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Aluminum Carbothermic Technology

Final Technical Progress Report for the
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Elkem ASA

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EXECUTIVE SUMMARY

This report documents the non-proprietary research and development conducted on the Aluminum Carbothermic Technology (ACT) project from contract inception on July 01, 2000 to termination on December 31, 2004. The objectives of the program were to demonstrate the technical and economic feasibility of a new carbothermic process for producing commercial grade aluminum, designated as the "Advanced Reactor Process" (ARP). The scope of the program ranged from fundamental research through small scale laboratory experiments (65 kW power input) to larger scale test modules at up to 1600 kW power input. The tasks included work on four components of the process, Stages 1 and 2 of the reactor, vapor recovery and metal alloy decarbonization; development of computer models; and economic analyses of capital and operating costs.

Justification for developing a new, carbothermic route to aluminum production is defined by the potential benefits in reduced energy, lower costs and more favorable environmental characteristics than the conventional Hall-Heroult process presently used by the industry. The estimated metrics for these advantages include energy rates at approximately 10 kWh/kg Al (versus over 13 kWh/kg Al for Hall-Heroult), capital costs as low as $1250 per MTY (versus 4,000 per MTY for Hall-Heroult), operating cost reductions of over 10 %, and up to 37 % reduction in CO_2 emissions for fossil-fuel power plants. Realization of these benefits would be critical to sustaining the US aluminum industries position as a global leader in primary aluminum production. One very attractive incentive for ARP is its perceived ability to cost effectively produce metal over a range of smelter sizes, not feasible for Hall-Heroult plants which must be large, 240,000 TPY or more, to be economical. Lower capacity stand alone carbothermic smelters could be utilized to supply molten metal at fabrication facilities similar to the mini-mill concept employed by the steel industry.

The accomplishments of the project are listed:

- The system thermo-chemistry was defined for the Advanced Reactor Process flow diagram.
- An operating diagram was developed based on available thermodynamics for the $Al_2O_3 – Al_4C_3$ system.
- Correlations for slag and metal alloy viscosities versus temperature and composition were predicted from developed mathematical expressions.
- Stage 1 was demonstrated at the 1 MW scale.
- Stage 2 critical components were demonstrated in a 500 kW module.
- The fundamentals of vapor recovery were experimentally determined, including reaction mechanisms and Al species vapor pressures.
- The detailed design and installation of an advanced Stage 1 system was completed, including a vapor recovery reactor.
- The feasibility of efficient Al – C separation was demonstrated.
- Capital and operating cost estimates for the process were updated.
- Computer models were developed for the vapor recovery system and are in progress for Stage 1, Stage 2 and the total process.
- A number of papers were presented and published in Light Metals and other journals and/or conference proceedings.

- Five US patents have been awarded; 3 patent applications are in process of being reviewed by the US Patent Office.

Based on these accomplishments it was concluded that (1) the thermodynamics of the process are valid; (2) the designs of the Stage 1 and Stage 2 reactor components successfully address the identified technical hurdles related to the pre-reduction and reduction process steps; (3) efficient decarbonization of the Al–C alloy product is feasible; (4) fundamentally, the vapor recovery process concepts are valid; (5) the process economics are favorable compared to the Hall-Heroult process for production of commercial grade Al; and (6) that the program should continue with emphasis on the engineering of the vapor recovery system, followed by the implementation of a 3 MW totally integrated reactor system to demonstrate all steps of the process and to develop additional design data for a large scale pilot reactor system.

It is recommended that the program be continued through the 3 MW integrated reactor evaluation. Based on the results of test campaigns with the integrated reactor, plus a further update on process cost estimates, the next phase of study would be the design and implementation of a large scale pilot reactor. Successful evaluation at the pilot scale would enable the design and implementation of one or more commercial plants sized to meet specific business opportunities.

INTRODUCTION

The Aluminum Carbothermic Technology project addresses the Aluminum Industry Technology Roadmap goal of making the U.S. aluminum industry more competitive in world markets. Alcoa's carbothermic process, the Advanced Reactor Process, is projected to reduce capital and operating costs, reduce process energy consumption, and reduce CO_2 emissions for smelting. The process is expected to attain an energy rate on the order of 10 kWH/kg of Al which is about 25% lower than the benchmark Hall-Heroult rate of 13.25 kWH/kg.

The carbothermic Advanced Reactor Process is a multi-stage system in which a molten slag bath containing alumina and carbon is reacted to produce aluminum carbide in a low temperature stage. The resulting alumina – aluminum carbide slag then flows into a high temperature stage where the aluminum carbide is reacted with the alumina to produce aluminum metal. The aluminum is less dense than the slag and accumulates as a layer floating on the slag. The low temperature and high temperature stages are located in a common reaction vessel and are separated by an underflow partition wall. The high temperature stage has an outlet for continuously tapping molten aluminum. Additional carbon material is supplied to the high temperature stage to satisfy the reaction stoichiometry

Energy required for the low temperature stage melting and pre-reduction is supplied by high intensity slag resistance heating using vertical carbonaceous electrodes submerged in the molten slag. Similarly, energy to the high temperature stage is high intensity slag resistance heating via a plurality of pairs of horizontally arranged electrodes through the sidewall of the reactor into the slag phase and below the metal phase.

Each reactor stage could have an off-gas reactor attached to capture the energy and aluminum values from volatile aluminum and aluminum sub-oxide leaving the hot reaction zones. These are referred to as vapor recovery reactors, or VRR's. In effect, the aluminum species are reacted with carbon to produce aluminum carbide that is recycled to the high temperature stage to satisfy the carbon stoichiometry for the reduction step.

The tapped molten aluminum product contains some amount of carbon as aluminum carbide. A metal–carbide separation is attained by cooling the mix to precipitate the carbide, followed by degassing prior to casting into ingots or using the molten aluminum as a feed to some other process. The carbide is an additional carbon source for recycle to the high temperature stage of the reactor.

The development program has been focused on empirical R&D whereby each stage of the Advanced Reactor Process was independently evaluated in modular components ranging in scale from bench (60 – 100 kW furnaces) to laboratory (up to 1500 kW). This includes reactor Stages 1 and 2, vapor recovery and metal product decarbonization. The program was aimed at solving identified engineering problems that were experienced by others in previous research attempts. These problems included efficient delivery of energy to attain the high temperatures required to effect reduction of alumina by carbon to produce aluminum; materials of construction issues; excessive losses of aluminum values and sensible heat due to volatilization; high electrode carbon consumption; and efficient separation of aluminum from carbon to recover commercial grade metal. An additional requirement was that potential solutions had to be economically viable.

Successful production of commercial grade aluminum would result in a generic metal that can be used in any of the typical applications and markets, including aerospace, automotive, packaging and building. If Carbothermic Aluminum Technology is successful, and if it replaced the existing process, the annual energy savings for the U.S. primary aluminum industry would be on the order of 1,500 MWe based on 2003 domestic production. The long term plan for commercialization includes completion of the process feasibility in a 3 MW integrated reactor system, scale up to a pilot unit and design of a commercial facility in the next 6 to 8 years.

BACKGROUND

The objectives of this project are to demonstrate the technical and economic feasibility of the Advanced Reactor Process. Technical feasibility will be demonstrated through completion of a number of tasks that include fundamental experiments related to the vapor recovery system; energy and mass calculations to assess impact of various flow schemes for the process; development of computer models for the reactor stages, the vapor recovery system and the total process; physical modeling to study dynamic parameters for the reactor stages; design, fabrication, assembly, installation and operation of process units both in modular form and as integrated systems, to include reactor Stages 1 and 2, the vapor recovery systems and the product decarbonization unit. Economic feasibility will be accomplished through capital and operating cost estimates continuously upgraded as new information is developed about the process.

Over the last 50 years, many previous attempts were made to develop a successful carbothermic approach to aluminum production. Reynolds worked on an electric arc process from 1971 through 1984. They designed, built and operated small furnaces, 100 to 200 kW size. Their process was a batch system that contained 3 phases of sequential operation: slag pool building using submerged electrodes; reduction and metal making using an open arc mode; and decarbonization of the product metal by alumina extraction of the aluminum carbide. Reynolds identified several major technical hurdles, including (1) an effective power delivery system that would supply heat at greater than 2100^{o}C while avoiding short circuiting and minimizing vaporization of aluminum; (2) efficient charge column operation to recover volatiles; and (3) effective decarbonization of the metal product. Reynolds terminated their efforts due to the perceived costs for scale-up R&D.

Pechiney conducted research on electric arc furnace carbothermic reduction from 1955 to 1967. Through 1960, they operated a variety of furnaces ranging from 150 kW single phase to 2.7 MW three phase and produced carbide saturated metal containing 60% aluminum. From 1960 to 1967, Pechiney ran a single phase furnace at up to 6 MW, producing 300 tons of carbide saturated metal; and a 2 MW, three phase unit that made 540 tons of 70-80 % Al. Their carbothermic processes turned out to be cost prohibitive due to high consumptions of alumina and carbon, high vaporization losses and high energy usage (18.75 kWH/kg).

Alcan acquired information from Pechiney and attempted to solve the problems that Pechiney had experienced. Alcan did employ a two stage concept to reduce the volatility issues. Two reaction chambers were used, requiring transfer and recycle of molten slag through resistance heated pipes. However, their design was difficult to implement and eventually they stopped their program in the early 1980's.

Alcoa tried to develop a blast furnace type carbothermic reactor from 1977 to 1982 for the production of Al-Si alloy. The reactor was similar to an iron making unit, with heat supplied by oxygen combustion of coke. This concept also failed. Volatile species flowing up through the downward moving charge condensed in the colder regions and plugged the bed. By the end of the Alcoa program, we were running a bench scale (100 kW) submerged arc furnace which did make Al-Si alloy. In 1999, at the start of our latest effort on carbothermic production of Al, Alcoa hired Mintek to conduct electric furnace tests to evaluate the effects of arc mode on reactor performance. Using a 200 kW unit, Mintek demonstrated that an open arc would not work well due to high volatile generation. Their results confirmed that a submerged arc process was critical to successful production and recovery of Al.

In 1999 at an Alcoa sponsored 3-day workshop on carbothermic approaches to Al, Elkem proposed the basic concept that has become known as the Advanced Reactor Process. As described, the process utilizes slag resistance heating through submerged arc operation. Elkem was an ideal partner to jointly develop the new process since they have a long history of expertise in high temperature metallurgical processes, much of which is founded in electric furnace systems.

Combined with Alcoa's know-how in aluminum smelting and purification, the Alcoa-Elkem team is very highly qualified to address the technical challenges posed by successful implementation of carbothermic reduction. Elkem employs their best design and process engineers located at both Oslo and at their R&D center in Kristiansand, Norway. Elkem also provides an excellent facility for the development work, including high bay space, electric power supplies, machine shops and analytical laboratories. They can operate electric furnaces ranging from 60 kW to over 3 MW.

Alcoa provides experienced engineers and technologists plus excellent facilities at the Alcoa Technical Center (ATC). Most of the fundamental research is being conducted at ATC as well as the development of decarbonization concepts that utilize Alcoa technology for purifying Al. In addition, Alcoa has contracted key consultants expert in high temperature metallurgy and in computer modeling. Carnegie Mellon University (CMU) is also under contract to work on advanced computer models of the process steps.

TECHNICAL PROGRESS

Work done under this contract can be categorized in the following subject:
Fundamental Research;
Computer Modeling;
Reactor Development;
Decarbonization Development;
Economic Analysis.

Fundamental Research

Thermodynamic Background

The overall reaction for carbothermic aluminum production can be written

$$\begin{array}{ccccc} Al_2O_3 + & 3\ C = & 2\ Al + & 3\ CO & \\ 25 & 25 & 2000 & 600 & ^\circ C \end{array} \qquad (1)$$

The temperatures of the products are reasonable estimates for the process. According to thermochemical data, the energy consumption for this reaction is 7.9 kWh/kg Al. Carbothermic processes often have an energy efficiency around 80 percent, and the expected energy consumption for very good operation then becomes 10 kWh/kg Al. The process can also get energy credit for the CO that can be used as fuel to produce power and/or as preheat for charge materials.

When Al_2O_3 and C is heated at atmospheric pressure, a rather complex product is formed. Much of the process chemistry can be understood from the phase diagram Al_4C_3-Al_2O_3, which is shown in Figure 1 (1). The species Al_2O_3 and Al_4C_3 can occur as separate phases, or they can combine to make a liquid Al_2O_3-Al_4C_3 slag. With fixed pressure the equilibrium is completely determined when the system has either three condensed phases or two condensed phases and one of them is slag with a given composition. Two completely determined combinations are possible: Al_2O_3-C-Al_4C_3 and Al_2O_3-Al_4C_3-Al. The species Al_4C_3 is stable only up to 2150°C; above it decomposes to Al and C. The Al phase always contains some C, and it can be considered as an alloy Al-C.

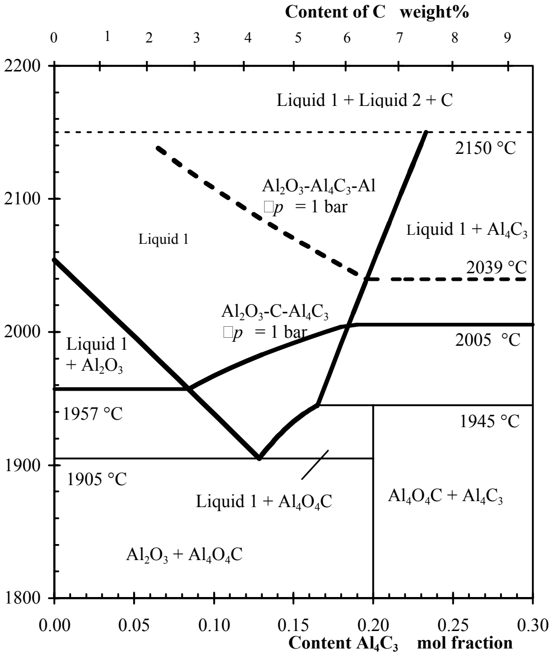

Figure 1: The Pseudobinary Phase Diagram Al_4C_3-Al_2O_3 with Equilibrium Temperatures for the Main Phase Combinations.

The high electrical conductivity of the melt Al_4C_3-Al_2O_3 indicates that it is ionic. Motzfeldt et al. assumed that it consists of the three monovalent ions AlO^-, AlO_2^- and AlC^- that form an ideal mixture according to Temkin. From this assumption they could reproduce the pseudobinary diagram Al_4C_3-Al_2O_3 fairly accurately. This fact does not prove that the suggested melt model is correct, but it shows that the experimental facts can be interpreted by a very simple melt model. The reactions in the system can be expressed as ionic reactions. For example, the dissolution of Al_4C_3 in the slag phase can be described by

$$Al_4C_3 + Al_2O_2^- = 2\ AlO^- + 3\ AlC^- \qquad (2)$$

Other reactions in the systems can be interpreted similarly.

An alternative diagram, Figure 2, was developed by Alcoa based on the thermodynamics for the Al_2O_3-Al_4C_3 system reported by Qui and Metselaar $^{(2)}$. In addition to the phases, the concentration of Al_4C_3 in the alloy product and the instantaneous percent of Al species vaporized are shown. The fact that the two thermodynamic systems are not in total agreement is a measure of the uncertainty of the thermochemical data.

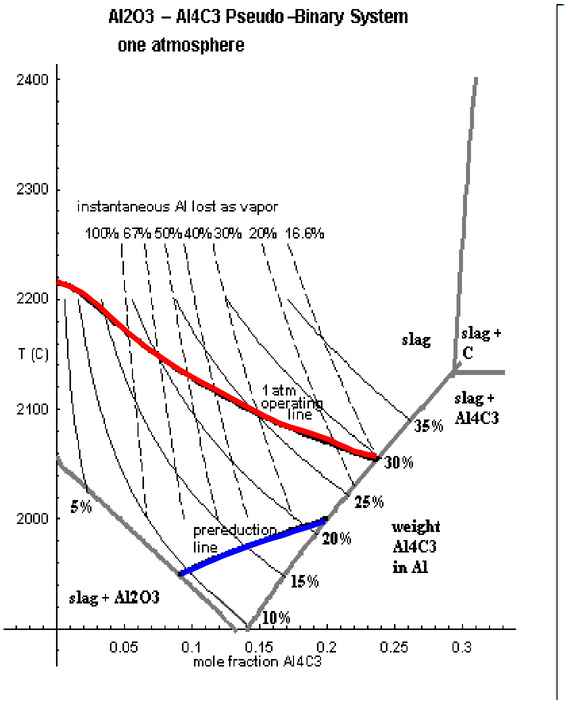

Figure 2: Alcoa Operating Diagram of the Al-C-O System.

The thermodynamic condition for reaction with a considerable rate is that the overall equilibrium vapor pressure of the reaction is larger than the ambient pressure, which is assumed to be 1 bar. The system has three gaseous species with significant amounts: CO, Al_2O and Al. The condition for reaction is therefore

$$p'_{CO} + p'_{Al2O} + p'_{Al} \geq 1 \text{ atmosphere}$$

where p'_X is the equilibrium pressure of the gas species X. Here the equal sign stands for the limiting equilibrium situation. The temperatures giving $\sum p' = 1$ atmosphere for the two combinations Al_2O_3-C-Al_4C_3 and Al_2O_3-Al_4C_3-Al are shown in Figure 1 as functions of the slag composition, and the corresponding equilibrium contents of Al_2O and Al are shown in Figure 3a and 3b.

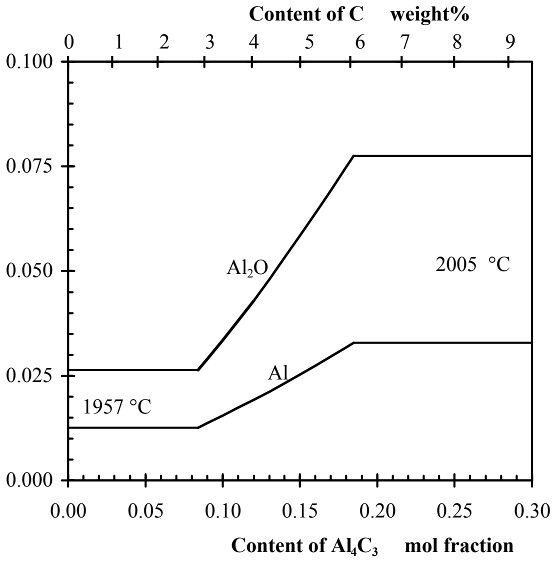

Figure 3a: Gas in Equilibrium with Al_2O_3-C-Al_4C_3.

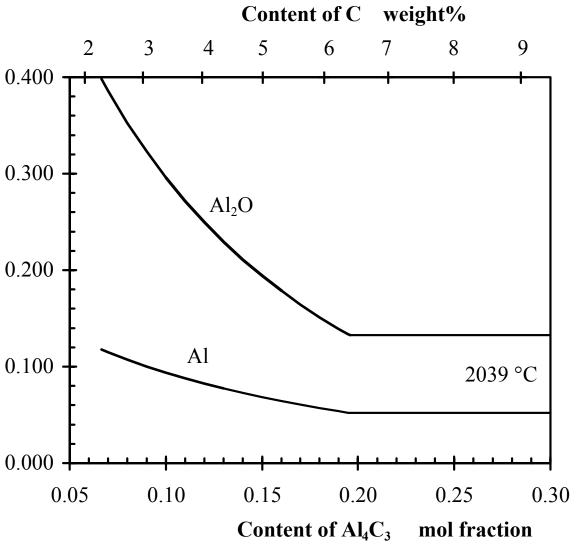

Figure 3b: Gas in Equilibrium with Al_2O_3-Al_4c_3-Al.

In a reactor at equilibrium temperature the reaction rate is very low, but it increases with rising temperature until a steady state is reached where the energy addition is equal to the heat consumption and loss to the surroundings. In steady state the reactor temperature giving $\sum p' = 1$ is a lower limit, and the real temperature is determined by the electrical load and the kinetics of the reactions. The reaction system is not in equilibrium, and the composition of the gas is determined by the relative rate of the partial reactions. The equilibrium of the systems Al_2O_3-C-Al_4C_3 and Al_2O_3-Al_4C_3-Al gives a first approximation for estimates of the gas composition, and equilibrium calculations for tentatively selected favored reactions can be used as a means for better estimates.

For aluminum production the charge will be $Al_2O_3 + \approx 3\ C$. If this mixture is heated to an appropriate temperature, it will react until the C is consumed and Al_4C_3 dissolved in the slag phase is the only C-containing species:

$$2\ Al_2O_3 + 9\ C = Al_4C_3 + 6\ CO \tag{3}$$

This is Stage 1 of the reaction, where free C is consumed. If the mixture is heated further, Al_4C_3 and Al_2O_3 react until one of them is consumed:

$$Al_4C_3 + Al_2O_3 = 6\ Al + 3\ CO \tag{4}$$

This is Stage 2 of the reaction. This division into stages is appropriate for sequential heating of a mixture. In both stages the gas from the reaction will contain Al_2O and Al. In this process picture, the alloy is produced by reaction between Al_2O_3 and Al_4C_3. If the charge to the alloy production reactor also contains an even flow of free C and sufficient energy is added to keep the temperature high enough for alloy production, the Stages 1 and 2 will run simultaneously. The Stage 1 of the free C reaction corresponds to an extra addition of CO, and this CO will have the same content of Al-containing species as the gas from alloy production. With free C in the charge, more of these species will be transported to the vapor recovery reactor per unit alloy produced than for a charge where all of the C is added as Al_4C_3. However, as long as there is enough free C in the recovery charge, the Al-containing species can be captured and the Al recovery for the overall process can be high. The process is self-stabilizing. If for some reason the amount of free C becomes extraordinarily large, more Al-containing gas species will flow to the vapor recovery reactor where it consumes more free C. Then less free C is left in the charge going to the alloy production reactor. This mechanism can give a high recovery as long as the amount of C available for the vapor recovery reactor is large enough. With a very high content of Al-containing species in the gas, the charge will not contain enough C for complete capture. This may set a lower limit for the acceptable Al_4C_3 content of the slag.

In the ACT-ARP concept, the necessary reactions are carried out in a combination of reactors. Figure 4 shows the material flows between them.

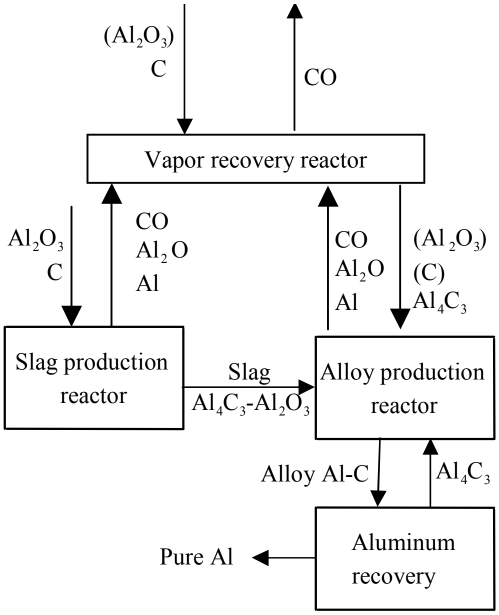

Figure 4: Flow Chart of the ACT-ARP Concept for Carbothermic Aluminum Production.

The reaction in the alloy production reactor gives off hot gas with a high content of Al_2O and Al. The process economics requires that the aluminum and the energy are recovered, and the vapor recovery reactor is added for that purpose. The recovery reactor charge is primarily C but could include some amount of Al_2O_3 in certain circumstances. The charge enters the recovery reactor at the ambient temperature, which for simplicity is set equal to 25°C. The recovery reactor can be visualized as a shaft where the charge passes through countercurrent to the gas. Since the Al-producing reaction needs temperature in excess of the equilibrium temperature, the gas from the reaction can heat the materials in the recovery reactor to a temperature above the temperature of alloy production. Then the only condensed species that are stable at equilibrium at this temperature are Al_4C_3 and Al, or Al_4C_3 and C if there is a surplus of C in the recovery reactor. Then the product from the recovery reactor must be either Al_4C_3-Al or Al_4C_3-C. However, if the recovery charge contains Al_2O_3, some of the reactions in the vapor recovery reactor are endothermic, and additional heat may be necessary to complete the reaction.

In a countercurrent reactor, the exit gas can be cooled to sufficiently low temperatures such that the content of the Al-containing species is practically zero. Thus the process can in principle emit pure CO. The alloy from Stage 2 flows to the aluminum recovery unit where it will undergo further treatment to remove C to commercial grade Al levels.

Slag and Metal Viscosities

Professor Sridhar Seetharaman from Carnegie Mellon was contracted to provide estimates of slag and metal viscosities as a function of compositions for a range of temperatures.

Professor Seetharaman developed mathematical expressions for the viscosities of Al_2O_3-Al_4C_3 slag compositions containing up to 0.4 mol fraction of Al_4C_3 over a temperature range of 1950°C to 2150°C using a model developed by Roscoe for handling two phase regions such as solids suspended in liquid slag. Predicted viscosities were on the order of 0.27 Pa.s at 0.4 mol fraction Al_4C_3. The correlations are shown in Figure 5.

Professor Seetharaman also developed an expression for the viscosity of Al- C over a range of C compositions up to 45 weight per cent for a temperature range of 1850°C to 2250°C. For example, the viscosity was 0.0028 Pa.s at 2025°C and 20% C. Correlations are shown in Figure 6.

The procedures for developing the fundamental expressions were complex. Professor Seetharaman has written a technical paper on the subject (3). The viscosity values determined by Professor Seetharaman will be used in dynamic computer models under development.

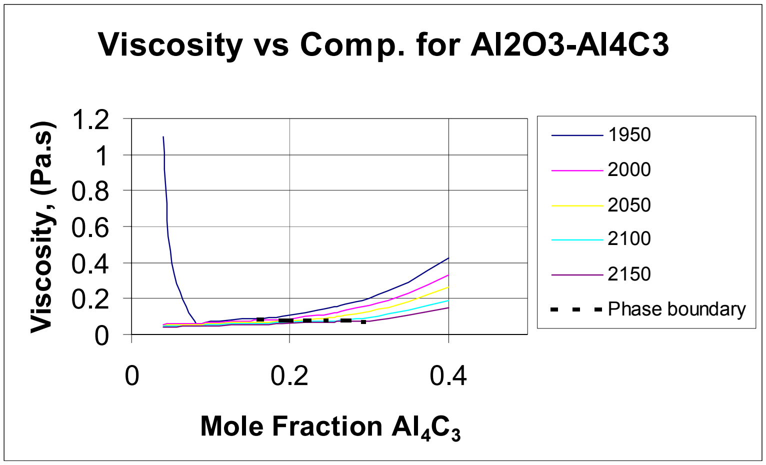

Figure 5: Viscosity vs. Composition for Al_2O_3-Al_4C_3.

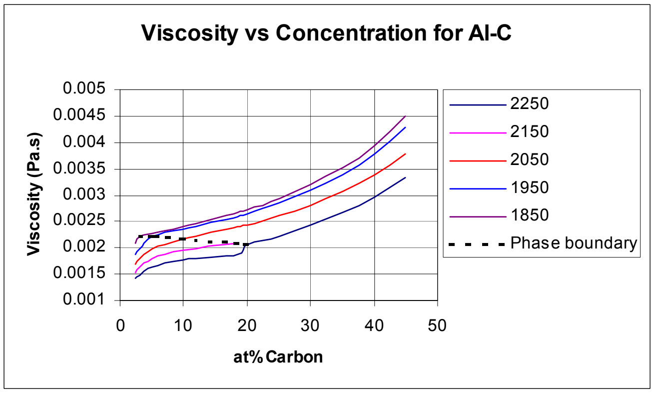

Figure 6: Viscosity vs. Concentration for Al-C.

Mechanism and Rate of Reaction of Al_2O, Al and CO Vapors with Carbon

Alcoa and Carnegie Mellon University collaborated on experimentally determining the mechanism and rate of reactions of gas containing Al and Al_2O with various types of carbon to form Al_4C_3 (4). This is the preferred method for recovering the aluminum values in the reactor off gases, with the carbide being recycled to Stage 2 of the reactor to satisfy the stoichiometry of the reduction step. The Al-Al_2O-CO gas was generated by reacting an Al_2O_3-Al_4C_3 melt with carbon at high temperatures (2000°C to 2050°C) in the Alcoa 65 kW induction heated furnace. The gas was then reacted with carbon at lower temperatures (1900°C to 1950°C). A schematic diagram of the experimental equipment is shown in Figure 7. The melts used to generate the vapors were heated in a graphite crucible (17.5 cm ID). About 7 kg of slag was charged. The temperatures of the melt and at the sample location were measured with a tungsten-rhenium (5% W-Re) – (26% W-Re) thermocouple which is capable of measuring temperatures up to 2200°C. A two color optical pyrometer was also used to measure the temperature. The two temperature measurement techniques agreed within 10°C. The furnace was continuously flushed with argon to avoid excessive oxidation. The off gas composition was measured by an inline mass spectrometer. The primary species were CO, Ar and N_2; all of the Al containing species either reacted or condensed before entering the mass spectrometer.

Several different types of carbon were tested, including wood charcoal, metallurgical coke, petroleum coke and graphite. Prior to reaction, the carbons used were examined in an SEM. Refer to Figures 8a and 8b. In addition, the bulk density, porosity and average pore size was measured. Results are shown in Table 1. The carbon samples were in the form of cylinders, about 25 mm diameter by 25 mm high. Each carbon sample was attached to a graphite rod.

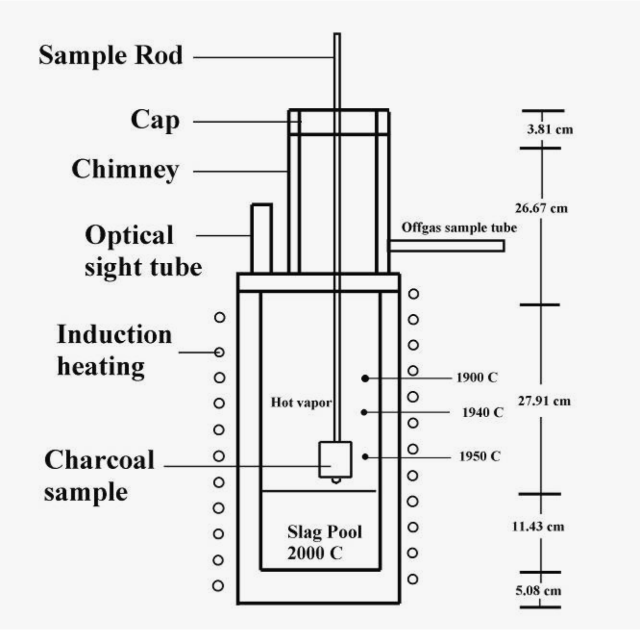

Figure 7: Schematic Diagram of Experimental Equipment.

Table 1: Properties of the Unreacted Forms of Carbon Tested

	Bulk Density g/ml	Average Pore Diameter, mm	Porosity % A	Porosity % B
Met. Coke 1	1.0378	0.0205	24.2	50.5
Pet Coke	1.6003	0.0302	24.7	23.8
Met. Coke 2	0.919	0.0907	50.3	56.2
Wood Charcoal	0.5165	0.0655	61.7	75.4

A Open pore Porosity
B Total Porosity

Once the desired temperature was achieved, and the vapors were being generated, the carbon samples were lowered into the upper “chimney” of the unit, reacted for a specified period of time and then withdrawn. The samples were rapidly transferred to a cooling chamber at room temperature which was continuously flushed with argon to avoid excessive oxidation of the reaction products or carbon. The samples were generally mounted and examined in a scanning electron microscope (SEM) and the phases analyzed with EDX. In a few cases the samples were analyzed chemically.

In several experiments the carbon samples were held higher up in the chimney where the temperature was about 1930°C. At this temperature, a (Al_2O_3-Al_4C_3) slag was formed. In subsequent experiments, after holding the samples at 1930°C for 15 minutes, they were lowered to where the temperature was 1950°C and the carbide was formed. These experiments were conducted to determine if the slag formed would inhibit diffusion of the Al_2O and Al into the carbon and therefore the formation of the carbide. This is an important concern since in the counter current vapor recovery unit (VRR) the carbon particles will first be at a lower temperature where the slag will form.

As seen in Figure 8a, the wood charcoal has a large uniform porosity. As a result, the wood charcoal reacted the best of all carbon types tested. Al_4C_3 formed both on and in the wood charcoal, whereas with pet coke there was some reaction, while with graphite only the condensation reactions occurred at the outer surface of the carbon sample. Figure 8b shows the metallurgical coke structure. SEM pictures of the carbide-carbon interface, of the carbide forming in the pores and of slag formation are shown in Figures 9, 10 and 11 for wood charcoal. As seen in Figure 9, the interface between the unreacted carbon and carbide phase is fairly distinct and easy to identify. There is a small region of partially reacted carbon. As shown in Figure 10a, the carbide crystals begin to grow into the porosity of the carbon and when there is primarily Al_4C_3 the porosity is greatly reduced, Figure 10b. The liquid slag is dense and most likely slows any further reaction as shown in Figure 11.

In addition to having the highest porosity and the most uniform pore structure, wood charcoal also contains the lowest amount of ash except for graphite, which does not react and is not a practical carbon source. This reduces the potential for contamination of the product metal phase.

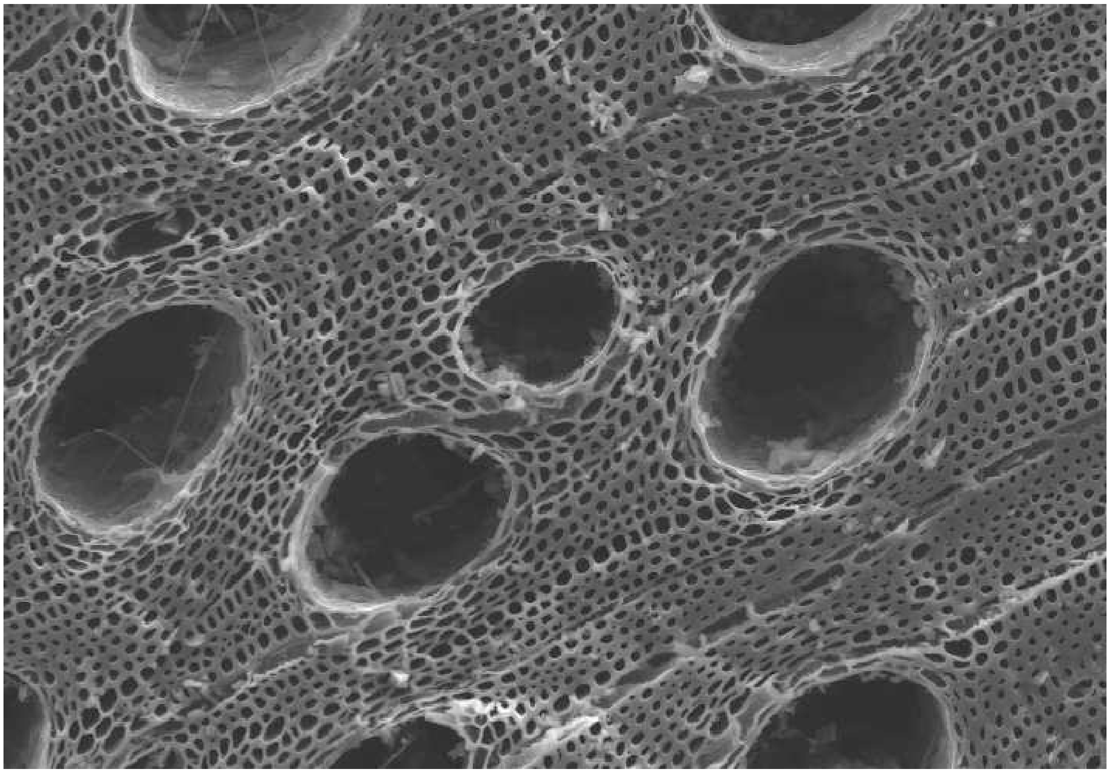

Figure 8a: Wood Charcoal Structure.

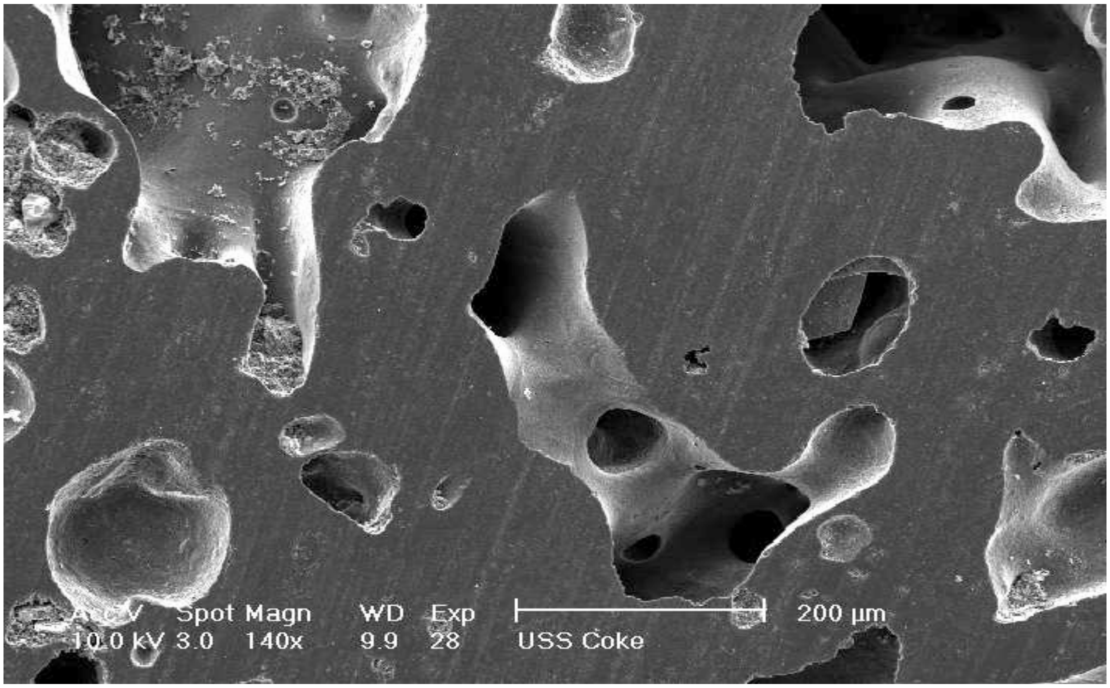

Figure 8b: Metallurgical Coke Structure.

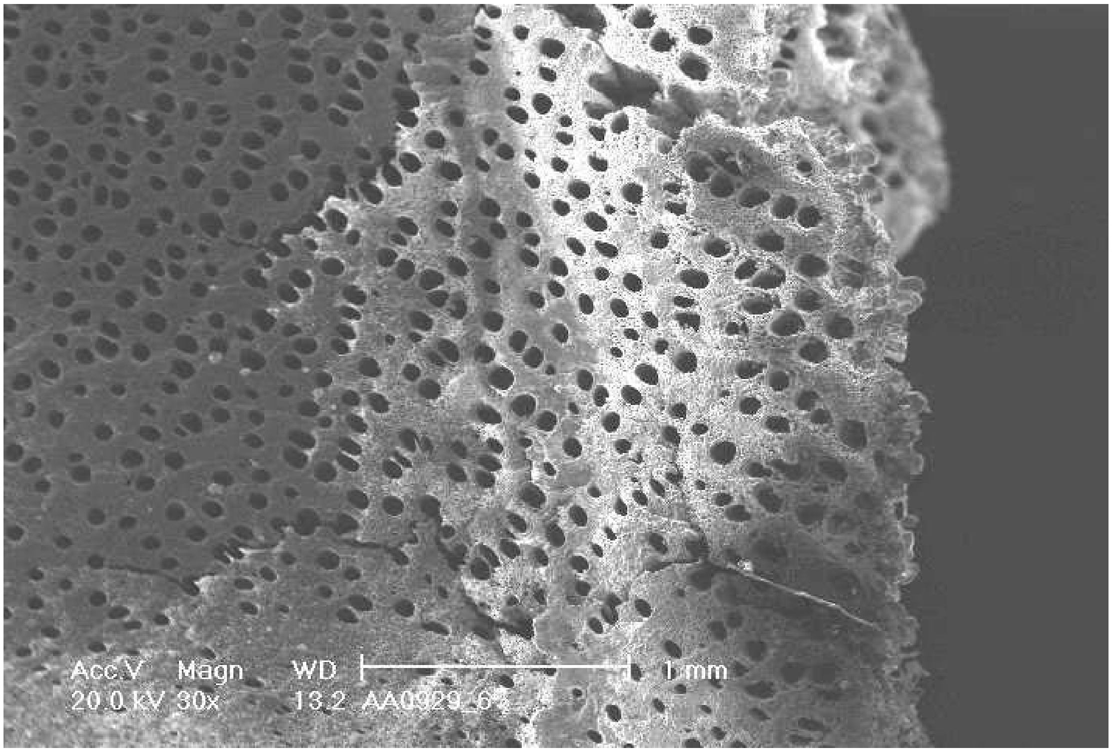

Figure 9: Reacted Wood Charcoal Indicating Carbon-Carbide Interface.

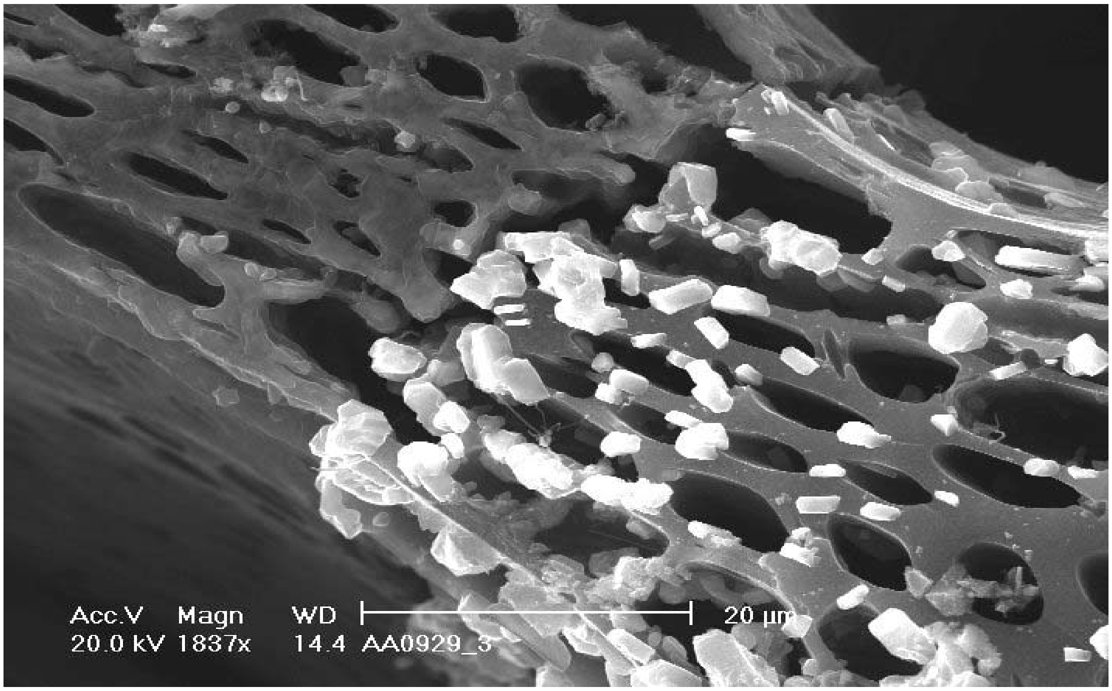

Figure 10a: Partially Reacted Wood Charcoal Showing Al_4C_3 Crystal Growth.

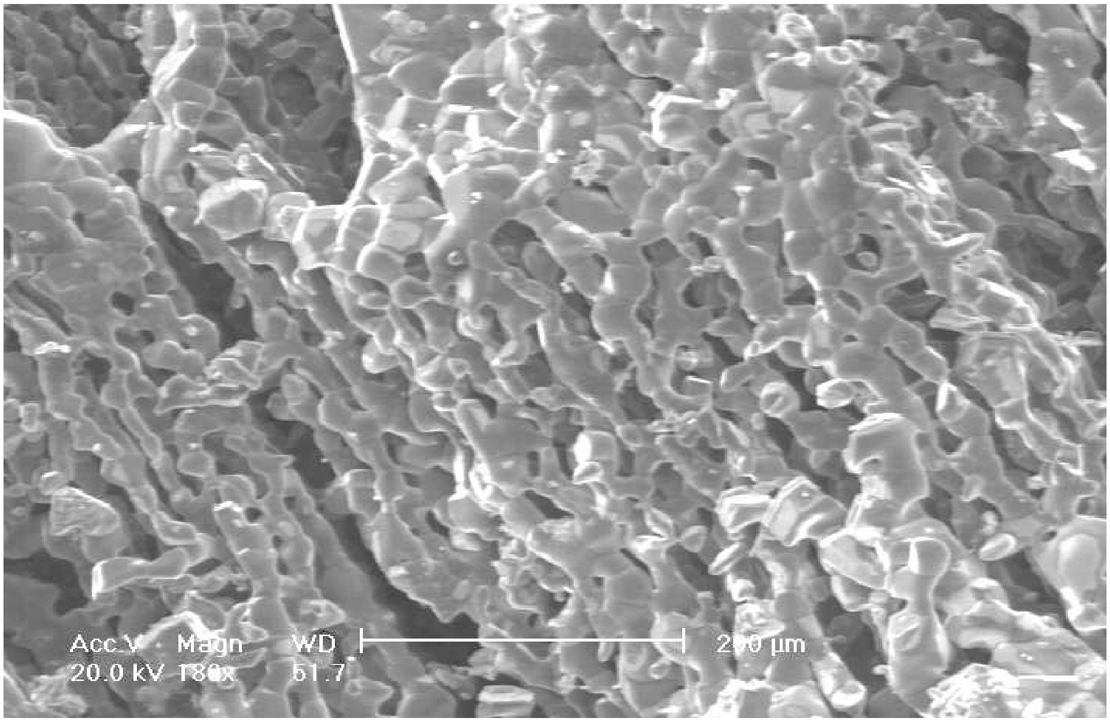

Figure 10b: Fully Reacted Wood Charcoal.

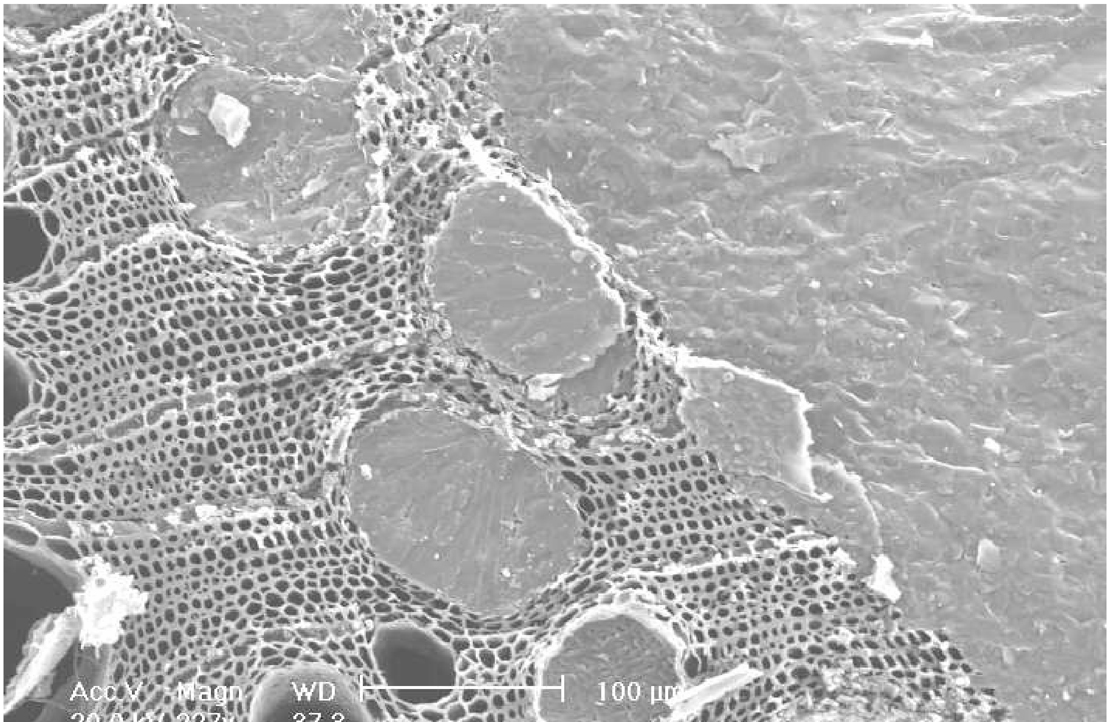

Figure 11: Dense Slag Formed on Wood Charcoal Surface.

The conclusions from the experimental results are as follows:

1. The rate of Al_4C_3 formation from Al_2O and Al gases in CO is controlled by the diffusion of the reactants through the Al_4C_3 product layer.
2. The critical parameters determining the rate are the effective diffusivities which were estimated to be 0.82 and 1.31 cm^2/s for Al_2O and Al respectively at 1950°C in the Al_4C_3 layer formed from wood charcoal.
3. Based on current knowledge of the thermodynamics of the relevant systems Al_2O is responsible for over 90% of the carbide formed. Its vapor pressure is much higher than that of Al and has two atoms of Al while its effective diffusivity is only about 37% lower.
4. The only carbon type tested that reacted extensively was wood charcoal. The wood charcoal has a high (60%) and uniform porosity. It is speculated that, when there is insufficient porosity, the increase in volume of the solid phases due to the formation of the carbide fills the pores and causes the reaction to stop. The wood charcoal also is very low in ash, which is a process requirement.
5. The largest uncertainty in the present work is accurately defining the driving force for diffusion, which depends on the thermodynamics of the system. Therefore, validation of the pressures of Al_2O and Al generated by the reactions was determined experimentally. That work is described in the next section.

Vapor Pressures of Al_2O and Al in Equilibrium with Al_4C -Al_2O_3 Slag at 1950°C to 2020°C

Knowledge of the vapor pressures of Al_2O and Al in equilibrium with $A1_4C_3$-Al_2O_3 slag at high temperatures (1950°C to 2020°C) is critical for evaluation and control of carbothermic reduction for producing aluminum. As indicated, the vapor pressures were experimentally determined (5). The experimental setup was similar to that used in the previous study on the reaction of Al_2O and Al gases with carbon. The change in weight of the slag and crucible and the weight and nature of the condensate on the crucible walls were measured. In addition, the total amount of CO released during the experiment was measured using a mass spectrometer. The mass spectrometer also measured the Ar, CO_2, H_2O, and N_2 concentrations, which were used in the data analysis. In theory, the weight loss of the crucible and slag should indicate the weight of all the species leaving the system (CO, Al_2O, and Al). The measured mass of CO can then be deducted to determine the total amount of Al_2O and Al lost from the melt. It is not possible to distinguish the loss of Al_2O from Al. Thermodynamics indicate that in the temperature range of interest (1950°C to 2020°C), the Al_2/Al molar ratio is 2.6 to 2.8. This ratio only depends on the free energy of formation of Al_2O and its uncertainty is estimated to be less than 10 pct. In any case, about 80% of the Al lost from the melt is as Al_2O. In the estimation of the Al_2O pressure, a value for the ratio of 2.7 was used in this work.

The volume of CO leaving the reactor was calculated from the mass spectrometer data and the Ar flow rate. The mole percentage ratio of CO to Ar (% CO/% Ar) was multiplied by the Ar flow rate (0.50 L STP per minute) and integrated with respect to time. The CO to Ar ratio remained relatively constant (±5 %) over long periods of time (10 to 30 minutes). The N_2 to Ar ratio was also measured and used to compute air ingress into the system and the amount of CO produced by oxidation of the graphite crucible by oxygen. The CO_2, typically 0.2 to 1.0 %, was added to the CO since it was formed from CO by reaction with oxygen in the air ingressed into the system.

The experimental results are presented in Table 2. The measured values of the vapor pressures are in general agreement with the thermodynamic predictions. Specifically, the activity of Al_2O_3 at $A1_4C_3$ saturation predicted from the solution models and the standard free energy of the reactions of Al_2O_3 with carbon to form Al_2O and Al vapors are consistent with the present measurements.

Table 2: Measured and Predicted Al_2O_3 Pressures During Slag Making

Temperature (°C)	Al_2O (Atm) Measured	Al_2O (Atm) Qui-Metselaar(2)**	Al_2O (Atm) Motzfeldt et al.(6)**	Ar (Atm)
1950	0.056	0.028	0.032	0.10
1965	0.040 to 0.045+	0.050	0.063	0.10
1980	0.090	0.079	0.095	0.30
2000	0.122	0.082	0.100	0.10
2020	0.110	0.112	0.146	0.10

* General uncertainty is ±15 pct.

** Degterov and Pelton's (7) evaluation of the Qui-Metselaar (2) model.

\+ Scatter due to large scatter in mass spectrometer.

COMPUTER MODELING

CMU Programs

The CMU modeling program was conducted by two PhD students working under the supervision of Professor Erik Ydstie. One program focused on (a) the development of a model for the vapor recovery reactor (VRR) distributed in time and one spatial dimension and (b) the development of a simple total process model. The other program focused on developing steady state fluid flow models of the second reactor stage including an electric potential model (distributed in 3D) and heat transfer and fluid flow models distributed in 2D. Both PhD students continued their work as Postdoctoral students for a period of time after they had successfully completed their PhD defense.

Program A: Vapor Recovery Reactor for Carbothermic Aluminum Production.
PhD Student: Vianey Garcia-Osorio

The primary objective of this research was to develop distributed parameter models for the vapor recovery reactor in the carbothermic aluminum process and then to include this model in a total process model. The latter was only partially successful due to the computational complexity involved in solving the coupled model structure and lack of efficient methods for stabilizing the simulation.

Three distinct models were developed for the VRR. All models treated the VRR as a packed bed filled with carbon particles that were small relative to size of the column. The aluminum containing gases entered at the bottom of the column and reacted with the carbon particles as they flowed up. The objective of the study was to explore carbon conversion factors and recovery rates for different column design parameters and operating conditions. The solid-gas reactions were based on the mass transfer limited (shrinking core) reaction scheme. This gives a mass transfer limited model with solid-vapor reaction rate determined by the mass transfer rate with the carbon particle. The diffusion rates for Al_2O and Al reactants and CO product in the particle were based on experimental studies performed at Alcoa. The models furthermore assumed the following:

1. The size of the particle was considered to be constant.
2. There was no sintering.
3. The reactions were reversible.
4. The diffusion of the gas through the product layer controlled the rate of mass transfer.
5. There was no transport in the radial direction.
6. Temperature gradients within the solid particle were neglected.

Model A1: The Stage-wise VRR Model: The VRR was modeled using four distinct reaction zones with preset temperature. The concentrations and heat duties for each of the stages were calculated and overall conversion factors determined. This model and the results were published (8).

Model A2: The Continuous Fixed Bed VRR Model: The VRR was modeled as a plug flow continuous fixed bed reactor with axial dispersion. There was no reaction in the vapor phase. The shrinking core model was used to determine the local reaction rate. A number of case studies were developed to study the sensitivity of the model outputs (conversion and recovery) versus design parameters (superficial velocity, column height and particle diameter). The model temperature and conversion predictions compared favorably (+-15% for conversion) with a small scale experimental column. The numerical method for solving the system relied on discretization using the method of lines. The MATLAB routine ODE15S was used to solve the resulting set of differential algebraic equations (9).

Model A3: The Moving Bed VRR Slag Model: The VRR was modeled as a plug flow continuous, counter current, moving bed reactor with axial dispersion. Reaction in the vapor phase was modeled by assuming that the Al-O-C system was at equilibrium at a given pressure and temperature. Equilibrium data was generated using model parameters from the FACT data base system. The shrinking core model was used to determine the local reaction rate inside the carbon pellet. The model was used to study the sensitivity of conversion and recovery with respect to design parameters like gas superficial velocity, carbon feed rate and gas composition. The model showed that slag could be generated in the column. The formation of slag may cause operational problems since the column can become very difficult to operate. The model description and results were published (10). A theoretical framework was also developed for studying the stability and convergence of control strategies for reaction diffusion convection reaction problems (11).

Model A4: The Total Process Model: The VRR model was combined with dynamic models for Stage 1 and Stage 2. These models were based on assumed values for a production system and connected together and integrated with thermo-physical properties models to establish the time dependent compositions of Stages 1 and 2. It proved to be very difficult to solve the resulting large scale system of differential algebraic equations. We therefore developed a new modular simulation method for integrating distributed simulation models. This approach is described and tested on a very simple system (12). The simulation model was not completed due to difficulties concerning the linking the FACT thermo-physical properties data base system with the MATLAB/SIMULINK system for process modeling and control system design.

A complete description of these models and related results is given in Dr V. Garcia-Osorio's PhD thesis.

Program B: CFD Modeling of Stage 2 of the Carbothermic Aluminum Process.
PhD Student: Dimitrios Gerogiorgis

The objective of this work was to develop CFD models to study the interaction of current, heat and fluid flow in the second stage of the carbothermic aluminum process. Several different models were developed.

Model B1: Thermo-physical Properties: In order to develop the CFD model it was first needed to develop temperature and composition dependent thermo-physical properties for the Al-O-C system in the temperature range 1900-2020°C. Very little data is available and in some instances we had to rely on data taken from other systems (e.g. substituting Al with Boron). Correlations were then developed for density, viscosity, thermal and electrical conductivity as well as melting points (13).

Model B2: Mixed Integer Nonlinear Programming Model for Optimal Voltage: A Mixed Integer Nonlinear Programming Model (MINLP) was developed for investigating the optimal voltage input to a furnace with 6multiple electrode pairs. The reactor was modeled as a compartmentalized system with multiple well mixed compartments. The concentration, temperature and energy requirements were modeled using a kinetic model for the Al system. The model was developed using the GAMS modeling environment for optimization. The nonlinear program was solved to local optimality using the GAMS MINLP model. The model solved robustly. The optimal energy inputs and process flows were determined using less than 30 minutes of computer time (14).

Model B3: CFD Model for Fluid Flow Calculation in Stage 2 of the Carbothermic Aluminum Process: The full reactor and homogeneous slag assumptions were used in order to simplify the many physical phenomena and study electric charge, heat and momentum balances. The goal was to solve the steady state PDE problems for the respective variables of the latter balances [potential (V), field intensity (E), temperature (T), velocity ($U_{x,}$ U_y), pressure (P)], obtaining reliable starting points so as to solve molar balances for species concentration profiles in a complete model reliable for performance evaluation. Constant thermo-physical properties were assumed, although a temperature-dependent electrical conductivity was used to illustrate the strong coupling between the charge balance and the Joule heat generation term. The standard k-ε model of Launder and Spalding was used in the momentum balance in order to analyze the turbulent slag flow in the reactor. A CFD model of the Stage 2 of the process was developed. The model is based on the assumption of incompressible fluid flow.

The finite element method was used to formulate the PDE problem on an unstructured triangular domain discretization. The developed finite element model of the reactor has been solved with quadratic finite element basis functions, using a commercial finite element simulation environment (FEMLAB® v. 2.3). Four FEMLAB® modules were used for these simulations: (a) “Conductive Media DC”, (b) “Convection and Conduction”, (c) “K-ε Turbulence Model” and (d) “General form PDE Model”. Imposed electrode voltages were crucial, affecting field intensity and current density profiles (hence Joule effect heat production). This in turn was expected to affect the uniformity of heat generation, thus the uniformity of temperature and gas fraction distributions. Slag convection was also influenced by the presence of electrodes. This study presents (a) pseudo-homogeneous slag CFD results derived without gas generation modeling and (b) two-phase flow CFD results that use a T-independent gas generation model.

There only experimental data available to test this model was the temperature data generated by the pilot experiments. The model matched temperature data very well. The two phase model predicted that there was considerable fluid mixing close to and above the electrodes.

The CPU time required for convergence below tolerance when solving the quadruple PDE problem for specific voltages (Vi) was about 30 min. (the corresponding grid has 3031 triangles). Solutions were obtained using reasonable computational resources (A dual processor Pentium III/1.2 GHz with 512 MB of RAM was used in these studies). Finer discretizations were used to enhance the accuracy. The feasibility of developing a 3D model was investigated. It was concluded that the FEMLAB system would not be able to handle this problem for the full scale system at the present time.

The CFD models and the results were published (15-22). A full description of the research results is given in the PhD thesis by Dr. Dimitrios Gerogiorgis.

Alcoa Programs

Early computer modeling work at Alcoa involved use of a program provided by Aspentech in which the FACT database was interfaced with Aspen. This software was employed to run mass and energy balances on various flow sheet concepts.

More recently, the Aspen software was upgraded to windows 11.1 and CHEMAPPS software was obtained since it is required to implement and trouble shoot Aspen/FACT. Mass and energy balances were calculated for several operating scenarios, with the base case being carbon saturation in Stage 2. Specific cases run included the effect of Al_4C_3–Al recycle from metal recovery on Stage 2; the effect of heat additions to the inlet zone of the vapor recovery operations; and the impact of adding Al_2O_3 to the vapor recovery step. Results expressed as net electrical energy required ranged from 7.84 to 14.1 kWh/Kg for the base case optimistic to pessimistic assumed conditions. With heat additions to vapor recovery, the range was 7.54 to 13.2 kWh/kg. For Al_2O_3 additions to vapor recovery in addition to heat, the energy rates were 6.38 to 11.2 kWh/kg for optimistic to pessimistic conditions.

The optimistic assumptions include utilization of the process waste heat from the vapor recovery step, the heat value of the CO off-gas and the sensible heat of the metal product to preheat input materials to the process, where the input materials are Al_2O_3 and petroleum coke to Stage 1, and vapor recovery solids discharge plus recycle dross fraction from Al-C separation to Stage 2. Heat additions to the inlet of the vapor recovery column are needed to drive the reactions of Al and Al_2O with carbon to form Al_4C_3. Alumina additions to vapor recovery capture the sensible heat of the reaction gases in the upper regions of the vapor recovery column by forming Al_2O_3 – Al_4C_3 slag which then converts to Al_4C_3 in the lower column zones.

In addition to the CMU and ATC calculations, independent calculations were conducted by Elkem based on simple equilibrium conditions at 100% thermal efficiency, varying carbon conversion to carbide in the vapor recovery step, some of the alumina feed going through the vapor recovery unit and all of the carbon feed going through as well. These calculations were done using Chemsheet software. Model results using Chemsheet were similar to those for Aspen/FACT. Thermodynamics do not appear to limit the potential of the process. In follow-up calculations, Elkem predicted a range of net energy requirements from 9.5 kWh/kg to 11.6 kWh/kg for a reactor system thermal efficiency of 80% and a credit for CO to power conversion at 35% efficiency.

The initial Alcoa work on a Stage 1 model was done using CFX4 computational fluid dynamic software. Progress was made in coupling current flow, joule heating, heat flow, natural convection and sidewall freezing. However, CFX did not handle the geometric complexities of the model and new software was considered. CFX 5 upgrade does have the capability to address the geometric complexities since it can create its own unstructured mesh. The Stage 1 model development is continuing using CFX5.

REACTOR DEVELOPMENT

Major design challenges from earlier efforts to develop a carbothermic reduction process for aluminum were reviewed and a tailor-made multi-stage reactor design and processing concept has been developed, based on utilizing Elkem's proprietary reactor technology.

A modular test program was designed to demonstrate the technical feasibility of the process concept. Several successful test campaigns were conducted verifying the technical feasibility of the first stage and critical elements of the second stage. Additional module tests were done on the vapor recovery step. The tests have been performed in large laboratory scale units designed to operate in the 0.5 – 1.6 MW range. All results from the modular tests will be used to design an integrated reactor, which will be constructed and operated to verify all of the stages combined.

Stage 1 campaigns were designed for equipment "shake-down", determination of reactor system characteristics, evaluations of process parameters and to establish the reactor operating strategies. These campaigns were highly successful and proved the feasibility of the pre-reduction stage:

- Pre-reduced slag with controlled carbon content was produced.
- The slag was manageable both in the reactor and during tapping.
- The test system functioned as planned and no flaws or weaknesses in the basic engineering design were detected.

The following photos indicate both the complexity of the test installation and the level of ambition for the test work.

Figure 12: Overview of the Experimental Site for Stage 1.

Figure 13: Front View of the Stage 1 Reactor.

Following the successful demonstration of Stage 1 feasibility, the laboratory facility was modified to develop Stage 2. A 500 kW module was installed and operated to evaluate horizontal, sidewall-entering electrode assemblies, electrode slippage, reactor sidewall controlled cooling systems, slag composition control and tapping of slag. Temperatures up to 2100°C were measured. A number of successful tests were run, verifying these critical components and providing valuable input for the design of a large scale integrated system. Figure 14 shows the Stage 2 module setup for an early test operated without a lid to study slag flow patterns during powering of the sidewall electrodes.

Figure 14: Stage 2 Module with Lid Removed Showing Molten Slag Flow.

The Stage 2 module also functioned as a generator of reaction gases for laboratory testing of a vapor recovery system. A prototype vapor recovery reactor module was installed and used to determine functional system solutions and design parameters. Hot process gas transport requirements were obtained. Gas inlet temperatures greater than 1820°C were measured. Gas, composed of 95 % CO, exited the column at greater than 1000°C.

On-line mass spectrometry was employed to analyze process gases. The use of metered Ar as a tracer in conjunction with the gas analysis provided an estimate of the total gas flow rate.

Test results from operation of the prototype vapor recovery module will be used to aid design of vapor recovery for the integrated system.

The focus for the 2004 program was on the design, assembly and evaluation of an advanced Stage 1 and VRR 1 system for the 3 MW integrated reactor. The engineering solutions chosen for the advanced Stage 1/VRR 1 system are identical to those which are required for the total integrated reactor system, especially with respect to materials of construction and achieving structural integrity. Installation of Stage 1/VRR 1 was completed. The new Stage 1 is a 1.5 MVA system designed to operate between 0.5 MW and 1.25 MW. The Vapor Recovery Reactor is a gas/solid counter-flow system with solids discharge. Auxiliary systems for feed preparation, off-gas handling, synthetic media cooling and process monitoring/control have been designed for maximum flexibility and conform to industrial EHS standards. Great emphasis was placed on system robustness and the whole test installation conforms to commercial engineering standards.

A shake-down test was run to check out the functionality of the equipment. The system is being prepared for a hot slag test in the first quarter of 2005.

The pictures in Figures 15 and 16 show the test site, the infrastructure and some of the auxiliary equipment.

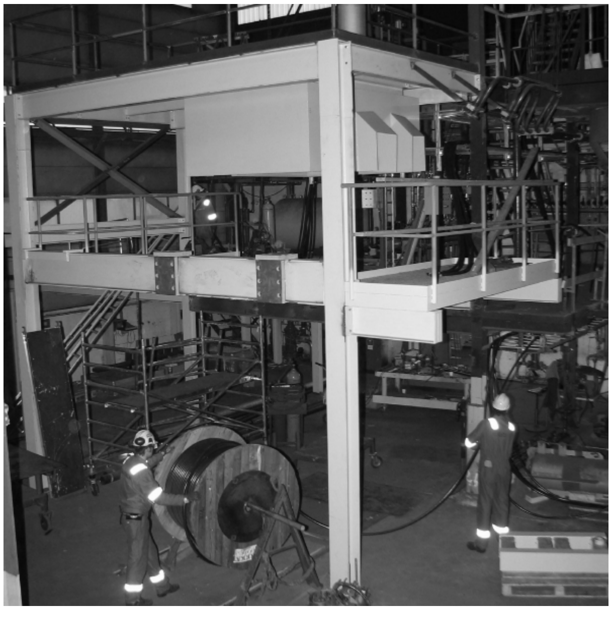

Figure 15: Test Site.

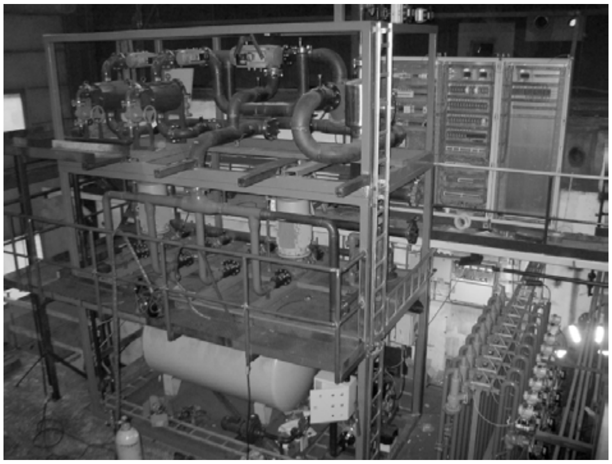

Figure 16: Oil Coiling System.

In addition to the Stage 1/VRR 1 system, research continued on VRR design and operation, and on a new concept for solids charging to Stage 1. Reliable vapor recovery tests must have the correct ratio between reaction gases and VRR charge flow. The ratio depends on the composition of the slag and the amount of carbon available for vapor recovery. Valuable information can be obtained from simple tests. Preferably such tests are small-scale simulations of the complete process. The temperature of the outgoing gas is determined by the extent of the reactions in the vapor recovery reactor, and the reactions between gas and VRR charge can be studied.

A series of static as well as moving bed VRR experiments were run in order to investigate the mechanism and kinetics of the vapor recovery reactions. These experiments took place in both single and double electrode furnaces in the 50-150 kW range, Figure 17.

Figure 17: Static Bed VRR Experiment in a Single Electrode Arc Furnace.

Countercurrent mechanical operation was demonstrated. Conditions for Al_4C_3 formation were established. Figure 18 is an example of almost complete conversion of VRR charge in a dynamic test.

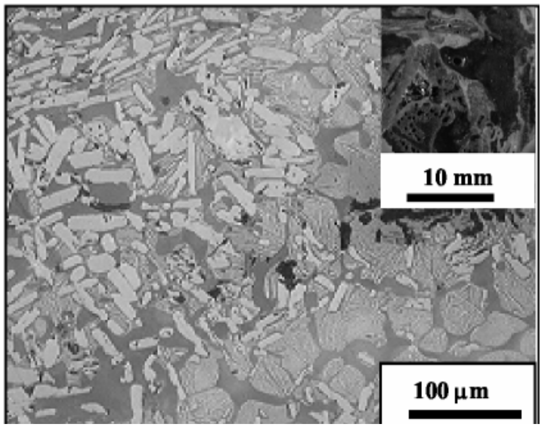

Figure 18: Converted VRR Charge.

Following the VRR tests, the small arc furnace was modified to facilitate evaluation of the new solids charging concept. The concept was demonstrated, although the scale of the experimental unit limited the ability to obtain quantitative data for operating parameters. It was determined that further testing would be more effective at a larger scale. Therefore, the charging system has been included in the advanced Stage 1/VRR 1 unit.

DECARBONIZATION DEVELOPMENT

Decarbonization is the fourth stage of the Advanced Reactor Process (ARP) and is critical to the recovery of commercial grade Al from the Al-C reaction product tapped from Stage 2 of ARP.

Both Pechiney and Reynolds have reported R&D on decarbonization of carbothermically produced Al-C alloys. Pechiney reported that alloys containing 30% Al_4C_3 would not tap from their electric furnace. Alloys with 15% Al_4C_3 did tap easily. As a result, Pechiney adjusted their slag concentration to reduce the carbon content of the metal product. The resulting alloy analyzed 85% Al – 13% Al_4C_3 – 2% Al_2O_3. Reports by Reynolds on Al_2O_3 extraction tests were studied. Reynolds used a mixture of 70% Al_2O_3- 30% slag (containing 85% Al_2O_3- 15% CaO), which equates to 95.5% Al_2O_3- 4.5% CaO. The CaO was added to reduce the melting temperature of the extractant. Starting at an average concentration of 8.4% Al_4C_3 in the metal, the average final concentration was 2.1% or a 75% reduction. Temperatures during extraction were in the range of 1700^{o}C to 1900^{o}C. Recovery of Al was about 50%. Although the addition of CaO was effective in providing a liquid phase extractant, the use of CaO commercially is unlikely since the oxide reduces to Ca which concentrates in the product metal phase. Alumina extraction is desirable, especially if it takes place in the reactor rather than in a separate furnace as patented by Reynolds.

Alcoa's work on this task was initiated in 2002. Several process options were considered, including Al_2O_3 extraction, controlled cooling of the Al-C alloy to effect phase separation of solid Al_4C_3 from liquid Al, and extraction by chloride salts.

The Reynolds Al_2O_3 extraction concept was evaluated. Several tests were run in alumina crucibles to avoid carbon contamination by reaction with graphite containers. Although some carbide was removed, the CaO attacked the alumina crucibles. Further testing of the Al_2O_3 extraction was put on hold to assess other options.

Feasibility of Al_4C_3 extraction by chloride salts was tested. The results were promising. Up to 65% of the charge was recovered as carbon free coalesced Al, which was at least 79% recovery of the available Al.

In 2003, separation tests were initiated on Al-C alloy produced by Elkem in the Stage 2 hot box module during a series of runs made in December 2002. Alloy feed compositions contained 1.26% C, equivalent to ~ 5% Al_4C_3 and 2.48% C, equivalent to 9.92% Al_4C_3. The alloy was charged to alumina crucibles and heated to 760°C – 960°C using a resistance-heated furnace. Various types of treatment were tested, including the effect of salt additions, inert gas sparging, mechanical stirring and dilution by Al additions. After treatment, the Al and "carbide dross" were separated by decanting. The dross was then screened through selected screen sizes. All resulting phases were analyzed for carbon content. The dross was also analyzed for free Al, oxygen and nitrogen. The metal was analyzed by ICP. For each test, the total mass balance and the Al product recovery were determined. Individual elemental balances were also determined for selected tests.

Major conclusions from the tests were as follows:

- Al recovered from the various separation methods was very low in carbon content, typically less than 0.06%.
- Inert gas sparging was effective in attaining good separation of Al from dross.
- Degree of separation was similar for the temperature range studied. Temperatures did not impact Al recovery.
- Dilution with Al did not improve the efficiency of separation for inert gas sparged tests.
- Based on a few tests, salt additions resulted in the highest Al recovery.
- Based on two tests, the initial carbon content of the alloy did not impact Al recovery.
- Mass balances were high for all tests; the lowest was 98.1%; the average was greater than 99%.

Simultaneous to the separation experiments on Stage 2 hot box alloy, Elkem developed a system for synthetically producing Al-C alloy to produce additional charge material for further separation trials. Temperatures of 2000°C or higher were attained in the melt. Alloy carbon concentrations ranged from about 1.5% to 3.5% in tapped alloy.

The Alcoa separation tests continued using the synthetic alloy made. Good Al recoveries were sustained for higher carbon (carbide) concentration alloys comparing results from processing of 3.5% C alloy versus 2.48% C alloy. In all separation tests, the dross phase has been dry, granular and free flowing. These properties are important to the dross recycle step of the Advanced Reactor Process.

Alcoa scaled up its separation tests by a factor of 10 using an induction furnace at Carnegie Mellon University (CMU). Synthetic alloy made at Elkem was charged, heated to 735°C-760°C and treated to effect separation of the Al from the C. Conditions used in the Alcoa small scale runs were repeated in the CMU furnace. Initial C concentrations ranged from 1.6% to 3.75% C. Al recoveries of 94% or higher were attained. Carbon concentrations of the recovered Al phase were 0.06% or less. The carbide dross was dry and granular, well suited for recycle to the reactor. The CMU results verified those obtained in the Alcoa small scale experiments.

Three CMU tests were done at high temperatures, 1910°C to 2140°C. In these tests, Al and C were charged to a graphite crucible, alloy was produced at 2.5% - 5.0% C and separation was carried out in-situ on the alloy at about 750°C. Good Al recoveries were attained.

ECONOMIC ANALYSIS

Successful development of ARP will potentially result in significant cost benefits for greenfield aluminum smelter installations, especially in locales that rely on fossil fuel power generation.

In 1999, prior to the start of the DOE project, a preliminary cost estimate was prepared to compare ARP with published world wide average costs for Hall-Heroult aluminum production. Table 3 shows the resulting total cost comparison between ARP and Hall-Heroult for a 400,000 metric ton per year smelter. The capital cost associated with a greenfield Hall-Heroult smelter was $4,000 per MTY or $1.6 billion, while the capital for ARP was $1,763 per MTY or $705 million. The preliminary operating cost comparison predicted a cash operating cost savings of $173 per metric ton, or $69.2 million for the sample plant. The energy rates used were 14.74 kWh/Kg Al for Hall-Heroult and 9.50 kWh/kg Al for ARP. The total costs for carbothermic were about 30% lower for a 12% rate of return, at an estimated $587 per metric ton savings. Energy, labor and capital charges were major positives and carbon cost was a negative for carbothermic.

Table 3: Estimated Total Cost Comparison for 400,000 MTY Al Production, $/MT

Cost Category	Hall-Heroult WW Average	ARP
Alumina	398	386
Carbon	144	248
Bath	14	0
Energy	307	199
Labor	120	43
R&M materials	66	30
Pig casting	31	31
Overhead	66	35
Other	78	78
Cash operating cost	1224	1051
Capital charge (12% A/T)	741	327
Total cost	1965	1378

It is estimated that ARP's production rate would be about 100 times greater than the largest Hall-Heroult cell (300 kiloamp). For a 400,000 MTY plant, Hall-Heroult would require 500 cells, whereas ARP would need 5 reactors. Obviously, this has a significant impact on reducing labor costs.

Later, the ARP cost comparison was upgraded to reflect the impact of a 29% lower predicted capital cost based on results from the development program through mid-2002. For the latest comparison, current benchmark cost estimates for Hall-Heroult were used. For this estimate, the energy rates used were 13.25 kWh/kg Al for Hall-Heroult and 9.50 kWh/kg Al for ARP. Table 4 shows the later comparison, for a 240,000 MTY facility. Total costs for carbothermic are about 35% lower than Hall-Heroult, again based on a 12%

return. The capital cost savings have the most significant impact on the cost reduction potential, similar to the 1999 study. Estimated capital costs for the 240,000 MTY plants are $960 million ($4,000 per MTY) for Hall-Heroult and $300 million ($1,250 per MTY) for ARP.

One scenario for ARP is to add scrap to the high temperature Al-C metal phase product. Benefits of this approach include cooling the metal phase for further processing (e.g., casting) by a method that effectively uses the metal phase sensible heat (i.e., melting the scrap). This has an energy cost value of about $22/MT Al for melting, plus an environmental benefit of eliminating the CO that would be generated by conventional combustion melting of the scrap.

Another consideration is to co-locate carbothermic plants with existing fabricating plants. Co-located carbothermic facilities creates the possibility of mixing primary metal with a continuous stream of recycled metal, which would offer significant economic advantages. In addition, carbothermic facilities could be sized according to fabricating plant needs, rather than rely on increasing capacity to offset capital costs, as is the case with Hall-Heroult plants. Economic savings, therefore, would vary by plant on a case-by-case basis.

Table 4: Estimated Total Cost Comparison for 240,000 MTY Al Production, $/MT

Cost Category	Hall-Heroult Benchmark	ARP
Alumina	359	359
Carbon	101	288
Bath	10	0
Energy	239	180
Labor	101	19
R&M materials	156	14
Pig casting	33	33
Overhead	45	2
Other	0	29
Cash operating cost	1043	924
Capital charge (12%)A/T)	741	232
Total cost	1784	115

The energy values for CO off-gas from the vapor recovery reactors is typically estimated by assuming a 30% efficiency in generation of power by combustion of the CO. In an effort to optimize capture of CO energy values, Fern Engineering was retained to conduct a paper study on CO energy utilization. Various concepts were defined, conversion efficiencies to power were predicted and capital costs were estimated. For the options evaluated, the net efficiencies ranged from about 31% to 47%; estimated capital costs varied from $267 per kW to $1507 per kW. The most promising option was a simple GE gas turbine fired on CO using a natural gas supplement to satisfy the inlet flow requirements for that specific turbine. This option did not include CO2 recovery.

Alcoa is exploring potential opportunities for commercialization of carbothermic in the United States, including automotive, extrusion and smelting applications. Scenarios being considered include smaller carbothermic reactors to supply Al to "mini-mill" type applications for casting plants in the range of 15,000 to 25,000 mt/yr production. Rolling mills can range from 14,000 mt/yr to 180,000 mt/yr. Extrusion plants also have a wide range of productivity, up to about 80,000 mt/yr. On-site smelting at a fabrication plant will save transportation costs to ship ingot plus the melting costs. This can be a 3 to 5 cent/lb savings. Also, power contracts are generally more available and lower cost for smaller segments of purchased power.

ACCOMPLISHMENTS

The project accomplishments are summarized in the following list.

- The system thermo-chemistry was defined for the Advanced Reactor Process flow diagram.
- An operating diagram was developed based on available thermodynamics for the $Al_2O_3 - Al_4C_3$ system.
- Correlations for slag and metal alloy viscosities versus temperature and composition were predicted from developed mathematical expressions.
- Stage 1 was demonstrated at the 1 MW scale.
- Stage 2 critical components were demonstrated in a 500 kW module.
- The fundamentals of vapor recovery were experimentally determined, including reaction mechanisms and Al species vapor pressures.
- The detailed design and installation of an advanced Stage 1 system was completed, including a vapor recovery reactor.
- The feasibility of efficient Al – C separation was demonstrated.
- Capital and operating cost estimates for the process were updated.
- Computer models were developed for the vapor recovery system and are in progress for Stage 1, Stage 2 and the total process.
- A number of papers were presented and published in Light Metals and other journals and/or conference proceedings.
- Five US patents have been awarded; 3 patent applications are in process of being reviewed by the US Patent Office.

CONCLUSIONS

Based on the progress through December 31, 2004 we have concluded that (1) the thermodynamics of the process are valid; (2) the designs of the Stage 1 and Stage 2 reactor components successfully address the identified technical hurdles related to the pre-reduction and reduction process steps; (3) efficient decarbonization of the Al–C alloy product is feasible; (4) fundamentally, the vapor recovery process concepts are valid; (5) the process economics are favorable compared to the Hall-Heroult process for production of commercial grade Al; and (6) that the program should continue with emphasis on the engineering of the vapor recovery system, followed by the implementation of a 3 MW totally integrated reactor system to demonstrate all steps of the process and to develop additional design data for a large scale pilot reactor system.

RECOMMENDATIONS

It is recommended that the program be continued through the 3 MW integrated reactor evaluation. Based on the results of test campaigns with the integrated reactor, plus a further update on process cost estimates, the next phase of study would be the design and implementation of a large scale pilot reactor.

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