

# De-chlorination and Stabilization of Waste LiCl Salt Wastes

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## 1. Introduction

The spent LiCl salt waste generated from the Advanced Spent Fuel Conditioning Process (ACP) in KAERI is highly soluble in water and contains a relatively high amount of volatile element such as Cs. Therefore, this waste is very difficult to stabilize by the conventional cementation or vitrification process because of the low chemical durability of the cement waste forms and easy vaporization of the volatile radionuclides during melting. We suggested a new two-step process for a safe treatment of LiCl salt wastes containing volatile radionuclides. First, the chemical form of the soluble LiCl waste was converted into the chloride-free and less soluble hydroxide compound in an electrochemical reactor equipped with an ion exchange membrane, where an electrolytic de-chlorination was performed without adding any chemical salt (electrolyte). Then a new stabilization concept, named the GRSS (Gel-Route Stabilization/Solidification) system aiming to greatly reduce the vaporization of radionuclides, was introduced to stabilize/solidify the hydroxide salt wastes. The product gels obtained from this gel-route reaction system can be fabricated to the more durable NZP(Na-Zr-P)-structure waste form through a high temperature process without or little vaporization of the radionuclides.

In this paper, we described the conversion of metal chloride into metal hydroxide based on the electrochemical reaction route and the GRSS system using water-soluble raw materials and H<sub>2</sub>O as a solvent, its materials system and experimental procedure. Also, the experimental results on their applications to treat spent LiCl salt wastes are presented.

## 2. Experimental

To investigate the possibility on the electrolytic de-chlorination/transformation of LiCl, an electrolytic cell with an IrO<sub>2</sub> anode and a Ti cathode equipped with an anion exchange membrane (Electrolytica, A7001) was used. The volume of each anodic and cathodic chamber was 16.5 ml. A 2 M LiCl solution as catholyte and 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution as anolyte were circulated into the cathodic and anodic chamber through their reservoirs with applying 80mA/cm<sup>2</sup> to the cell. For the continuous electrolytic de-chlorination/transformation of LiCl, a 4 cell-stacked electrolyzer equipped with the anion exchanger membrane was used, where the anolyte and catholyte solutions independently flowed in series through the anodic chambers and the cathodic chambers with the same flow rate of 2.5 ml/min. The volume of

each cell and electrodes of the stack were the same to those in bath experiment. During the electrolysis, each electrolyte solution coming out of the electrolyzer was regularly sampled to analyze the changes of pH and concentration of chloride ion of the solutions by on-line pH-meters and an ion chromatograph.

In the gel-route stabilization step, ZrCl<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, LiCl, and LiOH (99%, Aldrich) were used as raw materials for the synthesis of NZP-structure products and CsCl and SrCl<sub>2</sub> were used as surrogate nuclides. The mole ratio of ZrCl<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> was set at 1:1.5 based on the mole ratio of Zr and P in a NZP material. A mixture solution containing 0.1 mol of ZrCl<sub>4</sub>, 0.15 mol of H<sub>3</sub>PO<sub>4</sub> and 0.05 mol of metal compound (Li, Na, Cs or Sr compound) in H<sub>2</sub>O was prepared and strongly stirred for 1 hour. The mixture was put into the plastic bottle, tightly sealed, and then placed into the electric oven maintained at 70 °C for 7 days for a gelation reaction. The transparent and elastic product gels were dried at 110°C for 2 days and then heat-treated at 600, 700, 800 or 900°C for 2 hours. They were characterized by XRD (Rigaku, CuK $\alpha$ , Japan) and SEM (Perkin-Elmer, USA) analysis. And the 7-day PCT leach test was performed to assess the chemical durability of the final waste forms.

## 3. Result and discussion

### 3.1. De-chlorination of LiCl salt wastes

The experimental result of electrochemical de-chlorination of LiCl in a batch electrolytic cell is shown in Figure 1. The pHs in the cathodic and anodic chamber increased even to 14 and got down to 1, respectively. The concentration of Cl<sup>-</sup> in the cathodic chamber gradually decreased, but that in the anodic chamber slightly increased because the most of Cl<sup>-</sup> ion migrated went out of system as Cl<sub>2</sub>. The evolution of almost pure Cl<sub>2</sub> from the anodic chamber was experimentally observed. At that time, the cell voltage was changed, depending on the total conductivity within the system affected by the changes of the concentrations of Li<sup>+</sup> and Cl<sup>-</sup>, and the pHs of in the each chamber.

From the continuous de-chlorination experiments carried out by using a 4-cell stacked electrolyzer, the concentration of Cl<sup>-</sup> at the cathodic outlet decreased to about 50% of the feeding in a steady state that reached in 60 minutes, and that at the anodic outlet became below 0.02M. By using two stacks electrolyzer connected in series, about 90% of Cl<sup>-</sup> of the feeding solution was continuously removed.

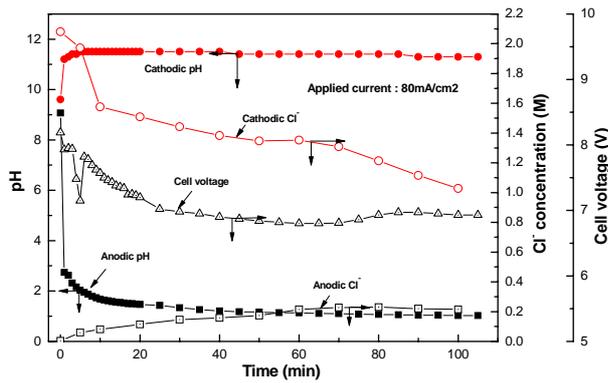


Figure 1. The changes of pH and concentrations of chloride ion in anodic and cathodic chamber of a batch electrolytic cell with circulating anolyte.

From these results, the chloride-free LiOH solution is considered to be effectively produced from the target LiCl waste salt by the electrochemical method. The XRD analysis of the reaction product prepared by drying the cathodic solution after the electrolytic de-chlorination revealed that the major constituent of the de-chlorination reaction was LiOH with containing a small amount of un-reacted LiCl.

### 3.2. Stabilization of de-chlorinated LiCl salt wastes

The XRD analysis of various reaction products after drying at 110°C for 2 days and heat-treated at 900°C for 2 hours showed that the crystallinity of the gel products was increased after heat-treatment. As the fraction of LiOH in the feed material was increased, the characteristic peak intensity of the desirable product, LiZP, became slightly stronger even if the difference between LiOH and LiCl system was not so much. Investigation was made on the change of crystalline products in the gel products when CsCl was added to the LiOH or LiCl feed material with a molar ration of Li:Cs = 0.7:0.3, which was determined from the chemical composition of the NZP. For the LiCl and CsCl system, Cs formed NZP-structure material, while Li formed  $\text{Li}_2\text{Zr}(\text{PO}_4)_2$ . When the metal compound (Cs, Li, Na, or Sr) is added by 60% excess to the stoichiometric amount of NZP in the LiOH and CsCl system, Cs or Na selectively reacts with Zr and P to form CsZP or NaZP rather than to form LiZP, respectively. Only in the Sr-Li system, the SrZP and LiZP were co-produced. This means the selective reactivity of Cs compared to the Li in the formation of the NZP-structure material. The compound  $\text{Zr}(\text{HPO}_4)_2$  has a selective ion exchange capability in the order of Cs, Sr, Na, and Li to form the durable NZP-structure material. Another notable result when LiOH was used instead of LiCl was that the formation temperature of the durable NZP-structure materials was lowered from around 900°C to 600°C. This can be a great advantage in the high temperature waste treatment process such as

vitrification or ceramization. The reduced processing temperature will greatly lower the vaporization of the radionuclides, diminish the need of off-gas treatment unit, reduce the amount of secondary wastes, and also help to reduce the construction and operation cost.

The chemical durability of the final waste form was found to be enhanced when LiCl was replaced with LiOH. The 7-day PCT leaching result with different leachant volume/sample weight ratios revealed that the leach rate of Li was reduced by 50% and that of Cs by 25% if LiOH was used, as shown in Figure 2. The Cs leach rate was about  $5 \times 10^{-4} \text{ g/m}^2\text{-d}$ , which was far less than that leached from the zeolite fixed product. Thermogravimetric analysis (TGA) is on-going now to find out the thermal behavior of the stabilization matrices and radionuclides and the result will be presented in the conference.

This experimental result shows the superiority of the gelation process (GRSS system) combined with or without the electrochemical de-chlorination step to the conventional methods.

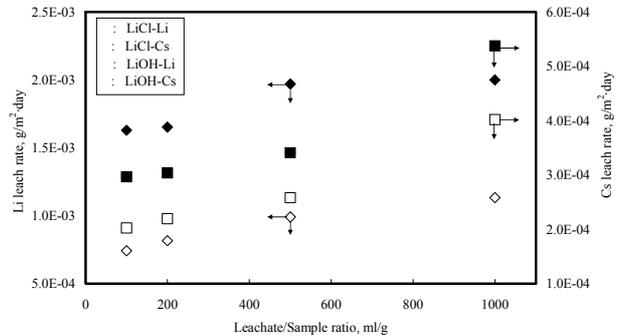


Figure 2. The 7-day PCT leach result for the LiOH and LiCl material systems.

## 4. Conclusions

It can be concluded that the chloride-free LiOH solution is considered to be effectively produced from the target LiCl waste salt by the electrochemical method and the replacement of LiCl with LiOH is very effective for the fixation of radionuclides in a durable waste form and for the decrease of processing temperature to reduce the possibility of the vaporization of the volatile radionuclides. The application of the electrochemical de-chlorination process and the subsequent gel-route stabilization process to treat soluble LiCl salt wastes was found to be very successful.

## REFERENCES

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