Proceeding Paper

ΣIDERWIN—A New Route for Iron Production [†]

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Abstract: Iron and steel production contributes to ~10% of global CO_2 emissions. In recent decades, different scenarios and low-emission pathways have been taken up by steelmaking industries with the collaboration of universities and research institutes to tackle this problem. One of the most promising novel methods to replace the current steelmaking process is the low-temperature electrolysis of iron oxide. This technology is currently being developed under the H2020 ΣIDERWIN project, a European project led by ArcelorMittal, the world's leading steel and mining company. The ΣIDERWIN project aims at developing an innovative electrochemical process to transform iron oxide into steel metal plates. This process produces steel by electrolysis without direct CO_2 emissions. In this operation, electrical energy and iron oxide are converted into chemical energy consisting of separated iron metal from the oxygen gas. It is a disruptive innovation that entirely shifts the way steel is presently produced. One of the advantages of this process is the fact that, in addition to iron oxide (hematite), it is possible to feed this process with other iron-containing raw materials. An alternative raw material which is being studied to be used in this process is bauxite residue (BR), the waste material from the Bayer process for alumina production. The iron oxide of the conversion of bauxite residue to metallic iron is under investigation, and insights are showing that it could follow up the electrochemical route for sustainable iron production. This research deals with the effect of the current density and temperature on current efficiency comparing two different raw materials, pure iron oxide–hematite and bauxite residue.

Keywords: bauxite residue; iron production; sustainability; CO_2 emissions

1. Introduction

Climate change forces the world of metallurgy to take big steps towards sustainability. Steel production has made a lot of progress throughout the last decade, attempting to reduce CO_2 emissions and energy consumption through maximizing scrap use and developing advanced technologies. The possible solutions that have been proposed to address this problem are CO_2 capture, utilization and storage (CCUS), the replacement of carbon with hydrogen and, finally, an electrowinning method using electrical energy [1].

The present paper is focused on the third mentioned technique, an electrolysis-based process that started developing during the ULCOWIN (Ultra Low Carbon Dioxide in Steelmaking) program supported by the European Commission and the steel industry in Europe at the beginning of the 2000s [2,3]. This technology consists of low-temperature electrolysis that produces metallic iron from iron oxide, basically hematite. The raw material is suspended in a high-alkaline electrolyte solution of 50% *w/w* NaOH-H_2O. Iron oxide particles are reduced at low temperature around 110 °C, achieving high current efficiencies with an applied current density of around 1000 A·m^{-2} [4–7]. A lot of studies have been carried out and shown that this process is valuable for the future of iron production, and pilot plant construction is ongoing in terms of the ΣIDERWIN process, the evolution of the

aforementioned ULCOWIN technology. Even though the process is approaching sustainability, by using a by-product as a feed, the impact will be maximized. The ΣIDERWIN project also deals with the research of possible secondary raw materials that would be a great fit as an alternative for iron production.

Bauxite residue (BR) is a raw material with a high content of hematite (35–45%), and previous work has shown that it has great potential to evolve in the ΣIDERWIN process [4]. Bauxite residue is the by-product of the Bayer process, an established method for producing alumina from bauxite ore. The valorization of this by-product has gathered interest in recent years due to the large quantities that are generated every year and its content in valuable metals such as iron and rare-earth elements [5,8]. The current efficiency of BR alkaline low-temperature electrolysis has reached 70% at a current density of 138 $A \cdot m^{-2}$, a lower value compared to the optimized current for hematite at 1100 $A \cdot m^{-2}$ [9]. As a result, the quantity of metallic iron produced is lower, and there are indications that the mechanism may differ.

2. Materials and Methods

2.1. Materials

Bauxite residue was provided by MYTILINEOS S.A. along with its chemical characterization by the plant's laboratory with the wavelength-dispersive X-ray fluorescence spectrometric method (XRF). The analysis is shown in Table 1.

Table 1. Chemical composition of bauxite residue analyzed by the XRF method at AOG.

Metal Oxides	Percentage (%)
Fe_2O_3	39.19
Al_2O_3	23.81
SiO	7.68
CaO	8.07
Na_2O	3.44
TiO_2	5.03

Analysis indicated that the iron oxide percentage in bauxite residue is 39.19%. Furthermore, mineralogical characterization was conducted by a Malvern-PANalytical™ X 'Pert Pro diffractometer with CuKa radiation, and the pattern is shown in Figure 1. As it can be seen, hematite is the predominant iron oxide. Pure hematite was supplied by Sigma Aldrich, with purity of >99.99%. Finally, the electrolyte was prepared with sodium hydroxide pelets supplied by Honeywell.
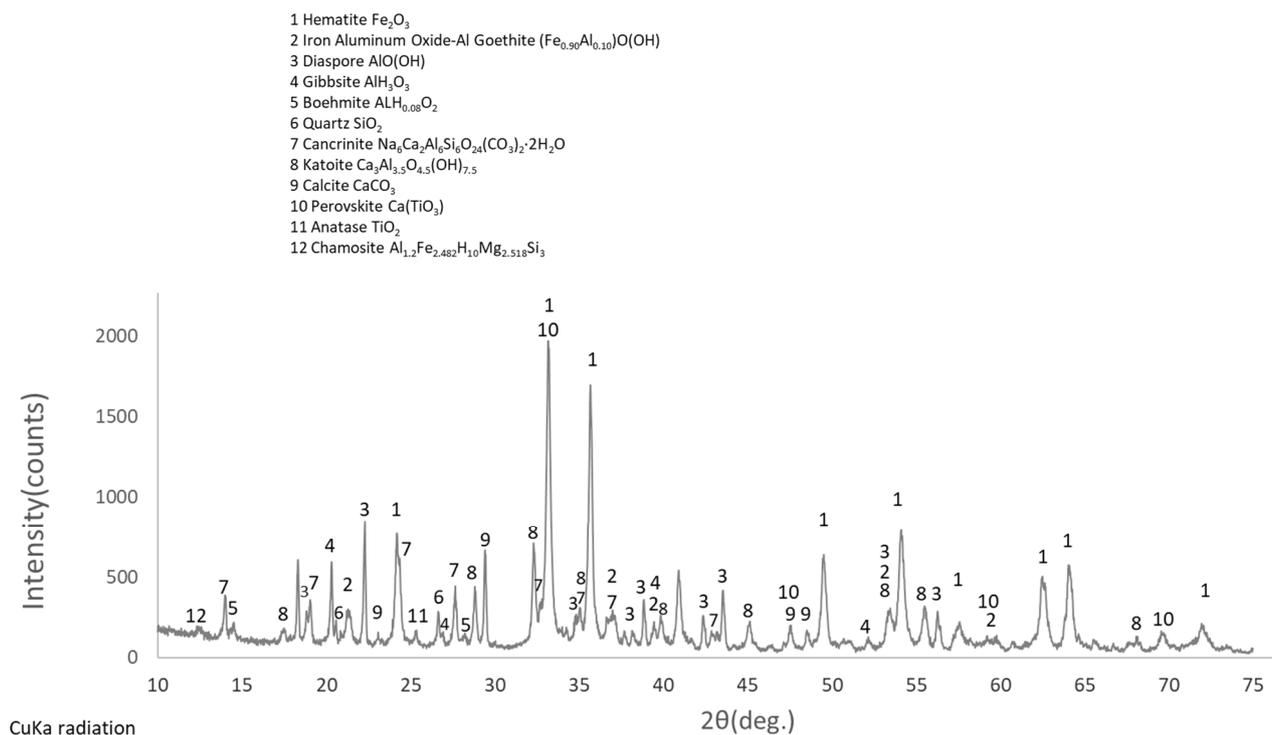
1 Hematite Fe_2O_3
2 Iron Aluminum Oxide-Al Goethite $(Fe_{0.90}Al_{0.10})O(OH)$
3 Diaspore $AlO(OH)$
4 Gibbsite AlH_3O_3
5 Boehmite $AlH_{0.08}O_2$
6 Quartz SiO_2
7 Cancrinite $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$
8 Katoite $Ca_3Al_{3.5}O_{4.5}(OH)_{7.5}$
9 Calcite $CaCO_3$
10 Perovskite $Ca(TiO_3)$
11 Anatase TiO_2
12 Chamosite $Al_{1.2}Fe_{2.482}H_{10}Mg_{2.518}Si_3$

Figure 1. X-ray diffraction of bauxite residue.

2.2. Experimental Set-Up and Parameters

A three-electrode configuration was used. The cathode was a rectangular-shaped stainless-steel V2A plate, while the counter electrode consisted of two rectangular-shaped nickel plates. All electrodes were centered according to the silicon bug's cylindrical axis in specially configured holes so that the electrodes were in certain positions and at a fixed distance to each other. The working electrode's surface area that was immersed in the solution was defined to be 9 cm^2. The reference electrode that was used was a commercial Hg|HgO|NaOH (1 M) electrode (RE-61AP, ALS), which was immersed in a distinct glass compartment containing 1 M NaOH. Cyclic voltammetry and electrolysis tests, under chronopotentiometry mode, were performed in a three-electrode cell connected to an electrochemical sourcemeter (2461 Series, Keithley), and the obtained experimental data were analyzed.

The focus of the present research is the comparison of BR and pure hematite regarding low-temperature alkaline electrolysis. Two series of galvanostatic experiments were performed to evaluate the effect of the following parameters: current density and pulp temperature. For that reason, two values of the applied current density were chosen: the optimum value for BR according to previous research is 138 $A \cdot m^{-2}$, and that for iron ore electrolysis is 1100 $A \cdot m^{-2}$ [2,4,6]. All other factors remained constant (50% *w/w* NaOH, 10% *w/w* BR or hematite, temperature 110 °C and stirring rate 500 RPM). While testing the effect of temperature, three values were selected: 70, 110 and 130 °C, with the other factors remaining constant (50% *w/w* NaOH, 10% *w/w* bauxite residue, current density 138 $A \cdot m^{-2}$ and stirring rate 500 RPM).

2.3. Faradaic Efficiency

The evaluation of the process is based on Faradaic efficiency that describes the charge that is transferred in the system facilitating the electrochemical reaction for the iron oxide reduction to metallic iron. The working electrode was weighed before the experiment, and when the electrolysis was over, the cathode was placed in a vacuum drier at 85 °C. After 12 h, the electrode was weighed again, and the deposited mass was calculated from

the mass difference prior to and after the experiment. The theoretical mass according to Faradaic law is calculated from Equation (1), and the ratio of the real deposited mass to the theoretical one from Equation (2) reveals the current efficiency.

$$\Delta m \ (Faradaic) = (M \times I \times t)/(z \times F) \tag{1}$$

$$Current \ efficiency \ (\%) = (\Delta m \ (real))/(\Delta m \ (Faradaic)) \times 100\% \tag{2}$$

where $\Delta m(Faradaic)$ is the theoretical mass; M stands for the molecular weight of the substance; I represents the applied current; t is the time; z is the number of electrons transferred; F is Faraday's constant; and $\Delta m \ (real)$ is the deposited mass.

3. Results and Discussion

3.1. Cyclic Voltammetry

Firstly, to compare the alternative raw material's electrochemical behavior with that of hematite, cyclic voltammetry tests were conducted. Cyclic voltammograms with a scan rate of 100 mV/s for the two materials are depicted in Figure 2. The comparison between the two cyclic voltammograms illustrates that the cathodic potential of the reduction of iron oxide to metallic iron is more negative than −1.2 V vs. Hg/HgO for both cases. Furthermore, the pure iron oxide voltammogram indicates higher current densities than those of the bauxite residue. The impurities that BR contains, such as silicoaluminate phases, possibly have a negative effect on the electrical conductivity of the process.
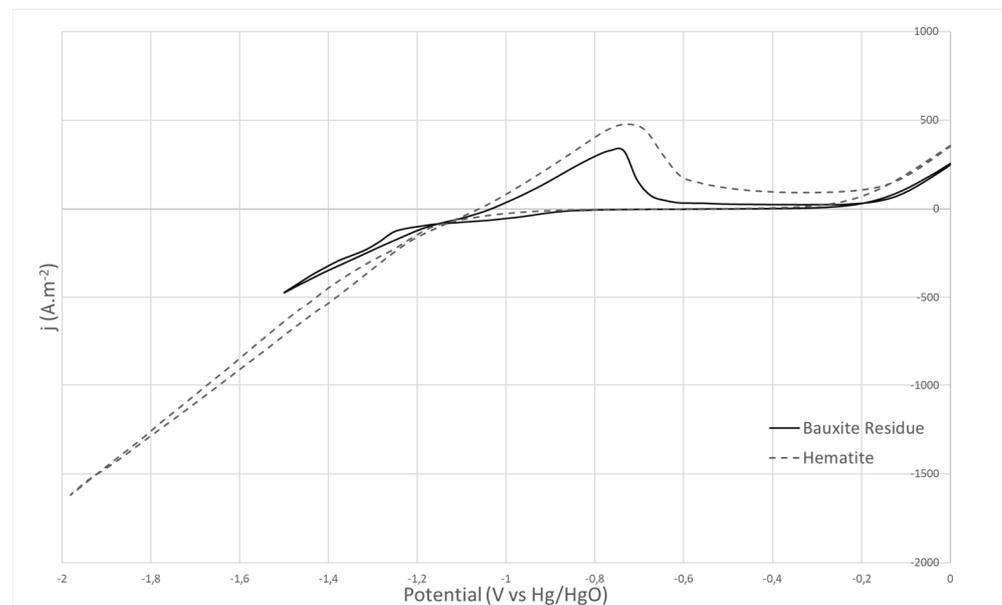

Figure 2. Cyclic voltammetry of BR and hematite with scanning rate of 100 mV/s.

3.2. Galvanostatic Experiments

Electrolysis tests were performed to study the aforementioned parameters. The Faradaic efficiency of the experiments as a factor of the current density is depicted in Figure 3. Concerning the hematite case, the decrease in the current density leads to a slight reduction in the efficiency, resulting in a 10% lower Faradaic yield. On the other hand, the trend for bauxite residue seems to differ since the diagram shows that the current efficiency decreases abruptly, from 72.8 to 36.1% for current densities of 138 and 1100 A·m^{-2}, respectively.
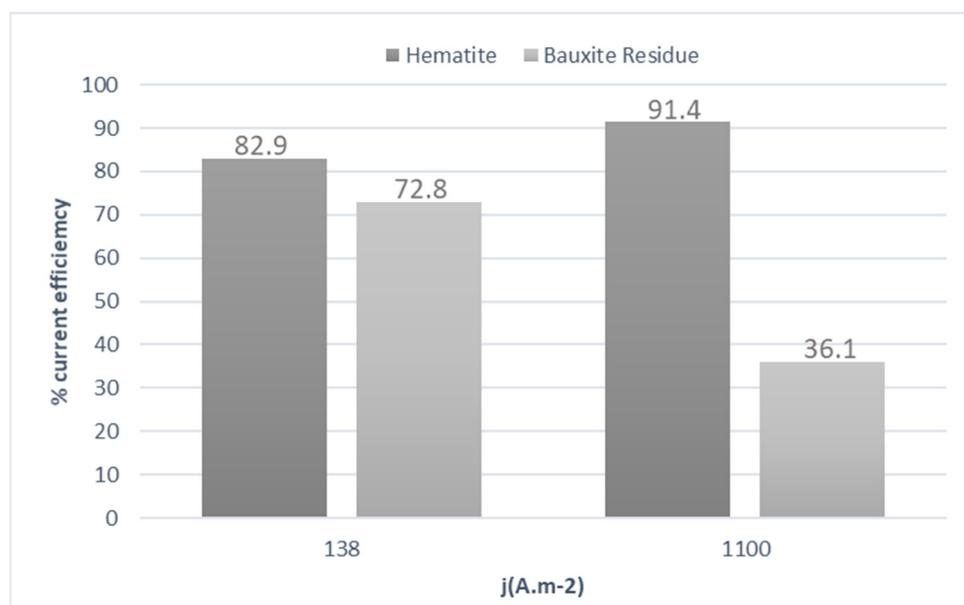
Figure 3. Current efficiency as a function of current density for hematite and bauxite residue.

Concerning the cathodic potential in the experiments with BR at a current density of 138 A·m^{-2}, the potential remains at the region of -1.24 V vs. Hg/HgO, while that of hematite is at -1.18 V vs. Hg/HgO. Increasing the current density to 1100 A·m^{-2} resulted in more negative cathodic potentials, with the BR range varying at 1.75 V vs. Hg/HgO and hematite at 1.69 V vs. Hg/HgO.

The second factor that was tested was the pulp temperature. The current density chosen was 138 A·m^{-2}, representing the most efficient value for the alternative raw material. The results are shown in Figure 4. It can be observed that the materials react differently. Hematite is more efficient at low temperatures, while BR's yield increases dramatically from 70 to 110 °C and then reaches a plateau. The cathodic potentials remained in the same range as the previous series according to the corresponding current, showing that temperature has no effect on the electrochemical reactions that take place during the experiments.
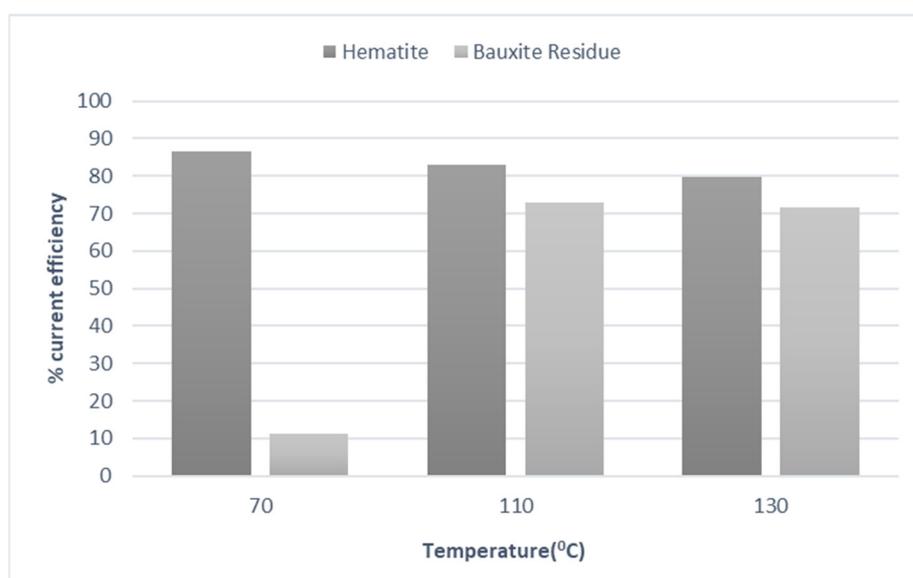

Figure 4. Current efficiency as a function of temperature for hematite and bauxite residue.

4. Conclusions

Low-temperature electrolysis of iron ore in alkaline environments is a breakthrough technology for the future of iron production. Alternative raw material use will strengthen the technology's sustainability. Bauxite residue is a strong candidate for the ΣIDERWIN process, but there are significant differences with pure Fe_2O_3 concerning the solution behavior and the electrochemical mechanism. The impurities that BR contains may be crucial regarding the electroactivity of systems. Processing of BR to remove impurities and long-term electrolysis experiments will be tested by the authors in subsequent work in order to optimize the process.

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