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Production of Aluminum-Silicon Alloy and Ferrosilicon and Commercial Purity Aluminum by the Direct Reduction Process

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CONS-5089-15
UC-95f

Unclassified

M.J. Bruno
Aluminum Company of America
Alcoa Laboratories
Alcoa Center, PA 15069

ALCOA

Work Performed Under
Contract DEAC01-77CS40079

First Interim Technical Report, Phase D
For the Period 1981 January 01 -
1981 March 31

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MARSHALL J. BRUNO

1981 APRIL

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
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FORWARD

This is the First Interim Technical Report, Phase "D", 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 1981 January 01 through 1981 March 31.

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ABSTRACT

Phase C of the basic three-year cost-sharing contract between the Department of Energy and Alcoa was completed on 1980-12-31. A Work Statement for additional tasks was submitted to DOE on 1980-11-21 to describe work proposed for Phase D, to go from 1981-01-01 to 1981-09-30. To provide adequate time for approval of the contract modification relating to Phase D, the basic contract was extended through 1981-02-25 at no additional cost. Therefore, the first two months of 1981 were administratively considered to be part of Phase C, with Phase D starting on 1981-02-26. For the purpose of technical reporting, the period 1981-01-01 through 1981-03-31 has been considered as the first quarter of Phase D since the work performed related to the Phase D Work Statement. At the end of the first quarter, the program for Phase D is estimated as 45% complete, with 87% of the total contract funding expended and 93% of the total contract completed.

Operation of the bench AF-reactor on burden with all reducing carbon exterior to the ore pellet resulted in low metal alloy product yields and prematurely terminated runs. These results were due respectively to a gas-solids reaction mechanism rather than liquid-solid, and to bridging in the cold zones from high volatile levels. The same results were obtained in reducing "lump" burden containing alumina balls, SiC chunks, and lump coke. Both types of runs demonstrated the need for intimate contact between alumina and carbon to produce oxycarbide liquid prior to reaction with solid silicon carbide. Carbon solubility tests made on 60Al-40Si alloys at 2200°C in graphite crucibles indicated continued reaction to form SiC over a period of one hour. Heat and material balances were calculated for closed and semi-closed submerged arc furnaces on a commercial scale (300,000 TPY eutectic Al-Si alloy from refining). The studies predicted dust losses to be handled and off-gas sensible heat to be recovered for both 70Al-30Si and 60Al-40Si alloy products, for each furnace type. The subroutine for arc furnace simulation in the computer models was completed. The VSR pilot unit was modified for solids discharge and operated as the Blast phase of the Blast-Arc to prereduce SiO_2 to SiC. Uncalcined burden charged to the VSR was dried, calcined, and prereduced as the material moved downward in the shaft. Efficiency of reduction to SiC ranged from about 68% to nearly 100% based on preliminary evaluations utilizing weight loss measurements. Conversions must be verified by chemical analyses. The A-C two-electrode submerged arc reactor pilot, SAR-II, was successfully operated on both alumina-clay-coke and alumina-silicon carbide-coke (from the VSR prereduction) burdens. Metal alloy was produced

and tapped in each of four runs. Operating with a low bed corresponded to low voltage, high current, and resulted in high unit heat and dust losses plus carbided alloy. Too high a bed produced high voltage, low current, and insufficient heat for complete reduction. Optimum conditions appeared to be 30-35 volts per electrode at 1600 amperes and a burden feed rate of 15-20 kg/hr. Optical phase analyses of AF-reactor products were typically Al-Si, $FeSi_2Al_4$, SiC, and Al_4SiC_4. The Al_4SiC_4 was predominant at the top portion of the ingots, and appeared to be formed by peritectic reaction of SiC with Al-Si alloy. SAR-II product alloy contained Al-Si, $FeSiAl_4$, $TiSi_2$, and either SiC or Al_4SiC_4.

The pilot crystallizer was operated to evaluate the two-stage ("stop and go") crystallization technique on obtaining high yields of Al in Al-Si eutectic, with a limit of 1.0%Fe and 0.1%Ti in the alloy product. The procedure involved cooling to 700°C in the first stage, followed by separation of liquid from crystals. This liquid was then further cooled to near eutectic temperature (576°C) and again separated from the crystal bed formed. The cooling cycles were controlled at a slow rate to effect more uniform temperatures across the melt. In a run starting with Al-31.2%Si-3.16%Fe-0.84%Ti an Al yield of 74% was attained in a product containing Al-13.6%Si-1.0%Fe-0.08%Ti. A second run conducted on starting alloy with no Ti and 4.12%Fe resulted in an Al yield of only 52% for a product alloy containing 1.0%Fe. The higher initial Fe content tied up more Al as Fe-Si-Al complexes in the crystal bed.

Primary activities in the second quarter of Phase D will include: evaluation of burden formulations using activated alumina as the binder in place of clay; measurement of the degree of SiC back reaction to SiO_2 during heating to 1600°C; determination of kinetics for conversion of alumina-clay-coke to SiC in a shaft reactor; conversion of the FLOWREAC computer program to RCYCREAC, which handles recycle; operation of the pilot VSR to prereduce SiO_2 in clay to SiC using CO sweep to simulate heat supply by coke combustion, and using O_2 to burn excess coke in the burden; operation of the pilot SAR to evaluate burdens containing activated alumina and SiC or SiO_2; completion of the submerged arc furnace conceptual, commercial flow sheets; development of an alumina hydrate-clay-green Wyoming coal pellet.

DISCUSSION

The primary objective of the contract is to determine technical feasibility of a Direct Reduction Process for producing aluminum and aluminum-silicon alloy. Goals for the fourth phase are to complete the evaluation of alternative reduction processes utilizing electric heat in the metal-producing zone and to develop an effective operating procedure for alloy refining in the pilot fractional crystallizer.

In the first quarter of Phase D, Koppers Company continued its engineering studies of the Arc and Blast-Arc process concepts. The Arc process is being evaluated for two cases, a closed furnace with off-gas recovery and a semi-closed furnace with recovery of off-gas heat values in a waste heat boiler. Preliminary block flow diagrams were prepared on several cases. Schematic studies of the Blast-Arc process revealed further technical problems which need to be resolved prior to completing an engineering study.

Carnegie-Mellon University's fundamental phase equilibria program examined the effect of silicon carbide on the temperature of formation of liquid oxycarbide from alumina. It was found that no reduction occurred below 1945°C and that in the absence of carbon there was no reduction of alumina by silicon carbide. It is also inferred that silicon carbide has little solubility in liquid oxycarbide at 1950°C. Small amounts of aluminum oxynitride were detected in the product samples, indicating the presence of nitrogen, either as an impurity in the carbon monoxide cover gas or as nitrogen absorbed on charge materials.

Professor Julian Szekely consulted a total of 6.75 days on heat transfer in arc systems. Dr. J.C. Agarwal consulted a total of 2 days on process flow sheets.

Technical progress was reviewed with the DOE project manager and Professor J.F. Elliott twice during the first quarter.

Progress for the two main tasks is reported by sub-task as identified in the Work Statement for Phase D submitted to DOE on 1980 November 21. It is estimated that for Phase D the Reduction task is 46% complete, and the Alloy Purification task is 38% complete at the end of the first quarter.

PROGRESS

A. Reduction - Phase D

Task No. 1: Effects of Process Variables

All bench scale reactor tests are included under this task, including optimization of formulations, evaluation of special burdens, solubility of carbon in Al-Si alloys, and kinetics of SiO_2 prereduction to SiC.

During the first quarter of 1981, the bench scale program continued to focus on determining if metal can be produced with all of the carbon exterior to the ore pellet at varying SiO_2/Al_2O_3 ratios. Previous tests at the high silicon end of the range of interest (Al/Si = 60/40) showed heavy volatilization of the ore in the metal-producing zone in the form of aluminum and silicon suboxide and metal vapors leaving an excess of carbon to form carbides with any metal that was produced. Metal production under these same conditions at the high aluminum end of the range (Al/Si = 70/30) was determined in the most recent runs. The details of these runs are shown in Table 1.

In a previous run, AF24, a large amount of reduced material was produced; however, it was carbided extensively. Phase analysis showed that in addition to an abundance of carbides, some of the product was in fact of a metallic phase. This same run was repeated in AF53 with the same chemical results, but with much less accumulation of reduced material and a considerable shortening of the run. The difference in these two runs was in the temperature profiles and temperature levels along the profile. The temperature profile in AF24 was shifted strongly toward the bottom of the reactor with much higher temperatures occurring below the grate. In AF53, the peak zones of the temperature profile were shifted to above the grate, but ranged from 50-100°C colder for comparable positions in the highest temperature zones of AF24. Apparently, the temperature did not change the chemical results and the effectiveness of production of a usable metal. The other three runs in this series gave similar results to AF53. Placing all of the carbon exterior to the ore pellet accentuates the gas-solid metal producing mechanism as compared to the liquid oxycarbide reaction with carbon and carbide to make metal. If the vapors formed do not react to form metal before they pass to colder zones of the bed, an excess of carbon will be left in the metal-producing zone to carbide the metal that is formed with an attendant increase of bridging due to the higher level of volatiles.

Burdens containing "lump" forms of reactants were evaluated in the AF reactor to provide flexibility of starting materials and eliminate solids processing steps involved in the production of agglomerates. As there is no lump alumina available except the balls made from activated alumina, 1/4" dia. XF100 balls were used with -4 +10 mesh SiC chunks and -8 +17 mesh pet coke in making two runs. The details of these runs can be found in Table 2. The results of these runs were similar to those discussed above when all the carbon was placed exterior to the ore pellet. Heavy bridging due to the refluxing of excess volatiles cut off the feed of burden to the metal-producing zone and forced these runs into early termination. The limited amount of metal produced easily formed carbides with the carbon left in the metal-producing zone due to incomplete reduction of the suboxide vapors before they migrated to colder regions of the bed. It was again demonstrated that Al_2O_3 and carbon must be intimately mixed in a pellet to produce the oxycarbide liquid and thus aid the production of metal by the liquid-solid carbide reaction mechanism.

Pure dense SiC does not appreciably back react as the surface quickly passivates with SiO_2 when heated in an oxidizing atmosphere. SiC powder ground to -200 mesh and contained in a pellet with Al_2O_3 and C may not passivate as effectively. Significant back reaction of SiC to SiO_2 would negate the value of prereducing SiO_2 to SiC in a separate stage such as the blast part of the blast-arc concept. In the lump ore runs of AF47 and AF48, there was no evidence of this back reaction using SiC chunks.

Also in this quarter, tests were continued on determining the optimum pellet and total burden carbon content as effected by varying SiO_2/Al_2O_3. The ore burden tested was the last of three burdens that have been studied in the alloy range of Al/Si of 70/30-60/40 and corresponded to the middle of the range at 65/35. These experiments comprised the last five of the 11 bench scale shaft reactor runs made during this quarter and since the chemical analyses are not yet completed, the details will be discussed in a later report.

Carbon solubility studies during this quarter consisted of testing melts of Al-Si alloys in graphite crucibles at 2200°C. The intent was to test Al rich alloys above the temperature of Al_4C_3 stability of 2156°C. In this case, the solid of equilibrium should be either graphite or SiC or possibly an aluminum-silicon carbide phase. Another possibility for the solid of equilibrium with the alloy is $Al_4Si_yC_z$ of which two different stoichiometries have been identified(1, 2). Motzfeldt(3) found in a preliminary report that Al_4SiC_4 decomposed at 2070°C and $Al_4Si_2C_5$ has been identified in some metal samples although no evidence of its temperature range of stability has been established.

Previous experience showed that an Al/Si = 60/40 alloy reacted extensively with graphite in the temperature range of 1900-2000°C and that SiC was only slightly attacked and probably was the solid in equilibrium with this alloy at these temperatures. The most recent tests in this composition range between 2100-2200°C as well as the previous tests indicated that the graphite was not passivated by SiC formations, and that SiC built up in the melt proportionally to the time (up to 60 min.) at temperature.

It appears that at 2150°C the liquid alloy is saturated with Al_4C_3 for $89.4/10.6 \le Al/Si \le 100/0$, $\alpha\ Al_4SiC_4$ for $79.6/20.4 \le Al/Si \le 80.5/19.5$, both βSiC and αAl_4SiC_4 for $Al/Si = 67.6/32.4$ and βSiC for $Al/Si \le 62.9/37.1$. Obvious gaps that exist in these data will be obtained in future runs.

Task completion is 40%.

Task No. 2: Calculate Heat and Mass Balances

Heat and material balances were determined for closed and semi-closed submerged arc furnaces. This was an update of previous calculations that utilized the SOLGASMIX equilibrium calculator program to determine the mass balances as controlled by equilibrium chemical conditions and required hand calculations to determine the stage to stage and overall heat balances. The major difference of these recent calculations is that complete convergence of the heat and material balances can now be achieved on the computer using the SOLGASMIX-REACTOR program which became available late in the fourth quarter of 1980. Other major changes in the calculations were as follows:

-Dust losses have been determined on a basis of 5% loss of SiO_2 with 3% SiO_2 loss from SiO and 2% SiO_2 loss from physical entrainment of fine particles abraded from the pellets fed to the furnace. The dust losses for alumina, carbon, and the impurities in the charge materials are basically those that occur from physical entrainment since almost all of the Al and Al_2O_3 back react in the furnace.

-The chemistry of the slag solution was treated as an ideal solution of hypothetical Al_4C_3 and Al_4O_4C liquids. The thermodynamic data for these liquids comes from the extrapolation of data for these solids to temperatures above their melting points.

-The previous heat balances included a 10% heat loss allowance from the furnace shell, roof, and electrical buswork. Since the arc furnace manufacturers predicted widely varying values for this energy loss, it was decided to include a value specific to the most desirable furnace design on the economic evaluations for which these calculations are intended. Therefore, the energy requirements used in the comparison of a closed and semi-closed furnace do not include these losses.

-Since a better convergence of the mass balance is now possible, the model predicts only a minor amount of residual slag or carbide to be tapped from the furnace. This residue was not recharged to the furnace as in the previous calculations.

-Equilibrium chemistry predicts Ti to be stable as TiC at metal-producing temperatures. However, experiments have shown that TiO_2 is reduced to metal and the equilibrium calculator cannot be used to determine the mass balance on Ti. The current calculations now include the effects of Ti in the overall heat and material balances, but not in those of the stage-to-stage equilibria.

In a closed arc furnace no air is bled into the furnace off-gases to burn the CO, H_2, COS, H_2S, and escaping suboxide vapors of SiO and Al_2O. The semi-closed furnace uses a manually operated stoking and charging machine mounted on top of the furnace to break crusts and charge ore onto the desired locations on top of the bed. The newer designed closed furnaces that are currently under development use remotely controlled mechanical devices to accomplish the stoking and charging, and it is believed that the furnace can be sealed against the large air leakage into the furnace off-gases. This will greatly decrease the amount of off-gas and heat recuperation from the off-gas that are required with the semi-closed furnace while increasing the fuel value of the off-gas from no fuel value for the semi-closed to

315.2 BTU/SCF for the closed furnace off-gas. Another important difference in the two processes is that the sulfur gases of COS and H_2S get oxidized to SO_2 in the semi-closed case and require caustic scrubbing for their removal, while these pollutants can be more economically removed in their reduced state as in the closed furnace case. Top temperatures due to combustion of the top gases will undoubtedly make the semi-closed furnace bed top much hotter and make it more difficult to back react and reflux the suboxides of Al and Si.

Table 3 compares these furnaces for two different operating schemes with respect to the sources of reduction carbon and for the production of Al/Si = 70/30 alloy. In all cases, it was assumed that 10% of the reduction carbon came from the electrode. For the closed furnace, the 60/30 and 80/10 cases assumed that 60% and 80% of the reduction carbon came from char in the pellet and 30% and 10% of the reduction carbon was from purchased furnace coke fed directly to the furnace. The coal to produce the furnace coke was not included in the material balances as shown in Figures 1, 2, and 3 and Table 3. For the semi-closed furnace the furnace coke was replaced with coal fed directly to the furnace. The coal chemicals will be readily burned by the bleed air in the semi-closed furnace, but may recondense and plug up the off-gas system in the closed furnace cases. Table 3 showed little variation in the power consumption for all the cases, but showed wide variation in the sensible heat to be recuperated from the off-gas. The dust losses for the semi-closed cases were lower because the carbon dust was burned by the bleed air and converted to gas. The 60/30 semi-closed dust losses were less than the 80/10 case because there was more volatile matter from the increased coal feed that entered the gas phase. The dust losses shown in Table 3 represent the solid particles to be recovered from the gas cleaning system and do not indicate a variation in the amounts of original solids leaving the furnace. The dust leaving the furnace is probably nearly equal for each case, but of a different composition and related to the different raw materials. The only disadvantage of the closed furnace is the requirement of furnace coke instead of directly fed coal. The closed furnace operation and design should greatly improve the economics of the Al-Si submerged arc operation.

The starting material and product compositions used in the calculations are shown in Table 4.

Heat and mass balances were also calculated for arc reactors on burdens containing alumina and carbon, and alumina-silica-carbon to facilitate comparison of the computer program output for pure materials to burdens containing impurities such as Fe and Ti.

Task completion is 60%.

Task No. 3: Mathematical Model Development

The subroutine for arc furnace simulation was completed and applied in calculating the heat and material balances reported in Task No. 2. Conversion of the FLOWREAC program to handle recycle has been initiated.

Task completion is 25%.

Task No. 4: Fundamental Phase Equilibria

This task is being performed by Carnegie-Mellon University. Current work effort was described in the Discussion section of the report.

Task completion is 33%.

Task No. 5: Process Demonstration

This task includes: 1) operation of the VSR (vertical shaft reactor) as the Blast part of a Blast-Arc Process, in which SiO_2 in the feed material is reduced to SiC prior to being charged into a submerged arc unit for further reduction to Al-Si alloy; and 2) operation of the SAR (submerged arc reactor) to demonstrate alloy production.

The Blast-Arc Process offers the possibility of about a 30% reduction in the electrical energy requirements for smelting Al-Si alloys compared to a submerged arc process. The electrical energy savings results from the use of combustion heat to reduce silica to SiC prior to charging into the arc furnace.

In order to study the technical feasibility of the first stage of the process, prereduction, the Vertical Shaft Reactor (VSR) was modified for solids discharge. The two major considerations in operating a prereduction reactor are kinetics and heat transfer. Specific kinetic data was not available during the first quarter. Bechtold(4) reported kinetic data on clay-coke agglomerates in which only enough carbon to form SiO was added to the agglomerate while the remaining carbon was external. A small batch of pellets (2 gms) was found to react completely to SiC within one hr. at 1500°C, while a larger batch (100 gms) took 8.5 hrs. at 1625°C. Since the pellets used in our study contain excess carbon for SiC reduction within the pellet and the aim temperature is 1550° to 1600°C, the kinetics for an individual particle should be more rapid than Bechtold reported. Therefore, heat transfer may limit the production rate of the VSR since heat is supplied at the wall and transferred by radiation to the center. In a combustion-heated reactor, heat would be supplied by a hot gas to each particle.

Heat transfer for the 8" VSR was modelled for the heating up of a coke bed with induction. The thermal lag between the wall and the center of the bed was about 25-60°K depending upon the temperature profile and the rate of descent of the charge. It was not possible to model a system where a strongly endothermic reaction occurred during heat-up. The result is that the time required to reduce the ore at the center of the reactor cannot be predicted without experimental data.

Four runs were made in the first quarter to calcine and prereduce Al_2O_3-Clay-Coke pellets to SiC. A sealed turntable was fitted in place of the product collection hearth to allow a controlled discharge of solids (Figure 4). The discharge rate was controlled by setting the drive mechanism to the minimum speed, about 0.7 rpm, and switching the motor on and off with a timer.

Argon was introduced below the turntable. The countercurrent flow of gas cooled the product before discharge and preheated the solids feed at the top of the reactor. A water trap in the offgas line condensed much of the water driven off during drying and calcining. A 2" diameter graphite plunger with 1/2" stubs at various levels was used to overcome the tendency to bridge. The plunger had an 8" stroke.

In the first three runs, both calcination and prereduction were performed. The maximum aim bed temperature was 1600°C with a residence time of about 4-5 hrs. and a production rate of 7-10 kg/hr. The first run, PR-1, was started with the reactor full of a low strength calcined ore which was discarded after discharge. Thermal and mechanical operation was satisfactory, but the run was terminated when a large amount of fines appeared in the product. Tests showed that fines generation was probably related to the combination of frequent plunger cycling and breakdown of the low strength ore. The reactor contents were removed, screened, and returned for the second run in which a shorter plunger was used. During the second run, PR-2, the drive mechanism jammed, causing a delay. Following the delay, the reactor was rapidly heated to 1600°C, but the lower zone overheated and the temperature exceeded 1700°C. The run was terminated due to the absence of product discharge. A 24" bridge was found below the limit of plunger travel. The delay and overheating probably contributed to bridge formation. In the third run, PR-3, the reactor contents were again screened and recharged. This run lasted about 11 hrs., and produced sufficient material to supply a run in the submerged arc reactor(SAR-II-4). Most material was run through the VSR twice since reduction was not complete after one pass. Considerable variation in strength was observed in the discharged pellets at the end of the run. CO was still being evolved at shutdown.

The fourth run, PR-4, was an attempt to calcine the ore in the VSR without prereduction. It was projected that a 500 lb. batch of ore could be processed in about 12 hrs. compared with about 4 days in the electrical furnace normally used. The reactor was started up on uncalcined material. Since radial heat transfer is primarily by radiation and effective thermal conductivity is low at calcination temperatures, large temperature differences between wall and center apparently existed. Considerable CO evolution was observed at temperatures well below those for SiC prereduction. The presence of CO can be explained by the water gas reaction ($H_2O + C = H_2 + CO$) which occurred because the H_2O being evolved in the core of the bed diffused toward the walls where C was present at a much higher temperature. One solution is to start up the reactor on calcined materials and provide sufficient sweep gas so that heat transfer is primarily by convection. Matching wall temperature to bed temperature would minimize radial temperature gradients. The bottom zone would be operated at about 1200°C to serve as a gas preheater.

Table 5 shows the nominal ore composition at various stages of processing: green, dried, calcined, and prereduced. During the runs, the extent of reduction was estimated from the difference between charge rate and discharge rate. Several assumptions were made:

1. Steady state operation.
2. Constant bed level
3. Water gas reaction ($C + H_2O = CO + H_2$) is negligible

Tables 6 and 7 show the charge and discharge rates and yields for runs PR-1, -2, and -3. In run -1, a 63% yield was achieved in the last two hrs. of operation compared to a 56.4% yield for complete reduction. This corresponds to about 68% reduction to SiC. In run-2, steady state operation was not achieved due to operating problems. In run-3, recycled material was charged in the last half of the run. It was assumed that there is no volume change upon calcination and prereduction and that the ore feed mechanism charges a constant volume. Average data from 2:00 through 8:00 shows a yield of 61%. This corresponds to nearly 100% prereduction.

Chemical analysis of the samples is in progress. The determination of the % prereduction is complicated because quantitative x-ray diffraction is difficult when many phases are present. A partially reacted pellet may contain alumina, graphite, silica (crystobalite), mullite, and SiC (α and β) plus small amounts of Fe-Si. If prereduction is based on elemental analysis, discrepancies in closure of the analysis can cause significant errors. Sampling is also a problem because the composition will vary from wall to center unless prereduction is complete. The variation in strength observed in the product from the end of PR-3 probably reflects the difference in % reduction. At low temperatures, the clay bonds due to hydration. At 1050°C, a glassy bond forms which is replaced by mullite at about 1250°C. Up to this point, strength increases. The removal of SiO_2 from the mullite as SiO + CO probably leaves a weaker porous Al_2O_3 matrix so strength would be expected to drop. At higher temperatures, α-Al_2O_3 formation might lead to an increase in strength. This hypothetical relationship between strength, temperature, and structure will be investigated in the second quarter. It may be desirable to prereduce to only 80% SiC from the standpoint of strength and production rate.

Four successful SAR-II runs were made in the first quarter. Each of the runs 2-5 was conducted with a clay, alumina, met coke pellet which had a SiO_2/Al_2O_3 ratio of 0.6 and contained 85% of the stoichiometric carbon. In all but SAR-II-4, the ore was fed directly after calcination. Charge for SAR-II-4 was preduced in the VSR prior to being fed to the arc. No additional coke was added to any run. In each case, metal was produced and tapped (Table 8).

Several modifications were made to the AC arc reactor. After an overheating problem in SAR-II-2, higher temperature insulation was used. Also, water jackets were added to the shell surface, the electrode sleeves, and the off-gas line and a radiation shield was placed beneath the lid. The need for even feed distribution was noted and splitters were positioned to distribute the charge around the reaction chamber. Between runs 4 and 5, a second taphole was added. The two tapholes were positioned with one under each electrode. Changes in internal chamber dimensions do not appear necessary.

SAR-II-2 was the first successful AC arc run. It lasted 4 hrs. and 20 min. (see Table 9) and tapped 4530g of metal. The metal was tapped in two parts, 880g after 2 hrs. and 40 min. at 1600 amps and 65 volts and 3650g after an additional 1 hr. 35 min. at 1250 amps and 72 volts. A material balance for the arc reactor between the first and second taps indicated a 34% yield* with 5% dust losses. The run was terminated because of excessive sidewall heating. Autopsy revealed large reaction cavities and a 2" metal pad.

SAR-II-3 ran for 4 hrs. 30 min. and had only one metal tap of 3101g. This tap came after 2 hrs. 15 min. at 62 volts and 1400 amps. A second tap was attempted after another 2 hrs. 15 min. at 66 volts and 1175 amps, but the taphole could not be reopened and the run was ended. Autopsy showed a deep bed with small cavities and a large amount of slag.

SAR-II-4, the only run to use prereduced burden, lasted 3 hrs. 20 min. The first tap of 2500g came after 2 hrs. 20 min. at 64 volts and 1650 amps. The second tap came 10 min. later and contained 2000g. One final tap was attempted after 50 min. at 80 volts and 1100 amps, but only 290g of metal could be removed. Autopsy revealed that voids had formed in the metal pad and the electrodes and cavities had risen high above the taphole. This contributed to a cold taphole making metal removal difficult.

The final run of the quarter, SAR-II-5 ran 4 hrs. 20 min. For this run, two tapholes were used, one under each electrode. The first tap was attempted after 1 hr. 45 min. at 53 volts and 1700 amps, but no metal was removed. The feed rate was then increased to produce a deeper bed and increase the voltage. The arc ran for another 2 hrs. 15 min. at 1600 amps and 58 volts. The tapholes were opened and 3095g of extremely viscous metal was tapped. The taphole could not be plugged and the run was terminated after 15 minutes.

Several important points were noted throughout the arc runs. The most crucial was the correlation between bed height and voltage. Low bed height corresponded to low voltage and high current. This led to high heat and dust losses because

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*$\%\text{yield} = \frac{\text{metal tapped}}{\text{theoretical metal}} \times 100$

of inadequate bed for condensation of the volatiles. It also contributed to carbiding of the product because of the large amount of suboxides escaping and leaving carbon behind.

On the other hand, if the bed was too high, voltage was high and current low and the power density on the cavity walls decreased. Also, the bed took heat away from the reaction zone and the ore was not completely reduced. Slag collected beneath the electrodes causing them to rise while not producing metal to tap. Optimum voltage for this system appeared to be 30-35 volts per electrode with 1600 total amps. A corresponding charge rate was between 15 and 20 kg/hr. Another important point was the need for even burden distribution. Uneven feed led to holes on the surface and cavity gases escaped directly to the off-gas. This also increased heat and dust losses.

Task completion is 50%.

Task No. 6: Process Flow Sheets and Economics

The heat and mass balances for the process flow sheets on closed and semi-closed submerged arc furnaces were reported under Task No. 2. Koppers Company, Inc. continued working on flow sheet concepts utilizing the heat and mass balances as a basis. Current work effort was described in the Discussion section of the report.

Task completion is 30%.

Task No. 7: Supply Burden Materials

Burden materials produced in the first quarter are described in Table 10. All burdens were pelletized in the Eirich mixer and calcined in an electric globar furnace. Materials used were hydrated alumina, Huber clay, and metallurgical coke.

Task completion is 50%.

Task No. 8: Supportive Analytical

Samples were analyzed as required. A total of 707 man-hours were expended in the Analytical Chemistry Division.

Detailed phase analyses by optical microscope were also completed on metal alloy products from AF-bench reactor runs AF-42, 43, 44, and 45 plus SAR-II runs 1 and 4.

The major phases in the AF-42 ingot were eutectic microstructure (Al-Si-$FeSiAl_5$), Si, $FeSi_2Al_4$, and SiC, with minor amounts of $TiSi_2$(Al), and traces of slag intergrown with SiC. The distribution of primary Al_4SiC_4 plates was variable. SiC morphology ranged from plates to subequant, rounded grains to blocky crystals. The extent of the peritectic reaction forming secondary Al_4SiC_4 (spheroids) from SiC and melt was generally greater in the upper zones of the ingot. However, the SiC plates appeared to be more susceptible to this reaction than the other SiC morphologies, although the presence of slag intergrown with SiC appeared to retard or stop the peritectic reaction within that grain. Phase composition as volume percent is shown in Table 11 for the AF-42 ingot, separated into five zones as per Figure 5.

Runs AF-43, 44, and 45 were made at the same operating conditions. Run AF-45 was completed, whereas 43 and 44 were terminated prior to completion. The burden formulation used in these runs contained bauxite, kaolinite, and coke with a SiO_2/Al_2O_3 ratio of 0.521, and approximately 90% of the stoichiometric proportion of carbon required for reduction of the oxides to metal. No additional CO sweep was used during these runs.

The three ingots were texturally homogeneous. These textural zones have been distinguished, based primarily upon microscopic differences in the type, morphology, and reaction relations of the carbides (zone 2 was probably present in the AF-44 ingot, but was not sampled). The textural zones for each ingot are shown in Figures 6, 7, and 8, and the modal compositions in Table 12 for the AF-43, AF-44, and AF-45 ingots, respectively. The contacts between adjacent zones were gradational. Most of the textural and compositional variation within the individual ingots was related to the distribution and morphology of SiC, primary or discrete Al_4SiC_4, and secondary carbide spheroids formed by peritectic reaction between SiC and the Al-Si melt.

The basal portion of these ingots was friable and very porous (up to 90%)., resulting from drainage of the Al-Si melt, leaving a friable network of carbides.

The remaining metal in all three zones consisted primarily of three-phase eutectic microstructure (Al-Si-$FeSiAl_5$), hypereutectic Si, and intermetallic $FeSi_2Al_4$; SiC, Al_4SiC_4, and secondary spheroids were also present, but the relative proportions vary widely. Al_4SiC_4 occurred both as primary platelets and intergrown with SiC in the secondary spheroids; these latter were formed by peritectic reaction between SiC and the Al-Si melt. The extent of this peritectic reaction was inversely proportional to the amount of primary Al_4SiC_4

present. SiC appeared to be more stable, with respect to the Al-Si melt, in the presence of primary Al_4SiC_4 than in its absence. In addition, the presence of small amounts of slag intergrown with SiC appeared to decrease the tendency of that SiC to form secondary carbide spheroids.

The eutectic microstructure had a random orientation in the lower part of the ingots. However, the microstructure became increasingly coarse-grained, and tended toward cellular or dendritic solidification structures, toward the top of the ingots. In addition, the morphology of the eutectic Si grains changed from predominantly planar to predominantly granular, or spheroidal, toward the top of the ingots. This gradual change in morphology also occurred, to a lesser extent, in the coarse grained primary Si.

Two metal ingots from Run SAR-II-1 were analyzed to determine the distribution of carbides. Both ingots contained primarily hypereutectic Si and intermetallic $FeSi_2Al_4$ and $TiSi_2$(Al) crystals in a matrix of eutectic microstructure (Al-Si-$FeSiAl_5$), with highly variable SiC distribution (Table 13).

Three textural zones were identified in the SAR-II-4 ingot, based primarily upon variations in abundance of Al_4SiC_4 and in the texture of the three-phase eutectic microstructure. These zones divided the ingot approximately into thirds. However, the contacts were chosen arbitrarily because of their gradational nature. Modal compositions of the three zones are listed in Table 14.

Zone 1, at the base of the ingot, consisted primarily of intermetallic $FeSi_2Al_4$/$FeSiAl_5$ and hypereutectic Si in a matrix of eutectic microstructure (Al-Si-$FeSiAl_5$), with minor amounts of $TiSi_2$(Al) and Al_4SiC_4. $TiSi_2$(Al), $FeSi_2Al_4$, and Si in zone 2 were similar to zone 1, although the extent of peritectic reaction of $FeSi_2Al_4$ tended to be greater. Al_4SiC_4 was much more abundant and coarser, ranging up to 0.25 mm in diameter.

With the exception of the eutectic microstructure, zone 3 was similar to zone 1 in phase composition and texture. The eutectic was more coarse-grained than in zone 1, and had a dendritic to cellular structure.

Task completion is 50%.

B. Alloy Purification

Task No. 1: Pilot Operations

Pilot experiments were carried out on a nominal Al-30%Si-3%Fe-1%Ti in order to simulate the purification of a hypothetical furnace alloy from an arc or blast-arc reactor using an Al_2O_3-Clay-Wyoming Char burden. The objective of the experiments was to produce a significant yield of casting alloy of near-eutectic composition with solute limits of 1.0%Fe and 0.1%Ti. Previous experiments (Runs 1-3) produced aluminum yields of 81, 57, and 68% for solute limits of 20%Si, 2.0%Fe, and .25%Ti. Since iron has deleterious effects on ductility and corrosion resistance, there is only a limited market for high iron alloys. In sand casting and permanent mold castings, the upper limit is usually 0.6-0.7% Fe(5), while the eutectic contains 0.7-0.8%Fe. The effects of iron can be ameliorated by iron correctors, Co, Cr, Mn, Mo, and Ni, but the extent of the "correction" is not known. Thus, 1%Fe seems to be a good compromise from the standpoint of alloy properties and process yields.

In order to reduce the Fe and Ti content of the purified alloy, it is necessary to separate liquid from solid at a temperature very close to the eutectic. Table 15 shows the temperatures and compositions of two invariant points at which four condensed phases are present. If it is assumed that the more recent data (Ref. 5) is correct, a drop in temperature of 20°C will reduce the %Fe in the liquid by 0.8% or .04%/°C.

TABLE 15

Phases	Ref. 5 Composition			Ref. 6 Composition		
	Si	Fe	Temp.	Si	Fe	Temp.
Peritectic Si, δ, χ, ℓ, v	14.0	1.5	596°C	13.6	2.0	595°C
Eutectic Al, χ, $\underline{\ell}$, Si, v	12.0	0.7	576°C	11.6	0.8	577°C

χ=$FeSiAl_5$ δ=$FeSi_2Al_4$ ℓ=liquid V=vapor

In previous runs, cooling was terminated at 590°C corresponding to 1.26%Fe which is above the 1% limit. To achieve a reasonable yield of an acceptable alloy, the melt must be cooled virtually to the eutectic temperature before remelting. During the remelt, iron will gradually increase in the liquid drain, but a considerable amount of the remelt should be acceptable when averaged in with the eutectic drain.

Several problems arise when attempting to separate liquid from solid at the eutectic. The amount of the eutectic drain seems to be related to the volume fraction of crystals present. The original pilot experiment on Al-Si which started with a 25%Si, no Fe or Ti alloy had more than twice as much eutectic drain (57.1% of charge) as Runs 1-, 2-, and 3-AP (18, 21, and 19% of charge). The introduction of Fe and Ti causes a marked increase in the amount of crystals due to the formation of $FeSi_2Al_4$, $FeSiAl_5$, and (Ti, Al) Si_2 intermetallics. Because the densities of these phases are not known, the volume fraction cannot be calculated exactly but an Al-30%Si-3%Fe-1%Ti alloy has roughly twice the volume of crystal bed that an Al-25%Si alloy has. This suggests the possibility of a two-stage process which would form approximately half of the crystal bed in each stage. Such a process has been called "stop and go". For the alloy considered above, the Al-Si-Fe phase diagram(6) indicates that in the "stop" stage, cooling from about 825°C will precipitate Si crystals until the double saturation line is reached at 700°C. After draining at 700°C, the liquid would be charged to a second stage where further cooling will precipitate Si and $FeSi_2Al_4$ down to 596°C and Si and $FeSiAl_5$ from 596°C to 576°C. The effect of Ti is not known since a Al-Si-Fe-Ti phase diagram is not available. The (Ti, Al)Si_2 probably precipitates with the Si at the higher temperatures.

Another problem in achieving a high yield of eutectic is due to the vertical temperature gradient caused by cooling at the surface. Rapid cooling causes a steep gradient with the result that the upper melt can reach the eutectic temperature and composition well before the bottom does. Slow cooling should minimize the temperature difference. If the crystals sink, the temperature difference should be smaller than if the crystals float. Since Si crystals are less dense than the melt, floating should occur in the "stop" stage while sinking should occur in the "go" stage due to the presence of iron intermetallics ($FeSi_2Al_4$, $FeSiAl_5$).

Given a certain volume fraction of crystals, various techniques may improve the draining of the bed. Presumably, beds of large crystals which have a lower ratio of surface area to volume and larger void volume should drain better. Slow cooling should cause larger crystals unless rapid nucleation occurs. Packing of the crystal bed should squeeze alloy from the crystal bed if it has the consistency of a sponge.

The experiments were performed in the pilot crystallizer. Two pairs of runs were made. In the first "stop and go" pair, the alloy contained 0.84%Ti, while in the second, the alloy was Ti-free.

Material balances for the four runs are shown in Tables 16-19. These tables show the cumulative yield vs. composition during the experiments. For the "go" runs, Tables 16 and 18, the yield at the 1%Fe level is based on interpolation. Figures 9-12 show the temperature vs. time throughout the run. Temperatures were measured at two depths during the freeze cycle. Figures 14-17 show the alloy composition of the metal drained vs. percent of initial charge.

In Run 4-AP ("go", with Ti), the temperature in the melt reached 578°C at the end of the freeze cycle, but the surface had a frozen crust. The gas-fired lid was used to soften the crust and packing was attempted during the drain. Very little compression of the crystal bed was observed during packing.

In Run 5-AP ("stop"), the initial alloy composition was 31.2%Si, 3.16%Fe, and 0.84%Ti while the cumulative alloy composition after remelt was 23.9%Si, 3.00%Fe, and 0.39%Ti at a 90% aluminum recovery yield. Figure 13 shows that the initial composition of the drain (18.4%Si, 2.12%Fe, 0.17%Ti) is well down the double saturation line. It should be noted that the data represented by this Al-Si-Fe phase diagram is: 1) equilibrium data which may not apply exactly at higher cooling rates; 2) probably affected by Ti; and 3) different from the older data of Gwyer and Phillips on the position of the double saturation line. The double saturation line is apparently reached at a temperature higher than 700°C as predicted by Gwyer and Phillips. Thus, in order to freeze half the hypereutectic crystals by dropping the temperature to 700°C, halfway from the liquidus at 825°C to the eutectic at 576°C, it is necessary to freeze some $FeSi_2Al_4$. If a low-iron crystal bed is desired, the freeze cycle must be interrupted at a higher temperature. During the remelt, the silicon increased steadily while the iron was relatively constant until the end. This seems to indicate that the kinetics of dissolution of $FeSi_2Al_4$ are slow (see Figures 14-17). Since the average titanium in the drain was slightly less than half its starting value at the end of 5-AP, $(Ti, Al)Si_2$ probably crystallizes continuously between the liquidus and the eutectic.

The starting composition for Run 4-AP ("go") was 22.2%Si, 3.35%Fe, and 0.40%Ti. This estimated composition for the "stop" drain was slightly low in silicon but high in iron compared to the actual drain while titanium was very close. The silicon and iron differences tend to offset each other when estimating the volume fraction of crystal bed to be expected, so the 90% aluminum yield on the "stop" stage should apply to the alloy actually charged to the "go" stage. In Run 4-AP, iron cut-off was reached at 64% aluminum yield. The remaining liquid containing 22.2%Si, 3.88%Fe, and 0.38%Ti would be recycled to the "go" stage. The overall eutectic yield through two stages with recycle would then be 74% aluminum (Figure 18). The goal for this process is an optimistic 90%, but this may be achievable with improvements in technique and crystal bed processing to separate a high aluminum fraction for recycle. The crystal bed from Run 5-AP ("stop") contained considerable iron so it would not represent a substitute for metallurgical-grade silicon. However, both crystal beds would be usable as a substitute for ferrosilicon.

In Run 7-AP ("stop"), the starting alloy composition was 29.2%Si and 4.12%Fe with no Ti while the cumulative alloy composition after remelt was 21.1%Si and 3.02%Fe at an 86% aluminum yield. The aluminum content of the crystal bed (193 lbs.) was considerably higher than in Run 5-AP (115 lbs.), possibly due to the higher iron in the starting alloy. Probing of the crystal bed during the run revealed a steadily increasing level of mushy crystals on the bottom. This seems to indicate that the double saturation line was hit quite early in the freeze cycle. The advantage of the co-precipitation of Si and $FeSi_2Al_4$ is that the heavier iron intermetallics seems to drag the silicon crystals to the bottom. This improves circulation by displacing liquid and avoids premature freezing of the melt surface.

The starting composition of Run 6-AP was 18.4%Si and 3.5%Fe which is considerably lower in silicon than the final average drain composition of 7-AP (21.1%Si). Thus, Run 6-AP does not fit well with Run 7-AP based on volume fraction of crystals. The drain from 6-AP was quite close to the eutectic, with a 38% cumulative yield at 12.4%Si and 0.83%Fe. Since the temperature at the end of 6-AP reached only 583°C, the actual eutectic is probably at <12.4%Si and 0.83%Fe. The 1%Fe limit was reached at 52% aluminum yield which was a lower yield than in 4-AP. A lack of titanium may have influenced the faster rise in iron as the remelt progressed.

Task completion is 75%.

Task No. 2: System Characterization

No progress.

Task completion is 0%.

PHASE D SECOND QUARTER PROGRAM

Administrative

The Baseline Cost Plan for DOE fiscal year 1981 will be submitted. Change purchase orders will be implemented for subcontractors/consultants to cover their work on the contract in calendar year 1981.

Technical

Reduction: A number of burdens will be tested in the AF-reactor including the following: activated alumina-silicon carbide-petroleum coke (simulating prereduced charge); activated alumina-silica-petroleum coke (to obtain very pure alloy product); "lump" silicon carbide plus activated alumina-coke; and alumina hydrate-clay-metallurgical coke containing 57% of reduction carbon in the pellet. The extent of back reaction of SiC to SiO_2 upon heating to 1600°C will be measured. Carbon solubility tests in Al-Si alloys using SiC crucibles will be initiated. Kinetics of SiO_2 conversion to SiC starting with an alumina-clay-coke burden will be determined in the bench crucible reactor to correlate residence time and temperature with percent conversion. Conversion of the FLOWREAC computer program to handle recycle (RCYCREAC) will be continued. A series of runs are planned in the pilot VSR to study prereduction of SiO_2 in clay to SiC. Included are measurement of the heat transfer lag from reactor wall to center when heating to 1600°C, a continuous run with CO sweep to simulate the effects of coke combustion on SiC formation, and a run with O_2 injection to combust excess coke added to the pelletized burden. A relationship will be established between temperature, strength and structure of the prereduced solid product. The various activated alumina burdens will be tested in the pilot submerged arc unit, SAR-II, including a charge containing activated alumina-silicon carbide-clay-hematite and metallurgical coke to simulate a prereduced material partially converted to SiC. The closed and semi-closed arc furnace conceptual flow sheets will be completed and estimation of capital costs will be started. Pelletization of a burden containing alumina hydrate-clay-green Wyoming coal will be developed in addition to supplying the regular clay and activated alumina binder materials. Phase equilibria studies of the Al-Si-O-C system will be continued.

Alloy Purification: Additional pilot crystallizer runs are planned to further determine the effects of cooling rate on product yield and purity. Density separation of silicon crystals from intermetallic crystals will be tried.

Cost Summary

Expenditures for the first quarter of Phase D totaled \$309,307. Distribution was \$291,567 for Reduction, \$14,282 for Alloy Purification and \$3,467 for burden adjustment. Total cumulative spending through the first 43 months of the contract was \$5,373,260. Actual spending for Phase D is compared to estimated spending in Attachment 1.

Assigned Personnel

The actual man-hours expended by engineers and technicians for the first quarter of Phase D are shown in Attachment 2 and compared to estimated man-hours. For engineers, actual was 1.1% below estimated. For technicians, actual was 3.7% above estimated. Total man-hours were 1.9% above estimated.

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5. L.F. Mondolfo, Aluminum Alloys: Structure and Properties, Butterworths, 1976, p. 759, p. 535.

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TABLE 1

OPERATING CONDITIONS FOR PRODUCTION OF Al/Si = 70/30 ALLOY WITH NO CARBON IN THE PELLET

RUN	SiO_2/Al_2O_3	Total %C	Consumed Ore	Reaction Zone Wt.	Reaction Zone Phase	Wt. Metal / Consumed Ore	%C Metal
AF50	.497	85.1	1.19 kg	.85 kg	oxide	---	---
AF51	.497	85.1	3.01	1.02	carbide/oxide	.089	8.0
AF52	.497	80.0	3.17	.75	oxide/carbide	.101	4.25
AF53	.469	80.0	2.09	.84	oxide/carbide	.036	15.7
AF24	.469	80.0	6.25	---	carbide	.325	19.7

TABLE 2

OPERATING CONDITIONS FOR SEPARATE Al_2O_3, SiC, C BURDEN MIXTURE

RUN	SiO_2/Al_2O_3	Total %C	Consumed Ore	Reaction Zone Wt.	Reaction Zone Phase	Wt. Metal Consumed Ore	%C Metal
AF47	.528	89.6	2.64 kg	1.02kg	carbide/oxide	.053	8.9
AF48	.663	89.2	6.15	.71	carbide	.097	10.5

TABLE 3

SUMMARY OF HEAT AND MATERIAL BALANCES OF CLOSED VS. SEMI-CLOSED ARC FURNACE OPERATIONS FOR 300,000 TPY Al, CHAR FROM WYOMING COAL, 330 DAY/YR., 90% Al RECOVERY IN CRYSTALLIZER (ALL UNITS ARE IN TPY DRY BASIS)

OPERATION	CLAY	Al_2O_3 HYDRATE	CHAR 86.15%C	FURNACE COAL 51.02%C	FURNACE COKE 86.15%C	ELECTRODES 86.15%C	SPECIFIC POWER	DUST LOSSES	TOP GAS	HEAT TO RECOVER
Closed Arc 80/10	640526.2	607875.8	333881.5	--------	41735.2	41735.2	5.189 kWh/#Al	43211.2	821023.3	.00016 kWh/#Al
Closed Arc 60/30	640526.2	607875.8	250411.2	--------	125205.6	41735.2	5.189 kWh/#Al	43211.2	821023.3	.00016 kWh/#Al
Semi-Closed Arc 80/10	634422.0	591206.5	326100.9	68833.4	------	40762.2	5.1955 kWh/#Al	31132.6	3,225,302.7	3.618 kWh/#Al
Semi-Closed Arc 60/30	631373.4	595566.4	240650.2	203178.3	------	40108.4	5.1949 kWh/#Al	29649.0	4,145,297.9	4.564 kWh/#Al

TABLE 4

MATERIAL ANALYSIS (wt %)

	Wyoming Coal	Char	Huber Clay	Bayer Hydrate
C	69.59	86.15	---	---
N_2	1.72	.61	---	---
O_2	17.18	.79	---	---
H_2	4.95	1.20	---	---
S	.86	.88	---	---
SiO_2	3.714	6.95	45.55	---
Al_2O_3	0.903	1.69	37.38	65.38
Fe_2O_3	1.052	1.68	1.71	---
TiO_2	0.031	.05	1.47	---
L.O.F.	---	---	13.89	34.62

PRODUCTS AFTER REFINING tpy 60/30 CASE

	Al	Si	Fe	Ti	Total
Eutectic	300000 (85%)	49412 (14%)	3176 (0.9%)	353 (0.1%)	352941
Crystals	33333 (23.64%)	93287.9 (66.16%)	9046.5 (6.42%)	5330.5 (3.78%)	140997.9
Raw Alloy	333333 (67.485%)	142699.9 (28.890%)	12222.5 (2.475%)	5683.5 (1.150%)	493938.9

PRODUCTS AFTER REFINING tpy 80/10 CASE

	Al	Si	Fe	Ti	Total
Eutectic	300000 (85%)	49412 (14%)	3176 (0.9%)	353 (0.1%)	352941
Crystals	33333 (23.60%)	93410.5 (66.14%)	9133.8 (6.47%)	5359.8 (3.79%)	141237.2
Raw Alloy	333333 (67.45%)	142822.5 (28.90%)	12309.8 (2.49%)	5712.8 (1.16%)	494178.1

% WEIGHT

	GREEN (7%H_2O)	DRIED	CALCINED	PREREDUCED
SiO_2	20.86	22.43	27.15	24.69 (SiC)
Fe_2O_3	1.08	1.16	1.40	1.34 (Fe)
TiO_2	0.66	0.71	0.86	1.17
Al_2O_3	34.77	37.39	45.27	61.68
C	18.33	19.71	23.86	10.34
S	0.21	0.23	0.60	0.82
VM	0.46	0.50	---	
L.O.F.	23.63	16.90	---	
Yield Fraction	---	.93	.826	.734
Cum (Green)	---		.768	.564
Cum (Dried)	---		---	.606

TABLE 5 - NOMINAL ORE COMPOSITION DURING PREREDUCTION STARTING WITH GREEN BURDEN

TABLE 6 - VSR PREREDUCTION

PR-1

Start-up: "Raspberries"
Feed: Air-Dried Ore

TIME	GMS CHARGE	GMS DISCHARGE	YIELD , %	PRODUCT
12:00	23638	23085	---	"Raspberries"
1:00	16502	7610	46.1	"Raspberries"
2:00	14272	8650	60.6	"Raspberries"
3:00	23192	8930	38.5	Mixed
4:00	16502	10500	63.6	Pellets
5:00	16056	10000	62.3	Pellets

PR-2

Start-up: PR-1 Reactor Contents
Feed: Oven-Dried Ore

TIME	GMS CHARGE	GMS DISCHARGE	YIELD, %	COMMENTS
12:15	26350	13745	--	
2:00	13600	10670	78.5	
3:00	7650	7297	95.4	Delay
4:00	7650	5760	75.3	
5:00	6375	6314	--	Bridge
END	---	4892	--	Bridge

TABLE 7 - VSR PREREDUCTION

PR-3

Start-Up: PR-2 Reactor Contents
Feed: Air-Dried Ore, Recycle

TIME	GMS CHARGE	GMS DISCHARGE	YIELD, %	FEED
11:00	6375	14654	--	Dried
12:00	10625	8761	82.5	Dried
1:00	8500	7255	85.4	Dried
2:00	12325	7877	63.9	Dried
3:00	11475	8022	69.9	Dried
4:00	19125	10007	52.3	Dried
5:00	13600	9166	67.4	Partial Recycle
6:00	16575	9243	55.8	Recycle
7:00	12325	6707	54.4	Recycle
8:00	8925	6550	73.4	Recycle
9:00	10200	10038	98.4	Recycle

TABLE 9

METAL ANALYSIS (WT%)

	SAR-II-2		SAR-II-3 *	SAR-II-4 *
	1st Tap	2nd Tap		
Al	53.4	55.1	48.8	52.5
Si	33.4	32.9	22.7	29.5
Fe	6.50	5.71	4.54	4.52
Ti	2.79	2.62	1.95	2.72
C	1.96	2.54	1.44	1.03

*Further analysis will be obtained to close metal balance.

TABLE 9 RUN PARAMETERS

	SAR-II-2	SAR-II-3	SAR-II-4	SAR-II-5
Box dimensions bottom	7.875" x 15.75"	8.875" x 15.75"	7.875" x 15.75"	7.875" x 15.75"
Tapholes	1-center	1-center	1-center	2-1 under each electrode
Feeder	1-center	1-center	1-center with splitter	1-center with 3 splitters
Electrode Spacing Center to Center	7.875"	7.375"	7.875"	7.875"
Initial Volts	65	62	64	55
Amps	1600	1400	1650	1700
Final Volts	72	66	80	65
Amps	1250	1175	1100	1550
Charge Rate (kg/hr)				
1st hr.		17.1	10.8	12.9
2nd hr.	18.6	18.0	23.8	9.4
3rd hr.	18.1	24.0	17.2	15.8
4th hr.	18.3	20.1	19.3	14.3
5th hr.	16.4	27.9		17.1
Total run time	4 hrs. 20 min.	4 hrs. 30 min.	3 hrs. 20 min.	4 hrs. 20 min.
Total metal tapped	4530g	3101g	4790g	3095g

Aluminum Company of America
ALCOA LABORATORIES

TABLE 10 BURDEN MATERIAL PREPARED 1981, JANUARY 1 TO 1981 MARCH 31
FOR DIRECT REDUCTION (74D1450601)

EXP. NO.	NOTEBOOK & PAGE NO.	PREP. METHOD	QUANTITY (LB)	RAW MATERIALS USED	BURDEN CHARACTERISTICS SIZE	YIELD (%)	SiO_2/Al_2O_3 % Red C	COMPRESSIVE STRENGTH (LB/IN^2)	
5A1292	199880 16,20,22	EIRICH	100	50.4% HUBER CLAY	4X10M	76	0.49	382	
				17.0% PROD.NO. 10 MET COKE			57%		
				33.6% HYDRATED ALUMINA					
5A1293	19988 17,20	EIRICH	100	61.0% HUBER CLAY	4X10M	91	0.76	457	
				16.7% PROD. NO.10 MET COKE			57		
				22.2% HYDRATED ALUMINA					
5A1335-1	19988 23,28	EIRICH	600	29.7% HYDRATED ALUMINA	3/8"X4M	61	0.60	300	
" -2	19988-29 34,38	EIRICH	600	47.3% HUBER CLAY	" "	-	87	AIR DRIED	
" -3	19988 40,45	EIRICH	600	23.3% PROD.NO. 10 MET COKE	" "	-		" "	
" -4	20038 3-9	EIRICH	700	ALL FOUR HAVE SAME COMPOSITION	"	-		" "	
5A1367	20038-11	EIRICH	100	39.7% HYDRATED ALUMINA	4X10M	89	0.49	355	
				44.4% HUBER CLAY			57%		
				15.9% PROD NO. 10 MET COKE					
5A1375	20038- 13,18	EIRICH	600	30.0% HYDRATED ALUMINA	3/8"X6M	-	0.60	302	
				48.0% HUBER CLAY		-	82%		
				21.9% PROD.NO. 10 MET COKE					

FORM 027 9-74)

TABLE 11 PHASE COMPOSITION OF AF-42 INGOT (VOLUME PERCENT)

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5
Al(in eutectic)	44%	40%	44%	33%	32%
Si	27	31	30	36	30
$FeSi_2Al_4$	13	10	6	7	6
$FiSiAl_5$	<1	<1	<1	<1	<1
$TiSi_2(Al)$	2	2	2	1	2
SiC	6	13	17	12	8
Al_4SiC_4	<1	-	1	7	22
Carbide Spheroids	7	5	<1	3	1
Slag	<1	<1	<1	<1	<1

TABLE 12 - PHASE COMPOSITIONS OF AF-43, 44, AND 45 INGOTS (VOLUME %)

	AF-43			AF-44		AF-45		
	ZONE 1	ZONE 2	ZONE 3	ZONE 1	ZONE 3	ZONE 1	ZONE 2	ZONE 3
Al (in eutectic)	42%	54%	53%	56%	47%	39%	40%	60%
Si	32	25	26	25	25	26	22	19
$FeSi_2Al_4$	10	11	7	9	7	12	9	6
$FeSiAl_5$	<1	<1	<1	<1	<1	<1	<1	<1
$TiSi_2(Al)$	1	<1	1	2	1	2	1	2
SiC	13	4	5	2	9	16	14	7
Al_4SiC_4	--	<1	6	<1	10	--	13	6
Carbide Spheroids	<1	5	1	6	1	5	<1	1
Slag	<1	<<1	<<1	<<1	--	<1	<<1	<1

TABLE 13- PHASE COMPOSITION OF SAR-II-1 INGOT (VOLUME %)

	First Tap	Second Tap			
		Base	Middle	Top	"Extruded Drop"
Al (in eutectic)	36%	41	36	38	47
Si	27	35	24	31	36
$FeSi_2Al_4$	19	17	17	18	16
$FeSiAl_5$	<1	<1	<1	<1	<1
$TiSi_2$(Al)	4	4	4	3	<1
SiC	11	3	18	10	<1
Slag	4	-	-	-	-

TABLE 14 PHASE COMPOSITION OF SAR-II-4 INGOT (VOLUME %)

	ZONE 1	ZONE 2	ZONE 3
Al (in eutectic)	42%	43%	50%
Si	34	29	31
$FeSiAl_5$	<1	1	1
$FeSi_2Al_4$	16	11	12
$TiSi_2$(Al)	5	4	2
Al_4SiC_4	3	11	4
Slag	–	<1	–

TABLE 16

RUN 4-AP

	Weight lb.	Content, %			
		Si	Fe	Ti	
Initial Alloy	2003	22.2	3.35	0.40	
Metal in Increment:					
0-2	131.9	12.9	0.92	0.07	
2-4	188.4	13.0	0.90	0.06	
4-6	188.4	13.0	0.90	0.06	
6-8	169.6	13.0	0.90	0.06	
8-10	188.4	13.7	0.96	0.08	
10-12	207.3	14.8	1.16	0.09	
12-14	179.0	18.0	2.04	0.20	
14-17	310.9	24.0	4.70	0.46	
Crystal Bed	439.0	(44.0)	(8.77)	(1.24)	(46 Al)

Metal Increment	Cum. Content, %			Cumulative Yield, %	Avail. Al Rec, %
	Si	Fe	Ti		
0-2	12.9	.92	.07	6	8
0-4	13.0	.91	.06	16	18
0-6	13.0	.90	.06	25	30
0-8	13.0	.90	.06	34	39
0-10	13.1	.92	.06	43	50
0-12	13.4	.96	.07	54	62
0-12+	13.6	1.00	.08	56	64
0-14	14.1	1.11	.09	62	72
0-17	16.1	1.83	.16	78	86
Reflux (12+ - 17)	22.2	3.88	.38	22	22

TABLE 17

RUN 5-AP

	Weight, %	Content, % Si	Fe	Ti	
Initial Alloy	1874	31.2	3.16	0.84	
Metal in Increment					
0-2	107.7	18.4	2.12	0.17	
2-4	153.3	20.0	2.82	0.22	
4-6	165.7	21.5	3.24	0.25	
6-8	165.7	21.6	2.97	0.22	
8-10	165.7	21.2	3.16	0.22	
10-12	165.7	21.4	3.01	0.24	
12-14	107.7	23.0	2.64	0.29	
14-16	145.0	25.7	2.53	0.36	
16-18	165.7	29.2	2.74	0.63	
18-20	165.7	34.8	4.24	0.19	
Crystal Bed	358	(61)	(3.8)	(2.7)	(32 Al)

Metal Increment	Cumulative Content, % Si	Fe	Ti	Cumulative Weight, %	Avail. Al Recovered, %
0-2	18.4	2.12	0.17	6	7
0-4	19.4	2.53	0.20	14	17
0-6	20.2	2.81	0.22	23	27
0-8	20.6	2.85	0.22	32	37
0-10	20.7	2.92	0.22	40	48
0-12	20.8	2.94	0.22	49	58
0-14	21.1	2.90	0.23	55	64
0-16	21.6	2.86	0.25	63	73
0-18	22.6	2.84	0.29	72	82
0-20	23.9	3.00	0.39	80	90

TABLE 18

RUN 6-AP

	Weight, lb	Content, % Si	Content, % Fe	
Initial Alloy	2082.5	18.4	3.5	
Metal in Increment:				
0-2	109.7	12.5	0.84	
2-4	168.7	12.4	0.83	
4-6	168.7	12.4	0.80	
6-8	168.7	12.4	0.82	
8-10	168.7	12.5	0.84	
10-12	168.7	14.0	1.46	
12-14	236.2	16.4	3.28	
14-16	168.7	18.3	5.5	
16-18	101.2	22.8	7.0	
18-20	168.7	25.7	7.6	
20-22	143.4	25.0	6.0	
Crystal Bed	311	(28)	(6.5)	(66 Al)

Metal Increment	Cumulative Content, % Si	Cumulative Content, % Fe	Cumulative Yield, %	Avail. Al Recovered, %
0-2	12.5	0.84	5	6
0-4	12.4	0.83	13	15
0-6	12.4	0.82	21	24
0-8	12.4	0.83	30	33
0-10	12.4	0.83	38	42
0-12	12.7	0.94	46	51
0-12+	12.8	1.00	47	52
0-14	13.4	1.40	57	62
0-16	14.0	1.91	65	70
0-18	14.6	2.27	70	74
0-20	15.6	2.60	77	81
[illegible] (12+-22)	19.9	[illegible]	30	29

TABLE 19

RUN 7-AP

	Weight, lb	Content, % Si	Fe	
Initial Alloy	2102	29.2	4.12	
Metal in Increment:				
0-2	66	18.8	2.36	
2-6	332	18.7	2.31	
6-10	332	19.0	2.32	
10-14	332	20.3	2.86	
14-18	332	22.7	3.43	
18-21	199	28.0	5.14	
Crystal Bed	508	(55)	(7.6)	(38 Al)

Metal Increment	Cumulative Content, % Si	Fe	Cumulative Weight, %	Avail. Al Recovered, %
0-2	18.8	2.36	3	4
0-6	18.7	2.32	19	22
0-10	18.8	2.32	35	41
0-14	19.3	2.49	50	59
0-18	20.1	2.71	66	77
0-21	21.1	3.02	76	86

ATTACHMENT 2

PHASE D MAN-HOUR SUMMARY

	FIRST QUARTER		SECOND QUARTER		THIRD QUARTER		CUMULATIVE		CUMULATIVE % DEVIATION
	Actual	Est	Actual	Est	Actual	Est	Actual	Est	
ENGINEERS	2044	2067		2060		2057	2044	2067	-1.1
TECHNICIANS	3475	3350		3340		3339	3475	3350	+3.7
TOTAL	5519	5417		5400		5396	5519	5417	+1.9

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

Coal req'd for char; 422849/563798.5

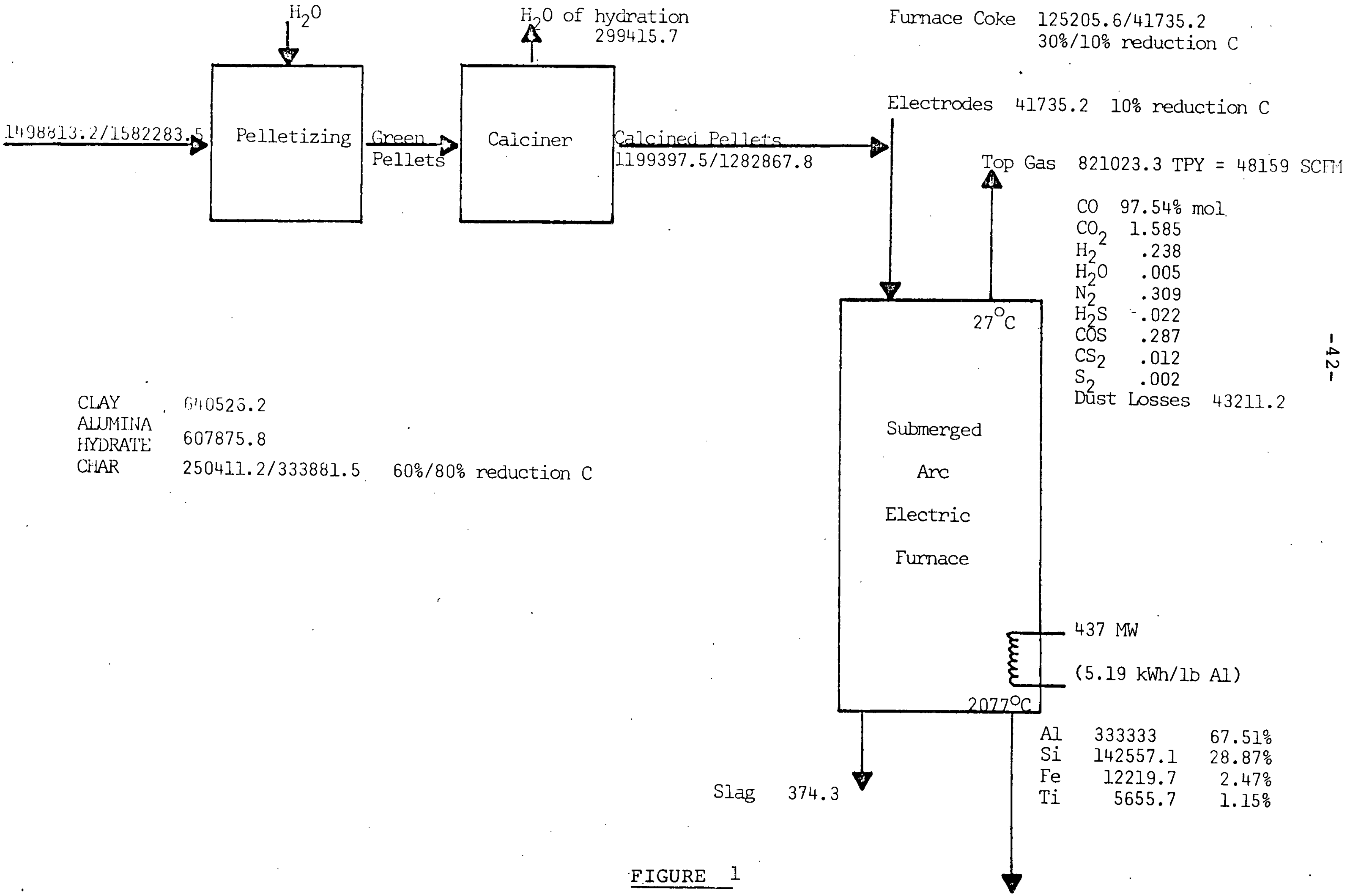


FIGURE 1

]

SEMI-CLOSED ARC FURNACE 80/10 CASE
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

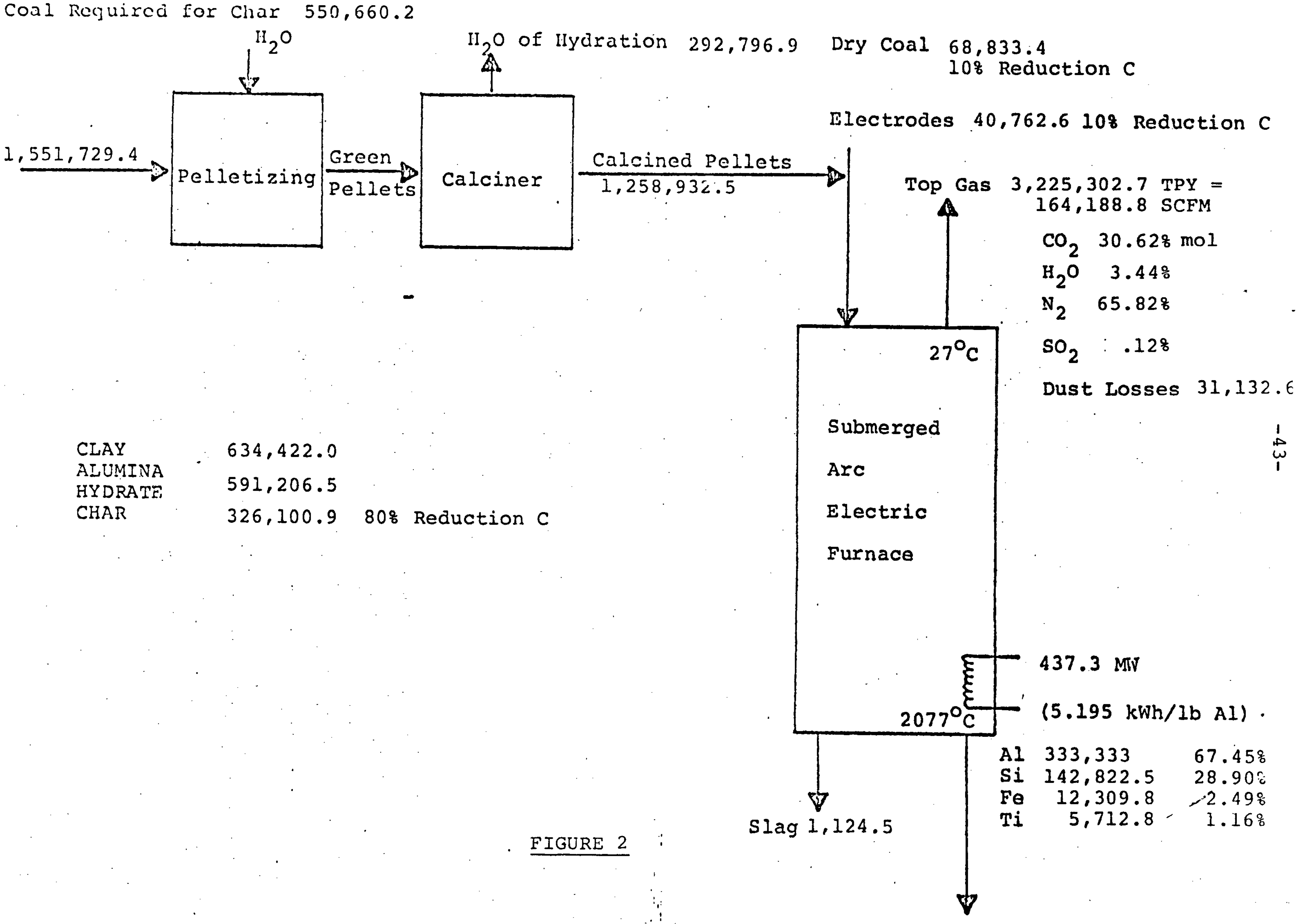


FIGURE 2

SEMI-CLOSED ARC FURNACE 60/30 CASE
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

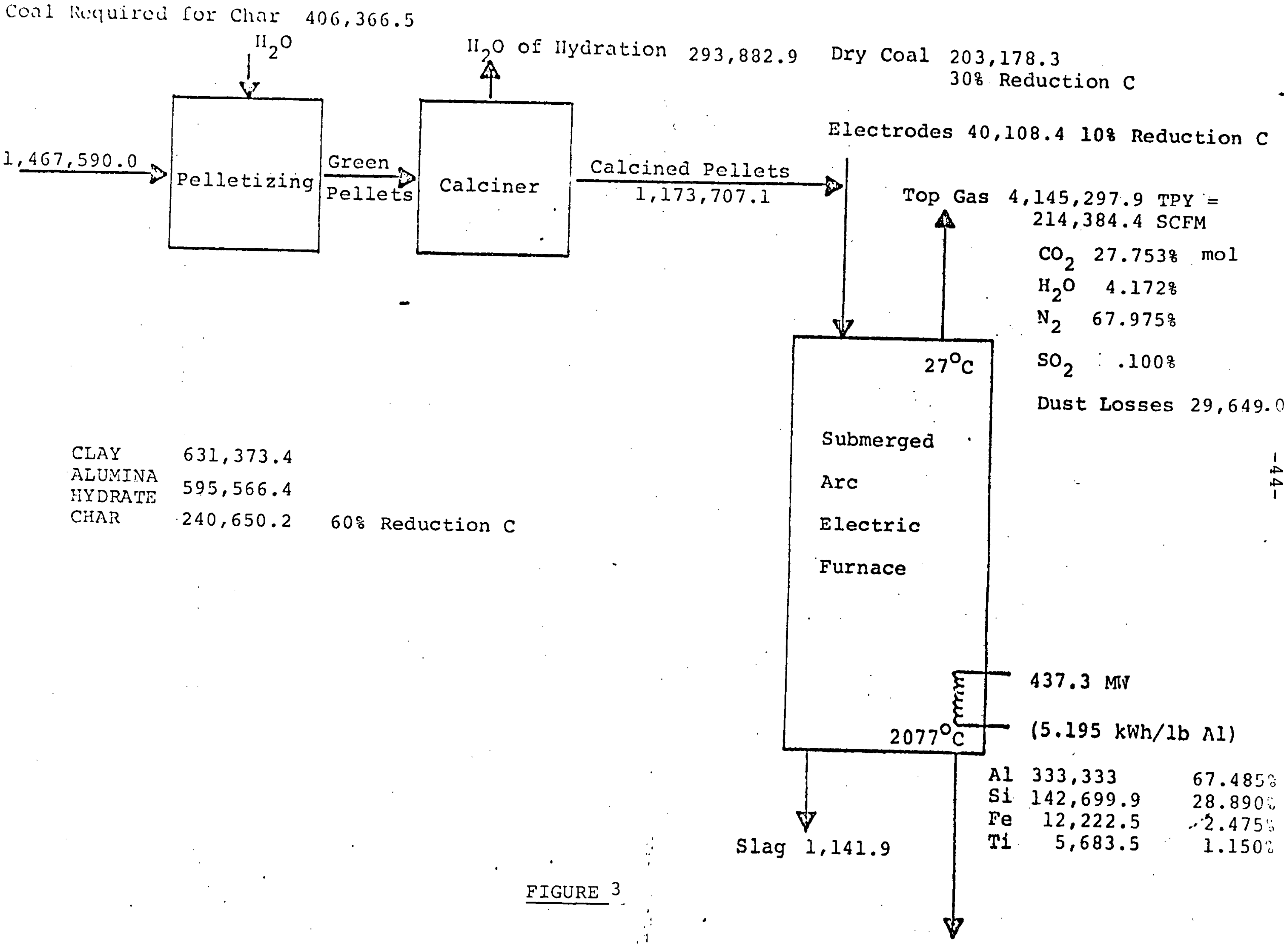


FIGURE 3

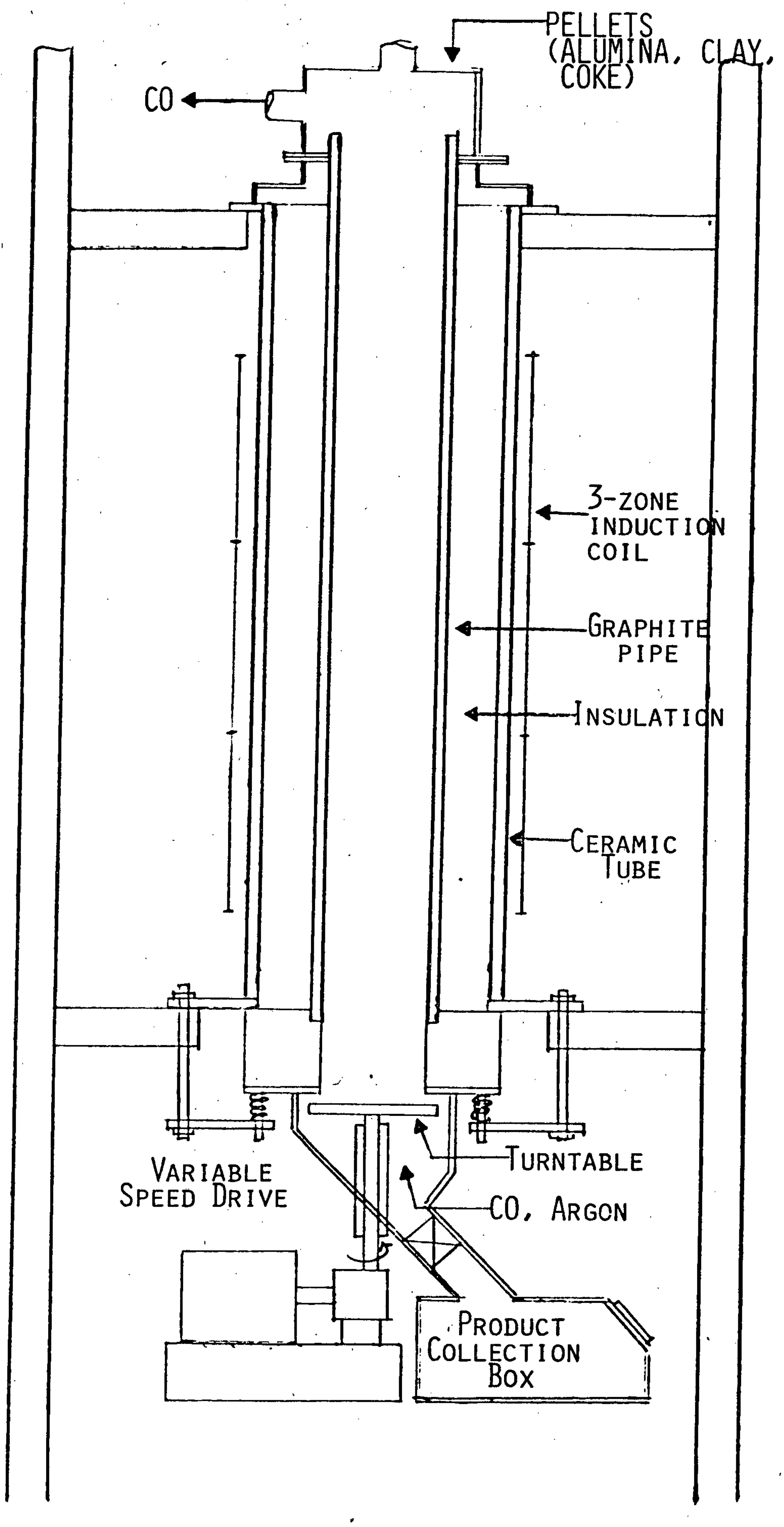


FIGURE 4

VERTICAL SHAFT REACTOR WITH SOLIDS DISCHARGE

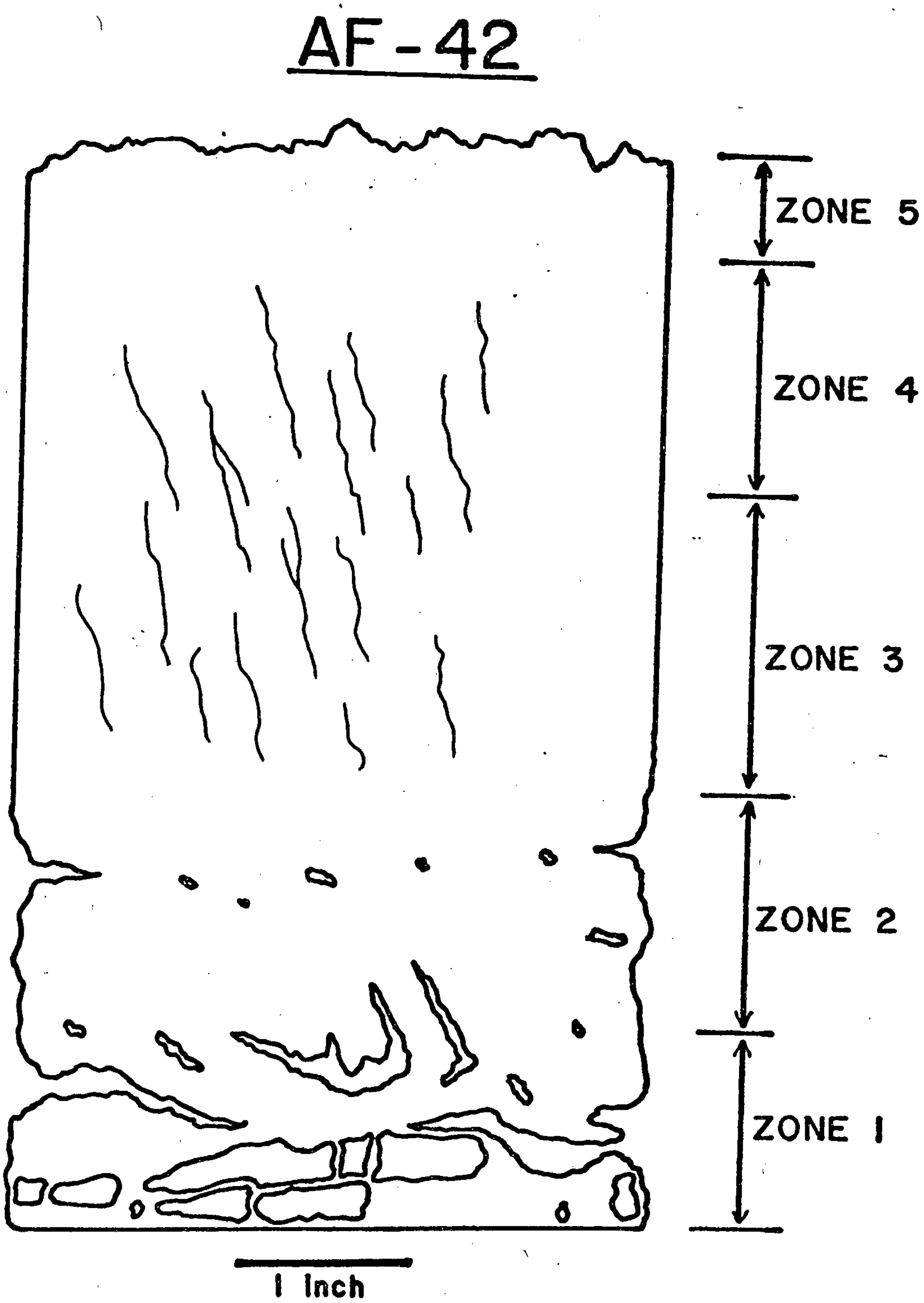


FIGURE 5 Schematic diagram at 1:1 scale of AF-42 ingot showing textural zones.

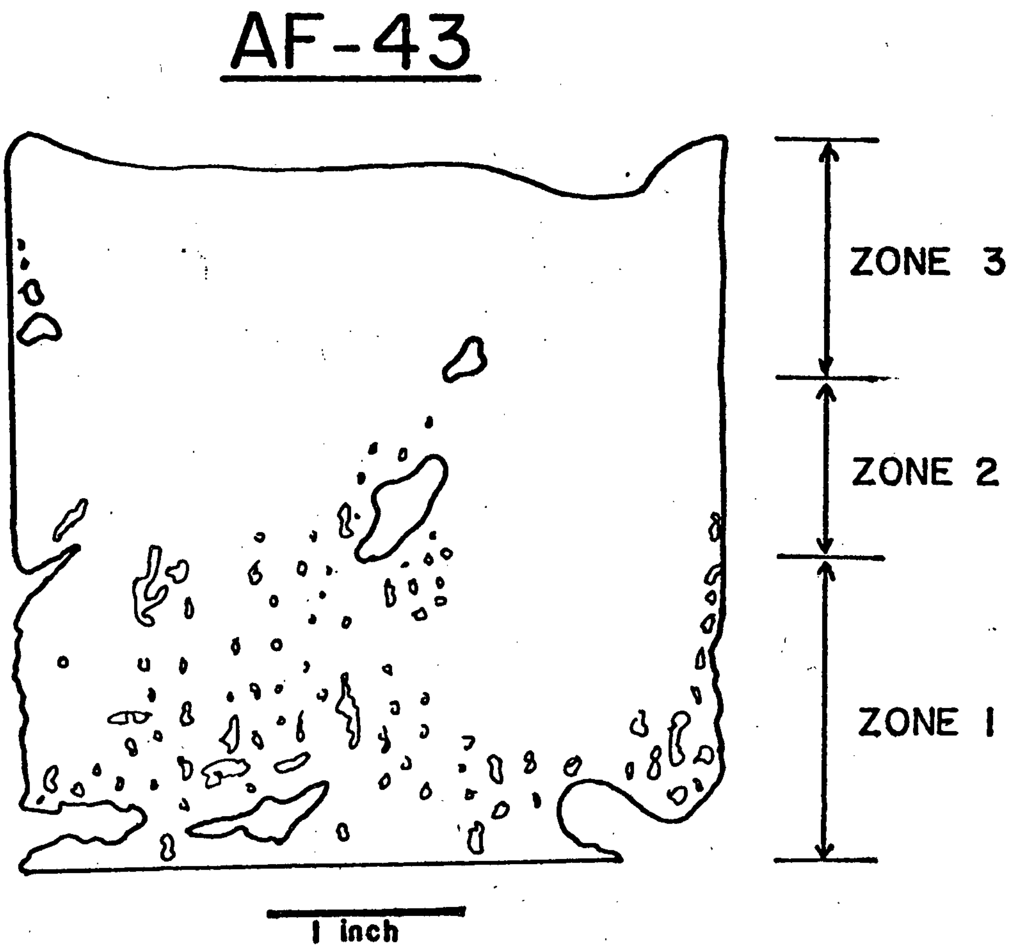


Figure 6 Schematic diagram at 1:1 scale of AF-43 ingots showing textural zones.

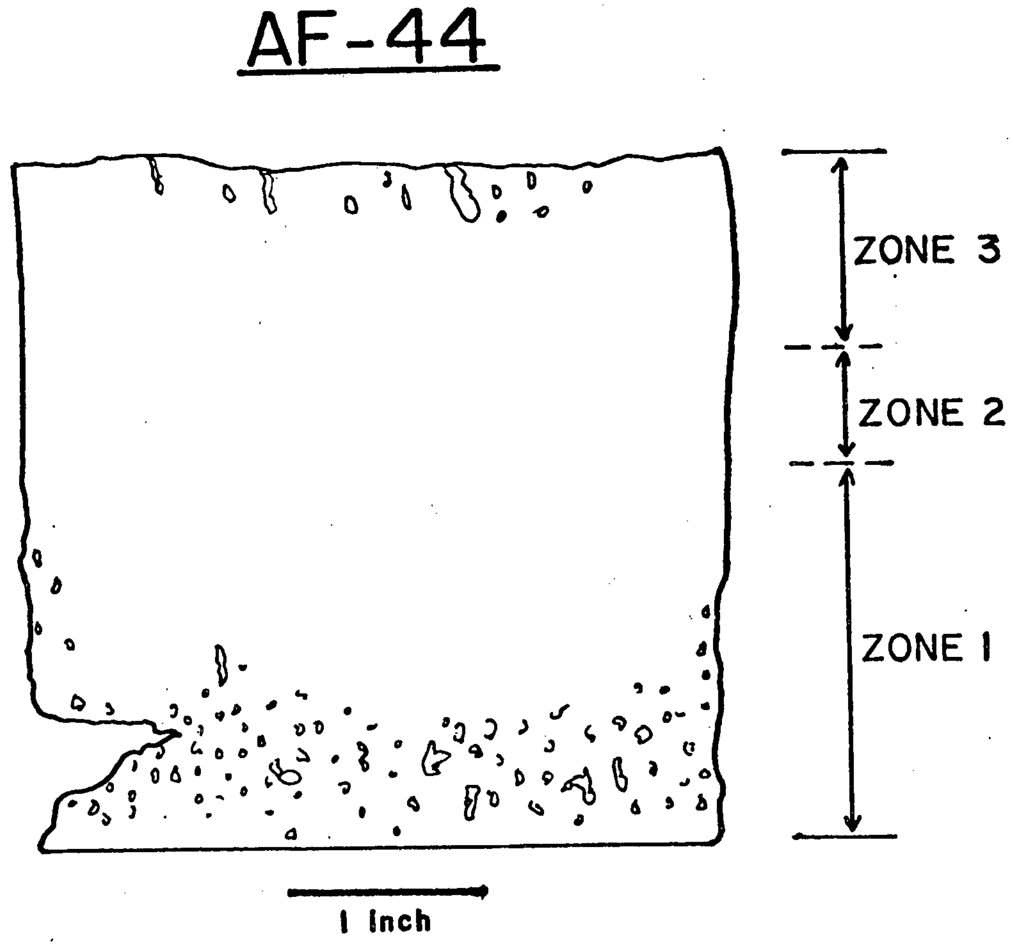


Figure 7 Schematic diagram at 1:1 scale of AF-44 ingot showing textural zones.

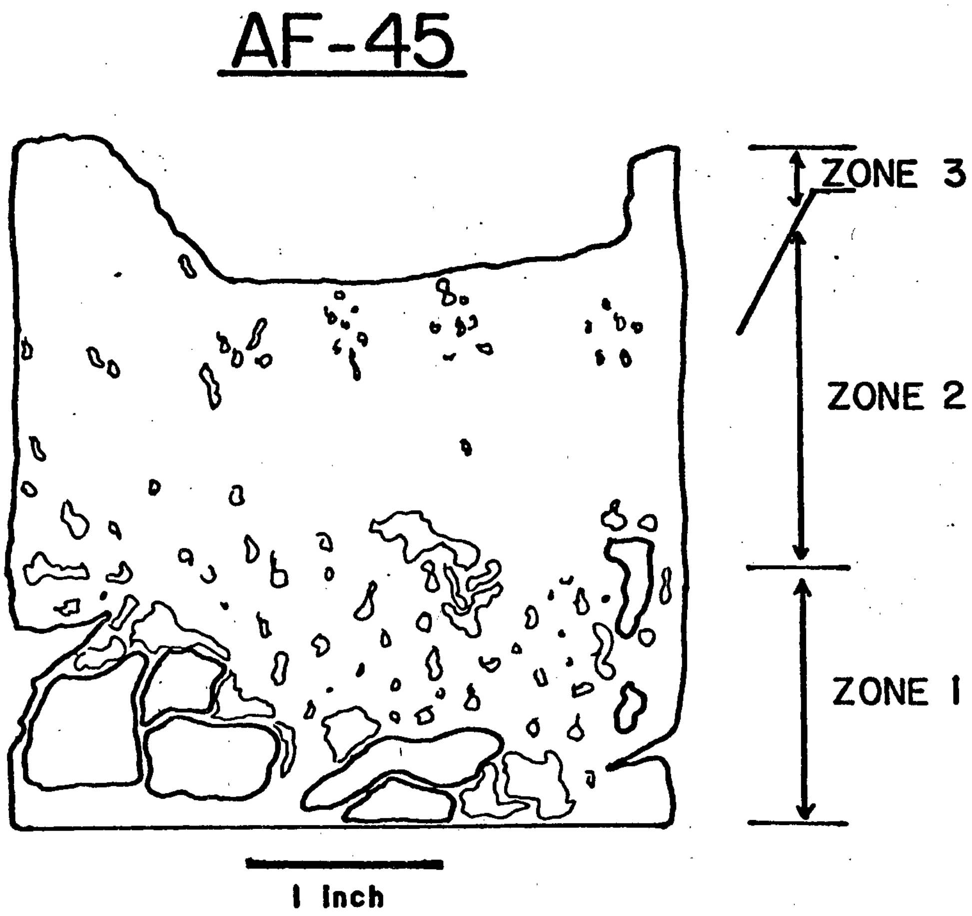
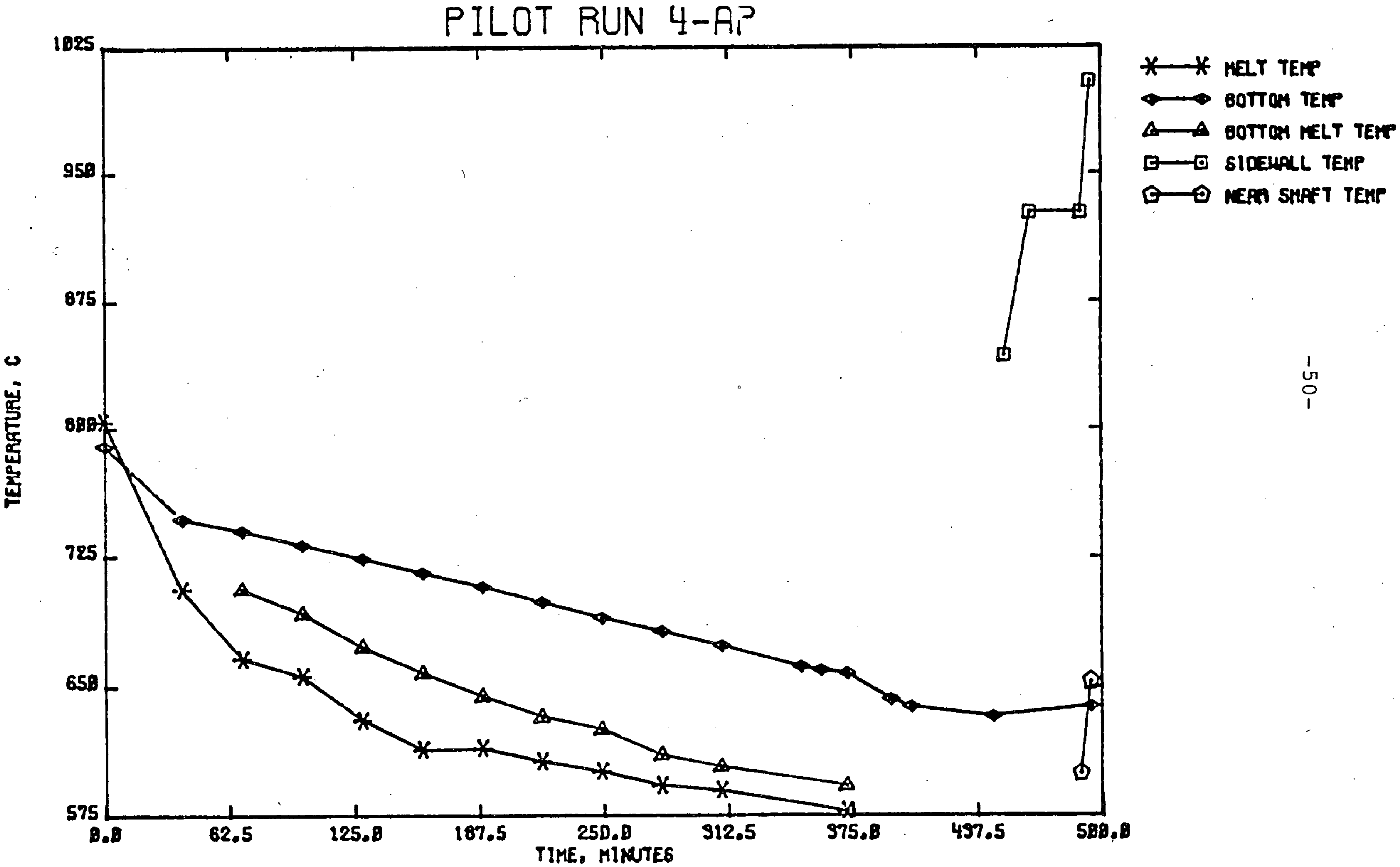


Figure 8 Schematic diagram at 1:1 scale of AF-45 ingot showing textural zones.

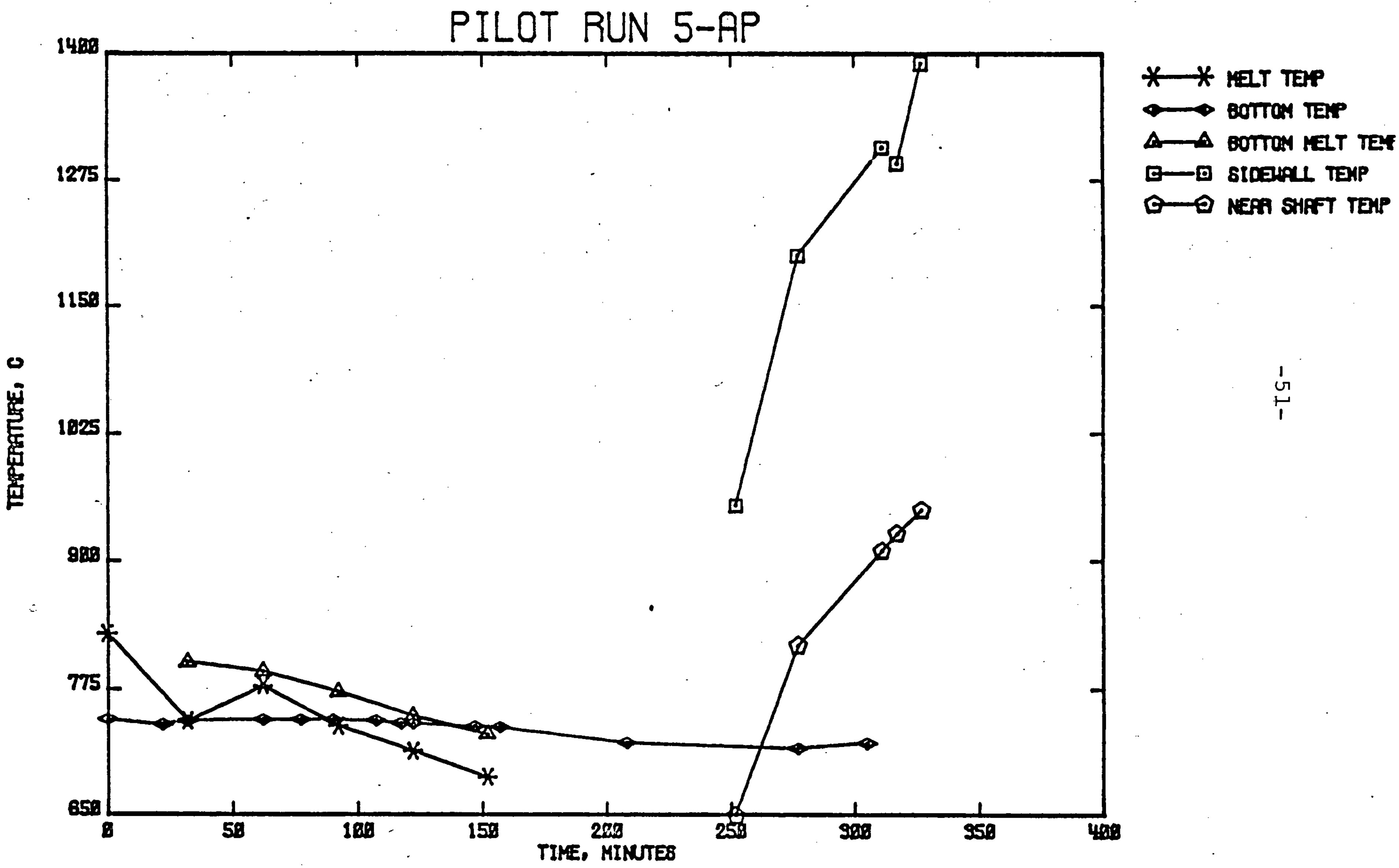
FIGURE 9



TEMPERATURE PROFILE

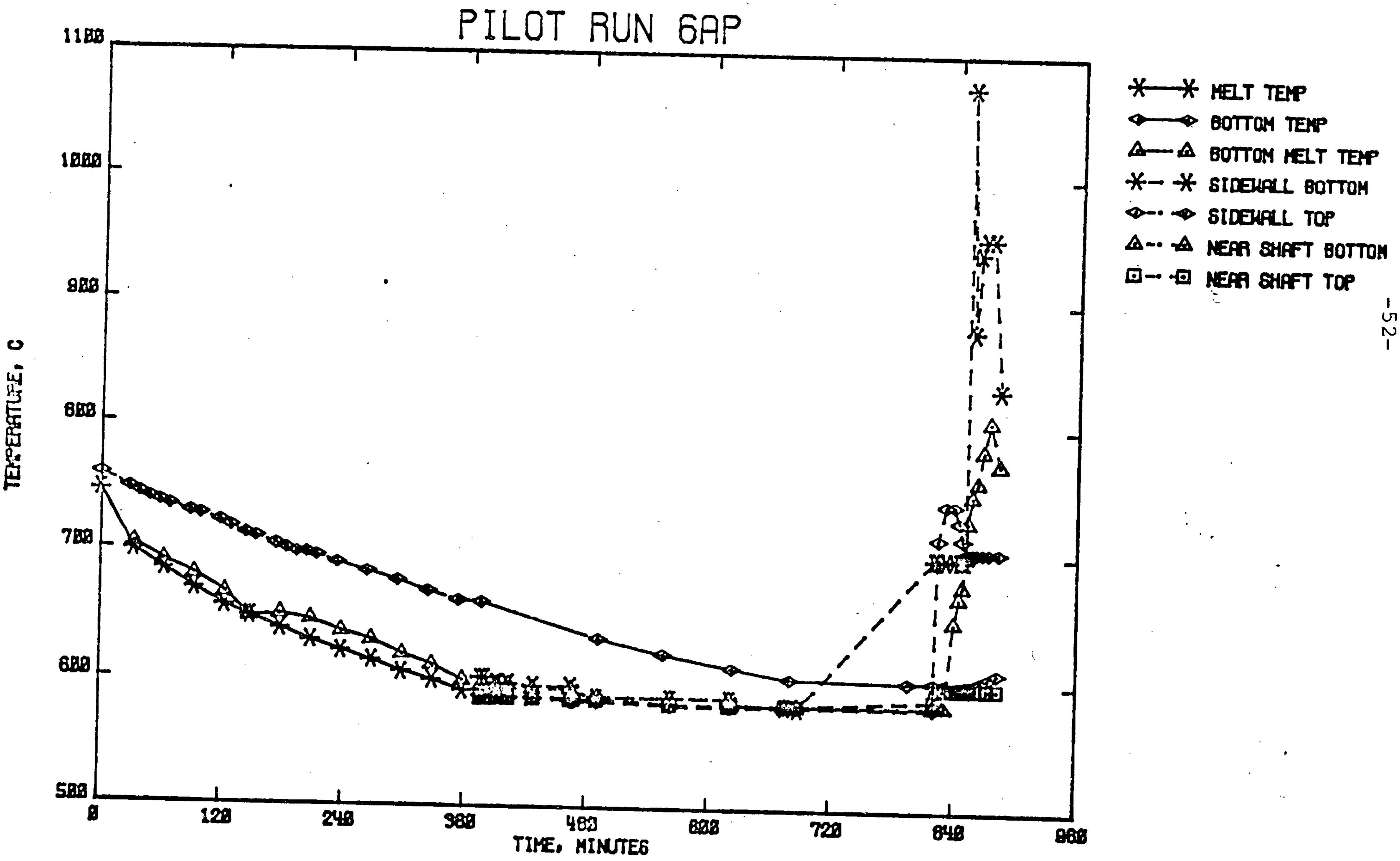
'GO' CRYSTALLIZATION

FIGURE 10



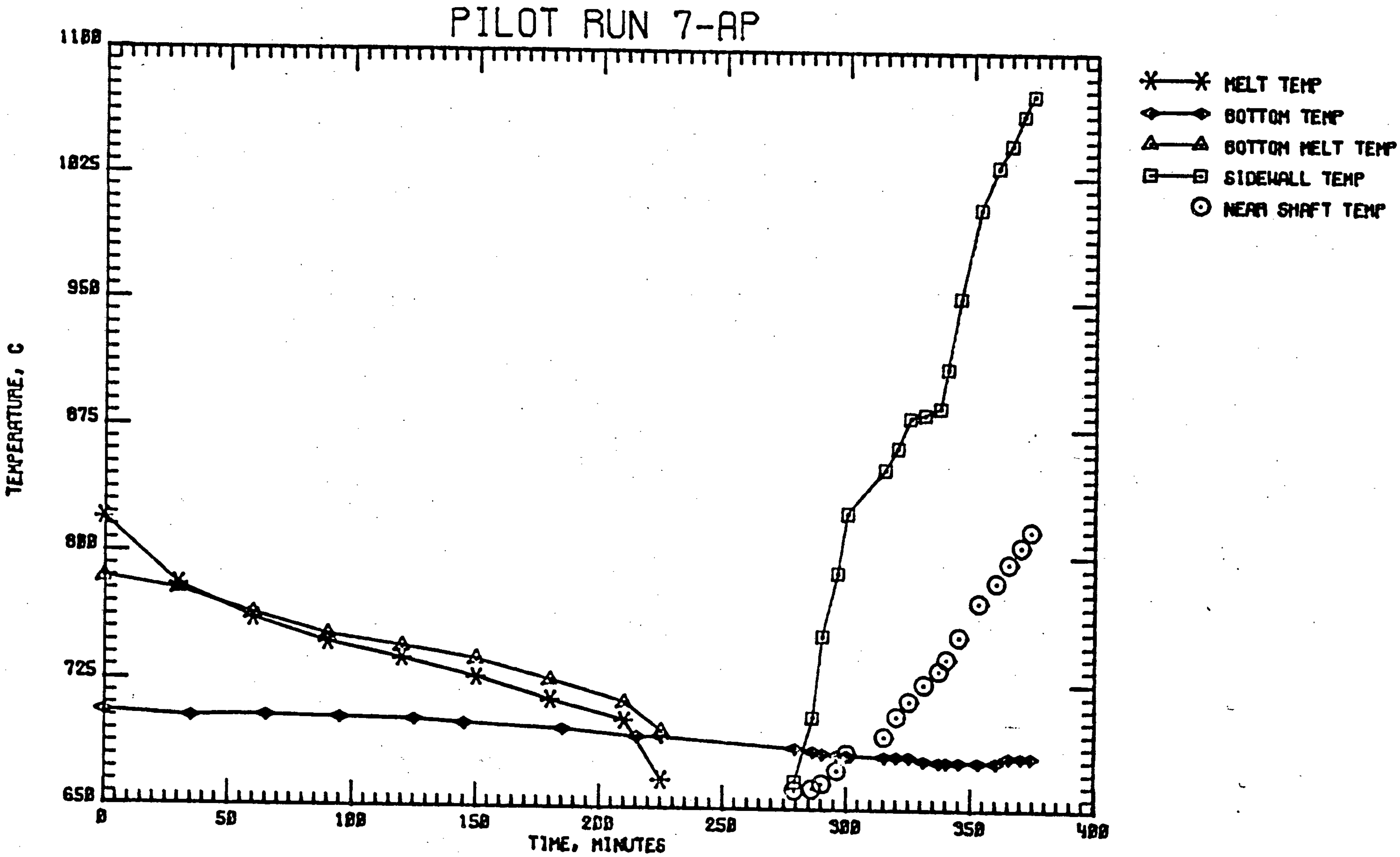
TEMPERATURE PROFILE
'STOP' CRYSTALLIZATION

FIGURE 11



TEMPERATURE PROFILE
'GO' CRYSTALLIZATION

FIGURE 12



TEMPERATURE PROFILE
'STOP' CRYSTALLIZATION

FIGURE 13

AL-SI-FE PHASE DIAGRAM
(AFTER MONDOLFO AND GWYER AND PHILLIPS)

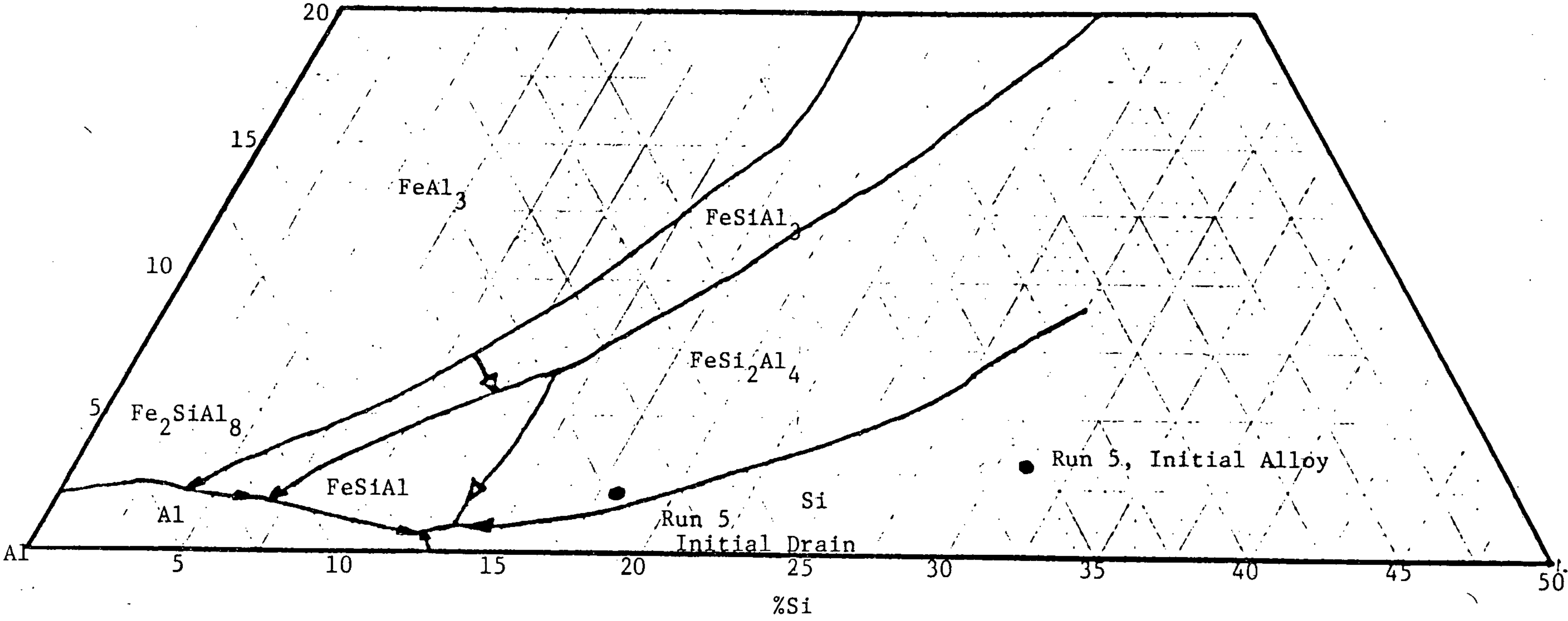
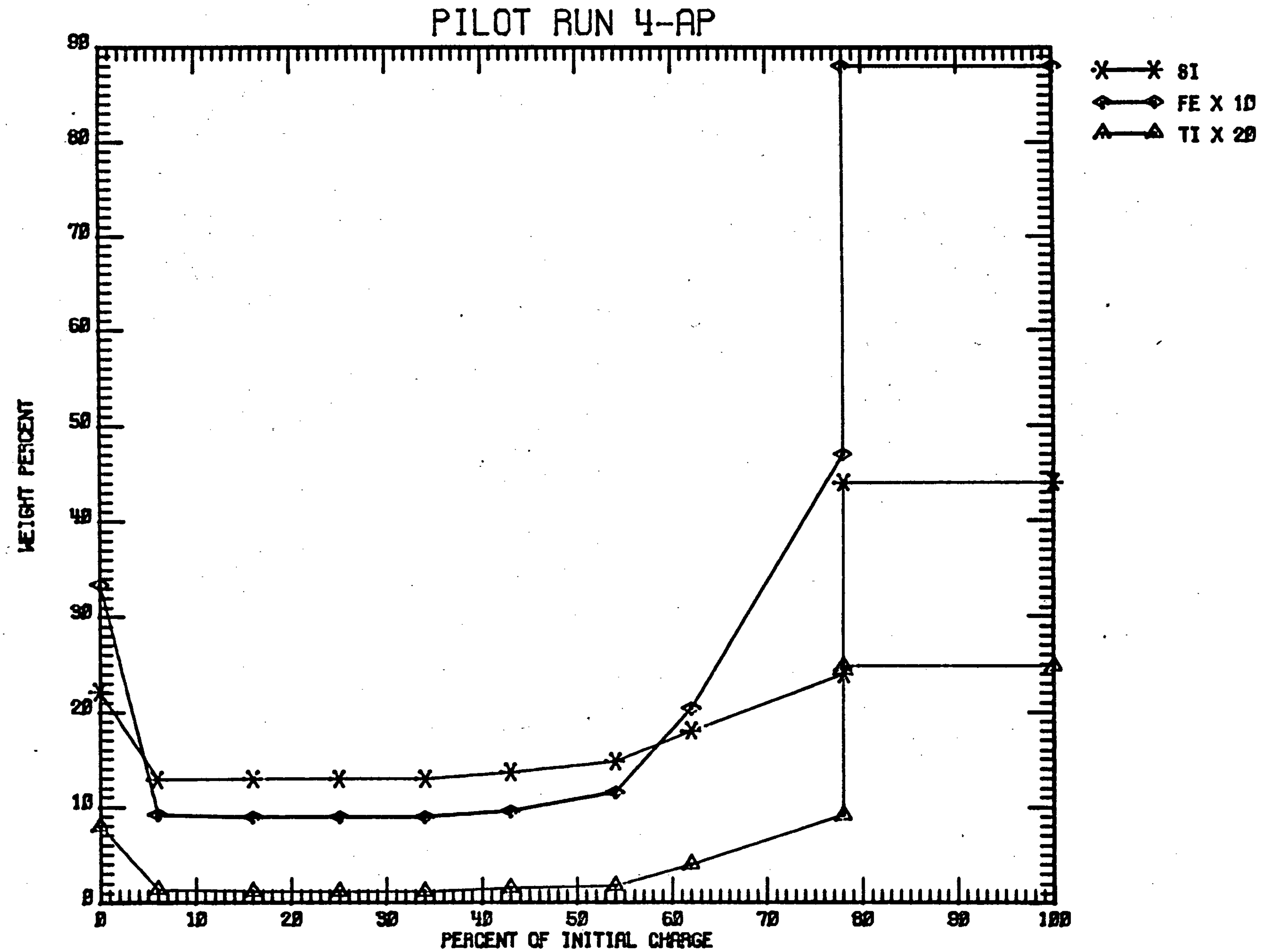


FIGURE 14



ALLOY COMPOSITION VS % INITIAL CHARGE

'GO' CRYSTALLIZATION

FIGURE 15

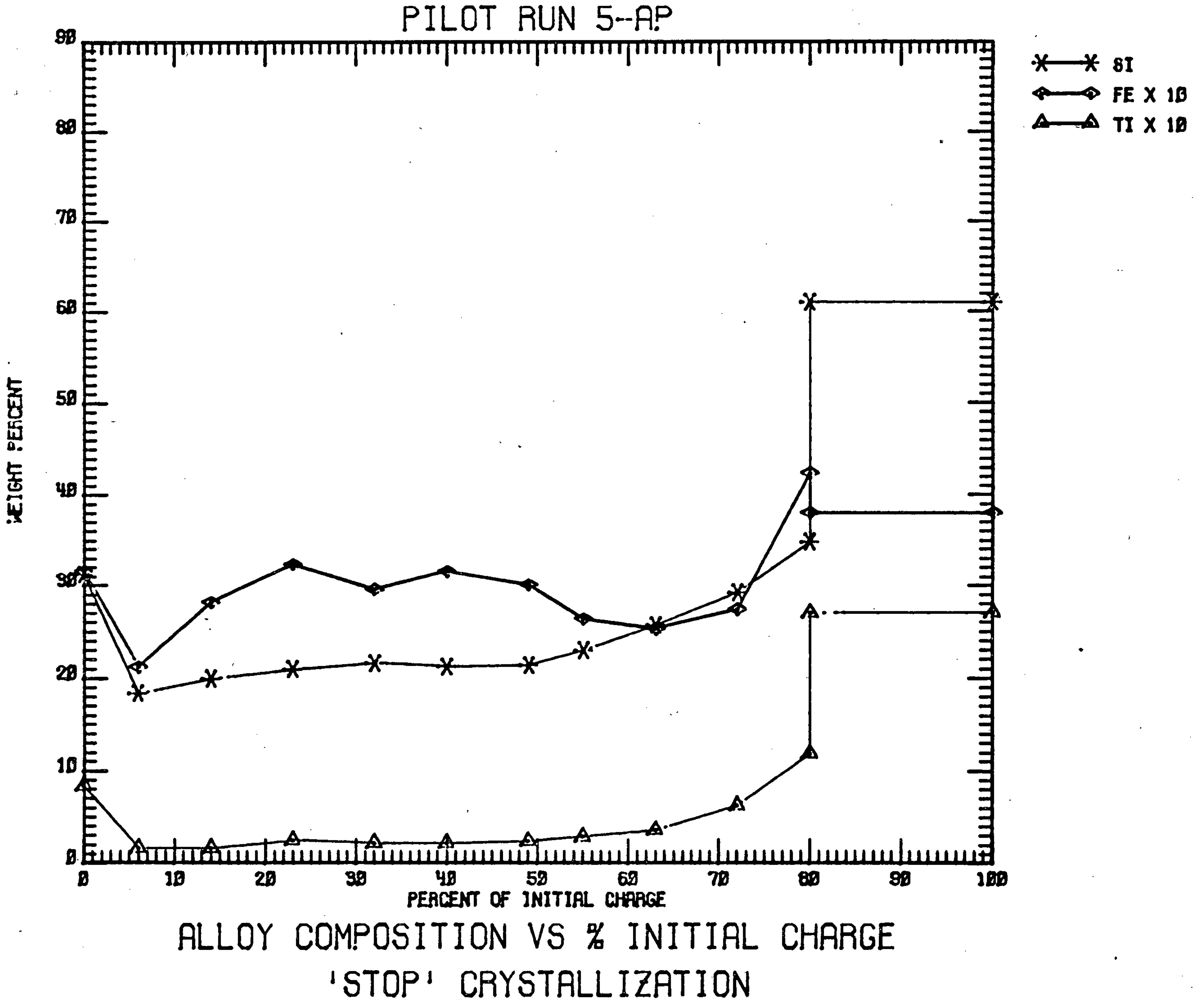
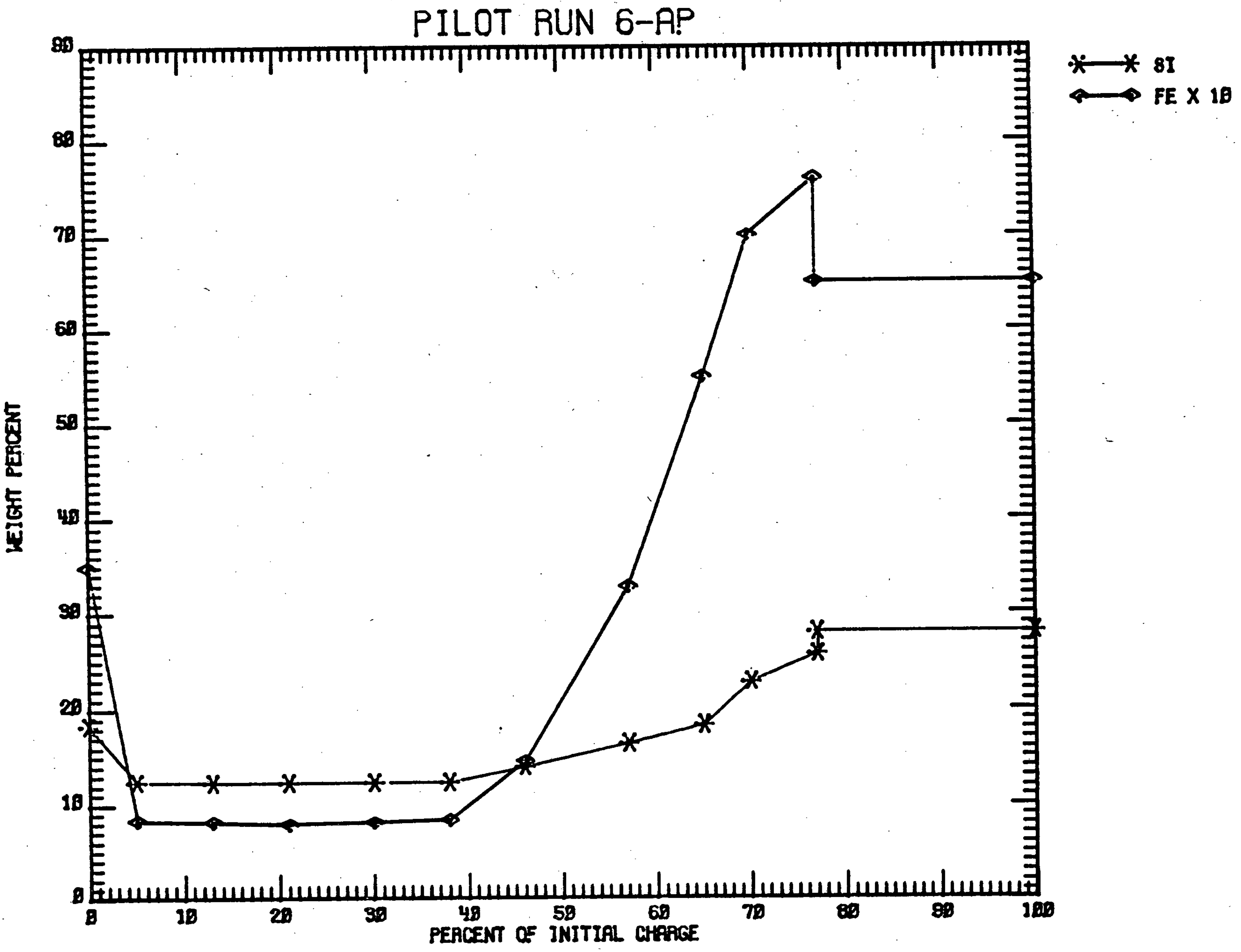

PILOT RUN 5--AP
SI
FE X 10
TI X 10
WEIGHT PERCENT
0
10
20
30
40
50
60
70
80
90
0
10
20
30
40
50
60
70
80
90
100
PERCENT OF INITIAL CHARGE
ALLOY COMPOSITION VS % INITIAL CHARGE
'STOP' CRYSTALLIZATION

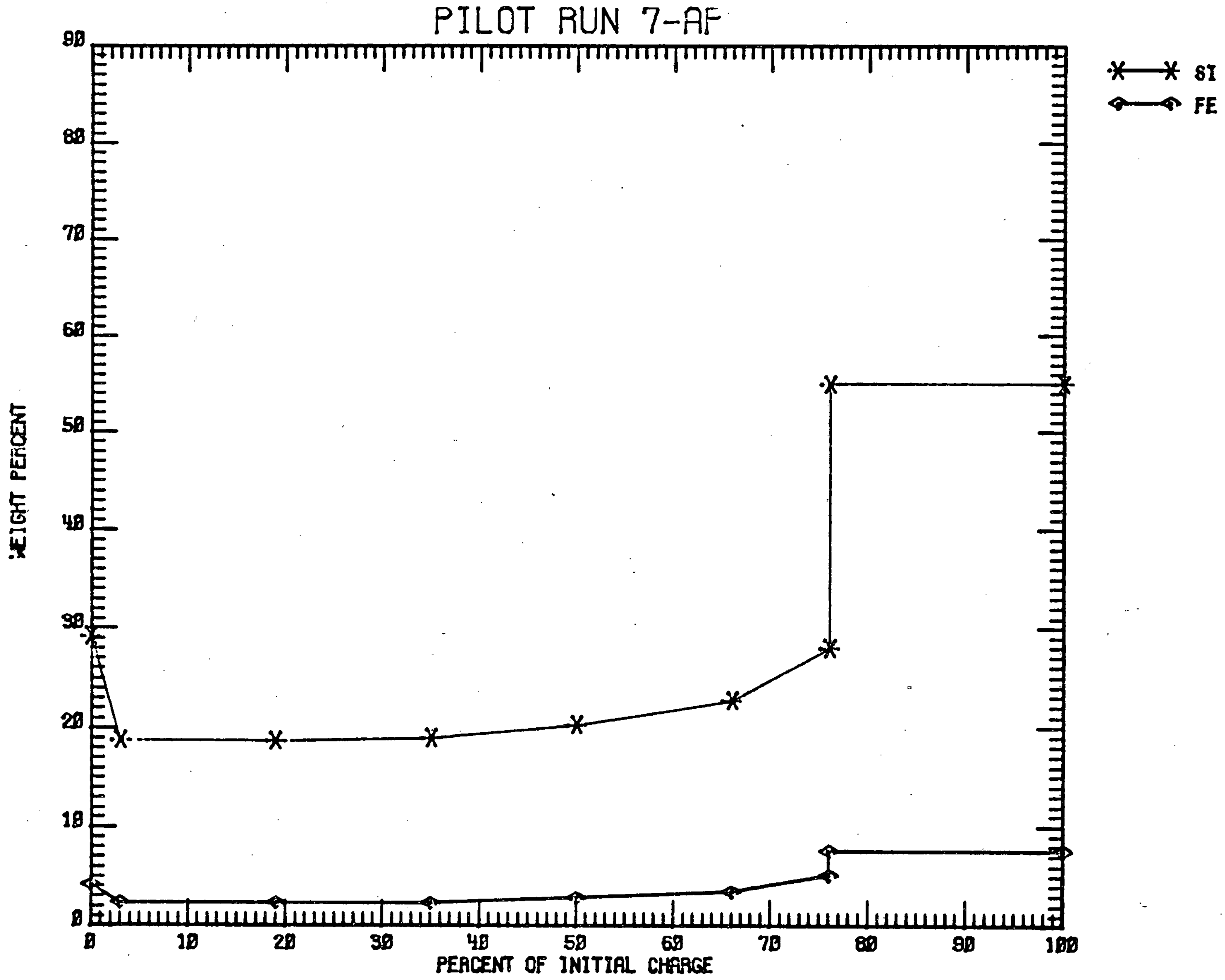
FIGURE 16



ALLOY COMPOSITION VS % INITIAL CHARGE

'GO' CRYSTALLIZATION

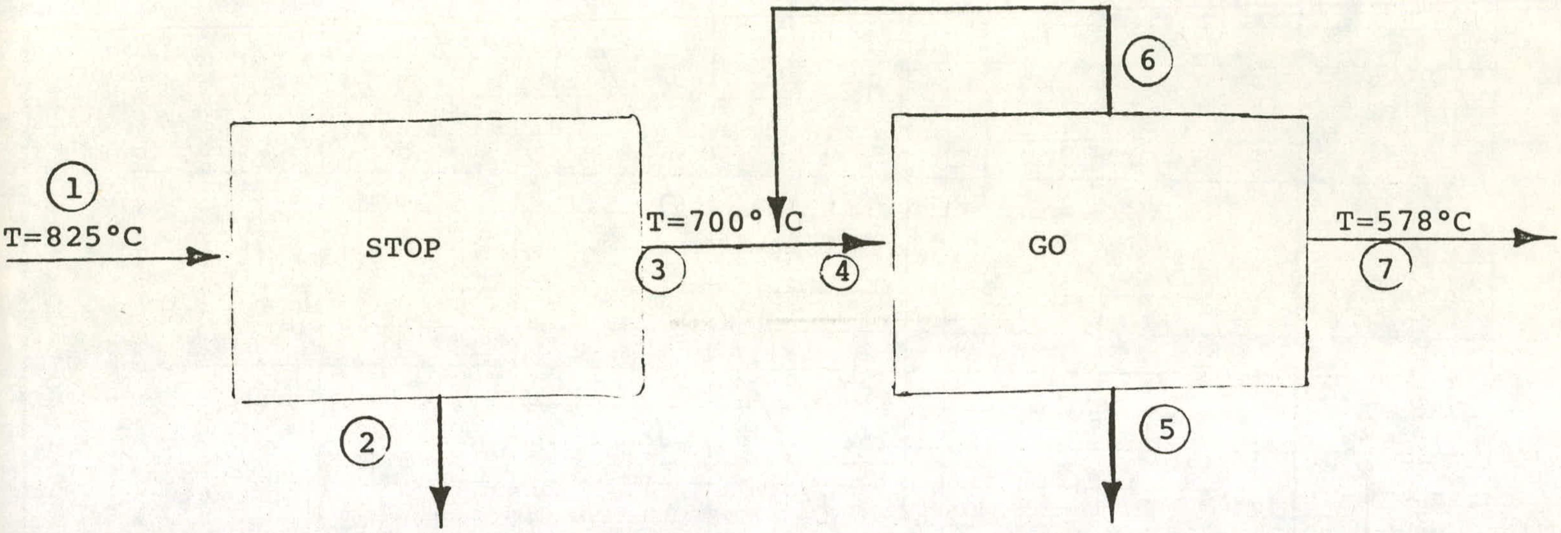
FIGURE 17



ALLOY COMPOSITION VS % INITIAL CHARGE
'STOP' CRYSTALLIZATION

FIGURE 18

TWO STAGE "STOP AND GO" FRACTIONAL CRYSTALLIZATION WITH RECYCLE: Al-30%Si-3%Fe-1%Ti BASED ON 4-AP AND 5-AP



	1	2	3	4	5	6	7
Si	31.2	61.	23.9	22.2	44.0	22.2	13.6
Fe	3.16	3.8	3.00	3.35	8.77	3.88	1.0
Ti	0.84	2.7	0.39	0.40	1.24	0.38	0.08
Yield, Wt.	--	19	81	--	22	22	56
Yield, Al	--	10	90	--	14	22	64

$$\text{Overall Yield} = .90 \times \frac{.64}{1-.22} = .74$$

ATTACHMENT 1

PHASE D COST CHART