Feasibility Examination of Machine Learning Based Process Monitoring Approach Using Cathode Potential in Electrorefining to Enhance Pyroprocessing Safeguards-ability

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1. Introduction

Pyroprocessing is an electrochemical recycling technology for used fuels. As an alternative of aqueous technologies with several advantages, it prevents pure plutonium separation, which provides proliferation resistance. For nuclear fuel cycle facilities, it is indispensable to implement a safeguards system that can be monitored and verified by the International Atomic Energy Agency (IAEA).

Current safeguards technologies mainly rely on a mass balance method, which is based on sample extraction and the use of destructive assay. Due to unique features of pyroprocessing, there is uncertainty to apply traditional safeguards methods to meet safeguard-ability requirements (defined as "timely detection of significant quantity of special nuclear material") in commercializing pyroprocessing, and new approaches and technologies have been suggested to enhance existing safeguards.

It is suggested that process monitoring (PM) can supplement existing safeguards technologies. By employing PM, it is possible to indirectly track a flow of special nuclear materials. Various types of signals can be produced in (near) real time from a variety of sensors installed in specific locations at the facility. Though the signal alone do not imply information about the operation state, the process can be diagnosed based on the statistical experience by collecting data and developing data library. On this wise, machine learning

The electrorefining (ER) process is a main unit process in pyroprocessing. The purpose of ER is to selectively separate uranium from used fuels. When the process begins, a variety of active elements including SNMs are dissolved out into molten salt electrolyte, and accumulated in the electrolyte. Only uranium is electro-deposited on a cathode according to the order of equilibrium potentials among existing elements. Therefore, ER is very important process in the safeguards aspect and requires to employ a reliable safeguards system.

In this study, the feasibility of using PM based on machine learning for improving safeguards-ability of ER was examined. Cathode potential was selected as a target signal to investigate the operation state (normal vs. off-normal). Cathode potential data was produced through a series of experiments in lab-scale. Surrogate materials, which have close standard reduction potentials leading to feasible environment for codeposition, were employed in the experiments. In safeguards perspective, if the co-deposition signal can be distinguished when a difference of reduction potential between elements is small, it is expected to clearly distinguish the co-deposition for elements having a larger difference in reduction potential such as uranium and plutonium. To support this statement, two types of binary systems were employed using lanthanum - cerium (La-Ce), or lanthanum - gadolinium (La-Gd). The composition of deposition was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-OES) to classify input data. Before learning, data preprocessing was conducted in terms of complicity and quantity to prepare appropriate data for learning. Both neural network (NN) and recurrent neural network (RNN) were used in learning.

2. Methods

2.1 Cathode Potential

The cathode potential is intuitive data providing a simple approach to detect co-deposition of Pu [1-2]. Cathode potential is an electric single recorded while metal ions are reduced to metal on a cathode. The cathode potential is defined as follows by the Nernst equation:

$$\mathrm{E} = E^{0`} + \frac{RT}{nF}\ln(C_{\mathrm{ox}}) \quad (1)$$

where E is the electrode potential [V], E_0` is the standard apparent reduction potential [V], R is the ideal gas constant [8.314 J/mol·K], T is the absolute temperature [K], n is the number of electrons involved in the oxidation-reduction reaction, F is the Faraday's constant [96,485 C/mol], and C_{ox} is the concentration of the reactant [mol/cm^3].

As shown in the equation 1, the number of electrons (n) and the standard apparent reduction potential (E_0`) are properties of an element, and the ideal gas constant (R) and the Faraday's constant (F) are constants. Therefore, the electrode potential is a function of the temperature (T) and the concentration of reactant (C_{ox}). Theoretically, since a standard reduction potential is a thermodynamic property of each element differing by element to element, it is possible to infer whether the process operation is normal state (pure uranium deposition) or off-normal state (co-deposition) by examining a flow of cathode potential. During pure uranium deposition, the potential is maintained constantly. Therefore, if other active elements start to deposit, the potential will shift to more negative value.

However, in actual, the electrode potential is a result of comprehensive and complex interactions of various elements in molten salt such as exchange current densities of elements which depend on their concentrations, limited current density affected by mass transfer of elements, and also continuing change of concentration and cathode surface area complicate the signal [3].

2.2 Machine Learning

To effectively manage and utilize the massive amounts of data collected, the use of machine learning — an application of artificial intelligence (AI) — have dramatically increased. In machine learning, existing data are used to enable a computer to learn how to conduct a given task by means of statistical inference, without explicit programming. The advantages of machine learning are enhanced when variables are inter-related. Therefore, it seems machine learning can be a good approach to maximize the benefits of PM.

Neural network (NN) is a subcategory of machine learning method. NN simulates the neural cell and its neural network in real life. A neuron (or a node) is connected to the other neurons via an input/output link ("network"). Recurrent neural network (RNN) is a type of NN that uses sequential data as input. RNN is an algorithm that is applied where previous data affects the current data, and it can be used for predictions such as time series forecasting. The RNN can be considered as a graph of a "circular NN cell" that performs the same operation on each sequential element and can solve various kinds of problems by rearranging the ways cell graphs are assembled.

NN have been applied in nuclear safeguards since 1990's [4-5]. As computing techniques surged, a number of research have been conducted as efforts to apply machine learning techniques to nuclear industry such as safety, security, and safeguards including PM in order to improve robustness of a process. Among them, some research proposed the application of machine learning to enhance pyroprocessing safeguards-ability [5].

3. Experiment

Electrodeposition experiments were conducted in a binary system with various cell compositions to produce cathode potential data. In the experiment, both a singular element deposition (normal operation) and two elements codeposition (off-normal operation) were produced. Three lanthanides (Lns); La, Ce, and Gd, were used as surrogate materials based on their close standard reduction potentials each other. It allows favorable environment for codeposition. Due to the similar behavior of Lns with that of actinides (Ans), commonly, Lns are used as surrogate materials of Ans. Since the order of reduction potential is $E_{Gd} > E_{Ce} > E_{La}$, Gd or Ce (higher reduction potential) was used as the surrogate material for U, and La was used instead of Pu to simulate co-deposition [3].

The composition of electrochemical cells were designed the same with [3] elsewhere for more detailed and general descriptions. Only a brief explanation of experiment cells design were provided here.

According to Nernst equation, the difference in equilibrium potentials is able to adjust by using the mole ratio of the cell components. Electrode potential differences were varied from 0.00 and 0.10 V for the Ce-La binary system and between 0.05 and 0.15 V for the Gd-La binary system. Each binary system used three experimental cells with 0.05 V interval. The experimental cells were named based on the Ce or Gd in the binary system and as their potential difference increase, the allocated number increase from 1 to 3. Considering that the electrolyte in an actual electrorefiner begins with approximately 10 wt% UCl_3, the experimental cells were also designed to contain approximately 10 wt% $GdCl_3$-$LaCl_3$ or $CeCl_3$-$LaCl_3$. An electrodeposition experiment was also conducted for a cell containing 10 wt% $LaCl_3$ to obtain pure singular deposition signal. The designed electrochemical cells are presented in Table I.

Table I. The composition of the experimental cells in the mass transfer study

ΔE [V]	$CeCl_3$-$LaCl_3$ Binary System		$GdCl_3$-$LaCl_3$ Binary System	
	Cell Name	X_{Ce}/X_{La}	Cell Name	X_{Gd}/X_{La}
0.00	Ce1	0.1	-	-
0.05	Ce2	1	Gd1	0.25
0.10	Ce3	10	Gd2	2.5
0.15	-	-	Gd3	25

The electrodeposition experiments were conducted as following conditions. Experiments were performed in a glove box under an inert atmosphere with less than 1 ppm of both oxygen and moisture. The operating temperature maintains as 773 K (±3 K) measured with a chromel-alumel thermocouple.

Three-electrode system was employed for experiments using a working electrode, a counter electrode, and a reference electrode. The working electrode was a molybdenum wire with a 1 mm diameter. The immersed length of the working electrode was 2 (± 0.2) cm. The counter electrode was an Ln metal (Ln = La, Ce, or Gd, rod located in a stainless steel basket. Electrodes were sheathed in alumina tubes to prevent electrical conduction between materials. A Ag/AgCl reference electrode was prepared using 1 wt% AgCl in a LiCl-KCl eutectic salt with a silver wire (0.5 mm diameter) contained in a thin mullite tube (4 mm inner diameter , 6 mm outer diameter). To prepare an electrolyte consisting of 59-41 mol% LiCl-KCl eutectic salt, LiCl and KCl were mixed in an alumina crucible and the mixture was pre-heated at 773 K for more than 3 hours to remove any moisture. After the cell was cooled down, it was re-heated with an addition of $LnCl_3$ to adjust the final molten salt concentrations in the cell. All reagents were purchased in Alfa Aesar with ACS grade/purity. A schematic of the electrochemical cell is shown in Fig. 1.

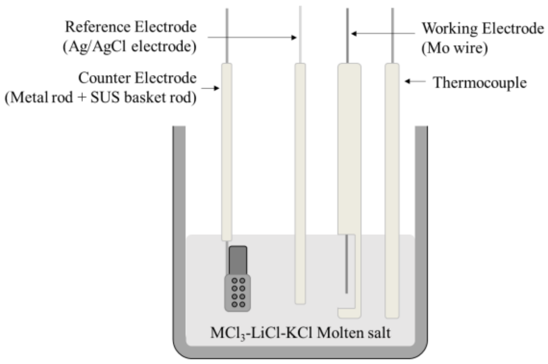

Fig. 1. Electrochemical cell design for the experiment

Cathode potential was recorded for 600 seconds with 100 hertz scale by supplying a constant electric current. To diversify the deposition ratio, the supplied current was varied from 100 to 500 mA in 50 mA intervals. Each experiment was repeated at least 3 times. Cathode sheathing alumina was designed to have a basket so that it can capture any fallen deposits to prevent loss in an electrodeposit sample as shown in Fig. 1. The electrodeposit experiments used a potentiostat/galvanostat (Biologic, SP-150) with EC-lab software.

After each experiment, the electrodeposits and the eutectic salts were sampled and analyzed for their quantities and associated compositions using ICP-OES (Agilent, Agilent ICP-OES 5110). The electrodeposit samples were prepared by cutting the bottom of the Mo electrode including deposition. The segment was weighed and then dissolved in 20 ml of 10 % HNO_3. Since 10% HNO_3 cannot dissolve Mo metal, the Mo was collected from the acid solution and weighed in order to subtract its weight from the initial sample weight. The salt sample was weighed and then dissolved in 20 ml of 2% HNO_3. Further dilution was conducted to ensure the sample concentration was between 0.1 to 10 ppm. The final acidity of ICP-OES samples was maintained at 2% HNO_3. The salt analysis results were used to remove effect of attached salt in codeposition ratio. The amount of attached salt was calculated based on the measured potassium amount and the Ln amount resulted from not deposition but salt were proportionately subtracted.

4. Experiment Results and Data Preparation

4.1 Experimental results

A range of codeposition ratio in each experimental cells are presented in Table II. The co-deposits had weak attachment with Mo electrode, resulting in a loss of electrodeposit samples. This phenomenon was more serious in Gd-La binary cell than Ce-La binary cell. The ranges of codeposition ratio were the result of ICP-OES data not the result of discrete experiment. To indicate the data number difference, the number of actually analyzed samples by ICP-OES were presented in parentheses.

As expected, when an electrode potential difference is small, two elements deposited together easily. Ce 1 cell where the electrode potential difference is zero, La, which has a more negative electrode potential than Ce, deposited more than Ce.

Table II. The results of electrodeposition experiment

	Normal deposition	The number of data		Off-normal deposition	The number of data
La	0%	27 (27)	Gd 2	10~25 %	27 (14)
Gd 3	~1 %	28 (16)	Ce 2	40~60%	29 (8)
Ce 3	2~5%	27 (5)	Gd 1	100~300 %	32 (24)
			Ce 1	300~1200%	30 (18)

*parentheses: the number of actually analyzed samples by ICP-OES

4.2 Data preparation for learning

The obtained data was labeled as normal (singular deposition) or off-normal (codeposition). To balance the number of normal and off-normal data, when codeposition ratio is less than 5%, the data is classified as normal data as Table II presented.

The advantages of machine learning can be maximized when appropriate data is available in terms of complicity and quantity. About 200 cathode potentials were collected for data. Although one cathode potential data consists of 60,000 points (100 hertz for 600 seconds), since it is 1-dimensional (1 column) time-series data, the simplicity of the data was not suitable for machine to find features in data. To overcome a lack of data (complicity and quantity), the data is preprocessed before use for learning.

The complicity was compensated by employing another data, a change of cathodic surface area. One factor influencing electrodeposition is current density. When a constant current is applied, the cathodic current density gradually increases due to the cathode growth, which can be estimated by Cottrell equation [3]. By predicting the effect of surface area growth (adding the second column), other unknown features may be easily found.

The quantity was augmented by slicing the 10 minutes data as 1 minute data (6,000 data points). However, initial section (until 5999th point) wasn't used to eliminate an unsteady state in the initial stage. This is a common feature in the cathode potential. As all of the reactants surrounding the electrode are consumed by the instantaneous reaction (electrodeposition), rapid potential drop occurs. The electrode potential is recovered as the concentration gradient becomes similar over time through diffusion and as cathodic surface area grows.

These two preprocessing methods are reasonable considering the characteristic of the data and necessary to make learning feasible.

5. Result and Discussion

Both NN and RNN were applied to classify the data as normal and off-normal. Softmax function is used as a classifier and Cross entropy error is used as loss function. To optimize the learning, various factors such as the number of layers and nodes, learning batch size, epoch, learning rate are differed. Several optimizers were also tried and optimizer Adam and AMSGrad showed meaningful results.

Fig. 2 presents the learning results of using two-layer RNN with optimizer AMSGrad, which showed the best learning result. Since the cathode potential is not high dimension data, deeper structure (increasing the number of layers) hindered learning and resulted in decrease of accuracy. The classification accuracy reached about 80%. However, as fig. 2 showed, variance between train and validation for both loss and accuracy were maintained and not stabilized. This is because the model cannot find optimized parameters.

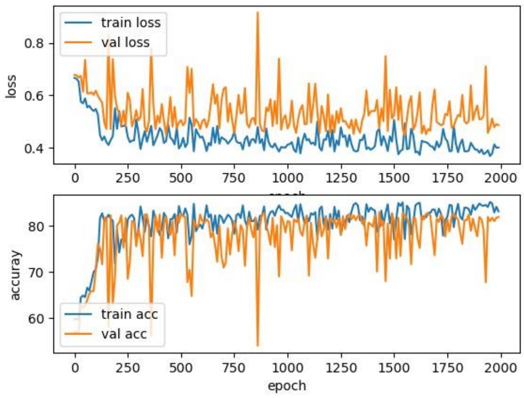

Fig. 2. Result of learning using two-layer RNN (32 hidden states, optimizer: AMSGrad, batch size: 16, learning rate: 0.0001)

As mentioned before, the electrode potential is a result of comprehensive and complex interactions of various factors related with electrolyte and electrode. In this study, the limited number of experiments and simplicity of data (two column data: cathode potential and estimated cathodic surface area) disrupted to maximize the benefits of machine learning. However, in actual field, there will be more available data such as temperature and concentration-related indicators. Availability of various data is achievable by designing facility considering such approach in advance which known as safeguards by design.

As more signals become available, the reliability of PM using ML approach can increase. Complexity of data allows profound ML techniques such as deep learning, and reducing the possibility of spoofing signals.

6. Conclusion and Future work

In this study, feasibility of ML based PM was examined to employ it as an approach for enhancing pyroprocessing safeguards-ability. Cathode potential recorded during electrodeposition in electrorefining process was suggested as a test case.

Cathode potentials were obtained experimentally and the obtained data was labeled as normal and off-normal data based on the results of ICP-OES analyses. Data preprocessing was conducted to overcome a lack of data and its simplicity. NN and RNN were employed in machine learning. To optimized the learning, various variables were tested. As a results, two-layer RNN with optimizer AMSGrad showed the best result, presenting more than 80% of classification accuracy.

To advance current result, further research is planned. Firstly, the assumption – clearer distinguishment of codeposition for elements having a larger difference in reduction potential – will be tested by dividing the validation dataset. Secondly, considering special characteristics of safeguards, which discourages the necessary of off-normal operation to acquire off-normal data, a classification model using only normal data (machine learning without negative data) will be developed.

If safeguards-ability can be improved with this method, this method would be applied not only to electrorefining, but also to overall facility including other unit processes.

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