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MASTER

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ABSTRACT

The operational performance of a "six-pack" of cermet anodes and corrosion rates was evaluated in a six kA pilot reduction cell at Reynolds' Manufacturing Technology Laboratory. Two separate test periods were conducted with the cermet anodes; the first period was in conjunction with the Pacific Northwest Laboratory and the second with ELTECH Research Corporation. Both tests used identical NiO-$NiFe_2O_4$-Cu anodes manufactured by Ceramic Magnetics, Inc.. The ELTECH testing involved the in situ coating of the anodes with cerium oxide. Primary evaluations for both test periods were conducted at target conditions of alumina saturation and 0.5 amp/cm^2 anode current density. Individual anodes remained in operation for 25 days during the two and one-half month testing period. Operational difficulties developed throughout the test due to breakage of the anode conductor stems, cracking and breaking of the cermet anodes, unequal anode current distribution, and alumina muck build-up in the cell. These operational problems are discussed as well as an estimate of anode corrosion rates based on metal impurity levels in the aluminum metal pad.

Separate papers will be presented by the Pacific Northwest Laboratory and ELTECH detailing the autopsies and results of microstructural and metallurgical analysis of the anodes removed from the cell.

INTRODUCTION

Pacific Northwest Laboratory (PNL) has been in a development program of inert anodes for the Hall - Heroult cell funded by the Department of Energy (DOE) since 1985. This work was following through on the development work previously conducted by Alcoa in using a NiO-$NiFe_2O_4$-Cu cermet material for the anode. The initial scale-up of the anode size was first done in 1989 (1,2) in a single anode test at Reynolds' Manufacturing Technology Laboratory. Following this evaluation, plans were made to further evaluate these anodes in a pilot cell test in which a "six-pack" arrangement of the cermet anodes would replace one standard carbon anode in the pilot cell operation.

ELTECH Research Corporation is developing a technology in which a cerium oxide coating is formed on the surface of the cermet anode, further reducing the corrosion rates of the anodes. As DOE was jointly funding both of these developments, it was decided to test the "CEROX" technology during the pilot cell testing using identically fabricated anodes.

Ceramic Magnetics was selected by PNL to supply the powder for the anodes as well as fabricate the anodes. After initial fabrication problems were resolved, anodes were manufactured for both of the pilot cell test periods.

EXPERIMENTAL DESIGN AND PROCEDURES

Pilot Reduction Design

MTL's pilot reduction cell, as shown in Figure 1, is a small self-heated cell with the capacity for running two industrial-size (15.5" X 21.5") carbon anodes. Special modifications were made to the system to accommodate the testing of the cermet anodes. One of the carbon anodes was replaced by an inert anode cluster consisting of six cermet anodes in a 2-by-3 arrangement as shown in Figures 2 and 3. The identification (A-F) of the anode positions is shown in Figure 2. The holder system allowed for the removal of individual anodes during operation. Current was supplied to the anode cluster by means of cables connected to the top of each stem. Current was monitored to each cermet anode by means of a calibrated current shunt located near the top of the anode superstructure. Each of the anodes was electrically isolated from the holder by means of a ceramic insulator (fused silica or alumina refractory). Current to the cermet anode cluster was supplied by separate rectifiers and was isolated from the adjacent carbon anode allowing individual control of current or voltage of the carbon anode and cermet anode cluster. This allowed the operation of the carbon anode at higher voltages or currents to provide sufficient heat for maintaining a proper thermal balance in the cell.

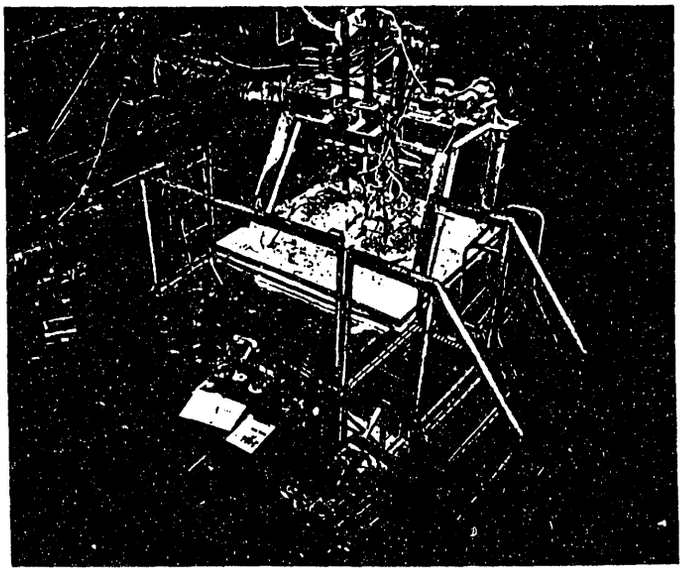

Figure 1 MTL's Pilot Reduction Cell

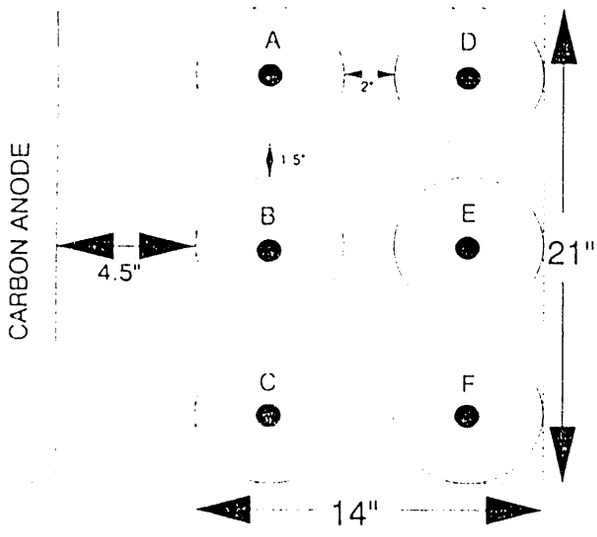

Figure 2 Cermet Anode Identification

Cermet Anode Design

The cermet anodes of the type $NiO\text{-}NiFe_2O_4\text{-}Cu$ were manufactured by Ceramic Magnetics Inc., Fairfield, N.J. These anodes contained approximately 42.9% NiO, 40.1% Fe_2O_3, and 17% Cu. The cermet anode design used in the pilot cell test is shown in Figure 4. The anodes were cylindrical with a radius of three inches and a height of three inches with an additional one inch lip extending above the top face of the cylinder. The bottom edges of the anodes were rounded with a radius of curvature of 1.5 inch. An 18-inch long, 1-inch diameter rod was screwed into the center of each cermet anode. Initially, nickel was used for the rod material, however, failures of these stems resulted in replacement anodes using either 304 stainless steel or Inconel 601. The stems were protected with an 1.25 inch diameter alumina sleeve placed over the rod, extending three inches up from the top of the cermet anode.

Pilot Cell Operation

Test Schedule

The pilot cell test of the cermet anodes was conducted from August 1 to October 10, 1991. A summary of the test program is summarized in Table I. The first test period of the cermet anodes was in conjunction with PNL from August 10-30. Following a re-stablization period of the pilot cell with standard carbon anodes, a second test period of the cermet anodes was conducted with ELTECH from September 15 through October 10.

Table I TEST SCHEDULE

Date	Comments
Aug. 1, 1991	Pilot Cell Start-up with Two Carbon Anodes
Aug. 2-5	Initial Stabilization of Cell
Aug. 5-9	Operation with "Six-Pack" Graphite Anode Cluster
Aug. 10-27	PNL Cermet Anodes at Standard Test Conditions
Aug. 27-30	PNL Cermet Anodes at Modified Test Conditions
Aug. 30 - Sept. 14	Re-stabilization of Cell with Two Carbon Anodes
Sept. 15-30	ELTECH Cermet Anodes at Standard Test Conditions
Sept. 30 - Oct. 10	ELTECH Cermet Anodes at Standard Test Conditions
Oct. 10, 1991	End of Cermet Anode Testing

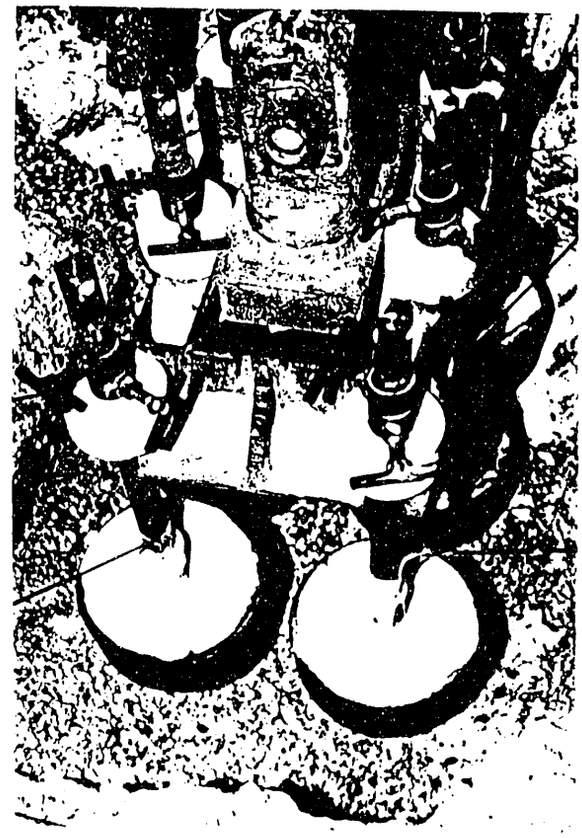

Figure 3 Pilot Cell Cermet Anodes in Cell for Preheating

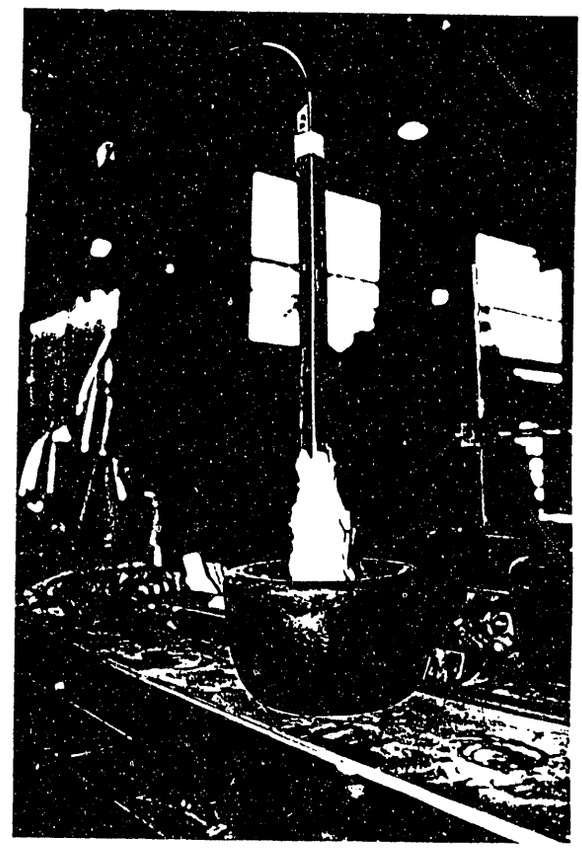

Figure 4 Cermet Anode Assembly

Cermet Anode Preheating and Installation

The preheating and installation of the cermet anodes was expected to be a critical part of the test due to the thermal shock characteristics of the material A "six-pack" of graphite anodes was installed in the cell initially to assure proper operation of the data collection system and to evaluate the individual change-out procedures for the cermet anodes The method for preheating and transferring the cermet anodes to the cell was as follows

1 Preheat the anodes to 300°C at a rate of 50°C/hour in an electric furnace The anodes would be bundled in Kaowool insulation to retard heat loss during transport to the cell

2 Remove one graphite anode from the cell, allowing sufficient opening in the crust for the cermet anode to be located in place

3 Remove one cermet anode from the preheat furnace, placing it into the cell, hanging several inches above the molten bath surface

4 As the temperature increases on the anode, lower it down toward the bath until it is eventually submerged

5 At this time the current lead will be connected and current passed through the anode

The first anode transferred in this manner (position B), cracked upon exposure to the open bath Figure 5 shows this anode As shown, the anode cracked radially down the center line including the nickel rod-cermet anode connection Thermal shock coupled with too large a CTE mismatch between the nickel rod and cermet anode was the probable cause of the cracking Following this initial failure in transferring a cermet anode, the preheating procedures were modified Two alternative procedures were evaluated

1 An anode, labeled AUX1, was positioned on the cell and allowed to preheat over the crust Then it was gradually lowered through the semi-solid crust into the bath This procedure generally took about 24 hours

2 An anode, labeled AUX2, was preheated in an electric furnace to 970°C, then transferred to the cell and inserted directly into the molten bath

Both of these methods worked satisfactorily, with option 1 proving to be the simplest in handling the anodes This procedure was used for installing all anodes in future exchanges For the ELTECH test, all six cermet anodes were installed in the cell at the same time by placing the anodes over the solid crust and then covering the tops with an insulating blanket and allowing them to preheat slowly, gradually moving the anodes into the molten bath as their temperature increased

PNL Testing

Operation with the cermet anodes in the pilot cell began on August 10 and continued until August 30 for the PNL phase of the testing During most of the time (until August 27), the cermet anodes were tested under "normal" conditions, i e , at nominal current densities of 0 5 amp/cm² and as close to alumina saturation as possible These conditions were found by PNL to produce the least amount of corrosion of the cermet anodes in laboratory tests Target test conditions for this phase of cell operation were as follows

Maximum individual anode current	90 amp
Anode immersion	1 5 inch
Bath ratio	1 3 - 1 4
CaF_2	4-6 wt%
Al_2O_3	100% saturation (7-8 wt%)

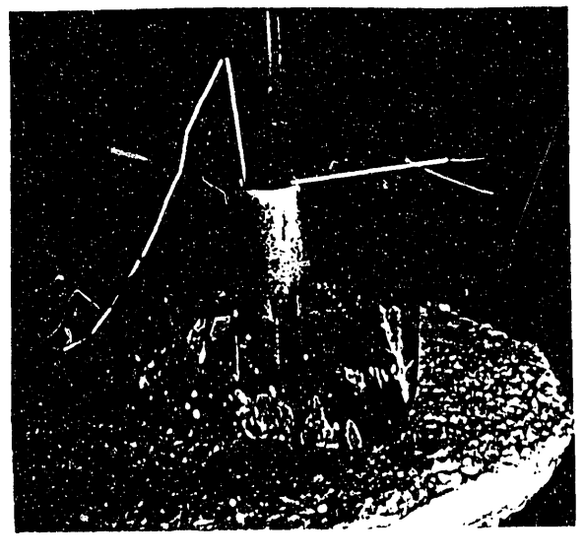

Figure 5 Cracked Anode After Exposure to Heat From the Bath

The test conditions were altered on August 27 with the alumina concentration being reduced to values significantly less than saturation Operation was further modified on August 28 when the current on each anode was increased to 180 amp (nominal) or about double the value under the "normal" conditions

Electrolyte Chemistry

Figures 6 and 7 show the primary chemical composition of the bath Maintaining bath ratio at target levels was difficult due to the changing volumes in the pilot cell as a result of the variability of bath temperatures Measured bath temperatures are shown in Figure 8 A large variability is seen in this as the dynamics of the cell are such that a quick response in temperature occurs with disturbances to the cell cryolite-alumina cover or energy input These disturbances were enhanced by frequent cell test measurements and material problems which will be discussed later

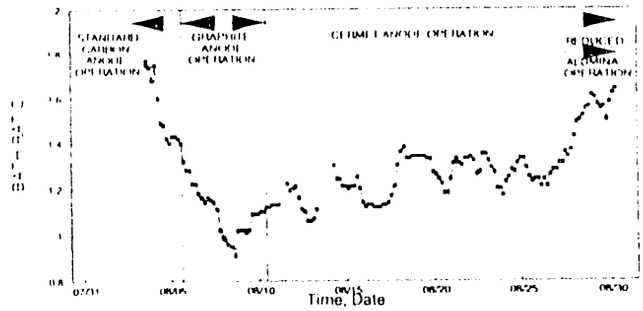

Figure 6 Bath Ratio During PNL Test Period

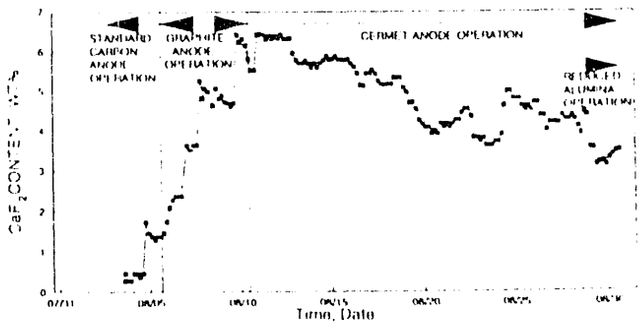

Figure 7 CaF_2 Content in the Bath During PNL Test Period

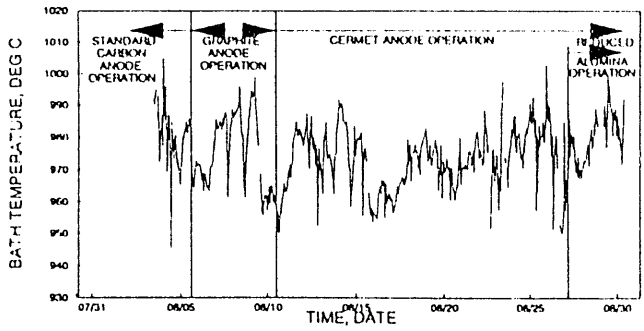

Figure 8 Bath Temperature During PNL Test Period

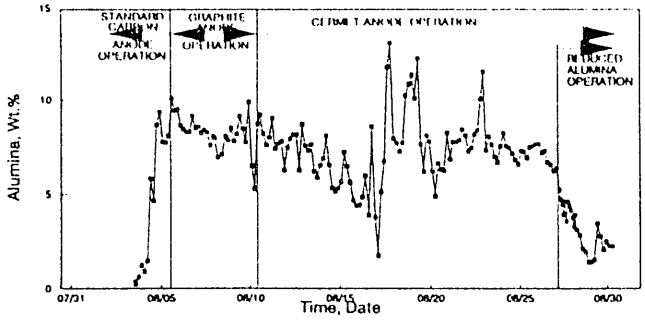

Figure 9 Alumina Weight Percent During PNL Test Period

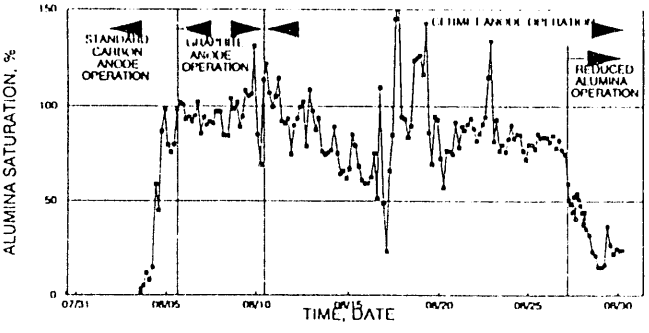

Figure 10 Alumina Content Expressed as Percent Saturation During PNL Test Period

One of the key operational control parameters was to maintain alumina content in the bath as close to saturation as possible during the majority of the test. Figures 9 and 10 show the results of the measured alumina content in the bath and the corresponding calculated alumina saturation throughout the test. As these plots indicate, the alumina content during the cermet anode operation was generally 7-8 wt% resulting in calculated percent saturation of 80-90%. During the test period at reduced alumina content, the content was 2-3 wt% or 20-30 percent saturation. Maintaining the cell near alumina saturation for an extended period of time resulted in a very difficult operation, enhanced by the temperature swings experienced in the cell. This problem is illustrated in Figure 11 which shows when severe temperature reductions occur, significant amounts of alumina will come out of solution. This is the type of operation which occurs in a small pilot cell, resulting in alumina muck deposits on the cell bottom.

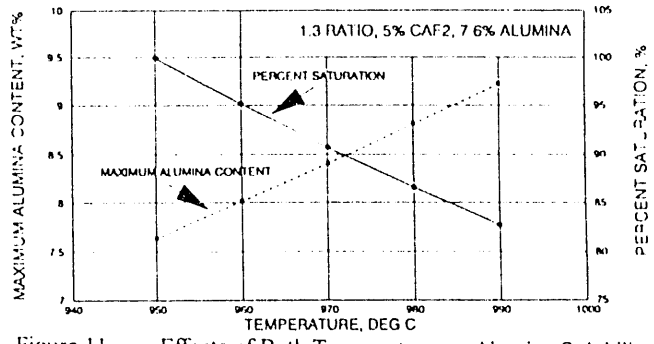

Figure 11 Effects of Bath Temperature on Alumina Solubility

Liquid Level Control

The target operating conditions included a depth of immersion for the anode equal to 1.5 inches. It was also planned that the anode-cathode distance (ACD) would be relatively large. Measured anode immersion levels during the test are shown in Figure 12. Generally, all anodes were maintained within 0.5 inches of each other. Typically only anodes in positions B and C were measured for immersion levels. It is evident from the plot information that the anode immersion varied more than desired, from one to three inches. This was due to the difficulty in adjusting anodes as a result of anode material problems and changing bath level as shown in Figure 13. As the pilot cell operation progressed and muck build-up occurred in the cell, the total liquid inventory decreased as shown by the reduced bath level. Initial operation with the cermet anodes was at eight inches of liquid bath, but by the end of the test the level had decreased to two to three inches. At the end of the run, approximately six inches of hard muck had built up in the cell bottom, primarily under the cermet anodes.

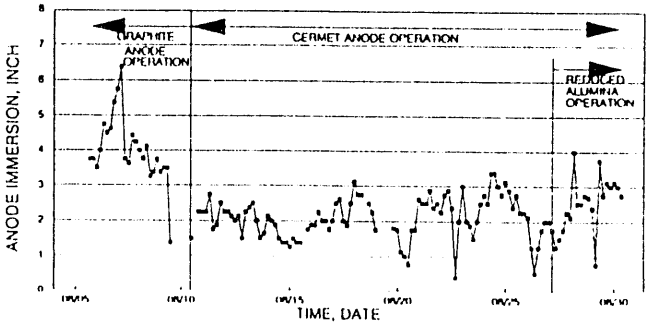

Figure 12 Anode Immersion Level During PNL Test

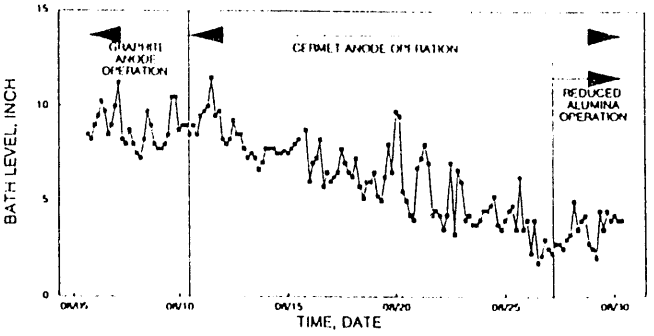

Figure 13 Bath Level During PNL Test

Cermet Anode Current Distribution

Throughout the test, the current was maintained so that the maximum for any one anode was 90 amp (except the last two days of operation when the target was raised to 180 amps). As shown in Figure 14, a current imbalance existed for the cermet anodes. The current imbalance was caused primarily by two factors: (a) significant conduction of current to the sidewall, and (b) the perturbing effects of the large carbon anode. The nature of this current imbalance on the cermet anodes also changed during the test because of changes in operating conditions, particular ACD. In general, the impact of the adjacent carbon anode current and sidewall conduction were lessened toward the end of the test as the ACD was reduced due to the lower bath levels. The effect of the large carbon anode was a unique part of the pilot cell operation due to the separate power supplied to the two sides of the cell and the need to operate the carbon anode at elevated power inputs to maintain sufficient heat input to the cell. Figure 15 shows the effects of various power inputs to the carbon anode upon the current of the cermet anodes.

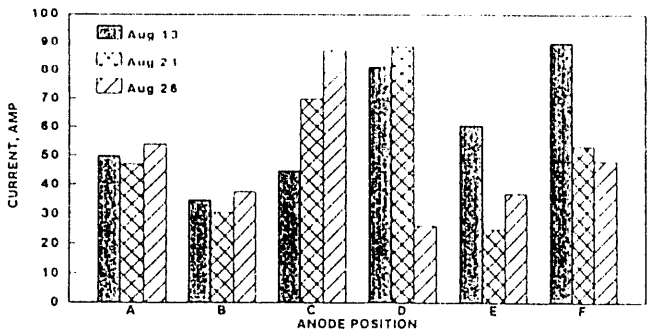

Figure 14 Cermet Anode Current Distribution During PNL Test

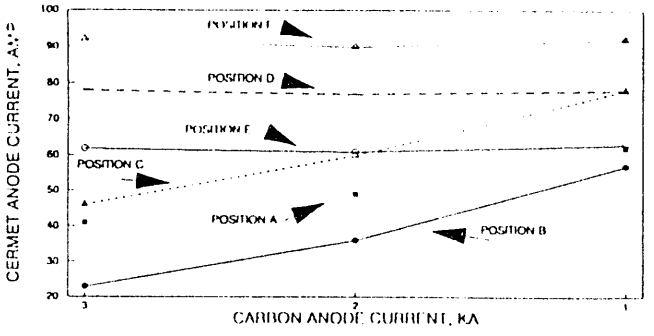

Figure 15 Effects of Adjacent Carbon Anode's Current on Cermet Anode Current Distribution

Meaningful voltage drop measurements could not be made due to the multiplicity of current paths caused by the adjacent carbon anode, cell condition (muck build-up), and sidewall conduction. Those taken indicate normal anode drop of 0.2 volts at 90 amps and 0.5 volts at 180 amps.

PNL Cermet Anode Evaluation

A total of 13 cermet anodes was used during the first test period. The anodes' identification, position installed in the cell, and life of each one is summarized in Table II. The longest time any individual anode remained in service was 314 hours (13 days). Two major problems affected the life of the anodes: (1) breakage of the nickel connector rods, and (2) cracking and breaking of the cermet anodes.

Table II PNL Anode Summary

Anode	Cell Position	Operation	Comments
1	A	9/15-23 213 hr.	Section of anode broke, removed.
2	B	9/14 1 hr.	Cracked down center of anode at start-up
3	C	9/15-26 275 hr.	Removed on schedule
4	D	9/15-10/10 614 hr.	End of test.
5	E	9/15-10/10 614 hr.	End of test.
6	F	9/15-10/10 614 hr.	End of test
7	A	9/27-10/10 312 hr.	End of test
8	B	9/27-10/10 312 hr.	End of test.
9	C	9/27-10/10 312 hr.	End of test

The nickel rods used for current conductors to the cermet anodes began to break very early in the pilot cell test. The anode, during operation, typically had a cryolite-alumina cover over the top of the anodes extending above the protective alumina sleeve as shown in Figure 16. Temperatures were measured in the 700° to 850°C range in the stem area submerged in the crust cover. It was in this area, approximately three inches (or less) above the top of the anode, that the failures of the nickel stem occurred. The chronological listing of the stem failures is summarized in Table III.

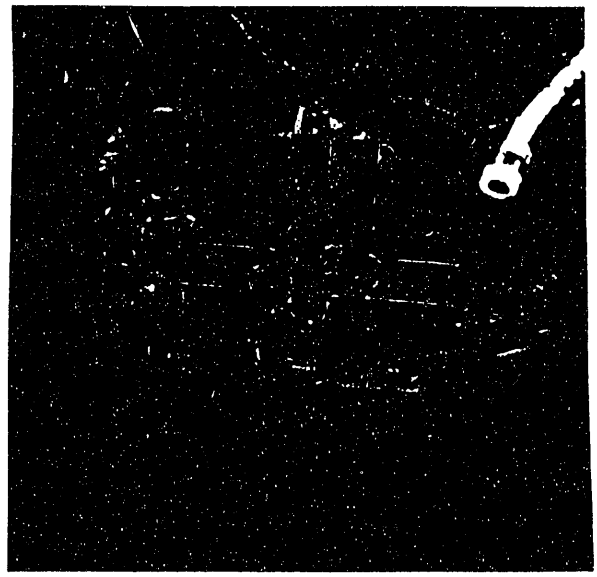

Figure 16 Cermet Anodes with Cryolite - Alumina Cover

Table III Chronological Listing of Anode Stem Failures

Date	Anode Position	Comment
Aug. 14, 9 a.m.	C	Replaced with sleeve
Aug. 15, 3 p.m.	B, F, and D	B and F replaced with sleeve, D anode replaced.
Aug. 18, 1 13 a.m.	B	Stem broke beneath sleeve, replaced anode
Aug. 18, 1 p.m.	A	Replace with new anode.

As shown in the Table, the stem failures first occurred four days after beginning operation, with only one stem (in position E) not failing. If sufficient stem length remained connected to the anode, a steel pipe was fitted over the stub and the anode continued operation. Replacement anodes for the remaining of the PNL testing used 304 SS for the stems, which proved to be satisfactory in combination with packing the alumina sleeve with a "pumpable" castable refractory. A similar system, but with Inconel 601 stems, worked well during the ELTECH test. SEM/EDS analysis of the fractured nickel rod surface indicated abnormally large grain/crystal and high sulfur content, suggesting embrittlement of the nickel rod had occurred. The prolonged operation at the elevated temperatures in the presence of the cryolite crust (which contains some sulfur) probably led to the very fast penetration of the grain boundaries, embrittlement and oxidation, and early failures of the stems. These failures of the anode stems dominated the events of the early part of the cell operation resulting in significant modification of the test schedule and operation.

The other significant problem which occurred during the test was the cracking/breakage of the cermet anodes during operation. As previously indicated, the first cermet anode that was transferred to the pilot cell broke immediately upon exposure to the heat from the open bath. Even though the transfer procedures were modified to reduce thermal shock, all of the anodes eventually developed cracks, although not as suddenly and catastrophically as the first anode. The cracking of all of the anodes had similar characteristics, i.e., radially down the center of the anode. Two anodes broke completely apart during cell operation: Anode A2 (position B, August 26), and Anode C1 (position C, August 18). Part of Anode C1 that broke off and fell into the cell and, unlike other large pieces that had broken off, was never recovered. Post-test analysis revealed significant penetration of electrolyte into most of the cracks indicating they were present during operation. It is also suspected that the strong alumina-cryolite crust prevented the anodes from falling apart in most instances. The problems with anodes cracking were not unexpected given the mismatch in thermal expansivities of the nickel rod and the cermet material as well as the high thermal shock sensitivity of the cermet material.

Metal Impurities

The primary indicator of the corrosion rate of the cermet anodes during operation was the rate of increase of nickel, copper, and iron impurity content in the aluminum metal. Metal samples were collected every four hours to track the concentration of these elements. These results are shown in Figures 17-19. The increase in metal concentrations was seen to increase at a nearly linear rate during the period of cermet anode operation at normal operating conditions (8/10-27) and experience a sharp increase with operation at reduced alumina content and increased anode current. During normal conditions, the rate of increase for the various impurities was as follows:

Fe	0.017% per day
Cu	0.008% per day
Ni	0.019% per day

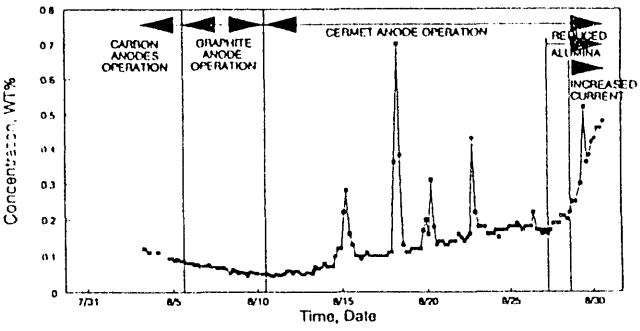

Figure 17 Copper Content in the Aluminum Metal During PNL Test

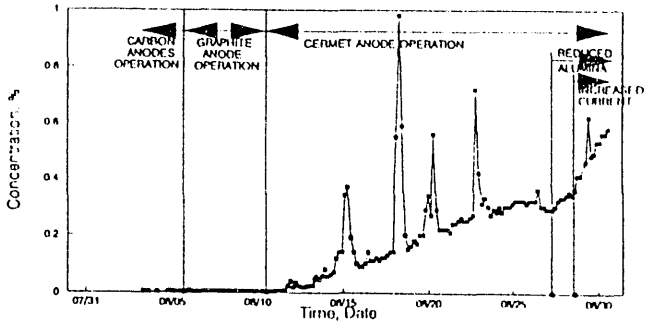

Figure 18 Nickel Content in the Aluminum Metal During PNL Test

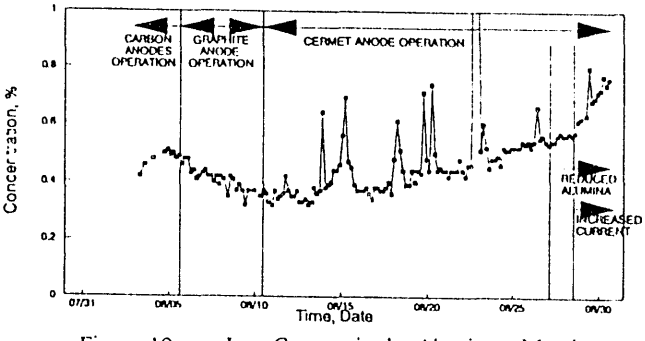

Figure 19 Iron Content in the Aluminum Metal During PNL Test

The metal loss from the cermet anodes during this period was estimated by fitting curves to the plots as shown in Figures 20-22. Very good correlations were obtained by using the following fixed amounts of metal impurities reporting to the aluminum metal pad each day.

Cu	0.13 lb per day
Ni	0.26 lb per day
Fe	0.31 lb per day

The ratio of these metal losses is 1.2:2.4 (Cu:Ni:Fe). The actual ratio of these three elements in the cermet is 1.1:98.1:65, which suggests that iron contamination may be supplemented by other sources. If all components came from the anodes uniformly, iron would have been released at a rate of 0.21 lb per day. Assuming these calculated rates are indicative of the dissolution rates of the anodes, it can be calculated that the rate of total material loss from the anodes was 0.76 lb per day. This corresponds to a volumetric loss of 57.5 cm^3, based on an anode density of 6 g/cm^3. Applying this uniformly to all surfaces of all the anodes gives a "wear rate" of 0.2 mm per day.

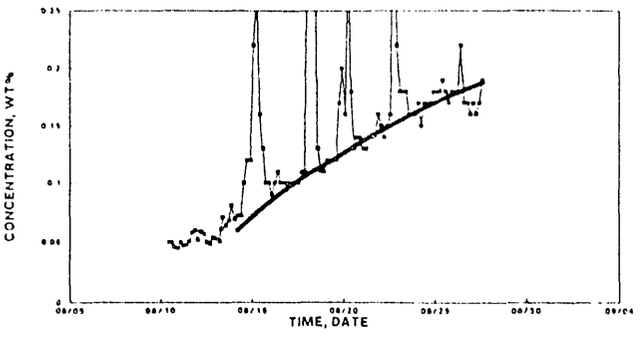

Figure 20 Model Prediction of Copper Content in the Aluminum Metal During PNL Test

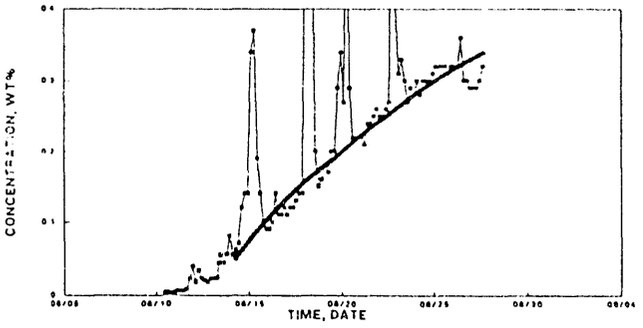

Figure 21 Model Prediction of Nickel Content in the Aluminum Metal During PNL Test

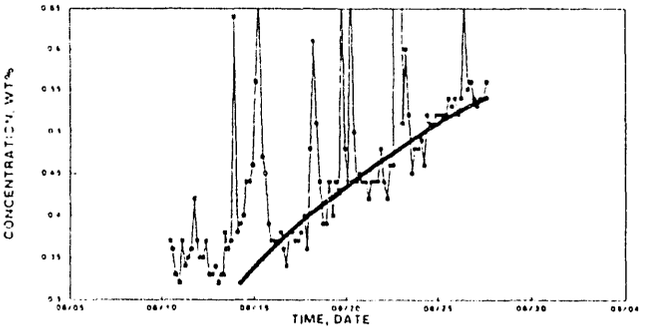

Figure 22 Model Prediction of Iron Content in the Aluminum Metal During PNL Test

ELTECH Testing

An evaluation was made of the ELTECH "CEROX" coating technology with the cermet anodes in the pilot cell for the second phase of the test from September 15 through October 10. Following the completion of the PNL testing, the cermet anodes were replaced with a standard carbon anode and the cell was operated in a manner to return the cell to normal conditions, i.e., achieving a clean cathode bottom (free of muck) and reducing the metal impurity concentrations to normal levels

The anodes used during the second test period were identical to those used for PNL. The primary difference in the pilot cell operation was the addition of CeF_3 to the cryolitic bath which forms an in situ cerium oxide, "CEROX," coating on the cermet anodes. Pre-heating and installation methods as previously described were used for these anodes

CEROX Cermet Anode Coating Procedure

The cermet anodes were coated with cerium oxide in the pilot reduction cell by controlling the additions of cerium fluoride to the electrolyte. For the coating to occur properly, it is essential to have sufficient concentrations of cerium fluoride in the cell bath. The majority of the cerium added to the bath reported to the aluminum metal pad. These values for cerium are shown in Figure 23. Typical equilibrium concentration values for the distribution of cerium between the bath and aluminum are as follows:

Cerium in bath	0.44%
Cerium in metal	3.23%

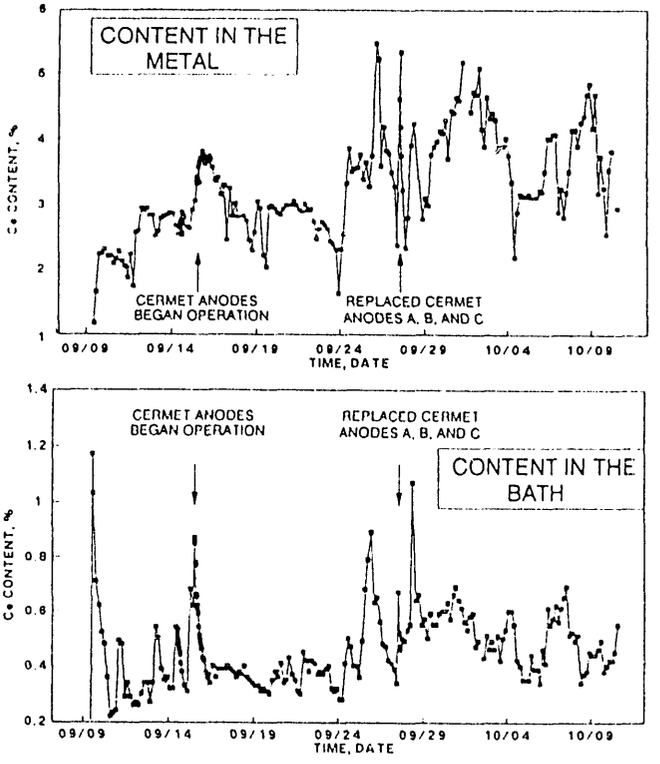

Figure 23 Cerium Content in the Metal and Bath During ELTECH Test

At the time (September 15 and 26) of the initial coating of the anodes, increased amounts of CeF_3 were added to the cell, temporarily achieving higher levels of cerium in the bath. A separate, small (reference) cermet anode (1.5 inch in diameter) was placed into the electrolyte, operating on a separate power supply, to evaluate the cerium coating process. This reference anode was operated for a few hours and then removed to evaluate the quality of the "CEROX" coating. The first evaluation was on September 13 at 1:30 p.m. in which no coating was observed on the anode after five hours of operation. A second evaluation was made on September 14 and, again, little or no coating of the cermet anode occurred. On September 15, after increased amounts of CeF_3 were added to the cell, a coating was observed on the anode. This anode and its coating is shown in Figure 24. As this photograph shows, a significant coating did occur, approximately 1/8" thick, on a portion of the cermet anode. The side of the cermet anode next to the carbon anode did not form a coating, as minimal current flow occurred from this area of the cermet anode. After obtaining the initial coating, a maintenance (25-60 g/hr) amount of CeF_3 was added to the cell to compensate for the cerium being removed from the bath by aluminum metal being produced

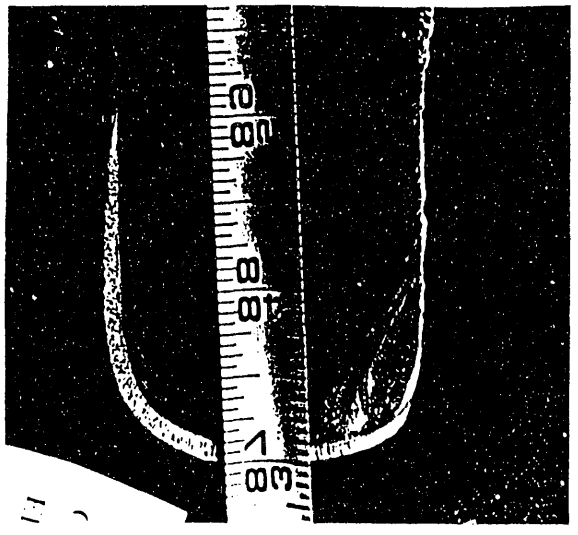

Figure 24 CEROX Coating on Reference Anode

Test Conditions

Similar to the PNL test schedule, the majority of the cermet anode testing was directed to "normal" ELTECH recommended test conditions, i.e., at nominal current densities (<=0.5 amp/cm²) and as close to alumina saturation as possible. Target test conditions for this phase of cell operation were as follows:

Maximum individual anode current	90 amp
Bath Ratio	1.4 -1.6
CaF_2	4-6 wt%
Al_2O_3 (100% Saturation)	7-8 wt %

On September 30, the test target operating conditions were changed such that maximum current to an individual cermet anode was increased to 115 amp. An additional change was made on October 6 with the target ratio being lowered to 1.2.

Operational Conditions

Electrolyte chemistry control was similar to that described for the PNL testing. Figures 25-27 show the measured results for ratio, bath temperature, and alumina content. As before, severe mucking conditions occurred in the cell cathode cavity resulting in a similar effect on bath levels, Figure 28, and anode immersion, Figure 29. An initial operational target was to maintain the anodes' immersion in the bath at 2-3 inches, and to minimize any movements of the anodes which may enhance anode cracking or breaking. To achieve this, metal was removed incrementally in quantities of 5-20 lb. Additionally, small amounts of bath were taken out of the cell to maintain the consistent immersion depth of the anodes.

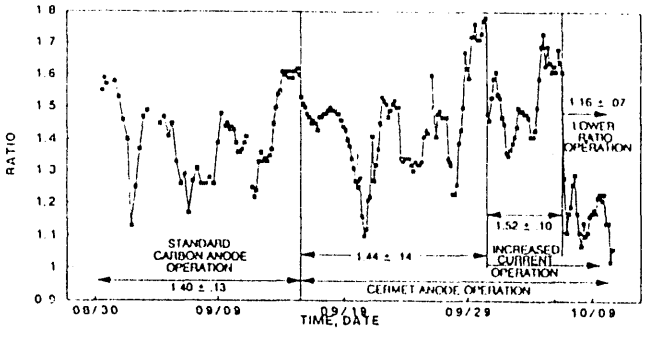

Figure 25 Bath Ratio During ELTECH Test

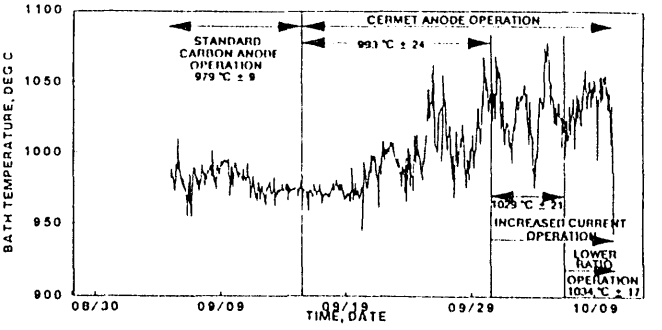

Figure 26 Bath Temperature During ELTECH Test

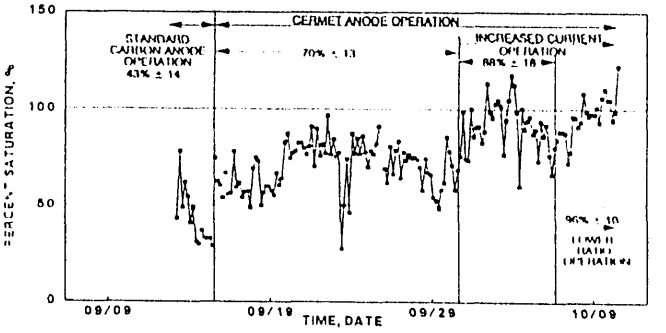

Figure 27 Alumina Saturation During ELTECH Test

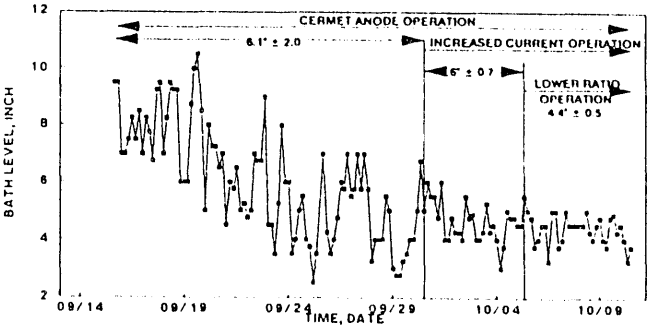

Figure 28 Bath Level During ELTECH Test

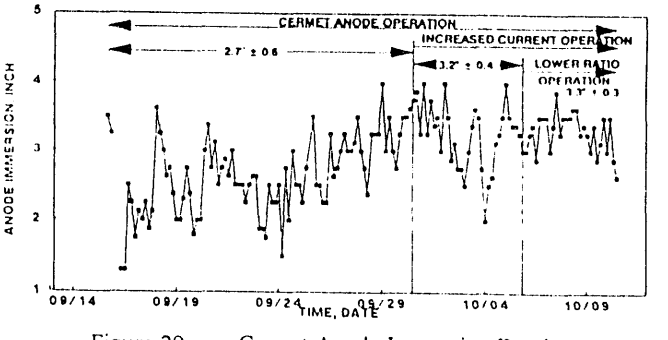

Figure 29 Cermet Anode Immersion Depths During ELTECH Test

The electrical current distribution among the six cermet anodes varied throughout the cell operation as shown in Figure 30. Generally, the current distribution was better than that experienced in the PNL testing. This can be attributed to operating a narrower inter-electrode distance which lessened the effects of the adjacent

carbon anode and sidewall conduction As the cell operation continued, it can be seen that the current conducted by positions D, E, and F was reduced while the current conducted by A, B, and C increased correspondingly. This was due to muck and frozen ledge building under the cermet anodes, minimizing any metal inventory under them, such that the current path was through the metal pooled under the carbon anode. This resulted in an extremely resistive path for those cermet anodes furthest away from the carbon anode. The uneven current distribution among the cermet anodes and on an individual anode has the added disadvantage of using the "CEROX" coating in that an uneven coating will occur on the anode. In the worse case, no coating was observed on sections of the anode directly adjacent to the carbon anode

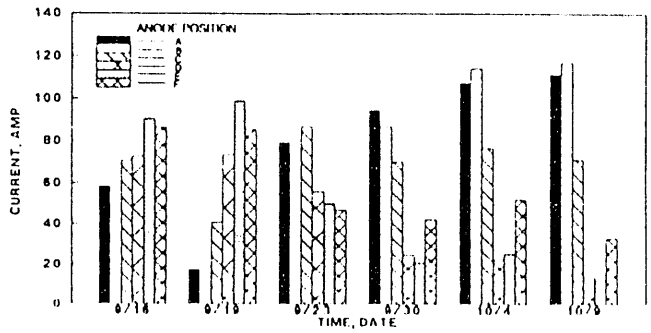

Figure 30 Cermet Anode Current Distribution During ELTECH Test

ELTECH Cermet Anode Evaluation

Nine cermet anodes were used during this phase of the pilot cell operation. Table IV summarizes the life of each anode Anodes 4-6, located in positions D, E, and F, remained in operation for the entire test period, 614 hours (25.6 days). Only anodes 1 (position A) and 2 (position B) were removed early due to cracking/breakage. Special efforts were made to minimize the movement and disturbances to the anodes during the reduction cell operation. This probably contributed to the reduced breakage of the anodes as compared with that experienced during the PNL test as well as the use of improved stem material and ceramic protectors While breakage was not the problem experienced previously, upon removal of the anodes, numerous cracks were found to exist in the anodes as shown in Figure 31

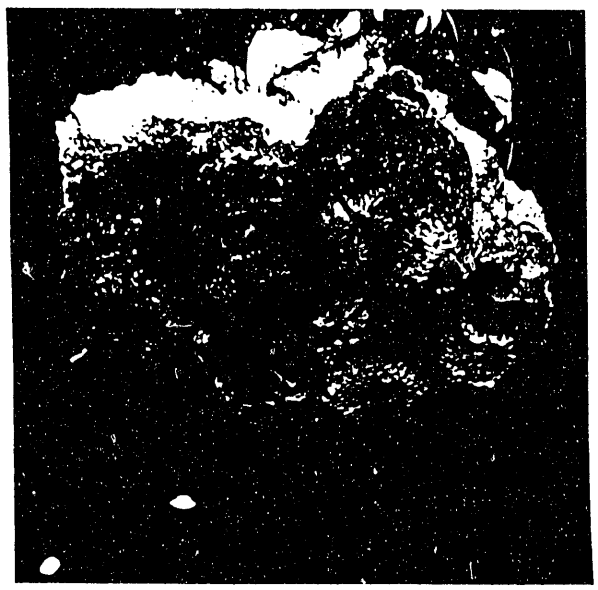

Figure 31 Removed Cermet Anodes at End of ELTECH Test

Table IV ELTECH Anode Summary

Anode	Cell Position	Operation	Comments
A1	A	8/10-18 193 hr	Removed due to broken stem.
A2	B	8/19-26 182 hr	Removed prior to reduced alumina, anode broke in half
B1	B	8/8 0 hr.	Broke at installation
C1	C	8/19-30 260 hr.	Removed at end of test.
D1	D	8/10-15 123 hr	Removed due to broken stem
D2	D	8/16-28 279 hr	Removed prior to increased current test
E1	E	8/24-30 135 hr	Removed at end of test
E2	A	8/19-30 260 hr	Removed at end of test
F1	F	8/10-23 314 hr.	Removed at end of test.
F2	F	8/24-28 96 hr	Removed prior to increased current test
AUX1	E	8/10-23 313 hr	Removed as scheduled
AUX2	B	8/10-18 181 hr.	Removed due to broken stem

Metal Impurities

Similar to the initial period, the rate of increase of nickel, copper, and iron impurity in the aluminum metal during cell operation was the primary indicator of the corrosion rate of the cermet anodes Figures 32-34 show the results of these analyses along with the predicted concentrations using a fixed amount of material reporting to the metal pad each day The data shows an initial increase in impurity levels with the introduction of the cermet anodes, but then a stabilization of the impurity concentrations occurred. It should be noted that the concentrations were much more sensitive to change than in the PNL test, as the cell was operated at a greatly reduced metal inventory (200 lb versus 750 lb) The data shows several spikes in the impurity concentrations which can be attributed to segregation of the metal pad within the cell preventing obtaining representative analysis of the metal The data does not clearly indicate any significant changes in corrosion rates with the changes in cell operation (increased current and lower ratio)

Similar to the PNL analysis, fixed amounts of the impurities reporting to the aluminum metal pad each day could be determined These amounts are:

Cu	0.075 lb per day
Ni	0.13 lb per day
Fe	0.30 lb per day

The ratio of these metal losses is 1:1.74:4 (Cu:Ni:Fe) as compared with the actual ratio in the cermet anode of 1:1.98:1.65 It is not surprising that the iron losses appear to be significantly higher than what would be expected from the anode as frequent dipping of the

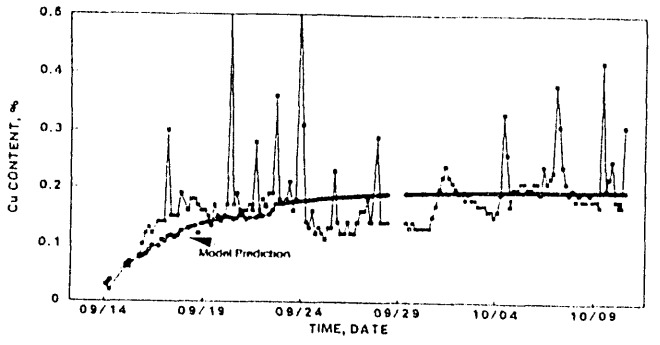

Figure 32 Copper Content in the Aluminum Metal During ELTECH Test

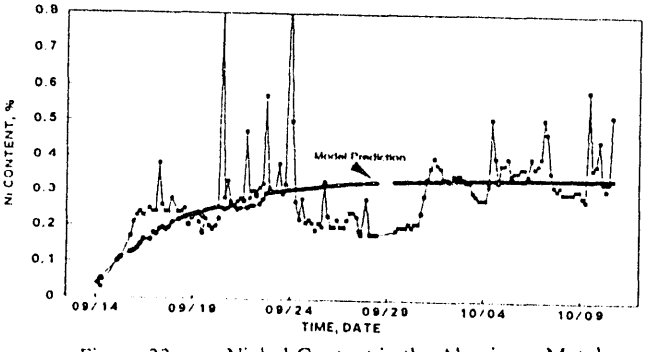

Figure 33 Nickel Content in the Aluminum Metal During ELTECH Test

metal from the cell was done with iron ladles. Based upon the composition of the anode, the iron losses should be at the rate of 0.12 lb per day, assuming uniform dissolution of the three components into the aluminum metal. It can then be calculated that a "wear rate" of 0.1 mm per day existed for these anodes during this test period or approximately half that found in the absence of "CEROX."

Discussion

The performance of the cermet anodes during the pilot cell test suffered from a number of limitations. These include the failure to be able to operate a conventional pilot reduction cell at desired target conditions of alumina saturation and constant current and voltage conditions, and the mechanical fracture problems with both the anode connections and the cermet anodes themselves. Despite these limitations, however, the pilot cell test was successful in that certain important and relevant information was learned about the cermet anodes under scaled-up conditions and the direction for further development of the cermet anode technology.

Cermet Anode Material and Stem Connections

The cracking of the cermet anodes and breaking of the stems indicate that significant design and material selection considerations must be given in these areas. The anode stem material breakage appears to be a manageable problem with proper selection of materials and the use of ceramic barriers to protect against electrolyte/vapor attack. The more difficult technical problem appears to be centered around the stem-to-anode connection and the thermal stress cracking which occurred in the cermet anodes. Regardless of the anode design used in any subsequent large-scale testing, it is recommended that additional testing of the physical and mechanical properties and modeling of thermal stresses be performed before the next phase of pilot evaluation. The requirements for controlled heat-up of the anodes mandates specialized start-up and operating techniques. These procedures will have to be modified using the current experience as a basis.

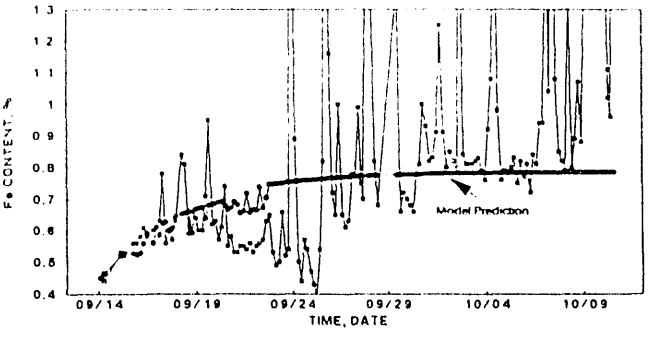

Figure 34 Iron Content in the Aluminum Metal During ELTECH Test

Operation at Low Current Density

The apparent need to operate at low anode current density will require the design of a reduction cell with significantly increased surface area with sufficient current conduction for the thermal stability of the aluminum reduction cell. This revised design must exhibit uniform current distribution and also meet the necessary requirements for minimization of thermal stress. It appears the most likely success for such a cell design would be in conjunction with refractory hard metal cathodes (such as the TiB_2-G type currently under development).

Operation at Alumina Saturation

While the test was not conclusive as to the effects of operation of the cermet anodes at reduced alumina concentrations, indications were that the corrosion rate did increase significantly with operation at reduced alumina. It is essentially impossible to operate for the long term at saturated conditions in a conventional reduction cell due to the increasing muck build-up which results in an increase in cathode voltage drop and a reduced liquid volume for the cell. The development of innovative cell designs will be required to address these problems.

Cermet Anode Corrosion Rate

The corrosion rates experienced for the cermet anodes during the tests were too high, resulting in unacceptable metal impurity levels in the aluminum. Despite showing significant corrosion rates for the cermet anodes, the pilot cell test did not conclusively demonstrate for or against the "inertness" of the cermet anodes. This was because of (1) the poor current distribution among the anodes as well as on the individual anodes, and (2) the impact of cracking and breaking of the anodes. Many fundamental and applied questions remain concerning both materials development and fabrication techniques.

CEROX Coating Technology

The CEROX coating appeared to significantly reduce the measured corrosion rate of the cermet anodes. The effectiveness of the coating was reduced somewhat because not all surfaces of the cermet anodes were coated, due to the current imbalance on the individual anodes. The corrosion rates were also probably reduced somewhat, as compared with the PNL test, due to reduced mechanical failures of the anodes and stems.

The use of the CEROX coating presents some additional challenges, including:

a) Increased importance on uniform anode current density,

b) Procedure for the initial coating of the anodes, including when existing coated anodes are in operation,

c) Management of the increased levels of cerium in the aluminum metal.

Acknowledgments

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