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Quartz Crystal Microbalance Corrosion Diagnostic

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New or novel analytical techniques or capabilities applicable to aging and reliability concerns

Current methods of detecting material aging and assessing material compatibility rely heavily on lengthy (12-18 month) exposure to predefined conditions. Rapid screening of materials for compatibility and corrosion susceptibility is consequently impossible. Alternatively, accelerated aging studies are sometimes performed; however, correlation of data obtained from such studies and model predictions lacks a basis in fundamental understanding, making model development and validation difficult. Both long-term and accelerated studies involve expensive, bulky, and resource-hungry instruments.

We are developing a quartz crystal microbalance (QCM) system as a new diagnostic tool for monitoring stockpile-relevant corrosion processes. This instrument can be used to detect changes in the surface composition of materials in real time upon exposure to, for example, humidity, solvents, corrosive gases, and elevated temperatures. Mass changes due to corrosion reactions can be detected with sub-monolayer sensitivity; consequently, the QCM is ideal for probing the early stages of surface reactions. With this capability in hand, we are performing experiments to measure corrosion reactions under a variety of conditions for critical metals in the stockpile, focusing in particular on aluminum and molybdenum. Rate constants and thermodynamic data extracted from these results will be used to develop quantitative models of the corrosion process.

The QCM monitors the process of corrosion at a surface by measuring the crystal resonance frequency and dissipation simultaneously. We successfully demonstrated that the QCM can detect salt-initiated corrosion of aluminum, using aluminum-coated QCM crystals with nanoscale dots of NaCl deposited by an ink-jet printing process. These substrates simulate localized pitting corrosion initiated by exposure to water vapor and CO_2. Gold QCM substrates with NaCl, for which no corrosion is expected, were evaluated as a control. We exposed these substrates to the following relative humidities (RH) at room temperature: 20%, 40%, 60%, 75%, 85% for 3 hours each. Both metal surfaces adsorb water vapor. The change in mass with each increase in RH is ~10-20 ng/cm^2, equivalent to ~ 0.2 monolayer and demonstrating the extremely high sensitivity of the QCM to small mass changes. Although both aluminum and gold surfaces with NaCl nanoparticles show similar mass uptake at RH $<$ 75%, at ≥75%RH the rate of mass uptake by the aluminum sample dramatically increases. Scanning electron microscopy reveals dendrite-like deposits on the aluminum surface, clearly indicating a chemical reaction has occurred. We also demonstrated that subtle changes in the amount of mass uptake as a function of temperature can be detected, indicating that it should be possible to extract an activation energy from these data. In future work, we plan more extensive measurements using a variety of salt-coated aluminum surfaces to obtain rate data and dependencies on RH level and temperature. In collaboration with ongoing computational modeling efforts, we expect these data will enable us to develop quantitative models useful for predicting aging and corrosion rates of components in the stockpile.

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