ANALYSIS OF THE SMELTING PROCESS FOR THE PRODUCTION OF SILICON-CALCIUM-IRON ALLOYS

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ABSTRACT

The smelting of ferro-silicon-calcium alloys is a complex process usually characterized by the formation of undesirable by-products.

Based on thermodynamic data it is established a model describing the possible sequence of reactions ocurring during the reduction process. This model may be confirmed by the examination of the crusts obtained from the dismantling of the furnace for repairs.

It is found as well as a very good relationship between the slag and metal, showing that the slag is an important step in the reduction process.

The thermal balance shows how the energy efficiency of the process can be improved.

INTRODUCTION

The technical literature is currently publishing papers covering the steel and iron treatment with calcium alloys. The calcium containing alloy most often used is a silicon base alloy, in which calcium content ranges usually between 29 and 33%. The total world market, including USSR, for silicon calcium alloys is relatively limited, far less below than 100,000t (1), and a few plants in the world are producing this alloy. It is also denominated calcium-silicon or calcium silicide or ferro-silicon-calcium, and a very small number of countries in the world are establishing standards for their composition, as shown in table I. As in the usual alloy compositions calcium is regularly found in the microestructure as the intermetalic fase $CaSi_2$ (2), the name calcium silicide is as well as applied.

Electrothermic smelting of silicon-calcium is presently a well developed process, based on accumulated experience from operators, resulting in the modification of the standard reduction furnaces in order to better fit the peculiarities needed for the production of the alloy. In this way a considerable know how was collected by present producers that only to a limited degree has found its way to technical papers.

Calcium silicide alloy have been produced industrially by three methods. One method, sometimes called the two-stage process, consists in the previous production of calcium carbide in a first submerged arc furnace. The resultant carbide is fed into a second submerged arc furnace along with quartz and an appropriate reducer, producing silicon calcium based on the overall simplified reaction:

$$2SiO_2 + CaC_2 + 2C = CaSi_2 + 4CO \qquad (1)$$

According to published information (3-5), power to produce 1000kg of silicon calcium alloy by this process ranges between 13,000 and 17,000kWh, taking into account the power consumed to produce the calcium carbide.

Because of the overall high power usage, plus problems related to the handling and storing calcium carbide, and the need for more furnaces and facilities, the single-stage process is now widely accepted as the more economical way of producing silicon calcium. This method, also called carbothermic process, consists of charging the furnace with a weighted mixture of lime, quartz and an appropriate reducer. In some plants it is used limestone instead of burnt lime. Under the proper conditions of the electric reduction furnace silicon-calcium alloy may be produced in accordance with the following overall simplified reaction:

$$2SiO_2 + CaO + 5C = CaSi_2 + 5CO \qquad (2)$$

A third method for producing silicon-calcium, known as silicothermic process as been proposed as an alternative for the two stage process. The technique is based in the reduction of CaO with Si contained in ferro-silicon, melting the charge in an electric arc furnace. It is produced an alloy and a slag in accordance with the following reaction:

$$3CaO + 3Si\ (alloy) = CaSi_2\ (alloy) + 2CaO.SiO_2 \qquad (3)$$

In spite of this process being considered by the developers as better than the others (6), it is seldom used in the western world and the single-stage process is still the most used.

At first glance, and without examining some of the thermodynamic aspects, the reaction (2) which describes the overall reaction of the

TABLE I - STANDARD COMPOSITIONS OF SILICON-CALCIUM ALLOYS

Standard	Grade	% Si	% Ca	% Fe max	% Al max	% C max	% P max	% S max	% Others
ABNT NBR 5912-88	SiCa	58-65	30-33	Balance	1,0	1,0	-	-	-
ASTM A 495-1976	CaSi	60-65	28-32	5 max	1,5	1,0	0,02	0,02	0,10% Ti max
DIN 17580-1968	Casi	-	29-33	Balance	1,8	1,2	0,07	0,06	90(Si+Ca) min
	CaSiC50	-	29-33	Balance	1,8	0,5	0,07	0,06	90(Si+Ca) min
JIS G2314-1978	CaSi 1	55-65	30 min	Balance	-	1,0	0,05	-	-
	CaSi 2	55-65	25-29	Balance	-	1,0	0,05	-	-
GOST 762-49	CaSi 0	-	33 min	Balance	1,5	-	0,05	0,04	90(Si+Ca) min
	CaSi 1	-	28 min	Balance	2,5	-	0,05	0,04	90(Si+Ca) min
	CaSi 2	-	23 min	Balance	3,0	-	-	0,04	85(Si+Ca) min

single-stage process might appear simple and easily obtained. Using pure reactants, if carried out as shown, it indicates that an alloy containing about 42%Ca and 58%Si should be obtained. Experience has demonstrated that this is not the case, however, even when employing, without considering economical aspects, the highest purity reactants available, suitable for use in a submerged arc furnaces. Production experience collected through tryals and errors has demonstrated that the smelting of silicon calcium alloys is one of the most trick and troublesome processes. As in the case of the other silicon base ferroalloys, the reduction process is acomplished by the formation of intermediate carbides and gaseous species, other than CO, which significantly complicate the making of this alloy. On the other hand, contrary to the production of silicon and ferrosilicon, which are basically slagless processes, the smelting of silicon-calcium is always acomplished by the formation of huge quantities of slag which are tapped at the same time as the alloy.

In the case of silicon metal and ferrosilicon, the carefull control of the composition of the raw materials and reducting materials allows the reduction process to proceed until pratically all charge is reduced. If any slag is formed, it will float on the molten alloy having still the opportunity to be reduced if the furnace conditions are properly adjusted. In the case of the smelting process for the production of silicon calcium, the simultaneous presence of lime and silica will easily allow the formation of important quantities of slag, which are denser than the alloy and sink loosing contact with the reduction zone of the furnace. This slag is strongly contaminated with calcium carbide, silicon carbide and alloy droplets, and a slag free process is impossible from the practical standpoint.

Consequently the silicon calcium smelting operation might be remotely compared to that of producing silicon metal.

In the typical mass balance of silicon-calcium smelting process the charge input is counter balanced to a output comprising of alloy, offgases and slag. Data collected from different operations shows that there is a wide range of operational parameters, as shown in table II. Taking into account the losses in the slag and in the offgases, calcium and silicon recovered in the alloy range to values as low as to respectively 55 to 73% and 60 to 70% (10). Considering Ca and Si losses in the offgases, about 10% each one, the slag tapped with the metal amounts 300 to 1050kg of slag per metric ton of alloy.

Considering the wide range of confliting operational data and the lack of scientific approach covering the smelting of silicon alloys, it was decided to proceed a systematic collection and analysis of the data obtained from regular production at Bozel plant, in order to develop a better understanding of the process.

Bozel plant at Minas Gerais is producing silicon-calcium alloys in two electric arc reduction furnaces, rated each one at 21MVA. The production is through the single-stage process using charcoal is main reduction material.

The thermochemistry of the process was studied through the chemical analysis of the metal and corresponding slag during the regular operation and through the examination of the crusts obtained from the furnace dismantling for repairs.

The Thermodynamics of the molten industrial alloys

The first difficulty in establishing a scientific approach to the production data is the settlement of the thermodynamical characteristics of molten silicon-calcium alloys at the high temperatures involved in the smelting process. The thermodynamic properties of the pure silicon-calcium alloys as established elsewhere (11) must be conveniently

TABLE II - TYPICAL CHARGES FOR THE PRODUCTION OF 1000kg OF STANDARD SILICON-CALCIUM AND COMPOSITION OF THE SLAG TAPPED WITH THE METAL

REFERENCE	Silveira(12)	Walter(3)	Elyutin (9)	Edneral(5)	Riss(7)	Perez (8)	Robiette (19)
CHARGE (kg/t)							
Quartz	1800	1650-2100	1890	1830	1900	1600	1950
Burnt lime	1100	-	640	710	720	-	970
Limestone	-	-	-	-	-	-	-
Calcium carbide	-	600-1020	-	-	-	650	-
Charcoal	1380	170-200	270	500	400	190	270
Coal	-	-	150	310	240	-	160
Coke	-	560-580	890	580	670	450	720
Soedeberg paste	-	80-120	140	160	230	-	120
SLAG COMPOSITION							
%CaO	53.5	40-60	40-57	15-25	15	50-60	-
$\%SiO_2$	26.4	30-50	25-55	45-50	54	14-24	-
$\%Al_2O_3$	0.7	-	-	4-5	2.5	2-8	-
%FeO	-	-	-	-	-	0.3-0.6	-
$\%CaC_2$	9.3	5-15	8-11	10-12	15	7-20	-
%SiC	9.3	3-13	3-12	8-10	9	7-20	-
SLAG RATE kg slag/t alloy		300-800	700	860	900	300	1050

adjusted to the composition of the industrial alloys, which are usually alloyed with iron, contain aluminum and carbon as main impurities and, depending of the tapping and casting conditions, may be contaminated with appreciable quantities of slag. (2)

Figure 1 shows the system Si-Ca-Fe as proposed by Schurmann et alli (22), with the composition of the industrial alloys represented in the shaded are. As shown elsewere (2), depending of the Si and Fe contents the microestructure of the alloy may present Si or Fe_2Si_5 as primary phases. In any case most of the Ca will be present as the phase $CaSi_2$.

In the structure of industrial alloys the phases precipitated from impurities are usually SiC, CaC_2 and FeAlSiCa (2).

Simple thermodynamical calculation shows that the stability at high temperature of the phases Fe_2Si_5, CaC_2 and CSi are of the same order of magnitude as $CaSi_2$. Consequently, as a first rough approximation, the effect of iron on the activity of calcium could be considered as a reduction in the silicon content proportionaly to the composition of the Fe_2Si_5 phase. The effect of the aluminum may deducted directly from the thermodynamic data on Fe-Ca-Si alloys (11): each 1%Al contained in the alloy is equivalent to 0.78%Si.

The effect of the carbon is more difficult to understand. However it can be assumed that at the very high temperature existing close to the electric arc all the carbon is dissolved in the alloy (20), and the precipitation of carbide occurs during the movement of the molten alloys to the colder zones of the furnace. It can be assumed as well as that it is established an equilibrium during carbides precipitation in accordance with

$$\underline{Ca} + 2SiC = 2\ \underline{Si} + CaC_2 \qquad (4)$$

with a calculated free energy given by

$$\Delta G^o = +\ 39450 - 14.75\ T \quad cal/mol$$

Considering that the activity of calcium is by far below that of the activity of the silicon respectively about 0.003 and 0.6, when considering an alloy containing 0.3 mols of Ca and 0.7 mols of Si (figure 2), and the high value of the free energy of the reaction (4) in the temperature of interest, it is reasonable to assume that practically all the carbon is precipitating as SiC, which usually corresponds to the microstructure of the commercial alloys (2). Consequently the effect of carbon contamination can be assumed as a decrease of the silicon content corresponding to the composition of the phase SiC.

As an example lets consider an industrial alloy containing 61%Si, 31%Ca, 5,5%Fe, 0,5%C and 0,5%Al. A simple calculations (Table III) shows that 1000g of the alloy will contain 19.07 mols of Si to combine with 7.75 mols of Ca. In accordance with the described criterion, this alloy is equivalent to a binary silicon-calcium alloy containing an atomic fraccion of calcium equals to 0.29 or 36.8%Ca by weight.

The silicon equivalent of the alloy is a way of better comparing thermo dynamic data of the alloys, and is a criterion to be used until a better approach is found.

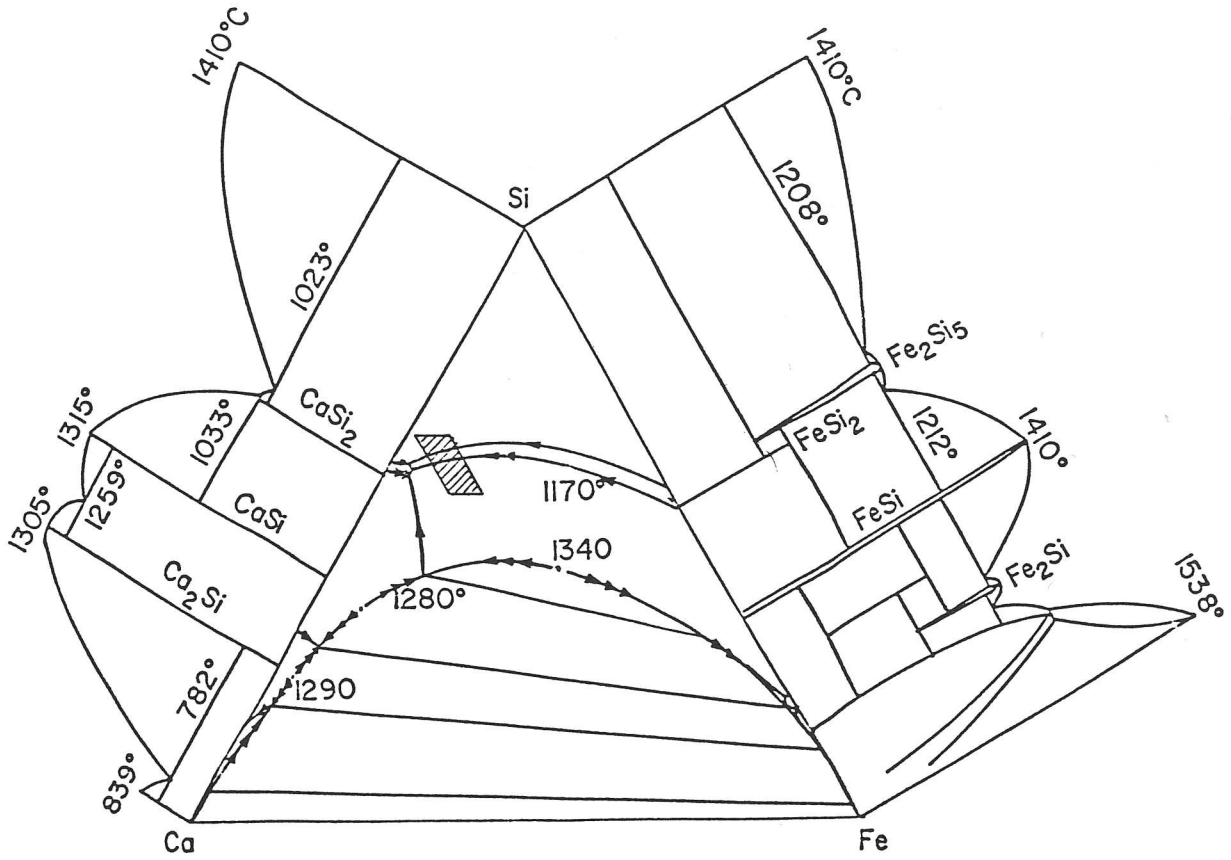

Figure 1 - Equilibrium diagram of the system Si-Ca-Fe (22). The upper shaded area represents the composition of the standard alloys (Table I). Depending of the Si and Fe contents, primary phase may be Si or Fe_2Si_5. In any case most of the Ca is present as $CaSi_2$ phase.

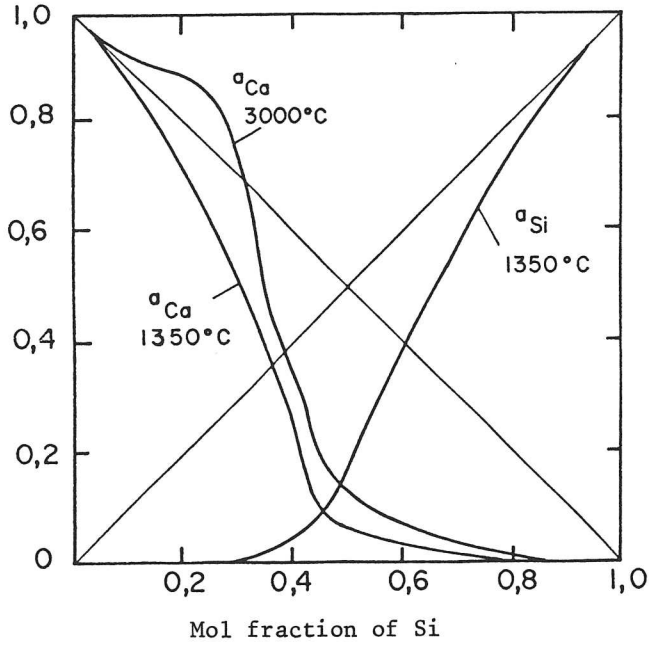

Figure 2 - Activities of Si and Ca in silicon-calcium binary alloys (11). Industrial alloys correspond to approximately 0.7 mols Si.

TABLE III - EXAMPLE OF EQUIVALENT SILICON CALCULATION

Element	Weight content %	Mols per 1000g of alloy	Calculus of equivalent Si
Ca	31.0	7.75	-
Si	61.0	21.79	+ 21.79
Fe	5.5	0.98	-2.5 x 0.98 = - 2.45
C	0.5	0.42	-1 x 0.42 = - 0.42
Al	0.5	0.19	+0.78x 0.19 = + 0.15
			Total = 19.07

$$X_{Ca} = \frac{7.75}{7.75 + 19.07} = 0,29$$

$$X_{Si\ eq} = \frac{19.07}{7.75 + 19.07} = 0.71$$

The thermochemistry of the smelting process of silicon alloys

The thermodynamic study of the smelting process of silicon calcium production is not easy in view of the number of species involved and the number of possible reactions. The simplest charge is composed of the oxides SiO_2 and CaO in the form of quartz and burnt lime, and C in the form of an appropriate reducer. The experience shows that Ca and Si are lost in the gases, consequently it should be expected that the gases Ca vapour, SiO and CO participate in the reduction process. With the metal, it is tapped an appreciable quantity of slag which contains basically calcium silicate, CaC_2 and SiC. Finally, the Soedeberg electrode contributes with Fe contamination, and all the charge brings contamination with at least Al_2O_3.

Due to the practical impossibility to the compounds reacting all together at once, it would be more reasonable to consider inicially the reactions occurring with each two components.

The reactions occurring when SiO_2 and C are heated together received an excellent approach from Schei (13, 14) and Müller et alli (15). The possible reactions are represented as a function of the partial pressure of equilibrium gases and temperature, as in figure 3. At low temperatures, some SiO must be formed to fulfil the equilibrium

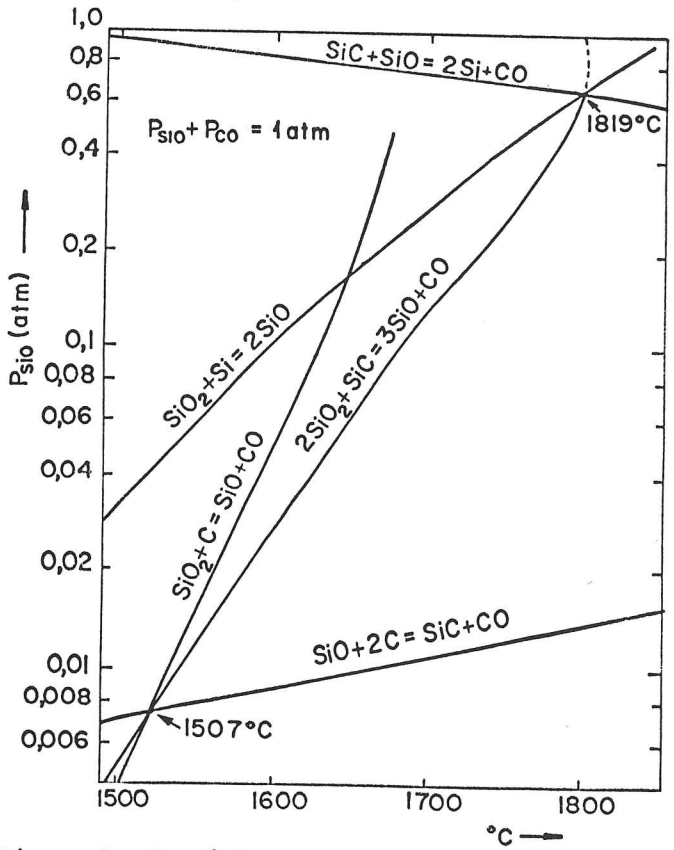

Figure 3 - Parcial pressure of SiO as function of temperature for reaction occurring when SiO_2 and C are heated together (14)

$$SiO_2 + C = SiO + CO \qquad (5)$$

At 1507°C SiC is a stable phase and will be formed in accordance to the reaction

$$SiO + 2C = SiC + CO \qquad (6)$$

There are then three condensed phases, and the system is non variant according to the phase rule. As the SiO partial pressure is low, the overall reaction at the non-variant point is near to

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

If all the carbon is consumed by this reaction, the temperature may rise. With increasing temperature, the SiO content of the gas will increase according to the equilibrium

$$2\ SiO_2 + SiC = 3\ SiO + CO \qquad (8)$$

until 1819°C when Si becomes stable. The equilibrium is then again non variant with p_{SiO}/p approximately 2/3. This gas composition must result from an over-all reaction

$$3\ SiO_2 + 2\ SiC = Si + 4\ SiO + 2\ CO$$

During its way to the colder zones of the furnace, the gas mixture cools and becomes unstable. The following condensation may occur

$$3\ SiO + CO = 2\ SiO_2 + SiC \qquad (8)$$

$$SiO + CO = SiO_2 + C \qquad (5)$$

$$2\ SiO = Si + SiO_2 \qquad (9)$$

$$SiO + 2C = SiC + CO \qquad (10)$$

The last reaction, formation of SiC through the reaction of SiO gas with the carbon contained in the reducer is considered as the most important step for the production of SiC. To be accomplished, the reduction material must have a convenient porosity, consequently charcoal is considered the best for silicon smelting (16).

Thermochemistry of the reactions between CaO and C

It can be established a similar approach when considering the reactions occurring when CaO, from burnt lime, and C from a reduction material are heated in contact. The study may be accomplished by representing the possible reactions as function of Ca vapour parcial pressure and temperature (figure 4).

When a mixture of CaO and C are heated, it is formed inicially calcium vapour and CO in accordance with

$$CaO + C = Ca\ (vapour) + CO \qquad (11)$$

At 1865°C, the partial pressure of calcium vapour reaches 0.011 bars, enough for the formation of CaC_2, when 3 condensed phases appear, and the system becomes non variant according to the phase rule.

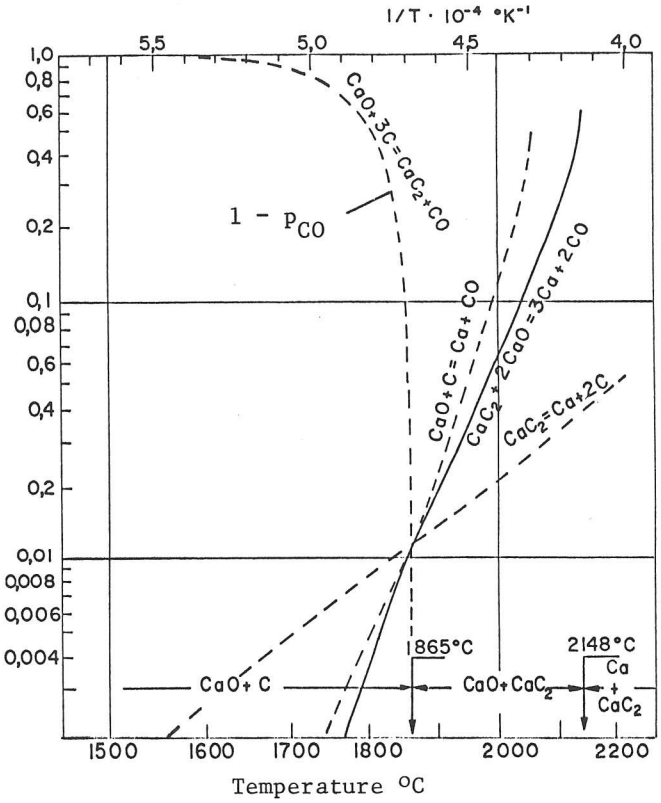

Figure 4 - Calculated partial pressure of Ca vapour for reactions occurring when CaO and C are heated together.

Possible reactions for the formation of CaC_2 are:

$$Ca\ (vapour) + 2C = CaC_2 \qquad (12)$$

$$CaO + 3 = CaC_2 + CO \qquad (13)$$

According to the phase rule the temperature will be maintained constant until one of the reactants is consumed. If there is not enough carbon, it will still remain some CaO after all C is reacted. Ca vapour can be formed,

$$CaC_2 + 2CaO = 3\ Ca\ (vapour) + 2\ CO \qquad (14)$$

and the partial pressure of Ca vapour increases with the temperature until 2148°C when the reaction is accomplished at a partial pressure of Ca vapour of 0.6.

If there is an excesses carbon, all the CaO will be converted to CaC_2 at 1865°C. With further increase in temperature the CaC_2 will partially decompose releasing Ca vapour according to

$$CaC_2 = Ca\ (vapour) + 2C \qquad (15)$$

During its way to the colder zones of the furnace, the Ca vapour will react with C restablishing CaC_2. A carefull study of the mass transfer related to the above reactions brings to the conclusion that the most important step for the formation of CaC_2 is the reaction of the Ca vapour formed in the hotter zones of the furnace with the carbon of the reducer in the colder zones of the furnace. Once again the porosity of the reducing material plays a quite important rule (17, 18).

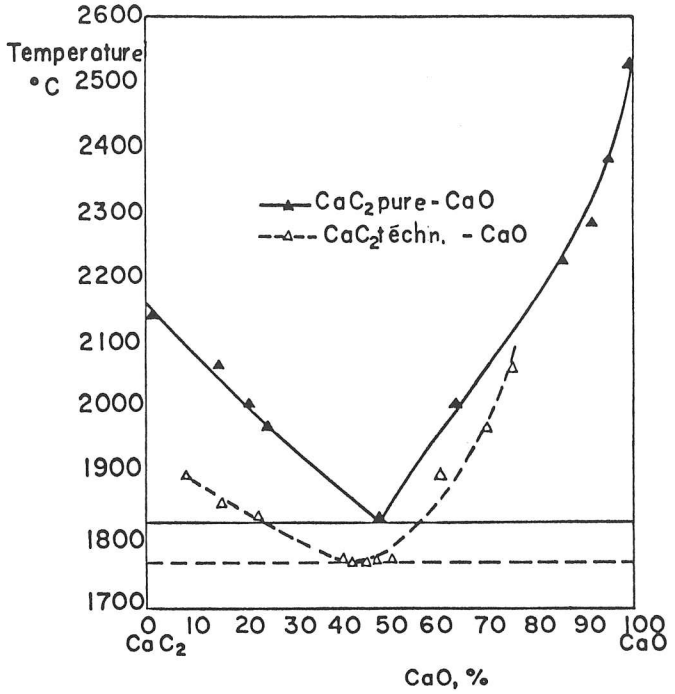

Figure 5 - Equilibrium diagram CaO-CaC_2 showing the liquidus solubility of the phases (3).

The reaction (13) of solid CaO with the reducer forms CaC_2 in the contact region. On further heating, according to equilibrium diagram represented in figure 5, the CaC_2 melts dissolving CaO, promoting the continuing of the carbide forming reaction. On the other hand the equilibrium temperature of the reaction (14) of Ca formation from CaO and CaC_2 is increased from 1865°C to 1920°C in view of the decrease in activity of the CaO and of the CaC_2.

Thermochemistry of silicon calcium smelting

According to Elyutin et alli (9), the single stage reaction of the smelting process is given by:

$$2\ SiO_2 + CaO + 5C = CaSi_2 + 5\ CO \qquad (2)$$

with an equilibrium temperature of 1853K. In view of the impossibility for a convenient simultaneous contact of the three components, above reaction is hardly to happen. It should be considered initially the formation of SiC, SiO, Ca vapour and CaC_2 from the contacts of the oxides SiO_2 and CaO with carbon.

Following two compounds reaction to be considered is of Ca (vapour) with SiO in accordance to:

$$Ca(v) + SiO(g) = Si(l) + CaO(s) \qquad (15)$$

The calculated product pressure of the gases is very low in the range of temperatures below 1850°C. At 1819°C,

$$P_{SiO} \cdot P_{Ca} = 0.0005$$

as calculated from thermodynamic data(21).

Consequently, if the temperature is not high enough, Ca(vapour) may precipate as CaO from the reaction with SiO. It appears clear that the possibilities for the formation of CaC_2 are relatively scarce, and SiC will be the predominant carbide in the region of highest temperature. The same conclusion is coming from the comparative examination of the figures 3 and 4. The Ca vapour partial pressure at a given temperature is far below the SiO vapour partial pressure at the same temperature.

Final reaction may be determined by SiC previously formed with CaO and with SiO_2 in the form of oxides or calcium silicate. In addition, the molten calcium silicate slag formed will react with the metal in order to establish the equilibrium between Ca and Si contained in the metal according the reaction

$$2\ \underline{Ca} + (SiO_2) = \underline{Si} + 2\ (CaO) \qquad (16)$$

where $\underline{Ca}$ and $\underline{Si}$ represent the metals dissolved in the alloy and (SiO_2) and (CaO) represent the oxides dissolved in the molten slag.

At high temperatures it may be possible to occur the formation of CaSi alloy by

$$SiC + CaO = CaSi + CO \qquad (17)$$

which reachs equilibrium at 1845°C with $p_{CO} = 1$. Due to the presence of SiO at higher temperatures, there is a decrease of the parcial pressure of CO, decreasing the temperature of the reaction (17), which is the most important in view of the small quantity of CaC_2. Partial pressure of CO for the important reactions at high temperature are given in figure 6. It appears reasonable to assume that the final reaction will happen at p_{SiO} slightly higher than 0.6, once reaction (17) is shifted to the right in view of the diluting effect for the formation of $CaSi_2$.

Final process may be envisaged as a combination of the three following reactions occurring in increasing temperatures,

$$SiO_2 + C3 \xrightarrow{1500C} SiC + 2\ CO \qquad (7)$$

$$CaO + SiC \xrightarrow{1800C} CaSi + CO \qquad (17)$$

$$SiO_2 + 2SiC \xrightarrow{1815C} 3Si + 2\ CO \qquad (18)$$

According to previous thinkings, the quantity of CaC_2 formed may be relatively small. Even so, it may be assumed as well as that CaC_2 will contribute to the formation of the alloy, according to the following combination of reactions:

$$Ca\ (vapour) + 2C \xrightarrow{< 1770C} CaC_2 \qquad (12)$$

$$CaC_2 + SiO_2 \xrightarrow{\sim 1770C} CaSi + 2CO$$

$$SiO_2 + 2SiC \xrightarrow{\sim 1815C} 3Si + 2CO \qquad (18)$$

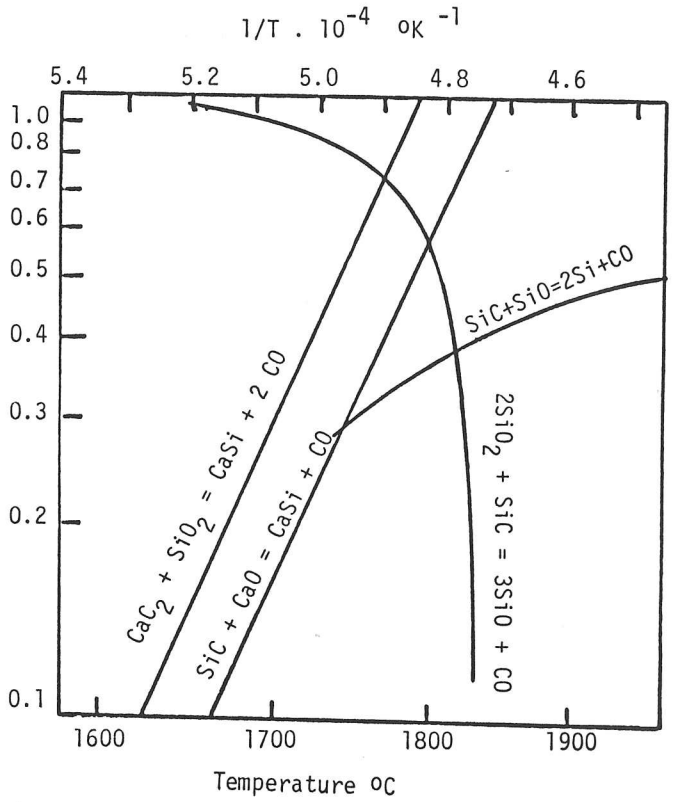

Figure 6 - Calculated partial pressures of CO for some reactions in the system CaO - SiO_2 - C

The examination of the chemical composition of the crusts near the crater wall, obtained when desmantling the furnace for repairs, shows that the main existing intermediate compound is the SiC. The phases CaC_2 and Si metal represents each one about one fifth of the SiC content. It was found as well as calcium silicate slag.

The crusts removed from the botton of the furnace are constituted basically of SiC, with minor quantities of CaC_2 and calcium silicate slag.

The findings brings some prove that the intermediate phase CaC_2 does not play an important rule for the silicon calcium process. It appears that the formation of the intermediate compound SiC and its further reaction with CaO and SiO_2 or even with the calcium silicate slag is the most probable sequence of reactions in the single phase smelting process.

The analysis of the furnaces crusts are more or less in agreement with a research previously done on a 500MVA furnace (23).

Slag metal relationship

The supply of raw materials used in our plant have been developed by selection of purer ores. Charcoal, which is caracterized by low ash content is the main reducer used. Consequently, the development of the process since the plant started operation, allowed to the regular production of silicon calcium alloy of a purity that is considered a premium quality elsewere.

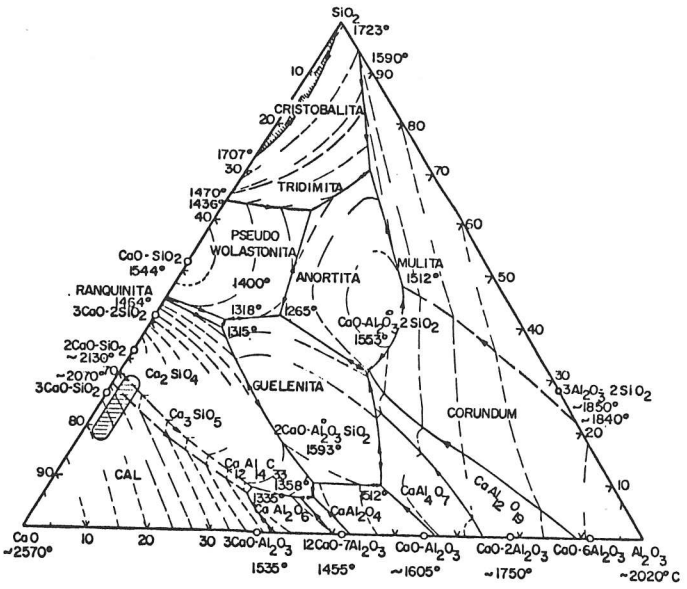

Figure 7 - $CaO-SiO_2-Al_2O_3$ system. The shaded are at the left near to the botton represents the composistion of the silicate phase of the slag.

In view of the large amount of slag formed, it is to be forecast that it is acchieved an equilibrium between the slag and the molten metal. This slag is composed of a silicate phase containing precipitated calcium and silicate carbides. Excluding the carbides, the silicate phase is composed of CaO, Al_2O_3, SiO_2 and a smaller content of FeO. Figure 7 represents the range of compositions of the silicate phase, plotted in the $CaO-SiO_2-Al_2O_3$ diagram. The melting temperature of the silicate phase is very high, reaching up 2300°C.

During the smelting of silicon-calcium, as the molten slag formed is denser than the alloy, the slag sinks to the botton of the furnace. Considering the very high temperature involved in the submerged arc furnace operation, it may be assumed that, when the slag is passing through the molten alloy layer, it is established an equilibrium given by the following reaction:

$$2\underline{Ca} + (SiO_2) = 2(CaO) + \underline{Si} \qquad (16)$$

where <u>Ca</u> and <u>Si</u> represent the elements dissolved in the alloy and (SiO_2) and (CaO) represent the oxides dissolved in the slag. The carefull examination of a number of slag compositions and their respective metals compositions show that this relationship exists in production melts, as shown in figure 8. In this figure it was plotted the alloy richness as function of the slag basicity index.

Alloy richness is here defined as the ratio X_{Ca}/X_{Si}, where X_{Ca} is the mole fraction of Ca in the alloy and X_{Si} is mole fraction of equivalent Si, calculated as previously described. The slag basicity index was calculated as the ratio $\%CaO/\%SiO_2+\%Al_2O_3$.

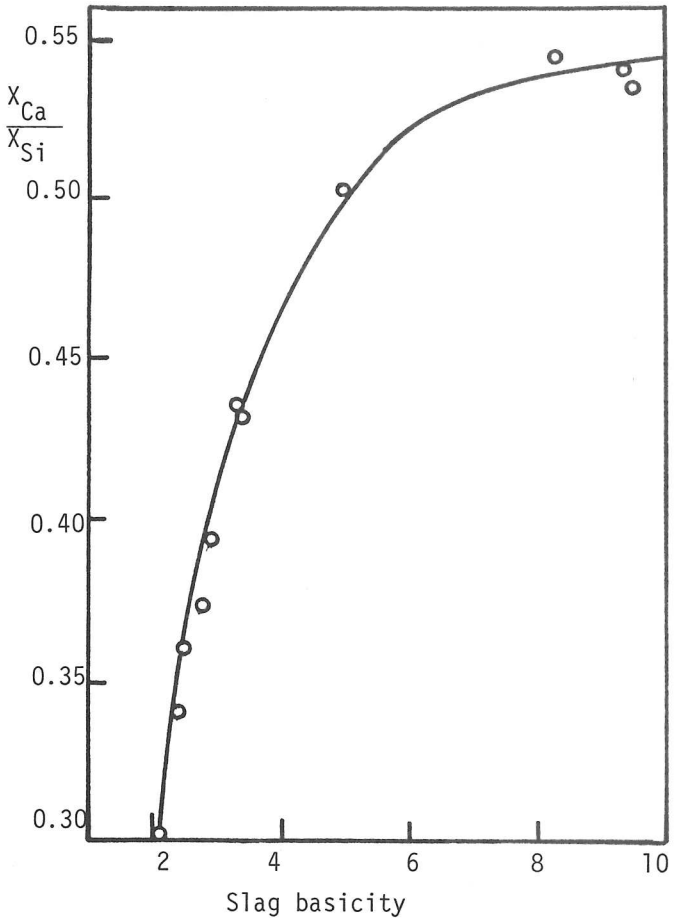

Figure 8 - Relationship between the silicate phase basicity with the alloy richness index.

It is clear in figure 8 that the alloy richness increases with the basicity of the slag.

Systematic analysis of the slags tapped with the alloy shows that they contain appreciable quantities of SiC and CaC_2. One question that arises is if these carbides are intermediate products formed during the smelting of the alloy or if they are resulting from the decrease in solubility of the carbon dissolved in the liquid slag. The study of the chemical analysis of the slag shows that there is a very good relationship between the slag basicity and the total carbon content of the slag as it can be seen in figure 9. However the relationship between slag basicity with CaC_2 content or with SiC content is not so clear.

Considering the tendency of the slag to enter in equilibrium with the metal, the CaC_2 content of the slag should have some proporcionality with the Ca content of the metal in accordance with the following reaction:

$$\underline{Ca} + 2(SiC) = (CaC_2) + 2\,\underline{Si} \qquad (20)$$

where <u>Ca</u> and <u>Si</u> represent the elements dissolved in the metal and (SiC) and CaC_2) represent the carbides contained in the slag. However, the examination of the available data did not show

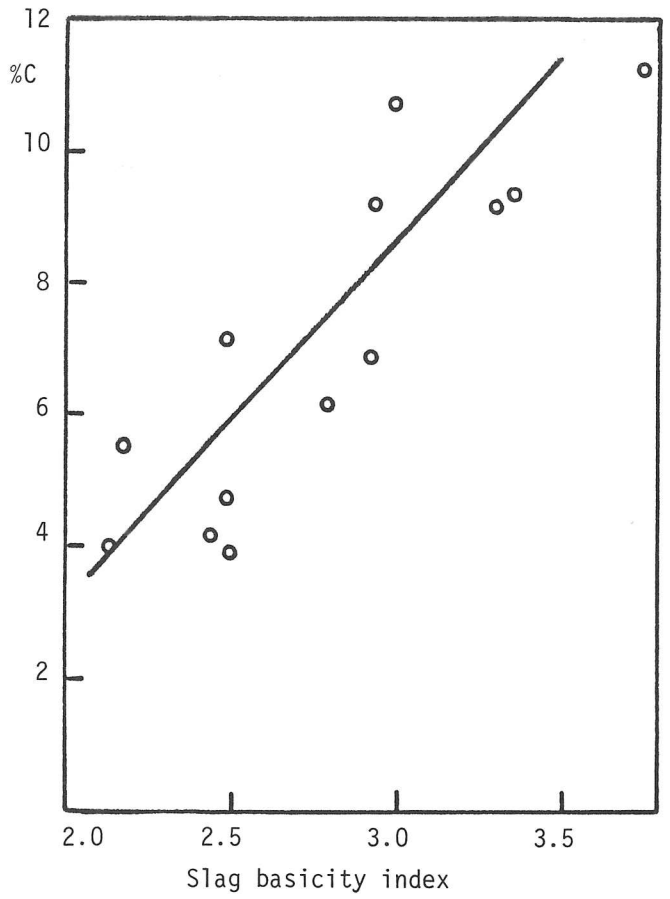

Figure 9 - Relationship between the slag basicity index and the carbon content of the slag.

any relationship in accordance with the reaction (20).

Energy balance of the process

As in the case of other silicon alloys, energy consumption usually constitutes the main factor cost and receives the best attention. Being a process of high temperature, the smelting of silicon-calcium depends on a constant energy supply. Any shut down of the electricity supply causes a decrease of the temperature in the reaction zone, which will represent a decrease in production proportionally higher than the down time. Statistic control of the operation shows an effect three times higher.

Other main factors contributing to increase of energy consumption, respectively decrease in production are: silicon losses as SiO, calcium losses as Ca vapour and increased quantities of slag.

Table IV sumarises the main factors that promote increased energy consumption.

TABLE IV - EFFECT OF SOME VARIABLES ON THE ENERGY CONSUMPTION FOR THE SMELTING OF SILICON-CALCIUM

Variable	Effect on energy consumption
1% down time	+ 3.0%
Increase of the slag rate in 50kg slag/t alloy	+ 1.5%
Increase in silicon losses as SiO in 10%	+ 6.5%
Increase in calcium losses as Ca vapour in 10%	+ 2.0%

CONCLUDING REMARKS

The smelting process for the production of silicon-calcium-iron alloys was studied, based on thermodynamic data. It was established a thermochemistry modelling based initially on the simple oxides reaction with carbon. It was proposed a sequence of reactions that fits relatively well to the chemical analysis of the crusts formed near to the crater wall.

Apparently the main intermediate phase is SiC, resulting from the reactions of SiO_2 with C and mainly of SiO with C. In view of the relatively low partial pressure of Ca gas, apparently this phase and CaC_2 do not bring a large contribution to the smelting process.

It was shown as well as that the slag phase is an important step in the final reaction. This slag is apparently in equilibrium with the metal.

The analysed slag presents an appreciable content of carbon, which precipitates as refractory carbides in the zones of the furnace that are not so close to the crater and electric arc. As it is impossible to avoid this precipitation, the encrusting of the furnace during normal operation is a normal rule.

As in the case of the smelting of other silicon base alloys, energy consumption is one of the elements of major concern. Some variables that contribute to increased energy consumption were mentioned. Even so, the accumulated experience and thermodynamic research shows that the biggest problem is still the formation of refractory crusts that are impossible to avoid and usually they clogg the furnace and reduce the extent of the campaign.

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