

## SOLAR-GRADE SILICON PREPARED BY CARBOTHERMIC REDUCTION OF SILICA

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### Abstract

An advanced carbothermic reduction (ACR) process was developed to produce solar-grade (SG) silicon from high-purity silica and carbon. Preparation of starting materials and operation of the arc-furnace to produce high-purity silicon is described. Solar cells prepared from single crystal SG-Si had efficiencies of up to 12.3%, practically identical to cells made from electronic-grade (EG) silicon. The ACR process is now in the pilot stage for further evaluation.

### 1. Introduction

Commercial solar cells presently available are manufactured exclusively from high-purity EG-silicon. For large scale application of photovoltaic devices this expensive material must be replaced by inexpensive SG-silicon. Numerous processes are presently under investigation and some have already reached the pilot-stage /1/.

Metallurgical-grade (MG)-silicon is commercially available for ~1\$/kg but its impurity level is much too high to render it suitable for solar cell applications. MG-Si is produced by carbothermic reduction (CR) of quartzite in large arc-furnaces, a process extensively employed world-wide.

The reasons for the CR to succeed as the most economical Si-process are as follows:

- Abundance of inexpensive starting materials (quartzite, coke, charcoal)
- Low energy consumption (~11 KWh/kg Si) and high Si-yield (~85%)
- High throughput (~1000 kg/h)
- Inexpensive process technology
- No toxic by-products are produced

These favourable attributes of the CR-process were the basis of our decision to embark on this method for the production of SG-silicon.

However, to obtain high-purity silicon suitable for solar cell production the commonly employed CR-process must be modified considerably. Fig.1 shows that the high impurity concentration in MG-Si is the result of impure starting materials (mainly carbon) and process technology such as furnace lining, electrodes, poking and tapping equipment.

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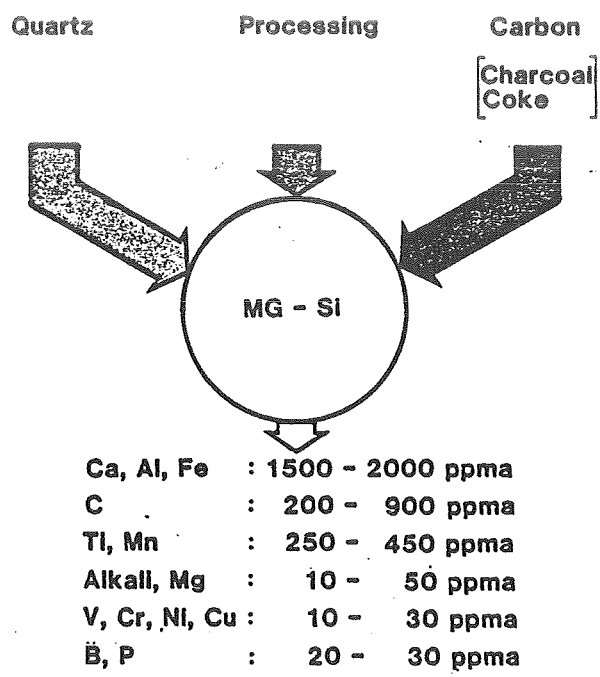


Fig.1 **Origin of impurities in metallurgical(MG)-silicon**

To eliminate these impurities we developed an advanced carbothermic reduction (ACR) process, using high-purity starting materials that are reacted under high-purity conditions in an arc-furnace /2/. A similar approach was first adopted by L.P.Hunt at Dow Corning /3/ and later in a joint Exxon/Elkem research project /4/. In the latter process silicon produced has to be further purified by acid-leaching, a method not employed in our ACR. By combining economy of production with high-purity conditions the ACR-process has a large potential for meeting cost and purity requirements for SG-silicon production.

2. Preparation of high-purity starting materials

For the ACR high-purity silicondioxide and high-purity carbon are employed. To meet the cost goal these materials should be inexpensive and abundently available. In addition, since impurities present in the starting materials will be incorporated into the silicon produced, it is extremely important to avoid those impurities difficult to remove from silicon by the subsequent crystallization process for sheet production /1/. In particular, the concentration of impurities such as boron and phosphorous with a large distribution coefficient of 0.8 and 0.2 resp. should be below 0.2 ppmw.

a) High-purity silica

The requirements mentioned above leave only a small number of silica sources to be considered for the ACR. High-purity quartz mined from various deposits located in Brazil, the USA or Canada is too expensive and because it is a natural product, it is likely to vary in purity.

Synthetic silica produced in large quantities by flame hydrolysis from silicon tetrachloride contains several ppm of B and P and is too expensive as well. An inexpensive material is the silica produced from waterglass. However, because of its high impurity content it can not be employed for the ACR.

Since neither natural quartz nor synthetic silica meet our specifications we developed a process in which inexpensive quartz sand is purified using a combined glass melting/fiber leaching (FL)-process /5/.

The quartz sand we use is mined from deposits in Germany and contains a high concentration of impurities such as Al, Fe, Ti etc. To remove these impurities incorporated in the bulk material, the sand is fused with glass forming oxides such as sodium oxide and calcium oxide to form a multicomponent glass. The glass melt is converted into fibers or granules to obtain a product with a large surface area. Treatment with hot HCL leaches out all metal oxides and impurities and high-purity silica is obtained as a result (Tab.1). Basically, the glass forming oxides merely serve as an acid-soluble solvent for the impurities present in the quartz sand.

Impurities	SiO <sub>2</sub> FL-Process (ppmw)
B	< 0,2 ΔNW
P	< 2 ΔNW
Na	< 0,1
Mg	< 0,1
Ca	< 0,1
Al	< 6
Fe	< 0,1
Ti	< 0,1
Zr	< 1
V,Cr,Mn,Co, Ni,Cu	< 0,1
Nb,Mo,Ta,W	< 0,1

Tab. 1 Impurity content of FL-SiO<sub>2</sub>

b) High-purity carbon

The carbon materials commonly used for producing MG-Si such as coal, coke and charcoal, have a very high impurity content and can not be employed in the ACR. High-purity materials such as graphite can not be used either since their reactivity is too low to obtain silicon with high yield.

Carbon of sufficient reactivity is commercially available in the form of various carbon blacks. These materials are produced on an industrial scale by thermal decomposition of C-H-compounds. A commonly applied method uses crude

oil as a starting material which is burned in an oxygen lean flame; the hot gas mixture containing the carbon black particles is subsequently quenched by water spraying.

The material produced usually has an impurity content of several hundred ppm, too high to be used directly for the ACR.

Carbon blacks much higher in purity can be obtained by decomposing acetylene or natural gas, but the high price renders this product unsuitable for our process.

To obtain high-purity carbon from inexpensive carbon black we treat commercially available products with hot HCl-solution to leach out harmful impurities. The purity of the material produced is comparable to the high-purity silica.

### 3. Granulation of silica and carbon

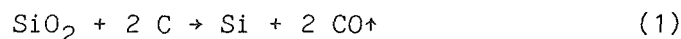
In an MG-Si producing furnace starting materials are commonly employed as chunks up to 10 cm in size. In our process, the silica and carbon prepared are finely powdered materials and must therefore be granulated before being used in the arc-furnace. This may be achieved by briquetting or by pelletizing with the aid of special binders. Regardless of the method employed, no impurities should be introduced by this process and granules produced must exhibit the following properties:

- High mechanical integrity up to temperatures of  $\sim 700^{\circ}\text{C}$   
to prevent premature disintegration and loss of material
- High reactivity to insure high silicon yield
- Optimal grain size for smooth furnace operation
- Sufficient electrical conductivity to obtain proper temperature distribution in the region of the electrodes.

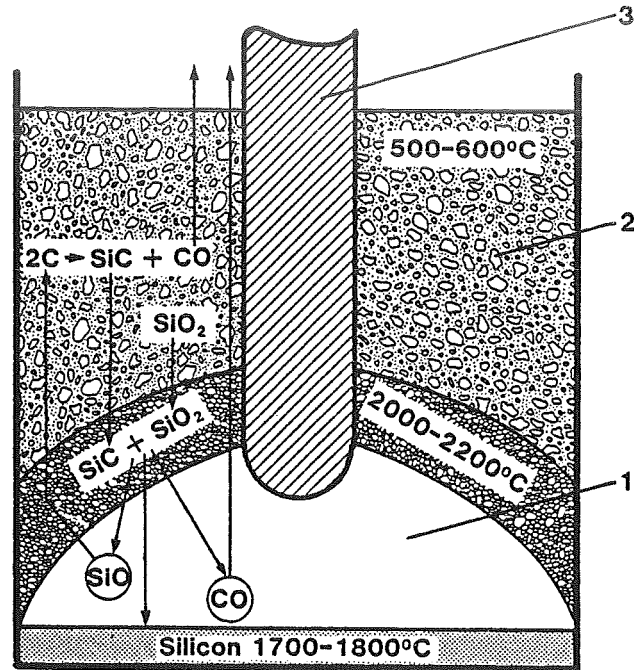
The granules may either contain only one component or may be composed of a  $\text{SiO}_2/\text{C}$ -mixture. Recently  $\text{SiO}_2/\text{C}$ -briketts were successfully employed in large industrial furnaces resulting in lower energy consumption and higher Si-yield when compared to the conventional charge. In our experiments both pellets and briketts were successfully tested; as a binder a phenol resin was used.

### 4. Carbothermic reduction of silica

The production of silicon in an arc-furnace may be described by the overall reaction



The simplicity of this reaction is deceptive, however, for the various reactions actually taking place in an arc-furnace are much more complex. In the high temperature zone in the region of the arc a large number of reactions are thermodynamically feasible between the principle species  $\text{SiO}_2$ ,  $\text{SiO}$ ,  $\text{Si}$ ,  $\text{SiC}$ ,  $\text{C}$  and  $\text{CO}$  /6/. Although a quantitative description of these reactions is not possible at present, a comparatively simple model can be used to describe the processes occurring in the furnace (Fig.2).



**Temperatur distribution in an arc furnace and simplified reaction model.**

Fig. 2      **1** Cavity (filled with SiO and CO),  
              **2** Charge (SiO<sub>2</sub> and C),  
              **3** Electrode

In the region of the arc at a temperature of more than 2000°C SiO<sub>2</sub> and SiC react to form volatile products (SiO, CO) and liquid silicon. This reaction leads to the formation of a cavity (1) filled with SiO- and CO-gas. Rising SiO-gas reacts with carbon to form SiC which, together with the SiO<sub>2</sub> travels into the hot zone, replacing the material that has already been reacted to liquid silicon. Fig. 2 shows that this reaction occurs primarily at the cavity wall, with liquid silicon accumulating at the bottom of the furnace. The CO-gas formed as a by-product rises through the reaction mixture and reacts with atmospheric oxygen to CO<sub>2</sub> at the surface.

To test our high-purity starting materials and to determine conditions necessary for SG-Si production a 70 kW single-electrode reduction furnace was set up (Fig.3).

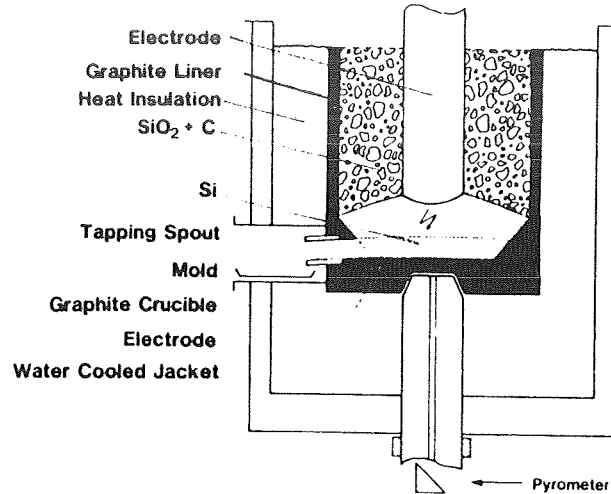


Fig. 3 Schematic of the 70 KW-Reduction furnace

All parts that come into contact with the starting materials and the silicon produced are made of high-purity graphite, including the electrode which supplies about 10% of the carbon necessary for the reduction. To monitor the temperature near the reaction zone, a hole was drilled through the lower electrode and the temperature measured at the bottom of the graphite crucible using a pyrometer.

Carrying out reduction experiments with various  $\text{SiO}_2$ -sources and acid-leached carbon black pellets, silicon of p-type was obtained in every case (Tab.2). The production rate was  $\sim 2\text{kg/h}$ , and the silicon was tapped continuously or every 1 to 2 hours.

Impurity	Quartz (1)	Selected Silica (2)	Synthetic Silica (3)	FL- $\text{SiO}_2$ (4)	Purified Carbon (5)
B	$\approx 1$	$< 1$	$< 0,01$	$< 0,5$	$< 0,1$
P	$< 0,5$	$< 0,5$	$< 0,1$	$< 0,5$	$< 0,5$
Al	30	15-20	$< 0,5$	$< 10$	$< 1$
Transition Elements	$\approx 20$	$< 20$	$< 1$	$< 5$	$< 5$

Tab. 2 Impurity content of  $\text{SiO}_2$ -sources and acid-leached carbon

To determine the limit of the carbothermic reduction process with respect to the purity of the silicon produced an experiment was carried out using synthetic  $\text{SiO}_2$  of the highest purity commercially available (Tab.2 Nr.3) and leached carbon pellets. High-purity silicon with a B-concentration below  $10^{16}\text{a/cm}^3$  (SIMS-measurement) was produced, the highest purity ever obtained in this process [7]. This shows that under suitable conditions the ACR process can be carried out under high-purity conditions so that purity of starting materials can be maintained.

On account of the promising results obtained in the preparation of starting materials and small scale reduction, a 550 kVA furnace was built for pilot production of SG-Si. This 3-electrode furnace has an inside diameter of 1.2m and a capacity for filling it with 1.2t of silica and carbon /2/. The electrode arrangement and the electronics for furnace operation are similar to those commonly used in large industrial furnaces. All parts of the furnace that come into contact with raw materials or liquid silicon are made from high-purity graphite to prevent contamination of the silicon produced. Using specially selected silica and carbon black briquettes silicon was produced at a rate of ~15kg/h. This furnace will be used to estimate the overall cost of our SG-Si process.

## 5. Processing of silicon

At 1750°C, the temperature liquid silicon leaves the furnace, about 500ppmw of carbon may be dissolved in the silicon melt /8/. In addition solid SiC-particles may also be present. Upon solidification carbon will precipitate and numerous SiC-particles may be detected. When using this material as feedstock for Czochralski-growth, at temperatures of 1420°C only 25-30ppmw carbon will dissolve the remainder being solid SiC-particles floating in the melt preventing single crystal growth. Consequently, to obtain first generation single crystal rods the carbon content of the silicon produced has to be reduced down to values below 25-30ppmw.

In principle, this can be achieved by physical or chemical methods:

### - Physical methods

Si-samples obtained from the furnace usually contain SiC-particles 10-20µm in size. Remelting this material in a crucible and holding the temperature close to the melting point SiC-particles will grow and, due to its larger density compared to the melt, sink to the bottom of the crucible. The supernatant melt may be removed and used for crystal growth. SiC-particles may also be removed by passing the melt through a suitable filter made from an inert material such as SiO<sub>2</sub> or SiC. Finally, by collecting the liquid silicon from the furnace in suitable moulds and carrying out a simple directional solidification carbon and SiC-particles can also be segregated effectively.

### - Chemical methods

These techniques rely on the reaction of carbon and SiC with oxidizing agents, i.e.  $\text{SiC} + 2 \text{SiO}_2 \rightarrow 3 \text{SiO} + \text{CO}$  (2). Whether this reaction is feasible is determined by thermodynamics. Neglecting the influence of the silicon melt, the vapor pressure of CO at a temperature of 1500°C is ≈0,15 Torr and ≈1 Torr at 1600°C ( $P_{\text{SiO}} = 3 P_{\text{CO}}$ ). Removing CO continuously by pumping or by working under flowing inert gas, reaction (2) is shifted to the right resulting in a reduced carbon content.

Using metallurgical silicon with a high carbon content as well as our own SG-Si and employing methods discussed above silicon was produced that could be converted into single crystal rods using one Cz-pull only. More work is necessary to determine the most economical technique to remove carbon.

## 6. Solar cell preparation

Silicon obtained by our ACR-process was converted into single crystal material using Cz-technique. Second generation ingots having a diameter of 100mm and 125mm and free of dislocations were sliced using ID-saw. Wafers obtained having a resistivity of 0,5 - 0,4  $\Omega\text{cm}$  and diffusion length of  $\sim 50\mu\text{m}$  (SPV-method) were converted into solar cells using conventional technique /7,9/. Best values obtained (AM1) were 11.1% for 100mm  $\emptyset$  cells.

Similar results were obtained when comparing cells made from EG-Si (0.5 $\Omega\text{cm}$ ).

The cells (5cm x 5cm) made from SG-Si and EG-Si (1.9 $\Omega\text{cm}$ ) having an improved grid structure had the following cell parameter:  $\eta = 12.2\%$  (EG-Si = 13.0);  $I_{\text{sc}} = 690\text{mA}$  (720mA);  $V_{\text{oc}} = 596\text{ mV}$  (593mV);  $\text{FF} = 74.3$  (76.0). In our opinion, the lower values for SG-Si cells are mainly due to the higher B-concentration of SG-Si ( $5 \times 10^{16}\text{cm}^{-3}$ ) as compared to EG-Si ( $7 \times 10^{15}\text{cm}^{-3}$ ).

In general, for Cz-material solar cell efficiency and diffusion length decrease for B-concentration  $> 5 \times 10^{16}\text{cm}^{-3}$  and little difference is observed between SG-Si and EG-Si of the same resistivity /10/. Similar findings were reported by Amick et al. /4/.

To produce solar cells of higher efficiency the B-concentration of our SG-Si should be lowered to  $\sim 2-3 \times 10^{16}\text{cm}^{-3}$ .

This was demonstrated by using high-purity silica (Nr.3 in Tab.2) and leached carbon pellets in our ACR process. Silicon obtained was converted into a 3" single crystal by Cz-technique rod.

Solar cells with conventional grid structure obtained from wafers (p-type 1 $\Omega\cdot\text{cm}$ ) had an efficiency of 12.3%,  $I_{\text{sc}} = 283\text{mAcm}^{-2}$ ,  $V_{\text{oc}} = 593\text{mV}$  and  $\text{FF} = 74\%$ , identical to the reference cell made from EG-Si (1 $\Omega\text{cm}$ ).

## 7. Conclusions

Using our ACR-process silicon was obtained that could be converted into solar cells having an efficiency of up to 12.2%. Carbon and SiC-particles were successfully removed from the tapped silicon using simple separation methods to obtain a feedstock suitable for single crystals growth.

The process is now in the pilot stage to estimate cost of SG-Si production.

## Acknowledgements

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## References

- /1/ Aulich, H.A.:  
Proc. 17th IEEE Photovoltaic Spec. Conf., May 1984, Kissimee, USA, p. 390
- /2/ Aulich, H.A.; Dietze, W.; Eisenrith, K.-H.; Schäfer, J.; Schulze, F.-W.;  
Urbach, H.-P.:  
4th E.C. Photovoltaic Solar Energy Conf., May 10-14, 1982, Stresa, Italy,  
p. 868
- /3/ Hunt, L.P.; Dosaj, V.D.:  
Proc. 2nd Photovoltaic Solar Energy Conf., April 23-26, 1979, p. 98
- /4/ Amick, J.A.; Dismukes, J.P.; Francis, R.W.; Hunt, L.P.; Ravishankar, P.S.;  
Schneider, M.; Matthei, K.; Sylvain, R.; Larsen, K.; Schei, A.:  
Electrochem. Soc. 132 (1985), p. 339
- /5/ Aulich, H.A.; Eisenrith, K.-H.; Urbach, H.-P.:  
J. Mater. Sci. 19 (1984), p. 1710
- /6/ Aulich, H.A.; Eisenrith, K.-H.; Schulze, F.-W.; Urbach, H.-P.:  
6th E.C. Photovoltaic Solar Energy Conf., April 15-19, London, U.K., p.951
- /7/ Schulze, F.-W.; Fenzl, H.J.; Geim, K.; Hecht, H.-D.; Aulich, H.A.:  
17th IEEE Photovoltaic Spec. Conf., May 1984, Kissimee, USA, p. 584
- /8/ Scace, R.J.; Slack, G.A.:  
J. Chem. Phys. 30 (1959), p. 1551
- /9/ Claeys, D.E.; Hecht, H.D.; Münzer, K.A.:  
6th E.C. Photovoltaic Solar Energy Conf., April 15-19, 1985, London, U.K.,  
p. 1021
- /10/ Aulich, H.A.; Cammerer, F.; Fenzl, F.J.; Schulze, F.-W.:  
1st Int. Photovoltaic Science and Engineering Conf., Kobe, Japan, 1984, p.777

DISCUSSION

MAYCOCK: Is the pre-chemical purification step also scaled up to the pilot plant level?

AULICH: We are in the process of doing that. In other words, we are setting up pilot plant level production for high-purity silica.

SCHMID: It seems that you have achieved some very impressive results with respect to getting the impurities like boron, phosphorus, and others down to low levels. The one situation that you did mention was the presence of silicon carbide, which is involved in the reaction. You mentioned a number of ways of reducing the silicon-carbide concentration. What do you believe is the most feasible way of doing this on a production scale?

AULICH: I believe a good way would be to use an inexpensive directional solidification process in which the ingot quality with respect to mechanical properties and its use for slicing, and so on, are not the primary objectives. That is, the procedure is used simply as a separation method. We know that this procedure works, but it must also be low cost because if this process is expensive, it is prohibitive. We have two possibilities now, and we are evaluating the economics of these processes.

CALLAGHAN: What are the schedules for the completion of the economic analysis of the pilot plant scale operation and for the installation of large-scale production that would provide \$10/kg silicon?

AULICH: We intend to evaluate the pilot plant operation in the next few years and, within this time frame, we will produce silicon, solar cells, and modules. Thus, we will evaluate the whole process from the starting material to the finished module. This decision for building a larger furnace should be reached in the next 3 years or so.

KOINUMA: I fear that the fiber purification of silica is poor in productivity, and I wonder if your process is really practical.

AULICH: Why do you think the productivity is poor?

KOINUMA: Because the amount of fiber is small.

AULICH: Oh, no. There is no problem in producing hundreds of thousands of tons of glass fiber. This is an established technology which is used in the building industry and, as I showed, leaching is done within a few minutes. Therefore, enormous amounts of high-purity silica can be produced with the correct technology. It is no problem.

SCHWUTTKE: I find it very surprising and rewarding that your baseline process gives you the same solar-cell efficiency as the use of boron-doped semiconductor-grade silicon of the same resistivity. This is very encouraging. I would like to propose that it would be worthwhile to use this type of material as a substrate for epitaxial deposition for integrated circuits.

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AULICH: Yes, we have done this. The results are quite good.

SCHWUTTKE: I would assume so.

WRIGHT: What was the base resistivity of the material used for the high efficiency cells?

AULICH: The cells prepared by our process had a resistivity of about 0.5 to 0.6 ohm-cm, and this was compared with 0.5 to 0.6 ohm-cm Czochralski material.

WRIGHT: I assume you use a carbon plug in the furnace tapping operation. How did you remove the carbon plug without introducing metal contaminants?

AULICH: We used the conventional technique. In the industrial process, an arc is produced between a graphite rod and the closure point. The temperature becomes high enough to melt the solidified silicon and molten silicon runs out. To produce high-purity silicon, the graphite rod must be of high purity. Of course, this can be done and it is our procedure.

RUSTIONI: We also have used similar electrode techniques for tapping the furnace. You mentioned a system for obtaining amorphous silica from fluosilicic acid, but this process is not expensive because a byproduct of the industrial production of phosphoric acid can be used. The process involves the precipitation of the sodium salt of fluosilicic acid. Can you comment on this?

AULICH: We looked at this process very carefully because fluosilicic acid is relatively inexpensive. The sodium salt can be produced without any problem, but there are a large number of problems involved in the decomposition step to produce silicon tetrafluoride. If this reaction is not carried out correctly, some compounds of boron and other elements remain in the silicon tetrafluoride, and other separation methods must be used. We looked at the large-scale production of silicon dioxide using this process, and we concluded that the environmental hazards using the fluorine compounds are very severe, at least in Germany. That makes the processing cost very high. On the other hand, there are no such problems melting glass and leaching with hydrogen chloride. Almost all the technology for leaching is available from the chemical industry. We concluded that it was much better to use our approach than to use silicon tetrafluoride.

RUSTIONI: What is the temperature used for the production of the glass fibers?

AULICH: It is the conventional glass-melting process. The temperature used is about 1300 to 1400°C. Window glass is produced in the same way. We don't spin the fibers. We melt and let the melt run into water producing the glass fibers.

RUSTIONI: During the purification of carbon black, you first prepared the pellets or briquettes and then the leaching was done. Do the pellets or the briquettes remain intact during the process?

OMIT

AULICH: It is important that they remain intact because if it is not done correctly, the product is a high-surface area carbon black which has to be filtered and this is a cumbersome procedure. We make pellets that remain intact during the leaching process and after leaching they are, of course, much purer.

RUSTIONI: After leaching, are you obliged to dry the pellets before feeding the arc furnace?

AULICH: Some drying must be done, but it doesn't have to be super dry.

RUSTIONI: Do you use three-electrode, three-phase in the pilot plant?

AULICH: It's a three-electrode, three-phase furnace.

MAYCOCK: When do you think this process will be commercial?

AULICH: As in my answer to Dr. Callaghan, we will develop this process in the next few years and also evaluate the economics. During this time, we will use the product silicon for our own purposes. In a few years, based on the evaluation as a technically sound, economic process, the decision will be made concerning large-scale production by us or licensing the process. I can't tell you exactly when this will occur, but it will take a few years.