ELECTRIC POTENTIAL FIELD CALCULATIONS
FOR THE FCF MARK-IV ELECTROREFINER

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ABSTRACT

The electric potential field and resulting current densities are studied for the FCF Mark-IV electrorefiner during the direct transport mode of operation. The results are used in estimating primary current distributions and ohmic resistances between components of the electrorefiner for various cell configurations. Each configuration is analyzed for operation with a single power supply, dual anodes and serial cathodes, and dual power supplies. The effect of cathode deposit growth from a bare mandrel to a 10" diameter cylinder is also studied. A comparison of the calculated results with data from initial electrorefiner experiments in direct transport mode indicates a good agreement for cell resistance and reference electrode readings at the beginning of an experiment. The difference between the calculated results and experimental data provides information regarding overpotentials that form on the surfaces of the electrorefiner components.

INTRODUCTION

Argonne National Laboratory (ANL) is currently demonstrating an electrometallurgical process for treatment of spent nuclear fuel from the Experimental Breeder Reactor-II (1). The project demonstration is being performed in the Fuel Conditioning Facility (FCF) that is located at ANL-West site in Idaho. The FCF Mark-IV electrorefiner consists of a 1 m diameter steel vessel filled with molten salt electrolyte at 500°C operating temperature. The electrolyte, molten LiCl-KCl eutectic (41 mol% KCl) with dissolved UCl₃, sits on top of the pool of molten Cd which is approximately 10 cm from the vessel bottom. In direct transport mode of operation of the electrorefiner, spent nuclear fuel pin segments are loaded into rotating rectangular anodic dissolution baskets that are assembled together in a cruciform arrangement. A rotating steel mandrel is used as the cathode. As dendritic deposit grows at the cathode, its size is limited by scraping the excess material. Both anode baskets and cathode mandrel are immersed in the electrolyte to a depth of 23 cm, about 10 cm above the Cd pool.

The FIDAP finite element analysis code(2) has been used to calculate the 3-D electric potential field within the electrorefiner using similarity between the potential distribution in an electrolytic solution and the temperature distribution in a heat
conducting medium. The results of the analysis have been used mainly in estimating the primary current distribution and ohmic resistances between components of the electrorefiner under various operating conditions, and in evaluation of the shorting of the anode baskets.

The electrorefiner is modeled as the electrolyte surrounded by the vessel and the cadmium pool with higher electrical conductivity than that of the molten salt. In direct transport mode, the vessel wall and the cadmium pool provide alternate current paths representing a potential for dendrite growth on the metallic surfaces near the electrodes. With no dendrites on the metallic surfaces near the cathode, typically only the portion of the vessel near the anode baskets can be expected to be electrically conducting. The metallic objects (baffles, scraper support assemblies, and the central cadmium mixer shaft) that change the topography of calculated equipotential surfaces are also included in the model.

The electrorefiner is equipped run with two direct current power supplies operating under controlled current conditions, each supporting a pair of anode cathode electrodes. However, most of the electrorefiner tests to this date have been performed with a single power supply. Thus, the cell voltage is determined by the cell configuration, operating conditions, and the chemical state of the electrorefiner. The electrode potentials are specified as boundary conditions, and the vessel and cadmium pool potential is assumed to be floating between the two values with no net current passing through the outer boundaries of the model (no ground connection).

**CELL CONFIGURATIONS IN DIRECT TRANSPORT**

Any metallic surface (either vessel wall or the cadmium pool) near the anodic dissolution baskets with electric potential less than that of the anode electrode is subject to ion deposition and dendrite formation provided the circuit can be closed by pulling current from the cadmium pool near the cathode. Similarly, any metallic surface near the cathode electrode with prior dendritic accumulation and electric potential greater than that of the cathode can give current into the system provided the circuit can be closed by passing current to the cadmium pool (or the vessel) near the anode baskets.

The concentration and surface overpotentials determined mainly by details of mixing conditions and the chemical state of the electrorefiner can introduce additional resistances to the flow of electric current and alter these current paths. For simplicity, the surface and concentration overpotentials are included in this analysis only as infinite contact resistances. Therefore, the calculated path resistances are the ohmic drops between the components of the electrorefiner and they are based only on geometric considerations. In other words, the calculated equipotential surfaces and resulting current densities do not include the effects of secondary currents that could form because of overpotentials. On the other hand, since the ignored overpotentials would reduce the total
current passed, the results of this analysis should provide a lower limit for the overall cell resistance for each configuration considered as long as the original geometry is not distorted by material accumulation.

During a direct transport run, depending on the conditions of the electorefiner from prior operations, four limiting modeling states can be identified, each with distinct characteristic cell resistance.

- **Insulated vessel and depleted pool (ivdp):** When the vessel is clean and the cadmium pool is depleted in current-carrying species, both the vessel wall and the cadmium pool establish insulated surfaces if the electrode potential difference is below the cut-off voltage. In this case, the equipotential surfaces are perpendicular to the vessel wall and molten salt-cadmium pool interface. The ohmic cell resistance is then determined by current paths within the electrolyte, directly from the anode baskets to the cathode cylinder(s). In direct transport mode, this state may be expected following a deposition run that depletes the pool.

- **Insulated vessel and saturated* pool (ivsp):** If the cadmium pool is not depleted, it behaves as an intermediate electrode by receiving current under the anode baskets and passing current (supplying ions) to the electrolyte under the cathode electrode. If we assume that the vessel wall is still insulated due to infinite contact resistance (overpotential), equipotential surfaces become parallel to the salt-cadmium pool interface, but perpendicular to the vessel wall. Then, the cell resistance is determined by the current paths between the electrodes and paths to and from the cadmium pool.

- **Conditioning vessel and saturated pool (cvsp):** When the vessel is clean and the cadmium pool is not depleted, part of the vessel wall and the cadmium pool near the anode baskets will provide alternate current paths as explained above. Collecting dendrites on the vessel is often referred to as “vessel conditioning.” Since the electrical conductivity of the vessel and the liquid cadmium is several orders of magnitude greater, part of the vessel that receives the ion current and the entire cadmium pool constitute an equipotential surface. Therefore, the cell resistance is determined by currents in and out of this surface and the direct current paths between the electrodes. Among the four configurations considered, this one is most likely to be at a given time during operation of the electorefiner.

- **Preconditioned vessel and saturated pool (pvsp):** If the vessel wall contains dendritic deposits from prior operations, besides passing current to the vessel, it is possible to pull current from the vessel into the electrolyte where the electric

* The cadmium pool does not have to be saturated to behave as an intermediate electrode. The term “saturated” is to emphasize that calculated resistances do not include effect of overpotentials.
potential is lower (near the cathodes). As an extreme case, the whole vessel (and the cadmium pool) can be considered conductive, resulting in the entire external boundary of the molten salt to form an equipotential surface. This configuration is the most general case in terms of available current paths and it yields the least cell resistance. The preconditioned vessel conditions may be expected after a cathode stripping operation. It can also occur, to some extent, following an anodic dissolution run or a direct transport run with an alternated anode port assignment.

Most of the earlier electrorefiner tests to date have been performed with a single power supply providing direct current for a pair of anode-cathode electrodes (1). More recently, a series of Mark-IV electrorefiner tests have been performed with dual power supplies, each operating under controlled current conditions and supporting a pair of anode-cathode electrodes. Both modes of operation are considered in this analysis. Furthermore, additional calculations for dual power supplies are performed to support analysis of a proposed mode with dual anode baskets and serial cathodes (one cathode at a time). As the cathode deposit grows in size from a bare mandrel to a maximum size of 10" diameter cylinder, the electric potential field and the resulting primary current distributions differ. These variations are studied for varying cathode deposit size assuming the cathode product maintains a cylindrical shape as it grows.

**RESULTS**

The typical electric potential field for the conditioning vessel and saturated pool (cvsp) case at the beginning of a direct transport run is shown in Fig. 1 for operations with single and dual power supplies. Ohmic drops between the electrodes, vessel, and the cadmium pool of the electrorefiner are characterized as individual resistors in an analogous circuit representing the lumped parameter equivalent of the electrorefiner. The lumped parameter approach forms the basis of chemical equilibrium models that are used to support process modeling activities. The path resistances and direction of currents in most general case (pvsp) with dual power supplies are described in Fig. 2.

The calculated results for a bare mandrel are provided in Table I. Since the Mark-IV experiments are performed with controlled current, only the potential difference between the electrodes, \(\Delta V\), is known. Individual electrode potentials are measured with respect to vessel and used as the boundary conditions in the calculations. The electric potential of the cadmium pool and the conducting portions of the vessel is assumed to be floating between the anode and cathode potentials.* The ohmic resistances are calculated from

\[
R_{\text{cell}} = \frac{\Delta V}{I_{a1} + I_{a2}}, \quad R_{pS1} = \frac{\Delta V}{I_{a1}}, \quad \text{and} \quad R_{pS2} = \frac{\Delta V}{I_{a2}}.
\]

* The electrode voltages in Table I are adjusted with respect to a zero vessel/pool potential.

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For all cases analyzed, $\Delta V = 0.4$ Volt with $V_{a1} = V_{a2}$ and $V_{c1} = V_{c2}$ (i.e., $R_{a1a2} = R_{c1c2} = 0$). Therefore, the cell resistance can also be determined in terms of path resistances from

$$\frac{1}{R_{\text{cell}}} = \frac{1}{R_{a1c1}} + \frac{1}{R_{a1c2}} + \frac{1}{R_{a2c1}} + \frac{1}{R_{a2c2}} + \frac{1}{R_{a1p}} + \frac{1}{R_{a1w}} + \frac{1}{R_{a2p}} + \frac{1}{R_{a2w}} + \frac{1}{R_{p1c1}} + \frac{1}{R_{p1c2}} + \frac{1}{R_{w1c1}} + \frac{1}{R_{w1c2}}$$

Based on the results in Table I, the resistance measured by individual power supplies in dual power supply mode is about the same as the resistance measured with a single power supply at the beginning of a direct transport run when the pool is saturated. However, the overall cell resistance with dual power supplies is about half the value calculated for single power supply. When dual anode baskets provide the current for a single cathode (serial cathodes), the decrease in the overall cell resistance is between 15 to 30% depending on the cell configuration. Compared to operation with a single power supply, the reduction in cell resistance with dual power supplies becomes more pronounced as the cathode product gradually grows to its full size.

The results also show that, unless the cadmium pool is depleted, much of the electrorefiner current comes through the pool. Even when the vessel is eliminated as a possible current path (cases with an insulated vessel), the current passed through the pool is between 40% and 60% of the total ER current; i.e., on average half the cathode current comes from the Cd pool. In more likely scenario (cvs), the pool current is between 50% and 75% of the total ER current as the vessel becomes part of the circuit and contributes to the current pulled from the pool. The relative importance of ER components (the pool and portions of the vessel near the electrodes) in providing alternate current paths is reflected in Table I as the calculated path resistances. The anode-cathode path resistances are much bigger when the pool and/or vessel are considered part of the circuit.

As the cathode product grows to its full size, the current density on the cathode product goes down due to increased surface area, but the total current passed increases by a factor of two for all cases considered. Consequently, the overall cell resistance decreases proportionally. The variations in the calculated ohmic cell resistance as a function of diameter of the cathode deposit is shown in Fig. 3 for operation with single power supply, dual anodes and serial cathodes, and dual power supplies.

At the beginning of a run, the current density on the cathode surface increases by 15% (cvs) to 32% (ivd) because of steeper electric potential gradient when dual anode baskets are used with a single cathode. As the cathode product grows, the difference between the two modes of operation becomes more pronounced--25% (cvs) to 35% (ivd) at the end of a run. When dual anode baskets are used with dual cathodes, the
calculated current densities on the cathode products increase two fold for the given ER voltage compared to operation with a single power supply. Since the ER is operated under controlled current conditions, operation with dual power supplies would mean a reduced electrode voltage difference for a given ER current.

**COMPARISON with the EXPERIMENTS**

The resistance measured by an individual power supply (R_{PS1} or R_{PS2}) exhibits large fluctuations during a direct transport run as overpotentials form due to depletion of the anode baskets, as the cathode product grows and excess material starts getting scraped, and as large chunks of dendrites fall under the cathode electrode. Therefore, a comparison of the calculated results with data from experiments is useful mostly at the beginning of a direct transport run when the cathode is bare mandrel and overpotentials are typically minimal. Even the measured initial resistance deviates from run to run depending on the parameters from previous operations. Large deposit drops from cathode during a previous run results in an initially low resistance due to reduced distance for ohmic drops. Also, an experiment followed by a series of direct transport runs exhibits heavy shorting of anode baskets to the vessel/pool caused by dendritic accumulation on scraper support hardware.

A comparison of the calculated results for a bare mandrel with data from the electrorefiner experiments is provided in Table II for various cell configurations. The experimental resistances in Table II are the average over a group of runs with identical operational parameters. The agreement between the calculated and experimental numbers is better when more runs are included in the average. The first electrorefiner experiment which is categorized as “insulated vessel and depleted pool” case indicates that, even when the U concentration in the Cd pool is well below saturation, the pool provides paths for current flow despite a large concentration overpotential. The preconditioned vessel cases are identified after a cathode stripping operation with substantial mass transfer. A comparison of calculated results with data from reference electrodes at the beginning of a direct transport run also indicates a good agreement consistent with results in Table II.

As noted above, the discrepancy between the experimental data and the calculated results grows as the cathode product gets larger and the overpotentials on the surfaces of the electrorefiner components alter the current distributions. Since the ignored overpotential terms would reduce the total current passed in the system, the results reported here provide a lower limit for the resistances measured by each power supply. Therefore, the difference between the calculated and observed values could be useful in understanding the electrode, vessel and pool overpotentials. Particularly, the limited comparisons for experiments with dual power supplies provide useful information on overpotentials on the anode and cathode, relative cathode deposit size, and vessel polarization using additional constraints during asynchronous operations.
The observed cell resistance in some electrorefiner experiments with single power supply is smaller than the calculated ohmic resistance even for the preconditioned vessel (pvs) case. This suggests a modified geometry, possibly caused by dendritic accumulation on the vessel near the rotating anode baskets. This hypothesis could be further substantiated by observed shorting of the anode electrode just after the beginning of these experiments as evident in anode electrode voltage signals. Such distortions in geometry, and subsequent shorting, have important implications on the electrorefiner performance: It deteriorates the anodic dissolution rate, but appears to improve the cathode deposit morphology and, as a result, the throughput. The effect of electrical shorting between the anode baskets and the electrorefiner vessel on the stability of cathode deposit morphology is also investigated (3).

CONCLUSIONS

Three-dimensional electric potential field within the FCF Mark-IV electrorefiner and the primary current densities on the surfaces of electrorefiner components have been calculated. The calculations are performed to analyze the operation of the electrorefiner in direct transport mode with single and dual power supplies by modeling the molten salt electrolyte, vessel wall, and the cadmium pool as electrically conducting media, each with characteristic conductivity. The results of the analysis are used to estimate ohmic resistances under various operating conditions and for varying cathode deposit size.

Calculations suggest that one would expect an initial cell resistance of as low as 10 mΩ with a single power supply and a clean vessel if the overpotentials can be ignored. With dual power supplies, effective cell resistance could be as low as 5 mΩ. The cell resistances could drop by half as the cathode deposit grows from a bare (thick) mandrel to a 10" diameter cylinder. The calculated results are generally in good agreement with data from the Mark-IV experiments for resistances measured by the individual power supplies at the beginning of a direct transport run. The discrepancy grows as the cathode product gets larger and the overpotentials form on the surfaces of the electrorefiner components. Since the calculated results provide a lower limit for cell resistance, the difference between the calculated and observed values provides insight into these overpotentials.

It appears that the cadmium pool plays an important role in the electrorefining process even in direct transport mode by acting as an intermediate electrode and providing alternate current paths, especially through the vessel wall. Unless it is depleted, a large fraction of the total electrorefiner current comes through the pool. The alternate paths through the vessel and pool result in ion deposition on the metallic surfaces near the anodic dissolution baskets, particularly on the sharp objects like scraper mount bolts and/or bottom scraper support rings. The dendritic growth on these objects may result in eventual shorting of the anode electrode as exhibited in some direct transport.
experiments. The effect of electrical shorting between the anode baskets and the electrorefiner vessel on the stability of cathode deposit growth is being investigated.

In an attempt to incorporate the surface and concentration overpotentials into the model, currently a series of iterative calculations are being performed by running the FIDAP and the chemical equilibrium codes in sequence. The path resistances provided by the FIDAP model are being used in predicting the overpotentials by the chemical equilibrium model and, in return, these overpotentials are being incorporated in the FIDAP model as contact resistances. Repeated use of this procedure is expected to provide more accurate distribution of ion currents between the electrorefiner components and eventually converge to a set of final path resistances through iterative use of the FIDAP and chemical equilibrium models.

ACKNOWLEDGEMENTS

Work supported by the U.S. Department of Energy, Nuclear Energy Programs under contract W-31-109-ENG-38.

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Fig. 1. The electric potential field for conditioning vessel and saturated pool (cvsp) case at the beginning of a direct transport run for operation with a single and dual power supplies, respectively.
Fig. 2. Current paths and characteristic resistances for direct transport mode of operation of the Mark-IV electrorefiner, and representative circuit diagram.
Table I. The Calculated results for the beginning of a direct transport run with cathode as bare mandrel.

| Electric Potential (Volt) | Single Power Supply |
|---------------------------|---------------------|
|                           | ivdp    | ivsp    | cvsp    | pvsp    |
| Cathode 1 Port A          | -0.20   | -0.27   | -0.31   | -0.29   |
| Cathode 2 Port C          | 0.00    | 0.00    | 0.00    | 0.00    |
| Anode 1 Port B            | 0.20    | 0.13    | 0.09    | 0.11    |
| Anode 2 Port D            | 0.00    | 0.00    | 0.00    | 0.00    |
| Cd Pool and Vessel        | 0.00    | 0.00    | 0.00    | 0.00    |

| Currents (Amp)            |             |                     |                     |
|---------------------------|-------------|---------------------|
| Cathode 1 Port A          | 25.75       | 36.43               | 40.70               |
| Cathode 2 Port C          | 0.00        | 0.00                | 0.00                |
| Anode 1 Port B            | -25.75      | -36.43              | -40.70              |
| Anode 2 Port D            | 0.00        | 0.00                | 0.00                |
| Cd Pool                   | 0.00        | 23.45               | 10.14               |
| ER Vessel                 | 0.00        | 0.00                | 19.09               |

| Overall Cell              | 15.54       | 10.98               | 9.93                |
| Power Supply #1           | 15.54       | 10.98               | 9.93                |
| Power Supply #2           | 34.43       | 34.43               | 34.43               |
| R_{151}                   | 5.53        | 8.55                | 8.39                |
| R_{152}                   | 5.65        | 8.88                | 8.61                |
| R_{251}                   | 5.65        | 8.88                | 8.61                |
| R_{252}                   | 5.65        | 8.88                | 8.61                |
| R_{351}                   | 5.65        | 8.88                | 8.61                |
| R_{352}                   | 5.65        | 8.88                | 8.61                |
| R_{45}                    | 5.65        | 8.88                | 8.61                |
| R_{46}                    | 5.65        | 8.88                | 8.61                |
| R_{56}                    | 5.65        | 8.88                | 8.61                |
| R_{24}                    | 5.65        | 8.88                | 8.61                |
| R_{34}                    | 5.65        | 8.88                | 8.61                |
| R_{35}                    | 5.65        | 8.88                | 8.61                |
| R_{45}                    | 5.65        | 8.88                | 8.61                |
| R_{46}                    | 5.65        | 8.88                | 8.61                |
| R_{56}                    | 5.65        | 8.88                | 8.61                |

| Dual Power Supplies       |
|---------------------------|
| ivdp | ivsp | cvsp | pvsp |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.00 | 0.00 | 0.00 | 0.00 |
Fig. 3. Variations in the calculated ohmic cell resistance as a function of cathode deposit size for operation with (a) single power supply, (b) dual anodes and serial cathodes, (c) and dual power supplies.
Table II. Comparison of the data from Mark-IV experiments with calculated resistances when the cathode is bare mandrel.

| Power Supply          | Cell Configuration | Mandrel | Temp. (°C) | Cathode #  | Resistance Measured by Power Supply (mOhm) |
|-----------------------|--------------------|---------|------------|------------|-------------------------------------------|
|                       |                    |         |            |            | Average | Calculated | % Diff. |
| Single power supply   | ivdp               | Thin/Long | 500 | 1 | 16.0 | 17.7 | 10.5 |
|                       | cvsp               | Thin/Long | 500 | 1,2 | 12.8 | 11.6 | 9.1 |
|                       | cvsp               | Thick/Short | 500 | 25,29,30 | 9.1 | 9.8 | 8.4 |
|                       | cvsp               | Thick/Long | 500 | 32,33,59,61,63,66,67 | 9.4 | 9.5 | 1.0 |
|                       | cvsp               | Thick/Long | 450 | 37,39,40,41,43,44,45,48,49,50 | 11.4 | 11.3 | 1.0 |
|                       | pvsp               | Thin/Long | 500 | 1,4 | 8.7 | 9.9 | 13.3 |
|                       | pvsp               | Thin/Short | 500 | 7 | 10.5 | 10.3 | 1.5 |
|                       | pvsp               | Thick/Long | 450 | 39 | 9.5 | 9.5 | 0.5 |
| Dual anodes, serial cathodes | cvsp   | Thick/Long | 500 | 71,72 | 17.0 | 17.0 | 0.1 |
| Dual power supplies   | cvsp               | Thick/Long | 500 | 55,56 | 9.5 | 9.4 | 1.4 |
|                       |                    |         |            | 54 (with larger cathode# 53) | 12.0 | 11.4 | 5.0 |