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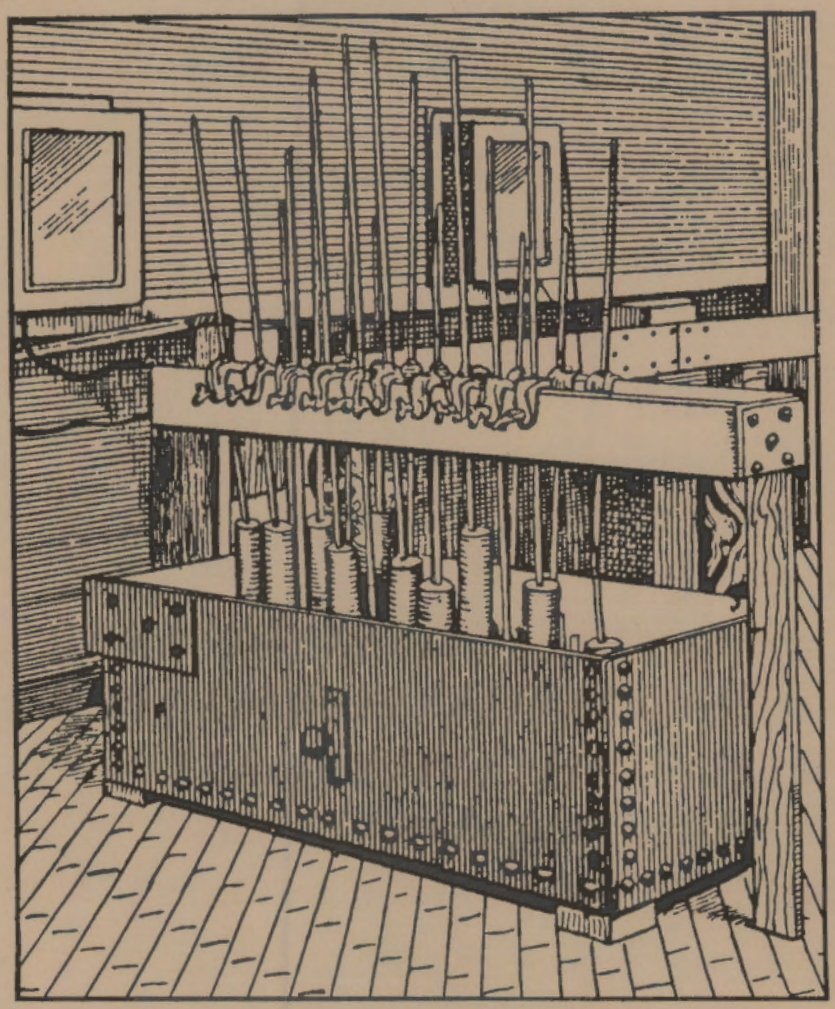
Inert Electrodes Program

Laboratory-Scale Testing of Non-Consumable Anode Materials



March 1989

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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PNL-6805

On the cover:

Aluminum reduction pots at the Pittsburgh Reduction Company's (Alcoa's) plant in 1889. Adapted from a photograph, courtesy of Alcoa.

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Inert Electrodes Program

LABORATORY-SCALE TESTING OF NON-CONSUMABLE ANODE MATERIALS

S. C. Marschman

March 1989

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

Development of inert anode materials for use in the electrolytic production of aluminum is one of the major goals of the Inert Electrodes Program sponsored by the U. S. Department of Energy, Office of Industrial Programs, at Pacific Northwest Laboratory. The objectives of the Materials Development and Testing Task include the selection, fabrication, and evaluation of candidate non-consumable anode materials. Research performed in FY 1987 focused primarily on the development and evaluation of cermets that are based on the two-phase oxide system $NiO-NiFe_2O_4$ and contain a third, electrically conductive metal phase composed primarily of copper and nickel.

The efforts of this task were focused on three areas: materials fabrication, small-scale materials testing, and laboratory-scale testing. This report summarizes the development and testing results of the laboratory-scale testing effort during FY 1987.

The laboratory-scale electrolysis testing effort was instrumental in partially determining electrolysis cell operating parameters. Although not optimized, $NiO-NiFe_2O_4$-Cu-based cermets were successfully operated for 20 h in cryolite-based electrolytes ranging in bath ratios from 1.1 to 1.35, in electrolytes that contained 1.5 wt% LiF, and at conditions slightly less than Al_2O_3 saturation. The operating conditions that lead to anode degradation have been partly identified, and rudimentary control methods have been developed to ensure proper operation of small electrolysis cells using non-consumable anodes.

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The author wishes to acknowledge the following individuals for their contributions to this project: D. E. Smith, N. C. Davis, J. L. Humason, O. H. Koski, and B. J. Wrona.

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INTRODUCTION

The Inert Electrodes Program is conducted by Pacific Northwest Laboratory (PNL)[a] for the U. S. Department of Energy, Office of Industrial Programs. The purpose of the program is to develop long-lasting, energy-efficient anodes, cathodes, and ancillary equipment for Hall-Heroult electrolysis cells used by the aluminum industry. In FY 1987 the program was divided into three tasks:

- Inert Anode Development - to improve the energy efficiency of Hall-Heroult cells by development of non-consumable anodes.
- Stable Cathode Studies - to develop methods for retrofitting Hall-Heroult cells with TiB_2-based cathodes.
- Sensor Development - to develop sensors for control of the electrolyte chemistry in Hall-Heroult cells being operated with stable anodes and cathodes.

One of the major objectives of the Inert Electrodes Program is the development of long-lasting, stable anode materials for use in the electrolytic production of Al. The most promising material to date is a cermet material based on a NiO-$NiFe_2O_4$ oxide matrix that contains a Cu-based metal phase. The performance of this material has been successfully demonstrated in small-scale electrolysis tests. High-purity Al has been produced during 20-h tests.

The purpose of this document is to present the supporting data for the selection of NiO-$NiFe_2O_4$-Cu-based materials as a leading non-consumable anode candidate material. The history of the development and testing effort is presented here, and several important discoveries regarding electrolysis cell operation and control are documented.

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CONCLUSIONS

The development of $NiO-NiFe_2O_4$-Cu-based cermet non-consumable anodes at PNL was continued in FY 1987. Research performed during that period indicates that the $NiO-NiFe_2O_4$-Cu-based cermets are potentially viable as non-consumable anodes for use in the electrolytic production of Al. This conclusion is supported by the results of successful laboratory-scale testing at PNL. High-purity Al was repeatedly produced in laboratory-scale cells, and anodes were operated virtually free of degradation in 20-h tests.

These successful results were obtained, however, by operating the experimental electrolysis cells at conditions slightly different from those found in commercial reduction facilities. To maintain the stability of a resistive "film" that appears to protect the non-consumable anodes, it was determined (for the present at least) that the experimental electrolysis cells had to be operated at lower anode current densities than found in commercial reduction cells. A process control device was developed for monitoring the performance of the non-consumable anodes, and future research will be conducted to yield methods to operate the anodes at higher anode current densities. Analysis of data obtained with the process control device has led to the development of a rudimentary system of control that can be used to correct conditions adverse to successful anode operation.

Although these results are promising, continued research is necessary. Before the aluminum industry will apply this technology, research must be conducted to expand operating parameters, demonstrate long anode life, and show that high-purity Al can be produced.

TECHNICAL PROGRESS

Research conducted during FY 1986 resulted in the recommendation of four candidate NiO-$NiFe_2O_4$-Cu-based cermet materials for further study. These candidates were evaluated, resulting in the selection of NiO-$NiFe_2O_4$-Cu-Ni-Al cermets as the most promising non-consumable anode material. New technical developments and discoveries made by PNL staff during FY 1987 indicate that these materials can be operated under a wide range of conditions. These efforts are described in detail below.

Testing of non-consumable anode materials involved the use of small-scale electrolysis test cells and laboratory-scale electrolysis test cells. This document focuses on the laboratory-scale testing effort.

The principal goal of the laboratory-scale testing effort was to evaluate non-consumable anode performance as a function of electrolyte chemistry. Many experiments were performed over the course of FY 1987, resulting in at least one major discovery regarding electrolysis cell operation using non-consumable anode technology. The electrolysis cell that was used to conduct these tests was described in a previous report (Hart et al. 1987), and for brevity will not be discussed here.

ELECTROLYTE VARIATION TESTS

A series of tests was designed to evaluate the performance of NiO-$NiFe_2O_4$-Cu-based anodes in a variety of electrolyte compositions. The electrolyte mixtures were selected statistically after careful review of the operating conditions found at commercial reduction facilities and consideration of results obtained from preliminary experiments. The concentrations of components of the electrolytes ranged as follows:

Bath ratio	1.0 to 1.5
Al_2O_3	2 to 10 wt%
CaF_2	0 to 10 wt%
MgF_2	0 to 6 wt%
LiF	0 to 5 wt%

Approximately 30 experiments designed to evaluate the effect of electrolyte chemistry on non-consumable anode performance were performed during FY 1987. These experiments are numbered 9 through 38 in Table 1. Of those experiments, four were considered to be reasonably successful. The experimental failures were largely attributed to variations in the electrolyte chemistry. All of the anodes from the four partially successful tests exhibited some type of degradation. Although relatively high electrolysis cell current efficiencies (89% maximum) and Al purities (~98.5%) were obtained, the degradation of the anodes was unsettling.

Anode degradation for the 30 tests ranged from severe, where the anodes were so badly corroded that they fell into the electrolyte (Figure 1), to only slight degradation of the anode edges (Figure 2). Four experiments (numbers 39, 40, 41, and 42 in Table 1) were performed in an attempt to duplicate the partially successful experiments, but the anodes were severely corroded in each of these experiments (Figure 3).

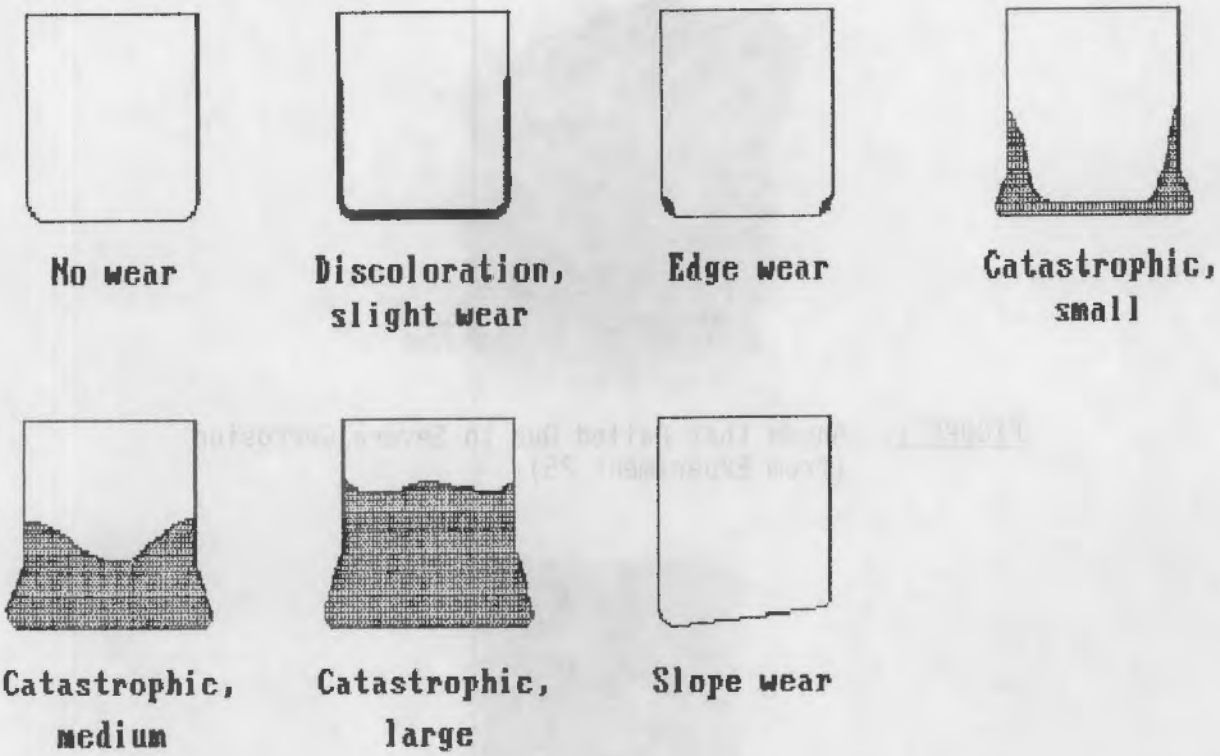
These unsettling results led to a reevaluation of the data obtained to that point, and a reevaluation of the experimental procedures. After careful review of the electrolysis cell operating parameters, several problems were identified. It was determined that the amount of electrolyte used in the cells was insufficient to provide adequate volume for the duration of the test. Electrolyte volatility was found to contribute to large electrolyte losses during a 20-h test.

Initially it was believed that placing a large (250-g) high-purity Al pad into the electrolysis cells would aid in coalescing the Al that was produced. Although the molten Al in each cell could be consolidated into a large pad, those pads did not remain stable. Post-test analysis of several cells indicated that the Al pads were sufficiently large to extend to the electrolyte surface. This resulted in electrical shorting of the anodes to the molten Al cathodes, which was most likely responsible for anode failure. As a result of electrolyte volatility, other cells contained so little electrolyte at the end of the tests that the Al metal pad was exposed to the electrolyte surface, again resulting in anode shorting.

TABLE 1. Experiments Performed Through FY 1987

EXP. NUMBER	ANODE NUMBER	DURATION (HOURS)	CURRENT (AMPS)	ANODE CURRENT DENSITY (A/cm2)	ALUMINUM PRODUCED (GMS)	COULOMBIC EFFICIENCY	BATH RATIO	AlF3	Al2O3	CaF2	MgF2	LiF	wt% Fe in Al metal	wt% Ni in Al metal	wt% Cu in Al metal	wt% Fe in bath	wt% Ni in bath	wt% Cu in bath	SUCCESS OR FAILURE	COMMENTS
58	102-1 & 101-2	20.0	20.1	0.5	0	0%	1.15	9.5	8.0	4.0	0	0	-----	-----	-----	-----	-----	-----	SUCCESS	2 Al-anodes, very slight edge wear
57	100-2	17.0	10.5	0.5	80.2	95%	1.35	3.7	8.0	5.0	0	0	-----	-----	-----	-----	-----	-----	SUCCESS	Cerox test; slight edge wear beneath coating
56	106-1	20.0	11.5	0.5	44.6	58%	1.15	9.5	8.0	4.0	0	0	-----	-----	-----	-----	-----	-----	SUCCESS	No wear
55	104-1	19.0	10.55	0.5	61.1	91.5%	1.15	9.5	8.0	4.0	0	0	-----	-----	-----	-----	-----	-----	SUCCESS	Al-anode, only very slight edge wear
54	105-2	20.0	11.0	0.5	68.7	93%	1.15	9.5	8.0	4.0	0	0	0.112	0.022	0.112	-----	-----	-----	SUCCESS	No wear
53	105-1	15.0	11.2	0.5	47.2	85%	1.15	9.5	8.0	4.0	0	0	0.103	0.013	0.061	-----	-----	-----	SUCCESS	No wear
52	103-2	20.0	10.8	0.5	64.3	88%	1.15	9.5	8.0	4.0	0	0	0.121	0.002	0.015	-----	-----	-----	SUCCESS	No wear
51	103-1	10.0	21.45	1.0	63.1	88%	1.15	9.5	8.0	4.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	Cerox, catastrophic, medium
50	100-2	20.0	21.8	1.0	No weight taken	---	1.0	14.7	2.0	10.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	slight edge, bottom, side wear
49	92-1	11.6	21.0	1.0	No weight taken	---	1.0	13.4	4.5	10.0	5.0	0	-----	-----	-----	-----	-----	-----	FAILURE	slight edge, bottom, side wear
48	98-3	15.0	20.6	1.0	No weight taken	---	1.0	14.7	2.0	10.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	catastrophic, med-large
47	96-2	14.0	20.4	1.0	No weight taken	---	1.0	13.4	4.5	10.0	5.0	0	-----	-----	-----	-----	-----	-----	FAILURE	catastrophic, med-large
46	97-2	20.0	22.0	1.0	111.0	75%	1.3	5.3	5.0	4.0	0	0	0.181	0.014	0.045	0.056	0.147	0.269	SUCCESS	very slight to nil wear
45	97-1	20.0	21.9	1.0	100.0	68%	1.1	10.8	5.0	10.0	0	0	0.235	0.165	0.245	-----	-----	-----	SUCCESS	very slight edge wear
44	82-2	20.0	21.9	1.0	No weight taken	---	1.07	11.7	11.6	4.0	0	0	ICP numbers not useable			0.032	0.022	0.020	SUCCESS	No wear
43	92-2	6.0	22.7	1.0	No weight taken	---	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	SUCCESS	very slight, even, edge, bottom, side wear
42	90-3	20.0	22.3	1.0	82.2	55%	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	catastrophic, med-large
41	90-2	20.0	20.7	1.0	120.8	87%	1.1	10.8	5.0	10.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	catastrophic, large
40	85-2	20.0	21.5	1.0	113.5	78%	1.0	14.7	2.0	10.0	0	0	ICP numbers not useable			0.166	0.106	0.413	FAILURE	cat. small-med
39	85-1	20.0	21.0	1.0	118.8	83%	1.1	10.8	5.0	10.0	0	0	ICP numbers not useable			0.093	0.300	1.070	FAILURE	cat. med.
38	86-4	30.0	14.95	1.0	123.8	82%	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. small-med
37	66-2	30.0	23.4	1.0	114.7	49%	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	slope wear
36	66-3	20.0	18.9	1.0	102.4	80%	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	SUCCESS?	good? not identified
35	66-1	20.0	16.9	1.0	99.0	88%	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	PARTIAL SUCCESS	slight edge wear
34	63-3	20.0	17.6	1.0	22.9	19%	1.3	5.0	8.0	6.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	slope wear
33	63-2	20.0	18.9	1.0	72.4	64%	1.2	7.8	6.0	6.0	2.0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med.
32	63-1	19.8	20.6	1.0	111.1	81%	1.0	14.1	5.0	4.0	6.0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. large
31	54-2	20.0	20.6	1.0	74.0	53%	1.0	13.4	4.5	10.0	5.0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med-large
30	62-4	20.0	20.6	1.0	101.4	74%	1.3	7.1	8.0	3.0	4.0	2.0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med.
29	62-2	20.0	19.8	1.0	82.2	62%	1.1	11.8	10.0	4.0	2.0	1.0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med.
28	62-1	20.0	21.0	1.0	111.7	79%	1.25	9.1	5.0	7.0	3.0	2.5	-----	-----	-----	-----	-----	-----	FAILURE	cat. med.
27	54-1	7.0	20.1	1.0	No weight taken	---	1.1	16.6	11.0	4.0	0	5.0	-----	-----	-----	-----	-----	-----	FAILURE	cat. no pics taken
26	54-3	20.0	21.4	1.0	126.6	86%	1.1	10.8	5.0	10.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	severe edge wear
25	54-4	12.2	20.9	1.0	No weight taken	---	1.25	9.1	5.0	7.0	3.0	2.5	-----	-----	-----	-----	-----	-----	FAILURE	anode fell off, cat. large
24	55-4	20.0	19.9	1.0	119.4	89%	1.0	13.4	4.5	10.0	5.0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. edge and side, bottom was minimal
23	55-1	17.5	21.2 ave	1.0	No weight taken	---	1.1	10.3	10.3	4.0	6.0	5.0	-----	-----	-----	-----	-----	-----	FAILURE	anode fell off, no pics
22	55-3	20.0	21.0	1.0	107.9	77%	1.3	5.3	5.0	4.0	0	0	-----	-----	-----	-----	-----	-----	PARTIAL SUCCESS	slight edge wear only
21	55-2	20.0	21.0	1.0	119.9	85%	1.0	14.0	5.0	4.0	6.0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. edge only
20	52-2	20.0	21.0	1.0	73.0	52%	1.0	13.4	2.0	10.0	5.0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. large
19	52-1	20.0	21.0	1.0	67.1	48%	1.1	10.3	10.3	4.0	6.0	5.0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med.-large
18	53-3	20.0	20.9 ave	1.0	130.2	88.5%	1.0	14.7	2.0	10.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. small
17	53-2	17.5	20.2 ave	1.0	41.2	35%	1.0	13.4	4.5	10.0	5.0	0	-----	-----	-----	-----	-----	-----	FAILURE	anode fell off, cat. large
16	42-2	30.0	21.2 ave	1.0	52.2	24%	1.1	16.8	11.0	3.8	0	5.0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med
15	40-1	30.0	20.7 ave	1.0	120.4	56%	1.1	10.3	10.3	3.9	6.0	5.0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med-large
14	42-3	30.0	18.9 ave	1.0	134.3	71%	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. small-med.
13	41-3	30.0	21.1 ave	1.0	114.9	54%	1.07	11.7	11.6	4.0	0	0	0.855	0.488	0.504	-----	-----	-----	FAILURE	slope wear
12	41-4	30.0	19.8	1.0	146.8	73%	1.07	11.7	11.6	4.0	0	0	0.611	0.414	0.282	-----	-----	-----	FAILURE	slope wear
11	52-3	30.0	19.5 ave	1.0	170.9	87%	1.1	11.8	10.0	4.0	2.0	1.0	0.265	0.186	0.714	-----	-----	-----	FAILURE	cat. edge & side, bottom ok
10	41-1	20.0	20.0	1.0	85.0	64%	1.1	12.7	10.0	4.0	4.0	2.0	0.700	0.587	0.568	-----	-----	-----	PARTIAL SUCCESS	bottom not flat
9	41-2	30.0	20.2	1.0	No weight taken	---	1.07	11.7	11.6	4.0	0	0	-----	-----	-----	-----	-----	-----	FAILURE	cat. med. no other data recorded

1 through 8 were scoping experiments and data not available.



Legend for Table 1, Comments column. Slight wear is meant to define wear of less than 0.5 mm, which is just visible to the eye. Edge wear is qualified the same as slight wear, however, only the edge of the anode is affected. Slope wear appeared on some anodes, and although the anode appeared sound, it did not maintain the original shape. Catastrophic failures were characterized by severe degradation of a portion of the anode cermet matrix.

These problems were easily solved. In subsequent experiments, sufficient electrolyte was used to maintain the level at 6 to 8 cm above the molten Al pad. Careful monitoring of electrolyte volatility ensured adequate electrolyte depth throughout the tests. The other problem was also effectively solved by lining the cell bottoms with a TiB_2-G[a] composite cathode material obtained from Great Lakes Research Corporation. Use of this Al-wetting cathode material allowed the size of the Al pad at the start of an experiment to be reduced by a factor of 4. Shorting between the anodes and molten Al cathodes was eliminated. These improvements were developed in Experiments 43 through 50 shown in Table 1.

(a) TiB_2-G is a composite material comprised of a TiB_2 matrix into which graphite is infiltrated. The process for fabricating these composites was developed by Great Lakes Research Corporation.

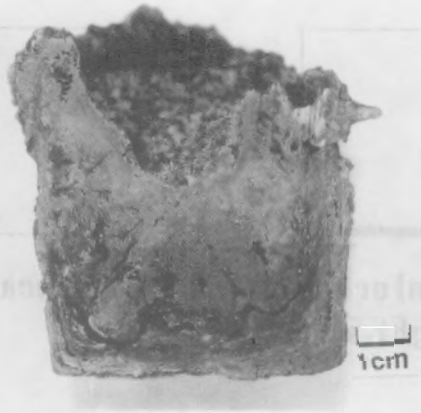


FIGURE 1. Anode that Failed Due to Severe Corrosion (from Experiment 25)

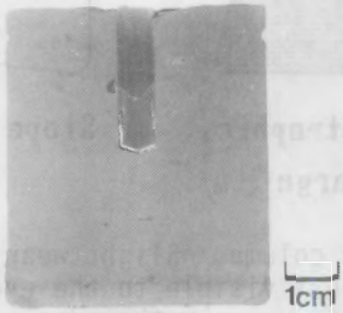


FIGURE 2. Anode that Exhibits Only Slight Corrosion at the Edge (from Experiment 35)

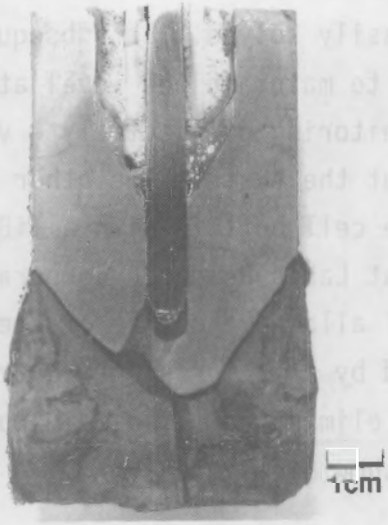


FIGURE 3. Anode from Experiment 41, Which Was an Attempt to Duplicate Previous Partially Successful Experiments

Verification Tests. Additionally, Experiments 45 through 50 (Table 1) were conducted in an attempt to reproduce the partly successful tests performed earlier using the improved cell operating procedures. Experiments 45 and 46 were successful, and little or no wear was apparent on the anodes (Figure 4). However, experiments 47, 48, 49, and 50 produced anodes that had degradation that could not be explained (Figure 5). These four cells were difficult to operate, and all required constant attention to maintain stable operation. The cell operating procedures were again scrutinized.

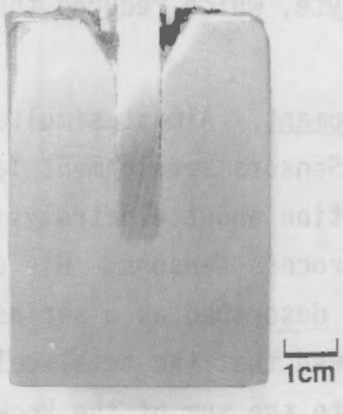


FIGURE 4. Anode from Experiment 46. Only slight wear is apparent.

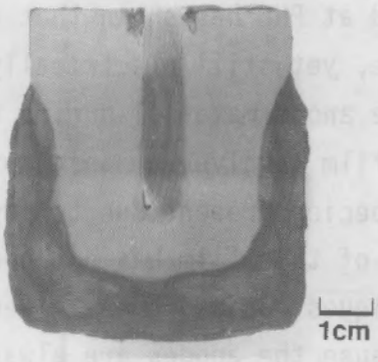


FIGURE 5. Anode from Experiment 48. Note the large amount of degradation.

The Al_2O_3 feed used in the experiments to that point was a highly calcined Al_2O_3 obtained from J. T. Baker Chemicals. Cell mucking (sludging) was a continual problem, which indicated the dissolution kinetics of the highly calcined Al_2O_3 were slow. After consultation with aluminum industry representatives, the type of Al_2O_3 fed to the cells was changed. "Metal grade" Al_2O_3 was obtained from Alcoa for the next tests. This Al_2O_3 was found to dissolve much more easily, and mucking problems were less severe. The equations used to calculate the saturation concentration of Al_2O_3 in the electrolyte were also reviewed. This resulted in lower quantities of Al_2O_3 being added to the electrolyte, which reduced the possibility of oversaturating the electrolyte.

Process Control Development. Almost simultaneously with the verification tests, O. H. Koski (Sensors Development Task) was conducting research designed to provide information about electrolysis cell operation that would aid in the development of process sensors. His experiments showed that Al electrolysis cells could be described as a series of resistive components. Examination of the data showed that the total cell resistance measured during electrolysis was not equal to the sum of the known cell resistances. Evaluation of the electrolysis process determined that a resistive film was formed or plated onto the surface of the anode (see Section 5.0).

The research performed at PNL has shown that anodes can be protected by this electrically resistive, yet still electrically conductive, film which forms on the surface of the anode material during the electrolysis process. It is postulated that the film involves an anion of some oxy-alumino-fluoride species or a metal oxide species present due to impurity contamination. The exact chemical composition of this film has not been determined; current analytical chemistry techniques appear to be inadequate. Post-test analyses cannot detect the film because the anodes are always coated with a thin layer of electrolyte, which interferes with analytical techniques. In-situ analyses (such as Raman spectroscopy) have not proven successful due to interference from the surrounding physical and chemical environment (electric furnace noise, overlapping spectra, etc.). However, the presence of the film can be confirmed by simple electrochemical techniques discussed below.

Maintenance of the conditions necessary to promote the formation of the protective film is essential to ensure proper anode performance. Research at PNL has shown that the integrity of the protective film is influenced by operating temperature, Al_2O_3 concentration in the electrolyte, and anode current density. The effects of temperature on the observed anode and electrolyte resistance are shown in Figure 6. Experiments were performed with Al_2O_3 concentrations ranging from 0 to 15 wt%. The observed resistance shows a marked increase at temperatures below 940°C over the Al_2O_3 concentration range of 0 to 10 wt%, and at temperatures below 965°C for an Al_2O_3 concentration of 15 wt%.

The observed increase in anode and electrolyte resistance can be attributed to the formation of a highly resistive film layer deposited on the surface of the anode. The formation of this film is suggested by the result that no major changes in the resistance of the anode material, lead wires, or electrolyte resistance occur during electrolysis. Precipitation of electrolyte or Al_2O_3 on the anode surface was not possible because of the high temperature maintained in the experiments. At temperatures above 940°C (0 to 10 wt% Al_2O_3) and 965°C (15 wt% Al_2O_3), the film resistance drops. Results of additional tests indicated that the highly resistive film is unstable and can be disrupted by events inherent in the electrolysis process, such as O_2 bubble nucleation. The film formed at the higher temperatures has been shown to be stable, and is not disrupted by bubble nucleation. It should be noted that the film composition may be identical at all temperatures, but the difference in resistance of the film may be accounted for if the film that is formed at the lower temperatures is thicker than that formed at the higher temperatures.

The formation of a highly resistive film at the lower temperatures has one major implication regarding electrolysis cell operation: electrolysis cells should not be operated at temperatures below approximately 965°C if acceptable operating voltages and anode performance are expected. For one thing, the highly resistive film acts as a barrier to the passage of electric current, and electrical energy is wasted. In addition, the unstable nature of the highly resistive film may contribute to the degradation of the anode material. Film disruption due to bubble nucleation can result in small areas

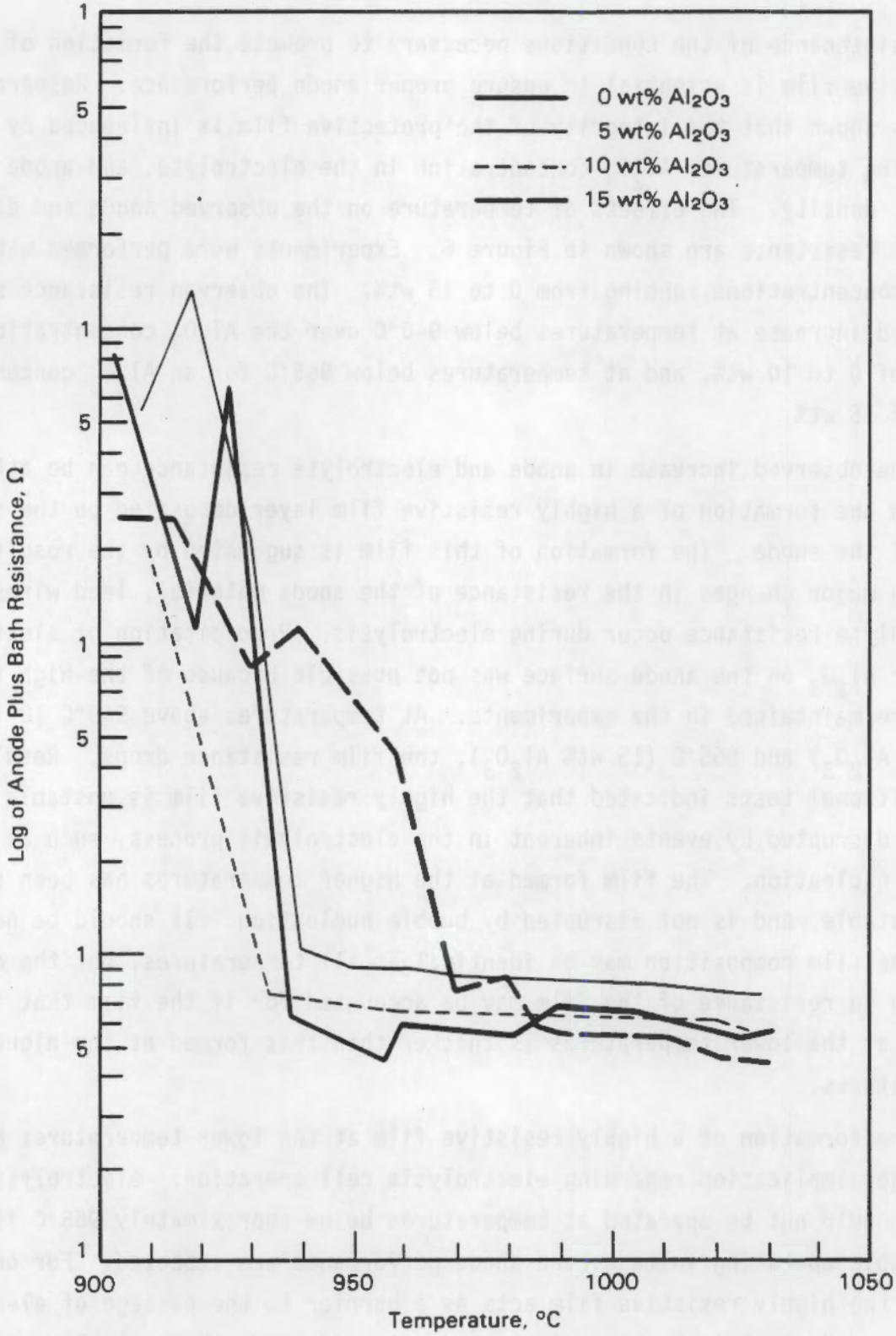


FIGURE 6. Cell Resistance, as a Function of Al_2O_3 Concentration, Versus Bath Temperature

of the anode material being exposed to the electrolyte without the benefit of a protective film. In these localized areas, the current density may be much higher than the overall anode current density. Under these conditions, the anode may undergo degradation.

This point is illustrated by the data presented in Figure 7. The voltage values are those observed for an electrolysis cell using a carbon cathode of undefined potential. That is, the voltages shown are not referenced against a liquid-Al cathode. The curves shown represent the observed cell voltages and the IR-corrected electrode potentials (cell voltage minus the IR drop of the cell) as a function of anode current density.

Resistance data for the 0 wt% Al_2O_3 electrolyte composition are presumed to be for the direct corrosion reaction of the Na_3AlF_6-based electrolyte with the cermet anode material. This reaction is initiated at about 0.5 V above the zero current potential for the cermet anode material, or about 2.7 V when corrected to a cell referenced against a liquid Al cathode.

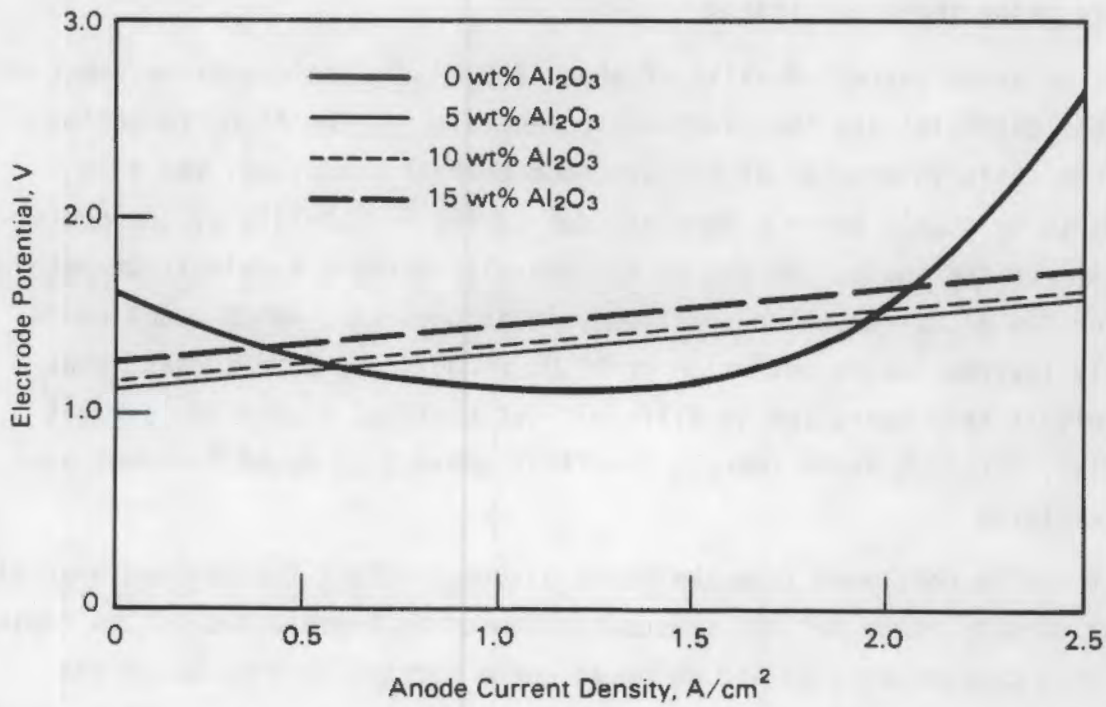


FIGURE 7. Electrode Potential Change with Variation of Anode Current Density

Electrode potential decreases with increasing anode current density until a current density of about 1.6 A/cm^2 is reached, at which point the electrode potential increases. This suggests that the corrosion reaction is self-catalyzing in the anode current density range from 0 to 1.6 A/cm^2.

The electrode potentials plotted for the three compositions of 5, 10, and 15 wt% Al_2O_3 illustrate the conditions under which Al metal is produced during electrolysis and a film is known to cover the anode. As is illustrated, the zero current potentials are approximately 0.5 V below those for the corrosion reaction. The electrode potentials remain below that observed for the corrosion reaction until an anode current density of about 0.5 A/cm^2 is reached. This implies that the corrosion reaction is not favored below 0.5 A/cm^2 anode current density and >5 wt% Al_2O_3. The film on the anodes is also known to be stable at these conditions. Above 0.5 A/cm^2 anode current density, the corrosion reaction is favored; the electrode potential for the corrosion reaction is lower than the electrode potential for the Al_2O_3 reduction reactions. The film on the anode has been shown to be generally unstable under these conditions.

At an anode current density of about 2.0 A/cm^2, the corrosion reaction electrode potential and the electrode potentials for the Al_2O_3 reduction reactions again intersect; at higher anode current densities, the film appears to be stable again. However, due to the instability of the protective film on the anode, and due to the overall increase in electrode potential for the Al_2O_3 reduction reactions, it is uncertain which reaction is actually favored--anode corrosion or Al_2O_3 reduction. Data suggest that electrolysis cell operation is difficult (at best) at high anode current densities, although anode current densities above 1.25 A/cm2 have not been fully explored.

It can be concluded from the above discussion that the desired operating current density range for non-consumable anodes is represented by the region above zero current density and below an anode current density where the electrode potentials of the Al_2O_3 reduction reactions and corrosion reactions are equally favored. Furthermore, the electrolysis cell must be operated at a sufficiently high temperature to encourage the development of a stable,

low-resistance film on the anode; the film is the primary corrosion protection mechanism for the anode material. These conditions cannot be expected to remain identical because electrolyte chemistry and other electrolysis cell parameters vary from one reduction facility to another.

A simple device has been developed for use in determining the stability of the protective film that forms on the anodes during operation. The device is basically a simple reference anode constructed from cermet material and fashioned into a small probe. The circuitry developed to use this device is illustrated in Figure 8. The probe is inserted into the molten electrolyte and fed a small dc current by means of a resistor connected to the main electrolysis dc current bus. The current fed to the probe provides a current density that is a small fraction of that found on the anode but ensures an electrochemical similarity between the anode and the probe. The dc voltage drop between the anode and probe is used as an analog of the anode-to-Na_3AlF_6 potential.

Stable electrolysis cell operation (stable anode film) is represented as a steady dc signal detected between the anode and probe. Any instability of the anode is easily detected as an unsteady dc signal between the anode and

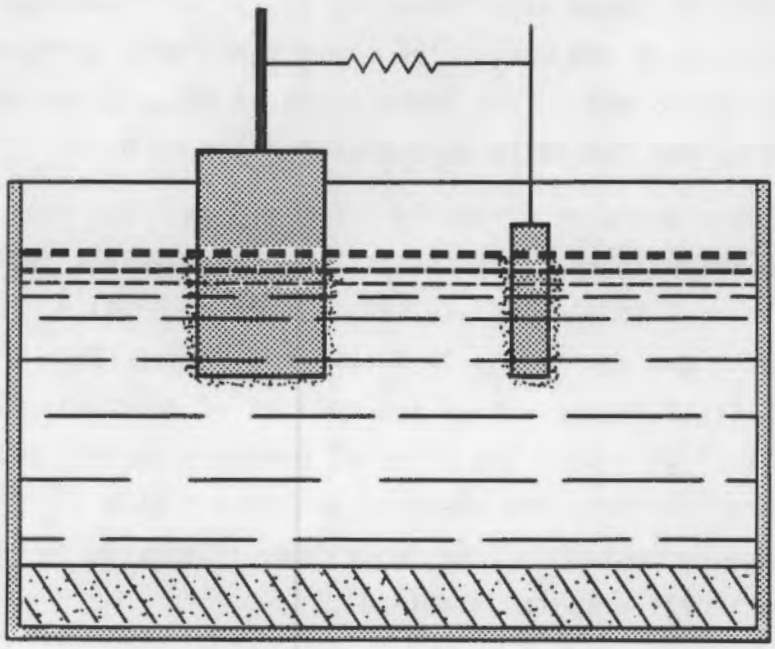


FIGURE 8. Schematic of Simple Process Control Sensor Used to Monitor Anode

probe. Electrolysis cell control is deduced from this signal. Assuming constant Al_2O_3 concentration and anode current density, the temperature can be varied until instability sets in, thus identifying the lowest temperature at which stable operation can be maintained. By similar methods the optimum anode current density and Al_2O_3 concentration can be identified for any electrolyte composition.

This device has been employed in laboratory-scale electrolysis cells at PNL. The operation of electrolysis cells has been greatly improved since the improvements discussed above were made in the operating conditions and the device has been used to monitor cell operating conditions.

Confirmation Testing. Experiments 52, 53, 54, 55, 56, and 58 were performed to study the behavior of $NiO-NiFe_2O_4$-Cu-based cermet anodes using the process control device described above. All of the experiments were performed at reduced anode current densities and actively monitored using the process control device. An immediate improvement in electrolysis cell operation and anode performance was realized.

Three experiments (52, 53, and 54) were performed using $NiO-NiFe_2O_4$-17%Cu anodes at 0.5 A/cm^2 anode current density. The initial bath ratio of the electrolyte used in these experiments was 1.15, and the experiments contained an additional 4 wt% CaF_2. The experiments were performed at or near Al_2O_3 saturation (8 wt%). The temperature of these experiments ranged from 960°C to 970°C, and the cells were operated for 20 h.

These cells were operated virtually trouble free. The cell voltages remained nearly constant throughout the tests. Fluctuations in the cell voltage could be traced to electrolyte volatilization or Al_2O_3 concentration variations due to slight variations in Al_2O_3 feed rates. None of the three anodes from these tests showed visual indications of degradation during the post-test analysis (Figure 9). The Al metal produced during these experiments was recovered and sent for chemical analysis (Table 1). The concentration data are corrected for the impurities introduced by the small Al pads placed in each cell prior to start-up.

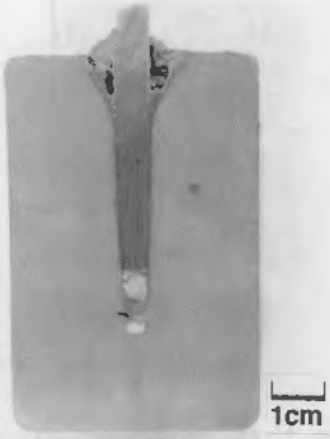


FIGURE 9. Anode from Experiment 52, Which Was Performed Using Process Control Device and Improved Operating Conditions. Crack in anode is a result of rapid air-cooling at end of experiment.

In Experiment 54, a cell was operated for 20 h using an $NiO-NiFe_2O_4$-17%Cu cermet anode. The electrolyte and temperature of this experiment are shown in Table 1. The cell was started using an anode current density of 0.5 A/cm^2 and allowed to reach stable operation. After 6 h of operation, the cell current was increased from 11 A to 25 A (0.5 to 1.1 A/cm^2) in an attempt to "push" the anode protective film. The Al_2O_3 feed rate was adjusted to account for the increase in Al production expected. The cell operated smoothly for about 3 h, at which point the signal monitored between the process control device and anode became unstable. The instability increased rapidly (within 5 min), and the cell current was returned to 11 amps (0.5 A/cm^2) in an attempt to stabilize the cell. The instability continued, and the cell current was further reduced to 5 amps (0.23 A/cm^2). At this current density the cell instability ceased. The cell was allowed to stabilize under these conditions for about 10 min, and then the cell current was increased to 11 amps (0.5 A/cm^2). The cell remained stable for the remainder of the test.

Post-test analyses of the anode again showed no signs of degradation (Figure 10). Apparently the protective film that develops on the surface of the anodes during operation can be "pushed" to higher current densities for short periods. The technique used to eliminate the cell (anode) instability

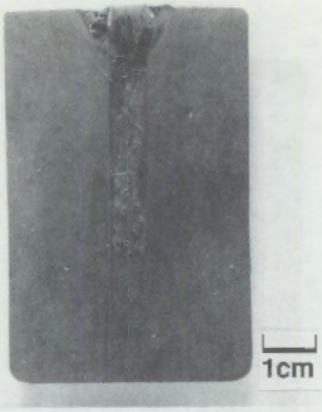


FIGURE 10. Anode that Underwent "Upset" Conditions During Experiment 54

is reproducible and can be used not only to recover from conditions of excessive anode current density but also to recover from the non-consumable anode equivalent of an anode effect.

Alumina starvation was induced during the course of operating several cells by simply turning off the cell feeders. The cells were allowed to operate until insufficient Al_2O_3 was present in the electrolyte to permit steady operation. Once the Al_2O_3 content of the electrolyte was sufficiently depleted, the cell voltage rose sharply at a rate of approximately 0.2 V/min. Left uncorrected, the cell voltage would continue to climb and begin to oscillate sharply. Degradation of the anode would occur unless corrective measures were taken.

During conditions of depleted Al_2O_3, the protective film on the anode is either destroyed or redissolved into the electrolyte. This leaves the anode exposed to the electrolyte with no protection other than its inherent corrosion resistant properties. Research at PNL has shown that the degradation process can be halted before damage results to the anode by following a corrective procedure similar to that described above. After a condition of depleted Al_2O_3 has been identified, the following procedure can be used to re-establish the protective film on the anode:

- Feed the cell a quantity of Al_2O_3 sufficient to eliminate the depleted condition.
- Reduce the cell current to about 1/2 the operating value.

- Allow the cell to operate for a period of approximately 5 min, and observe the cell voltage.
- If the cell voltage increases, reduce the cell current by 1/2 a second time, and allow the cell to operate for another 5 min. When the cell voltage decreases, the conditions have been reached that will promote re-establishment of the film.
- Hold the cell at the highest current that still results in a condition of decreasing cell voltage.
- Allow the cell to stabilize and maintain this operation for at least 10 min.
- Return the cell to the original anode current density.
- If the cell voltage begins to increase, repeat the procedure described above and lengthen the stabilization period.
- If the cell voltage remains stable, resume cell operation and Al_2O_3 feeding.

This procedure has been used successfully many times to recover from Al_2O_3-depleted conditions. It has failed only when the cell has been depleted in Al_2O_3 for extended periods and the cermet anode damaged beyond "repair." The procedure may be applicable to commercial cell operations, though refinement of the technique will be required. Since the process control device will provide the same information as the cell voltage, individual devices could be used to monitor each anode in a commercial cell and allow independent maintenance of each anode.

<u>NiO-$NiFe_2O_4$-Cu- Ni-Al Cermet Experiments</u>. Two experiments (numbers 55 and 58) were performed to test the NiO-$NiFe_2O_4$-Cu-Ni-Al cermet anode material. One experiment (number 55) used a single anode, the other experiment contained two anodes. The first experiment (number 55; single anode) was performed in an electrolyte with an initial bath ratio of 1.15, 4 wt% additional CaF_2, and Al_2O_3 saturation (8 wt%). The cell was operated for 20 h at 965°C, using the process control device. Post-test analyses of the anode showed no visual corrosion (Figure 11).

The second test (number 58) was performed in a larger, 15-cm-diameter electrolysis cell. Two anodes were placed in tandem to test the feasibility of using clustered anodes and one process control sensor for two anodes. The

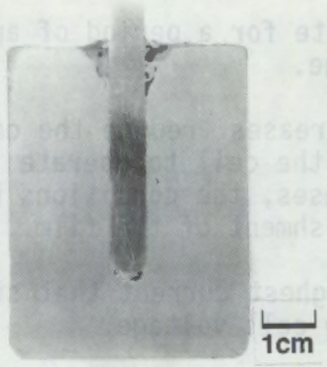


FIGURE 11. $NiO-NiFe_2O_4$-Cu-Ni-Al Anode Used in Experiment 55

electrolyte was the same as in the first test. The cell was operated at 965°C for 20 h without incident. The process control device was effective in monitoring the performance of the two anodes, though it would not have been possible to distinguish between the two anodes if a problem had developed with one and not the other. Post-test optical microscopy of the anodes indicated virtually no corrosion; only one of the anodes showed evidence of a slight amount of corrosion at the edge. The effect of geometry on anode performance may need to be investigated further.

FUTURE DIRECTIONS

Research performed through the end of FY 1987 has lead to new discoveries about the use of non-consumable anodes for the electrolytic production of Al. The importance of cell control and anode monitoring has been realized, and these techniques must be made applicable to commercial electrolysis cells if this technology is to be implemented by commercial industry. Future research will focus on the verification and confirmation of the operation techniques discussed in the preceding section, and on expansion of the range of electrolytes that can be used with the cermet anodes. Although the $NiO-NiFe_2O_4$-Cu-Ni-Al cermet material appears to be the most promising non-consumable anode material developed (high electrical conductivity, good performance in cells), the standard $NiO-NiFe_2O_4$-17%Cu anode material may prove cheaper and easier to produce. This issue will also be addressed in FY 1988.

The final goal of the future work is, of course, implementation of non-consumable anodes by the aluminum industry. Continued success and promising results should allow the realization of that goal.

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