PLASMA SMELTING OF SILICON

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SUMMARY

Dow Corning Corporation has been working since 1984 to bring forth new technology aimed at reducing the manufacturing cost of metallurgical silicon. This paper discusses the results of an extensive development effort aimed at a new, plasma-arc technology for smelting of silicon. Three extended tests of more than 50 hours each were made to establish the feasibility of the new process technology. Future work is planned aimed at evaluating various raw material possibilities and then optimizing on the selected ones. Scale-up data must be obtained from these results to move the new technology into commercialization.

INTRODUCTION

The Dow Corning Corporation, a 50/50 joint venture between the Dow Chemical Company and Corning Glass Company, uses large quantities of silicon metal in the manufacture of silicones. Approximately 4,500 different silicone products are made and distributed to over 40,000 customers of Dow Corning. Dow Corning purchases most of its silicon metal needs from the producers who are distributed across the globe. The Springfield, Oregon plant which has a 25,000 kVA submerged arc electric furnace manufactures a portion of Dow Corning's silicon metal for captive use. The purchase of this plant in 1979 launched an effort aimed at improving silicon manufacturing technology and reducing production costs within Dow Corning. In 1984, a new department was formed to bring new technology from concept to commercialization. It is through the efforts of the Engineers and Scientists in this department that the new silicon smelting concepts being described in this paper have evolved. This technology for smelting silicon is being jointly developed by the Dow Corning Corporation and Voest-Alpine. In this joint development, the expertise of Dow Corning in silicon smelting technology is combined with the expertise of Voest-Alpine in transferred-arc plasma technology.

EXISTING SMELTING PROCESS

Typically, silicon is produced in a submerged electric arc furnace via the carbothermic reduction of silicon dioxide by a mixture of solid carbonaceous reducing agents such as coal, coke, woodchips or charcoal. The overall reduction reaction can be represented as:

$$SiO_2+2C = Si+2CO \qquad (1)$$

The two key intermediates essential for the production of silicon are silicon monoxide and silicon carbide. The reaction being:

$$SiO+SiC = 2Si+CO \qquad (2)$$

and

$$SiO_2+2SiC = 3Si+2CO \qquad (3)$$

Silicon monoxide is produced by the reaction of SiO_2 with carbon, silicon carbide, or silicon, according to the following reactions:

$$SiO_2+C = SiO+CO \qquad (4)$$

$$2SiO_2+SiC = 3SiO+CO \qquad (5)$$

$$SiO_2+Si = 2SiO \qquad (6)$$

Silicon carbide is produced by the reaction of carbon with SiO_2 or SiO, as shown below:

$$SiO_2+3C = SiC+2CO \qquad (7)$$

$$SiO+2C = SiC+CO \qquad (8)$$

In a submerged arc furnace process as shown in Figure 1, a stoichiometric mixture of carbon and silica is added to the top of the furnace. As the mixture descends down, silicon monoxide and silicon carbide are formed according to reactions (4) through (8). Production of excessive silicon monoxide that does not react with carbon or condense in the furnace results in loss of silicon recovery. The most dominant reaction for production of silicon monoxide in the upper zone of the furnace is by equimolar reaction of quartz with carbon according to reaction (4).

In a typical arc furnace operation, silicon recovery accounts for 75%-85% of the inbound silicon in quartz. The remaining 15%-25% exits the furnace in the form of SiO which oxidizes to SiO_2 upon coming in contact with air. Present arc furnaces for silicon production are also very inefficient from the standpoint of energy utilization. Only 31% of the total energy input to the furnace, both in the form of electrical energy and chemical energy from the reductants (coal, coke, woodchips), is used for reduction of quartz. The remaining 69% of the energy is lost, most of which is in the form of by-product off-gas accounting for up to 52.5% of the input energy in BTU value.

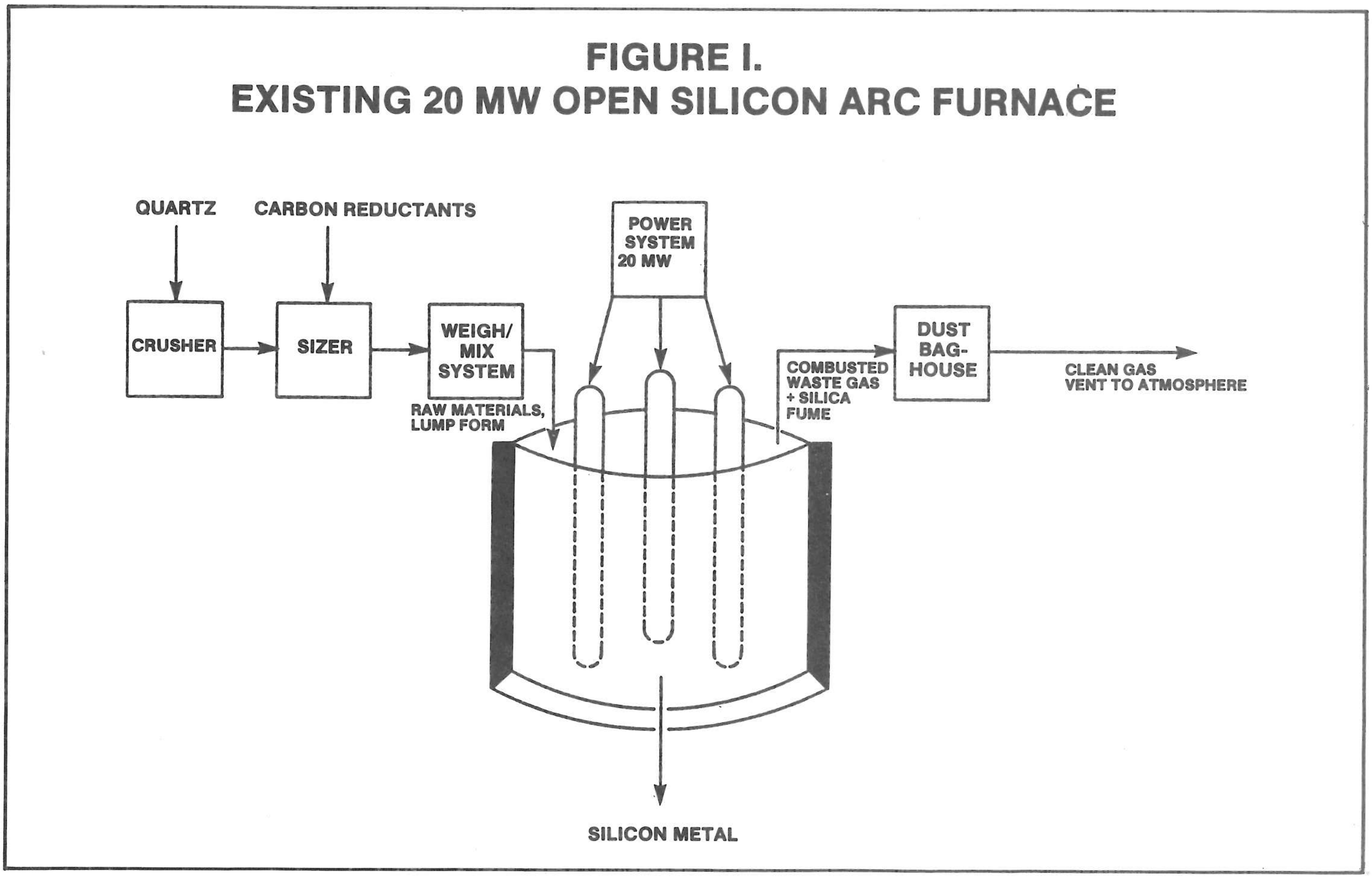

FIGURE 1
Existing 20 MW OPEN SILICON ARC FURNACE

NEW PLASMA SMELTING PROCESS

The plasma smelting concept involves producing silicon by the reaction of silicon dioxide with silicon carbide in a shaft reactor. The plasma torches are introduced through the side of the reactor. This configuration allows loading the reactor with stoichiometric amounts of carbon. The initial feed to the reaction zone is essentially an equimolar mixture of SiC and SiO_2. Upon applying energy with a plasma, silicon is produced along with SiO and CO by the reaction of SiO_2 with SiC. The gaseous SiO, upon passing the shaft filled with carbon, reacts to form SiC and CO. The converted silicon carbide is mixed with an equimolar quantity of SiO_2 and the mixture is stoked down into the plasma reaction zone. The shaft is then reloaded with two moles of carbon. By feeding the quartz and carbon separately in the plasma process, the SiO generation by reaction (4) is eliminated, thus minimizing any loss of Si as SiO.

The plasma approach to smelting silicon using a closed reactor also allows the recovery of the energy contained in the furnace off-gas. The BTU value of the off-gas energy amounts to approximately 50% of the total energy input to the silicon smelting process [1].

A schematic of a proposed plasma furnace is shown in Figure 2.

This technology is covered by U.S. patent 4,680,096 [2] and patent application no. DC3056 [3].

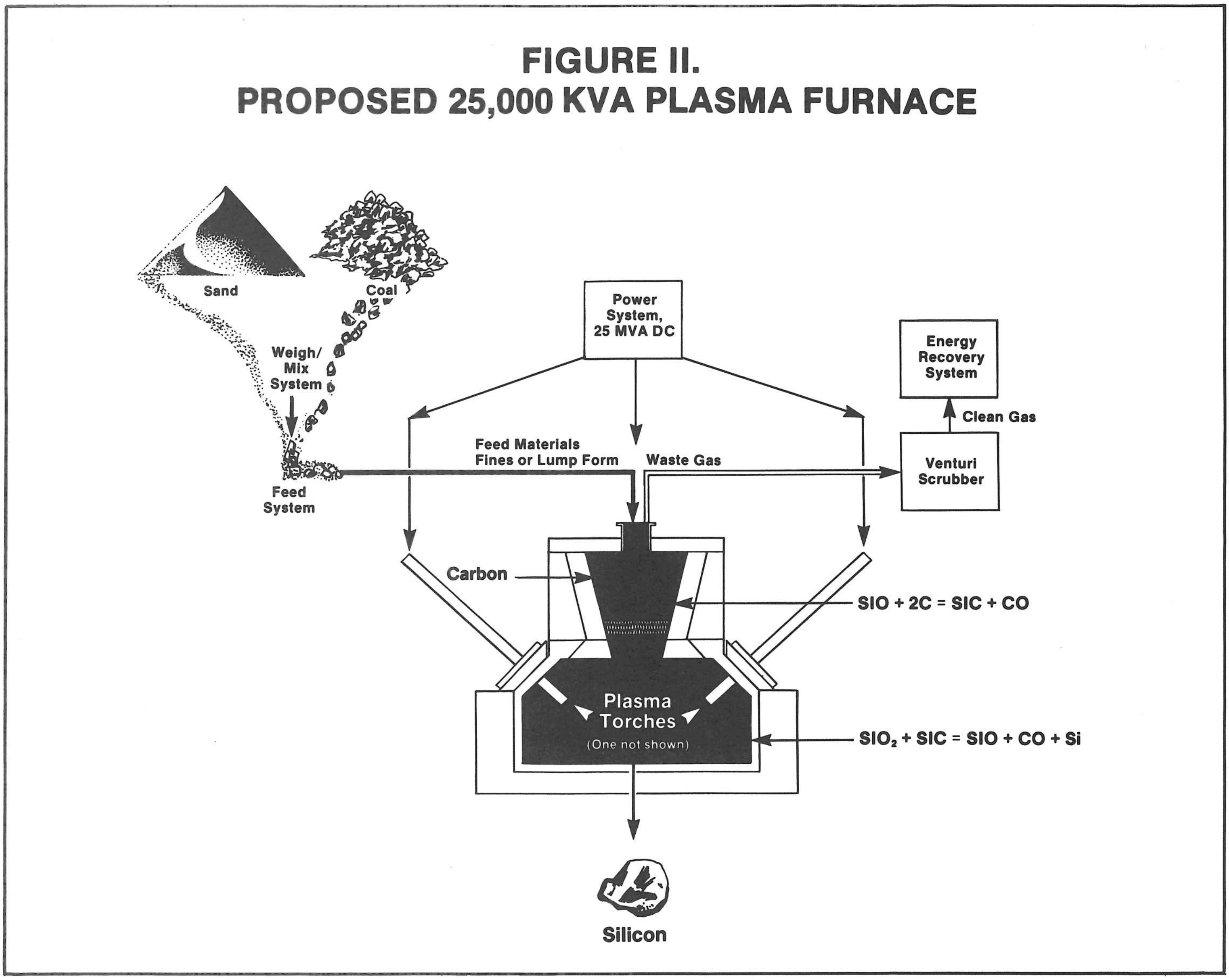

FIGURE 2
PROPOSED 25,000 KVA PLASMA FURNACE

BACKGROUND ON PLASMA-ARC

The novel concept of smelting silicon was demonstrated using Voest-Alpine's direct current transferred arc plasma torch. The plasma arc is formed between the tungsten cathode in the torch and the furnace charge which is in contact with the bottom electrode (anode). The torch jacket and the cathode are water cooled. Argon is normally used as the plasma gas. The plasma arc is initiated using a non-transferred direct current pilot arc. Once the space between the cathode and the anode becomes conductive by the pilot arc, the main arc is ignited and the pilot arc is switched off. The achievable active power with the plasma torches range from 20kW to 7.5 MW.

SMELTING RESULTS

The initial tests for smelting silicon in a plasma reactor were aimed at demonstrating the reactor and plasma operation for a 60-hour period without damaging the reactor. Due to refractory meltdown during earlier tests, the shaft smelting concept could not be evaluated due to the plugging of the taphole with solidified refractory. Once the reactor improvements were accomplished by using novel high temperature materials of construction, the refractory meltdown problems were solved. Water leaks from the plasma torches were a handicap during the early tests. As the torch operation improved, it was possible to produce silicon. Significant improvement in silicon recovery was achieved by improving the reactor design with respect to the dimensions of the carbon shaft and by controlled energy distribution into the plasma zone and the carbon shaft.

Three test results with improved reactor design are reported. The first successful test was of 53-hour duration. The test was started with a plasma torch operating at a flow rate of 900 litres/hour of Argon. The flowrate was maintained for the entire test. An equimolar mixture of Si/SiO_2 was added to the plasma zone and charcoal was placed in the shaft of the reactor. Upon conversion of the charcoal to silicon carbide after 7.5 hours of operation, one mole equivalent of SiO_2, for each 2 moles of carbon placed in the shaft, was mixed with the converted silicon carbide and pushed into the plasma reaction zone. This procedure was repeated every 2 to 3 hours of operation. The carbon theory for the entire test was maintained at 90% and silicon was first tapped after 13 hours of operation. A total of 37 kg silicon was produced. During the stable operation of the last 13-hour period the silicon yield was 88.3%. Silicon was tapped every two hours with 180-200 kWH energy input. A plot of arc current and voltage vs. time for the period of 41-53 hours is shown in Figure 3. During this stable operating period, the arc voltage was maintained between 90-120 volts. The corresponding arc current was controlled to be between 1000-1200 amps. The figure also shows the down times for torch inspection and charging of raw materials. The plot of power input and cumulative kWH input vs. time for the same period is shown in Figure 4. The power input was maintained between 100-120 kW. The total power input for the test was over 4000 kWH.

The off-gas samples were periodically collected during a smelting cycle. The off-gas composition provided a means to determine instantaneous silicon production rate. The gas samples were analysed for it's composition using a gas chromatograph. Based on known flow rate of argon into the reactor, the CO production rate was calculated from the composition of the off-gas sample. A typical off-gas sample composition over a smelting cycle is plotted in Figure 5. From the calculated CO production rate the silicon production rate was calculated. The results when compared to tapped silicon give a good correlation.

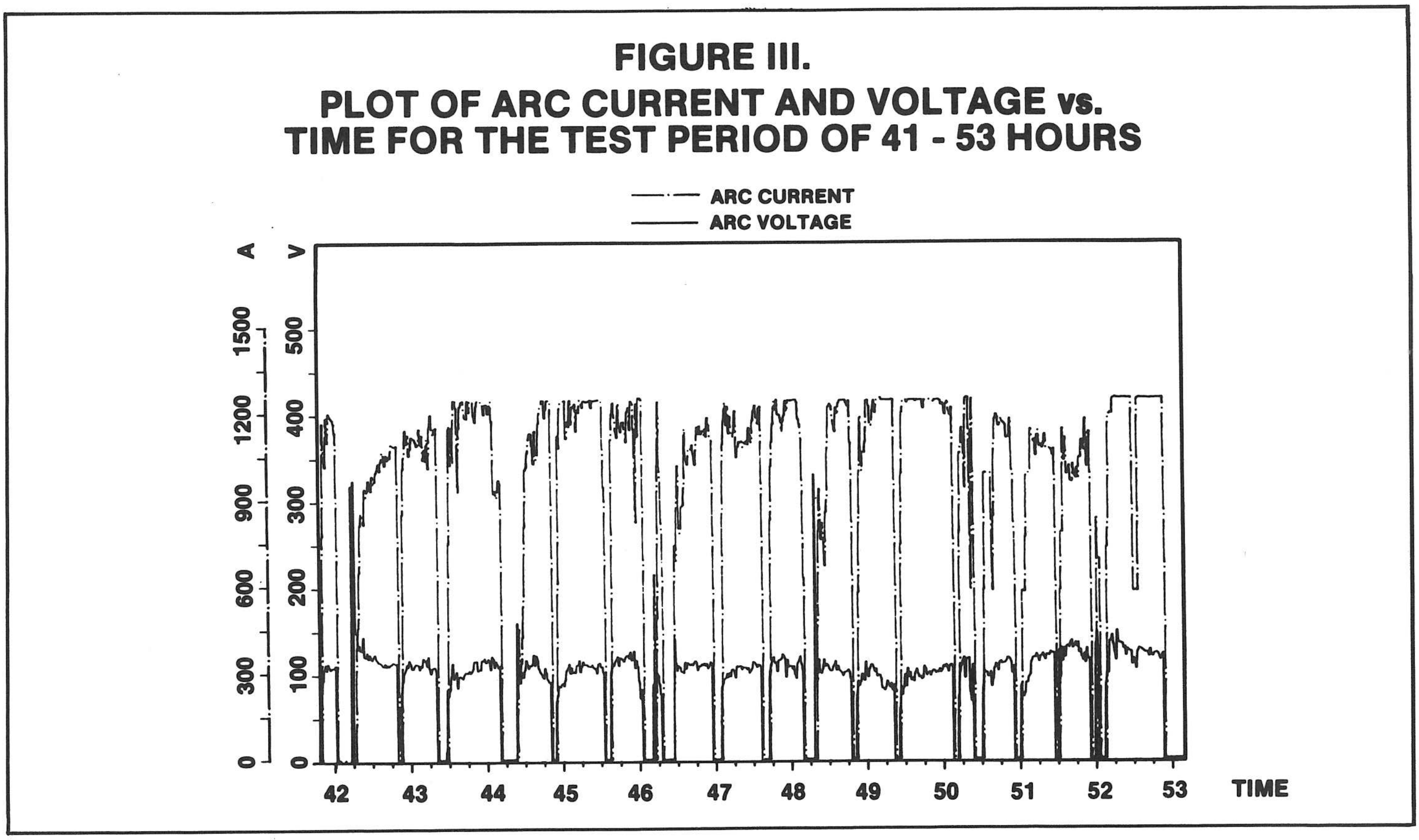

FIGURE 3
PLOT OF ARC CURRENT AND VOLTAGE VS. TIME FOR THE
TEST PERIOD OF 41-53 HOURS

FIGURE IV.

PLOT OF POWER INPUT AND CUMULATIVE kWH INPUT vs. TIME FOR THE TEST PERIOD OF 41 - 53 HOURS

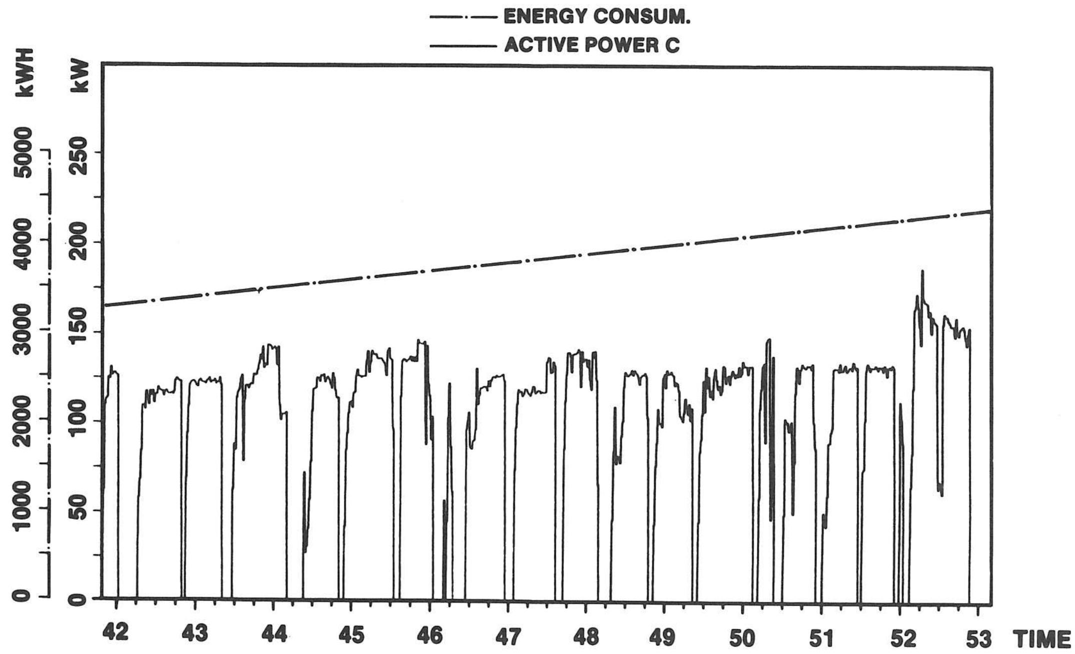

FIGURE 4
PLOT OF POWER INPUT AND CUMULATIVE kWH INPUT VS.
TIME FOR THE TEST PERIOD OF 41 to 53 HOURS

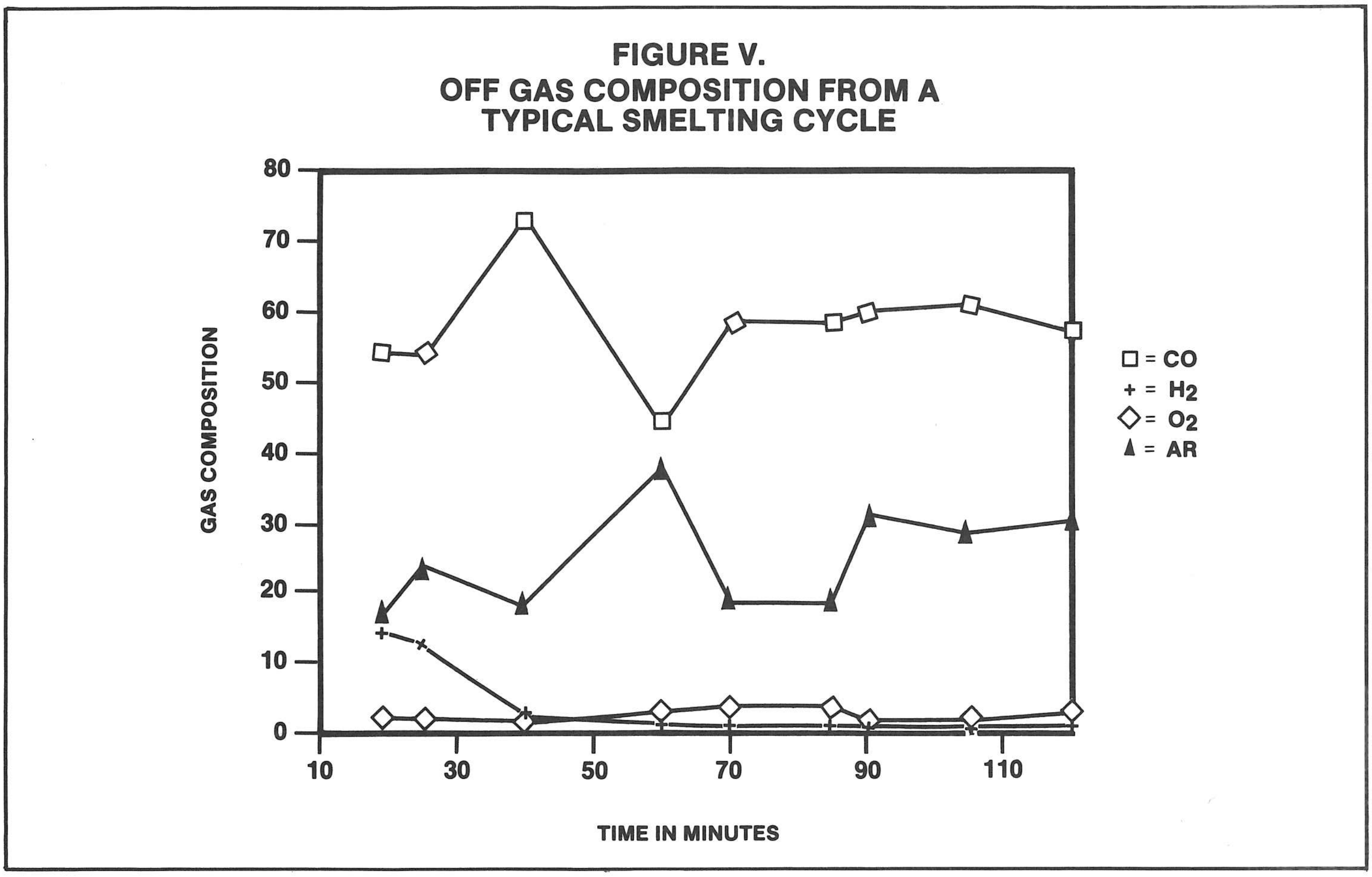

FIGURE 5
OFF-GAS COMPOSITION DURING A
TYPICAL SMELTING CYCLE

The second test was of 68-hour duration. A total of 41 kg silicon was tapped during the test. A silicon recovery of 91% was recorded for the last 10 hours of operation. The energy consumption during this period was 54 kWH/kg at a silicon production rate of 2.9 kg/hour. The energy input rate for the test averaged 88 kW.

For the third test, 42 kg silicon was produced over a 56-hour period. The average energy input for this test was 97 kW. A silicon recovery of 80% was recorded during the last 16 hours of operation. The energy consumption during this period was 56 kWH/kg at a silicon production rate of 1.57 kg/hour.

FUTURE WORK

Future work will be aimed at obtaining a statistical baseline with the present raw materials and evaluating the feasibility of using lower cost materials such as petroleum coke. Other areas of recognized cost improvement are represented by use of cheaper raw materials such as sand and carbon fines.

As progress is made in the above-cited areas with the 200 kW reactor, effort is being made to obtain scale-up information necessary for successful commercialization of the technology.

CONCLUSIONS

The feasibility of smelting silicon using a new plasma smelting process concept was successfully demonstrated. Silicon recovery in excess of 90% was achieved during the stable operating period. Plasma smelting of silicon provides a unique opportunity for smelting of metallurgical silicon in a novel configuration allowing silicon recovery in excess of 95%.

As is the case with the development of any new technology, challenges presented have to be overcome for a commercialization of the technology.

Continuous feeding and mixing of materials and improvement of thermal efficiency for operating with plasma are the two most significant issues. Effort is underway to address and resolve these issues.

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