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INFORMATION TECHNOLOGY AND DATA MINING FOR SPENT FUEL TREATMENT*

by

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ABSTRACT

Information technology is being used to provide interactive access to data collected from the electro-metallurgical treatment of spent fuel. The data are results from many hundreds of experiments performed to better characterize the processes by which uranium is separated from the waste products. Web-based display and relational database query capabilities facilitate the identification of trends in the data and the relating of these trends to the underlying electrochemistry. The objectives are to ensure that the process behavior is well understood, to make readily accessible the necessary data for development and validation of models, and to identify unexpected trends in the data as indications of phenomena not yet represented in the models.

1. INTRODUCTION

Electro-metallurgical methods for processing spent nuclear fuel have been under development at Argonne National Laboratory since the mid-1980s. Many hundreds of experiments have been performed to develop and better characterize the processes by which uranium is separated from the waste products in spent nuclear fuel. The basic process involves the electrochemical dissolution of the uranium in the fuel and its subsequent collection on a cathode with minimal carry-over of impurities.[McPheeters, 1997]

The ensemble of experiments performed to date represent a rich body of data for the electrometallurgical process. The greatest information is extracted from these experiments when they are regarded as a related set tied together by the underlying electrochemistry and conservation laws, rather than a set of experiments independent of each other. To help with extracting this cross-experiment information the experiment data have been placed in a database that can be accessed through the World Wide Web by authorized personnel. This paper describes mining the database and some findings that have led to improved understanding of the electrorefining process.

Data mining involves the use of software tools to facilitate the identification of trends and patterns in data sets too large to be captured through traditional paper bound methods. In the case of the Spent Fuel Treatment project the number of experiments is very large, the experiments are spread out over many years, there are several experimenters involved, and the experiment data was spread across several geographically separate facilities. A method was needed to make all the data accessible to those in the project.

This paper describes how information technology has been used to make electrorefiner data accessible for analyses. Examples are given of how the database has supported: (1) development and validation of models; (2) data inspection to ensure that process behavior is well understood; and, (3) identification of unexpected trends that indicate phenomena not yet represented in the models.

2. DESCRIPTION OF THE ELECTROREFINER

The electrorefiner consists of a 36 in. cylindrical vessel containing a pool of molten cadmium of uniform depth in the range of 7 to 15 cm. deep at the bottom of the vessel. A salt pool of LiCl-KCl electrolyte approximately 37 cm. deep floats on the cadmium pool. The tank cover has four ports, one for a salt pool mixer, another for a cadmium pool mixer, an anodic dissolution port for dissolving material, and a cathode port for growing deposits. In the port used to grow deposits there are ceramic scrapers designed to shape the deposit into a right circular cylinder as it grows. The electrorefiner salt pool is normally maintained at 500^0 C. A schematic of the electrorefiner is shown in Fig. 1.

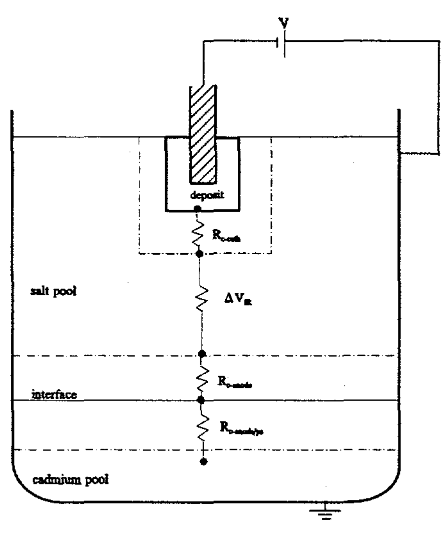

Fig. 1 Electric Circuit Equivalent of Electrorefiner

3. INFORMATION TECHNOLOGY

The use of information technology made it possible to provide electronic desk top access to experiment records formerly distributed across several locations and in several different media. The data included experiment log books in hardcopy form, monthly reports of post-experiment results in word processor format, images of equipment and process product as photograph negatives, chemical analysis of samples in hardcopy form, and computer files of digital acquisition system data recorded during each experiment. The data, however, is now stored in database tables and can be viewed as Web pages. Access is limited by IP address to ANL personnel working on the project.

3.1 Relational Database Model

The experiment data and records described above are stored using the Oracle Relational Database Model (RDBM). The RDBM provides tables for housing the data, permits definition of logical relationships among tables, and supports the retrieval of information by data association. A Master table associates a unique key with each experiment. The key is used to identify the row in each of five lower level tables that contain information on the experiment. These tables are Run Description, Initial Conditions, Time Dependent Process Variables, Deposition Results, and Analytic Chemistries.

3.2 Web Interface

The capability for interactive access to the data by modelers, analysts, and experimenters is provided by an Internet interface to the database. The Common Gateway Interface (CGI) approach of linking database tables was adopted. In this approach the World Wide Web serves as an efficient medium for retrieving information from the database.

3.3 Query Modes

The contents of a single run can be *browsed*, the runs that satisfy user specified conditions can be *searched* for, and the values of parameters across a subset of runs meeting user conditions can be *trended* using scatter plots or a cluster analysis. All this can be done interactively over the World Wide Web from the user's browser.

4. DATA MINING

Three cases are described where the understanding of electrorefining on an engineering scale has been improved through use of the database.

4.1 Search on Conditions: Experiment Selection

An application involved identifying experiments suitable for use in estimating a value for the exchange current density for uranium. This parameter represents a fundamental limit on the rate that uranium can be electrotransported out of the cadmium pool. The parameter appears in electrochemical models and influences the proportioning of the applied voltage across the various loss terms (surface overpotential, concentration overpotential, and ohmic) and hence plays a key role in the carry over of impurities to the cathode product. The absence of a published value led us to estimate a value.

The search capability was used to identify experiments in the database satisfying certain conditions. These conditions ensure that the data reflect processes consistent with the models to which data was fit. The conditions are: 1) uranium is electrotransported exclusively from the cadmium pool and there is no contribution from the vessel wall; 2) the anode surface is flat with no scraped dendrites heaping up above it under the deposit; and, 3) there is no shorting, that is, dendrites are not bridging spaces that are normally open. The runs are not, however, labelled explicitly in the database as to whether each condition is met. Instead inspection of the transport mode, applied voltage, and uranium content in the cadmium pool data by the analyst was needed to make that determination. The list of candidate runs was reduced to about ten runs from an initial number of about 200 after the database was used in this inspection.

A value for the exchange current density was obtained by fitting the model to data from the experiments. The most reliable value is obtained for an electrorefiner state where the controlling rate process is the surface overpotential at the salt-cadmium interface. In this regime the current is very sensitive to the value of the exchange current density parameter. The associated electrorefiner state exists for certain values of the ratio of uranium to zirconium concentration in the cadmium pool and relative current fractions. The database was used to further classify with respect to these measures among those runs already meeting the three conditions above. The runs and the class they belong to are given in Table 1. These runs were used to estimate the uranium and zirconium exchange current densities.

The values obtained provide a measure of the role of surface overpotential in electrorefiner performance. As the original source of uranium is depleted an increase in impurity transport and reduction in current will occur due to surface overpotential increase. The depletion level at which this occurs depends on the value of the exchange current density. The nominal value obtained for exchange current density at 500^0 C is 22 milliamps/cm^2 for uranium dissolved in cadmium to saturation and is 2200 milliamps/cm^2 for solid uranium. The experimental uncertainty in these values is 50 percent. There is a further uncertainty associated with the lumped parameter approach for representing the cadmium pool. A CFD calculation in the future will eliminate this source of uncertainty. These values indicate that impurity transport and reduced current due to increasing surface overpotential should not be an issue until the uranium in pin segments is depleted down to a few percent and until uranium in the cadmium pool is depleted down to a few percent of the value at saturation.

Table 1 Classification of Deposition Runs

Class	Criteria [a]	Expected Trend	Runs	$[U]_{dep}/[Zr]_{dep}$	$[U]_{Cd}/[U]_{Cd-sat}$	$[Zr]_{Cd}/[Zr]_{Cd-sat}$
A	$f_{i_U} \approx 1$, $[U]_{Cd} < [U]_{Cd-sat}$	surface overpotential dominates	129	40	0.003	0.05
			69	8.3	0.13	0.63
B	$f_{i_{Zr}} \approx 1$, $[U]_{Cd} < [U]_{Cd-sat}$, $[Zr]_{Cd} \approx [Zr]_{Cd-sat}$	surface overpotential dominates	64	0.22	0	1
C	$f_{i_U} \approx f_{i_{Zr}}$, $[Zr]_{Cd} \approx [Zr]_{Cd-sat}$, $[U]_{Cd} < [U]_{Cd-sat}$	surface overpotential dominates	63	0.63	0.05	1.0
			97	1.3		0.4

[a] f_i = current fraction, $[U]_{Cd}$ = cad pool U concentration, $[Zr]_{Cd}$ = cad pool Zr concentration, sat = saturation

4.2 Timeline Analysis: Long Term Behavior of Zirconium

Even though electrorefining of spent fuel proceeds on a batch basis, the chemical state of the electrorefiner evolves on a continuous basis. The content of the electrorefiner changes as material is added at the start of a run, is removed at the end of the run, and as the constituents react over time. Tracking the contents through time through a mass balance and comparing this to expected behavior is useful for discovering unexpected trends. The process of doing so revealed zirconium was behaving in the electrorefiner differently than expected.

The behavior was initially hinted at by the difficulty found in recovery operations when growing zirconium cathodes. The time history of the zirconium content of the electrorefiner shown in Fig. 1 and the dissolution rate of zirconium solids in the electrorefiner shown in Fig. 2 were prepared from the database. The data indicate that for zirconium in excess of what the cadmium pool could dissolve, the rate at which this zirconium later dissolves back into an unsaturated cadmium pool correlates more strongly with when zirconium metal was last introduced rather than the means used to bring it out of solid form. One possibility is that zirconium combines over time with other materials in the electrorefiner to form a substance from which the zirconium is not nearly as readily dissolved either passively or electrochemically as the pure metal. Samples taken from the electrorefiner showed the presence of a solid substance composed of zirconium, uranium, and cadmium. These findings pointed to the need for a better understanding of the long term behavior of zirconium if the zirconium inventory is to be managed.

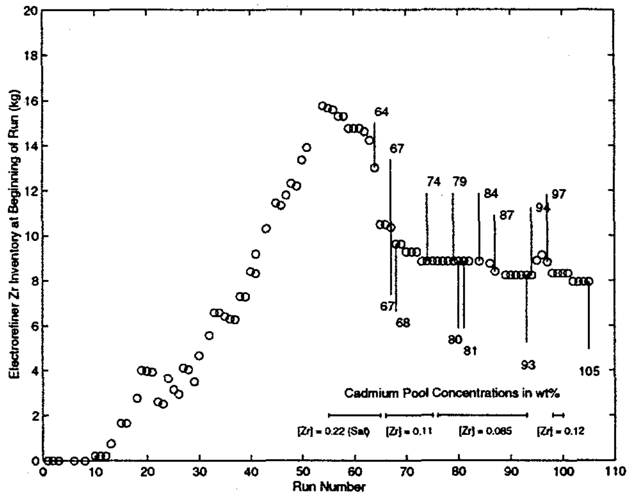

Fig. 2 Electrorefiner Zirconium Inventory

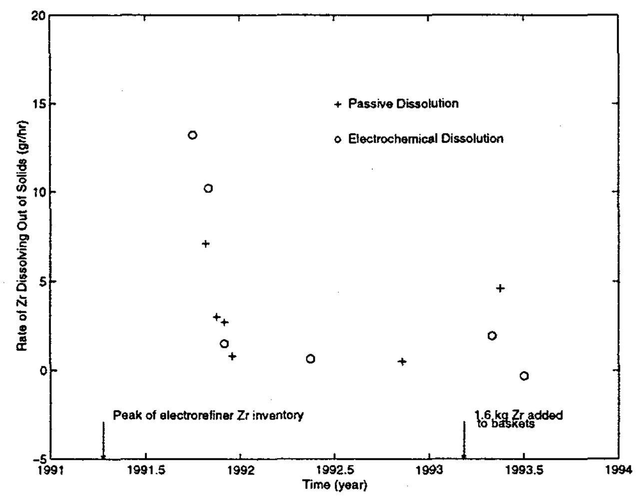

Fig. 3 Rate of Zirconium Dissolving Out of Solids

4.3 Process Inference: Deposit Morphology Factors

A compelling understanding of how a process behaves emerges when patterns in the data identified by empirical means prove consistent with fundamental electrochemical principles. In one such instance the conditions giving rise to the plate-like crystalline deposit morphology were identified through data inspection and first principles analysis after correlating below average collection efficiencies with plate-like morphology. Collection efficiency is a measure of the amount of electricity needed to produce a given mass and should be maintained high to maximize throughput. Because of the low efficiency associated with this morphology, the electrorefiner should be operated to avoid it.

Analysis of data in the database linked plate-like crystalline growth with low mixing and low current density as seen in Fig. 4 and 5. But this is the result expected from the electrochemical theory for dendrite growth. According to the standard

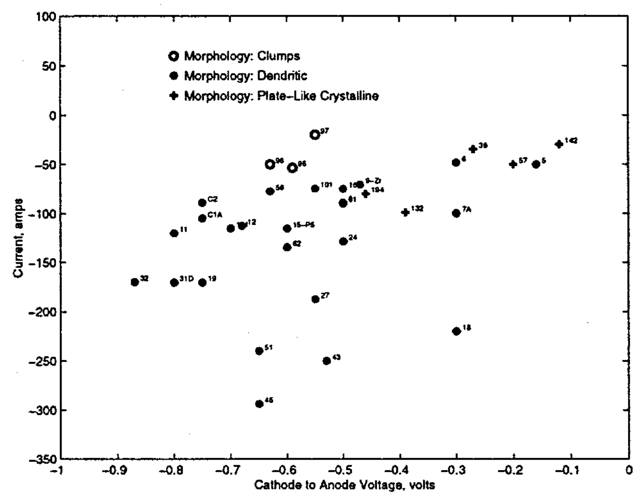

Fig. 4 Current Versus Voltage Partitioned by Deposit Morphology

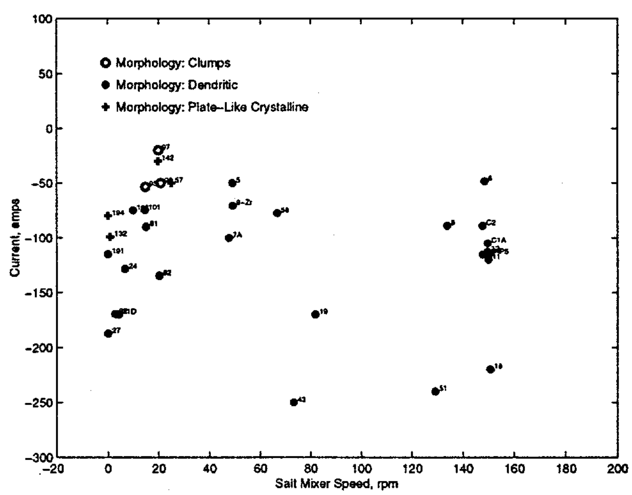

Fig. 5 Current Versus Salt Mixer Speed Partitioned by Morphology

electrochemical model a concentration boundary layer surrounds all surfaces of the cathode.[Bockris, 1993] A dendrite is created locally when a solid surface grows further out into the concentration boundary layer where the fluid has a higher ion concentration. The rate of growth accelerates and gives rise to a dendrite. There are two dependencies.

First, as the thickness of the concentration boundary layer is reduced, the probability that a surface will reach sufficiently concentration rich fluid to accelerate growth so that a dendrite will form increases. Second, as the concentration gradient is increased an increased rate of growth concentrated in fewer dendrites occurs giving rise to a more dendritic deposit. Low mixing favors a thicker concentration boundary layer and low current density favors a smaller concentration gradient. Thus, these two conditions favor plate-like growth rather than dendritic growth.

5. CONCLUSIONS

Information technologies including Web-based display and relational database capabilities are being used to provide access to data collected from the electro-metallurgical treatment of spent fuel. The objectives are to make readily accessible the necessary data for development and validation of models and for analysis to ensure that the process behavior is well understood and that unexpected trends in the data which would indicate phenomena not yet represented in the models are identified. Examples of three such applications were described.

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