LLNL-SR-850866

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Electrorefining Bismuth Using AC Superimposed DC Waveforms

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June 28, 2023

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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Section 1

Overview

Bismuth has been successfully electrorefined using both direct current (DC) and alternating current (AC) superimposed DC waveforms on a kilogram scale at Brigham Young University (BYU) in Provo, Utah. Finding a suitable surrogate for Pu Electrorefining has always been a technical challenge. This work allows the possibility to improve Pu electrorefining with nonradioactive material at universities, which greatly reduces the cost at Lawrence Livermore National Laboratory (LLNL) for improving Pu Electrorefining. Several possible surrogates (Ce, In, Sn, Zn, and Bi) were selected based on their ability to mimic the Pu electrorefining process. Ce and In electrorefining experiments were conducted at the same temperature as Pu electrorefining in $CaCl_2$ while Sn, Zn, and Bi, electrorefining experiments were conducted at a lower temperature in a eutectic molten salt composed of LiCl, KCl, and $CaCl_2$. The electrorefining experiments using Ce with a Ga impurity did not produce a cathode ring. While the remaining Ce anode after electrorefining was significantly less than what was initially added, Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) analysis showed that the Ce had been oxidized and formed a colloid with the surrounding molten salt. This is supported in the literature by analysis of Ce-rich $CaCl_2$ mixtures. All the electrorefining experiments except for the Ce electrorefining experiments did not introduce an impurity to the system. Electrorefining experiments with In showed that the $InCl_3$ volatilized out of the molten salt to an extent that only a low current (<<1 A) could be supported without decomposing the molten salt. Zn electrorefining experiments had marginal success, however an easily separable product was not formed. The Zn had to be rinsed from the salt after the experiment. Of the identified potential surrogates. Investigated, only Bi and Sn yielded an easily separable product ring, which enables quantitative analysis of yields and coulombic efficiencies. Bismuth was first identified as a surrogate at BYU, while Sn was identified as a surrogate at LLNL later. Thus, the electrorefining experiments conducted at BYU using AC superimposed DC waveforms used Bi as the metal to be electrorefined.

Six experiments were conducted using different waveforms, each yielding a product ring, like the ones shown in Figure 1. Two DC runs were conducted to use as a baseline, one before (DC 1 Figure 1a) and one after (DC 2 Figure 1f) the four AC superimposed DC runs to account for any operational variance. The AC superimposed DC electrorefining experiments were run by combining low frequency (LF) and high frequencies (HF) with low amplitudes (LA) and high amplitudes (HA) for the AC sine wave, as shown in Table 1. The setup used for the experiments can be easily implemented at LLNL. Table 2 shows the starting mass of Bi along with the purity from the certificate of analysis for the Bi used for all 6 experiments.

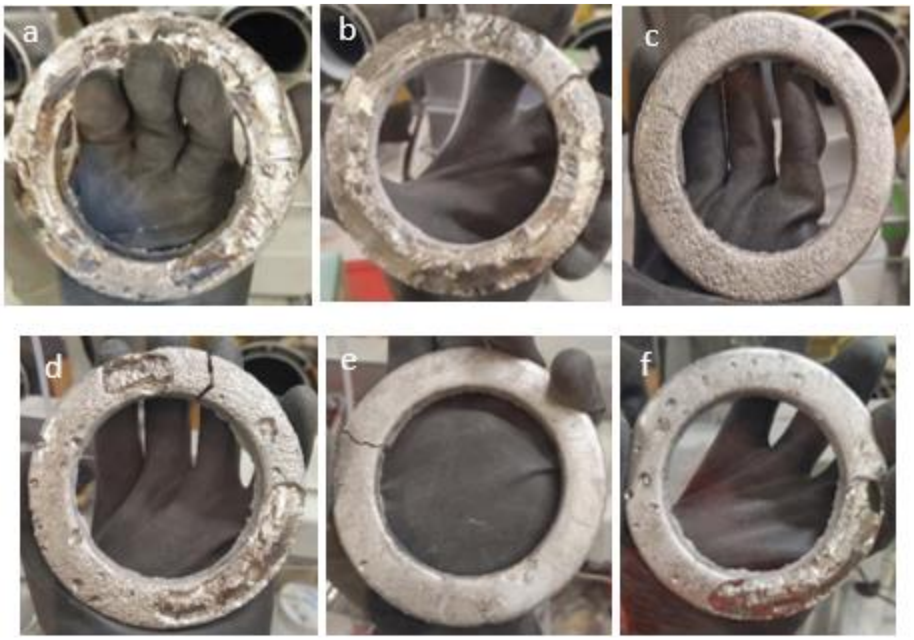

Figure 1. Top of the Bismuth Rings from the Electrorefining Experiments. a.) DC 1; b.) LF LA AC; c.) HF HA AC; d.) HF LA AC; e.) HF HA AC; f.) DC 2

Table 1. Power supply settings for each experiment

Experiment ID	DC voltage	AC frequency	AC amplitude
DC 1	2.18 V*	N/A	N/A
LF LA AC	1.85 V	100 Hz	1.23 V
LF HA AC	1.85 V	100 Hz	2.83 V
HF LA AC	1.85 V	1000 Hz	0.99 V
HF HA AC	1.85 V	1000 Hz	2.4 V
DC 2	1.85 V	N/A	N/A
*Represents average voltage, some variation in DC voltage occurred in the first 5 hours			

Table 2. Masses and purity of bismuth in the anode for each experiment

Experiment ID	Starting Bi Mass	Certificate of Analysis Purity
DC 1	800.03 g	99,99+% Bi, Al < 0.0005% , Cu < 0.0007% , Pb < 0.0009%, Tl < 0.0002%, As < 0.0002%, Cd < 0.0005% , Fe < 0.0010%, Sn < 0.0005%, Zn < 0.0004%
LF LA AC	800.57 g	
LF HA AC	801.49 g	
HF LA AC	799.83 g	
HF HA AC	800.06 g	
DC 2	799.32 g	

The power supply used was an off-the-shelf Asterion 3001A that can be placed on a shelf or rack and is simple to wire. While the Asterion power supply was simple to install, it has rigid software programing that was designed for avionics testing. This made executing the electrorefining runs labor-intensive. The Asterion control software only allows for voltage control because of a malfunction in the power supply’s communication interface, an external control system could not be used to turn the power supply on and off. To meet the milestones of the project as soon as possible, the power supply was not returned to be modified by Asterion. Hence, the power supply had to be turned off manually to measure the back EMF at specified intervals. This required the presence of the operator for the duration of the experiment. An external control system is feasible, when the power supply is modified by Asterion to enable an external control program to automate the control of the power supply. Due to these factors, BYU would recommend exploring the idea of building a custom power supply. A custom power supply could be made to be more adaptable, user-friendly, and seamless to operate. The custom power supply would consist of a DC power supply and an AC power supply wired together in series and could leverage existing DC power supplies in facilities.

Section 2

Key Results

The experiments conducted did not show any clear results for the possible benefits of using an AC superimposed DC waveform in Bi electrorefining, more runs are needed to show clear results. The runs had differences in yield, coulombic efficiency, and current profiles. It could not be determined if these differences were due to the difference in waveform or due to some other unexplained variable. The only runs that were repeated (DC 1 and DC 2) showed significant differences between the two experiments. Each of the AC superimposed DC runs variations were only performed once, which did not allow for any statistical analysis. While an experimental set-up to perform AC superimposed DC electrorefining was established successfully, additional experiments are needed to determine if statistically significant improvements in yield and efficiency are achieved using AC superimposed DC waveforms.

Table 3 shows the yield and coulombic efficiency of the bismuth electrorefining experiments conducted, and the experimental time. All the AC superimposed DC runs had a higher efficiency than the DC1 run. The DC2 run had a comparable efficiency to the AC superimposed DC runs. The yield and coulombic efficiency were highest for the HF -HA-AC runs. The DC2 run had nearly the same coulombic efficiency with almost 7% less yield than the HF HA AC run. The HF-LA-AC run had a higher yield but a lower coulombic efficiency than the DC2 run. The LF-LA-AC and the LF-HA-AC runs both had significantly lower yields than the DC2 run. The LF-LA-AC run had a lower coulombic efficiency while the LF-HA-AC run had a seemingly high coulombic efficiency compare to DC2. However, that efficiency of the LF-LA-AC run may be compromised by the possibility of calcium co-depositing with bismuth during that experiment. These inconsistent results highlight the need to perform more runs to eliminate confounding variables (e.g., Ca co-deposition) and establish better statistics for efficiency and yield for DC and AC superimposed DC runs to reach any conclusive finding.

Table 3. Power supply settings for each experiment

Experiment ID	Coulombic Efficiency	Yield	Experiment Duration
DC1	77.0%	82.8%	50 hrs
LF-LA-AC	80.8%	82.9%	50 hrs
LF-HA-AC	100.5%	63.2%	35 hrs
HF-LA-AC	91.9%	89.6%	45 hrs
HF-HA-AC	98.1%	93.8%	31 hrs
DC2	96.5%	87.1%	31 hrs

The voltage was controlled using the different waveforms explained in Table 1 for each of the electrorefining runs. The DC offset voltage for each run besides the DC 1 run was 1.85 V. While the offset voltage and the average voltage of each run was the same, the experiment durations for the DC2 and the HF-HA-AC runs were both significantly lower than the DC1, the HF-LA-AC, and the LF-LA-AC runs. The reduction in experiment time is primarily attributable to the higher current of electrorefining for the DC2 and the HF-HA-AC runs. While the LF-HA-AC run was also shorter, that was primarily due to the lower yield. Figure 2 shows the currents measured during each of the bismuth electrorefining experiments. The reason for the higher currents on some of the experiments is unknown without more repeatable experiments. The experimental set-up did not change between experiments. All 6 experiments were conducted as similarly as they could be within the abilities of the operators. The DC 1 run did have a different voltage profile due to it being the first run conducted. The appropriate voltage for the experiments was still being determined. This could partially explain the differences seen between the DC1 run and the DC2 run. The most likely reason for the higher currents seen in the HF HA AC run and the DC2 run is that they were the last two runs conducted. While there was no difference in the experimental set-up, to the knowledge of the operators, the dramatic differences seen between the first four runs (DC1, LF-LA-AC, LF-HA-AC, and HF-LA-AC) and the last two runs (HF-HA-AC and DC2) seem indicative of some change that occurred in the system between run HF-LA-AC and run HF-HA-AC). While differences were seen, there is no way to determine what caused the significant differences seen in these experiments with the data currently available. Further experiments might determine whether the differences seen can be attributed to the waveform used or not. Observing the consistency of the results when using the same waveform will determine this.

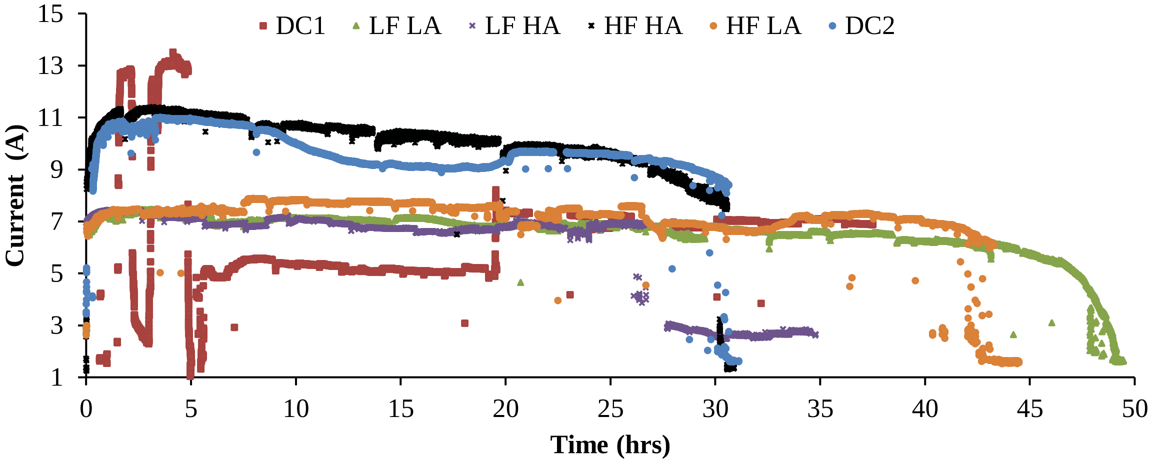

Figure 2. Electrorefining Currents Measured During the Six Bismuth Electrorefining Runs Conducted

While the average voltage applied was the same for each experiment, there were differences seen in the current response of each different run. Alternatively, the current for the LF-LA-AC, the LF-HA-AC, and the HF-LA-AC runs all started out at about 7 amps. After differing amounts of times, the current decreased at different rates until the run was terminated. The current decreasing at different rates is indicative of different rates of change in the resistance experienced in the electrochemical cell. The DC2 and HF-HA-AC runs started around 8 amps and then increased over a short time to 11 amps. After which, the current slowly decreased until the runs terminated at approximately the same time as after a steep decrease in current. The current for the DC 1 experiment was sporadic. This was due to changes in the electrorefining voltage initially. Initially, the electrorefining voltage was set too high as the back EMF reached 2 V which indicates that calcium was being deposited at the cathode. In each of the subsequent runs, the offset voltage was set to 1.85 V and the back EMF did not reach 2 V for any of those runs.

These results show that AC superimposed DC waveforms were successfully used to electrorefine bismuth with varying results for the first set of experiments. Due to the limited number of runs, any statistical certainty is not possible. Additionally, the differences in the experiments do not have any easily identifiable reason for the different performances. AC superimposed DC runs showed improvement in both efficiency and yield in comparison to DC1, with exception of the yield for LF-HA-AC, which was cut short. However, DC2 showed that a DC only waveform could potentially perform at the same level as AC superimposed DC waveforms. Future experiments, performed in the same manner, could be used to better quantify, and optimize the impact of the AC superimposed DC method on average. It may be that the level of yield and efficiency from DC2 is less common in DC only electrorefining runs. The AC superimposed DC runs showed that those levels of yield and efficiency may be commonly achieved. More ER runs would allow the determination of the relative amount of consistency seen between experiments conducted using just a DC waveform and an AC superimposed DC waveform with the same experimental conditions. Furthermore, the most optimal setting for AC superimposed DC ER may not have been tested yet. Due to the limited number of runs, only two frequencies and two amplitudes could be tested.

Section 3

Summary and Future Work

The initial motivation for experimenting with an AC superimposed DC waveform in actinide electrorefining was due to the positive effects seen in other electrorefining systems. Conventionally, DC waveforms of constant current or potential have been used to electrorefine actinides. Using an AC superimposed DC waveform is an alternative that has been shown to improve the efficiency and throughput of copper electrorefining in aqueous solutions [1]. While AC superimposed DC waveforms have been used in various applications, the findings have been conflicting depending upon the experimental system being studied. While some studies have seen an increase in efficiency or rate [2–5] , other studies have seen a decrease [6,7]. Some of the benefit of superimposing AC over DC is that solid deposits formed are more uniform, smooth, and compact [8–12]. The decrease in polarization of the electrodes is an additional benefit of an AC superimposed DC waveform for metal deposition [13–16]. Some studies have noted that the beneficial effects were only seen when the AC amplitude was greater than the direct current applied [17–19]. AC superimposed DC waveforms have only been used in systems that use solid electrodes. One study on the deposition in a deep eutectic solvent was found [20], but no studies had been conducted using a molten salt.

The findings of this study were inconclusive, but an experimental system to conduct kilogram scale electrorefining with an actinide surrogate able to use AC superimposed DC waveforms was successfully established with six runs conducted. The liquid metal electrodes adds an additional dynamic to the effects of AC superimposed DC that is still not well understood. The average efficiency for AC superimposed DC electrorefining was higher than the average DC electrorefining efficiency. Because of the limited runs, it is not possible to determine if the improved efficiency is significant and consistently observed. More measurements are required with greater control and repeated runs are needed to determine if there are any benefits from AC superimposed DC electrorefining.

The following actions are recommended to improve future electrorefining runs using an AC superimposed DC waveform. A custom power supply or external control program tailored to electrorefining could be built and tested. The external control system would be explored first as this will be the lowest cost route for the project because the existing power supply can be used with a data acquisition system and software to integrate other observables (e.g., temperature) and provide improved control and feedback. This will aid in identifying and controlling any variables unrelated to the changes in power supply settings. Further experiments are needed to determine if the waveform applied for electrorefining affects the results because the findings of these experiments were not statistically significant. More electrorefining runs conducted would indicate the level of consistency seen in electrorefining experiments when using the same voltage control waveform. There are three primary avenues to quantify more precisely the impact of AC superimposed DC waveforms on electrorefining:

1.) Repeating the runs using the established setup to assess reproducibility and the statistical significance of the observed differences in yield and coulombic efficiency.
2.) Conducting electrorefining runs at more varying frequencies and amplitudes to determine the most impactful frequency and amplitude for electrorefining with an AC superimposed DC waveform.
3.) Using electrorefining models and simulations to better understand the physical processes that may be affecting the observed electrorefining results.

The key accomplishments of this work are:

1.) Establishing a viable surrogate for Pu ER.
2.) Establishing an experimental testing capability for electrochemistry of Pu surrogates.
3.) Established gaps in understanding and a plan for addressing those to determine if AC over DC would be beneficial.

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