DEVELOPMENT AND USE OF SILGRO CARBON-SILICA BRIQUETTES IN SILICON METAL FURNACES

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PART I

INTRODUCTION, PROBLEM DEFINITION

Raw Materials Used For The Manufacture Of Silicon:

A modern silicon-producing electric arc furnace uses chunks of quartz ranging from walnut to fist-size in combination with various carbon sources which differ considerably in shape, size, physical properties and chemical behavior. The carbon sources all fulfill specific functions:

- Wood to provide charge stability and good gas permeability.
- Charcoal, peatcoke and cokes from bituminous and lignite coals for the rapid conversion of the SiO.
- Bituminous coal to facilitate good gas permeation and for rapid reduction of SiO.
- Petroleum coke for decreasing undesirable metals such as iron, aluminum, calcium and others.
- All carbon sources, including electrodes contribute their fixed carbon to the reduction of SiO2, a complicated process occurring in several stages.

The mechanical stability of these mentioned carbon sources is relatively poor, with the exception of the electrodes. For this reason, a carbon dosage control becomes difficult and a major problem of the furnace operation. After all, the carbon usage is judged according to the consumption of electrodes. It should also be mentioned that the properties, attributed to the individual carbon sources, cannot be utilized in a controllable manner. One need consider only the low ash bituminous coal which undergoes a coking process in the electric furnace during which it degases, expands and shrinks again.

Even though the electrical properties of the carbon sources can be measured at time of delivery, when they pass through the furnace, satisfactory measuring techniques, which might assist the furnace operator, simply do not exist.

Bases Of The SiO2 - Reduction:

Although it is necessary to consider thermodynamic aspects regarding Si-manufacture, they contribute very little to an optimization of the electric furnace operation. The chemical kinetics and its process-technological interpretation will more quickly lead to a good furnace operation and high productivity.

Contacts between the individual large-sized materials result in no appreciable chemical conversions, even though expected by the thermodynamics. When applied to the Si-furnace, this means that the quartz chunks can react with the carbon sources only when they exceed their melting temperature at over 1700 degrees C. Beginning at this temperature, the conditions in the electric furnace are similar to those in a distillation column filled with condensators (such as Raschig-rings). The melted quartz drips or runs on its downward path over the carbon sources, on a self-created cushion of gas resulting from the chemical reaction. The carbon sources are consumed; the smaller the carbon source particle the larger the specific surface the quicker the total conversion. The larger carbon particles guarantee the gas permeability of the drip-lattice for a longer time period.

One can imagine that the hottest reaction space, also called the crater, is surrounded by a zone which represents the region of isotherms in which the quartz melts. If the crater is poorly extended on its sides, a simplistic sketch shows that the chemical happenings occur within a narrow hood containing a lot of molten SiO2 per unit of area. The result is a thick melting zone where all conceivable reactions occur in parallel:

$$SiO2\ (liq) + C\ (solid) \rightarrow SiO\ (gas) + CO$$
$$SiO2\ (liq) + 3C\ (solid) \rightarrow SiC\ (solid) + 2CO$$
$$SiO2\ (liq) + 2SiC\ (solid) \rightarrow 3Si\ (liquid) + 2CO$$

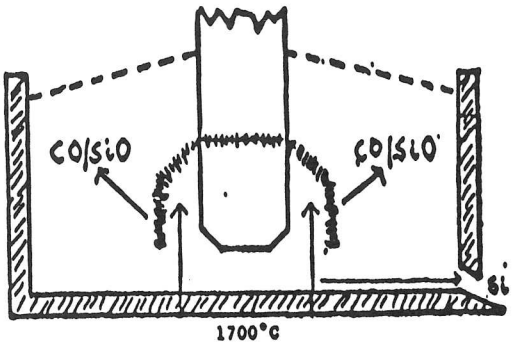
The SiO-gas escapes from this zone without having found sufficient opportunity to use free carbon source surfaces for a further reaction. The velocity of the gas mix CO/SiO is high because of the narrow available flow channel driven by the high temperatures in the vicinity of the electrodes. Furthermore, the reduction sources become covered by the liquid quartz.

Each escape of SiO, however, represents a simultaneous loss of materials and energy.

$$SiO2 + 2C = Si + 2CO \quad H = 6600\ KWH/TSi$$
$$SiO2 + C = SiO + CO \quad H = 4660\ KWH/TSiO$$

The data is valid for 2000 degrees K. They indicate that the partial reaction to SiO already consumes 70% of the total energy demand. Relative to the 636 Kg Si contained in a ton of SiO, the result becomes even more dramatic:

7327 KWH/1000 Kg Si are lost with SiO.



MAIN REACTION SPACE
ELECTRIC FURNACE WITHOUT BRIQUETTES
FIG. 1

The challenge is to slow down the reaction in such a manner that part of the chemical reaction can be completed before the quartz melts. The following reaction is suitable since it already starts at 1500 degrees C and utilizes around 5000 KWH/T SiC:

$$SiO2 + 3C \rightarrow SiC + CO.$$

SOLUTION TO THE PROBLEM

Isolation Of The SiC-Reduction:

No solution can be visualized with the current raw materials used in the Si-furnace. AIMCOR's approach has been toward bringing the reactants SiO2 and C closer to each other by means of compaction so that a SiC formation can occur as a solid-solid reaction beginning at 1500 degrees C since the diffusion paths have been shortened.

While the desire for a compacted charge is not new, it is erroneous to create a stoichiometric agglomerate according to the following reaction

$$SiO2 + 2C \rightarrow Si + 2CO.$$

Even small additions of carbon do not solve the problem. The explanation is simple. Since the SiC formation begins very early, requiring 3 moles of carbon, a part of the SiO2 consumes the entire carbon. The agglomerate then disintegrates into SiO2 and SiC with severe disruptions to the furnace operation. The only solution is to produce an agglomerate which maintains sufficient hardness even after the SiC-reaction. Many experiments pointed the way to produce a briquette containing a surplus of carbon relative to the general reaction. This excess carbon must however form a structure which continues to hold the briquette together after the SiC-reaction has been completed.

A briquetting technology was chosen which utilizes liquified coal as binder. After heating and homogeneously mixing the coal with hot sand and petroleum coke, the briquettes are formed at 500 degrees C. The technology has been known for decades under the name of "ancit," and is used today to produce SILGRO 1, among other things. So far 160,000 tons have been supplied to the Si metal industry.

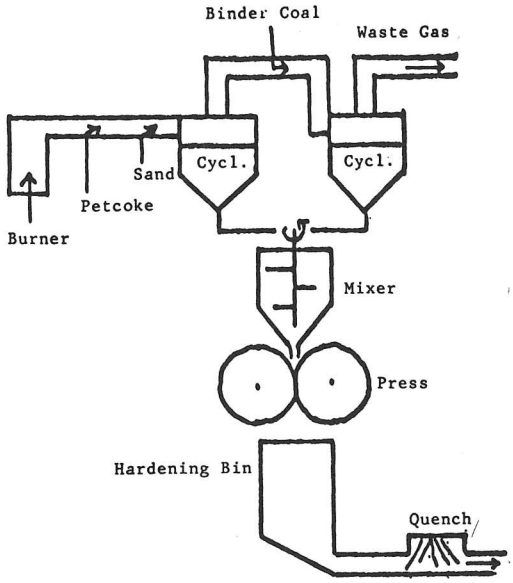


FIG. 2: DIAGRAM OF ANCIT-PROCESS

Unless otherwise requested, the normal mixture consists of 40% sand, 30% petroleum coke and 30% coal.

The essential characteristics of the briquettes may be stated as follows:

Carbon	About 50%
Sand	About 42%
Volatile matter	About 4%
Iron	< 0.1%
Aluminum	< 0.25%
Calcium	< 0.08%
Point pressure hardness	120-160 Kg
Weight of briquette	27-20 g
Specific weight of briquette (density)	1.4-1.5 g/cm3

A simple calculation shows that this formulation gives a mole ratio of around 6.0 between SiO2 and fixed carbon, twice as much as required by the SiC-reaction.

Therefore, when the sand reaches around 1500 degrees C, the SiC reaction can begin and be completed without destroying the integrity of the briquette. Intact samples have been found at the head of the electrodes which show the presence of SiC, Si, C and remainders of

SiO2 (presumably from reoxidized SiO). Also found were briquettes which had an enrichment of silicon in their centers.

SILGRO 1 After The SiC-Reaction:

The SiC-reaction in the briquette takes heat from the rising gas and cools it. The reaction also changes the briquette radically, since the solid-solid reaction between carbon and sand results in fine SiC-crystals and a highly-active carbon structure.

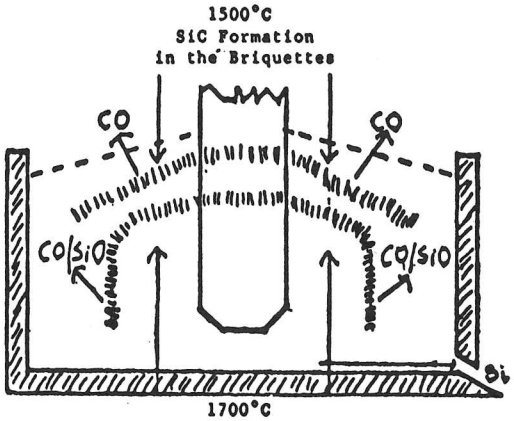
The changed, but still sufficiently strong, briquette sinks into the furnace toward the temperature at which lumps of quartz melt. The following reaction now begins to occur:

$$SiO2 + 2SiC \rightarrow 3\,Si + 2CO$$

from which SiO also escapes and can be reduced by the already-activated briquettes located higher up in the charge. The inner surface of the briquette has grown from 1-2 M2/G after production to 8-22 M2/G after the SiC-reaction and thus is in a position to reduce SiO rapidly. Corresponding measurements show that the briquettes behave like other most highly active reducing agents.

The metallic silicon in the center of the briquette seems to be confirmation of this.

In addition to the energy consumption from the SiC-reaction, there is the energy required for the conversion of SiO to Si. It now becomes also clear that the pre-reduction improves the main-reduction by decreasing the evolution of the CO above 1700 degrees C which drives the SiO at high flow velocity.



MAIN REACTION SPACE
ELECTRIC FURNACE WITH BRIQUETTES
FIG. 3

The reaction SiO2 (liquid) + 2SiC --> 3Si + 2CO which shows the conditions between the pre-reduced briquette and the melted quartz, illustrates the ratio of 3 moles of Si to 2 moles of CO, a strong relief for the main reaction zone in which all reactions must begin and end simultaneously.

Changes In The Furnace Behavior:

All these references, theories and concepts are only of value if they translate into large-scale effects which can be observed and measured. Without jumping ahead to the second part of this presentation, the following results have generally been observed:

- With increasing proportion of SILGRO 1 as carbon source, the gas permeability of the charge becomes noticeably better. The fringe areas of the furnaces become warmer. The number of blowers decreases.

- The movements of the electrodes decrease significantly. A very calm furnace operation results with deeply seated electrodes.

- The tapping temperatures rise.

- The waste gas temperatures decrease.

- The escape of SiO decreases. Waste gas scrubbers show less SiO2.

Commercially interesting consumption data is shown within the framework of results from different furnaces in Europe, USA and Canada:

Electrode consumption- minus 20-60 Kg/TSi
Energy consumption - minus 1500-3000 KWH/TSi
Silicon metal yield - plus 10-15%
Productivity - plus 10-25%

The proportion of SILGRO 1 in the charge has varied. Advantages can reasonably be obtained without exception by replacement of 50-60% of the carbon with SILGRO. From there to 100% replacement has different results, relative to individual experience. One furnace with a 100% SILGRO 1 (2 T SILGRO 1, and 2 T lump-quartz) has operated for several months with full satisfaction. Other furnaces have not yet achieved this. We are working on an explanation for this discrepancy. With a strong upward expansion of the crater, we suspect that the energy input in some operations exceeds the needs of the reaction when using briquettes. At the same time, this upward expansion may reduce the available distance between the SiC activation zone for the briquette and the main reaction zone, again concentrating the production of CO into an area similar to a standard charge operation.

OUTLOOK

The development work with SILGRO 1 has been fundamentally completed. Operations will be optimized over longer operating periods. The current objective is to reduce substantially the need to refine the Si-metal. Considering this aspect, AIMCOR is developing a new generation of briquettes which we call SILGRO 2. This product is expected to have a degree of purity that will revolutionize, in combination with other developments, the manufacture of silicon metal.

PART II

USE OF SILGRO CARBON-SILICA BRIQUETTES IN KEMANORD'S SILICON METAL FURNACES

Ever since the 1950s, a varying part of KemaNord's R&D efforts have been aimed at finding a way of briquetting quartz sand and carbon raw materials, giving a product strong enough to withstand the conditions prevailing in a Silicon Metal Furnace. We did not succeed.

In 1984, AIMCOR introduced a new generation of briquettes which we tested with open-minded cooperation.

The early efforts all had in common to produce a briquette with the "right" stoichiometric composition, and we had seen a lot of different ideas about binders, etc., fall apart in pieces when they reached the furnace. Now, we all of a sudden had a briquette that stayed together until it was completely consumed.

During the 4 years that have passsed since then, we have gathered a lot of positive experiences from using SILGRO briquettes as a raw material for silicon production in our two silicon furnaces in Ljungaverk, Sweden.

The two furnaces used for the trials were:

- Furnace 12, 14 MW, built in 1964 as an Elkem furnace, rebuilt in 1968 resp. 1971 into Demag-style.
- Furnace 11, 22 MW, a Demag furnace built in 1971.

In total, about 17,000 tonnes of briquettes have been charged to these furnaces, divided between them and spread over time as stated in Table 1.

TABLE I

BRIQUETTES CONSUMED BY KEMANORD

Year	Furnace 11 Tonnes	Furnace 12 Tonnes
1984	344	1890
1985	674	2720
1986	0	2045
1987	3601	1825
1988	2727	1545

Early trials showed that maximum improvement of yield and consumption figures per ton briquettes was obtained by charging the furnaces with 40-50% of the total fixed carbon charge originating from the briquettes. Consequently, further trials have mainly been aimed at finding optimal operation conditions and briquette composition at this level.

Availability of the briquettes has been limited, and this has prevented us from using them as a regular raw material in our silicon production. To start with, we only used the briquettes for experimental purposes, but very soon we also found them quite useful as a "furnace conditioner." That means that we used them to increase the active reaction volume in the furnaces, if excessive carbide formation had occurred.

As a base for evaluation of the results achieved during briquette trials, I have used operation data from periods before and after each presented trial.

The normal charge used during these periods consists of:

- Spanish quartz gravel
- Belgium low ash coal
- Up to 10% of total fixed carbon as petcoke
- Wood chips (mainly fresh birch)

The same raw materials were also used together with the briquettes.

FURNACE BEHAVIOR WITH SILGRO BRIQUETTES

One observation that we made very rapidly when we started the first trials with the new generation of briquettes, was that the charge surface cooled down remarkably.

Of course we had periods of disturbed operation also with the briquettes, especially when we were testing what the different

boundaries for safe operation are. But during stable operating conditions, the gas phase distribution in the charge is excellent.

Over extended periods we got the impression that the only silicon losses occurred during stoking of the furnace, preparing it for charging new raw materials.

Electrode control is also positively influenced by the briquettes. It is possible to keep movement of the electrode columns at a minimum, giving further evidence of extremely stable conditions in the reaction zone.

Another natural consequence of the improved operating conditions is that the temperature of the tapped silicon is some 50 degrees C higher than normal. As we always use continuous tapping, this is of great advantage to us.

FURNACE CLEANING

On many occasions, when a furnace, for some reason, has suffered from excess silicon-carbide formation, we have been able to return it to good operating condition again, simply by running it on briquettes for a few days. For such "medical treatment" of a furnace, we use lower carbon to quartz ratio than normal, thereby consuming the silicon-carbide that makes the reaction volume restricted.

INFLUENCE OF DIFFERENT FURNACE SIZE

We have had a limited number of furnaces available for testing the SILGRO briquettes, as mentioned earlier, one 14 MW and one 22 MW furnace. Our experiences of furnace size influence are based on those two sizes. We judge, that with normal charge, the 22 MW furnace is more difficult to run with good production results than the small one. This difference stays unchanged also with SILGRO briquettes in the charge.

The initial trials on the big furnace were not successful, but after changing electrode spacing and electrical parameters, the results improved.

RESULTS ON FURNACE 12

The first trials with the SILGRO briquettes were performed on Furnace 12, and with immediate success.

The results from these trials are presented in Table II, as well as in Figure 1-3.

TABLE II

IMPROVEMENT IN YIELD AND CONSUMPTION FIGURES WITH BRIQUETTES ON FURNACE 12

Consumption figure	Base level	Trial results	Improvement%
Yield, %	83.0	93.2	12.3
Energy, MWh/ton	12.620	10.840	14.1
Electrodes Kg/ton	124	85.8	30.8

It is to be noted, that some days with major production disturbances, as well as adjacent days, are not included in the material.

These previously achieved results have been verified during later trials.

Figure 1

Silicon yield on Furnace 12

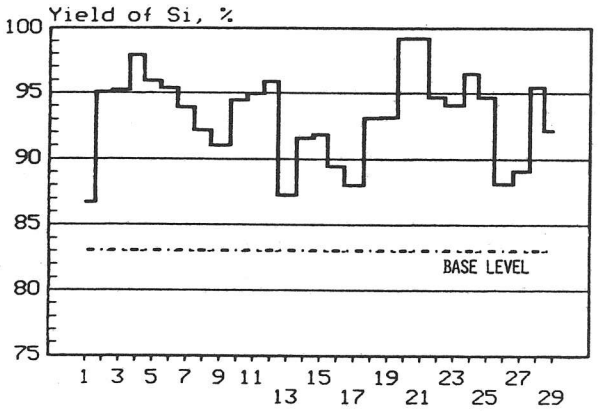


Figure 2

Electrode consumption on Furnace 12

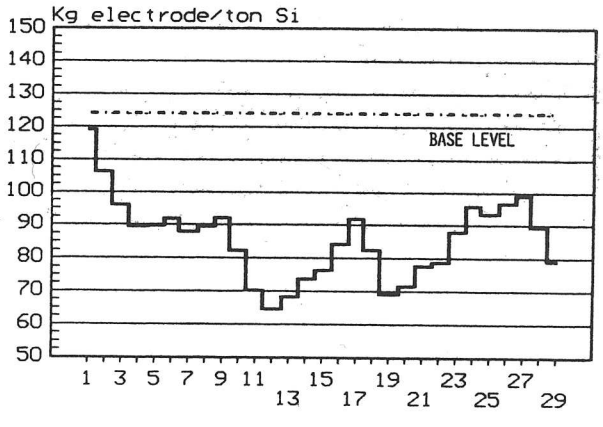
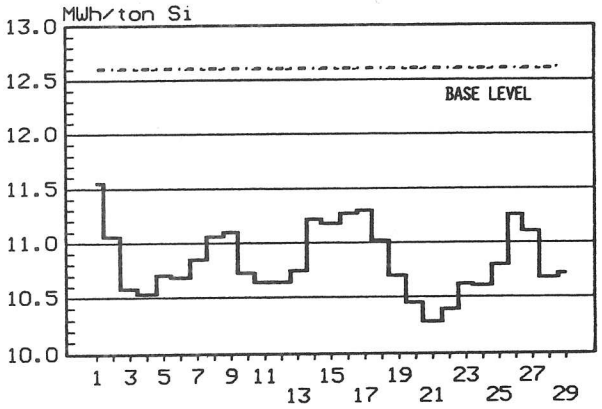


Figure 3

Energy consumption on Furnace 12



RESULTS ON FURNACE 11

The results achieved on Furnace 11 after changing electrode positions and electric parameters compared with the initial trials on this furnace, are presented in Table III as well as in figure 4-6.

TABLE III

IMPROVEMENT IN YIELD AND CONSUMPTION FIGURES WITH BRIQUETTES ON FURNANCE 11

Consumption figure	Base level	Trial results	Improve-ment %
Yield, %	81.5	84.8	4.0
Energy, MWh/ton	12.600	11.430	9.3
Electrodes, Kg/ton	135	114	15.6

Our feeling is that these results can be further improved. We have not had enough briquettes available yet to find optimal operation parameters.

Figure 4

Silicon yield on Furnace 11

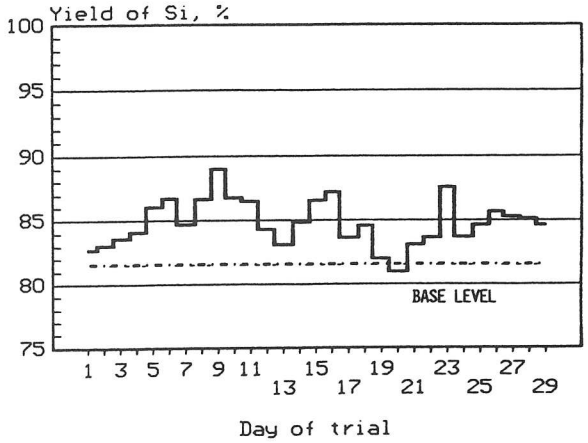


Figure 5

Electrode consumption on Furnace 11

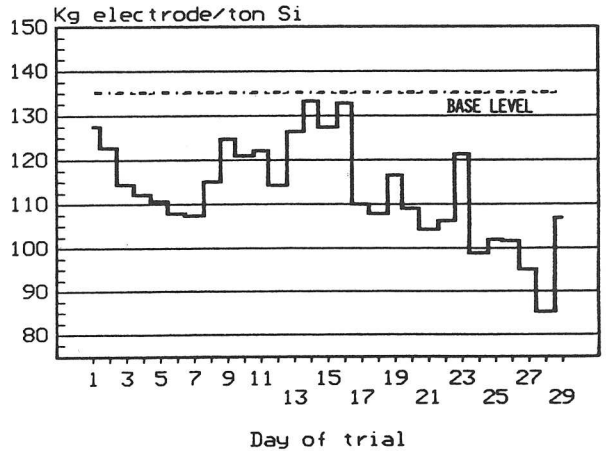
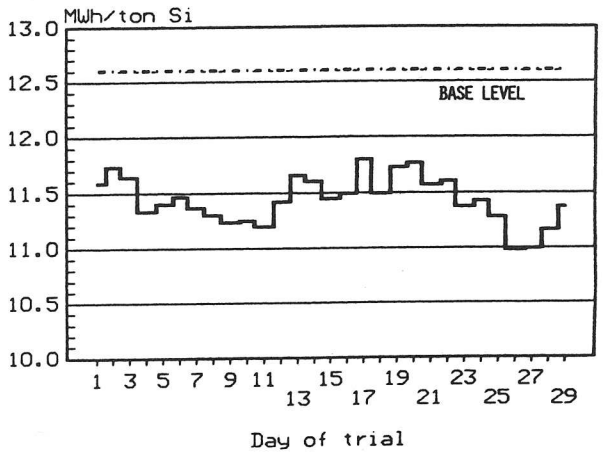


Figure 6

Energy consumption on Furnace 11



WISHES FOR THE FUTURE

One of the most important conditions of success in the noble art of silicon production is to have consistency in the raw material feed. Minimal variation in quality and composition is vital to the furnace operation.

With normal raw materials these variations tend to be unacceptably high.

My wish for the future is to have the possibility to use a briquetted charge supplied at a beneficial cost.

Using quartz sand with high purity and petroleum coke as ingredients in the briquettes would assure me a stable raw material and a high quality silicon product.