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Technical Summary of MIS Studies of Cl Transport and Reactivity

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Chloride containing deposits have been detected during destructive examination (DE) of 3013 inner and convenience containers that had contained impure plutonium oxide/salt mixtures. The deposits were found on surfaces that were not in direct contact with the oxide/salt mixtures. EDX analysis of deposits associated with corrosion pits in the inner container closure weld region (ICCWR) show Cl but no metal cations from the oxide/salt mixture (Na, K, Ca, Mg, or Pu) that would indicate particulate transport of the chlorine to that location. Powder x-ray diffraction analysis identified a coating found on the wall of a convenience container as ammonium chloride (NH₄Cl).¹ The location of the NH₄Cl coating on the wall above the material suggest that it was made by a gas-phase reaction, one possibility being a reaction between ammonia (NH₃) and hydrogen chloride (HCl) gases as shown in equation (1). It has been shown that NH₃ can be formed in a gas-phase reaction between nitrogen (N₂) and hydrogen (H₂) in a radiation environment, equation (2).^{2,3}



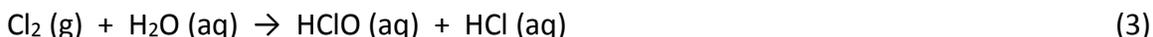
Chlorine as Cl₂ is found trapped within the crystal lattice of γ -irradiated CaCl₂ crystals with a few weight percent of excess water.⁴ Water is required to generate Cl₂ because Cl₂ is not observed with anhydrous CaCl₂. Trace amounts of Cl₂ are detected in γ -irradiated NaCl solids.⁵ These studies also show that HCl is not a direct radiolysis product and is likely generated from a secondary reaction with water. Thermal hydrolysis of alkaline earth chloride salts do not generate HCl at the low temperatures reached by the enclosed material and is not the source of HCl required by equation (1).

It is evident that the chlorine is transported from the stored material to the headspace as a chlorine containing gas-phase specie, but the form of the species being transported and subsequently responsible for headspace pitting corrosion in the ICCWR of 3013 containers is unknown.

Transport of Cl Specie(s) into the Headspace

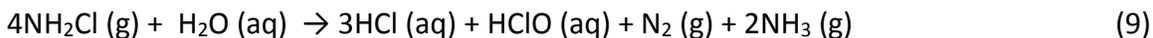
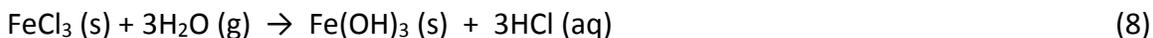
From the above studies, we can assume that Cl₂ is a primary radiolysis product in the stored plutonium oxide/salt mixture of 3013 containers and that HCl is not. Once

formed, the Cl₂ can either migrate into the headspace, as it is a stable volatile specie, or the Cl₂ can react with water present in the plutonium oxide/salt mixture, equation (3). All materials packaged in 3013 containers contain some, small percentage of moisture. The hypochlorous acid (HClO) and HCl generated from equation (3) are also stable volatile species that can migrate into the headspace.⁶



Reactions of Cl Specie(s) in the Headspace

Once in the headspace, these chlorine containing gas-phase species (Cl₂, HCl, or HClO) can continue to react with background headspace gases (NH₃, H₂O, H₂, O₂, CO₂, CO, N₂) present in the 3013 containers. A few potential reactions are shown in equation (1) and (4 – 6).^{7,8} These chlorine containing gas-phase species could also adsorb onto the surface in the ICCWR of 3013 containers and initiate pitting corrosion. For example, it has been shown that Cl₂ reacts with steel at temperatures of 77 °C and above to form FeCl₃, equation (7).^{9,10} The resulting FeCl₃ solid could then absorb moisture from the headspace and form an aqueous acidic solution (deliquesce) which can initiate chloride-induced corrosion pitting, equation (8).



The NH₂Cl generated in equations (6) and (7) has been shown to be a transport mechanism for chlorides resulting in SCC of austenitic stainless steels.⁸ Any NH₂Cl reaching the ICCWR can react with surface adsorbed water to generate HClO along with a decrease in pH, equation (9). It is known that HClO is a very aggressive corrosive specie capable of initiating chloride-induced corrosion pitting and SCC.

Capture of Cl Species

In order to determine the chlorine containing gas-phase specie(s) participating in headspace pitting corrosion including in the ICCWR of 3013 inner containers, one must capture them in their gaseous form. Chlorine containing gas-phase species like Cl₂ and HCl have been captured by solid alkene compounds under anhydrous and non-radiological conditions.¹¹⁻¹⁵ The environment inside 3013 stainless steel containers is not anhydrous and so the capture of Cl₂ and HCl gases under hydrous conditions needed

to be tested. This was done by exposing solid alkene compounds to two different gaseous environments inside constant humidity cells.¹⁶ Exposure of solid *trans*-Stilbene to a gaseous mixture composed of Cl_2 , HCl , HClO and H_2O gases resulted in capture of Cl_2 gas, Figure 1. This Figure shows the physical and photophysical changes that occur to *trans*-Stilbene upon exposure to this gas mixture for 22 days at room temperature. The white shiny crystalline solid, which luminescence blue under irradiation from a black light, upon exposure to the gas mixture changes to a white opaque solid and experiences a luminescence quench. Analytical analysis of this white opaque solid revealed addition of Cl_2 to the aliphatic double bond of *trans*-Stilbene making chlorinated *trans*-Stilbene.

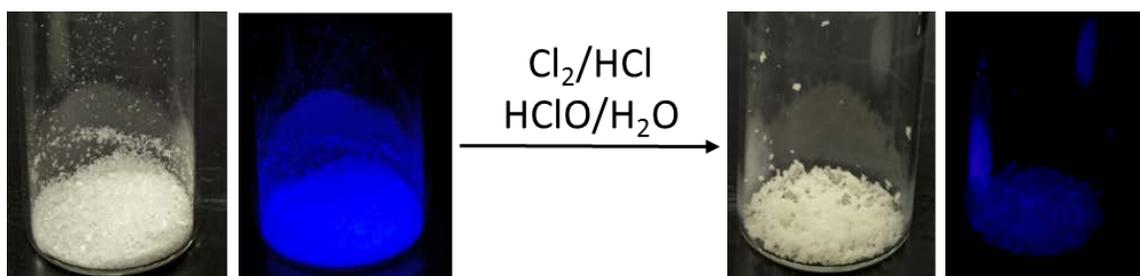


Figure 1. *trans*-Stilbene (left) and chlorinated *trans*-Stilbene (right) under both ambient light and black light.

Exposure of 4-(Dimethylamino)stilbene to a gaseous mixture composed of HCl and H_2O gases resulted in capture of HCl gas, Figure 2. This Figure shows the photophysical changes that occur to 4-(Dimethylamino)stilbene upon exposure to this gas mixture for 27 days at room temperature. The orange solid, which luminescence blue under irradiation from a black light, upon exposure to the gas mixture the color of the solid persists but its luminescence becomes yellow/green. In this case, analytical analysis of the product revealed HCl protonation of the amino group in 4-(Dimethylamino)stilbene and no addition of HCl to the aliphatic double bond.

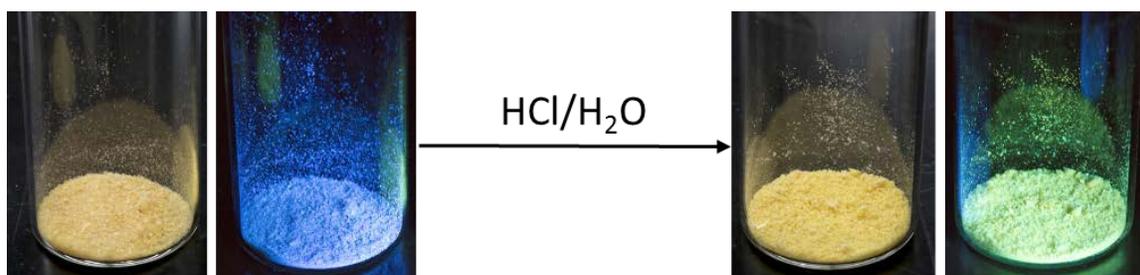


Figure 2. 4-(Dimethylamino)stilbene (left) and protonated 4-(Dimethylamino)stilbene (right) under both ambient light and black light.

Using these two compounds, it is possible to distinguish between Cl_2 and HCl , and to quantify the amounts of each. We will expose these two compounds to the atmosphere above an impure plutonium oxide/salt mixture known to cause headspace corrosion. If sufficient chlorine containing gases are produced by the material, we can monitor the

reaction progress using changes in the physical and photophysical appearance of the solid alkene compounds. The successful identification chlorine containing gas-phase species associated with headspace pitting corrosion in the ICCWR of 3013 containers will aid in evaluating the risk for SCC in 3013 inner containers.

Conclusion

In conclusion, the analyses presented here assume, based on literature, that Cl₂ is a conceivable radiolysis product in the stored plutonium oxide/salt mixture and that not only HCl but also HClO results from secondary reactions. These chlorine containing gas-phase species are stable and can potentially reach the ICCWR of 3013 containers where they can initiate chloride-induced corrosion pitting/SCC. Identifying and quantifying the chlorine containing gas-phase species will aid in evaluating the risk for SCC in packaged inner containers.

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