Date: March 23, 1982

Subject: Primary Processes R & D
Monthly Report - March 1982

From/Location: E. L. Cambridge/by J. C. Withers

To/Location: J. G. Kaufman

REDUCTION RESEARCH

AD-108 Process

Composite powder anode further investigations are awaiting non-conducting diaphragm materials. A reticulated fused alumina foam has been received and a porous boron nitride material is due in shortly which will be used to continue these investigations. In the meantime, prebaked anodes have been utilized for investigation with the sophisticated intrumentation of the Potentiostat and voltameter. Prebaked anodes of standard composition and containing 3% and 6% aluminum metal powder from skim were utilized in all fluoride melts containing high (35%) aluminum fluoride. Current-voltage sweeps were made utilizing the previously developed aluminum reference electrode. Utilizing a typical anode current density in a modern cell of 0.7 amps/cm^2, 1½ inches ACD, the major contributor to overall cell voltage was the increase in anode potential with respect to the reference electrode.

This increase is quite surprising since the aluminum powder was added to decrease anode resistance. This anomaly could be due to density decrease in anode fabrication or carbide formation during baking.

A standard anode comparison in the low (9.2%) and high AlF_3 melts at 4.76 cm ACD and 0.7 amp/in^2 anode current density showed a total cell voltage of 3.26V for low AlF_3 compared to 3.9V* for high. In the low AlF_3 melt, the cathode potential was 0.2V higher which indicates a concentration overvoltage and surprisingly 0.9V lower through the anode. A bath potential drop of 0.12V/inch in the low AlF_3 melt versus 0.22V/inch in the high AlF_3 melt shows a 42% increase in conductivity for the low AlF_3 melt. However, current efficiency for an approximately 500 amp/hr run showed 46% for the low AlF_3 melt compared to 82% for the high AlF_3 melt. This low CE is not necessarily discouraging for an isolated run. AlF_3 concentrations in all fluoride melts will be further investigated to optimize conductivity, CE, cathode and anode potentials.

*These absolute cell voltages can vary from run to run depending on length of the anode and the bus connection made to it.

Potentiostatic current-voltage sweeps using the cyclic voltametric technique were conducted employing a carbon anode and composite anode in a high AlF_3 all fluoride melt. The cyclic voltamonograms for the carbon anode showed a very small peak for CO_2 formation and a major peak for CF_4 formation (i.e. anode effect). This indicates that the alumina concentration in this melt is

very low and the anode reaction is diffusion controlled. The composite anode on the other hand, showed no current peaks even at very fast scan rates (2V/sec). This result indicates there are no diffusion limited reactions which leads to the conclusion that the alumina is electrochemically dissolved in the melt. Since chemical diffusion is not a limitation, as is the case in the Hall cell, the major consideration of a composite anode is carrying anodic current to the anode melt interface. This has been confirmed in the previous loose particle anode test and amplifies the importance of the electrically nonconductive diaphragm containing particles that must have a good anode contact through the anode buss connector.

Further studies will utilize the potentiostat to screen different anode configurations, their anodic contact methodology, and modified baths utilizing various aluminous feed materials.

A mathematical model for analyzing the voltage components taken from cell operating data has been set up and is being debugged in the computer.

Hydrogen level in prebaked composite anodes utilizing trihydrate dried at 110°C and 400°C, and MGA were 0.42%, 0.45% and 0.22%. There is no distinguishable difference between trihydrate dried to 110° and 400°C. Standard carbon anodes for Hall cell operation contain about 0.2% hydrogen. If a partially calcined trihydrate is used to make prebaked composite anodes, the effect on CE and fluoride emissions must be assessed relative to the residual hydrogen.

An additional test has been attempted on modeling the self-baking composite anode during which time the furnace burned out. The furnace is being modified and repaired for further testing.

AD-116 - Potlining Resource Recovery

Three processes for potlining resource recovery were examined by the joint Anaconda/Alcan study group. During that examination, heat and material balances, chemical reactions, equipment flowsheets, materials of construction, and capital and operating costs were scrutinized and change recommendations were made.

In an effort to reduce capital costs, the soda ash recovery section of both the Anaconda-S and Mini-L processes was eliminated and a sodium hydroxide concentrator added.

New heat and material balances and equipment flowsheets were completed for the Anaconda-S and Alcan-D processes. New capital and operating cost statements are being compiled.

Carbon

Ashland-240 pitch investigations at Columbia Falls (CF) continues with minor property improvements being achieved. Ashland-240 has a higher peak volatile emission rate than coal-tar pitch and thus would be expected to yield lower anode density at comparable bake conditions. To offset this

phenomena, slower bake rates are being investigated. Generally, the bake density and related property values of anodes utilizing Ashland-240 remain unsatisfactory.

During the Tucson Anode Technology Committee meeting of March 16-17, meetings were held with Fisher, Payne and Ryan of Columbia Falls concerning Tucson submitting a proposal leading to upgrading anodes to at least Mitsubishi technology quality. Meetings were also held with Hoffman and Woodall concerning improving raw materials specifications and the advantages of utilizing a coke consulting service.

The Anode Technology Committee meeting appeard to have been quite successful. These meetings will continue on a semiannual basis. Arco coke has performed well in anode tests at Columbia Falls but particle size (insufficient +4 mesh) remains a problem. Reduction of calcination has been suggested and with an increase in the coarse fraction would result in satisfactory Arco coke for Columbia Falls.

The Tucson presentation of penalties associated with pitch and coke deterioration was well received and provoked much discussion, particularly on the association of vanadium with reduce CE. There was considerable disagreement among the committee members of the effect of CE on anode quality, but a consensus that CE in the plant context versus vanadium should be determined.

The Columbia Falls carbon technology seminar is scheduled for March 29 and for Sebree April 19. During the Columbia Falls seminar the related subject of improved cathode support and life will be covered.

Arco Coal has submitted several samples of bituminous coal for evaluation as anode carbon. Utah tar sands are also being considered for anode carbon. Both these sources of carbon may only, at best, become of practical value in about a decade.

KHD visited Tucson and the order placed for a laboratory vibratory compactor that will produce anodes in 2, 3, 6 and 10 inch diameter. Vibration frequency, amplitude and pressure are all independently variable. Delivery is expected by the end of the year.

BASIC RESOURCES

AD-117

Experimental work has continued on removal of P_2O_5 from alumina. An eight experiment campaign evaluating the effect of H_2SO_4, HF and alumina calcination temperature on the leaching of P_2O_5 has been completed. Experiments designed to test the effect of washing raw clay with sulfuric or hydrochloric acids on removal of P_2O_5 have been conducted. These are an attempt to remove phosphorus at the beginning of the clay process rather than from the alumina end product. For the same reason the possibility of removing phosphate from the initial HCl/clay leach mixture by contacting it with raw clay has been attempted. The underlying rationale here is the

known ability of kaolin particles to bind phosphate ions. Analytical results for these experiments are inconclusive at present. Removal of phosphorus as PH_3 from alumina by reaction with hydrogen gas at 500°C has been attempted. Analytical results are not yet available.

A literature search on the effect of phosphorus on Hall-Heroult cells has been obtained.

AD-105

Samples of ammonoalunite have been prepared from clay on a 100g scale for use in thermal decomposition studies and for the determination of impurity levels in the alumina derived from that compound. These studies will be important in deciding if a clay process based on an $H_2SO_4/(NH_4)_2SO$ system is a viable alternative. Personnel have been diverted for the immediate future to work on aspects of the Al_2O_3/Cl_2 system.

Bauxite Evaluation

A literature search on methods of Bauxite analysis has been obtained from Ms. Donna Mendenhall. Contacts with ANSI, ASTM and NBS have been made with regard to standard procedures and standard test samples.

AD-120 - Anhydrous $AlCl_3$ Process

The most significant result for this period is the PCB levels in the $AlCl_3$ product. Anhydrous $AlCl_3$ produced from reductive chlorination at 550°C using partially calcined coke under nitrogen and partially calcined ACH was found to contain about 0.05% PCB (i.e. $\sim$50,000 ppm). Similarly, anhydrous $AlCl_3$ produced from reductive chlorination at 800°C using fully calcined coke and partially calcined ACH, was found to contain about .002% PCB (i.e. 2000 ppm). However, the product from the reductive chlorination at 550°C using either CO or partially calcined green coke which had been previously calcined in air, showed no increase in the PCB level of the background deionized water used for the preparation of the same. The air calcined green coke and partially calcined ACH which appears not to result in producing PCB's is our base case economic model used in comparing the Anaconda $AlCl_3$ process with the Alcoa HTFB process.

Our base case of not resulting in PCB formation is very encouraging, however, it should be considered preliminary, as a larger sample will be required to determine just how low the PCB level is in the anhydrous $AlCl_3$ produced from the chlorination of ACH using partially calcined green coke under controlled air atmosphere. This area is receiving top priority in the AD-120 process studies.

The results of fractional factorial design experiments employed to determine the effect of temperature, calcination time, particle size heating rate, carrier gas and flow rate on the residual hydrogen and surface area of ACH indicate that; (1) temperature has the largest effect on reducing the residual hydrogen, (2) particle size has a small but significant effect on hydrogen, and (3) none of the other factors have a significant effect, nor was an

interaction obtained. From this set of experiments, the average residual hydrogen obtained at 400°C was 0.56% and at 700°C was 0.27% H_2. A 0.24% hydrogen is acceptable for the proposed process. Surface area data of the ACH treatments is being analyzed. These results indicate that calcination of ACH at temperatures claimed by CSIRO patent (250-400°C) will result in an unacceptable hydrogen level in the product. A campaign of statistically designed experiments to narrow down the optimum operating temperature, time and particle size of ACH will be conducted to further lower the H_2 content of the ACH to be used in reductive chlorination to produce anhydrous $AlCl_3$.

In addition, a set of experiments examining the possible effect of a two-stage calcination of ACH on residual hydrogen, chlorine, LOI and BET surface area have begun. The first stage is 300°C calcination in a rotary kiln. Stage two is either calcination in vacus at temperatures between 400 and 1000°C or calcination in a fluidized bed at 500°C using different fluidizing gases. The purpose of this work is to explore ways of reducing the hydrogen content while maintaining a high level of activity in the alumina.

The result from fractional factorial design experiments employed in the partial calcination of green petroleum coke to determine the effect of calcination temperature, calcination time, particle size, and carrier gas (nitrogen vs air) on the residual hydrogen and surface area of coke indicate that (1) temperature alone has the largest significant effect on reducing the residual hydrogen, and (2) temperature, calcination time, particle size, and carrier gas have a signficant effect on the coke surface area. Surface area as large as 22 m^2/g was found for calcination at 650°C for 30 minutes and for particle size of -100 mesh using air at a flow rate of 600 cc/minutes. However, the residual hydrogen for this condition is unacceptably high (1.92% H_2). A calcination temperature of 850°C, particle size of -100 mesh, 30 to 120 minutes calcination time and air flow from 200-600 cc/minute will produce coke with an acceptable hydrogen level and a surface area of about 6 m^2/gm. Further work is scheduled to optimize treatment with H_2 level and maximum surface area. Reductive chlorination rate experiments of PC/ACH with various reductants have continued and data are being analyzed.

Tenneco Chemicals visited Tucson concerning the supply of a pure CO feed for the reductive chlorination of ACH. If capital numbers hold up, that Tenneco is supplying in more detail, there exists a possibility of obtaining CO at about 5¢/lb. Previous economic analysis showed 7¢/lb was break even with carbon as a reductant.

Paul A. Nelson and G. F. Vandergrift of Argonne National Laboratory visited Tucson concerning producing anhydrous $AlCl_3$ by solvent extraction. Chris Anderson of Solar and John Sibert from Los Angeles also attended the meeting. While some very unusual solvent extraction techniques were revealed, the initial conclusion is that the process is probably uneconomical, although John is further checking out the economics.

In our search and evaluation for a more stable refractory than Sialon (believed to be the preferred material of Alcoa) we have found compositions of $AlN-MgF_2$ to be equal or better than the Sialon in 24 hour tests. A computer model based on NASA thermodynamics is being used to evaluate and predict

compositions. A preliminary feasibility conclusion involving extended test times should be possible within the month on the viability of these type refractories.

DEVELOPMENT & TECHNICAL SERVICES

Lithium Fluoride

The lithium fluoride test continues at Sebree on three cells. These test cells ran 91.7% current efficiency for February with continued improvements into March. Although definitive conclusions cannot be made now, the improvements in test cell operations and project control are encouraging.

As the performance characteristics of Hall cells continue to improve, it becomes increasingly more difficult to realize the full economic benefits of lithium in cells. A techno-economic model is thus useful in avoiding expensive experimentation and statisticaly designs for evaluations. Such a model has been written for computer terminals and printers at Tucson. The technical and economic constants were from Sebree (plant avg. 1981) financial data and P & C reports. The following conclusions have been drawn, thus far, in the Sebree context.

Using aluminum price at $1507/ton, electrical energy cost at $0.027/kwh, lithium carbonate cost at $1.45/lb, with no change in cell current and anode effect frequency, lithium carbonate consumption rate at 4 lbs/ton Al, the following increase in current efficiency must be gained in order to realize a benefit-to-cost ratio of 1 (ROI = 0%):

% LiF	Increase in CE (%)
1	1.0
2	1.4
3	1.8
4	2.2

An additional gain of 0.5% in the current efficiency will have to be made to offset an increase of anode effect frequency of 1 anode effect/day.

The results of the model will be presented and discussed with Sebree during the week of March 22 and at a future time at Columbia Falls. A set of statistical designed plant experiments should be the result of these meetings.

Sebree Large Anode Project

The test to reduce the unit power consumption at Sebree by using larger area anodes is phasing out with the last large anode to be pulled on March 29. A statistical study of the test data is being conducted at Sebree. Future plans include a twenty-one pot test for a period of six months to a year. The anodes used in the extended test may be slightly smaller in dimensions than those used in the initial test to reduce carbon setting problems.

Fort Meade Aluminum Fluoride

Sebree is experiencing no problems in their test of Fort Meade Aluminum Fluoride as an alternative supply.

FACILITIES

Construction of the Carbon and Reduction Research laboratory continues within budget and is estimated to be slightly ahead of schedule. Occupancy may be as much as two weeks ahead of schedule, but there may be a problem with on-time delivery of the 50 kva transformer. A smaller transformer is available and will be utilized until the larger one arrives.

E. L. Cambridge/by J. C. Withers

E. L. CAMBRIDGE

ELC:pm

cc: R.W.Bartlett
File: 0.8.1