
Development and Optimization of Voltammetric Methods for Real Time Analysis of Electrorefiner Salt with High Concentrations of Actinides and Fission Products

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ABSTRACT:

This proposed project addresses the problem of achieving accurate material control and accountability (MC&A) around pyroprocessing electrorefiner systems. Spent nuclear fuel pyroprocessing poses a unique challenge with respect to reprocessing technology in that the fuel is never fully dissolved in the process fluid. In this case, the process fluid is molten, anhydrous LiCl-KCl salt. Therefore, there is no traditional input accountability tank. However, electrorefiners (ER) accumulate very large quantities of fissile nuclear material (including plutonium) and should be well safeguarded in a commercial facility. Idaho National Laboratory (INL) currently operates a pyroprocessing facility for treatment of spent fuel from Experimental Breeder Reactor-II with two such ER systems. INL implements MC&A via a mass tracking model in combination with periodic sampling of the salt and other materials followed by destructive analysis. This approach is projected to be insufficient to meet international safeguards timeliness requirements. A real time or near real time monitoring method is, thus, direly needed to support commercialization of pyroprocessing. A variety of approaches to achieving real time monitoring for ER salt have been proposed and studied to date—including a potentiometric actinide sensor for concentration measurements, a double bubbler for salt depth and density measurements, and laser induced breakdown spectroscopy (LIBS) for concentration measurements. While each of these methods shows some promise, each also involves substantial technical complexity that may ultimately limit their implementation. Yet another alternative is *voltammetry*—a very simple method in theory that has previously been tested for this application to a limited extent. The equipment for a voltammetry system consists of off-the-shelf components (three electrodes and a potentiostat) which results in substantial benefits relative to cost and robustness. Based on prior knowledge of electrochemical reduction potentials for each of the species of interest, voltammetry can be used to quantify concentrations of a variety of elemental species—including uranium, plutonium, minor actinides, and rare earths. Various methods have been tested by other researchers to date—including cyclic voltammetry, square wave voltammetry, normal pulse voltammetry, etc. In most cases, it has been observed that there is a very limited concentration range for which the output can be readily correlated with concentration in the salt. Furthermore, testing to date has been limited to simple ternary salts with only a single element being quantified. While incomplete for application to MC&A for pyroprocessing, these results lead us to believe that voltammetry can be optimized based on salt properties and fundamental electrochemical rate processes to yield a highly accurate and robust method. This proposed project is divided into four tasks jointly executed by three university research groups. This includes experimental measurement of key physical data on the systems of interest, development of a predictive voltammetry model, experimental validation of the voltammetry model, and design/verification of an optimized measurement method. This project supports the goals of the US-ROK Joint Fuel Cycle Study in addition to the NA-24 office of the National Nuclear Security Agency and the International Atomic Energy Agency (IAEA).