Mechanochemical Approach for Oxide Reduction of Spent Nuclear Fuels for Pyroprocessing

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Solid-state mechanochemical reduction combined with subsequent melting consolidation was suggested as a technical option for the oxide reduction in pyroprocessing. Ni ingot was produced from NiO as a starting material through this technique while Li metal was used as a reducing agent. To determine the technical feasibility of this approach for pyroprocessing, which handles spent nuclear fuels, thermodynamic calculations of the phase stabilities of various metal oxides of U and other fission elements were made when several alkaline and alkali-earth metals were used as reducing agents. This technique is expected to be beneficial, not only for oxide reduction but also for other unit processes involved in pyroprocessing.

Keywords: Spent nuclear fuel, Pyroprocessing, Oxide reduction, Mechanochemical reaction

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1. Introduction

Korea Atomic Energy Research Institute is developing oxide fuel pyroprocessing with an aim to couple the back-end fuel cycle of pressurized water reactors (PWRs) that use oxide fuels with a closed-loop fuel cycle of sodium-cooled fast reactors (SFRs) that use metal fuels [1-2]. Oxide reduction (OR) is a key technology of pyroprocessing because the oxide-phase spent nuclear fuels (SNFs) generated from the PWRs are converted to metallic states through the OR [3-7]. The OR product is further treated to fabricate fresh metal fuels for the SFRs [1-2].

High-temperature (~650°C) electrochemical reactions using LiCl-based molten salt (generally containing Li_2O) as an electrolyte, which is also called electrolytic reduction (ER), have been widely investigated for the OR technique [3-7]. The reaction mechanism can be briefly expressed as given below:

$$\text{Cathode: } 4Li^+ + 4e^- = 4Li \qquad (1)$$

$$\text{Cathode: } UO_2 + 4Li = U + 2Li_2O \qquad (2)$$

$$\text{Anode: } 2O^{2-} = O_2(g) + 4e^- \qquad (3)$$

$$\text{Electrolyte: } 2Li_2O = 4Li^+ + 2O^{2-} \qquad (4)$$

$$\text{Net reaction: } UO_2 = U + O_2(g) \qquad (5)$$
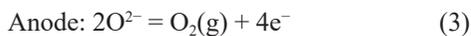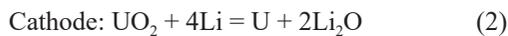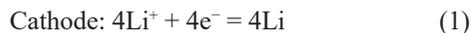
The in-situ formation of Li metals via reaction 1 is beneficial because, in an ideal case, only SNFs without any additives are used as the feed materials for ER operations, as shown in reaction 5. The formation rate (reaction 1) and the elimination rate (reaction 2) of the Li metal should be matched to keep the reaction constant. However, typically 120−200% of the theoretical charge is supplied during the ER operation, indicating unbalanced reaction rates [3-7]. Such difference in the reaction rates can become more critical upon the scale-up of the ER reactors. Indeed, the

consumption of Li_2O, which leaves excess Li metal, in the electrolyte was observed during large-scale (17 kg-UO_2) ER operations [3]. The excess Li metal could form Li metal clusters in the LiCl molten salt, causing anomalous physical behavior [8].

Here, we propose a mechanochemical reduction (MR)-based process as a simple and scalable OR technique. High mechanical impact can provide sufficient energy to overcome activation barriers of certain chemical reactions, even in solid states at low temperatures [9-10]. The strong mechanical energy is generally supplied to the reactants using simple milling equipment. Recently, Cho et al. reported that 5 L-scale SiO_2 can be mechanochemically reduced to Si metal by using Mg metal as a reducing agent with the following reaction [9]:

$$SiO_2 + 2Mg = Si + 2MgO \qquad (6)$$

The MgO byproduct was easily removed from the reaction product (i.e., Si-MgO composite) by acid treatment to obtain Si nanoparticles [9]. Similarly to this case, the oxide SNFs are expected to be reduced to metallic states by using highly reactive alkaline or alkali-earth metals as reducing agents (for instance, reaction 2). However, treatment of the SNFs with aqueous processes is strongly prohibited worldwide (especially in the Republic of Korea). In this respect, we adopted melting consolidation (MC) to remove the byproducts (i.e., alkaline or alkali-earth metal oxides) and, at the same time, to fabricate the consolidated metal ingot products. As the byproducts have low densities to the U metal, they could float on the liquid-phase metal surface during melting.

The feasibility of the MR-MC process to fabricate the metal ingot from its oxide phase was verified using NiO as a surrogate oxide material and Li metal as a reducing agent. The thermodynamic calculation of U and various fission elements was carried out to predict their phase stabilities with the presence of the alkaline and alkali-earth elements during the MR-MC process.

Table 1. U and fission elements used in the thermodyamic calculation

Category	Element	Oxides
U	U	UO_2, U_3O_8
Transuranic	Pu	PuO_2, Pu_2O_3
	Np	NpO_2, Np_2O_5
	Am	AmO_2, Am_2O_3
	Cm	CmO_2, Cm_2O_3
Rare-earth	Nd	Nd_2O_3
	Ce	CeO_2, Ce_2O_3
	La	La_2O_3
	Pr	PrO_2, Pr_2O_3, Pr_6O_{11}
	Sm	Sm_2O_3
	Y	Y_2O_3
	Eu	EuO, Eu_2O_3, Eu_3O_4
	Gd	Gd_2O_3
Group II	Ba	BaO
	Sr	SrO
Noble metal	Zr	ZrO_2
	Mo	MoO_2, MoO_3
	Ru	RuO_2
	Tc	TcO_2, TcO_3, Tc_2O_7
	Pd	PdO
	Rh	Rh_2O, RhO, Rh_2O_3

2. Experimental Methods

The MR experiment was done using a planetary ball-mill machine (Pulverisette 6, Fritsch). A stoichiometric amount of NiO (Samchun Chemical, 97%) and Li metal foil (Alfa Aesar, 99.9%), as well as stainless steel balls, was put together into a stainless-steel canister, which was subsequently sealed inside an Ar-filled globe box. The canister was installed in the ball-mill machine and then rotated at 300 RPM for 7 h (repeating 20 min operation and 10 min break). The reaction product was collected inside the glove box. The ball-mill product was treated inside an arc-melting furnace (Y&I Tech) under a vacuum environment for the consolidation. An energy dispersive X-ray spectroscope (EDS) (Horiba, X-MAX) coupled with a scanning electron microscope (Hitach, SU-8010) was used to identify the atomic ratio of the consolidated reaction product.

A thermodynamic investigation was made using HSC Chemistry 9 software (Outotec) [11]. Table 1 categorizes the elements and their oxides in the SNFs that were
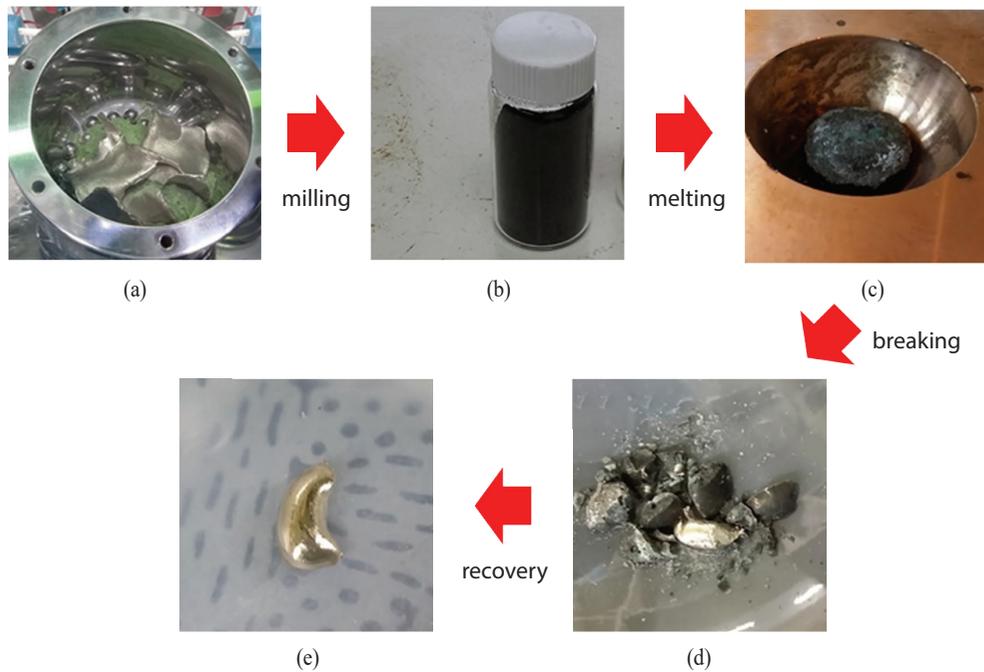
Fig. 1. Photographs of Ni ingot production process from NiO using the MR-MC process:
(a) before milling, (b) after milling, (c) after melting, (d) after breaking, and (e) after recovery.

considered in the calculation. Gibbs free energy change (ΔG) of chemical reactions between the oxides and the reducing agents (i.e., Li, Na, K, Mg, and, Ca) was calculated at a temperature range of $0-1,200°C$ to predict the phase stabilities during the MR-MC process.

3. Results and Discussion

3.1 Feasibiilty Test Using NiO

Since the MR reaction using the radioactive materials (e.g., UO_2) are not available due to legal regulations at this time, a surrogate test was carried out using NiO and Li metals to identify the technical feasibility of this process. Fig. 1(a) shows green-colored NiO powders and a bulky Li metal foil inside the canister before the MR operation. After the ball-milling, black-colored powders were obtained, as shown in Fig. 1(b), suggesting that the original NiO and Li

metals were lost via the following reaction 7:

$$NiO + 2Li = Ni + Li_2O \qquad (7)$$

The black powers were arc-melted, and then a consolidated button was obtained (Fig. 1(c)). The button was easily broken, even with a weak mechanical impact (Fig. 1(d)), leaving a shiny Ni metal ingot (Fig. 1(e)). The EDS anaylsis of the ingot was carried out to identify how well the OR reaction took place. The Ni content was more than 95 at.% in the metal ingot, showing that the MR technique combined with MC would be a promising strategy for the OR.

3.2 Thermodynamic Investigation

The actual SNFs are complicated systems composed of various oxide phases [12-13]. Some fission elements tend to form solid-solution phases with UO_2 grains while others would precipitate to form separate phases at the grain

Table 2. Summary of thermodyamic calculation results of U and TRU elements

Element	Oxide	With Li	With Mg	With Ca	Reoxidation
U	UO_2	Reduced	Reduced	Reduced	UO_2 with Li_2O
	U_3O_8	Reduced	Reduced	Reduced	
Pu	PuO_2	Reduced	Reduced	Reduced	
	Pu_2O_3	Reduced	Reduced	Reduced	
Np	NpO_2	Reduced	Reduced	Reduced	NpO_2 with Li_2O
	Np_2O_5	Reduced	Reduced	Reduced	
Am	AmO_2	Reduced	Reduced	Reduced	Am_2O_3 with Li_2O
	Am_2O_3	Reduced	Reduced	Reduced	
Cm	CmO_2	Reduced	Reduced	Reduced	
	Cm_2O_3	Reduced	Reduced	Reduced	
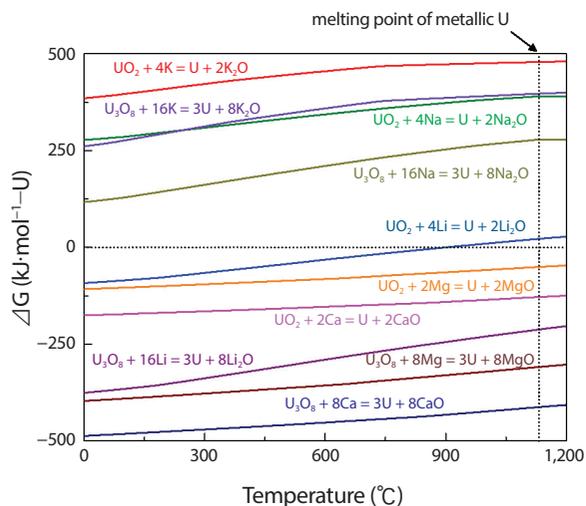
Fig. 2. Thermodynamic calculation of UO_2 and U_3O_8 with Li, Na, K, Mg, and Ca metals.

boundaries. In this thermodynamic study, we only focused on the chemical reactions of single-metal oxides with the reducing agents listed in Table 1. Nonetheless, we believe that this thermodynamic approach on the binay oxides is meaningful because of the following reasons:

- The goal of the MR-MC process is to produce metal ingots from the oxide SNFs.
- Non-reduceable elements (i.e., oxides) do not need to

be considered because they can be separated after the MC step.

Thus, the phase stability investigation on the reduced elements (i.e., metals) is enough to distinguish whether they can be stable after the MR-MC process.

3.2.1 U and Transuranic Elements

Recovering U and transuranic (TRU) elements is the major purpose of pyroprocessing to be recycled in the SFRs [1-2]. The goal of the OR process is to convert SNF constituents, especially U and TRU elements, so that subsequent electrochemical recovery (i.e., electrorefining and electrowinning) processes can work with the metal fuels [1-2]. Fig. 2 shows the ΔG of the chemical reactions of UO_2 and U_3O_8 with Li, Na, K, Mg, and Ca metals. Both UO_2 and U_3O_8 can be reduced in the typical MR condition (less than few hundreds °C) when Li, Mg, and Ca were used as the reducing agents. Na and K metals, therefore, were not considered further. Note that the U metal is not stable above ~900°C with a presence of Li_2O as UO_2 becomes stable at an elevated temperature (reverse direction of reaction 2). The melting point of the U metal is ~1,132°C. Thus, the reduced U metal can be oxidized back to UO_2 during the MC step when the Li reducing agent is used. Such

Table 3. Summary of thermodyamic calculation results of RE elements

Element	Oxide	With Li	With Mg	With Ca	Reoxidation
Nd	Nd_2O_3	Non-reduced	Non-reduced	Reduced	
Ce	CeO_2	Reduced	Reduced	Reduced	
	Ce_2O_3	Non-reduced	Non-reduced	Reduced	
La	La_2O_3	Non-reduced	Non-reduced	Reduced	
Pr	Pr_6O_{11}	Reduced	Reduced	Reduced	
	PrO_2	Reduced	Reduced	Reduced	
	Pr_2O_3	Non-reduced	Non-reduced	Reduced	
Sm	Sm_2O_3	Non-reduced	Non-reduced	Reduced	
Y	Y_2O_3	Non-reduced	Non-reduced	Non-reduced	
Eu	EuO	Non-reduced	Reduced	Reduced	
	Eu_2O_3	Reduced	Reduced	Reduced	Eu_2O_3 with Li_2O
	Eu_3O_4	Reduced	Reduced	Reduced	EuO with MgO
Gd	Gd_2O_3	Non-reduced	Non-reduced	Reduced	

high-temperature oxidation behavior of the U metal by Li_2O was experimentally and theoretically investigated in the previous studies [13-15].

A similar calculation was also made in the case of TRU elements, as summarized in Table 2. It was predicted that all TRU oxides can be converted to metallic states using Li, Mg, and Ca. Similarly to the U metal case, Np and Am metals were found to be oxidized to form NpO_2 and Am_2O_3, respectively, at an elevated temperature with the Li reducing agent. Consequently, using Mg and Ca as the reducing agents is suitable for the effective MR-MC process of the U and TRU oxides. During the MC step, all the U and TRU metals should be melted to form a liquid-phase alloy compound. The Cm metal has the highest melting point (~1,340°C) among these, and it seems that the MC step needs to be conducted above this temperature. Or the U-based alloy formation may lead to a decrease in the melting point since U is the most dominant element in the SNFs (UO_2 composition > ~95%), and thus the MC temperature could be lowered (near the melting point of the U metal). The residual reducing agents can be evaporated (boiling point of Li/Mg/Ca = 1,330/1,091/1,484°C) during the MC step to be separated from the reaction product.

3.2.2 Rare-Earth Elements

The U and TRU metal products are supposed to be recovered after the OR stage via electrorefining (U) and electrowinning (residual U and TRU) processes that utilize the LiCl-KCl-UCl_3 electroytes [1-2]. Rare-earth (RE) elements (either oxides or metals) in the SNFs contaminate the LiCl-KCl-UCl_3 electrolyte by consuming UCl_3 as described below with an example of the Nd_2O_3 case [16]:

$$2Nd_2O_3 + 3UCl_3 = 3UO_2 + 3NdCl_3 + Nd \qquad (8)$$

$$Nd + UCl_3 = U + NdCl_3 \qquad (9)$$
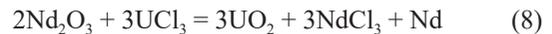
The electrowinning process utilized a liquid Cd cathode (LCC) technique, through which TRU chlorides, as well as UCl_3, are reduced to form a U-TRU-Cd alloy product [1-2, 17-18]. At the same time, the RE chlorides act like TRU chlorides to be co-reduced in the LCC product [17-18].

Table 4. Summary of thermodyamic calculation results of group II and NM elements

Element	Oxide	With Li	With Mg	With Ca	Reoxidation
Sr	SrO	Non-reduced	Reduced	Reduced	SrO with MgO
Ba	BaO	Reduced	Reduced	Reduced	BaO with Li_2O
Zr	ZrO_2	Reduced	Reduced	Reduced	ZrO_2 with Li_2O
Mo	MoO_2	Reduced	Reduced	Reduced	
	MoO_3	Reduced	Reduced	Reduced	
Ru	RuO_2	Reduced	Reduced	Reduced	
Tc	TcO_2	Reduced	Reduced	Reduced	
	TcO_3	Reduced	Reduced	Reduced	
	TcO_7	Reduced	Reduced	Reduced	
Pd	PdO	Reduced	Reduced	Reduced	
Rh	Rh_2O	Reduced	Reduced	Reduced	
	RhO	Reduced	Reduced	Reduced	
	Rh_2O_3	Reduced	Reduced	Reduced	

This phenomenon is critical for the SFR fuel application, as RE elements are well-known as neutron absorbers that should be restricted in the metal fuel to prevent its effect on the core physics [19]. An additional RE separation technique has been developed to minimize the RE content in the metal fuel products [1-2, 20-21]. Hence, it is beneficial to remove the RE elements from the feed materials of the electrochemical recovery processes.

Table 3 summarizes the thermodynamic calculation results of the RE elements. As some RE elements have various oxidation states, they can have a number of oxide phases. It should be noted that the reduced RE metals can be oxidized back upon the MC step if at least one stable oxide phase exists at a high temperature, regardless of the starting materials. Let us use the CeO_2 case as an example. CeO_2 can be reduced to Ce by the MR reaction using Mg through reaction 10, while Ce_2O_3 cannot. However, the Ce metal reduced from CeO_2 cannot be stable to form Ce_2O_3 (with an excessive amount of MgO generated from UO_2) during the MR or MC steps (reaction 11). Finally, reaction 12 is the reaction pathway of CeO_2.

$$CeO_2 + 2Mg = Ce + 2MgO \qquad (10)$$

$$2Ce + 3MgO = Ce_2O_3 + 3Mg \qquad (11)$$

$$2CeO_2 + Mg = Ce_2O_3 + MgO \qquad (12)$$
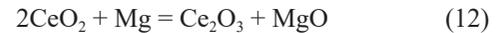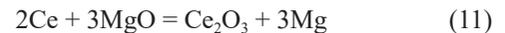
A similar approach can also be made in the re-oxidized phases of Eu. Thus, with the Li and Mg reducing agents, all RE elements are expected to have an oxide form after the melting step. If the floating RE oxides (mixed with Li_2O or MgO) are separated after the ingot production, the process load on the U and TRU recovery processes can be reduced. The Mg reducing agent maybe more promising because of the re-oxidation behavior of the U and TRU metals in the Li case. In contrast, Ca is the most powerful, and the RE oxides, except for Y_2O_3, can be reduced to metallic states, which are stable after the MR-MC process.

3.2.3 Other Elements

In the conventioanl ER process, the group II elements (e.g., Sr, Ba) are supposed to dissolve into an LiCl electrolyte
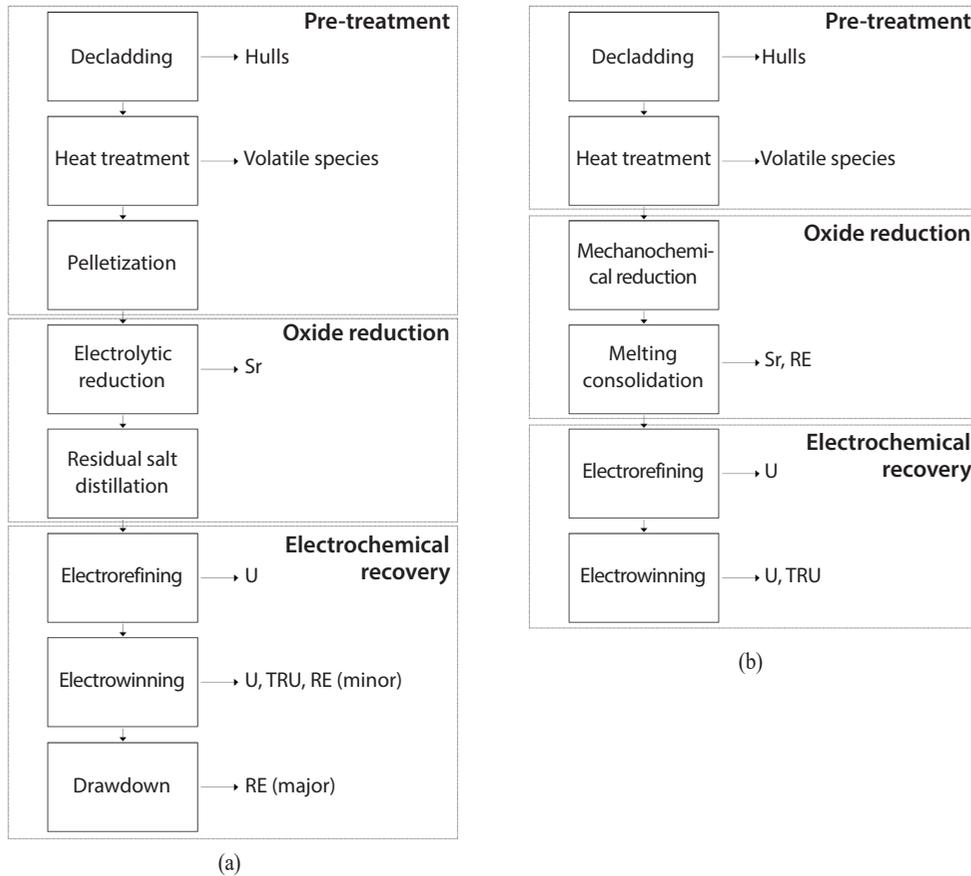
Fig. 3. Flow diagram of (a) conventional pyroprocessing based on the ER process and (b) modified pyroprocessing based on the MR-MC process.

for subsequent storage/disposal processes [22]. Hence, it is important to investigate their behaviors to replace the ER process. Table 4 shows the calculation results of the group II elements. SrO cannot be reudced with Li, and Mg-reduced Sr can be reconverted to SrO during the MC step. The Ba metal can also be oxidized to form BaO with Li_2O at a high temperature. Sr metal can be evaporated during the melting step (boiling point of Sr metals = ~1,377°C), and thus the off-gas should be carefully treated to prevent their exposure. The boiling point of the Ba metal is quite high (~1,845°C), and it is believed that the Ba metal can be incorporated into the U/TRU ingot, which will be transferred to the electrochemical recovery processes.

Noble metal (NM) elements generally have a low affinity to the O^{2-} ion; they can be easily converted to metallic phases, regardless of the reducing agents (Table 4). Only the reduced Zr metal can be oxidized back to ZrO_2 with the presence of Li_2O. They are supposed to form solid-solution phases with the excessive U metals, or they might be segregated depending on the heating and cooling conditions.

3.3 Modification of Pyroprocessing

The MR-MC process was suggested here to replace the state-of-art ER process. Fig. 3 briefly illustates the modified pyroprocessing flow diagram adopting the proposed OR process with comparison to the conventional one. The Mg
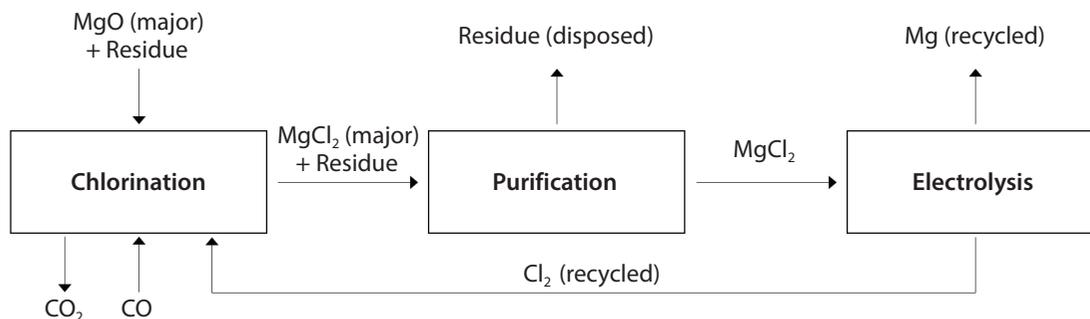
Fig. 4. Flow diagram of an example of the MgO recycling process.

reducing agent was considered here for removing the RE elements before the electrochemiacl recovery proceeses. During the MR step, the Mg could reduce U/TRU and other elements in the oxide SNFs, as given in Tables 2-4. Several elements (e.g., RE and Sr) are supposed to be reconverted to the oxide phases during the MC step (Tables 2-4), leading to the physical separation from the liquid-phase alloy compound.

The conventional OR process is composed of two unit processes: One is the ER to deoxidize the SNFs, and the other is residual salt distillation, also known as cathode processing (CP), to remove the residual LiCl electrolyte from the ER product [23]. Both the ER and CP equipments are composed of complicated modules, such as heaters, reactors, electrodes, electrochemical power systems, and gas exhaustion systems [3, 23]. On the other hand, the MR process only needs a simple milling equipment, which is highly scalable [9]. Various miling systems have been widely developed at an industrial level already. The MC process is also well commercialized.

In the ER process, porous pellet is used as a feed form to enlarge the contact area facing the LiCl electrolyte. Therefore, a complicated pelletizing process is required in the pre-treatment stage. Though it was denoted as one step of "pelletization", this process is, in fact, comprised of several sub-processes, including mixing, pelletizing, and then sintering [24]. In contrast, any feed forms are available in the MR process because the feed material is continuously

ground inside the reactor during the milling, which consequently forms a powder product. Thus, the complicated pelletization process can be removed by adopting the MR process. It is expected that the RE contamination of the LiCl-KCl-UCl_3 electrolyte can be reduced with the Mg reducing agent as descibed above. Thus, the consumption of UCl_3 can be minimized and the U/TRU ingot product quality can be improved with the MR-MC process. The RE drawdown process also can be removed when the RE separation effectively works during the MR-MC process.

Nevertheless, the accumulation of MgO byproducts, mixed with other unreduced oxide compounds, becomes serious with respects to waste management. In the case of the ER process, the Li_2O byproduct keeps getting recycled in-situ to generate the Li reducing agent, as described in reactions 1-5, to prevent the accumluation. The recycling of MgO could be a way to overcome this issue. Fig. 4 shows an example of the MgO recycling process. $MgCl_2$, made by chlorinating MgO, can be electrolyzed to form Mg and Cl_2. It was reported that MgO can be chlorinated using the Cl_2-CO mixed gas generating O_2 and CO_2 as gas products to be exposed [25]. The chloride puficiation process developed to treat pyroprocessing chloride waste can be used to decontaminate the produced $MgCl_2$ [26-27]. The $MgCl_2$ electrolysis is a well-established process in a commercial scale [28]. The obtained Mg is used as the reducing agent of the MR reaction, and the Cl_2 gas is supplied back to the chlorination process.

4. Conclusions

A new OR technique based on mechanochemical reactions was investigated for pyroprocessing. A Ni metal ingot was successfully produced from NiO through the MR reaction coupled with subsequent MC steps, suggesting the feasibiilty of this technique. Thermodynamic investigation was done to predict the behavior of U and the fission elements in the oxide SNFs during the MR and the MC processes. Mg was found to be a suitable reducing agent for the MR reaction in terms of stabilizing the U and TRU metals upon the MC step and separating the RE element prior to the electrochemical recovery processes. Because the MR-MC process utilizes commercially well-developed systems, the suggested technique is thought to have an advantage for the scale-up. It is necessary to mention that the negative ΔG values considered for the thermodynamic calculations are bottom lines for a chemical reaction to proceed, and the energy supplied from the MR process should be high enough to overcome the activation energy of each reaction. Therefore, experimental verification on the reduction and separation efficiencies should be made to distinguish whether the suggested strategy is viable. When this simple and scalable technique replaces the conventional electrochemical OR technique (i.e., ER), the process load during the pre-treament, OR, and electrochemical recovery processes of pyroprocessing will decrease substantially.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

Acknowledgements

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