PRODUCTION OF METALLIC IRON WITH ALKALINE ELECTROLYSIS UNDER LOW TEMPERATURES

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Abstract

Under the ULCOWIN and the SIDERWIN projects a novel process for carbon-free iron production has been developed. Iron ore is reduced to metallic iron through electrolysis in aqueous alkaline solutions. This research paper investigates the use of Bauxite Residue from the alumina industry, as an alternative raw material for iron production under the same technology. The process is investigated, in a high alkaline environment and under low temperature and ambient conditions. Several parameters, as well as their effect in the efficiency of the system, were examined at lab scale. Under the optimum combination of parameters studied iron production was achieved at current efficiencies exceeding 70%. Bauxite Residue has therefore the potential to be used as an alternative raw material in iron production through this novel sustainable process.

Introduction

Steel is one of the world's most essential material and at the same time its industry generates between 7 and 9% of direct emissions from the global use of fossil fuel [1]. It operates highly efficient processes and is considered difficult to decarbonize. However, the competitive deployment of renewable electricity might provide an opportunity for the decarbonization of a portion of the industry, through the direct use of electricity. Deep electrification of iron production could provide a contribution to the abatement of the overall Green House effect Gases emissions [2].

In the past a technique for the electrolytic production of iron from suspensions of iron oxide particles in a highly concentrated NaOH solution at 110^{0}C was demonstrated in Lab Scale and achieved Faradaic yield between 80 to 95% [3] [4] [5] [6].

The present paper is present a technology for alkaline pulp iron electrowinning for first time to a secondary mineral source, namely the Bauxite Residue of the alumina refining industry. The Bauxite Residue has been selected as possible raw material for iron production due to its high content of iron oxides (≈40%). The process is based into the reduction of iron oxides of the Bauxite Residue, in a high alkaline environment and under low temperature (110-130°C) and ambient conditions. This technique is referred to the H2020-SIDERWIN project that proposes to develop a breakthrough innovation compared the present-day steel production process by applying electrochemical technique to iron metal production [7].

Experimental

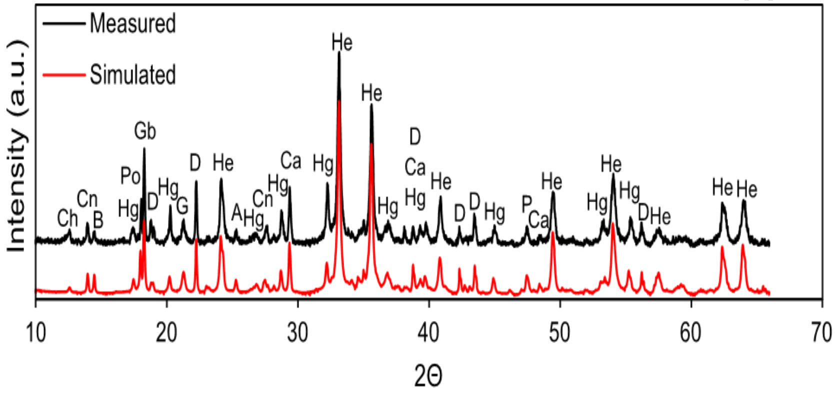
Chemical Analysis

Bauxite residue was supplied by Mytilineos-Aluminium of Greece (AoG). Samples were solubilized via fusion method according to which a quantity of bauxite residue remained at 1000°C for 1 hour with a mixture of $Li_2B_4O_7/KNO_3$ followed by direct dissolution in 6.5% HNO_3 solution. Chemical analysis was performed by Atomic Absorption Spectroscopy (AAS) with the use of Perkin Elmer 2100 Atomic Absorption Spectrophotometer. The chemical analysis of the samples used in this study is shown in *Table 1*. The chemical analysis showed that Fe_2O_3 is the main content (44.77%) of Bauxite Residue.

	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	CaO	Na_2O	LOI
Wt.%	44.77	18.75	6.69	6.65	9.77	2.93	9.17

***Table 1:** Bauxite Residue chemical analysis*

Mineralogical analysis of bauxite residue is shown in Figure 1 proved that the main iron oxide phase is Hematite while a small amount of Goethite also exists. The Hematite to Goethite mass ratio in Bauxite Residue is 4,2 [8].



He	Hematite
Hg	Hydrogarnet
D	Diaspore
Cn	Cancrinite
G	Goethite
Ca	Calcite
P	Perovskite
Ch	Chamosite
Gb	Gibbsite
B	Boehmite
Po	Portlandite
R	Rutile
A	Anatase

Figure 1: Bauxite residue mineralogical analysis

Electrolysis Experiments

A borosilicate glass beaker (250 ml) closed with a specially configured cylindrical silicon bung (45 cm diameter) was used as an electrolysis cell with a three-electrode configuration. The cathode was a rectangular shaped stainless steel V2A plate (110 mm height, 10 mm length, 1 mm width), the anodes were two rectangular shaped nickel plates (100 mm height, 10 mm length, 2 mm width). All electrodes were centered according to the silicon bung's cylindrical axis in specially configured holes so that the electrodes were in certain positions and at fixed distance to each other. The working electrode's surface area that was immersed in the solution was defined to be

8 cm^2. The reference electrode that was used was a commercial Hg|HgO|NaOH (1M) electrode (RE-61AP, ALS) which was immersed in a distinct glass.

The electrolyte was a 50 wt.% NaOH aqueous solution corresponding to molarity of 25 mol/kg, in which it was added an amount of 10 wt. % Bauxite Residue solid particles. The slurry temperature was measured via a probe that was wrapped in a PTFE shrink tubing to avoid current leakage. The slurry was stirred using a 1 cm ringed cylindrical magnetic bar and magnetic hot plate (IKA-Werke RCT Basic) at a rotational speed of 500 rpm to keep bauxite residue particles suspended. The small size of the magnetic bar was chosen to minimize the attraction of magnetite particles to the stirrer.

Before the electrolysis experiments, a cyclic voltammetry carried out with platinum wires as both working and counter electrode while the reference electrode that was used was the mentioned above Hg/HgO commercial electrode.

Electrolysis experiments were performed under galvanostatic mode. The duration of its experiment was 2 h. The difference between the mass of the cathode prior to and after the end of electrolysis was considered as the mass of the deposit. This value was used to deduce the current efficiency according to faradaic law.

Determination of metallic iron

According to previous studies, hematite reduction mechanism to form metallic iron on the cathode has magnetite as an intermediate product [4]. For that reason, a quantitative determination of the deposit took place to identify the percentages of both metallic iron and magnetite phases. The principle of the method is based on the selective dissolution of metallic iron from a 2% bromine solution in ethanol when it is in mixtures with its oxides. According to the procedure of the method 100 ml of bromine (ACROS ORGANICS) solution 2% in ethanol (EMSURE) was prepared and 0,2 g of sample powder was added in a 250 ml conical flask. The solution was let to stir at ambient temperature for 90 minutes and then filtered using a 47 mm diameter glass fiber filter (WHATMAN) [9]. The resulting solution was titrated into a 500 ml flask with deionized water and is measured in atomic absorption spectrophotometer (Perkin Elmer 2100).

Results and Discussion

Cyclic Voltammetry

A cyclic voltammetry of Bauxite Residue (10 wt.%) in 50 wt.% NaOH solution in 110^{0}C and with Scan Rate 100 mV/sec is shown in Figure 2. Iron oxide from Bauxite Residue (mainly hematite) is reduced to metallic iron in the region of cathodic potentials from -1,2 V to -1,4 V with a peak at -1,36 V. Hydrogen evolves at more negative potentials lower than -1,4 V. The plateau observed at cathodic potentials in-between -1,0 V and -1,2 V is attributed to reduction of hematite to magnetite which is always taking place in the system under study as is seen in Raman spectra of a typical deposit in Figure 3. The peak observed at anodic scanning at about -0,7 V is attributed to the reversible oxidation of iron. The peak observed at anodic scanning at about -0,7 V is attributed to the reversible oxidation of iron.

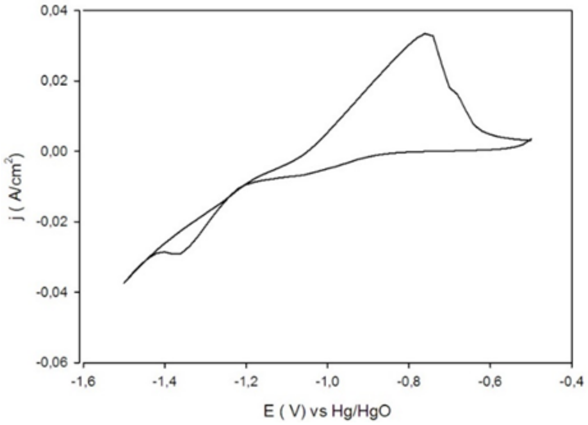


Figure 2: Cyclic Voltammetry in pulps of Bauxite residue (10% wt.%) in 50 wt.% NaOH solution at 110^0C and 100 mV/sec

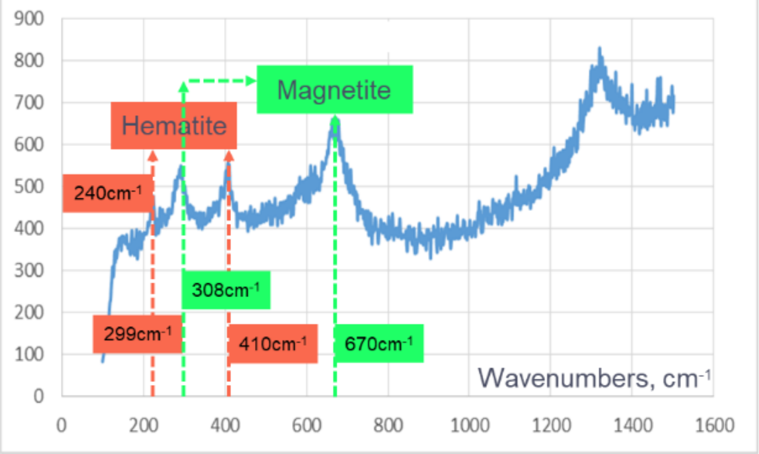


Figure 3: Raman Spectra of cathodic deposit

The iron oxide's reduction of Bauxite Residue was experimental tested by two different series of galvanostatic experiments. The two parameters that were studies was the current density and the slurry's temperature.

Effect of Current Density

Galvanostatic experiments carried out with different current densities while all other factors remained constant (50 wt.% NaOH, 10 wt.% Bauxite Residue, temperature 110°C, and stirring rate 500RPM). The cathodic potential vs Hg/HgO is shown in Figure 4. As it was expected, the increase of the applied current results in more negative values of cathodic potential indicating more intense reductive conditions at the cathode. The applied currents in-between 62,5 to 312,5 A/m^2 gave constant cathodic potential values for the whole duration of electrolysis experiments from -1,2 to -1,4V which coincide fully with the region of hematite reduction to metallic iron as is shown in the voltammogram of Figure 2. With current density higher than 312,5 A/m^2 the cathodic potential is moving towards the hydrogen evolution region (<1,4V) as is seen in Figure 4.

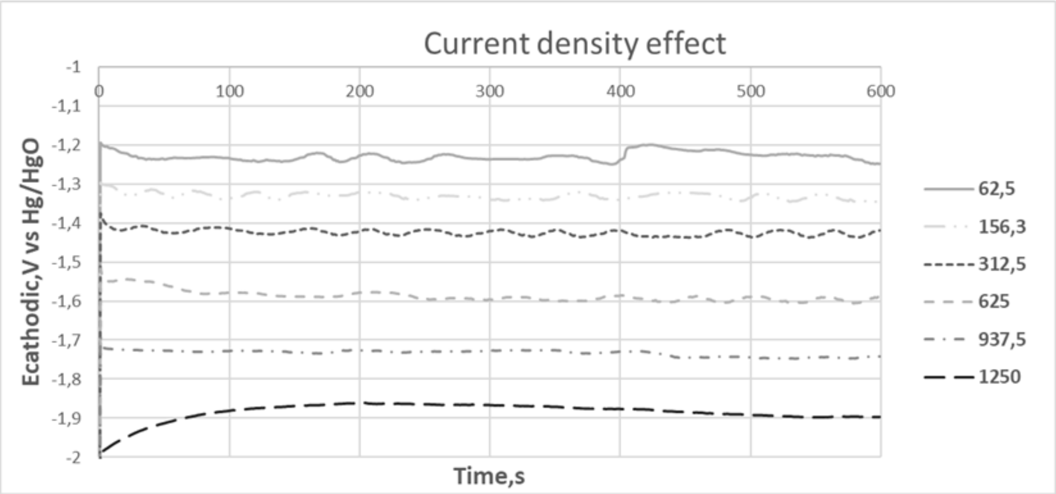


Figure 4: Cathodic potentials during galvanostatic experiment at different applied currents

The calculated faradaic efficiency for each experiment, taking into account the purity in metallic iron of the cathodic deposition that was determined to be 89-91% in all experiments, is shown in Figure 5. As is seen the lower the applied current the higher the faradaic efficiency is. The current density in the region of 62,5 to 156,25 A/m^2 gave the highest current efficiencies which were very close to 50%.

Current density(A/m^2)	Current Efficiency
62,5	48,48%
156,25	48,84%
312,5	41,19%
625	25,28%
937,5	35,14%
1250	33,74%

Figure 5: Current efficiency of galvanostatic experiments for the investigation of the applied current effect

Effect of Temperature

The temperature effect was studied between 70^o to 135^{o}C while the other parameters were kept constant (50 wt.% NaOH, 10 wt.% Bauxite Residue, and stirring rate 500RPM).The current density was selected to be 156,5 A/m^2 as this value resulted in the highest faradaic yield (48,84%) in the previous experimental series. The cathodic potentials vs Hg/HgO are shown in Figure 6. As is seen the cathodic potentials within the whole duration of all electrolysis experiments were remained in the region from -1,2 V to -1,4 V which coincides with the region where the hematite is reduced to metallic iron Figure 2. In addition, there is a tendency for less negative cathodic potentials (milder reductive conditions) as the process temperature increases.

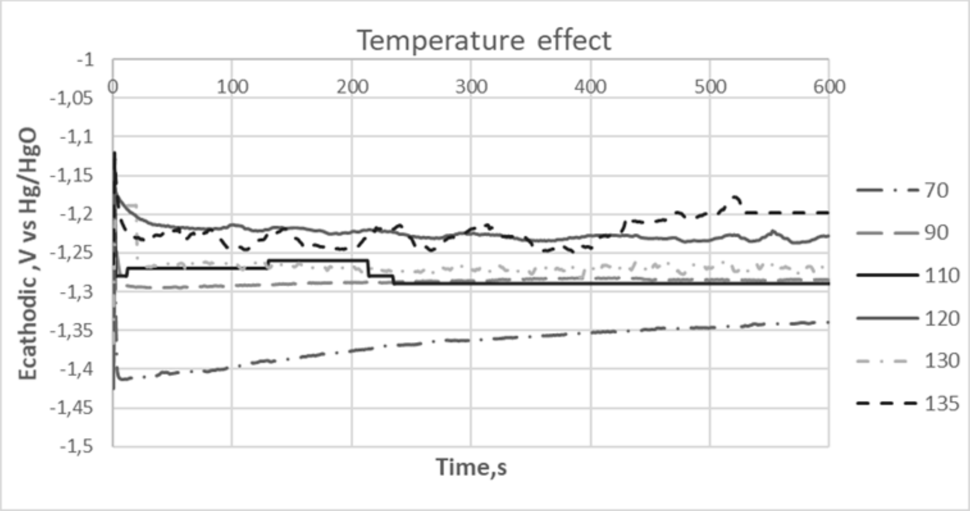


Figure 6: Cathodic potentials during galvanostatic experiment at different pulp's temperatures

The calculated faradaic efficiencies are shown in Figure 7**.** The increase of temperature from 70 to 130°C resulted a steady almost linear increase of faradaic efficiency from 11,23 to 71,58%. Step up temperature to 135°C caused a slight decrease in current efficiency to 59,76% which is still higher than the one at 120°C.

T(⁰C)	Current Efficiency (%)
70	11,23
90	24,48
110	48,84
120	54,94
130	71,58
135	59,76

Figure 7: Current efficiency of galvanostatic experiments for the investigation of pulp's temperature effect

Conclusions

The present work has demonstrated the possibility to electrochemically reduce iron from bauxite residue in alkaline pulps. The most crucial parameter for the process that affects the faradaic efficiency proved to be the temperature. At the current level of process development, a faradaic efficiency of 71,58% was achieved at pulp density of 10 wt.%BR in a 50 wt.% NaOH solution at 130°C. The desirable cathodic potential is higher than -1,4 V vs Hg/HgO (in 1M NaOH) in order to avoid the hydrogen evolution which takes place at cathodic potentials lower than -1,4V.

The present process has great potential for integration in the established Bayer process for production of alumina. As Bayer process, takes place in an alkaline environment at temperatures 120-150°C, the electrolytic process disclosed in this work, could become a symbiotic part of the Bayer process, valorizing the iron content of the bauxite ore, and significantly reducing the amount of the produced bauxite residue. Work in performing the electrolysis in larger electrochemical reactors and for extended periods of time is underway by the authors

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