Iron Recovery from Red Mud as Zero-Valent Iron Metal Powder Using Direct Electrochemical Reduction Method

Franky Michael Hamonangan Siagian, Affan Maulana, Himawan Tri Bayu Murti Petrus, Panut Mulyono, Widi Astuti

Abstract—In this study, the feasibility of the direct electrowinning method was used to produce zero-valent iron from red mud. The red mud sample came from the Tayan mine, Indonesia, which contains high hematite (Fe_2O_3). Before electrolysis, the samples were characterized by various analytical techniques (ICP-AES, SEM, XRD) to determine their chemical composition and mineralogy. The direct electrowinning method of red mud suspended in NaOH was introduced at low temperatures ranging from 30-110 °C. Current density and temperature variations were carried out to determine the optimum operation of the direct electrowinning process. Cathode deposits and residues in electrochemical cells were analyzed using XRD, XRF, and SEM to determine the chemical composition and current recovery. The low-temperature electrolysis current efficiency on Redmud can reach 11.8% recovery at a current density of 796 A/m². The moderate performance of the process was investigated with red mud, which was attributed to the troublesome adsorption of red mud particles on the cathode, making the reduction far less efficient than that with hematite.

Keywords—Alumina, electrochemical reduction, iron production, red mud.

I. INTRODUCTION

INDONESIA is one of the countries with the most abundant bauxite mineral potential in the world. According to the US report Geological Survey (USGS) in 2022, Indonesia is the sixth largest country for bauxite reserves, with total reserves of 1.2 billion tons [12]. Bauxite ore is usually extracted to obtain alumina, which is a source of aluminum metal. The process of extracting bauxite into alumina uses sodium hydroxide at temperatures above 200 °C, known as the Bayer process. The production of alumina from bauxite through the Bayer process is associated with the formation of red mud as the primary waste material. The main chemical components of red mud include 12-24% SiO_2, 29-42% Fe_2O_3, 7-13% Na_2O, 1-2% TiO_2, and other minerals with a range of 10-22% [1]. Red mud has a brick-red color and is sticky, with a pH of around 11-12. It is usually removed from the factory site by transporting it and storing it in tailings dams, lakes or landfills.

In reality, the environmental problems caused by red mud are related to two aspects: The red mud produced is present in large quantities, to produce 1 ton of alumina will produce around 1.5-2.5 tons of red mud [2]. Second, about 2 tons of caustic liquid (such as Na_2CO_3) with a concentration of about 5-20 gpl is generated in every ton of red mud solids [3]. Due to the high risk of red mud to the environment and also the handling of red mud waste which requires large waste storage areas, new innovations are needed regarding the utilization of red mud. Most researchers have made use of red mud and suggested using this residue (i) as a building material [4], (ii) as a pollutant absorbent [5], and (iii) as a source of rare earth elements [6]. In this application, there is no mass application of red mud. Each year only 15% of red mud can be reused or recycled; the rest is stored in final disposal or tailings dams [7].

Red mud is a raw material with a high hematite content (35-45%), so the hematite in red mud has great potential for further processing. Currently, electrolysis-based processes for the electrodeposition of iron have emerged as an alternative route for directly converting suspended iron oxides to metallic ferrous (Fe^0) without greenhouse gas emissions, replacing the traditional method of iron production in blast furnaces [8]. This process has been carried out in the Ultra Low Carbon Dioxide in Steelmaking (ULCOS) project supported by the European Commission and the European steel industry. The ULCOS electrowinning process is carried out by dissolving iron ore in an alkaline sodium hydroxide solution at a temperature of 110-110 °C, where the resulting product is solid iron [9]. The ongoing project on low-temperature electrolysis for steel production is also carried out by SIDERWIN, supported by the European Commission on the Horizon 2020 research and innovation funding program. The commissioning of the first pilot plant to produce iron by electrolysis is still in development [10].

Based on this report, a method for obtaining zero-valent iron (zvi) from red mud has been proposed in this study. The hematite in the red mud is reduced to zvi by an electrochemical process. Treatment conditions, such as current density, temperature, and electrode type, have been investigated in this study. It is hoped that this research can improve the beneficiation of red mud originating from bauxite mines in Indonesia with a high iron composition and transfer the knowledge gathered in studies on electrolytic reduction of

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World Academy of Science, Engineering and Technology
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hematite to more complex red mud beneficiation cases.

II. MATERIALS AND METHODS

A. Chemicals Reagent

A red mud sample was obtained from the Tayan mine, West Kalimantan, Indonesia. The sample as received was analyzed for the particle size using sieve analysis. A series of sieve mesh with an aperture size of 60 mesh, 70 mesh, 100 mesh, 120 mesh, 170 mesh, and 200 mesh were used for screening the samples. The particle size analysis result is shown in Fig. 1; red mud had a particle size of D_{90} 219 μm. The chemical analysis of the samples used in this study is shown in Table I. The chemical analysis showed that Fe_2O_3 is the main content of red mud. Furthermore, mineralogical characterization was conducted by X-Ray Diffraction (XRD), and the pattern is shown in Fig. 2. As can be seen, hematite is the predominant iron oxide. A 12.5 mol/L NaOH solution was prepared by dissolving sodium hydroxide pellets (purity 98%, Emsure Merck, Germany) in deionized water. The 1 mol/L hydrochloric acid solution used to clean the electrodes was prepared from 37% hydrochloric acid (Emsure Merck, Germany).
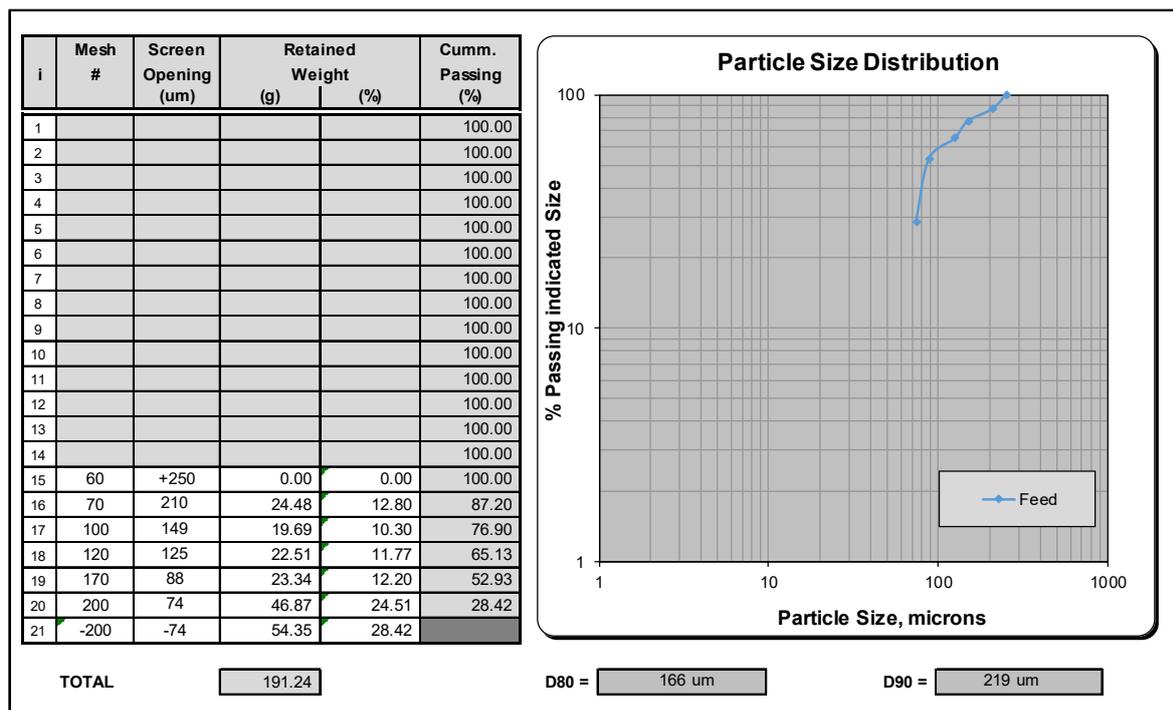
i	Mesh #	Screen Opening (um)	Retained Weight (g)	Retained Weight (%)	Cumm. Passing (%)
1					100.00
2					100.00
3					100.00
4					100.00
5					100.00
6					100.00
7					100.00
8					100.00
9					100.00
10					100.00
11					100.00
12					100.00
13					100.00
14					100.00
15	60	+250	0.00	0.00	100.00
16	70	210	24.48	12.80	87.20
17	100	149	19.69	10.30	76.90
18	120	125	22.51	11.77	65.13
19	170	88	23.34	12.20	52.93
20	200	74	46.87	24.51	28.42
21	-200	-74	54.35	28.42	28.42
TOTAL			191.24		

D80 = 166 um   D90 = 219 um

Fig. 1 Particle size distribution of red mud

TABLE I
CHEMICAL COMPOSITION OF RED MUD ANALYZED BY THE XRF

Metal Oxides	Percentage (%)
Al_2O_3	14.63
CaO	2.89
Fe_2O_3	57.11
SiO_2	20.12
TiO_2	3.29
Other	1.96

In most experiments, the suspensions were prepared by adding the required red mud to the NaOH solution to obtain a solid:liquid ratio of 1:3 g/mL. Electrolysis tests were performed under galvanostatic mode. The duration of the experiment was 3 h. At the end of each test, the cathode was dismantled from its support and then rinsed thoroughly with deionized water before drying at 100 °C for 24 hours. Once dried, the cathode was weighed to determine the mass of the deposit. According to Faradaic law, this mass value was used to deduce the current efficiency. Subsequently, the deposit was detached from the cathode substrate by rinse and sonicator at 1 mol/L hydrochloric acid solution for 1 hours. After that, the solution was filtered using a membrane (MF-Millipore 0.8 um MCE membrane) and then dried at 90 °C for 24 hours to obtain the iron deposit. The chemical composition of the deposit was obtained by X-ray fluorescence. The morphology of the iron deposits was observed by scanning electron microscopy. EDX analysis of the surface confirmed that deposits were mainly formed by iron metal. The crystal structure of deposited iron was analyzed by X-ray diffraction.

Experimental Apparatus

The electrochemical cell (Fig. 3) consisted of a cylindrical double-walled borosilicate glass (70 mm diameter, 80 mm height) cell with a total volume of 300 mL. The experiment used 150 mL of 12.5 mol/L NaOH solution, and 75 g of red mud was introduced into the cell based on previous work [11]. The electrolytic suspension temperature variation was maintained by the circulation of oil in the jacket. Oil circulation in the jacket made it possible to control the electrolyte solution's temperature accurately. The slurry temperature was measured

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via a HANNA-HI98501 digital thermometer. A three-electrode configuration was used in the electrochemical system. The working electrode was a cylindrical graphite rod (6 mm diameter, 80 mm length, Krakatau steel), and a platinum-coated titanium grid was used as counter electrodes. A reference electrode Hg/HgO (E° = 0.098V vs NHE at 25 °C) in a 1 M KOH electrolyte, equipped with a glass extension with a sintered junction filled with KOH 1 M, was used for measuring the potential of the two electrodes.
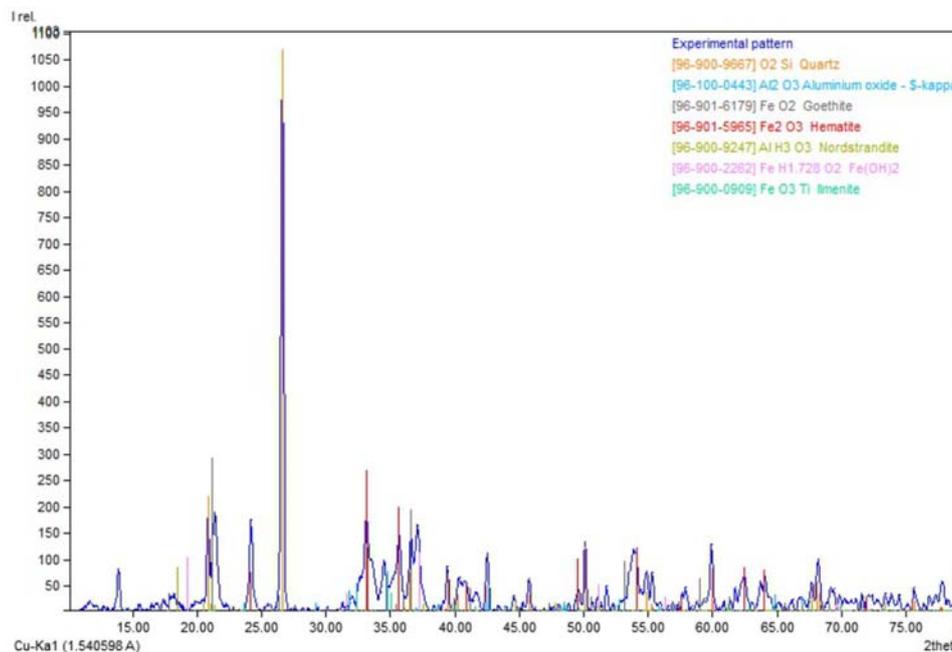
Fig. 2 X-ray Diffraction of Red mud
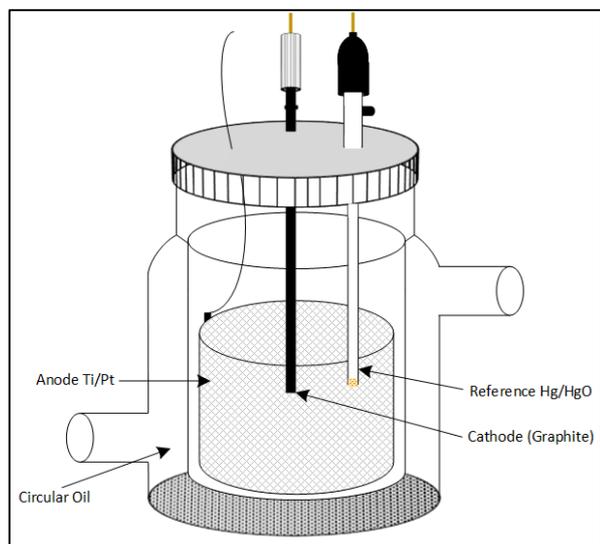
Fig. 3 Electrolysis experimental apparatus

The suspension was stirred at 200 rpm by a PTFE-coated stirrer mixer (250 mm long and 7 mm in shaft diameter). The PTFE-coated stirrer mixer was chosen to minimize contamination stainless steel rod to the electrolyte. The cathode, anode, and reference electrodes were connected via their respective terminal to a potentiostat (Corrtest instruments) that acted as the current source, driven by a user-developed CS Studio5 program for command of the electrochemical device, together with data acquisition and treatment.

Faradaic Efficiency

Faraday efficiency is commonly used in the evaluation of electrochemical processes. To determine the theoretical mass amount of iron metal quantity $m_{Fe,theor}$, can be calculated using Faraday's law:

$$m_{fe,theor} = \frac{MW_{fe} \times I \times t}{n \times F}$$

where MW_{fe} is the molar weight of the metal (55.85 g/mol), I is the current (A), t is the duration of the experiment, n is the number of electrons involved and F is the Faraday constant (C/mol). The faradaic efficiency was determined by dividing the mass of the deposit with the theoretical. To determine deposit mass, the working electrode was weighed before the experiment, and when the electrolysis was over, the cathode was dried at 100 °C. After 12 h, the electrode was weighed as a final weighed, and the deposited mass was calculated from the mass difference final to and initial of the experiment.

$$Faradaic\ yield\ (\%) = \frac{Deposit\ mass}{m_{fe,theor}} \times 100$$

III. RESULTS AND DISCUSSION

Cyclic Voltammetry

The cyclic voltammetry tests were conducted on cylindrical graphite (1 cm^2) with 12.5 mol/L NaOH solution at 100 °C and

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scan rate 20 mV/s, and the result is voltammetric curves are presented in Fig. 4. Cyclic voltammetry was used to determine

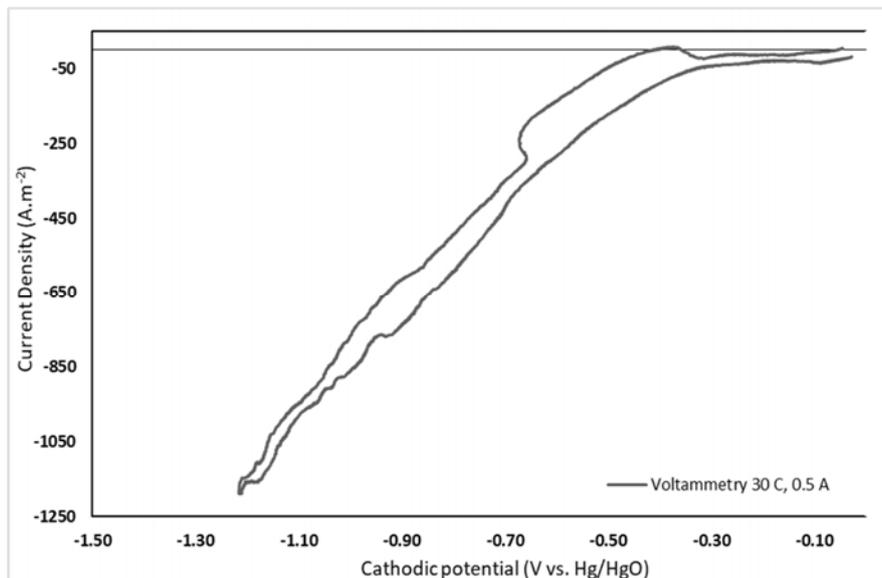mechanism several reactions are involved in the red mud electrolysis process.

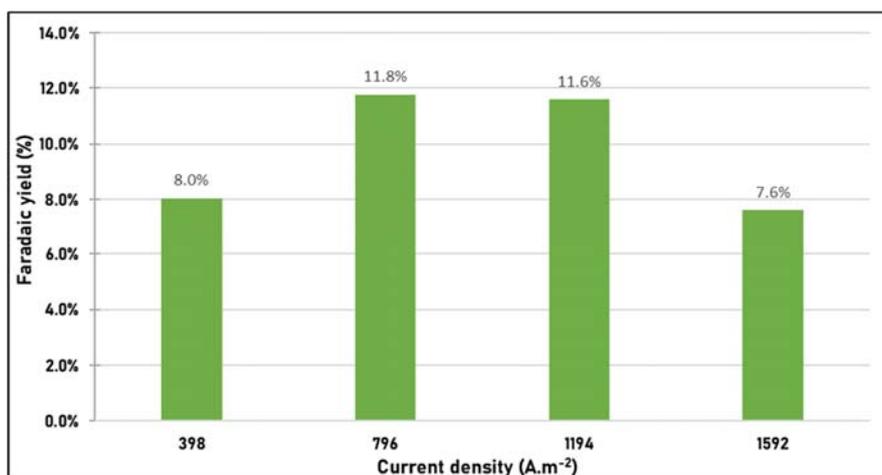Fig. 4 Cyclic voltammetry in red mud with 12.5 mol/L NaOH solution at 100 °C and scan rate 20 mV/s

Fig. 5 Influence of the current density on faradaic yield in red mud electrolysis at 12.5 mol/L NaOH in a solid/liquid ratio of 1/3 g/mL for 3 h at 110 °C

Iron oxide from red mud is reduced to metallic iron in the region of cathodic potentials from –0.9 V to –1.2 V with a peak at –1.1 V. Side reaction, reduction of water to hydrogen (hydrogen evolution), occurs simultaneously with the iron oxide reduction process and will increase at a lower negative potential than –1.1 V. The peak observed at cathodic potentials between –0.8 V and –1.2 V is attributed to reduction of hematite to magnetite which is always taking place in the system under study. The peak observed at anodic scanning at about –0.4 V is attributed to the re-oxidation of iron.

Influence of Current Density on Red Mud Electrolysis

Current density can be defined as the rate of flow of charge across any cross-section of the electrode. Current density (cd) is an important factor for evaluation of electrochemical

processes since it governs the production rate, depending on the faradaic yield. To determine the optimal current density, variation applied currents were used in Galvanostatic mode experiments at 398 A/m^2, 796 A/m^2, 1194 A/m^2, 1592 A/m^2. This variation was performed in constant condition (temperature 110 °C with a solid/liquid ratio of 1/3 g/mL and stirring rate 226 rpm). As shown in Fig. 3 (a), the faradaic efficiency of the red mud electrolysis process depends on the current density level. At a very low current density (398 A/m^2), the faradaic efficiency was found at 8.0%. When the cd was set at 796 A/m^2, the efficiency increased to 11.8%. On the other hand, for a larger current density, the faradaic yield was decreased to 7.6% at 1592 A/m^2. The cathodic potential vs. Hg/HgO is shown in Fig. 5. The cell voltage varied from 0.9 to 1.2 V for current density varying from 398 A/m^2 to 1592 A/m^2

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which coincide fully with the region of hematite reduction to metallic iron as shown in Fig. 6.
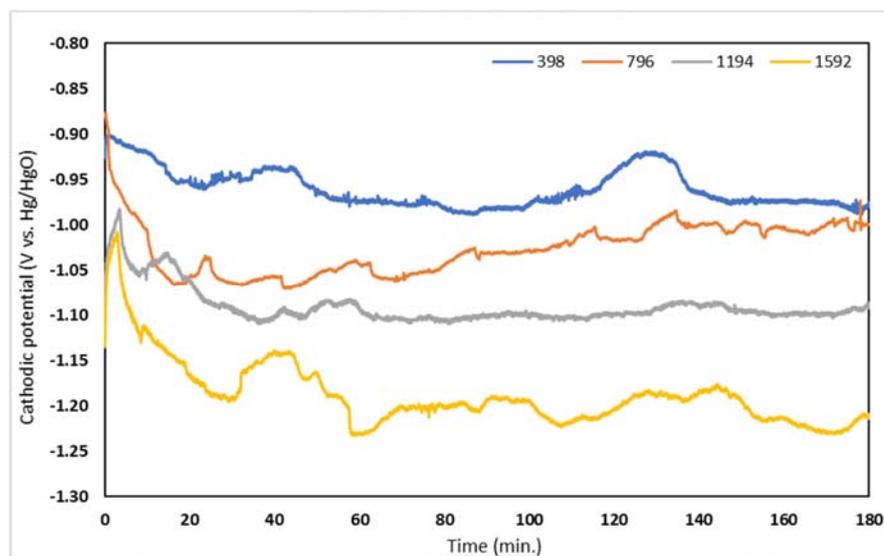
Fig. 6 Cathodic potentials during a galvanostatic experiment at different current densities (A/m^2)

Iron production from the electrolytic treatment of red mud appears to be a poorly efficient process. According to previous studies [11], the low faraday efficiency of red mud is due to the higher viscosity of red mud (7 cP at 110 °C) compared to hematite suspension (2.7 cP at 110 °C). At a high current density, unwanted cathodic reactions, such as the hydrogen evolution reaction, take place in the system. The production of gas evolution will increase with the increased current density, causing the gas bubbles to be hardly lifted to the surface. In the electrolyte suspension, a three-phase foam is formed, apparently increasingly stabilized by the more viscous suspension, resulting in lower electrical conductivity because there is a gas phase contained in the suspension. In addition, the low Faraday efficiency can be explained by a mechanism with adsorbed red mud particles at the cathode; the cathode is covered by electroactive hematite particles and non-electroactive particles coming from the bauxite residue. The non-electroactive particles are all the other phases in bauxite residue, such as diaspore, cancrinite, calcite, hydrogarnet, perovskite, gibbsite, boehmite and anatase. Therefore, the current distribution on cathode is non-uniform, giving rise to areas with charge accumulation (where the non-electroactive species are concentrated) and thus, more negative potential than the other areas where the electroactive hematite particles are located.

Influence of Temperature on the Faradaic Yield

Different temperatures were studied to understand the influence of the temperature condition on faradaic yield and to find the optimum temperature condition at red mud electrolysis. The temperature effect was studied in the range 30-110 °C while the other electrolysis parameters were kept constant (12.5 mol/L NaOH, solid/liquid ratio of 1/3 g/mL and stirring rate 226 rpm). As shown in Fig. 7, the faradaic efficiency of the red mud electrolysis process is increased with the increase in temperature. When electrochemical processes occur, the cathode surface is covered with electroactive and non-electroactive particles from the red mud. The electroactive particles are strongly attached to the cathode surface due to their partial reduction to metallic iron, while the non-electroactive particles are loosely attached. An increase in temperature causes an increase in the heterogeneous nucleation rate of water bubbles on the particle surface due to the vapor pressure increase. Therefore, the probability of removing the attached non-electroactive particles from the cathode surface increases and thus, the probability of replacing the non-electroactive ones with electroactive particles will increase. At higher temperatures, the percent coverage of the cathode with electroactive species increases; thus, the amount of metallic iron attach in the cathode increases, making faradaic efficiency increase.

Next, the effect of temperature on electrolysis time was investigated. Increasing the temperature increases the cathodic current efficiency at higher temperatures. The increase in current efficiency can be attributed to the increase in the rate of diffusion of iron ions in the electrolysis cell due to a decrease in the viscosity of the electrolyte and an increase in the rate of the reduction reaction of iron ions on the cathode surface to produce iron metal ($Fe^{2+} + 2e^- \rightarrow Fe(s)$).

Influence of Impurities

The influence of impurities is also briefly discussed in this study. Direct electrochemical process of red mud in this study did not carry out the impurity removal stage first. So, it is possible that impurities composition in red mud have an influence on the results of low flow efficiency. It can be seen in Table I the results of the XRF analysis of red mud, there are impurities Al_2O_3 (14.6%), SiO_2 (20.1%), V_2O_5 (0.3%), etc.

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which have quite significant concentrations. The presence of impurities can affect the resistivity of the solution. The higher the concentration of impurities present, the higher the viscosity and resistivity, which can cause an increase in cell voltage.
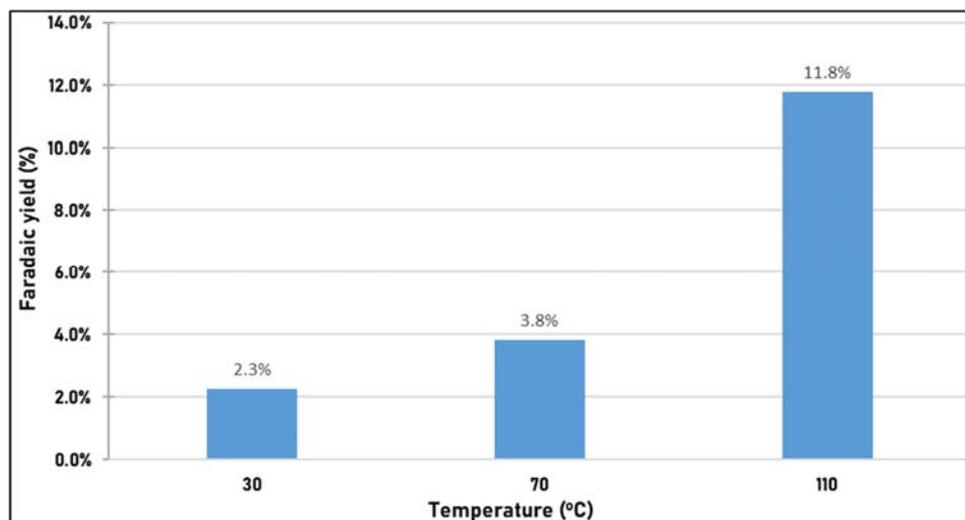

Fig. 7 Influence of the current density on the different temperatures in red mud electrolysis at 796 A/m^2, 12.5 mol/L NaOH in a solid/liquid ratio of 1/3 g/mL for 3 h

IV. RESULTS AND DISCUSSION

We have demonstrated the electrochemical reduction of red mud in concentrated NaOH electrolyte to produce zero-valent iron. Red mud samples were first analyzed by different techniques (ICP-AES, SEM, sieve analysis and XRD) to determine their chemical and mineralogical compositions and their particle size distribution. The red mud investigated had a particle size D$_{90}$ 219 μm and mainly contained Fe, Si, Al, Ti, and Na in the form of hematite, aluminosilicates and perovskite. The effect of the current density and temperature for high faradaic yield for the optimum faradaic yield was studied. The best faradaic yield was 11.8% at 796 A/m^2 with red muds. These laboratory-scale results demonstrate that direct electrolysis of red mud is feasible, and a potential route for the low-CO$_2$ production of iron from this naturally occurring ore. The low Faraday efficiency was investigated with red mud, we suspect that red mud particles do not have the same electrochemical reactivity as commercial hematite, particularly because of the presence of impurities e.g. cancrinite or perovskite, which might affect particle adsorption on the cathode surface.

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