



Application of normal pulse voltammetry to on-line monitoring of actinide concentrations in molten salt electrolyte

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Abstract

The applicability of electroanalytical methods – square wave voltammetry (SWV) and normal pulse voltammetry (NPV) – to on-line monitoring of actinide concentrations in molten chlorides was investigated for use in pyrometallurgical processes. For SWV curves for plutonium, the concentration dependence of the peak current was not linear at high concentration. However, the limiting currents for uranium and plutonium determined by NPV were proportional to their concentrations up to about 1.7 wt%. The fission product elements do not seem to affect the accuracy in determination of actinide concentrations because the limiting currents for uranium and plutonium were not influenced by the addition of gadolinium. It was found to be difficult to determine neptunium concentration in the presence of plutonium due to the overlap of the output current waves. From those results, NPV was considered more promising although the optimization of applied potential waveform is necessary for use at higher concentrations. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The metallic fuel cycle has been proposed as an innovative nuclear fuel cycle technology which has excellent economic, safety, and non-proliferation features [1,2]. In this cycle, the spent fuel from a metal-fueled fast reactor is recycled with pyrometallurgical process.

The main step in the pyrometallurgical process is molten salt electrorefining [3], where the most part of the actinide elements are recovered and decontaminated from the fission products. Fig. 1 shows the schematic flow for normal operation of this electrorefining step. The spent fuel is immersed in molten chloride electrolyte and the actinide elements in the spent fuel are anodically dissolved. The chemically active fission products such as alkali, alkaline earth, and rare earth metals exchange

with the actinide chlorides in the electrolyte and accumulate in the molten salt in the form of chlorides. Uranium is selectively reduced and collected at the solid cathode due to its higher standard electrode potential than those of other actinide elements [4,5]. Plutonium and minor actinide elements (neptunium, americium, and curium) are recovered into the liquid cadmium cathode making use of their low activity coefficients in liquid cadmium [4–8].

The concentration of plutonium in the electrolyte increases as uranium is selectively collected to the solid cathode. In reverse, the concentration of uranium increases when plutonium is recovered into the liquid cadmium cathode. Calculation with the electrorefining simulation code [9] showed that the concentration ratio between plutonium and uranium in the electrolyte widely changes during the electrorefiner operation. Such a change of the electrolyte composition has to be monitored quickly to obtain information for switching the two types of cathodes.

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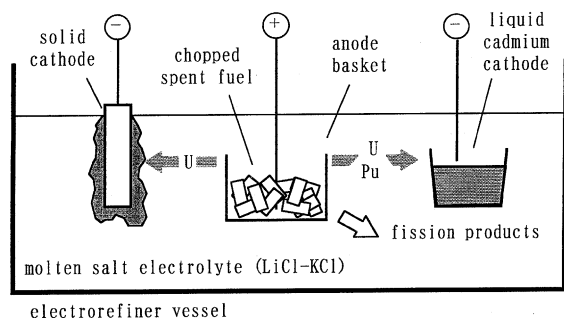


Fig. 1. Schematic flow of routine operation of the electrorefining step.

After many batches of fuel are processed, the molten salt electrolyte which contains a large amount of fission products would be sent to the waste treatment process. Before the waste treatment process, it is planned to collect the actinides in the electrolyte by electroreduction with cadmium–lithium anode [10]. In this step, the concentration of actinides is lowered by dissolution of lithium at the anode and simultaneous deposition of the actinides at the cathode. The concentration of actinides should be measured frequently in this step in order to monitor the progress of the electroreduction.

As described above, an on-line monitoring method for prompt determination of the actinide concentrations in the molten salt electrolyte is required for practically quick and smooth process control. Electroanalytical methods are considered suitable for this purpose because they are rapid in situ measurement techniques which produce no sample waste and save cost of analytical load. Furthermore, sufficient basic data useful for qualitative analysis, such as standard electrode potentials, are available for most of the elements in the system. In Argonne National Laboratory, the square wave voltammetry (SWV) was examined as a process monitoring method for the pyrometallurgical treatment [11]. In that study, SWV was carried out in molten chlorides containing zirconium, uranium, plutonium, and dysprosium. However, little discussion was made about the appropriate potential waveform and concentration dependence, especially the relation between the output current and the actual concentration in the practically high concentration region.

In this report, the applicability of two electroanalytical techniques was studied as the on-line monitoring method for the actinide concentrations in molten chloride electrolyte. One is SWV, and another is the normal pulse voltammetry (NPV). The concentration dependence and performance of these methods in a multi-component system were specifically studied. The standard electrode potentials of the elements fed from the metal-fueled fast reactor to the pyrometallurgical reprocessing are shown in Table 1. In the major steps in

Table 1
Standard redox potentials of the elements fed to pyrometallurgical reprocessing

Element	E^0 (V vs. Cl_2/Cl^-)
Te	-0.316
Pd	-0.430
Rh	-0.447
I	-0.471
Ru	-0.518
Ag	-0.853
Mo	-0.854
Eu	-0.860
Sb	-0.886
Ni	-1.011
Co	-1.207
Sn	-1.298
Fe	-1.388
Se	-1.463
Nb	-1.472
Cd	-1.532
Cr	-1.641
V	-1.749
Sm	-2.035
Mn	-2.065
Zr	-2.186
U	-2.500
Np	-2.697
Mg	-2.796
Pu	-2.803
Am	-2.865
Gd	-3.027
Nd	-3.078
Pr	-3.078
Ce	-3.094
Y	-3.106
La	-3.141
Na	-3.356

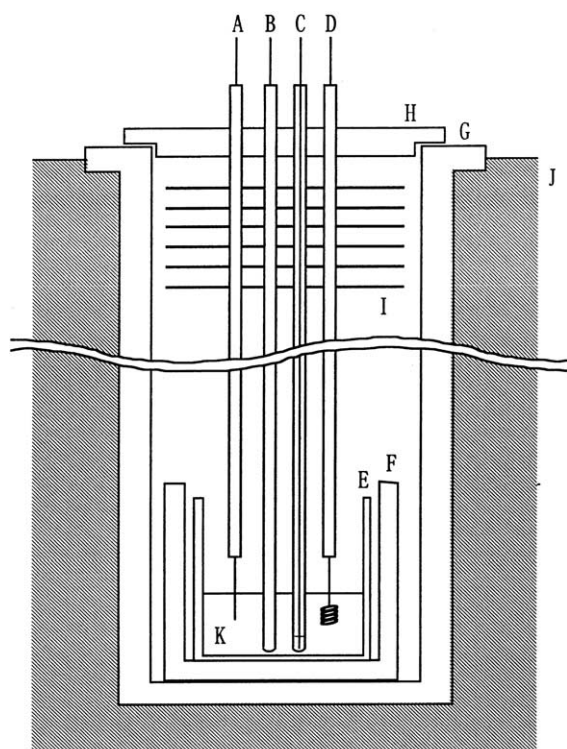
the pyrometallurgical process, the elements which have lower standard electrode potentials than that of zirconium exist in the molten salt electrolyte in the form of chlorides, and the other elements remain at the anode as metals. From the viewpoint of process control, usually concentrations of uranium and plutonium need to be separately determined because the expected amount of the other actinides, such as neptunium or americium, in the spent fuel is much smaller than those of uranium and plutonium.

2. Experiment

2.1. Apparatus

All the experiments were carried out in a high purity argon atmosphere glove box. Both oxygen and moisture levels in the atmosphere were kept lower than 2 ppm

during the tests. Fig. 2 is the schematic view of the experimental apparatus. About 50 g of lithium chloride–potassium chloride (LiCl–KCl) eutectic mixture was put in a high purity (>99.5%) alumina crucible. It was placed in the magnesia secondary crucible and the stainless steel outer crucible. These crucibles were heated with the electric furnace and the temperature of the molten salt was kept to 773 ± 1 K by a proportional-integral-differential (PID) controller. The working electrode was made of tungsten wire of 1 mm diameter. About 10 mm of the lower end of the wire was immersed in the molten salt. The surface area of the working electrode could not be estimated from the immersed length because of an expected large error due to the wetting of the electrode surface by the molten salt. The tantalum wire of 1 mm diameter was coiled and used as the counter electrode. A



- A : tungsten wire working electrode
- B : thermocouple
- C : Ag/AgCl reference electrode
- D : tantalum wire coil counter electrode
- E : alumina crucible
- F : magnesia secondary crucible
- G : stainless steel outer vessel
- H : flange
- I : heat shield
- J : electric furnace
- K : molten LiCl–KCl eutectic mixture

Fig. 2. Schematic view of the experimental apparatus.

silver–silver chloride (1 wt% AgCl in LiCl–KCl) electrode contained in a thin Pyrex glass tube was used as reference electrode. The potential of the reference electrode was very stable at 773 K throughout the measurements.

2.2. Chemicals

LiCl–KCl and rare earth chlorides (GdCl_3 and CeCl_3) were purchased from Anderson Physical Laboratory. Because the purity of these chlorides was no less than 99.99% and their moisture content was negligibly low, they were used without additional purification procedure. The concentration of uranium and plutonium in the molten salt was adjusted by the addition of LiCl–KCl–23 wt% UCl_3 and LiCl–KCl–20 wt% PuCl_3 which were prepared prior to these measurements [12]. The LiCl–KCl– UCl_3 mixture was prepared by the reaction of uranium metal with cadmium chloride in LiCl–KCl. The LiCl–KCl– PuCl_3 was prepared by the following three steps: (a) carbothermic reduction of PuO_2 to produce PuN [13], (b) formation of PuPt_3 by the reaction of PuN with platinum metal, and (c) exchange reaction between PuPt_3 and cadmium chloride in LiCl–KCl/liquid cadmium system. Metals for the electrode material (tungsten, tantalum and silver) were also of high purity (>99.95%). They were polished and cleaned with dilute nitric acid before use.

2.3. Analytical procedures

EG&G Princeton Applied Research potentiogalvanostat Model 273A and EG & G270/250 Research Electrochemistry Software were used for the electroanalytical measurement. The concentration of the actinide elements in the molten salt was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) of the samples.

3. Results and discussion

3.1. Result from SWV measurements

3.1.1. Potential waveform for the SWV measurement

Before the experiments with actinide elements, the effect of the half height and the frequency of the square wave on the SWV result were examined with cerium [14]. The peak current for cerium reduction increased approximately in proportion to the half height of the square wave except for the largest case at 100 mV (Fig. 3). The peak was also broadened to the positive direction with the increase of the square wave half height. Sharp peaks are preferable from the viewpoint of peak separation in a multi-component system and the peak height at the small square wave half height shown in

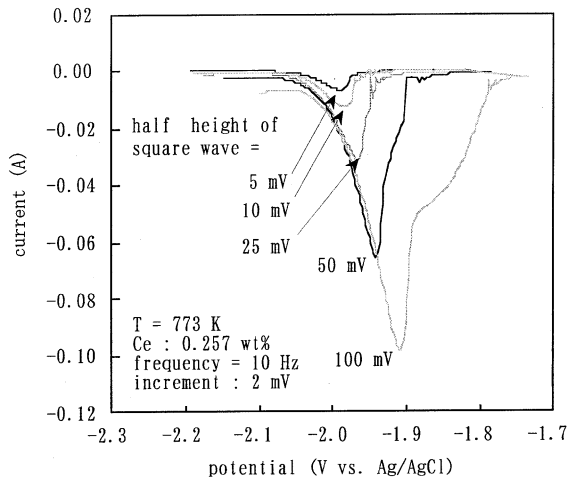


Fig. 3. Effect of half height of square waveform on results of SWV in LiCl–KCl–CeCl₃.

Fig. 3 was considered large enough for detection and the succeeding data processing. Then a square wave half height of 5–10 mV was selected for the SWV measurement in this study. The increase of the square wave frequency also brought growth in the current peak width to the negative direction as seen in Fig. 4. At low frequency, the sharp current peaks are observed which can be more easily separated from each other although the required time for measurement becomes longer. In this study, 5–10 Hz was adopted for the measurement with uranium and plutonium. The entire square wave parameters are tabulated in Fig. 5. When the potential is scanned from –1.0 to –2.2 V with a frequency of 5 Hz

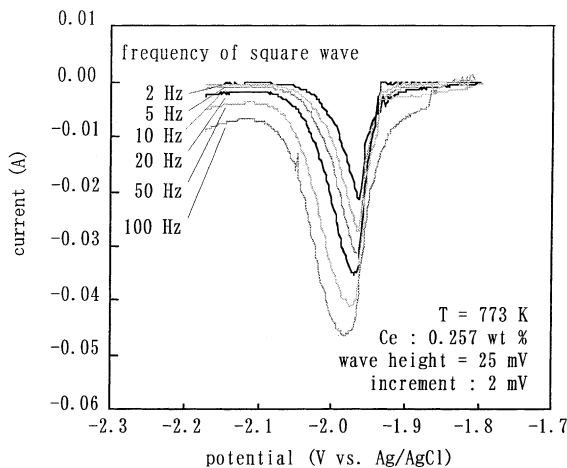


Fig. 4. Effect of frequency of square waveform on results of SWV in LiCl–KCl–CeCl₃.

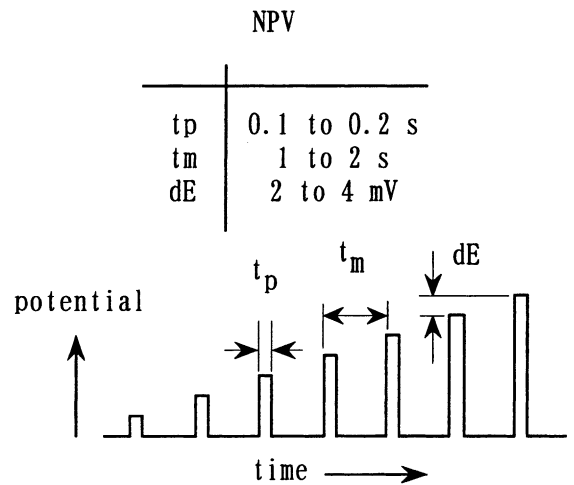
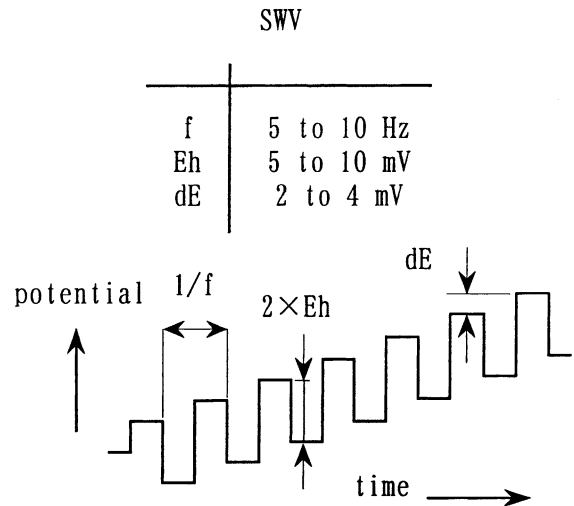


Fig. 5. Potential waveform parameters for SWV and NPV used in this study.

and a potential increment of 4 mV, the turnaround time required for one measurement becomes 60 s.

3.1.2. Applicability of SWV for on-line monitoring of actinide elements

Fig. 6 shows the result of SWV for LiCl–KCl–PuCl₃ in a relatively higher concentration range (0.14–3.35 wt%-Pu). Distinct and sharp current peaks by reduction of plutonium were observed at around –1.7 V in all cases. However, the height of the peak current did not show a linear relation to the actual concentration of plutonium over this concentration range as shown in Fig. 7. Below the deposition potential, the surface area of the working electrode is expected to be a little larger when reverse step current is measured than when forward step current is measured due to the deposition of

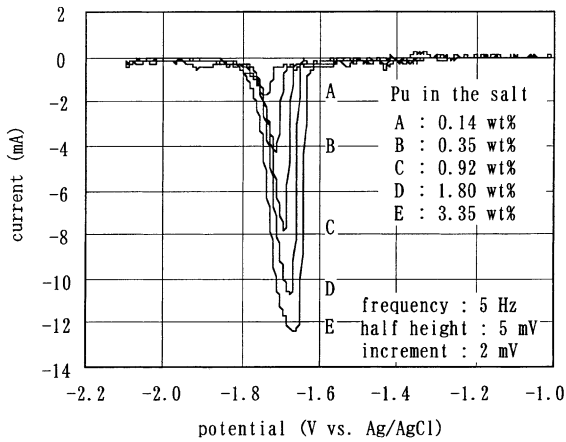


Fig. 6. SWV curves for LiCl-KCl-PuCl₃.

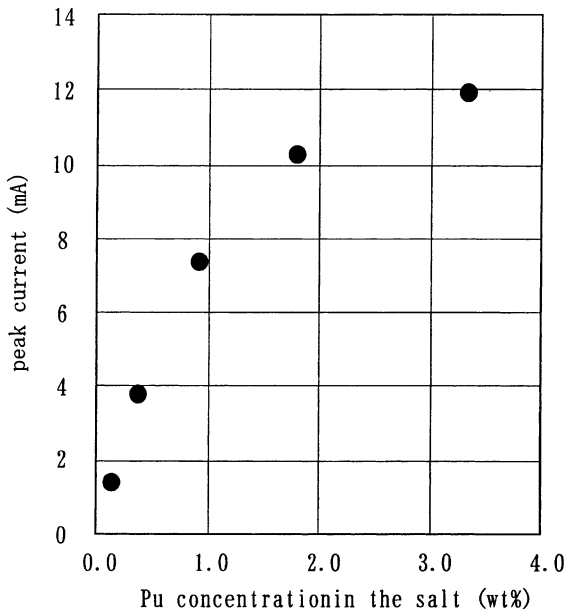


Fig. 7. Concentration dependence of peak height in SWV curves for LiCl-KCl-PuCl₃.

plutonium metal. Because SWV output is obtained by subtracting the reverse current from forward current in each step, the final output value would be smaller than expected especially at higher concentration. This is considered to be the reason for the non-linearity of the peak current to the plutonium concentration.

At concentration range of plutonium lower than 0.1 wt%, the linearity of the peak current to the concentration was better as shown in Fig. 8. In this figure, extrapolation of the linear trend to zero current crosses the x-axis at about 0.02 wt%. This concentration is considered to be an inevitable detection limit of NPV

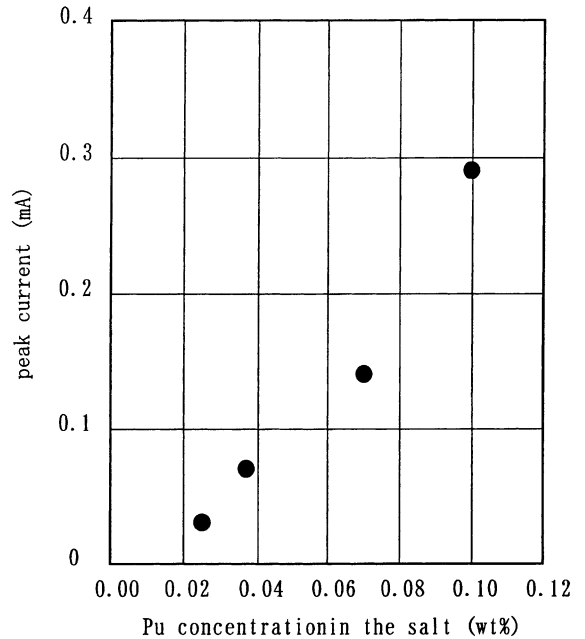


Fig. 8. Concentration dependence of peak height in SWV curves for LiCl-KCl-PuCl₃ (at lower Pu concentration).

method on the conditions of this study. This limit is, however, much smaller than expected concentration range to be monitored for the process control. Experimental results in LiCl-KCl-UCl₃-PuCl₃ showed that the peaks for reduction of uranium and plutonium were clearly separated because there was very little overlap between the output current waves of those elements.

From the above results, it was considered to be difficult to apply SWV to the process where the concentration of actinides in the molten salt electrolyte is higher than a few wt% such as the electrorefining step in normal operation [10]. However, SWV has many advantages when it is applied at very low concentrations of less than 0.1 wt% because of its high sensitivity and easy separation among the current peaks. It is still a candidate as an on-line monitoring method in the electroreduction step and the waste treatment process, where the concentrations of actinides are decreased to a very low level.

3.2. Result from NPV measurement

3.2.1. Potential waveform for the NPV measurement

NPV with various t_m and t_p was also carried out in LiCl-KCl-CeCl₃ [14] before the actinide elements were used in order to find out the potential waveform adequate for this method, where t_p is the pulse width and t_m is the period between the two succeeding pulses. Fig. 9 shows a few examples. In this case, t_p was fixed to 100

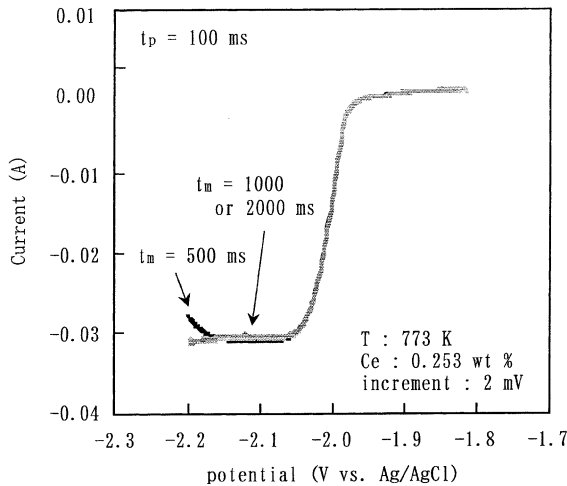


Fig. 9. Effect of t_m on results of NPV in LiCl–KCl–CeCl₃.

ms and t_m was varied. With longer t_m , the limiting current for cerium reduction was clearly defined. On the other hand, the cerium reduction current was found to decrease to some extent after the current once reached the maximum value when t_m was shorter than about 10 times t_p . It indicates that t_m of about 10 times t_p , at least, is needed for restoration of the concentration profile around the working electrode to the initial state. At a constant t_m , higher sensitivity can be theoretically expected with shorter t_p . In the preliminary tests with cerium, the reduction current of cerium was approximately proportional to square root of t_p in the range of 50–200 ms [14]. In the potential step experiment with uranium and plutonium, however, a significant delay was found in the reduction current rise until about 90 ms after the start of measurement (Fig. 10). In this figure, theoretical value was calculated on assumption that the reduction of uranium and plutonium are both reversible and diffusion-controlled. The configuration of the electrochemical cell and structure of the electrodes were practically same in the tests with cerium and actinides. It is unlikely that the mechanism and the kinetics of reduction significantly differ between the cases for lanthanides and actinides in this system. Then the delay in the reduction current was considered attributed to over 10 m of wiring from the electrodes through the plutonium glove box wall to the potentiostat (in contrast with the case with cerium where length of the wiring was less than 3 m), and it was thought to be inevitable in the present circumstances. With those results, the parameters for NPV measurement in this study were determined as shown in Fig. 5. When the potential is scanned from -1.0 to -2.2 V with t_m of 2000 ms, t_p of 100 ms and potential increment of 4 mV, the turnaround time required for one measurement becomes 600 s.

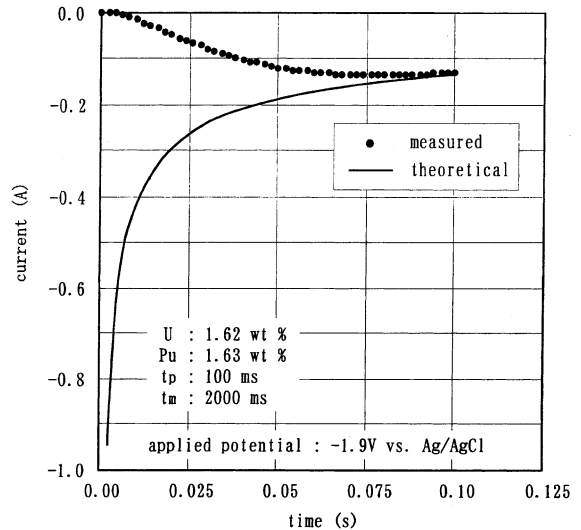


Fig. 10. Result of potential step experiment in LiCl–KCl–UCl₃–PuCl₃ compared with theoretical solution.

3.2.2. Determination of uranium and plutonium

Fig. 11 shows the result of NPV measurement in molten LiCl–KCl at various uranium and plutonium concentrations. It was found that the reduction current rises in two steps: one is around -1.4 V by reduction of uranium and the another around -1.7 V by reduction of plutonium. The reduction current by uranium and plutonium increased with the increase of concentrations of these elements in the electrolyte.

In order to determine the concentrations of uranium and plutonium from the NPV data, the contribution of the reduction of each element to the output current should be separately determined. For this purpose, the current output of NPV was differentiated with respect to

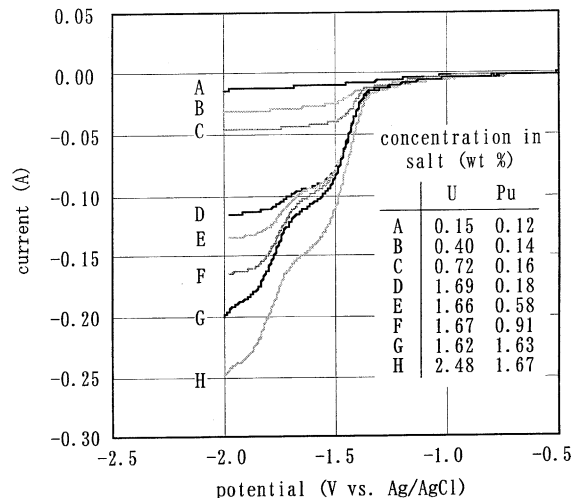


Fig. 11. NPV curves for LiCl–KCl–UCl₃–PuCl₃.

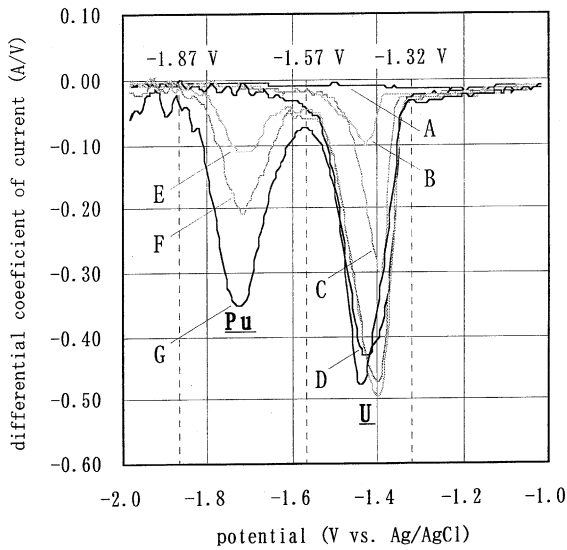


Fig. 12. Differentiated NPV curves for LiCl-KCl-UCl₃-PuCl₃.

the working electrode potential as shown in Fig. 12. The increase of reduction current was transformed to clear peaks by this treatment. Although the accurate criteria for the determination of tails of those peaks have not been fixed at present, the width of the peaks corresponding to the reduction of uranium and plutonium was tentatively determined to be -1.32 to -1.57 V and -1.57 to -1.87 V, respectively, as seen in Fig. 12. The increase of output current by reduction of each element was defined as the area of the corresponding peak in Fig. 12. A plot of the reduction currents defined in this way against the actual concentration determined by ICP-AES is shown in Fig. 13. The excellent linearity in this plot demonstrates the applicability of NPV to on-line monitoring in the pyrometallurgical process. There is one point for plutonium that deviates from the linear relationship. This is the case where the concentration of coexisting uranium in the molten salt was the highest (2.48 wt%) in this study. Under this condition, it is expected from the results of uranium electrorefining study [3] that reduced uranium forms dendritic deposit which increases the effective surface area of the working electrode. This is considered to occur when the reduction current for plutonium at this point was a little larger than that expected from the linearity among the other data. This problem would be avoided by optimization of the applied potential waveform, i.e. reduction of the pulse width t_p , although it was not demonstrated in this study due to the long wiring as described in Section 3.1.

3.2.3. Effect of coexisting fission products

Fig. 14 shows the change of differentiated NPV current measured in molten LiCl-KCl containing uranium, plutonium, and gadolinium. The concentration of gad-

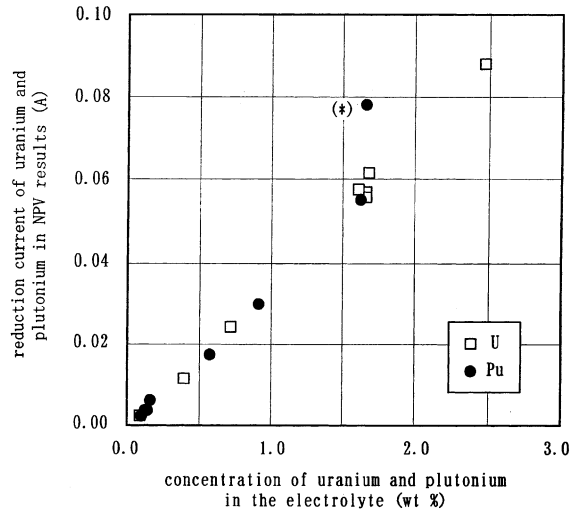


Fig. 13. Concentration dependence of reduction current in NPV curves for LiCl-KCl-UCl₃-PuCl₃.

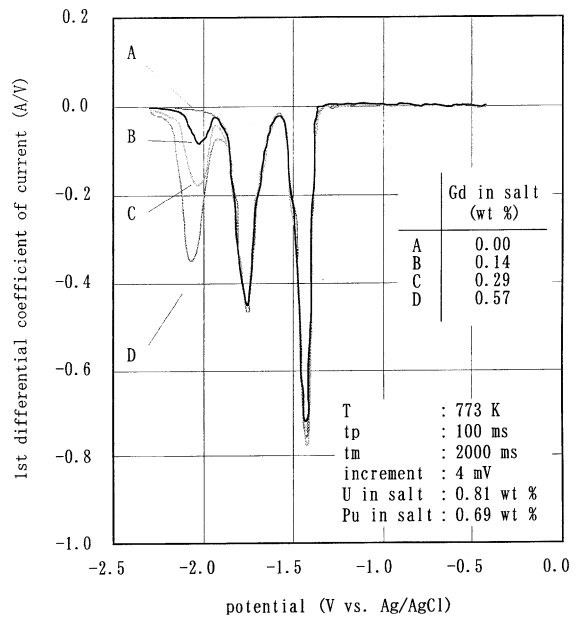


Fig. 14. Differentiated NPV curves for LiCl-KCl-UCl₃-PuCl₃-GdCl₃.

olinium in the molten salt was calculated from the amount of its chloride added to the electrolyte because the error of this method had been found to be very small in our past studies. The peaks of these elements in the differentiated NPV data were easily separated each other. The area of the peaks corresponding to the reduction current of uranium and plutonium were not influenced by the addition of gadolinium. Since the standard electrode potentials of the other fission product

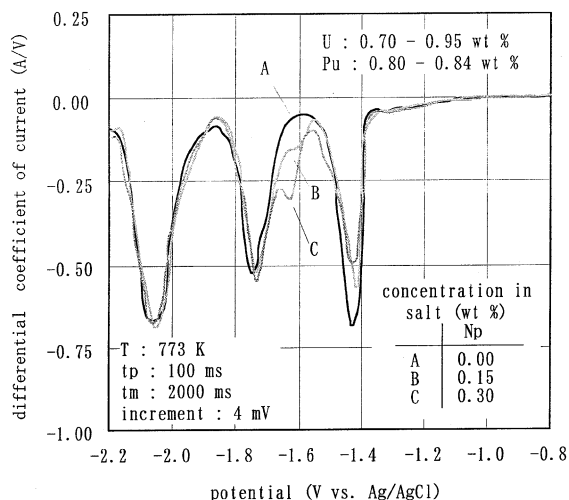


Fig. 15. Differentiated NPV curves for LiCl-KCl-UCl₃-PuCl₃-GdCl₃-NpCl₃.

elements in the electrolyte are lower than that of gadolinium (Table 1), it is expected that the concentrations of uranium and plutonium can be determined by NPV without any interference by fission products even in the practical multi-component systems.

3.2.4. Determination of minor actinide elements

In order to discuss the determination of minor actinides, NPV was carried out in molten LiCl-KCl containing uranium, plutonium, gadolinium, and neptunium. Fig. 15 shows the differentiated NPV results. A slight increase by the reduction of neptunium can be found between the peaks corresponding to the reduction of uranium and plutonium. However, the reduction current of neptunium could not be determined exactly due to the overlap with the plutonium peak. Because the amount of neptunium in the molten salt electrolyte is thought to be much smaller than that of plutonium in the normal operation of the electrorefiner, determination of neptunium by NPV seems to be difficult. Determination of americium concentration by NPV is expected to be more difficult because the standard electrode potential of americium is closer to that of plutonium than in the case of neptunium. It is possible, however, that NPV or SWV is applied to determine the minor actinides in cases where the concentrations of all the actinide elements are very low, such as in the electroreduction step or in the waste treatment process.

4. Conclusion

The applicability of two electroanalytical methods – SWV and NPV – to on-line monitoring of actinide

concentrations in molten lithium chloride–potassium chloride eutectic mixture was investigated for use in the pyrometallurgical processes. The potential waveforms for both methods were fixed based on the results of the preliminary tests using rare earth elements. For SWV of plutonium, the concentration dependence of the peak current was not linear at relatively high concentration, although SWV showed the advantage in high sensitivity and easy separation among the peaks in multi-component systems. The reduction currents for uranium and plutonium determined from the differentiated NPV data were proportional to their concentrations up to about 1.7 wt%. The fission product elements do not seem to affect the determined concentrations of uranium and plutonium because the reduction currents for these elements were not influenced by the addition of gadolinium which has the nearest standard electrode potential to those of the actinides among the fission product elements. It was found to be difficult to determine neptunium in the presence of plutonium due to the overlap of the output current waves. From those results, NPV was considered to be more promising for on-line monitoring in molten salt although the optimization of applied potential waveform is necessary for use at the higher concentrations expected in the normal operation of the electrorefiner in the pyrometallurgical reprocessing.

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