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REFINING OF METALLURGICAL-GRADE SILICON

J. Dietl
Heliotronic GmbH
D-8263 Burghausen, Postfach 1129, Germany

ABSTRACT

A basic requirement of large-scale solar cell fabrication is to provide low-cost base material. Unconventional refining of metallurgical-grade silicon represents one of the most promising ways of silicon meltstock processing. The refining concept is based on an optimized combination of metallurgical treatments. Commercially available crude silicon, in this sequence, requires a first pyrometallurgical step by slagging, or, alternatively, solvent extraction by aluminum. After grinding and leaching, "high purity" quality is gained as an advanced stage of refinement. To reach solar-grade quality a final pyrometallurgical step is needed: liquid-gas extraction.

INTRODUCTION

Different possibilities can be seen in the field of low-cost silicon meltstock processing for large-scale solar cell fabrication. Processing routes via the refinement of metallurgical-grade silicon seem to offer best chances of producing solar-grade silicon at costs of lowest possible levels. The present paper follows the steps of previous reviews (see e.g. references 1-4) concentrating mainly on a material concept of an optimized sequence of metallurgical refining steps.

The target of any economy-oriented program can be seen here in a 10 % minimum AM1 conversion efficiency based on a 10 x 10 cm² multicrystalline silicon solar cell (5). Its concept has to consider comparably strong reduction of costs in every subtechnology such as material refining, crystallization, and ingot slicing as well. The final systems balanced against each other, then, would allow optimum economical conditions.

SOLAR-GRADE SPECIFICATION

It has been widely discussed, that the term "solar-grade" should be used only as a rather vague material specification. "Solar-grade" characterizes a category of silicon quality which, though less pure than electronic-grade silicon, can nevertheless be used for solar cell fabrication. Often the therm "solar-grade"

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does not sufficiently distinguish between chemical, crystallo-graphic or device-related properties. In this paper this expression is primarily confined to the impurity situation of the silicon meltstock.

Fig. 1 illustrates various categories of silicon quality, covering about eight orders of magnitude from metallurgical-grade silicon to hyperpure silicon. The solar-grade or better the terrestrial solar-grade (TSG) quality range - to emphasize the real low-cost character of this product - should be seen as an approach assessing the chemical properties of the starting material modified by the influence of crystallization process and cell technology. The solar cell allows for reduced purity in general, but, as indicated by the dotted range in Fig. 1, demands hyperpure quality in terms of recombination-active elements. The introduction of terms such as "high purity 1" (HP1) or "high purity 2" (HP2) ist a rather arbitrary way of defining certain intermediate quality stages of refining.

Impurities in silicon affect the efficiency of solar cells in a variety of ways. At high impurity concentrations crystal growth can be perturbed by inclusions, precipitates, or defects which may finally cause structural breakdown. Semiconductor properties are influenced by electrically active impurities which reduce the minority carrier lifetime. The objective of the wellknown Westinghouse project (6) has been to determine thresh-old values for a lot of impurity elements. This basic investi-gation revealed the detrimental influence of transition metals in particular. In order to understand the specific behavior and interaction of certain elements typical impurities have to be pursued by trace analysis on their way through the different refining stages. Profound analytical characterization of start-ing materials, intermediate qualities, and final products has to be seen as an indispensible task in the framework of solar-grade silicon development.

METALLURGICAL ROUTES TO SOLAR-GRADE SILICON

One of the most evident ideas, namely to win solar-grade silicon by typical metallurgical techniques, has attracted increasing attention. Three economically feasible routes for preparing solar-grade silicon meltstock are shown in Fig. 2. This schematic flow-diagram indicates the currently most-dis-cussed processing sequences leading from different quartz qualities via intermediate purity stages to silicon of TSG-quality.

Two of these routes utilize the carbothermic reduction of quartz. Whereas route A proceeds from the low-purity arc furnace product - which will be discussed more in detail later on - route C is based on an impurity-improved thechnique from the very beginning. This alternative way, investigated for the first time at Dow-Corning (7) and continued by Elkem/Exxon (8), is not to refine metallurgical-grade silicon but to rather use raw materials of higher purity. Siemens (9) is developing a process in which quartz sand is purified using a combined glass melting/-fiber leaching treatment, and carbon black is upgraded by leaching with hot hydrochloric acid. A specially designed arc furnace system is demanded to preserve the much higher degree of purity from where solar-grade quality can be reached by final pruification procedures, e.g. by controlled solidification.

The aluminothermic reduction of quartz at comparatively low temperatures - as indicated by route B in Fig. 2 - represents another promising way to produce solar-grade silicon. A suitable technical process on this basis, being under investigation at Heliotronic (10), requires two liquid and immiscible phases - represented by an AlSi alloy and a flux system - acting as solvents for the reduction products Si and Al_2O_3. In Fig. 3 a schematic flow-diagram indicates the regeneration cycle of the flux system combined with the recovery of Al and the recrystallization of Si in form of platelets which acts as a very effective integrated refining treatment. After separation of the Si-platelets the remaining Al level has to be removed by a final pyrometallurgical purification step to achieve solar-grade meltstock quality.

REFINING OF MG-SILICON

The production of metallurgical-grade silicon in electric arc furnaces is a technically well established large-scale process. The nominal capacity of all existing furnaces in the Western World is known to be between 600.000 and 650.000 tons per year (11). In the carbothermic reduction process impurities from SiO_2, carbon mixtures, electrodes and other auxiliary materials contaminate the crude silicon to an amount of one to two percents. In Table 1 metallurgical-grade silicon products from different suppliers are characterized by impurity analysis.

Table 1: Concentration of impurities (ppmw) in MG-Si from
         different suppliers

Element	MG-Si I	MG-Si II	MG-Si III
Mn	260	500	50
Cr	25	20	50
Cu	25	50	20
Ni	110	30	10
Fe	3800	3500	5000
Al	1600	2400	2500
Ca	2700	2200	500
Mg	60	50	70
Ti	150	250	150
B	10	20	15
P	40	30	20

The predominant impurities Fe, Al and Ca are typically present in the range of some 1000 ppmw. Among the impurities below 100 ppmw the doping elements B and P can be seen. Another unavoidable impurity which is found in MG-Si in excess of saturation limits is carbon – mainly precipitated as SiC particles – in the concentration range between 100 and 1000 ppmw.

These impurity concentrations are far above the levels allowed for solar-grade meltstock. Nevertheless, the low cost of the metallurgical-grade product makes the refining by likewise economical metallurgical techniques increasingly attractive. Basic hydrometallurgical and pyrometallurgical refining procedures with special purification effects with regard to certain impurities and element groups are given by

- Solid-liquid extraction (acid leaching)
- Liquid-liquid extraction (slagging)
- Liquid-gas extraction (gas blowing and evaporation)
- Solvent extraction (recrystallization from Al solution)

Practice-oriented approaches have been started at several places to reveal the potentiality of these extractive processes. Optimization of the refining sequence is inseparably combined with economic aspects but also with the conditions of subsequent crystallization and device processing.

LIQUID-LIQUID EXTRAKTION

Liquid-liquid extraction as one of the pyrometallurgical processes is applied to remove impurities from MG-Si in the molten state. Successful utilization requires a slag system that has a higher chemical affinity to certain impurities than silicon. The slag melt should be immiscible with molten silicon, which means that besides being chemically stable in contact with molten silicon it does not contaminate the silicon too much or dissolve major amounts of elemental silicon. Slags based on alkaline earth metal silicates have been found to fulfill these criteria.

To optimize the purification effect by slagging the high temperature chemistry of liquid-liquid extraction has to be investigated. As the elemental impurities are reduced or oxidized at the liquid silicon-slag interface, first order thermodynamic predictions can be made on the basis of their oxidative/reducive behavior. Elements forming oxides of higher stability than SiO_2 are expected to get oxidized and slagged. This has proven to be valid for elements like Ca, Mg and Al. On the other hand, elements like Fe, Cr and Mn, which form oxides of lower stability than SiO_2, get transferred into the silicon melt.

In Fig. 4 a schematic drawing of the liquid-liquid extraction process is given. In a carbon ladle liquid-liquid contact between $CaSiO_3$ and MG-Si is established using the electroslag procedure as a more or less convenient heating technique. After realizing equilibrium extraction conditions by appropriate choice of extraction duration and temperature prerefined Pl-Si quality is obtained . Insertations in Fig. 4 comparing the situation of impurities in MG-Si and Pl-Si demonstrate the pruification effect by slagging in the case of Al and the non-metal contaminants B and C.

The carbon level it lowered due to the reaction of dissolved carbon and SiC particles with the silicate slag forming volatile CO. Despite intensive contact of the molten silicon-slag system with the carbon ladle, carbon concentrations below detection limits of combustion analysis in the range of 50 ppma are attainable by appropriate control of the kinetics of opposing chemical and physical phenomena.

Following the above stated rule with regard to B no purification by liquid-liquid extraction is expected, as its free energy value of oxide formation is somewhat below that of silicon. To understand the opposite experimental finding a more careful analysis has to take into account second order thermodynamic effects. Accordingly, the observed transference of B into the slag phase becomes understandable by special bonding conditions of boronoxide in the silicate phase. The potentiality to remove B makes the liquid-liquid extraction process an important step of the metallurgical refining sequence.

In Fig. 5 B concentrations of pyrometallurgically refined MG-Si are plotted versus resistivity values of multicrystalline samples. The observed dependence fits well in the correlation of ASTM standard F 723-82. B concentrations reaching levels below 1 ppma correspond to resistivity values up to nearly $0,5\,\Omega\,cm$, p-type. Doping levels in Si for solar application currently are settled in the $0,5 - 5\,\Omega\,cm$ range. They may experience, for primary economic reasons, a slide towards even lower resistivity values, as soon as modified cell concepts will be optimized.

SOLID-LIQUID EXTRACTION

The formation of impurity precipitates in polycrystalline low-grade silicon is a precondition of solid-liquid extraction known as acid leaching. The formation of precipitates in form of silicides, oxides, silicates or metal eutectics is enhanced by both low segregation coefficient and low solid solubility. A striking correlation is very helpful in the field of hydrometallurgical meltstock processing: The lower the permissible level of the impurity element in question, the lower the segregation coefficient and, thus, the more effective the purification.

During solidification of low-grade Si such as the above mentioned Pl-Si, impurities with low segregation coefficients and concentrations exceeding solid solubility accumulate mainly along grain boundaries of the polycrystalline material. For effective refining, the silicon has to be milled in order to set second phase inclusions free for subsequent attack by acid mixtures. In Fig. 6 a flow-chart of the hydrometallurgical refining process is given. Lumps of Pl-Si are crushed by a sequence of jaw and roll crushers and finally pulverized in a vibration mill. Milling under wet conditions allows a hydrocyclone to be used to classify the milled product.

Extensive experimental work has been done in optimizing particle size of the pulverized Si, type, mixture and concentration of acids as well as temperature and duration of the leaching procedure (12). Fig. 7 demonstrates the effect of particle size on the purification of Pl-Si powder in the treatment with aqueous solutions of hydrochloric acid and hydrofluoric acid. The experimental data cover a range from 10 to 150 µm of average particle size. Fe, Ca and Ti stand for the leaching behavior of certain groups of metal impurities in Pl-Si. The effectiveness of hydrometallurgical refining is improved by grinding the silicon down to a particle size well below the average grain diameter of the polycrystalline material. In the case of extremely fine milling, the improvement in purification, however, has to be balanced against the increasing difficulty of handling and melting the powder in the subsequent pyrometallurgical process.

The leaching equipment in Fig. 6 consists mainly of a filter-extractor in which the pumpable silicon-acid slurry is leached by appropriate acid mictures followed by rinsing and drying operations. Starting from P1-quality the main impurities Fe and Ca in the range of some 1000 ppma are eliminated down to low ppma levels, whereas in the case of nearly all other metal impurities even sub-ppma levels are attainable. Remaining impurities with unfavourable segregation coefficients such as the doping element P are distributed nearly homogeneously in solid silicon and cannot be selectively attacked by acid leaching.

LIQUID-GAS EXTRACTION

Liquid-gas extraction is another procedure in the field of metallurgical meltstock processing. Blowing reactive gases through molten silicon has been and is currently employed by MG-Si manufacturers for achieving higher material qualities. The conceptual approach is to form impurity compounds which can be slagged or removed by evaporation. The knowledge of both the chemistry of possible high temperature reactions and physical properties such as vapor pressure and solubility of the reaction products in molten Si is a prerequisite of selecting the proper experimental approach. The high reactivity of Si itself, however, limits the effective application of gaseous reactants much more than in the case of steel refinement.

Evaporation of elemental impurities from molten silicon represents a possibly more advantageous performance of liquid-gas extraction. Elements with higher vapor pressure than Si in principle are expected to evaporate from the silicon melt. In Fig. 8 the recovery of elemental impurities in the arc furnace process at temperatures around 1650°C is plotted versus vapor pressure. In fact the recovery has been found to be inversely related to the vapor pressure of the elements in question. This finding shows the possibility to further remove impurity elements such as Al, Ca and especially P.

In Fig. 9 a simplified drawing of the liquid-gas extraction process is given. To enhance the evaporation effect it is advantageous to treat the Si melt to be purified under vacuum conditions. Concentrations of impurities mostly affected by gaseous reactants and/or vacuum treatment are listet before and after liquid-gas extraction in Fig. 9. The obtained HP2-Si quality is characterized by metal concentrations each below 1 ppma, by oxygen below 10 ppma - starting from levels in surface oxide layers in the range of 5000 ppma - and by concentrations of phosphorus as a doping impurity reproducibly reduced to values below 0,5 ppma.

PROCESSING SEQUENCE

To define an optimum sequence of processing steps in the refinement of metallurgical-grade silicon is of central importance in terms of both systematic purification and economical conditions. The final combination of procedures may be different mainly due to special qualities of the starting material but also due to purity requirements of the subsequent crystallization technique. Differences in refining concepts, moreover, may be caused by the commercial availability of auxiliary materials of both adequate quality and dimension. Up to now all the efforts to find auxiliary materials suitable for use in the field of pyrometallurgical purification yielded refractory materials based exclusively on silicon compounds such as silicon oxide, silicon nitride and silicon carbide, respectively. This also applies in principle to carbon as this material in its Si-resistant quality protects itself by forming a dense layer of silicon carbide.

In Fig. 10 the flow-chart of an optimized refining cycle based on metallurgical refining steps is schematically drawn (14). Commercially available metallurgical-grade silicon – of selected quality with regard to certain impurities – in a first step is purified by liquid-liquid extraction. This slagging procedure yields prerefined silicon of the above discussed P1 quality typified by low B and C concentrations. Alternatively to liquid-liquid extraction solvent extraction by recrystallization from Al may be applied.

After grinding and acid leaching in the framework of an optimized hydrometallurgical technique high purity quality HP1-Si is reached. This advanced stage of refinement is characterized by drastically lowered levels of metal impurities. To accomplish Si meltstock of terrestrial solar-grade quality, a second pyrometallurgical step by liquid-gas extraction using reactive gas blowing and/or vacuum treatment is required. Directional solidification for instance carried out in form of multicrystalline ingot casting technique (15) can be considered as the final purification step due to nearly theoretical segregation phenomena. From a different point of view, however, it also represents the first step in crystallization technology.

CONCLUSION

To design a basic low-cost concept of large-scale material production, availability and costs of both starting and auxiliary materials as well as total amount of investment, energy consumption, throughput, and environmental compatibility have to be considered.

Solar-grade silicon at costs in the range of US $ 5 - $ 10 will only be realized by utilizing unconventional techniques. The metallurgical way of silicon meltstock processing can meet this target by bringing into action a minimum number of complementary hydro- and pyrometallurgical steps. To transfer the initial advantage of an impurity-optimized starting material to the final goal of large-scale terrestrial solar cell production, crystallization and cutting processes as well as cell technologies of adequate low-cost character are demanded. To reach industrial maturity, technical feasibility as well as economy of the different processes have to be finally investigated via pilot stages of adequate dimensions.

ACKNOWLEDGEMENT

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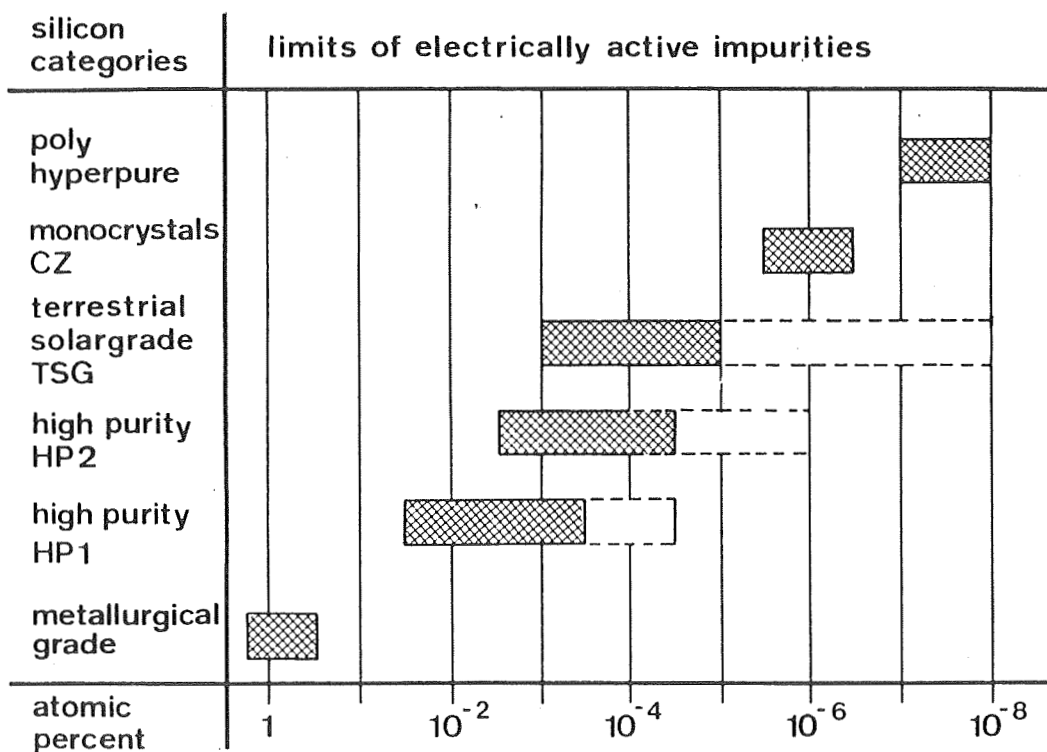(15) D. Helmreich, J. Phys. (Paris), Collog. C1, 43, 289 (1982)

silicon categories	limits of electrically active impurities				

Fig.1. Impurity ranges of different silicon qualities

Fig. 2

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        (A)                    (B)                    (C)

┌─────────────────┐   ┌─────────────────┐   ┌─────────────────┐
│ Quartzite + Coke│   │ Quartz +Aluminum│   │ Quartz + Carbon │
└─────────────────┘   └─────────────────┘   └─────────────────┘
      Carbo-               Alumino-              Multistage
      thermic              thermic                Refining
      Reduction            Reduction
┌─────────────────┐                         ┌─────────────────┐
│   Mg-Silicon    │─ ─ ─ ─ ─ ─ ─ ─ ─ ─ ─   │  Pure SiO₂+C    │
└─────────────────┘       Al-Solvent        └─────────────────┘
      Hydro-and           Extraction            Reduction
      Pyrometal.
      Refining        ┌─────────────────┐   ┌─────────────────┐
                      │ Silicon Platelets│  │  Pure Silicon   │
                      └─────────────────┘   └─────────────────┘
                      Final Purification

                   ┌──────────────────────┐
                   │  Solar-Grade Silicon │
                   └──────────────────────┘
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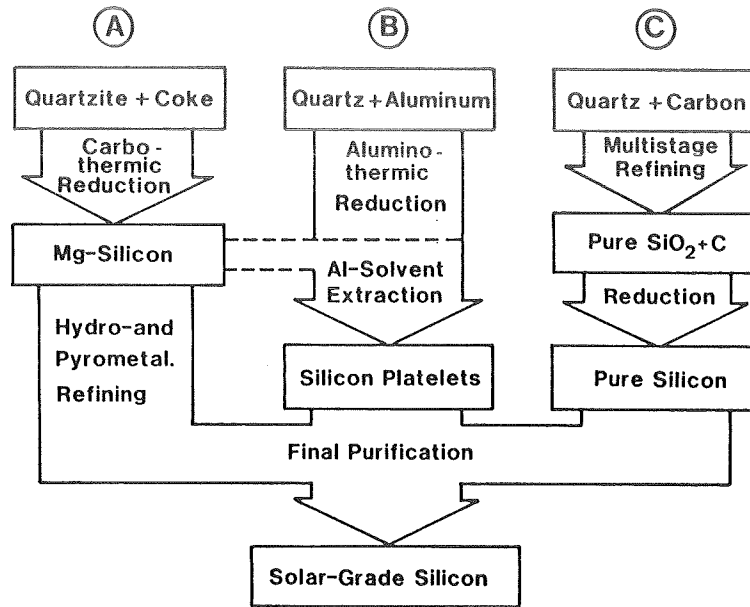
Fig.2. Different approaches to large-scale production of solar-grade silicon
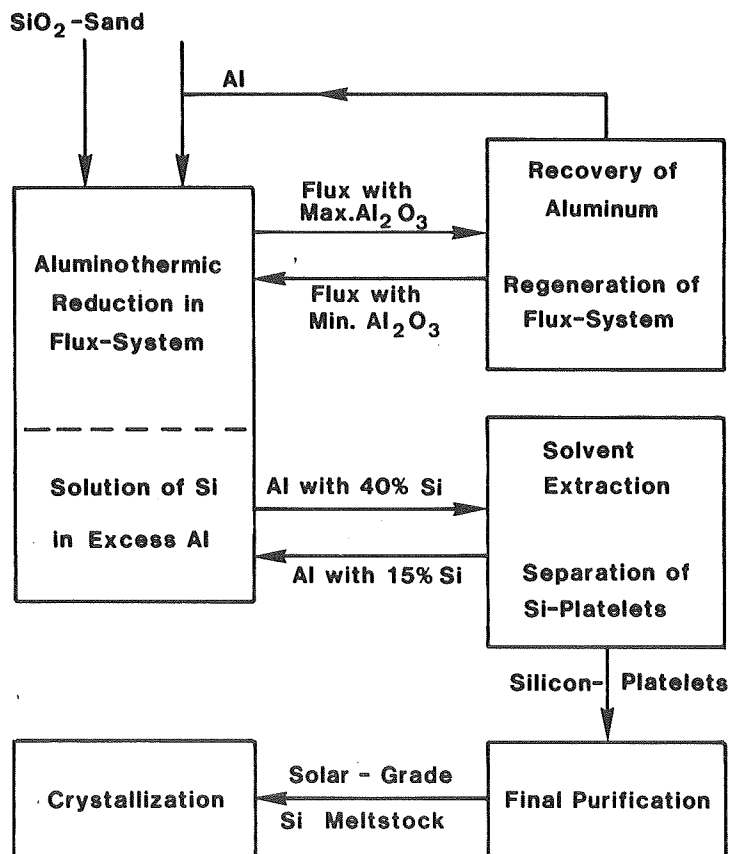
Fig. 3

Fig.3. Schematic flow-diagram of aluminothermic production of solar-grade silicon
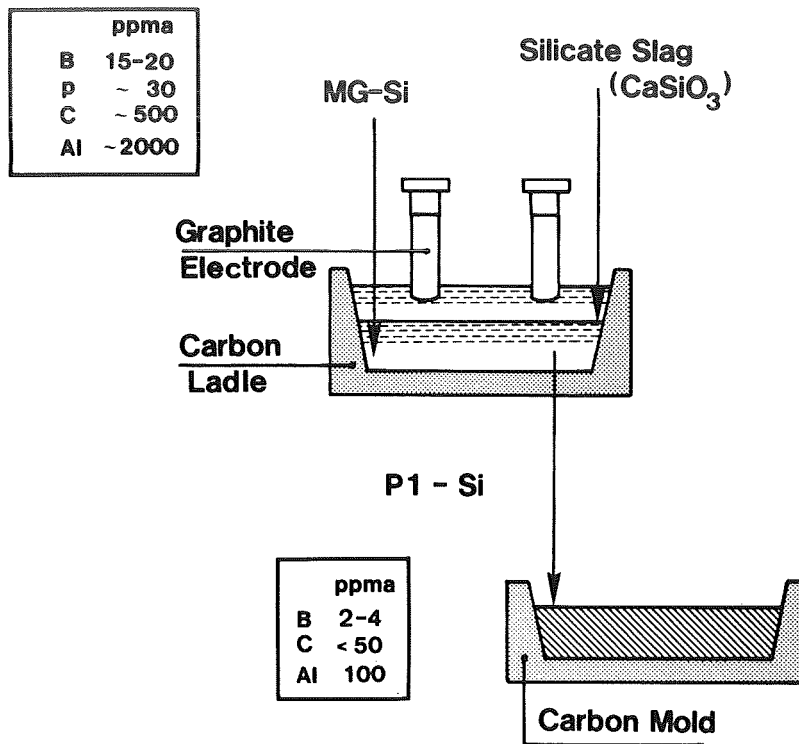
Fig.4. Schematic of the liquid-liquid extraction process
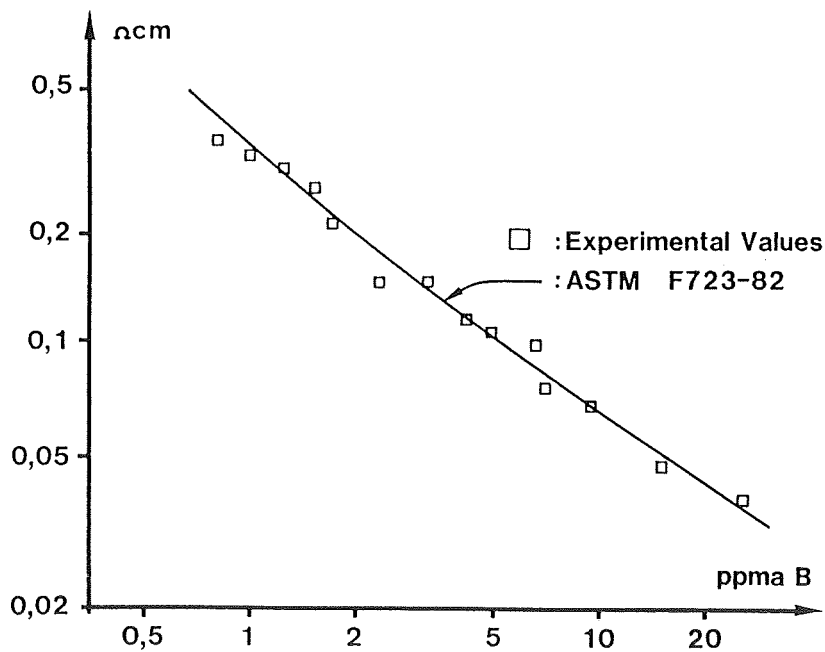yielding prerefined P1-Si

Fig.5. Correlation of boron concentrations with resistivity
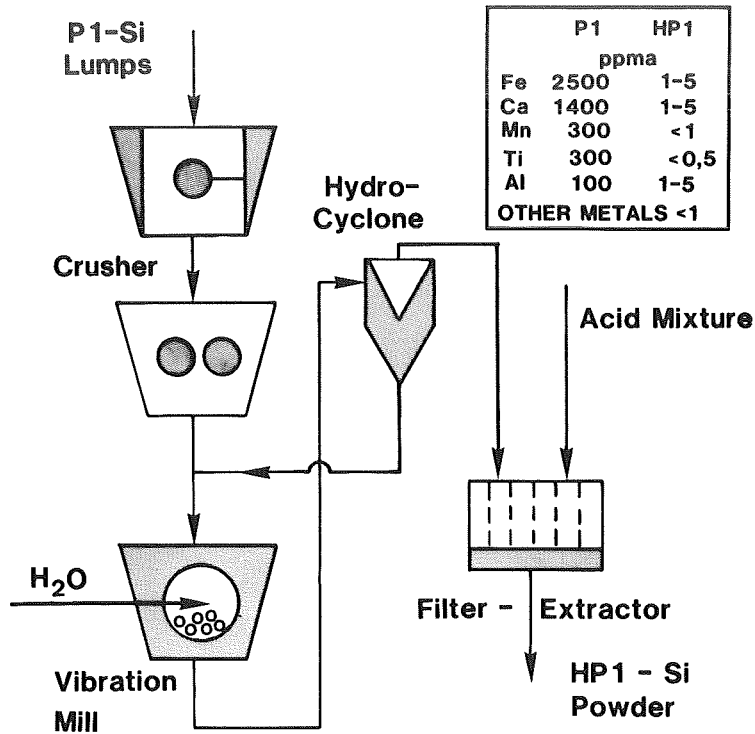values in pyrometallurgically refined silicon

P1-Si
Lumps

Crusher

Hydro-
Cyclone

	P1	HP1
	ppma	
Fe	2500	1-5
Ca	1400	1-5
Mn	300	<1
Ti	300	<0,5
Al	100	1-5
OTHER METALS <1		

Acid Mixture

H_2O

Vibration
Mill

Filter – Extractor

HP1 – Si
Powder

Fig.6. Flow-chart of the hydrometallurgical refining process
yielding HP1-Si (high purity 1)
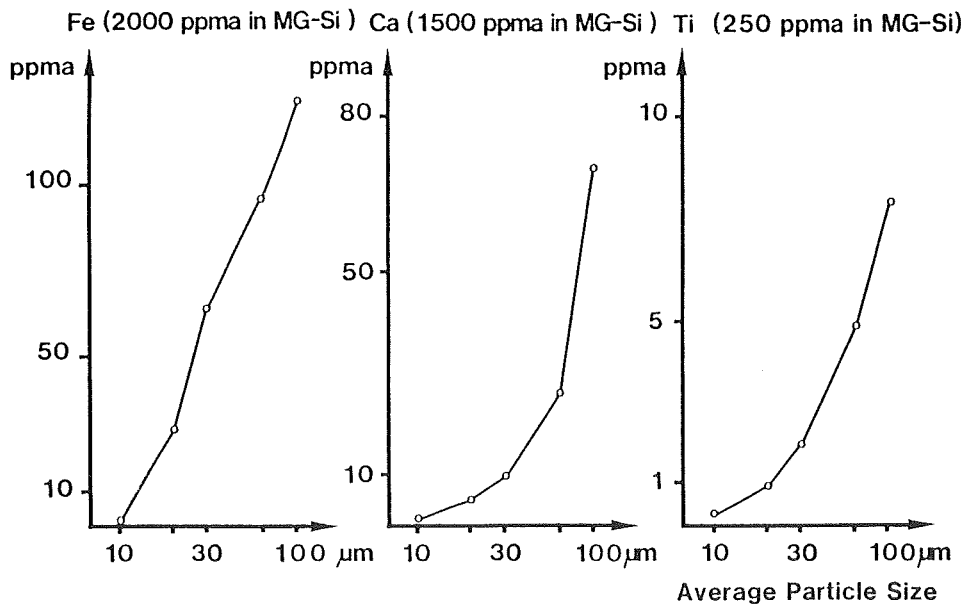
Fig.7. Effect of particle size on the purification of P1-Si
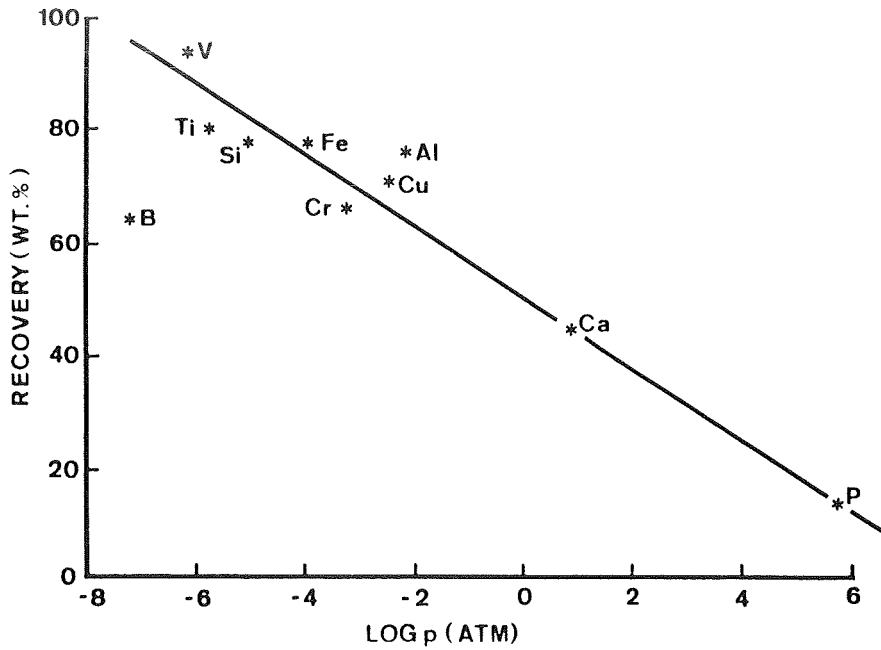powder by leaching with aqueous HCl/HF mixtures

Fig.8. Recovery of impurities in the arc furnace plotted
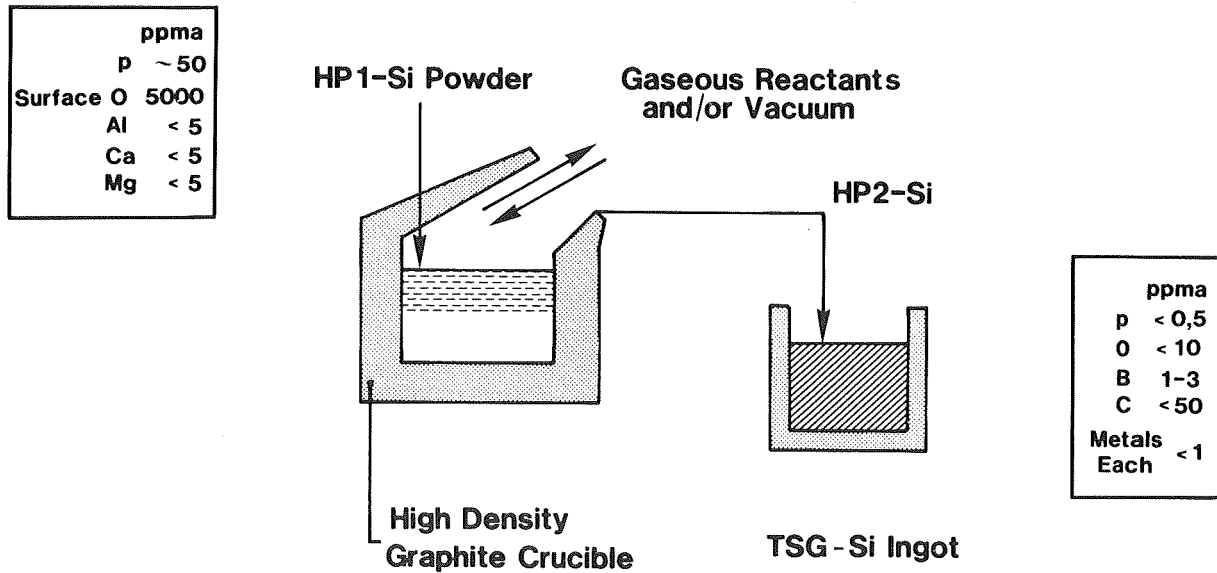versus elemental vapor pressure (13)

Fig.9. Schematic of the liquid-gas extraction process
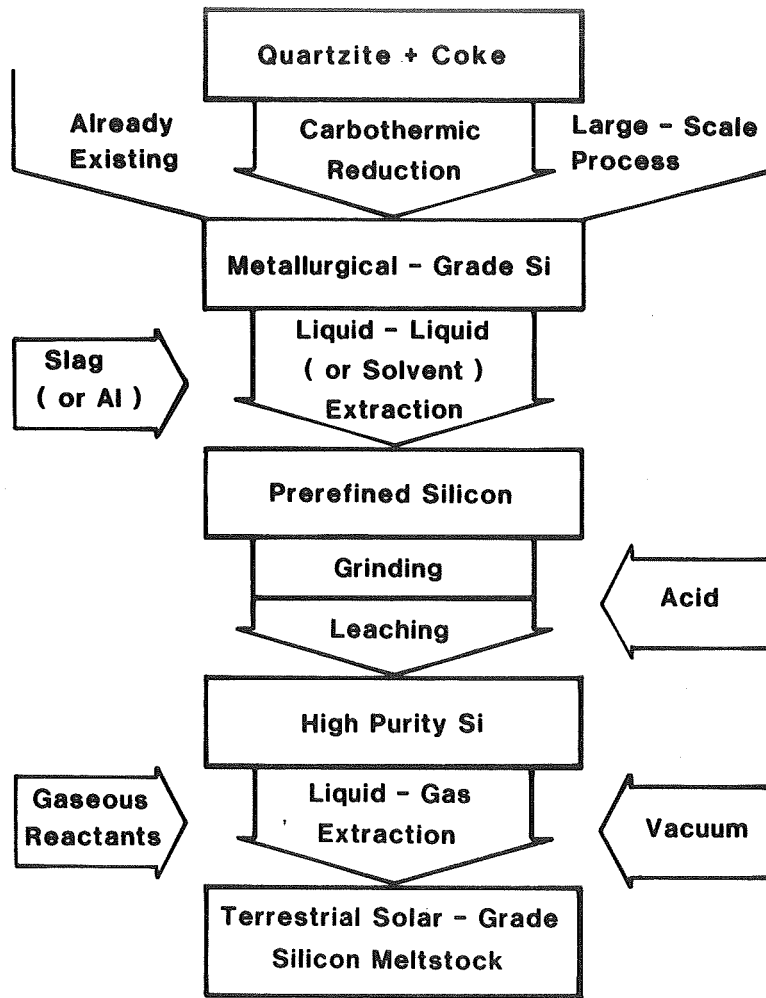yielding HP2 (high purity 2) quality

Fig.10. Schematic flow-diagram of the processing sequence for metallurgical refining of MG-Si

DISCUSSION

MAYCOCK: Could you estimate when Wacker could offer a commercial product based on this general research area?

DIETL: More years of basic development remain to be done. In perhaps 3 or 4 years we hope to achieve the state of development that will allow us to make decisions regarding production. The first production of this conventional silicon material will probably be the early 1990s.

RUSTIONI: We worked several years ago in this field. I remember that we had a problem of the formation of foam during the leaching treatment, especially with fine powder present. This was a very difficult problem to solve. We tried to use some surfactant substances in order to decrease this phenomenon. Have you noticed this formation also?

DIETL: In the beginning, we had the same problem. We tried to overcome this problem first by using a very effective classification to remove all of the very fine particles and, secondly, to use a filter extractor in which the worst effects of the foam are decreased.

WRIGHT: We were working on a very similar metallurgical approach in the early days at Solarex. Would you comment on the drop in yield for each step of the process?

DIETL: We have used a pilot two-stage process up to this time. This means batch quantities of about 100 kg in the pyrometallurgical step. We obtain yields ranging from 95 to 98% for those batches, depending on the process being examined.