At the United States Department of Energy’s Hanford tank reservation, approximately 50 million gallons of liquid radioactive waste from cold war weapons production is stored in 177 underground storage tanks. Prior to permanent disposal in a geologic site, the waste will be vitrified into glass logs. However, the double shelled carbon steel storage tanks now used for storage will continue in operation until the vitrification plant construction is finalized and waste processing operations completed, which could be still several decades. It is essential that tank leak integrity be assured through control of corrosion and cracking. The wastes are generally highly alkaline, from pH 10 to hydroxide concentrations in excess of 6 M. The steel is passive in these environments, but is susceptible to localized corrosion and stress corrosion cracking because of the generally high nitrate concentrations and elevated temperatures. Maintaining the pH above the specification of 13 requires addition of considerable amounts of hydroxide to balance the neutralizing effects of CO₂ from the atmosphere. These additions have deleterious influences on the vitrification process. On the other hand, nitrite ion, which is present to varying extents in the wastes, is known to be a potent inhibitor for corrosion and cracking in nitrate environments.

In this work, an experimental study was performed to investigate the ranges of susceptibility to localized corrosion and stress corrosion cracking as a function of potential and tank chemistry. Potential and nitrite ion concentration were shown to have a dominant influence, with pH in the range of 10-14 being less important. These results have led to the development of new approaches to control corrosion through tank chemistry. Two other issues must be addressed when considering a change in the tank chemistry specifications: atmospheric corrosion of the tank above the liquid and attack at the liquid/air interface (waterline attack). Both phenomena have been observed and result from local differences in chemistry relative to the bulk liquid composition. The liquid/air interface has been probed by Raman spectroscopy, which shows that key compositional differences can develop with time.

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