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MASTER

PRODUCTION OF ALUMINUM-SILICON ALLOY AND
FERROSILICON AND COMMERCIAL PURITY
ALUMINUM BY THE DIRECT REDUCTION PROCESS

Third Annual Technical Report for the Period
January 1–December 31, 1980

By
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January 1981

Work Performed Under Contract No. AC01-77CS40079

Aluminum Company of America
Alcoa Laboratories
Alcoa Center, Pennsylvania

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

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DIRECT REDUCTION PROCESS

THIRD ANNUAL TECHNICAL REPORT
FOR THE PERIOD 1980 JANUARY 01 - 1980 DECEMBER 31

MARSHALL J. BRUNO

JANUARY 1981

ALUMINUM COMPANY OF AMERICA
ALCOA LABORATORIES
ALCOA CENTER, PA 15069

PREPARED FOR THE
DEPARTMENT OF ENERGY
OFFICE OF THE ASSISTANT SECRETARY FOR
CONSERVATION AND SOLAR APPLICATIONS
DIVISION OF INDUSTRIAL ENERGY CONSERVATION
UNDER CONTRACT DEAC01-77CS40079

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FORWARD

This is the third annual technical report submitted in accordance with the requirements of Contract DEAC01-77CS40079, a three-year cost sharing agreement between the Department of Energy and the Aluminum Company of America. The report describes work performed during the period 1980 January 01 through 1980 December 31.

ABSTRACT

Phase C of a three year cost-sharing contract between the Department of Energy and Alcoa was started on 1980-01-01. At the end of the fourth quarter, the program for Phase C is estimated as 100% complete, with 96.7% of the funding expended.

The effects of calcination temperature and burden composition on pellet strength were determined for several mixtures of kaolinitic clay and alumina hydrate. Strength increased with both increasing clay content and higher calcination temperature. Beneficiation of bauxite by high intensity wet magnetic separation to remove Fe and Ti was not successful. Pilot reactor VSR-3 was operated with 75-120 SCFH O_2 to supply part of the process heat requirements by combustion of coke. No alloy was made and burden bridging persistently stopped operations. Updated thermochemical data for Al_2O_3 significantly changed the calculated reflux loading for a one-atm blast furnace, predicting almost total reflux and no alloy recovery. Based on these calculations and the experimental problems with combustion heated operation, VSR-3 was modified to study an alternate reduction concept--the blast-arc--which utilizes combustion heat to reduce SiO_2 to SiC at $1600^\circ C$, and electrical heat to complete the reduction of Al_2O_3 and the production of alloy. The upper shaft of VSR-3 was tapered 14° from the vertical and the auger was replaced by a vertical stroke ram. A preheater was assembled to facilitate injection of $1800^\circ C$ CO to the stage one reaction zone to simulate the effects of combustion products on the SiO_2 to SiC reaction. The taper/ram revisions were successful in maintaining bed movement, resulting in several continuous runs in which large quantities of burden were fed and metal product was recovered. Flows of 100-200 SCFH of preheated CO were injected at the first stage SiC reaction zone. The 200 SCFH CO rate represented 67% of the combustion products predicted for supplying first stage heat requirements. Higher rates resulted in unacceptably high top gas temperatures. The VSR-3 hearth was further modified to facilitate tapping molten alloy during operation. Attempts to tap were only partially successful due to high metal viscosity from excess carbides. The gas-fired crucible reactor was converted to a 1000 ampere D.C. submerged arc furnace with two in-line, straight polarity vertical electrodes. The unit was operated successfully, with alloy being produced and tapped. The arc furnace was redesigned as a two-electrode, 2000 ampere A.C. unit. Modifications were started on shaft reactor VSR-3 to convert to a continuous granular solids discharge system for the purpose of developing the "blast" section of a blast-arc, and to produce prereduced burden for use in the A.C. submerged arc furnace. The SOLGASMIX

computer program was modified to treat ideal and non-ideal solution chemistry. Heat and material balances were calculated for three reduction processes, combustion, blast-arc, and electric. The electric process is most energy efficient, followed by the blast-arc, and the combustion process respectively. The effect of pressure on carbon fuel rate, metal-producing temperature and reflux loading for a combustion-heated blast furnace was calculated using the SOLGASMIX computer program. High pressures reduce reflux and fuel rate and increase temperature. Detailed heat and mass balances were determined for the blast-arc and submerged arc process concepts. Both midwestern coal and low ash, low iron Wyoming coal were considered for the fuel and reduction carbon source in the blast-arc cases. The SOLGASMIX-REACTOR computer program was developed to handle recycle for the Al-Si-C-O-Fe system. Additional program modifications were made to include feed control schemes for the blast-arc and arc processes. The bench scale reactors were operated to determine the effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, CO sweep, carbon stoichiometry, location source of reduction carbon on alloy product yield, and carbon solubility in the alloy product. Starting up with substoichiometric carbon was beneficial to smooth operation, although steady state was not quite attained. Optimum carbon stoichiometry appeared to be 85-90% of theoretical. At 0.785 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the optimum carbon was 90% of theoretical. At 0.755 ratio, the optimum conditions were 87.5% of theoretical for total carbon with 80% of theoretical carbon contained in the ore-coke pellet. In general, total carbon at 85-90% and carbon in the pellet at 78-95% also applied for a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 0.486. Attempts to reduce burdens with no carbon in the ore-coke pellet (all reduction carbon was exterior to the ore pellet) failed to produce metallic alloy. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio did not significantly affect metal yield at low CO sweep conditions. However, no metal was produced at CO sweep rates of 22.5 l/m (50% higher than the normal CO rate) due to severe bridging from volatiles. The practical upper limit for $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 1.2; higher ratios generated extreme volatilization. A detailed study was made for the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ (0.485) burden that considered the roles of S, Fe_2O_3 , SiC, Ti, Fe, and carbon. Analyses of metal products indicated that Al_4SiC_4 increased as $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio decreased and that hypereutectic Si did not increase with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. At 0.43-0.58 ratio, Al_4SiC_4 was stable in the alloy produced (0.38-0.51 Si/Al ratio). Solubility tests showed a low solubility of carbon in the alloy; rather, carbon was dissolved as SiC. Phase identification of bench reactor metal product showed no significant variations of phases in

samples at the various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. However, the microstructure and slag concentrations did vary. More slag was found at the 0.79 to 1.0 ratios, probably due to increased slag fluidity. Pilot VSR samples were also analyzed. The major phases contained Si and FeSi_2Al_4 intermetallics in a matrix of eutectic Al-Si. Analyses of tests on the extractive purification effect of tin additions to Al-Si-Fe-Ti alloys showed no solubility of tin with any of the intermetallics. Analyses of metal produced in the D.C. arc furnace were similar to results on VSR metal samples except that the major carbide present was Al_4SiC_4 rather than SiC.

Design, fabrication, and installation of the pilot crystallizer system was completed. Three runs were made on the pilot crystallizer to determine the effects of alloy composition, cooling rate, tamping rate, remelt temperature, and rate on eutectic Al-Si yield. The yields varied from 48-72% for a starting alloy with a nominal composition of 66%Al-30%Si-3%Fe-1%Ti. Tests were run on solution leaching of the crystal bed to remove Al and Fe impurities for recovery of Si. Hydrochloric acid was effective; sodium citrate/nitric acid was not. The bench reactor was operated to determine the effects of copper additions on alloy yield for impure alloy containing greater than 10%Fe. The technique did reduce the Fe level in the alloy product and increased yield. Data from the bench and pilot operations were evaluated using regression analysis to correlate the effects of charge alloy composition on product alloy yield. Titanium concentration was not significant as an element. Increased levels of Si, Fe, and Fe-Ti complexes reduced product alloy yield.

The pilot membrane cell was fabricated and installed. The bench scale cell was operated to test graphite cements used in assembly of the pilot unit, different electrolyte compositions, and the resistance to metal penetration for the membrane cloth. Bath properties had a significant effect on the metal head limit, with penetration ranging from 63-217 cm. A new bench unit was built to study polarization effects during electrolysis.

Primary activities in the first quarter of Phase D will include: revision of the in-line electrode, direct current submerged arc furnace to a two-electrode, alternating current unit with a rating of 100KVA; startup and operation of the A.C. unit; modification of the VSR unit to a continuous, bottom solids discharge; startup and operation of the modified VSR to simulate the blast part of the blast-arc process, prereducing SiO_2 to SiC; development of a ball-forming technique to produce activated Al_2O_3 -SiC-coke burden as simulated prerduced feed for the A.C. arc furnace; operation of the bench scale reactors to determine total carbon requirement, amount of total carbon included in the ore-coke pellet, and carbon solubility in Al-Si alloys; calculation of updated heat/mass/energy balances for commercial size submerged arc furnaces; evaluation of

"stop and go" operation for the pilot crystallizer to obtain increased product alloy yield from Al-Si-Fe-Ti charge alloys.

DISCUSSION

The primary objective of the three-year program is to demonstrate technical feasibility of a pilot sized Direct Reduction Process for producing aluminum and aluminum-silicon alloy. The process includes three major tasks, Reduction to produce impure alloy, Alloy Purification, and Purification to Commercial Grade Aluminum. Goals for the third phase are to determine the feasibility of supplying high temperature reaction heat by oxygen combustion of coke in the vertical shaft reactor, to evaluate alternative reduction processes utilizing electric heat in the metal-producing zone, to complete construction and installation of the purification pilot units, and to demonstrate alloy refining and purification in the pilot units.

In Phase C, Alcoa was assisted on the Reduction Task by Koppers Company, Inc., Carnegie-Mellon University, Professor Julian Szekely, and Dr. J.C. Agarwal, Charles River Associates, Inc. Also, Professor J.F. Elliott contributed to the technical evaluation of the Reduction step in his role as DOE technical monitor for the contract.

The contributions of the above consultants and subcontractors were reported for the first three quarters of Phase C in the respective quarterly reports. In the fourth quarter, the following work was done. Koppers continued its engineering studies of the Arc and Blast-Arc process concepts, with a goal of providing preliminary engineering and cost estimates on the developmental processes. A report was submitted on the arc process that utilized information provided by two leading suppliers of electric smelting furnaces. In preparation for completing more comprehensive studies on both concepts, Koppers held meetings with three suppliers in December to establish concept heat/mass/energy balances, and to request more detailed information concerning capital requirements of commercial process flow sheets.

Carnegie-Mellon revised its optical pyrometry system for measuring experiment reaction temperatures to eliminate varying emissivity conditions and obtain improved, consistent measurements. A previously unidentified reaction line at 1850°C for reactor samples was found to be one that produces silicon metal. It was postulated that an invariant reaction was occurring in which metastable SiO_2 combined with stable SiC to form Si , SiO , and CO . Therefore, charging of SiO_2 into the reactor was discontinued in favor of high purity SiC . Experiments to determine phase equilibria data were continued.

Professor Szekely consulted a total of 7.5 days, and Dr. Agarwal consulted a total of 3.5 days on process economics, process strategy, process flow sheet concepts, and future programs for the project.

Alcoa participated in meetings scheduled by Koppers with Lectromelt Corporation, Elkem A/S, and Mannsmann-Demag to discuss submerged arc furnace technology.

Technical progress was formally reviewed with the DOE project manager and Professor J.F. Elliott once during the fourth quarter.

Alcoa submitted for DOE approval a Work Statement of additional tasks and a Cost Proposal to cover Phase D, to extend from 1981 January through 1981 September. Also, a modification to the contract was approved to extend the current contract, Phase C, through 1981 February at no additional cost. Phase D will start as soon as DOE approval is granted, probably in 1981 March.

Progress for the three main tasks is reported by sub-task as identified in the modified project outlines submitted on 1980 March 26. It is estimated that for Phase C the Reduction task is 100% complete, the Alloy Purification task is 100% complete, and the Purification to Commercial Grade Aluminum task is 100% complete at the end of the fourth quarter.

PROGRESS

A. Reduction - Phase C

Task No. 1: Supply Burden Material

Table 1 lists the burdens prepared during Phase C. All burdens were agglomerated as balls, made in the Eirich mixer or the bench scale Sprout-Waldron disk pelletizer. Most burdens were prepared from -200 mesh Tyler feedstocks. The alumina source was either bauxite, alumina hydrate, or calcined alumina. The silica source was Huber clay. The carbon source was COED char or metallurgical coke. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios ranged from 0.5 to 1.0; percent of stoichiometric carbon from 57 to 87. An average fired compressive strength of 2.80 MPa (406 lb./in.²) was attained for 3.2 mm. (0.125 in.) dia. balls using clay, bauxite, and char. Strengths over 5 MPa (700 lb./in.²) were measured on 6.3 mm. (0.25 in.) dia. balls when using clay, calcined alumina, and metallurgical coke.

In the fourth quarter, three of the burden materials were calcined at different temperatures to determine the effect of calcination temperature and burden composition upon burden strength. The results (Table 2) showed that burden strength is a function of both kaolinite clay content and calcination temperature. The high strengths obtained by calcining at 1500°C were due to the formation of mullite-alpha alumina bonds.

Task completion is 100%.

Task No. 2: Burden Beneficiation

Experiments using Rebolado bauxite demonstrated that no significant reduction in either iron or titanium can be obtained for this material by high intensity wet magnetic separation. For the conditions tested, iron showed an average decrease of 1.3 wt% Fe_2O_3 (from 12.0 to 10.7 wt% Fe_2O_3) while titanium showed essentially no change. The well dispersed nature of the magnetically susceptible minerals indicated in the tests suggests simple physical separation method will not produce the desired lowering of the iron or titanium levels.

Task completion is 100%.

Task No. 3: Effects of Pilot Operating Parameters

In the first quarter, four runs were conducted in an attempt to make metal while burning coke and oxygen. The details of these runs are shown in Table 3. No alloy was produced. During these runs, the oxygen rate was systematically lowered from 120 CFH to 75 CFH to decrease the CO sweep and vapor species recycle and enhance metal production.

Recent thermodynamic equilibrium calculations reflecting an update of Al_2O suboxide Gibbs Free Energy data indicated a much larger reflux requirement for the operation of a fully combustion heated carbothermic Al-Si process than was previously expected. These calculations show that at one-atmosphere total pressure the recycle of metal species is 100% indicating no metal production, but that some yield can be expected at three atmospheres. Based on this three-atmosphere case for a $.518 \text{ SiO}_2/\text{Al}_2\text{O}_3$ weight ratio, 1.217 gm total charge/gm O_2 are required to make the energy and mass balance. In all runs, except for VSR 30 and 31, CO sweep from combustion was excessive.

A series of experiments was conducted to determine if oxygen is present across the entire cross-section of the pilot reactor at the tuyere level.

Graphite rods (3/16-in. O.D.) were imbedded in the grate during runs 32 and 33 to detect the presence of oxygen in the radial direction across the reactor. These graphite rods extended approximately 4-in. above the centerline of the tuyeres. Pure oxygen at 60 SCFH was injected through one tuyere during VSR-32 and 33 after the vessel was brought to temperature by induction heating. The burning profile of the graphite rods revealed that the blast was not penetrating across to the opposite wall. This implied that reduced constituents (metal) could pass the tuyere region at the wall opposite to a single O_2 injection tuyere in the pilot reactor without being reoxidized.

Pilot reactor testing in March was redirected toward investigating the feasibility of operating an alternative combined "blast-arc" technique for producing metal. In this arrangement 40 to 60% of the energy of the process would be supplied by combustion in the upper stack to convert silica (SiO_2) to silicon carbide (SiC). Coke in the bed could be combusted by means of oxygen injection into the stack or a series of char (or coal)-oxygen burners could be placed around the circumference of the reactor. Silicon carbide would be

produced at bed temperatures between 1550 to 1850°C by the reductant carbon contained in the bauxite-clay-coke pellets in an atmosphere of combustion products (primarily CO) and ascending volatile species. In the lower section of the shaft Al-Si alloy would be produced by means of energy from an electric arc or induction system. Silicon carbide formed in the stack and unreacted carbon in the pellets would complete the reduction of Al_2O_3 at 2125°C to the metallic Al-Si phase.

In order to commence demonstration of the "blast-arc" concept, the pilot reactor was modified during March to inject preheated carbon monoxide at approximately 1850°C into the Stage I region to simulate the effects of combustion products on the formation of SiC. A schematic of the redesigned reactor is illustrated in Figure 1.

Carbon monoxide (150 SCFH) was successfully preheated to 300°C in the external packed bed and was passed upward through the reactor. Based on the temperature of the tube in the internal packed bed (obtained by sighting through the bottom glass prism) and heat transfer calculations, the CO gas was successfully heated to 1850°C at the point of injection.

Tests were continued during the second quarter to demonstrate the feasibility of operating a combined "blast-arc" for the production of Al-Si alloy. The upper section of the vertical-shaft reactor (VSR) was tapered and a vertical-stroke ram was added to the design in an attempt to prevent bridging problems which occurred during previous experimental runs. These design changes are illustrated in Figure 2.

The taper and ram proved successful in preventing bridge formations during the initial pilot run (VSR-36). An average bed movement of over 7 kg of ore/hr was established. This corresponds to the best solids flow obtained during the pilot reactor campaign. Furthermore, this rate of movement was maintained when 100 SCFH of preheated CO was injected at 1850°C at a point in the Stage I reaction zone to simulate the "blast-arc" gas flow pattern. A further increase in the CO injection rate was prevented by a high temperature in the upper stack and an irregular rate of feeding (charging) pellets. A substantial ingot was produced during VSR-36.

Several horizontal pegs were added to the ram prior to VSR-38 to combat condensate bridges in this upper area. Apparently the injection of CO gas into Stage I transfers a substantial

amount of heat to the upper shaft. Therefore, the power distribution from the induction system was adjusted to maintain a lower stack temperature. The packed bed for preheating CO and the catchbasin were also altered at this time to permit future tapping experiments to be conducted (see Figure 3).

The "blast-arc" was successfully simulated in run VSR-39. A CO injection rate of 200 SCFH was reached, which corresponds to 67% of the CO generated by a char-oxygen burner meeting the energy requirements of Stage I. Following a scheduled shutdown, an autopsy of the reactor revealed that a record 14.1 kg ingot had been produced during VSR-39. Since 50.3 kg of ore (pellets) had been consumed, the alloy to charge yield was 28%. This corresponds to 82% of the theoretical maximum rate of metal production anticipated from raw ore at steady state.

After demonstrating in part the feasibility of the "blast-arc" concept, the experimental program shifted to the installation of a system for tapping Al-Si alloy from the pilot reactor. Intermittent tapping would permit the pilot unit to be operated for extended periods where steady-state conditions could hopefully be attained. Furthermore, trials to purify the alloy (by filtering and/or ladle additions) could be conducted prior to delivering the alloy to the two downstream refining steps. A schematic of the initial location of the taphole and the detailed taphole design features are presented in Figures 4 and 5.

Upon completion of the taphole installation, an attempt (VSR-42) was made to produce alloy directly from ore pellets and to simultaneously drain the metal into the outside crucible prior to solidification. Burden movement during this run was very smooth resulting from improved control of the vertical-stroke ram. The ore pellets were composed of bauxite, clay, and coke breeze and very little condensation or dusting was evident.

After consuming 54 kg of ore, the water-cooled pipe was removed from the taphole and a stream of very viscous metal slowly flowed for a short time into the tercod crucible. Metal at times had to be raked from the graphite tapping tube with a graphite or steel rod. A total of 4.5 kg of Al-Si alloy was collected in the crucible.

An autopsy of the reactor showed that 8.1 kg of Al-Si ingot remained in the catchbasin and did not drain at a temperature of 1500°C. This ingot was similar in appearance

to the solid residue in the VSR-40 run and contained an excess of carbides.

During the third quarter, two runs were made in the VSR reactor with the aim of tapping more metal than was tapped in run VSR-42. Although significant amounts of alloy product were made in both runs, tapping was not successful. The viscosity of the alloy was too high, probably due to relatively high concentrations of carbides. The amount of carbide exceeds the amount which would precipitate if the alloy were saturated with carbon and then cooled to the tapping temperature. Filtration of the alloy through a bed of graphite rings or rods was somewhat effective in separating the carbides, but the alloy recovery was relatively low. Fluxing of the alloy with molten fluoride or chloride salts has been reported in the literature, so several experiments were performed to evaluate this approach.

In a preliminary test, a sample of a VSR ingot was submerged in a Tercod crucible containing cryolite at 950°C and agitated. The sample broke up and several globules of coalesced alloy were recovered from the crucible. A larger quantity of ingot alloy was added in the next experiment under the same conditions. The alloy was very fluid and separated readily from the bath. Analyses of a book mold sample and a sample from the furnace-cooled alloy layer were compared with an analysis of a sample from the original ingot. SiC was reduced from 17 volume per cent to an undetectable level based on quantitative metallographic techniques.

Towards the end of the third quarter, the gas-fired crucible reactor was converted to a D.C. submerged arc reactor, SAR-I (Figure 6). The D.C. reaction vessel was a 22.86 cm I.D. graphite crucible inside a 30.48 cm Starbide crucible. The D.C. arc was made between two inline vertical graphite electrodes ($\phi = 7.6$ cm), with straight polarity (top negative and bottom positive). Extending the bottom electrode about 7.6 cm into the reaction vessel allowed it to support a graphite grate. The grate enabled product to collect beneath it, out of the reaction zone. The gas fire was used to offset heat losses in the small reactor. Power was supplied by a Linde 1000 amp D.C. arc welder.

Four D.C. submerged arc reactor runs were made in the last quarter. SAR-I-1 lasted for only 25 minutes, and no arc was established. The startup was attempted with SiC covering the grate and activated carbon on the electrode.

SAR-I-2 was modified by tapering the top electrode and placing an aluminum disk on the bottom electrode. Also, carbon was placed on the grate instead of SiC. The arc was easily established and the run lasted 4 hrs., 18 mins. The arc length was about 2.5 cm with between 1000 and 1100 amps and 35 volts. A total of 25886 g of ore ($\text{SiO}_2/\text{Al}_2\text{O}_3 = .67$, 87% stoichiometric C in pellet plus an additional 4% as lump coke) was charged to the reactor. 1485 g of material were found below the grate and 4630 g above the grate. The material above the grate consisted of mixtures of SiC/slag and metal in varying proportions. SiC/slag predominated at the periphery, while alloy predominated at the center. The larger alloy drops contained very few SiC crystals, but did contain some mixed SiC/slag inclusions. The major phase in the alloy below the grate was Al_4SiC_4 (15-25% estimated) in a eutectic matrix with minor amounts of SiC, Si, and intermetallics.

SAR-I-3 was started as in SAR-I-2, but with oversized ore on the grate. The arc started easily, but the run was terminated because of power supply problems. After correction of the problems, the arc was restarted in a preheated reactor and continued for a total run time of 4 hrs., 41 mins. 23630 g of ore ($\text{SiO}_2/\text{Al}_2\text{O}_3 = .79$, 78% stoichiometric C) were charged to the reactor. Again, the average arc length was 2.5 cm with between 900 and 1000 amps and about 27 volts. 1800 g of slag and alloy were collected below the grate. The material above the grate consisted of a dish-shaped mass of mixed SiC and slag containing a pool of alloy. SiC was moderately abundant in the lower half of the alloy, but the top half was free of carbides.

SAR-I-4 was modified by removing the grate and using neither an aluminum disk, nor carbon lumps for startup. Total run time was about 4.5 hrs., but the arc was not stable. 37800 g of low carbon ore ($\text{SiO}_2/\text{Al}_2\text{O}_3 = .6$, 51% stoichiometric C in pellet plus an additional 21% as lump coke) were charged and a large amount of fuming was noted. The arc was again about 2.5 cm, but with between 600 and 1000 amps and 27 to 35 volts. Autopsy indicated that a large amount of unreacted material had accumulated in the hot zone. This may have been caused by a low power density, excessive stoking, and/or low %C in the pellets.

Task completion is 100%.

Task No. 4: Pilot Modifications

In the first quarter, the upper geometry of the shaft was altered to reduce the tendency for bridging of molten

material. Figure 1 illustrates a tapering of the reactor susceptor to an angle of 86° similar to the stack batter on a commercial blast furnace. The divergence of material in the lower taper section with the assistance of a reduced diameter auger or vertical stroke "ram" (not shown) was designed to prevent future bridging problems.

Figure 2 illustrates the reactor alterations made in the second quarter prior to run VSR-36. The 6-in. dia. rotating auger was replaced with a 1-7/8-in. dia. vertical "ram". This ram has an 8-in. vertical stroke designed to break ore bridges in the diverging section of the reactor shaft.

Further modifications were made to the pilot unit prior to VSR-38 (see Figure 7). The points of CO injection into Stage I were moved to the reactor outer wall. Several horizontal pegs (3/4-in.) were added to the ram to combat weak condensate bridges in the narrow section (6-in. dia.) of the shaft. The packed bed and catchbasin were elongated to permit future tapping of the reactor through the ceramic region of the shell.

After successfully demonstrating the initial phase of the "blast-arc" program (VSR 38 and 39) with these modifications, a system for tapping alloy from the pilot unit was installed. Figure 4 shows the general location of the new taphole. A graphite tube (2-in. O.D.) was inserted at an angle of 19° through the ceramic shell, insulation, and graphite susceptor. Castable insulation was set between flanges A and B to minimize heat losses and to protect the metal components from alloy splashing. A tercod crucible placed on refractory brickwork was positioned at the outer end of the tapping tube to collect the molten alloy. The entire tapping arrangement was enclosed in an aluminum partition equipped with an exhaust. Nitrogen and argon were injected into the enclosure near the end of the tapping tube to prevent air-burning of graphite and oxidation of the alloy. Levels of carbon monoxide in the aluminum enclosure were monitored to provide for operator safety.

In the third quarter, a tapping furnace was constructed for the purpose of maintaining the reactor tapping tube at an elevated temperature, and providing a preheated crucible so that the tapped alloy would coalesce. A schematic of this furnace is shown in Figure 8. A tercod crucible was set in a resistance-heated furnace with an added top section which accepted the tapping tube and provided access for the tap hole plug.

In run VSR-44, the reactor was fitted with two grates and a catchbasin lined with a 36 cm high section of alumina refractory. This arrangement is shown in Figure 9. The purpose of the lower grate was to support a filter bed consisting of a layer of graphite cylinders. The distance between grates was 43 cm, leaving a sump 22 cm high into which the tapping tube was screwed.

Experiments in the VSR reactor were terminated temporarily in September so that construction of an arc-heated reactor could begin. A gas-fired crucible reactor which was originally used in coke-oxygen combustion experiments has been converted to a submerged arc furnace. The reaction chamber was a graphite cylinder 23 cm in dia. The cylinder sat in a tercod crucible 30 cm in dia. which in turn sat in a gas-fired furnace 56 cm in dia. Graphite felt insulation was used to fill the gap between the graphite cylinder and the tercod crucible. The gas-fired furnace was able to maintain the tercod crucible at a temperature as high as 1200°C in order to reduce heat loss. A grate was installed 8 cm above the reactor bottom to provide a sump capacity of about 6 kg. A single graphite electrode 76 mm in dia. was used. The power supply was a DC welder capable of 1000 amps at 13-48 volts. The electrode position was changed with an electrically operated jack screw. It was possible for ore to be fed in batches from a tank through ball valves operated by a timer. The arc reactor top was closed so reduction CO was captured and burned in a flare. A single poker extended through the reactor top.

In the fourth quarter, a two-electrode single-phase arc reactor, SAR-II, was designed. This configuration has the advantage that interelectrode effects such as electrode spacing and charge conductivity can be investigated. These effects would not show up in a single electrode furnace with a conductive bottom, such as the DC reactor, SAR-I. The two-electrode configuration does not have the disadvantages associated with the three-phase delta configuration, in which each electrode interacts with the two other electrodes. In the delta configuration, optimization of conditions at all three electrodes is difficult. Since optimization of power density under the electrode is thought to be critical in the smelting of Al-Si alloys, the configuration of the pilot reactor is an important consideration.

Two views of SAR-II are shown in Figures 10 and 11. The reactor has a rectangular steel shell and, unlike SAR-I, is not fitted with a gas burner to offset preheat. The unit is lined with J.M-28 brick, J.M. thermo 12 board, Fiberfrax durablanket, and graphite felt. The reaction

chamber is a graphite box with 5 cm walls and internal dimensions of 20 cm x 40 cm x 27 cm deep. The electrode diameter is 8.9 cm and the electrode spacing is 20 cm, but can be decreased if necessary. A Rapid Electric Co. single-phase A.C. power supply capable of a maximum of 75 volts, 2000 amps, and 150 KVA has been delivered. The reactor construction has been completed.

The Vertical Shaft Reactor (VSR) is presently being modified to discharge granular solids. This reactor will be used during Phase D to provide quantities of prereduced burden for use in the submerged arc reactor. The modification consists of the replacement of the reactor hearth with an enclosed turntable. The solids discharged by the turntable are collected in a sealed box which can be emptied after closing an isolation valve. The same 24.6 cm O.D. x 20.6 I.D. graphite susceptor used in early runs will be carried over to the new configuration. The reactor top will remain essentially unchanged. The turntable will be driven by a variable speed motor which can be switched with a timer for very slow feed rates. Argon, CO, or N₂ will be introduced in the bottom in sufficient quantities to cool the reacted solids to a safe discharge temperature. This sweep gas will also preheat the solids entering the top of the reactor, so a minimal amount of power will be required for preheating. It is estimated that 80% conversion of SiO₂ to SiC can be achieved in one hr. at 1550°C. If the entire coil height (152 cm) were maintained at 1550°C, then about 36 kg/hr. could be processed with a one-hr. residence time.

Task completion is 100%.

Task No. 5: Reactor Scale-Up Design

A preliminary flow sheet was conceived for production of 300,000 TPY aluminum using a hybrid reactor combined with fractional crystallization and electrolytic purification. It was assumed that an Al, 40% Si alloy diluted by 2% Fe and 1% Ti would be produced from a pellet containing clay, Bayer alumina, and coke. It was assumed that the charge would be preheated and pre-reduced to SiC using heat supplied by a coal-O₂ burner. This would supply about 50% of the thermal requirements. The remaining energy would be supplied electrically but off-gas CO would be used to generate electricity at 35% efficiency to offset most of the electrical requirement. Thus, less than 2 kWh/lb aluminum would need to be purchased.

If silicon and ferrosilicon production must be minimized, relatively pure raw materials must be used; aluminum content in the alloy must be maximized; silicon recycle must be maximized; and the charge will probably have to be briquetted at a higher cost than pelletizing. It may not be possible to design a process operating at less than 4 kWh/lb aluminum if metallic by-product production must be minimized.

The smelting behavior of prereduced (SiC containing) burdens in an electric arc must be studied in order to determine E-I characteristics and productivity/in. of electrode diameter. Carbon content of the alloy must also be determined under arc smelting conditions.

Calculations were made for a pressurized combustion-heated reactor to determine the effect of pressure on Al and Al_2O_3 volatility. The use of a pressurized reactor and a diluent such as iron would lower volatility sufficient so that a combustion-heated process might be feasible under some conditions. This possibility was investigated using the SOLGASMIX equilibrium program by reacting $\text{Al}_4\text{O}_4\text{C}$, $\text{Fe}(l)$, CO , and excess SiC at a temperature just above the point where $\text{Al}_4\text{O}_4\text{C}$ is completely consumed. This was done at pressures of 1, 3, 6, 9, and 12 atmospheres with various $\text{Fe}/\text{Al}_4\text{O}_4\text{C}$ ratios at a constant $\text{CO}/\text{Al}_4\text{O}_4\text{C}$ ratio of 15.5. The percentage of combustion heat represented by that ratio varied from 93-97% of the heat requirement which included oxygen preheat. It was assumed that oxygen would be preheated to 1200°K so that the heat balance would allow for about 10% heat loss. The program assumed that Al, Si, and Fe form an ideal solution.

When pressure is doubled, the reaction temperature increases by 80-95°K. Increased temperature should increase the solubility of carbon in the alloy which is undesirable. The magnitude of this effect is unknown since reliable data on C solubility is not yet available.

A high reflux loading implies a low specific reactor productivity, difficulties in operation due to bridging or complete plugging of the bed, and a high fuel rate due to degradation of the high temperature heat input. Based on the calculations, a 45% iron alloy could be made at one atm with a recycle loading of 91% and a fuel rate of 42 mol C/mol Al. At 12 atm, a 10% iron alloy could be made with a recycle loading of 65% and a fuel rate of 11 mol C/mol Al. Thus, while one atm operation would produce an unacceptably high fuel rate, 12 atm operation should lead to a fuel rate comparable to that of the earlier optimistic calculations. If 25% iron could be tolerated, the reflux loading could be reduced to 52%.

In the fourth quarter, meetings were held with Lectromelt, Demag, and Elkem. Representatives of Koppers Company were

in attendance. The purpose of these meetings was to discuss the technology of smelting Al-Si alloys in an arc furnace and to establish a basis for capital cost estimates of a commercial plant.

The pros and cons of rectangular vs circular furnaces were discussed. Lectromelt favored rectangular furnaces; Demag favored the rectangular configuration for large furnaces and the circular configuration for smaller furnaces; Elkem favored circular furnaces in all sizes. Large furnaces with electrodes of 1900 mm or greater were said to be difficult to operate. 50 MW was thought to be the maximum size of a circular furnace with three electrodes. Larger furnaces with six electrodes would be possible with a practical limit of 70-75 MW with 1800 mm electrodes. Larger electrodes (2000 mm) would allow close to 100 MW, but operation would be difficult.

Self-baking electrodes (Soderberg) are about 1/3 the cost of prebake electrodes, but conventional types contribute about 2% iron to the alloy. Various designs for iron-free self-baking electrodes have been proposed. The Japanese have tested aluminum casings, but these are limited to less than 1m ϕ . Demag reported that a plant in Italy extrudes electrodes with fins which eliminates the casing and reduces the iron to 0.3% in the alloy.

Task completion is 100%.

Task No. 6: Calculate Heat and Mass Balance

The SOLGASMIX computer program for calculation of chemical equilibria was modified to treat ideal and non-ideal solution chemistry. Heat and materials balances were calculated for three reduction processes: electric, hybrid, and combustion, and a Reichardt diagram was constructed for the latter case. Using corrected data for Al_4O_4C and Al_2O , it was found that a one-atmosphere combustion-heated process will have insignificant one-pass yield ($\sim$ 100% recycle ratio), while a three-atmosphere process will have a one-pass yield ranging from 0-25% depending upon the assumed activity of aluminum and silicon in the alloy.

Review of the early modeling work revealed several problems that resulted in incorrect predictions for the atmospheric pressure, combustion-heated process at the start of the contract. The problems included significant changes in the published thermochemical data for Al_2O , revisions in the published activities for Al and Si based on more current

measurements, errors in $\text{Al}_2\text{O}_4\text{C}$ data entry, and an unbalanced heat transfer calculation.

The carbothermic reduction process can be separated into three main reaction stages assumed to occur in a shaft reactor with primary heat input at the bottom.

These reactions are incomplete as written since the volatile species, Al, Al_2O , and SiO are not considered. The Stage III reaction has the flexibility to produce an alloy where composition ranges from approximately Al_3Si_2 to Al_2Si_3 . The computer considers the alloys to be a series of compounds, Al_xSi_y , where $x + y = 10$. Ti, Fe, and C in solution are not considered nor are the possibilities of an oxycarbide (Al-O-C) "slag" solution or alloy solution with continuously variable composition.

Table 4 shows the complete heat balance by stages for the electrically heated, atmospheric pressure process. Since the thermal mass ratio is about 0.5, the CO is assumed to be cooled to the entering solids temperature. The total heat requirement for the electric process is 3909 kJ/mol Al_3Si_2 . This value could be lowered slightly by taking credit for the condensation of SiO from Stage I.

The hybrid process is assumed to be electrically heated in Stages II and III, and combustion-heated in Stage I and the preheat zone. It is assumed that C and O_2 are combusted adiabatically and supply heat at 1840°K, the temperature of Stage I. The heat balances for Stages II and III are identical in the electric and hybrid cases. The hybrid Stage I was recalculated with ARLEQUIL to determine the effect of the additional CO sweep on the heat requirement due to additional SiO formation. Table 5 shows the complete heat balance by stages for the hybrid process. The enthalpy of the gas is greater than that of the solids, so the gas exists at an elevated temperature. The hybrid process requires 2461 KJ/mol Al_3Si of electric heat and 19.9 mols of C to supply the combustion heat. This represents a 37% reduction in electrical heat requirements.

The combustion-heated process was separated into five stages by including a mullite formation stage and separate stages for SiC formation from mullite and excess silica. In order to be consistent with previous reports, Stage III was initially computed for reduction of $\text{Al}_4\text{O}_4\text{C}$ by SiC. An

initial run indicated that the one-pass aluminum yield for a combustion-heated process was nearly zero at one-atmosphere pressure. The pressure was then increased to three atmospheres for all the stages and significant one-pass yield was found, although the alloy composition shifted to $\text{Al}_3\text{Si}_{1.29}$.

The case presented here was slightly deficient in high temperature heat so the O_2 was assumed to be preheated to 630°K . The one-pass aluminum yield for Stage III was 38.9% which means 61.1% of the aluminum was volatilized and assumed to recycle. A more realistic case was run with 25% more combustion heat. The one-pass aluminum yield for Stage III dropped to 33.9%. Carbon consumption rose from 49.73 to 60.38 moles/mole $\text{Al}_3\text{Si}_{1.29}$.

In order to compare the combustion-heated processes to the electric and the hybrid processes, Stage III was recalculated with the addition of Al_2O_3 in order to make Al_3Si_2 . Combustion heat input was increased by 10% over that required to balance Stage III. The one-pass aluminum yield decreased to 25.2% while the carbon consumption rose to 84.64 moles/mole Al_3Si_2 .

The heat and material balances discussed above were used as the basis for a comparison of the energy requirements for the three thermal processes. Table 6 shows the calculations of the electric and coal energy requirements and the CO and metalloid by-product credits for the three processes. In Table 7, three variations of the electric and hybrid processes are compared with the combustion process. The variations are: coke as the solid fuel and reductant at 80% efficiency, coal as the solid fuel and reductant at 100% efficiency; coal with electricity generated by combustion of CO at a 35% efficiency.

The significant feature of these calculations is that the relative positions of the three thermal processes with respect to energy efficiency are reversed from the initial calculations. The arc is more efficient than before because a 10% rather than a 28% heat loss is assumed. The higher heat loss was based on a pilot arc furnace. The combustion process is much worse than before because of the higher volatility of Al_2O and the higher CO sweep required to supply the 10% heat loss above the critical temperature. The high recycle ratio greatly increases the high temperature heat requirement. The most efficient process is the electric process using coal as a reductant. If minimal purchased electricity energy is desired, the hybrid process using coal is most efficient since the

electrical energy requirements can be substantially reduced by burning CO to generate electricity.

In the third quarter, more complete heat and material balances were developed for the electrical and hybrid processes. Improvements and assumptions for these calculations were as follows:

- Fe was included in the mass balances and the metal was represented as an ideal solution of Al, Si, Fe pure liquids.

- Although C solubility in this alloy was not handled directly, the mass balance was forced to have a minor amount of excess SiC remain after all oxides were reduced. This represented approximately 2wt% carbon in the alloy as SiC and not as C in solution.

- Ti was excluded from the current equilibrium calculations, but was included in the overall mass balance for two of the cases studied.

- A char-oxygen burner was assumed to supply heat for the production of SiC at temperatures below 1840°K in the hybrid process. A carrier gas for the powdered char is required, and the sensible heat to raise these reactants as well as the combustion oxygen to the Stage I temperature was taken into account.

- Sulfur in the carbon source ash and S, H, and N in the carbon source volatile matter and carrier gas for the char in the char-oxygen burner were included in the mass balances.

- No slag solutions were considered in these balances.

- For these balances, an alloy containing an Al/Si ratio of 70/30 was assumed. It was determined by equilibrium calculation that all high temperature stages of the process for this ratio were endothermic and the heat balances between the temperature at which the first metal appears (2185°K) and all oxides disappeared (2345°K) could be combined to determine a net energy to be supplied by electric-arc heat. Thus, Stages II and III were lumped together, which greatly simplified the calculations. For the hybrid

process, the chemical heat in the gas above 2184°K as well as the sensible heat in the gas above 1840°K were used to balance the endothermic heats of reduction and sensible heat in the solids above 1840°K to leave the net endothermic heat to be supplied from the arc. This electric heat was then arbitrarily increased by 10% to allow for high temperature heat loss.

-The char and oxygen combustion required to maintain the Stage I heat balance in the hybrid process is determined by a trial and error technique using both the net heat of reaction to make SiC, and the energy required to preheat the char from 1200°K and the O₂ and carrier gas from 1089°K. These preheat temperatures were estimates related to the solids exit temperatures from the hot char-producing step, and need further refinement. Heat losses were arbitrarily set at 7.5% of the net chemical heat to produce SiC, and were included in the char-oxygen calculation.

-The top gas temperature calculation is a trial and error solution of balancing to zero the sensible and chemical heat in the gas between 1840°K and the top gas temperature, and the sensible heat in the solid entering the top of the furnace being heated from room temperature to 1840°K.

-The arc furnace heat balance is a great deal simpler with the required electric energy being determined by the net energy between all endotherms and exotherms plus 10% of this net for heat losses. Because carbon deposition by the decomposition of CO at lower temperatures is not believed to behave in an equilibrium fashion, the top gas compositions and refluxing was determined at 1205°K to limit this exothermic back reaction from effecting the heat balance

Preliminary heat and material balances for three cases were calculated according to the procedures and assumptions as stated above. The hybrid process heat and material balance for the Western Kentucky Coal case was significantly effected by the analysis and amount of ash in the coal. Higher ash in the coal requires more combustion of carbon and oxygen to preheat this ash as well as the attendant increases in carrier gas and combustion oxygen.

The hybrid process and arc furnace process as shown in Figures 12 and 13 respectively, can be directly compared because the carbon source, alloy recovery in the crystallizer, and other raw materials were identical. The only variations

were those related to heating Stage I by combustion and not by heat from an electric arc.

The furnace top gases from either process along with the same coal utilized for the production of char and formcoke were used to calculate the coal to generate the required electrical power for each process in a conventional coal-fired steam power plant. The top gas and coal burned for electricity generation was assumed to be converted with a 36% efficiency with 9600 BTU/lb coal and 316 BTU/SCF and 312 BTU/SCF for the heating value of the hybrid and arc furnace top gas respectively. This coal was assumed to be wet containing 20.3% H₂O. The same coal on a dry basis has a heating value of 12,040 BTU/lb, and the numbers in parenthesis in Table 3 reflect the use of dry coal.

In terms of the solids handled and the coal consumed, the two processes are equivalent for these calculations. Because there is 1.73 times more char consumed and 1.45 times more top gas produced in the hybrid process, there are probably more gases handled for that process.

In the fourth quarter, further improvements were made to the computer programs and a revised heat and mass balance calculation was initiated for a closed arc furnace operation. The study was based on using char from Wyoming coal, Huber kaolin clay, hydrated alumina, furnace coke, and electrode paste for self-baking electrodes. When completed, the study will be the basis for economic analysis of a commercial process to produce 300,000 tons/year of aluminum as Al-Si-Fe-Ti alloy.

Task completion is 100%.

Task No. 7: Process Mathematical Modeling

The FLOW REAC computer program for steady-state calculations was updated in the areas of reaction rate expression input, reaction heat assignment, treatment of external heat input or loss, and assignment of temperature limits.

The kinetics computer model was simplified, eliminating the uncertainties involved in modeling kinetics parameters and adapting it to calculation of equilibrium heat and mass transfer. Two versions of the chemical equilibrium/heat transfer model were developed, FLWEQUIL and FLWEQSEP, differing in their handling of backward-flowing phases.

The SOLGASMIX program was modified to correctly treat ideal and nonideal condensed phase solutions, and a series of databases incorporating various solutions was set up.

A program exchange was effected with Professor Gunnar Eriksson and KemaNord of Sweden in which Alcoa obtained SOLGASMIX-REACTOR. This program automatically makes converged equilibrium mass balances on reactor systems.

The SOLGASMIX-REACTOR program was converted to the ATC computer systems and has been expanded for conversational dialog, database management, improved program output, and automatic convergence control. Subroutines have been written and tested to provide external feed control on tuyere char and oxygen, top char, and top clay inputs to the blast-arc reactor. A converged simulation of the steady-state recycling blast-arc reactor has been produced which satisfies all requirements in the Al-Si-C-O-Fe system.

In the fourth quarter, modifications to the SOLGASMIX-REACTOR computer program to provide more complete and self-explanatory output as well as to provide a convergence monitoring strategy were completed. Feed control schemes were developed for both the blast-arc (which can also apply to a straight blast furnace) and arc processes.

These control schemes control the tuyere feed rate (in blast or blast-arc cases) to achieve heat balance with user-specified heat loss and control the top char and clay feed rates to achieve carbide balance (silicon carbide is recycled in the proposed process, so the model controls SiC production to be equal to SiC feed rate) and to achieve a user-specified product alloy Al/Si ratio. In the arc reactor scheme, damping factors were incorporated to control oscillations brought about, in part at least, by the lower top segment temperature's effect on the off-gas CO/CO₂/CS/CS₂ content.

Task completion is 100%.

Task No. 8: Effects of Process Variables

Nine runs were made in the bench reactor in the first quarter. The main variables were the SiO₂/Al₂O₃ ratio and the source of reduction carbon in the ore pellets. Runs AF-8 through AF-11 were made to decrease the axial temperature gradient in the back-reaction or bridging zone to prevent a concentration of these reactions over too small a volume. It was believed that by forcing the back-reactions to be distributed over a long zone, less severe bridging would occur, and a continuous operation could be obtained. Sufficient carbon for 100% reduction of oxides was charged and in all cases large accumulations of residue containing mostly carbide were found on top of the grate extending up to the bottom of the auger.

Also, the temperature in the susceptor at the bottom of the auger was above 1900°C and often evidence of liquid material could be found on top of the carbide accumulations at the bottom of the auger.

Initially, the suboxide vapors left the metal-producing zone, resulting in accumulations of unconsumed reduction carbon from the burden and the metal formed easily carbided. As these back-reacted suboxides recycled to the metal-producing zone, the accumulated carbides were consumed by the excess oxides that would accompany the downcoming burden. It appeared, however, that as the carbides formed and filled up the bottom of the furnace, the metal-producing zone was raised to higher levels until these endothermic reactions were either quenched on the bottom of the auger, which acted as a heatsink, or was raised out of the temperature region which was sufficiently hot enough to make metal.

To compensate for this effect, the next series of runs were started with a substoichiometric burden, then gradually charged with a higher carbon burden to prevent the accumulation of too much oxide slag in the metal-producing zone. Since the internal furnace hardware and auger were made of graphite, the ore burden was formulated with less than 100% stoichiometric carbon.

In AF-12 through AF-15, the burden contained only 80% of the reduction carbon requirement and the bottom of the auger was kept cooler by compressing the induction coil into the high temperature metal-producing region. As a result, each run was stopped only after the reservoir was full of metal. Each of these runs had an accumulation of slag on top of the grate and minor amounts dripped through the grate to the reservoir below. The first metal formed poorly coalesced in the bottom of the reservoir and the ingot structures were very heterogenous and difficult to characterize as to the composition and constituents of the continuous phase of operation. However, the ingot structure generally had a zone of metal with high concentrations of carbide, intermetallic, and slag on top of the poorly coalesced metal with a purer metal component near the top of the ingot.

Analyses indicated that Al_4SiC_4 was found in the metal phase for $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the burden of .6 and .5 but not for ratios of .78 and .99. Increases of SiO_2 in the ore did not necessarily result in increases in the hypereutectic Si phase. The first metal formed solidified as uncoalesced droplets with a skin of SiC at the surface and a typical solidification pattern of metal rich in slag, carbide, and intermetallics at the bottom

of the droplet and purer metal near the top. This tendency for non-coalescence increased as the ore $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio decreased. The slag content of the ingot increased with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

It did not appear that a steady-state was reached in any of these runs as the incoming ore Si/Al ratio did not equal that of the metal product. However, each run appeared to approach a steady-state. The analyses also indicated that Si was accumulated in the furnace either as SiC or recycled SiO more preferentially than Al.

A comparison of the weight ratio of metal to consumed charge with and without CO sweep, as shown in Table 8 indicated that CO sweep decreased metal production during runs of limited duration due to increased reflux. The CO ratios reported for the four CO sweep runs in Table 8 represented approximately 13% of the CO sweep that would be required in a three-atmosphere fully combustion heated reactor.

In general, it appeared that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the ore did not greatly affect metal yield and that metal could be easily produced with 13% of the CO sweep and 80% of the reduction carbon over a .5 to 1.0 ratio.

Table 9 listed the various reduction carbon sources and the distribution of the carbon in the charge. In all cases, sufficient carbon was contained in the ore pellets to reduce all SiO_2 to SiC. Within the conditions of these tests, it did not appear the source of carbon and location of carbon internal and external to the ore pellet had drastic effects on the experimental results. It was also noted that the ore pellet sizes used were -3/8 +6 mesh and -6 mesh +10 mesh in AF-12 and AF-15 respectively, and that this variable did not seem to significantly affect the results.

Thirteen bench-scale reactor runs were conducted during the second quarter. The details of each run are shown in Tables 8 and 9. The program focused on producing metal at higher levels of CO sweep and at the practical extremes of the ore burden $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. In addition, a program was begun to determine the optimum metal producing temperature and reduction carbon stoichiometry vs $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the ore burden.

Also, carbon solubility tests in Al-Si alloys were initiated. Experimental techniques were developed to run the tests at 2000°C without losing the alloy to vaporization, extreme wetting of container surfaces, or penetration into the container walls.

Previous CO sweep runs had been conducted at 1 atm total pressure and 15 litre/min of CO flow which represented only a small fraction of the sweep gas that would result from a fully combustion heated reactor. In AF-16 the CO sweep was increased by 50% to 22.5 litre/min, but the run had difficulty reaching temperature. The induction coil was repositioned for AF-17 to better preheat the incoming CO sweep gas. In both runs, no metal was collected in the reservoir below the grate, although phase analysis of the reaction zone material showed some metal had been produced. Each run was terminated prematurely due to severe bridging. These two runs can be directly compared with run AF12 which was identical in all variables except CO sweep. The process operation during AF-12 was smooth, and shutdown occurred only after the reservoir was full of metal.

Clay-coke burdens at 1.22 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio were tested in runs AF-20 through AF-23. Runs were terminated prematurely by bridging and no metal was collected in the reservoir. Even with no CO sweep, operation was erratic. It was concluded that the recycle loading of volatiles was higher for the clay-coke burdens than for lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ores, and that a ratio of 1.22 approached the maximum limit for making metal in the bench scale reactor.

Previous tests of metal production with all of the carbon placed external to the pellet were conducted under a CO sweep of 13 litre/min with a layer charging in the L bench reactor. It was decided to retest some of the critical variables studied in the L reactor program in the continuous operation AF reactor. AF-24 was a non-CO sweep run wherein the carbon-free ore extrudates were mixed with the pet coke chunks and not as a segregated or layer charge as was previously used. Metal was produced, but was heavily carbided. Also, the graphite support grate was almost completely consumed. It was difficult to decide whether the results of this run were tied to the fact that the reduction carbon was located exterior to the pellet or to the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 0.469 which was the lowest run in the AF reactor to date. Chemical analysis verified that the carbided ingot contained considerable metal; therefore, more tests would be required to determine if the severe bridging was caused by the low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio or the location of the reduction carbon. In AF-25, an 0.68 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio burden with 85% reduction carbon was tested and the ingot was again severely carbided. The coil had been lowered to better preheat the CO sweep gas during previous runs and was now overheating the metal collection reservoir such that severe attack of the graphite

reservoir by the metal was converting the metal to carbides. The induction coil was raised for AF-26 and this carburizing problem was eliminated. These results indicate that the metal of $0.34 < \text{Si/Al} < 0.96$ weight ratio is not in equilibrium with solid carbon but SiC and possibly Al_4SiC_4 .

In runs AF-27 and 28 the graphite rods normally placed on the grate to assist metal drain to the reservoir were replaced by SiC chunks. These tests were non-CO sweep runs with substoichiometric reduction carbon. None of the SiC chunks could be found after each run, and it appeared in AF-27 that the charge was reacting from the SiC bed. The SiC chunks probably reacted with the substoichiometric charge and not the metal.

Metallographic phase analysis of all the metal produced in the AF reactor to date have been compared to the Si/Al weight ratio of the metal at various parts of the ingot as shown in Table 10. X-ray diffraction analysis showed that Al_4SiC_4 was present in ingots made from 0.502 and 0.469 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ore (corresponding to 0.443 and 0.414 Si/Al ratio for the equivalent metal composition) and that $\text{Al}_4\text{Si}_2\text{C}_5$ was also found in metal coming from 0.502 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ore. Although there was no indication of Al_4SiC_4 by x-ray diffraction in AF7 at an 0.6 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the metallographic analysis showed a presence of this phase. The x-ray diffraction and quantitative analysis were done on essentially the same sample while the metallographic samples were taken from nearby areas in each case. Due to the heterogeneity of the bench scale ingots, these comparisons can only be approximated. Compilation of the data in Table 10 suggests that Al_4SiC_4 is stable with liquid metal of between $0.38 < \text{Si/Al} < 0.51$ coming from an ore of $0.43 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 0.58$ or an alloy typical of 7.25% Al - 27.5% Si to 66% Al - 34% Si.

Generally, large accumulations of SiC have been found in the AF bench scale as well as pilot plant ingots of Al-Si alloy, and have never been correlated with the metal Si/Al ratio and carbon chemical analysis. This problem of carbide formation causes great difficulty in the flow of the liquid alloy because the metal is easily entrapped in a honeycomb network of solid carbides. It is, therefore, very difficult to tap metal from the furnace, and filtering of the carbides from the metal is necessary before any solidification or crystallizing technique for alloy purification can occur. Limiting the chemical attack of the furnace walls and hearth area by the reduction reactions and liquid metal respectively is also of great practical importance. The most desirable circumstance is to keep carbide formation to a low level

such that all of these operating problems are alleviated.

The inability to correlate the data suggests that equilibrium between carbon and metal does not exist. In order to resolve this problem as well as to pinpoint the stabilities of various carbide phases in the Al-Si-C system, it was desired to study the solubility of carbon in alloys of varying Si/Al ratio at different temperatures in different crucible materials. In experiments to date, we have tested one initially carbon-free alloy of 0.685 Si/Al ratio in graphite, glassy carbon, and SiC crucibles of varying sizes and material density. At temperatures in the order of 2000°C, the alloy has fairly high metal vapor pressures, easily wets many solids and appears to be highly reactive with carbon and any low to medium density crucible material. The metal flows right through medium density SiC crucible walls. In order to maintain a pressure inside the crucible of one-atm, graphite lids were used with a small 1/8" hole to allow pressure equalization. Significant metal losses due to vaporization and crawling of the liquid metal through this small hole still occurred. It was finally decided to accept whatever pressurization might occur inside the crucible as it is not likely to effect the results to a measurable extent. Such experimental conveniences are typical for high temperature carbon solubility studies of volatile metals.

The results to date show that the alloy studied dissolves carbon as SiC from graphite crucibles, and that this reaction of C from the wall and Si in the metal will likely continue until one or the other is exhausted. The buildup of SiC crystals growing from a graphite wall is generally directed proportional to the time at a temperature of 2000°C. The same alloy contained in dense SiC crucibles shows little to no attack of the crucible wall; however, some carbon is found in the solution. It is not certain whether this minor amount of carbon pickup (less than 2wt%) comes from the SiC crucible or the metal that wets the graphite lid and drips back into the liquid sample in the bottom of the crucible. It is certain at this time that the carbon pickup from dense graphite crucibles is much greater than from dense SiC crucibles and that SiC may be the solid in equilibrium with this alloy.

If this is true, very low solubilities of carbon may exist in the alloys. It would then be advisable to use SiC hearth materials or possibly those of Al_4SiC_4 to limit carbon pickup and alleviate the problems in tapping the metal from the furnace and carbide removal before purification. These preliminary results also show that the consumption of dense SiC chunks on the grate as discussed above was due to the reaction with slag and not metal.

During the third quarter, two runs were made in the bench scale reactor. A summary of important variables for these runs along with all the other runs to date in the AF reactor program are presented in Table 8 and 9. The runs in AF-26, 28, and 29 are related in that the only intended variable was the carbon stoichiometry of the burden. It was desired to compare the metal yield with respect to carbon stoichiometry and find the optimum carbon level which would minimize the accumulations of slag or carbide resulting from too low or too high a burden carbon. Comparisons of these three runs showed that very little slag or carbide accumulations occurred for a 90% carbon stoichiometry in the burden at a .785 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Comparing AF-26 and 29 showed that no appreciable increase in metal production for an increase in burden carbon was observed. The increase in metal production in AF-28 could be related to the slightly higher burden carbon and metal-producing temperature, but this was a shortened run that was plagued with operating problems.

During the fourth quarter, 16 runs were made in the auger-feed bench scale reactor. The purpose of the runs was to determine the optimum total reduction carbon required in the burden as well as the amount of that carbon contained in the ore-coke pellet, to achieve smooth operation and produce acceptable alloy. Production of metal with all of the reduction carbon exterior to the ore pellet was also evaluated.

It has been perceived that at metal-producing temperatures for an Al/Si ratio of greater than 56/44, the reaction of carbon with ore and alloy is effected by the amount and location of the carbon, but not by the physical and chemical form of the initial carbon source. The high metal-producing temperatures of 2000°C or greater appear to graphitize the different forms of carbon, making them equally reactive. There are a number of reactions in the carbothermic reduction of Al-Si alloys where the location and amount of carbon is important.

If too much carbon is located inside the pellet, the metal produced will be carbided insitu before it has a chance to coalesce and separate from the reacting pellet.

Since the heat for metal production is supplied by an electric arc at a carbon electrode tip, a certain amount of carbon from the electrode is consumed as a reductant. If too much carbon is placed in the burden, the metal alloy carbon content will increase and excess carbides will form before the metal has a chance to coalesce and separate from the reaction zone. This carbide formation will cut off the feed of burden to the electrode tip or fill up the hearth or reaction zone volume, forcing the metal production zone and electrodes to a higher position in the furnace. Therefore, there is a

desirable maximum of carbon inside the pellet and in the burden mix.

If there is less than the maximum permissible carbon in the pellet, more of the liquid oxycarbide and suboxide and metal vapors will have to find additional carbon outside the pellet to complete their reaction to liquid metal. This is acceptable if the slag does not coalesce and separate from the reaction zone or the vapors do not escape to colder regions of the bed before they complete their reaction to liquid metal with adjacent carbon sources near the electrode tip. This increase in liquid oxycarbide and vaporous metal and suboxides reacting external to the pellet may affect the proportions of the reduction carbon coming from the burden mix and the electrode, but there will be no change in total carbon consumption if there is no net accumulation of carbides or oxycarbide slag and only SiC saturated metal is tapped from the furnace. It is expected for this condition of decreased pellet carbon that there will be an increase in electrode consumption and a decrease in total burden carbon. If the pellet carbon is decreased to a low enough level, there will be incomplete reduction producing an excess of recyclable vapors, an accumulation of oxycarbide slag, a decrease in liquid metal, and a possible further increase in electrode consumption. This criterion establishes a minimum of carbon in the pellet and in the burden mix, and a maximum acceptable electrode consumption.

Zero carbon in the pellet was desired providing the largest degree of flexibility for the process and the greatest economic advantage.

Before testing zero carbon burdens, the proper burden mix carbon for the ore $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in question had to be determined. Table 11 represents the testing of the total burden mix carbon for burdens near the composition for an Al/Si metal ratio of 60/40 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = .755$). Some runs reported on in previous quarters have been included in this comparison.

In each run, the goal was to feed between 9-10 kg of ore as the metal produced would completely fill the metal reservoir of the bench scale shaft reactor. The shutdown of each run occurs before all of the ore reaches the reaction zone so that the conditions in the reactor can be observed after the fact. A normal successful run will result in the actual consumption of at least 8 kg of ore. Consumption of less than 8 kg indicates that operating problems occurred resulting in a premature shutdown. Most of these shutdowns are caused by carbide formation shutting off the ore feed to the metal-producing zone or plugging of the bed due to high volatile

reflux resulting in an auger failure or loss of bed movement. Slag accumulations have never caused a shutdown.

The results in Table 11 showed that the maximum total burden carbon for .755 oxide ratio was in the range of 87.5-90% and that the results were partially affected by the amount of carbon in the pellet. Runs AF28, 31, and 33 all contained 84.5% or greater carbon in the pellet and resulted in early shutdowns. Runs AF28 and 31 were shutdown due to carbide formation while AF33 was terminated due to heavy bridging. Where the carbon in the pellet was below 78.5%, there were oxide accumulations in the metal-producing zone even though the total burden carbon ranged between 84.5-90.0%. In general, the higher total burden carbon gave carbide accumulations, but this was interdependent with the amount of carbon inside the pellet. Runs AF36 and 29 were successful runs based on the ore fed, but the conditions found after the runs indicated that they were close to termination due to bridging. A total burden carbon of 90% is probably too high. However, if a pellet carbon between 78.5-80.5% had been tested at this total carbon level, there may have been a better balance of oxides and carbon. The results suggested that 87.5% total carbon with 80% carbon in the pellet was a good estimate of optimum conditions to give a smooth operation, with 90% total burden carbon as the upper limit and the internal carbon lying between 78.5-84.5%.

The same type of experiments were run for ore pellets near the composition for a 70/30 Al/Si alloy ($\text{SiO}_2/\text{Al}_2\text{O}_3 = .486$) and the results were tabulated in Table 12. In general, runs where 84.5% carbon was contained in the pellet continued to result in early shutdowns due to carbide formation as occurred in the previous set of runs for 60/40 = Al/Si alloys. These runs, AF42 through 45, all had bridging in the bottom of the auger which created severe loads on the auger, causing the shear pins on the drive to fail or the auger shaft to break. These bridges were very low in oxide and high in carbides. Run AF46 was a mixture of two burdens with one containing 84.6% carbon in the pellet comprising 69% of the burden and the other containing 51.0% of the carbon in the pellet for a net total carbon in the pellet of 74.3%. This run behaved much like runs AF42 through AF45 which had 84.6% carbon in the pellet and showed the limitation of mixing different burdens of widely varying pellet carbons. Run AF27 was a successful run and one typical of runs in the previous tests where less than 78.5% of the reduction carbon was in the pellet. More runs would be required in this series to establish the best total burden carbon and pellet carbon relative to this $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

The last set of runs made in this quarter were attempts to make a 60/40 = Al/Si alloy with no carbon in the pellet. These runs are summarized in Table 13. Production of any metal at this oxide ratio proved to be very difficult. Only run AF41 began to show any signs of success. The analyses of the reaction zone material were typical of a situation where most of the oxides vaporized away from the hot zone, leaving an excess of carbon to form carbides with any metal that was produced.

Progress for carbon solubility studies in Al-Si alloys was limited to production of the master alloys to be used in these studies and some initial tests in graphite crucibles at 2200°C.

Task completion is 100%.

Task No. 9: Supportive Analytical

Analyses were completed as required. Man-hr. expenditures were as follows:

first quarter	422
second quarter	635
third quarter	381
fourth quarter	476

Task completion is 100%.

Task No. 10: Supportive Phase Identification

A series of metal alloy samples produced in the VSR reactor were subjected to remelt experiments to determine the effectiveness of fractional melting for separation of Al-Si alloy from the carbides and Fe- and Ti- bearing intermetallics in the reactor product. The remelt samples were then submitted for phase analyses. Results of the analyses were used to interpret the AF-reactor runs reported in Table 10.

SiC and TiSi_2 (Al, Fe) were concentrated in the refractory fractions, leaving a low-melting liquid slightly enriched in Al, Si, and Fe. Fe-Si-Al intermetallics were slightly enriched in the low-melting fraction; peritectic reactions with the melt resulted in the formation of FeSiAl_5 at the expense of high-temperature phases which have a lower Al content, reducing the amount of Al readily available for the formation of Al-Si alloy.

Phase analyses were done on metal produced in a series of AF-Bench Reactor runs with varying burden compositions in order to determine the effects of changing burden composition on the metal produced. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the burden was varied as follows: AF-13, 0.5; AF-7, 0.6; AF-12, 0.788; AF-14 and AF-18, 1.0; AF-20, 1.22.

No significant variations were found in the metal phases in the samples from AF-12, 13, and 14; all consisted primarily of three-phase eutectic microstructure, Si, and SiC, with minor amounts of $\text{FeSi}_2\text{Al}_4/\text{FeSiAl}_5$, and $\text{TiSi}_2(\text{Al}, \text{Fe})/\text{TiSi}_2(\text{Al})$. However, there were differences in the microstructure of the ingot, and in the amount of slag contained in the ingot. AF-12 and AF-14 contained increasing amounts of slag in the ingot with increasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. In addition, the metal overlying the slag in AF-14 (in which slag comprised 40-50% of the ingot) contained very abundant Fe-Si-Al inter-metallics, due to fractionation of iron into the metal from the large volume of slag. There was also a strong tendency for metal from the low- SiO_2 burden compositions to rapidly form a SiC "skin" in the reservoir; this "skin" of SiC on the surface of the droplets restricted coalescence of the droplets, resulting in very high interstitial porosity, including open voids, near the base of the ingot. The tendency to form this "skin" decreased at successively higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios.

Metal produced in bench reactor run AF-20 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.22$, 80% stoichiometric carbon, 15 l/min CO sweep) was not significantly different from metal produced in previous runs at lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios. Comparison of this ingot, in which the burden consisted only of kaolinite and coke, with no bauxite, with earlier ingots confirmed the previously indicated trend toward more accumulation of slag in the metal reservoir at higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, possibly due to formation of a less viscous slag. However, separation of the slag and SiC from the liquid metal within the reservoir was more efficient in earlier runs, at lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, than in AF-20.

Metallic product samples from pilot reactor runs VSR-35 and VSR-39 were submitted for phase analysis in order to determine the effects of a change in the temperature profile within the reservoir on the metal product. Phases were identified by optical microscopy, based upon phase compositions determined previously by electron microprobe. Modal compositions were determined by counting 450-550 grains on each sample.

Samples VSR-35 (1), VSR-35 (2), and VSR-35 (3) were taken from the base, middle, and top of the metal ingot formed

in the reactor reservoir. Modal compositions of the three samples are listed in Table 14. The major phases were three-phase eutectic microstructure (Al-Si-FeSiAl₅), SiC, and hypereutectic Si, with minor to trace amounts of FeSi₂Al₄/FeSiAl₅ and TiSi₂(Al, Fe)/TiSi₂(Al) intermetallics. The metal was coarse-grained, with intermetallic crystals up to 3 mm in length and SiC plates up to 10 mm in length.

The three-phase eutectic microstructure exhibited a dendritic morphology which is typical of the alloy purification and product remelt samples, but which has not previously occurred in the primary metal ingots. This morphology consisted of branched dendritic crystals of either Al or FeSiAl₅ with interstitial metal of eutectic composition. Individual dendritic crystals of Al were up to 1 mm in length, whereas individual dendritic crystals of FeSiAl₅ were up to 0.5 mm in length; the latter were occasionally in crystallographic continuity with hypereutectic FeSiAl₅ forming a peritectic reaction rim on the surface of intermetallic FeSi₂Al₄ crystals, indicating nucleation of eutectic FeSiAl₅ on previously formed hypereutectic crystals.

Two samples from Run VSR-39, designated top one-third and bottom one-third, were taken from the center of the cylindrical ingot at approximately one-third and two-thirds of the distance from the top of the ingot. The phase composition of the metal samples is also listed in Table 14.

Both metal samples consisted of Si and FeSi₂Al₄ intermetallics in a matrix of eutectic microstructure. In the lower sample, SiC occurred as discontinuous radial aggregates of fine platelets. In the upper sample, large bladed SiC crystals up to 8 mm in length formed an open framework, in which some of the interstices were filled with metal. TiSi₂(Al, Fe) was intergrown with SiC in both samples, suggesting co-crystallization of the two phases over a limited temperature range, with continued crystallization of SiC at higher and/or lower temperatures.

In the third quarter, phase determination by quantitative metallography was performed on ingots from four bench runs with SiO₂/Al₂O₃ ratios of .504, .785, .788, and 1.22. Typically, the ingots were texturally heterogeneous with three to five textural zones arranged vertically. Large variations in carbide distribution were found between zones. The amount of SiC generally decreased with increasing height, while Si showed a tendency to increase. Lower SiO₂/Al₂O₃

ratio ingots contained increasing amounts of Al_4SiC_4 . The relative amount of hypereutectic silicon did not increase with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, possibly due to the influence of carbon.

Two alloys were prepared in order to determine whether tin would form intermetallic compounds when added to Al-Si-Fe-Ti alloys. The alloy compositions were as follows:

	<u>AT-1</u>	<u>AT-2</u>
Sn	50%	50%
Al	28.1	26.4
Si	19.2	18.2
Fe	1.9	5.5
Ti	0.9	----

Back scattered electron and x-ray pictures taken by electron microprobe indicated that there was no solubility of Sn with any of the intermetallic phases for either alloy composition. It was concluded that multi-component Al-Si alloys could not be purified by extraction of Fe or Ti with Sn.

In run VSR-42, during which some alloy was tapped, a large quantity of alloy did not drain from the reactor. A metallographic analysis of the ingot which remained in the reactor showed 32% SiC, <1% Al_4SiC_4 , 4% slag, and 5% $\text{TiSi}_2(\text{Al}, \text{Fe})$ by volume. The SiC occurred as irregular plates contouring intergrown Al_4SiC_4 , and as agglomerated masses of semi-concentric SiC balls. Slag was generally associated with these agglomerates. $\text{TiSi}_2(\text{Al}, \text{Fe})$ was associated with the SiC plates, suggesting that $\text{TiSi}_2(\text{Al}, \text{Fe})$ may have crystallized in the SiC plates. By comparison, the alloy which drained from the tap hole contained only 0.72% C which is equivalent to about 2.5% SiC by volume.

In the fourth quarter, phase analyses were completed on six AF-bench reactor runs, AF-30 through AF-35. Volume percent results are shown in Tables 15 and 16 for 3-4 sections/ingot. Zone 1 was the first metal produced, zone 2 next, etc.

The major phases in the AF-30 ingot were three-phase eutectic (Al-Si-FeSiAl_5), Si, FeSi_2Al_4 , SiC, and Al_4SiC_4 . The Al_4SiC_4 was predominant in metal produced later in the run (zones 2, 3 of ingot).

Runs AF-31, 33, and 34 were made at the same reactor operating conditions; however, only run AF-34 was completed. The ingots were similar, containing primarily Al-Si-FeSiAl_5 eutectic, Si, FeSi_2Al_4 , SiC, and Al_4SiC_4 .

Run AF-32 ingot contained minor amounts of mixed SiC/slag in the top zone in addition to the normal phases present in all of the AF runs. Also, the carbide spheroids, formed by the peritectic reaction of SiC with the metal, were distributed throughout all of the zones.

Phase analyses were also determined for runs 2 and 3 made in the in-line electrode D.C. submerged arc reactor (SAR). For SAR-2, one sample was taken from the material accumulated above a graphite grate (below the electrode) and a second sample was obtained from the metal collected below the grate. The samples were extremely heterogeneous.

The above grate sample consisted of mixtures of SiC/slag and metal in varying proportions. SiC/slag predominated at the periphery of the sample, and metal predominated at the center. The polycrystalline slag appeared to be similar to that in earlier VSR runs. Its composition could not be determined by optical microscopy. SiC in the slag varied from fine platelets (less than 50 microns) to medium-sized plates (up to 300 microns) or small equidimensional tablets (less than 100 microns). The SiC/slag also contained small disseminated droplets of metal. The mixed SiC/slag generally was separated from the larger metal drops by a layer of SiC-free slag.

The larger metal droplets contained very few SiC crystals, but did contain some mixed SiC/slag inclusions. The metal consisted of Si, FeSi_2Al_4 , and large (up to 0.5 mm) $\text{TiSi}_2(\text{Al})$ crystals, in a matrix of eutectic microstructure (Al-Si-FeSiAl_5).

The major phase in the metal sample from below the grate was Al_4SiC_4 (15-25% estimated) in a matrix of eutectic microstructure, with minor amounts of SiC, Si, and FeSi_2Al_4 , and traces of $\text{TiSi}_2(\text{Al, Fe})$ and $\text{TiSi}_2(\text{Al})$. Al_4SiC_4 formed small (less than 0.5 mm) thin platelets. SiC occurred as larger (up to 1 mm) thick plates, typically with Al_4SiC_4 peritectic reaction rims. Hypereutectic Si occurred as prismatic crystals up to 0.6 mm in length; FeSi_2Al_4 crystals were tabular, up to 0.4 mm in length. The eutectic microstructure contained abundant sub-micron sized crystals of eutectic Si and FeSiAl_5 , giving it a "dirty" appearance.

In general, these samples were texturally similar to analogous samples from previous VSR runs. The major difference was the lack of SiC in the above grate metal, and the preponderance of Al_4SiC_4 over SiC in the metal accumulated below the grate.

Samples submitted for analysis from SAR-3 consisted of: (1) a large "bird's nest" structure consisting of metal, SiC, and slag; (2) an accumulation of metal which formed beneath the upper electrode, on top of the bird's nest; and (3) an accumulation of slag from the sump area below the grate. Modal compositions of the first two samples are listed in Table 17. These analyses include the metal fraction only; the intergrown SiC/slag mixture was excluded from the modal analysis because of the extreme variations in its abundance. Modal analysis was also not possible on the lower slag sample because of its poor polishing characteristics.

The metal accumulated within the SAR-3 bird's nest consisted of coarse-grained Si, FeSi_2Al_4 , $\text{TiSi}_2(\text{Al}, \text{Fe})$, and $\text{TiSi}_2(\text{Al})$ in a matrix of eutectic microstructure $(\text{Al-Si-FeSiAl}_5)_2$. SiC was moderately abundant in the lower half of the metal, but the top half was free of carbides. Both hypereutectic Si and Ti-bearing phases were unusually abundant in this metal, possibly due to reaction (or lack of reaction) with slag. The bird's nest structure itself consisted of fine-grained mixture of SiC and slag, with variable proportions of metal inclusions.

Metal accumulated beneath the upper electrode, on top of the bird's nest, was also free of carbides and high in Si, but had a more typical Ti content.

Task completion is 100%.

Task No. 11: Supportive Mechanical Engineering

Machining fabrication and engineering design were provided as needed. Man-hrs. expended were as follows:

first quarter	165
second quarter	87
third quarter	77
fourth quarter	109

Task completion is 100%.

B. ALLOY PURIFICATION

Task No. 1: Pilot Unit Installation

In the first quarter, the design, fabrication, and purchasing of all major hardware items were completed, including the multipurpose furnace, furnace instrumentation/controls, crystallization vessel, crystallizer gas-fired heating systems, agitation system for the crystallizer, and the gas-fired holding ladle. All of the supporting equipment and tools were also built, except for the false bottom product removal hardware.

The crystallization unit assembly was completed in the second quarter. Equipment modifications and installation were completed and the shakedown run was made during the last week in May.

Task completion is 100%.

Task No. 2: Effects of Pilot Operating Parameters

During the first quarter, experiments were continued on copper additions to improve casting alloy yield, extending the iron content of the alloy above 10%. Past experiments showed that yields of up to 33% were possible with starting alloys of 30%Si-10%Fe-2%Cu-rem. Al. Current experiments were not as successful, indicating that iron levels in excess of 10wt% will be difficult to process. Three experiments were performed, with initial compositions as follows:

Exp. 48	30%Si-10%Fe-2%Cu-rem. Al
Exp. 49	30%Si-15%Fe-2%Cu-rem. Al
Exp. 50	30%Si-15%Fe-4%Cu-rem. Al

Experiment 48 essentially was a repeat of Experiment 41, where a 30% yield was obtained. Experiment 48 had a 26% yield, a comparable result. Experiments 49 and 50 had increased iron contents, and the copper content was also varied. The yields were much lower, 8% and 2%, respectively. The lower yields suggested that copper additions can improve yields, but that there was a limit to their effectiveness at approximately 10% Fe. The results also indicated that a 2% Cu addition was an optimum level over a wide range of iron contents. See Table 18 for a summary of experiments on high Fe alloys.

Phase analyses were performed on the crystal samples from Experiments 33 and 41, with initial compositions:

Exp. 33	30%Si-10%Fe-rem.Al
Exp. 41	30%Si-10%Fe-2%Cu-rem.Al

The phase analyses indicated that the copper did not form intermetallics with the iron or silicon, but was present as very small (<4 um) crystals in the aluminum matrix.

The results of Experiments 49 and 50 indicated that some means of reducing iron levels to 10wt% or lower was necessary if the reactor product iron levels could not be reduced sufficiently by ore and carbon source selection. One method which has been briefly investigated is the use of a stripping solution to preferentially dissolve iron from an alloy. Preliminary results were favorable. The tests were conducted at room temperature, with soaking times of 40 hrs. and 72 hrs. In the experiment with the 72 hr. soak, more aluminum was dissolved than was desired, indicating that a short soak time is preferable to a long soak.

In the third quarter, three experiments were made in the pilot crystallizer on an alloy with a nominal initial concentration of 66%Al-30%Si-3%Fe-1%Ti.

The major process variables studied in the pilot unit were initial alloy composition, cooling rate, tamping rate, remelt rate, and final remelt temperature. The process variables are listed in Table 19 for Runs 1-AP, 2-AP, and 3-AP. The material balances are shown in Table 20. At regular intervals, stream samples were taken of the liquid alloy drained from the crystallizer. Selected samples were analyzed to determine approximate yields of casting alloy. The crystal bed was also analyzed to complete the material balance. Yields for the runs are shown in Tables 21, 22, and 23.

Samples were analyzed by atomic absorption (AA), and inductively-coupled plasma (ICP) for Si, Fe, Ti, and Al. Samples have also been submitted for neutron activation analysis (NAA). The poor closure obtained (92-96%) may have been due to oxide formation or carbon contamination. NAA on crystal bed samples from Runs 2-AP and 3-AP showed oxygen levels of 0.53 and 1.3% respectively. These results indicated either contamination of the bed with carbon or continued incomplete dissolution of samples for analysis.

The crystal beds were leached in two media: hydrochloric acid to remove free metal, and a sodium citrate/nitric acid solution to preferentially remove iron. The analyses are shown in Table 24.

A key assumption in the scale-up of alloy refining for the Direct Reduction Process is that high surface to volume ratios decreased yields in the bench equipment, and that drainage and casting alloy yields would improve as the scale of the equipment increased. Table 25 shows the yield information for Experiment 10 (bench), which had a starting alloy very similar to the composition of Run 2-AP. The amount of material drained at the end of the freeze cycle was much higher for Run 2-AP, 21% vs 7% for Experiment 10; however, the casting alloy yield was remarkably similar, 60% for Run 2-AP vs 55% for Experiment 10.

Referring to Table 19, Runs 1-AP and 2-AP were very similar, with a moderate cooling rate, and a slow tamping rate. The tamper stroke was short, 4-in. and 5-in., respectively. The major input difference between these runs was the titanium level; however, the casting alloy yield varied considerably, 72% for Run 1-AP and 48% for Run 2-AP. Run 3-AP had an even higher level of titanium, but the major operating change in reduction was to allow the cooling to more closely approach the equilibrium liquidus and to avoid supercooling. Run 3-AP also had better instrumentation, with a melt temperature profile during the freeze cycle, and better temperature monitoring during remelt. The casting alloy yield for Run 3-AP was 58%.

The crystal beds from the experiments were examined for chemical composition and morphology. The chemical composition is reported in Table 24, and the morphology is reported below.

<u>Experiment</u>	<u>Morphology</u>
Run 1-AP	72%Si, 25%Al, 2%FeSi ₂ Al ₄ , trace of FeSiAl ₅
Run 2-AP	70%Si, 26%Al, <1%TiSi ₂ Al, 3%FeSi ₂ Al ₄ , trace of FeSiAl ₅

The morphology agrees well with the chemical analysis. Six samples were taken of the crystal bed for Run 3-AP. The chemical analyses are:

<u>Sample Position</u>	<u>Composition, %</u>			
	<u>Si</u>	<u>Fe</u>	<u>Ti</u>	<u>Al</u>
1	60.8	2.7	2.5	30.4
2	61.0	1.4	5.5	30.0
3	57.7	1.5	3.9	29.6
4	54.8	2.6	2.6	38.0
5	61.8	1.9	3.4	32.0
6	49.9	5.2	3.8	32.9
average	57.7	2.5	3.6	32.2

Several observations were made:

1. More titanium bearing intermetallics were found near the top of the crystal bed.
2. Iron bearing intermetallics tended to concentrate near the shaft and the bottom of the bed.
3. The highest aluminum content occurred at the bottom of the bed, near the shaft. This was due to poor drainage and the generally lower temperatures along the axis.

The results of the leaching showed that hydrochloric acid was effective in reducing aluminum and iron levels in the crystal bed. The effect of the sodium citrate/nitric acid leach was minimal.

A sample of the crystal bed was tested to determine whether the Al could be separated from the Si by grinding to a fine particle size and screening. Partial separation was achieved by grinding the sample to -100 mesh Tyler. The Al was concentrated in the coarser fractions.

In the fourth quarter, data from the bench and pilot programs were analyzed using regression analysis to determine correlation of compositional variables on the casting alloy product. These variables were silicon content, iron content, titanium content, and an interaction term between the iron and titanium contents. The percentage of initial charge usable as casting alloy with limits of 20% silicon and/or 2% iron was used as the response variable. Regression analysis was performed using the ALSTAT program available on the DEC-10 computer. The regression model was determined to be $Y = 156 - 3.2 (\text{Si Content}) - 4.7 (\text{Fe Content}) - 3.7 (\text{Fe} \times \text{Ti Contents})$. These variables were significant at the 95% confidence level. Titanium level was found to be not significant at the 95% confidence level although it is important in the interaction term with the iron content. As expected, increasing the levels of silicon, iron, and iron x titanium reduce the casting alloy yield, as evidenced by negative coefficients in the model. This verifies the results of the bench program, where it was seen that iron alone (less than 7%) and titanium alone (up to 1.6%) did not appear to drastically affect the amount of casting alloy yield. When both iron and titanium were present, however, the casting alloy yield was drastically reduced.

The oxygen analyses on the crystal bed samples for the three pilot runs are shown below. The crystal beds were analyzed for oxygen primarily to improve closure on the material

balance for the runs. The oxygen levels were not very high, 2% or less, and did not contribute significantly to the material balance closure problem. Closure on the crystal bed samples are in the range of 96-98%. As mentioned in the Third Quarter Report, it is difficult to analyze these samples by solution chemistry.

<u>Crystal Bed</u>	<u>%O (by NAA)</u>
1AP	2.0
2AP	0.53
3AP	1.3

Task completion is 100%.

Task No. 3: Pilot Unit Modifications

The tamper unit used on the shakedown start-up was an existing assembly from an old Alcoa unit. The new, improved tamper built for the Direct Reduction pilot crystallizer required some modifications to the main bearing. These were completed and the new tamper was used for the experimental runs. The false bottom crystal bed removal system was modified after the first run following a premature failure. The revised false bottom worked well during the remaining runs.

Task completion is 100%.

Task No. 4: Supportive Analytical

Samples were analyzed as required. Man-hrs. expended were the following:

first quarter	31
second quarter	0
third quarter	147
fourth quarter	73

Task completion is 100%.

Task No. 5: Supportive Mechanical Engineering

Mechanical design and fabrication supporting Task No. 1 were provided in the first two quarters. Pilot modifications (Task No. 3) were supported in the third quarter. Man-hrs. were 370, 204, and 57 respectively.

Task completion is 100%.

C. PURIFICATION TO COMMERCIAL GRADE ALUMINUM PHASE C

Task No. 1: Pilot Unit Installation

In the first quarter, the anode box was assembled and installed in the unit. Fabrication and installation was also completed for the unit lid, top insulation, and electrode collector bars.

Procurement of materials and equipment was continued, including quartz and graphite for collector bar sleeves, inconel for startup heaters, components for the vacuum tapping product removal system, and instrumentation.

Instrumentation requirements and control function logic were determined for unit pressure, inert gas purges, pressure tapping of molten salt into the cell, vacuum tapping of product and temperature control.

Fabrication was started on the molten salt (bath) melter, the vacuum tapping vessel, the inconel strip heaters, and the control panels.

In the second quarter, two product removal vessels equipped with jet ejectors for vacuum tapping aluminum from the sump region of the cell were completed. These units consist of a steel shell, lined with two in. of insulating block (HW-177) and three in. of insulating castable (SJP). Molten Al will be tapped into a graphite mold positioned within the refractory-lined vessel. Molten metal will be transferred from the cell through a preheated fiberfrax-lined steel pipe. The completed unit is equipped with manual and automatic vent valves and a high intensity viewing lamp.

Aluminum buswork was installed between the cell electrodes and the DC rectifier. This buswork has been designed for 15,000 amps (DC) service. It consists of three 1-in. thick, 12-in. high aluminum pieces connected to the four anode and cathode electrodes.

Buswork was also connected from the cell electrodes to the 30 KVA AC transformer. AC power will provide heat to the cell to maintain the temperature of the bath when the DC rectifier has been switched off.

Water-cooling jackets were installed on the shell of the cell to remove heat generated during the electrolytic

process, and to maintain a desirable freeze line of bath in the refractory insulation. A piping system to individually supply and meter H_2O to each of the jackets in the shell was completed.

The system for supplying molten bath at temperatures above $650^{\circ}C$ to the cell has been completed. A 25 KVA AC power supply was installed for melting bath in the inconel chamber. A portable tapping station was constructed so that the transfer of molten bath to the cell can be controlled and regulated in a safe manner.

In the third quarter, final changes were made to the control logic, and wiring of the electrical circuitry was initiated. The membrane cell, tapping kettle, and bath melter have been equipped with pressure gauges and automatic as well as manual vent valves. Strip chart recorders for monitoring trends in voltage, current, and temperatures were procured.

The final design of the isolation chamber was completed. A graphite cylinder was fitted with an inner quartz sleeve to inhibit the penetration of bath from the cell. The isolation chamber will be used as an entry port for the introduction of molten and/or solid Al-Si alloys.

Four fabricated inconel strips wired in series to the main DC power supply were placed in the cell. These heaters will provide 20 KW of power to preheat the cell to startup condition ($660^{\circ}C$).

A water-cooled copper resistor with a voltage drop of 1.5-2.0V at 10,000 amps was incorporated into the aluminum buswork to permit the DC power supply to operate normally. Previous tests indicated that satisfactory control can be obtained in this range by means of manual adjustments to the rheostat on the DC rectifier.

Task completion is 100%.

Task No. 2: Effects of Pilot Operating Parameters

Operation of the electrolytic purifier was deleted from Phase C of the contract and will be completed in a future phase if the Reduction step is successful.

Task completion is 0%. Task deleted.

Task No. 3: Pilot Unit Modifications

This task is also deleted from Phase C.

Task completion is 0%.

Task No. 4: Support Pilot Operations

The nominal bath composition for startup of the cell has been changed from 90%LiCl, 10%AlCl₃ to 45%LiCl, 45%NaCl, 10%AlCl₃ in order to reduce the risks associated with the very high LiCl bath. These include higher volatility, greater penetration of the refractory wall, and higher and more uncertain heat transfer losses. The new bath will require an increase in operating temperature of the bath melter from 620°C-660°C to 660°C-700°C, because of a higher liquidus point.

Graphite cements were tested to determine if the bond for the membrane cloth would be adequate. Once bench scale techniques were applied, reasonably strong bonds were obtained with C-38 cement.

Electrode polarization contributed significantly to the cell voltage in previous bench-scale experimentation. A bench-scale cell was constructed to study the polarization effects with the aim to reduce their impact in pilot cell operation.

The limit at which metal starts penetrating the membrane was established for one set of conditions. For a G5502 continuous filament (FMI) graphite cloth, a penetration pressure of 2.3 psi was established with aluminum in a 90%LiCl-10%AlCl₃ electrolyte at 725°C.

The observed pressure of 2.3 psi would correspond to the pressure produced by 180 cm of aluminum, i.e., it corresponds to the pressure produced at the bottom of a 180 cm deep aluminum layer which is counterbalanced by a 180 cm deep layer of electrolyte.

In the third quarter, the design of the apparatus to establish the limit at which metal starts penetrating the membrane was revised.

In the revised procedure, metal was placed in the graphite tube. Without applying any gas pressure or flow, it was melted with the tube end immersed in the electrolyte. After equilibration at the desired temperature, normally 725°C, the graphite tube was raised so that 1 in. (2.54 cm) was

immersed in the electrolyte. Argon pressure was then increased stepwise and the occurrences at the membrane monitored by closed-circuit television.

The experimental conditions and the observed penetration pressures are listed in Table 26. The metal heights corresponding to these pressure values were calculated taking into account a counter-balancing effect of the bath pressure on the other side of the membrane. A density of 2.3 g/cm³ was assumed for pure aluminum, 2.4 g/cm³ for the aluminum-silicon alloy, 1.4 g/cm³ for the bath containing 90%LiCl, and 10%AlCl₃, and 1.47 g/cm³ for the NaCl-LiCl-AlCl₃ bath.

Some tests were performed with pure aluminum, others with aluminum-silicon alloy containing 11.7% silicon. The electrolyte was 90%LiCl-10%AlCl₃ or 45%LiCl-45%NaCl-10%AlCl₃. Two tests were run to establish the penetration test in air.

Results obtained were scattered. Penetration pressures between 0.45 and 2.3 psi were observed. The equivalent metal head varied from 63 to 217 cm. There was a distinct tendency to lower penetration pressures when the bath was filtered. Removal of oxide affected surface tension characteristics of the bath.

A strong indication that bath properties rather than membrane properties or imperfections are crucial was obtained in Run 80-09-09. After some measurements with and without electrolysis, a new membrane assembly was substituted. The same low penetration pressure of 0.45 psi was obtained with this new membrane.

Task completion is 100%.

Task No. 5: Supportive Analysis

Samples were analyzed as required. Expended man-hrs. were as follows:

first quarter	5
second quarter	4
third quarter	12
fourth quarter	0

Task completion is 100%.

Task No. 6: Supportive Mechanical Engineering

Assistance was provided for Task No. 1 as per the following expended man-hrs.:

first quarter	65
second quarter	80
third quarter	94
fourth quarter	0

Task completion is 100%.

PHASE D FIRST QUARTER PROGRAM

Administrative

Alcoa and DOE will negotiate an extension of the contract to go through September 30, 1981 (fiscal year 1981) to complete the experiments and cost estimates required to make complete recommendations regarding future work on Direct Reduction. Pending approval of the extension, increased expenditure limits for subcontractors/consultants will be requested to cover Phase D work.

Technical

Reduction: The direct current, single electrode submerged arc furnace will be revised to a two-electrode, alternating current type with a rating of 100 KVA. The A-C unit will be operated to evaluate the effects of electrode position and spacing, and burden concentration on metal yield. Tapping of molten alloy will be demonstrated. The modified VSR (with bottom solids discharge) will be operated to dry, calcine, and pre-reduce pellets containing aluminum hydrate-Huber clay-metallurgical coke. The unit will be operated in a continuous mode to establish the effects of time, temperature, and charge composition on conversion of SiO_2 to SiC . If successful, the pre-reduced material will be charged to the A-C arc furnace to complete the simulation of a blast-arc direct reduction process. As an alternative, a ball forming technique will be developed to produce activated alumina-silicon carbide-coke burden to simulate pre-reduction. Use of this material obviates the need for early success of VSR prior to evaluation of the arc, metal-producing step. The bench scale reactors will be operated to determine the total carbon required (percentage of theoretical) for optimum reduction, as well as the limiting amount of the total carbon that should be present in the ore-coke pellet. Also, the study of carbon solubility in specified Al-Si alloys will be continued. Updated heat/mass/energy balances will be calculated for several conditions in commercial size semi-open and closed submerged arc furnaces using the latest version of the improved mathematical models. These calculations will be the basis for obtaining capital cost estimates from furnace manufacturers as part of the economic evaluation of commercial direct reduction process flow sheets. Carnegie-Mellon University will continue to determine phase equilibria data for the Al-Si-C-O system.

Alloy Purification: Several runs will be made on the pilot crystallizer to evaluate the "stop and go" technique for obtaining high yields of Al-Si eutectic and hypereutectic alloys from initial alloy containing 30%Si-3%Fe-1%Ti. "Stop and go" incorporates liquid drain at an intermediate temperature between alloy and eutectic melting point to concentrate the Fe in the crystal bed.

Cost Summary

Expenditures for the fourth quarter of Phase C totaled \$352,192. Distribution was \$345,163 for Reduction, \$10,263 for Alloy Purification, and a credit of \$3,234 for Purification to Commercial Grade Aluminum. Cumulative spending for Phase C was \$1,667,908. Total cumulative spending through the 40 months of the contract was \$5,063,953. Actual spending for Phase C is compared to estimated spending in Attachment 1.

Assigned Personnel

The actual man-hrs. expended by engineers and technicians for the fourth quarter of Phase C are shown in Attachment 2 and compared to estimated man-hrs. For engineers, actual cumulative was 3.0% above estimated. For technicians, actual cumulative was 15.5% below estimated. Total cumulative man-hrs. were 9.8% below estimated.

Task/Milestone Schedule

Attachment 3 shows the task-time relationship for the three major tasks from initiation in DOE fiscal year 1977 (fourth quarter) through completion of the current contract in DOE fiscal year 1981 (first quarter). Completed milestones are noted by filled-in circles.

References:

1. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, First Interim Technical Report, Phase C, 1980 October, CONS-5089-11, UC-95f.
2. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, Second Interim Technical Report, Phase C, 1980 October, CONS-5089-12, UC-95f.
3. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, Third Interim Technical Report, Phase C, 1980 October, CONS-5089-13, UC-95f.
4. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, Special Technical Report: Technical Feasibility of Combustion-Heated Process for Producing Aluminum-Silicon Alloys, 1980 September, CONS-5089-9, UC-95f.

ATTACHMENT 1
PHASE C COST CHART

PROJECT EXPENDITURES, 1000 DOLLARS

2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0

TIME, MONTHS

○ BASELINE COST PLAN
● ACTUAL EXPENDITURES

ATTACHMENT 2

PHASE C MAN-HOUR SUMMARY

	<u>FIRST QUARTER</u> <u>ACUTAL</u>	<u>EST.</u>	<u>SECOND QUARTER</u> <u>ACTUAL</u>	<u>EST.</u>	<u>THIRD QUARTER</u> <u>ACTUAL</u>	<u>EST.</u>	<u>FOURTH QUARTER</u> <u>ACTUAL</u>	<u>EST.</u>	<u>CUMULATIVE</u> <u>ACTUAL</u>	<u>EST.</u>	<u>CUMULATIVE</u> <u>% DEVIATION</u>
ENGINEERS	3227	2705	2560	2780	2499	2437	2206	2265	10492	10187	+3.0
TECHNICIANS	<u>6464</u>	<u>6539</u>	<u>6227</u>	<u>6262</u>	<u>3694</u>	<u>6001</u>	<u>3007</u>	<u>4152</u>	<u>19392</u>	<u>22294</u>	<u>-15.5</u>
TOTAL	9691	9244	8787	9042	6193	8438	5213	6417	29884	33141	-9.8

ALCOA LABORATORIES

Attachment 3

Direct Production Project

Test/Milestone Schedule

[illegible]

TABLE 1

BURDEN MATERIAL PREPARED IN 1980 FOR DIRECT REDUCTION
(74D1450601)

<u>EXPT. NO.</u>	<u>BOOK AND PAGE NO. METHOD</u>	<u>RAW MATERIALS USED</u>			<u>CARBON</u>	<u>QUANTITY</u>	<u>SIZE</u>	<u>YIELD</u>	<u>FIRE COMPRESSIVE STRENGTH</u>
5A1091	EIRICH BALLS 19185-18	64.331 H. CLAY (64.331%)	10.375 B. BXTE. (10.375%)	25.294 COED. CHAR. (25.294%)	1.0 OXIDE RATIO @80% RED. CARB.	100#	3/8" x 6M		298.0#/sq in
5A1092	EIRICH BALLS 19185-19	H. CLAY (39.033%)	B. BXTE. (37.445%)	COED. CHAR. (23.522%)	.5 OXIDE RATIO @80% RED. CARB.	100#	3/8" x 6M		217#/sq in
5A1097	EIRICH BALLS 19185-20	276.51 H. CLAY (55.302%)	100.185 B. BXTE. (20.037%)	123.305 COED. CHAR. (24.661%)		500#	3/8" x 6M	63.9%	139.5# sq in 1/4" dia
5A1103	SMALL DISK 19185-31	9.52 H. CLAY (75.19%)	3.14 COED. CHAR. (24.80%)			12.66#	3/8" x 6M		98.72#/sq in
5A1105	SMALL DISK 19185-32	6.97 H. CLAY (55%)	2.55 B. BXTE. (20.14%)	3.14 COED. CHAR. (24.82%)		12.66#	3/8" x 6M		

TABLE 1, cont.

BURDEN MATERIAL PREPARED IN 1980 FOR DIRECT REDUCTION
(74D1450601)

<u>EXPT. NO.</u>	<u>BOOK AND PAGE NO. METHOD</u>	<u>RAW MATERIALS USED</u>			<u>CARBON</u>	<u>QUANTITY</u>	<u>SIZE</u>	<u>YIELD</u>	<u>FIRE COMPRESSIVE STRENGTH</u>
5A1106	EIRICH BALLS 19185-35	288.13 H. CLAY (57.626%)	100.855 B. BXTE. (20.171%)	111.015 MET. COKE (22.203%)	.788 OXIDE RATIO @80% RED. CARB.	500#		63%	
5A1107	EIRICH BALLS 19185-40	76.61 H. CLAY (76.61%)	23.39 MET. COKE (23.39%)		80% RED. CARB. SiO_2 / Al_2O_3 RATIO	100#	3/8" x 6M		212#/sq in
5A1117	EIRICH BALLS 19185-42	285.95 H. CLAY (57.19%)	99.55 B. BXTE. (19.91%)	114.50 MET. COKE (22.90%)	.788 OXIDE @80% RED. CARB.	500#	3/8" x 6M	59%	178#/sq in
5A1126	EIRICH BALLS 19185-48	264 H. CLAY (52.8%)	107 B. BXTE. (21.4%)	129 COKE BREEZE (25.8%)	.787 OXIDE RATIO @80% RED. CARB.	500#	3/8" x 4M	55%	287/sq in 1/4" dia
5A1149	SMALL DISK	4.375 H. CLAY (35%)	5.875 WARR. COAL (47%)	2.250 CALC. Al_2O_3 (18%)		12.5#			
5A1167	EIRICH BALLS	265 H. CLAY (53.0%)	129 PROP. #10 M. COKE (25.8%)	107.5 CALC. Al_2O_3 (21.5%)		500#	3/8" x 4M	56%	728#/sq in 1/4" dia

TABLE 1, cont.

BURDEN MATERIAL PREPARED IN 1980 FOR DIRECT REDUCTION
(74E1450601)

<u>EXPT. NO.</u>	<u>BOOK AND PAGE NO. METHOD</u>	<u>RAW MATERIALS USED</u>			<u>CARBON</u>	<u>QUANTITY</u>	<u>SIZE</u>	<u>YIELD</u>	<u>FIRE COMPRESSIVE STRENGTH</u>
5A1186	SMALL DISK	6.621 H. CLAY (53%)	3.22 PROD. #10 M. COKE (26%)	2.68 CALC. Al_2O_3 (21%)		12.5#			278#/sq in 1/4" dia
5A1194	SMALL DISK	43.4 H. CLAY (43.4%)	21.7 PROD. #10 M. COKE (21.7%)	35.5 HYDRATED Al_2O_3 (35.5%)		100#	3/8" x 4M		143.4#/sq in 1/4" dia
5A1195	EIRICH BALLS	267.4 H. CLAY (43.4%)	130.2 PROD. #10 M. COKE (21.7%)	213.0 HYDRATED Al_2O_3 (35.5%)		603.6#	3/8" x 4M	62.8%	464.5#/sq in 1/4" dia

ALCOA LABORATORIES

TABLE 1 - BURDEN MATERIAL PREPARED 1980 OCTOBER 01 - 1980 DECEMBER 31
FOR DIRECT REDUCTION (74D1450601)

EXPT. NO.	NOTEBOOK & PAGE NO.	SAMPLE TYPE	RAW MATERIALS			RAW MAT'L QUANTITY	BURDEN CHARACTERISTICS			
			RAW MATERIALS	USED			SiO ₂ / Al ₂ O ₃	SIZE	YIELD	FIRE COMPRESSIVE
							CARBON			STRENGTH
5A1232	19609- 38,42,43	EIRICH BALLS	H.CLAY (54.18%)	HYDRATED Al ₂ O ₃ (45.82%)	100#		0.48	4 X 10M	80%	569#/SQ IN
							OXIDE RATIO			3/16" DIA.
5A1233	19609- 39,42,43	EIRICH BALLS	H.CLAY (64.152)	HYDRATED Al ₂ O ₃ (35.85%)	100#		0.61	4 X 10M	77%	735#/SQ IN
							OXIDE RATIO			3/16" DIA.
5A1234	19609- 40,42,43	EIRICH BALLS	H.CLAY (74.43%)	HYDRATED Al ₂ O ₃ (25.57%)	100#		0.75	4 X 10M	85%	500#/SQ IN
							OXIDE RATIO			3/16" DIA.
5A1252	19609- 44,50 19888-1	EIRICH BALLS	H.CLAY (51.88%)	PROD.#10 MET.COKE (16.51%)	HYDRATED Al ₂ O ₃ (31.61%)	600#	0.6 OXIDE RATIO @ 56% RED	3/8" X 4M CARB	68%	352#/SQ IN 1/4" DIA
5A1275	19888- 8,14	EIRICH BALLS	H.CLAY (47.29%)	PROD.#10 MET.COKE (22.98%)	HYDRATED Al ₂ O ₃ (29.73%)	600#	0.6 OXIDE RATIO @ 87% RED	3/8" X 4M CARB.	65%	480#/SQ IN 1/4" DIA.
5A1292	19888-16	EIRICH BALLS	H.CLAY (50.45)	PROD.#10 MET.COKE (16.96%)	HYDRATED Al ₂ O ₃ (33.6%)	100#	0.49 OXIDE RATIO @ 57% RED	4 X 10M CARB.	*	*
5A1293	19988-17	EIRICH BALLS	H.CLAY (61.04%)	PROD.#10 MET.COKE (16.72%)	HYDRATED Al ₂ O ₃ (22.24%)	100#	0.76 OXIDE RATIO @ 57% RED	4 X 10M CARB.	*	*
*ANALYSIS IN PROGRESS										

TABLE 2

EFFECT OF CALCINATION TEMPERATURE UPON BURDEN STRENGTH¹

Experiment No.	5A1232	5A1233	5A1234
Kaolinite Clay (%)	54.2	64.2	74.4
Hydrated Al ₂ O ₃ (%)	45.8	35.9	25.6

<u>CALCINATION TEMPERATURE</u>	<u>FIRED COMPRESSIVE STRENGTH (LB/IN²)</u>		
1000°C	834	948	1586
1400°C	1031	1229	1555
1500°C	3952	4268	5208

1. LABORATORY NOTEBOOK 19988, P. 2

2. 1/8 IN. DIAMETER EIRICH MIXER BALLS

TABLE 3

OVERALL MASS BALANCE SUMMARY FOR PILOT REACTOR COMBUSTION RUNS

<u>VSR</u>	<u>O₂ RATE CFH @ 20°C</u>	<u>O₂ TIME HRS</u>	<u>TOTAL COKE G</u>	<u>TOTAL ORE G</u>	<u>TOTAL O₂ G²</u>	<u>INITIAL CHARGE G</u>	<u>FINAL BED WEIGHT G</u>	<u>CONSUMED CHARGE O₂</u>	<u>O₂ RATIO</u>
23	240	5.417	45182	15818	48978	21356	19701	.843	1.443
24	240	7.417	58509	28840	67061	21500	27632	.890	1.367
26	120	3.183	16343	12523	14390	20616	22990	.408	2.980
27	120	5.950	36023	15180	26899	17393	23609	1.026	1.186
28	120	5.350	29568	17111	24186	18327	25942	.857	1.419
29	120	4.383	31538	5399	19815	17974	19025	.904	1.346
30	90	3.583	27057	11630	12148	16766	17480	1.746	.697
31	75	5.633	24596	19647	15916	16278	19873	1.531	.795

$$\text{O}_2 \text{ Ratio} = \frac{\text{O}_2 \text{ supplied in pilot reactor test}}{\text{O}_2 \text{ required to fully combustion heat a 3 atm. shaft furnace}}$$

$$\text{Consumed Charge} = \text{Total Coke} + \text{Total Ore} - \text{Final Bed Weight.}$$

HEAT BALANCE BY STAGES - 100% ELECTRIC, ONE ATMOSPHERE
BASIS = 1 MOLE Al_3Si_2 (81g Al)

<u>PREHEAT</u>		<u>ΔH</u>				
<u>REACTANTS</u>	<u>TEMP. RANGE, °K</u>	<u>MOLES</u>	<u>KG</u>	<u>KJ/MOLE</u>	<u>KJ/KG</u>	<u>HEAT KJ</u>
Al_2O_3	300 - 1840	1.50		187.52		+281.28
SiO_2	300 - 1840	2.07		107.99		+223.53
C	300 - 1840	8.60		31.33		+269.46
CO^*	1840 - 300	8.59		50.45		<u>-433.39</u>
						+340.88
<u>STAGE I</u>						
ΔH^R	1840		0.5178		2136.59	+1106.33
<u>STAGE II</u>						
ΔH^R	2205		0.3857		1588.93	+612.85
Al_2O_3	1840 - 2205	1.58		50.41		+ 79.59
SiC	1840 - 2205	2.08		19.71		+ 41.01
C	1840 - 2205	2.54		9.00		+ 22.92
CO^*	2205 - 1840	4.61		13.26		<u>- 61.14</u>
						+695.23
<u>STAGE III</u>						
ΔH^R	2300		0.2483		7019.78	+1743.01
$\text{Al}_4\text{O}_4\text{C}$	2205 - 2300	.866		25.84		+ 22.38
SiC	2205 - 2300	2.22		5.19		+ 11.53
CO	2300 - 2205	3.07		3.48		<u>- 10.70</u>
						+1766.22
Net Heat (Electric)=						3908.66

TABLE 5

HEAT BALANCE BY STAGES - HYBRID, ONE ATMOSPHERE
BASIS = 1 MOLE Al_3Si_2 (81g Al)

<u>PREHEAT</u>						ΔH
<u>REACTANTS</u>	<u>TEMP. RANGE °K</u>	<u>MOLES</u>	<u>KG</u>	<u>KJ/MOLE</u>	<u>KJ/KG</u>	<u>ΔH, KJ</u>
Al_2O_3	300 - 1840	1.50		187.52		+281.28
SiO_2	300 - 1840	2.19		107.99		+236.50
C	300 - 1840	8.70		31.33		-272.57
CO	1840 - T_{exit}	28.39		27.84		-790.35
						0
<u>COMBUSTION</u>						
ΔH_R	1840	19.9		59.61		-1185.96
<u>STAGE I</u>						
ΔH_R	1840		1.0805		1097.6	+1185.96
<u>STAGE II</u>						
ΔH_R	2205		.03857		1588.93	+612.85
Al_2O_3	1840 - 2205	1.58		50.41		+ 79.59
SiC	1840 - 2205	2.08		19.71		+ 41.01
C	1840 - 2205	2.54		9.00		+ 22.92
CO	2205 - 1840	4.61		13.26		- 61.14
						+695.23
<u>STAGE III</u>						
ΔH_R	2300		0.2483		7019.78	+1743.01
Al_4O_4C	2205 - 2300	.866		25.84		+ 22.38
SiC	2205 - 2300	2.22		5.19		+ 11.53
CO	2300 - 2205	3.07		3.48		- 10.70
						+1766.22
Net Heat (Electric) =						2461.45

TABLE 6

ENERGY REQUIREMENTS FOR ELECTRIC, HYBRID, AND COMBUSTION PROCESSES

ELECTRIC PROCESS

Electric Energy:

$$\left[\frac{3908.66}{(81)(.90)} + 2.3 + 10.1 + 2.78 + 18.6 \right] / .425 = \frac{\text{KJ/gAl}}{181.9}$$

(See Table 2) $\frac{\text{Fe, Ti}}{\text{C}}$, pellets refining purification efficiency

Coal Energy:

$$(5.98) (.2854) (32.79) / .8 = 70.0$$

Reduction & Solution

CO Credit:

$$(5.98) (.2626) (23.59) = -37.0$$

Reduction

Metalloid
By-Product
Credit

-129.0

= 109.7

HYBRID PROCESS

Electric Energy:

$$\left[\frac{2461.45}{(81)(.90)} + 2.3 + 10.1 + 2.78 + 18.6 + \frac{(19.9)(16)(1.32)}{81} \right] / .425 = 171.1$$

(See Table $\frac{\text{Fe, Ti}}{\text{C}}$, pellets refining purification O_2 plant 3)

Coal Energy:

$$[(19.9)(12)/81 + (5.98)(.2854)] (32.79) / .8 = \frac{190.8}{361.9}$$

combustion reduction & solution

CO Credit:

$$[(19.9)(12)/81 + (5.98)(.2626)] (23.59) = -106.6$$

combustion reduction

Metalloid
By-Product
Credit

= -129.0

126.3

TABLE 6
Continued

COMBUSTION PROCESS

Electric Energy:

$$[2.3 + 10.1 + 2.78 + 18.6 + \frac{(84.64)(16)(1.32)}{81}] + .425 = 131.4$$

Coal Energy:

$$[(84.64)(12)/81 + (5.98)(.2854)](32.79/.8) = \frac{583.9}{715.3}$$

CO Credit:

$$[(84.64)(12)/81 + (5.98)(.2626)](23.59) = -332.8$$

Metalloid

By-Product

Credit

=

-129.0

253.5

TABLE 7

COMPARISON OF ENERGY REQUIREMENTS FOR VARIOUS
PROCESSES FOR PRODUCING ALUMINUM

Energy Requirements, KJ/g, (kWhr/#)							
<u>Process</u>	<u>Fuel</u>	<u>Electric Equiv.</u>	<u>Coal</u>	<u>Total</u>	<u>CO Credit</u>	<u>Credit for Ferrosilicon</u>	<u>Net</u>
Electric	Coke	205.7 (11.0)	70.0	275.7	37.0	129.0	109.7
	Coal	205.7 (11.0)	56.0	261.7	37.0	129.0	95.7
	Coal, CO* Credit for Electricity	175.2 (9.4)	56.0	231.2	0	129.0	102.2
Hybrid	Coke	171.1 (9.2)	190.8	361.9	105.6	129.0	126.3
	Coal	171.1 (9.2)	152.6	323.7	105.6	129.0	88.1
	Coal, CO* Credit for Electricity	83.3 (4.5)	152.6	235.9	0	129.0	106.9
Combustion	Coke	131.4 (7.0)	583.9	715.3	332.8	129.0	253.5

*CO credit for generating electricity at 35% efficiency.

TABLE 8

EFFECT OF $\text{SiO}_2/\text{Al}_2\text{O}_3$ CARBON STOICHIOMETRY AND CO SWEEP ON METAL PRODUCTION

<u>Run</u>	<u>Ore $\text{SiO}_2/\text{Al}_2\text{O}_3$ Wt. Basis</u>	<u>Consumed Charge CO</u>	<u>% Total C</u>	<u>Wt. Metal Consumed Charge</u>	<u>Reaction Zone Wt.</u>	<u>Metal Producing Temperature</u>
AF7	0.6	---	100 %	0.210	---	2050
AF12	0.784	1.815	80.55	0.164	1280 gm	2050
AF13	0.502	2.199	80.0	0.161	1341	2055
AF14	0.993	2.035	80.0	0.177	759	2060
AF15	0.788	1.950	80.0	0.191	718	2065
AF16	0.784	1.042	80.55	---	558	2030
AF17	0.784	0.579	80.55	---	362	2140
AF18	0.993	1.393	80.0	0.195	927	2060
AF20	1.224	0.730	80.0	0.209	122	2100
AF21	1.224	0.491	80.0	---	200	2060
AF22	1.224	1.173	85.0	---	150	2090
AF23	1.224	---	85.0	0.239	334	2075
AF24	0.469	---	80.0	0.325	---	2060
AF25	0.68	---	85.0	0.282	475	2020
AF26	0.785	---	84.5	0.274	927	2020
AF27	0.502	---	84.7	0.334	661	2035
AF28	0.785	---	91.3	0.294	127	2140
AF29	0.786	---	90.0	0.269	---	2030
AF30	0.642	---	85.0	0.289	---	2050

CONSUMED CHARGE = TOTAL ORE FED - REMAINING LOOSE CHARGE IN THE AUGER

TABLE 9

CARBON STOICHIOMETRY OF ORE BURDEN

Run	Ore SiO ₂ /Al ₂ O ₃ Wt. Basis	% C Ore	% C for SiC	% Total C	Carbon Source
AF7	0.6	71.0	58	100	met and pet coke
AF12	0.784	80.55	67	80.55	met coke
AF13	0.502	64.24	51	80.0	char and pet coke
AF14	0.993	63.75	76	80.0	char and pet coke
AF15	0.788	56.74	67	80.0	char and pet coke
AF16	0.784	80.55	67	80.55	met coke
AF17	0.784	80.55	67	80.55	met coke
AF18	0.993	63.75	76	80.0	char and pet coke
AF20	1.224	72.62	84	80.0	met and pet coke
AF21	1.224	72.62	84	80.0	met and pet coke
AF22	1.224	72.62	84	85.0	met and pet coke
AF23	1.224	72.62	84	85.0	met and pet coke
AF24	0.469	---	49	80.0	pet coke
AF25	0.68	77.67	63	85.0	met and pet coke
AF26	0.785	74.94	67	84.5	char, met, and pet coke
AF27	0.502	64.24	51	84.7	char and pet coke
AF28	0.785	91.30	67	91.3	char and met coke
AF29	0.786	80.53	67	90.0	char, met, and pet coke
AF30	0.642	79.33	61	85.0	met coke

TABLE 10
METALLOGRAPHIC PHASE ANALYSIS IN VOLUME %

Run	% Total Carbon	Ore SiO ₂ /Al ₂ O ₃ Wt. Basis	Uncoalesced Metal				Si/Al Wt. % Basis
			Slag	Si	SiC	Al ₄ SiC ₄	
AF7	100	0.6	--	16	12	2	--
AF12	80	0.784	9	15	15	--	--
AF13	80	0.502	6	19	17	1	--
AF14	80	0.993	2	18	22	--	--
AF15	80	0.788	3	16	11	--	0.48
AF18	80	0.993	5	10	42	--	0.60
AF20	80	1.224	5	27	15	--	--
AF23	85	1.224	--	8	64	--	1.37
AF26	84.5	0.785	--	12	51	1	0.62
AF27	84.7	0.502	--	11	45	1*	0.99

* Al-Si carbide verified by both x-ray diffraction and metallography

** Al₄Si₂C₅ identified by x-ray diffraction

TABLE 10 (Continued)
METALLOGRAPHIC PHASE ANALYSIS IN VOLUME %

Run	Metal Below Slag Layer					Metal Above Slag Layer					Top Metal				
	Slag	Si	SiC	Al ₄ SiC ₄	Si/Al Wt. % Basis	Slag	Si	SiC	Al ₄ SiC ₄	Si/Al Wt. % Basis	Slag	Si	SiC	Al ₄ SiC ₄	Si/Al Wt. % Basis
AF7	2	18	31	9	0.43	2	14	30	2	0.46	—	27	10	2	0.45
AF12	10	21	18	—	0.59	—	15	31	—	0.84	—	20	15	—	0.61
AF13	5	15	23	3**	0.38	1	18	16	6	0.39	1	20	11	2	0.51
AF14	20	9	53	—	—	—	24	9	—	0.92	—	25	2	—	0.66
AF15	16	16	23	—	0.58	—	—	—	—	1.08	—	24	11	—	0.44
AF18	15	6	60	—	0.86	—	—	—	—	—	2	22	14	—	0.53
AF20	—	—	—	—	—	5	9	27	—	0.80	2	25	28	—	0.80
AF23	—	15	38	—	0.80	—	13	23	—	0.53	—	24	1	4	0.42
AF26	—	11	52	2	1.13	—	18	17	4	0.46	—	18	22	7	0.44
AF27	—	12	45	6*	0.99	—	17	27	7*	0.39	—	6	23	9	0.42

* Al-Si carbide verified by both x-ray diffraction and metallography

** Al₄Si₂C₅ identified by x-ray diffraction

TABLE 11

OPERATING CONDITIONS FOR Al/Si = 60/40 ALLOY

<u>Run</u>	<u>SiO₂/Al₂O₃</u>	<u>Total %C</u>	<u>%C In Pellet</u>	<u>Consumed Ore</u>	<u>Reaction Zone wt.</u>	<u>Reaction Zone Phase</u>	<u>Wt. Metal Consumed Ore</u>	<u>%C Metal</u>
AF26	.785	84.5	74.9	10 kg	.93 kg	oxide	.273	9.0
AF28	.785	91.3	91.3	4.4	.13	carbide	.294	13.1
AF29	.786	90.0	80.5	8.4	--	ox/carb	.269	7.8
AF31	.755	87.0	84.5	5.5	--	carbide	.305	8.2
AF32	.75	85.0	78.5	8.7	1.62	oxide	.228	7.2
AF33	.75	87.4	84.6	5.95	.63	oxide	.243	5.8
AF34	.75	87.5	77.4	9.65	.83	oxide	.255	9.3
AF35	.75	90.0	78.4	9.6	1.12	oxide	.257	9.0
AF36	.75	92.5	80.4	8.3	--	carbide	.329	11.7

TABLE 12

OPERATING CONDITIONS FOR Al/Si = 68.5/31.5 ALLOY

<u>Run</u>	<u>SiO₂/Al₂O₃</u>	<u>Total %C</u>	<u>%C In Pellet</u>	<u>Consumed Ore</u>	<u>Reaction Zone wt.</u>	<u>Reaction Zone Phase</u>	<u>Wt. Metal Consumed Ore</u>	<u>%C Metal</u>
AF42	.521	87.5	84.6	7.88 kg	--	carbide	.285	4.8
AF43	.521	90.0	84.6	5.36	--	carbide	.247	4.4
AF44	.521	90.0	84.6	5.38	--	carbide	.242	5.2
AF45	.521	90.0	84.6	5.83	--	carbide	.177	5.9
AF46	.545	86.1	74.3	3.17	.19 kg	carbide	.148	4.8
AF27	.502	84.7	64.2	9.5	.66	oxide	.334	10.2

TABLE 13

OPERATING CONDITIONS FOR PRODUCTION OF AL/SI = 60/40
ALLOY WITH NO CARBON IN THE PELLET

<u>Run</u>	<u>SiO₂/Al₂O₃</u>	<u>Total %C</u>	<u>Consumed Ore</u>	<u>Reaction Zone wt.</u>	<u>Reaction Zone Phase</u>	<u>Wt. Metal Consumed Ore</u>	<u>%C Metal</u>
AF37	.764	87.5	2.97 kg	.45 kg	carbide	.061	7.17
AF38	.764	87.5	3.36	.58	carbide	.045	7.33
AF39	.764	87.5	2.71	.62	carbide	.080	8.17
AF40	.764	82.5	2.60	.67	carbide	----	-----
AF41	.764	87.5	4.64	~.60	carbide/ox.	.049	6.46

TABLE 14

PHASE COMPOSITION OF VSR-35 AND VSR-39
METAL INGOT (VOLUME %)

	<u>VSR-35(1)</u> <u>BASE</u>	<u>VSR-35(2)</u> <u>MIDDLE</u>	<u>VSR-35(3)</u> <u>TOP</u>	<u>VSR-39(1)</u> <u>BOTTOM 1/3</u>	<u>VSR-39(2)</u> <u>TOP 1/3</u>
AL	37%	42%	36%	49%	44%
Si (1)	19	20	24	16	19
FeSi ₂ Al ₄	7	9	11	6	6
FeSiAl ₅ (2)	7	6	8	<1	<1
TiSi ₂ (Al, Fe)	10	6	8	5	1
TiSi ₂ (Al)	1	1	1	-	-
SiC	19	18	13	24	31

(1) Included both eutectic and hypereutectic Si

(2) Includes both eutectic and intermetallic FeSiAl₅; estimated 80% of this is in eutectic microstructure.

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TABLE 15 - PHASE COMPOSITION, VOLUME PERCENT
RUNS AF-30, AF-31, AF-32

	AF-30			AF-31				AF-32		
	ZONE 1	ZONE 2	ZONE 3	ZONE 1	ZONE 2	ZONE 3	ZONE 4	ZONE 1	ZONE 2	ZONE 3
Al (in eutectic)	39	41	40	36	39	38	43	43	36	29
Si	18	20	21	19	20	15	18	18	21	18
FeSi ₂ Al ₄	9	11	11	12	10	6	11	8	8	10
FeSiAl ₅	<1	2	3	2	4	4	4	<1	<1	<1
TiSi ₂ (Al)	2	1	2	<1	1	1	2	<1	<1	<1
Ti, Si ₂ (Al,Fe)	-	-	-	-	-	-	<<1	5	5	5
SiC	31	15	8	30	24	30	18	13	17	14
Al ₄ SiC ₄	<1	8	13	1	2	6	4	2	3	9
Carbide Spheroids	-	2	2	-	-	-	-	11	10	14
SLAG	-	-	-	-	-	-	-	-	-	2

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TABLE 16 - PHASE COMPOSITION, VOLUME PERCENT

RUNS AF-33, AF-34, AF-35

[illegible]

TABLE 17 PHASE COMPOSITION OF SAR-3 METAL (VOLUME %)

	ZONE 1(1)	ZONE 2(1)	ZONE 3(2)
Al (in eutectic)	25%	29%	35%
Si	36	36	36
FeSi ₂ Al ₄	23	16	27
FeSiAl ₅	<1	1	<1
TiSi ₂ (Al,Fe)	4	13	1
TiSi ₂ (Al)	4	5	2
SiC	10	-	-
Slag	<1	-	-

(1) Bottom and top, respectively, of metal accumulation inside bird's nest.

(2) Metal accumulation underlying top electrode.

TABLE 18

COMPARISON OF YIELD
SUMMARY OF FE-HANDLING TECHNIQUES EXPERIMENTS
FE CONTENT 10% OR GREATER

<u>Experiment</u>	<u>Starting Alloy Content, %</u>				<u>Comments</u>
	<u>Si</u>	<u>Fe</u>	<u>Cu</u>	<u>Mg</u>	
26	29.2	10.2	--	--	
34	31.6	15.3	--	--	Pooled high Fe cuts
35	28.5	14.5	--	--	Stop at 820°C
40	31.2	10.3	4.4	--	Cu addition
41	31.0	9.4	1.9	--	Cu addition
48	28.4	10.7	1.9	--	Cu addition
49	26.8	13.9	1.9	--	Cu addition
50	27.8	13.7	4.0	--	Cu addition

<u>Experiment</u>	<u>Casting Alloy Content, %</u>				<u>Cumulative Yield, %</u>	<u>Avail. Al Recovered, %</u>
	<u>Si</u>	<u>Fe</u>	<u>Cu</u>	<u>Mg</u>		
26	14.1	1.1	--	--	<1	1
34	--	--	--	--	--	--
35	--	--	--	--	--	--
40	19.3	3.7	6.3	--	28	37
41	20.0	3.8	3.0	--	31	39
48	20.0	3.8	3.0	--	26	33
49	20.6	5.5	4.1	--	8	10
50	18.9	3.3	7.5	--	2	3

TABLE 19

PROCESS VARIABLES FOR PILOT RUNS

<u>PARAMETER</u>	<u>RUN 1-AP</u>	<u>RUN 2-AP</u>	<u>RUN 3-AP</u>
Initial Alloy Composition	30 Si - 3 Fe - 1 Ti - Rem. Al, ALL RUNS		
Cooling Air Rate	158 CFM	154 CFM	116 CFM
Stroke	4"	5"	8"/4"
Freeze Cycle	2.8 hr.	2.5 hr.	2.9 hr.
Remelt Cycle	2.3 hr.	2.6 hr.	2.7 hr.

TABLE 20
MATERIAL BALANCES

	<u>RUN 1-AP</u>	<u>RUN 2-AP</u>	<u>RUN 3-AP</u>
STARTING COMPOSITION	27.7 Si - 2.3 Fe - 0.58 Ti - REM. AL	30.0 Si - 2.8 Fe - 0.78 Ti - REM. AL	28.3 Si - 3.2 Fe - 0.87 Ti - REM. AL
WEIGHT OF MATERIAL IN, LB	1958	2001	1894
WEIGHT OF MATERIAL DRAINED, LB	542	413	366
WEIGHT OF REMELT MATERIAL, LB	1209	1244	1156
WEIGHT OF CRYSTAL BED, LB	178	309	250
YIELD: % MATERIAL DRAINED	28%	21%	19%
% MATERIAL <20% Si, 2% Fe	72% 81%*	48% 57%*	58% 68%*

*AL BASIS

TABLE 21
EXPERIMENTAL RESULTS
RUN 1-AP

	WEIGHT, LB.	CONTENT, %		
		SI	FE	II
STARTING ALLOY (828°C)	1958	27.7	2.33	0.58
LIQUID DRAINED IN INTERVAL:				
SAMPLE 1	----	18.9	2.49	0.17
1 - 2	107.6	16.6	1.83	0.12
3 - 5	262.6	15.2	1.31	0.10
6 - 10	430.5	20.7	1.97	0.24
11 - 15	430.5	23.8	2.24	0.41
16 - 18	258.3	29.5	4.2	0.79
19 - 21	258.3	44.0	4.0	1.7
CRYSTAL BED	178	90.0	1.0	0.6*

CUMULATIVE LIQUID DRAINED	AVERAGE CONTENT, %			CUMULATIVE YIELD, %	AVAIL. AL RECOVERED,
	SI	FE	II		
SAMPLE 1	18.9	2.49	0.17	--	--
1 - 2	17.8	2.16	0.14	5	6
1 - 5	16.7	1.74	0.12	19	22
1 - 10	17.4	1.69	0.15	41	48
1 - 15	19.0	1.83	0.21	63	72
	(20.0)+	(2.00)	(0.26)	(72)	(81)
1 - 18	20.4	2.07	0.28	76	85
1 - 21	22.8	2.37	0.42	89	96

*AL 8.4%. VALUES ADJUSTED TO PERMIT CLOSURE.

+INTERPOLATED VALUES.

TABLE. 22
EXPERIMENTAL RESULTS
RUN 2-AP

	WEIGHT, LB.	SI	CONTENT, % FE	LI
STARTING ALLOY	2001	30.0	2.80	0.78
LIQUID DRAINED IN INTERVAL:				
SAMPLES 1 - 2	65	16.8	1.97	0.13
3 - 5	261	17.0	1.79	0.12
6 - 10	457	21.5	2.12	0.26
11 - 15	413	24.0	2.69	0.36
16 - 20	457	44.4*	3.9	1.8
CRYSTAL BED	308	56.1	2.7	2.2**

CUMULATIVE LIQUID DRAINED	SI	AVERAGE CONTENT, %		CUMULATIVE YIELD, %	AVAIL. AL RECOVERED, %
		FE	LI		
SAMPLES 1 - 2	16.8	1.97	0.13	3	4
1 - 5	16.9	1.90	0.12	16	20
1 - 10	18.2	1.93	0.17	39	47
	(18.9)+	(2.00)	(0.19)	(48)	(57)
1 - 15	19.8	2.09	0.22	60	70
1 - 20	23.8	2.42	0.45	83	91

*ASSUMED VALUE

**35.5% AL

+INTERPOLATED VALUES

TABLE 23
EXPERIMENTAL RESULTS
RUN 3-AP

	WEIGHT, LB.	CONTENT, %			
		Si	Fe	Li	
STARTING ALLOY	1894	28.3	3.15	0.87	
LIQUID DRAINED IN INTERVAL:					
SAMPLES 1 - 2	98	16.6	1.57	0.11	
3 - 5	342	15.3	1.34	0.10	
6 - 10	407	21.8	2.17	0.25	
11 - 15	440	28.2	5.14	1.32	
16 - 17	244	37.8	5.88	2.07	
17 - 18	98	43.0	4.97	1.93	
CRYSTAL BED	250	60.1	2.64	3.77*	
CUMULATIVE LIQUID DRAINED	Si	AVERAGE CONTENT, %		CUMULATIVE YIELD, %	AVAIL AL. RECOVERED.
		Fe	Li		
SAMPLES 1 - 2	15.3	1.34	0.11	5	6
3 - 5	16.1	1.48	0.10	23	28
6 - 10	17.3	1.61	0.14	45	54
	(18.8)+	(2.00)	(0.25)	(58)	(68)
11 - 15	19.9	2.29	0.34	68	78
16 - 17	22.0	2.80	0.57	81	89
17 - 18	23.1	2.96	0.66	86	93

*33.5% AL, AVERAGE VALUES, NORMALIZED

+INTERPOLATED VALUES

TABLE 24
LEACHING MEDIA AND RESULTS

SAMPLE	LEACH MEDIA	CRYSTAL BED							
		BEFORE LEACH, %				AFTER LEACH, %			
		SI	FE	TI	AL	SI	FE	TI	AL
RUN 1-AP	HCL (7N)	82.5	0.9	0.6	7.7	88.2	0.0	2.4	1.3
	NACITRATE/HNO ₃	70.0	1.1	1.5	19.5	67.5	1.2	1.5	22.3
RUN 2-AP	HCL	56.1	2.7	2.2	35.5	78.1	0.4	3.6	1.9
	NACITRATE/HNO ₃	56.1	2.7	2.2	35.5	63.0	1.6	2.7	25.2
RUN 3-AP	HCL	67.8	3.2	1.6	26.5	83.2	1.9	2.0	4.9
	NACITRATE/HNO ₃	66.6	3.8	1.6	28.8	58.2	3.3	1.6	35.2

TABLE 25

BENCH SCALE RESULTS, AL-SI-FE-TI SYSTEM
EXPERIMENT 10

	<u>WEIGHT, g</u>	<u>CONTENT, %</u>		
		Si	Fe	Ti
STARTING ALLOY AFTER SKIM REMOVAL AND SAMPLING	2206	28.2	2.71	0.7
DRAIN (586°C)	158.4	13.0	0.79	0.08
REMELT CUT #1 (1040°F)	423.6	17.7	1.24	0.16
#2 (1070°F)	343.7	21.3	1.87	0.32
#3 (1140°F)	182.0	25.4	2.63	0.47
#4 (1260°F)	112.5	22.0	3.06	0.28
#5 (1340°F)	124.7	27.5	5.4	0.59

	<u>AVG. CONTENT, %</u>			<u>CUMULATIVE YIELD</u>	<u>AVAIL. AL RECOVERED</u>
	Si	Fe	Ti		
DRAIN	13	.79	0.08	7%	9.0%
DRAIN + REMELT CUT 1	16.4	1.12	0.14	26%	31.8%
DRAIN + REMELT CUTS 1, 2	18.2	1.40	0.21	42%	49.2%
DRAIN + REMELT CUTS 1, 2, 3	19.4	1.60	0.25	50%	57.8%
DRAIN + REMELT CUTS 1, 2, 3, 4	19.6	1.73	0.25	55%	63.4%
DRAIN + REMELT CUTS 1, 2, 3, 4, 5	20.4	2.07	0.28	61%	68.9%

TABLE 26 RESULTS - PENETRATION TESTS

<u>Run No.</u>	<u>Metal</u>	<u>Electrolyte</u>	<u>Penetration Pressure (psi)</u>	<u>Equivalent Metal Head cm.</u>
79-12-12	Al	LiCl-AlCl ₃	2	217
80-01-22	Al	LiCl-AlCl ₃	2.3	203
80-08-05	Al	LiCl-NaCl-AlCl ₃ (filtered)	0.6	81
80-08-12	Al	LiCl-NaCl-AlCl ₃	1.0	115
80-08-14	Al	LiCl-NaCl-AlCl ₃	0.8 -2.05	98-204
80-08-15	Al	Air	1.75-2.0	66.4-202 (air)
80-08-21	Al-Si	LiCl-NaCl-AlCl ₃ (LiCl and NaCl filtered)	1.9 -2.3	172-202
80-08-28	Al-Si	Air	1.35-1.7	52- 60 (air)
80-08-29	Al-Si	LiCl-NaCl-AlCl ₃ (filtered)	1.05-1.5	108-138
80-09-09	Al-Si	LiCl-NaCl-AlCl ₃ (filtered, with and without electrolysis)	0.45	63
	Al-Si	same electrolyte, new membrane	0.45	63
	Al-Si	same electrolyte, CaCl ₂ added, with and without electrolysis	0.8	89

FIGURE 1. ⁻⁸⁵⁻ MODIFIED PILOT
VSR REACTOR

FIGURE 2
PILOT REACTOR PRIOR TO VSR-36

- *VERTICAL STROKE "RAM" AND SHAFT TAPER ADDED
- *EXCELLENT BED MOVEMENT (7KG ORE/HR)
- *MOVEMENT MAINTAINED AT 100 SCFH OF CO INJECTION
- *6KG INGOT

FIGURE 3

PILOT REACTOR PRIOR TO VSR-38

HEIGHT 1 BLOCK = 1"
WIDTH 4 BLOCKS = 1"

A) SUSCEPTOR THICKNESS $25/32"$ B) SHELL O.D. $19.5"$ I.D. $8\frac{1}{8}"$
C) CATCH BASIN $\frac{1}{2}"$ BELOW 2ND SUSCEPTOR PIECE SHIPPLAP

FIGURE 4

VSR TAPPING LAYOUT

FIGURE 5
VSR TAPHOLE DESIGN

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FIGURE 6

Submerged Arc Reactor Using Linde DC Welder (1000 amp)

VSR-38 START-UP

*HORIZONTAL PEGS ADDED TO RAM

*STARTUP WITH "BIRDSNEST" FROM VSR-37 TO DEMONSTRATE COMMERCIAL STARTUP AFTER SHUTDOWNS OR DELAYS

*NO CO INJECTION

*SOLIDS MOVEMENT EXCEEDED 8.7 KG PER HR

*55 KG OF ORE CONSUMED

FIGURE 8

TAPPING FURNACE SCHEMATIC - VSR REACTOR

FIGURE 9

DOUBLE GRATE AND ALUMINA LINER - VSR REACTOR

FIGURE 10

1. Graphite
2. Graphite felt
3. SiC supports
4. Durablanket
5. Jons-Manville thermo 12
6. J.M.-28 brick

A.C. SUBMERGED ARC FURNACE
SIDE SECTIONAL VIEW

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FIGURE 11

A.C. SUBMERGED ARC FURNACE
FRONT SECTIONAL VIEW

BLAST-ARC FURNACE
MATERIAL BALANCE FOR 300,000 TPY ALUMINUM PRODUCTION
(QUANTITIES IN TPY ON DRY BASIS)
CHAR FROM WYOMING COAL, 330 DAY/YR, 90% AL RECOVERY IN CRYSTALLIZER

FIGURE 12

ARC FURNACE
MATERIAL BALANCE FOR 300,000 TPY ALUMINUM PRODUCTION
 (QUANTITIES IN TPY ON DRY BASIS)
 CHAR FROM WYOMING COAL, 330 DAY/YR, 90% Al RECOVERY IN CRYSTALLIZER

FIGURE 13