SUPERNATANT LIQUID SAMPLING IN WASTE TANKS (U)

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Supernatant Liquid Sampling in Waste Tanks (U)

SUMMARY

Supernatant liquid samples are periodically taken and analyzed for corrosive and inhibiting species concentrations as part of the waste tank chemistry control program. These samples are taken at or near the surface of the waste. This is the preferred location for sampling since the liquid phase at this location is the most corrosive liquid phase in the tank as a result of the highest nitrate to nitrite ratio and the lowest hydroxide concentration.

INTRODUCTION AND DISCUSSION

High-level nuclear wastes are stored at the SRS in underground carbon steel tanks. The waste consists of three forms; water insoluble metal oxides and hydroxides (sludge), crystallized water soluble salts (salt cake), and supernatant liquid. Three types of corrosion can occur during the storage and processing of nuclear wastes at SRS; general corrosion, stress corrosion cracking and localized or pitting corrosion.^{1,2} To limit and/or prevent these types of corrosion, the temperature and composition of the liquid phase are maintained within certain limits. These limits are based on tests which have determined the minimum inhibitor concentrations required to prevent corrosion as a function of the concentration of corrosive species and the temperature of the liquid phase.³

In order to determine the concentration of corrosive and inhibiting species in solution, the supernatant liquid in each tank is sampled and analyzed on a periodic basis. Based on the results of this analysis, a decision is made whether to add inhibitor(s) to the tank contents. This sample is taken at or near the surface of the liquid phase. Samplers have also been developed to take samples at variable depths. However, these samplers are not routinely used in the tank chemistry control program.

The concentration of chemical species in the high-level waste stored at the SRS can vary within the liquid phase due to radiolytic reactions, chemical reactions, and additions of waste having varying compositions. In order to assess whether the composition of the liquid phase of HLW is adequately inhibited, samples of the supernatant liquid are taken and analyzed on a periodic basis. Since the composition of the liquid phase can vary within a tank, the selection of the sampling location(s) must include that which would exhibit the most corrosive solution.

Nitrate is converted into nitrite by radiolysis.^{4,5} Nitrite is an effective corrosion inhibitor. With the exception of the ITP process, there are no reactions which rapidly consume nitrite during storage and processing of HLW.⁶ Thus, as the waste ages, the nitrate concentration decreases and the nitrite concentration increases. As a result, the corrosivity of the waste decreases. Thus, the most corrosive solution in a waste tank would be that which has been most recently added to the tank since the ratio of nitrate to nitrite would be highest in this fraction. Since this fresh waste would be at the top of the tank, the preferred sampling location would be at or near the top of the waste stored in the tank.

Sludge

Settled sludge consists of about 20% metal oxide and hydroxide solids and 80% supernatant liquid. Because of the high concentration of fission products in the sludge solids, the absorbed dose of the supernatant liquid in the settled sludge is greater than that in the supernatant liquid above the sludge. Therefore, the nitrite concentration is higher and the nitrate concentration is lower in the settled sludge region than in the supernatant liquid above the sludge which was originally part of the same waste transfer into the storage tank.

Supernatant Liquid

All waste tanks are actively ventilated with air to prevent the buildup of flammable vapor mixtures of hydrogen.⁷ Alkaline solutions such as the supernatant liquid in the waste storage tanks are known to absorb carbon dioxide from air, which reacts with the hydroxide in solution producing bicarbonate and carbonate species.⁸ No attempt is made to exclude carbon dioxide from the air which passes through the storage tanks. Thus, carbon dioxide is continuously absorbed by the waste. Absorption of the carbon dioxide continues until the partial pressure of carbon dioxide over the solution equals that of the air entering the tank.⁹

For a relatively stagnant tank which has not reached steady-state conditions with respect to the absorption of carbon dioxide, a concentration gradient in hydroxide would develop extending down from the liquid/vapor interface to the bottom of the tank. Thus,

the lowest hydroxide concentration in the tank would occur at the supernatant liquid/vapor interface. This location would thus have the greatest possibility of being corrosive, and would be the preferred sampling location to ensure that a sufficient amount of hydroxide is present to prevent attack of the tank steel.

Salt Cake

Salt cake is produced by cooling evaporated supernatant liquid. During evaporation, the supernatant liquid is concentrated a factor of about three. Thus, the salt concentration in the uncooled liquid is increased by a factor of about three. Upon cooling, salts crystallize, according to their solubility limits. Sodium hydroxide has the greatest water solubility of the major salts and thus, the cooled supernatant liquid is enriched in hydroxide. After allowing the salts to settle, the supernatant liquid is decanted leaving a small layer of supernatant liquid covering the salts. This process is repeated until the tank is filled with salt cake.

The salt cake is comprised of crystalline salts and interstitial supernatant liquid. The major salt components in the crystalline solids are the sodium salts of nitrate, nitrite, aluminate and hydroxide. The interstitial liquid is enriched in hydroxide because of the higher solubility of sodium hydroxide. As carbon dioxide is absorbed and reacts with the hydroxide in solution, it would be replenished from hydroxide in the crystalline salts. As discussed earlier, the minimum hydroxide concentration in the liquid phase would occur at the liquid/vapor interface, and thus sampling at this location would represent the most corrosive composition in the tank.

Due to the absorption of atmospheric carbon dioxide, the relative younger age, and the decreased concentration of fission products, the liquid phase at the top of a waste tank will exhibit the highest nitrate to nitrite ratio and the lowest hydroxide concentration. This combination of higher nitrate to nitrite ratio and lower hydroxide concentration results in the liquid phase at this location being potentially more corrosive than lower regions. Thus, this location is the preferred sampling location in order to determine the need for additional corrosion inhibitor(s).

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