown to be possible but with both lower current density and current efficiency than for pure hematite. After deposition tests at a fixed current density, further experiments in simulation tests have been carried out for better understanding. In particular, hematite particles were tested with and without impurities introduced in the solution. Presence of little soluble impurities at the particle surface appear to hinder the reactivity of the suspended particles at the cathode surface, whereas side-hydrogen reaction still occurs.

Keywords
Iron production; electrodeposition; iron ores; red mud; surface reactivity.

Introduction

Iron production by reduction of hematite or other iron oxides by coal carbon at high temperature is per se a significant source of CO_2. Although reported decades ago, the electrolytic alternative has appeared an attractive secondary way for iron production with far lower CO_2 emissions and possibly lower energy demand per ton of iron produced. Most works conducted until recently concerned the direct reduction of hematite (α-Fe_2O_3) particles suspended in a hot concentrated alkaline solution [1-6]. It was shown that the reduction of trivalent iron proceeds through a particular pathway with formation of intermediate magnetite only upon direct contact of the hematite particle with the cathode: metal iron can then be produced from concentrated suspensions of hematite in 50 wt.% NaOH at 110 °C at 1000 A/m^2 with a current efficiency near 80 %. This particular mechanism involves the adsorption of hematite particles on the cathode surface, as shown by zeta potential measurements in such concentrated NaOH media, and complementary electrochemistry tests [7,8]. Direct reduction of dissolved Fe(III) at concentrations at a few 10^{-3} M also occurs but at far lower current density and with poor current efficiency [2], corresponding to production rates far lower than that through the above solid-solid electrochemical reaction.

Because hematite can be considered as an already refined, reactive iron-containing mineral, other iron oxides e.g. goethite [9] and magnetite [9,10] have been tested for electrolytic production of metal iron. As a matter of fact, the equilibrium – thermodynamic - cell voltage for the reduction of the above metal iron oxides at 110 °C were calculated to be at 1.25 V ± 50 mV [11] depending on the iron oxide. Nevertheless, tests conducted at similar electrolyte composition, temperature and cell voltage led to the following performance: Hematite > Goethite >> Magnetite for both the cell current and the current efficiency. Apart from the various existing iron oxides, the cases of rawer materials such as iron ores before removal of the gangue after their extraction has also been studied [11]. Feeding the electrolytic cell with iron ore concentrate particles in the alkaline medium would avoid the stage for gangue dissolution, then reducing the cost of electrolytic iron production. With concern to iron-containing waste, the waste of Bayer process for purification of bauxite – often called “red mud” - represents a huge potential source of iron since its contents in hematite vary from 35 to 60 %, depending on the process conditions and on the bauxite ores considered [12]. In addition to their very high production rate at approx. 70 million tons per year, the alkaline feature of the concentrated suspensions of iron mud, which should be disposed of, represents a potential hazard to environment, as observed by the ruptures of lagoon dams in Hungary and in Brazil in the last decade [13]. Despite various works and processes developed for the valuable use of red mud [12], their year production rate largely exceeds that of their use in industry.

We investigated here at the lab scale the potential of the electrochemical reduction of red mud suspension, making profit of their alkaline nature in the preparation of the strongly alkaline electrolytic medium. The manuscript presents the electrolytic treatment of this solid after thorough characterization of the mineral phases contained, with their potential and limits, in comparison to the “ideal” case of hematite.

Experimental section

Chemicals used

Sodium hydroxide solutions have been either taken from VWR Prolabo Chemicals 47–51 wt.% solutions of by dissolution of VWR sodium hydroxide pellets, in both cases without further purification. More dilute solutions have been prepared by dilution of mother NaOH solutions. Hydrochloric and nitric acids respectively at 37 and 65 wt.% were analytical grade solutions from VWR or EMSURE.

Sodium metasilicate as a solid powder was from Alfa Aesar and kaolinite (Al_2O_3 $2SiO_2$, $2H_2O$) also solid was a technical VWR Prolabo product.

Two raw materials that can be suitable for iron production by electrolysis in an alkaline medium have been used:

- Commercial Hematite (VWR), *i.e.* α-iron oxide Fe_2O_3;
- Red mud samples (Alteo, France) recovered after production of alumina from bauxite by the Bayer process by partial dissolution of silica and silicocaluminates in 15-25 wt.% NaOH liquors at temperature and pressure up to 200 °C and 20 bars, respectively.

Lab-scale electrolytic cells and deposition tests

Because of the presence of suspensions of little soluble particles, electrodeposition experiments have been carried out with thorough stirring of the medium by a 3.5 cm magnet at 600 rpm in a cylindrical double walled reactor with oil recirculation via a thermostated bath (Huber). The volume of the reactor was equal to 0.8 L. The 19.4 cm^2 graphite cathodic rod was surrounded by a Ti/Pt grid (area near 150 cm^2), allowing fairly uniform deposition rate on the cathode surface.

The electrochemical reduction of the red mud sample was compared to the reference case of commercial hematite conducted in the same cell. Temperature was fixed at 110 ^oC under steady nitrogen stream for all experiments. Red mud (150 g) was suspended in 450 mL 12.5 M NaOH solution: the appreciable alkali content of the red mud partly compensated the NaOH concentration here somewhat lower than that in former works [2-4,9]. Runs were carried out a fixed current using a Bio-Logic SP150 Potentiostat coupled to a 10 A booster (Bio-Logic).

After deposition, the cathode was carefully rinsed with deionised water, then dried with a paper cloth and weighted. Eventually the deposit was detached from the graphite rod and submitted to microscopic observations and analysis (see following section). Current efficiency was estimated from the weight of the solid recovered: as a matter of fact, the deposits were shown to consist of iron at more than 97 wt.%, which justified the estimation method. Most tests were replicated: deviations below 5 % were usually reported for the current efficiency.

Characterization techniques of the solids

Particle size distributions of the solid phases investigated have been measured using a granulometer with laser diffraction (Mastersizer 2000, Malvern Ltd): hematite particles consisted of fines with a diameter in the order of one micrometre or below, and larger particles with an average size near 15 µm (Figure 1). The red mud investigated had a very broad size distribution, from less than 1 µm up to 300 µm or so for agglomerates of appreciable mechanical stability (Figure 1).

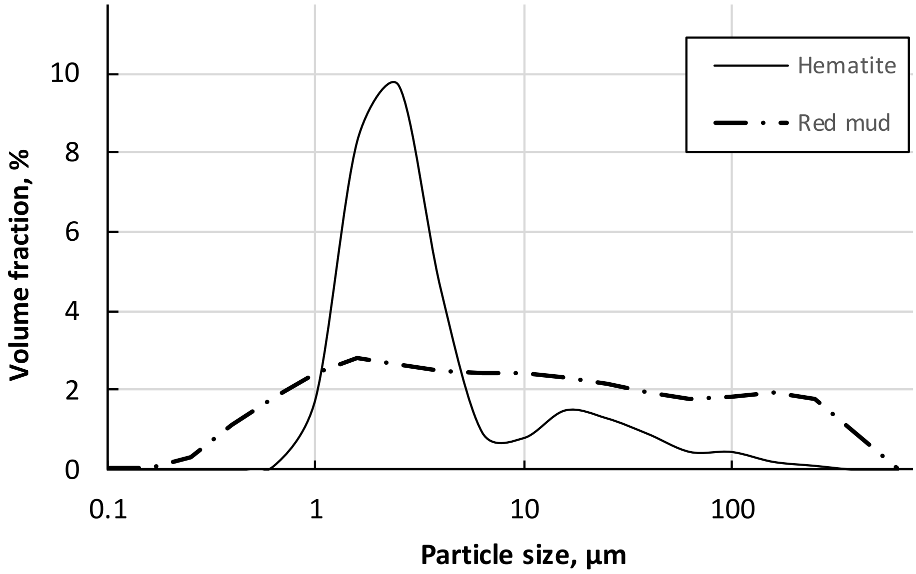

Figure 1. *Particle size distribution of the two Fe-rich solids investigated*

Chemical characterization of the two materials have been conducted either by X-Ray fluorescence or by ICP-OES (Agilent Technologies, S100) analysis of the liquid solutions produced after alkaline fusion with lithium salts ($LiBO_2$ and $LiBO_3$) at 1050 °C and dissolution into nitric acid.

Identification of the various phases present in the two solids was conducted by X-Ray diffraction with use of Topas® Software for quantification. The metal deposits were observed by SEM-EDX (JSM-6490, JEOL Ltd) and XRD (Bruker D8 Advance), respectively for chemical analysis of the surface and phase identification, in complement to quantitative XRD and ICP analysis.

The equivalent viscosity of suspension of red mud in alkaline media was measured by using a Brookfield viscosimeter.

Chemical and phase composition of the solids tested

The weight contents in the various metals or elements have been expressed as their oxide contents in Table 1. Titanium is very significant in the red mud and Ti-oxide minerals contained in the starting bauxite are very little soluble in alkaline media. The appreciable amounts of sodium, calcium and potassium in the red mud, can originate from the Bayer treatment. Finally, vanadium, a transition metal with multiple valences was also found and assayed in the red mud fraction.

Table 1. *Weight contents of the various elements (in their oxide equivalents) in the solids. The sum of the contents can slightly differ from unity*

	Content, wt.%								
	Fe_2O_3	SiO_2	Al_2O_3	CaO	TiO_2	Na_2O	K_2O	MnO_2	V_2O_5
Hematite	98.67	0.08	0.21	0.22	0.04	-	-	0.36	-
Red mud	52.7	4.19	13.9	4.1	7.40	2.10	14.0	-	0.28

Iron is mainly in the form of hematite in the two fractions investigated. Presence of goethite is visible in the XRD spectra of the red mud (Figure 2). Quartz (silica) is also present in the red mud. Aluminium contained in the red mud was in the form of cancrinite - $Na_8(Al_6Si_6O_{24})(OH)_{2.04}$, $(H_2O)_{2.66}$- and liottite $(Na, Ca, K)_{24}(SiAl)_{36}O_{72}(SO_4ClF)_{10}$ (Figure 2).

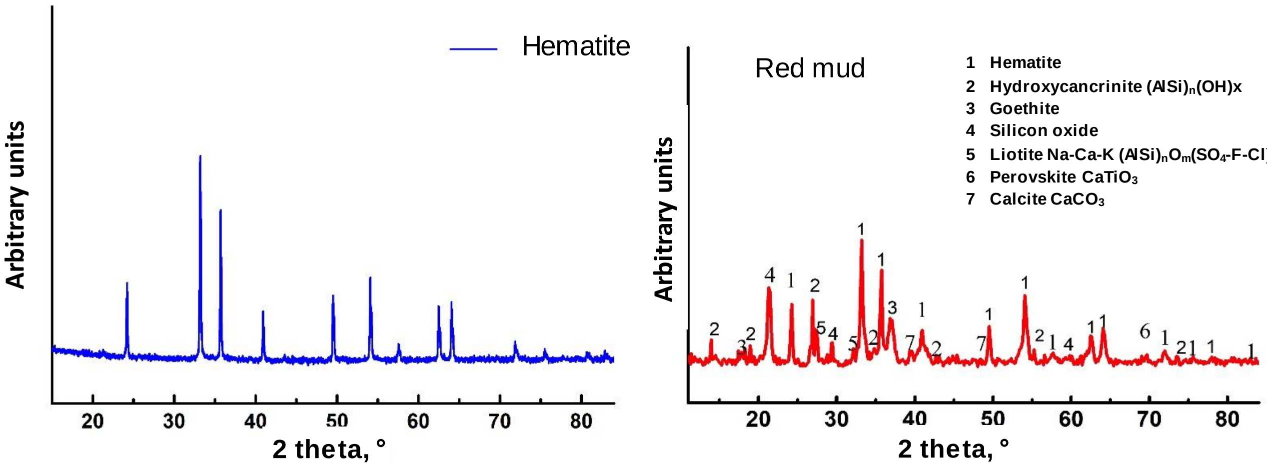

Figure 2. *XRD spectra of the two Fe-rich solids investigated*

Presumably, these two crystalline aluminates were formed from kaolinite, or mixed aluminates and silicates contained in the native bauxite through formation of an amorphous phase. This phase rapidly dissolves while forming crystalline phases, *e.g.* cancrinite whose solid entities gradually mature in the alkaline solution during the Bayer process [15,16]. Calcium in the red mud is also visible as calcite and calcium titanium oxide (perovskite) $CaTiO_3$, as shown in Figure 2.

Solubility of particular minerals in the electrolytic solutions at 110 °C and for various NaOH concentrations have been predicted by simulation using PHREEQC® software with Minteq.v4 database [14]. For this purpose, the chemical composition of the commercial hematite of the red mud sample (Table 1) was used.

Results and discussion

Deposition tests from red mud and hematite

First deposition tests from red mud suspensions were done at 1000 A/m^2 and led to faradaic efficiencies in the order of 20 %. Tests with other red mud samples produced in Canada and South Korea led to comparable results, in spite of the partly different natures of impurities (data not shown). It was then preferred to test lower current density levels: as shown in Figure 3, the faradaic efficiency of Fe deposition from red mud suspension decreases with the current density, peaking at 71 % at 45 A/m^2: although fair, this result corresponds to very low production rates from the metallurgical waste. In comparison, hematite particles suspended in a 12.5 M NaOH solution can be reduced to iron with a current yield larger than 80 % for current density in the range 200 - 1000 A/m^2. The poor performance of Fe deposition exhibited by the red mud is presumably related to the high contents of the various impurities (Table 1), most of them being crystallized minerals, *e.g.* cancrinite, calcite or calcium titanium oxide.

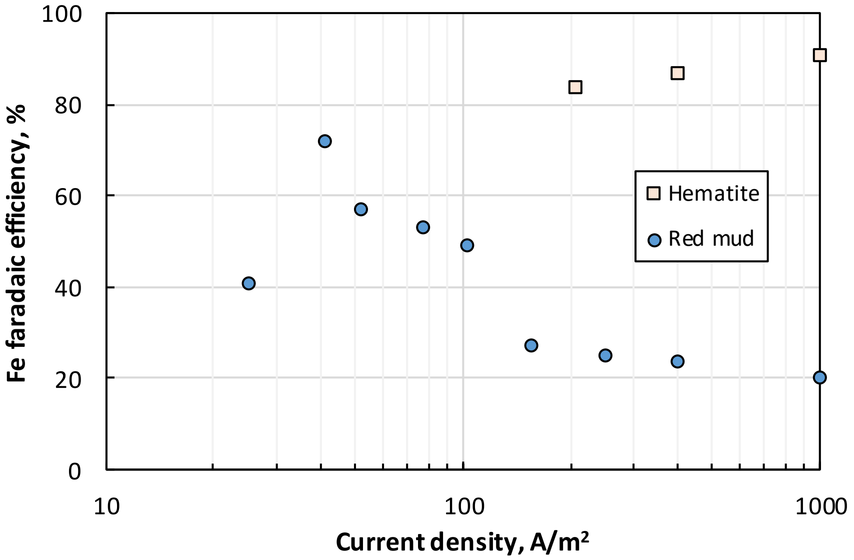

Figure 3. *Current efficiency of Fe deposition with hematite and red mud depending on the applied current density*

To conclude, the lower, but unequal performance exhibited by the two solids led us to investigate its possible causes. Presence of these impurities can affect the reduction efficiency through their inhibiting effect either at the solid surface (solid form effect), or after their dissolution into the electrolytic bath, that might lead to surface inhibition. Successive series of experiments have therefore been carried out for better understanding.

Dissolution of impurities into the electrolytic bath

Preliminary calculations with PHREEQC on the red mud sample together the results of XRD measurements led to consider the presence of hematite, goethite, cancrinite and perovskite for

NaOH concentration ranging from 1 to 12 M. The solubility of these various phases in the 12.5 M NaOH solution is shown in Figure 4, in comparison with that of kaolinite ($Al_2Si_2O_7,2H_2O$) Hematite and goethite were found to have a solubility near 2.3 10^{-3} and 1.5 10^{-3} M respectively, in good agreement with the experimental determinations reported in [2,9]. Solubilities of cancrinite, titania and calcium titanium oxide (perovskite) were predicted at 0.90x10^{-3}, 1.15x10^{-3} and 0.46x10^{-3} M. Thus, considering the high solid/liquid ratio used here, the three minerals can be considered as dissolving to insignificant extent. Kaolinite is actually highly soluble, with a solubility near 1.9 M under these conditions. These predictions have been made assuming that the mineral phases are accessible to the alkaline solution, and not entrapped in complex agglomerates by refractory solid phases. Traces of kaolinite remaining in the red mud after the Bayer process – not quantified – might dissolve in the course of electrodeposition tests. However, the single silicate and aluminate ions produced are also to crystallize in the formation of little soluble cancrinite and sodalite as explained above [15,16].

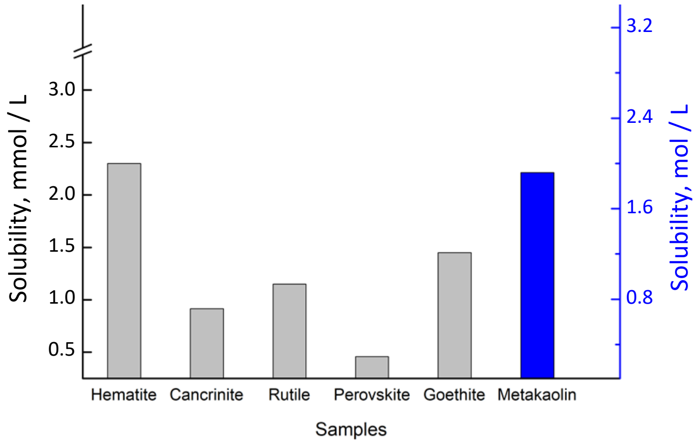

Figure 4. *Solubility of mineral phases present in the red mud samples placed in NaOH 12.5 M and at 110 °C*

Effect of introduced impurities in the electrolytic bath

The principle of this series of experiments is to perform the electrochemical reduction of hematite after addition of salt impurities contained in the red mud and to compare the run performance with the data obtained with pure hematite or with the less refined solids.

To emulate the solid, the effect of two impurities, namely silicoaluminates and vanadium, has been studied here. Vanadium ions have actually been reported as hindering the deposition of particular metals *e.g.* gallium [17] even at concentrations far below 1 g/L, presumably because of the capacity of vanadium to generate galvanic cells with antagonistic reactions at the two electrodes resulting in very poor production rates.

Kaolinite has been employed as silicoaluminate source. In both cases, impurities have been introduced in a concentration range exceeding the actual species content in the red mud. The presence of kaolinite reduced significantly the faradaic efficiency conducted at 41 A/m^2 (Figure 5a). This effect might be caused by the progressive formation of cancrinite and sodalite on the surface of the particles [18] – this could not be directly evidenced - then resulting in lower faradaic efficiency, found at 38 % upon addition of 30 wt.% kaolinite. Another effect of kaolinite addition is the significantly increased viscosity of the suspension, as shown in Figure 6: presence of 30 % kaolinite in the solid introduced made the suspension viscosity at 110°C increase from 2.8 mPa s to approx. 16 mPa s (Figure 6)

The effect of kaolinite addition has been also tested at higher current density (Figure 5b). With 10 wt.% kaolinite – a content in the order of that of (Si-Al)-based impurities, the faradaic efficiency was found at 62 and 70 % at 400 and 1000 A/m^2 respectively: although lower than the reference value without silicoaluminate, the faradaic efficiency is nevertheless far larger than that with the red mud investigated.

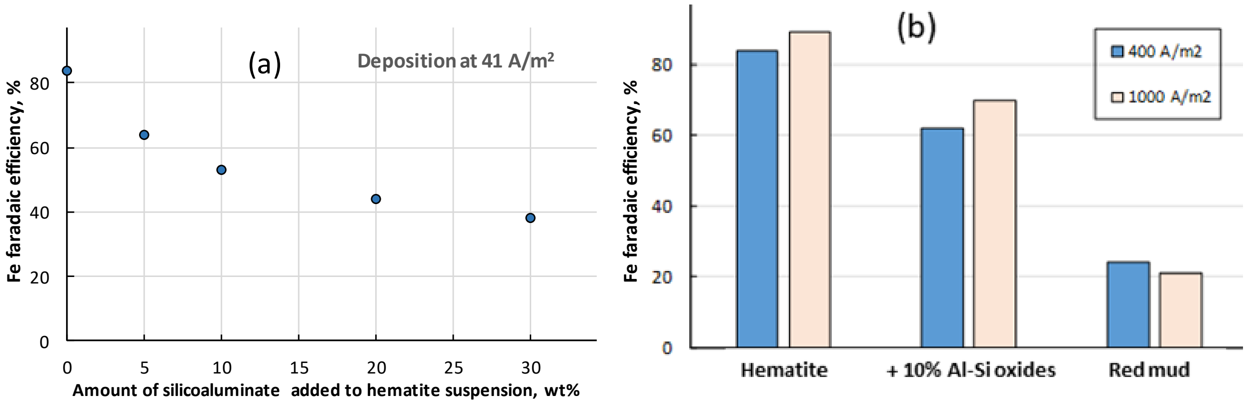

Figure 5: Effect of silicoaluminate added on the current yield for Fe deposition: (a) low current density; (b) at higher current density, with 10 % silicoaluminate, with comparison of data with hematite and red mud

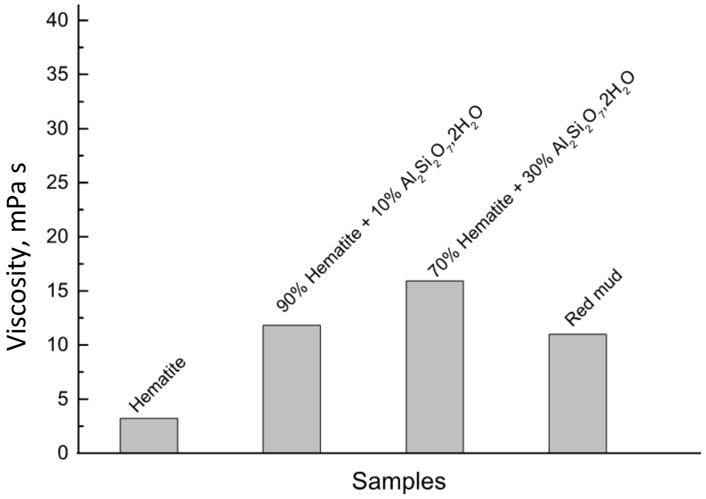

Figure 6: Equivalent viscosity of suspensions of solids (1 g / 3 mL solution) in NaOH 12.5 M at 110 °C.

Vanadium in the form of V_2O_5 was added at various contents to the electrolytic bath, with V element content ranging from 150 to 1500 mg/L. The lowest content did not really affect Fe deposition conducted at 1000 A/m^2, with faradaic efficiency near 85 %. Increasing vanadium concentration to 500 and 1500 mg/L resulted in slightly lower faradaic efficiency near 76 %. Although not favourable, the presence of vanadium species cannot actually explain the low deposition rates of iron with red mud.

Discussion and conclusion

Replacing hematite by less pure Fe-containing minerals can be considered, principally in view to cheaper processes for Fe electrodeposition from alkaline media, but the case study reported here clearly shows the poor potential of red muds for Fe deposition. The red mud sample considered for such electrolytic treatment is first less electrochemically reactive, and with far lower current efficiency. The presence of impurities in the solids investigated seems to act mainly on the surface reactivity, as formerly reported in [18]. It could be supposed that the presence of the Ti- and Si-oxides phases on the hematite particle surface would modify its zeta potential, then affecting the efficiency of particle adsorption on the cathode surface.

Whereas iron ores instead of refined hematite had been shown to be of interest for Fe deposition from alkaline media [11], beneficiation of red mud by an electrochemical route still appears difficult, principally because of the low reactivity of the solid particles and the huge cost for particle activation through dissolution of the refractory minerals present.

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References

[1] D. Oster, Electrochemical reduction of suspended iron oxides suspended in water-sodium hydroxide mixture (between 25 and 140 °C). Investigation of conditions for production of electrolytic iron, PhD dissertation, Univ. Paris [in French] (1979).
[2] A. Allanore, H. Lavelaine G. Valentin, J. Birat, F. Lapicque, *Journal of the Electrochemical Society* **154** (2007) E187-193.
[3] A. Allanore, Experimental study of the production of electrolytic iorn in alkaline media: mechanisms of oxides reduction and design of a cell. PhD dissertation, INPL Nancy [in French] (2007).
[4] A. Allanore, H. Lavelaine, G. Valentin, J. Birat, P. Delcroix, F. Lapicque, *Electrochimica Acta* **55** (2010) 4007-4013.
[5] B. Yuan, O. E. Kingstein, G. M. Haarberg, *Journal of the Electrochemical Society* **156** (2009) D64-D69.
[6] S. Gu, X. Zou, X. Lu, *Applied Mechanics in Materials* **595** (2014) 8-13.
[7] M. Siebentritt, P. Volovich, K. Ogle, G. Lefevre, *Colloids and Surfaces A: Physicochemcial and Engineering Aspects* **440** (2014) 197-201.
[8] A. Allanore, J. Feng, H. Lavelaine, K. Ogle, *Journal of the Electrochemical Society* **157** (2010) E24-E30.
[9] V. Feynerol, H. Lavelaine, P. Marlier, M. N. Pons, F. Lapicque, *Journal of Applied Electrochemistry* **47** (2017) 1339-1350.
[10] J. F. Moteiro, Y. A. Ivanova, A. V. Kovalesky, D. K. Ivanou, J. Frade, *Electrochimica Acta* **193** (2016) 284-292.
[11] V. Feynerol, Treatment of iron ores by alkaline leaching followed by their electrolysis in an alkaline medium. PhD dissertation, University of Lorraine [in French] (2018).
[12] Ab. Maihatchi, M.N. Pons, Q. Ricoux, F. Goettmann, F. Lapicque, submitted to *Journal of Environmental Management* (2019).
[13] W. M. Mayes, I. T. Burke, H. I. Gomes, A. D. Anton, M. Molnar, V. Feigl, E. Ujaczki, *Journal of Sustainable Metallurgy* **2** (2016) 332-343
[14] D. L. Parkhurst, K. L. Kipp, P. Engesgaard, S. R. Charlton, *Geochimica and Cosmochimica Acta* **69** (2005) Supplement S, A156-A156
[15] M. C. Barnes, J. Addai-Mensah, A. R. Gerson, *Colloids and Surface A: Physicochemical and Engineering Aspects* **147** (1999) 283–295.
[16] H. Peng, D. Seneviratne, J. Vaughan, *Industrial and Engineering Chemistry Research* **57** (2018) 1408-1416.
[17] L. Liu, M.Y. Wang, Z. Wang, Y. Zhang, *Hydrometallurgy* **146** (2014) 76-81.
[18] B. Rusch, K. Hanna, B. Humbert, *Colloids and Surface A: Physicochemical and Engineering Aspects* **353** (2010) 172-180.