

EXTRACTING LITHIUM FROM A LITHIUM ALUMINATE COMPLEX BY VACUUM ALUMINOTHERMIC REDUCTION

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Abstract

The molten salt electrolysis of LiCl–KCl is presently the primary method of producing lithium, but it is costly and has environmental issues in addition to other disadvantages. Vacuum thermal reduction may be used extensively in the future because it offers low energy consumption, a high purity product and short cycle times. The present study investigated a novel process for the extraction of lithium from Li_3AlO_4 clinker by vacuum aluminothermic reduction. The Li_3AlO_4 clinker was prepared in ambient air using lithium hydroxide, alumina and calcium oxide. The results show that this process can proceed in conjunction with a lower ratio of raw materials to lithium (8.89:1) and provides lithium reduction rates in excess of 97%. In addition, the reduction slag consists mainly of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, which can be used to produce aluminum hydroxide. Thus, this process represents a highly efficient and environmentally-friendly method of generating lithium.

Keywords: Lithium; Vacuum; Aluminothermic reduction

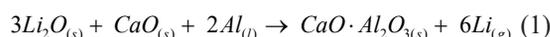
1. Introduction

Lithium is the lightest metal and is widely used in many fields, including in lithium ion batteries, alloying with aluminum and magnesium, aerospace applications and thermonuclear fusion [1,2]. Molten salt electrolysis and vacuum thermal reduction are the two main methods of lithium extraction. At present, over 90% of the world's lithium is produced by the former process, although the latter is continuously researched because it involves short production cycles, does not generate corrosive gases and results in a product with low levels of sodium and potassium [3,4].

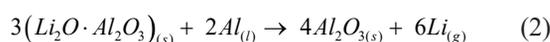
Vacuum thermal reduction was first proposed by Bappen in 1894, who used magnesium as a reductant and obtained coarse lithium containing approximately 50% magnesium. Many subsequent improvements have been proposed to reduce costs and improve the reduction efficiency and lithium purity. These newer processes can be divided into three types, based on the reduction agent: carbon thermal reduction, hydrogen reduction and metal thermal reduction. Common metal reduction agents include magnesium, aluminum, silicon and their alloys. The U.S. Bureau of Mines has investigated the carbon thermal reduction of spodumene at 1680 °C, and it is thought that various carbide formations were present in these reaction mixtures [5].

Lin extracted lithium from lithium carbonate using

calcium carbide and carbon reduction in conjunction with a vacuum metallurgy method, although the product was only 54.34% pure because of the reaction between the lithium vapor and CO [6,7]. Nevertheless, it is anticipated that vacuum thermal reduction using aluminum, silicon or Al-Si alloys as reduction agents will become an important industrial process in the future. The aluminothermal reduction of lithium was described in a U.S. patent as early as 1935 [8], and Kroll and Schlechten have since reported that CaO must be added to the reaction mixture [9]. The overall reaction in this process is as follows.



Stauffer extracted lithium with a 92.2% yield via the vacuum thermal reduction of a mixture of spodumene, aluminum and CaO, but found that the direct reduction of spodumene without CaO was not successful [10]. Fedorov and Shamrai studied the reduction of lithium aluminate by aluminum [11], based on the reaction equation below.



Kroll also prepared metallic lithium using the vacuum silicon thermal reduction method on the laboratory scale [5], while Smeets studied the bench scale reduction of lithia and spodumene with

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aluminum and silicon as the reductants [12]. The extraction of metallic lithium by vacuum thermal reduction has been investigated by many researchers at KUST in China. These studies employed lithium carbonate as the raw material together with CaO, employing various reductants, including aluminum, silicon, calcium carbide, carbon and iron [13,14]. The results demonstrated that aluminum and silicon are the most suitable reductants and that large amounts of CaO are required to lower the reduction temperature.

In the present work, a new aluminothermic reduction process was developed, with the aim of increasing the lithium reduction efficiency and recovery rates, while lowering the amount of residue. This process employs lithium hydroxide, alumina and calcium oxide as the raw materials and is summarized in Fig. 1. In this process, a mixture of the raw materials is initially calcined to produce Li_5AlO_4 clinker under ambient air. Metallic lithium is subsequently extracted from the Li_5AlO_4 using aluminum as the reductant under vacuum, while also producing a side-product containing calcium aluminate. This material can be recycled to produce high-whiteness $\text{Al}(\text{OH})_3$ or Al_2O_3 . The preparation of lithium-rich Li_5AlO_4 clinker has been previously reported [15]. However, in this work, the optimal calcination conditions for the reduction reaction were determined and the extraction of lithium from the Li_5AlO_4 clinker by a vacuum aluminothermic process was examined.

2. Experimental

2.1 Materials

The raw materials used in present work were obtained from the Sinopharm Chemical Reagent Co.,

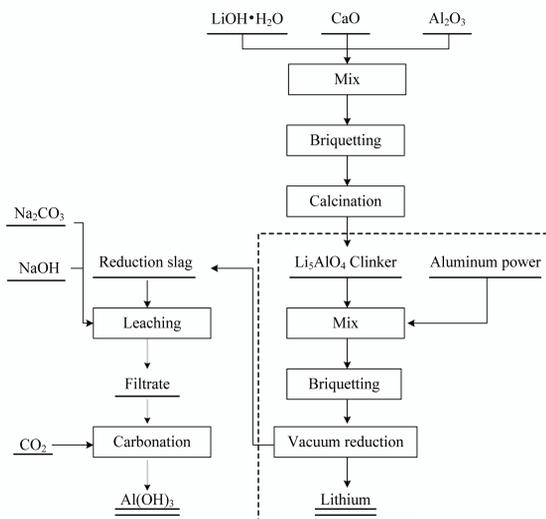


Figure 1. A flow chart summarizing the novel aluminothermic reduction of lithium

Ltd. Their compositions are listed in Table 1-3. The aluminum used as the reduction agent was 99% pure on a mass basis.

Table 1. Major chemical components of lithium hydroxide hydrate / wt%

LiOH·H ₂ O	Li ₂ CO ₃	Na	K	sulfate
≥95.0	≤2.0	≤0.05	≤0.05	≤0.02

Table 2. Major chemical components of alumina / wt%

Al ₂ O ₃	alkali metal	chloride	Ignition loss
≥95.0	≤0.5	≤0.01	≤5.0

Table 3. Major chemical components of calcium oxide / wt%

CaO	alkali metal	sulfate	Ignition loss
≥98.0	≤0.5	≤0.1	≤2.0

2.2 Apparatus

The experiment apparatus employed in this work is shown in Fig. 2.

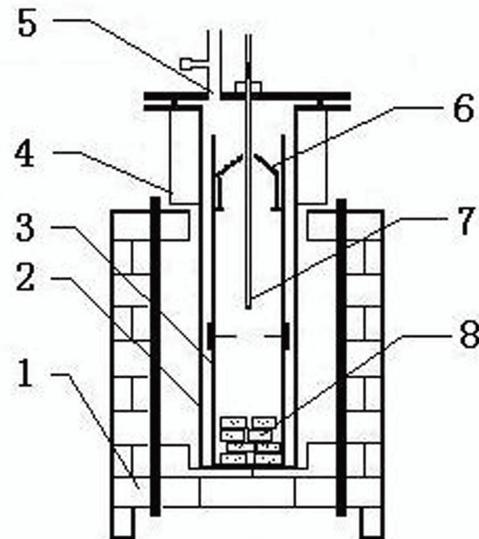
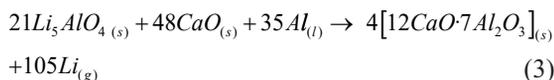


Figure 2. A diagram of the vacuum reduction furnace. 1-furnace; 2-reactor; 3-briquettes bucket; 4-cooling water; 5-vacuum tube; 6-condenser; 7-thermocouple; 8- briquettes

2.3 Experimental method

Lithium hydroxide, alumina and calcium oxide were combined in the molar ratio of 70:7:32. The subsequent reaction was as follows.





In this reaction, the theoretical mass ratio between the raw materials and lithium is 8.54:1. The mixture was pressed into pellets by applying a set pressure and these pellets were then calcined under ambient air. The calcined material was milled into a powder and subsequently combined with aluminum powder to form a new mixture that was also pressed into pellets. These pellets were loaded into the reactor for the reduction experiments. During the reduction, lithium was reduced by aluminum under vacuum and at high temperature and the product was collected on the condenser while the reduction slag was left in the briquettes bucket. The lithium reduction rate (η_{Li}) was calculated using the formula

$$\eta_{\text{Li}} = m_{\text{Li}} / M_{\text{Li}} \times 100\% \quad (4)$$

where M_{Li} is the amount of lithium originally in the raw material mixture and m_{Li} is the quantity of lithium collected on the condenser after the vacuum aluminothermic reduction process.

3. Results and discussion

The effects of briquette pressure, calcination temperature and time on the burning loss rate and lithium reduction rate have been previously investigated [15]. The burning loss rate was found to remain constant at approximately 34% when employing a briquette pressure of 30 MPa, a calcination temperature of 750–800 °C and a calcination time of 60–90 min. Thus, in the present work, Li_5AlO_4 was prepared under these same conditions. Reaction temperature, time and add amount of aluminum powder are major factors on aluminothermic reduction process [16], so effects of these factors on lithium reduction rate were investigated as follows.

3.1 Effect of reduction temperature on reduction rate

The reduction of Li_5AlO_4 is endothermic, and so higher temperatures increase the reaction rate. The effects of reduction temperature on the reduction rate are summarized in Fig. 3. It is evident that the reduction rate increases with increase in the reduction temperature, although this effect plateaus around 1100 °C. There are two main stages of this increase in the reduction rate. The first stage is from 900–1100 °C, over which the rate rapidly increases by about 70%, while the second stage is over the range 1100–1200 °C, and involves a slower increase. The reduction rate is above 93% at 1200 °C at a reduction time of 90 min.

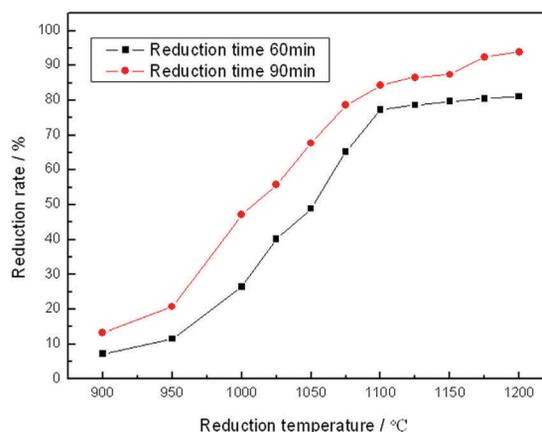


Figure 3. The lithium reduction rates as functions of reduction temperature

3.2 Effect of reduction time on reduction rate

In present work, the reduction time is defined as the time span at a constant temperature after the apparatus reaches that temperature. Fig. 4 plots the results of experiments at various reduction times. It can be seen that the lithium reduction rate increases as the reduction time is extended. At a reduction time of 75 min at 1200 °C, the reduction rate is above 90%.

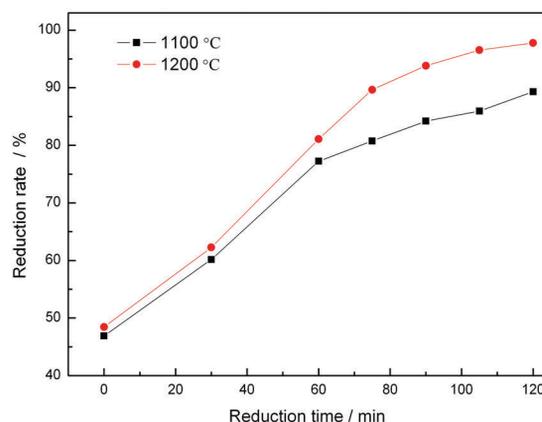


Figure 4. The lithium reduction rates as functions of the reduction time

3.3 Effect of aluminum excess coefficient on reduction rate

Herein, the aluminum excess coefficient is defined as the percent difference between the actual amount of aluminum in the reaction mixture and the amount of aluminum required on a stoichiometric basis. Fig. 5 shows the effects of this parameter on the reduction rate of lithium. There are two stages in this plot. The first stage is from 0% to 6%, over which an excess of aluminum increases the contact area between the



reductant and the lithium oxide and so increases the reaction rate. In the second stage, the reduction rate decreases at coefficient values above 6%, meaning that the aluminum powder is used less efficiently. This phenomenon differs from observations obtained during experiments with vacuum reduction based on magnesium [17].

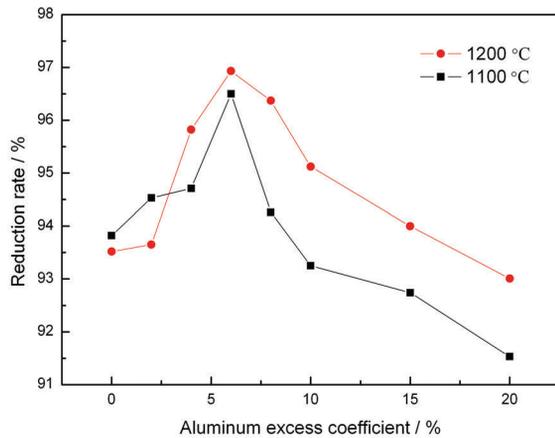
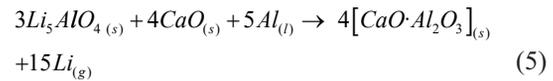


Figure 5. The lithium reduction rates as functions of the aluminum excess coefficient (reduction temperature 1100 °C and 1200 °C, reduction time 90 min)

The composition and morphology of the reduction slag were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in an attempt to explain the effects of the excess aluminum coefficient. The XRD patterns are presented in Fig. 6. The data for the reduction slag indicate the presence of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$, $\text{CaO}\cdot \text{Al}_2\text{O}_3$ and CaO at aluminum excess coefficients below 6%. In contrast, $\text{CaO}\cdot \text{Al}_2\text{O}_3$, $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$, CaO , LiAlO_2 and aluminum are present at a coefficient of 20%, indicating that the reduction reaction was incomplete. These reaction products in the residue allow us to determine the primary chemical reactions, which

include that in equation (3) as well as the reaction in equation (5), below.



SEM micrographs of the reduction slag are shown in Fig. 7, and demonstrate the presence of numerous pores through which lithium vapor can diffuse. Fig. 7 (a) presents a micrograph of the reduction slag obtained under the conditions of reduction temperature 900 °C, reduction time 90 min and Al excess coefficient 0%, there is almost none pore on the surface of the particle, and the lithium reduction rate is below 15% (Fig. 3). Fig. 7(b),(c),(d) show the micrographs of the reduction slag obtained with different reduction time under reduction temperature 1200 °C and Al excess coefficient 0%. It can be seen that the number of pore increases as the reduction time is extended, and at the same time the lithium reduction rate also increases (Fig. 4). In other words, the number and size of pores on the surface of particle are closely related to the lithium reduction rate. Therefore, it can be considered that lithium vapor diffused from those pores on the surface of particles. Fig. 7(f) presents a micrograph of the reduction slag generated using an aluminum excess coefficient of 20%. The surface of the particle indicates a molten state and the diameters of the holes are smaller than those in Fig. 7(e), which was obtained with a coefficient of 6%. Fig. 8 shows photographic images of the reduction slag obtained under different reduction conditions. It is evident that higher coefficients generate a more cohesive surface structure.

These images indicate that an excess of aluminum powder results in a coating of liquid aluminum on the surface of the reduction mixture, which presumably constrains the lithium vapor. Thus, the reduction rate

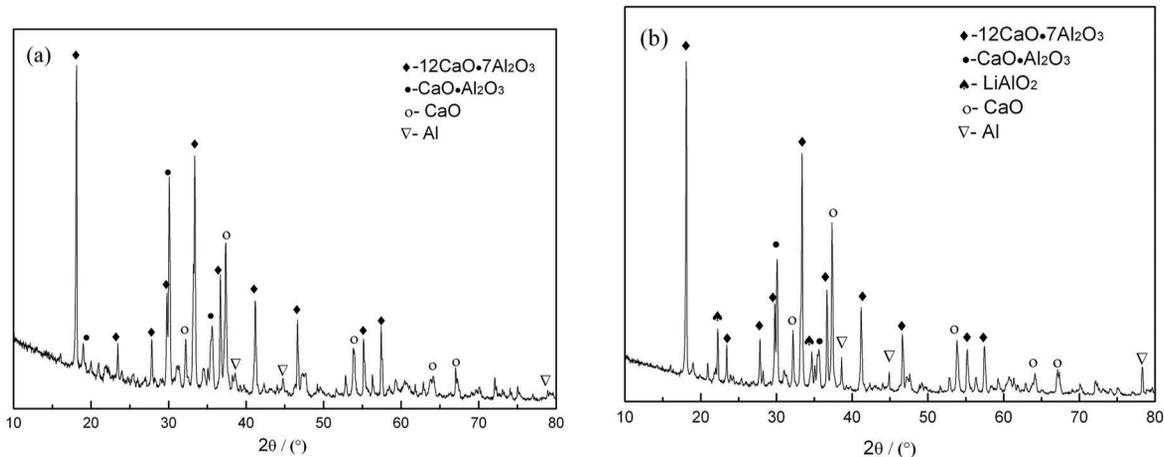


Figure 6. XRD patterns of the reduction slag obtained using an aluminum excess coefficient of (a) 6% and (b) 20%

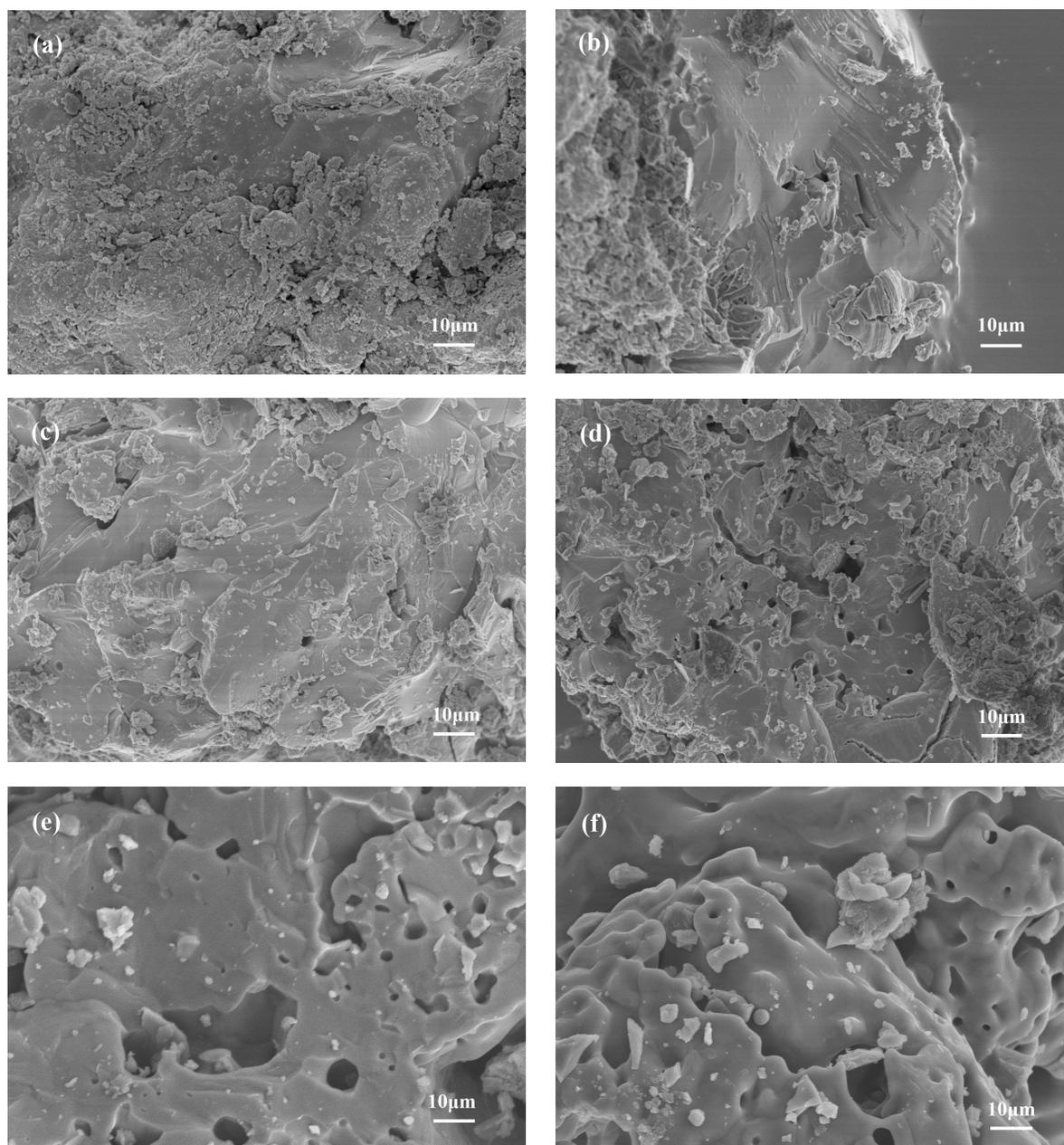


Figure 7. SEM images of the reduction slag obtained under the reduction conditions: (a) temperature 900°C, time 90 min, Al excess coefficient 0%, (b) temperature 1200°C, time 0 min, Al excess coefficient 0%, (c) temperature 1200°C, time 30 min, Al excess coefficient 0%, (d) temperature 1200°C, time 90 min, Al excess coefficient 0%, (e) temperature 1200°C, time 90 min, Al excess coefficient 6% and (f) temperature 1200°C, time 90 min, Al excess coefficient 20%

and the aluminum utilization decrease when a large excess of aluminum is employed. For these reasons, an optimal quantity of aluminum should be used to ensure a high reduction rate and suitable utilization of the aluminum.

Finally, previous work has confirmed that high-whiteness aluminum hydroxide can be obtained from $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ reduction slag [18-20], and so the slag

resulting from the present lithium extraction process could be recycled by alkali leaching and carbonation precipitation.

4. Conclusions

The extraction of lithium from Li_5AlO_4 clinker by aluminum thermal reduction is feasible in a vacuum

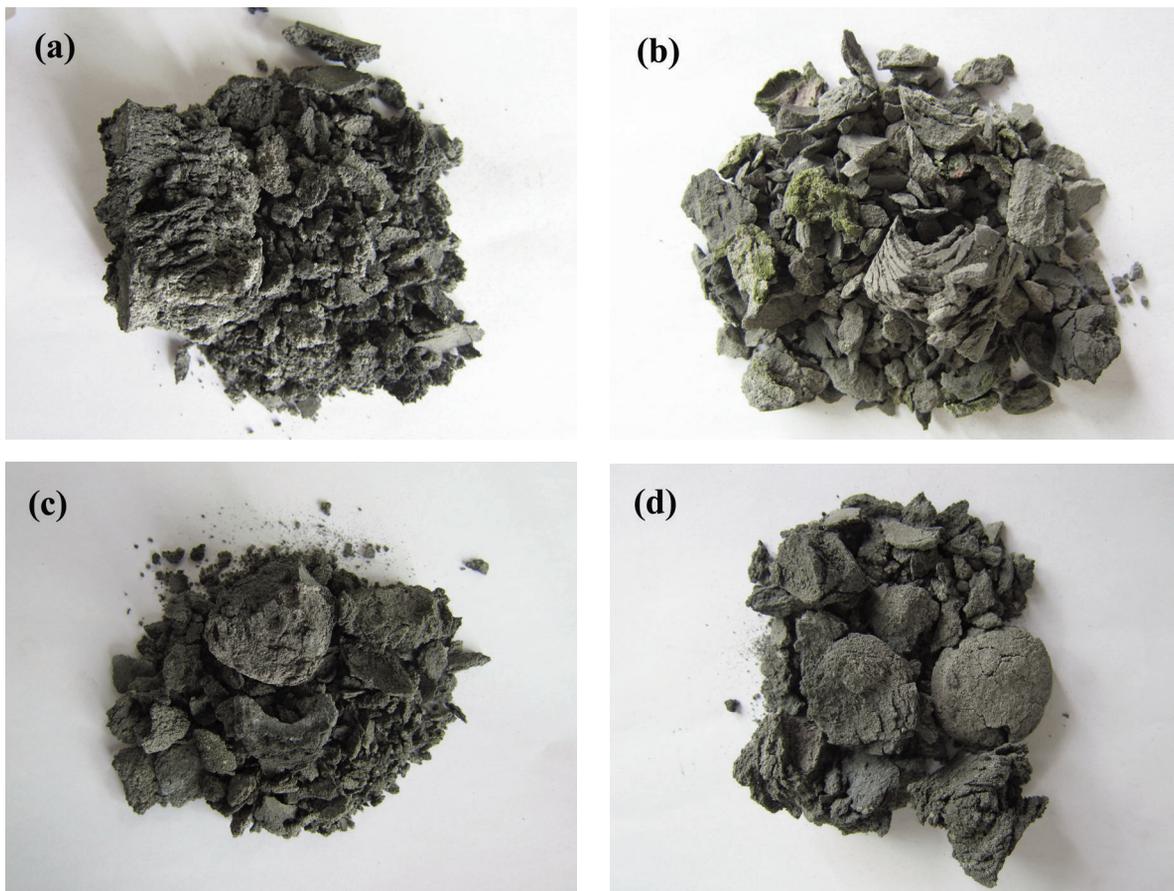


Figure 8. Photographic images of the reduction slag obtained using an aluminum excess coefficient of (a) 0%, (b) 6%, (c) 10% and (d) 20%

system. A lithium reduction rate in excess of 97% can be obtained at a reduction temperature of 1200 °C in conjunction with a reduction time of 90 min and an excess aluminum coefficient of 6%, together with a raw material to lithium ratio of 8.89:1. The reduction slag consists primarily of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ and $\text{CaO}\cdot\text{Al}_2\text{O}_3$ and could be leached with sodium carbonate and sodium hydroxide to obtain aluminum hydroxide by carbonation precipitation from a sodium aluminate solution. Thus, the overall aluminothermic lithium reduction process is highly efficient and results in a reduction slag that can be recycled as aluminum hydroxide using a hydrometallurgical method.

Acknowledgement

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DOBIJANJE LITIJUMA IZ KOMPLEKSA LITIJUM ALUMINATA POSTUPKOM ALUMINOTERMIČKE REDUKCIJE U VAKUUMU

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Apstrakt

Elektroliza rastopa soli LiCl–KCl trenutno predstavlja primarni metod dobijanja litijuma, ali je to skup postupak i pored ostalih nedostataka, takođe predstavlja problem za životnu sredinu. Termička redukcija u vakuumu se može intenzivnije koristiti u budućnosti zato što nudi nisku potrošnju energije, proizvod visoke čistoće i kratak vremenski ciklus trajanja. Tokom ovog istraživanja ispitivao se novi postupak dobijanja litijuma iz Li_5AlO_4 klinkera postupkom aluminotermičke redukcije u vakuumu. Klinker Li_5AlO_4 je pripremljen u prirodnim uslovima koristeći litijum hidroksid, aluminijum i kalcijum oksid. Rezultati pokazuju da se ovaj postupak može odvijati kada je sirovina u manjoj razmeri u odnosu na litijum (8.89:1), kao i da omogućuje stopu redukcije litijuma od preko 97%. Osim toga, redukciona šljaka se uglavnom sastoji od $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ koji može da se koristi za dobijanje aluminijum hidroksida. Stoga, ovaj postupak predstavlja veoma efikasan i ekološki prihvatljiv metod dobijanja litijuma.

Ključne reči: Litijum; Vakuum; Aluminotermija

