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WHC-SA-1985-FP

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Prepared for the U.S. Department of Energy
Office of Environmental Restoration and Waste Management

Westinghouse Hanford Company Richland, Washington

Hanford Operations and Engineering Contractor for the U.S. Department of Energy under Contract DE-AC06-87RL10930

Conf-940222--8

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Date Published
November 1993

To Be Presented at
NACE Corrosion 94
Baltimore, MD
February 28 - March 4, 1994

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CORROSION MONITORING OF HIGH-LEVEL WASTE TANKS

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ABSTRACT

High-level nuclear wastes are currently being stored in carbon steel tanks at the Hanford Site. The wastes are stored in both single-shell tanks (SSTs) and double-shell tanks (DSTs). The SSTs have already exceeded their design life and some of these tanks have already leaked waste into the surrounding soil. The DSTs, on the other hand, were fabricated and put into operation more recently and have not been observed to show any leakage of wastes. One of the objectives at the Hanford Site is to monitor the degradation of the DSTs with the aid of in-tank corrosion probes. Outside the nuclear industry, electrochemical and resistance corrosion probes are in common use. The application of these probes to nuclear waste storage is generally complicated by the high radiation and complexed caustic environment. This paper deals with the details of a proposed development of commercial probes to monitor corrosion of the DSTs at the Hanford Site. Once the corrosion probes are successfully developed, the technology can be applied to SSTs and also transferred to other U.S. Department of Energy (DOE) Sites.

Keywords: double-shell tanks, electrochemical, resistance, corrosion probes, carbon steel, caustic, radiation, development

INTRODUCTION

High-level wastes from nuclear spent fuel processing operations are currently being stored in carbon steel tanks at the Hanford Site. The wastes are stored in both SSTs and DSTs. The SSTs were constructed and operated during the

1940s through the 1960s and have already exceeded their design life. Some of the SSTs have already leaked waste into the surrounding soil. The DSTs, on the other hand, were fabricated and put into operation during the 1970s and the 1980s and have not shown any leaks.

In the interest of minimizing leakage of waste to the soil, recommendations have been made to monitor the corrosion of the DSTs with the aid of in-tank corrosion probes. Corrosion probes are available commercially, and both electrochemical and resistance corrosion probes are routinely used outside the nuclear industry. The application of these probes to nuclear waste storage is complicated by the high radiation and complexed caustic environment. This paper deals with the details of a proposed development of commercial probes to monitor corrosion of DSTs at the Hanford Site.

BACKGROUND

The high-level wastes stored in the carbon steel tanks at the Hanford Site contain nitrates, nitrites, organic chemicals used as chelating agents, and aluminates. The major chemical species that may be important from a tank wall corrosion standpoint are OH^-, F^-, Cl^-, NO_3^-, NO_2^-, and AlO_2^-. The pH of the DST wastes is specified to be >11.5. According to Pourbaix diagrams, iron is passivated under oxidizing conditions for pH>8. Test results with simulated wastes indicated uniform corrosion rates <0.5 mils per year (mpy) in most cases. The redox potential of the NO_2^-/NO_3^- couple at the operating temperature of the DSTs is near zero, which implies it is either slightly oxidizing or slightly reducing depending on the temperature. Under these conditions, iron is expected to be passivated (except for pH>14), which agrees well with the experimental data on simulated wastes. The presence of nitrate in the wastes is a cause for concern due to the possibility of nitrate stress corrosion cracking (SCC) of carbon steel. However, if enough hydroxide is present in the waste, the nitrate SCC could be totally mitigated. The above facts led to the development of the operating specifications for high-level waste tanks based on the work performed at the Savannah River Laboratories (SRL) and Pacific Northwest Laboratory (PNL). Therefore, it is believed that for those tanks meeting the operating specifications, corrosion rates are below the design criteria (1 mpy) in the liquid phase.

However, both PNL and SRL have expressed concern that the corrosion rates at the liquid/vapor interface and in the vapor phase may be excessive. Also, it is important to verify that the corrosion behavior under actual waste storage conditions is consistent with the predicted behavior.

All of the DOE sites that store high-level nuclear waste are being requested to demonstrate that the storage tanks are sound and not deteriorating at an excessive rate. A program is underway to perform non-destructive evaluation of the Hanford DSTs. The waste tanks at the Hanford Site are currently not being monitored for corrosion.

CORROSION PROBE DESCRIPTION

There are two basic types of commercially available probes - one based on the loss of metal in the sensing element which results in a change in the resistance of the probe and the other based on the electrochemical corrosion reaction that occurs at the sensor surface. The former is called an "electrical resistance" probe (ER probe) and the latter a "polarization resistance" probe (PR probe).

Mechanism of Operation

Electrical Resistance Probe - The sensing element of the ER probe is a thin sheet, tube, or wire for which any metal loss translates into a "significant" percentage of the total metal present. Consequently, because the electrical resistance is proportional to the metal thickness, the metal loss is readily detected by the change in the resistance of the probe. The loss of metal per unit time is the corrosion rate, and, therefore, the change of resistance as a function of time is directly proportional to the corrosion rate.

Polarization Resistance Probe - From electrochemical relationships, it may be shown that the current density at an electrode is proportional to the exponential of the applied potential. From this relationship, it can be shown mathematically that for sufficiently small applied potentials, the current density is linearly proportional to the potential. Because this proportionality is analogous to Ohm's law, the proportionality factor is referred to as the "polarization resistance." For a given system, the polarization resistance is constant and by the application of a small potential, the current density can be calculated; the current density can be converted to corrosion rate.

PROBE AVAILABILITY AND APPLICABILITY

Availability

Both types of probes are commercially available. If special conditions are present, for example, high temperature, radiation, high caustic, or the need to decontaminate, the probes can be made to order using special materials or fabrication techniques. The two major suppliers are Cortest and Rohrback Cosasco. There are also other vendors who make the probes as replacement items.

Applicability

The applicability of both types of probes has been shown in numerous non-nuclear industrial systems. They are currently undergoing testing at West Valley Nuclear Services, New York, in caustic nuclear waste. Results to date suggest that the ER probes are generating data generally consistent with laboratory tests. The results of the PR probe are inconclusive in that it has not been determined whether the data generated are a result of the waste chemistry, the probe type and design, or whether other effects are present. No comparisons have been made with weight loss coupons installed in the tank.

PROPOSED APPROACH FOR PROBE DEVELOPMENT

The probes fabricated according to the current industry standard are acceptable for use except for the need to improve their life in the caustic and radiation environments such as the tank wastes. In addition, there has been no significant development of probes suitable for monitoring pitting or SCC.

Westinghouse Hanford Company (WHC) will manage the project and team with ChemMet and PNL for the development of the corrosion probes. Pacific Northwest Laboratory has the laboratory facilities in which the required experimental work for probe development could be performed, while ChemMet and WHC will provide the technical expertise and coordination necessary for the task.

Initially, commercial probes will be procured and tested for applicability for use in the high level waste tanks. The probes will then be tested for any indications for the formation of conductive films that would affect the measurements. In addition, the PR probes will be tested for the presence of any electrochemical reactions. Then, a computerized data collection system will be procured and modified to provide data in a readily usable format. Examination of some of the operating characteristics of the PR probes in caustic solutions is already in progress at PNL.

Once the testing and evaluation of the operating characteristics of the probes are completed in the laboratory, it is expected that suitably designed probes will be installed in one or more of the Hanford waste tanks in the out years for demonstration of the probe system. Data collection and interpretation will continue with the simultaneous collection of tank operating data into the same data base to assess the response of the probe to changing operating parameters.

Plans are already in place to embark on a collaborative effort with SRL and West Valley Nuclear Services in the probe development effort. This will be done to assure that the research at the Hanford Site is complimented by the work at the other DOE sites. The corrosion probes that are proven to be compatible with Hanford tank wastes will be made available for installation in tanks at other DOE sites. Therefore, successful probe development at Hanford is expected to provide improved corrosion monitoring capability at all DOE sites.

CONCLUSIONS

Westinghouse Hanford Company will team with ChemMet and PNL for the development of corrosion probes to monitor corrosion of DSTs at the Hanford Site. Pacific Northwest Laboratory has the laboratory facilities where the probe development work will be performed. Westinghouse Hanford Company will manage the project and ChemMet and WHC will provide the technical expertise and coordination necessary for the developmental effort. Commercial probes will be procured and modified based on the results of the developmental research to be compatible with the Hanford tank wastes. Final modifications to the probe design will be accomplished after exposing the probes to actual tank wastes. The corrosion probes that are proven to be compatible with Hanford tank wastes will be made available for installation in tanks at other DOE sites. The developmental technology will be transferred to other DOE sites to avoid duplication of effort. Thus, successful probe development at the Hanford Site will provide improved corrosion monitoring capability at all DOE sites.

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DATE FILMED

3/29/94