

## Appendix B

### Pilot scale excavations

Further information about the state of the furnace is available from careful excavations after the run. Schei and Sandberg smelted silicon and ferrosilicon in a 50 kW one-phase furnace with one electrode and bottom contact (Schei, 1967; Schei and Sandberg, 1966). A summary of several excavations is given in Figure B.1. The intention was to operate the furnace in the same way as an industrial furnace, but owing to the small size, some modifications were necessary. The following cycle is typical: the furnace was filled with charge; the charge was heated for some time; produced metal was tapped; the upper layer of the charge was stoked down by wooden stokers; the furnace was charged again; etc. Most of the time, the gas rose smoothly from the surface. It contained some white fumes, which became increasingly apparent with time from charging.

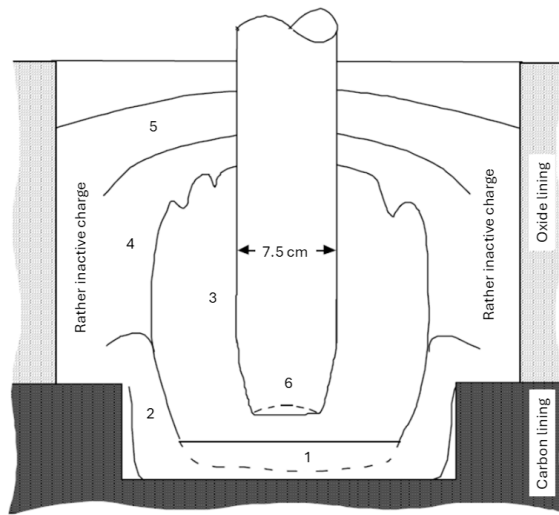


**Figure B.1** *Excavation after smelting of ferrosilicon in a 40 kW one-phase furnace with a graphite electrode 75 mm diameter (Schei, 1967). The furnace was planned for convenient excavation. It was flanged so it could be split to make the contents open for observation. The drawing is based on several experiments. The current was shut down with the electrode in working position, and the furnace was allowed to cool. The charge was quartz, gas coke, and sintered iron ore pellets to give 75 per cent silicon.*

1. Ferrosilicon.
2. Coarse crystals of silicon carbide, the pores between the crystals partly filled with ferrosilicon.
3. Cavity.
4. Greenish layer consisting of quartz pieces partly turned glassy, green porous lumps, and ferrosilicon drops glued together with a slightly porous, brownish glassy substance. The green lumps contain SiC, some free C and some  $\text{SiO}_2$ . Towards the cavity, the walls are partly covered by a 2–3 mm thick brownish glaze substance, mainly  $\text{SiO}_2$ .
5. Mainly charge materials in original form with deposits of a brown substance consisting of  $\text{SiO}_2 + \text{Si}$ . This substance is especially abundant on and near the electrode.
6. Graphite electrode somewhat tapered towards the lower end. The lower end is concave.

The particles in the upper charge layer were glued together by a dense, brown substance that was especially abundant on and near the electrode. In the optical microscope, the brown substance consisted of small white droplets in a dark matrix. In the electron microprobe, the droplets were identified as Si and the matrix as  $\text{SiO}_2$ . A greenish dense substance was also found; it consisted of SiC in a matrix of  $\text{SiO}_2$ . This mass often appeared as a thin layer on the brown substance. The crater wall was partly covered with a brownish glaze that resembled the brown substance, but in the microscope it proved to contain only a few small drops of silicon.

The small-scale operation described above, together with an equilibrium discussion, has suggested that the two reactions



and



are very important. Two experiments were run in a modified small-scale furnace to elucidate these reactions further (Schei, 1967). The furnace pot was as before, but the electrode was hollow, and pellets [ $\text{SiO}_2 + \text{C}$ ] were fed through the hole. According to the stoichiometry, these pellets should give a gas mixture [ $\text{SiO} + \text{CO}$ ]; however, since the vapourization is not an equilibrium reaction, the composition of the gas will vary somewhat.

In the first of the mechanism experiments, the furnace was charged with only coke. This charge gave stable electric resistance and a gas that burnt, giving negligible amounts of white smoke. The coke layer gradually became red-hot up to the top. The excavation showed an irregular cavity at the electrode tip. Above and around the cavity, several consecutive layers were found, in the direction from the hottest zone: coarse crystalline SiC; light green transformed coke particles rich in SiC; a thin layer of black coke covered with a thin layer of the above-mentioned brown substance of  $\text{SiO}_2$  and Si; and, at the top, black coke. The layer of green particles ended rather abruptly at a distance below the top. The reason is probably that the kinetics of SiC formation requires a high temperature, and that the strongly heat-producing condensation to brown substance is necessary to heat the carbon to a sufficiently high temperature.

Reaction [3.3] was studied with the set-up of the previous experiment, except that the furnace was filled with  $\text{Al}_2\text{O}_3$ -pellets. This experiment is a larger-scale variant of a study of the condensation of  $[\text{SiO} + x \text{CO}]$  by Poch and Dietzel (1962). These pellets were thought to be as inert as possible in the condensing gas. The electric resistance was fairly stable, and the furnace produced a gas that burnt with negligible amounts of white smoke. The charge gradually became hot at the top. The charge slid down, and some refilling was necessary. The result of the excavation is shown in Figure B.2. At the bottom there was a layer of alumina-containing slag and a considerable amount of silicon with a high aluminium content. Above a small cavity there was a roof of sintered substance, and further up there were pellets with the surface covered by a thick deposit. The deposit on the pellets changed with the height from the bottom. At the lowest level it was greenish throughout; then brown with an outer greenish layer; and towards the top brown throughout. The experiment demonstrates that evaporation and condensation of SiO may be an important reaction mechanism in the process. At first, the condensate consists of the brown substance, with very small drops of Si in a matrix of  $\text{SiO}_2$ . The Si and the  $\text{SiO}_2$  may separate at higher temperatures, or the Si may pick up carbon from CO in the gas and give a greenish substance of SiC in a silica matrix.

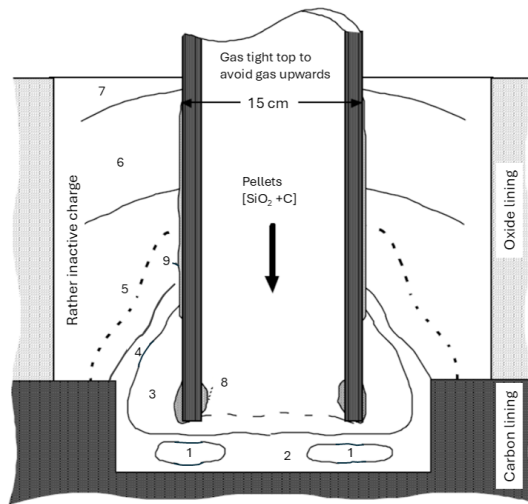


**Figure B.2** *Excavation after an experiment with cooling of a gas mixture  $\text{SiO} + \text{CO}$  on a layer of alumina pellets.*

1. Alloy (about 85% Si, 9% Al, 4% Fe, 0.2% C).
2. Slag (88%  $\text{Al}_2\text{O}_3$ , 6%  $\text{SiO}_2$ , 0.7% C).
3. Cavity.
4. Sintered oxidic material with metal drops.
5. Pellets with a green outer layer. In the inner part of this zone, the green shell lies directly on the oxidic core, and in the outer part there was a brown layer between the oxidic core and green shell.
6. Pellets covered with a brown substance, which was up to 3 mm thick.
7. White pellets partly blackened.
8. Deposits on the electrode (oxide, metal, silicon carbide).
9. Thick layer of brown substance deposited on the electrode.

Small furnaces are well suited for excavation, and new ideas for operation can be tested. Still, it is always a question whether the results obtained are typical for large-scale and extended-time industrial operation. Large furnaces are occasionally dug out for repair in industrial operation. Even with rapid removal of the furnace content, interesting observations can be made. Metre-sized blocks of silicon-containing silicon carbide are taken out, showing that the deposit at the furnace bottom may be very thick in a large furnace. Kurosawa *et al.* dug out a 6500 kVA three-phase rotating furnace that had produced silicon metal (Kurosawa *et al.*, 1972). The furnace charging was stopped immediately before the electric shut down. In their sketch of the furnace, the cavity was very small, but they did not comment on it. The electrode tip had a position about 50 cm above the bottom carbon lining at excavation. They took out samples in a grid at several depths and sectional positions, and investigated them by chemical analysis, X-ray diffraction, and microscopy. In the charge areas close to the wall and in the centre, they found a considerable amount of SiC high up in the furnace. In the electrode path in the rotating furnace, the upper layers contained less SiC and more Si and SiO<sub>2</sub>. These facts indicated that the charge had been consumed mainly in and close to the electrode path in the rotating furnace. Below the electrodes, the deposit consisted of Si-containing SiC and some SiO<sub>2</sub>.

## References

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