

Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Original Article

A preliminary study of pilot-scale electrolytic reduction of UO_2 using a graphite anodeSung-Wook Kim^{*}, Dong Hyun Heo, Sang Kwon Lee, Min Ku Jeon, Wooshin Park, Jin-Mok Hur, Sun-Seok Hong, Seung-Chul Oh, Eun-Young Choi

Pyroprocessing Division, Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 34057, Republic of Korea

ARTICLE INFO

Article history:

Received 6 March 2017

Received in revised form

12 May 2017

Accepted 23 May 2017

Available online xxx

Keywords:

Anode

Carbon

Electrolytic Reduction

Pilot Scale

Pyroprocessing

Spent Fuel

ABSTRACT

Finding technical issues associated with equipment scale-up is an important subject for the investigation of pyroprocessing. In this respect, electrolytic reduction of 1 kg UO_2 , a unit process of pyroprocessing, was conducted using graphite as an anode material to figure out the scale-up issues of the C anode-based system at pilot scale. The graphite anode can transfer a current that is 6–7 times higher than that of a conventional Pt anode with the same reactor, showing the superiority of the graphite anode. UO_2 pellets were turned into metallic U during the reaction. However, several problems were discovered after the experiments, such as reaction instability by reduced effective anode area (induced by the existence of Cl_2 around anode and anode consumption), relatively low metal conversion rate, and corrosion of the reactor. These issues should be overcome for the scale-up of the electrolytic reducer using the C anode.

© 2017 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Electrolytic reduction is a key technique in pyroprocessing, which is being developed to manage and recycle spent fuels generated in pressurized water reactors [1–3]. Spent fuels, a complex mixture of metal oxides (mainly UO_2), are electrochemically converted to metallic states [e.g., $\text{UO}_2 = \text{U} + 2\text{O}_2(\text{g})$] after electrolytic reduction using $\text{LiCl-Li}_2\text{O}$ molten salt as an electrolyte [1–3]. Pt has been widely used as an anode material evolving O_2 gas ($2\text{O}^{2-} = \text{O}_2(\text{g}) + 4\text{e}^-$) [4–7]. However, it has been identified that the Pt anode is gradually damaged during the operation owing to (electro)chemical side reactions [5–7]. The cost of the raw material of Pt is extremely high, and thus its limited lifetime is a major hurdle for pyroprocessing.

Several candidates have been extensively investigated to replace the Pt anode [8–16]. Among these, C is an attractive material because of its low cost and reasonable electrical and mechanical properties [14–16]. Under moderate operation conditions (~3.0 V) based on the CO/CO_2 evolution reaction ($\text{C} + x\text{O}^{2-} = \text{CO}_x + 2x\text{e}^-$) of the C anode, accumulation of the Li_2CO_3 by-product in the $\text{LiCl-Li}_2\text{O}$ electrolyte cannot be prohibited, which makes the reuse of the electrolyte

impossible [14,17]. Recently, a high-voltage electrolytic reduction technique was proposed using the C anode in small-scale experiments (up to 50 g UO_2) [15]. The dissociation voltage of LiCl [$2\text{LiCl} = 2\text{Li} + \text{Cl}_2(\text{g})$] is approximately 3.46 V [14]. When a sufficiently high voltage is applied, Cl_2 is expected to be evolved preferentially at the C anode instead of O_2 and CO/CO_2 [15]. In the presence of Cl_2 , Li_2CO_3 , which is the major side reaction product of the C anode, can be removed via various chemical reaction pathways [15]. At the same time, metallic Li formed at the cathode assists the reduction of UO_2 to metallic U ($\text{UO}_2 + 4\text{Li} = \text{U} + 4\text{Li}_2\text{O}$) [15]. It has been confirmed that the high-voltage operation effectively prevents Li_2CO_3 accumulation, meaning that the electrolyte can be reused [15].

Scale-up is an important issue for the commercialization of pyroprocessing [1]. In this study, preliminary test of the electrolytic reduction of 1 kg UO_2 was performed using graphite as the C anode. Three experiments were conducted to examine its feasibility and to verify the technical issues associated with scale-up. An identical reactor, which was used to investigate the Pt anode at the 1-kg scale, was used to compare the cell's performance [18].

2. Materials and methods

An electrolytic reducer was installed inside an Ar-filled glove box to prevent air and O_2 exposure. Further description of the

^{*} Corresponding author.

E-mail address: swkim818@kaeri.re.kr (S.-W. Kim).

<http://dx.doi.org/10.1016/j.net.2017.05.004>

1738-5733/© 2017 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

electrolytic reducer is given in the literature [18]. The electrolytic reducer can be equipped with one cathode and two anodes as shown in Fig. 1A. A stainless steel basket (STS 314L) with a perforated wall was used as the cathode (Fig. 1B). UO_2 pellets (1 kg) were loaded into the cathode basket (length \times width \times height = 100 \times 25 \times 120 mm). The electrochemical performance of two types of rod-shaped graphite anodes (diameter = 8 mm and length = 20 cm/diameter = 15 mm and length = 10 cm) (R8500; SGL Carbon group, Wiesbaden, Germany) was examined. The graphite anode was held by a stainless steel lead as shown in Fig. 1C. The anode shroud was made with a 3 wt.% MgO-stabilized ZrO_2 tube (bottom) (outer/inner diameter = 28/22 mm) and stainless steel pipe (top) (Fig. 1D). The effect of the anode shroud was investigated by controlling the immersion depth. The initial electrolyte used was dehydrated LiCl (6 kg) (99%; Alfa Aesar, Ward Hill, United States of America) without any additives. The reaction temperature was 650°C, which is high enough to melt the electrolyte. The LiCl was replenished after the reaction to maintain an adequate electrolyte height. The electrolytic reduction was carried out with a constant current operation using an external power supply (EX30-240; ODA Technologies, Incheon, Republic of Korea), and cell voltage was monitored with a digital multimeter (34405A; Agilent Technologies, Santa Clara, United States of America) simultaneously. The gas product evolved at the anode surface was exhausted through off-gas line connected to highly concentrated NaOH solution to eliminate the Cl_2 within it. The concentration of Li_2O and Li_2CO_3 in the electrolyte was determined by an autotitrator (G20; Mettler-Toledo, Greifensee, Switzerland) using 0.1N HCl solution. X-ray diffraction (XRD) (D8 Advance; Bruker) analysis was carried out for phase identification.

3. Results and discussion

3.1. Effect of anode shroud

Prior to the electrolytic reduction runs, the effect of the anode shroud was investigated using one graphite anode (diameter = 8 mm) as shown in Fig. 2. Electrochemical reaction was done with the constant current operation to keep the measured cell voltage at around 7.0 V. When the whole graphite anode was covered with the shroud (immersion depth = 4.5 cm), the electrochemical reaction was not stable and the cell voltage abruptly reached the voltage limit of the power supply within a few minutes (Fig. 2A). Such abnormal behavior was not observed in the small-scale experiment [15]. In this experiment, the cell current was 30 A, with a current density of 2.54 A/cm², which is higher than that observed in the small-scale experiment (~1.94 A/cm²). It is speculated that the high current density increases the concentration of gas bubbles generated at the graphite anode. The gas bubbles would reduce the effective anode area and increase the anode overpotential significantly, preventing the sustenance of the electrochemical reaction. It is worth noting that the open-circuit voltage was approximately 3.3 V, comparable to the LiCl decomposition voltage, when the electrochemical reaction was stopped. This implies that a large amount of Cl_2 gas existed around the graphite anode inside the shroud, which was not properly removed. The existence of the Cl_2 gas around the anode should be negative on the reaction stability. It has been reported that Cl_2 bubbles tend to remain for a long time at the C anode in the LiCl–KCl electrolyte [19,20]. These suggest that removing Cl_2 bubbles around the anode is important for the application of the graphite anode.

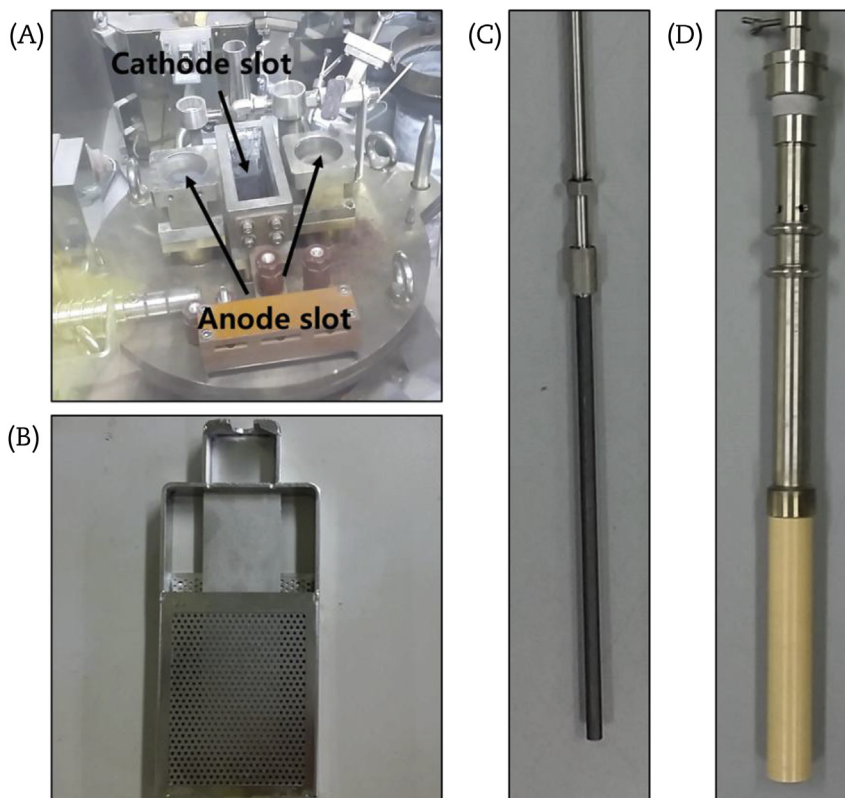


Fig. 1. Electrolytic reduction equipment. (A) Flange. (B) Cathode basket. (C) Graphite anode. (D) Anode shroud.

Download English Version:

<https://daneshyari.com/en/article/8084005>

Download Persian Version:

<https://daneshyari.com/article/8084005>

[Daneshyari.com](https://daneshyari.com)