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Deliquescence of eutectic LiCl-KCl diluted with NaCl for interim waste salt storage

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Abstract — *Molten eutectic LiCl-KCl salt is a widely used electrolyte for electrorefining uranium from spent nuclear fuel. Due to the hygroscopic nature of this salt, such operations must be performed under controlled atmospheric conditions, and waste salts require careful storage to avoid deliquescence and corrosion of container materials. This study investigated a potential processing path for reducing the degree of deliquescence through dilution to varying extents with NaCl. The hydration behavior of LiCl-KCl salts diluted with NaCl was evaluated in terms of mass gain due to water absorption, degree of deliquescence (including first appearances of standing water), and evidence of corrosion to stainless steel containers in a humid air environment (40°C, 20% relative humidity). In this humid air environment, pure eutectic LiCl-KCl exhibited a 50 mass% increase due to water absorption and showed evidence of standing water after 24 hours. Waste salt diluted with NaCl required loadings of 89 mass% NaCl in order to prevent deliquescence and exhibited a 3 mass% increase due to water absorption. After 48 hours, standing water was observed near all ingots with the exception of 89 mass% NaCl samples. Dilution with 89% NaCl was also found to reduce evidence of corrosion when stored in stainless steel crucibles. While dilution with NaCl greatly decreases steady state hydration, the storage volume is increased ~10x through this procedure.*

Keywords — *Electrochemical processing, electrorefiner salt, eutectic LiCl-KCl, waste salt, deliquescence*

I. INTRODUCTION

The electrorefiner is a key unit of operation for electrochemical processing of irradiated metallic fast reactor fuel.[1] In the electrorefining process, chopped metallic fuel segments are loaded into anode baskets and immersed in molten salt. They are then electrochemically separated into transition metals which remain in the anode basket and refined uranium which reports to the cathode, leaving alkali, alkaline earths, lanthanides, and transuranic elements to accumulate in the salt.[2] The molten salt is composed primarily of eutectic LiCl-KCl and variable concentrations of UCl_3.[3,4] The uranium chloride reacts with the active metal fission products to form the chloride salts that partition into the molten salt bath. During processing, the electrorefiner must be kept in a dry, inert gas environment as the eutectic LiCl-KCl is hygroscopic and reactive with the ambient atmosphere.[5] There are many processing constraints that call for the disposal of the electrorefiner salt such as criticality and safety, electrorefiner volumetric limit, fission product concentration, etc.[6-8] This saturated waste salt must be safely stored and eventually immobilized.[9-15]

Argonne National Laboratory demonstrated the immobilization of waste salt through occlusion within zeolite-4A and pressureless sintering in the presence of borosilicate glass frit for ceramic waste form (CWF) production.[9,16-18] Lengthy processing times and large space claim for a variety of specialized equipment complicate the economics of CWF synthesis.[11] One low-cost alternative to CWF processing is through direct disposal of salt in a suitable waste package and repository.[19] However, this can pose issues as electrorefiner salt waste is extremely hygroscopic and can deliquesce, forming a liquid salt solution upon contact with moist air.[20,21]

The release of waste salt through aqueous phase reactions may result in the dissolution and dispersal of radionuclides into the local environment. Even if the hydrated salt is contained, dehydrating after interim storage will most likely be required before subsequent waste form processing. Absorbed water can interfere with waste processes, such as vitrification.[22] There is also the potential for HCl gas production during drying into an anhydrous state.[23]

A potential means of minimizing deliquescence of electrorefiner salt waste during temporary storage to permanent disposal involves the dilution with a less hygroscopic material. NaCl is one candidate for dilution given its low price, solubility in eutectic LiCl-KCl, and greater stability in humid environments.[24,25] It is hypothesized that water uptake of eutectic salts can be decreased by dilution with NaCl. In this research, eutectic LiCl-KCl salts were diluted to differing extents with NaCl. The hydration behavior in a humid environment was observed, as well as the changes in composition associated with dissolution of the salts, with a qualitative examination of corrosion of stainless-steel crucibles exposed to the deliquescent salts.

II. MATERIALS AND METHODS

II.A. Salt Ingot Synthesis

Salts composed of near-eutectic LiCl-KCl (56 mol% LiCl, 44 mol% KCl) and diluted with NaCl at different ratios (8 – 89% NaCl, 4 – 80% NaCl, 2 – 67% NaCl, 1 – 50% NaCl, and 0 – 0% NaCl) were mixed in an inert atmosphere glove box into 40-g batches using reagent-grade anhydrous chemicals (Fisher Scientific – Hampton, NH). Each ingot had dimensions of ca. 3.5 cm diameter × 3 cm high. Premixed batches containing NaCl were loaded into glassy carbon crucibles, heated at 10°C min-1, held at 800°C for 60 minutes, and left to cool slowly inside of the furnace. The LiCl-KCl batches followed the same heating procedure but were held at 400°C instead of 800°C. These temperatures were selected based on calorimetric measurements of different salt mixtures. Differential scanning calorimetry (DSC) was used to determine liquidus temperatures for different (LiCl-KCl)-NaCl compositions. Thermograms were collected on additional (LiCl-KCl)-NaCl samples batched separately with masses in the range of 15-30 mg that were heated at 10°C min^{-1} up to 825°C under ultra-high-purity argon flowing at 50 ml min^{-1}.

II.B. Hydration Testing in Glass

The hydration behavior of salt ingots evaluated using a TE-101H-F model humidity chamber (Test Equity LLC, Moorpark, CA). Testing was performed at 40°C and 20% relative humidity (RH). The humidity chamber was calibrated using an SDL500 hygro-thermometer (Extech Instruments – Nashua, NH). Two separate calibration runs were performed under steady-state conditions at 40°C and 20% RH. During each run, temperature and humidity data were collected at one-minute intervals over ten-minute periods. Salt ingots (made with 0, 50, 67, 80, and 89 mass% NaCl) were loaded into glass petri dishes (60 ml) or beakers (250 ml) and placed in the humidity chamber (40°C and 20% RH) to assess rehydration capacity. The beakers were removed periodically to measure mass gain over time, and digital photographs were collected to evaluate any apparent degradation of specimens. Three samples for each condition were evaluated.

II.C. Hydration Testing in Stainless Steel

Both electrorefiner operations and long-term waste storage involve the use of steel containment vessels. Thus, any steel corrosion due to water absorption in the waste must be characterized. Incremental mass gain measurements and specimen images were collected on salt powders (pure LiCl-KCl and 89 mass% NaCl samples) loaded in 10-mL 304 stainless steel crucibles. Salt powders were used in place of ingots to simulate a worst-case scenario for corrosion with a high surface area. Powders were sieved to a particle size range of 45 to 250 μm. Duplicate 5-g batches of waste were used from each condition and were kept in the humidity chamber at 40°C and 20% RH. Specimens were removed periodically for mass measurements. Images were also taken during each interval to track apparent changes in corrosion behavior during hydration.

III. RESULTS AND DISCUSSION

III.A. Differential Scanning Calorimetry

Thermograms for five salt dilution ratios are shown in Figure 1. Melting endotherms were observed at 792°C for the 89% NaCl mixture. These measured values confirm that the melting runs performed at 800°C for 60 minutes for these samples resulted in sufficient superheating for melting to occur.

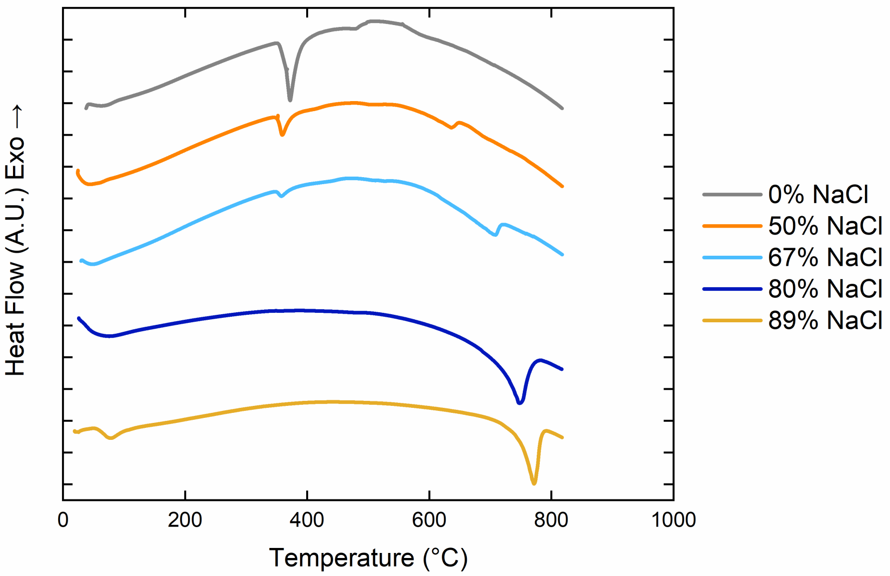


Fig. 1. DSC thermograms for salts made with different amounts of NaCl added to LiCl-KCl.

III.B. Salt Hydration

The average relative humidity values for each run are reported in Figure 2. The hygro-thermometer values are slightly lower than the humidity reported by the chamber. However, the values measured by one device are within the uncertainty bands of the other values. The uncertainty was calculated using the bias uncertainty reported for each device (probe: ±3.0% RH, chamber: ±2.5% RH) and the random uncertainty of the averages calculated over each 10-minute period (0.6-0.7% RH for each measurement).

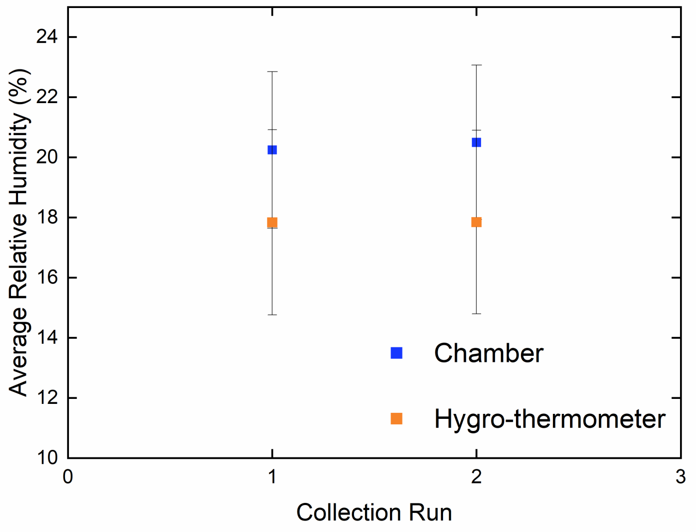
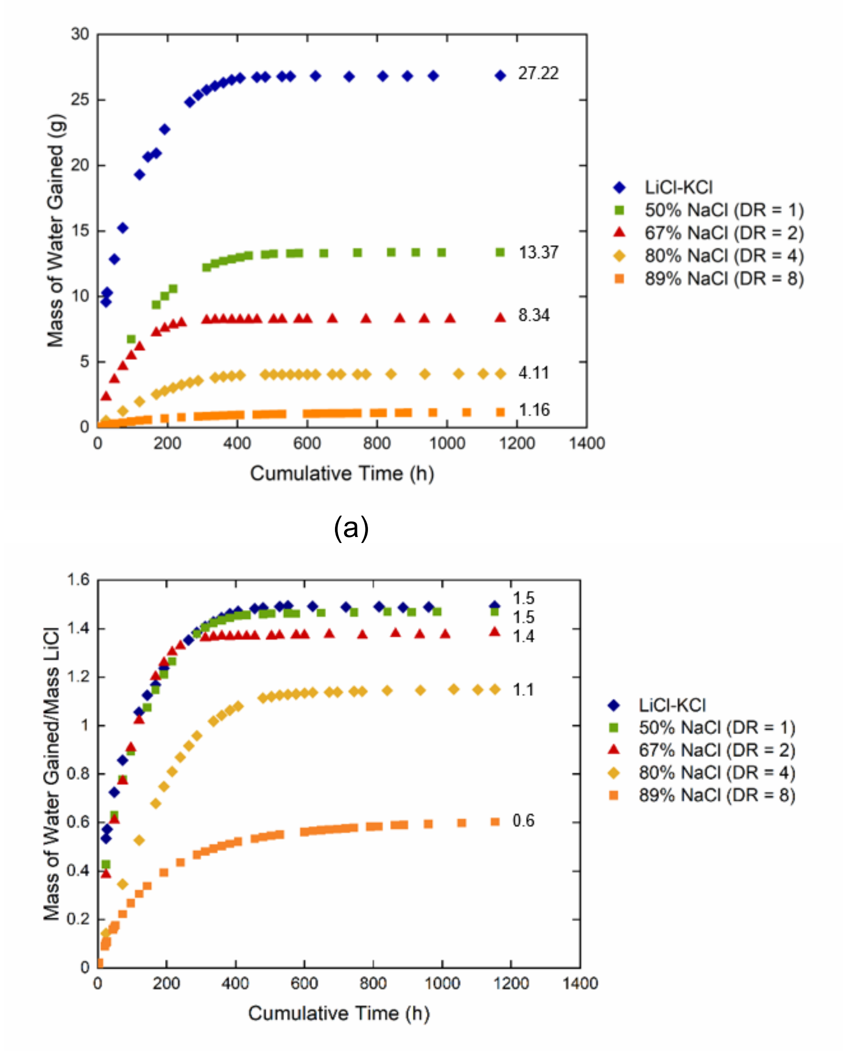


Fig. 2. Steady state humidity measurements inside of the chamber were compared to values collected using an external hygro-thermometer. Each set of measured values is within the uncertainty bands of the other set.

The masses of a series of salt ingots (synthesized with varied amounts of NaCl) were recorded over a 48-day period. Figure 3 shows the average mass increases due to hydration of the ingot and any standing water. In each case, the forward rate of moisture uptake attenuated over time, eventually reaching steady state hydration. Figure 3a shows the total mass gain in grams for each sample, while the ordinate of Figure 3b is normalized to the mass of LiCl present in each sample. This normalization helps in comparing results for a fixed amount of LiCl. From 0 – 67 mass% NaCl, the normalized hydration rates are similar, with the steady-state hydration of the 67 mass% slightly lower than the pure LiCl-KCl or 50 mass% NaCl. Dilutions made with 80 and 89 mass% NaCl show increasingly lower hydration rates and steady-state hydration rates.



(a)

(b)

Fig. 3. Average salt ingot hydration rates (a) presented in absolute mass gain and (b) normalized by the mass of LiCl in each composition. A similar steady state value to LiCl-KCl indicates that any decrease in absolute water uptake is due only to NaCl dilution. Samples made with 80 and 89 mass% NaCl exhibited lower steady state water uptake. Error is within the marker.

Figure 4 shows images of ingots collected before and after 48 days of hydration testing and shows the increased collection of moisture over time. The petri dishes shown have an inner diameter of 5 cm. Table 1 lists the elapsed time when standing water was first observed in the bottom of each specimen container, as well as the mass of water gained before and after standing water was observed. At 20% relative humidity (RH), these tests were performed well above the deliquescence relative humidity (DRH) of LiCl (11.6% at 40°C).[26] Because of this, LiCl is expected to dissolve when exposed to water. As this RH is well below the DRH of KCl (82% at 40°C) and NaCl (75.4% at 40°C), deliquescence is expected to be driven by the amount of LiCl present in each sample. For samples with $\leq$80 mass% NaCl, there is a high enough concentration of LiCl on the surface to lead to deliquescence. For samples with $\leq$67 mass% NaCl, it appears as though enough solution was present to dissolve some KCl and

NaCl, exposing more of the underlying surface, and resulting in higher total water gains. However, the absence of standing water at 89 mass% NaCl indicates that LiCl was not in a high enough concentration at the surface to lead to any appreciable deliquescence. If there is too low of an LiCl concentration in a given area, not enough water can be absorbed to deliquesce, which prevents dissolution of the ingot.

These lower amounts of water uptake in NaCl-loaded waste samples come at the cost of large volume increases (~10x) resulting from dilution. Furthermore, this diluted waste would require further processing to remove moisture (risking HCl gas production via hydrolysis) prior to immobilization in a qualified waste form. Any effort to incorporate NaCl-loaded salt into a waste form may be complicated by higher salt liquidus temperatures.

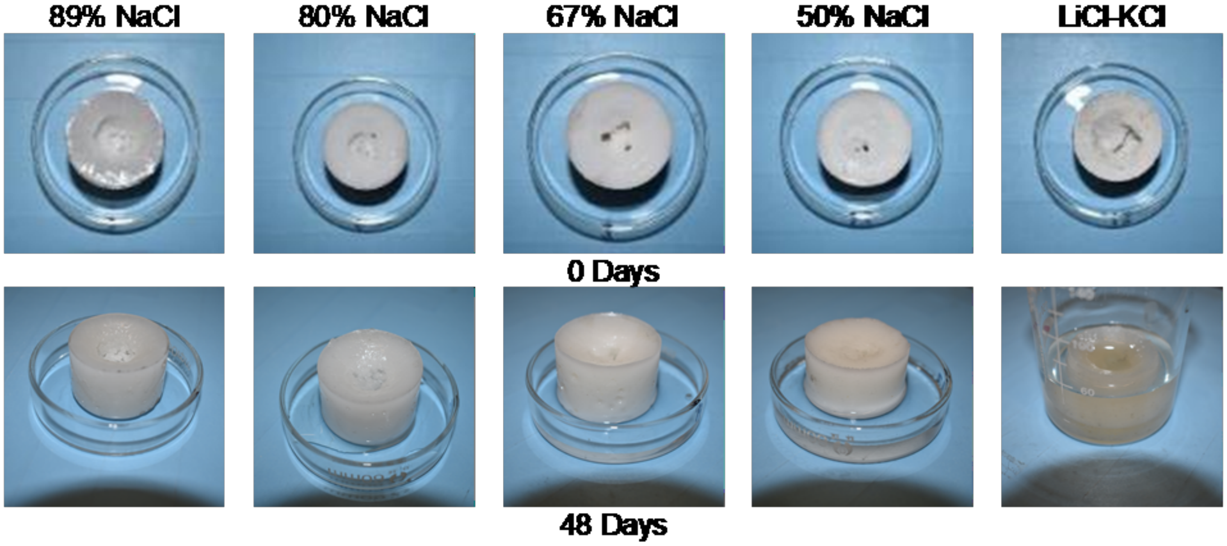


Fig. 4. Ingot appearances after formation and after 48 days in the hydration chamber. Standing water was observed in all samples except those with 89% NaCl. The petri dishes shown have an inner diameter of 5 cm.

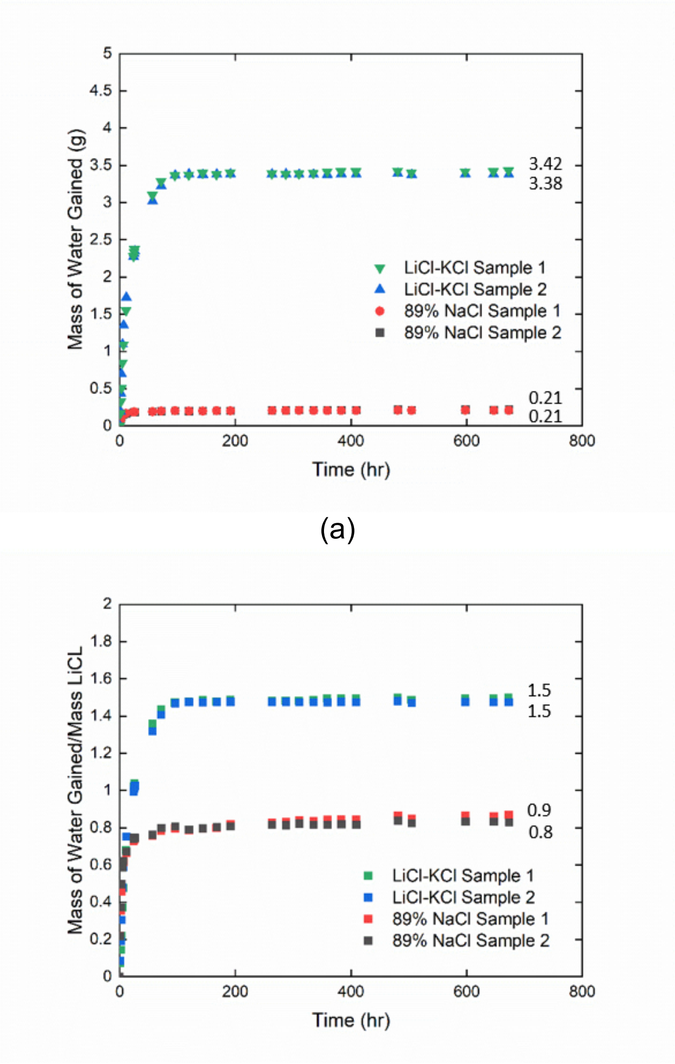
Table 1. Elapsed time when standing water was first observed adjacent to each ingot during hydration experiments. Masses of water gained before and after the first evidence of standing water, as well as the total water gained after reaching steady state.

Mass % NaCl	First Evidence of Standing Water (h)	Mass gained prior to observation of standing water (g)	Mass gained after observation of standing water (g)	Total water gained (g)
0	17	9.91	17.31	27.22
50	24	3.65	9.72	13.37
67	48	3.39	4.94	8.34
80	192	2.79	1.32	4.11
89	NA	1.16	NA	1.16

III.C. Effect of Hydration on Corrosion of Stainless Steel

The measured mass increases of salt powders contained in stainless steel crucibles are reported in Figure 5. Pure LiCl-KCl powder in stainless steel reached steady-state hydration after 100 hours. This is much faster than the LiCl-KCl ingot (400 hours, see Figure 3), as expected. Figure 6 shows photos of the salt-crucible interface with accumulation of standing water in pure LiCl-KCl (standing water was first observed at 24 hours). Evidence of corrosion was also observed in LiCl-KCl samples (both on crucible bottoms and on inner walls just above the water line) after 24 hours. No such standing water was observed in crucibles containing 89% NaCl powder, though small amounts of brown staining were observed on the salt. An empty crucible was also placed inside the humidity chamber as a reference for mass uptake from corrosion in the absence of any salt. This reference crucible exhibited no mass gain and appeared pristine after eight days inside the humidity chamber.

Based on these findings, the deliquesce of pure LiCl-KCl provides an electrolyte for corrosion reactions at steel canister surfaces. These conditions are untenable for long-term storage of waste salt. Alternatively, salt loaded with 89% NaCl eliminates deliquescence, limits water absorption, and significantly inhibits evidence of corrosion in the moist test environment.



(a)

(b)

Fig. 5. Hydration behavior of salt powders (LiCl-KCl and 89% NaCl samples) in stainless steel crucibles.

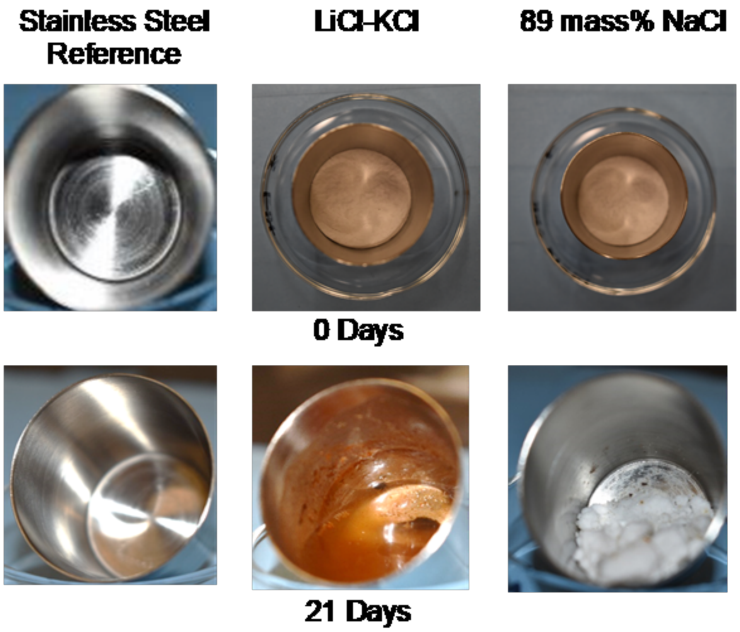


Fig. 6. Images of salt-stainless steel interfaces with evidence of standing water and corrosion and crucibles containing pure LiCl-KCl. Evidence of corrosion is minimal in crucibles with 89% NaCl. The crucibles have a top inner diameter of 3 cm.

IV. CONCLUSIONS

This work reported on a prospective processing path for minimizing water uptake upon atmospheric failure of electrorefiner operations and during the interim storage of electrorefiner salt: waste dilution via solid solution with NaCl. Deliquescence reduced with increasing NaCl and was eliminated at an NaCl concentration of 89 mass%. When deliquescence was inhibited, only minimal evidence of corrosion on the stainless steel vessels was observed.

While acceptable for short-term storage, this processing path does not eliminate the need to further process the salt to immobilize it for permanent disposal as liquid water will rapidly dissolve the NaCl-LiCl-KCl into a corrosive brine. There is also a large increase in the total waste volume (~10x). Additionally, removal of absorbed water may prove difficult due to the potential for HCl generation via hydrolysis. Despite these drawbacks, NaCl dilution could be an indispensable solution in emergency situations.

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