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CONS-5089-13

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

Third Interim Technical Report, Phase C, July 1—September 30, 1980

By
M. J. Bruno

October 1980

Work Performed Under Contract No. AC01-77CS40079

Aluminum Company of America
Alcoa Laboratories
Alcoa Center, Pennsylvania

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

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Price: Printed Copy A04
Microfiche A01

CONS-5089-13
Distribution Category UC-95f

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THIRD INTERIM TECHNICAL REPORT, PHASE "C"
FOR THE PERIOD 1980 JULY 01 - 1980 SEPTEMBER 30

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 DEACOL-77CS40079

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This is the third interim technical report, Phase "C", submitted in accordance with the requirements of Contract No. DEAC01-77CS40079, a three-year cost-sharing agreement between the Department of Energy and Alcoa. The report describes work performed in the third quarter of the third year of the program

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Abstract

Phase C of a three year cost-sharing contract between the Department of Energy and Alcoa was started on 1980-01-01. At the end of the third quarter, the program for Phase C is estimated as 78.8% complete, with 70.9% of the funding expended.

Pilot reactor VSR-3 operation in the third quarter was directed to tapping molten alloy product. Modifications to the hearth region included a tapping furnace to maintain taphole temperature, a graphite ring filter to separate carbides from metal and an alumina liner to eliminate carbiding from reaction of alloy with the graphite hearth walls. Tapping was not successful, however, due to high alloy viscosity from a large concentration of carbides. Fluxing the alloy with molten cryolite resulted in a clean separation of fluid eutectic alloy from carbides. The gas-fired crucible reactor was converted to a submerged arc furnace with a single graphite electrode. The effect of pressure on carbon fuel rate, metal-producing temperature and reflux loading for a combustion-heated blast furnace was calculated using the SOLGASMIX computer program. High pressures reduce reflux and fuel rate and increase temperature. Detailed heat and mass balances were determined for the blast-arc and submerged arc process concepts. Both midwestern coal and low ash, low iron Wyoming coal were considered for the fuel and reduction carbon source in the blast-arc cases. The SOLGASMIX-REACTOR computer program was developed to handle recycle for the Al-Si-C-O-Fe system. The correlation of SiO_2/Al_2O_3 ratio with carbon stoichiometry was continued in bench scale reactor experiments. At 0.785 ratio, the optimum carbon was 90% of stoichiometric. A detailed study was made for the low SiO_2/Al_2O_3 ratio burden (0.485) that considered the roles of sulfur, iron oxide, silicon carbide, titanium, iron and carbon. Microscopic phase identification analyses of metal products indicated that Al_4SiC_4 increased as SiO_2/Al_2O_3 ratio decreased, and that hypereutectic silicon did not increase with SiO_2/Al_2O_3 ratio. Tests on the extractive purification effect of tin additions to Al-Si-Fe-Ti alloys showed no solubility of tin with any of the intermetallics.

Three runs were made on the pilot crystallizer to determine the effects of alloy composition, cooling rate, tamping rate, remelt temperature and rate on eutectic Al-Si yield.

The yields varied from 48 to 72% for a starting alloy with a nominal composition of 66%Al-30%Si-3%Fe-1%Ti. Tests were run on solution leaching of the crystal bed to remove Al and Fe impurities for recovery of Si. Hydrochloric acid was effective; sodium citrate/nitric acid was not.

The pilot membrane cell installation was almost completed at the end of the quarter. Experiments were conducted in the bench scale cell to correlate electrolyte composition with membrane metal penetration. Bath properties had a significant effect on the metal head limit, with penetration ranging from 63 to 217 cm.

Primary activities in the fourth quarter of Phase C will include: operation of the large bench scale submerged arc furnace to determine the effects of process parameters on alloy production; modifications of VSR-3 to provide continuous solids removal for evaluation of the blast region of a blast-arc process; optimization of carbon stoichiometry and concentration in the ore pellet in relation to the SiO_2/Al_2O_3 ratio; determination of carbon solubility in Al-Si alloys at temperatures lower than 1600°C and higher than 1800°C; mathematical modeling of high pressure, combustion-heated blast furnace and submerged electrical arc furnace; completion of the SOLGASMIX-REACTOR computer program; operation of the pilot crystallizer on Al-Si-Fe and Al-Si-Ti alloys.

Discussion

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

In the third quarter of Phase C, the following work was performed by subcontractors and consultants. Koppers Company completed a preliminary study on conceptual engineering and capital cost estimates for a commercial blast-arc process. Professor Julian Szekely consulted a total of 5.5 days, and Dr. J.C. Agarwal consulted a total of 5 days on process economics, process strategy, development of process flow sheets, and future programs for the project. Carnegie-Mellon University ran thermogravimetric analyses on alumina-silica charges in graphite crucibles. At temperatures below 2000°C, one atmosphere of CO and carbon saturation, the oxycarbide stability was lower than expected. Oxycarbide liquid was observed at alumina to silica ratios of four to one or greater. No oxycarbide was detected at lower ratios.

A special technical report titled, "Technical Feasibility of Combustion-Heated Process for Producing Aluminum-Silicon Alloys" (CONS-5089-9) was submitted to DOE in September, 1980. The Abstract is included in Appendix III of this report.

Alcoa submitted additional cost substantiation data to DOE relating to the projected cost overrun.

Two contract modifications were executed, increasing DOE obligated funds and revising the Statement of Work with respect to Phase C sub-tasks under the three main tasks.

As requested by DOE, Alcoa submitted a number of photographs depicting various parts of the process equipment.

Technical progress was reviewed for the DOE Project Manager and Professor J.F. Elliott one time during the quarter.

Progress for the three main tasks is reported by sub-task as identified in the modified porject outlines submitted on 1980 March 26. It is estimated that for Phase C the Reduction task is 78% complete, the Alloy Purification task is 96% complete, and the Purification to Commercial Grade Aluminum task is 71% complete at the end of the third quarter.

A. REDUCTION - PHASE C

Task No. 1: Supply Burden Materials

Materials prepared in the third quarter are listed in Table 1.

Task completion is 75%.

Task No. 2: Burden Beneficiation

This task was completed in the second quarter.

Task completion is 100%.

Task No. 3: Effects of Pilot Operating Parameters

During the third quarter, two runs were made in the VSR reactor with the aim of tapping more metal than was tapped in run VSR-42. In run VSR-43, a tapping furnace was attached to the reactor tapping tube in order to keep the tapping tube temperature above the liquidus of the alloy. This is described under Task 4 and shown in Figure 1. A layer of mixed graphite cylinders and tubes (4.7 kg) was placed in the bottom of the catchbasin for the purpose of filtering carbides from the alloy. The reactor was charged with calcined alumina-clay-coke pellets with an SiO_2/Al_2O_3 ratio of 0.60 and 89% stoichiometric carbon. A small amount of coke was added in order to bring the charge to 92% stoichiometric carbon. After reaching operating temperature, ore was charged for 6.0 hrs at a rate of 7.2 kg/hr. The tap hole plug was then removed and a rod was used to poke into the catchbasin. The rod met resistance from the graphite shapes. Very little metal was tapped. Considerable air burning occurred around the tapping tube due to overheating and shrinkage of the packing between the ceramic shell and the tapping tube. The loss of carbon felt around the catchbasin may have contributed to the poor fluidity of the alloy. An 8.0 kg ingot was recovered from the catchbasin during the autopsy.

In run VSR-44, a double grate and alumina liner were installed as described in Task 4 and shown in Figure 2. The tapping furnace was not used. A layer of SiC lumps was placed on the upper grate, and a layer of graphite cylinders on the lower grate. The reactor was charged with hydrated alumina-clay-coke pellets with an SiO_2/Al_2O_3 ratio of 0.52 and 85%

stoichiometric carbon. Coke was added to bring the charge to 91% stoichiometric carbon. After reaching operating temperature, ore was charged for 6.2 hrs at a rate of 7.5 kg/hr. An attempt was made to tap the reactor after 5 hrs of charging. No alloy was tapped so power was increased to the alloy collection zone (coil C) and the zone temperature increased from 1760°C to 1950°C. After approximately 15 hrs, the tap hole was again opened but no alloy was tapped. Upon autopsy, a large ingot weighing about 12 kg was recovered. The upper half and top of the ingot surface was covered with gold-colored crystals, probably Al_4SiC_4. The alumina sleeve had melted and slumped so that it covered only the lower half of the ingot. Uncoalesced globules of alloy were found in the filter bed. About 0.15 kg of slag was found below the grate and some frozen drops hung from the grate bottom. The slag contained Al_2O_3, Al_4O_4C, Al, and Si. Apparently, the alloy was too viscous to flow through the filter. The mechanism by which large amounts of carbides accumulate in the metal should be better understood before further tapping runs are made. Experiments in the bench reactor should help elucidate the mechanism.

Difficulties in tapping the alloy are related to the presence of a large volume fraction of carbides which makes the alloy quite viscous. The amount of carbide exceeds the amount which would precipitate if the alloy were saturated with carbon and then cooled to the tapping temperature. Filtration of the alloy through a bed of graphite rings or rods was somewhat effective in separating the carbides, but the alloy recovery was relatively low. Fluxing of the alloy with molten fluoride or chloride salts has been reported in the literature, so several experiments were performed to evaluate this approach.

In a preliminary test, a sample of a VSR ingot was submerged in a Tercod crucible containing Hall cell bath at 950°C and agitated. The sample broke up and several globules of coalesced alloy were recovered from the crucible. A larger quantity of ingot alloy was added in the next experiment under the same conditions. After solid pieces could no longer be detected by poking, alloy was ladled from the crucible and samples were poured into a book mold. The alloy was very fluid and separated readily from the bath. In the next experiment, ingot alloy was melted under the same condition, but allowed to furnace cool. Figure 3 shows a schematic of the layers which were found when the cold crucible was broken away. The bottom alloy layer was fairly well coalesced, although there was a rather ill-defined interface between the alloy and a middle layer of sludge, a mixture of bath and carbides.

The interface between the sludge and the top layer of clean bath was well defined. Analyses of a book mold sample and a sample from the furnace-cooled alloy layer were compared with an analysis of a sample from the original ingot. SiC was reduced from 17 volume per cent to an undetectable level based on quantitative metallographic techniques. Iron intermetallics were considerably increased during fluxing due to dissolution of an iron rod used to stir the bath. A comparison of the top of the alloy layer with the bottom shows that the iron and titanium intermetallics sink. $TiSi_2$ intermetallics are reduced by the fluxing procedure, indicating that $TiSi_2$ had begun to precipitate well above 950°C.

In the next experiment, a chloride salt bath was used. The bath was initially at 700°C when the ingot was submerged. The bath temperature was gradually increased to 885°C where fuming was heavy. Very little coalesced alloy was recovered.

In the final experiment of this series, a chloride bath containing 10% cryolite was used. The ingot alloy was introduced to the bath at 810°C and bath temperature was gradually increased to 975°C where fuming was heavy. A small globule of metal was recovered, but the carbide framework remained intact.

These experiments indicate that the carbide framework is broken up by a fluoride bath but not by a chloride bath. Obviously, further experimentation would be needed to verify this conclusion over a wide range of compositions. Fluxing would be used in practice to treat a liquid alloy containing a much smaller fraction of solids and a chloride bath might be effective under those conditions.

Task completion is 80%.

Task No. 4: Pilot Modifications

A tapping furnace was constructed for the purpose of maintaining the reactor tapping tube at an elevated temperature, and providing a preheated crucible so that the tapped alloy would coalesce. A schematic of this furnace is shown in Figure 1. A tercod crucible was set in a resistance-heated furnace with an added top section which accepted the tapping tube and provided access for the tap hole plug.

The plug was not water-cooled. The furnace was purged with argon. This arrangement was used in run VSR-43.

In run VSR-44, the reactor was fitted with two grates and a catchbasin lined with a 36 cm high section of alumina refractory. This arrangement is shown in Figure 2. The purpose of the lower grate was to support a filter bed consisting of a layer of graphite cylinders. The distance between grates was 43 cm leaving a sump 22 cm high into which the tapping tube was screwed.

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

The arc-heated reactor will be started up in October after completion of wiring to the power supply and a job safety analysis. The reactor will be run initially on straight polarity (movable electrode negative) although reverse polarity will also be investigated. At a later time, the reactor may be run on AC.

Task completion is 80%.

Task No. 5: Reactor Scale-Up and Design

Early calculations on the combustion-heated reactor concept were based on free energy data for Al_2O and Al-Si alloys which gave optimistic results. Newer data corroborated by experiments indicates that the concept as originally conceived is not viable due to greater volatility of Al and Al_2O.

The use of a pressurized reactor and a dilutent such as iron would lower volatility sufficient so that a combustion-heated process might be feasible under some conditions. This possibility was investigated using the SOLGASMIX equilibrium program by reacting Al_4O_4C, Fe(l), CO, and excess SiC at a temperature just above the point where Al_4O_4C is completely consumed. This was done at pressures of 1, 3, 6, 9, and 12 atmospheres with various Fe/Al_4O_4C ratios at a constant CO/Al_4O_4C ratio of 15.5. The percentage of combustion heat represented by that ratio varied from 93-97% of the heat requirement which included oxygen preheat. It was assumed that oxygen would be preheated to 1200°K so that the heat balance would allow for about 10% heat loss. The program assumed that Al, Si, and Fe form an ideal solution. Figure 4 shows the effect of pressure on the temperature of the reaction $15.5\ CO + Al_4O_4C + x\ SiC + q\ Fe = a\ \underline{Al} + b\ \underline{Si} + c\ \underline{Fe} + d\ CO + e\ Al + f\ Al_2O + g\ SiO$, where q = .13, .26, .52.

When pressure is doubled, the reaction temperature increases by 80-95°K. Increased temperature should increase the solubility of carbon in the alloy which is undesirable. The magnitude of this effect is unknown since reliable data on C solubility is not yet available. Figure 5 shows the variation of fuel rate expressed as mol C/mol Al with weight percent iron in the alloy at various pressures. Figure 6 shows the reflux loading on a similar plot. A reflux loading of 80% means that 80% of the Al_4O_4C reaching the Stage III reaction zone refluxes while 20% is converted to alloy.

A high reflux loading implies a low specific reactor productivity, difficulties in operation due to bridging or complete plugging of the bed, and a high fuel rate due to degradation of the high temperature heat input. Based on the calculations, a 45% iron alloy could be made at one atm with a recycle loading of 91% and a fuel rate of 42 mol C/mol Al. At 12 atm, a 10% iron alloy could be made with a recycle loading of 65% and a fuel rate of 11 mol C/mol Al. Thus, while one atm operation would produce an unacceptably high fuel rate, 12 atm operation should lead to a fuel rate comparable to that of the earlier optimistic calculations. If 25% iron could be tolerated, the reflux loading could be reduced to 52%. Although 10% iron is probably too high to handle economically with fractional crystallization and 52% reflux may still cause operating problems, the low energy consumption potential provides an incentive for further investigation. SOLGASMIX REACTOR, a program which is not operational, will be used to model a high pressure combustion-heated reactor. This will provide a much more complete analysis and will be used as a basis for an energy balance on the whole process.

Task completion is 75%.

Task No. 6: Calculate Heat and Mass Balances

In order to obtain a useful economic evaluation of the hybrid (blast arc) and straight arc processes, a more complete heat and material balance was developed for these cases. As in the past, the SOLGASMIX program was utilized to determine the equilibrium compositions of each phase present and the heat of reaction of all species at temperature. All sensible heats were determined by hand calculations as well as the final heat balances. The new improvements and assumptions used in these calculations encompassed the following items.

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

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

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

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

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

-No slag solutions were considered in these balances, but they may be included in the future.

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

Thus, Stages II and III were lumped together, which greatly simplified the calculations. For the hybrid process, the chemical heat in the gas above 2184°K as well as the sensible heat in the gas above 1840°K were used to balance the endothermic heats of reduction and sensible heat in the solids above 1840°K to leave the net endothermic heat to be supplied from the arc. This electric heat was then arbitrarily increased by 10% to allow for high temperature heat loss. A better estimate of these heat losses will be attempted in the future (See Appendix I).

-The char and oxygen combustion required to maintain the Stage I heat balance in the hybrid process is determined by a trial and error technique using both the net heat of reaction to make SiC, and the energy required to preheat the char from 1200°K and the O_2 and carrier gas from 1089°K. These preheat temperatures were estimates related to the solids exit temperatures from the hot char-producing step, and need further refinement. Heat losses were arbitrarily set at 7.5% of the net chemical heat to produce SiC, and were included in the char-oxygen calculation (See Appendix I).

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

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

Preliminary heat and material balances for three cases were calculated according to the procedures and assumptions as stated above. The hybrid process heat and material balance for the Western Kentucky Coal case was significantly effected by the analysis and amount of ash in the coal (See Table 2).

Even though the assumptions used for the hybrid process with Western Kentucky Coal and Wyoming Coal differ slightly, the basic effects of these two coals are clear. Higher ash in the coal requires more combustion of carbon and oxygen to preheat this ash as well as the attendant increases in carrier gas and combustion oxygen. The carbon in the combustion char required for the Western Kentucky Coal and Wyoming Coal cases is 1.74 lb C/lb Al and 1.50 lb C/lb Al respectively. This translates into 2.34 lb char/lb Al for the Western Kentucky coal case and 1.74 lb char/lb Al for Wyoming coal. Another major effect of these two coals is the Fe content of the metal resulting from the lb Fe/lb C attributed to these two coals. The Western Kentucky coal is very similar to the Indiana coals, and the results show that compared to a Wyoming sub-bituminous coal with lower ash and lower Fe in the ash, these Midwestern steam coals would raise the lb Fe/lb Al in the alloy by a factor of 2.7 times in the hybrid process. The Al recoveries in the crystallizer have yet to be determined and have been estimated in these three studies. However, a lower yield of Al in the crystallizer due to Fe contamination is to be expected, and it is shown how this difference would effect the quantities of material that would have to be processed through the reduction reactor to obtain the same net Al production.

The hybrid process and arc furnace process as shown in Figures 8 and 9 respectively, can be directly compared because the carbon source, alloy recovery in the crystallizer, and other raw materials were identical. The only variations were those related to heating Stage I by combustion and not by heat from an electric arc.

The furnace top gases from either process along with the same coal utilized for the production of char and formcoke were used to calculate the coal to generate the required electrical power for each process in a conventional coal-fired steam power plant. The top gas and coal burned for electricity generation was assumed to be converted with a 36% efficiency with 9600 BTU/lb coal and 316 BTU/SCF and 312 BTU/SCF for the heating value of the hybrid and arc furnace top gas respectively. This coal was assumed to be wet containing 20.3% H_2O. The same coal on a dry basis has a heating value of 12,040 BTU/lb, and the numbers in parenthesis in Table 3 reflect the use of dry coal.

In terms of the solids handled and the coal consumed, the two processes are equivalent for these calculations. Because there is 1.73 times more char consumed and 1.45 times more

top gas produced in the hybrid process, there are probably more gases handled for that process. This entire analysis does not include the power consumption for production of oxygen or Bayer alumina. There may be no large economic or energy differences between the two processes, but the arc process is definitely more technologically likely, and will result in less Fe and Ti in the alloy. These preliminary analyses will be updated in the future with capital costs.

Task completion is 85%.

Task No. 7: Process Mathematical Modeling

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

The SOLGASMIX programs have been converted to run on the new ATC DEC-10 computer (KL processor). This will enhance their availability. Conversion of the SOLGASMIX-REACTOR program will be done when its development is complete, which should be in the next quarter.

Task completion is 80%.

Task No. 8: Effects of Process Variables

During the quarter, two runs were made in the bench scale reactor. The details of the two AF runs are shown in Figures 10 and 11. A summary of important variables for these runs along with all the other runs to date in the AF reactor program are presented in Tables 4 and 5. The runs in AF26, 28, and 29 are related in that the only intended variable was the carbon stoichiometry of the burden. It was desired to compare the metal yield with respect to carbon stoichiometry and find the optimum carbon level which would minimize the accumulations of slag or carbide resulting from too low or too high a burden carbon. Comparisons of these three runs show that very little slag or carbide accumulations occur for a 90% carbon stoichiometry in the burden at a .785 SiO_2/Al_2O_3 ratio. Comparing AF26 and 29 shows that no appreciable increase in metal production for an increase in

burden carbon was observed. The increase in metal production in AF28 could well be related to the slightly higher burden carbon and metal-producing temperature, but this was a shortened run that was plagued with operating problems and needs repeating for any conclusion to be made.

From the heat and material balances, as reported in Task 6, certain information regarding possible reaction mechanisms and important operating criterion surfaced that are worth noting. All of the items discussed below relate to a process run with .485 SiO_2/Al_2O_3 ratio burden, and many of these will change as this ratio is varied. The following items have been deduced from these calculations, and some of them are represented in one form or another in Figures 12 through 15. These figures represent the phases and temperature ranges of stability for the primary species present in the two streams of mass flow in the reactor.

-The heat balances have been calculated to give the lowest possible electric power consumption by assuming complete equilibrium. With respect to the vaporous species Al, Al_2O, and SiO, if serious channeling of the gas occurs, the chemical heat of refluxing of these species due to condensation and back reaction will be released at much higher reaction positions and lower furnace temperature than would be predicted by equilibrium, and a very large increase in the electric power consumption would occur. High temperature reactions generally very closely approach chemical equilibrium, and it is hoped this will be true in this case.

-Along this line, equilibrium calculations predict very little Al and Al_2O in the gas below 2185°K. If the gas is cooled below 1500°K before leaving the furnace and chemical equilibrium prevails, no SiO will be present in this gas. Therefore, no dust losses are predicted by the model as the top gas temperatures calculated from the heat and material balances are all below 1500°K.

-For a 70/30 Al/Si ratio in the alloy, there is a small temperature range where Al_4C_3 is stable. It is not known, if an oxycarbide slag solution of varying composition was included in the thermodynamic calculations, whether this phase would continue to appear. These results do suggest that this phase might not be stable under these conditions.

-With Fe in the system, metal appears at a lower temperature than it would for a straight Al-Si alloy. The metal, as it first appears at 2185°K, is basically Fe with a minor amount of Al and with increasing temperatures, the Al content raises much faster than that of Si. These are the behavior that are predicted for an ideal solution of Al-Si-Fe.

-From our experimental work, Ti ends up exclusively in the metal. When Ti is included in the metal solution in future thermodynamic calculations, it will be interesting to see if this occurs rather than the formation of TiC as is now predicted.

-Silicon carbide is the major reductant for all aluminum oxide species and not carbon.

-Iron oxide is reduced to Fe metal long before the Al-Si-Fe alloy is formed, and probably would be present as a carbon saturated iron-carbon alloy until this multi-component alloy is formed. The equilibrium model predicts that liquid Fe_3C will be present until the first alloy appears. Although the model predictions are not strictly correct, they do assimilate the consumption of carbon and formation of the Fe-C alloy.

-The presence of sulfur indicates another refluxing species of SiS that is stable above 1450°C and results in a reflux of only Si. Iron vapor, vaporous sulfur species, and FeS liquid work together to reflux both Fe and S. The predominant sulfur species leaving the furnace are H_2S and COS with minor amounts of CS_2 and CS. These reduced forms of S are more easily removed than oxidized forms and there are good possibilities for an economic sulfur clean-up of the furnace gases to prevent pollution and produce elemental sulfur.

-The equilibrium model predicts that carbon is deposited along with Si and Al in the refluxing reactions. The results show that twice as much Al_2O_3, SiC, and C enters Stages II and III than is supplied from Stage I.

Many of these points will be studied further with respect to varying SiO_2/Al_2O_3 ratio using the new SOLGASMIX-REACTOR program.

Task completion is 75%.

Task No. 9: Supportive Analytical

Analyses were completed as required. A total of 381 man-hrs were expended.

Task completion is 75%.

Task No. 10: Supportive Phase Identification

Phase determination by quantitative metallography was performed on ingots from four bench runs with SiO_2/Al_2O_3 ratios of .504, .785, .788, and 1.22. Typically, the ingots were texturally heterogeneous with three to five textural zones arranged vertically. Large variations in carbide distribution were found between zones. The amount of SiC generally decreased with increasing height, while Si showed a tendency to increase. Lower SiO_2/Al_2O_3 ratio ingots contained increasing amounts of Al_4SiC_4. The relative amount of hypereutectic silicon did not increase with SiO_2/Al_2O_3 ratio, possibly due to the influence of carbon. These results are reported in more detail under Task 8.

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

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

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

In run VSR-42, during which some alloy was tapped, a large quantity of alloy did not drain from the reactor. A metallographic analysis of the ingot which remained in the reactor showed 32% SiC, <1% Al_4SiC_4, 4% slag, and 5% $TiSi_2$(Al, Fe) by volume. The SiC occurred as irregular plates contouring

intergrown Al_4SiC_4, and as agglomerated masses of semi-concentric SiC balls. Slag was generally associated with these agglomerates. $TiSi_2$ (Al, Fe) was associated with the SiC plates, suggesting that $TiSi_2$ (Al, Fe) may have crystallized in the SiC plates. By comparison, the alloy which drained from the tap hole contained only 0.72% C which is equivalent to about 2.5% SiC by volume.

Task completion is 75%.

Task No. 11: Supportive Mechanical Engineering

A total of 87 man-hrs of machining and mechanical assistance were expended.

Task completion is 75%.

B. ALLOY PURIFICATION - PHASE C

Task No. 1: Pilot Unit Installation

Task was completed in second quarter.

Task completion is 100%.

Task No. 2: Effects of Pilot Operating Parameters

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

The major process variables studied in the pilot unit were initial alloy composition, cooling rate, tamping rate, remelt rate, and final remelt temperature. The process variables are listed in Table 6 for Runs 1-AP, 2-AP, and 3-AP. A temperature profile is available for the freeze and remelt cycles on Run 3-AP. The material balances are presented in Table 7. At regular intervals, stream samples were taken of the liquid alloy drained from the crystallizer. Selected samples were analyzed to determine approximate yields of casting alloy. The crystal bed was also analyzed to complete the material balance. They yield information for the runs is presented in Tables 8, 9, and 10.

Analysis of the crystal beds for these runs was difficult due to the high silicon content of the samples. Samples were analyzed by atomic absorption (AA), and inductively-coupled plasma (ICP) for Si, Fe, Ti, and Al. Samples have also been submitted for neutron activation analysis (NAA). It is possible that the door closure obtained (92-96%) is due to oxide formation or carbon contamination. NAA on crystal bed samples from Runs 2-AP and 3-AP showed oxygen levels of 0.53 and 1.3% respectively. These results would indicate either contamination of the bed with carbon or continued incomplete dissolution of samples for analysis.

The crystal beds were leached in two media: hydrochloric acid to remove free metal, and a sodium citrate/nitric acid solution to preferentially remove iron. The analyses are presented in Table 11.

The major objective of the pilot crystallizer runs was verification of bench results on fractional crystallization of synthetic reactor product. The nominal starting composition of Al-30%Si-3%Fe-1%Ti was chosen to be within the iron and titanium concentration limits established by the bench scale program. It was hoped that, with a small number of experiments, several assumptions could be verified and also produce improved yields. A key assumption in the scale-up of this portion of the Direct Reduction Process is that high surface to volume ratios decreased yields in the bench equipment, and that drainage and casting alloy yields would improve as the scale of the equipment increased. Table 12 shows the yield information for Experiment 10 (bench), which had a starting alloy very similar to the composition of Run 2-AP. The amount of material drained at the end of the freeze cycle was much higher for Run 2-AP, 21% vs 7% for Experiment 10; however, the casting alloy yield was remarkably similar, 60% for Run 2-AP vs 55% for Experiment 10. It must be remembered that Experiment 10 was performed in a resistance-heated crystallizer, and that the pilot experiments are only the first efforts at operating the pilot crystallizer for alloy purification.

Referring to Table 6, Runs 1-AP and 2-AP were very similar, with a moderate cooling rate, and a slow tamping rate. The tamper stroke was short, 4-in. and 5-in., respectively. The major input difference between these runs was the titanium level; however, the casting alloy yield varied considerably, 72% for Run 1-AP and 48% for Run 2-AP. Run 3-AP had an even higher level of titanium, but the major operating change in Run 3-AP was a 25% lower cooling rate. The purpose of this reduction was to allow the cooling to more closely approach the equilibrium liquidus and to avoid supercooling. Run 3-AP also had better instrumentation, with a melt temperature profile during the freeze cycle, and better temperature monitoring during remelt. These temperature profiles are presented in Figure 16. The cooling rate was 1°C/min. During the remelt cycle, two thermocouples were suspended from the inert lid, and pushed into the crystal bed when it had softened somewhat. One thermocouple was approximately 4-in. from the sidewall, and the other approximately 4-in. from the shaft of the false bottom. The temperature of the bed near the sidewall increased more rapidly than in the center of the unit, although some equilibration did eventually occur. This temperature differential can be contributed to the "skin effect" of induction heating. The casting alloy yield for Run 3-AP was 58%. As stated in previous reports,

iron and titanium have a synergistic effect on casting alloy yields. The yield on an experiment with both iron and titanium is lower than the yields on experiments with similar levels of either iron or titanium.

The remelt cycle length showed a slight variation among the three experiments. Since the temperature monitoring was inadequate for Runs 1-AP and 2-AP, no significance is attached to this variation. In future runs, the remelt cycle will be terminated when the crystal bed reaches 900°C, with less than a 25°C difference in thermocouple readings.

The crystal beds from the experiments were examined for chemical composition and morphology. The chemical composition is reported in Table 11, and the morphology is reported below.

Experiment	Morphology
Run 1-AP	72% Si, 25% Al, 2% $FeSi_2Al_4$, trace of $FeSiAl_5$
Run 2-AP	70% Si, 26% Al, <1% $TiSi_2Al$, 3% $FeSi_2Al_4$, trace of $FeSiAl_5$

The morphology agrees well with the chemical analysis. Six samples were taken of the crystal bed for Run 3-AP, as indicated in Figure 17. The chemical analyses are:

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

Several observations were made:

1. More titanium bearing intermetallics are found near the top of the crystal bed.

2. Iron bearing intermetallics tend to concentrate near the shaft and the bottom of the bed.

3. The highest aluminum content occurs at the bottom of the bed, near the shaft. This is due to poor drainage and the generally lower temperatures along the axis.

The results of the leaching work (Table 11) show that leaching with hydrochloric acid is effective in reducing aluminum and iron levels in the crystal bed. The effect of the sodium citrate/nitric acid leach is minimal. Although the iron and aluminum levels in the citrate/nitric solution increase during the leaching, and the iron pickup is generally greater than that of aluminum, the amount of iron and/or aluminum leached is so small as to be insignificant.

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

Task completion is 90%.

Task No. 3: Pilot Unit Modifications

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

Task completion is 100%.

Task No. 4: Supportive Analytical

Analytical work on samples from the pilot runs and leaching experiments was completed during this quarter. A total of 147 man-hrs were expended.

Task completion is 90%.

Task No. 5: Supportive Mechanical Engineering

A total of 57 man-hrs was expended in support of Task No. 3.

Task completion is 100%.

C. PURIFICATION TO COMMERCIAL GRADE ALUMINUM - PHASE C

Task No. 1: Pilot Unit Installation

Final changes were made to the control logic, and wiring of the electrical circuitry was initiated. Alarms for high and low conditions for voltage, current, temperatures, and cooling water flow rates have been incorporated into the control package. The membrane cell, tapping kettle, and bath melter have been equipped with pressure gauges and automatic as well as manual vent valves. Strip chart recorders for monitoring trends in voltage, current, and temperatures are being procured.

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

Four fabricated inconel strips wired in series to the main DC power supply were placed in the cell. In series (total resistance of .0192 ohms) these heaters will provide 20 KW of power to preheat the cell to start-up condition (660°C).

The available DC power supply is oversized for the membrane cell. Testing conducted in late 1979 indicates that control in the low voltage range required for normal cell operation will be marginal. Therefore, a water-cooled copper resistor with a voltage drop of 1.5-2.0 V at 10,000 amps is being incorporated into the aluminum buswork to permit the DC power supply to operate normally. Previous tests indicate that satisfactory control can be obtained in this range by means of manual adjustments to the rheostat on the DC rectifier.

Task completion is 100%.

Task No. 2: Effects of Pilot Operating Parameters

No progress.

Task completion is 0%.

Task No. 3: Pilot Unit Modifications

No progress.

Task completion is 0%.

Task No. 4: Support Pilot Operations

The design of the apparatus to establish the limit at which metal starts penetrating the membrane was revised. The redundancy of safety features was increased and the design shown in Figure 18 submitted for safety approval after a formal hazard review had been conducted.

In the present procedure, metal was placed in the graphite tube. Without applying any gas pressure or flow, it was melted with the tube end immersed in the electrolyte. After equilibration at the desired temperature, normally 725°C, the graphite tube was raised so that 1 in. (2.54 cm) was immersed in the electrolyte. Argon pressure was then increased stepwise and the occurrences at the membrane monitored by closed-circuit television.

The experimental conditions and the observed penetration pressures are listed in Table 13. The metal heights corresponding to these pressure values were calculated taking into account a counter-balancing effect of the bath pressure on the other side of the membrane. A density of 2.3 g/cm^3 was assumed for pure aluminum, 2.4 g/cm^3 for the aluminum-silicon alloy, 1.4 g/cm^3 for the bath containing 90% LiCl, and 10% $AlCl_3$, and 1.47 g/cm^3 for the NaCl-LiCl-$AlCl_3$ bath.

Some tests were performed with pure aluminum, others with aluminum-silicon alloy containing 11.7% silicon. The electrolyte was 90%LiCl-10%$AlCl_3$ or 45%LiCl-45%NaCl-10%$AlCl_3$. In the last run listed, 3% $CaCl_2$ was added to the electrolyte. Two tests were run to establish the penetration test in air.

Results obtained were scattered. Penetration pressures between 0.45 and 2.3 psi were observed. The equivalent metal head varied from 63 to 217 cm. Although, even according to the lowest number obtained, the metal would not leak through the membrane in the pilot cell, the safety margin would not be as high as desired.

There was a distinct tendency to lower penetration pressures when the bath was filtered. Removal of oxide affects surface tension characteristics of the bath. The interfacial tensions at the membrane play a significant role.

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

Electrolysis currents of 2A were applied in two cases, but the same penetration pressures were observed.

Task completion is 100%.

Task No. 5: Supportive Analytical

Required analyses were performed. A total of 12 man-hrs were expended.

Task completion is 100%.

Task No. 6: Supportive Mechanical Engineering

Assistance was provided for Task No. 1. A total of 12 man-hrs were expended.

Task completion is 100%.

PHASE C FOURTH QUARTER PROGRAM

Administrative

The Baseline Cost Plan for DOE fiscal year 1981 and a Statement of Work for calendar year 1981 program will be submitted. Approval to proceed with Phase D will be requested. A list of current time and materials subcontracts will be submitted.

Technical

Reduction: The large bench scale submerged arc furnace will be operated to evaluate the effects of operating parameters on metal production. Burden composition, carbon location, charge height above the arc, electrode size, electrical characteristics, and electrode to vessel geometric relationships will be studied. The VSR-3 reactor will be modified to facilitate continuous solids removal so that the blast section of the blast-arc concept can be evaluated. Bench scale reactor tests will be continued on optimization of carbon stoichiometry in relation to SiO_2/Al_2O_3 ratio and determination of the minimum reduction carbon in the ore pellet. Master alloys of Al-Si will be prepared for use in carbon solubility experiments at less than 1600°C in graphite crucibles and greater than 1800°C in SiC crucibles. The submerged electrical arc and high pressure, combustion-heated blast furnace processes will be mathematically modeled. The SOLGAS-REACTOR computer program for the Al-Si-C-O-Fe-N-H-S system will be completed.

Alloy Purification: The pilot crystallizer will be operated on Al-Si-Fe and Al-Si-Ti starting alloys to establish the effects of each impurity on Al-Si refining, independent of the interaction that may occur when both Fe and Ti are present.

Purification to Commercial Grade Aluminum: The development of this step of the Direct Reduction Process will be deferred to a future program pending the success of the Reduction task.

Cost Summary

Expenditures for the third quarter of Phase C totaled $328,446. Distribution was $252,228 for Reduction, $27,170

for Alloy Purification, and $49,048 for Purification to Commercial Grade Aluminum. Cumulative spending for Phase C was $1,208,642. Total cumulative spending through the first 37 months of the contract was $4,604,687. Actual spending for Phase C is compared to estimated spending in Attachment 1.

Assigned Personnel

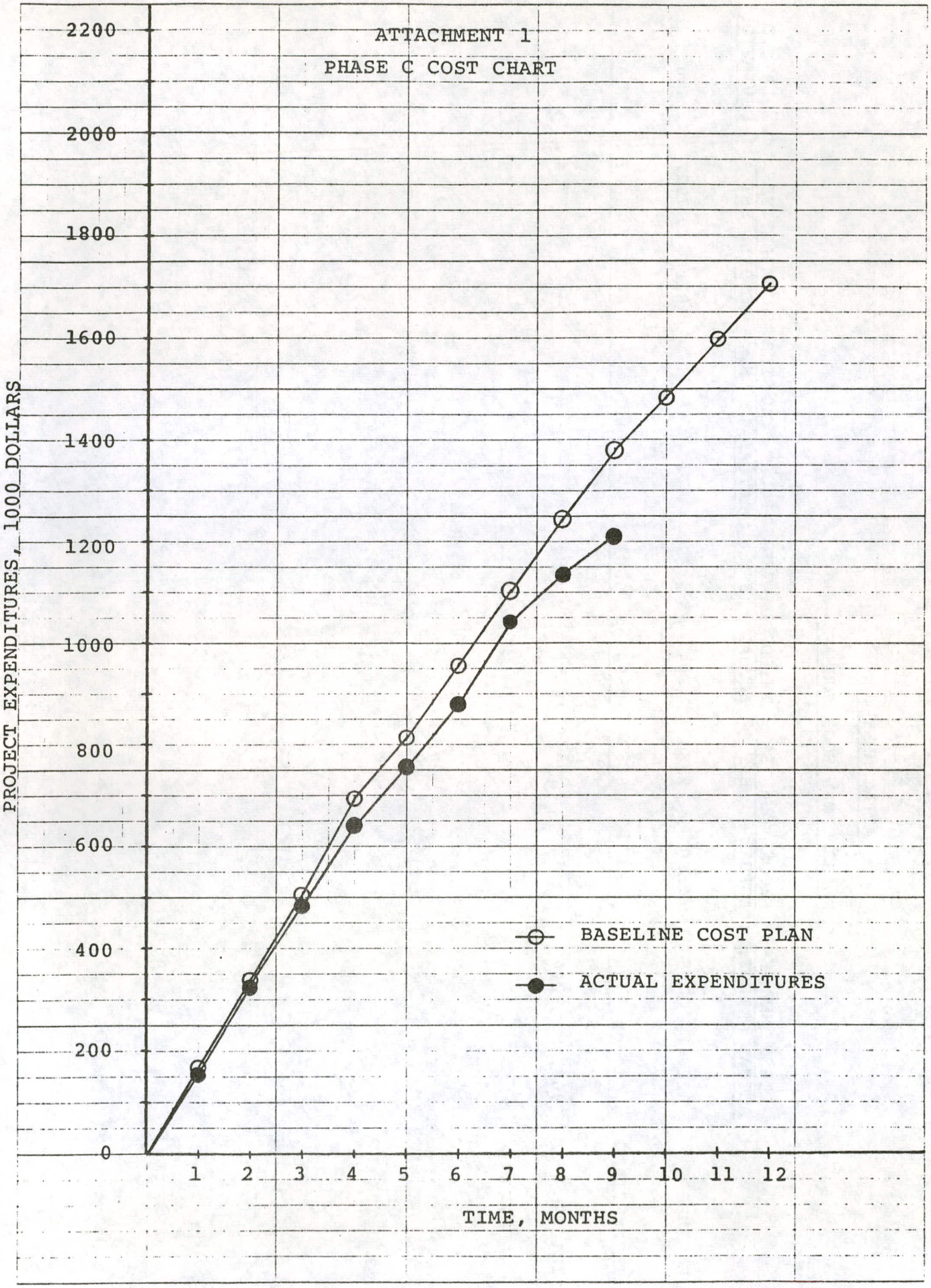
The actual man-hrs expended by engineers and technicians for the third quarter of Phase C are shown in Attachment 2 and compared to estimated man-hrs. For engineers, actual was 4.6% above estimated. For technicians, actual was 12.9% below estimated. Total cumulative man-hrs were 7.7% below estimated.

Task/Milestone Schedule

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

ATTACHMENT 1

PHASE C COST CHART



ATTACHMENT 2

PHASE C MAN-HOUR SUMMARY

	FIRST QUARTER		SECOND QUARTER		THIRD QUARTER		FOURTH QUARTER		CUMULATIVE		CUMULATIVE
	ACTUAL	EST.	ACTUAL	EST.	ACTUAL	EST.	ACTUAL	EST.	ACTUAL	EST.	% DEVIATION
ENGINEERS	3227	2705	2560	2780	2499	2437			8286	7922	+4.6
TECHNICIANS	6464	6539	6227	6262	3694	6001			16385	18802	-12.9
TOTAL	9691	9244	8787	9042	6193	8438			24671	26724	-7.7

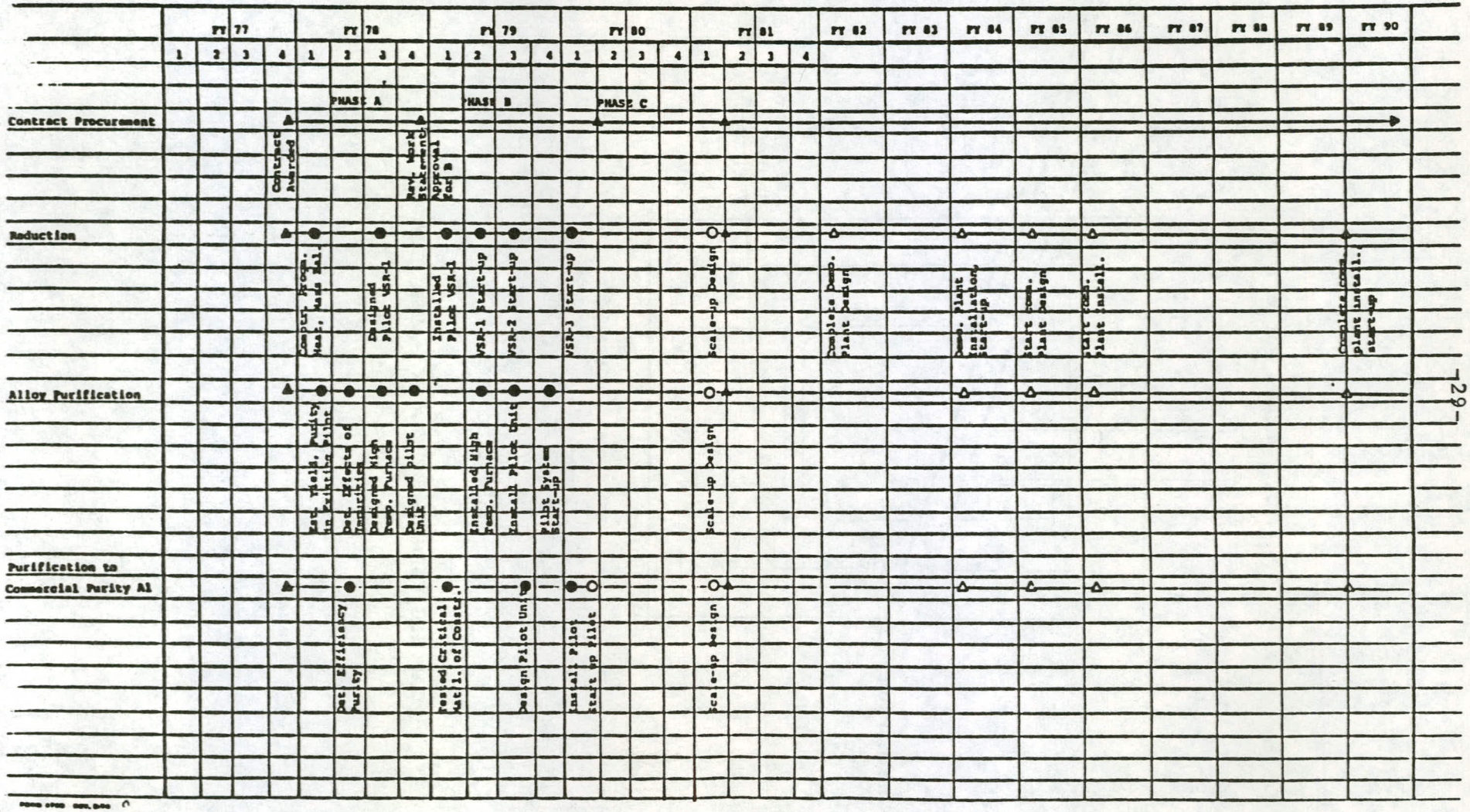
ALUMINUM COMPANY OF AMERICA

ALCOA LABORATORIES

Attachment 3

Direct Reduction Project

Task/Milestone Schedule



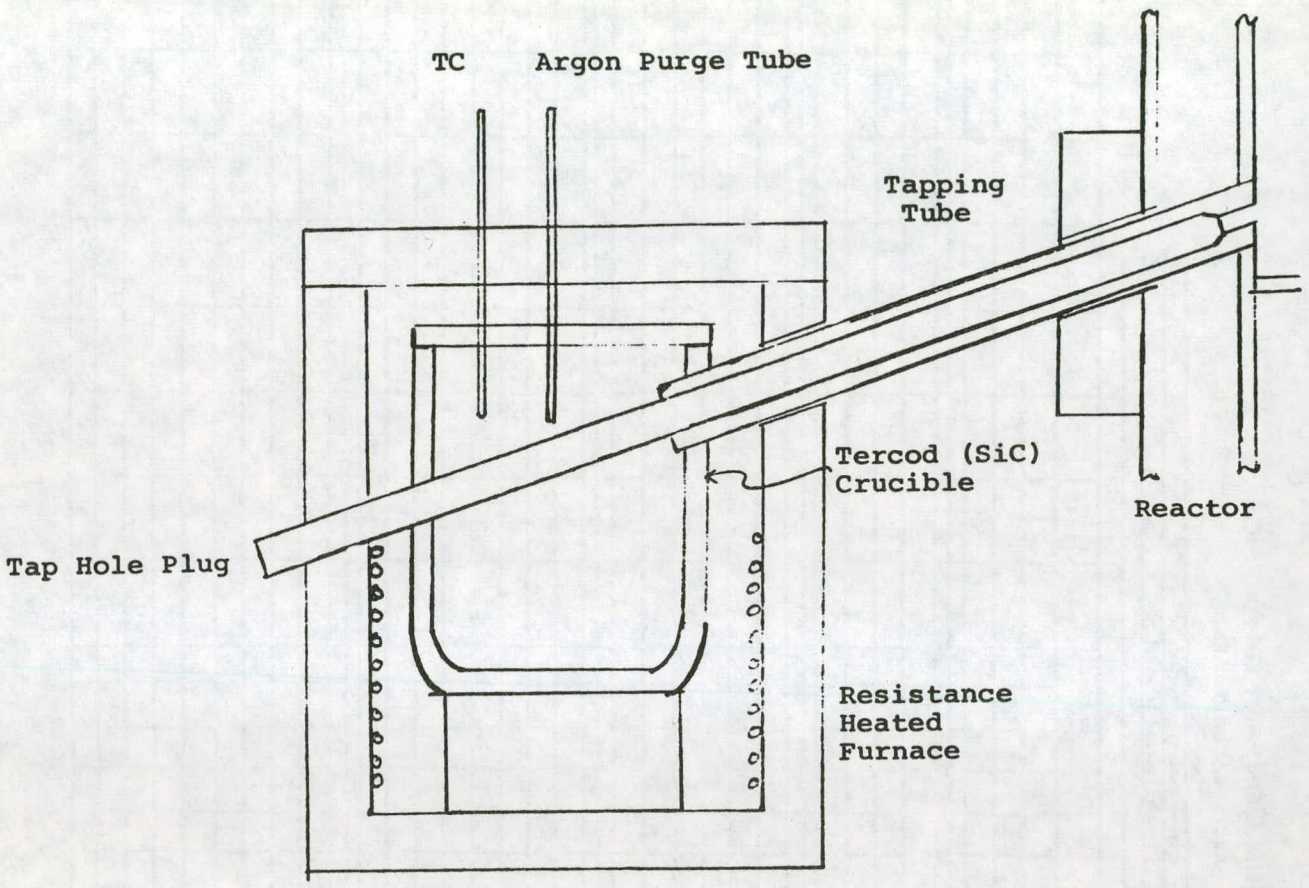


FIGURE 1

TAPPING FURNACE SCHEMATIC - VSR REACTOR

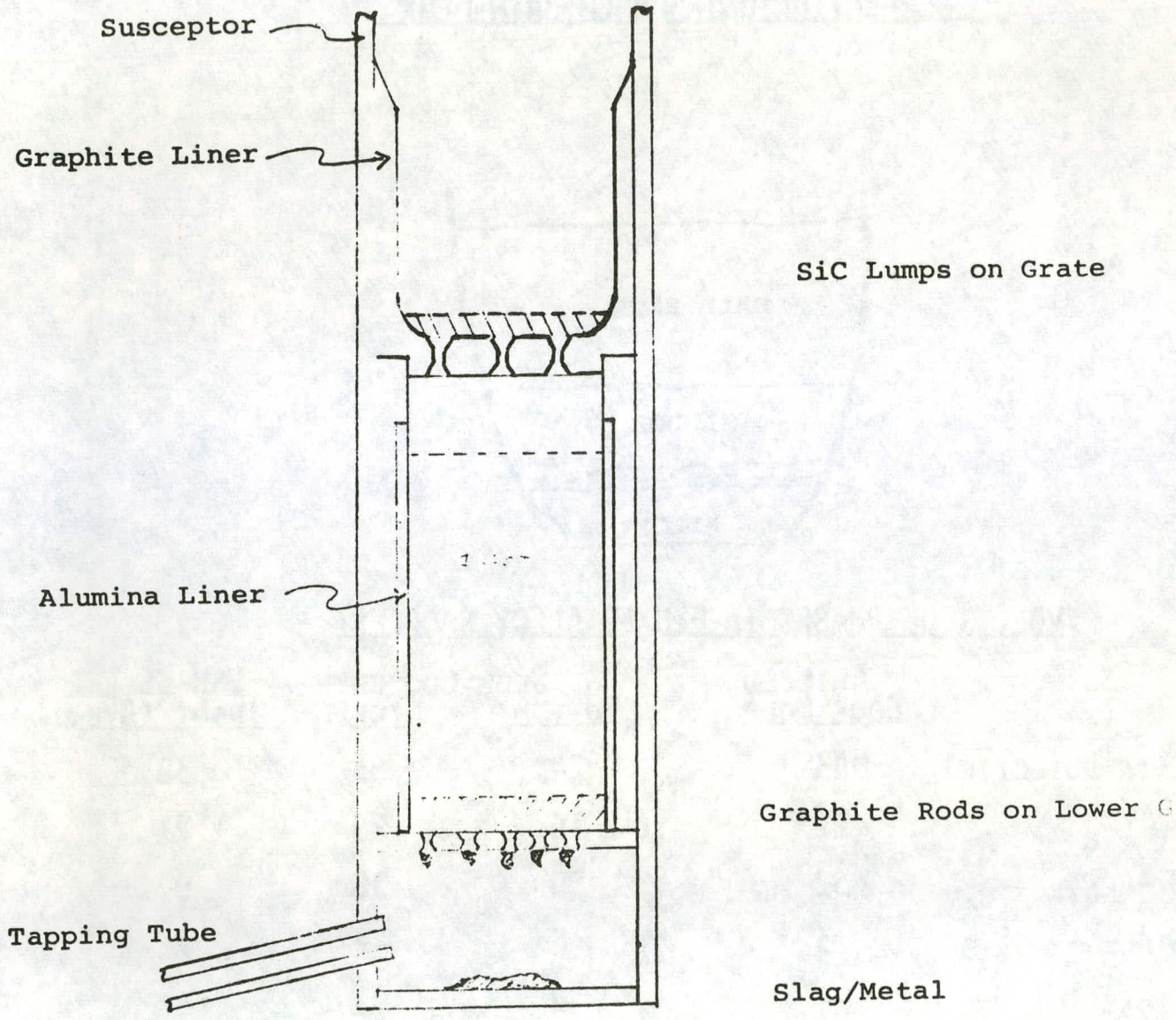
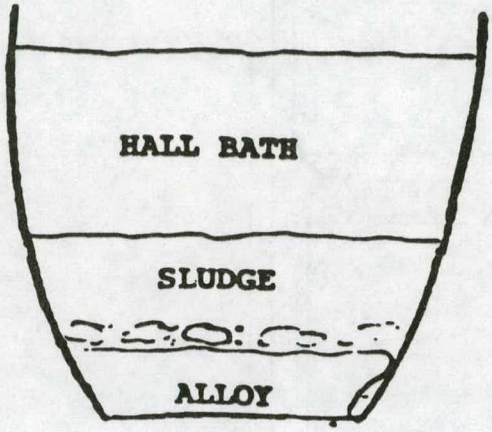


FIGURE 2

DOUBLE GRATE AND ALUMINA LINER - VSR REACTOR

FIGURE 3

INGOT DISSOLUTION AND CARBIDE/ALLOY SEPARATION USING HALL BATH FLUX



VOL. % OF PHASES IN FLUXED ALLOY SAMPLES

	Chilled Book Mold	Slow Cooled Bottom	Slow Cooled Top	VSR-35 Ingot (Ave.)
Al (in eutectic)	43	24	53	38
Si	22	16	29	21
$FeSi_2Al_4$	32	50	16	9
$FeSiAl_5$	3	6	2	7
$TiSi_2$(Al)	--	4	<1	8
$TiSi_2$(Al,Fe)	--	<1	--	1
SiC	--	--	--	17

% Fe increased from about 6% to about 10% due to pick-up from iron tools.

FIGURE 4

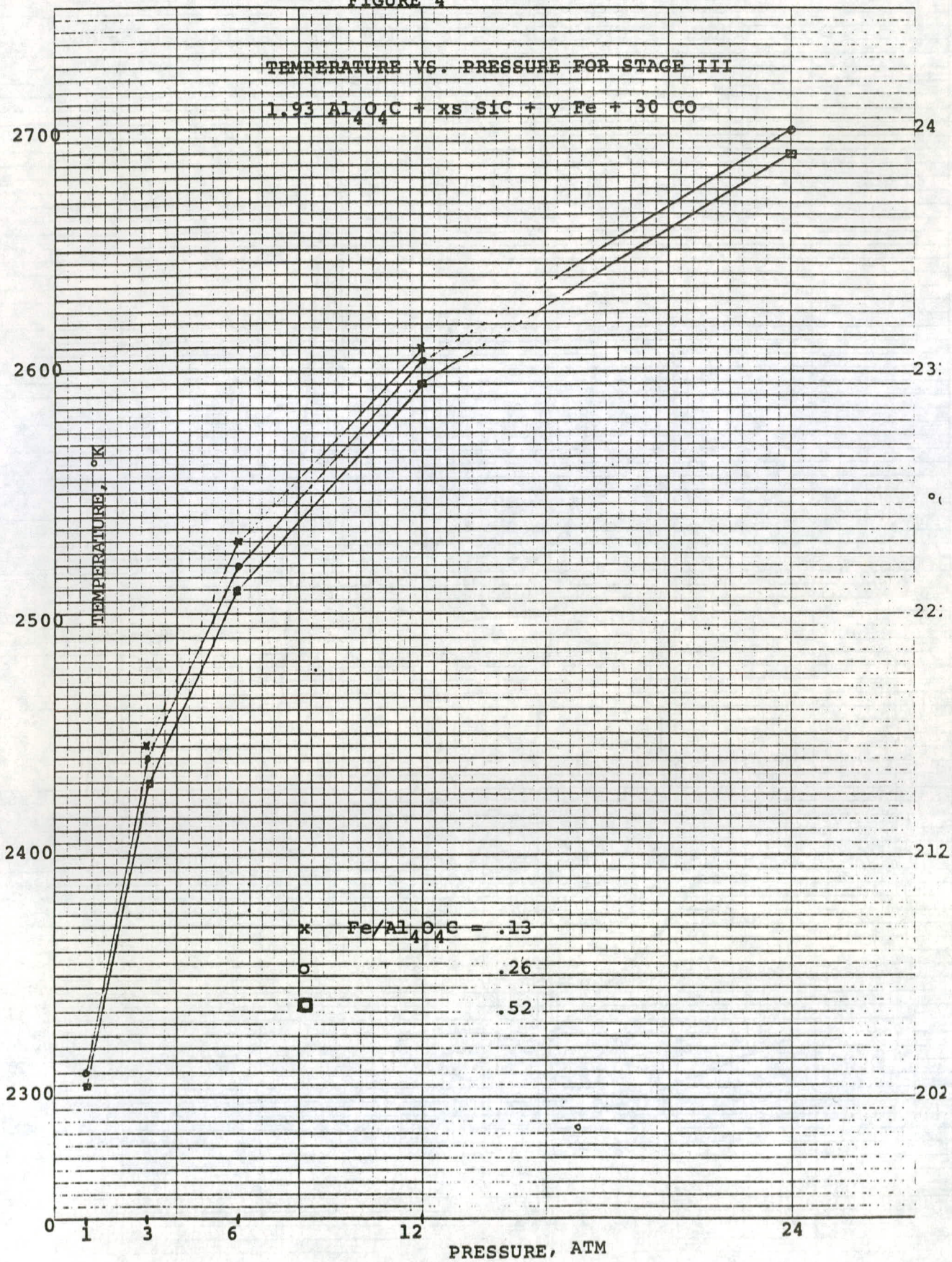

TEMPERATURE VS. PRESSURE FOR STAGE III
1.93 Al_4O_4C + xs SiC + y Fe + 30 CO
TEMPERATURE, °K
2700
2600
2500
2400
2300
0
1
3
6
12
24
PRESSURE, ATM
x Fe/Al_4O_4C = .13
o .26
□ .52

FIGURE 5

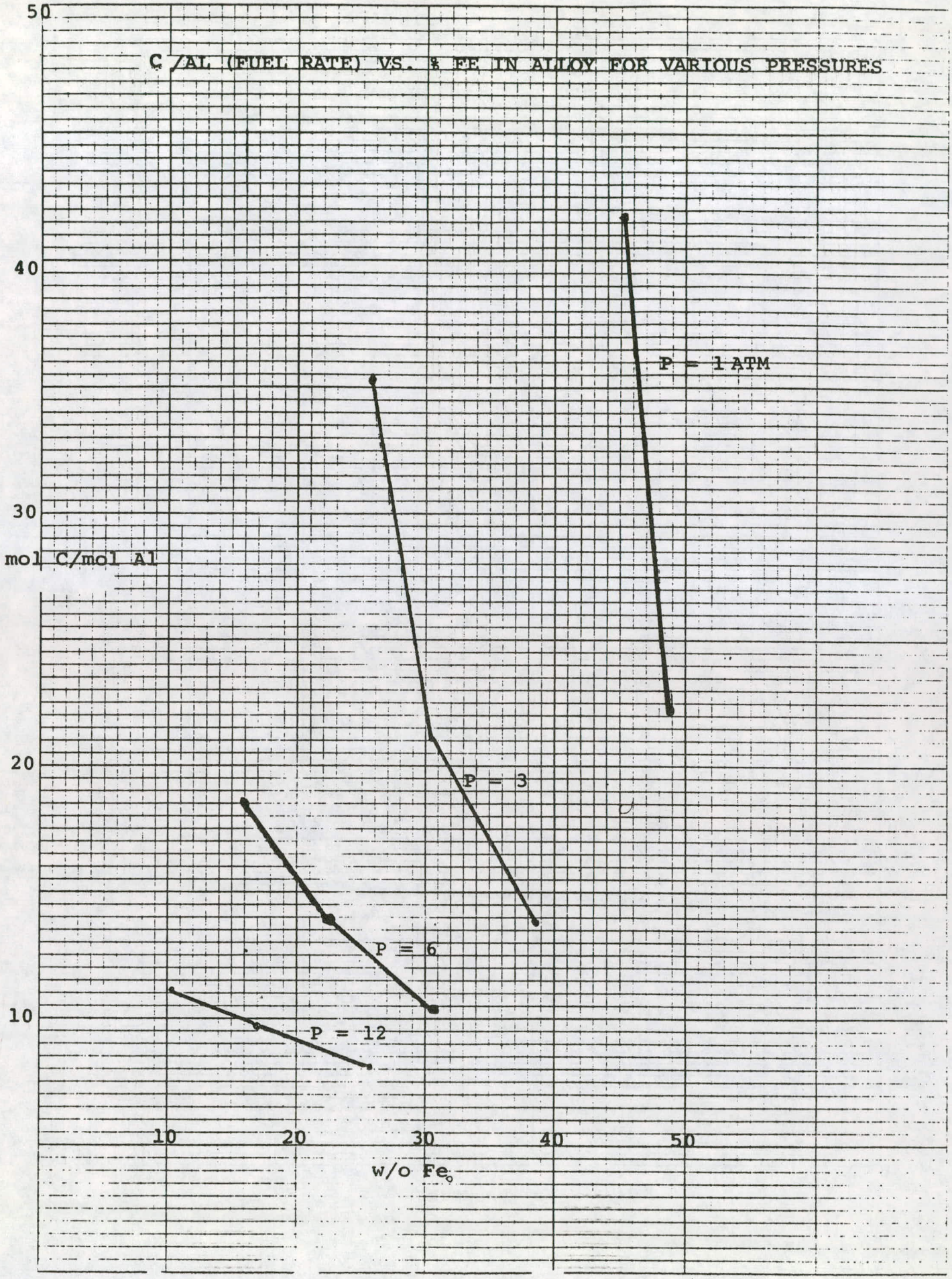
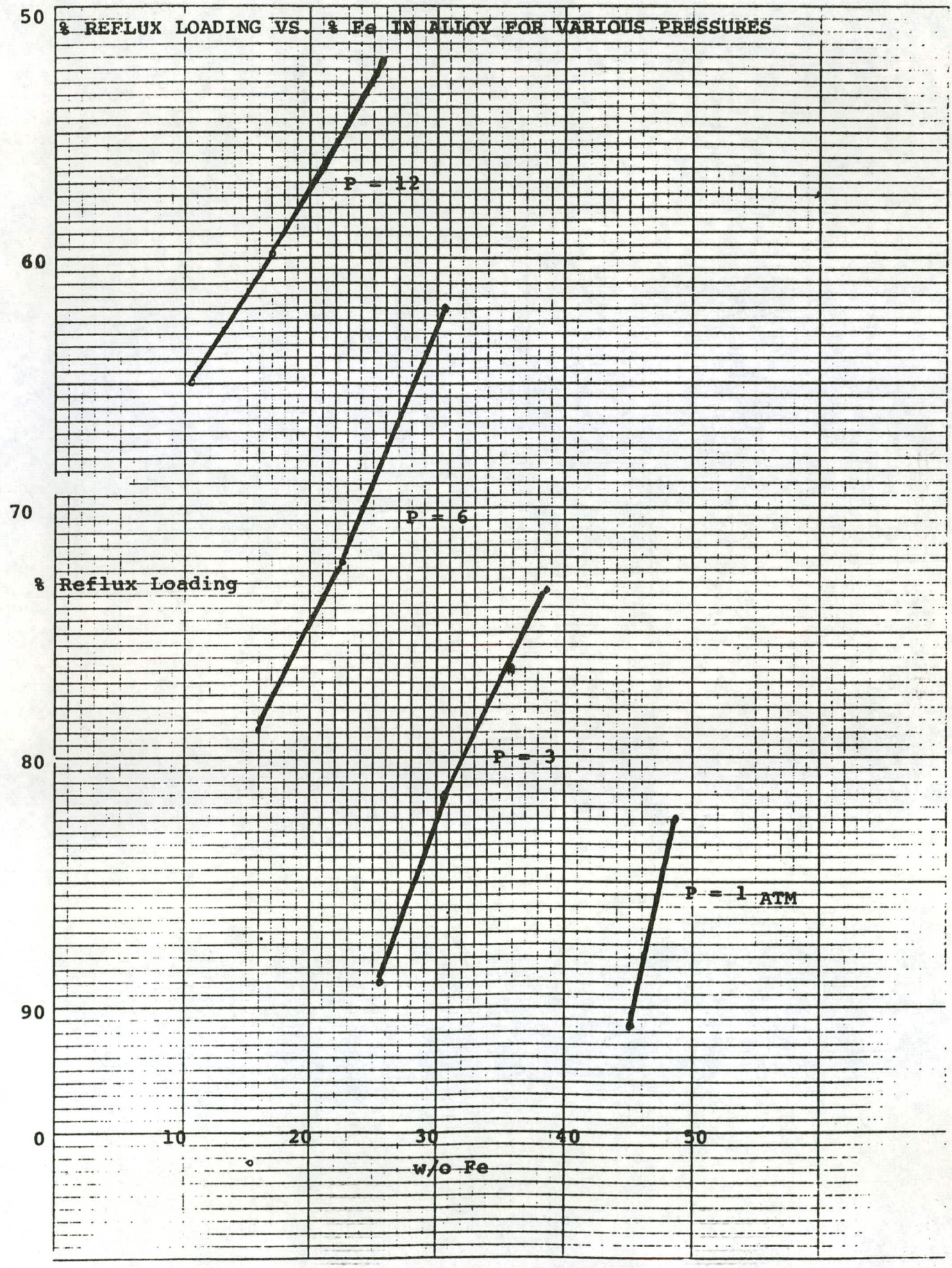

C /AL (FUEL RATE) VS. % FE IN ALLOY FOR VARIOUS PRESSURES
50
40
30
20
10
mol C/mol Al
P = 1 ATM
P = 3
P = 6
P = 12
10
20
30
40
50
w/o Fe

FIGURE 6


% REFLUX LOADING VS. % Fe IN ALLOY FOR VARIOUS PRESSURES
P = 12
P = 6
P = 3
P = 1 ATM
% Reflux Loading
50
60
70
80
90
0
10
20
30
40
50
w/o Fe

BLAST-ARC FURNACE
MATERIALS BALANCE FOR 300,000 TPY ALUMINUM PRODUCTION
CHAR FROM WESTERN KENTUCKY COAL 365 DAY/YR, 70% Al RECOVERY IN CRYSTALLIZER
(QUANTITIES IN TPY ON DRY BASIS)

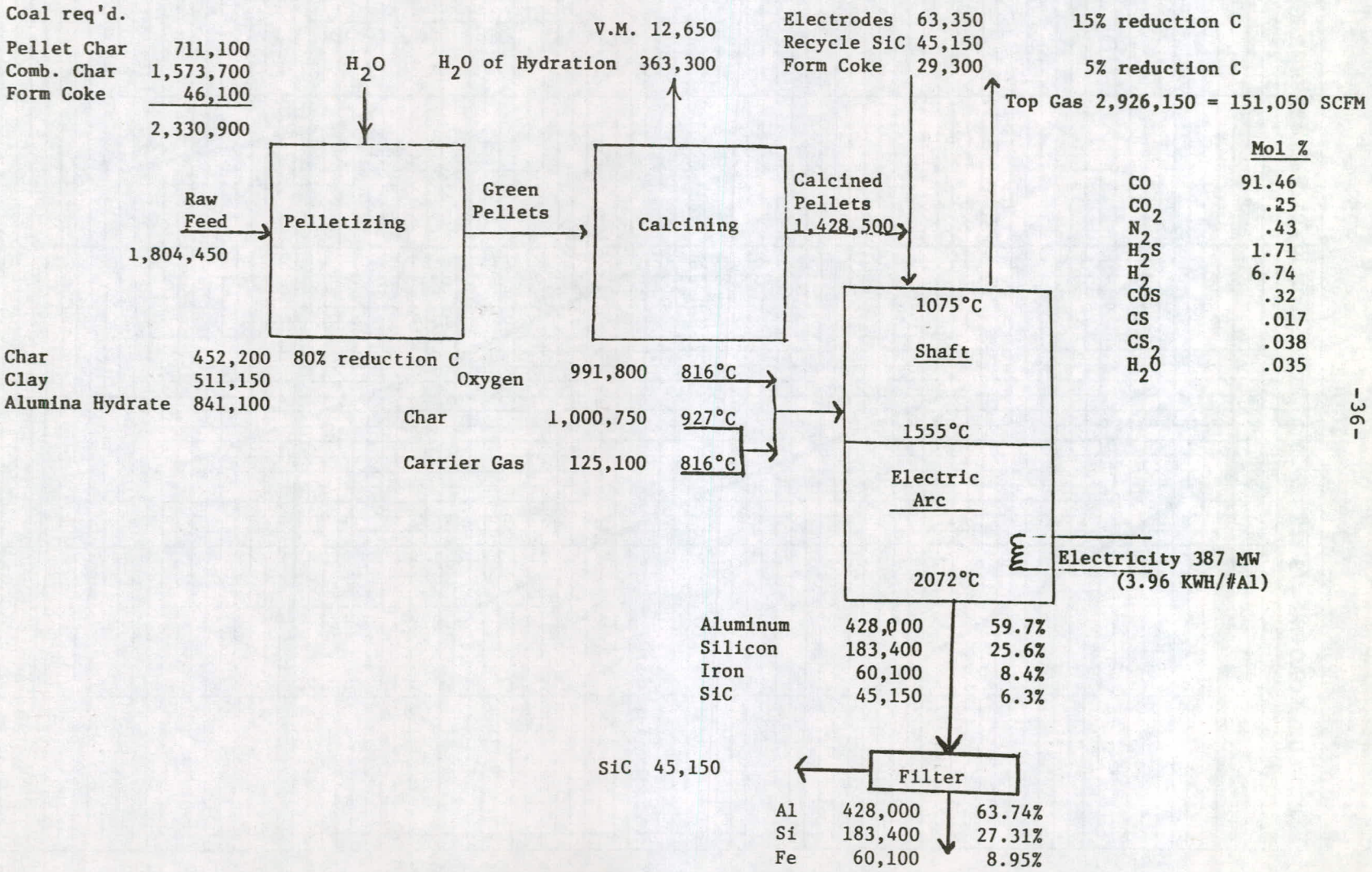


FIGURE 7

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

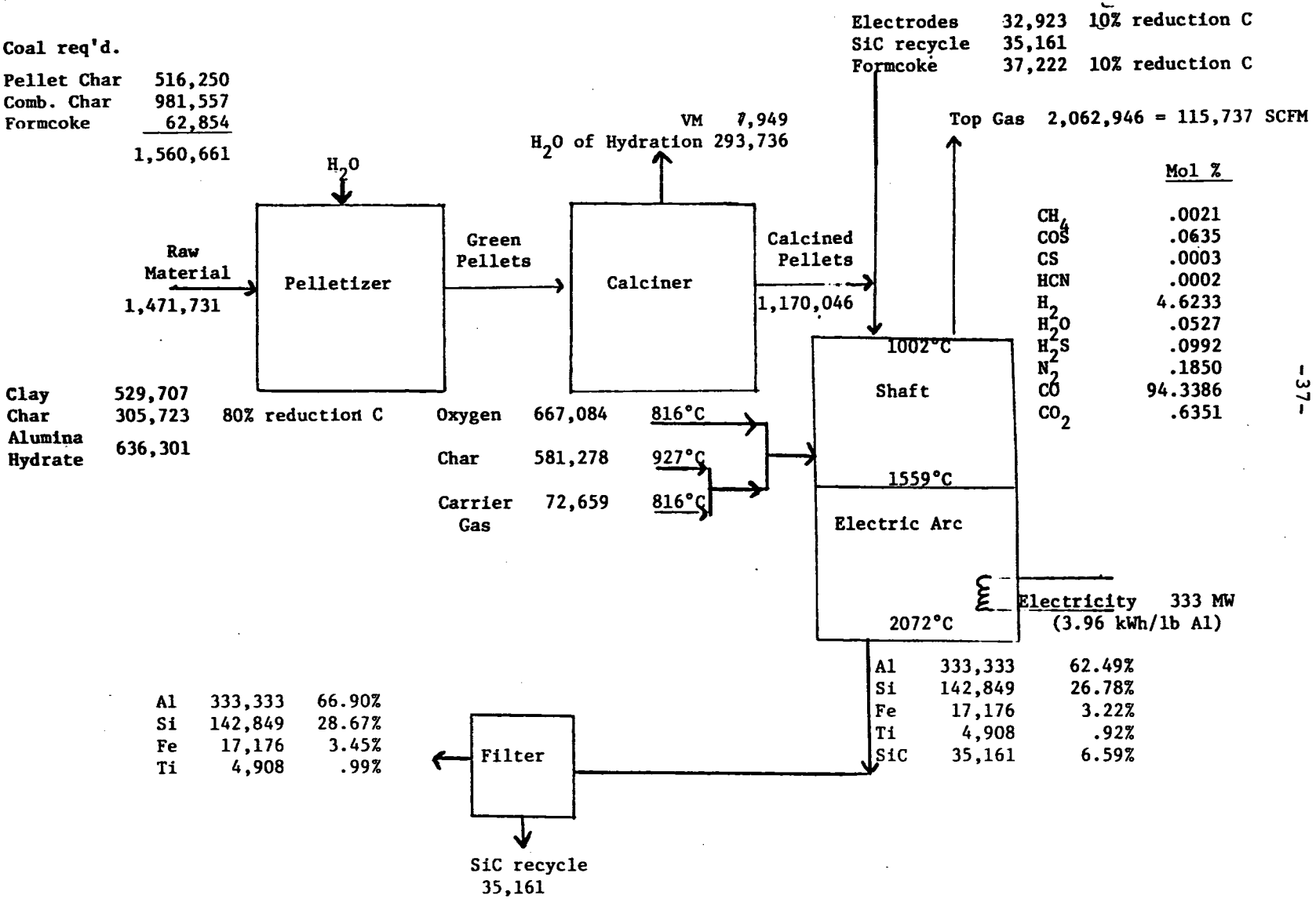


FIGURE 8

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

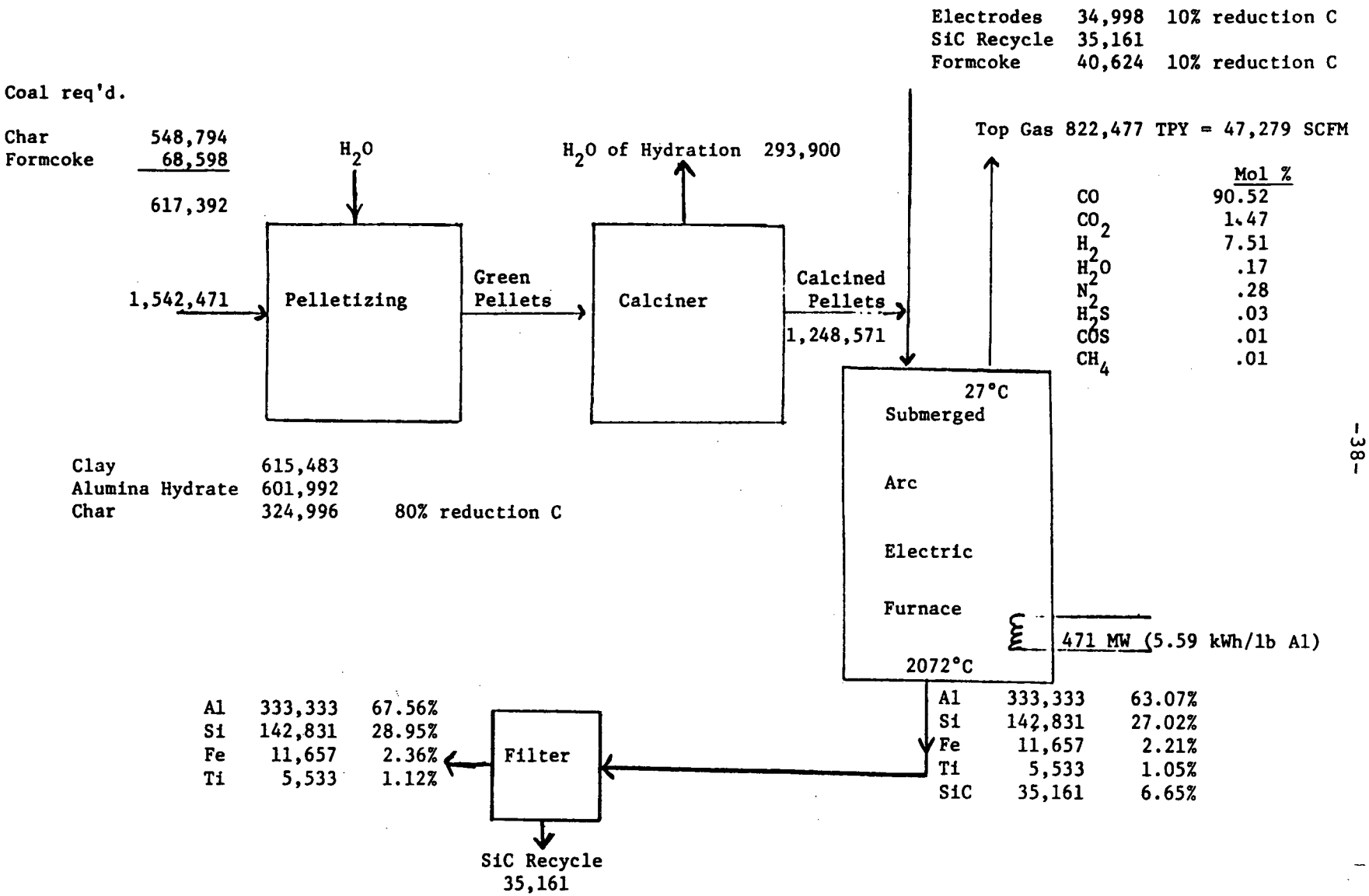


FIGURE 9

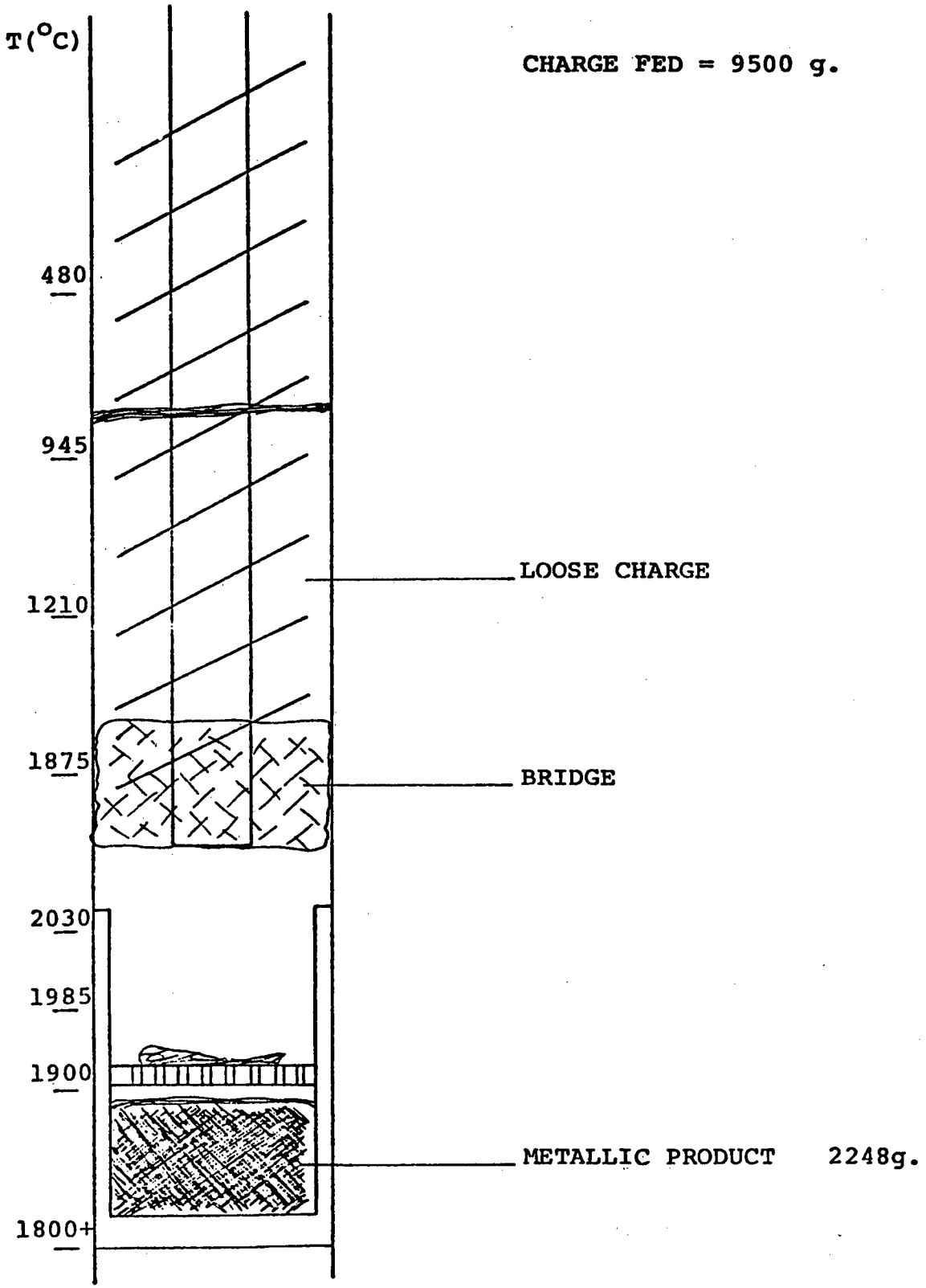

T(°C)
CHARGE FED = 9500 g.
480
945
1210
LOOSE CHARGE
1875
BRIDGE
2030
1985
1900
METALLIC PRODUCT 2248g.
1800+

FIGURE 10

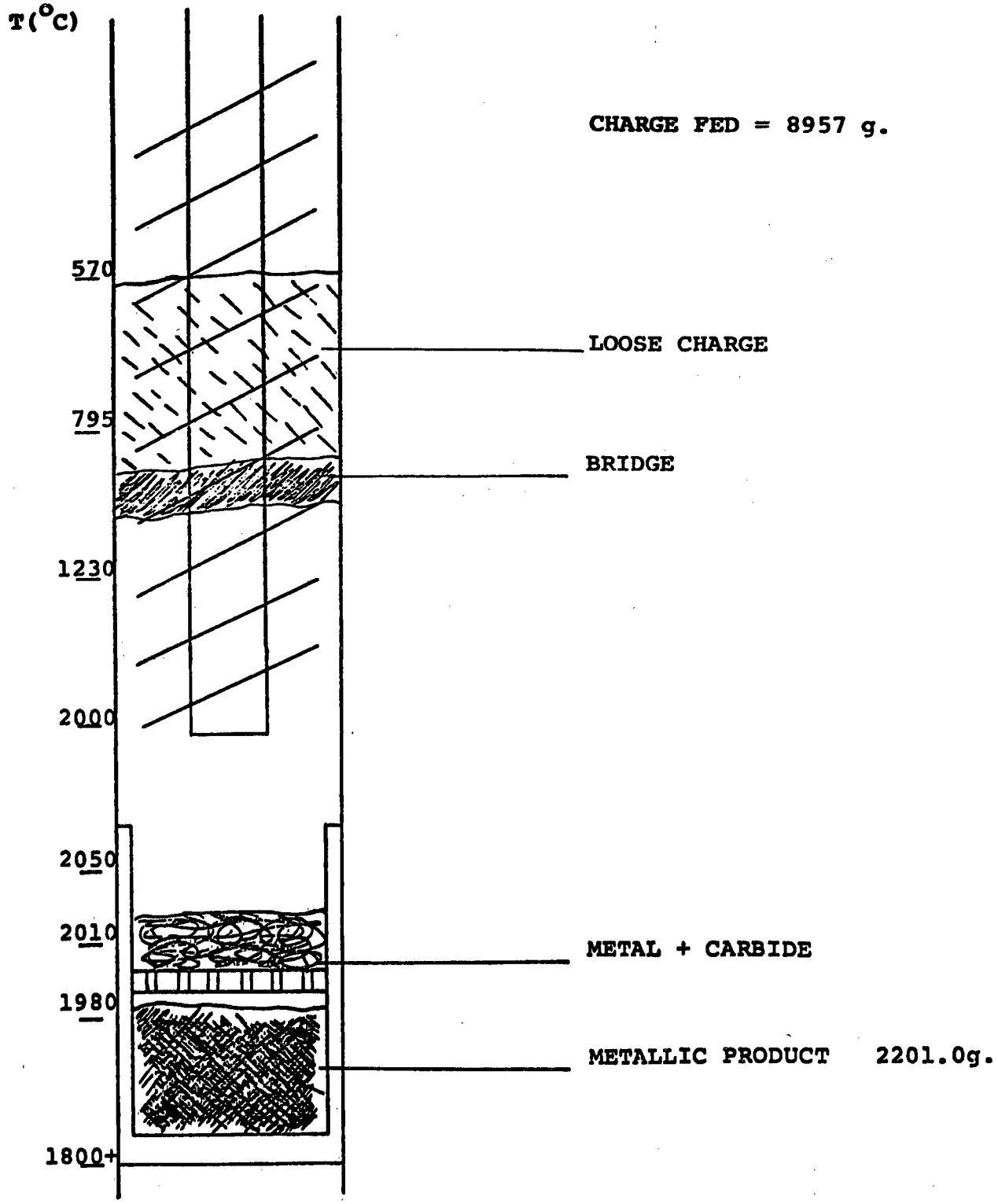

T(°C)
570
795
1230
2000
2050
2010
1980
1800+
CHARGE FED = 8957 g.
LOOSE CHARGE
BRIDGE
METAL + CARBIDE
METALLIC PRODUCT 2201.0g.

FIGURE 11

FIGURE 12

Behavior of Si and Al in Hybrid Process
For 70/30 Alloy

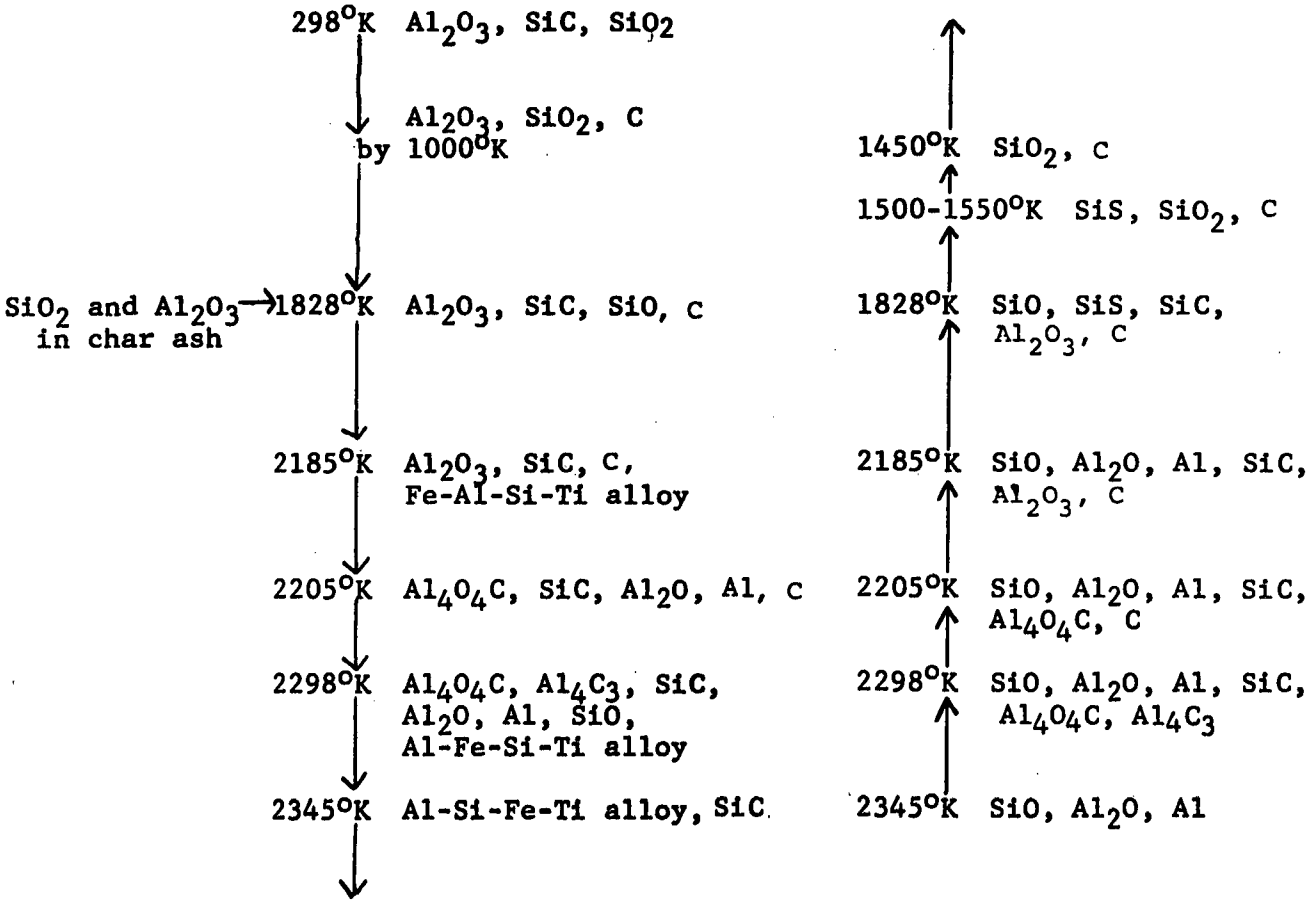


FIGURE 13

Behavior of Fe in Hybrid Process for 70/30 Alloy

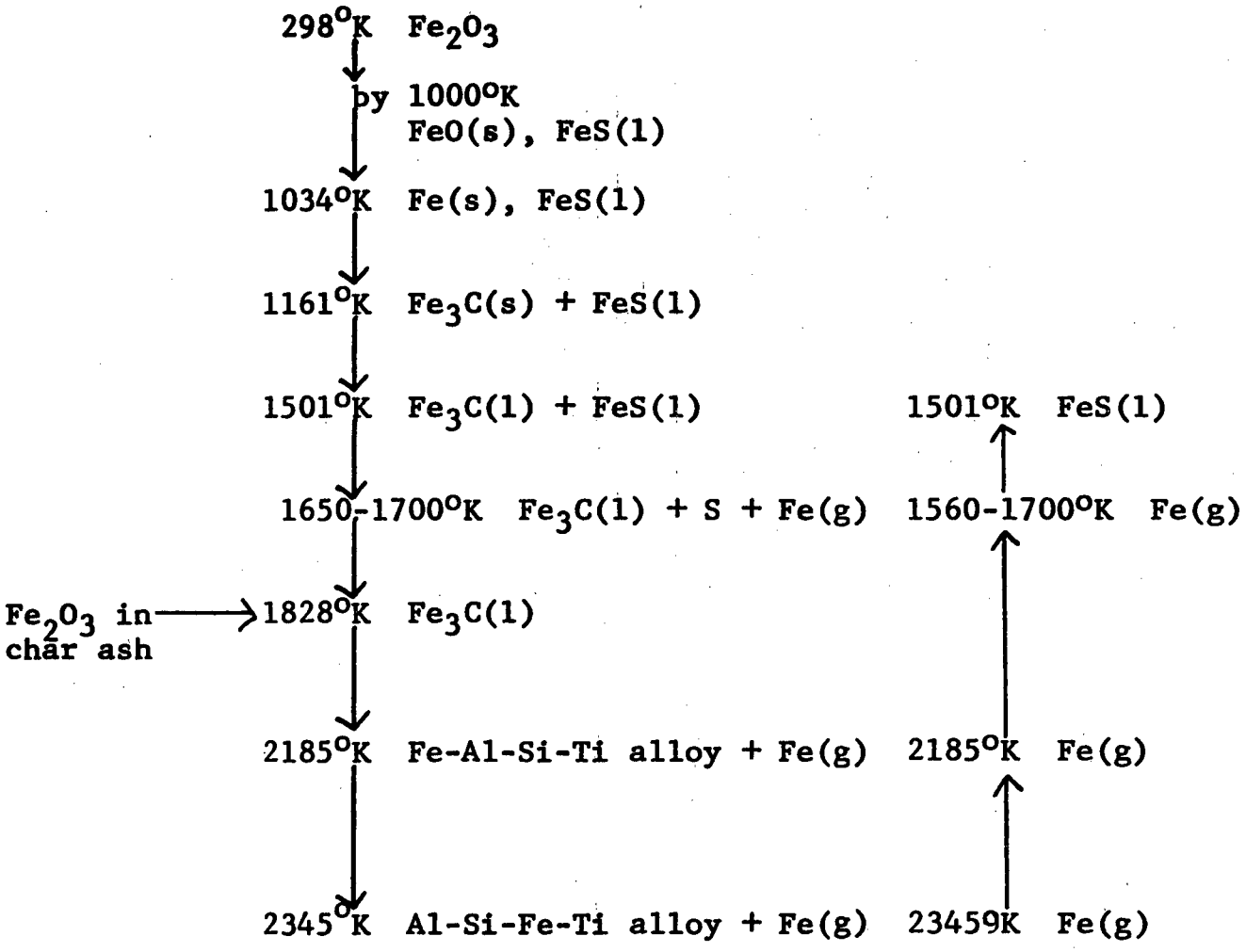


FIGURE 14

Behavior of Ti in Hybrid Process
for 70/30 Alloy

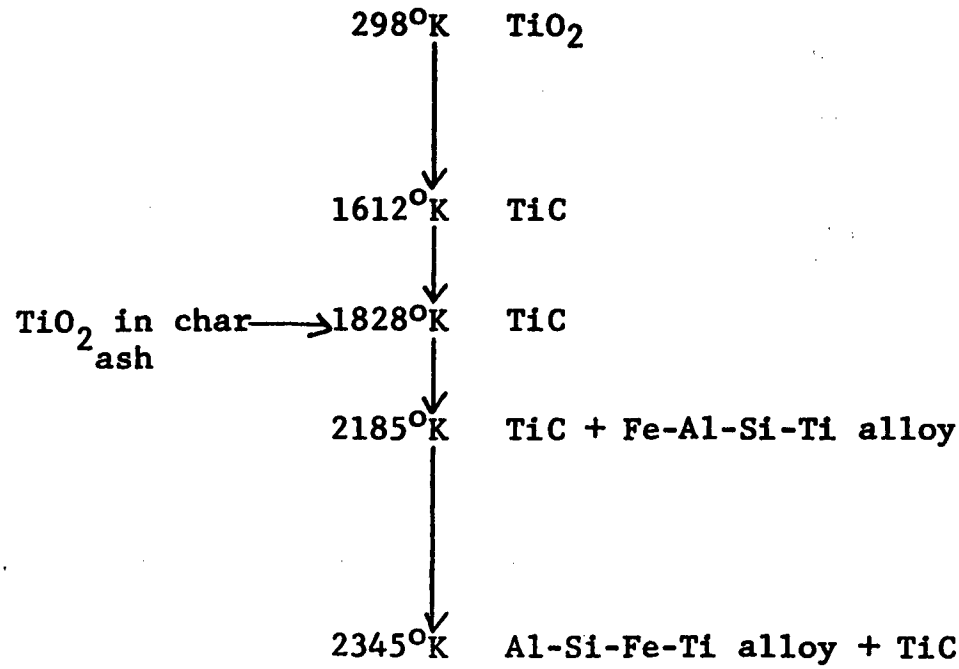


FIGURE 15

Behavior of S in Hybrid Process for 70/30 Alloy

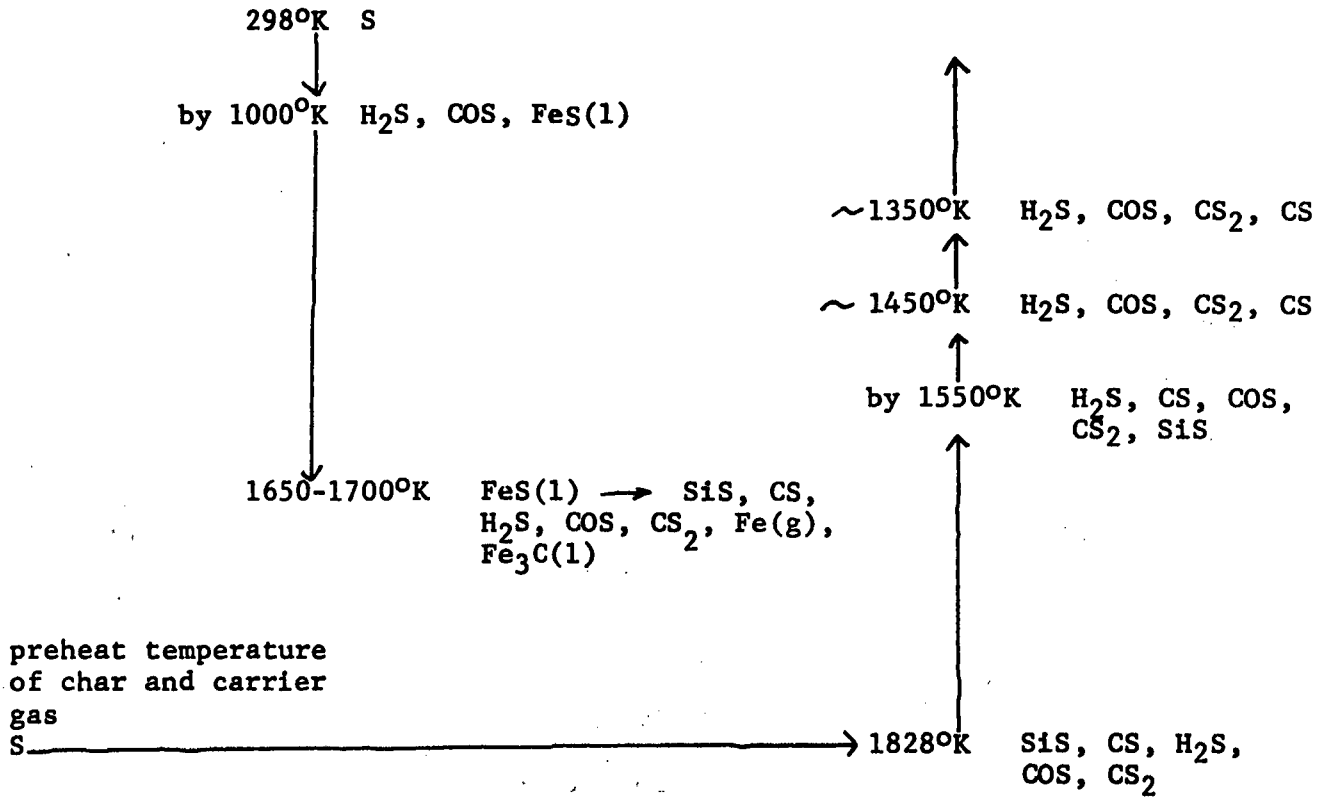


FIGURE 16

TEMPERATURE PROFILE FOR RUN 3-AP

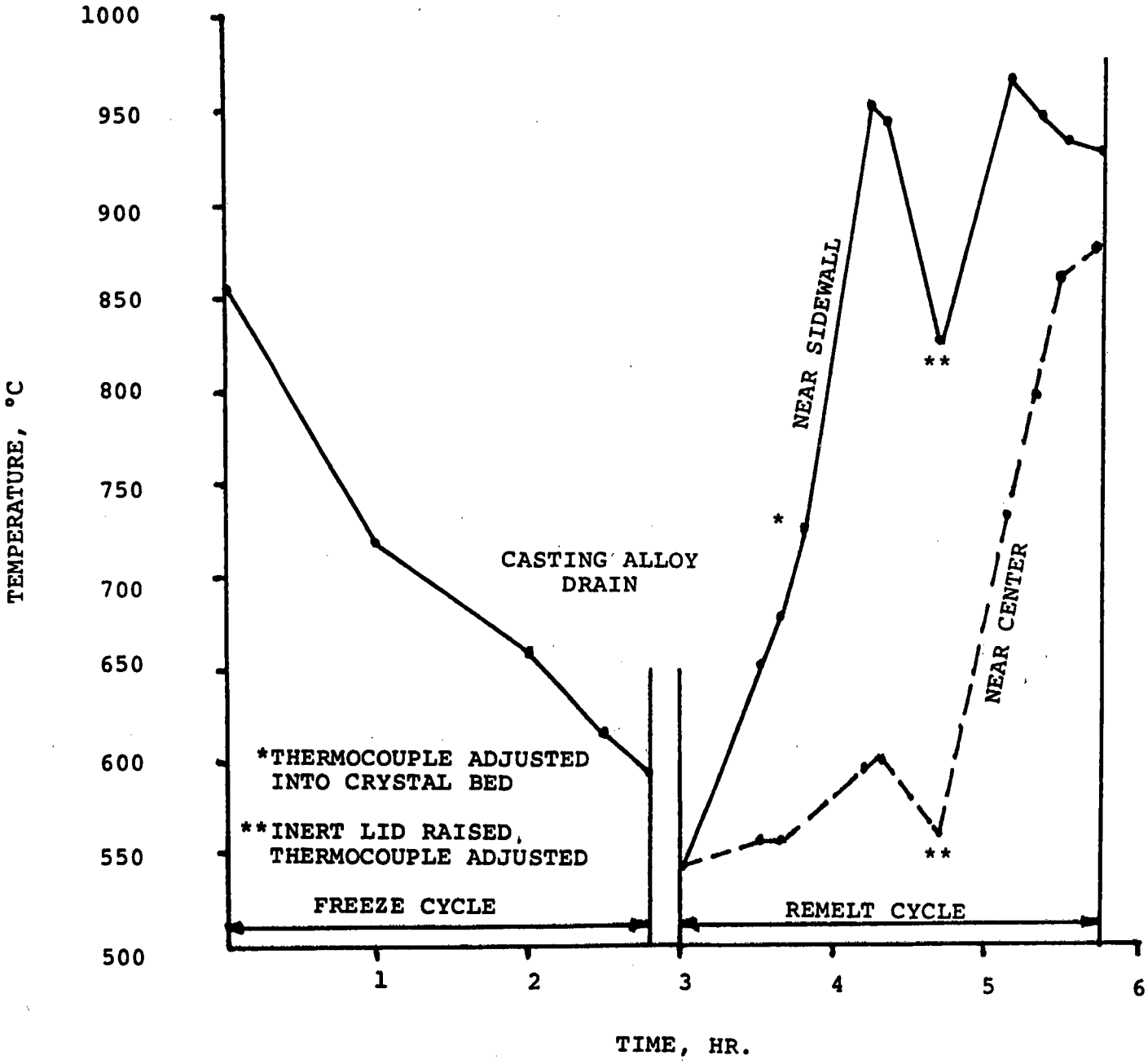
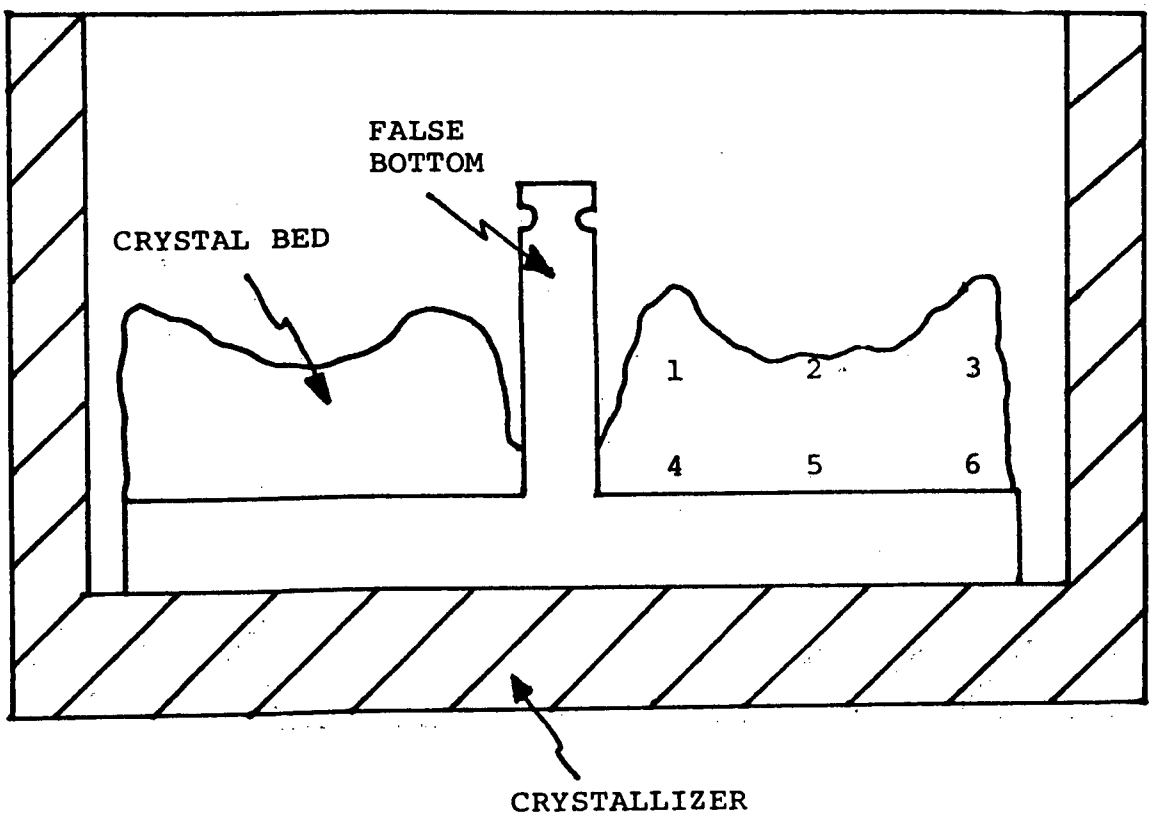


FIGURE 17

SAMPLING POSITIONS FOR CRYSTAL BED FROM RUN 3-AP



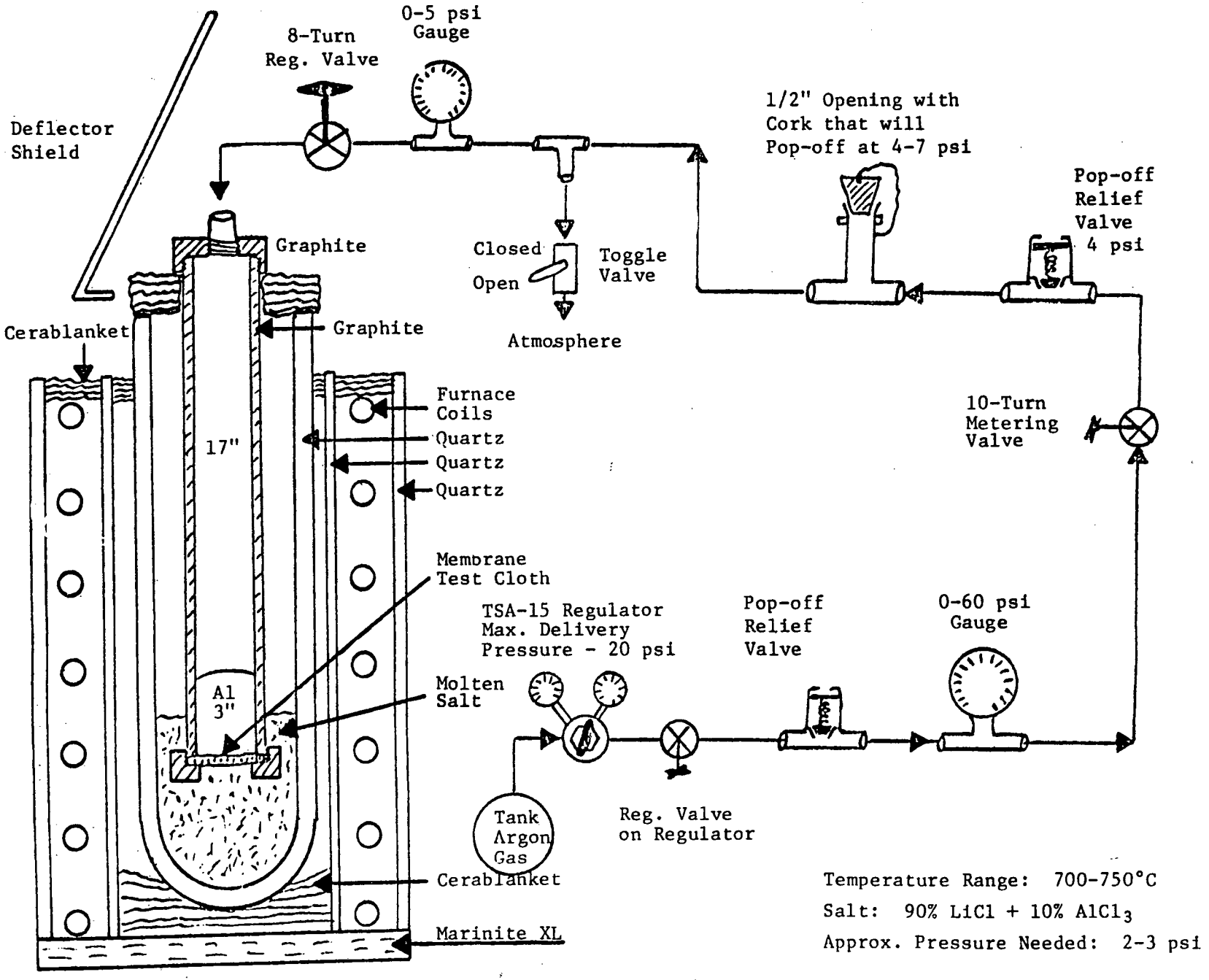

0-5 psi
Gauge
8-Turn
Reg. Valve
Deflector
Shield
1/2" Opening with
Cork that will
Pop-off at 4-7 psi
Pop-off
Relief
Valve
4 psi
Graphite
Closed
Open
Toggle
Valve
Atmosphere
Cerablanket
Graphite
Furnace
Coils
Quartz
Quartz
Quartz
17"
10-Turn
Metering
Valve
Membrane
Test Cloth
TSA-15 Regulator
Max. Delivery
Pressure - 20 psi
Pop-off
Relief
Valve
0-60 psi
Gauge
Molten
Salt
Al
3"
Tank
Argon
Gas
Reg. Valve
on Regulator
Cerablanket
Marinite XL
Temperature Range: 700-750°C
Salt: 90% LiCl + 10% $AlCl_3$
Approx. Pressure Needed: 2-3 psi

FIGURE 18

TABLE 1

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

EXPT. NO.	BOOK AND PAGE NO. METHOD	RAW MATERIALS USED			CARBON	QUANTITY	SIZE	YIELD	FIRED COMPRESSIVE STRENGTH
5A1186	SMALL DISK	6.621 H. CLAY (53%)	3.22 PROD. #10 M. COKE (26%)	2.68 CALC. Al_2O_3 (21%)		12.5#			278#/sq in 1/4" dia
5A1194	SMALL DISK	43.4 H. CLAY (43.4%)	21.7 PROD. #10 M. COKE (21.7%)	35.5 HYDRATED AL_2O_3 (35.5%)		100#	3/8" x 4M		143.4#/sq in 1/4" dia
5A1195	EIRICH BALLS	260.4 H. CLAY (43.4%)	130.2 PROD. #10 M. COKE (21.7%)	213.0 HYDRATED Al_2O_3 (35.5%)		603.6#	3/8" x 4M	62.8%	464.5#/sq in 1/4" dia

TABLE 2

COAL SOURCES USED IN THE HEAT AND MATERIAL BALANCES

Western Kentucky Coal		Wyoming Coal
Proximate Analysis Coal		**Proximate Analysis Coal**
Fixed C	47.85%	51.02%
Volatile Matter	39.35	42.84
Ash	12.80	6.14
S	3.36	.86
Ash Analysis		**Ash Analysis**
SiO_2	51.64%	67.06%
Al_2O_3	21.48	16.30
Fe_2O_3	25.83	16.16
TiO_2	1.05	.48
Char Analysis		**Char Analysis**
C	74.4%	86.15%
N	.8	.61
H	1.3	1.2
O	.7	.79
S	2.7	.88
Ash	20.1	10.37

TABLE 3

MATERIAL AND POWER CONSUMPTION COMPARISONS OF AN ARC AND HYBRID PROCESS BASED ON WYOMING COAL

	HYBRID	ARC FURNACE	ARC VS HYBRID PERCENT CHANGE
Power Consumption kWh/lb Al	3.96	5.59	29.2% increase
Coal Consumption lb coal/ lb Al	4.68	1.85	152.8% decrease
Reactor Solids Processed lb solids/lb Al	8.18	5.50	48.6% decrease
Top Gas Produced SCFM/lb Al	.35	.14	144.8% decrease
Char Consumption lb char/lb Al	2.66	.97	172.9% decrease
Coal Consumption for Power Generation lb coal/ lb Al	1.19 (.95)	4.43 (3.54)	73.1% increase
Total Solids Processed lb solids/lb Al	9.37 (9.13)	9.93 (9.04)	5.6% increase (1.0% decrease)
Total Coal Consumption lb coal/lb Al	5.87 (5.63)	6.28 (5.39)	6.5% increase (4.4% decrease)

TABLE 4

EFFECT OF SiO_2/Al_2O_3 CARBON STOICHIOMETRY AND CO SWEEP ON METAL PRODUCTION

Run	Ore SiO_2/Al_2O_3 Wt. Basis	Consumed Charge CO	% Total C	Wt. Metal / Consumed Charge	Reaction Zone Wt.	Metal Producing Temperature
AF7	0.6	---	100 %	0.210	---	2050
AF12	0.784	1.815	80.55	0.164	1280 gm	2050
AF13	0.502	2.199	80.0	0.161	1341	2055
AF14	0.993	2.035	80.0	0.177	759	2060
AF15	0.788	1.950	80.0	0.191	718	2065
AF16	0.784	1.042	80.55	---	558	2030
AF17	0.784	0.579	80.55	---	362	2140
AF18	0.993	1.393	80.0	0.195	927	2060
AF20	1.224	0.730	80.0	0.209	122	2100
AF21	1.224	0.491	80.0	---	200	2060
AF22	1.224	1.173	85.0	---	150	2090
AF23	1.224	---	85.0	0.239	334	2075
AF24	0.469	---	80.0	0.325	---	2060
AF25	0.68	---	85.0	0.282	475	2020
AF26	0.785	---	84.5	0.274	927	2020
AF27	0.502	---	84.7	0.334	661	2035
AF28	0.785	---	91.3	0.294	127	2140
AF29	0.786	---	90.0	0.269	---	2030
AF30	0.642	---	85.0	0.289	---	2050

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

TABLE 5

CARBON STOICHIOMETRY OF ORE BURDEN

Run	Ore SiO_2/Al_2O_3 Wt. Basis	% C Ore	% C for SiC	% Total C	Carbon Source
AF7	0.6	71.0	58	100	met and pet coke
AF12	0.784	80.55	67	80.55	met coke
AF13	0.502	64.24	51	80.0	char and pet coke
AF14	0.993	63.75	76	80.0	char and pet coke
AF15	0.788	56.74	67	80.0	char and pet coke
AF16	0.784	80.55	67	80.55	met coke
AF17	0.784	80.55	67	80.55	met coke
AF18	0.993	63.75	76	80.0	char and pet coke
AF20	1.224	72.62	84	80.0	met and pet coke
AF21	1.224	72.62	84	80.0	met and pet coke
AF22	1.224	72.62	84	85.0	met and pet coke
AF23	1.224	72.62	84	85.0	met and pet coke
AF24	0.469	---	49	80.0	pet coke
AF25	0.68	77.67	63	85.0	met and pet coke
AF26	0.785	74.94	67	84.5	char, met, and pet coke
AF27	0.502	64.24	51	84.7	char and pet coke
AF28	0.785	91.30	67	91.3	char and met coke
AF29	0.786	80.53	67	90.0	char, met, and pet coke
AF30	0.642	79.33	61	85.0	met coke

TABLE 6

PROCESS VARIABLES FOR PILOT RUNS

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

TABLE 7

MATERIAL BALANCES

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

*Al basis

TABLE 8
EXPERIMENTAL RESULTS
RUN 1-AP

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

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

*AL 8.4%. VALUES ADJUSTED TO PERMIT CLOSURE.

+INTERPOLATED VALUES.

TABLE 9
EXPERIMENTAL RESULTS
RUN 2-AP

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

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

*ASSUMED VALUE

**35.5% AL

+INTERPOLATED VALUES

TABLE 10
EXPERIMENTAL RESULTS
RUN 3-AP

	WEIGHT, LB.	CONTENT, % Si	Fe	Ti
STARTING ALLOY	1894	28.3	3.15	0.87
LIQUID DRAINED IN INTERVAL:				
SAMPLES 1 - 2	98	16.6	1.57	0.11
3 - 5	342	15.3	1.34	0.10
6 - 10	407	21.8	2.17	0.25
11 - 15	440	28.2	5.14	1.32
16 - 17	244	37.8	5.88	2.07
17 - 18	98	43.0	4.97	1.93
CRYSTAL BED	250	60.1	2.64	3.77*

CUMULATIVE LIQUID DRAINED	AVERAGE CONTENT, % Si	Fe	Ti	CUMULATIVE YIELD, %	AVAIL AL. RECOVERED,
SAMPLES 1 - 2	15.3	1.34	0.11	5	6
3 - 5	16.1	1.48	0.10	23	28
6 - 10	17.3	1.61	0.14	45	54
	(18.8)+	(2.00)	(0.25)	(58)	(68)
11 - 15	19.9	2.29	0.34	68	78
16 - 17	22.0	2.80	0.57	81	89
17 - 18	23.1	2.96	0.66	86	93

*33.5% AL, AVERAGE VALUES, NORMALIZED

+INTERPOLATED VALUES

TABLE 11

LEACHING MEDIA AND RESULTS

		CRYSTAL BED							
		BEFORE LEACH, %				AFTER LEACH, %			
SAMPLE	LEACH MEDIA	Si	Fe	Ti	Al	Si	Fe	Ti	Al
Run 1-AP	HCl (7N)	82.5	0.9	0.6	7.7	88.2	0.0	2.4	1.3
	NaCitrate/HNO_3	70.0	1.1	1.5	19.5	67.5	1.2	1.5	22.3
Run 2-AP	HCl	56.1	2.7	2.2	35.5	78.1	0.4	3.6	1.9
	NaCitrate/HNO_3	56.1	2.7	2.2	35.5	63.0	1.6	2.7	25.2
Run 3-AP	HCl	67.8	3.2	1.6	26.5	83.2	1.9	2.0	4.9
	NaCitrate/HNO_3	66.6	3.8	1.6	28.8	58.2	3.3	1.6	35.2

TABLE [59] 12

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

EXPERIMENT 10

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

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

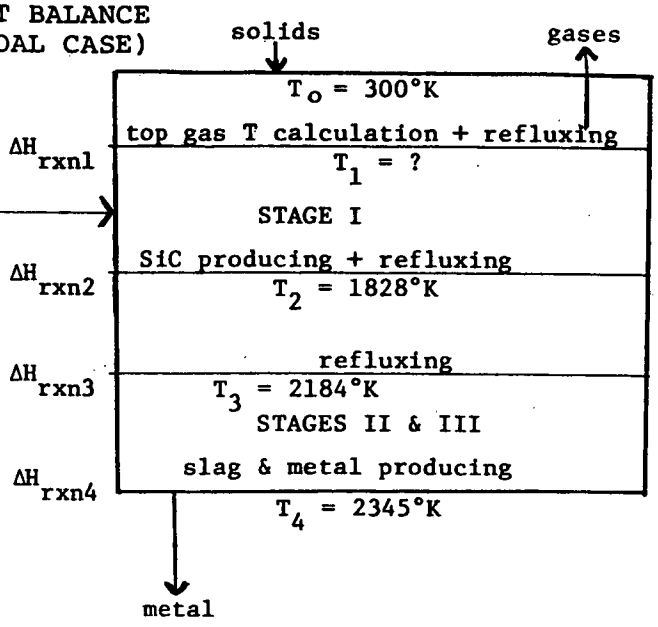
TABLE 13 RESULTS - PENETRATION TESTS

Run No.	Metal	Electrolyte	Penetration Pressure (psi)	Equivalent Metal Head cm
79-12-12	Al	$LiCl-AlCl_3$	2	217
80-01-22	Al	$LiCl-AlCl_3$	2.3	203
80-08-05	Al	$LiCl-NaCl-AlCl_3$ (filtered)	0.6	81
80-08-12	Al	$LiCl-NaCl-AlCl_3$	1.0	115
80-08-14	Al	$LiCl-NaCl-AlCl_3$	0.8 -2.05	98-204
80-08-15	Al	Air	1.75-2.0	66.4-202 (air)
80-08-21	Al-Si	$LiCl-NaCl-AlCl_3$ (LiCl and NaCl filtered)	1.9 -2.3	172-202
80-08-28	Al-Si	Air	1.35-1.7	52- 60 (air)
80-08-29	Al-Si	$LiCl-NaCl-AlCl_3$ (filtered)	1.05-1.5	108-138
80-09-09	Al-Si	$LiCl-NaCl-AlCl_3$ (filtered, with and without electrolysis)	0.45	63
	Al-Si	same electrolyte, new membrane	0.45	63
	Al-Si	same electrolyte, $CaCl_2$ added, with and without electrolysis	0.8	89

APPENDICES

APPENDIX I

HYBRID PROCESS HEAT BALANCE
(WESTERN KENTUCKY COAL CASE)



$\Delta H_{rxn3} + \Delta H_{g4} + \Delta H_{g3} - \Delta H_{s4} - \Delta H_{s3}$

$- \Delta H_{rxn4} = .9$ KWH

$\Delta H_{loss4} + \Delta H_{loss\ 3} = .1$ KWH

Electric Power = KWH = 3.96 KWH/#Al

ie. $\Delta H_{g4} = \Delta H_{gas\ 2345°K} - \Delta H_{gas\ 2184°K}$

ie. $\Delta H_{s4} = \Delta H_{solids\ 2345°K} - \Delta H_{solids\ 2184°K}$

$\Delta H_{rxn2} = \Delta H_{rxn_{SiO_2 \rightarrow SiC}} - \Delta H_{rxn\ reflux}$

$\Delta H_{combustion} = \Delta H_{rxn2} + \Delta H_{preheat} + \Delta H_{loss}$ combustion char calculation

$$\Delta H_{preheat} = \int_{T_{incoming}}^{T = 1828°K} (\Delta C_{p_{char}} + \Delta C_{p_{O_2}} + \Delta C_{p_{carrier\ gas}})\, dT$$

$\Delta H_{loss} = .075\ \Delta H_{rxn_2}$

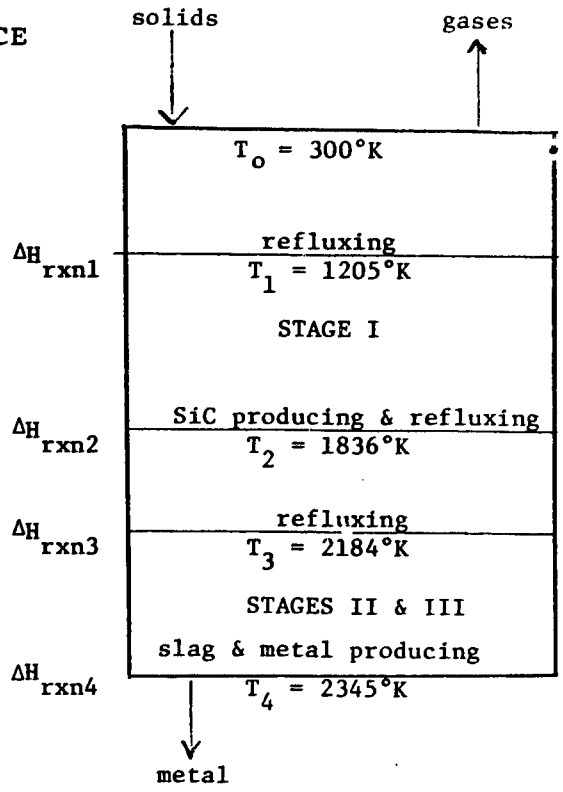
$\Delta H_{rxn1} + \Delta H_{g2} - \Delta H_{s2} - \Delta H_{s1} = 0$ top gas temperature calculation

$\Delta H_{g2} = \Delta H_{gas\ 1828°K} - \Delta H_{gas\ top\ T}$

$\Delta H_{s2} + \Delta H_{s1} = \Delta H_{solids\ 1828°K} - \Delta H_{solids\ 300°K}$

APPENDIX II

ARC FURNACE HEAT BALANCE
(WYOMING COAL CASE)



$\Delta H_{rxn3} + \Delta H_{rxn1} + \Delta H_{g4} + \Delta H_{g3} + \Delta H_{g2} + \Delta H_{g1}$

$- (\Delta H_{rxn4} + \Delta H_{rxn2} + \Delta H_{s4} + \Delta H_{s3} + \Delta H_{s2}$

$\Delta H_{s1}) = .9KWH$

$\Sigma\Delta H_{loss} = .1$ KWH

Electric Power = KWH = 5.59 KWH/#Al

ΔH_{rxn1} determined at 1205°K

$\Delta H_{g1} = \Delta H_{g1205} - \Delta H_{g\ 300°K}$

top gas composition determined at 1205°K

APPENDIX III - SPECIAL TECHNICAL REPORT
TECHNICAL FEASIBILITY OF COMBUSTION-HEATED PROCESS
FOR PRODUCING ALUMINUM-SILICON ALLOYS

Abstract

As part of a contract to develop a process for the carbothermic reduction of aluminum-silicon alloys, the technical feasibility of an atmospheric combustion-heated reactor was investigated. Potentially, such a reactor could have lower energy and capital requirements than current processes for producing aluminum and silicon.

Reduction reactions were modelled using two chemical equilibrium computer programs which predicted the aluminum recovery in the reduction zone and the carbon rate needed to meet the energy requirements of the process. Calculations made prior to the initiation of the contract had indicated that the process might be feasible. Recent revisions in the data for Al_4O_4C, Al_2O and activities of aluminum and silicon, made under the contract, indicated that the process would not be feasible at one atmosphere pressure. The equilibrium was found to be very sensitive to the vapor pressures of Al, Al_2O, and SiO due to the large amounts of CO generated by combustion heating.

Experiments in the bench reactor generally verified the results of the equilibrium model since relatively low CO sweep rates caused bridging which could not be overcome. Based upon the model, it is estimated that the equivalent of about 25% of the high temperature heat was supplied by CO.

Pilot reactor experiments indicated that combustion rates required by physical considerations were so high that zero yield was predicted. In addition, alloy was found to react readily with excess carbon supplied for combustion.

The equilibrium model predicted that certain combinations of elevated pressure and temperature, oxygen preheat, and dilution of the alloy with other elements might allow the process to work. The model does not consider physical problems associated with high temperature and pressure reactors or difficulties in controlling the oxygen/carbon ratio and overcoming bridging.

Arc and hybrid blast-arc processes are under consideration as alternatives to the combustion heated process.

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