



# Application of multivariate analysis techniques to safeguards of the electrochemical treatment of used nuclear fuel



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## ARTICLE INFO

### Article history:

Received 29 September 2014

Accepted 17 November 2014

### Keywords:

Pyroprocessing

Safeguards

Electrorefiner

Voltammetry

Principal component analysis

Partial least squares

## ABSTRACT

Several countries have shown interest in developing the electrochemical treatment of used nuclear fuel (UNF), commonly termed pyroprocessing. From a proliferation perspective, an advantage of pyroprocessing is its inability to isolate pure plutonium. However, because plutonium is present in the process, it needs to be effectively safeguarded to protect against diversion of plutonium-containing materials that could be post-processed elsewhere. The most complicated unit to safeguard in the process is the electrorefiner where UNF is chemically separated into several material entities. Molten LiCl–KCl serves as the electrolyte into which actinides (including uranium and plutonium), rare earths, and other active metals from the fuel are partitioned after being oxidized to chloride salts. Various voltammetric methods are being developed to measure the concentration of actinides in the molten salt in near-real-time. However, these methods have mostly been applied to molten salt mixtures containing a single actinide. Unfortunately, the presence of multiple actinides will create interferences in the electrochemical responses which could make traditional analysis of voltammetric data inaccurate for determining individual species concentrations. It is proposed to use multivariate techniques to more accurately predict concentrations of multiple actinides from voltammetric data. Two techniques, principal component analysis and partial least squares, are demonstrated on experimental and simulated data for molten salt mixtures containing uranium and plutonium. These techniques consistently yielded more accurate predictions of uranium and plutonium concentrations than simply using peak height. Possible methods of employing multivariate techniques in safeguarding an electrorefiner are also demonstrated.

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## 1. Introduction

The electrochemical treatment of used nuclear fuel (UNF), commonly termed pyroprocessing, is being developed by several countries including non-nuclear weapons states (NNWS) such as Japan and Republic of Korea. Because plutonium (Pu) and uranium (U) are present in the process, the International Atomic Energy Agency (IAEA) needs to develop reliable safeguards and material accountability methods for pyroprocessing in anticipation that the technology will be commercialized by these and other NNWS's. From a safeguards perspective, an advantage of pyroprocessing is its inability to isolate Pu from other elements in used fuel, which either remains in the salt with other transuranics (TRU) or is co-extracted with U and TRU. However, the amount of Pu and U in the process still needs to be accurately tracked throughout the

process to ensure that mixtures containing Pu or U are not diverted and processed elsewhere.

Several variations of pyroprocessing exist (National Research Council, 2000; Lee et al., 2013), and no standard design for a commercial facility has been developed. However, the general features are similar among the process variations. The process generally starts with disassembly and chopping of UNF pellets or slugs. If the UNF is from oxide fuel, it must first be reduced to its metal form by electrolytic reduction. If the UNF is from metal fuel, this step can be bypassed. Once in metallic form, UNF is loaded into an electrorefiner where active metal fission products and TRU elements are oxidized into molten eutectic LiCl–KCl salt. Noble metal fission products (FP) and cladding hulls remain in the anode. U and/or TRU can be electrotransported to a cathode from the salt or the undissolved fuel in the anode baskets. There are principally two modes in which an electrorefiner (ER) can operate. In one mode, the ER is designed to solely recover U. In the other mode, the ER is designed to simultaneously recover U and TRU as a co-deposited actinide alloy. The product from the ER, whether U or

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U/TRU, is then distilled to remove residual salt and consolidated into an ingot for waste storage or fabricated into fuel. The variations in the process largely deal with salt treatment, waste form fabrication, and recycle of actinides.

A significant amount of special nuclear material (SNM) can build up in the eutectic LiCl–KCl salt in the ER. Under normal operation, the most prevalent actinide in the ER salt is U (3.5–6.9 wt%) while other actinides and lanthanides, most notably plutonium (Pu) are also present in small amounts (<1 wt%) (Simpson and Sachdev, 2008; Li and Simpson, 2005; Li et al., 2009). Over the course of electrorefining, the U concentration decreases while the concentration of TRU increases. This is because  $UCl_3$  in the salt serves as an oxidant and reacts with the more active metals (Group I, II, rare earths, and TRU). The TRU metals react with  $UCl_3$  to form chlorides if not hindered by diffusion limitations. Different measures are taken to maintain an adequate level of U and reduce the concentration of TRU in the ER salt. One method is to occasionally add  $CdCl_2$  to the ER salt which then reacts with U metal to form  $UCl_3$  and Cd metal, which settles at the bottom of the ER (Li et al., 2009). Another method is to use a liquid cadmium cathode (LCC), which reduces the concentration of TRU in salt while increasing the concentration of U (Vaden et al., 2008). In order to maintain process control, models are currently used in pyroprocessing facilities, such as INL's Fuel Conditioning Facility (FCF), to predict the effect of these operations. Current process monitoring technology is insufficient to provide even near-real-time (NRT) feedback regarding concentration changes. State of the art practice is to sample the salt and wait weeks for analytical chemistry results to be returned.

NRT concentration measurements could assist both the host country and the International Atomic Energy Agency (IAEA) by providing a continuity of knowledge of salt composition which could be relatively uncertain otherwise. The host country's operators could use NRT measurements to determine when to add  $CdCl_2$ , employ the LCC or clean the salt in general. The IAEA could use NRT concentration measurements to help close mass balances and detect the suspension of salt cleaning activities which would allow TRU to accumulate in the salt and to be diverted in the salt waste or on a solid cathode. Additionally, NRT measurement of the salt composition could assist in general process monitoring and control to help optimize the performance of the ER, avoid criticality, and minimize process interruptions due to salt cleaning and inspections. Thus, NRT measurements could reduce the cost-burden of safeguards on both the IAEA and the host country.

Because it is already an electrochemical environment in the ER, electroanalytical techniques utilizing electrode probes (cyclic voltammetry, chronoamperometry, etc.) can be readily applied to make *in situ*, NRT quantitative measurements of ER salt composition. Cyclic voltammetry (CV) is a favorable method because of its reliability over a broad range of concentrations in molten LiCl–KCl eutectic (Kim et al., 2014). Additionally, normal pulse voltammetry (NPV) and square wave voltammetry (SWV) have been applied to the measurement of actinide ion concentrations in molten LiCl–KCl eutectic, but were found to be only suitable at low concentrations (Iizuka et al., 2001). In addition to these two studies, the electrochemical behaviors of several actinides in LiCl–KCl eutectic have been well studied. Zhang provided an extensive review of these studies (Zhang, 2014). These studies support the development of electrochemical sensors for NRT concentration measurements by providing important parameters and properties of actinide elements. Unfortunately, these studies have mostly focused on single actinides in eutectic LiCl–KCl with exception of Iizuka et al. (2001). In an actual ER, several of the actinides are present at varying concentrations. The presences of multiple actinides can interfere with each other's signals.

Typically, steady-state current, peak current, peak area or cumulative charge is related to concentration. However, if multiple actinides are present, their peaks or currents could overlap making it difficult to establish baselines for peaks or attribute the measured current to a single species. For example, in CV, current peaks are formed by scanning the potential at a sensing electrode. As long as these peaks are linearly related to the concentration of a species, they can be reliably used to predict the concentration. However, if another species is present and forms a peak in close proximity to the other species, the peaks will overlap. The peaks will need to be deconvoluted in order to extract reliable concentration predictions. This could involve stalling the scan just after the peak potential or semi-differentiating the CV curve, but these methods require a certain amount of separation between the peak potentials and discard a majority of the data (Bard and Faulkner, 2001; Palys et al., 1991). Alternatively, multivariate analytical techniques, which utilize the complete CV curve rather than a couple data points at the peaks, could provide more reliable and accurate predictions, potentially even when peak almost completely overlap (Rappleye et al., 2014a). Multivariate analytical techniques could also provide additional insights into the conditions of the ER and the measurement device. The capability of multivariate analytical techniques to predict elemental concentrations and provide other information relevant to safeguards is demonstrated in this work.

## 2. Multivariate analytical techniques

Two closely related multivariate analytical techniques are investigated in this paper: (1) principal component regression (PCR) and (2) partial least squares (PLS). Only a brief explanation of PCR and PLS will be provided here which is specific to the analysis of voltammograms. Readers are referred elsewhere for more detailed and general descriptions (Rappleye et al., 2014a; Keithley et al., 2009; Kramer, 1998). However, it is worth noting the PCR and PLS can be applied to any signal that is affected by any set of variables in any process.

PCR and PLS are multivariate analysis methods which use a greater amount of the data collected in voltammograms than the univariate analysis of peak height. PCR and PLS analyze a set of data, called a training set, to determine the main contributors to variance, called principal components (PCs). In this work, a training set is an  $n \times m$  matrix of voltammetric curves with  $n$  data points collected at  $m$  different species concentrations that span the expected range of concentrations for each species. A PC is calculated from the training set,  $A$ , using singular value decomposition, as shown below:

$$A = USV^T \quad (1)$$

where  $U$  is an  $n \times n$  matrix containing the PCs, or the eigenvectors of  $AA^T$ ,  $S$  is  $n \times m$  matrix containing the eigenvalues on its diagonal, and  $V^T$  is a  $m \times m$  matrix containing the eigenvectors of  $A^T A$ . The important thing to note is that  $U$  is orthonormal and the columns of  $U$  are the PCs. Thus, a PC is a vector that is transformed from  $A$  into a space where it is uncorrelated from all other PCs which helps mitigate co-variance when regression is performed. Also, the PCs in  $U$  are ranked according to the amount of the variance captured from  $A$  by the PC. Thus, column 1 of  $U$  is the PC that accounts for the most variance. The main difference between PCR and PLS are the considerations made when determining the PCs. In PCR, the PCs are selected and ranked based on the amount of variance that they capture from the training set without considering the relation between the data and concentration. In PLS, the values of concentration are taken into account when calculating the PCs from the training set, which can result in slightly more accurate predictions of concentration.

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