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Recycling of Li_2ZrO_3 as LiCl and ZrO_2 via a Chlorination Technique

Min Ku Jeon[1,2,*], Sung-Wook Kim[1], Keun-Young Lee[1], and Eun-Young Choi[1,2]
[1]*Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea*
[2]*University of Science and Technology, 217, Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea*

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In this study, a chlorination technique for recycling Li_2ZrO_3, a reaction product of ZrO_2-assisted rinsing process, was investigated to minimize the generation of secondary radioactive pyroprocessing waste. It was found that the reaction temperature was a key parameter that determined the reaction rate and maximum conversion ratio. In the temperature range of 400−600℃, an increase in the reaction temperature resulted in a profound increase in the reaction rate. Hence, according to the experimental results, a reaction temperature of at least 450℃ was proposed to ensure a Li_2ZrO_3 conversion ratio that exceeded 80% within 8 h of the reaction time. The activation energy was found to be 102 ± 2 kJ·mol^{-1}·K^{-1} between 450 and 500℃. The formation of LiCl and ZrO_2 as reaction products was confirmed by X-ray diffraction analysis. The experimental results obtained at various total flow rates revealed that the overall reaction rate depends on the Cl_2 mass transfer rate in the experimental condition. The results of this study prove that the chlorination technique provides a solution to minimize the amount of radioactive waste generated during the ZrO_2-assisted rinsing process.

Keywords: Chlorination reaction, Oxide reduction, Lithium zirconate, Lithium chloride, Molten salt rinsing

*Corresponding Author.
Min Ku Jeon, Korea Atomic Energy Research Institute, E-mail: minku@kaeri.re.kr, Tel: +82-42-868-2435

ORCID

Min Ku Jeon	http://orcid.org/0000-0001-8115-3241	Sung-Wook Kim	http://orcid.org/0000-0002-5537-4793
Keun-Young Lee	http://orcid.org/0000-0001-7144-9014	Eun-Young Choi	http://orcid.org/0000-0003-1693-7642

1. Introduction

Oxide reduction (OR) is a key process that enables the use of oxide fuels discharged from pressurized water reactors (PWRs) in electrochemical pyroprocessing [1]. Recycling of the metallic fuels, employed in the Experimental Breeder Reactor-II (EBR-II) sodium-cooled fast reactor (SFR), via pyroprocessing was successfully demonstrated in the USA [2]. An integrated system of pyroprocessing and SFR is under intensive research in South Korea with the aim of recycling the transuranic (TRU) nuclides existing in the used nuclear fuels (UNFs) of PWRs as a fuel for SFRs [3-4].

The OR process liberates oxygen atoms from oxide fuels so that the resulting metallic fuels can be processed via subsequent electro-refining and electro-winning processes to recover U and TRU nuclides. Normally, LiCl containing 1−3wt% Li_2O is employed as a molten salt in the OR process at around 650℃ [5-8]. In order to construct an electrochemical circuit for the OR process, oxide fuels are loaded into a metal basket to serve as the cathode, with platinum employed as the anode. The reactions occurring at the cathode and anode are listed below:

<Cathode>

$$4\ Li^+ + 4\ e^- \rightarrow 4\ Li \quad (1)$$

$$UO_2 + 4\ Li \rightarrow U + 2\ Li_2O \quad \text{(Chemical mechanism)} \quad (2)$$

$$UO_2 + 4\ e^- \rightarrow U + 2\ O_2^- \quad \text{(Electrochemical mechanism)} \quad (3)$$

<Anode>

$$2\ O^{2-} \rightarrow O_2(g) + 4\ e^- \quad (4)$$

There are two mechanisms, chemical and electrochemical, which explain the reaction behavior at the cathode. In the chemical mechanism, Li metal is generated through reaction (1) and then reacts with UO_2 to produce U and Li_2O via reaction (2). In the electrochemical mechanism, UO_2 is directly converted to U via an electrochemical reaction (3). As the operation potential of the two mechanisms are close, both pathways can occur simultaneously during the OR operation. In the anode, oxygen ions liberated from UO_2 are oxidized to O_2 gas through reaction (4). Regardless of the cathode reaction mechanism, the overall reaction equation of the OR process can be expressed as reaction (5).

$$UO_2 \rightarrow U + O_2(g) \quad (5)$$

When the OR operation is complete, the cathode basket is discharged from the reactor along with any residual salt adhering to the metallic fuel and basket. The cathode basket is transferred to a salt distillation process, during which the residual salt is removed by heat and a vacuum to obtain clean metallic fuel [3, 4, 9]. During this process, Li_2O dissolved in the residual salt reacts with U metal, resulting in a reoxidation reaction through reaction (6), expressed below, which is a reverse reaction of reaction (2) [10, 11].

$$U + 2\ Li_2O \rightarrow UO_2 + 4\ Li \quad (6)$$

Here, the consistent removal of Li, with a melting point of 454 K and a boiling point of 1615 K, using heat and a vacuum is a key driving force that keeps reaction (6) going. In addition, it was documented that a higher Li_2O concentration or distillation temperature can lead to a higher degree of reoxidation [10, 11].

This reoxidation phenomenon will cause a significant reduction in the overall process efficiency, as the reoxidized product, UO_2, is not recoverable through electro-refining. Recently, Choi et al. proposed a ZrO_2-assisted rinsing process as an alternative to the salt distillation process [12]. In this process, the cathode basket is immersed in a separate bath of molten LiCl such that Li_2O in the residual salt is diluted. Here, ZrO_2 is utilized as a Li_2O scavenger to prevent the accumulation of Li_2O in the rinsing bath via the following reaction mechanism [13, 14]:

$$ZrO_2 + Li_2O \rightarrow Li_2ZrO_3 \quad (7)$$

Although the rinsing technique was successfully demonstrated through repeated experiments, the reaction product, Li_2ZrO_3, should be replaced by ZrO_2 periodically. The resulting Li_2ZrO_3 can be handled as a radioactive waste for disposal after several treatments. As a result, the ZrO_2-assisted rinsing technique will produce additional radioactive waste, Li_2ZrO_3, unless it can be recycled. In this work, a chlorination technique was applied to recycle Li_2ZrO_3 through reaction (8) below, with the goal of recycling LiCl and ZrO_2 in the ZrO_2-assisted rinsing process.

$$Li_2ZrO_3 + Cl_2(g) \rightarrow 2\ LiCl + ZrO_2 + 1/2\ O_2(g) \quad (8)$$

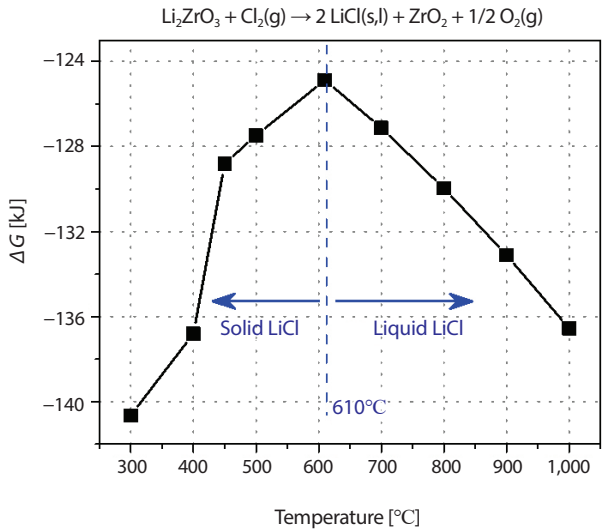

Fig. 1. ΔG values of the reaction between Li_2ZrO_3 and Cl_2 (Eq. 8) at various temperatures calculated using the HSC chemistry software.

2. Experimental

The Gibbs free energy change (ΔG) values of the Li_2ZrO_3 chlorination reaction (reaction (8)) were derived using the HSC chemistry software (version 9.5.1) as a function of the reaction temperature [15]. Chlorination experiments were conducted using a quartz tube reactor with a diameter of 4 cm. The reactor was equipped with an electrical furnace to control the reaction temperature. Before the reaction began, the weight of the Li_2ZrO_3 powder (Sigma-Aldrich) was measured before and after the sample was loaded into an alumina boat. Approximately 0.50 g of Li_2ZrO_3 was used for each experiment. The boat was placed in the middle of the quartz reactor and both ends were then connected to a gas control system. On the inlet side of the reactor, a gas feed system with two mass flow controllers (MFCs, Kofloc co., Japan) for Ar (Model 3660) and Cl_2 (Model 5440) was connected. A dry scrubbing system for the removal of unreacted Cl_2 was connected to the other side of the reactor. After purging the reactor with Ar for at least 2 h, the reactor was heated to the reaction temperature at a ramping rate of 10°C·min^{-1} under an argon flow. When the reactor temperature is settled at the target temperature, each MFC was set at the reaction flow rate and then maintained for the reaction time. Upon the completion of the reaction, the Cl_2 flow was stopped and the reactor was cooled to room temperature under an argon flow. After discharging the alumina boat, the weight of the sample was measured with or without the alumina boat to quantify the weight change. The highest reaction temperature in this work was set to 600°C in order to minimize the volatilization loss of LiCl during the reaction. Experiments were repeated for various reaction temperatures (300−600°C), durations, and total flow rates (Q = sum of the Ar and Cl_2 flow rates).

The phase change of the samples was analyzed using an X-ray diffraction system (XRD, Bruker D8 Advance). The analysis was conducted in the 2θ range of 10–80° with a step size of 0.0104° and measurement time of 0.15 s during each step.

3. Results and discussion

The ΔG values of the Li_2ZrO_3 chlorination reaction were derived using the HSC chemistry software. These results

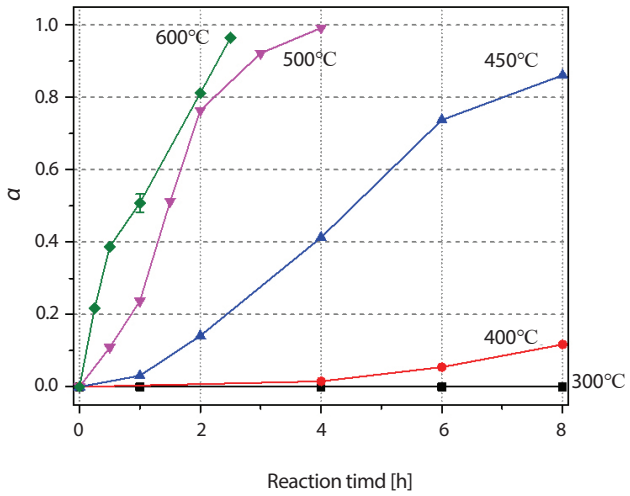

Fig. 2. Experimental results obtained at various reaction temperatures and times with a flow rate of 98 mL·min^{-1} Ar + 2 mL·min^{-1} Cl_2.

are shown in Fig. 1. The ΔG value represents the change in the chemical potential when the reaction proceeds, which is negative when the sum of the chemical potentials of the reaction products is smaller than that of the reactants. In other words, a negative ΔG indicates that the reaction is thermodynamically feasible. In Fig. 1, negative ΔG values were observed throughout the temperature range (300−1,000°C), suggesting that the Li_2ZrO_3 chlorination reaction is thermodynamically feasible. The volcano shape of the figure came from phase change of LiCl from a solid to a liquid at 610°C, which is the melting point of LiCl. The following equation, where ΔH and ΔS correspondingly represent changes in enthalpy and entropy, accounts for the volcano shape because the melting of LiCl leads to an increase in the ΔS value.

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

However, an experimental approach should be utilized in order to verify the actual operating temperature as the activation energy and rate of the reaction are not included in the ΔG values.

The effects of the reaction temperatures and times were also investigated, as shown in Fig. 2. In the figure, the term α, the conversion ratio, is noted, representing the ratio of Li_2ZrO_3 reacted with Cl_2 over the input of Li_2ZrO_3. This value was calculated using the following equation,

$$\alpha = (W_f - W_i) / (W_i) / ((2 \times M.W._{LiCl} + M.W._{ZrO2} - M.W._{Li2ZrO3}) / M.W._{Li2ZrO3}) \quad (10)$$

where W_f and W_i represent the final and initial weight of the samples, respectively, and $M.W._{LiCl}$, $M.W._{ZrO2}$, and $M.W._{Li2ZrO3}$ correspondingly represent the molecular weight of LiCl (= 42.39 g·mol^{-1}), ZrO_2 (=123.2 g·mol^{-1}), and Li_2ZrO_3 (= 153.1 g·mol^{-1}). Interestingly, no signs of the reaction were found at 300°C, while the reaction proceeded slightly at 400°C (α = 0.117 after 8 h of reaction). It is clear here that the reaction temperature should be at least 400°C to overcome the activation energy of the Li_2ZrO_3 chlorination reaction, although the reaction is very slow at 400°C. In addition, this outcome shows why the experimental approach should be used in conjunction with thermodynamic calculations. With an increase in the reaction temperature to 450 and 500°C, a profound increase in α was observed. The reaction was found to be complete after 4 h at 500°C. A further increase in the reaction temperature to 600°C brought a significant increase in the value of α, especially in the region of $\alpha \leq 0.5$. It is obvious from this result that the reaction temperature is a key parameter which determines the reaction rate and maximum value of α, especially in the temperature range of 400−600°C. Reproducibility of the experiments was verified by repeating identical experiments three times at 600°C for 1 h under a 98 mL·min^{-1} Ar + 2 mL·min^{-1} Cl_2 flow. These results are shown the error bar in Fig. 2, where the resulting α value was 0.508 ± 0.025. This outcome proves the acceptable reproducibility of the experiments conducted in this work.

Activation energy of the Li_2ZrO_3 chlorination reaction was derived using the data of Fig. 2. In a gas-solid reaction, the reaction rate can be expressed using the following equation,

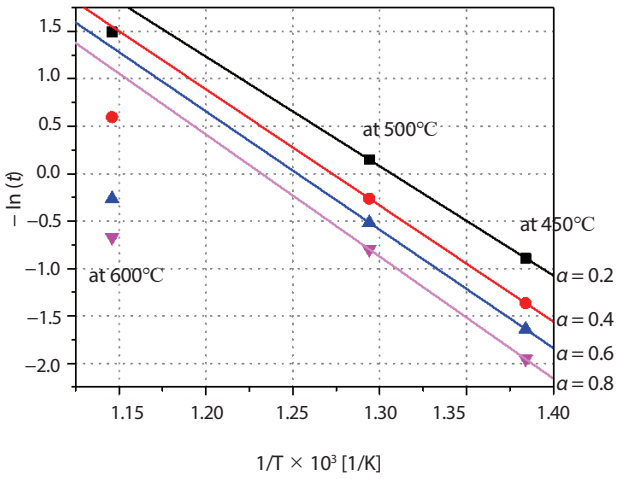

Fig. 3. Plot of $-\ln(t)$ versus $1/T\times10^3$ for the calculation of activation energy at α values of 0.2, 0.4, 0.6, and 0.8 under a 98 mL·min^{-1} Ar + 2 mL·min^{-1} Cl_2 flow.

$$R = \frac{d\alpha}{dt} = k(T)F(pCl_2)G(\alpha) \tag{11}$$

where $k(T)$, $F(pCl_2)$, and $G(\alpha)$ represent the effects of reaction temperature, chlorine partial pressure, and morphological changes, respectively. Applying the Arrhenius equation in $k(T)$ and integration of Eq. (11) results in the following equation,

$$-\ln(t) = C(\alpha) - \frac{E_a}{R_g}\frac{1}{T} \tag{12}$$

where $C(\alpha)$ represents combination of $F(pCl_2)$ and $G(\alpha)$ at a constant pCl_2, E_a is an activation energy, and R_g is the gas constant (8.314 J·mol^{-1}·K^{-1}). Here, the E_a value can be derived from the slope of $-\ln(t)$ versus $1/T$ plot for a given α. The experimental results at α values of 0.2, 0.4, 0.6, and 0.8 are shown in Fig. 3 with linear fitting results. Here, linear interpolation was applied to the α and t values. It should be noted that the results at 600°C were not included in the linear fitting calculations because of significant discrepancy in the trend. The activation energy calculated from the results at 450 and 500°C was 102 ± 2 kJ·mol^{-1}·K^{-1}. These results also propose that the reaction regime is changing between 500 and 600°C.

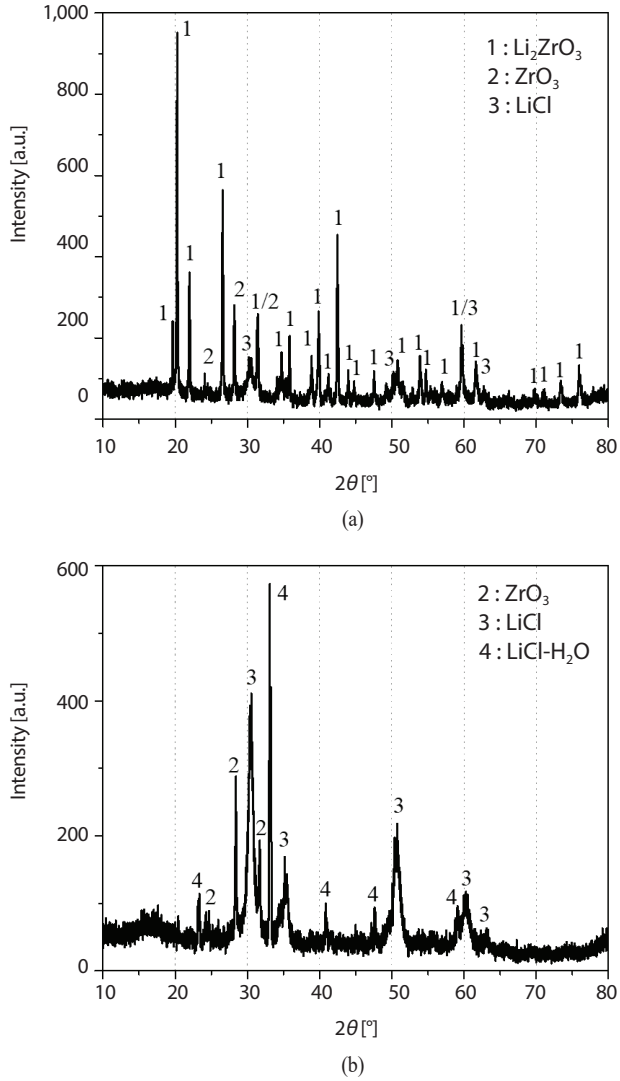

Fig. 4. XRD measurement results of Li_2ZrO_3 reacted at 500°C for (a) 1.0 and (b) 4.0 h under a 98 mL·min^{-1} Ar + 2 mL·min^{-1} Cl_2 flow.

Phase changes in the samples prepared at 500°C for 1.0 and 4.0 h were analyzed by XRD measurements, as shown in Fig. 4. After 1.0 h of the reaction (α = 0.2374), the XRD peaks could be assigned according to the three phases of Li_2ZrO_3 (PDF #01-070-8744), ZrO_2 (PDF #01-078-0047), and LiCl (PDF #01-074-1972). Peaks of Li_2ZrO_3 were not observed after 4.0 h of the reaction (α =0.9922), as shown in Fig. 4(b), whereas peaks of LiCl-H_2O (PDF #01-070-9971) were noted. Considering the hygroscopic characteristic of

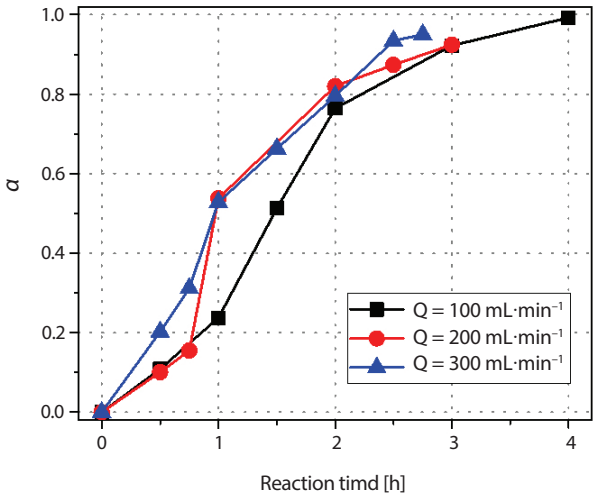

Fig. 5. Experimental results obtained at 500°C for various Q values of 100 (= 98 mL·min^{-1} Ar + 2 mL·min^{-1} Cl_2), 200 (= 196 mL·min^{-1} Ar + 4 mL·min^{-1} Cl_2), and 300 mL·min^{-1} (294 mL·min^{-1} Ar + 6 mL·min^{-1} Cl_2).

LiCl, the LiCl-H_2O phase may have been generated during the sample handling process for the XRD measurements. These outcomes prove that the weight-based calculation of α was a reasonable approach for the experiments conducted at 500°C, assuming that the weight was measured as soon as the samples were exposed to air. In addition, the absence of unexpected reaction by-products was confirmed by XRD measurement results.

In a solid-gas reaction system, the reaction rate is controlled by either or both of mass transfer rate of gas, Cl_2 in this work, and chemical reaction rate. Under a mass transfer rate controlled condition, an increase in the *Q* value leads to an increase in the reaction rate because the amount that is transferred to the surface of reactant, Li_2ZrO_3, affects the overall reaction rate. On the other hand, the reaction rate is independent of *Q* under the chemical reaction rate controlled condition. In order to identify the reaction mechanism of this work, the effect of *Q* at 500°C was investigated by repeating experiments under various flow rates of 98 mL·min^{-1} Ar + 2 mL·min^{-1} Cl_2 (Q = 100 mL·min^{-1}), 196 mL·min^{-1} Ar + 4 mL·min^{-1} Cl_2 (Q = 200 mL·min^{-1}), and 294 mL·min^{-1} Ar + 6 mL·min^{-1} Cl_2 (Q = 300 mL·min^{-1}) for various

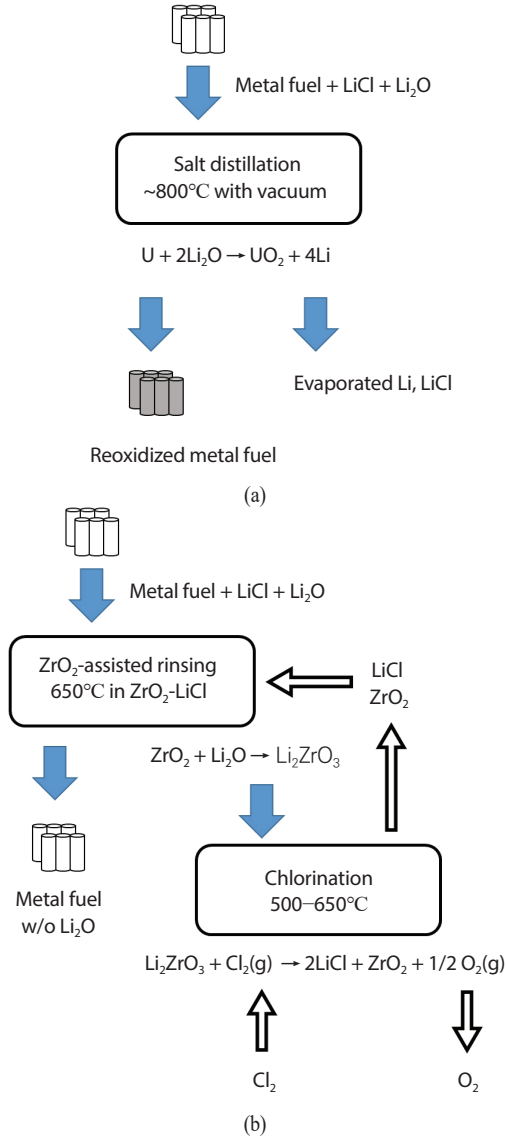

Fig. 6. Flow diagrams of (a) the conventional salt distillation process and (b) the ZrO_2-assisted rinsing process combined with Li_2ZrO_3 chlorination.

reaction times as shown in Fig. 5. Note that the ratio of Cl_2 was kept constant at 2% of *Q* in order to eliminate the effect of Cl_2 partial pressure. In the figure, an increase in the *Q* value leads to an increase in the reaction rate suggesting that the reaction is under the influence of Cl_2 mass transfer rate at 500°C. It is interesting to observe the results with *Q* of 200 mL·min^{-1}, which exhibited similar values to those with 100 mL·min^{-1} in the low (< 0.2) and high (> 0.9) α regions,

and with 300 mL·min^{-1} in the middle ($0.5 < \alpha < 0.85$) region. Here, it is worth to note that the reaction time for high conversion (> 90%) reduced less significantly, though it is clear that an increase in *Q* accelerates the reaction rate under the condition of this work.

A combined flow diagram of the ZrO_2-assisted rinsing and Li_2ZrO_3 chlorination processes is displayed in Fig. 6 in comparison with the conventional salt distillation process. The concept of combining the ZrO_2-assisted rinsing and chlorination processes involves the use of ZrO_2-dispersed LiCl salt during the rinsing process. After a certain level of ZrO_2 is converted into Li_2ZrO_3 by reacting with Li_2O, bubbling chlorine gas through the rinsing salt can eliminate the need for a separate reactor for the chlorination process. When scaling up these processes, the bath size and the ZrO_2 input of the rinsing process may be the key parameters determining the capacity of the rinsing bath and frequency of Li_2ZrO_3 chlorination. In addition, various aspects such as the process cost, operation time, and total process efficiency should be compared between the conventional salt distillation process and the ZrO_2-assisted rinsing step combined with the chlorination process.

4. Conclusions

A chlorination reaction of Li_2ZrO_3 to recycle it as LiCl and ZrO_2 via a ZrO_2-assisted rinsing process was successfully demonstrated in various experiments. It was found that the reaction temperature is a key parameter of the reaction to achieve a high conversion ratio, suggesting an operating temperature of at least 450℃. The activation energy was estimated to be 102 ± 2 kJ·mol^{-1}·K^{-1} at 450 and 500℃. The effect of *Q* on the α value at 500℃ indicated that the reaction rate of this study is under control of Cl_2 mass transfer rate under the condition of this work. The outcomes of this work suggest that the chlorination technique can solve the problem of extra waste (Li_2ZrO_3) generation during the ZrO_2-assisted rinsing process.

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