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Second Annual Technical Report, September 1, 1978–December 31, 1979

October 1980

**Aluminum Company of America
Alcoa Laboratories
Alcoa Center, Pennsylvania**

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

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

SECOND ANNUAL TECHNICAL REPORT
FOR THE PERIOD 1978 SEPTEMBER 01 - 1979 DECEMBER 31

MARSHALL J. BRUNO

OCTOBER 1980

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

FORWARD

This is the second 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 1978 September 01 - 1979 December 31.

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ABSTRACT

Phase B of a three-year cost-sharing contract between the Department of Energy and Alcoa was started on 1978 September 01. Phase B is 16 months long and has included four quarterly reports preceeding this "annual" report. The program for Phase B is estimated as 81% complete. Certain sub-tasks were deferred to the next phase or deleted as not applicable, and other sub-tasks relating to the installation of the purification systems will be continued and completed in Phase C.

A new computer program was developed for simultaneously solving heat and mass balance at steady state for a flowing one-dimensional chemical reactor. Bench scale reactor results confirmed that minimum final stage reaction temperature is 1950-2000°C, depending on the Fe_2O_3 concentration in the burden. Additions of Fe_2O_3 to the charge produced significant increase in metallic yield. A new bench reactor was designed, built, and operated to facilitate semi-continuous operation, using O_2 injection to burn coke supporting the burden, resulting in burden movement. Validity of the equipment and test procedures was demonstrated by successfully operating the reactor as an iron blast furnace at 1500°C. However, operation of the O_2 injection reactor for Al-Si production was erratic and inconsistent due to formation of burden bridging by condensation of volatile suboxides. The addition of CaO decreased the tendency to form thick, strong bridges but did not completely eliminate bridging. Implementation of a rotating auger resulted in improved operation and production of metallic alloy at yields of 19 to 49% for low Fe_2O_3 burdens. Construction of the pilot reactor (VSR-1) was completed. The unit was operated successfully with O_2 injection after resolving shell leakage problems through use of an impermeable fused silica tube. Similarly to the bench reactor, VSR-1 experienced problems with burden bridging, both chemically from volatile condensation and mechanically from excess fines. Cold modeling studies confirmed that mechanical bridging was caused by plugging of voids in the bed with fines generated in the raceway. Proper sizing of coke particles minimized fines formation. After adding a rotating auger, providing heat at the hearth and improving the grate/liner design, a series of induction heated runs were made in VSR-3. Continuous operation produced significant quantities of coalesced metal alloy. Metal yields for Al ranged from 64 to 76% for high Fe_2O_3 burdens and 79% for low Fe_2O_3 material. Further modifications were made to the tuyere seals at the reactor shell and a series of runs were made using coke/oxygen combustion. No significant metal was produced due to problems of bridging, high heat losses at the tuyere region, and difficulty in controlling carbon concentration at the metal producing zone. Extensive phase analyses were completed on VSR-3 and bench reactor metal product samples by optical microscope techniques,

resulting in identification of phases and understanding of phase relationships. Ball forming agglomeration was developed for bauxite-clay-coke mixes and the bonding mechanism of the clay was established. A char injection system was designed for the VSR pilot reactor. Calculations for char-oxygen combustion in a burner indicated that preheat to 1000°C would be required to maintain the carbon consumption and CO sweep values of a blast furnace type combustion of coke in the burden.

Bench scale fractional crystallizer runs were continued to determine the impurity effects of Fe up to 6.9% and Ti up to 1.25% on alloy product purity and yield. High initial impurity concentrations resulted in less pure Al-Si product and product yield below 50% due to Al and Si losses as Fe-Si-Al and Ti-Si-Al intermetallics. Several special techniques for processing very high Fe alloy (10%) were tested, including pooling the high Fe remelt cuts and additions of Cu and Mg to reduce Fe levels. Copper additions increased product yield from a few percent to about 30%. Extensive microscopic phase analyses of bench scale crystallizer product samples quantitatively identified intermetallics and phase structure relationships. Detailed design and fabrication of the pilot crystallizer and auxiliaries were completed. Installation is 20% complete. Installation and shake-down of the induction heated multipurpose furnace were completed.

Long term testing was continued in the large bench scale membrane cell to evaluate woven cloth membrane and other construction materials, operating procedures, and effects of operating parameters on cell performance. Included in the latter were starting alloy composition, current density, anode-cathode spacing, and electrolyte composition. The best membrane material tested was a continuous filament, twill weave graphite cloth. Metal skim and oxide additions had no significant effect on cell operations. Metal penetration tests indicated that the cloth membrane could support up to 150 cm of Al without breakthrough. Tests were run to demonstrate the use of alternating current to resistively heat the cell during "off-electrolysis" periods. Pilot system detailed design was completed and fabrication was started, including the cell shell and refractory lining, major internal graphite components, cell lid and electrolyte (bath) melting furnace.

Primary activities for the first quarter of Phase C include the following: pilot reactor VSR-3 will continue to be operated using external induction heat and internal coke/oxygen combustion with an auger to establish the maximum O₂ rate feasible; the blast-arc reactor concept will be evaluated in VSR-3 using pre-heated CO to simulate the gas mass flow in the shaft (blast) region; the pilot reactor shaft will be redesigned to incorporate a taper to reduce burden bridging; heat and mass balances will be calculated for several alternative reduction processes; the chemical equilibria computer program will be refined to include non-ideal solutions; the bench scale reactor will be operated to evaluate CO sweep, SiO/Al₂O₃ ratio and reduction carbon source; construction and installation of the pilot crystallizer and membrane cell will be continued.

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 second phase are to build and operate a vertical shaft pilot reactor, to modify the reactor design for optimum performance, to complete detailed design, construction and installation of the purification pilot units, and to start up the purification units.

In Phase B, Alcoa was assisted on the Reduction Task by Koppers Company, Inc., Professor Julian Szekely, Carnegie-Mellon University, Professor Ketil Motzfeldt, and Professor Thorvald Engh. In addition, Professor John Elliott contributed to the technical evaluation of the Reduction step in his role as DOE technical monitor of the contract.

The contributions of the above consultants and subcontractors were reported for the first four quarters of Phase B in the respective quarterly reports. In the last "quarter," a four-month period from September to December 1979, the following activities were carried out. Koppers prepared a preliminary flow sheet for a plant to produce hot char under pressure from coal or lignite; made suggestions pertaining to the use of anthracite, formed coke and char as alternative process carbon sources, including a literature survey of articles on anthracite; designed a new oxygen tuyere for pilot reactor VSR-3 with the features of larger nozzle diameter and lower process heat loss to the tuyere jacket; toured Alcoa's burden preparation facilities and made recommendations on equipment use and burden characterization; consulted on aspects of char injection and raceway formation; and coordinated a tour for Alcoa personnel at the Bethlehem Steel, Sparrows Point "L" blast furnace.

Carnegie-Mellon University started up their carbon resistance furnace and initiated a series of experiments directed at reducing aluminum vapor losses. Carbon crucibles, 3/4 inch diameter x 3/4 inch high, were charged with various combinations of Al_2O_3 , C, SiC, or Al_4C_3 , heated to 2150°C and quenched. Products were weighed. Losses occurred in all runs; however, the addition of SiC to the charge did reduce the losses, indicating that recycled SiC would lower Al vapor losses.

Professor Szekely consulted seven days on computer modeling, raceway formation, alternative reduction processes, and process economic evaluations including a study on the credits for carbon monoxide by-product as a fuel or a chemical feedstock.

Professor Motzfeldt completed a series of experiments relating to the Al-Si-C system and observed the following: (1) the compound Al_4SiC_4 does not have a high degree of stability relative to Al_4C_3 and SiC; (2) SiC goes into solid solution with Al_4C_3 up to about 0.85-0.90 mols of SiC per mol of Al_4C_3 , with solid solubility expected to decrease as temperature is decreased; (3) carbon solubility in molten alloy decreases significantly when Si is added to Al.

Professor Engh submitted a final report of his study on "Consumption of Electricity and Heating Carbon: Carbothermic Production of Al-Si, Si and Al Calculated from a Chemical Equilibrium Model." The report describes calculations for continuous, steady-state counterflow carbothermic production of Al, Si or Al-Si alloy. A chemical equilibrium model was used to determine mass balances for the metal producing zone and predict process energy requirements, both total and electrical. For Al-Si, expressed as Al_2Si_3 and Al_4Si_3 , the total energy result is 10 kWh/kg alloy (4.5 kWh/lb alloy). Half would be supplied to the metal producing zone as electrical energy, and the remaining 5 kWh/kg alloy would be generated from combustion of carbon in the upper sections of the shaft.

The status of the project was reviewed with the DOE project manager and Professor Elliott once during the fifth period.

Approval was requested by Alcoa and granted by DOE for publication and release of a technical paper titled, "Computer Aided Model of Coke Fired Reduction of Alumina-Silica." The paper is to be presented at the 1980 annual AIME meeting. DOE also approved release of an article, "Method of Carbothermically Producing Aluminum-Silicon Alloy," to be published in the German technical journal Aluminium sometime in 1980. Alcoa also received DOE approval to disclose certain mathematical models formulated under the contract to Kema Nord AB, Sweden. The disclosure facilitates an exchange of technical information on similar techniques for process mathematic modeling.

Permission was requested to proceed with Phase C of the contract beginning 1980 January 1.

Progress for the three main tasks is reported by sub-task, as identified in the modified project outline submitted on 1978 August 16. It is estimated that for Phase B the Reduction task is 97% complete, the Alloy Purification task 68% complete, and the Purification to Commercial Grade Aluminum task is 52% complete. One task under Reduction, Task No. 15 - Develop Ore Beneficiation Methods, was deferred to Phase C. Under Alloy Purification, Task No. 2 - Determine Cooling Effects on Morphology was deleted as not required. Task No. 12 - Start and Shake Down Crystallization System was deferred to Phase C since the pilot system

installation was not complete. Work on Task Nos. 6, 9 and 10 relating to fabrication, installation, instrumentation and controls for the pilot crystallizer will continue and be completed in Phase C. For Purification to Commercial Grade Aluminum, Task Nos. 3-9 relating to fabrication and installation of the pilot system will continue and be completed in Phase C. Task No. 11 - Supportive Phase Identification was deleted as not applicable in Phase B.

PROGRESS

A. REDUCTION - PHASE "B"

Task No. 1: Calculate Heat and Mass Balances

Heat balance calculations were made simulating heat-up and steady state operation of pilot reactor VSR-1. Initial computer simulation was made on a burden charge containing all petroleum coke. Heat-up times of 1.3 to 2.5 hours were predicted to attain a bed temperature of 1327°C, using full and half induction power inputs respectively. Steady state simulation indicated a bed depth of 0.1 meters for solids heat-up to 1600°K. Radial temperature distributions were calculated for the vertical shaft reactor for several assumed susceptor (reactor wall) temperatures between 2000°C and 2200°C, and various insulation and shell materials. Results indicated that operating temperatures were within acceptable limits for quartz and fireclay shells, but not for transite. The distributions are shown in Figures 1 to 5.

A new computer program was developed for simultaneously solving heat and mass balance at steady state for a flowing one-dimensional chemical reactor (titled FLOWREAC). The program description and method of computation are shown in Appendix 1.

A series of energy balances were calculated for three alternative thermal processes to produce Al-Si alloy. The balances assumed recovery of material and energy values of volatiles-theoretically achievable but not experimentally demonstrated. The processes were (1) Arc Furnace; (2) Blast Furnace; and (3) Combined Blast-Arc Furnace. Total net energy requirements were 90 KJ/g, 59 KJ/g, and 70 KJ/g respectively. These values can be compared to present production of Al-Si eutectic by combined Bayer-Hall Al and arc furnace Si which requires 215 KJ/g net energy.

Task completion for Phase B is 100%. This task continues in Phase C.

Task No. 2: Continue Reaction Kinetics Studies

The chemical rate equations in the kinetics computer model were revised, resulting in integration of the SiO_2/C test case past complete conversion of SiO_2 to SiC . Also, the

range of input rate equations was expanded, and the effects of external heating or cooling were included in the model. A composition was completed for silicon production in a low shaft furnace as a means of checking the mechanics of the kinetic model. Production of silicon under reasonable conditions was predicted. Further development of a full chemical kinetics model will be deferred in Phase C due to the complexity of the system, and the need to concentrate on models for steady state, equilibrium heat and mass transfer calculations.

Experimental procedures for measuring reaction kinetics were altered to facilitate studying high temperature phases by fast cooling of samples in a quench zone, thus eliminating effects of extended time at temperature. Cooling rates of approximately 7°C per second were attained. The parameters of charge content, reaction stage temperature, and time at temperature were varied. Results confirmed that minimum metal formation temperatures are 1950°-2000°C depending on the concentration of Fe_2O_3 in the charge. With no Fe_2O_3 additions, 2000°C and two hours were required to produce significant quantities of metal. With Fe_2O_3 , metal was made in 0.33 hours at 2000°C. Product analyses also indicated that Fe_2O_3 additions resulted in improved Al and Si recoveries, and more complete reduction of oxide ores.

Tests were made in the bench scale reactor to determine the effect of a cooler metal reservoir on product collected. No appreciable change in product weight was found for runs in which the reservoir was 180° to 250°C cooler than normal.

A series of runs were made to determine the effect of volatile flow rate on metal product recovery and burden bridging. At volatile rates of 2L/m the location of bridge formation was a function of temperature gradient and concentrated over a short height of bed. As the volatile rate increased to 30L/m, condensation of suboxides was spread over a greater height. Product recovery in the reservoir decreased from 193 grams to 128 grams to 106 grams for 2, 13, and 30 L/m volatile flows respectively.

Task completion is 100%

Task No. 3: Continue Reaction Mechanism Studies

A series of runs were made to determine the effects of CaO and Fe_2O_3 additions on metallic yield and burden bridging.

The purpose of these additives was to form liquid phases at the cooler, high-up regions of the bed, causing a "washing" action of the suboxide condensate as the liquids flowed down through the bed. Bridging was not eliminated by these additives. Over 60% of the Ca was found in the metallic product and the carbide slag. Very high concentrations of Fe_2O_3 , 25 to 50% of the burden charge, produced metal yields of 44 to 64%.

The reactions related to burden bridging by suboxide condensation were studied via computer calculations and empirically. SiO can back react to SiO_2 or SiC , or disproportionate to Si and SiO_2 . SiC is the major compound found in tests. Al_2O primarily back reacts to Al_2O_3 , and does not go to oxycarbides, carbides, or free Al .

Metallic samples from both the pilot and bench scale reactors were remelted to determine the effects of metal concentration on flowability through a drilled graphite plate, as well as separation of metal species from carbides. Results are shown in Table 1.

Bench scale sample L-17 was the first to melt at a reasonably low temperature (1325°C). This sample was made from the reduction of pure Al_2O_3 , SiO_2 , Fe_2O_3 , and petroleum coke (low ash). The elimination of Ti apparently resulted in a more fluid alloy. In all material collected below the plate, except for VSR3-18, the carbon and Ti concentrations were lower than in the starting material, indicating that both these elements contributed to alloy melting and flowability characteristics. Microscopic studies were made on VSR3-18 and VSR3-19 samples. The carbide shapes in VSR3-18 were spheroids not interconnected through the matrix. The carbides in VSR3-19 were intergrown, interlocking platelets. Both samples remelted at almost the same temperature, indicating that the shape of the carbide solids does not affect the liquid drain characteristics.

A series of computer calculations were made to determine the effect of the $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{C}$ ratio on metallic yield for a non-refluxing mechanism, without combustion O_2 or CO sweep from combustion of carbon. The charge was varied in a systematic pattern to change the ratios. Figure 6 is a plot of the predicted metallic yield in percent as a function of charge composition. Iso-yield curves are indicated where there is sufficient data. These curves indicate a region of high yield at higher Al_2O_3 and C . The yield decreases rapidly

as either the SiO_2 or Al_2O_3 is increased. The symbols next to the yield points represent the solid or liquid phases in equilibrium with the Al-Si alloy for the given charge compositions. Any charge that is oxide rich has $\text{Al}_4\text{O}_4\text{C}$ as the second product. Any C rich charge has SiC or SiC and C as the extra products.

Four experimental runs were made in the bench reactor to evaluate the effect of carbon concentration on reactor operation and alloy product formation. Carbon levels of 77, 89, 94, and 100% of stoichiometric for reduction were tested. The data is summarized in Table 2. The highest alloy yield was obtained at 89% of stoichiometric carbon. Burden movement was similar for all runs. The results indicate that the startup charge to a refluxing reactor should contain less than stoichiometric carbon to obtain maximum yield with no carbide accumulation. These conclusions apply to an externally heated reactor with no additional carbon for combustion.

Task completion is 100%.

Task No. 4: Supply Burden Materials

Various burden materials were crushed, sized, blended, and agglomerated to supply solid feed for reactor operations. Agglomerate forms included briquettes, extrusions, and balls. Raw material compositions and quantities are listed in Table 3.

Task completion is 100%.

Task No. 5: Evaluate Burden Preparation Methods

At the start of Phase B ball forming of metallurgical coke, Theile clay and Boke bauxite mixtures were evaluated using a ball mill. Particle grinding was done by two methods, a 19 cm dia. ball mill and a laboratory size hammermill. The balls made from the finer ground materials (ball mill) were superior to the coarser mix (hammermill) as shown below.

Burden Mix Composition: 63.6% coke, 18.7% clay,
19.9% bauxite

Compressive Strength (Calcined): Ball Mill Burden 23.2 MPa
Hammermill Burden 13.7 MPa

Calcined extrudates (5A1043) and briquettes (5A1044) made from metallurgical coke, bauxite, kaolinitic clay, and hematite were compared for compressive strength and abrasion resistance. Both agglomerates had similar abrasion resistance but the fired briquettes were 3.4 times stronger than the fired extrusions.

Extrusions were also compared to balls made in an Eirich mixer. The balls (5A1055) had very good abrasion resistance and acceptable compressive strength. The extrudates (5A1046) were lower in both properties. These test results indicated that ball forming is the best method for burden preparation.

To evaluate the effect of producing balls in commercial type equipment, burden materials from the same feedstock mix were charged to a 100 cm dia. Dravo Disk (5A1068) and to the laboratory Eirich mixer (5A1075). The Eirich balls were four times stronger and had excellent abrasion resistance. In addition, both materials were tested for breakdown after being dropped 22 ft. The Eirich balls were 10 times stronger in this comparison. It should be noted that the Eirich burden composition did contain 7% more clay and 9% less metallurgical coke than the Dravo Disk burden, which would account for part of the improved properties.

The physical characteristics of the above comparisons are shown in Table 4.

The effect of calcination rate on ball physical characteristics was determined on Eirich balls (5A1060). The faster heat-up rate was preferred. Balls fired at the "standard" rate of 25°C/hr had a compressive strength of 0.81 MPa (118 psi) and an abrasion breakdown of 9.5%; whereas material fired at 285°C/hr had values of 1.21 MPa (176 psi) and 0.2%. Another batch of Eirich balls (5A1063) with the same composition was interrupted during calcination at 400°C, cooled, and was then reheated and taken to the endpoint temperature of 1000°C. These balls had lower strength, 0.57 MPa (82 psi), and higher breakdown, 3.7%, than the fast-fired material.

During Phase B, ball-forming of mixtures of coking coal with non-coking carbonaceous material was demonstrated in the Eirich mixer. The coking coal provided the fired bonding strength up to 4.92 MPa (714 psi) depending on the ratio of coking coal to non-coking material.

Task completion is 100%.

Task No. 6: Evaluate Burden Materials

Various burden materials were evaluated qualitatively for retention of shape and strength after exposure to operating conditions for producing alloy in the bench reactors. Results are shown in Table 5. Taconite was included as a comparison material.

Fired extrudates (to 1000°C) containing 28% Fe_2O_3 showed a shrinkage of 7% and a weight loss of 15% when heated to 1400°C in an inert atmosphere. Analysis indicated that quartz, mullite, hematite, and minor alpha alumina were replaced by major alpha alumina and metallic iron.

Firing tests on ball-formed kaolinitic clay and Boke bauxite showed that only the clay provides bonding strength to burden materials containing clay, bauxite, and coke. An evaluation of Eirich balls (5A1058) made from bauxite, hematite, coke, and calcined clay resulted in low compressive strength and very high breakdown on both tumbler abrasion and 22 ft drop tests, verifying the importance of forming the clay bond during calcination of the agglomerated mixture. Values of strength and breakdown for 5A1058 compared to 5A1055 (same burden with uncalcined clay) were 0.37 MPa (54 psi) vs 1.07 MPa (155 psi) and 66.8% vs 1.5%, respectively. The drop test breakdown for 5A1058 was 48%.

Tumbler tests were performed on Eirich mixer balls (5A1075) and calcined metallurgical coke to determine the amount of fines generated by each material. Fines (minus 6 mesh Tyler) generation was higher for the coke due to its angular particle size. The high abrasion resistance of the balls caused mixtures of these materials to generate slightly more fines than the coke alone. The results are listed:

	<u>Minus 6 Mesh</u>
Eirich mixer balls	0.1%
33.3% balls + 66.7% coke	3.6%
50% balls + 50% coke	3.9%
Metallurgical Coke	3.1%

Task completion is 100%.

Task No. 7: Develop Analyses and Properties of Critical Compounds

Alternate methods were investigated to more rapidly analyze

product samples from reactor operations. The best procedure was analysis of Al, Si, Fe, and oxygen by Neutron Activation Analysis plus total carbon by combustion and Ti by Atomic Absorption. Quantometer dilution remelt and x-ray fluorescence analyses were not successful due to the high melting point and x-ray absorption properties of the alloys produced. X-ray diffraction is used to qualitatively identify phases and compounds. Microscopic analyses provide quantitative compound identification. Details of the latter method are included under Task 16.

Task completion is 100%.

Task No. 8: Complete Construction of Pilot Reactor, VSR-1

Construction of VSR-1 was completed. A schematic of the reactor is shown in Figure 6. Gas leaks through permeable ceramic shells were eliminated by using impervious quartz. Leaks at joints were stopped by water cooling critical areas sealed with silicone. Improvements were made to the induction heating system relating to zone control and total power availability. The power input is adequate to heat the charged reactor to 2000°C in several hours. System safety was controlled by use of CO monitors in strategic locations to alarm or automatically shutdown the reactor if the CO set point limit was exceeded. Data taking and process control was improved by use of accurate digital meters and a mini-computer which included automatic solids charging.

Several water-cooled oxygen tuyeres were designed during Phase B. The type used in VSR operations is specified in Figure 7. The oxygen port was 0.180 in. dia, flaring out to 0.375 in. at the exit.

Task completion is 100%.

Task No. 9: Effects of VSR Operating Parameters

In the second quarter, six runs were made to study combustion of coke with oxygen. The parameters of coke size, O₂ flow rate, and bed height were evaluated. The goal was to achieve coke bed movement at temperatures of 1600°-2000°C under steady state conditions with heat input from induction and combustion. Tuyere port size was held constant at

0.180 in. dia. Large petroleum coke particles, $-3/8$ in x 4 mesh, did not move well and required "slipping" to attain movement. The gas flow pattern was predominantly peripheral. Poor movement was attributed to incomplete combustion of the large coke in the raceway, allowing fine coke particles to accumulate in the center of the bed, causing plugging and reducing permeability. Also, the large coke was subject to interlocking between particles due to greater surface roughness. To offset these conditions, the coke size was reduced to $-4 +8$ mesh. This coke tended to fluidize, even at lower O_2 rates and higher bed heights. Therefore, an intermediate coke size of $-1/4$ in $+6$ mesh was tested. This material did feed smoothly without buildup of pressure in the bed after a short conditioning period. For 300 SCFH of O_2 and a 30 in. bed height, about 30 minutes were required. After movement of the coke bed was established, a mixture of 50% Fe_2O_3 extrudates (with clay, bauxite, and coke) and dolomite flux was charged. The bed bridged after about one hour of ore feed at a level 43 in. above oxygen entry ($\sim 1700^\circ C$). The run was repeated with improved hardware for monitoring bed level. Run VSR-1-6 ran well at 310 SCFH O_2 and a hot zone temperature of $2000^\circ C$.

Simultaneously with the VSR runs, a two-dimensional Plexiglas model was constructed to study the relative relationships between tuyere diameter, gas flow rate, solid particle size, and bed height at ambient conditions. The model size was 10 in. long x 22 in. high x 2 in. deep. VSR operations were simulated by injecting high velocity air into sized coke particles. It was determined that the raceway size was a direct function of gas velocity at the tuyere exit for low flow rates only. As velocity increased, coke fines generated by abrasion in the raceway plugged the bed and restricted further growth of the raceway. This condition could be stopped temporarily by shutting off gas flow, allowing the bed to collapse, and restarting flow (in effect, a simulation of "slipping"). However, after some time, the same condition of plugged bed would develop. In a hot reactor, the coke particle size would decrease by both combustion and abrasion, and a similar effect of fines generation causing bed plugging would eventually lead to bridging by mechanical means in addition to the chemical bridging from condensation of suboxide volatile compounds. Proper initial sizing of coke particles appears to be the best method to avoid fluidization by "too fine" material and generation of fines from abrasion and incomplete combustion of "too coarse" coke, both resulting in poor bed movement culminated by bridging.

Four continuous runs were made with oxygen combustion in the third quarter. VSR-1-7 was operated on metallurgical coke, -1/4 in. +6 mesh, the first attempt to use a high ash carbon source in the pilot reactor. The run was terminated after a short time due to premature venting through a rupture disk. During the run, "slipping" of the bed was necessary for about 20 seconds every five minutes to maintain bed movement. A weak bridge was formed at the top of the bed. Most of the coke ash was blown out of the bed rather than form an oxide slag. Graphite pegs installed vertically across the burden support grate provided an indication of the tuyere-injected oxygen combustion pattern. At 100 SCFH O_2 , the raceway penetrated to the center of the reactor. VSR-1-8 started on metallurgical coke, with 10% Fe_2O_3 extrudates and fresh coke added in alternating layers after establishing good bed movement. This run was eventually terminated by a false indication of bed level which resulted in a low, carbon deficient charge. Metallic product was found at the grate level between the tuyeres. The molten alloy solidified around the graphite pegs rather than flow through the grate perforations to the hearth, probably due to high heat losses in the tuyere-grate region. VSR-1-9 was a repeat of VSR-1-8 with the addition of an improved level probe and the grate raised slightly to get above the bottom induction coil and decrease heat loss. Run results were similar to VSR-1-8: metal was produced but collected at the grate, and a bridge formed at the top of the bed. Remelt analyses of the metal products in these two runs indicated that the alloy was primarily FeSi with up to 14% Al and 4% Ti and/or C. The low Al content was due to insufficient temperature and/or residence time, with the temperature influenced by unit heat losses in the metal producing zone, primarily to the water-cooled tuyeres. The fourth run, VSR-2-11, implemented an induction heated hearth. However, balance problems were experienced with distribution of power to the three induction coils when the bottom coil was relocated to the hearth region and the run failed to produce molten alloy.

In order to establish steady state metal production, the pilot reactor was modified by adding a motor-driven rotating auger in the upper zone to reduce or eliminate burden bridging. In the fourth quarter, a series of six runs were made in VSR-3 using 100% induction heat. Due to problems with the auger, this series can be regarded as three pairs of runs with premature shut-downs of the

first runs followed by long, successful operating periods for the second runs. CO sweep was introduced in runs VSR-3-15, 16, and 17 through the O_2 tuyeres to simulate the products of O_2 -coke combustion. The burden materials used (refer to Table 6) included both high and low amounts of Fe_2O_3 , SiO_2/Al_2O_3 ratios of 0.575 to 0.614 and substoichiometric reducing carbon in the agglomerates. High Fe_2O_3 concentrations reduce Al and Si activities in the alloy and improve single pass metal yield, but results in undesirable levels of Fe for alloy refining. Table 7 shows the run conditions and results.

An autopsy of run VSR-3-13 indicated that the reactions occurred first at the walls of the reactor. The highly endothermic nature of the reactions makes it difficult to heat the charge uniformly using the induction wall heat source. The 12.1 kg of alloy produced in this run was quite fluid. CO sweep was injected for the last two hours of run VSR-3-15. The maximum temperature of $2050^\circ C$ was $100^\circ C$ lower than VSR-3-13, and the amount of reducing carbon was significantly deficient, resulting in less metal production (8.3 kg) and an accumulation above the grate of more partially reduced material (20.0 kg). No metal was produced in VSR-3-16 due to the low temperature experienced. Adjustments to the induction heating system resulted in a reaction temperature of $2180^\circ C$ for VSR-3-17. About 2.5 kg of metal was made before the auger failed. It was apparent that the CO sweep in runs VSR-3-16 and 17 caused substantial condensation of suboxides near the top of the bed, cemented to the auger.

This series of runs demonstrated the following: metal was produced continuously, although steady state has not been attained; substoichiometric carbon resulted in lower metal yields and greater accumulation of partially reacted burden; start-up conditions will require some level of substoichiometric carbon to balance the initial formation of volatile suboxides; in very carbon deficient charges, molten Al_2O_3 slag was formed; the alloy produced was very fluid.

Material balances for VSR-3-13 and 15 were calculated based on the analyses submitted. Results are shown in Tables 8 and 9. No chemical analyses were obtained on the prereacted material above the reaction zone, but x-ray diffraction did identify the phases present. It was assumed that only Fe_2O_3 was reduced to Fe in the prereaction zone. The percent of each element accounted for shows reasonable closure, ranging from 85% to 98%. The high recovery of all major

metal species indicated satisfactory refluxing of back reacting vaporous Al and Si species. In both runs, the reaction zone contained Al_2O_3 , SiC, Al-Fe-Si intermetallic and no SiO_2 or free C. The metallic products included Al, Si, Al-Fe-Si intermetallic and SiC. Phases, elemental analyses, and run-starting conditions are related to material locations in the various zones of the reactor for runs VSR-3-13 (Figs. 8 and 9), -15 (Fig. 10), and -17 (Fig. 11).

In the "fifth" quarter of Phase B, the last four months of a 16 month phase, a total of 10 pilot runs were made. Runs VSR-3-18, 19, and 21 were totally heated by induction, and no CO sweep was used. Run VSR-3-21 was a special batch operation with no charge fed to assess the effect of excess carbon on alloy yield and fluidity. VSR-3-20, 22, 23, 24, 25, 25, and 27 were combustion heated runs that included injection of O_2 .

VSR-3-18 and 19 were a continuation of the induction heated series previously discussed. The purpose of these two runs was to reduce the accumulation of slag and intermetallics by increasing the reducing carbon and decreasing the hematite contained in the pelletized burden. An auger was used in the runs to prevent bridging. Substantial quantities of alloy were produced. The ores charged contained only 71% stoichiometric carbon so additional activated carbon granules were mixed with the ore to increase the available carbon. Figures 8 and 9 show the important characteristics of these runs. In run 18, a problem with heating of the graphite/carbon felt insulation resulted in low power input and high shell heat losses. When this was corrected in run 19, the reaction zone heat input increased from 37 to 46 kW while heat losses decreased. The increased heat input resulted in an increase in temperature from less than 2000°C to 2100°C , an increase in charging rate from 3.9 to 6.7 kg/hr and an increase in metal production from 3.5 kg to 15.0 kg. In run 18 the carbon level was maintained at 85% of stoichiometric while in run 19, the carbon level increased from about 85% to greater than 100%, averaging about 100% overall. Less carbon is required during start-up since the reflux of suboxides has not yet reached steady state. Differences in carbon level had a significant effect on the reaction. In run 18, the material above the grate was a conglomerate of SiC, Al_2O_3 , and alloy. Only 50% of the carbon required to

reduce the Al_2O_3 was available in the SiC . In run 19, the material below a parabolic interface was a friable conglomerate of alloy and carbides with little, if any, Al_2O_3 indicating an excess of carbon in that zone. Above the parabolic interface there was a granular bed of SiC , $\text{Al}_4\text{O}_4\text{C}$, C , and Al_2O_3 indicating a Stage II reaction zone as predicted by the thermochemical model. The optimal carbon level is between 85 and 100%, but calculations based on material balances are not consistent. The product formed in run 19 contained considerably more SiC than that in run 18, but both remelted between 1000 and 1085°C.

Material balances for VSR-3-18 and 19 are shown in Tables 10 and 11. The data for VSR-3-19 indicates a significantly larger recovery of Si (probably as SiC) and a slight decrease in Al recovery probably due to the higher reaction temperature and the attendant higher volatility of Al and Al_2O_3 .

Several observations from the induction run program are important when considering the various effects on the process. Over 30 kg of ore must be charged to the VSR-3 pilot reactor before metal begins to accumulate in the catchbasin when using no additional CO sweep. Metal can be made in a substoichiometric and a stoichiometric reducing carbon condition of operation resulting in accumulations of slag and carbide, respectively. Even though the operation of the reactor appeared constant at shutdown, it is impossible to say a steady state had been reached and that the slag or carbide would not continue to accumulate with an extended run. For the first time, $\text{Al}_4\text{O}_4\text{C}$ was found in the reaction zone of the pilot reactor in VSR-3-19. The two main differences that occurred in this run as compared to other long induction runs was that stoichiometric carbon and only clay, bauxite, and coke were used in the burden.

Run 21 shown schematically in Figure 10, contained a batch charge consisting of alternate layers of ore and carbon materials, followed by a mixture of ore and coke, topped off by a bed of coke was placed in the reactor. No auger was used and no material was charged during the run. The reactor was heated to 2060°C and held until the CO in the off gas dropped to a low level indicating the completion of the reaction. An autopsy revealed that product had formed in the ore layers above the layers of graphite cylinders and SiC chunks, and had drained through those materials. Most of the product coated the graphite

cylinders and the grate while about 100 grams were in the catchbasin. The 2-in. thick layers of ore sandwiched between coke layers apparently reacted to alloy which penetrated the coke layers, reacting with them to form carbide "pancakes". The only trace of the ore in the 1-in. layers and the ore mixed with the coke was carbide-coated coke. This run seems to indicate that thick layers of ore and large size carbon materials result in a product which coalesces and drains while a mixed bed of heating coke and ore may have no yield even under the best conditions.

The program was then switched to making runs in which heating coke was fed to the top of the reactor along with the ore, and combustion oxygen was injected into the reactor just above the grate. In general, the goal was to feed enough ore to the reactor to expect an accumulation of metal while burning varying degrees of coke and oxygen. Only VSR-3-23, 24, 26, and 27 ran for any length of time, but in no case was the run long enough to feed 30 kg or more of ore. Since this is the guideline for a non-CO sweep run to make metal, it would likely require the consumption of considerably more ore than this amount to expect to make metal while burning coke and oxygen.

In runs 22 through 27, ore was mixed with coke in a ratio of 1:1. Carbon bushings were used around the tuyeres to try to reduce heat loss to the cooling water. The bushings burned through at the beginning of run 22, but were modified and used successfully for the next four runs. (Run 25 which was terminated immediately after initiation of O_2 was continued as run 26.) Runs 23 and 24 were made at 80 CFH O_2 per tuyere while runs 26 and 27 were made at 40 CFH. Table 12 shows the amounts of materials charged and recovered from those runs. In each case, Al_2O_3 and SiC accumulated in the reaction zone, thus decreasing the relative amount of excess carbon. The most extreme case was run 24 in which sufficient O_2 was blown to react virtually all the coke carbon in the lower part of the reactor. Thus, the likelihood of making alloy product should have increased towards the end of the run as the reaction zone was swamped with reactants and excess carbon was progressively removed. The deficiency of heating carbon may have caused the combustion zone to expand over the entire cross section reoxidizing any alloy which formed. The only evidence of product in the combustion heated runs was a metallic coating on the top of the layer of graphite cylinders between the raceway and the grate. This was the same location where considerably larger accumulations

of metallic product were found in runs 8 and 9. The latter runs utilized a high iron (10% Fe_2O_3) agglomerate to increase the yield.

The lack of success in these runs was mostly a result of the difficulty of maintaining a continuously moving bed and the repeated failure of the auger. The details of these runs can be found in Figs. 11 through 21 and Table 13. Three different augers at two different rotational speeds and two positions with respect to the height above the tuyere were systematically tried to prevent bridging and maintain bed movement. Different levels of total oxygen flow rate were also utilized in the range of 100 CFH to 240 CFH.

Although no metal was made during these runs, there were other results relating to heat losses, the carbon/oxygen balance, and the phases present in the reaction zones that were informative. It was believed that the tuyere cooling water presented a heat sink which limited the endothermic metal producing reactions in the hot zone of the furnace. The tuyeres were shrouded with carbon tubes and caps instead of those made from graphite. Using the lower conducting carbon insulators, we expected to retard the heat loss to the tuyere cooling water. Although this idea makes sense in principal, measurements of the tuyere inlet and outlet cooling water temperatures have not given clear indication of the success of this concept. Another operating problem that is the result of irregular bed movement is evidenced by the ratio of the required coke feed to the actual coke fed during each run. When the bed is hanging up, no ore or coke can be charged to the reactor until more room is available in the top of the bed. Consequently, there are periods when voids may be formed below the bridge, and there are momentary insufficiencies of carbon for reduction due to combustion by oxygen or the metal may be reoxidized before it can drain into the crucible below the grate. The required coke/actual coke ratio is therefore an indicator of how smoothly the reactor is operating. This ratio varied from 1.63 to 1.43 indicating a quite irregular behavior of bed movement as 1.0 would relate to perfect control. It should be mentioned that the ore and coke were always fed in a ratio sufficient to match the intended continuous oxygen rate plus reduction requirement even if the proper oxygen/coke ratio could not be maintained. Phase analysis of the bridge materials and samples of the most metallic looking product to be found on the grate indicated little or no metal production.

It is also noteworthy that $\text{Al}_4\text{O}_4\text{C}$ continued to show up in the bridge and metal producing zones as well as both SiC and Al_4SiC_4 .

Task completion is 100%.

Task No. 10: Effects of Operating Parameters in Bench Reactors

A new bench scale reactor was designed and built to facilitate operating in a semi-continuous mode, and to more closely simulate the VSR pilot reactor. Bottom entry oxygen was injected to produce a combustion zone and to effect burden movement by consumption of coke supporting the burden. However, the O_2 fed does not provide a significant quantity of heat (about 10% of total input at 13 l/min O_2 rate).

The new reactor (Figure 22) is approximately 130 cm (50 in) high and 23 cm (9 in) in diameter. The outer shell consists of four sections of R-680 ceramic each 30 cm (12 in) high. The carbon liner is 107 cm (42 in) high and 12 cm (5 in) in outside diameter. The liner and graphite insulation are permanently mounted in the reactor. At the bottom of the liner, a carbon crucible is inserted which is easily removable. This crucible is 25 cm (10 in) high and 10 cm (4 in) in outside diameter and 8.9 cm (3.5 in) in inside diameter.

A water-cooled stainless steel tuyere (Fig. 23) protrudes approximately 5 cm (2 in) into the bottom of the crucible. This tuyere is sheathed with carbon to facilitate removal after a run and to provide protection from liquid metal attack. Four horizontal holes through the ceramic and insulation permit temperature measurement of the outside of the graphite liner.

Nine runs were made in the new unit (designated BF reactor) during the first quarter of Phase B. Tables 14 and 15 summarize the operating data and results. Table 16 shows the burden compositions used. The carbon to oxide ratio has been maintained in the range 1.4 to 2.0. This is the range calculated for the ratio required in a self-heated furnace. Pilot operations typically ran 75-150 l/min (150 to 300 CFH) of oxygen in the 15 cm (6 in) diameter crucible reactor. Comparable flows in the 9 cm (3.5 in)

bench reactor are 26-52 l/min of oxygen. The bench reactor is typically operated at 13 l/min of oxygen, which is just half of the lower end of the range. Higher flow rates may be examined at some time in the future.

Run BF1 was strictly a shakedown run to test the equipment without oxygen or charge. Run BF2 with a coke charge tested the oxygen tuyere assembly. The burden moved about as expected and no crucible attack was evident. Due to the high heat losses from the small bench unit, the amount of heat generated by the oxygen-coke combustion at six liters per minute of oxygen is only 5% of that supplied by the induction power supply. Thus, it is highly unlikely that the bench unit can ever be run without the induction power.

Run BF3 was charged with B-1 briquettes made from pure SiO_2 and Al_2O_3 , enid coke, and pitch. Soon after introducing the oxygen, the sight glass on the bottom port disappeared. Air entering through the hole rapidly consumed a large quantity of the graphite felt insulation requiring an early termination of the run. Upon attempting to remove the charge, it was discovered that a bridge had formed. This is surprising considering the short duration of the run. It can probably be explained from a consideration of the charge materials. Since pure SiO_2 , Al_2O_3 , and C were used to make the briquettes, the activities of all three reactants are equal to one. They are thus in their most reactive chemical state. SiO_2 , Al_2O_3 , and Al vapor formation will be increased due to the high reactant activities. Any charge containing pure SiO_2 or Al_2O_3 will be prone to high volatile losses. These high oxide activities can only be reduced by complexing either in solid state minerals like mullite or liquid state slags. Burden materials containing pure oxides are probably the ones most likely to bridge and, thus, least likely to be successful.

The E-3 extrudates used in run BF4 are a mixture of Rebolado bauxite, Huber clay, and metallurgical coke. A large void 38 cm high was formed but the burden did not move. The unreacted material was heavily coated with white deposits. An analysis of the product around the tuyere showed only SiC and C. These extrudates were made from real ores and contain various impurities. Apparently these impurities are not present in sufficient quantities to lower the activities of the reactant oxides enough to reduce the volatility losses.

Pellets containing 50% Fe_2O_3 (run BF5) were tried next. Coalesced metallic product was recovered in the reservoir

and large quantities of metallic product were found around the tuyere tip and in the lower part of the burden. The metallic product near the tuyere formed a cavity approximately 2.5-4 cm dia, perhaps providing an indication of the raceway size. The burden did move a significant amount. Two bridges were formed, however. Coked ore (run BF6) is an agglomerate made by coking bauxite, clay, and coking coal. The materials are held together by the carbon bond formed during coking. Very little of the material reached the tuyere at temperatures above reaction temperature due to the bubbling of oxygen through the mercury bubbler relief valve. This required shutdown occurred only twenty minutes after the hot zone reached 2000°C. Two bridges were again formed, though neither showed any signs of liquid formation. The bottom bridge probably formed while cooling since there was no void below the bottom bridge. The upper bridge was typical of other bridges with large quantities of white-green condensate. The present coked ore material is particularly susceptible to volatile formation since it contains part of the heating carbon. Thus, the oxides are exposed to the high temperatures in the combustion zone (flame temperature). A coked ore material that contained only the reduction carbon would be better than the present material.

It was postulated that burden movement could be increased by using a low bulk density carbon, i.e., charcoal. In run BF7, charcoal was substituted for part of the coke charge (1/3 in preheat coke, 1/2 in ore coke). A metallic plus carbide product was found near the tuyere. The central cavity was similar to that in BF5, confirming the approximate size of the raceway. Even though the charcoal was coated with white condensate, large quantities of condensate still escaped. A white plume was observed at the end of the gas exit tube. After the oxygen bubbler started releasing oxygen, the plunger was rapped to try to move the bed. This apparently compressed the bed since the bubbling increased dramatically causing shutdown.

Since the only burden that had moved freely was petroleum coke, a run (BF8) was attempted to simulate an iron blast furnace. If this charge had bridged, it would be a strong indication that the bridging is due to equipment not process problems. Taconite, dolime, and metallurgical coke were charged and a large quantity of metal and slag was produced. The run was terminated due to oxygen venting through the bubbler. This was due to flooding of the tuyere, however, not bridging. The depth of metal and slag produced had covered the tuyere. The burden had moved significantly.

One part of the charge was not easily removed, but this was definitely a liquid phase at temperature. Since there was no void below this bridge, it probably would have continued to move down as the coke below it was consumed.

As noted above, one way to reduce the quantity of volatiles formed is by reducing the chemical activity of the reactant materials. It is highly unlikely that the carbon chemical activity can be reduced. The reactivity of the carbon can be changed by using different sources of carbon (charcoal vs coke), but reactivity is a rate phenomena not an equilibrium phenomena. The activities of the reactant oxides can be reduced by either solid or liquid state complexing. The Fe_2O_3 in the high iron run (BF5) may have formed an $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ slag and thus reduced the SiO , Al_2O , and Al volatiles somewhat. FeO may reduce out of the slag at such a low temperature ($\sim 1500^\circ\text{C}$) as to be ineffective in lowering volatile formation at process temperatures.

To test the idea of reducing the oxide activities, CaO was added to form a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ complex which should be stable to at least 1800°C . If the correct composition is chosen, this slag will liquefy at $1400\text{-}1500^\circ\text{C}$. It will tolerate rather large SiO_2 changes without solidifying. Thus, it could condense SiO (increase SiO_2 content), or form SiC (decrease SiO_2 content) without solidifying. The major advantage is the reduction in the amount of SiO formed which never has to be recondensed. There are several disadvantages: 1) The CaO is yet another material that must be charged, heated to temperature, and removed from the furnace; 2) Ca may recycle; and 3) Ca will be reduced to the metal phase to some extent and will have to be removed in the purification step.

Run BF9 was a preliminary attempt to examine the effects of a CaO addition. The desired slag was approximately 43% CaO , 5% MgO , 33% Al_2O_3 , and 20% SiO_2 . This slag has a liquidus temperature of approximately 1500°C . High Fe_2O_3 briquettes (50%) were the ore charge. Any FeO that is formed will act to lower the liquidus temperature. The run was terminated due to oxygen burning through the graphite crucible, liner, and felt insulation. A metallic-carbide layer was found directly above the tuyere. There was a significant quantity of coke above this in the crucible below the bridge. Apparently the metallic-carbide layer diverted the oxygen sideways against the wall. Also, some liquid metal had dropped onto the outer edge of the tuyere, causing localized melting.

Though BF9 had some bad results, it did produce 550 gms of metal and 34 cm of bed movement. This run was similar to BF5 which only produced 24 gms of metal with 18 cm of bed movement. The CaO additions thus increased both metal yield and bed movement significantly. The bridge was a liquid phase bridge that might have continued to move down if the material below it had been consumed.

In the second quarter, ten runs were made in the BF reactor in an attempt to overcome the bridging problem. The runs examined a wide variety of burden materials and operating techniques such as columnar charging, reduced flame temperature, small burden size, and high flow rates. The runs were terminated for many different reasons including bridging, tuyere flooding, tuyere plugging, and one planned shutdown.

Tables 17, 18, and 19 contain the summaries of the burden data, operating data, and results of runs BF10 through BF19.

As before, the carbon to oxide ratio was maintained between 1.4 to 2.0. The oxygen flow initially was 13.0 l/min. Four of the runs used oxygen flow rates of 26 l/min which is equivalent to 75 l/m (150 CFH) in the pilot reactor. The present oxygen flow rate in the pilot reactor is now up to 120-150 l/m (240-300 CFH). The bench reactor is therefore run at approximately half that of the pilot.

Run BF10 was charged with 10% Fe_2O_3 extrudates. This charge composition had shown high yields (~70% metallic) in the bench crucible reactor. The run lasted 54 minutes with O_2 at 13 l/min. It was terminated due to high pressures at the tuyere (0.024 MPa or 0.24 atm). A thick scull of metallic product had covered the tuyere.

Since BF9 attained good burden movement and high metallic yield, run BF11 was designed to have approximately the same slag composition (43% CaO, 5% MgO, 33% Al_2O_3 , and 20% SiO_2). The charge for run BF11 contained approximately 10% Fe_2O_3 as compared to 40% Fe_2O_3 in run BF9. Thus the metal produced should have had higher levels of aluminum and silicon. The coil length was shortened to reduce the amount of charge exposed to the hot zone at one time and decrease the amount of volatiles produced. This run was terminated due to high tuyere pressures (0.024 MPa or 0.24 atm). Upon disassembling the reactor, there was no sign of a bridge. The tuyere was partially plugged with a piece of oxide material.

Volatile formation is a function of the temperature and the amount of gaseous sweep. When hot C is combusted with pure O_2 , very high flame temperatures ($\sim 3500^\circ C$) are possible. This very hot flame may produce much greater volatilization than the normal high temperature zone of the furnace. It has been suggested that perhaps the flame temperature should be reduced by additions of some other gas or solid to the O_2 . CO_2 reacting with C to form CO at high temperatures is an endothermic reaction. Carefully balancing the quantities of O_2 and CO_2 can produce any desired flame temperature. Two runs (BF12 and BF13) were made to see if any advantages could be detected when a lower flame temperature was used.

BF12 used 25% Fe_2O_3 extrudates which has a composition between those of runs BF5 and BF10. The CO_2 - O_2 ratio was chosen to give a flame temperature of approximately $2500^\circ C$ compared to $3500^\circ C$ for pure O_2 . This run was terminated due to high tuyere pressures. The pressure was basically due to a scull of metal at the tuyere openings. The reduced flame temperature did not have any apparent effect on the location, size, or appearance of the bridge.

The tuyere flooding problem is caused by a pool of liquid metal or slag which collects above the tuyere. This liquid greatly increases the resistance to flow of the O_2 from the tuyere. Several changes were made in run BF13 in an attempt to keep the tuyere open longer. A smaller particle size charge (-4+8 mesh) and a higher gas flow rate of 26 l/m should produce more penetration of the gas into the charge. This larger raceway should keep the liquid product away from the vertically oriented tuyere. This run was shut down when vigorous bubbling at the exit bubbler could only be stopped by reducing the O_2 flow rate to 2 l/m. The agglomerate above the tuyere tip was not solid but contained a passageway through which the O_2 was able to flow. This run did not fail due to tuyere flooding indicating the small charge - high flow rate was successful. Unfortunately, most of the burdens are not -4 +8 mesh so this technique cannot be used for all burdens. The BF13 burden was Koppers briquettes (bauxite, clay, coke) with separately added CaO. A CO_2 - O_2 mixture was used to reduce the flame temperature as in run BF12. Again, there was not apparent effect of the reduced flame temperature. The bridge formed in a typical location in the shaft and there was no metallic product.

Since BF11 had had no apparent bridge, an identical run, BF14 was made. The results were quite similar to BF11. This run was terminated when the bubbling from the exit bubbler

could only be stopped by reducing the O_2 flow rate almost to zero. There was no apparent bridge.² The tuyere was flooded with a deep liquid pool which probably caused the resistance to flow.

Since this burden had shown good burden movement with no apparent bridging, one more attempt was made with a special columnar charging technique. In BF15, the heating coke was charged inside a paper tube directly above the tuyere. The burden of 10% Fe_2O_3 extrudates and CaO was charged in an annular pattern between the paper tube and the liner wall. The paper tube was withdrawn from the reactor in stages as it was filled. The central coke charge should feed the tuyere minimizing the amount of liquid metal formed in the tuyere region.

All previous runs had had a grate level higher than the tuyere. A careful examination of some of the grates and skulls suggested that as the O_2 reacted with the grate, a funnel was formed. This funnel concentrated the liquid that formed into a pool on the tuyere tip that could not flow away from the tuyere. For BF15, the grate was lowered so that the tuyere extended 0.6 cm above the grate. Thus, the solid C of the grate could not act as a miniature crucible to contain the liquid above the tuyere tip.

Unfortunately, this combination of changes did not help the tuyere flooding problem. The tuyere opening was plugged with a piece of metallic rod approximately 2 cm long. A small quantity of liquid metal flowed into the tuyere and froze due to the cooling effect of the tuyere water. This plug was probably responsible for the high tuyere pressure which required shutdown. BF15 was the third time this charge had failed due to tuyere problems.

All previous runs containing CaO were formulated by separate CaO additions. To improve the potential for forming liquid slags, extrusions were made with CaO as part of the agglomerate. Four batches of extrudates designated C-1 to C-4 containing varying levels of CaO, Fe_2O_3 , bauxite, clay, and coke were prepared (see Table 20).² The four batches all had the same $CaO/Al_2O_3/SiO_2$ ratio. Only the quantity of Fe_2O_3 and/or C was changed. Two of the batches were made without any reduction carbon. Finely divided coke in intimate contact with this oxide slag may greatly increase the viscosity of the slag. Removing the coke from the extrudate should increase the probability of these oxides forming a fluid liquid slag at least within each extrudate.

BF16 and BF17 compared the effect of a high CaO, low Fe_2O_3 burden in the absence and presence of reduction carbon. In both runs, a large quantity of liquid slag (perhaps containing some SiC or C) was formed which collected in the reservoir. The solid agglomerate above the tuyere contained an open vertical raceway approximately 3 cm in diameter and 10 cm high. In both runs there was a large quantity of unagglomerated coke on the grate near the wall. This supports the idea that the burden flow pattern is a funnel shape directed at the tuyere where the coke is being consumed. This unreacted wall coke is the "deadman" for this reactor configuration. BF16 had a large void (18 cm), while BF17 had none. Neither bridge was very strong though the bridge in BF16 was 3 cm thick and not supported. There was no void under the BF17 bridge indicating that it may have formed on cooling. There was no burden movement in BF16 whereas there was 10 cm of movement in BF17. The charge in BF17 with reduction carbon moved in a more fluid manner. This should be qualified by the fact that a different heating pattern was used due to difficulties with the induction equipment during BF16. BF17 showed some promise of keeping the burden moving without a void forming under the bridge.

BF18 was essentially a repeat of run BF9 which had good burden movement and good metal production. This burden contained both Fe_2O_3 and CaO along with the bauxite, clay, and coke. No preheat coke was used, and the burden was columnar charged to the grate. Since no preheat coke was used, the reactor was heated to 1800°C with Ar before the O_2 was introduced. Thus the burden was not exposed to an oxidizing environment at temperatures below metal producing temperatures. A large quantity of metal and slag were produced, more than in run BF9. There was no significant pressure buildup; the run was shutdown when approximately 80% of the heating coke should have been consumed. The bridge must have been very weak since it collapsed in the process of removing the liner from the reactor.

Runs BF9 and BF18 with 50% Fe_2O_3 and 20% CaO had produced large quantities of metal. Runs BF11, BF14, and BF15 with 10% Fe_2O_3 and 37% CaO had produced only small quantities of metal. The charge composition for run BF19 was 26% Fe_2O_3 and 26% CaO, intermediate between the other two sets of runs. This burden was charged in a columnar manner to

the grate as in BF18. The run was terminated due to high tuyere pressures and large quantities of O_2 being vented through the mercury bubbler. The metal formed in this run must have been carbon saturated by the time it reached the grate since it did not consume the high surface area carbon felt that was on top of the grate. This felt prevented the metal from dripping into the reservoir. The liquid metal accumulated on the grate until it flooded the tuyere. There was only a small amount of burden movement indicating a bridge formed. However, upon removing the crucible, the charge dropped out of the reactor. Once again the bridge was very weak.

The above series of runs indicate that the burdens with high CaO form thin weak bridges. Therefore, if difficulties are encountered in mechanically breaking strong Al_2O_3 or SiC bridges, then CaO containing charges might be investigated to weaken the bridge.

In the third quarter, the bottom entry oxygen tuyere was replaced by a side entry assembly in the BF reactor to eliminate the problem of tuyere plugging and/or flooding. Ten runs were made in the revised unit. Burden composition, operating conditions, and results are shown in Tables 21, 22, and 23. The first two runs (BF20 and BF21) were shakedown runs with coke to see if the burden would move with just coke. Run 20 used -4 +8 mesh enid coke. The oxygen flow was 13 L/m initially and 26 L/m for the last 20 minutes. The run was shut down since there was no burden movement. There was no definite sign of a bridge. Only the two graphite rods in the grate directly in front of the tuyere were consumed. Several rods on the periphery showed some oxidation.

Run BF21 used -3/8 +4 mesh metallurgical coke. The oxygen flow rate was 13 L/m initially and 26 L/m for the last 45 minutes. This run was also shut down since there was no burden movement. There was a bridge roughly 20 cm above the tuyere. Only a small amount of coke was still on the grate. The grate pegs were consumed almost to the opposite wall in a rising pattern as the wall was approached. The apparent large raceway may have been due to the small amount of coke, i.e. there was no coke head to resist the growth of the raceway. Thus, the raceway spread, oxidized and consumed the pegs on the far side of the grate.

The burden used in BF11, BF14, and BF15 had shown signs of movement without bridging. The runs were shut down due to back pressure probably related to tuyere flooding. Since

tuyere flooding should be reduced with a side entry tuyere, this same burden was used again in BF22. BF22 was similarly shut down due to back pressure which must have been from the bridge since there was no tuyere flooding. Though this charge had not bridged in BF11 and BF14, there was a strong thick bridge only 10 cm above the tuyere in BF22. The reservoir product consisted of an FeSi metallic phase and a $\text{CaO-Al}_2\text{O}_3$ slag phase.

The charging procedure used in the VSR reactor produces alternating layers of extrudates and coke. BF23 was layered charged with 10% Fe_2O_3 extrudates and metallurgical coke. The metallic product formed in an ore layer might have a better chance of coalescing and dripping through the coke bed than metallic product formed from separate extrudates. This was one of the shortest runs, however. The back pressure gauge tacked off scale after only 14 minutes. The charge had agglomerated against the wall. No product was found in the reservoir, though there was some metallic mixed with coke above the grate.

One possible method to eliminate the bridging problem is to spread out the condensation zone. This should reduce the chances of forming a thick strong bridge that stops burden movement. In BF24, the coil was lengthened to try to increase the temperature in the bridging zone. The spread coil had the desired effect on the gradient: it increased the temperature 1000°C (from 700°C to 1700°C) at a point 23 cm above the tuyere. The bridge location was moved up to a much higher location than in previous runs. It was still a strong bridge of relatively short height indicating the condensation was still occurring over a short vertical distance. During the run, the high pressure dropped once abruptly before climbing a second time. Upon disassembling the reactor, the liner was separated at its midpoint seam. The bridge above the seam had caused the pressure to build up sufficiently to make the liner separate as a pressure relief. The final back pressure was caused by liquid metal on the grate that flooded the side entry tuyere. Some metallic product had drained to the tuyere but there were a lot of metallic globules dispersed through the coke.

Coked ore is a new agglomeration material made specifically for this process. Coked ore was tested in run BF6 but the results were inconclusive. A second attempt, BF25, was made with several changes: smaller preheat coke weight, larger coked ore size, and a side entry tuyere. Fuming near the

tuyere caused an early shutdown of the run. This was apparently due to bake out of the BN or cement, not oxygen attack of the liner. Upon disassembling, the burden dropped indicating no bridge formation. Since reaction temperature had not been attained, this was not a good test of the coked ore.

Run BF26 had a dual purpose: 1) to see if larger briquettes and coke could be run without bridging and 2) to provide large samples that could be sectioned to study the microscopic signs of any reactions that occur. Larger particles should have fewer contacting points and hopefully fewer condensation sites. The condensate that does form may not be enough to support the larger particles. The larger briquettes also allowed discrete samples to be removed as a function of temperature. These large samples can be sectioned and examined to see at what temperature signs of reduction are obvious. BF26 formed two bridges, an upper bridge of solid green-white condensate and a lower mechanical bridge. The condensate coated the charge, completely bridging across the contact points between discrete particles. The lower bridge again confirms the problem of mechanical bridging of large particles in a small diameter reactor.

Two runs, BF27 and BF28 were made with activated charcoal of small particle size (-4+6 mesh) at different oxygen flow rates. BF27 at 26 L/m oxygen produced a large void (56 cm) though a bridge did exist at the top of the void. Only 5 cm of coke were found above the tuyere. The run was terminated due to smoke at the sight port opposite the tuyere. BF28 was similar to BF27 except the oxygen flow rate was 48 L/m. A high bridge was again formed, though this bridge was impermeable to gas flow causing a back pressure buildup requiring shutdown. These flow rate-particle size combinations have produced burden movement in the VSR reactor. The difference may be the low temperatures at the top of the BF reactor which cause a much higher percentage of the volatiles to condense. In the VSR these same volatiles exit the reactor due to the high top temperature of the reactor.

Another approach for solving the BF start-up problems is to charge prereduced charge to the lower hotter part of the reactor. The L reactor was used in two separate runs to produce "Stage I" product at 1700°C and "Stage II" product at 1850°C. These materials were mixed with the appropriate amounts of coke and charged as a function of height in the BF reactor. The top was filled with unreacted material.

This charge bridged very early and very low in the reactor. The oxygen then penetrated across the reactor, burned through the graphite liner and graphite insulation, and melted the inner surface of the ceramic outer liner. The prereduced "Stage II" material apparently reacted somewhat with the added coke and formed a bridge. Prereduction does not appear to be a viable start-up technique.

In the fourth quarter, a BF bench reactor with a series of pressure taps was built and operated to determine the location and time relationships of bridging formation by monitoring the pressure profile during operation. Two runs were made. Burden, operating conditions, and results for runs BF-30 and 31 are listed in Tables 24, 25, and 26. Pressure vs time plots for the five pressure tap locations are shown in Figures 24 and 25. As expected, the pressure decreased toward the top of the reactor. In run 30, the pressures at the tuyere, 80 cm and 70 cm down increased rapidly at 120 minutes; whereas the 60 cm and 50 cm pressures remained low. The run autopsy indicated a bridge at 62 cm down.

In run BF31 the burden was 10% Fe_2O_3 extrudates with stoichiometric carbon, but the ore to heating coke ratio was 3/1 rather than the normal 1/1 ratio to determine the effect on metal yield. A significant quantity of metallic product (67 g) was collected in the reservoir. This was the first reservoir product made with a relatively low iron charge in the oxidizing conditions of the BF reactor. The metallic product in most previous runs froze in front of the tuyere. Only runs with high Fe_2O_3 or CaO additions had produced metal that flowed to the reservoir. This run definitely proves that metallic product can be produced and separated from the burden in an environment that contains both excess heating coke and oxygen.

The pressure profile data for BF31 was not as straightforward as for run BF30. The start of a bridge was indicated at 80 minutes. The O_2 flow was off between 80 and 120 minutes. From 120 to 150 minutes the pressures were erratic. Ultimately, the bridge was found at 67 cm down. The pressure data does not provide a reliable indication of when or where the bridge forms.

In the fifth quarter, a graphite auger was developed for the bench reactor to mechanically eliminate bridging. The auger for the AF (auger feed) unit was a continuous two-flute

design. Prior to use at temperature, the auger operating characteristics were determined by cold modeling in a Plexiglas tube with the same diameter as the reactor liner.

The effect of charge depth on auger rotation speed was determined first. In Table 27, the bottom of the auger is zero depth. As charge was added incrementally, the time for one revolution was monitored. For both one and three rpm, the time per revolution increased as the level of the charge increased. This change was much larger (29%) at one rpm than at three rpm (9%). The change in the auger speed at a constant motor setting should permit the load on the auger to be monitored continuously. This may be indicative of bridging or liquid formation on the auger.

The tests described above were made by filling the Plexiglas tube with the auger running. If the auger was intentionally stopped, it could be restarted without any problem. However, if the Plexiglas tube was filled with the auger off, the auger could not be started. Instead, the shear pin would break.

A test was also made to check the effect of reversing the auger. The normal direction of rotation is to lift burden upwards. Reversing the auger forces the burden down. Upon reversing the auger, the burden dropped two cm. The auger could not be restarted since the shear pin broke.

Visual examination of coke particles mixed with the burden indicated that a large amount of mixing occurred behind the auger flute as it rotated. This mixing included some movement in the radial direction though most of the particle movement is in the axial direction. Vertical movement of the charge upwards may be a problem in the AF reactor.

Six runs were made in the AF (auger feed) reactor. The quartz shell and graphite susceptor are the same sizes as those in the BF (blast furnace) reactor, 23 cm O.D., 19 cm I.D., 122 cm high and 14 cm O.D., 10 cm. I.D., 112 cm high respectively. The auger is 91 cm long, 7.6 cm O.D., with a 3.2 cm shaft. The feed system consists of two hoppers and ball valves to permit continuous feeding of charge. Three vertical holes in the wall of the susceptor permit CO to be introduced inside the susceptor and crucible just below the grate. By passing to CO down the walls of the susceptor, it should be adequately preheated when it enters the reaction zone.

Tables 28, 29, and 30 contain the burden, operating variable, and results data for the AF-runs. Runs AF-1, 2, and 3 failed due to problems in the external motor and gear box system used to drive the auger.

Run AF-4 was the first run in which reaction temperature was attained and significant amounts of charge were fed. The reactor was above 2270 K (2000°C) for 65 minutes. The auger slowed down over the course of the run from 3.1 to 2.2 rpm. The run was again terminated due to a shear pin breaking. The auger was stopped by a massive deposit of roughly 10 cm thickness on its bottom. This material was definitely liquid at temperature, indicating that the auger was too deep in the reactor or that the hot zone was too high.

The metallic product weighed 371 g which is only a 19% yield of the material that made it to the hot zone. A large part of the rest could be found in the bridge, on the walls and in the CO purge holes. This low yield is partly due to the worst case assumptions made to perform the yield calculation. The weight of the remaining loose charge is subtracted from the initial charge weight to obtain a reacted charge weight. The theoretical metallic weight is calculated from this. The yield is the actual metallic product weight divided by the theoretical metallic weight. No credit is taken for the above grate or bridge materials, nor is the reacted charge weight reduced by the above grate or bridge weights. In addition, the loose charge in the reactor may have reacted partially, thus perturbing the reacted charge weight even higher. More accurate yield figures will require elemental analyses of samples from all parts of the reactor.

In AF-5 several changes were made to correct the problems of AF-4. The hot zone was dropped to reduce the temperature at the bottom of the auger so that the auger would be breaking solid bridges, not stirring a liquid-solid paste. Finally, graphite rods were placed above the grate to support the burden.

The reactor was above 2273K (2000°C) for 219 min (AF-4 = 65 min) yet much less ore was charged (AF-4 = 7860g and AF-5 = 6000g). AF-5 was much hotter than AF-4, yet the reaction appeared to proceed much slower. Apparently a bridge formed early beneath the auger and prevented charge from reaching the hot zone. The auger ground a large amount of the loose charge into dust. As this dust packed around the auger, the auger slowed and eventually broke a shear pin. The graphite rods prevented any loose charge from falling into the reservoir and only reacted to a limited extent. The

metallic product weighed 315 g which was a 25% yield of the material that made it to the hot zone.

Since AF-4 had bridged on the auger and AF-5 had bridged under the auger, the coil was moved up for AF-6 to a point midway between AF-4 and AF-5. This did not have the desired effect since the bridge again formed under the auger. There are two possible explanations for the concentration of the condensation at the bottom of the auger. First, the induction coil ends here and the temperature profile drops abruptly. The volatile back reactions may be occurring over a very short height causing a bridge. Extending the coil higher vertically with a few widely spaced turns may spread the temperature profile, spread the condensation zone, and permit the auger to break solid bridges. However, if the hot zone is raised, the problem of AF-4 (liquid bridge on the auger) may return.

A second explanation for the condensation at the end of the auger could be the auger itself. With its high thermal conductivity, the auger may be acting as a heat sink. It would thus be an ideal location for the exothermic back reactions to occur. This may also be solved by extending the coil since this would probably minimize the temperature difference between the end of the auger and the surrounding charge.

AF-6 ran for 170 min above 2273 K (2000°C). A diligent effort was made to keep the hot zone temperature below 2373 K (2100°C). Towards the end of the run, the auger again ground alot of the charge to dust. The run was terminated when the auger motor stalled. The metallic product weighed 850 g which is a 49% yield of the material that reached the hot zone. This apparently much higher yield must be tempered by the knowledge that part (2770 g) of the charge was previously used in AF-5 and thus may have been prereduced.

Task completion is 100%.

Task No. 11: Evaluate Materials of Construction

The construction and operation of the BF bench reactor involved testing of various materials that were also used in the pilot VSR unit. A special castable ceramic and cement used as the outer shell held up well. However, the

ceramic was permeable and allowed CO to leak in the VSR. Horizontal sight ports located at various levels along the reactor axis to optically measure temperatures were difficult to keep intact. Super 3000, carbon, SiC, and BN cements were tested. The most successful assembly was a BN tube cemented to the ceramic shell with BN cement. The internal extension of the port tubes from the shell to the graphite liner used several materials. The top port at relatively low temperature had a closed-end alumina tube. The second port had an open-end zirconia tube. The third port at the hot zone had an alumina tube mechanically joined to a graphite tube where the graphite was against the graphite liner. The second and third ports were usually measured with an optical pyrometer, and argon gas was used to keep the tube clear.

Zirconia components were tested as protective sheaths for the BF reactor oxygen tuyere. The material held up in areas where it was partially cooled, but failed in direct contact with combusted coke and molten metals.

Quartz shells for the VSR reactor were gastight but did develop cracks. Two potential substitute materials were tested. Transite pipe failed in the drying out stage. Fireclay pipe also failed during the initial heat-up. Subsequent computer heat transfer calculations verified that transite could not be used and fireclay was limited for the VSR sized reactor due to a deficiency in insulation.

Task completion is 100%.

Task No. 12: Evaluate Alternative Heating Processes

Although it is desirable to supply process reaction heat by combustion of carbonaceous materials, the metal producing zone must be carefully controlled to maintain a proper balance between carbon burned and carbon in contact with alloy product to avoid carbide formation and attack of the carbon refractory reactor lining. Burning of coke charged into the top of the furnace may be difficult to control accurately. Therefore, a char-oxygen injection system was designed for VSR-1 by Koppers Company as an alternative approach to supplying heat by combustion while providing better control. The char system could be incorporated at the normal tuyere level as well as at other locations up the shaft. Details of the design are included in Appendix 2.

In addition to process control, the use of char improves process economics by eliminating costly metallurgical coke. However, the use of cold char results in increased total carbon consumption and CO sweep, which could offset the economic gains and decrease product yield. Therefore, calculations were made to evaluate the effects of preheating char and oxygen. Results of the study indicated that both the char and O_2 must be preheated to $1000^\circ C$ to maintain carbon consumption and CO sweep at the level of the base case-combustion of metallurgical coke preheated to $2100^\circ C$ with ambient temperature oxygen. Preheating of O_2 to high temperatures is not done routinely. However, it is known that O_2 is preheated to $1000^\circ C$ in a process for making pigment grade TiO_2 from $TiCl_4$, and that O_2 can potentially be heated to over $2000^\circ C$ in a plasma arc heater. As the O_2 preheat temperature increases, the quantity of heating coke decreases. The correlation is shown in Table 31. The detailed report is included in Appendix 3.

Task completion is 100%.

Task No. 13: Modify VSR Design

In the second quarter, the VSR-1 reactor shell developed vertical cracks, each about 55 in. long, above the North and South tuyeres. These cracks were probably initiated when cracked fused silica tuyere tubes were removed. The cracks propagated when the reactor was heated and pressurized. High temperature epoxy and fiberglass tape were used to seal the cracks but these patches last only one to three runs. Another fused silica upper shell was ordered. One major change in the new shell was the entry of the tuyeres to a level 20 inches higher than the first shell to permit one coil section to be placed below the tuyere level.

A steep temperature gradient existed below the tuyeres due to the conduction of heat down the graphite susceptor. The water-cooled tuyeres were also heat sinks. This heat loss made it more difficult to achieve high temperatures in the combustion zone and, especially, made it difficult to coalesce and separate alloy at the grate level. The precipitation of carbides as the alloy cools is likely to increase the alloy's viscosity and aggravate the problem. A coil below the tuyeres should solve the heat loss problem and keep the alloy fluid.

Another problem with the three coil induction system was the inability to put full rated power (50 kW) into the coil just above the tuyeres. Only about 27 kW could be

fed to this coil by itself, yet, when the middle coil was turned on at its lowest setting, full power could be fed to the bottom coil. This was thought to be related to an improvement in efficiency due to larger height-to-diameter ratio of the total inductor when two coils were used. Since the coil below the tuyeres is likely to be on at all times in the new configuration, the coil above the tuyeres should have full power capability even if the top coil is off. This should improve the flexibility of the heating system.

A third problem was associated with the low bed heights which were being run. With a 30-in. bed height, the top of the bed was 54 inches below the reactor top. This made it difficult to extend probes and mechanical devices into the bed from above. In the new reactor this distance was shortened by 20 inches. Two separately-controllable induction heated zones and an 18-in. preheat zone provided an available reactor height of 60 inches. This new reactor, designated VSR-2, was modified in the third quarter.

In the third quarter, it was attempted to offset the "cold" hearth zone below the bottom induction coil by making temporary modifications to VSR-1 until the new quartz shell was delivered to facilitate the planned changes for VSR-2. An initial attempt to heat the reactor bottom was made by placing half of the coil section below the split flange. A full length coil section would not fit. The half coil section did not effectively heat the lower end of the susceptor even though considerable voltage was applied to the coil. Apparently, the small length-to-diameter ratio of the coil and the proximity of the steel (ferromagnetic) reactor bottom contributed to the poor efficiency.

At this point an attempt to seal the cracked quartz shell of VSR-1 with a special high temperature epoxy (Cotronics 700) resulted in severe spalling of the quartz, apparently due to contraction of the epoxy during curing. It was determined that that shell was unsuitable for further runs so a search for a readily available quartz substitute commenced. Five candidate construction materials were considered: Transite, clay pipe, glass reinforced cement, glazed R-680 ceramic, and aluminum.

Two 6.5 ft lengths of Transite pipe, 18.72 in. O.D., 16 in. I.D., were obtained, one with tuyere holes and one without.

The pipes were heated to about 500°F over several days in order to drive off excess water and test the pipes at approximately operating temperature. The pipe without holes explosively spalled in the furnace. This indicated unpredictable behavior since Transite is rated at 600°F. Furthermore, steady-state heat transfer calculations indicated that the inside of the Transite would exceed 600°F in service. Transite was therefore rejected as a possible material.

A clay pipe, 18.5 in.O.D. x 15 in.I.D., was used to construct the initial version of VSR-2. During the first heat-up attempt, the shell cracked. Thermal stresses in the thick wall evidently exceeded the fracture strength of the fired clay. Although the clay pipe might have survived a slower heat-up, the probability of eventual failure led to a rejection of clay.

The initial version of VSR-1 showed that R-680 ceramic was very good structurally, but was highly permeable. Ceramic Section attempted to reduce the permeability by glazing the material. Although the results were encouraging, the permeability of material was still high due to the presence of uncoated pores and overall crazing.

Glass reinforced cement is a transite-like material in which asbestos fibers are replaced by glass fibers. Factory representatives indicated that a pipe could be made but price and delivery information was unavailable. Temperature limitations were the same as Transite. Therefore, the material was not ordered.

Calculations run by Ajax Magnethermic Corporation, the supplier of the VSR induction system, indicated that an aluminum shell with a diameter of 40 in. to 60 in. could be used to enclose the present coil. Power losses would range from 1-6 kW, decreasing as diameter increases.

The microcomputer-based charging system was further developed. The computer can charge layers of ore and coke when a level probe switch indicates that the level is below the set point. Each minute the cumulative number of ores and cokes is printed on a terminal along with the number of five sec. intervals in which O₂ flow was on. The computer shuts the oxygen off for 20 sec's. every five minutes and also monitors the manual O₂ switch. Intervals and other parameters can be

updated through the terminal keyboard during the run. Programs to handle these functions were written.

In order to prevent chemical bridging from terminating a VSR run, an auger was developed to keep the burden in a continual gentle motion in the bridge forming zones of the furnace. Two augers were tested in a Plexiglas shaft model to observe many design and operating parameters. The second of these augers was tested twice in the crucible pilot reactor while burning metallurgical coke with oxygen. The ash in the coke supplied the condensate suboxides that cause chemical bridging. Both of these runs were very successful in preventing bridge formation in the bed where the auger was located. It was found that the auger must span the entire bridge formation zone to be completely effective. The auger also acted as a high heat conduction path and a channel for the rising gases.

Based on this information, an auger was built for the VSR-3 reactor. The new auger assembly was multi-sectioned with a break in the spiral flutes between each section to prevent the gas from channeling up the face of one continuous flute as occurred in the previous crucible reactor tests. Also, a lower conductivity carbon spacer was placed in between each graphite section to decrease the heat conduction up the auger assembly. The new auger was long enough to stir the bed beginning 15 in. above the tuyere up to the top of the bed.

In the fourth quarter VSR-2 (new quartz shell plus full coil below the tuyeres at the hearth) was further modified to include installation of the auger, an improved liner/grate assembly and better sealing of tuyere ports at the quartz shell. The unit was designated VSR-3.

In run VSR-3-12 a five section auger was used while in runs -13 through -17 a four section auger was used. The use of multiple sections simplified removal of the auger after a run and permitted a variable angle between adjacent auger sections. The combination of spacer and angle between sections provided a break in solid and gas flow over the auger in order to minimize channeling. The auger was driven by an air motor through a 600:1 gear reducer and right angle drive. The auger was rotated at about 1.1 rpm in a direction which lifted the bed.

The auger broke during runs VSR-3-12, -14, -16, and -17. In run -12, the break occurred between the upper two and

lower three sections. In the other three runs, the break occurred at the joint above the top section. To strengthen the auger, the original carbon spacers were replaced by Graphitite spacers. To minimize stress, rotation of the auger was started before any charge material was fed around the auger.

It was also attempted to strengthen the top joint where the shaft connected to the auger assembly. This top joint was the weak link, and a new auger has been designed to eliminate this critical joint and if at all possible, all joints. In order to achieve a continuous steady-state refluxing system for the bench scale program, a similar auger design was developed for a 4-in. dia bench scale reactor.

During run VSR-3-13, extensive metal leakage around the product crucible and attack of the susceptor made it necessary to break the susceptor in order to remove the product. In order to obtain longer susceptor life, a one-piece grate and sacrificial liner 44 cm (17.5 in.) high was fabricated for each run. Previously, a separate grate and 13 cm (5 in.) liner were used.

Sealing of the tuyere entry and sight tube ports to the quartz shell was improved by fabricating close fitting waterjacketed assemblies which were sealed with a thin layer of RTV silicone. The purpose of the water cooling was to maintain the sealing properties of the RTV when the quartz shell temperatures exceeded the level at which uncooled RTV fails.

Problems with the induction heating equipment continued during the quarter. Since all runs were heated by induction it was necessary to obtain maximum heat input. During runs VSR-3-12 through -15, about 60 kW was available when the system was hot. During runs VSR-3-16 and -17 more power was available. In these later runs, an Airco-Speer graphite susceptor was used instead of the usual Union Carbide susceptors. Whether the improvement was due strictly to the change in graphite is uncertain. In all cases, power was limited by current overload.

In the last quarter of Phase B, a new tuyere seal was designed and implemented, consisting of a water-cooled "donut" which fits flush on the quartz shell to facilitate unrestricted positioning of the induction coil sections. In particular, the middle and lower coils were moved closer

together and the tuyeres were inserted between coil turns. Due to the high heat loss associated with the water-cooled tuyeres and injection of cold O_2 , it was desired to operate with a high power input to the tuyere zone.

In order to obtain significant alloy yield in the combustion heated reactor, it was planned to improve the reactor thermal profile and minimize recarbiding of metal produced. Also, burden size and distribution was selected to prevent flooding in the prereduction zone. These effects are discussed below.

1. Improve the thermal profile.

In a combustion heated reactor, the combustion zones surrounding the raceways are the sources of heat. The maximum induction heat input in the VSR reactor is supplied in the middle of coil B which is about 28 cm above the tuyeres. Temperature measurements made just above the tuyeres and through the tuyeres range generally from 1900-2000°C while the temperature in the middle of coil B is generally greater than 2100°C. Thus, alloy product would tend to form well above the tuyeres and would be required to drip a considerable distance through excess carbon at an elevated temperature. This configuration encouraged carbiding and vaporization. The zone of maximum induction heat should be brought into coincidence with the combustion heated zone. This can be accomplished by lowering coil B; constructing the tuyere zone from a higher resistivity graphite which suscepts more efficiently than that used in the middle of coil B; reducing the heat loss to the tuyeres; and increasing the input of combustion heat by blowing more oxygen.

The option to lower coil B is now available since flush tuyere seals have been installed. Stackpole 2020 graphite which has twice the resistivity (at room temperature) of typical extruded graphite might be used to modify the thermal profile. The use of carbon rather than graphite may also be effective. Heat loss to the tuyere has been measured and attempts to reduce the loss by insulation of the tuyeres with carbon have been made. Heat loss was found to be roughly proportional to O_2 flow in four runs where carbon bushings were installed around the tuyeres. When the O_2 was turned on, the water temperature increased by 1.4°F @ 40 CFH/tuyere and 3.0°F @ 80 CFH/tuyere. The overall temperature rise was 4.8°F @ 40 CFH and 9.0°F @ 80 CFH. This increased water temperature reflects the higher tuyere temperatures at the higher O_2 flows. However, the

net high temperature heat input calculated as the heat generated by combustion above 2000°C less the heat lost to the water is only slightly positive, being about 0.9 kW at 40 CFH x 3 tuyeres and 2.7 kW at 80 CFH x 3 tuyeres. In order to make substantial gains in the tuyere heat balance, more efficient insulation must be used and more than 80 CFH O₂ per tuyere must be blown.

A higher O₂ blowing rate requires a larger tuyere in order to maintain the same raceway size.* The tuyere used thus far consists of a diverging nozzle which tapers from 4.6 mm (0.18 in.) to 9.5 mm (0.375 in.). A new tuyere which was designed by Koppers Company has a straight 10.2 mm (0.4 in.) nozzle (Figure 26). Although the outlet of the new tuyere is only slightly larger than the old one, the old tuyere did not have well developed flow due to the taper and probably behaved like a tuyere smaller than 9.5 mm. The new tuyere can be bored out to between 11.4 mm (0.45 in.) and 12.7 mm (0.50 in.) if required. The larger tuyere will permit larger coke to be used and this will allow still more O₂ to be blown.

2. Burden size and distribution

In run VSR-3-21, alloy product seemed to drain through a layer of large graphite cylinders (1/2 in x 3/4 in) and SiC chips, but was held up by layers of smaller coke. No evidence of product was found when the ore and excess coke were intimately mixed. This run suggests three possibilities for improving yield: larger coke, SiC deadman, and layer charging. Drainage of product through various beds is imperfectly understood, but the alloy does appear to be very fluid and to wet graphite. Wetting may influence the rate of carburizing since contact between the alloy and carbon surface is maximized. Carburizing might be minimized by reducing the available surface area of the excess carbon. This implies larger, smoother coke with narrow size distribution so that the bed is very permeable. In the next series of runs, the coke size will be increased from -1/4 in.+6 mesh to -3/8 +4 mesh. The use of still larger coke may be possible due to the small diameter of the reactor, 6-5/8 in. at the tuyeres.

* $D_R \sim W_{O_2} / (D_T \sqrt{D_p})$ where W_{O_2} is O₂ flow rate, D_T is tuyere diameter and D_p is coke particle diameter.

According to the equilibrium phase diagram SiC should be less reactive with alloy product than coke so the use of SiC may be beneficial in the deadman, a conical zone of stagnant solids through which liquid drains. The wetting behavior of SiC and the possibility that SiC layers develop on the coke need further investigation. A preformed SiC deadman is an option for future runs.

In run VSR-3-21, layers of ore placed between layers of coke reacted to alloy product which infiltrated the coke layers and converted almost completely to carbides. This represents evidence that alloy can form and coalesce in a local environment of stoichiometric carbon even though excess carbon is nearby. The problem lies in draining the metal faster than carbides can form. In the present VSR reactor, the use of the auger causes vertical mixing which breaks up separate layers. While the auger is ideal for induction heated runs, it may be a disadvantage in combustion heated runs. In runs VSR-3-8, 9, and 11, layers were charged and bed movement was maintained by "slipping" the furnace, i.e. turning the O_2 off for 10-20 seconds every five minutes, and using a level probe to poke the top of the bed. Eventually, the burden did "hang" but success was achieved for a time. This offers the possibility that a combination of means might be as effective as the auger.

Means to aid burden movement include:

1. Use a tapered section in the bridge zone. This could be done by installing a 30.5 cm (1 ft) high section with a 17 cm/m (2 in/ft) taper between the present susceptor in the bosh and a 15 cm (6 in) x 10 cm (7.5 in) graphite pipe in the stack. The tapered section would be centered at the bottom of the present auger.
2. Use a low bed extending no higher than the top of the top coil. This will prevent bridging above the tapered section, by causing some vapors to blow out as a fume.
3. Use the pneumatic level probe as a poker. Three could be installed to provide more uniform poking.
4. Slip the furnace on a regular cycle. This technique should be more effective above the taper since the higher velocity through the smaller cross section will result in larger aerodynamic forces.

5. Development of a rotating wall design of the type used in arc furnaces. Rabble arms are another possibility.

Models of the solids flow of a layered charge should be tested to be sure that the layers do not mix and to aid in optimizing layer thickness and reactor profile.

Calculations have indicated that carbon/graphite felt layers in insulation in VSR-3 should preferentially heat relative to the graphite susceptor. This is due to the combination of geometric factors and high frequency (10 KHz) and should not be a problem in the smaller AF bench reactor or in a larger reactor. Typically, the walls of the optical pyrometer sight tubes are observed to be much hotter than the susceptor during the early part of a run. This felt heating behavior may be minimized by using outer wraps of Fiberfrax ceramic blanket, providing breaks in the carbon/graphite felt blanket, using a slower heating to avoid overheating the Fiberfrax and using a higher resistivity graphite in the susceptor.

In the fifth quarter, a mechanically driven auger was used in almost every run. The original auger containing four 6-in fluted sections was used successfully in VSR-3-18 and 19. During VSR-3-23, a continuous fluted auger with no joints was tested. Later, slots were cut in the flutes of this auger to limit the upward transport of the burden in the auger. The auger itself did not fail, but the shear pin in the coupling continually broke under the load of bridging. Changing of the position and rotational speed of the auger in itself did not sufficiently change the loads on the auger and thus prevent the shear pin from breaking. Once a shear pin failed during a run, the auger could not be restarted. Details of auger performance are shown in Table 13.

Task completion is 100%.

Task No. 14: VSR Design Modification Construction

Most of the design modifications implemented in Phase B were discussed under Task No. 13 and involved the VSR shell, liner, tuyeres, induction heating system, auger, and microcomputer control system. In order to improve data collection during runs, some renewed effort has been expended on the microcomputer data acquisition and control system and instrumentation. A 16-channel multiplier

was added to the digital voltmeter. Presently eight signals can be read and printed on the terminal every minute. Instrumentation which will be connected to the system include:

(3) B.K. Precision Temperature probes for tuyere water temperatures

Pyro automatic pyrometer for coil B middle temperature

Land optical thermometer for above-tuyere temperature

Setra differential pressure transducer for off gas flow measurement

Unimeasure pressure transducer for tuyere O₂ pressure

Lyra gas analyzer for off gas CO

All of the above can be read directly with the digital voltmeter although improved accuracy will result from scaling the signals with operational amplifiers. An op-amp board will be added during the next quarter.

The control system will operate the ore and coke feeders and the O₂ valve while monitoring the panel-mounted O₂ switch. The charging system will charge a sequence of n ores and m cokes with an adjustable valve cycle time whenever the charging switch is closed. The accumulated number of ores and cokes will be printed each minute. The O₂ can be shut off according to an adjustable off-on cycle by the computer. The accumulated O₂-on time is printed each minute.

Task completion is 100%.

Task No. 15: Develop Ore Beneficiation Methods

This task was considered premature to the project objectives for the current phase and will be deferred to Phase C.

Task completion is 0%.

Task No. 16: Supportive Phase Identification

Optical data was developed to facilitate identification of

the following phases by microscopic techniques:

Si	$\beta\text{-FeSiAl}_5$
Al	$\alpha\text{-FeSi}_2\text{Al}_4$
SiC	$\text{Si}_7\text{Ti}_4\text{Al}$, $\text{Si}_8\text{Ti}_4\text{Al}$

The microscopic analysis provides phase composition, model composition (proportion of each phase present) and textural variations.

In the fourth quarter, metal samples from pilot run VSR-3-13 were examined by optical microscopy and electron microprobe. Major phases present (>10 volume %) were FeSi_2Al_4 , Al-Si eutectic, and SiC; minor phases (3-10 volume %) were FeSiAl_5 and $\text{Ti}_2\text{Fe}_2\text{Si}_3\text{Al}_3$ (approximate formula); traces of FeSiAl_3 , Si, and CaSi_2Al_2 were also detected. Textural relationships indicated that $\text{Ti}_2\text{Fe}_2\text{Si}_3\text{Al}_3$ and CaSi_2Al_2 were the first phases to crystallize. The initial Fe-Al or Fe-Si-Al phase to crystallize could not be determined. However, the following solid-liquid reaction relationships were observed in the samples, listed in order of decreasing temperature:

- (1) $\text{Liquid} + \text{FeSiAl}_3 \rightarrow \text{FeSi}_2\text{Al}_4 + \text{FeSiAl}_5$
- (2) $\text{Liquid} + \text{FeSi}_2\text{Al}_4 \rightarrow \text{FeSiAl}_5 + \text{Si}$
- (3) $\text{Liquid} \rightarrow \text{FeSiAl}_5 + \text{Si} + \text{Al}$

Reaction (1) progressed almost to completion, leaving only traces of FeSiAl_3 in the metal. Reaction (2) has been quenched, resulting in large crystals of FeSi_2Al_4 with reaction rims of FeSiAl_5 .

Samples VSR-3-13 (1), VSR-3-13 (2), and VSR-3-13 (3) were taken from the base, middle, and top, respectively, of the metal ingot formed in the reservoir. VSR-3-13 (4) and VSR-3-13 (6) are samples of icicles formed in the susceptor area beneath the reservoir. VSR-3-13 (5) is a sample of metal frozen between the reservoir wall and the graphite reactor lining.

Modal compositions of four samples are listed in Table 32. With the exception of CaSi_2Al_2 , the same phases were found in all samples. However, the heterogeneity of these samples makes the modal analysis useful only for showing trends in phase composition; the actual phase compositions may vary locally by 20-30% of the amount present.

Sample (2) contained abundant void space between the metal grains, whereas samples (1) and (3) contained only scattered shrinkage cracks. Peritectic reaction relationships can be identified from textural relationships. The major phase, FeSi_2Al_4 , occasionally contained rounded cores of FeSiAl_3 (especially in sample (2)), and reaction rims of FeSiAl_5 which penetrate the larger crystals along cracks. Al-Si eutectic occurred in the interstices between earlier formed crystals.

A phase approximating $\text{Ti}_2\text{Fe}_2\text{Si}_3\text{Al}_3$ in composition was found in all samples. This phase tends to form regular hexagonal crystals. The development of regular crystals faces indicated that this phase was one of the first to crystallize.

SiC occurred as needles in polished section, although the grains were probably flakes in the third dimension. The individual crystals usually occurred in groups with an hour-glass shape, with Al-Si eutectic occurring between the SiC needles. Microprobe analysis indicated that, whereas most of the grains were pure SiC , others also contained some Ti and Al. Optical examination showed the presence of small amounts of other unidentified carbides intergrown with the SiC . The carbides were erratic in abundance, being more abundant adjacent to the graphite walls.

In the fifth quarter, samples were analyzed from runs VSR-3-15, 17, 18, and 19. Samples VSR-3-15 (1), VSR-3-15 (2), VSR-3-15 (3), and VSR-3-15 (4) were taken from the top, upper middle, lower middle, and bottom, respectively, of the metal ingot formed in the reactor reservoir. These samples represent a vertical section through the outer edge of the ingot, whereas the samples from VSR-3-13 represent a vertical section near the center of that ingot. Modal compositions of the four samples are listed in Table 33.

A polycrystalline slag of unknown composition was associated with SiC in the ingot, and was concentrated in large, continuous masses along the ingot periphery.

SiC also occurred within the metal as radiating clusters of tabular crystals, usually accompanied by interstitial Si-Al eutectic. The Si-Al eutectic was interstitial to all other phases, except for occasional semi-spherical "droplets" extending into the slag.

As in VSR-3-13, $Ti_2Fe_2Si_3Al_3$ crystallized at high temperature, forming large crystals with well developed crystal faces. Some grains had rounded inclusions of Si-Al eutectic, but inclusions of other phases were rare. The slight concentration of $Ti_2Fe_2Si_3Al_3$ at the base of the ingot, and its depletion at the top, suggested accumulation by settling through the liquid metal.

$FeSiAl_3$ occurred as rounded grains within $FeSi_2Al_4$; both phases were approximately equal in abundance. The degree of reaction between these two phases varied from grain to grain. No $FeSiAl_5$ occurred in any of these samples. The peritectic reaction forming $FeSiAl_5$ by reaction of liquid with higher temperature phases may have been limited by the availability of low-melting Si-Al liquid. This relationship was also suggested by the data from VSR-3-15 (2), which had the highest ratio of $FeSiAl_3:FeSi_2Al_4$ (1.32) and the lowest Si-Al content (10.8%) of any of the samples. The presence of a small amount of intergranular porosity in this sample indicated that some of the low-melting liquid drained through the previously formed crystals into the base of the ingot, decreasing the amount of Si-Al eutectic remaining in sample (2) and freezing the higher temperature phases, relative to the other samples, by removing a reactant phase.

Comparison of the data in Table 33 with that from VSR-3-13 (Table 32) indicated that the VSR-3-15 samples contained less Si-Al eutectic (16-26%) than those from VSR-3-13 (16.26%). This difference may have been related to sample locality; the samples from VSR-3-13 were taken from near the center of the ingot, whereas the VSR-3-15 samples were taken from the periphery of the ingot. However, if the difference in the amount of Si-Al eutectic produced was real, rather than resulting from sampling variations, then the limited amount of Si-Al liquid available for reaction in VSR-3-15 could have been responsible for the relatively high proportion of $FeSiAl_3$ and the lack of $FeSiAl_5$ in VSR-15.

For run VSR-3-17, a sample of metallic "icicle" formed below the pilot reactor hearth was analyzed. The burden formulation used in this run contained approximately 70% of the carbon necessary for stoichiometric reduction of the metal oxides (hereafter referred to as stoichiometric carbon). The burden formulation also contained only the Fe_2O_3 present in the raw materials; no additional Fe_2O_3 was used to achieve a high-iron burden composition, as in VSR-3-13 and VSR-3-15.

Modal composition of the "icicle" is listed in Table 34. The major phases were a three-phase eutectic (Al-Si-FeSiAl₅) and SiC, with minor amounts of Fe-Si-Al, Si, and TiSi₂ (Al, Fe) intermetallics.

The three-phase eutectic averaged 49% of the metallic icicle. The eutectic was more abundant at the top of the icicle than at the tip, probably because of settling of crystals through the melt prior to solidification. Al was the dominant phase in the eutectic with Si and FeSiAl₅ exsolved from the Al matrix along preferred crystallographic directions.

Fe-Si-Al occurred as blocky to tabular crystals within the eutectic. Most of these grains consisted of a partially reacted core of a high-temperature Fe-Si-Al phase and a rim of FeSi₂Al₄ formed by peritectic reaction between the high-temperature phase and the metal. This reaction relationship was not shown on existing phase diagrams; the high-temperature core may be a previously unreported compound in the Fe-Si-Al system.

SiC occurred within the eutectic as small bladed crystals 5-200 μ m in length, and in a hypereutectic phase as slightly larger prismatic crystals.

TiSi₂(Fe, Al) occurred as euhedral to subhedral, hexagonal crystals indicating that, as in previous runs, it was one of the first phases to crystallize. Recent x-ray pictures taken by electron microprobe indicate that the composition of this phase was highly variable, with varying levels of substitution of Fe or Al for either Ti or Si, or both. This highly variable composition was almost certainly characteristic of this phase in other reactor runs, although it was not mentioned in earlier reports.

Comparison of the metal ingots from pilot reactor runs VSR-3-18 and VSR-3-19, which contained no added Fe₂O₃ in the burden, with those from runs VSR-3-13 and VSR-3-15, which contained 10% Fe₂O₃ added to the burden, indicated that the liquid metal followed a different series of peritectic reactions. Hypereutectic silicon was a major phase with the low-iron burden compositions, but occurred at trace levels in the high-iron compositions. In addition, a previously unreported high-temperature Fe-Si-Al phase has been found in the low-iron metal.

The proportion of carbon in the burden has been shown to affect the morphology of the carbides in the metal.

Stoichiometric amounts of carbon produced an interlocking framework of SiC platelets in VSR-3-19. The use of sub-stoichiometric carbon (85%) in VSR-3-18 produced aggregates, or bundles, of SiC platelets which are not interconnected through the Al matrix; these bundles of SiC reacted with the Al-Si eutectic to form a reaction rim of Al_4SiC_4 .

Sample locations for VSR-3-18 and 19 were the following. Samples VSR-3-18 (1), VSR-3-18 (2), and VSR-3-18 (3) were from a vertical traverse through the middle of the metal ingot formed in the reactor hearth. Samples VSR-3-18 (2), VSR-3-18 (4), and VSR-3-19 (5) provided a radial traverse from the center to the periphery of the ingot. Samples VSR-3-19 (2) through VSR-3-19 (5) provided a vertical traverse through the ingot.

Modal compositions of the metal samples are listed in Tables 35 and 36. The major phases in all samples are three-phase eutectic (Al-Si- FeSiAl_5), carbides (SiC, with Al_4SiC_4 in VSR-3-18), and Si; minor to trace amounts of FeSi_2Al_4 and TiSi_2 (Al) intermetallics were also present. These metal samples differed from those previously reported in the presence of abundant intermetallic Si and three-phase eutectic, and in the scarcity of Fe-Si-Al intermetallic compounds.

The three-phase eutectic comprised 48-62% of the metal in both runs. Al was the dominant phase in the eutectic, with lesser amounts of Si and traces of FeSiAl_5 . This eutectic phase assemblage agreed with that platelets exsolved parallel to the crystallographic dimensions of the Al and as irregular grains within the Al. The diameter of these latter grains ranged from 20 μm to sub-microscopic ($<0.25 \mu\text{m}$).

FeSi_2Al_4 occurred as blocky to tabular crystals within the eutectic in both runs. No reaction relationship could be observed between the FeSi_2Al_4 and the eutectic. However, many of the larger FeSi_2Al_4 grains contained a partially reacted core of a high-temperature Fe-Si-Al phase. Although this phase had the same morphology as the FeSiAl_3 observed in earlier runs, the optical properties differed from FeSiAl_3 . This phase is probably more Si-rich and Fe-poor than FeSiAl_3 , and has undergone peritectic reaction with the liquid to form FeSi_2Al_4 .

SiC occurred in all of these samples, although its morphology differed between VSR-3-18 and VSR-3-19. As in previous runs, there was an SiC reaction zone along the contact between the metal ingot and the graphite reservoir wall. The SiC within

the metal in VSR-3-19 (~100% stoichiometric carbon), and in the basal 1.5 cm of the ingot in VSR-3-18 [VSR-3-19 (3) base], occurred as intergrown, interlocking platelets up to 5 mm in length. Solution experiments in which the Al was dissolved in dilute HCl indicated that these platelets formed an interlocking framework with very high porosity, but with questionable permeability to molten metal; the interlocking framework may retard or stop the flow of metal in remelt experiments.

In contrast, SiC was associated with Al_4SiC_4 in VSR-3-18 (85% stoichiometric carbon). SiC occurred both as hourglass-shaped bundles, and as spheroids up to 2-3 mm in diameter; in both cases, the individual SiC agglomerates were not interconnected through the eutectic matrix. In both morphological types, Al_4SiC_4 occurred as intergrowths with SiC, and as a reaction zone between the SiC and the Al matrix. The Al_4SiC_4 reaction zone usually enclosed the entire matrix. The Al_4SiC_4 reaction zone usually enclosed the entire particle in the spheroidal SiC; however, it only occurred near the ends of the bundles, not at the neck. Al_4SiC_4 also occurred as smaller spheroids up to 0.5 mm diameter with no SiC core. In both cases, the Al_4SiC_4 crystal zone also contained the three-phase eutectic derived from trapped interstitial liquid. The data of Table 35 indicated that, within any given area of the VSR-3-18 ingot, SiC occurred either as a framework, or as spheroids; the two morphologies do not occur together.

Si occurred both within the eutectic, as discussed above, and as a hypereutectic, intermetallic phase. Earlier runs in which Fe_2O_3 was added to the burden contained only traces of hypereutectic Si. However, with the low-iron burden used in VSR-3-18 and VSR-3-19, hypereutectic Si was a significant phase in the metal. The abundance of hypereutectic Si, combined with the apparent absence of FeSiAl_3 , suggested that this low-iron metal crystallized along a difference peritectic reaction path than the earlier high-iron metal.

$\text{TiSi}_2(\text{Al})$ occurred as tabular crystals, often with well-developed crystal faces. As in earlier runs, this phase was probably one of the first to crystallize. Comparison of the electron microprobe analysis with established phase diagrams suggests that this phase is TiSi_2 , with variable amounts of Al substituted for either Ti or Si, or both.

Task completion is 100%.

Task No. 17: Supportive Analytical

A very large number of samples were analyzed for the Reduction Task during Phase B as indicated by a total of 1749 man-hours expended in the Analytical Division. This effort does not include the phase identifications reported under Task No. 16.

Task completion is 100%.

B. ALLOY PURIFICATION - PHASE B

Task No. 1: Support Pilot Plant Operations

A test furnace was constructed to evaluate the use of an aluminum/aluminum-phosphate foam insulation as a metal penetration barrier in the pilot crystallizer. A major advantage of this material is its low thermal conductivity, on the order of 0.5 to 1.0 BTU-in/hr·ft²°F. No penetration was observed even though a 1/16-in. wide path was left in the inner lining between the molten metal cavity and the foam. The foam was slightly compressible and could absorb some of the thermal expansion of the inner refractory lining. In compression, however, a network of cracks formed and it was possible that metal penetration through a crack could occur in a thin layer of foam (one in. or less). The chance for metal penetration decreases as foam thickness increases.

Task completion is 100%.

Task No. 2: Determine Cooling Effects on Morphology

This task cannot be carried out until the pilot crystallizer is in operation. Therefore, it is deferred to Phase C.

Task completion is 0%.

Task No. 3: Establish Effects on Impurities

Bench scale experiments to determine the effects of Fe and Ti impurities on crystallizer operation were continued from Phase A. Iron impurity levels up to 6.9 wt% and Ti levels up to 1.25 wt% have been studied. The experiments performed this quarter are listed in Table 37. Also listed in Table 37 are the observed liquidus temperatures, equilibrium liquidus temperatures where available and the maximum melt temperature for each experiment. There was marked supercooling in the Al-Si-Fe experiments at Fe levels below 5 wt%. Equilibrium liquidus temperatures are not available for the Al-Si-Ti and Al-Si-Fe-Ti systems.

The presence of impurities during fractional crystallization of Al-Si alloys has two effects: increased impurity levels in the eutectic material drained off, and formation of intermetallic compounds which tie up aluminum, decreasing the amount of eutectic drain. Since the eutectic material is expected to be used as a casting alloy, at least to some extent, increased impurity levels, especially Fe, would decrease its marketability without further purification. Compositions of starting alloys and drain material are given in Table 38. Maximum limits on casting alloys are typically 18% Si and 0.7% Fe although some casting alloys contain up to 3% Fe. Increased formation of intermetallic compounds not only affects the amount of eutectic material obtained, but also places restrictions on the products obtainable from further treatment of the crystal bed. These restrictions could be advantageous as in the case of production of ferrosilicon from a high Fe-containing remelt cut. Titanium impurity tends to remain in the Si bed, forming Al-Si-Ti ternary intermetallics. The effect on silicon product formation is not known. Experiments 17 and 18, containing large amounts of both Fe and Ti, had no liquid phase below 700°C, and the liquid obtained at these high temperatures had unacceptable levels of Si (greater than 20%). Experiments with Fe impurity only at comparable levels had acceptable Si contents (13-14% Si) in metal drained near the eutectic temperature. During Experiment 23, 29.0% Si-5.0% Fe-0.8% Ti-remainder Al, it was possible to obtain a eutectic drain at 590°C, but even at this low temperature, the composition of the metal drained was 20.5% Si-2.6% Fe-0.39% Ti-remainder Al. It is possible that sidewall freezing may be influencing the amount of metal drained and to some extent, its composition.

In the second quarter, induction remelts for runs 20-23 were completed. Starting alloy compositions were:

Experiment 20	Al-29% Si-6.9% Fe
Experiment 21	Al-30% Si-1.13% Ti
Experiment 22	Al-29% Si-1.25% Ti
Experiment 23	Al-29% Si-5.0% Fe-0.9% Ti

The remelt experiments were performed using a graphite lined induction furnace powered by a 20 kW radio frequency generator. The high frequency prevented continuous temperature measurement, introducing some error into the tapping temperature measured, probably +10°C. The problem was caused by the very high frequency involved, approximately 450,000 cps, which induced sufficient heat in the thermocouple to open the "bead". Other facets of the remelt

went very well. In this series of experiments, fiberfrax taphole cones were used, eliminating the need for dry asbestos. Figures 27-31 showed the progress of the remelts for Experiments 20-23, plotting liquid alloy content versus liquid alloy removed. As seen in previous experiments, the eutectic impurities silicon and iron were reduced in the drain and initial remelt. The Al-Si-Fe-Ti system must also be a eutectic system at low titanium concentrations, as titanium content was also reduced initially. Figures 27 and 31, representing experiments containing iron, both showed evidence of high iron content remelt cuts. This is caused by the remelting of iron-containing intermetallic compounds, each of which melts over a specific temperature range (with some overlap). Use of this phenomenon is crucial when handling charge alloy with a high iron content.

Results pertaining to production of casting alloy are listed in Tables 39-42 for Experiments 20-23, and summarized in Table 43. As discussed at length in previous reports, iron or titanium in small amounts (Fe <5%, Ti ~1.0%) does not significantly reduce product yields, with yields above 50% attainable with bench scale equipment (these figures would improve considerably as the equipment is scaled up to pilot and commercial sizes). However, at higher concentrations, the yield figures fall below 50%, with Al-29% Si-7% Fe yielding only 23% of the charge as a casting alloy.

In the third quarter, fractional crystallization and induction remelt portions of the experiments were combined and completed in sequence in the same furnace. Formerly, these portions were conducted separately in a bench crystallizer heated resistively and an induction remelt furnace. The labor expenditure has been reduced from three man-days to less than one/experiment. Nine experiments were completed during this quarter, Experiments 24-32. Experiments 24 and 25 investigated the Al-Si-Fe-Ti system at two levels of titanium content. Experiments 26 and 27 had high initial iron contents, while Experiments 28-31 investigated higher initial silicon content. Experiment 32 is the first in a series to study sidewall freezing and its effect on the results of bench scale experiments. Tables 44-50 and Figures 32-40 show the bench scale results for the experiments, except Experiments 30 and 32.

In the quaternary system Al-Si-Fe-Ti, increasing titanium levels affected the quantity of eutectic material through formation of Al-Si-Ti intermetallics. In Experiments 24 (29% Si-2.9% Fe-0.6% Ti-remainder Al) and 25 (29% Si-2.9%

Fe-1.2% Ti-remainder Al), approximately one-third of the charges were recovered as casting alloy. Silicon and titanium were concentrated in the crystal product, with contents approximately 1.5 times the charge composition. Iron was concentrated in the remelt cut taken between 760°C and 840°C with similar increases. Increasing the titanium content from 0.6% to 1.2% did not appear to have an effect on the amount of eutectic material drained at 590°C. Since very little aluminum is tied up in the Al-Si-Ti intermetallics, the titanium level may have to be increased significantly to see an effect.

Current estimates of reactor product indicate that high levels of iron may be present. Experiments 26 (29% Si-10% Fe-remainder Al) and 27 (29% Si-13% Fe-remainder Al) investigated the effect these levels may have on alloy purification. As expected, there was virtually no liquid at 590°C (eutectic temperature is 577°C), and none of the remelt cuts contained less than 18% Si (upper limit for casting alloys). However, greater than 50% of the iron present was contained in the remelt cut between 760°C and 840°C, and no iron remained in the crystal product at 940°C. These results implied that for these alloys the iron was bound in intermetallics which formed over specific temperature ranges. In general, the iron content decreased as the temperature was lowered, releasing more iron into the liquid to form intermetallics with further cooling.

In addition to higher iron contents, the expected reactor product had higher silicon levels. Experiments 28-31 had nominal silicon levels of 40%, with varying amounts of iron and titanium.

Experiment 28 - 37% Si-2.6% Fe-remainder Al
Experiment 29 - 38% Si-9.6% Fe-remainder Al
Experiment 30 - 39% Si-2.5% Fe-0.9% Ti-remainder Al
Experiment 31 - 33% Si-3.1% Fe-1.6% Ti-remainder Al

Silicon at ~40% and iron at ~3% resulted in casting alloy yields of 10% or less. The high Fe experiment in this series (Experiment 29) had no casting alloy yield at all.

Calculations on ore burdens predicted the minimum iron content of reactor product at 10-12%, based on metallurgical coke, bauxite, and clay as feed materials. Previous crystallizer experiments have shown that iron levels above 7% significantly reduced the casting alloy yield and that above 10%, no casting alloy was obtained with

standard fractional crystallization. Several approaches to this problem have been considered, including pooling the high iron content remelt cuts (obtained between 760°C and 840°C).

Experiment 34 did not involve a change in the crystallization procedure. High iron-containing remelt cuts from Experiments 26, 27, and 33 were combined to form a charge with a composition of 32% Si-15% Fe-remainder Al. There was no liquid at 580°C or 700°C. The high iron cut obtained in the standard crystallization procedure occurs between 760°C and 840°C and contains more than 50% of the charge. In this experiment, however, the "high iron cut" contained 11% Fe (29% Si) and was 25% of the charged weight. The higher temperature cut, 840° to 940°C, contained 17% Fe (32% Si) and 46% of the charged weight. Figure 41 shows the weight distribution of the remelt cuts vs the silicon and iron contents of each cut. The concentration of iron in the higher temperature cuts was minimal, as shown in Table 52. In the large cut, 42% of the available aluminum and 46% of the available iron were present, similar to results of experiments without pooling.

During the fifth quarter, several techniques were tested for production of casting alloy. These techniques included copper and magnesium additions. Based on patent literature, it was decided to pursue additions of copper (1 to 4%) and magnesium (0.1 to 1%) to reduce silicon and iron levels in the alloy product.

Experiments 40 and 41 investigated initial alloys of 30% Si, 10% Fe, with copper additions of 4.4 and 1.9 respectively. Standard crystallization procedure was employed, and yields of approximately 30% were obtained, a marked improvement over previous experimentation. Tables 52 and 53 present the experimental data. The next experiments investigated the addition of both copper and magnesium. See Tables 54 and 55 for data compilation. The product yield was not as high as when copper alone was added, and the crystal bed was much harder, in one instance necessitating destruction of the crucible to remove the bed. Yields were approximately 20% compared to 30% for Experiments 40 and 41.

This task is 100% complete.

Task No. 4: Fabricate and Install Multipurpose Furnace

In the second quarter, the multipurpose induction furnace and auxiliary equipment were received from Inductotherm

Corporation. The furnace was installed complete except for the refractory lining.

In the third quarter, the furnace was lined with LA8521, a Norton refractory. Lid improvements were also made to obtain better sealing for reduced heat loss.

A description of the furnace is given in Appendix 4.

Task completion is 100%.

Task No. 5: Install Furnace Instruments and Controls

The electrical and mechanical installations were completed in the second quarter. Preliminary electrical shakedown and leak testing were performed. A temperature controller with high and low temperature shut-off limits was installed in the fourth quarter.

Task completion is 100%.

Task No. 6: Fabricate, Install Crystallization Vessel and Heating System

In the second quarter, the induction coil heating system was designed and equipment was ordered. The unit design layouts were initiated.

In the third quarter, the coil was received. The refractory lining material and insulation were purchased and the unit lid shell was fabricated.

Two problems were encountered which caused significant delays in this task. Transite has been eliminated as the shell material because it contains asbestos and also can explode on rapid heatup due to its water content. A search for substitutes has provided an alternate material, GRC Board from Cem-Fil, Inc. This material has no asbestos and less water than transite with about the same mechanical properties. Tests are underway to verify its acceptability. Heat transfer analyses of the taphole block revealed unacceptably high temperature in the region that the block contacts the shell. Modifications in the design were necessary to reduce this temperature. Thermal shock of the block is also of concern when metal first contacts the flow path. Heat transfer calculations show that the

standard taphole burner planned for this job is capable of maintaining this surface at sufficient temperature to prevent shock damage.

The design of the system was 90% complete at the end of the fourth quarter. Drawings of the completed items were issued for construction. All refractory and lining materials have been acquired. A taphole mold and a top refractory plate mold were built and the casting of these parts was scheduled for the fifth quarter. The GRC ceramic fiber board, which will be used as the shell material, was received and its machining is also scheduled for the fifth quarter. The crystallizer combustion lid was fabricated and lined with refractory.

In the fifth quarter, the design, fabrication, and purchasing of all components was completed. Erection or assembly of the unit is underway and is approximately 20% complete.

The main burner and the air/fuel train for the crystallizer combustion lid and auxiliary systems were completed. The electrical controls were also built and will be installed in the first quarter of Phase C.

The unfired crystallizer lid was designed and built.

Task completion is 80%. Installation of the system will be continued in Phase C.

Task No. 7: Fabricate and Install Agitation System

The agitation (tamper) system design was completed in the third quarter. Fabrication of the unit was completed in the fourth quarter. The pneumatic/electric control system was installed in the fifth quarter.

Task completion is 100%.

Task No. 8: Fabricate and Install Cooling System

Design of the cooling system was completed in the third quarter. The system consists of a series of steel pipes with sized orifices at their ends to control and direct the cooling air flow onto the surface of the metal to be crystallized. The pipe assembly was installed on the agitator support frame in the fourth quarter.

Task completion is 100%.

Task No. 9: Fabricate and Install Product Removal System

The liquid product will be drained into a gas-fired holding ladle and then either cast into pigs or used to supply molten feed to the aluminum purification unit. In the third quarter, detailed drawings for the ladle were completed and all materials received. Fabrication of the shell, lid, pouring trunion, and combustion system platform were completed.

The ladle refractory lining was installed in the fourth quarter. The combustion piping system was installed in the fifth quarter. Electrical cabinets were also assembled. The cabinets will be installed and wired in the first quarter of Phase C.

Task completion is 95%. Electrical wiring will be completed in Phase C.

Task No. 10: Install Crystallizer Instruments and Controls

Installation of the controls was started in the fourth quarter. Completion of this task is dependent upon the completion of Task No. 6. Both tasks are scheduled for completion during the first quarter of Phase C.

Task completion is 80%.

Task No. 11: Start and Shake Down Multipurpose Furnace

The induction power supply and multipurpose furnace were tested in the third quarter. Sintering of the furnace lining (LA 8521) was accomplished by a combination of induction power to the steel mold plus a gas fired torch. An Al-Si alloy (3000 lb) was made up using the furnace. The unit held the 3000 lb of alloy at 760°C with a total power of 125 kW and the lid imperfectly seated. Inductotherm tuned the power supply to deliver up to 290 kW total power. The unit was shut down after testing and will be restarted upon completion of the holding ladle and crystallization unit.

Task completion is 100%.

Task No. 12: Start and Shake Down Crystallization System

Since the crystallization system installation will not be completed until Phase C, this task is deferred to Phase C.

Task completion is 0%.

Task No. 13: Supportive Analysis

The Analytical Chemistry Division provided analyses of samples as follows: compositions of starting alloys, eutectic drain material, and remelt cuts by dilution quantometer. A total of 364 man-hours were expended during Phase B.

Task completion is 100%.

Task No. 14: Supportive Mechanical Engineering

In the first quarter, the concrete foundation, platform, and structural steel designs for the multipurpose furnace and crystallizer were completed. Electrical installation and piping layout designs were completed.

In the second quarter, the site preparation was completed including installation of a cooling tower and fabrication of transfer troughs, emergency tap-out pans, grating supports, and floor drain covers.

During the entire Phase mechanical engineering support was provided to complete the designs and layouts relating to Tasks 4, 5, 6, 7, 8, 9, 10, 11, and 16.

Task completion is 100%.

Task No. 15: Supportive Phase Analysis

In the first quarter, Alloy Technology Division provided phase analyses of several samples using electron microprobe and X-ray diffraction techniques.

Mircoprobe analysis of crystal product from Experiments 19 and 20 (Al-Si-Fe) alloys revealed the presence of β and δ Al-Fe-Si intermetallic compounds. Approximate

compositions were very close to the equilibrium compounds FeSiAl_5 and FeSi_2Al_4 . A crystal sample from Experiment 21 (Al-Si-Ti alloy) contained an intermetallic compound of composition $\text{Ti}_8\text{Si}_4\text{Al}$.

X-ray diffraction was done on samples from Experiment 10 (Al-Si-Fe-Ti alloy) and Experiment 16 (Al-Si-Fe). The samples consisted of the fine powder left after acid leaching (the large Si crystallites were removed by passing the powder through a 48 mesh sieve). Any Fe present would have been removed during the acid leaching. Both powder patterns and Guinier analysis were made of the samples. A phase with composition $\text{Ti}_7\text{Al}_5\text{Si}_{12}$ was found in the sample from Experiment 10, with a small amount of $\alpha\text{-Al}_2\text{O}_3$, a large amount of Si, and a very small unidentified phase. Experiment 16 had the expected Si, a very small amount of $\alpha\text{-Al}_2\text{O}_3$, a trace of aluminum, and an unidentified phase.

In the third quarter, phase analysis of run 23 was obtained using the electron microprobe and scanning electron microscopy. A volume fraction of phases present was completed on three high Fe content samples from remelt cuts at 760°C, 845°C, and 940°C. The volume fraction of Al-Si-Fe intermetallics was 16.0%, 24.5%, and 22.4% respectively.

In the fourth quarter, six metal purification samples were submitted for modal analysis of phases present. The samples were identified as follows:

S#496961	Run #10	Al-30% Si-3% Fe-0.8% Ti
#495972	Run #11	Al-25% Si
#495983	Exp #12	Al-35% Si
#496176	Exp #19	Al-28% Si-8% Fe
#496180	Exp #20	Al-28% Si-7% Fe
#496184	Exp #21	Al-30% Si-1.5% Ti (nominal)

Phase identification and compositions were determined by electron microprobe. Modal compositions were determined by counting 550-700 grains on each sample. All modal compositions were presented as volume percentages.

Modal compositions of the samples are listed in Table 56. Four intermetallic phases were identified (Si, β -Al, Fe, Si, δ -Al, Fe, Si, and $\text{Si}_8\text{Ti}_4\text{Al}$) in a matrix of Al and Al-Si eutectic. The distribution of intermetallic phases was variable; none of the samples contained all four intermetallic phases.

Silicon occurred in three forms in these samples: as large equant to lath-shaped crystals, as acicular needles, and as eutectic Si. The large crystals ranged from 0.5 μm to 2.5 mm in length; crystal faces were moderately well developed. The acicular needles ranged up to 0.75 mm in length. The eutectic Si formed irregular masses interstitial to aluminum metal. Both the eutectic Si and the acicular Si were included as part of the matrix component in the modal analyses. All of the visible matrix silicon in S #594961/972/983 occurred as the irregular eutectic form, whereas most of the matrix silicon in S #496176/180/184 occurred as the acicular form; this relationship suggested that both forms of matrix Si have formed by exsolution from the Al phase, possibly at different temperatures.

β -Al, Fe, Si occurred in the S #495961/972/983 series as irregular equant grains, with little development of crystal faces. The grains were 0.04-0.5 mm in diameter. Microprobe analysis indicated that this phase was approximately FeSiAl_4 ; this composition probably corresponded to the stoichiometric compound FeSiAl_4 , and will be reported as such.

Both β -Al, Fe, Si, and δ -Al, Fe, Si occurred in S #496176/180. δ -Al, Fe, Si occurred as subequant grains 0.03-0.8 mm in diameter. Most grains were partially mantled and/or embayed by β -Al, Fe, Si, although both phases also occurred independently of one another. Cracks were common in the β -Al, Fe, Si in all of the samples suggesting that this phase may have undergone brittle deformation. The occurrence of δ -Al, Fe, Si in addition to β -Al, Fe, Si appeared to be related to an increase in the amount of iron in the samples. Microprobe analyses indicated that the δ -Al, Fe, Si was approximately FeSi_2Al_3 ; this composition probably corresponded to the stoichiometric compound FeSi_2Al_4 , and will be reported as such.

$\text{Si}_8\text{Ti}_4\text{Al}$ occurred only in S #495961 and S #496184, as subequant to lath-shaped crystals with well-developed crystal faces. The grains were 0.25-1.5 mm in length in S #495961, and 0.05-0.5 mm in length in S #496184. The microprobe analyses indicated minor compositional

differences between the $\text{Si}_8\text{Ti}_4\text{Al}$ in these samples and the $\text{Si}_7\text{Ti}_4\text{Al}$ found in a previous series of samples; petrographic study confirms that these are different phases, because they exhibit different optical properties.

Aluminum occurred as the matrix enclosing the intermetallic compounds. No structures can be detected, although it appears to be very finely crystalline ($<5\mu\text{m}$ grain diameters).

Data have been accumulated at this time to permit the routine identification of Al, Si, FeSiAl_5 , FeSi_2Al_4 , $\text{Si}_8\text{Ti}_4\text{Al}$, and $\text{Si}_7\text{Ti}_4\text{Al}$ by their optical properties alone. The electron microprobe will only be necessary for identification of new phases, as they are encountered.

Two alloy purification samples were submitted for phase analysis in the fifth quarter. The samples and initial alloy compositions were identified as follows:

Exp. #33-Al-30% Si-10% Fe
Exp. #41-Al-30% Si-20% Fe-2% Cu

Phases identified in both samples by optical microscopy were 3-phase eutectic (Al-Si-FeSiAl_5), Si, and FeSiAl_5 (Table 57); a Cu-Al phase also occurred in Exp. #41.

FeSiAl_5 occurred as large blocky crystals up to 1 mm long and as small irregular patches in the eutectic. No higher temperature Fe-Si-Al phases were found. Si occurred as large, subhedral, prismatic crystals up to 2 mm in length, and in the eutectic as irregular patches exsolved from Al.

The Cu-Al phase occurred in the Al matrix in Exp. #41 as very small anhedral crystals. The grains were too small ($<4\mu\text{m}$ diameter) to permit quantitative microprobe analysis; however, x-ray pictures indicated no Si or Fe in this phase. The binary phase diagram for the pure system Cu-Al suggested that these grains may be CuAl_2 intermetallic.

Task completion is 100%.

Task No. 16: Supportive Facilities Engineering

All work submitted to outside subcontractors was coordinated by the resident Facilities Engineer. Included were concrete foundation installation, structural steel assemblies, installation of water cooling tower, all painting, and

electrical and mechanical jobs associated with site preparation.

Task completion is 100%.

C. PURIFICATION TO COMMERCIAL GRADE ALUMINUM

Task No. 1: Support Pilot Plant Work

In the first quarter, long-term testing was continued in the large bench scale unit to evaluate construction materials, operating procedures, and effects of operating parameters on unit performance. The most critical items were the tests on woven carbon fabric membranes (discussed in Task No. 2), assessment of maximum acceptable alloy height that the membrane will support without breakthrough, and the determination of membrane blinding mechanisms.

In the second quarter, a series of experiments were initiated to correlate cell performance with anode-cathode distance. All tests were run with continuous filament twill weave graphite cloth.

In the third quarter, the tests on effects of anode-cathode distance were continued. Five experiments were conducted. It is desirable to operate at the lowest anode-cathode distance possible to reduce resistive loss through the electrolyte and decrease the power consumed per unit of metal produced. The minimum distance is limited by the potential for short circuiting at too close a gap.

The bulk of the experimental work in the fourth quarter was directed toward answering some fundamental questions regarding the operation of the pilot cell. In all previous experiments the electrolyte was formulated with reagent grade anhydrous lithium chloride. To identify any unexpected problems, an experiment was conducted with commercial purity anhydrous lithium chloride, 99.3% pure. No problems were encountered in cell operation.

The use of alternating current to resistively heat the membrane cell exhibited no problems. Two types of experiments were conducted. The first consisted of immersing two graphite rods into the molten LiCl-AlCl_3 electrolyte and passing alternating current between them. No deterioration of the graphite rods was observed. The two electrodes in the second type of experiment were the graphite crucible and a membrane "anode" containing molten aluminum-silicon (11.7%) alloy. Alternating current was passed between the two electrodes. Again the woven graphite membrane showed no deterioration. The conclusion from these experiments is that the membrane cell may be resistively heated using an a.c. voltage without harming the cell.

The experimental results achieved in the fifth quarter reaffirmed the basis for the design of the pilot cell, particularly in regard to electrode geometry, materials selection, and heat management.

Materials to be used in the construction of the pilot cell were exposed to the standard electrolyte (10% AlCl_3 , 90% LiCl) in a laboratory cell during electrolysis (interrupted for overnight periods). The results are summarized in Table 58. All materials except Foamsil 28 displayed satisfactory performance in these tests. Test temperatures exceeded the acceptable range for the use of Foamsil 28, and the failure of this material is probably due to this fact.

A new laboratory cell was designed and used to test membrane anodes of a greater height. A test was run for 31.5 hrs at current densities in the range of 1.0 to 3.1 amps/cm². The unit ran well.

A resistance heating system has been designed to bake out the membrane cell and heat it to near operating temperatures. Four units consisting of inconel strips will fit into the cell. They can be connected in series to produce a total resistance of .02 ohms. In this mode, 5 kW (10V, 500 amps) is produced for low temperature bakeout. Connected in parallel these same units can produce a total power rating over 28 kW (6V, 4800 amps total) which is more than adequate to reach startup conditions of 630°C to 660°C. Heat transfer calculations for this power rating show an inconel temperature of 900°C to 960°C which is acceptable.

Task completion is 100%.

Task No. 2: Continue Evaluation of Membrane Types

Four candidate membrane materials were tested in the first quarter. The experimental data appear in Table 59.

Run No. 22 was essentially a repeat of the large-scale Run No. 21 from last quarter. The cell was kept at the operating temperature for 34 days and electrolysis was conducted for 150 hrs. Visual and manual examination of the graphite cloth after the experiment indicated that the material was not weakened by this prolonged exposure. No quantitative measurement was made. Metal produced in this run was well coalesced.

The three new materials (Run Nos. 23-25) are twill weave carbon fabrics that are stronger than the plain weave fabric of Run No. 22. The experiment with the best cell performance used a membrane that was woven with continuous graphite filaments. Data supplied by Fiber Materials, Inc., Table 60 show that fabric made from continuous fibers is stronger than the same fabric made from staple (discontinuous) fibers.

Physical property data have also been received for a number of RVC products. These materials, however, are no longer being seriously considered because of their cost and brittle nature.

An experiment was conducted in the second quarter to simulate the accumulation of oxide in the membrane cell. Aluminum oxide in the form of PCA (partially calcined alumina) was added to both the bath and the anode metal. Two PCA additions to the bath (25g + 50g) made the bath ~3% PCA. Four PCA additions to the anode metal (8g + 8g + 8g + 25g) resulted in >10% PCA in the metal. No significant effect on cell operation was observed.

An experiment to evaluate the long term performance of the GC 5502 membrane material was started in the large bench-scale cell. During the third day, the bath leaked through the graphite crucible and through a failed weld of the nickel crucible. The run was stopped when the furnace elements burned out and it was found that the salt electrolyte had soaked into a large amount of the furnace refractory. Reconstruction of the furnace and the cell has delayed a second startup.

In the third quarter, an experiment designed to evaluate the long-term performance of the GC 5502 membrane material was again prematurely stopped due to experimental problems. The cell failed to hold bath, the container was badly corroded, and the heating elements shorted to the electrolysis power supply destroying some of the circuit elements. Due to the lowering of the bath level, air burning of the membrane material occurred. The experiment was terminated after being held at temperature for 10 days and after electrolyzing for 40 hrs. The parameters of the experiment are presented in Table 61.

In the fourth quarter, continuing concern about accumulated oxides plugging the porosity of the membrane, or blinding the membrane, lead to an experiment wherein aluminum skim

was added to the membrane anode. Initially 303g of aluminum-silicon (11.7%) alloy was charged to the anode and electrolysis was started. Then skim additions totalling 945g were stirred into the anode metal. The nominal composition of the alloy which formed the skim, designated 356 skim, is aluminum with 7% silicon, 0.35% iron, 0.12% copper, 0.35% magnesium, and 0.10% zinc. It is felt that this skim would be similar to that which may form in the pilot cell. The experimental parameters of the experiment are presented in Table 62. In this test, current densities greater than $4A/cm^2$ were not maintained for as large a portion of the run time as experienced in experiments where skim was not added. This experiment was purposely designed to depict the prolonged accumulation of oxides in the cell and indeed, decreased cell performance was seen. Blinding of the membrane with oxides would probably be a very gradual process and most likely it would not severely decrease cell performance.

A test to evaluate the service life of the GC 5502 membrane cloth was terminated after being held at temperature for 22 days and after 97 hrs of electrolysis. A hole formed in the cloth and the metal leaked out. Many times through the run the bath level dropped to expose the membrane to the air. Thus, air burning of the graphite filaments may be responsible for the failure. Yellowish traces, presumably aluminum carbide, were observed on the face of the cloth that was in contact with the anode metal. This may also cause a general weakening of the material. This GC 5502 cloth, however, is still recommended for use in the pilot cell because previous tests with a membrane woven from the same continuous graphite filaments but with the less structured plain weave, showed no visible deterioration after exposure to the cell environment for 34 days.

In the fifth quarter, an experiment was designed to establish the limit at which either metal starts penetrating the membrane or the membrane ruptures.

A membrane is attached to a graphite tube of 1.9 cm inner dia. The tube is filled with a known amount of aluminum metal and immersed into bath of standard composition. A gauged argon pressure is applied to the metal and the point observed when metal droplets penetrate the membrane. A gold-plated quartz furnace which permits observation in the furnace is employed for this experiment.

In a preliminary run, metal started to penetrate the graphite membrane to be used in the pilot cell at a pressure of 0.2 atm. This pressure corresponds to the pressure resulting from about 150 cm of aluminum metal in electrolyte.

Task completion is 100%.

Task No. 3: Fabricate, Install Pilot Unit

The pilot unit design was reviewed. Design concepts were established to provide adequate circulation and collect impurities. Sidewall construction design details were completed based on heat transfer calculations. High strength graphite was ordered for use as structural cell components. Insulating refractories and electrode graphite materials were selected.

In the third quarter, design details of the shell, electrode connections and refractory lining assembly were completed. The membrane material, graphite cloth GC 5502, was received. A low voltage, high amperage transformer for an AC power supply was ordered to maintain heat on the unit when DC electrolysis is not going on. Additional aluminum buswork was installed to the existing system to increase the allowable amperage to greater than 15,000 amps.

In the fourth quarter, construction of the steel shell was started. Additional refractory and insulation lining materials were received. Work on detailed design drawings was continued. Design modifications were made to the electrode assemblies to offset increased heat losses predicted by revised heat transfer calculations. Stress analyses calculations were made for critical aspects of the membrane installation.

The main components for the pilot cell were received in the fifth quarter. The shell fabrication was completed. Installation of the insulation and refractory walls was started. Most of the graphite components have been machined and several of the major internal components were assembled. Construction of the cell lid was started.

Task completion is 60%. Task to be continued in Phase C.

Task No. 4: Fabricate, Install Residue Removal System

Design of the residue removal system was continued. Impurities will be collected in a separate chamber and periodically removed from the chamber with a specially designed lifting device. Several materials and methods of construction relating to the chamber were selected for consideration.

In the second quarter, calculations were made to determine the effects of residue concentration on the design and operation of the residue removal system. The feed to the membrane cell should contain between 0.8 to 3% Fe and 0.1 to 0.3% Ti depending on the impurity content of the product from reduction. It may be possible to recover much of the Si content in the feed as metallurgical grade Si after acid leaching treatment to remove Al and Fe impurities.

In the fourth quarter, techniques for sealing the residue removal chamber as well as critical dimensions of the chamber were determined. A purchased graphite crucible with an inner refractory lining will be used.

Task completion is 25%. Task to be continued in Phase C.

Task No. 5: Fabricate, Install Product Removal System

Based on the successful formation of coalesced Al in the bench scale units, it was decided to effect product removal by vacuum tapping from a collection sump. Tapping tube materials, size, and location were selected.

Task completion is 15%. Task to be continued in Phase C.

Task No. 6: Fabricate, Install Alloy Charging System

The cell will be charged through an isolated chamber since the alloy layer is accessible there and space is limited. The feed will be the drainable product from the alloy crystallization pilot. One crystallization pilot run produces sufficient product for up to three days of membrane cell operation. It is preferred that the feed be charged as a solid in the form of 25 lb (11.3kg) pigs and melted in the chamber using the heat from the cell. A melting function is emphasized by covering the chamber with a lid. An alternating operating mode seems workable. For example, charging plus melting would proceed for 6 hrs, followed by

6 hrs. of crystallization, etc.

Charging molten alloy to the membrane cell will also be tested but this is less logistically convenient. The receiving crucible being built for the crystallization pilot can be used to maintain the alloy molten. This will place some restrictions on crystallization pilot operations in terms of run frequency or type. In the event the crystallization pilot is shut down for repair or modification, the induction melting furnace and possibly the holding crucible could be used to make up synthetic molten alloy for the membrane cell. The hold-up in the chamber should permit up to 16 hrs of continuous cell operation between charge additions.

Task completion is 30%. Task to be continued in Phase C.

Task No. 7: Install Instruments and Controls

A multipoint temperature recorder was ordered in the first quarter. Several other instruments and meters plus controls for the DC power supply are available for use.

The temperature recorder was received and installed in the second quarter.

In the fourth quarter, access ports were designed into the cell lid to provide capability for measurement of temperature, metal and bath levels and continuous monitoring of electrolyte concentration.

Task completion is 15%. Task to be continued in Phase C.

Task No. 8: Fabricate, Install Bath Handling System

Detailed design of the bath melter-transfer system proceeded during the second and third quarters.

In the fourth quarter, design sketches for an 800 lb (364kg) capacity, bath melting system were nearly completed. An inconel crucible surrounded by electric heating coils will be used in the melter. An inconel cup test with pure LiCl has been initiated.

The bath sumps and anode-cathode gap regions within the cell are designed to hold 370 lb (168kg) of bath. At startup, penetration into the graphite cathode and refractory regions increases the amount required to about 750 lb (340kg). This degree of bath penetration would be expected during the startup procedure within a few hrs of the initial bath pour. At operating temperature, bath penetration would be expected to continue for several days such that the total amount of bath in the cell could be over 1300 lb (590kg).

Once at operating temperature, the bath melter will be capable of melting 30 to 60 lb/hr (13.6 to 27.2 kg/hr) of pure lithium chloride (liquidus point $\sim 610^{\circ}\text{C}$). A small amount of aluminum chloride will be added to convert lithium oxides and hydroxides into alumina; and this material will be filtered from the melt during vacuum tapping into the cell.

In the fifth quarter, the inconel cup test with molten LiCl was completed. After 12 days of continuous exposure, no deterioration of the cup was observed. It was concluded that an inconel crucible surrounded by electric heating coils will make a simple bath melter for the membrane cell. Inconel plate and piping required for the inner crucible and transfer system have been ordered. The outer steel shell and support structure for this unit have been fabricated and refractories ordered.

Pressure tapping of the bath is preferred for transfer to the membrane cell. Stress analyses of the inner container were done to determine if pressure vessel criteria could be met using 1/2-in plates for the top and bottom, and a 1/4-in plate for the cylindrical wall. The total pressure required in the system is less than 4 psig. At this pressure and 1400°F , only creep is a problem, and considering that the system will be pressurized for less than 15 minutes for each tap, it is not necessary to meet a 100,000 hr creep criterion. The low pressure involved coupled with an outer steel container provides a reasonably safe system even if a weld failure did occur.

Task completion is 30%. Task to be continued in Phase C.

Task No. 9: Startup and Shake Down System

In the second quarter, a unit startup procedure was established. In the third quarter, approximately 3,000 lbs of Al-Si alloy

feed for the cell was produced in the alloy purification induction heated multipurpose furnace. No further work can be done on this task until the system installation is completed.

Task completion is 10%. Task deferred to Phase C.

Task No. 10: Supportive Analytical

During Phase B analyses were completed as required. A total of 84 man-hrs were expended.

Task completion is 100%.

Task No. 11: Supportive Phase Identification

Due to the nature of the operations in Phase B, phase identification analyses were not required. Therefore, no progress was reported on this task.

Task completion is 0%. Task deleted.

PHASE C FIRST QUARTER PROGRAM

Reduction: Pilot unit VSR-3 will continue to be operated using a combination of external induction heat and internal coke/oxygen combustion heat with an auger to establish the maximum O_2 rate feasible. The flow profile of the tuyere injected O_2 will be determined by installing graphite rods at the grate and observing the burn-off pattern. Larger size fuel coke will be burned to attempt to decrease recarbiting of alloy product. The diverging tuyere nozzle (0.125-in. dia flaring out to 0.375-inches) will be replaced by a straight-through design with a diameter of 0.4 inches to obtain a favorable ratio of coke particle to O_2 outlet size.

An alternative to the blast furnace is a blast-arc concept that utilizes electrical heat for the high temperature, metal-producing stage preceded by a partially reduced burden, heated by coke combustion. An evaluation of this concept will be initiated in VSR-3 using preheated CO to simulate the gas mass flow in the shaft region. It is also planned to taper the shaft to reduce burden bridging problems and perhaps eliminate the auger.

Heat and mass balances will be calculated for several alternative reduction processes. Development of the chemical equilibria computer program will be refined to include non-ideal solutions. The bench scale AF reactor will be operated to evaluate the effects of CO sweep, SiO_2/Al_2O_3 ratio and source of reduction carbon on alloy yield. Detailed microscopic phase analyses will be done on both VSR and AF reactor products to define product composition and structure.

Alloy Purification: All incomplete phases of construction and installation will be continued for the pilot crystallizer. Bench scale crystallizer operation will emphasize development of techniques to reduce iron while maintaining high product recovery.

Purification to Commercial Grade Aluminum: Fabrication and installation of the pilot unit and auxiliary systems will be continued. Bench scale experiments will be run to evaluate

electrolyte composition, polarization effects and resistance of cloth membranes to metal penetration. In addition, several candidate refractory cements will be tested to determine their applicability to the pilot unit construction.

Cost Summary: Expenditures for the fifth period (four months) of Phase B totaled \$681,074. Distribution was \$368,414 for Reduction, \$190,252 for Alloy Purification and \$122,408 for Purification to Commercial Grade Aluminum. Total expenditures for Phase B was \$2,457,237. Total cumulative spending through the first 28 months of the contract was \$3,396,045, representing 73.6% of the original contract value of \$4,614,288. Actual spending for Phase B is compared to estimated spending in Figure 42.

Assigned Personnel: The actual man-hrs expended by engineers and technicians for the final four months of Phase B are shown in Table 63 and compared to estimated man-hrs. For Phase B, cumulative engineer man-hrs were 4.5% above estimate. Cumulative technician man-hrs were 18.9% above estimate. Total cumulative man-hrs for Phase B were 13.2% above estimate. Also shown in Table 63 are the total actual and estimated man-hrs for the contract through Phases A and B. Deviations from the estimated man-hrs were 4.0% below estimate for engineers, 11.2% above estimate for technicians, and 4.8% above estimate for total cumulative man-hrs.

Task/Milestone Schedule: Attachment 2 shows the task-time relationship for the three major tasks from initiation of the contract in DOE fiscal year 1977 (fourth quarter) through the first quarter of DOE fiscal year 1980. 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 B, 1978 December, CONS-5089-5, UC-95f.

2. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, Second Interim Technical Report, Phase B, 1979 March, CONS-5089-6, UC-95f.
3. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, Third Interim Technical Report, Phase B, 1979 June, CONS-5089-7, UC-95f.
4. Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process, Fourth Interim Technical Report, Phase B, 1979 September, CONS-5089-8, UC-95f.

TABLE 1 PRODUCT REMELT TESTS

<u>SAMPLE</u>	<u>LOCATION</u>	<u>% AL</u>	<u>% SI</u>	<u>% FE</u>	<u>% TI</u>	<u>% C</u>	<u>T-FIRST LIQUID, °C</u>	<u>% WT. PASSED THROUGH GRATE</u>
VSR-1-9	I	1.8	25.5	41.0	5.2	23.4	1970	27
	A	1.6	26.0	34.7	5.5	29.4		
	B	2.6	23.7	59.3	3.9	3.0		
VSR-1-8	I	21.9	15.7	28.7	5.4	12.7	2000	46
	A	12.2	20.8	31.8	10.2	20.0		
	B	14.5	24.5	50.2	3.5	4.3		
L22A	I	32.1	20.0	31.5	3.7	6.1	2040	46
	A	32.0	25.4	30.1	4.5	7.2		
	B	32.9	22.4	34.3	3.4	5.4		
L17	I	40.0	26.2	19.9	---	8.1	1325	30
	A	34.2	29.5	16.5	<.1	11.4		
	B	49.4	20.2	12.5	<.1	1.7		
VSR-3-18	I	60.1	25.6	4.0	4.3	4.6	995	48
	A	57.5	26.4	3.8	4.2	5.3		
	B	60.4	25.1	3.8	4.1	4.1		
VSR-3-19	I	50.6	30.0	3.5	3.7	8.7	1000	49
	A	47.6	31.6	2.8	4.6	9.8		
	B	51.0	29.1	2.9	4.0	8.4		

I = Initial Sample

A = Material Remaining Above Grate

B = Material Collected Below Grate

Table 2 Effect of Substoichiometric C

<u>Charge</u>	<u>L44</u>	<u>L46</u>	<u>L47</u>	<u>L45</u>
Burden No.	5A1060	5A1060	5A1060	5A1060
C Content	19.8%	22.9%	24.3%	25.7%
Additional C added (g)	0	64	98	120
Ore wt (g)	1700	1600	1600	1500
% Stoich C	77	89	94	100
 <u>Procedure</u>				
CO flow rate (L/min)	13	13	13	13
T-CO on (°C)	1065	1130	1100	1110
T-max (°C)	2140	2120	2140	2130
t-CO on (min)	30	35	30	30
t-CO off (min)	175	175	175	175
t-at temp (min)	80	80	80	80
 <u>Results</u>				
Burden Movement (cm)	5	4	5	5
Bridge above grate (cm)	16	19	13	11
Bridge thickness (cm)	3	9	6	8
Shutdown	Planned	Planned	Planned	Planned
 <u>Product</u>				
Above Grate (g)	31	9	63	80
Reservoir (g)	64	111	0	0

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ALCOA LABORATORIES

TABLE 3

BURDEN MATERIAL PREPARED IN 1979 FOR DIRECT REDUCTION
(74C1450601)

EXPT. NO.	NOTEBOOK & PAGE NO.	METHOD	RAW MATERIALS USED						
5A1006	18470-36	EXTRUDATES	(21.1 Kg H. Clay)	(7.4 Kg R. Bxte.)	(15.4 Kg Hydrated Lime)	(25 grams Methylcellulose)			
			(48.06%)	(16.85%)	(35.07%)				
5A1007	18470-41	"	(20.2 Kg H. Clay)	(B.Bxte. 6.3 Kg)	12.2 Kg Hydrated Lime)	(11.4 Kg Met.Coke)			
			(40.31%)	(12.57%)	(24.35%)	(22.75%)			
5A1008	18470-41	"	(12.9 Kg H. Clay)	(8.6 Kg Hydrated Lime)	(22.8 Kg Hematite)	(5.7 Kg B. Bxte.)	(1/2 lb Methyl-cellulose)		
			(16.20%)	(10.79%)	(28.64%)	(7.16%)	(1.38%)		
5A1009	18470-41	"	(10.0 Kg H. Clay)	(4.5 Kg B.Bxte.)	(6.9 Kg Hydrated Lime)	(18.3 Kg Hematite)	(11.0 Kg Met Cc)		
			(19.72%)	(8.87%)	(13.60%)	(36.09%)	(21.69%)		
2A983	18470-42	"	(42.33 Kg Thiele)	(23.73 B.Bxte)	(25.19 Kg Met Coke)	(8.75 Kg Hematite)			
			(42.33%)	(23.73%)	(25.19%)	(8.75%)			
5A1023	18470-43	"	56.6 Lbs H.Clay)	(31.7 Lbs B.Bxte)	(11.7 Lbs Fe ₂ O ₃)				
			(56.6%)	(31.7%)	(11.7%)				
5A1024	18470-43	"	(42.3 Lbs.H.Clay)	23.7 Lbs B.Bxte)	(25.2 Lbs.Met Coke)	(8.8 Lbs. Fe ₂ O ₃)			
			(42.3%)	(23.7%)	(25.2%)	(8.8%)			

Aluminum Company of America

ALCOA LABORATORIES

TABLE 3 CONT.

BURDEN MATERIAL PREPARED IN 1979 FOR DIRECT REDUCTION

(74C1450601)

EXPT. NO.	NOTEBOOK & PAGE NO.	METHOD	RAW MATERIALS USED				% STOICH CARBON	QUANTITY	SIZE	YIELD	FIRE COMPRESSIVE STRENGTH
5A1043	19016-3	EXTRUDATES	23.73 B.Bxte.	42.33 H.Clay	25.19 M.Coke	8.75 Hematite	Non-stoich	100 lbs	3/8" x 3/8"	83%	97.3#/sq in
			(23.73%)	(42.33%)	(25.19%)	(8.75%)					
5A1044	19016-3	BRIQUETTES	5.9 B.Bxte.	10.6 H.Clay	6.3 Met.Coke	2.2 Hematite	Non-stoich	25 lbs	3/4" x 7/16"	95%	
			(23.67%)	(42.4%)	(25.2%)	(8.80%)					
5A1046	19016-4	EXTRUDATES	12.66 B.Bxte.	22.58 H.Clay	10.08 Met.Coke	4.67 Hematite	Non-stoich	50 lbs	3/8" x 3/8"	84%	90#/sq in
			(25.32%)	(45.16%)	(20.16%)	(9.35%)					
5A1047	19016-4	BRIQUETTES	6.33 B.Bxte.	11.29 H.Clay	5.04 Met.Coke	2.33 Hematite	Non-stoich	25 lbs	1/4" x	85.6%	
			(25.32%)	(45.16%)	(20.16%)	(9.32%)	Low TiO ₂				
5A1053	19016-11	BRIQUETTES	49.82 Hydrated Al ₂ O ₃	22.19 Quartz Sand	9.40 Hematite	35.85 Wharton Coal	29.9% V.Matter	100 lbs	3/8" x 3/8"	94%	226#/sq in
			(42.48%)	(18.92%)	(8.01%)	(30.57%)					
5A1055	19016-19	EIRICH BALLS	5.93 B.Bxte.	10.58 H.Clay	6.30 Met.Coke	2.19 Hematite	Stoich. 10% Fe ₂ O ₃	25 lbs	3/8" x 3/8"	81%	155#/sq in
			(23.72%)	(42.32%)	(25.20%)	(8.76%)					
5A1057	19016-17	EIRICH BALLS	118.6 B.Bxte.	211.6 H.Clay	126.0 Met.Coke	43.8 Hematite	Stoich.C 10% Fe ₂ O ₃	500 lbs.	1/4" x 6M	56%	90.2#/sq in
			(23.72%)	(42.32%)	(25.20%)	(8.76%)					
5A1058	19016-21	EIRICH BALLS	128.06 B.Bxte.	200.21 Cal.Clay	133.02 Met.Coke	38.71 Hematite	Stoich.C 10%	500 lbs.	5/8" x 6M	62.7%	535#/sq in
			(25.61%)	(40.04%)	(26.60%)	(7.74%)					

Aluminum Company of America

ALCOA LABORATORIES

TABLE 3 CONT.

BURDEN MATERIAL PREPARED IN 1979 FOR DIRECT REDUCTION

(74C1450601)

EXPT. NO.	NOTEBOOK & PAGE NO	METHOD	RAW MATERIALS	USED IN LBS.	% STOICH. CARBON	QUANTITY	SIZE	YIELD	FIRED COMPRESSIVE STRENGTH
5A1060-A	19016-29	EIRICH BALLS	25.95 B.Bxte. (25.95%)	48.22 H.Clay (48.22%)	25.83 Met.Coke (25.83%)	Stoich Low Carbon 100 lbs	3/8" x 6M	-	-
5A1060-B	19016-31	EIRICH BALLS	138.05 B.Bxte. (27.12%)	241.10 Raw Clay (47.36%)	129.85 Met.Coke (25.50%)	Stoich Low Carbon 500 lbs	3/8" x 6M	58.7%	176.2#/sq i
5A1063	19016-43	EIRICH BALLS	129.75 B.Bxte. (25.95%)	241.10 Huber Clay (48.22%)	129.15 Met.Coke (25.83%)	80% Stoich Carbon 500 lbs	3/8" x 1/8"	84.6%	82.4#/sq ir
5A1068	19016-45	DRAVO DISK	91.594 B.Bxte. (18.07%)	254.233 H.Clay (50.16%)	161.036 Met.Coke (31.77%)	80% Stoich Carbon 500 lbs	1/4" x 6M	33.6%	115.5#/sq
5A1072	19016-48	SMALL DISK	11.87 Al ₂ O ₃ (47.48%)	5.37 SiO ₂ (21.48%)	7.76 Wharton Coal (31.04%)	25 lbs	1/8" x 1/4"		-82-
5A1074	19016-49	EIRICH BALLS	23.57 Hyd Al ₂ O ₃ (23.57%)	48.94 H.Clay (48.94%)	27.49 Met.Coke (27.49%)	Low Fe ₂ O ₃ Low TiO ₂ 100 lbs			
5A1075	19185-1	EIRICH BALLS	60.0 B.Bxte. (20.0%)	172.20 H.Clay (57.4%)	67.80 Met.Coke (22.6%)	80% Stoich Carbon 300 lbs	3/8" x 6M	73.5%	469.6#/sq
5A1077	19185-9		15 Wharton Coal (30%)	30 Met.Coke (70%)		50 lbs	1/4" dia.		33.75#/sq

TABLE 3 CONT.

(74C1450601)

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TABLE 4

COMPARISON OF BURDEN PREPARATION METHODS

<u>TYPE</u>	<u>EXPT. NO.</u>	<u>FIRE COMPRESSION</u> <u>STRENGTH</u>		<u>ABRASION BREAKDOWN %</u>	<u>22 FOOT DROP, BREAKDOWN - %</u>
		<u>MPa</u>	<u>PSI</u>		
EXTRUSION	5A1043	0.67	97	15	--
BRIQUETTE	5A1044	2.26	328	15	--
EIRICH BALL	5A1055	1.07	155	1.5	--
EXTRUSION	5A1046	0.62	90	3	--
EIRICH BALLS	5A1075	3.23	470	0.1	2.8
DRAVE DISK BALLS	5A1068	0.79	115	6.0	27.4

TABLE 5

QUALITATIVE BURDEN EVALUATION

<u>BURDEN</u>	<u>MAX. TEMP, °C - RETAINED SHAPE</u>	<u>STRENGTH AT MAX. TEMP.</u>
EXTRUDATES	1800	Retained initial strength
50% Fe ₂ O ₃ PELLETS	1800	Slightly weaker than initial
COKED ORE	2000	Retained initial strength
TACONITE	1200	Retained initial strength
10% Fe ₂ O ₃ EXTRUDATES	Shrank at 1600	Not strong after firing
25% Fe ₂ O ₃ EXTRUDATES	----	Good fired strength
CaO EXTRUDATES	>1500	Very strong fired
BAUXITE-CLAY EXTRUDATES	Shrank at 1600	Good strength
EXTRUDATES, BALLS, AND BRIQUETTES MADE FROM -200 MESH PARTICLES	----	Very strong at 2130°C

TABLE 6

Ore Composition

<u>Designation</u>	<u>Agglomerate Type</u>	<u>% Fe₂O₃</u>	<u>SiO₂/Al₂O₃</u>	<u>% Stoichiometric Carbon</u>
5A1055	Crushed/screened extrudates	11.8	0.614	89.0
5A1057	Crushed/screened extrudates	12.8	0.610	68.8
5A1060	Eirich-Mixer Balls	2.3	0.575	71.5

TABLE 7

Operating Parameters for VSR-3 Runs

Run No.	Run Time hr >2000°C	Max. Temp. °C	Ore Designation	Ore Charged, kg	Alloy Wt. kg	Accumulation Above Grate, kg	CO Sweep SCFH, (hr)	Grate Location	Power kW	Run Termination
VSR-3-12	1.75	2075	5A1055	0	.16	0	0	Above Tuyeres	62-58	Broken feed tube and auger
VSR-3-13	10.25	2150	5A1055	50	12.1	10.7	0	"	60	Planned
VSR-3-14	2.50	2075	5A1057	0	.62	0	0	Below Tuyeres	61	Broken auger
VSR-3-15	9.00	2050	5A1057	50	8.3	20.0	70 (2)	"	62	Planned
VSR-3-16	*	1990	5A1060	11	---	Not removed	225 (3.5)	Above Tuyeres	76	Broken auger
VSR-3-17	5.50	2180	5A1060	30	2.5	13.8	60-170 (3.25)	"	72	Broken auger

*Did not reach 2000°C

TABLE 8

VSR-3-13 MATERIAL BALANCE

<u>MATERIAL</u>	<u>C</u>	<u>AL</u>	<u>SI</u>	<u>FE</u>	<u>TI</u>	<u>O</u>	<u>TOTAL</u> <u>WT.</u> <u>(G)</u>
INGOT & ICICLE	2.97	42.0	21.15	23.4	3.41	2.26	95.19 11773
LIGHT METAL	.12	45.8	19.9	27.7	1.50	1.0	96.02 294
REACTION ZONE	7.2	37.24	19.0	13.8	2.07	19.24	98.55 15549
PREREACTIONED CHARGE	21.48	21.01	11.39	8.76	1.45	32.67	96.76 15420
ORE CHARGED	22.8	19.71	10.69	8.22	1.36	34.18	96.96 79584

<u>ELEMENT BALANCE</u>	<u>% ELEMENT ACCOUNTED FOR</u>	<u>% METALLIC YIELD</u>
AL	89.95	76.31
SI	85.33	67.12
FE	96.81	93.14
TI	87.89	75.60

TABLE 9

VSR-3-15 MATERIAL BALANCE

<u>MATERIAL</u>	<u>C</u>	<u>AL</u>	<u>SI</u>	<u>FE</u>	<u>TI</u>	<u>O</u>	<u>TOTAL</u>	
							<u>%</u>	<u>WT. (G)</u>
INGOT	2.91	38.2	24.45	25.6	3.64	1.88	96.68	8300
REACTION ZONE	5.99	36.18	19.4	14.22	2.50	20.0	98.29	19999
PREREACTIONED CHARGE	17.28	22.79	12.27	9.62	1.60	35.34	98.90	22767
ORE CHARGED	19.00	21.25	11.44	8.97	1.49	36.81	98.96	81647

<u>ELEMENT BALANCE</u>	<u>% ELEMENT ACCOUNTED FOR</u>	<u>% METALLIC YIELD</u>
AL	89.88	64.37
SI	93.17	76.09
FE	97.75	92.80
TI	95.88	85.76

TABLE 10 -90-

VSR-3-18 MATERIAL BALANCE

<u>MATERIAL</u>	<u>C</u>	<u>Al</u>	<u>Si</u>	<u>Fe</u>	<u>Ti</u>	<u>O</u>	<u>TOTAL</u>	
							<u>%</u>	<u>wt gm</u>
Ingot	4.56	60.1	25.6	4.02	4.34	1.46	100.08	3499
Reaction Zone	8.93	41.1	20.6	2.90	2.90	25.7	102.13	11387
Pre-Reacted Charge	19.53	24.22	12.30	1.64	1.65	36.67	96.01	21130
Ore Charged	19.8	23.92	12.14	1.62	1.63	36.91	96.02	52054

ELEMENT BALANCE% ACCOUNTED FOR% METALLIC YIELD

Al	95.60%	79.34%
Si	92.40	65.08
Fe	96.99	84.74
Ti	97.79	89.51

TABLE 11

VSR-3-19 MATERIAL BALANCE

<u>MATERIAL</u>	<u>C</u>	<u>Al</u>	<u>Si</u>	<u>Fe</u>	<u>Ti</u>	<u>O</u>	<u>%</u>	TOTAL <u>wt gm</u>
Ingot & Icicle	8.28	52.8	27.5	3.69	3.71	1.98	97.96	14940
Reaction Zone	17.8	32.4	30.9	1.81	2.13	12.62	97.66	10130
Pre-Reacted Zone	19.96	23.82	13.31	1.46	1.63	37.46	97.64	13758
Ore Charged	20.20	23.56	13.17	1.44	1.61	37.66	97.64	70361

ELEMENT BALANCE

% ELEMENT ACCOUNTED FOR

% METALLIC YIELD

Al	87.09%	78.65%
Si	97.86	95.39
Fe	92.29	87.59
Ti	87.64	79.80

TABLE 12

Materials Balances on Combustion Runs

	Run No.			
	<u>23</u>	<u>24</u>	<u>26</u>	<u>27</u>
(1) Initial Coke, g	21356	21500	20616	17393
(2) Coke charged, g	23826	36399	9200	18630
(3) O ₂ Blown, ft ³	1280	1720	360	840
(4) Coke Consumed, g	40051	53818	12855	29994
(5) Coke Remaining, g	5131	4081	16961	6029
(6) Ore Charged, g	15818	27546	8250	15180
(7) (5) + (6)	20949	31627	25211	21209
(8) Material Recovered, g	19701	27863	22990	23609
(9) Final C/O = (5)/(6)	0.32	0.15	2.06	0.40

TABLE 13

AUGER PERFORMANCE

<u>Run</u>	<u>Auger Length</u>	<u>Auger Bottom To Tuyere</u>	<u>Grate Position Relative to Tuyere</u>	<u>RPM</u>	<u>Miscellaneous</u>	<u>Reason for Failure</u>
VSR-3-18	25-1/4" 4 Sections	24"	+3-1/2"	1.07	Induction run, no gas, graphite chunks on grate, low Fe ₂ O ₃ ore pellets, remaining auger remnants being used, 5# activated 100# ore was added.	No failure
VSR-3-19	25-1/4" 4 Sections	24"	+4-1/2"	1.13	Same as VSR-3-18 except Ar gas flowing through 1 tuyere, and ~8# act. C/100# ore was added.	No failure
VSR-3-20	25-1/4" 4 Sections	24"	-1-1/2"	1.0	Coke combustion run using 1 tuyere, same auger as VSR-3-19, low Fe ₂ O ₃ ore pellets and pet coke in ~2.8:1 wt ratio was added. A hole burnt through the liner opposite the tuyere.	Heavy bridging in bottom section of auger, failed between sections 1&2,
VSR-3-21						No auger used
VSR-3-22	25-1/4" 4 Sections	24"	-2"	1.05	Coke combustion run using 3 tuyeres, same auger as VSR-3-19, 10% Fe ₂ O ₃ ore pellets and pet coke charged to bin, pet coke charged to bed, shutdown due to hot spots 15 min. after O ₂ turned on	No failure during run. Auger broke during disassembly

TABLE 13 cont.

AUGER PERFORMANCE

<u>Run</u>	<u>Auger Length</u>	<u>Auger Bottom to Tuyere</u>	<u>Grate Position Relative to Tuyere</u>	<u>RPM</u>	<u>Miscellaneous</u>	<u>Reason for Failure</u>
VSR-3-23	30" full section 6" reduced section 1 pc. continuous flutes	24"	-1-1/2"	1.08	Coke combustion run using 3 tuyeres and new 1 pc. auger, 50% 5A1060 $\text{SiO}_2/\text{Al}_2\text{O}_3=.5752$, $\text{C}=71.03\%$ and 50% 5A1068 $\text{SiO}_2/\text{Al}_2\text{O}_3=.783$, $\text{C}=110.27\%$ O_2 @ 80 ² scfh/tuyere normal shutdown after 43 slugs of ore were fed	No failure
VSR-3-24	30" full and 6" reduced sections 1 pc. auger	20"	-1-1/2"	1.07	Identical conditions as VSR-3-23 except for lowering of auger by 4". Fed 78 slugs of ore.	No failure.
VSR-3-25	30" full and 6" reduced section, 1 pc. auger	20"	-2-1/2"	1.08	Combustion coke run. Slots cut in each flute 180° or 6" apart, 9 slots cut in all. Met coke and 40 scfh O_2 /tuyere fed along with two ore mixtures 50% 5A1060/50% 5A1068 and 73% 5A1063/27% 5A1068.	Actual shutdown due to breaking of shear pin. Bottom 3/4" of auger burned off.
VSR-3-26	1 pc. auger with slots	20"	-2-1/2"	.98	Same as VSR-3-25 using the same charge materials. 3/8" graphite shear pin replaced by 1/8" brass pin.	Shutdown after 25 ore slugs due to breaking of shear pins.
VSR-3-27	1 pc. auger with slots	20"	-2-1/2"	1.7/1.99	Same as VSR-3-26 with only 73% 5A1063/27% 5A1068 ore mixture in use. Shear pin moved to horizontal part of right angle drive.	Shutdown due to shear pin failure after 46 slugs of ore were fed.

Table 14 Burden for BF Runs

<u>Run</u>	<u>Burden</u>	<u>Preheat Coke Height (cm)</u>	<u>Preheat Coke Weight (g)</u>	<u>Burden Height (cm)</u>	<u>Ore Weight (g)</u>	<u>Coke Weight (g)</u>
BF1	None	Empty	--	--	--	--
BF2	Coke	89	4000	--	--	--
BF3	B-1 Briquettes	15	560	71	1800	2200
BF4	E-3 Extrudates	15	560	71	1800	2200
BF5	50% Fe ₂ O ₃ pellets	30	1390	68	2000	2000
BF6	Coked Ore	30	1300	68	2700	560
BF7	E-3 Extrudates + Charcoal	30	460	68	620	620
BF8	Taconite	15	560	74	5000	1500
BF9	50% Fe ₂ O ₃ Extrudates and Lime	15	560	66	2170	1820

Table 15 Operating Variables for BF Runs

<u>Run</u>	<u>O₂ Flow Rate (ℓ/min)</u>	<u>T-O₂ On (°C)</u>	<u>t-O₂ On (min)</u>	<u>t-O₂ Off (min)</u>	<u>Tmax (°C)</u>
BF1	None	--	--	--	1910
BF2	3.0/6.0	1600	210	370	2020
BF3	13.0	1550	105	112	1600
BF4	13.0	1670	80	192	2110
BF5	13.0	1020	35	160	2140
BF6	13.0	1010	34	120	2050
BF7	13.0	1210	45	93	2120
BF8	7.8 O ₂ 18.2 Ar	820	35	105	1520
BF9	13.0/2.0	1060	40	205	2140

Table 16 Results of BF Runs

<u>RUN</u>	<u>BRIDGE HEIGHT ABOVE TUYERE (cm)</u>	<u>BRIDGE THICKNESS (cm)</u>	<u>BURDEN MOVEMENT (cm)</u>	<u>PRODUCT</u>	<u>COMMENTS</u>
BF1	--	--	--	--	--
BF2	None	None	13	--	--
BF3	27	13	None	None	Sight glass problem
BF4	38	18	None	SiC, C	--
BF5	25 Lower 50 Upper	15 28	18	24 g metal	P relief valve
BF6	20 lower 43 upper	13 30	13	None	plunger
BF7	38	8	18	metallic & carbide	Coil moved down
BF8	None	--	37	1500 g metal 500 g slag	metallurgical coke
BF9	25	8	34	550 g metal	P gauge

Table 17 Burden for BF Runs

<u>Run</u>	<u>Burden</u>	<u>Preheat Coke Height (cm)</u>	<u>Preheat Coke Weight (g)</u>	<u>Burden Height (cm)</u>	<u>Ore Weight (g)</u>	<u>Coke Weight (g)</u>
BF10	10% Fe ₂ O ₃	15	560	70	2000	2000
BF11	10% Fe ₂ O ₃ + CaO	15	560	65	2400	1600
BF12	25% Fe ₂ O ₃	15	560	68	2000	2000
BF13	Koppers & CaO -4m + 8m	15	560	66	1930	2070
BF14	10% Fe ₂ O ₃ + CaO	15	560	67	2400	1600
BF15	10% Fe ₂ O ₃ + CaO	15	560	81	2650	2040
BF16	C-1	15	560	74	1600	2400
BF17	C-3	14	560	75	2000	2000
BF18	C-4	None	None	99	3870	1690
BF19	25% Fe ₂ O ₃ + CaO	None	None	84	2710	2050

Table 18 Operating Variables for BF Runs

<u>Run</u>	<u>O₂ Flow Rate (ℓ/min)</u>	<u>CO₂ Flow Rate (ℓ/min)</u>	<u>T Gas On (min) C</u>	<u>t Gas On (min)</u>	<u>t Gas Off (min)</u>	<u>Tmax (C)</u>
BF10	13.0	--	1000	36	92	2020
BF11	13.0	--	990	46	95	1700
BF12	8.9	4.1	1000	55	125	2000
BF13	16.1	9.9	980	40	78	2100
BF14	13.0	--	970	37	77	1900
BF15	26.0	--	980	35	70	2000
BF16	13.0	--	990	60	100	1760
BF17	13.0	--	995	30	90	1820
BF18	26.0	--	1820	43	93	1940
BF19	26.0	--	1800	50	70	1990

Table 19 Results of BF Runs

<u>RUN</u>	<u>BRIDGE HEIGHT ABOVE TUYERE (cm)</u>	<u>BRIDGE THICKNESS (cm)</u>	<u>BURDEN MOVEMENT (cm)</u>	<u>PRODUCT</u>	<u>COMMENTS</u>
BF10	25 lower 38 upper	3 3	None	Metallic - 30 g	Scull on tuyere
BF11	None	None	13	Metallic - 20 g	5 turn coil tuyere plugged
BF12	23	7	8	Metallic - 10 g	Scull on Tuyere
BF13	14	20	8	Slag -10 g	--
BF14	None	None	5	Metallic - 10 g	Scull on Tuyere
BF15	27	8	8	Carbide	Columnar Charge + Grate Lowered
BF16	33	3	None	Slag - 76 g	Coil lowered Rathole
BF17	13	2	10	Slag - 116 g	Rathole
BF18	48	3	6	Metallic - 910 g Slag - 400 g	Columnar Charge Scull on Tuyere
BF19	28	3	3	Metallic - 48 g	Columnar Charge Scull on Tuyere

TABLE 20 EXTRUDATES CONTAINING CaO

<u>Batch</u>	<u>Fe₂O₃</u>	<u>CaO</u>	<u>Al₂O₃</u>	<u>SiO₂</u>	<u>C</u>
C-1	--	30	38	32	--
C-2	50	15	19	16	--
C-3	--	22.6	28.6	24.1	24.6
C-4	39.2	11.8	14.9	12.5	21.6

Table 21 Burden for BF Runs

<u>Run</u>	<u>Burden</u>	<u>Preheat Coke Height (cm)</u>	<u>Preheat Coke Weight (g)</u>	<u>Burden Height (cm)</u>	<u>Ore Weight (cm)</u>	<u>Coke Weight (g)</u>
BF20	Pet Coke -4m+8m	-	-	89	0	4330
BF21	Met Coke -3/8+4m	-	-	91	0	3340
BF22	10% Fe ₂ O ₃ +CaO	10	560	85	2760	1850
BF23	10% Fe ₂ O ₃	-	-	90	2200	2200
BF24	25% Fe ₂ O ₃	13	560	61	2000	2000
BF25	Coked Ore	13	560	84	4260	0
BF26	Koppers (uncrushed)	13	480	84	2110	2310
BF27	Activated Charcoal	-	-	86	0	3500
BF28	Activated Charcoal	-	-	89	0	3500
BF29	Prereduced 10% Fe ₂ O ₃	-	-	82	2280	2780

Table 22 Operating Variables for BF Runs

<u>Run</u>	<u>O₂ Flow Rate (L/min)</u>	<u>T-O₂ on (°C)</u>	<u>t-O₂ on (min)</u>	<u>t-O₂ off (min)</u>	<u>T max (°C)</u>
BF20	13/26	1125	30	85	1940
BF21	13/26	965	24	105	2130
BF22	13	1085	23	88	2050
BF23	26	1800	51	65	1950
BF24	26	1500	60	94	2070
BF25	13	1020	40	61	1550
BF26	26	1500	35	56	1980
BF27	26	960	26	115	2290
BF28	48	1005	31	70	1855
BF29	26	1800	78	92	1910

Table 23 Results of BF Runs

<u>Run</u>	<u>Bridge Height Above Tuyere (cm)</u>	<u>Bridge Thickness (cm)</u>	<u>Burden Movement (cm)</u>	<u>Product</u>	<u>Comments</u>
BF20	?	?	0	None	Side Entry Tuyere
BF21	20	8	0	None	
BF22	10	10	14	Metallic 30g Slag 140g	
BF23	13	8	0	None	Layered Charge
BF24	46 upper 8 lower	3 8	0	Metallic 58g	Coil Spread
BF25	None	None	None	None	Equipment Failure
BF26	33	?	0	None	Large Charge
BF27	56	10	11	None	
BF28	41	3	0	None	
BF29	6	3	0	Metallic + Carbide	Burn Through

Table 24 Burden for BF Runs

<u>Run</u>	<u>Burden</u>	<u>Preheat Coke Height (cm)</u>	<u>Preheat Coke Weight (g)</u>	<u>Burden Height (cm)</u>	<u>Ore Weight (g)</u>	<u>Coke Weight (g)</u>
BF30	10% Fe ₂ O ₃ 5Al ₂ O ₃	10	560	84	1950	1950
BF31	10% Fe ₂ O ₃ 5Al ₂ O ₃	10	560	76	3300	1100

Table 25 Operating Variables for BF Runs

<u>Run</u>	<u>O₂ Flow Rate (L/min)</u>	<u>T-O₂ on (°C)</u>	<u>t-O₂ on (min)</u>	<u>t-O₂ off (min)</u>	<u>T max (°C)</u>
BF30	13	1840	110	158	2130
BF31	13	1880	50	on-off (~60 total)	2300

Table 26 Results of BF Runs

<u>Run</u>	<u>Bridge Height Above Tuyere (cm)</u>	<u>Bridge Thickness (cm)</u>	<u>Burden Movement (cm)</u>	<u>Product</u>	<u>Comments</u>
BF30	28	3	3	None	Scull on Tuyere 66 g
BF31	23	2	2	Metallic in Reservoir 67 g	Scull on Tuyere 100 g 3/1 Ore Coke Ratio

Table 27 Cold Modeling of Auger

<u>Charge Depth</u> <u>(cm)</u>	<u>1 rpm</u> <u>(sec/rev)</u>	<u>3 rpm</u> <u>(sec/rev)</u>
0	52	17.0
4	52	17.6
10	56	--
15	58	17.6
23	60	17.8
33	--	18.2
43	67	18.5

Table 28 Burden for AF Runs

<u>Run</u>	<u>Burden</u>	<u>Ore (wt)</u>	<u>Additional C (wt)</u>	<u>% Stoich C</u>	<u>Ore Size</u>	<u>Coke Size</u>
AF-1	5A1060/63	3240	260	100	-6+8	-1/4+6
AF-2	5A1060/63	2780	220	100	-8+16	-8+16
AF-3	5A1060/63	2780	220	100	-8+16	-8+16
AF-4	5A1060/63	7280	580	100	-8+16	-8+16
AF-5	5A1060/63	5560	440	100	-6+8	-8+16
AF-6	5A1060/63	6100	490	100	-6+8	-8+16

Table 29 Operating Variables for AF Runs

<u>Run</u>	<u>CO Flow Rate (L/min)</u>	<u>T-CO (on) (°C)</u>	<u>t-CO on (min)</u>	<u>t-power off (min)</u>	<u>t at T > 2000°C (min)</u>	<u>T (max) (°C)</u>	<u>Auger rpm</u>
AF-1	7.5	25	0	65	0	1850	0.8
AF-2	15	25	0	1	0	--	3.2-2.6
AF-3	0	--	--	130	0	1165	1.3-0.5
AF-4	15	995	35	180	65	2100	3.1-2.2
AF-5	15	1085	27	321	219	2300	3.0-2.4
AF-6	15	1130	15	240	170	2120	3.1-2.1

Table 30 Results of AF Runs

<u>Run</u>	<u>Bridge Height above grate (cm)</u>	<u>Bridge Thickness (cm)</u>	<u>Product</u>	<u>Termination</u>	<u>Cause</u>
AF-1	--	--	--	set screw shear pin	poor alignment
AF-2	--	--	--	shear pin	thermal expansion
AF-3	--	--	--	shear pin	thermal expansion
AF-4	11	10	371g (19%)	shear pin	liquid bridge
AF-5	11	5	315g (25%)	shear pin	bridge under auger
AF-6	9	5	850g (49%)	motor stalled	bridge under auger

TABLE 31

<u>O₂ Preheat Temperature</u> <u>(°K)</u>	<u>Heating Coke</u> <u>Requirements, %</u>
298	100.00
500	96.89
1000	89.48
1273 (1000°C)	85.70
1500	82.70
2000	76.56
2273 (2000°C)	73.44
2500	70.98
3000	65.92
3273 (3000°C)	63.36
3500	61.33
4000	57.15
4273 (4000°C)	55.04
4500	53.36
4985 (4712°C)	50.00

TABLE 32 MODAL COMPOSITION OF VSR-13 METAL SAMPLES (VOLUME %)

	<u>Al-Si</u>	<u>FeSiAl₅</u>	<u>FeSi₂Al₄</u>	<u>Ti₂Fe₂Si₃Al₃</u>	<u>SiC</u>	<u>Si</u>	<u>CaSi₂Al₂</u>
(3)	26	9	41	10	13	2	trace
(2)	16	12	47	12	11	1	-
(1)	18	20	37	8	17	1	-
(4)	32		48	9	11	1	trace

TABLE 33 MODAL COMPOSITION OF VSR-15 METAL SAMPLES (VOLUME %)

	Al-Si	FeSiAl ₃	FeSi ₂ Al ₄	Ti ₂ Fe ₂ Si ₃ Al ₃	SiC	Si	Slag
(1)	11	20	18	6	14	1	31
(2)	11	34	26	7	12	2	8
(3)	13	31	25	8	9	1	12
(4)	12	31	26	12	15	-	5

TABLE 34 MODAL COMPOSITION OF VSR-17 ICICLE (WT %)

Al	38%
Si	11%
FeSiAl ₅ (total eutectic)	trace (49%)
Fe-Si-Al	10%
Si	9%
TiSi ₂ (Fe,Al)	10%
SiC	21%

TABLE 35 MODAL COMPOSITION OF VSR-18 METAL SAMPLES (VOLUME %)

Spl. No.	Eutectic				Spheroids			Intermetallics			
	Al	Si	FeSiAl ₅	(Total)	Al ₄ SiC ₄	SiC	(Total)	Fe-Si-Al ¹	Si	TiSi ₂ (Al)	SiC
(1) ¹	45	14	2	(61)	8	9	(17)	4	13	3	trace
(2)	35	12	1	(48)	10	11	(21)	8	13	9	trace
(3) top	40	16	3	(59)	8	10	(18)	8	4	11	trace
(3) base	39	16	1	(56)	3	1	(4)	5	8	6	21
(2) ²	35	12	1	(48)	10	11	(21)	8	13	9	trace
(4)	42	15	2	(59)	7	10	(17)	6	8	8	1
(5)	44	13	2	(59)	7	12	(19)	6	12	5	0

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1. Samples (1), (2), and (3) top are a vertical traverse from top to bottom in the ingot. Sample (3) base is the basal zone containing SiC platelets.
2. Samples (2), (4), and (5) are a radial traverse from the center to the edge of the ingot. Sample (5) does not include the peripheral SiC envelope adjacent to the graphite wall.
3. Tentatively identified as FeSi₂Al₄, with unreacted cores of an unidentified high-temperature Fe-Si-Al phase.

TABLE 36 MODAL COMPOSITION OF VSR-19 METAL SAMPLES (VOLUME %)

Spl. No.	Eutectic				Intermetallics			
	Al	Si	FeSiAl_5	(Total)	Fe-Si-Al^1	Si	$\text{TiSi}_2(\text{Al})$	SiC
(2)	45	13	2	(60)	3	7	6	24
(3)	48	11	3	(62)	4	5	6	25
(4)	45	8	2	(55)	4	9	6	26
(5)	45	13	1	(59)	3	6	8	25

1. Tentatively identified as FeSi_2Al_4 , with unreacted cores of an unidentified high-temperature Fe-Si-Al phase.

TABLE 37

Observed Liquidus Temperatures in Al-Si Alloys

<u>Alloy Composition</u>	<u>Observed Liquidus Temp. (°C)</u>	<u>Equilibrium Diagram Liquidus Temp. (°C)</u>	<u>Max. Melt Temp. (°C)</u>	<u>Remarks</u>
Al-25% Si	771	750	960	
Al-28% Si	785	795	841	
Al-35% Si	766	890	981	Note Supercooling
Al-30% Si-3% Fe (1)	754	820	872	Note Supercooling
(2)	758	820	808	Note Supercooling
Al-29% Si-6.9% Fe	803	802	878	
Al-28% Si-8% Fe	855	810	928	
Al-35% Si-3% Fe	854	895	977	Note Supercooling
Al-34% Si-4.4% Fe	866	905	957	Note Supercooling
Al-28% Si-0.7% Ti	756	-	782	
Al-29% Si-1.2% Ti	802	-	882	
Al-30% Si-1.1% Ti	795	-	890	
Al-28% Si-3% Fe-0.8% Ti	785	-	838	
Al-29% Si-5% Fe-0.9% Ti	803	-	942	
Al-25% Si-5% Fe-1.4% Ti	876	-	1007	
Al-35% Si-5% Fe-2.9% Ti (5% SiC)	911	-	1033	

TABLE 38

Composition† of Starting Alloys and Eutectic Drains
Direct Reduction Alloy Purification

<u>Experiment</u>	<u>Si Content, wt.%</u>		<u>Fe Content, wt.%</u>		<u>Ti Content, wt.%</u>	
	<u>Initial</u>	<u>Drain</u>	<u>Initial</u>	<u>Drain</u>	<u>Initial</u>	<u>Drain</u>
11	24.0	15.6	--	--	--	--
12	35.0	15.1	--	--	--	--
7	29.7	--	3.0	--	--	--
8	28.2	13.0	2.9	0.8	--	--
*20	28.9	13.9	6.9	1.0	--	--
*19	28.4	13.7	8.0	1.1	--	--
13	34.2	14.6	2.9	1.0	--	--
14	34.3	--	4.4	--	--	--
16	36.7	13.4	3.1	0.9	--	--
9	28.2	15.3	--	--	0.70	0.2
*21	30.1	14.4	--	--	1.13	0.15
*22	28.8	18.3	--	--	1.25	0.40
10	28.2	13.0	2.7	0.8	0.70	0.08
*23	29.0	20.5	5.0	2.6	0.90	0.39
17	35.0	--	4.6	--	1.4	--
18	35.0	--	5.3	--	2.9	--

†Remainder Al

*Experiments performed First Quarter, Phase II.

TABLE 39

BENCH SCALE RESULTS, AL-SI-FE
EXPERIMENT 20

	<u>WEIGHT, g</u>	<u>CONTENT, %</u>	
		<u>Si</u>	<u>Fe</u>
STARTING ALLOY AFTER SKIM REMOVAL AND SAMPLING	2397.6	28.9	6.9
DRAIN (588°C)	288.2	13.9	1.0
REMELT CUT #1 (700°C)	265.1	25.7	5.0
#2 (800°C)	758.5	22.5	3.7
#3 (900°C)	665.5	36.3	11.0
#4 (>900°C)	121.9	38.7	9.6

	<u>AVG. CONTENT, %</u>		<u>CUMULATIVE YIELD</u>	<u>AVAIL. AL RECOVERED</u>
	<u>Si</u>	<u>Fe</u>		
DRAIN	13.9	1.0	12%	16%
DRAIN + REMELT CUT 1	19.6	2.9	23%	28%
DRAIN + REMELT CUT 1,2	21.2	3.4	55%	64%
DRAIN + REMELT CUT 1,2,3	26.3	5.9	82%	87%
DRAIN + REMELT CUT 1,2,3,4	27.0	6.2	88%	91%

TABLE 40

BENCH SCALE RESULTS, AL-SI-TI
EXPERIMENT 21 CONTINUOUS DRAIN

	<u>WEIGHT, g</u>	<u>CONTENT, %</u>	
		<u>Si</u>	<u>Ti</u>
STARTING ALLOY AFTER SKIM REMOVAL AND SAMPLING	2179.7	30.1	1.13
DRAIN (590°C)	729.1	14.4	0.15
REMELT CUT #1 (730°C)	489.5	23.5	0.54
#2 (730-865°C)	230.5	33.8	1.0
#3 (865-990°C)	297.1	44.1	1.8

	<u>AVG. CONTENT, %</u>		<u>CUMULATIVE YIELD</u>	<u>AVAIL. AL RECOVERED</u>
	<u>Si</u>	<u>Ti</u>		
DRAIN	14.4	0.15	33%	42%
DRAIN + REMELT 1	18.0	0.31	56%	66%
DRAIN + REMELT 1,2	20.6	0.42	66%	76%
DRAIN + REMELT 1,2,3	24.6	0.65	80%	87%

TABLE 41

BENCH SCALE RESULTS, AL-Si-Ti SYSTEM
EXPERIMENT 22

	<u>WEIGHT, g</u>	<u>CONTENT, %</u>	
		<u>Si</u>	<u>Ti</u>
STARTING ALLOY AFTER SKIM REMOVAL AND SAMPLING	2392.7	28.8	1.25
DRAIN (590°C)	960.1	18.3	0.40
REMELT CUT #1 (700°C)	409.0	23.2	0.67
#2 (800°C)	153.8	27.6	0.59
#3 (900°C)	219.1	35.5	1.24
#4 (935°C)	177.4	42.1	2.1

	<u>AVG. CONTENT, %</u>		<u>CUMULATIVE YIELD</u>	<u>AVAIL. AL RECOVERED</u>
	<u>Si</u>	<u>Ti</u>		
DRAIN	18.3	0.40	40%	47%
DRAIN + REMELT 1	19.8	0.48	57%	65%
DRAIN + REMELT 1,2	20.6	0.49	64%	72%
DRAIN + REMELT 1,2,3	22.4	0.58	73%	80%
DRAIN + REMELT 1,2,3,4	24.2	0.72	80%	86%

TABLE 42

BENCH SCALE RESULTS, AL-SI-FE-TI
EXPERIMENT 23

	<u>WEIGHT, g</u>	<u>CONTENT, %</u>		
		<u>Si</u>	<u>Fe</u>	<u>Ti</u>
STARTING ALLOY AFTER SKIM REMOVAL AND SAMPLING	2450.8	29.0	5.0	0.90
DRAIN (590°C)	794.9	20.5	2.6	0.39
REMELT CUT #1 (700°C)	213.2	23.1	3.4	0.36
#2 (760°C)	305.4	25.6	5.0	0.45
#3 (845°C)	416.7	31.4	8.0	0.89
#4 (940°C)	312.3	38.6	7.3	1.7

	<u>AVG. CONTENT, %</u>			<u>CUMULATIVE YIELD</u>	<u>AVAIL. AL RECOVERED</u>
	<u>Si</u>	<u>Fe</u>	<u>Ti</u>		
DRAIN	20.5	2.6	0.39	32%	38%
DRAIN + REMELT 1	21.0	2.8	0.38	41%	48%
DRAIN + REMELT 1,2	22.1	3.3	0.40	54%	61%
DRAIN + REMELT 1,2,3	24.3	4.4	0.41	71%	77%
DRAIN + REMELT 1,2,3,4	26.5	4.9	0.61	83%	87%

TABLE 43

Casting Alloy Product Yields Based on Bench Scale Results

<u>Alloy Composition</u>	<u>Drain</u>			<u>Cumulative Product</u>		
	<u>Si Content</u>	<u>Avail. Al Rec.</u>	<u>Yield</u>	<u>Si Content</u>	<u>Avail. Al Rec.</u>	<u>Yield</u>
Al-28% Si	13.1%	35%	28%	17.3%	78%	66%
Al-28% Si-3% Fe	13.0%	32%	25%	17.4%	71%	59%
*Al-29% Si-7% Fe	13.9%	16%	12%	18.0%	28%	23%
Al-28% Si-0.7% Ti	15.3%	38%	32%	16.8%	75%	64%
*Al-30% Si-1.1% Ti	14.4%	42%	33%	18.0%	66%	56%
*Al-29% Si-1.2% Ti	18.3%	47%	40%	18.3%	47%	40%
Al-28% Si-2.7% Fe-0.7% Ti	13.0%	9%	7%	18.2%	49%	42%
*Al-29% Si-5.0% Fe-0.9% Ti	20.5%	38%	32%	20.5%	38%	32%

*Experiments performed Second Quarter, Phase B

TABLE 44

Bench Scale Results, Al-Si-Fe-Ti System

Experiment 24

	<u>Weight, g</u>	<u>Content, %</u>		
		<u>Si</u>	<u>Fe</u>	<u>Ti</u>
Starting Alloy After Sampling and Skim Removal	2428.0	28.4	2.90	0.64
Drain (590°C)	748.0	16.0	1.08	0.15
Remelt Cut #1 (715°C)	516.5	25.3	3.67	0.47
Remelt Cut #2 (800°C)	392.5	34.7	0.68	0.06
Remelt Cut #3 (900°C)	97.5	37.0	4.30	1.41
Remelt Cut #4 (1000°C)	267.5	43.7	3.70	1.76

	<u>Average Content, %</u>			<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>	<u>Ti</u>		
Drain	16.0	1.08	0.15	31%	37%
Drain + Remelt Cut 1	19.8	2.14	0.28	52%	60%
Drain + Remelt Cuts 1,2	23.3	1.79	0.23	68%	75%
Drain + Remelt Cuts 1,2,3	24.1	1.93	0.29	72%	78%
Drain + Remelt Cuts 1,2,3,4	26.7	2.16	0.49	83%	86%

TABLE 45

Bench Scale Results, Al-Si-Fe-Ti System

Experiment 25

	<u>Weight, g</u>	<u>Content, %</u>		
		<u>Si</u>	<u>Fe</u>	<u>Ti</u>
Starting Alloy After Sampling and Skim Removal	2407.3	29.4	2.94	1.20
Drain (590°C)	829.9	18.4	1.49	0.37
Remelt Cut #1 (700°C)	139.5	26.8	4.19	0.63
Remelt Cut #2 (760°C)	573.0	25.3	5.02	0.42
Remelt Cut #3 (840°C)	156.0	34.6	4.45	1.27
Remelt Cut #4 (940°C)	212.0	40.7	4.05	2.07

	<u>Average Content, %</u>			<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>	<u>Ti</u>		
Drain	18.4	1.49	0.37	34%	41%
Drain + Remelt Cut 1	19.6	1.88	0.41	40%	47%
Drain + Remelt Cuts 1,2	21.7	3.04	0.41	64%	72%
Drain + Remelt Cuts 1,2,3	22.9	3.17	0.49	70%	78%
Drain + Remelt Cuts 1,2,3,4	24.9	3.27	0.67	79%	85%

TABLE 46

Bench Scale Results, Al-Si-Fe System

Experiment 26

	<u>Weight, g</u>	<u>Content, %</u>	
		<u>Si</u>	<u>Fe</u>
Starting Alloy After Sampling and Skim Removal	2571.4	29.2	10.2
Drain (590°C)	16.6	14.1	1.12
Remelt Cut #1 (700°C)	625.0	24.8	6.7
Remelt Cut #2 (760°C)	503.4	27.9	9.1
Remelt Cut #3 (840°C)	823.7	32.0	16.3
Remelt Cut #4 (940°C)	362.5	34.0	15.6

	<u>Content, %</u>		<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>		
Drain	14.1	1.1	1%	1%
Drain + Remelt Cut 1	24.5	6.6	25%	28%
Drain + Remelt Cuts 1,2	26.0	7.7	44%	49%
Drain + Remelt Cuts 1,2,3	28.5	11.3	76%	76%
Drain + Remelt Cuts 1,2,3,4	29.4	12.0	91%	88%

TABLE 47

Bench Scale Results, Al-Si-Fe System

Experiment 27

	<u>Weight, g</u>	<u>Content, %</u>	
		<u>Si</u>	<u>Fe</u>
Starting Alloy After Sampling and Skim Removal	2589.2	29.2	12.7
Drain	--	--	--
Remelt Cut #1	316.3	23.0	7.5
Remelt Cut #2	337.5	25.1	5.9
Remelt Cut #3	1499.8	30.7	17.6
Remelt Cut #4	173.6	30.5	19.3

	<u>Content, %</u>		<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>		
Drain	--	--	--	--
Drain + Remelt Cut #1	23.0	7.5	12%	15%
Drain + Remelt Cuts 1,2	24.1	6.7	25%	30%
Drain + Remelt Cuts 1,2,3	28.7	14.3	83%	82%
Drain + Remelt Cuts 1,2,3,4	28.8	14.6	90%	87%

TABLE 48

Bench Scale Results, Al-Si-Fe System

Experiment 28R

	<u>Weight, g</u>	<u>Content, %</u>	
		<u>Si</u>	<u>Fe</u>
Starting Alloy after Sampling and Skim Removal	2490.2	36.6	2.57
Drain (590°C)	195.9	14.3	0.92
Remelt Cut #1 (700°C)	765.4	23.6	2.74
Remelt Cut #2 (760°C)	358.0	26.7	4.80
Remelt Cut #3 (840°C)	113.0	31.2	4.40
Remelt Cut #4 (940°C)	101.0	37.4	6.40

	<u>Avg. Content, %</u>		<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>		
Drain	14.3	0.92	8%	11%
Drain + Remelt Cut 1	21.7	2.37	39%	48%
Drain + Remelt Cuts 1,2	23.1	3.03	53%	64%
Drain + Remelt Cuts 1,2,3	23.7	3.14	58%	69%
Drain + Remelt Cuts 1,2,3,4	24.6	3.35	62%	73%

Bench Scale Results, Al-Si-Fe System

Experiment 29

	<u>Weight, g</u>	<u>Content, %</u>	
		<u>Si</u>	<u>Fe</u>
Starting Alloy After Sampling and Skim Removal	2478.4	38.0	9.6
Drain (590°C)	--	--	--
Remelt Cut #1 (700°C)	250.7	23.8	4.1
Remelt Cut #2 (760°C)	276.8	26.8	6.5
Remelt Cut #3 (840°C)	1010.0	33.4	12.6
Remelt Cut #4 (940°C)	131.3	37.4	11.4

	<u>Content, %</u>		<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>		
Drain	--	--	--	--
Drain + Remelt Cut 1	23.8	4.1	10%	14%
Drain + Remelt Cuts 1,2	25.4	5.4	21%	28%
Drain + Remelt Cuts 1,2,3	30.6	10.1	62%	70%
Drain + Remelt Cuts 1,2,3,4	31.2	10.2	67%	75%

TABLE 50

Bench Scale Results, Al-Si-Fe-Ti System

Experiment 31

	<u>Weight, g</u>	<u>Content, %</u>		
		<u>Si</u>	<u>Fe</u>	<u>Ti</u>
Starting Alloy After Sampling and Skim Removal	2411.9	33.1	3.08	1.65
Drain (590°C)	601.3	22.1	2.04	1.12
Remelt Cut #1 (700°C)	523.3	22.6	2.68	0.65
Remelt Cut #2 (760°C)	155.6	24.9	3.49	0.74
Remelt Cut #3 (840°C)	166.9	28.8	4.94	0.80
Remelt Cut #4 (940°C)	208.6	36.0	4.91	1.42

	<u>Content, %</u>			<u>Cumulative Yield</u>	<u>Avail. Al Recovered</u>
	<u>Si</u>	<u>Fe</u>	<u>Ti</u>		
Drain	22.1	2.04	1.12	25%	30%
Drain + Remelt Cut 1	22.3	2.34	0.90	47%	56%
Drain + Remelt Cuts 1,2	22.6	2.48	0.88	53%	63%
Drain + Remelt Cuts 1,2,3	23.4	2.76	0.87	60%	70%
Drain + Remelt Cuts 1,2,3,4	24.9	3.03	0.94	69%	78%

TABLE 51
Bench Scale, Experiment 34

Al-Si-Fe

Pooled High-Fe Cuts

	<u>Weight, g</u>	<u>Content, %</u>	
		<u>Si</u>	<u>Fe</u>
Starting alloy after skim removal and sampling	2350.7	31.6	15.3
Drain (580°C)	--	--	--
Remelt Cut #1 (700°C)	--	--	--
#2 (760°C)	64.1	24.8	5.3
#3 (840°C)	531.0	29.4	10.8
#4 (940°C)	1006.8	31.9	16.4

	<u>% Available Fe</u>	<u>% Available Al</u>	<u>Cumulative Yield</u>
Drain	--	--	--
Remelt Cut #1	--	--	--
#2	1	4	0.2
#3	16	25	25
#4	46	42	68

TABLE 52

Bench Scale Results
Experiment 40

	Weight, g	Content, %		
		Si	Fe	Cu
Starting alloy after sampling and skim removal	2646.1	31.2	10.3	4.4
Drain (590°C)	--	--	--	--
Remelt Cut #1 (700°C)	497.0	18.0	3.1	6.6
Remelt Cut #2 (760°C)	249.5	21.9	4.9	5.9
Remelt Cut #3 (840°C)	756.0	26.6	10.0	3.9
Remelt Cut #4 (940°C)	802.3	33.0	14.2	2.4

	Content, %			Cumulative Yield, %	Avail. Al Recovered %
	Si	Fe	Cu		
Drain	--	--	--	--	--
Drain + Remelt Cut #1	18.0	3.1	6.6	19	25
Drain + Remelt Cuts #1, 2	19.3	3.7	6.3	28	37

TABLE 53
Bench Scale Results
Experiment 41

	<u>Weight, g</u>	<u>Content, %</u>		
		<u>Si</u>	<u>Fe</u>	<u>Cu</u>
Starting alloy after sampling and skim removal	2649.4	31.0	9.4	1.9
Drain (590°C)	155.0	15.1	1.5	3.4
Remelt Cut #1 (700°C)	343.5	17.2	2.1	3.2
Remelt Cut #2 (760°C)	318.2	25.4	6.6	2.5
Remelt Cut #3 (840°C)	568.4	26.2	7.0	2.4
Remelt Cut #4 (940°C)	787.5	31.7	15.5	1.4

	<u>Content, %</u>			<u>Cumulative Yield, %</u>	<u>Avail. Al Recovered %</u>
	<u>Si</u>	<u>Fe</u>	<u>Cu</u>		
Drain	15.1	1.5	3.4	6	8
Drain + Remelt Cut #1	16.5	1.9	3.3	19	26
Drain + Remelt Cuts #1, 2	20.0	3.8	3.0	31	39

TABLE 54

Bench Scale Results
Experiment 44

	<u>Weight, g</u>	<u>Content, %</u>			
		<u>Si</u>	<u>Fe</u>	<u>Cu</u>	<u>Mg</u>
Starting alloy after sampling and skim removal	2558.0	30.0	10.4	0.9	0.2
Drain (590°C)	150.3	15.9	2.2	2.2	0.3
Remelt Cut #1 (700°C)	346.6	20.8	3.6	1.6	0.4
Remelt Cut #2 (760°C)	406.8	25.2	5.6	1.5	0.3
Remelt Cut #3 (840°C)	744.7	30.6	11.4	0.8	0.2
Remelt Cut #4 (940°C)	511.1	33.3	16.3	0.4	0.1

	<u>Content, %</u>				<u>Cumulative Yield, %</u>	<u>Avail. Al Recovered %</u>
	<u>Si</u>	<u>Fe</u>	<u>Cu</u>	<u>Mg</u>		
Drain	15.9	2.2	2.2	0.3	6	8
Drain + Remelt Cut #1	19.3	3.2	1.8	0.4	19	25

TABLE 55

Bench Scale Results
Experiment 45

	<u>Weight, g</u>	<u>Content, %</u>			
		<u>Si</u>	<u>Fe</u>	<u>Cu</u>	<u>Mg</u>
Starting alloy after sampling and skim removal	2522.8	28.8	9.6	1.4	0.8
Drain (590°C)	222.6	19.4	4.0	2.1	1.1
Remelt Cut #1 (700°C)	315.9	19.6	2.5	2.2	1.3
Remelt Cut #2 (760°C)	316.8	25.5	5.9	1.9	1.0
Remelt Cut #3 (840°C)	652.8	28.9	9.5	1.4	0.8
Remelt Cut #4 (940°C)	586.2	32.6	17.8	0.7	0.4

	<u>Content, %</u>				<u>Cumulative Yield, %</u>	<u>Avail. Al Recovered %</u>
	<u>Si</u>	<u>Fe</u>	<u>Cu</u>	<u>Mg</u>		
Drain	19.4	4.0	2.1	1.1	9	11
Drain + Remelt Cut #1	19.5	3.1	2.2	1.2	21	26

TABLE 56 MODAL COMPOSITION OF METAL PURIFICATION SAMPLES (VOLUME %)

Sample No.	Matrix (Al + eutectic Si)	Si	β -Al, Fe, Si (FeSiAl ₅)	δ -Al, Fe, Si (FeSi ₂ Al ₄)	Si ₈ Ti ₄ Al
495961	73.5	20.2	5.6	-	0.7
495972	76.9	22.7	0.4	-	-
495983	77.1	22.3	0.6	-	-
496176	59.3	22.1	9.9	8.7	-
496180	74.0	19.1	4.5	2.4	-
496184	67.5	30.6	-	-	1.9

TABLE 57- MODAL COMPOSITIONS (VOLUME %)

	<u>EUTECTIC</u>						
	Al	Si	FeSiAl ₅	(Total)	Si	FeSiAl ₅	Cu-Al
Exp. #33	42	15	3	(60)	16	25	-
Exp. #41	46	13	1	(60)	19	19	2

Table 58 Results of Material Testing

<u>Material</u>	<u>Test Period</u>		<u>Result</u>
	<u>Electrolysis</u>	<u>Total</u>	
HW 177 (3 samples)	17 hrs	50 hrs	no signs of erosion, black discoloration
Foamsil 12	25	75	excellent condition
Foamsil 28	25	75	swelled, one-third of sample lost

Initial Bath Composition: 10% AlCl_3 , 90% LiCl
 Temperature: 680-725°C

Table 59 Experimental Parameters and Results of Electrolyses

No.	Initial Anode Comp. (%)		Electrolyte	Membrane	Current Efficiency (%)	Maximum Current Density A/cm ² (A/in. ²)	% at Maximum Current	Power Consumption MJ/kg (kWh/lb)	Temp. (°C)	Cathode Metal Purity (%)
22*	14.1 Si 1.46 Fe 0.16 Ti		LiCl-NaCl-AlCl ₃ 60-30-10 wt %	Graphite Cloth (25x21)	94	3.2 (21)	4	20 (2.6)	705- 745	99.96- 99.2
23	11.7 Si 0.21 Fe		LiCl-AlCl ₃ 90-10 wt %	G-5502 Graphite Cloth, Twill Weave, Continuous Filament	97.5	5.3 (34)	1	18 (2.3)	740- 750	99.980
24	"	"	"	G-5525 Graphite Cloth, Twill Weave, Staple Fiber	95	3.5 (23)	25	20 (2.5)	720- 750	99.985
25	"	"	"	Vitreous Carbon Cloth, Twill Weave	98	3.5 (23)	33	18 (2.3)	730- 750	

*large bench scale

TABLE 60

PHYSICAL PROPERTY DATA FOR WOVEN GRAPHITE CLOTHS

	<u>Tensile Modulus (psi)</u>	<u>Ultimate Elongation (%)</u>	<u>Tensile Strength (psi)</u>
G-5502 (Continuous filament)	$(2.74 \pm 0.09) 10^6$	0.93 ± 0.07	$(22.8 \pm 3.3) 10^3$
G-5525 (Staple filament)	$(0.87 \pm 0.03) 10^6$	0.74 ± 0.10	$(6.4 \pm 0.3) 10^3$

Table 61 Results of the Large Bench-Scale Cell

<u>Run</u>	<u>Current Efficiency %</u>	<u>Current Density A/cm² (A/in.²)</u>	<u>% at C.D.</u>	<u>Power Consumption MJ/Kg (kWh/lb)</u>	<u>Temp. (°C)</u>	<u>Cathode Metal Purity (%)</u>
34	80	3.5 (23)	26	23	690-	99.91
		2.9 (19)	40	(2.9)	740	
		2.4 (15)	27			
		1.8 (11)	7			

Note: The electrolyte was LiCl-AlCl₃ (90-10 wt.%) and the initial anode metal was aluminum with 11.7% Si and 0.21% Fe.

Table 62

Skim Added to the Anode Metal

<u>Current Efficiency</u>	<u>Power Consumption MJ/kg (kWh/lb)</u>	<u>Current Density A/cm² (A/in.²)</u>	<u>% at C. D.</u>	<u>Temp (°C)</u>	<u>Metal Purity (%)</u>
93.6%	17 (2.2)	4.7 (30)	17	715- 730	99.927
		4.1 (27)	19		
		3.5 (23)	12		
		2.9 (19)	24		
		2.4 (15)	16		
		1.8 (11)	12		

TABLE 63

Summary of Man-Hours Expended

	Months 1-3		Months 4-6		Months 7-9		Months 10-12		Months 13-16		Cumulative		Cumulative Per Cent Deviation
	Man-hr		Man-hr		Man-hr		Man-hr		Man-hr		Man-hr		
	<u>Actual</u>	<u>Est.</u>	<u>Actual</u>	<u>Est.</u>	<u>Actual</u>	<u>Est.</u>	<u>Actual</u>	<u>Est.</u>	<u>Actual</u>	<u>Est.</u>	<u>Actual</u>	<u>Est.</u>	
Engineers	3190	2737	3355	3230	3556	3475	3659	3658	4895	4749	18655	17849	+4.5
Technicians	<u>4714</u>	<u>4046</u>	<u>5026</u>	<u>5287</u>	<u>5676</u>	<u>5664</u>	<u>7565</u>	<u>4853</u>	<u>9206</u>	<u>7224</u>	<u>32187</u>	<u>27074</u>	+18.9
TOTAL	7904	6783	8381	8517	9232	9139	11224	8511	14101	11973	50842	44923	+13.2

Cumulative Summary For Phases A and B

	<u>Actual</u>	<u>Estimated</u>	<u>Per Cent Deviation</u>
Engineers	29441	30677	-4.0
Technicians	<u>46747</u>	<u>42034</u>	+11.2
TOTAL	76188	72711	+4.8

TEMPERATURES VS RADIUS SUSCEPTOR INNER WALL 2273, 2373, 2473 K
VSR WITH PET COKE BED, QUARTZ SHELL 1979-04-17

FIGURE 1

TEMPERATURES VS RADIUS SUSCEPTOR INNER WALL 2273, 2973, 2473 K
VSR WITH PET COKE BED, QUARTZ SHELL, EXTRA DURA-H 1979-04-17

FIGURE 2

TEMPERATURES VS RADIUS SUSCEPTOR INNER WALL 2273, 2373, 2473 K
VSR WITH PET COKE BED, FIRECLAY SHELL 1979-04-19

FIGURE 3

TEMPERATURES VS RADIUS SUSCEPTOR INNER WALL 2273, 2373, 2473 K
VSR WITH PET COKE BED, FIRECLAY SHELL, DURA-H OUTSIDE 1979-04-19

FIGURE 4

TEMPERATURES VS RADIUS SUSCEPTOR INNER WALL 2273, 2373, 2473 K
VSR WITH PET COKE BED, TRANSITE SHELL 1979-04-17

FIGURE 5

FIGURE 6

SCHEMATIC PILOT REACTOR

	INCH mm	INCH mm	INCH mm
	O.D.	I.D.	WALL
304 S.S. PIPE: $\frac{1}{2}$ " SCH. 40	0.84"	0.622	0.109
	21.336	15.7988	2.7686 mm
MONEL TUBING: $\frac{1}{2}$ " O.D. X .035	0.50"	0.43	0.035
	12.70	10.922	0.889 mm
304 S.S. TUBING: $\frac{1}{4}$ " O.D. X .035	0.25"	0.18	0.035
	6.35	4.572	0.889 mm
304 S.S. TUBING: $\frac{3}{8}$ " O.D. X .035	0.375"	0.205	0.035
	9.525	7.747	0.889 mm

INCHES	MM
0.840	21.336
0.622	15.798
0.500	12.700
0.430	10.922
0.250	6.350

$\omega = 0.096132 \text{ IN}^2$
 $A = 0.107508 \text{ IN}^2$

FIGURE 7

MB-200-77 (O₂ TUBE)

R.B./MAY, 1977

VSR-3-18

Burden Formulation

5Al060B low Fe₂O₃ pellets
Bauxite-clay-coke

Amount Ore Fed

Initial Charge = 52054g ore +
2611g act. carbon

Feed Material During Run:

Ore 26054g/60 = 434g/slug

C 1311g/15 = 87g/slug

4.4 g C/100 g ore

Actual

$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	C
--	---

.575 71.03%

86.81%

Sample

C Al Si Fe Ti O

Phases

Reaction
Zone

Edge

Center

Graphite
Deadman

Ingot

Reacted
Alumina
Insulation

8.30	41.4	22.4	2.63	3.12	23.2	Al, SiC, Al ₂ O ₃ , Si
9.57	40.8	18.8	3.17	2.67	28.1	SiC, Al ₂ O ₃ SiC, Graphite, Al
4.56	60.1	25.6	4.02	4.34	1.46	Al, Si, SiC, Ti-Si-Al
						Al ₂ O ₃ , Al ₄ O ₄ C

VSR-3-19

Burden Formulation

5Al063 low Fe₂O₃ pellets
Bauxite-Clay-Coke

Amount Ore Fed

Initial = 70361g ore +
Charge 6202g act. C

Feed Material During Run:

Ore 44946g/110 = 408g/slug
C 4446g/50 = 89g/slug

Start 11" layer 6.1g/100g ore
balance 8.7g/100g ore

Actual	
$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	C

.63 71.06%

92.52%
101.67%

Sample

C	Al	Si	Fe	Ti	O	Phases
---	----	----	----	----	---	--------

17.6	39.1	13.8	1.74	1.95	23.9	SiC, Al ₄ O ₄ C C, Al ₂ O ₃
18.0	25.6	47.9	1.88	2.31	1.33	Al, SiC, Si Trace Al-Fe-Si
11.2	44.9	31.2	2.97	3.51	2.48	Al, Si SiC Trace Al-Fe-Si
7.86	52.4	29.1	3.78	3.88	1.19	
7.11	54.4	27.4	3.74	3.64	1.98	
6.93	59.3	22.3	4.26	3.79	2.28

VSR-3-20

Burden Formulation - 5A1063 low Fe_2O_3 pellets,
-3/8 + 6 mesh made from bauxite-clay-coke.

$$\text{SiO}_2/\text{Al}_2\text{O}_3 = .63 \quad \text{C} = 71.06\%$$

Heating Carbon -1/4" + 6 mesh pet coke

Initial Charge - First 12" 3481 g pellets,
3481 g pet coke, next 12" to bottom of auger
5004 g pellets, 2502 g pet coke, bottom to top
of auger 9000 g pellets, 3000 g pet coke.

Feed Material

Ore 7 slugs x 408g/slug = 2856 gm

Pet coke 7 slugs x 147g/slug = 1029 gm

Operating Conditions

1 tuyere operation 100 CFH O_2 (1.80 fps
max CO sweep)

O_2 on 77 minutes

12 piece liner/grate used with graphite
block installed around the tuyere end
extending 1" inside the liner.

Standard 4 section auger was utilized
Auger speed 1.0 RPM

Reason For Shutdown - Bed was not moving.
Heavy bridging broke the auger spacer between
the top two sections. Oxygen burned through
the liner opposite the tuyere.

VSR-3-22

Burden Formulation - 5A1058 10% Fe_2O_3 pellets,
-1/4 +6 mesh, made from bauxite-clay-iron ore-
coke

$$\text{SiO}_2/\text{Al}_2\text{O}_3 = .626 \quad \text{C} = 69.1\%$$

Heating Carbon -1/4" +6 mesh pet coke

Initial Charge - Filled up the reactor with
23205 gm -1/4" +6 mesh pet coke

Feed Material - No material fed before
forced shutdown

Operating Conditions

3 tuyere operation 70CFH O_2 /tuyere
(3.78 fps max CO sweep)

O_2 on 15 minutes

1 piece liner/grate is used with
the exposed end of each tuyere
covered with a carbon cup. The
side walls of the cup extend back
through the susceptor to form a
bushing around each tuyere. Standard
4 section auger was utilized.

Auger speed 1.05 RPM

Reason for Shutdown

Hot spots occurred in the quartz shell
around 2 tuyeres shortly after O_2 was
turned on. Hot spots were believed
to be related to the deflection of
 O_2 from the carbon cups covering the
front face of each tuyere as there were
holes burned through the susceptor and
liner at the bushing interface.

FIGURE 13

6-80-13

VSR-3-23

DUST { Mullite
βSiC
αAl₂O₃

BRIDGE { Mullite
βSiC Al₄O₄C
αAl₂O₃

GRATE { Mullite
βSiC Al₄SiC₄ Al₄O₄C
αAl₂O₃

Oxygen Rate - 80 CFH/tuyere

Max. Gas Velocity - 4.32 ft/sec

O₂ Blow Time - 5 hr - 25 min.

Weight Ore Feed - 15.8 kg

Ore Size - -3/8 +6 mesh

Coke Size - -1/4 +6 mesh pet coke

VSR-3-23

Burden Formulation - 50% 5A1060/50% 5A1068
Mixture of low Fe_2O_3 pellets, -3/8 +6 mesh,
made from bauxite-clay-coke

Mixture $\text{SiO}_2/\text{Al}_2\text{O}_3 = .668$ Mixture C = 90.65%

Heating Carbon - -1/4 +6 mesh pet coke

Initial Charge - Filled up the reactor with
21356 gm -1/4 +6 mesh pet coke

Feed Material

Ore 15818 gm/43 slugs = 368 gm/slug

Pet Coke 23826 gm/184 slugs = 129 gm/slug

Operating Conditions

3 tuyere operation 80 CFH O_2 /tuyere
(4.32 fps max CO sweep)

O_2 on ~5 hrs - 25 minutes

required coke/actual coke = 1.633

2 piece liner/grate with
carbon bushings around each
tuyere but no cups covering
the front face of each tuyere.

New one piece auger with bottom
positioned at same height
as in previous auger runs.

Auger speed 1.08 RPM

Reason For Shutdown

Heavy condensate obscured
sight ports. Couldn't
verify the bed was moving.

VSR-3-24

DUST { β SiC
 α Al₂O₃ Graphite

Bridge { Mullite
 β SiC
 α Al₂O₃ Al₄SiC₄

Oxygen Rate - 80 CFH/tuyere

Max Gas Velocity - 4.32 ft/sec

O₂ Blow Time - 7 hr - 25 min

Weight Ore Feed - 28.8 kg

Ore size - -3/8 +6 mesh

Coke Size - -1/4 +6 mesh pet coke

FIGURE 16

6-80-13

VSR-3-24

Burden Formulation - 50% 5A1060/50% 5A1068
Mixture of low Fe_2O_3 pellets, -3/8 +6 mesh,
made from bauxite-clay-coke

Mixture $\text{SiO}_2/\text{Al}_2\text{O}_3 = .668$ Mixture C - 90.65%

Heating Carbon -1/4 +6 mesh pet coke

Initial Charge - filled up the reactor with
21500 gm -1/4 +6 mesh pet coke

Feed Material

Ore 28840 gm/368 gm/slug = 78 slugs

Pet Coke 37009 gm/129 gm/slug = 286 slugs

Operating Conditions

3 tuyere operation 80 CFH O_2 /tuyere
(4.32 fps max CO sweep)

O_2 on ~7 hrs - 25 min.

Required coke/actual coke = 1.445

Same 2 piece liner/grate and set of
carbon bushing around each tuyere as
used in VSR-3-23

New 1 piece auger positioned at 20" above
the tuyere centerline as in the original
auger runs.

Auger speed 1.07 RPM

Reason For Shutdown

Auger shear pin broke just prior
to planned shutdown. Heavy
bridging overloaded the shear pin
coupling. Bed was overfilled
due to loss of visual reference
of bed height from heavy
condensate plugging the sight
ports.

VSR-3-25

Burden Formulation - 50% 5A1060/50% 5A1068
and 73% 5A1063/27% 4A1068
Mixtures of low Fe_2O_3 pellets, -3/8 +6 mesh,
made from bauxite-clay-coke

50%/50% Mixture $\text{SiO}_2/\text{Al}_2\text{O}_3 = .668$ C=90.65%
73%/27% Mixture $\text{SiO}_2/\text{Al}_2\text{O}_3 = .668$ C=81.63%

Heating Carbon -1/4" +6 mesh met coke

Initial Charge - Up to bottom of auger 14710
gm -1/4 +6 met coke mixed with 4416 gm 73%/
27% ore mix

Feed Materials

50%/50% ore mix - 5 slugs x 368 gm/slug =
1840 gm
Met coke - 18 slugs x 97 gm/slug = 1746 gm

Operating Conditions

3 tuyere operation 40 CFH O_2 /tuyere (2.16
fps max CO sweep)

O_2 on ~2 minutes $\frac{\text{moles C}}{\text{moles O}_2}$

Coke/ O_2 feed rate = 2.0
extra coke is added to bring ore mixes up
to 100% stoichiometric C

Same liner/grate configuration and tuyere
bushings as in VSR-3-24 but with patching
in liner and a new grate.

Auger is positioned the same as in
VSR-3-24, but slots have been cut
in each flute every 6" for increased
agitation.

Auger speed 1.08RPM

Reason for Shutdown

Auger shear pin broke due to heavy con-
densate bridging. Fire was visible on
the top of the bed due to an air leak.

VSR-3-26

BRIDGE

{
BSiC
AlN
TiSi₂
Graphite

Oxygen Rate - 40 CFH/tuyere

Max Gas Velocity - 2.16 ft/sec

O₂ Blow Time - 3 hr - 11 min

Weight Ore Feed - 8.3 kg

Ore Size - 3/8 +6 mesh

Coke Size - 1/4 +6 mesh met coke

VSR-3-26

Burden Formulation - Same material as in VSR-3-25 50% 5A1060/50% 5A1068 and 73% 5A1063/27% 5A1068 ore mixes

Heating Carbon -1/4 +6 mesh met coke

Initial Charge - left material in the reactor from VSR-3-25 up to auger 9840 gm pet coke, around auger 10776 gm 73%/27% ore mix and met coke

Feed Materials

ore from both mixes 25 slugs x 330
g/slug = 8250 g
-1/4 +6 met coke 80 slugs x 115
g/slug ~9200 g

Operating Conditions

3 tuyere operation 40 CFH O₂/tuyere (2.16
fps max CO sweep)
O₂ on ~3 hrs - 11 min
Required coke/Actual coke = 1.428
Liner/grate and slotted auger are the
same as in VSR-3-25 but shear pin is
now made of brass instead of graphite.
Auger speed .98 RPM

Reason For Shutdown

Auger shear pin broke due to heavy
condensate bridging.

VSR-3-27

BRIDGE

{ β SiC

Al_4O_4C
 Al_4SiC_4
Graphite
AlN

GRATE

{ SiC

Graphite
Al-Fe-Si

Oxygen Rate - 40 CFH/tuyere

Max Gas Velocity - 2.16 ft/sec

O_2 Blow Time - 5 hr - 57 min

Weight Ore Feed - 15.2 kg

Ore Size - 3/8 +6 mesh

Coke Size - 1/4 +6 mesh met coke

VSR-3-27

Burden Formulation

Same ore and heating carbon as in VSR-3-26

Initial Charge - filled up reactor with 17393 gm
-1/4 +6 mesh met coke

Feed Material

Ore from both mixes 46 slugs x 330
g/slug = 15180 g
Met Coke 162 slugs x 115 g/slug =
18630 g

Operating Conditions

3 tuyere operation 40 CFH O₂/tuyere
(2.16 fps max CO sweep)
O₂ on 5 hrs - 57 min
Required Coke/Actual Coke = 1.628
Liner/grate and slotted auger are
the same as in VSR-3-26. The
liner and susceptor have been
repatched and the brass shear
pin has been moved to a
different coupling on the
auger drive system.
Auger speed 1.7/2.0 RPM

Reason For Shutdown

Auger shear pin broke due to heavy
bridging. Could not successfully
restart auger after shear pin
was repaired and auger was raised 3".

FIGURE 22 NEW REACTOR WITH WATER COOLED TUYERE

FIGURE 23 - BENCH REACTOR BOTTOM ENTRY TUYERE

CUSTOMER	ALCOA RESEARCH LAB.	CONTRACT NO.	MB-209-77
TITLE	OXYGEN TUYERE (SK-2)	SHEET NO.	1
		NO. OF SHEETS	1

Figure 24 Pressure Data for Run BF30

Figure 25 Pressure Data for Run BF31

Engineering and Construction Div., Koppers Company, Inc.
Pittsburgh, Penna. 15219
KOPPERS

CALCULATIONS
Name _____ Date _____
Made _____ NOV. 7, 1979
Checked _____

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FIGURE 26 - PILOT REACTOR LARGE TUYERE

CUSTOMER ALCOA RESEARCH LAB
TITLE OXYGEN TUIERE TIP (R-3)

SCHEDULE ITEM	SECTION
CONTRACT NO. MS-200-77

Fig. 27 Content of Liquid Removed from Crystal Bed
Experiment 20 Al-Si-Fe

Fig. 28 Content of Liquid Removed from Crystal Bed
Experiment 21 Al-Si-Ti Continuous Drain

Fig. 29 Content of Liquid Removed from Crystal Bed
Experiment 22 Al-Si-Ti

Fig. 30 Content of Liquid Removed from Crystal Bed
Experiment 23 Al-Si-Fe-Ti

Fig. 31 Content of Liquid Removed from Crystal Bed
Experiment 23 Al-Si-Fe-Ti

FIGURE 32

Content of Liquid Removed from Crystal Bed
Experiment 24, Al-Si-Fe-Ti System

FIGURE 33

Content of Liquid Removed from Crystal Bed
Experiment 24, Al-Si-Fe-Ti System

FIGURE 34

Content of Liquid Removed from Crystal Bed
Experiment 25, Al-Si-Fe-Ti System

FIGURE 35

Content of Liquid Removed from Crystal Bed
Experiment 25, Al-Si-Fe-Ti System

FIGURE 36

Content of Liquid Removed from Crystal Bed
Experiment 26, Al-Si-Fe System

FIGURE 37

Content of Liquid Removed from Crystal Bed
Experiment 27, Al-Si-Fe System
No eutectic drain

FIGURE 38

Content of Liquid Removed from Crystal Bed
Experiment 28R, Al-Si-Fe System

FIGURE 39

Content of Liquid Removed from Crystal Bed
Experiment 29, Al-Si-Fe System
No eutectic drain

FIGURE 40

Content of Liquid Removed from Crystal Bed
Experiment 31, Al-Si-Fe System

FIGURE 41

Content of Liquid Removed from Crystal Bed
Experiment 34, Al-Si-Fe System
Pooling High-Fe Cuts

K·E
5 X 5 TO THE INCH • 7 X 10 INCHES
KEUFFEL & ESSER CO. MADE IN U.S.A.

46 0410

FIGURE 42- Phase "B" Cost Chart: Total Expenditures vs. Time

ALUMINUM COMPANY OF AMERICA

ALCOA LABORATORIES

Attachment 1

Direct Reduction Project

Task/Milestone Schedule

	FY 77				FY 78				FY 79				FY 80				FY 81				FY 82	FY 83	FY 84	FY 85	FY 86	FY 87	FY 88	FY 89	FY 90
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4									
					PHASE A				PHASE B				PHASE C																
Contract Procurement				▲				▲					▲															▶	
				Contract Awarded				Rev. Work Statement Approval for B																					
Reduction				▲	●		●		●	●	●	●	●				○	▲			▲		▲	▲	▲			▲	
				Comptr. Progm. Heat. Mass Bal.			Designed Pilot VSR-1	Installed Pilot VSR-1	VSR-1 Start-up	VSR-2 Start-up	VSR-3 Start-up						Scale-up Design			Complete Demo. Plant Design			Demo. Plant Installation, Start-up	Start Com. Plant Design	Start Com. Plant Install.		Complete Com. plant install. start-up		
Alloy Purification				▲	●	●	●	●	●	●	○	○					○	▲					▲	▲	▲			▲	
				Est. yield, Purity in Existing Pilot	Det. Effects of Impurities	Designed High Temp. Furnace	Designed pilot Unit	Installed High Temp. Furnace	Install Pilot Unit	Pilot System Start-up							Scale-up Design												
Purification to Commercial Purity Al				▲	●			●	●	○	○						○	▲					▲	▲	▲			▲	
				Det Efficiency Purity			Tested Critical Mat 1. of Constr.	Design Pilot Unit	Install Pilot Start up Pilot								Scale-up Design												

APPENDIX 1

FLOW REAC

CHAPTER 1

INTRODUCTION

In the course of investigations relating to carbothermic reduction of aluminosilicates it was found desirable to model various heat transfer and chemical aspects of the flowing reactor system. A FORTRAN program code was constructed to perform these tasks. The program was so arranged as to be generally useful, however, in that the processor was set up to apply to any one-dimensional flowing reactor system. This system may contain up to three phases (solid, liquid and gas), and the details of the chemistry and configuration of the system being simulated are specified in data files external to the processor. With appropriate data files any one-dimensional flowing reactor can be studied.

Heat transfer is permitted between the three flowing phases. Chemical reactions are kinetically modelled, using Absolute Reaction Rate Theory forms for the rate equations, but with departures from equilibrium specified in the quantity terms instead of absolute quantities. This approach acts to absolutely prevent the system from exceeding equilibrium conditions. Reactions may be specified as heat transfer or mass transfer limited. An equilibrium computation routine is incorporated as part of the program, and is used at each step to provide the equilibrium constraints on the chemical reactions. Heat effects of chemical reactions are included in the heat balance of the reactor, and heat requirements or production of any reaction in either direction may be assigned to any of the three phases. For simulation of blast furnace type reactors, provision is included for the specification of oxygen injection tuyeres at various levels in the reactor. Provision is also made for satisfaction of split boundary conditions by iteration (i.e., inlet and exit conditions and stream compositions may be specified both ends of the reactor).

The SOLGASMIX equilibrium solver (G. Eriksson, University of Umea, Sweden) and DIFSUB differential equation solver (C. Gear, University of Illinois) are incorporated into the program to perform specific functions. Use is also made of a general-purpose subroutine for matrix inversion, MIG, which is part of the AMIS SLMATH subroutine library.

The rest of the code was generated in house.

This manual will assume a good level of familiarity on the part of the reader with the IBM 370 computer on which FLOWREAC runs, and its Job Control Language, JCL. Readers not familiar with OS/VS2 and/or JCL are advised to obtain relevant material and study it before proceeding.

CHAPTER 2

METHOD OF COMPUTATION

The general approach to the computation has been set out in the Introduction. This chapter will discuss the details of the theory used to model the system, with the objective of providing the reader with appreciation for the capabilities and limitations of the method.

A general-purpose coupled differential equation solver (DIFSUB) is used to integrate the differential equations governing the system starting at one end of the reactor to the other end. The details of the method used in this differential equation solver will not be covered here. In the event that split boundary conditions are to be satisfied (this would be typical of a countercurrent flow reactor) integration is started from one end and the values of the relevant variables are compared with the constraints specified at the other end. Based on the differences observed, corrections to the unconstrained variables at the starting end are computed by a multi-dimensional equivalent of the secant method, and the integration performed again. This process is continued until the integrated values of the constrained variables agree with the constraint values within some user-specified criterion at the far end.

All that remains to be specified to completely describe the computation is the differential equations themselves. These equations fall into three major categories, 1) those which cover heat balance; 2) those which cover overall mass balance (i.e., which predict the variation of flow rates of each phase without considering the composition of each phase); and 3) those which cover the detailed mass balance (i.e., which predict the variation in composition (mole fractions) of species within the phases).

In the equations which follow, a few conventions will be used for simplicity of notation. A superscript/subscript (p) will denote a variable phase specification, and can take on the values (s), (l) or (g). Note that a subscript p without parentheses is used to denote constant-pressure heat capacity. Stoichiometric coefficients in a chemical reaction equation or its associated rate equation will be denoted as a_{is} , where the subscript i indicates the reaction number being specified and s indicates the number of the

chemical species involved. Negative values of a_{is} indicate reactants, positive values indicate products. Thus, a chemical reaction in this notation can be simply written:

$$\sum_s a_{is} S_s = 0$$

where the S_s are the chemical species involved in the reaction and the a_{is} are their respective stoichiometric coefficients. As before, species with negative a_{is} 's will be consumed when the reaction runs forward, and species with positive a_{is} 's will be created when the reaction runs forward. Provisions are made for reactions to run either forward or backward. If a given reaction is not to run in a certain direction, then the rate for the appropriate reaction and direction should be set to zero by setting its pre-exponential factor to zero. (See below for further discussion of pre-exponential factors.)

SI units are used throughout the program, with molar amounts expressed in kg-moles, temperatures in Kelvins, energies in Joules, etc. A note to this effect is placed on the program output. In equations below, Kronecker delta functions are used to indicate omission of certain terms in summations, based on comparison of summation indices with other indices. The Kronecker delta is denoted δ_{ij} and assumes the value zero unless $i=j$, in which case it assumes the value 1.

Distance along the reactor is denoted by y . The identification of origin for this distance is arbitrary, but vertical-reactor terminology has been used in the program. In the adopted coordinate system, the "top" end of the reactor has been identified as $y=0$. An input variable named HT is used to specify the "height" of the reactor, and the value of y at the "bottom" end is $y=HT$. Normal integration sequence starts the integration from the "top" end. However, in some situations it is desirable to start from the other end, so an input parameter called BTST is provided for this purpose. If BTST is specified, integrations are carried out starting from the "bottom" end. In this case, an "internal" coordinate system is used in which the "bottom" end is $y=0$. This simplifies the coding. The user need not concern himself with this complication unless he has need to study the detailed output which the program can be instructed to produce. Normal production runs should not need to produce detail output, which is used primarily for debugging. On this detail output, values of y which are in the internal coordinate system are identified as YINT, whereas values of y in the user's ("top"=0) coordinate system are identified as simply Y . No use of YINT is made on the primary program output, which contains lists of relevant variables at specific locations along the reactor, selected by the user.

Up to three class 1 equations can be generated for

$$\frac{d(C_p^{(p)} G^{(p)} T^{(p)})}{dy} = \sum_{i=S, R, g} (1 - \delta_{(i), (p)}) h_{(i), (p)} a_{(i), (p)} (T^{(i)} - T^{(p)}) + \sum_{i=1}^{n_r} [\delta_{(p), (p_f^i)} r_i^r \Delta H_i - \delta_{(p), (p_r^i)} r_i^f \Delta H_i]$$

in which $C_p^{(p)}$ is the constant-pressure heat capacity of phase (p), $G^{(p)}$ is the molar flow rate per unit reactor cross section of phase (p), and $T^{(p)}$ is the temperature of phase (p). The first Kronecker delta expression $(1 - \delta_{(i), (p)})$ is used to prevent consideration of heat transfer from phase (p) to itself, which is mathematically inconsistent. $h_{(i), (p)}$ is the heat transfer coefficient (including radiation if solid and gas are involved) between phase i and phase (p). $a_{(i), (p)}$ is the specific area (square meters/cubic meter of reactor) between phases i and (p), and $T^{(i)}$ is the temperature of phase i. The second sum considers the heat effects of all reactions which have had their heat effect assigned to phase (p). Thus, in the first term of the sum, the Kronecker delta removes from consideration all reactions which have not had their reverse heat effect assigned to phase (p) (i.e., those for which (p_r^i) does not equal (p)). The second Kronecker delta does the same for the forward direction. n_r is the total number of reactions in the model, and the r_i^f and r_i^r are the forward and reverse rates of reaction i, respectively. Either r_i^f or r_i^r can be nonzero at a time, but not both. ΔH_i is the molar heat effect of reaction i in the forward direction. The method of computation of the reaction rates will be explained below. All other variables in these equations are supplied by the user as constants or polynomial equations in temperature except for the Kronecker deltas, the flow rates (G) and the temperatures (T), which are calculated by the program.

Up to three class 2 equations can be generated, which have the following form:

$$\frac{d(G^{(p)} x_s^{(p)})}{dy} = \sum_{s=1}^{n_s} \delta_{(p), (p_s)} \frac{d(G^{(p)} x_s^{(p)})}{dy}$$

in which $x_s^{(p)}$ denotes the mole fraction of species s in phase (p), and the Kronecker delta removes from consideration all species which are not part of phase (p) (i.e., removes solids and liquids from consideration when $(p)=(g)$). n_s is the number of species in the model. The individual terms in the sum are computed as part of the detailed mass balance, below.

One class 3 equation is generated for each species considered. A species is one phase form of a chemical compound. Thus, Al(s), Al(l) and Al(g) are all different species. Each equation has the form:

$$\frac{d(G^{(p)} x_s^{(p)})}{dy} = \sum_{i=1}^{n_r} (a_{is} r_i^f - a_{is} r_i^r)$$

in which a_{is} is the stoichiometric coefficient of species s

rate of reaction i , respectively.

The only variables not yet specified are the reaction rates themselves. At each step, the SOLGASMIX subroutine is first called to specify the equilibrium state for the temperature and pressure of interest. The temperature given to SOLGASMIX is the gas temperature. This feature can be fairly readily altered if required, but requires modification of the program code. The mole numbers given to SOLGASMIX are the product of $G^{(n)}$ and $x_s^{(n)}$ for each species present. SOLGASMIX in turn calculates a series of equilibrium mole fractions, x_s^{eq} , which are normalized at each step, as are the actual mole fractions computed at each step.

For rate-limited and mass transfer-limited reactions the following form is used to arrive at a reaction rate:

$$r_i^f = k_{eff}^f a_{lm}^f \prod_{\substack{\text{all } s \text{ with} \\ a_{is} < 0}} (x_s^{(p)} - x_s^{eq})^{e_{is}}$$

in which k_{eff}^f is an effective rate constant, which will be specified below. The e_{is} are exponents of species s in reaction i . These exponents can be input by the user, or calculated by the program if not input. If the user does not specify one of the e 's, it will be calculated by setting it equal to the absolute value of the appropriate a_{is} if the species involved is a gas. If the species involved is a liquid or solid, e_{is} is set to 0.66666667. The a_{lm}^f term in the rate equation is an "appropriate" reaction specific surface area (square meters per cubic meter of reactor). The value for this term depends on the phases of the reactants which enter into the reaction in the direction being considered. (For the reverse direction, an equation analogous to the one above with r superscripts is used.) For instance, if the reaction being considered involves solid and gas in its forward direction as reactants, then the specific area between solid and gas will be used. Provisions are available, however, for a special area term to be specified for any reaction. If a particular reaction and direction involves only one phase (i.e., a solid-solid reaction), an area term will still be included (identified as a_{ss} or a_{ll}) unless all the reactants are gaseous. In this case, the area term is set to unity. Reactions which involve solid, liquid and gas all in one direction are not permitted.

k_{eff}^f is calculated by:

$$k_{eff}^f = \left(\frac{1}{k_{MT}^f} + \frac{1}{k_i^f \exp(-E_i^f/RT)} \right)^{-1}$$

in which k_{MT}^f is a user-specified mass-transfer rate constant (if left unspecified its term in the equation is dropped) and k_i^f and E_i^f are user-specified pre-exponential and activation energy constants, respectively. The temperature, T , used in this equation is the average of all temperatures

METHOD OF COMPUTATION

for phases which enter into the reaction in the direction selected for computation. I.e., if the reaction being considered involves only solid and gas in its reverse direction as reactants, then an average will be taken of the solid and gas temperatures and this average will be used as T for the reverse direction.

Reactions are permitted to run only if they do not carry any of their reactants or products away from equilibrium in the directions in which they are flowing. To arrive at a final rate for a particular reaction, the rates of both forward and reverse directions are computed separately, and the direction which has the largest magnitude of rate is selected, with an appropriate sign on the rate, depending on the direction finally decided upon.

Heat transfer-limited reaction rates are calculated from the following equation form:

$$r_i^f = h_{lm}^f a_{lm}^f (T - T_r) / \Delta H_i$$

in which T_r is a user-specified temperature at which significant reaction begins in the forward direction. This would be the melting point for melting reactions and the boiling point (or somewhat below it) for vaporization reactions. The h_{lm}^f term in this equation is selected in a manner analogous to the a_{lm}^f term in non-heat transfer limited reaction rates, except that phases of both reactants and products are included in the selection process.

Tuyeres are handled by introducing a step change in the flow rate and mole fraction of the appropriate species when the tuyere height is passed during the integration.

These general forms may be somewhat difficult to decipher. A means of gaining better footing may be to turn to Chapter 7, where explicit examples of the equations above are shown for an example problem. Studying the equations developed for that model may allow the reader to more easily sort out the implications of the general forms above.

PILOT REACTOR CHAR INJECTION SYSTEM DESIGN
PROCESS DESCRIPTION

The injection system consists of three separate but identical units each capable of metering and transporting char with either carbon monoxide or argon as the carrier into one of three reactor tuyeres. One such unit is described here; numbers refer to items on drawings MB-200-77-2A1 and 2A2.

Enough char for one day's test run is loaded by hand into the cylindrical cone bottomed batch feed bin, V-1, 2 & 3, after which the blind flange is securely bolted to the 4-inch filling nozzle. This permits the bin to operate under pressure.

The feed bin is suspended from a tension-type load cell, WE V-1-1, 2 & 3. All connections between it and other equipment are flexible in the vertical direction so as not to distort the reading. The bin is protected from horizontal sway and twist by four check rods that run between it and the supporting steelwork.

A vibrating screw feeder, L-1, 2 & 3, moves the char at a constant rate from the feed bin to the injection head, V-2-1, 2 & 3. The char feed rate is adjusted by changing the rotation speed of the screw through manual adjustment of the mechanical variable speed transmission. The weight of the char in the bin is continually displayed on the digital indicator (WI V-1-1, 2 & 3) actuated by the load cell. Also, the weight rate of flow can be monitored by observing the slope of the line drawn on the strip-chart recorder, WR V-1-1, 2 & 3.

When the char is transported into the injection head it falls by gravity from the end of the screw and is blown out through the 1/2-inch bottom exit by a jet of carrier gas that issues from the 1/4-inch inlet pipe extending vertically through the blind flange at the top. A horizontal transport tube runs from a point downstream of the injection head directly to the char injection tuyere, X-5-1, 2 & 3. The shutoff valve and pipework between the head and the tube are constructed without abrupt changes in diameter so that the char particles will accelerate to the higher velocity in the small tube through as smooth a transition as possible.

The injection head has a second function: it is connected by a pressure equalizing line to the top of the feed bin. This helps to maintain a nearly zero pressure differential across the screw feeder which is not capable of sealing against more than a minimal amount. Equalizing the pressure on both sides of the screw also helps to smooth out variations in solids flow rate caused by surges in system pressure.

The char and carrier gas flow through the stainless steel transport tube to the tuyere at velocities high enough to keep the solids in suspension.

PROCESS DESCRIPTION (Continued)

The diameter remains constant all the way to the tuyere nozzle (Drawing MB-200-77-7A1) where the gas and char enter the reactor. Oxygen, in the correct proportion to burn the carbon in the char to carbon monoxide, is also injected through the tuyere through four separate tubes that surround the char tube. The ends of the oxygen tubes are restricted by orifices drilled in such a way that the oxygen and char will mix downstream of the nozzle. The tuyere nozzle and tubes are continually cooled by water flowing through a double pipe jacket that also forms the outside shell of the tuyere.

The transport gas, either carbon monoxide or argon, comes from cylinders equipped with pressure regulators that hold 50 psig in the supply lines. Each gas flows through a separate inline flow indicator controller (FIC V-1-1, 2 & 3-1 for CO and FIC V-1, 2 & 3-2 for Ar). These are rotameters with the capability of holding a constant volume flow rate.

Piping and valves are also provided in the argon system that permit the manual purging of the feed bin, the feeder and the injection head before startup and after shutdown. In order to achieve good distribution the purge gas for the feed bin is piped into the bottom of the cone through four 1/8-inch connections located on 90-degree centers. When purging the air or carbon monoxide are released to the vent stack through a bleed connection and valve located at the highest point on the feed bin.

If the pressure in the feed bin should approach the 14.9-psig design pressure the safety shutdown and purge are activated through the pressure switch (PS V-1-1, 2 & 3). This blows a horn, closes a solenoid valve to shut off the carbon-monoxide or argon transport gas, opens a solenoid valve to bleed the feed bin and opens a solenoid valve to start the argon purge into the bin. If the pressure should continue to rise, the gas is released to the stack through a relief valve (RV V-1-1, 2 & 3).

DESIGN BASIS

The data, sources, and assumptions used as a basis for the more important design features of the char injection system are:

1. Char

The char is available from a supply stored by the Department of Energy at Bruceton, Pennsylvania. It was produced from a high-volatile Western Kentucky bituminous coal by the FMC Corporation in their COED pilot plant at Princeton, New Jersey.

Typical analyses are:

Proximate Analyses - Wt.%

	<u>As Received</u>	<u>Dry</u>
Fixed Carbon	54.18	55.97
Volatile Matter	25.45	26.29
Ash	14.27	14.74
Sulfur	2.90	3.00
Moisture	3.20	0.00
	<u>100.00</u>	<u>100.00</u>

Ultimate Analyses - Wt.%
(Used for Design)

	<u>As Received</u>	<u>Dry</u>
C	74.27	75.55
H	1.79	1.82
N	1.38	1.40
S	3.99	4.06
O	2.66	2.71
Ash	14.21	14.46
Moisture	1.70	0.00
	<u>100.00</u>	<u>100.00</u>

Screen Analyses (Wt.% Retained)

<u>Screen Size, mm</u>	<u>As Received</u>	
	<u>Individual</u>	<u>Cumulative</u>
2	1.2	1.2
1	11.7	12.9
0.5	23.2	36.1
0.25	21.7	57.8
0.125	18.5	76.3
0.063	12.3	88.6
-0.063	11.4	
	<u>100.0</u>	

DESIGN BASIS (Continued)

Screen Analyses (Wt.% Retained) (Continued)

Screen Size, Microns	Ground Sample	
	Individual	Cumulative
125	2.4	2.4
90	2.3	4.7
63	12.7	17.4
50	1.1	18.5
40	12.5	31.0
30	27.5	58.5
20	28.4	86.9
10	7.6	94.5
-10	5.5	
	100.0	

Apparent particle density = 99.2 Lb./Ft³
 Bulk Density (as received) = 28 Lb./Ft³

2. Char Rate

When using metallurgical coke in the pilot reactor the range in total oxygen feed rates to all three tuyeres has been between 150 and 350 SCFH (70°F, 30 In.Hg). If all of the metallurgical coke were replaced by char the range of char rates equivalent to these oxygen rates would be about 4 to 10 pounds per hour per tuyere. At a bulk density of 28 pounds per cubic foot the range in char volume flow rates is about 0.14 to 0.36 cubic feet per hour per tuyere.

3. Char Feeder

In order to hold a precise material balance within the reactor the char must flow at a constant rate that is correctly proportioned to the oxygen flow. The choice of commercially available mechanical feeders that can handle minute quantities of solids at constant rates is small. The two leading choices among the various types are a rotary valve and a screw feeder.

Because a rotary valve contains a multiplicity of separate pockets the ordinary unit, especially when operating at the low PRM occasioned by the very small desired throughput rate, delivers the solids in pulses. These valves can be designed with pockets that are askew to the axis of rotation. If properly designed the skewed rotor can deliver a steady flow. When it is necessary to meter the solids in precise amounts the rotary valves are not as consistent as screw feeders because the pockets do not always fill and do not always empty by the same amount. In the case of the FMC char which is highly flowable it is unlikely that this problem would be severe. However the char might run completely out of a skewed pocket as soon as the leading end reaches the discharge point thus causing a cycling feed rate.

DESIGN BASIS (Continued)

3. Char Feeder (Continued)

The screw feeder that has both the low capacity and a design which should provide a steady feed rate for fine powders is the Vibra Screw Feeder. Reportedly it only deviates one to two percent on either side of the set point.

Though the quoted price for the Vibra Screw Feeder is sixty percent higher than the equivalent rotary valve it was selected as being more likely to give the desired performance. Because the rotary valve must be custom designed and built the estimated delivery time is 15 weeks after receipt of the order whereas the equivalent Vibra Screw is only 6 weeks.

The vibrating-screw feeder selected has a stepless variable speed drive that will provide a range of solid flows between 0.052 and 0.52 cubic feet per hour. This is sufficient to handle the desired range of 0.14 to 0.36 cubic feet per hour and should encompass the desired range of weight flow rates even if the bulk density should be considerably different than the previously determined value. Also the feeder's capacity range can easily be altered by interchanging screws and barrels.

The feeder will be modified by the manufacturer for leak-free operation at internal pressures up to 14.9 psig.

4. Measurement of Char Rate

Though the feeder is expected to hold a constant char rate over long periods it is not likely that it can remain consistent enough to calibration to rely upon it as a flow measuring device. The most accurate way to determine the char flow rate is to relate the change in the weight of the feed-bin contents with time.

The ability to sense weight changes in the four to ten pound per hour range with sufficient accuracy to be meaningful is difficult primarily because the tare weight of the feed bin, being about 250 pounds, represents a considerable portion of the total weight. The feed bin is sized to hold a large enough batch of char, 120 pounds, to run at the maximum rate of ten pounds per hour for twelve hours. The load cell is attached to a digital weight indicator that is sensitive to the nearest 0.02 pounds. The accuracy of the load cell and the digital display is only about plus or minus 0.3 pounds when pertaining to the absolute weight, but the combination should sense a change in weight close to 0.02 pounds.

To determine a weight rate of flow with the indicating instrument requires observing the weight change over a period of time. A strip-chart recorder is also specified; the slope of the line traced

4. Measurement of Char Rate (Continued)

thereon is an indication of the char flow rate. Here again the accuracy of this instrument when pertaining to the absolute weight is not too good, but the difference between readings should be sufficiently close to the weight difference to register changes in char flow rate by changes in slope.

If the char were free to flow through the 6-inch opening at the bottom of the feed bin at least part of the contents would be supported by the screw feeder rather than the load cell. It is then necessary to restrict the flow from the bottom of the bin to the point where only a negligible amount of the bin contents is supported by the feeder but not to the point where the feeder ceases to be the flow controlling device. If a valve were used to restrict flow it would not only add greatly to the tare weight but would be unsatisfactory in that the correct setting could not be duplicated from run to run. A set of flanges has been provided to hold a horizontal orifice plate. The orifice size will be determined by experiment. This can be done by making calibration runs during which changes in the load cell readings are compared with the weight of the discharged material while the bin and screw outlet are open to the atmosphere. It is possible that an annular orifice may work better than the circular orifice shown on Dwg. MB-200-77-2A2 (MK "EH").

5. Injection Velocity

The carrier gas, whether it be carbon monoxide or argon, acts as a coolant in the bottom of the reactor. Therefore, from the standpoint of fuel requirements it should be kept to a minimum.

The saltation velocity for the ground char flowing through the 0.18-inch, i.d., tubing at ten pounds per hour is calculated to be about 15 feet per second. Double this rate is considered a safe minimum superficial velocity for the carbon monoxide.

On the other hand there is the possibility that a low velocity may cause the char to burn so close to the face of the tuyere that it may be damaged. Therefore the carbon monoxide and argon flow meters have been sized for mid-scale readings equivalent to a velocity of about 100 feet per second at the upstream end of the transport tube. This velocity is based on an average pressure in the tuyere zone of 2.5 psig and a calculated friction drop in ten feet of injection tube of 2.4 psig when transporting ten pounds per hour of char at a carbon monoxide velocity of 100 feet per second.

6. Char Injection Tuyere

The char injection tuyere is designed for char rates of 4 to 10 pounds per hour; carbon monoxide velocities of 30 to 100 feet per second, and oxygen rates of 50 to 120 SCFH. The latter is equivalent to the expected maximum and minimum oxygen rates that have been used with metallurgical coke.

One of the design criteria was to attain as small an outside diameter as possible to facilitate the insertion of the three tuyeres in the 8 1/8-inch, i.d., column. The smallest commercial pipe that could contain the double-pass water jacket, and the five inner tubes has a 1 1/4-inch nominal diameter. The outside diameter is 1.66 inches.

The tip of the tuyere is crucial from a cooling standpoint. Consequently the water passage inside the tip is narrow in order to create a high velocity which lowers the film coefficient.

It was not considered feasible at this time to try to design for a specific oxygen flow pattern at the tuyere nozzle that would provide the best mixing for partial combustion of the char. It is expected that the best size and direction for the oxygen orifices can be determined by experiment. This would be done by observing the flame in the open atmosphere while conveying the char with argon. The ends of the four oxygen tubes would be filled with weld metal and drilled to suit.

EQUIPMENT SPECIFICATIONS

ITEM NO. L-1, 2 & 3

VIBRATING FEEDERS

QUANTITY:

Three (3)

PURPOSE:

To transfer char at a nearly constant rate from feed tank V-1-1, 2 & 3 to injection head V-2-1, 2 & 3.

SERVICE:

Continuous for each test run of up to twelve hours duration.

DESCRIPTION:

Standard Vibra Screw Live Bin Feeder, excluding the hopper, equipped with a 5/8-inch diameter screw in a 7/8-inch, o.d. tube; 1/3 HP, 230 Volt A-C, 3-phase, 60 cycle XP motor with mechanical variable speed transmission (HFC L-1, 2, 3) and a 10 to 1 turn-down ratio. Feeder contains carbon-steel wetted parts and is modified for 14.9 psig service including a 2-inch flexible sleeve for connection to the inlet to the injection head, V-2-1, 2, & 3, and a 6-inch flexible sleeve for connection to feed tank V-1-1, 2, & 3.

CAPACITY:

Feeder will move minus 200-mesh coal char at variable speeds between 0.052 and 0.52 cubic feet per hour.

SUPPORT:

Feeder will be mounted at an elevation of about 4 feet, 2 inches above the laboratory floor on an independent steel structure to be designed in the field.

ITEM NO. V-1-1, 2 & 3

FEED BINS

QUANTITY:

Three (3)

PURPOSE:

To contain one batch of minus 200-mesh coal char for one test run of up to twelve hours duration, to hold it under a carbon-monoxide or argon atmosphere at operating pressures up to 14.9 psig while it is withdrawn at controlled rate by vibrating feeder L-1, 2 & 3.

EQUIPMENT SPECIFICATIONS (Continued)

ITEM NO. V-1-1, 2 & 3 (Continued)

FEED BINS

DESCRIPTION:

A vertical cone-bottomed carbon-steel tank with dished head having an inside diameter of 1 foot, 6 inches and a cylindrical height of 1 foot, 10 inches. The included angle of the cone bottom is to be 30 degrees. The 6-inch cylindrical bottom char outlet is flanged to fit a 6-inch, o.d., extension which fits within the flexible sleeve provided with vibrating feeder L-1, 2, 3. The flow restricting orifice, "K "EH", together with the proper gaskets will be inserted between the flanges. The size of this orifice is to be determined by experiment.

PRESSURE:

Tank is to be designed for 14.9 psig internal pressure and fabricated to U.P.V. Code but not stamped.

CONNECTIONS:

Tank is to be equipped with a 4-inch flanged feed nozzle located on the vertical centerline and closed with a blind flange. Flange is to be high enough above dished head to allow the connection of a 1/2-inch threadolet between the flange and the head for attachment of the bleed line. Also attached to the head is a 1-inch threaded connection for the pressure relief valve. A 1/2-inch threadolet for the pressure equalizing line is attached to the cylindrical shell 1-inch below the dished head. Four 1/8-inch threadolets for the purging sparger are spaced on 90-degree centers around the cone, one inch above the bottom. Separate 1/2-inch threadolets are provided for a pressure indicator and a pressure switch.

CAPACITY:

Tank will hold about 4.25 cubic feet of char when filled to within 4 inches of the top of the cylindrical portion.

SUPPORT:

Tank is suspended from a tension-type load cell (WE V-1-1, 2 & 3) by three wire cables attached to the dished head through lugs.

EQUIPMENT SPECIFICATIONS (Continued)

ITEM NO. V-2-1, 2 & 3

INJECTION HEADS

QUANTITY:

Three (3)

PURPOSE:

To catch the char as it falls from the vibrating screw, L-1, 2, & 3 and allow it to be entrained by the transport gas into the injection tube. It also connects to the feed bins, V-1-1, 2, & 3 through a pressure equalizing line.

DESCRIPTION:

A vertical 2-inch SC. 40 carbon-steel pipe, 5 3/4 inches long, flanged at the top end and having a 2" x 1/2" swaged nipple at the bottom. A blind flange is attached to the top fitting and is drilled at the center line for the insertion of a 1/4-inch SC. 40 pipe for injecting the transport gas. The 1/4-inch pipe is welded to the blind flange and extends into the 2-inch pipe for a distance of 3 inches. Also connected to the 2-inch pipe are a 1/2-inch threadolet located 1 3/4 inches from the top for the pressure equalizing line and a 2-inch horizontal branch inlet located 4 inches below the top for connection to the screw feeder, L-1, 2 & 3, through the flexible coupling provided with the feeder.

ITEM NO. X-1-1, 2 & 3

FLEXIBLE HOSE

QUANTITY:

Three (3)

PURPOSE:

To connect the 1/2-inch bleed fitting at the top of the feed bin, V-1-1, 2 & 3 to the atmospheric vent line in such a way that the vertical movement of the bin will not be hindered enough to distort the reading of load cell (WEV-1-1, 2 & 3).

DESCRIPTION:

A 1/2-inch single braided flexible carbon-steel corrugated metal hose (Penflexweld 201-10, or equal) having a live length of 10 3/4 inches, fitted at one end with a 1/2-inch NPT carbon-steel nipple with integral hex nut (Style WHN) and the other end with a 1/2-inch NPT carbon-steel female pipe union (Style WUF).

EQUIPMENT SPECIFICATIONS (Continued)

ITEM NO. X-2-1, 2 & 3

FLEXIBLE HOSE

QUANTITY:

Three (3)

PURPOSE:

To connect the outlet of the pressure relief valve, PRV V-1, 2 & 3, to a line leading to the stack (not part of this specification) in such a way that the vertical movement of Feed Bin V-1-1, 2 and 3, will not be hindered enough to distort the reading of load-cell (WE V-1-1, 2 & 3).

DESCRIPTION:

A 1-inch single braided flexible carbon-steel corrugated metal hose (Penflexweld 201-10, or equal) having a live length of 11 1/2-inches, fitted at one end with a 1-inch NPT carbon-steel nipple with integral hex nut (Style WHN) and at the other end with a 1-inch NPT carbon-steel female pipe union (Style WUF).

ITEM NO. X-3-1, 2 & 3

FLEXIBLE HOSE

QUANTITY:

Three (3)

To connect the 1/2-inch pressure equalizing line to Feed Bin, V-1-1, 2 & 3, in such a way that the vertical movement of the bin will not be hindered enough to distort the reading of load cell (WE V-1-1, 2 & 3).

DESCRIPTION:

Identical to Item X-1-1, 2, 3.

ITEM NO. X-4-1, 2 & 3

FLEXIBLE HOSE

QUANTITY:

Three (3)

PURPOSE:

To connect the Argon purge system to the sparger pipe located near the bottom of Feed Bin V-1-1, 2 & 3, in such a way that the vertical movement of the bin will not be hindered enough to distort the reading of load cell (WE V-1-1, 2 & 3).

EQUIPMENT SPECIFICATIONS (Continued)

ITEM NO. X-4-1, 2 & 3

FLEXIBLE HOSE

DESCRIPTION:

Identical to Item X-1-1, 2 & 3.

ITEM NO. X-5-1, 2 & 3

CHAR INJECTION TUYERE

QUANTITY:

Three (3)

PURPOSE:

To facilitate the injection of two separate streams, one containing coal char and carbon monoxide or argon and the other containing oxygen, into the carbothermic reactor (not part of this specification) in such a manner that the char and oxygen will react within the raceway.

SERVICE:

Continuous for each test run of up to twelve hours duration.

DESCRIPTION:

The char entrained with carbon monoxide or argon flows through the 1/4-inch o.d. (0.18-inch i.d.) stainless-steel center tube which is welded to the water-cooled nozzle. The oxygen enters through four 3/16-inch, o.d., (0.02-inch wall) stainless steel tubes which symmetrically surround the center tube. The ends of the oxygen tubes are connected to the nozzle and will be plugged. Oxygen orifice will be drilled through the plugs to suit in the field. The five tubes are surrounded with a double water jacket made of a 1-inch Sc 10 stainless-steel pipe surrounded by a 1 1/4-inch Sc 10 stainless-steel pipe. The cooling water enters through the outside channel and leaves through the inside passage where it contacts the oxygen and char tubes. The upstream ends of the several tubes and pipes pass through specially designed glands to provide for the relative expansion. See drawing MB-200-77-7A1 for details.

CAPACITY:

Char rates of 4 to 10 pounds per hour, carbon monoxide velocities of 30 to 100 feet per second and oxygen rates of 50 to 120 SCFH.

DRAWING LIST

DRAWING NO.

TITLE

MB-200-77-2A1

Carbothermic Reduction
Laboratory Column
Char Injection System
P & I Flow Diagram

MB-200-77-2A2

Carbothermic Reduction
Laboratory Column
Char Injection System
General Arrangement and Details

MB-200-77-7A1

Carbothermic Reduction
Laboratory Column
Char Injection Tuyere

MB-200-77-2A2

ELEVATION

DETAIL "A"
SCALE: 3"=1'-0"

SECTION "A-A"

PIPING ARRANGEMENT

DETAIL MK. "G"
SCALE: FULL SIZE

SECTION "C-C"

SECTION "B-B"

DETAIL MK. "EH"

NOZZLE ORIENTATION

DETAIL
MK. "B"

SCHEDULE OF OPENINGS

NO.	QTY.	SIZE	TYPE	DESCRIPTION
(A)	1	4"	150° RF FLG.	FEED NOZZLE
(B)	1	1"	3000 COUR.	RELIEF VALVE
(C)	2	1/4"	3000 THREADED	PRESSURE EQ. & PRESS. SW.
(D)	4	1/8"	- DO -	SPARGING
(E)	1	1/4"	- DO -	BLEED
(F)	1	1/4"	3000 COUR.	PRESSURE GAUGE

NOTES -

- CHAR FEED BIN TO BE DESIGNED AND FABRICATED IN ACCORDANCE WITH ASME CODE FOR UNFIRED PRESSURE VESSELS BUT NO STAMP IS REQUIRED. DESIGN PRESSURE - 14.9 PSIG. DESIGN TEMPERATURE - AMBIENT. OPERATING CONDITIONS - 200 MESH COAL CHAR IN CARBON MONOXIDE OR ARGON ATMOSPHERE.
- PROVIDE INDEPENDENT SUPPORT FOR VIBRATING SCREW FEEDER L-1.
- THREE SYSTEMS REQUIRED AS SHOWN.
- THE PIPING ARRANGEMENT SHOWN IS SUGGESTED ONLY.

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CUSTOMER: ALCOA - NEW KENSINGTON, PA.
Engineering and Construction Group, Koppers Company, Inc. W.L.S. 2100
Pittsburgh, Penna. 15229
KOPPERS

SCALE: 1" = 1' FT.	LABORATORY REDUCTION
LAB. NO. MB-200-77-2A2	LAB. COL. - CHAR INJECTION SYSTEM
KEY: W.L.S. 2100-1	GENERAL ARRANGEMENT & DETAILS
AREA: T.T.	CONTRACT: MB-200
DR. J.A. WOOD	DATE: 4-3-79
CR. MINICH	DATE: 5-24-79
APP. [Signature]	DATE: 5-24-79
REV.	DESCRIPTION

MB-200-77-2A2

MB-200-77-7A1

-A23-

SECTION A-A

TUYERE GENERAL ARRANGEMENT

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CUSTOMER: ALCOA - NEW KENSINGTON, PA.		Engineering and Construction Group, Koppers Company, Inc.	
KOPPERS			
SCALE	WT. PY.	CARBOTHERMIC REDUCTION	
REV. NO.		LAB. COLUMN	
REV. NO.		CHAR INJECTION TUYERE	
DATE		CONTRACT	REVISION
DR. D. J. BURCHETT	8/11/78		
CK. R. B. KING			
APP.			
MB-200-77-7A1			

REV.	DESCRIPTION	CHECKED BY	DATE
1			
2			
3			

EFFECT OF PREHEAT ON CHAR OXYGEN SYSTEM

Abstract

In the process to make Al-Si alloys carbothermically, reactions of the liquid metal product with the large amounts of coke required to heat the metal producing zone can result in extensive carbide formation causing a reduction in metallic yield and considerable operating problems. Preheating of oxygen and the utilization of an oxygen-char burner have been evaluated as a substitute source of energy for the metallurgical coke used to heat the process.

Using heat and material balances, each case has been compared to the base case of burning coke preheated to the metal producing temperature and unpreheated oxygen. The loss in preheat by substituting cold char for preheated coke increases the carbon consumption and CO sweep by 2.5 times at complete replacement. Preheating of the oxygen and char to 1000°C results in no increase in CO sweep up to 50% replacement. The advantages of preheating oxygen are clearly evident whereas the utilization of char offers a set of tradeoffs not always resulting in an apparent advantage.

1.0 Introduction

In the technical proposal to the DOE for the development of a carbothermic reduction process for production of aluminum-silicon alloys(1), it was proposed that metallurgical coke for heating the process would be charged with the ore burden into the top of a countercurrent shaft reactor. The coke would be preheated by the rising hot gases and combusted by unpreheated oxygen injected into the metal producing zone near the bottom of the furnace. This process concept is very similar to the iron blast furnace except unpreheated oxygen is used in place of the preheated air blast.

Dilute iron alloys saturated with carbon are in equilibrium with graphite or the commonly formed metastable iron carbide Fe_3C , which melts above 1225°C.(2) Therefore, there are no solid carbides which are formed at the metal producing temperatures near 1600°C, and an homogeneous liquid alloy is easily tapped from the furnace. Aluminum has a high solubility of carbon(3) at its metal producing temperature near 2100°C which results in extensive carbide formation upon cooling only a few hundreds of degrees centigrade. Furthermore, the solids in equilibrium with liquid Al-Si-C alloys are Al_4C_3 and SiC below 2156°C and C and SiC above 2156°C.(4) This means that carbides can be precipitated from Al-Si-C alloys at metal producing temperatures if excess carbon in the form of heating coke reacts with the molten alloy. Both of these conditions hinder the separation of the alloy from the burden and the handling of the molten alloy.

An obvious solution to this problem is to replace all or some of the heating coke with an alternative energy source. It also may be desirable to reduce the consumption of metallurgical coke to effect the economics of the process. This report addresses the relative effects of using preheated oxygen and preheated powdered char in an oxygen-char burner to replace metallurgical coke for heating the process. These effects are evaluated in terms of coke and char consumption and the relative changes in CO sweep gas coming from the combustion of these carbon sources.

2.0 Procedure

The basis for comparison of the various carbon sources and reactant preheats is the standard case of obtaining all the process heat from metallurgical coke combusted by unpreheated oxygen in the metal producing zone of the shaft furnace. It is assumed that the metal producing stage or highest temperature stage of the process is where the thermal pinch point occurs. This means that, at least for the standard case, if sufficient heat is supplied for the highly endothermic final stage reduction reactions, there is enough sensible and chemical heat to fulfill all of the other thermal requirements in the solids bed from the hot gases rising up the reactor. Therefore, if the same amount of heat above the hot stage reaction temperature is supplied while replacing coke with char or preheated oxygen, the same amount of oxides would be reduced.

The heat balance equations used to determine the amount of coke and char required for each case considered are given in Appendix I. These heat balances are based on the enthalpy equations for determining the heat contents of the reactants and products of combustion which are found in Appendix II. Mass balances on carbon and CO resulting from changes in heating carbon for each case are given in Appendix III. An analysis for the metallurgical coke and the determination for the carbon to reduce the coke ash have been previously reported.(5) The analysis for the char obtained from Koppers(6) is given in Table I along with that of the coke. The molar quantities of the reactants required for combustion are given in Table II.

The additional assumptions required to make the calculations are as follows:

- Each ore agglomerate contains enough carbon to reduce all of the oxides in the ore and coke ash in the agglomerate.
- The carbon to reduce the ash in the heating coke and char comes from the heating coke or char respectively. The char needs 4.7 g carbon/g char and the coke 3.8 g carbon/g coke to reduce this ash.

- Char is conveyed to the oxygen-char burner by CO at the same temperature of preheat as the char. It takes approximately 1 mole of CO to convey 9 moles of carbon in powdered char. (6)
- The coke charged to the furnace is preheated to the metal producing temperature of 2100°C (2373°K) by the rising hot gases.
- The gas resulting from the combustion of the heating carbon cools to within 50°C of the metal producing temperature of 2100°C as it passes the assumed pinch point of the process.
- The maximum preheat of oxygen and char to be fed through a tuyere or oxygen-char burner is 1000°C (1273°K).
- Any S or H_2 in the coke or char is combusted to supply heat for reduction, but their sweep gas effect is not included in the CO sweep determination. The CO sweep includes only the CO from conveyance of char and the CO resulting from combustion of heating carbon and not the reduction reactions.
- The heat of reduction of the ash in the heating coke and char is not considered in the combustion heat balance calculation. It is assumed to be reduced along with the ore with the heat supplied by combustion of carbon.
- All flame temperatures are adiabatic calculations with no dissociation of the products of combustion included.
Note that the stability of CO in the flame is very high. (7)

3.0 Results

The results along with the equations used to calculate the flame temperatures at the extremes of each case are presented in Appendix IV. The results are further summarized in Figures 1 through 3.

The value of preheating coke, char and oxygen to decrease the carbon consumption and CO sweep is clearly shown by the results. It also appears that utilization of unpreheated char (Case B) to any great degree is unpractical due to the large increases in carbon consumption and CO sweep. Note that char could be used effectively to reduce carbiding without increases in CO sweep if both the char and oxygen (Case C) were preheated to 1000°C . The practicality of using preheated char and unpreheated oxygen (Case D) depends on whether the attendant increases in CO sweep can be tolerated.

4.0 Discussion

Eventually we will formulate a burden that gives us the best results for a given reactor wherein we will probably choose our ore materials to balance the Al_2O_3 , SiO_2 , Fe_2O_3 and possibly TiO_2 in our charge taking into account the ash in the carbon sources. The amount of heating carbon for a given oxide balance in each reactor would not change with varying source material of ore and carbon, because the same amount of oxides to be reduced and heat loss would result from any mix of materials. This statement is true provided the metal producing and refluxing efficiency do not change with source of material, and the preheat of the reactants and source of combustion oxygen remain the same.

If the preheat of a replacement heating carbon source was lower than the heating coke, more carbon would have to be combusted to make up this thermal difference resulting in an increase in the CO sweep gas. Since char conveyed to a burner requires CO carrying gas, the use of char would generally increase the CO sweep gas. Both of these situations are represented to varying degrees in Cases B, C and D. Preheating the oxygen would lower the required heating carbon and thus decrease the CO sweep gas as shown in Case A.

We cannot currently evaluate the effect of CO sweep gas on metal production and refluxing efficiency or the effect of replacing heating coke on carbiding of the product, but we need to point out that replacement of heating coke has a number of tradeoffs that need careful consideration to evaluate the methods discussed in this report. If CO sweep gas increases, caused by replacement of heating coke, unfavorably effect the metal producing and refluxing efficiency, even greater consumptions of carbon per unit of alloy produced will occur with their attendant further increases in CO sweep. Although the sensible heat in the sweep gas increases as the sweep gas rate increases (Cases B, C and D), no additional solids preheat can be obtained beyond the temperature of the gas. Unless the bed can be made higher, top temperatures will increase. However, raising the bed height increases the heat losses, therefore any increase in CO sweep rate decreases the thermal efficiency of a given shaft furnace. Decreases in the flow rate of hot rising gases (Cases A and C) would not reduce the solids preheat temperature if there was an equivalent decrease in the thermal requirement in the bed above the metal producing zone. In fact even if there is not an equivalent decrease in the thermal load, only a decrease in the top temperature may occur with an improvement in thermal efficiency of the process.

Preheating the oxygen is the only clearcut positive step to take to decrease carbiding without having numerous negative side effects. While a 14.3% decrease in coke consumption and CO sweep could be realized by this process change, it remains to be seen whether such a decrease would sufficiently reduce carbiding. Although the engineering of an oxygen preheating step may not be trivial, it remains a possible alternative to reach our goal.

The ability to use char made from cheap coal sources to replace expensive by-product metallurgical coke may be a good argument for cases C and D, but this cost advantage may decrease when the use of char and formcoke made from the same coal are compared. If elimination of carbiding by substantial or complete replacement of heating coke is required, the utilization of an oxygen-char burner may be the only alternative. An oxygen-char burner operated at flame temperatures of greater than 3350°C (Case D), wherein the burner is placed in a low heat sink chamber and the hot gases from combustion flow into an adjacent moving bed to provide heat for reduction may not be an easy engineering task.

5.0 Summary

The effects of replacing heating coke with preheated oxygen and char in the carbothermic reduction process for production of aluminum-silicon alloys have been evaluated in terms of the relative carbon consumption and the resulting changes in the CO gas sweeping through the solids bed. Each case evaluated was compared to the standard case of burning metallurgical coke preheated to 2100°C with unpreheated oxygen.

The use of unpreheated char to replace a sizable amount of heating coke does not seem practical as the CO sweep and char consumption would be greatly increased relative to the amount of coke replaced. If the practical limit to preheat char and oxygen is 1000°C, they must both be preheated to this temperature to replace significant amounts of heating coke without large increases in CO sweep and C consumption. Straight preheating of oxygen offers the only clearcut advantages as it results in decreased coke consumption and CO sweep. In either case engineering development would be required to utilize these technologies.

6.0 References

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TABLE I

COED Char and Metallurgical Coke Analysis

	<u>COED Char Wet (6)</u>	<u>Met. Coke Wet (5)</u>
Al ₂ O ₃	3.11%	3.00%
SiO ₂	6.37	5.55
Fe ₂ O ₃	3.84	1.40
TiO ₂	.14	.17
Na ₂ O		.06
CaO	.43	.28
MgO		.10
P ₂ O ₅		.02
K ₂ O	.30	.14
MnO		.004
CuO		.002
ZnO		.004
Cr ₂ O ₃		.004
V ₂ O ₅	.02	
LOF	1.70	1.13
Fixed C	74.27	87.64
S	3.99	.95
H ₂	1.79	
O ₂	2.66	
N ₂	1.38	
	<u>100.00%</u>	<u>100.45%</u>

TABLE II

Moles of Reactants for Combustion of 100 g of Coke and Char

	<u>COED Char Wet Analysis</u>	<u>Met Coke Wet Analysis</u>
Al_2O_3	.03050	.02942
SiO_2	.10601	.09236
Fe_2O_3	.02405	.00877
TiO_2	.00175	.00213
Na_2O		.00048
CaO	.00767	.00499
MgO		.00248
P_2O_5		.00014
K_2O	.00318	.00149
MnO		.00006
CuO		.00003
ZnO		.00005
Cr_2O_3		.00003
V_2O_5	.00011	
C (combustion)	5.79219	6.98027
C (ash reduction)	.39131	.31637
S	.12443	.02963
H_2	.88790	
O_2 (in char)	.083125	
O_2 (pure gas)	3.38175	3.520625
N_2	.04926	
H_2O	.09436	.06272

APPENDIX I

Heat Balance Equations for Cases A, B, C, and D

a = Net heat above 2150°C from burning 100 g of 2100°C metallurgical coke with 25°C oxygen

b = Heat in preheated oxygen required to burn 100 g of metallurgical coke

c = Net heat above 2150°C from burning 100 g 25°C char with 25°C oxygen .

d = Net heat above 2150°C from burning 100 g of 2100°C metallurgical coke with 1000°C oxygen

e = Net heat above 2150°C from burning 100 g of 1000°C char with 1000°C oxygen

f = Net heat above 2150°C from burning 100 g of 1000°C char with 25°C oxygen

x = Weight of coke in grams

y = Weight of char in grams

Case A - Metallurgical coke at 2100°C - Oxygen at variable preheat temperatures

$$a = (x/100) a + (x/100) b$$

Case B - Metallurgical coke at 2100°C - Oxygen and char at 25°C

$$a = (x/100) a + (y/100) c$$

Case C - Metallurgical coke at 2100°C - Oxygen and char preheated to 1000°C

$$a = (x/100) d + (x/100) e$$

Case D - Metallurgical coke at 2100°C - Char preheated to 1000°C - Oxygen at 25°C

$$a = (x/100) a + (y/100) f$$

APPENDIX II

Heat Contents of the Reactants and Products of Combustion^(8, 9)

1. Heat content in the reactants and products from burning 100 g of metallurgical coke with oxygen

Preheat in coke

$$(\Delta H_{T-298K})_{\text{coke}} = 33.046T + 790.735 \times 10^{-5}T^2 + 1554200.31T^{-1} - 13832.693$$

$$(\Delta H_{2373-298K})_{\text{coke}} = 109767.725 \text{ cal}$$

Preheat in oxygen

$$(\Delta H_{T-298K})_{\text{oxygen-coke}} = 25.208T + 176.0 \times 10^{-5}T^2 + 140825 - 8140.777$$

$$(\Delta H_{1273-298K})_{\text{oxygen-coke}} = 26911.76 \text{ cal}$$

Heat of combustion of C and S in coke

$$(\Delta H^{\circ}_{\text{rxn.}})_{\text{coke}} = -186499.95 \text{ cal}$$

Heat in products of combustion of coke and oxygen (for $T \geq 1700^{\circ}\text{C}$ and all ash oxides melted)

$$(\Delta H_{T-298K})_{\text{products-coke}} = 51.971T + 400.278 \times 10^{-5}T^2 + 169334.04T^{-1} - 14489.016$$

$$(\Delta H_{2423-298K})_{\text{products-coke}} = 135006.64 \text{ cal}$$

2. Heat content in the reactants and products from burning 100 g of char with oxygen, char conveyed by CO

Preheat in CO conveyance

$$(\Delta H_{T-298K})_{\text{CO conveyance}} = 4.665T + 33.6655 \times 10^{-5}T^2 + 7557.6T^{-1} - 1445.460$$

$$(\Delta H_{1273-298K})_{\text{CO conveyance}} = 5044.58 \text{ cal}$$

Preheat in char - $1154^{\circ}\text{K} < T \leq 1700^{\circ}\text{K}$

$$(\Delta H_{T-298K})_{\text{char}} = 36.663T + 423.796 \times 10^{-5}T^2 + 1313431.21T^{-1} - 14381.378$$

$$(\Delta H_{1273-298K})_{\text{char}} = 40188.85 \text{ cal}$$

APPENDIX II (cont'd.)

Preheat in oxygen

$$(\Delta H_{T-298K})_{\text{oxygen-char}} = 24.213T + 169.0 \times 10^{-5} T^2 + 135270T^{-1} - 7819.655$$

$$(\Delta H_{1273-298K})_{\text{oxygen-char}} = 25848.45 \text{ cal}$$

Heat of combustion of C, S and H in char

$$(\Delta H^{\circ}_{\text{rxn.}})_{\text{char}} = -213159.06 \text{ cal}$$

Heat in products of combustion of char and oxygen + CO for conveyance
(for $T \geq 1700^{\circ}\text{C}$ and all oxides melted)

$$(\Delta H_{T-298})_{\text{products-char}} = 57.510T + 502.3235 \times 10^{-5} T^2 + 186238.67T^{-1} - 15980.823$$

$$(\Delta H_{2423-298})_{\text{products-char}} = 152933.83 \text{ cal}$$

APPENDIX III

Mass Balance for CO Sweep Determination

These determinations do not include the carbon for reduction of the oxides as this is assumed to remain constant for changes in heating carbon.

g = mass fraction of carbon in coke = .8764

h = mass fraction of carbon in char = .7427

j = mass fraction of carbon in coke for reducing coke ash = .038

k = mass fraction of carbon in coke for reducing char ash = .047

CO = relative change in CO sweep as compared to the standard case

Case A - Metallurgical coke at 2100°C - oxygen at variable preheat temperatures

$$CO = \frac{\text{Weight of coke with O}_2 \text{ preheat}}{\text{Weight of coke without O}_2 \text{ preheat}} = \frac{\text{Wt. coke with O}_2 \text{ preheat}}{100 \text{ g}}$$

Case B - Metallurgical coke at 2100°C - oxygen and char at 25°C

l = CO for conveyance of char mass fraction + CO mass fraction from
combustion of char

$$l = h/9 + (h-k) = .7427/9 + (.7427-.047) = .7782$$

$$CO = \frac{\text{Wt. coke (g-j)} + \text{wt. char (l)}}{100 \text{ g coke (g-j)}} = \frac{\text{wt. coke .8384} + \text{wt. char .7782}}{83.84}$$

Case C - Metallurgical coke at 2100°C - oxygen and char preheated to 1000°C

Same as Case B

Case D - Metallurgical coke at 2100°C - char preheated to 1000°C - oxygen at 25°C

Same as Case B

APPENDIX IV

Results of the Heat and Material Balances

Case A - Metallurgical coke at 2100°C - oxygen at variable preheat temperature

Flame temperature heat balance no oxygen preheat

$$51.971T + 400.278 \times 10^{-5}T^2 + 169334.04T^{-1} - 310756.691 = 0$$

Preheat Temp. (°K)	O ₂ Preheat (cal)	Products at 2423°K (cal)	Net Heat Above 2423°K (cal)	Flame Temp. (°K)	Coke	CO
298		135006.64	161261.035	4452	100.0	1.000
350	1299.98				99.20	.992
400	2576.09				98.43	.984
500	5184.87				96.89	.969
600	7852.33				95.36	.954
700	10568.40				93.85	.939
800	13328.05				92.37	.924
900	16128.50				90.91	.909
1000	18968.05				89.48	.895
1100	21845.65				88.07	.881
1200	24760.58				86.69	.867
1273	26911.76	115698.50	161261.035	4755	85.70	.857

For combustion 85.70 g of coke

$$(\Delta H_{T-298K})_{\text{products-coke}} = 44.538T + 343.032 \times 10^{-5}T^2 + 145116.527T^{-1} - 12416.767$$

$$(\Delta H_{2423-298K})_{\text{products-coke}} = 115698.50 \text{ cal}$$

Flame temperature heat balance, oxygen preheated to 1273°K

$$44.538T + 343.032 \times 10^{-5}T^2 + 145116.527T^{-1} - 289376.389 = 0$$

APPENDIX IV (cont'd.)

Case B - Metallurgical coke at 2100°C - oxygen and char at 25°C

Flame temperature heat balance burning char only

$$57.510T + 502.3235 \times 10^{-5}T^2 + 186238.67T^{-1} - 229139.883 = 0$$

Products at 2423°K (cal)	Net Heat Above 2423°K (cal)	Flame Temp. (°K)	Coke (g)	Char (g)	CO
135006.64	161261.035	4452	100		1.000
			90	26.78	1.149
			80	53.55	1.297
			70	80.33	1.446
			60	107.11	1.594
			50	133.88	1.743
			40	160.66	1.891
			30	187.43	2.040
			20	214.21	2.188
			10	240.99	2.337
152933.83	60225.245	3128	--	267.76	2.485

Case C - Metallurgical coke at 2100°C - oxygen and char preheated to 1000°C

Flame temperature heat balance burning char only

$$57.510T + 502.3235 \times 10^{-5}T^2 + 186238.67T^{-1} - 300221.759 = 0$$

Products at 2423°K (cal)	Net Heat Above 2423°K (cal)	Flame Temp. (°K)	Coke (g)	Char (g)	CO
115698.50	161261.035	4755	85.70		.857
			80	8.17	.876
			70	22.50	.909
			60	36.83	.942
			50	51.16	.975
			40	65.49	1.008
			30	79.82	1.041
			20	94.15	1.074
			10	108.48	1.107
152933.83	131307.15	3895	--	122.81	1.140

APPENDIX IV (cont'd.)

Case D - Metallurgical coke at 2100°C - char preheated to 1000°C - oxygen at 25°C

Flame temperature heat balance burning char only

$$57,510T + 502.3235 \times 10^{-5}T^2 + 186238.67T^{-1} - 274373.310 = 0$$

Products at 2423°K (cal)	Net Heat Above 2423°K (cal)	Flame Temp. (°K)	Coke (g)	Char (g)	CO
135006.64	161261.035	4452	100		1.000
			90	15.29	1.042
			80	30.58	1.084
			70	45.87	1.126
			60	61.17	1.168
			50	76.46	1.210
			40	91.75	1.252
			30	107.04	1.294
			20	122.33	1.336
			10	137.62	1.377
152933.83	105458.66	3623	--	152.91	1.419

INDUCTOTHERM CORP.

A SUBSIDIARY OF INDUCTOTHERM INDUSTRIES, INC.

March 27, 1978

10 INDEL AVENUE RANCOCAS, NEW JERSEY, USA 08073 (609) 267-9000 TWX (510) 683-9392

QUOTATION NO. 32778-1-CHF

To

ALUMINUM COMPANY OF AMERICA

Alcoa Technical Center

Alcoa Center, Pennsylvania

Covering

180 CYCLE "TRI-LINE" INDUCTION MELTING EQUIPMENT

As follows:

ITEM I: POWER SUPPLY - Bulletin 50-250

One INDUCTO 250 KW TRI-LINE power and control unit:

- A. RATED: 250 KW/290 KW
 480 volts, 3 phase, 60 cycles - 350 KVA input required
 750 volts, 1 phase, 180 cycles - output

B. POWER COMPONENTS:

Enclosed in heavy gauge, front access, steel cubicles:

1. One three-pole, solenoid-operated, main-line contactor complete with overload relays.
2. Inductotherm-developed frequency-tripling transformers, self-stabilizing, vacuum encapsulated, high efficiency, grain oriented, toroidal type, water cooled, with sufficient internal reactance to limit short circuit currents to self-protecting values.
3. Primary capacitor bank to correct the line power factor.
4. Secondary capacitor bank complete with magnetically operated capacitor contactors to resonate the induction coil through its full range of melting conditions. The secondary capacitors will be equipped with the new INDUCTO-developed capacitor fault detector and indicator.
5. One 480/110 volt control power transformer, properly sized and fused.
6. Necessary potential transformers, properly fused, and current transformers for instrument and control circuits.
7. Miscellaneous bus bar, overcurrent and overvoltage relays, switches, fuses, terminal blocks, power and control wiring, water lines, hoses, etc. all installed within the cubicle.

March 27, 1978

C. CONTROL & INSTRUMENTATION COMPONENTS

Mounted on a hinged door of a power cubicle:

1. Three large face type instruments:
 - a. Ammeter for 60 cycle income line
 - b. Voltmeter for 180 cycle circuit
 - c. Kilowattmeter for 180 cycle circuit
2. Push buttons and indicating lights for main-line contactor.
3. One fine tuning power selector to provide stepless power control to adjust power to the desired level.
4. One INDUCTO interlock circuit monitor with indicating lights, test and reset buttons and relays to indicate circuit troubles on all safety devices and interlocks.
5. One INDUCTO continuously monitoring ground and molten leak detector unit with double indicating lights, milliammeter, by-pass switch, sensitivity rheostat and test push button for testing the circuit.
6. Miscellaneous terminal blocks and wiring, installed.

PRICE - F.O.B. Rancocas, New Jersey ----- \$41,835.00

ITEM I-A: POWER SUPPLY - Alternates

- A. One 200/230 KW Tri-Line power supply, 275 KVA, 3 phase, 60 hertz input.

PRICE ----- \$35,870.00

- B. One 300/350 KW Tri-Line power supply, 425 KVA, 3 phase, 60 hertz input.

PRICE ----- \$50,200.00

- C. One 350/400 KW Tri-Line power supply, 475 KVA, 3 phase, 60 hertz input.

PRICE ----- \$56,700.00

ITEM II: FURNACE SELECTOR SWITCHES - Optional

Two (2) double-pole, single-throw selector switches mounted on the control cubicle and properly interlocked to permit selection of furnaces for alternate operation. These switches may be used with any of the above power supplies.

PRICE - F.O.B. Rancocas, New Jersey ----- \$ 1,600.00

Quotation No. 32778-1-CHF

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ITEM III: STEEL SHELL TYPE MELTING - Bulletin 10-10 -

- A. One (1) special INDUCTO 5000 lb. steel capacity steel shell melting furnace (for aluminum and aluminum alloys), trunnion mounted, with integral hydraulic tilting mechanism, using two hydraulic cylinders of adequate capacity to power the tilting and righting of the furnaces in smooth, easy movements. The furnace will be complete with tilting stanchions and water-cooled leads. (Refractory working linings by customer.)

PRICE - F.O.B. Rancocas, New Jersey ----- \$27,700.00

- B. One (1) special INDUCTO 3000 lb. steel capacity steel shell melting furnace (for aluminum and aluminum alloys), trunnion mounted, with integral hydraulic tilting mechanism, using two hydraulic cylinders of adequate capacity to power the tilting and righting of the furnaces in smooth, easy movements. The furnace will be complete with tilting stanchions and water-cooled leads. (Refractory working linings by customer.)

PRICE - F.O.B. Rancocas, New Jersey ----- \$20,145.00

ITEM IV: LIFT-SWING COVERS

The above furnaces may be equipped with lift-swing hydraulically operated covers to minimize the radiation loss during "holding periods".

PRICE - 5000 lb. furnace ----- \$ 2,110.00
PRICE - 3000 lb. furnace ----- \$ 1,875.00

ITEM V: HYDRAULIC POWER SUPPLY

One (1) hydraulic power supply, consisting of hydraulic pump, motor, motor starter, reservoir, relief valve, pressure valve, and gauge. One initial filling of fluid is included.

PRICE ----- \$ 2,415.00

ITEM VI: WATER COOLING AND RECIRCULATING EQUIPMENT - Two Alternates

A. OPEN TYPE SYSTEM:

One (1) cooling water recirculating system for use in the Pittsburgh, Pennsylvania area to provide cooling for one 250 KW Tri-Line unit and two 5000 lb. steel shell furnaces.

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This system will consist of:

One (1) open type cooling tower.

One (1) combination hot and cold well assembly, epoxy painted and prepiped with two (2) pumps, strainers, isolation valves, auto make-up water controls, side stream filter and immersion heater.

Four (4) temperature switches to control the hot well pump, cooling tower fan, overtemp alarm and hot well immersion heater.

One (1) prewired control panel complete with all push buttons, lights, relays, motor starters, fuses and alarm circuit, all contained in a NEMA-12 dust-tight enclosure.

The entire system will be completely designed with the exception of any water treatment equipment which may be required to meet the following specifications:

Hardness	50 PPM or less
Conductivity	350 Micromhos/cm or less
Suspended Solids	10 PPM or less
Alkalinity or Acidity (pH)	7.0 to 7.8

It is recommended that the purchaser contact local water treatment companies to determine the proper treatment necessary to meet these standards. Not included in the quoted price is the inlet, interconnecting and drain piping, interconnecting wiring, or any other parts or components required, except as specified above.

PRICE - F.O.B. Shipping Points ----- \$ 7,800.00

B. OPEN TYPE SYSTEM WITH ISOLATION HEAT EXCHANGER

One (1) cooling water recirculating system for use in the Pittsburgh, Pennsylvania area to provide cooling for one 250 KW Tri-Line unit and two 5000 lb. steel shell furnaces.

This system will consist of:

One (1) open type cooling tower.

One (1) combination hot and cold well assembly, epoxy painted and prepiped with two (2) pumps, strainers, isolation valves, auto make-up water controls, heat exchanger(s), two (2) side stream filters and immersion heater(s).

Quotation No. 32778-1-CHF

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Four (4) temperature switches to control the hot well pump, tower fan, overtemp alarm and hot well immersion heater (if necessary).

One (1) prewired control panel complete with all push buttons, lights, relays, motor starters, fuses and alarm circuit, all contained in a NEMA-12 dust-tight enclosure.

The entire system will be completely designed with the exception of any water treatment equipment which may be required to meet the following specifications:

<u>FURNACE SIDE:</u>	Hardness	50 PPM or less
	Conductivity	350 Micromhos/cm or less
	Suspended Solids	10 PPM or less
	Alkalinity or Acidity (pH)	7.0 to 7.8
<u>TOWER SIDE:</u>	Dissolved Solids	1500 PPM or less after treatment for scaling and corrosion.
	Suspended Solids	50 PPM or less
	Alkalinity or Acidity (pH)	6.5 to 7.5

It is recommended that the purchaser contact local water treatment companies to determine the proper treatment necessary to meet these standards. Not included in the quoted price is the inlet, interconnecting and drain piping, interconnecting wiring, or any other parts or components required, except as specified above.

PRICE - F.O.B. Shipping Points ----- \$14,030.00

ITEM VII: ELECTRIC BUS BAR

To minimize transmission losses between the power supply and melting furnace, Inductotherm recommends electric bus bar. Pricing for the electric bus bar is available once the layout configuration is determined along with final equipment sizing.

ITEM VIII: STEP-UP AUTO-TRANSFORMER

If the customers voltage source is not 480 volt, 3 phase, 60 hertz, a step-up auto-transformer is available to step the voltage up to 480 volt, 3 phase, 60 hertz. The pricing is as follows:

A. 250 KW Tri-Line.

PRICE ----- \$4510.00