Electrolytic Reduction of Metal Sulfides/Oxides in Molten Salts for Sustainable Metal Production

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ABSTRACT

The metal production industry is a significant contributor to global CO_2 emissions due to the use of fossil fuels such as coal and coke. To mitigate these emissions and meet climate goals, innovative and sustainable technologies are required. Molten salt electrolysis is a promising technology that directly produces metals from their precursor sulphides or oxides using electricity. When combined with renewable electricity and an inert anode, the electrolysis process can be carbon neutral.

This paper presents the results of two pilot-scale studies on the electrolytic reduction of metal oxides and sulphides in molten salts. The first study focuses on the electrolytic reduction of chalcopyrite in molten NaCl-KCl salt. The results demonstrate that in situ separation of copper, iron, and sulphur is possible, enabling the extraction of all valuable elements without CO_2 emissions. Furthermore, the findings underscore the capability to eliminate impurities like zinc, antimony, arsenic, and mercury from the electrolysis product. The second study investigates the electrolytic reduction of pure/synthetic chemicals of wustite, hematite, and magnetite, as well as a magnetite-type iron ore in molten NaOH salt. The findings reveal a stepwise reduction of iron oxides from high valence to low valence, ultimately leading to the production of metallic iron electrolytically. Notably, this study underscores the challenges associated with the selection of an economically viable and durable inert anode material for efficient oxygen generation.

These results indicate that molten salt electrolysis provides a sustainable and green route for base metal production. The use of this technology has the potential to significantly reduce CO_2 emissions in the metal production industry, contributing to achieving climate goals.

1 INTRODUCTION

The base metal production industry is a major emitter of CO_2 due to its heavy reliance on fossil fuels for reduction and heating processes. For instance, steelmaking in blast furnaces and basic oxygen furnaces emits 1800 kg of CO_2 per metric tonne of steel produced (Suopajärvi et al., 2018). Achieving carbon neutrality in this industry requires transitioning to renewable energy sources or agents for metal extraction from compounds, typically sulphides and oxides. Promising candidates for renewable energy sources or agents include bio-based materials like biocarbon, green hydrogen, and renewable electricity. While bio-based materials show potential to replace fossil fuels in metallurgical processes, their supply is limited (Pei et al., 2020). Hydrogen, produced via water electrolysis using renewable electricity, serves as a green energy and reducing agent for metal oxide reduction. However, its application is limited by thermodynamic constraints, particularly in reducing metal sulphides and oxides like chromium oxide (Davies et al., 2022), manganese oxide (Safarian, 2022), and silicon oxide (Itaka et al., 2015). Moreover, the two-step process of hydrogen production and subsequent metal oxide reduction lowers process efficiency. Electrons derived from renewable electricity are potent reducing agents suitable for electrolysis processes to convert metal compounds to metals. Two notable examples of electrolysis approaches are molten salt electrolysis (FFC process (Chen & Fray, 2020; Mohandas & Fray, 2004)) and molten oxide electrolysis (MOE process (Allanore et al., 2011, 2013; Sadoway, 2017)). The FFC process involves controlled liberation of oxygen or sulphur ions from metal oxides or sulphides within a molten salt electrolyte, primarily chloride salt, positioned at the cathode. This process yields sponge-like metal at the cathode while generating oxygen or sulphur at an inert anode (Cox & Fray, 2008; Tan et al., 2016). Operating at lower temperatures compared to conventional methods, the FFC process reduces energy consumption. The MOE process dissolves iron ore in a molten oxide electrolyte, leading to electrolytic reduction of iron ions and continuous liquid metal production with an inert anode and renewable electricity, thereby avoiding CO_2 emissions. Despite the environmental benefits, challenges remain in both processes, particularly in finding durable and economically viable anode materials (Allanore et al., 2013).

This study investigates the electrolytic reduction of chalcopyrite and iron oxides in molten NaCl-KCl and NaOH salts in a pilot-scale electrolysis reactor to further explore the potential of molten salt electrolysis for sustainable metal production.

2 METHODLOGY

2.1 Materials and their preparation

2.2.1 Materials and preparation for electrolytic reduction of chalcopyrite/pyrite

Two samples, designated as Concentrate A and Concentrate B, were chosen for the electrolysis trials. Concentrate A, a chalcopyrite material, is composed of 33.9% iron (Fe), 31.2% copper (Cu), and 18.5% sulfur (S). In contrast, Concentrate B, a pyrite material, contains 50.6% Fe, 0.75% Cu, and 22.7% S. These materials were subjected to thorough analysis utilizing X-ray Fluorescence (XRF) for elemental composition, LECO combustion for carbon and sulfur content, and X-ray Diffraction (XRD) for mineralogical characterization. The analyses confirmed that Concentrate A is primarily chalcopyrite (CuFeS2), with a Fe to Cu ratio of approximately 1.1:1. Meanwhile, Concentrate B is predominantly composed of pyrite (FeS2), with a substantially higher Fe to Cu ratio of 67.5:1 and a marked presence of impurities such as antimony (Sb) and arsenic (As).

To prepare these concentrates for the electrolysis experiments, they were processed into briquettes. This involved first sieving the concentrates to ensure 90% of the particles were finer than 250 μm (D90=250 μm). Following sieving, the concentrates were mixed with 2% bentonite and 2% water to form a mixture. This mixture was then compacted under a pressure of 200 kN for 5 minutes, resulting in briquettes measuring 40 mm in diameter and 6 mm in thickness (Φ40×6 mm). The final step involved drying and sintering the briquettes in an oven set at 150 °C for about 40 hours. Once completed, the briquettes were stored in plastic bags, ready for subsequent use in electrolysis processes.

2.2.2 Materials and preparation for electrolytic reduction of iron oxides

Wustite, hematite, magnetite, and iron ore concentrate served as the primary materials in this study. Wustite was synthesized through the thorough blending of chemical-grade iron powder and magnetite powder in a precise stoichiometric ratio. This mixture was then subjected to a heat treatment process in a vertical furnace at 900°C for 24 hours, under a continuous flow of argon gas. The successful formation of wustite was subsequently verified through X-ray Diffraction (XRD) analysis. Both hematite and magnetite used in the experiments were of high purity, classified as pure chemicals. The iron ore concentrate (total iron content 64.6%), characterized as a magnetite-type ore with a particle size where 80% of the material is below 82 μm (D80=82 μm), was procured from a local iron ore producer. For the electrolysis experiments, the iron oxides underwent a process to form briquettes, employing a methodology akin to that previously described. This process ensures the creation of briquettes from the iron oxide materials to facilitate their use in the electrolysis experiments.

2.2 Experimental setup and procedure

Figure 1 shows the experimental setup for the electrolytic reduction of chalcopyrite and pyrite. A steel crucible (inner diameter 230 mm and height 508 mm) with lid was placed in a pit furnace and then the crucible was filled with ca. 25 kg mixture of chemical pure NaCl (purity >98%) and KCl (purity >99.8%) of equal mole. The salt in the crucible was heated to a desired temperature (around 680-870 °C) into a molten salt at a heating rate of 10 °C/min. Two electrodes (namely, anode and cathode) were placed in the molten salt. The anode is a graphite block connected on copper conductor; the cathode is a molybdenum net, which is used to hold the as-prepared briquettes. The net was made by folding molybdenum mesh into a bag hold either 2 or 4 briquettes. The net was connected to a stainless-steel plate and then to a copper conductor. This is to avoid the damage of the molybdenum net and copper conductor, which could otherwise easily get oxidized at the molten slag/gas interface by oxygen and the generated sulphurous gas.

During the electrolysis the chamber above the molten salt was purged by N_2 or Ar gas in order to protect the electrodes from oxidation and expel the generated sulphurous gas. For electrolytic reduction of iron oxides, a similar experimental setup, as it is shown in FIG 1, was applied. In this case, the steel crucible was filled with ca. 25 kg NaOH (purity >99.8%) and the operation temperature was set to be ca. 500 °C.

FIG 1 – Experimental setup for molten salt electrolysis at SWERIM.

In all the electrolysis trials, constant voltage electrolysis was conducted. Each electrolysis trial began with a short series, during which the voltage was increased from 0 to 2.5 V for chalcopyrite electrolysis in molten NaCl-KCl salt or 1.7 V for iron oxides in molten NaOH salt. The electrolysis process was terminated after several hours. After each experiment, the molybdenum net with sample was detached from the cathode. FIG 2 shows the appearances of the obtained sample. The sample with the net was placed in distilled water. Then the glass was put in an ultrasonic water bath to make the salt in the sample dissolved in the water. Thereafter, the sample for the chalcopyrite/pyrite trials was able to be separated into two sub-samples. These samples were carefully washed with distilled water and filtrated several times to get rid of the salt. The sample from the iron oxide trials only has one single sample for each experiment. The resulting samples were then filtered out and dried in an oven at a temperature of 105°C for over 12 hours to remove any remaining water. Selected samples were analysed by XRD, XRF and SEM methods.

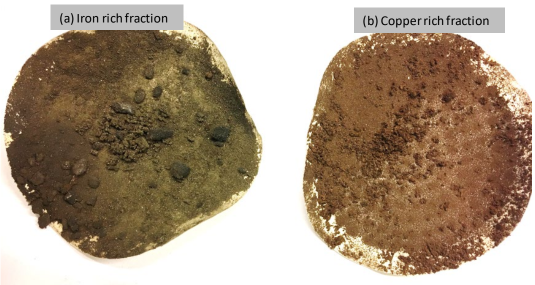
FIG 2 – Appearance of the cathode sample after electrolysis.

3 RESULTS AND DISCUSSION

3.1 Electrolytic reduction of chalcopyrite/pyrite

Sulphur content in the sample or subsample is an important index to evaluate the extent of electrolytic reduction. A lower sulphur content in the sample indicates a higher degree of electrolytic reduction. After electrolysis, the sulphur contents in the samples were analysis by LECO analysis. It is seen that the samples had quite low S contents (as low as 0.01%) compared to that in the original samples (18.5% S in the chalcopyrite sample and 22.7% S in the pyrite sample). This indicates an almost complete reduction of chalcopyrite/pyrite in the electrolysis trials.

FIG 3 shows an example of the obtained two sample fractions from one electrolysis trial using chalcopyrite. It is seen that the one sample fraction had reddish colour, while another sample fraction had dark green colour. The difference in colours in the two sample fractions is attributed to the difference in chemical compositions that later confirmed by chemical analysis. The reddish fraction is referred to as Cu-rich fraction and the dark green fraction as Fe-rich fraction. The chemical analysis results show that the Cu-rich fractions contain 43.1% Cu and 40.1% Fe, while the Fe-rich fractions contain 4.9% Cu and 55.3% Fe. The high amount of Fe in the Cu-rich fraction is attribute to the fact that during scratching the coagulated materials from the Mo net, some iron particles were also taken down. Further, it should be noted that the collected Cu-rich fraction is far below the balanced amount according to the amount of the charged materials during electrolysis. This is due to that some copper particles were lost in the molten salt. These results clearly indicate that during electrolytic reduction of chalcopyrite, the in-situ separation of copper, iron and sulphur is possible.


(a) Iron rich fraction

(b) Copper rich fraction

FIG 3 – Appearances of the obtained samples of iron-rich and copper-rich fractions from one electrolysis trials using chalcopyrite.

After electrolytic reduction of pyrite, it was found that the materials coagulated on the Mo were found quite less and not be able to be collected. Therefore, this electrolysis sample was taken a whole and analysed by XRD and XRF methods. By combining the LECO analysis result for the same sample, it can conclude that iron and copper were completely reduced after the electrolysis of pyrite, the leading phase in the obtained product is iron. The SEM analysis of the reduced pyrite sample shows that the reduced iron particles have a cubic shape in the scale of several to several tens of microns.

It is known that in the used pyrite sample it contains several trace elements, the concentrations of which are in noticeable level. To evaluate how these trace elements behave during the electrolysis, the removal efficiency of these trace elements was calculated, by combining the chemical compositions of the original pyrite and the reduced products. It is seen that elements Zn, Sb, As and Hg can be removed; elements Pd and Cd can be partially removed after electrolysis.

3.2 Electrolytic reduction of iron oxides

During electrolytic reduction of wustite, it is found that wustite was reduced to iron in a single step. However, for the electrolytic reduction of hematite, magnetite, and magnetite ore, co-existence of FeO, Fe_2O_3, and Fe_3O_4 were found in the incompletely reduced samples. This indicates a stepwise reduction of iron oxides from high valence to low valence, ultimately leading to the production of metallic iron electrolytically. It should be noted, during electrolytic reduction of iron oxides, graphite was used as the anode. This has led to the generation of CO/CO_2. The future research focus will be investigating the use of inert anode to reach the carbon neutrality of the process. Scaling up the process to a scale comparable to the conventional ironmaking process can be quite challenging;

however, the process may still find its use to produce high-quality iron product or product other metal products that cannot be produced in a conventional or sustainable way.

CONCLUSIONS

A pilot-scale molten salt electrolysis reactor was established at SWERIM to study the molten salt electrolysis of sulphur ore, chalcopyrite and pyrite, and various iron oxides, including wustite, hamatite, magnetite, and magnetite-type iron ore. The results from electrolytic reduction of chalcopyrite/pyrite demonstrate that in situ separation of copper, iron, and sulphur is possible, enabling the extraction of all valuable elements without CO2 emissions. Furthermore, the findings underscore the capability to eliminate impurities like zinc, antimony, arsenic, and mercury from the electrolysis product. The results from electrolytic reduction of iron oxides/ore demonstrate the stepwise reduction of iron oxides from high valence to low valence, ultimately leading to the production of metallic iron.

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