

Electrorefining of Cerium in LiCl-KCl Molten Salts

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Electrorefining of cerium from cerium-gallium alloys has been demonstrated in lithium chloride-potassium chloride salts at temperatures below 500°C, with excellent current efficiencies and high product yields. These experiments are being carried out as non-active trials for a process for the purification of impure actinide metals.

The results reported show anodic current efficiencies consistently close to 100%, and in several experiments complete oxidation of the cerium in the feed occurred. The cathodic product is hard and metallic, and incorporates a significant amount of salt into its structure. The product can be consolidated into a dense, pure metal by melting under calcium chloride at 850°C. The yield of this consolidation step varies between 16 and 75%, seeming to depend on the total mass of metal being consolidated and the quality of inert atmosphere.

A small-scale electrochemical cell has been demonstrated which will be used in initial active experiments.

A. INTRODUCTION

Actinides can be purified by electrolysis in a molten salt. Depending on the melting points of the actinide and the salt system used, the metal may be in either a solid or molten state. In a review of the literature, Willitt et al [1] reported that for Uranium, electrorefining normally takes place below the melting point of the pure metal. This can be either via a solid anode/solid cathode process, or by the use of liquid alloys, such as uranium-cadmium anodes or uranium-nickel cathodes.

In contrast, plutonium is typically purified with both the feed and product in the liquid state, e.g. in sodium chloride-potassium chloride (NaCl-KCl) salt [1]. The efficiency of the process is limited because a build-up of impurities causes the anode to freeze towards the end of the process, leaving a Pu residue which cannot be processed further. Work at Argonne reported by Blumenthal and Brodsky [2] has demonstrated that electrorefining of Pu is possible in the solid state; high purities are possible, and the process is not limited by the build-up of impurities. Further work by Miller et al [3] suggests that impurities would collect as a liquid at the surface of the feed and drip down, revealing fresh plutonium surface. Ideally, a reference electrode is required to ensure that impurities are not oxidised from the anode.

In recent years our group has worked to develop a “solid anode” process for the purification of impure actinides. This focussed on demonstrating the feasibility of the process using cerium as a non-active simulant [4]. The generation of cerium oxychloride has also been investigated; cyclic voltammetry in some runs suggested that concentrations would increase throughout the experiment [5]. However, this effect was not consistently reproducible.

This paper reports further investigations into solid anode electrorefining of cerium, including the effect of operating temperature and the development of a small-scale electrochemical cell for active trials.

B. EXPERIMENTAL AND PROCEDURE

Lithium chloride (LiCl, Fisher Scientific, 98%), potassium chloride (KCl, Fisher Scientific, 99%) and calcium chloride dihydrate (CaCl₂·2H₂O, Fisher Scientific, Analytical reagent grade) were dried by heating under vacuum to at least 150°C (LiCl) or 200°C (KCl, CaCl₂), and stored in an inert

atmosphere glovebox prior to use. Cerium chloride (CeCl_3 , Alfa Aesar, 99.5%) and silver chloride (AgCl , Alfa Aesar, 99.9%) were used as-procured. LiCl-KCl eutectic salt (44.7wt% LiCl) with 1wt% CeCl_3 was mixed, fused in a 750°C furnace (element temperature) under argon, and the cast block broken into smaller pieces for use in experiments.

The cathode was made from silver steel (high carbon steel, 0.95-1.25wt% carbon). In Experiments 1-4, this was a 2mm diameter rod, whilst in Experiments 5-6 this was a 1mm diameter rod with a 15mm x 15mm paddle welded onto the end. In Experiments 1-4 a 2mm tungsten rod was also present to use as the working electrode for cyclic voltammetry. The anode was a steel basket which could hold the feed. Cerium-gallium alloy (Ce-Ga , 10wt% Ga) was procured from Johnson Matthey (REacton grade) in glass ampoules. This was cut to the required size within an inert atmosphere glovebox, and polished with a metal file and glass paper prior to use.

The reference electrode consisted of a Pythagoras ion-conductive tube procured from Multi-Lab. This contained approximately 1g of a finely ground $\text{LiCl-KCl-2wt\% AgCl}$, previously fused under argon at 750°C , and a 0.5mm silver wire (Alfa Aesar, 99.9%). When the top of the reference electrode would be exposed to the air, the top was sealed using epoxy resin.

An alumina stirrer was present in all experiments; in Experiments 1-4 this was a “cricket bat” stirrer 25mm wide, whilst in Experiments 5 and 6 a smaller, 12mm wide stirrer was used. The use of a smaller stirrer would be expected to slow the mass transport of Ce^{3+} ions through the salt.

Experiments were prepared in an inert atmosphere glovebox to limit the exposure to moisture. Chunks of fused $\text{LiCl-KCl-1wt\%CeCl}_3$ salt were added to a ceramic, (alumina or zirconia-coated alumina) crucible. This was then heated in a top-loading furnace within either an inert atmosphere glovebox or an argon-purged vessel within a fume cupboard. The cell design for Experiments 5 and 6 is shown in Figure 1.

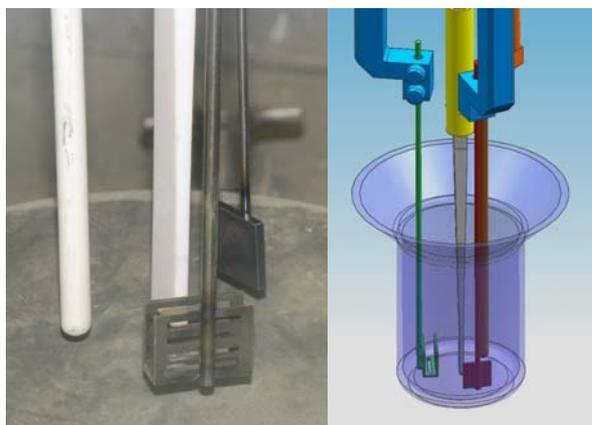


Figure 1: Electrodes and stirrer used for Experiments 5 and 6

Electrochemistry was conducted using an Autolab™ PGSTAT30 potentiostat with a current booster capable of delivering up to 20A. This was controlled by a desktop PC running the General Purpose Electrochemistry Software (GPES) application. Electrorefining was typically conducted using the Chronoamperometry (CA; constant potential) setting, although in a few instances the Chronopotentiometry (CP; constant current) setting was used. Cyclic Voltammograms (CVs) were conducted using the “staircase” setting. CVs require a working electrode of a small surface area, and preferably of an inert material (e.g. tungsten). It was not therefore possible to perform CVs in Experiments 5 and 6 where only larger, steel electrodes were present.

Experiments 1-4, which took place in an argon-purged vessel within a fume cupboard, were conducted in a systematic manner to investigate oxychloride production. Electrorefining was interrupted at regular intervals and cyclic voltammetry used to investigate the presence of oxychloride. Between experiments, the temperature and electrode potential were varied, whilst other variables were kept as consistent as possible; experimental parameters are shown in Table 1. In Experiment 3, the temperature was increased after 24 hours to investigate the effect on current.

Experiments 5 and 6, which took place under argon in a glovebox furnace, tested the small-scale electrochemical cell developed for active use, allowing as little as 150g of salt to be used. However, in this set-up there is no electrode present which can be used as a working electrode for cyclic voltammetry. The temperature in both experiments was approximately 475°C (530°C element temperature).

Table 1: Parameters for experiments conducted

Exp #	Salt (g)	Temp (°C)	Cathode	Stirrer diameter (mm)	Electrode Potential (V, vs Ag/AgCl)	Feed mass (g)
1	306	395	2mm rod	25	0.2	11.5
2	300	490	2mm rod	25	0.2	10.7
3	302	395*	2mm rod	25	0.4	12.6
4	354	490	2mm rod	25	0.4	11.4
5	220	475	15mm paddle	12	0.2-0.3	4.6
6	315	475	15mm paddle	12	0.2-1.0	6.4

*Temperature increased to 490°C after 24 hours

On breaking out the experiment, the used feed was removed from the anode basket, and rinsed with hot water to remove adhered salt; the length of wash was brief (typically less than one minute) to limit the chemical oxidation of cerium. The feed was then weighed to allow a mass loss to be calculated. The cathode was sealed in a bag as soon as possible to limit any reaction with the atmosphere. The salt was removed from the crucible, which in most cases required breaking. The salt was carefully broken open to see whether any product fell from the cathode, with any product-rich areas saved for consolidation.

To consolidate the metallic product, the product-rich salt or cathode (as applicable) were placed at the bottom of a small, round-bottomed crucible, and covered by a layer of CaCl₂ salt to limit reaction with any traces of oxygen or moisture present in the argon atmosphere. This was then heated to above 800°C (950°C element temperature), and gentle stirring used to help the beads of metallic cerium to coalesce. The consolidation data reported includes the consolidation of products from electrochemistry runs other than those described above.

C. RESULTS AND DISCUSSION

Results of all experiments are summarised in Table 2.

Table 2: Results of all experiments reported

Exp #	Charge passed (C)	Mass loss from anode (g)	Anode current efficiency* (%)	Product on cathode	Product in salt
1	6856	3.7	111	Light granular deposits	Yes
2	11989	5.9	102	Light granular deposits	Yes
3a	3370	NA	NA	NA	NA
3b [†]	10919	5.4	102	Dense, bulky deposits	Yes
4	21009	10.3	101	Electrode frozen into salt; similar to Experiment 3b	
5	8530	4.4	106	Dense, bulky deposits	No
6	5000	2.5	103	Dense, bulky deposits	No

* Based on theoretical mass oxidised, as calculated from Formula 1 from Formula 1
[†] Includes charge passed after temperature increased to 490°C

C.1. Experiments 1-4

Each experiment varied according to the temperature and applied potential as follows; Experiment 1, 395°C and 0.2V vs Ag/AgCl; Experiment 2, 490°C and 0.2V; Experiment 3, 395°C and 0.4V; Experiment 4, 490°C and 0.4V. All other parameters were kept as similar as possible.

C.1.1. Cyclic Voltammograms

The intent for these experiments was to establish the conditions in which cerium oxychloride would be generated. However, only traces of oxychloride were seen throughout the experiments, and unlike previous experiments there was no consistent growth of peak height with time. Figure 2 shows a CV taken from Experiment 2. The Ce^{0/3+} couple can be clearly seen, with a reduction peak at -2.20V vs

Ag/AgCl and an oxidation peak at -1.98V. The suggested $\text{CeO}^{0/+}$ couple can be seen with a reduction peak at -2.0V and oxidation peak at -1.55V or -1.39V.

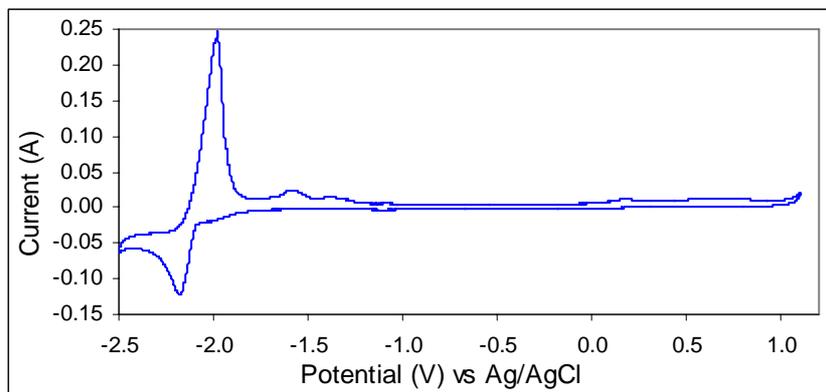


Figure 2: Cyclic Voltammogram from Experiment 2

Although the peaks attributed to oxychloride were seen only sporadically, the peak positions show a reasonable fit with those seen in previous work, and with those reported by Smolenski et al [6], see Table 3. It should be noted that the Smolenskii work took place in NaCl-KCl, and therefore differences in potentials would be expected; however separations between Ce^{3+} and CeO^+ should be similar. There is no clear correlation of experimental parameters when significant generation of oxychloride has occurred. One suggested cause which has not been investigated is the presence of loose oxide powder left in the crucible during manufacture.

Table 3: Comparison of electrode potentials assigned to cerium and cerium oxychloride

	Reduction Potential			Oxidation Potential		
	Ce^{3+}	CeO^+	Difference	Ce^{3+}	CeO^+	Difference
Previous Work	-2.19	-2.01	0.18	-1.96	-1.24	0.73
This work	-2.18	-2.00	0.18	-1.98	-1.39	0.59
Smolenskii et al [6]	-1.82	-1.55	0.27	-1.72	-0.92	0.80

C.1.2. Electrorefining (chronoamperometry)

The chronoamperometry data (Figure 3) for the four experiments shows an effect from temperature that had not previously been observed. Experiments 2 and 4, which took place at higher temperatures, showed a high initial current which gradually decayed through the course of the experiment. In contrast, Experiments 1 and 3, which took place at lower temperatures, showed consistently low currents except during the first two hours, where the temperature was slightly higher (420°C in exp 1 and 410°C in exp 3) due to the heating profile used. This temperature dependence was tested further in Experiment 3; after 14 hours at 390°C and very low currents, the temperature was increased by 100°C over one hour. The response of the current was prompt and linearly proportional to the temperature increase (Figure 4).

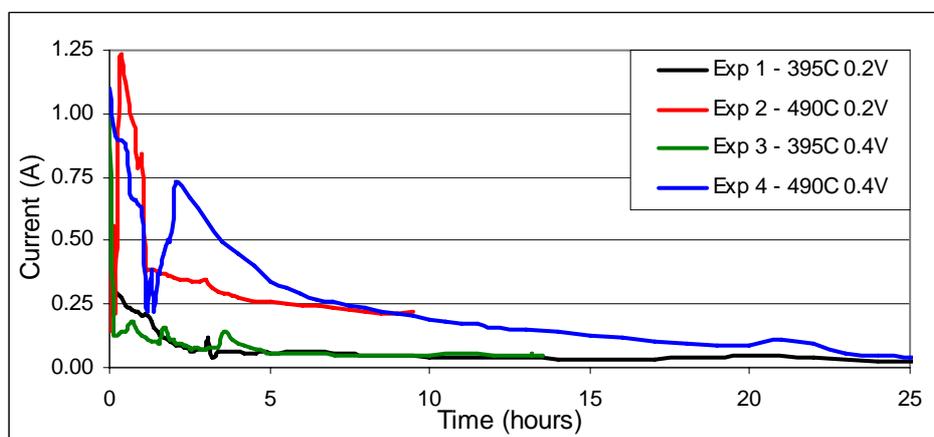


Figure 3: Chronoamperometry data from Experiments 1-4

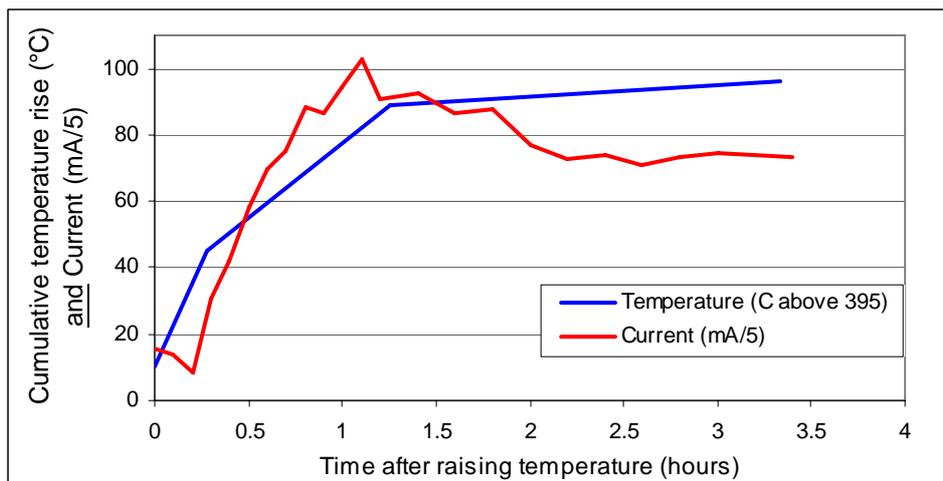


Figure 4: Comparison of current and temperature from Experiment 3

The reason for the very low currents at temperatures below 400°C is not clear. It is unlikely to be only due to increased diffusion through the salt at higher temperatures, as other alloys, e.g. zinc-tin, have been successfully electrorefined at temperatures below 400°C [4]. However, it may be related to the fact that at the higher temperatures the cerium-gallium alloy is close to its melting point of around 500°C. As suggested above in Experiment 3, there may be a direct relationship between the maximum current and the temperature.

Differences in the electrode potential did not prove significant in these experiments. Experiments 1 and 3 (both at 395°C, but at 0.2V and 0.4V vs Ag/AgCl respectively) showed similar chronoamperometry behaviour, as did Experiments 2 and 4 (both at 490°C, but at 0.2V and 0.4V respectively). Experience has suggested that the current is dependent on a range of factors, including mass transport (stirring), applied potential, temperature, and the amount (weight or surface area) of feed available for oxidation. This suggests that in this experiment, the current was limited by a factor other than potential, but does not mean that the potential does not have an effect on the currents obtained.

Current efficiencies were calculated based on the charge passed, and the mass loss from the anode, by Formula 1, which for cerium electrorefining reduces to Formula 2. Experiments 1-4 all gave current efficiencies at slightly more than 100%. However, small amounts of cerium may have been removed from the feed during the process of washing salt from the used feed; if this is the case then the calculated value of current efficiency would be slightly too high.

$$\text{Current Efficiency (\%)} = 100 \times \frac{\text{mass loss} \times n \times F}{M \times Q} \quad (1)$$

$$\text{Current Efficiency (\%)} = 206600 \times \frac{\text{mass loss}}{Q} \quad (2)$$

(n = electrons, F = Faraday constant, M = elemental mass, Q = charge)

C.1.3. Products

In Experiments 1 and 2, only small quantities of dull grey metal were on the electrode when withdrawn from the salt. After washing, these appeared granular (Figure 5a) and turned white rapidly on exposure to air. However, larger quantities of metal were found in the salt directly below the cathode, presumably having fallen off the cathode when withdrawn from the salt.

In Experiment 3, a dense deposit of metal approximately 20mm in diameter remained on the electrode after being withdrawn from the salt (Figure 5b), with a further quantity in the salt below. The cathode from Experiment 4 was frozen into the salt because of a failure of the argon gas; this appeared similar to the product of Experiment 3, with a dense product around the cathode, and some areas of a less dense product slightly further away (Figure 5c).

In all of the experiments at least some of the metal product fell from the cathode, suggesting that a cathode with a larger surface area is required to enable the product to cling to it, and for this reason the small “paddle” stirrer was acquired for the next set of experiments.



Figure 5a (left): Light granules from Experiment 2
Figure 5b (centre): Dense product from Experiment 3
Figure 5c (right): Product in salt from Experiment 4

C.2. Experiments 5 and 6

Two experiments were undertaken using the scaled down equipment designed for initial active experiments. Results for the Experiments are shown in Table 2.

C.2.1. Chronoamperometry

Experiment 5 ran to completion, with the current-time trace (Figure 6) showing a gradual decline with time; from an initial value of 0.4A, to 0.2A after 4 hours, to 0.1A after 8 hours, to zero after 19 hours. Each time electrochemistry was restarted there was a significant drop in current in the first few minutes, e.g. from ~1.5A to ~0.3A; a much greater drop than seen in Experiments 1-4. This type of behaviour has previously been associated to conditions with relatively poor mass transport, and may be attributable to the smaller stirrer used.

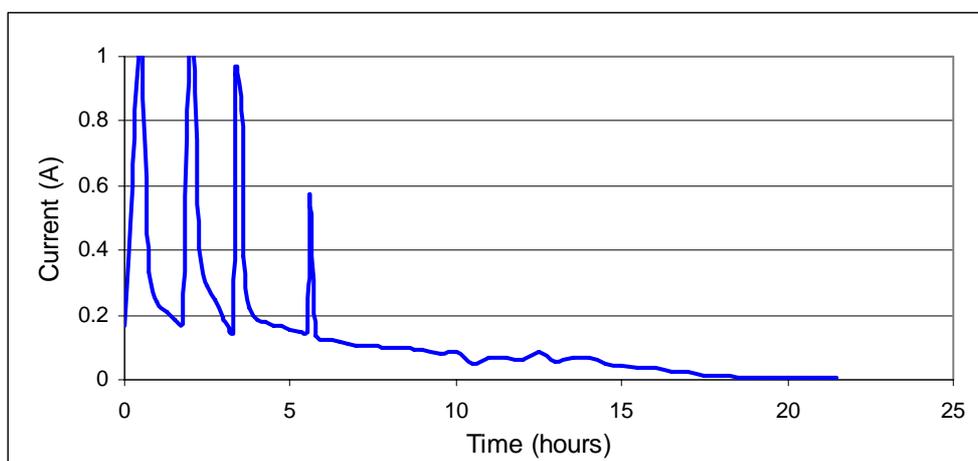


Figure 6: Chronoamperometry data from Experiment 5

In Experiment 6, currents were stable at around 0.3A for 2 hours before becoming erratic, with sudden jumps to large positive or negative currents. This type of behaviour has previously been attributed to a problem with the reference electrode; in this case, it began clashing with the stirrer at the same time as currents became erratic.

After this it was run under constant current conditions for a further two hours, with the applied potential gradually rising from -1.3V (vs Ag/AgCl) to -1.0V, at which point the experiment was terminated. The total charge passed, approximately 5000C, corresponds to oxidation of approximately one-third of the feed.

C.2.2. Products

The cathode product of Experiments 5 and 6 were similar, with hard, thick deposits of metallic product approximately 25mm across. Both cathodes gained substantially more weight than the total feed going into the experiment, suggesting that the deposits incorporated 50-75wt% of salt. When first removed from the furnace the deposits lost their metallic lustre over the course of several hours, and developed a white surface layer of oxide when stored in a glovebox over a period of weeks.

Experiment 5 appeared to run to completion; the feed remaining at the anode was small and dark, and fell apart with no obvious reaction when immersed in hot water. This was filtered to give 0.2g of a fine, black powder. In contrast, in Experiment 6, a distinct piece of feed was left behind which visibly reacted with hot water, producing 0.4g of a flocculent grey-white deposit in addition to 3.5g of used feed which remained intact. The observation of Experiment 6 suggest cerium reacting to form cerium oxide, with the differing observations in Experiment 5 suggest little or no cerium remained at the anode.

If it is assumed that all the Ce in Experiment 5 was oxidised (90% of a 4.6g feed, or 4.15g), the total charge passed corresponds to 100% current efficiency at the anode. In Experiment 6, the recorded mass loss suggests an anode current efficiency of 103%.

In both experiments no metal was seen in the salt, suggesting that the entire product remained on the cathode. The alumina crucible used in Experiment 5 had reacted strongly with the salt and had to be broken to remove the salt. Experiment 6 used a zirconia-coated alumina crucible with tapered side. The frozen salt block could be removed from this by inverting and tapping firmly on the glovebox floor, with the crucible appearing to be suitable for reuse. The zirconia coating gives a much smoother surface than the untreated alumina, which seems to limit the amount of sticking which occurs when reactive species such as $CeCl_3$ are present.

C.3. Consolidation

Five consolidation processes have been undertaken, including the products from Experiments 2, 4 and 5. Recoveries and process parameters are included in Table 4.

Table 4: Data obtained from consolidation experiments to date

Consolidation Run	Experiment ID in this paper	Mass loss from anode (g)	Consolidated metal (g)	Consolidation recovery (%)*
1	NA	9.2	3.2	35
2	2	3.7	1	17
3	4	10.3	6.6	64
4	NA	4	3.1	78
5	5	4.4	1.3	31

* Actually combined yield of cathodic efficiency and consolidation yield

After successful consolidations, the bulk of the salt is a clean white with no deposits present. The product is found at the bottom of the crucible as spherical, or slightly flattened, metal pieces of 1-10mm diameter. These are shiny and have a slightly yellowy surface finish (see Figure 7). The salt immediately surrounding the metal product is often light –medium grey, possibly suggesting slight oxidation of the metal.



Figure 7: Product of the third consolidation run, using metal from Experiment 4

The casting efficiency from consolidation is variable, ranging from <20% to ~75% as a percentage of the amount of cerium removed from the anode. It is not possible to separate the yield of the consolidation step with the yield from the cathode reduction, as the mass of product on the cathode cannot be accurately determined due to the inclusion of salt. In the case of the fifth consolidation run, using the product of Experiment 5, it is believed that the low recovery was due to an inadequate flow of argon gas, as demonstrated by oxidation to the steel hardware. Unlike other experiments, the salt was not a clean white but was pale grey throughout, which may be another indication of cerium oxidation.

When more product metal is present, larger pieces are formed, and the recovery yield is better, suggesting that this process will be increasingly successful as larger scale experiments are performed.

D. CONCLUSION

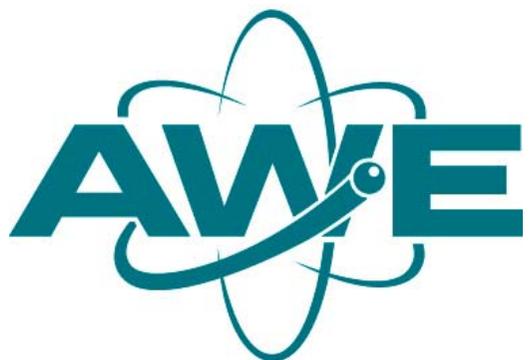
A cell design has been produced which has been used to electrorefine cerium-gallium alloys as an analogue for impure actinides. The current efficiency is consistently high, typically close to 100%, and in several experiments all of the cerium has been oxidised from the feed. Using a steel paddle-ended cathode, the product can be removed from the salt as a hard metallic deposit incorporating entrained salt. These deposits can be recovered as solid metal pieces through a consolidation process under molten salt.

Further work is planned to study this technique on actinide materials.

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