

MAGNESIUM DECLADDING OF URANIUM BY MOLTEN SALT ELECTROREFINING

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ABSTRACT

Recovery and potential recycle of irradiated metallic uranium fuel rods often requires removal of a protective cladding material such as magnesium, zirconium or aluminum. The majority of this cladding may often be stripped mechanically, It may also be worth removing any residual layers whilst minimizing the loss of uranium in order to reduce the generation of radioactively contaminated waste. In this study, magnesium is used as an example of a cladding material that is chemically more reactive than uranium. Molten salt electrorefining has been studied as a possible technique for surface removal of magnesium since it forms a more stable chloride than uranium under standard conditions. A low temperature LiCl-KCl electrolyte has been used for electrorefining with 5 mol. %. MgCl_2 addition. Stainless steel cathodes have been used. Separate U and Mg rods were electrically connected for this study. Process variables of cathodic current density, temperature and anode (U/Mg rods) compositions have been studied to minimize the cathodic transport of uranium during magnesium electrorefining.

In a related investigation, purity of cathodic deposit during magnesium electrorefining has also been optimized as a function of magnesium chloride content in the process salt for a fixed level of uranium chloride. For this part of the study, depleted uranium was clad with magnesium. The exposed uranium surface area gradually changed as electrorefining progressed. ICP-MS has been used to measure the residual uranium and magnesium contents in the cathodic deposit and in the salt. The study has determined the critical current densities for electrorefining. The temperature was found to have little effect on the process within the range studied.

INTRODUCTION

Molten salt electrometallurgy is the primary technique used for producing and refining reactive metals, such as aluminum, magnesium, lithium, beryllium, etc. The oxides and other compounds of these metals are thermodynamically too stable to allow reduction by carbon, hydrogen or other metals. Aqueous electrochemistry is not viable due to lower discharge potentials of these reactive metals compared with hydrogen gas. Thus molten salt electrometallurgy is used where the reactive metal compounds are either melted (MgCl_2) or dissolved in a proper stable electrolyte (alumina in cryolite) and the metal is electrowon. Molten salts also provide a suitable medium for separation of products when metallothermic reduction is used for producing reactive metals, such as uranium, lanthanides and other actinides. Mixtures of low melting alkali halide salts are useful media for electrorefining from an impure reactive metal anode. Typical considerations in molten salt electrorefining are melting points of the anode, the metallic cathodic product and the electrolyte, electrical conductivities and the densities of the salt and products as well as the thermodynamic stability of the salt with respect to the metal compounds. In addition, material considerations are important towards the selection of the cell container material and the electrodes.

Laidler (1) has developed a pyrochemical method for the separation of fission products from the actinide elements present in spent fuel and for further separation of pure uranium from the transuranic elements. This pyroprocess utilizes elevated-temperature to prepare spent fuel for fission product separation by molten salt electrorefining that provides efficient (>99.9%) separation of transuranics. The resultant waste forms from the pyroprocess are stable and highly leach-resistant.

Gay et al. (2) have described a pyrometallurgical process for recycling spent metal fuels from the Integral Fast Reactor (IFR) that involves electrorefining spent fuel in a molten salt electrolyte (LiCl-KCl-UCl_3) at 500 °C. The total heavy metal chloride concentration in the salt was about 2 mol %. The heavy metal concentration in the salt was reduced before removing the fission products from the salt. The operation used a lithium-cadmium alloy anode, a solid mandrel cathode with a ceramic catch crucible below to collect heavy metal that falls off it, and a liquid cadmium cathode. Good separation was achieved while removing uranium and rare earths from the salt. The uranium concentration in the salt was reduced to 0.05 ppm after uranium and rare earths were transferred from the salt to a solid mandrel cathode with a catch crucible. Rare earth concentrations in the salt were reduced to less than 0.01 wt % in these operations.

Burris et al. (3) have described an electrorefining process employing a molten salt electrolyte and a molten cadmium anode for the separation of uranium and transuranics from fission products and cladding material in discharged IFR driver fuel. The use of a liquid cadmium anode, which is the unique feature of the process, permits selective dissolution of the fuel from the cladding and prevents electrolytic corrosion of the steel container and contamination of the product by noble metal fission products.

Kobayashi et al.(4) have performed molten salt electrorefining experiments using a liquid metal anode made of cadmium-lithium alloy to recover uranium to a solid cathode from the spent molten salt. The concentration of U^{3+} in the molten salt effectively decreased from 1.38 wt% to less than 0.01 wt%. However, it was revealed that about 10 to 40% of uranium was not recovered by the solid cathode. This U deficit was caused by chemical reduction around the Cd-Li anode.

Koyama et al. (5) have studied molten salt electrorefining of uranium using solid iron cathode and liquid cadmium cathode. Design and operational conditions of the cathode were improved for obtaining much greater quantity of deposit, resulting in recovery of 723 g of dendritic uranium on a single solid cathode, and of 232 g of uranium in 2,344 g of a liquid cadmium cathode. The decontamination factors of fission products simulating elements from uranium were tentatively determined as $>2,000$ for deposition to solid cathode and as >7 for deposition to liquid cadmium cathode, respectively.

Willit et al. (6) have prepared a comprehensive review of the molten salt electrorefining of uranium over the last five decades.

The irradiated magnesium-clad uranium fuel rods require decladding for recovery and reuse of the reactive metals. Since the interaction at the interface is minimal, most of the magnesium can be removed by physical methods, such as machining. However, the complete separation of the metals requires chemical or electrochemical means. It is also desired that the separated metals be free from significant cross-contamination, i.e. separated magnesium should be free from uranium and vice-versa, to the best possible extent. For the purpose of the removal of last layers of magnesium from uranium, molten salt electrorefining has been used in this work. This concept was proposed to BNFL by the Chemical Technology Division of Argonne National Laboratory. A low-melting eutectic KCl-LiCl salt mixture has been used in this study. The selection of molten salt electrorefining is based on the thermodynamic stability sequence of uranium chloride (UCl_3), magnesium chloride (MgCl_2) and the salt mixture where the salt is the most stable. The comparative thermodynamic stability of uranium and magnesium chloride is primarily dependent on the activities of the metal ions in the salt and the concentration of metals in the anode. The standard free energies of formation at 1000 K temperature are -58 kcal and -51 kcal per g-atom of chlorine for MgCl_2 and UCl_3 , respectively. At unit metal and magnesium chloride activities, the theoretical uranium chloride activity is 4×10^{-5} . If the magnesium chloride activity in the salt is lower, the uranium chloride activity will be even smaller. Thus, magnesium can be preferentially ionized from the anode. However, if there is a relative increase in the uranium chloride concentration (activity) in the salt, uranium will preferentially deposit on the cathode due to the fact that uranium chloride is less stable (higher ΔG°) than magnesium chloride. This argument can be extended to other impurities in the anode and the salt. Metal impurities that form less stable chlorides than magnesium will be retained at the anode and impurity chlorides that are more stable than magnesium chloride will be retained in the salt.

This research program was undertaken to experimentally investigate and analyze two tasks:

- (1). The removal of residual surface-clad magnesium on uranium by selective electrorefining of magnesium using low-temperature molten salt electrolyte under low concentration of uranium chloride in the salt.
- (2). The electrorefining of magnesium with depleted uranium by molten salt electrolysis using cleaned anodes from (1) where the uranium chloride content of the salt was deliberately maintained at a high level of 2 mol. % to initiate uranium deposition.

The objectives of the research program were to identify optimum conditions for electrorefining process, including current density; electrolyte temperature and electrolyte composition. This paper presents the results from Task (1).

EXPERIMENTAL PROCEDURE

Facilities

The experiments were performed in a stainless-steel inert atmosphere glove-box equipped with a 1200°C resistance-heated furnace, atmospheric control units for nitrogen, moisture and oxygen, molten salt stirring facility and vacuum inter-lock for materials handling. During an experimental run, several samplings of electrolyte were taken for chemical analysis. The cathodic product was sampled at the end of an experiment. Chemical analysis was done by Inductively Coupled Plasma (ICP) Mass Spectrometry (MS) technique and X-ray diffraction analysis was used for the structure and compound analyses of the electrolyte. A gas chromatograph and moisture meter were also periodically used to monitor the atmosphere of the glove box. The sampling procedure for the salt comprised the collection of salt sample from approximately the same location of the bath using an alumina tube. The salt sample froze at the tip of the tube that was collected for analysis.

Electrorefining Apparatus

The apparatus, as shown in Figure 1, is constructed inside a temperature and atmosphere-controlled vertical furnace. The whole furnace and the apparatus within are mounted underneath an argon-protected glove box for safe handling of the materials, especially since magnesium and uranium need to be removed from the molten salt bath. The glove-box is attached to a Ni-train and a Dri-Train for nitrogen and moisture control, respectively. Additional atmospheric protection during the electrorefining process itself is provided by a continuous argon-flow through the molten salt chamber. To reduce concentration polarization, the molten salt electrolyte was stirred by the rotating anode. Both uranium and magnesium rods are bolted to this rotating anode and they both have the same electrical potential. The maximum length of the anode immersed in the salt bath is 200 mm. The cathode is made of stainless steel and has a circular shape to surround the rotating anode, so that at any angle of rotation the process condition is symmetrically maintained with uniform throwing power. It was also observed that almost all the metal deposition occurred on the inner side of the cathode facing the anode.

Electrolyte

To attain the lowest melting point of the salt bath, a eutectic composition of KCl-LiCl binary system has been referenced. This composition requires a mixture of 60 mol % KCl and 40 mol % LiCl. To accelerate initial ionization and to ensure continuous dissolution of magnesium from the anode, up to 5 mol % MgCl₂ was introduced to the salt bath as a replacement to LiCl. The electrorefining process was performed over a range of voltage from 0.1 to 0.25 V depending on the duration of the electrolysis and conductivity of the bath. The theoretical dissociation potentials for various chlorides per gm-atom of chlorine ion are listed below:



These voltages imply that if uranium chloride is produced in the salt due to near complete depletion of magnesium chloride, than uranium chloride will preferentially dissociate and the uranium electrodeposited on the cathode. Therefore, for the magnesium electrorefining process, a critical minimum amount of MgCl_2 must be maintained in the bath by anodic dissolution of magnesium. However, as long as this critical value is maintained, the theoretical electrorefining potential will be 0.0 V and only the cell resistance needs to be compensated which comprises solution and contact resistances. For the uranium electrorefining process, it was expected that a reference amount of 2 mol. % UCl_3 in the electrolyte would be needed to minimize magnesium electrodeposition in the cathode.

Experimental Design and Program

The following experimental parameters were studied to investigate the optimum conditions for magnesium decladding process as well as the uranium electrorefining process.

Magnesium electrorefining investigation was done in two parts:

- ◆ Separate Uranium and Magnesium rods electrically connected to form a composite anode to create the extreme reference case, since the surface area ratio of Mg/U was LOW
- ◆ Magnesium-clad uranium anode to create the other extreme of a very HIGH Mg/U surface area ratio.

The electrorefining process was investigated using a reference electrolyte at a composition of 55 mol. % LiCl, 40 mol. % KCl, and 5 mol. % MgCl_2 . This salt melts eutectically at approximately 350°C.

Curves of uranium and magnesium concentration in electrolyte and in electrodeposited cathode product against time for different current density/voltage conditions, and other parameters, as shown in Table I, were produced.

RESULTS AND ANALYSES

Measurement of electrolyte composition and cathodic products were initially done using the X-ray diffraction analysis. Subsequent analysis utilized ICP-MS technique to quantify the amount of elements both in the electrolyte and in the cathodic product.

Electrorefining of Separate Mg and U Anodes:

Magnesium electrorefining experiments were performed using two different sampling methods. In the ‘**batch**’ sampling method, collection of salt and cathodic product, as well as measurement of magnesium weight loss, were done by interrupting the process. Especially for the measurement of magnesium weight loss from anode, the anodic shaft assembly was allowed to cool due to safety concerns. Subsequently, the magnesium anode was disassembled from the shaft for weight measurement. In the mean time, the cathode assembly was removed from the salt bath and replaced by a new one. Also, around 5 grams of salt sample was taken from the crucible with stainless steel utensil.

In the batch sampling method, the uranium content in the salt bath continuously increased with process time. Each electrolytic run appeared to add uranium to the salt that increased without any apparent limit. It was assumed that the build up of uranium in the salt bath was caused by the formation of uranium chloride over a long period of time. To restart a process from the beginning for each data point, the salt bath had to be refined for uranium until its content reached the same range of value, before the next experiment could be done. To achieve this, a cleaning electrolytic process was carried out before each data assessment. This cleaning process involved running a cathodic current density of approximately 36 mA/cm². This cleaning process took at least half an hour using only magnesium anode and the stainless steel cathode, that were dedicated for the cleaning purpose. In most cases, the cleaning step managed to reduce the amount of uranium in the salt bath by as much as 50 percent. Since it was found that the cleaning step was unable to return the uranium content back to the same value, a variation in the initial uranium content of as much as 100 wt. ppm was observed. It should also be noted, that a significant part of this variation originated from variability associated with the ICP-MS measurement. To minimize errors in uranium measurement, a set of data with the same current density, were generated in sequence with increasing process time. When the uranium content exceeded 1000 wt. ppm, the salt bath was replaced with a leaner solution. High current density usually produced uranium dissolution already in thousands of wt. ppm values in each run. Replacement of salt bath in every experimental run was undesirable because of the limitation on hazardous waste disposal in the research facility.

In the ‘continuous’ sampling method, only the salt sample was collected at selected time intervals during a continuous electrolytic process. The salt sample was collected from the crucible by immersing an alumina rod in the salt bath. Cathodic product samples were only collected at the end of each experiment.

Magnesium electrorefining from separate U and Mg anodes was conducted to investigate the effect of two parameters: (a) electrolyte temperature and (b) current density. The volume (approx. 700 cc.) and composition of the electrolyte, the immersed depth of the electrodes and the Mg/U area ratio (1:1) on the anode were held constant.

Temperature Dependencies: The initial set of experiments were carried out to determine the practical range of process temperature, without producing excessive uranium build up in the salt bath. Cathodic current density was held constant at 36 mA/cm² (Process current: 7.5 amps., anodic current density: 200 mA/cm², cell voltage: 0.2 V).

Figure 2 shows the anodic dissolution at the three selected temperatures. The magnesium anodic dissolution was shown to depend mainly on the current density, while temperature has virtually no effect on magnesium anodic dissolution. The anode was cleaned in warm water to remove the adhering salt before weight measurements. The corresponding uranium anodic dissolution in the salt bath is shown in Figure 3. This figure shows that the level of cathodic current density used has already produced uranium dissolution well beyond the upper limit of 100 wt. ppm. In addition, there is a tendency for uranium to stay dissolved in the salt bath when the salt bath temperature increases. On the other hand, uranium deposition on the cathode from the salt bath is enhanced as the temperature decreases. The precision of the uranium measurement from cathodic product is low because uranium macrosegregation may occur at the cathode, particularly at lower temperatures when the salt viscosity is high. This segregation may be related to the coating of salt on the cathode. It is likely that the uranium measured from the cathode was mainly from the salt that deposited on the cathode. In general, at any process condition, the uranium content in the cathode was always higher than

that in the salt bath. Uranium on the cathode has two components – one carried by the salt and the other deposited electrolytically. The deposited component should be directly related to the uranium chloride activity in the salt with respect to magnesium chloride. The carried over component is related to the salt viscosity and its uranium content. Thus, it was decided that the subsequent experimental runs require only measurement of uranium in the salt to find the upper limit of cathodic current density. The upper limit of the current density is that value which does not rapidly accumulate uranium in the salt bath.

Based on Figure 3, low uranium dissolution in the salt bath can be maintained if the process temperature is kept at 400 °C or below. It should be noted that solid binary compound of uranium and potassium chloride becomes stable at low temperatures (7). 400°C was selected as the process temperature for further experiments since an increase of up to 450 °C does not raise the uranium dissolution significantly.

Time and Current Density Dependencies: The subsequent experiments focused on the transient behavior of magnesium and uranium dissolution for three levels of cathodic current densities. The voltage across the electrolyte for all three current densities was found to be less than 0.1 Volt. On the basis of previous data, the salt bath temperature was set at 400 °C. Figure 4 shows the magnesium dissolution of the anode, which appeared to be linear for all of the current density levels. Comparison of the experimental magnesium dissolution rate with the theoretically calculated rate shows current efficiency in the range of 90 to 95 %. Also, as shown in Figure 5, the magnesium content in the salt bath remained constant during and between experimental runs. This result implies that there is a steady state mass transfer of magnesium from anode to cathode because there was no significant magnesium accumulation in the salt bath.

The uranium dissolutions for the three levels of cathodic current densities are shown in Figures 6 to 8. Particularly for the batch process, the initial uranium content for each set of data did not start from zero. In the continuous process, a cleaning process was not required. However, the electrolyte was not refreshed before running the next experiment with higher current density. Therefore, the uranium content continuously accumulates in the salt bath when continuous processes are conducted at one current density and another. The process was done in sequence with increasing time and increasing current density. The results for both processes then have to be interpreted by the incremental difference between the data points.

Figures 6 and 7, for current densities 6 and 12 mA/cm², show that the uranium dissolution in the salt bath reaches a steady state value. Current density of 6 mA/cm² produced uranium steady state dissolution between 75 to 100 wt. ppm, while 12 mA/cm² produced uranium steady state dissolution of 200 wt. ppm. Finally, Figure 8 shows that the uranium dissolution in the salt bath did not have a tendency to reach a steady state value, but continued to accumulate with process time. In addition, the level of uranium addition to the salt bath was extremely high at high current densities compared to those at the lower current densities. Uranium dissolution can be minimized by using low salt bath temperature (400 °C) and the cathodic current density should be limited to 12 mA/cm² to maintain a steady state value of uranium dissolution in the salt bath.

Electrorefining of Mg-Clad Uranium Anode:

Cladding of uranium with magnesium was accomplished by a tight compression fitting of hollow magnesium cylinder onto a uranium rod. During hydraulic pressing, with compression force of approximately 60 kgf, the hollow magnesium cylinder slid over the uranium rod until it finally covered the whole uranium surface. After the hydraulic pressing, the magnesium cylinder outer surface was carefully ground to reduce its thickness to approximately 1mm. The initial surface area ratio of magnesium to uranium after cladding was 30. The initial clad assembly is shown in Figure 9. All the data in these experiments were recorded in the continuous mode.

Magnesium electrorefining from Mg-clad uranium anode was conducted to investigate the effect of three parameters: (a) Magnesium to uranium surface area ratio; (b) MgCl_2 content in the electrolyte and (c) Stirring rate. Parameters that were held constant were, (a) Electrolyte temperature, at 400 °C; (b) Cathodic current density at 12 mA/cm^2 , and (c) Volume of electrolyte (700 cc.)

Effect of Mg/U surface area ratio: One Mg-clad uranium anode was used for the investigation of the Mg/U ratio of surface area. The anode was electrorefined at the cathodic current density of 12 mA/cm^2 . The change of the Mg/U ratio of surface area during the electrorefining process is shown in Figure 10.

Figure 11 shows the variation of uranium content in the electrolyte during the magnesium electrorefining process. The figure shows that uranium dissolution in the electrolyte reaches a steady state value of 400 wt. ppm as long as the Mg/U ratio of surface area remains constant at the initial value of 30 i.e., there is full coverage of magnesium on the uranium surface. The steady state content of uranium in the electrolyte also remained constant until the Mg/U ratio of surface area further reduced to 5. Beyond this point, as soon as the surface area of uranium was more than that of magnesium, uranium continued to accumulate in the electrolyte. This continuous accumulation of uranium in the electrolyte at the lower end of Mg/U ratio of surface area is similar to observations made in the experiments with separate but coupled electrodes reported earlier. It is evident that the threshold condition for continuous accumulation of uranium in the electrolyte depends both on the current density and the Mg/U ratio of surface area.

The corresponding magnesium electrodisolution from the Mg-clad uranium anode, as measured by its weight loss, is shown in Figure 12. The magnitudes of weight loss of the two extreme Mg/U ratios of surface area are essentially identical, between 1.0 gram (after 100 minutes of processing) and 1.2 grams (after 120 minutes of processing). This result implies that magnesium electrotransport predominates the electrorefining process at 5 mol. % MgCl_2 addition in the electrolyte, as long as there is still some residue of magnesium clad on to the uranium anode surface. Also as an additional supporting evidence, the magnesium electrotransport efficiency for Mg-clad uranium anode with 5 mol. % MgCl_2 in the electrolyte was found to be approx. 100 %. This efficiency is in good agreement with the efficiencies obtained for the separate-anodes experiments. In addition, the voltage necessary to maintain the cathodic current density of interest (12 mA/cm^2) was only slightly lower than that for the separate anode experiments at 0.06 V.

Effect of MgCl_2 content in the electrolyte: The effect of MgCl_2 content in the electrolyte was studied by additions of MgCl_2 to the electrolyte at three different levels of 1, 2.5, and 5 mol.

%. The anode used in this study was a new Mg-cladding of the same uranium rod used previously. After the hydraulic pressing, the clad was kept as thick as 2 mm, so that there would be no variation of the Mg/U ratio of surface area during the investigation. The ratio of Mg/U surface area remained at 30 during the whole course of investigation.

The time dependency of electrolyte uranium content at the three levels of MgCl_2 is shown in Figure 13. In general, the rate of uranium accumulation in the electrolyte was high when the MgCl_2 content was also high. Such a higher accumulation rate of uranium may be attributed to two possibilities: either a faster rate of uranium electrodisolution into the electrolyte or slower rate of uranium electrodeposition on the cathode. The corresponding uranium deposit in the cathode decreased when the MgCl_2 content in the electrolyte was increased. From the mass balance consideration, this observation of the cathodic products implies that faster accumulation of uranium in the electrolyte was more likely due to a slower rate of uranium electrodeposition on the cathode. In other words, electrodeposition was the controlling step of uranium electrotransport when the MgCl_2 content in the electrolyte was high. Upon further observation of Figure 13, one can see that the uranium content reached a steady state value of 400 wt. ppm, with 5 mol. % MgCl_2 in the electrolyte. Similarly, the 2.5 mol.% addition also caused the uranium to reach the same steady state content, even though the process started with a much higher initial uranium content. It was expected that the uranium content with the 1 mol. % MgCl_2 addition would also reach the same steady state value, given sufficient time.

The disadvantage of lower MgCl_2 content in the electrolyte can be shown in the light of electrotransport efficiency. The efficiency of magnesium electrotransport changed from 100 % with 1 mol % MgCl_2 in the molten salt to approximately 45 % with 5 mol. % MgCl_2 . The corresponding magnesium electrotransport rates, as measured by the anodic weight loss, are shown for the different levels of MgCl_2 in Figure 14. To achieve the same process current, the electrorefining process with low MgCl_2 content should allow more uranium to codeposit to the cathode. The higher uranium deposit on the cathode at lower MgCl_2 content in the electrolyte, as shown in Figure 13, is a clear evidence of the above suggestion. However, low magnesium electrotransport efficiency in process with low MgCl_2 addition may be related to the possibility that uranium content in the electrolyte has not reached its steady state value. Hence, after a longer process time, the final electrotransport efficiency of magnesium might get back up to 100 %.

Assessment for the effect of stirring rate: Two stirring rates were used for electrorefining of the Mg-clad uranium anode for an hour each. The anode was also thick enough to get a constant ratio of Mg/U surface area ratio during the course of experimental runs. As shown in Figure 15, a lower steady state value of uranium was achieved when the experiment was conducted with stirring rate of 4 Hz than that with 1 Hz. This result is in contradiction to the usually observed trend when the stirring rate is lower. It is believed that the apparent reduction of uranium in electrolyte was unique in this experiment which was carried out with a high starting content of uranium. Should the starting content of uranium be very low, one would observe an increase of uranium content up to the steady state value associated with high stirring rate of 4 Hz. One possible cause of such a lower steady state content is that the higher stirring rate minimizes the gravitational sinking of uranium in the electrolyte, and thus allows more uranium to migrate to the cathode. The other possibility is that the higher stirring rate breaks any viscous layer of dissolved uranium off from the anode, which also helps uranium to electrodeposit on the cathode. In either case, the uranium deposition on the cathode should be higher with increasing stirring rate, as confirmed by Figure 16.

The measurement of the magnesium dissolution rate at the higher stirring rate was not attempted. However, drawing parallels to the observation made in the previous section, a lower steady state content of uranium would very likely be associated with the ease of uranium electrodeposition to the cathode along with magnesium, as supported by earlier observations. Therefore, higher stirring rate, which causes a lower steady state content of uranium in the electrolyte, will have a lower magnesium electrotransport efficiency as well as higher uranium contamination.

SUMMARY

The molten salt electrorefining process has been studied to selectively remove magnesium layers from depleted uranium rods. The limiting cathodic current density at 400 °C in a LiCl-KCl electrolyte, for a steady state uranium dissolution in the salt bath at 200 wt. ppm. was 18 mA/cm² at the uranium to magnesium surface area ratio of 1. The corresponding anodic current density is 200 mA/cm². At any cathodic current density, magnesium electrorefining proceeded with 100 % current efficiency and was independent of temperature.

Uranium content in the cathodic product was always higher than in the salt bath. Once uranium dissolves in the salt, its deposition on the cathode competes strongly with magnesium. Predominant magnesium deposition on the cathode can only be achieved by keeping a higher activity of magnesium in the salt.

Under the optimal conditions of 400 °C temperature and below 18 mA/cm² of cathodic current density, minimal uranium contamination in the electrolyte can be achieved by holding MgCl₂ content in the electrolyte greater than 2.5 mol.% and higher stirring rate, such as 4 Hz.

There is an inverse relationship between the current density and the Mg/U ratio of surface areas that determine the condition where uranium continuously accumulates in the electrolyte. Low magnesium electrotransport efficiency, which is accompanied by increase of uranium electrotransport efficiency, is associated with low steady state uranium content in the electrolyte. Higher stirring rate appears to lower the steady state uranium content throughout the whole process, while lower MgCl₂ content may cause such an effect temporarily during the transient period of the process.

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Table I. Parameters for Mg decladding Experiments

<u>(a) Separate U and Mg anodes</u>	<u>(b) Thin Mg-cladding layer on U anode</u>
Temperature: 400, 450, and 500°C	
MgCl ₂ content in electrolyte: initially 5 mol. %, and lower	
Current density (voltage): derived from the upper limit for the uranium contamination in electrolyte or cathodic product. Limit initially set at ~100 ppm U in electrolyte which is expected to correspond to 0.2-0.3 V operating potential	
Mg/U surface area ratio: around 1:5, 1:1, 5:1, and 30:1	
Stirring rate: 1Hz and 4 Hz	

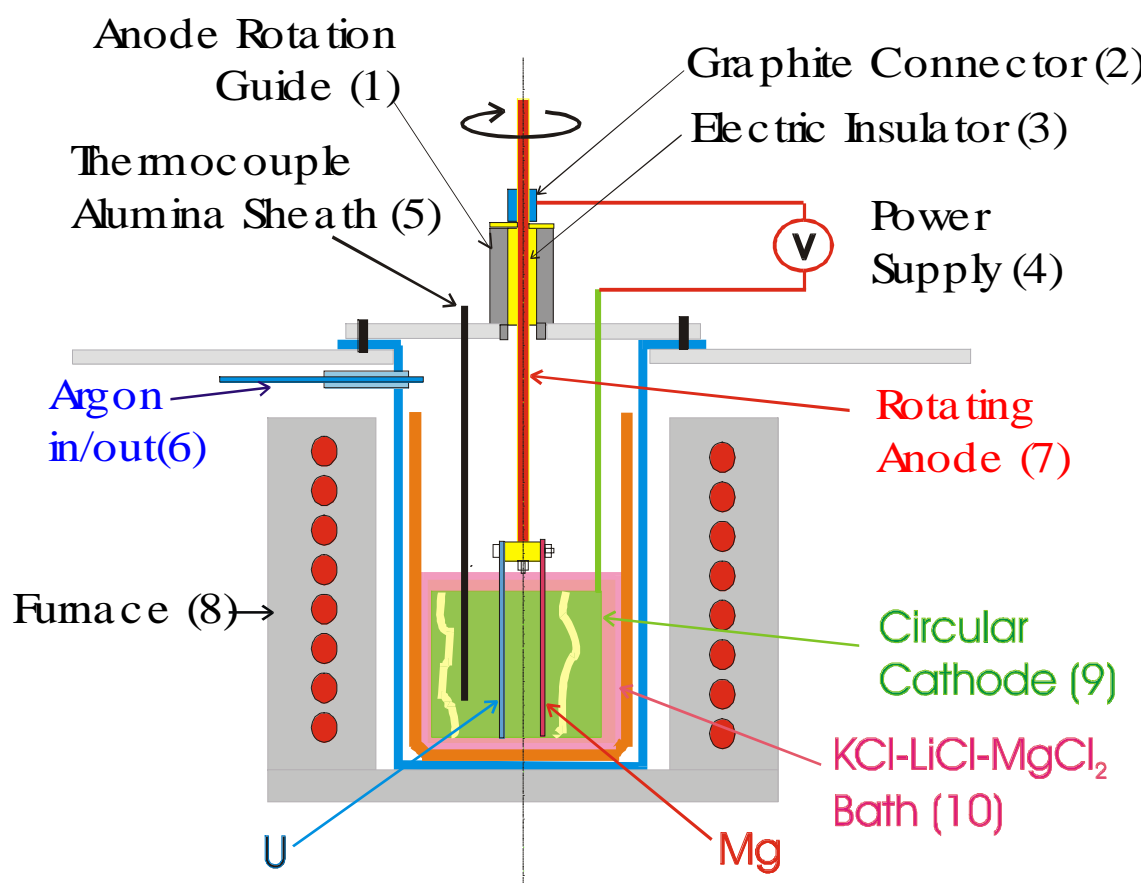


Figure 1. Schematic diagram of the electrorefining apparatus.

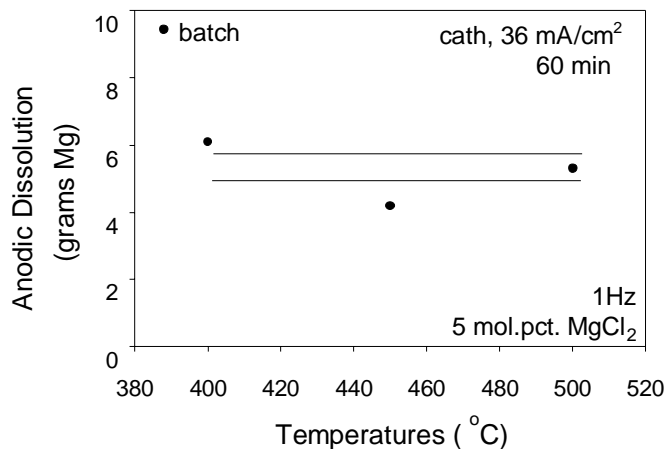


Figure 2. Magnesium Anodic dissolution as a function of salt bath temperature for electrolytic process with separate uranium and magnesium anodes.

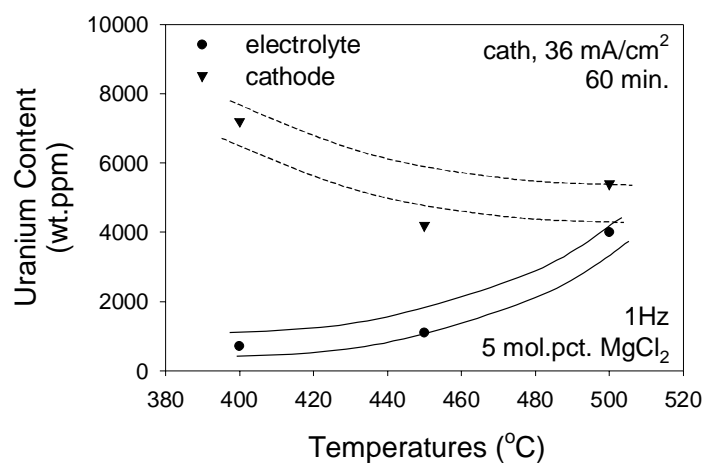


Figure 3. Uranium dissolution in the salt bath as a function of temperature for electrolytic process with separate uranium and magnesium anodes.

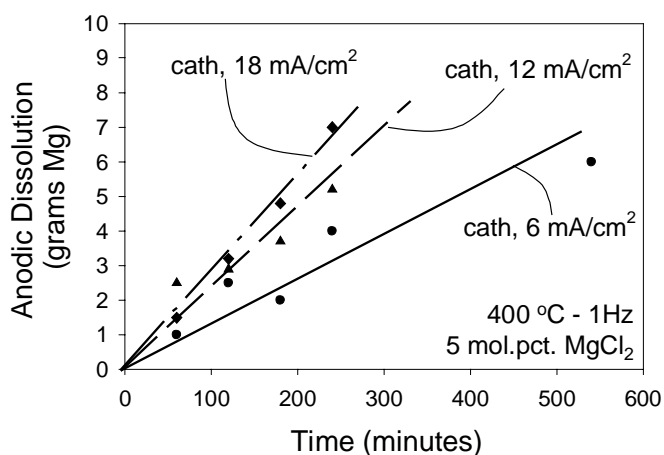


Figure 4. Magnesium anodic dissolution as a function of time at 400 °C. The magnesium weight loss was measured from the batch method.

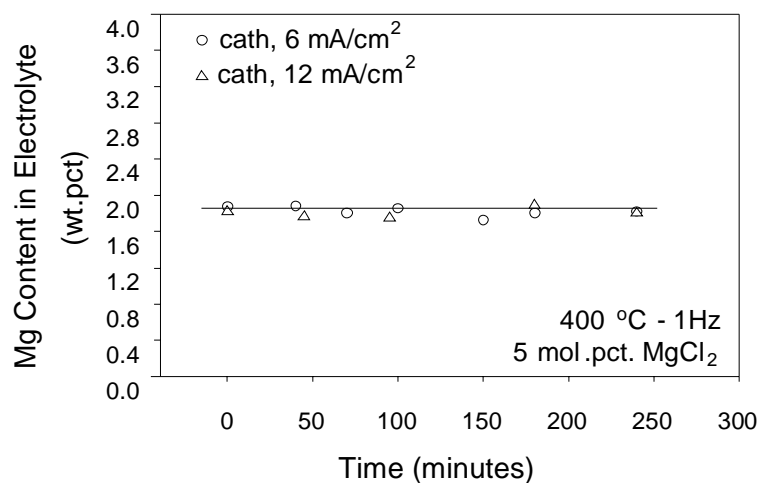


Figure 5. Magnesium content in the salt bath from continuous process experiments at 400 °C

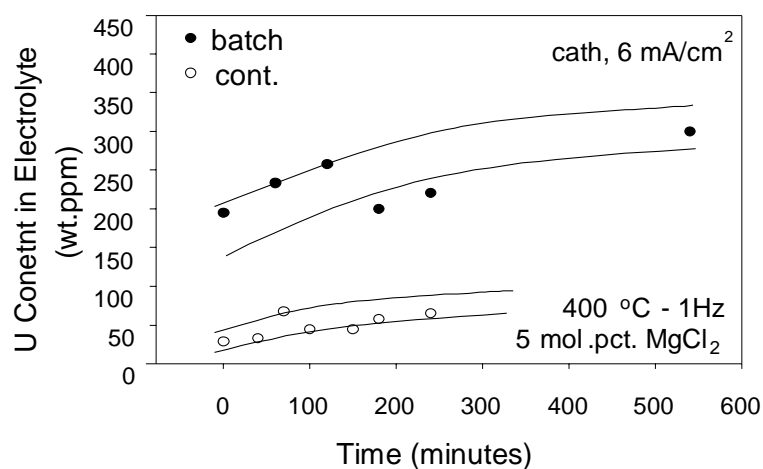


Figure 6. Uranium dissolution in the electrolyte at cathodic current density of 6 mA/cm² and temperature of 400 °C.

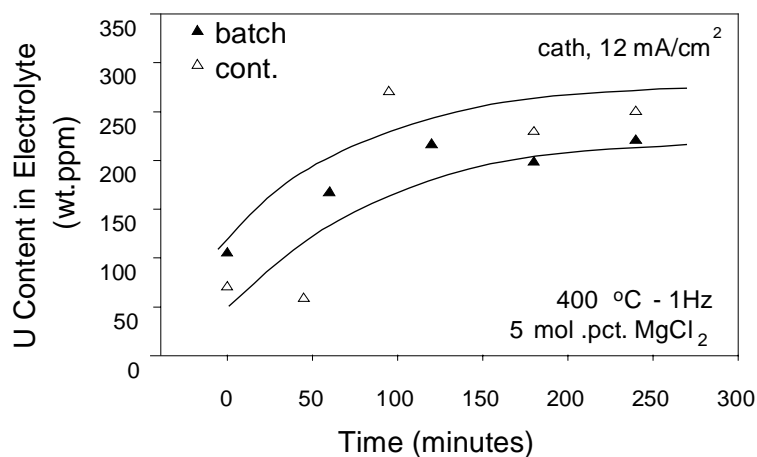


Figure 7. Uranium dissolution in the electrolyte at cathodic current density of 12 mA/cm² and temperature of 400 °C.

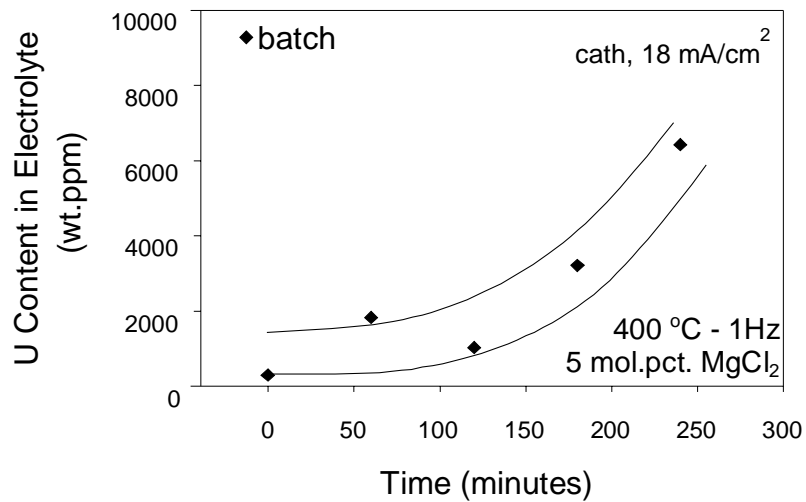


Figure 8. Uranium dissolution in the electrolyte at cathodic current density of 18 mA/cm² and temperature of 400 °C.

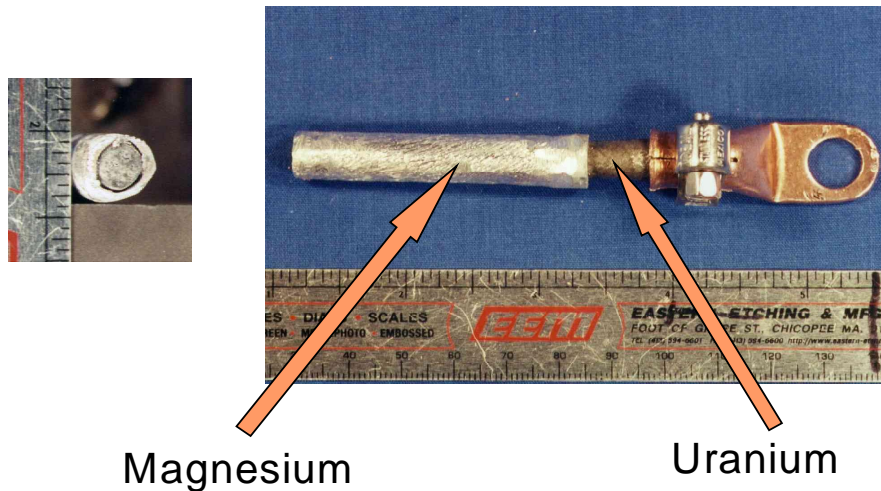
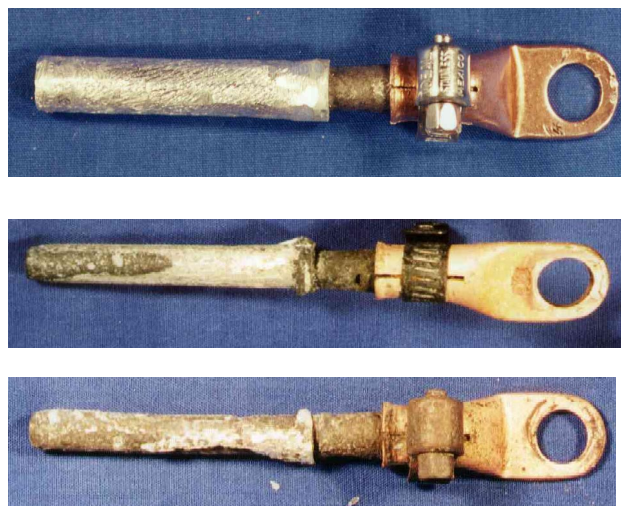


Figure 9. The assembly of Mg-Clad uranium anode.



Mg/U = 30
Initial

Mg/U = 5
120 min.

Mg/U = 0.2
220 min

Figure 10. The variation of Mg/U ratio of surface area during electrorefining

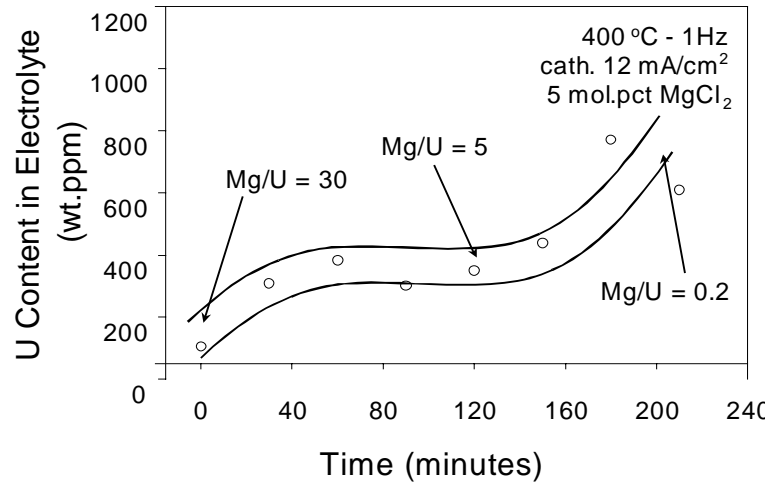


Figure11. Variation of uranium content in the electrolyte with time at 400 °C during magnesium electrorefining of Mg-clad uranium anode.

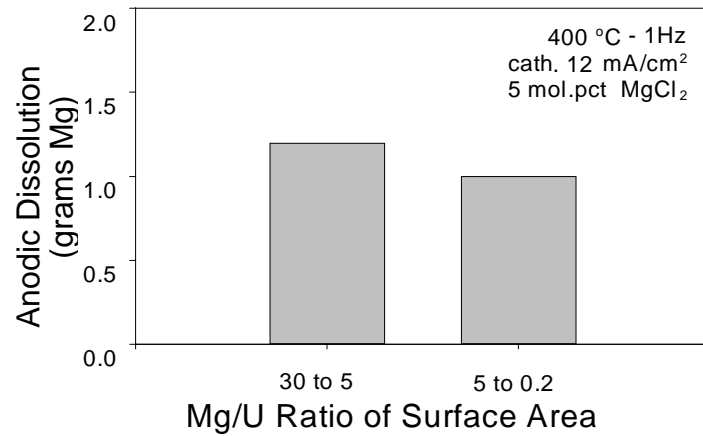


Figure 12. Magnesium dissolution from the Mg-clad uranium anode, measured after the electrorefining process. Magnesium electrorefining of Mg-clad uranium anode.

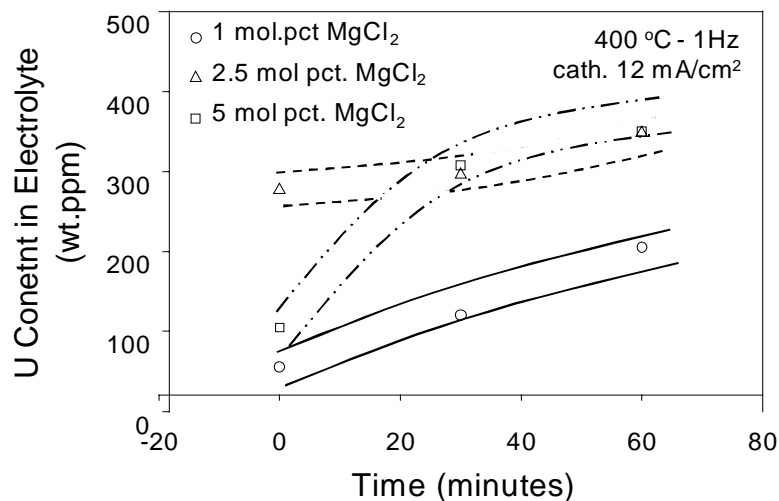


Figure 13. Variation of uranium content in the electrolyte with time, at a cathodic current density of 12 mA/cm². Magnesium electrorefining of Mg-clad uranium anode.

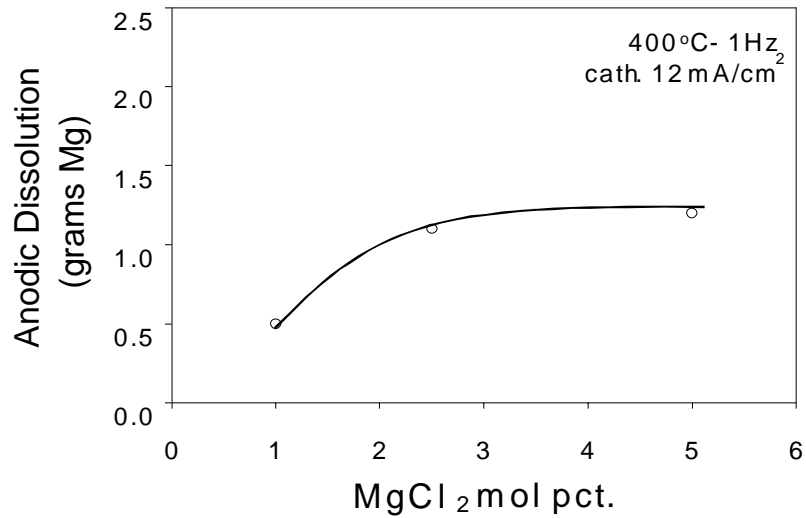


Figure 14. Magnesium dissolution from the Mg-clad uranium anode at cathodic current density of 12 mA/cm² and at 400 °C during magnesium electrorefining process of Mg-clad U.

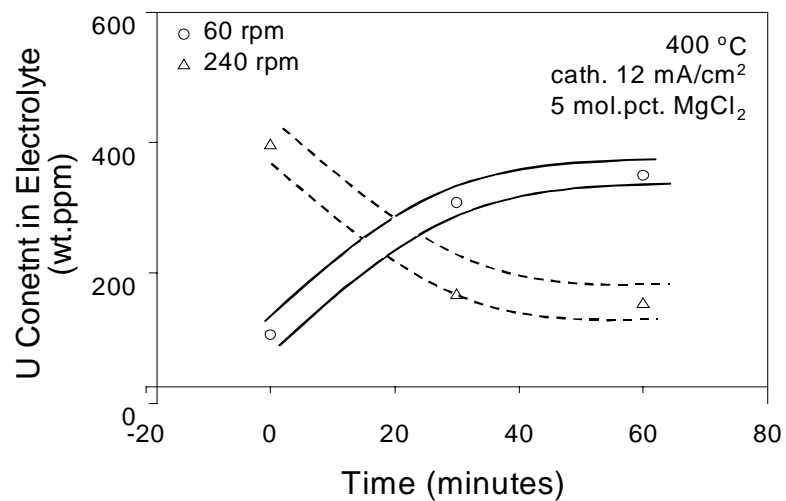


Figure 15. Uranium content in in the molten salt as a function of time, at cathodic current density of 12 mA/cm² and at 400 °C.

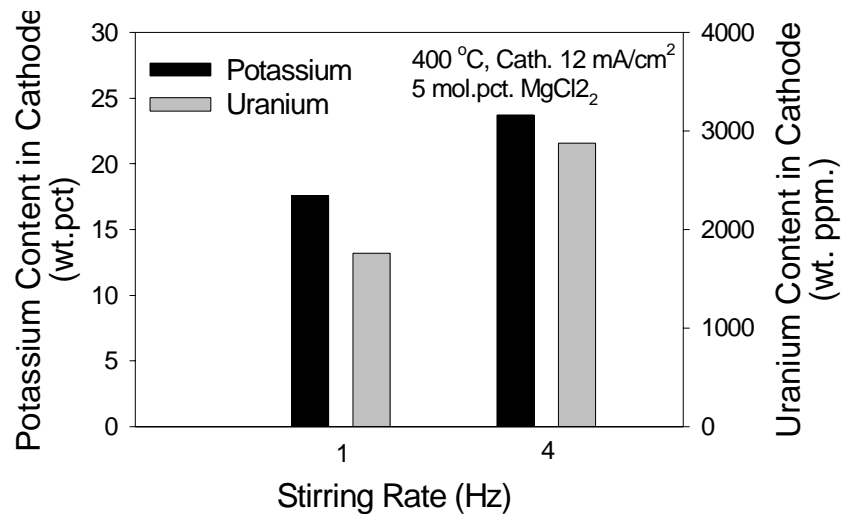


Figure 16. Potassium and uranium content in the cathodic product as a result of electrorefining process of Mg-clad uranium anode at different stirring rates.