Distribution of Al and Ca between Ferro-Silicons and CaO-Al$_2$O$_3$-SiO$_2$ slags at 1450°C.

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Several ferro-silicon liquid alloys (65wt% Si called FeSi65) were equilibrated in SiC-coated graphite crucibles with CaO-Al$_2$O$_3$-SiO$_2$ liquid slags at 1350, 1450 and 1550°C. 12h to 48h duration were requested to reach a thermodynamic equilibrium, depending on the viscosity of the slag. Chemical analysis of the phases after quenching in air allowed to find a correspondence between the slag composition and the residual amounts of Al and Ca in the alloys. Results were interpreted in terms of infinitely diluted solution of these trace elements in the ferro-silicon. The isoconcentration lines of Al and Ca in a ferro-silicon alloy at 65% Si are presented for the CaO-Al$_2$O$_3$-SiO$_2$ liquid slags at 1450°C. Activity coefficient values are proposed for Al and Ca at infinite dilution in FeSi65.

I.   INTRODUCTION

Al, Ca and Ti are the three major impurities contained in industrial ferro-silicon. To remove Al and Ca an oxidizing treatment of the liquid alloys may be used. Gaseous oxygen and/or silica are brought into contact with the primary alloy as soon as it is poured from the electric carboreduction furnace. In this process chemical exchanges take place at various temperature ranging from about 1750°C to 1350°C. It leads to the formation of a CaO-Al$_2$O$_3$-SiO$_2$ slag, often silica-rich. To better understand the oxidizing process it is useful to know the thermodynamic limits of Al and Ca removal corresponding to the equilibrium between these two liquid phases. For this, equilibrium experiments were undertaken with synthetic ferro-silicons having amounts of Al and Ca comparable to or higher than the amounts usually present in industrial alloys. These experiments were carried out in SiC lined graphite crucibles because industrial ferro-silicons are usually SiC saturated at the exit of the reduction furnace.
Similar experiments have already been carried out by Tuset (1)(2)(3) at 1550°C and by Weiss & Schwertfeger (4) at 1500 and 1600°C. It is the reason why the present experiments were focussed on a lower temperature despite the inherent difficulties. Indeed the silica rich slags are known to be very viscous and their components have a low diffusion coefficient. Thus the reaction kinetics may be low, even at 1450°C. Diffusion couples were realized to evaluate this problem and a simple kinetic study was carried out to make sure that the equilibrium experiments lasted long enough to reach conditions as close as possible to a thermodynamic equilibrium.

II.   EXPERIMENTAL

A. Experimental set-up

The equilibrium experiments were carried out with premelted Fe-Si alloys at 65wt%Si(FeSi65), obtained from pure iron (99.3%) and pure silicon (99.999%) with additions of Al and Ca ,and with premelted slags. The slags were prepared from pure natural minerals and melted in a water-jacket furnace. The initial compositions of the alloys are given in Table I and the initial composition of the slags are in Table II.

Equilibration was achieved in a 30mm inner diameter SiC coated graphite crucible that was placed in a larger inductively heated graphite crucible as shown on Fig.1. Argon was blown inside the heating crucible to prevent the presence of oxygen (as CO at high temperature) in order to avoid the superficial oxidation of the alloy before the slag has been melted and thus has covered the metal. The argon flow (1 to 2 l/min) was maintained during the treatment until the sample were cooled. The temperature was measured by a PtRH6%/PtRh30% thermocouple placed inside the heating crucible, by the equilibration crucible, as shown on Fig 1.

Pieces of alloy (60g) were first introduced in the equilibration crucible and melted by induction in a vacuum chamber filled with Ar-10%H_2. The temperature (1550 to 1600°C, measured with an optical pyrometer) was maintained for about 20 min. This preparation was necessary to avoid the presence of a thick layer of oxide, at the surface of the alloy pieces, that could form if the alloy and the slag were heated together in the equilibration furnace. Such a layer resulted in some cases in a blockage of the mass transfer between the metal and the slag and also formed alloy containing "oxide bags" that were mangled with slag, impeding a good sampling of the two phases.

After cooling under Ar-H_2 the equilibration crucible with its monolithic load of ferro silicon received about 60g of crushed slag and was placed inside the heating graphite crucible. The atmosphere was flushed by argon and the temperature was raised up to 1450°C in about 40 min. This procedure did not allow to get rid of the oxide later on the alloy but limited its thickness.The temperature was then manually maintained within +/- 5°C. It is to be noticed that the temperature shift has always been slow: <20°C/24h.

At the end of the equilibration period the equilibration crucible was quenched in air and broken to extract the metal and the slag that separated. The surfaces of the metal block and the slag block were usually polluted by adhering phases such as slag on the metal or metal on the slag but also by SiC or graphite from the crucible. These blocks were ground down until no extra phase was apparent under magnifying glass (10x). The mean weight of the samples submitted to chemical analysis was 50g for the metal and 40g for the slag.

The results are presented in Tables III to V.

B. Kinetics & Equilibrium achievement

Two kind of observation were made to figure out the time necessary to achieve equilibrium and to precise the initial conditions that were requested for this.

The first set of experiment aimed at showing that the same phase composition can be reached with an initial excess or lack of Al in the ferro-silicon. The experiments were repeated for equilibration time of 12h and 48h. The results for FeSi65 is given on Fig.2. The experiments were carried out at 1450°C with the same slag (15.1% Al_2 O_3–9.84% CaO–51.7% SiO_2) but with FeSi65 alloys containing various amounts of Al and Ca.

When the initial Al content of the alloy was too far from equilibrium this one was never reached. By examination of the samples it was observed that the metal/slag interface is covered by anorthite for the highest Al concentration in the metal and by silica when the ferro-alloy is Al depleted. This diffusion blockage for Al is likely due to the initial conditions underwent by the samples. With the Al rich alloys the oxidation kinetics is initially fast because the system is far from equilibrium. The alumina which is produced by silica reduction

is accumulated at the interface with the alloy because it cannot diffuse at the same pace it is produced. This forms an layer of anorthite which may remain as a diffusion barrier for a long time. When the alloy has no reducing agents (Al or Ca) the silica layer, formed when the metal was heated under slightly oxidizing atmosphere before slag melting, cannot be reduced and the silicon of the metal is unable to reach the alumina in the bulk slag.

When the initial metal composition is close to the equilibrium composition the final composition is independent of the initial one.

The second set of experiment was devoted to look more closely to the presence of a diffusion barrier or a diffusion gradient in the slag. For this diffusion couples were formed with slices of slag and metal as shown on Fig.3. The interface diameter was 10mm and the thickness of the slices were 5 to 10mm. After a thermal treatment under the same conditions as for the equilibrium experiments, except their introduction in a hot crucible to get a more precise melting time, the diffusion couples were air quenched, cut and submitted to microscopic observation and microanalysis.

Even for alloys initially close to equilibrium an alumina–rich layer may be found at the metal slag interface for short period of time, as shown on Fig.4. This micrograph illustrates the specific behavior of alumina or anorthite layer in the mass transfer. Small silicon-rich metallic particles were observed on the slag side of the solid layer that separated the metal from the monophasic slag. As already seen in similar circumstances (5), this phenomenon may be attributed to the fact that the anorthite layer in pervious to aluminum ions but not to silicon ions. Mobile solvated electrons or holes, produced by Al oxidation at the alloy surface, may carry the charges necessary to reduce silica into metallic silicon inside the slag. An electrochemical reaction could thus take place even without direct contact between the oxidizing agent and the reducing one.

The silicon-rich particles are lined up along what seems a thin continuous oxide layer from which anorthite lamellae have grown toward the metal interface. This continuous layer may originate in the alumina skin that covered the metal before its contact with the reacting slag. The growth of anorthite lamellae perpendicular to this skin on its metal side, i.e. where Al ions were formed, may have resulted in a progressive separation of the skin and the metal surface where it has initially formed. The space between these two surfaces has been filled both by the Al ions produced on the metal and by slag flowing through scarce holes in the oxide skin.

Large amount of Ca in the alloy did not lead to the same behavior, likely because Ca ions diffuse easily in the silicate slag and also because calcium-rich solid phases are not as stable as aluminosilicates in the present case.

Concentration profiles of Al, Ca and Si in the slag are presented on Fig.5. They were measured after 2h at 1450°C for an FeSi65 alloy with 0.2%Al and 0.2%Ca in contact with a 10%Al_2O_3-30%CaO-60%SiO_2 slag. The presence of anorthite (CaO-Al_2O_3-2SiO_2) at about 100µm from the metal/slag interface explains the sharp concentration bump. The concentration gradient zone is limited to a 200µm layer of slag.

As a conclusion on these observations it may be stated that the main phenomenon impeding the mass transfer kinetics is the formation of an alumina layer on the metal that leads later on to the formation of an anorthite layer that slowly dissolves in the slag. No steep concentration gradients have been observed out of a 200µm zone with initial Al and Ca concentration in the metal close to the equilibrium values. When the initial Al concentration in the ferro-silicon is high the anorthite accumulation is so high than even 48h at 1450°C did not allow the excess alumina to diffuse in the slag.

It is to be noticed that in an industrial oxidation process there is no initial oxide layer at the metal-slag interface. However an anorthite layer may form when the Al concentration in

the ferro-silicon is high. The present experiments do not permit to fix a concentration limit for this because some alumina layer was initially present in all runs.

III.   THERMODYNAMICS
A. Thermodynamics.
    By assuming that an equilibrium is achieved between the thermodynamic constituents Al, Ca, Si, Al_2O_3, CaO and SiO_2 one may express the equilibrium constants of the two following reactions:

$$4Al + 3SiO_2 \Leftrightarrow 2Al_2O_3 + 3Si \qquad 1$$
$$2Ca + SiO_2 \Leftrightarrow 2CaO + Si \qquad 2$$
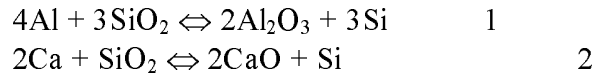
by:

$$LogK_{Al} = 2Log a_{Al2O3} - 3Log a_{SiO2} + 3Log a_{Si} - 4LogX_{Al} - 4Log\gamma^{\circ}{}_{Al} \qquad 3$$

$$LogK_{Ca} = 2Log a_{CaO} - Log a_{SiO2} + Log a_{Si} - 2LogX_{Ca} - 2Log\gamma^{\circ}{}_{Ca} \qquad 4$$

The metallic elements are dissolved in a ferro silicon and the corresponding oxides are the

constituents of the slag in contact with the ferro-silicon. a_i designates the activity of the

constituent i, X_i the molar fraction of a diluted species j in the liquid alloy and $\gamma^{\circ}{}_i$ its activity coefficient at infinite dilution.
It is assumed that Henry's law is applicable to Al and Ca for all the alloy compositions. Indeed their concentration were below 0.6 wt% and often below 0.1 wt% in the present experiments. In such a case, for a given ferro-silicon, the silicon activity is independent of the impurity content and so is the activity coefficient of the impurities. Thus the concentrations of Al and Ca depend only on the slag composition through the activities of the oxides. Isoconcentration lines for Al and Ca may thus be drawn on a ternary diagram representing the slag composition. Any change in the iron to silicon ratio in the ferro-silicon would only change the value of concentration for each line by a ratio deduced by differentiating equations 3 and 4:

$$4\Delta LogX_{Al} = 3\Delta Log a_{Si} - 4\Delta Log\gamma^{\circ}{}_{Al} \qquad 5$$

$$2\Delta LogX_{Ca} = \Delta Log a_{Si} - 2\Delta Log\gamma^{\circ}{}_{Ca} \qquad 6$$

where ΔX designates the difference between the two values taken by X when the silicon content of the ferro-alloy is changed without changing the slag composition.
It is to be noticed that silicon activity change with usual industrial composition is small:

a_{Si} = 0.37 / 0.82 / 0.88 / 1 (6) for the silicon molar fraction (0.6 / 0.8 / 0.86 / 1) corresponding to the theoretical weight contents of the industrial alloys: 45% / 65% / 75% / metallurgical Si. The change in equilibrium concentration should be mainly due to the change in the activity coefficients of Al and Ca with the solvent composition.
The isoconcentration lines for Al and Ca in a ferro-silicon at 65 wt% Si are presented in Fig. 6 for the equilibrium experiments carried out at 1450°C.

B. Temperature.
The experiments were mainly carried out at 1450°C. However in the case of ferro-silicon at 65 wt% Si results were also obtained at 1550°C and 1350°C for the same slag compositions. The effect of temperature is illustrated in Fig. 8 by the values of the Al and Ca concentration ratios: $X_T / X_{1450°C}$. The aluminum concentration increases with temperature for all the slag compositions. This effect is more pronounced when the alumina concentration is high.

On the contrary the effect of temperature is not obvious for the Ca content, as shown on Fig.9. The values are scattered and no clear trend appears.

C. Activity coefficient of Al in FeSi65.

The activity coefficient of Al in the ferro-silicon was calculated from the experimental results, the equilibrium constant of reaction 1 taken from JANAF tables (7), the oxide activities calculated in the slag phase by the model proposed by Eriksson & Pelton (8) and by the silicon activity at saturation with SiC given by the optimization of Lacaze & Sundman(9). This coefficient should have been independent of the Al and Ca content in the metal. The results shown in Fig.10 indicate that its apparent evolution with alumina activity is likely the result of a departure of the calculated activities from the actual ones for low alumina activities.. This anomalous behavior may be due to the fact that the model proposed by Eriksson & Pelton is extrapolated in the low alumina content composition range, leading to a shift toward underestimated alumina activity. The mean value for γ°_{Al} is 0.65+/-0.2 at high alumina activity where the model well represents the measured values. This value is in agreement with the value of 0.55+/-0.1 determined by mass spectrometry by Dumay (10) and with the value 0.53 given for pure silicon by Weiss & Schwerdtfeger (4). The value 0.19 in pure silicon at 1550°C given by Tuset (3) seems underevaluated.

D. Activity coefficient of Ca in FeSi65.

The activity coefficient of Ca in the ferro-silicon was determined by the same technique used for Al. The value was found to be 0.003+/-0.001, with no dependence on Ca content or lime activity but with a large scattering due to the low Ca level in the metal that renders a pollution of the sample by the slag very deleterious. From that point of view any pollution would increase the Ca content and lead to an underevaluation of its activity coefficient.

IV. CONCLUSIONS

The distribution of Al and Ca between a CaO-Al$_2$O$_3$-SiO$_2$ liquid slag at 1450°C and a 65 wt % Si liquid ferro-silicon was measured by equilibration in graphite crucibles. The results lead to the presentation, on a ternary diagram representing the slag composition, of isoconcentration lines for the Al and Ca contents in the alloy. It was found that the aluminum concentration in the metal increases with temperature but no clear dependence on temperature was found for calcium.

The mass transfer kinetics is slow at 1450°C and thermodynamic equilibrium is reached only if no solid oxide precipitation occurred in the slag at the beginning of the reaction. Otherwise a solid oxide layer forms that creates a diffusion barrier impeding the equilibration process and maintaining the liquid alloy in "oxide bags" for time up to a day, as demonstrated by diffusion couple experiments.

In oxidizing processes used for Al and Ca elimination in industrial ferro-silicons the mass transfer at 1450°C should remain limited and most of it should take place at higher temperature only. Metal drops shut up in "oxide bags" are not likely to coalesce, during the industrial processing at this temperature, because diffusion is not fast enough to dissolve the oxide bag. However all this detrimental effects may disappear when the initial Al and Ca content in the alloy are close enough to the equilibrium ones.

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Table I: Alloy composition before equilibration.

Alloys: (FeSi65)	Si (%)	Fe (%)	Al (ppm)	Ca (ppm)	C (ppm)
A1	67.0	33.0	15	<10	
A2	65.0	34.1	350	<10	410
A3	64.8	34.3	2600	1900	270
A4	65.0	33.7	2300	55	240
A5	66.1	33.4	650	1800	170

Table II: Slag compositions before equilibration. The standard deviation on the concentrations found for about 10 samples of the same slag was about 0.5% for each element.

Slag N°:	$\%Al_2O_3$	$\%CaO$	$\%SiO_2$
1	< 0.2	29.2	70.6
2	5.6	24.9	69.5
3	5.5	32.3	62.2
4	5.5	45.9	48.6
5	7.7	28.5	63.8
6	11.3	15.9	72.8
7	10.3	25.5	64.2
8	10.4	30.6	59.0
9	10.3	35.3	54.4
10	10.1	43.0	46.9
11	11.0	48.4	40.6
12	15.1	9.8	75.0
13	21.9	14.4	63.7
14	20.7	30.8	48.5
15	20.7	36.9	42.4
16	19.4	44.5	36.1
17	28.9	19.3	51.7
18	30.5	29.2	40.2
19	35.4	31.3	33.3
20	40.7	28.4	30.8

Table III: Chemical analysis after equilibration at 1450°C

Initial Slag & Alloy	Equil. time	Al_2O_3 (%)	CaO (%)	SiO_2 (%)	Al (ppm)	Ca (ppm)
S2+A2	12h	5.3	25.0	71.2	68	15
S2+A5	12h	5.6	25.0	70.6	38	20
S2+A2	48h	5.76	25.0	69.0	58	13
S2+A1	48h				37	20
S3+A2	12h	5.4	32.5	64.0	42	17
S3+A5	12h	5.6	32.6	62.4	43	39
S3+A2	48h	5.57	32.5	62.2	30	45
S3+A1	48h				38	35
S4+A2	12h	5.4	45.9	48.6	172	229
S4+A5	12h	5.7	45.9	48.2	211	310
S4+A2	48h	5.4	45.5	48.5	159	254
S4+A1	48h				140	190
S5+A2	12h	7.7	28.4	64.4	48	21
S5+A5	12h	7.6	28.5	63.1	76	23
S5+A2	48h	7.78	28.6	64.0	44	67
S5+A1	48h				41	26
S6+A2	12h	10.9	15.8	74.0	150	17
S6+A5	12h	11.3	16.0	73.2	126	29
S6+A4	48h	11.6	16.0	72.4	227	19
S6+A1	48h				90	< 10
S7+A2	12h	10.3	25.9	65.5	76	24
S7+A4	12h	10.4	25.9	65.5	100	18
S7+A2	48h	10.5	25.7	63.9	61	12
S7+A1	48h				69	38
S8+A2	12h	9.92	30.4	60.8	140	55
S8+A4	12h	10.4	30.6	61.0	89	33
S8+A2	48h	10.3	30.2	59.5	78	35
S8+A2	48h	10.3	30.3	59.2	94	46
S9+A2	12h	10.0	35.4	56.0	100	41
S9+A3	12h	10.7	35.5	53.9	152	62
S9+A2	48h	10.4	35.6	54.3	96	50
S10+A2	12h	10.0	44.1	48.1	360	450
S10+A5	12h	9.89	43.1	47.5	370	290
S10+A2	48h	10.3	43.2	46.9	330	270
S10+A4	48h	10.5	43.0	46.9	263	147
S10+A2	48h				440	270
S11+A2	48h	11.0	49.1	41.1	1300	1700
S11+A4	48h	11.2	48.8	41.2	1200	1600
S12 + A2	12h	14.9	9.7	76.4	300	10
S12 + A4	12h	15.3	9.8	76.5	*660*	*8*
S12+ A2	48h	15.3	9.84	73.9	300	7
S12+A3	48h	15.4	10.0	74.2	*550*	*11*
S12+A1	48h				*89*	*<10*
S12+A5	48h				340	<10
S13 + A2	12h	21.4	14.3	65.2	330	<10
S13 + A3	12h	21.2	14.2	65.2	*950*	*29*
S13+ A4	48h	22.1	14.4	63.4	*680*	*98*
S13+ A2	48h				380	18
S14 + A2	12h	20.3	30.9	50.7	310	70
S14 + A3	12h	20.5	30.9	50.2	760	47
S14+ A4	48h	21.0	30.6	48.1	370	120
S14+ A2	48h				420	64
S15 + A2	12h	20.3	37.1	44.8	*680*	*290*
S15 + A3	12h	21.1	37.0	42.2	937	349
S15+ A4	48h	21.1	37.0	42.5	840	255
S15+ A2	48h				910	250

S16+ A2	48h	19.5	44.9	36.6	2100	1400
S16+ A4	48h	19.8	45.0	36.4	2400	1700
S17 + A2	12h	28.9	19.3	51.5	474	14
S17 + A3	12h	28.3	19.2	50.9	*1800*	*52*
S17+ A2	48h	28.9	19.2	52.5	430	19
S17+ A4	48h	29.2	19.5	51.6	*1400*	*42*
S17+ A1	48h				460	12
S18 + A2	12h	30.6	29.5	41.7	*960*	*78*
S18 + A3	12h	30.8	29.8	41.2	1400	140
S18+ A4	48h	31.3	29.4	39.2	1200	100
S18+ A2	48h				1400	110
S19+ A2	48h	35.8	31.6	34.1	2300	210
S19+ A3	48h	35.9	31.7	33.8	2700	280
S20 + A2	12h	41.1	28.6	30.8	*2300*	*239*
S20 + A3	12h	41.1	28.7	30.8	3400	177
S20+ A4	48h	40.9	28.5	30.9	2700	154
S20+ A2	48h	stirring			3200	170
S20+ A3	48h	stirring			3700	190

Table IV: Chemical analysis after equilibration at 1550°C

Initial Slag & Alloy	Equil. time	Al_2O_3 (%)	CaO (%)	SiO_2 (%)	Al (ppm)	Ca (ppm)
S2 + A2	12h	5.65	25.2	70.9	**54**	**21**
S2 + A5	12h	5.67	25.6	71.0	**65**	**51**
S2 + A2	48h				**47**	**26**
S3 + A2	12h	5.5	32.3	62	**46**	**35**
S3 + A5	12h	5.6	32.7	61.8	**43**	**38**
S4 + A2	12h	5.4	45.8	48.6	**239**	**347**
S4 + A5	12h	5.5	45.9	48.6	**208**	**325**
S6 + A2	48h				**150**	**29**
S6 + A5	48h				**130**	**12**
S8+ A2	12h	13.3	30.5	59.6	**107**	**38**
S8+ A5	12h	10.4	30.6	59.3	**102**	**34**
S12 + A2	12h	15.1	9.9	76.3	**350**	**14**
S12 + A4	12h	15.1	9.8	76.1	*1100*	*<10*
S12+ A2	48h				**340**	**20**
S13 + A2	12h	22.0	14.3	63.5	**535**	**57**
S13 + A4	12h	22.3	14.3	63.0	*1124*	*17*
S13+ A2	48h	22.3	14.8	62.5	**502**	**11**
S13+ A2	48h				**550**	**<10**
S14+ A2	12h	20.6	30.9	48.6	**524**	**108**
S14+A3	12h	20.9	31.0	47.9	**610**	**82**
S14+ A2	48h	21.0	31.5	47.6	**491**	**52**
S14+ A2	48h				**650**	**80**
S15+ A2	48h	20.7	37.9	42.5	**1200**	**330**
S15+ A2	48h	20.8	38.5	42.1	**1300**	**380**
S19+ A2	48h	35.8	32.0	33.8	**3800**	**330**
S19+A4	48h	35.8	31.5	33.4	**3900**	**350**
S20 + A2	12h	40.8	28.4	31.1	**4900**	**738**
S20 + A3	12h	41.0	28.5	30.9	**5200**	**254**
S20+A2	48h	41.0	28.6	31.0	**4500**	**211**
S20+A4	48h	stirring			**4800**	**240**

Table V: Chemical analysis after equilibration at 1350°C

Initial Slag & Alloy	Equil. time	Al$_2$O$_3$ (%)	CaO (%)	SiO$_2$ (%)	Al (ppm)	Ca (ppm)
S6 + A2	48h	11.4	16.1	73.1	110	24
S6 + A5	48h	11.3	16.1	72.3	110	47
S15+A2	48h	20.9	37.2	42.7	520	250
S15+A3	48h	21.1	37.0	41.9	610	240
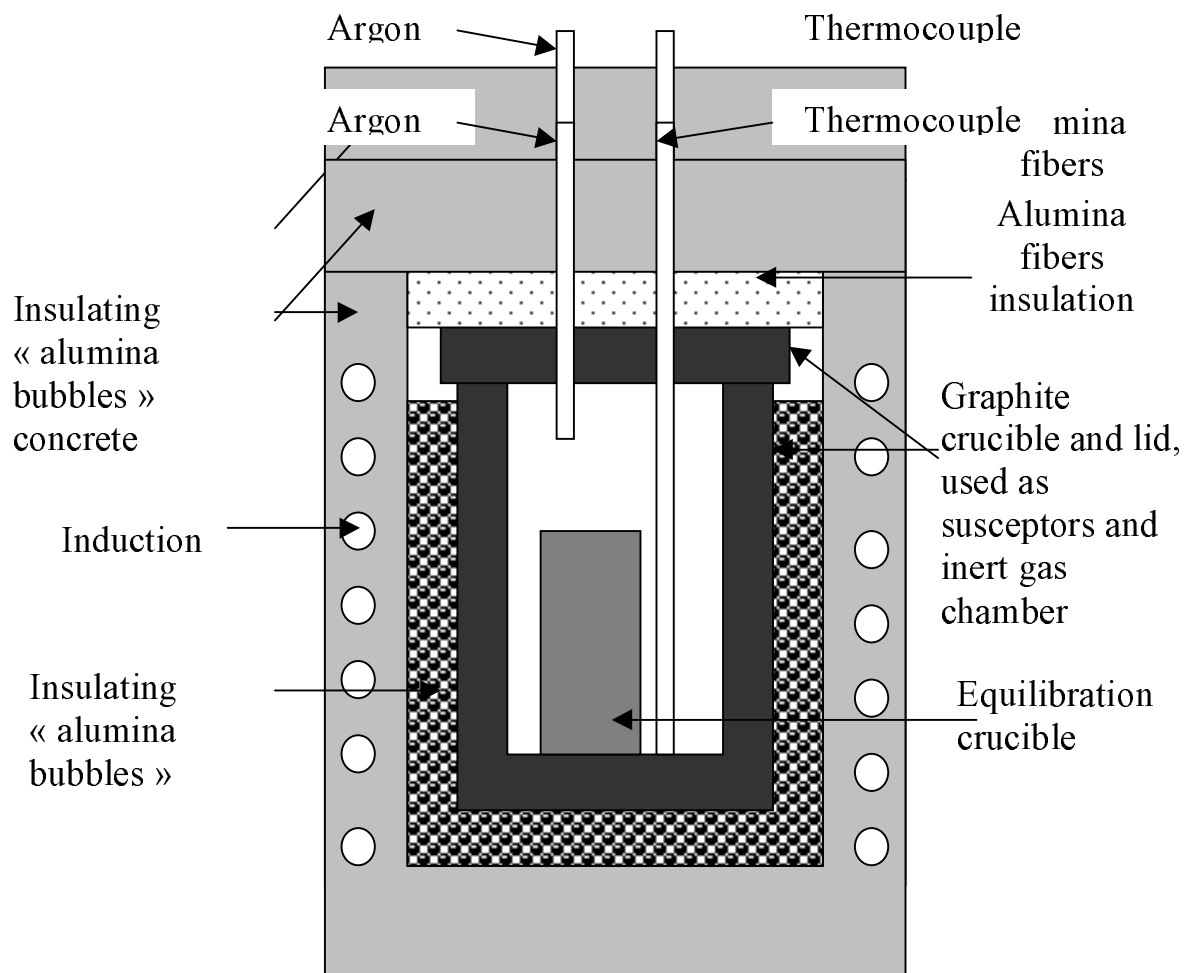
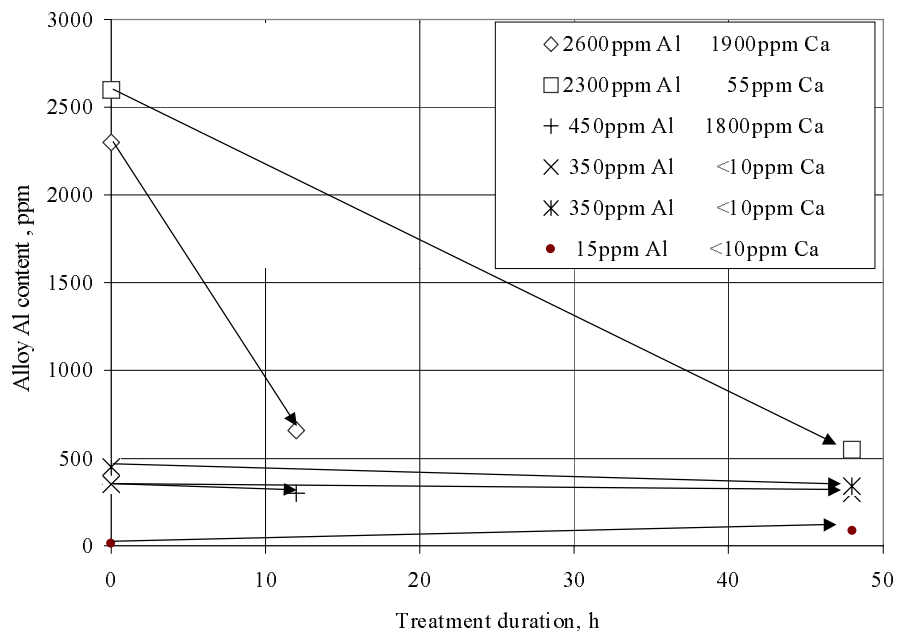Figure 1 : Experimental assembly used to equilibrate ferro-silicons with slags for 12 to 48h at 1450°C.

Fig.2: Evolution toward equilibrium of FeSi65 with various impurity contents in contact with slag S12 at 1450°C.
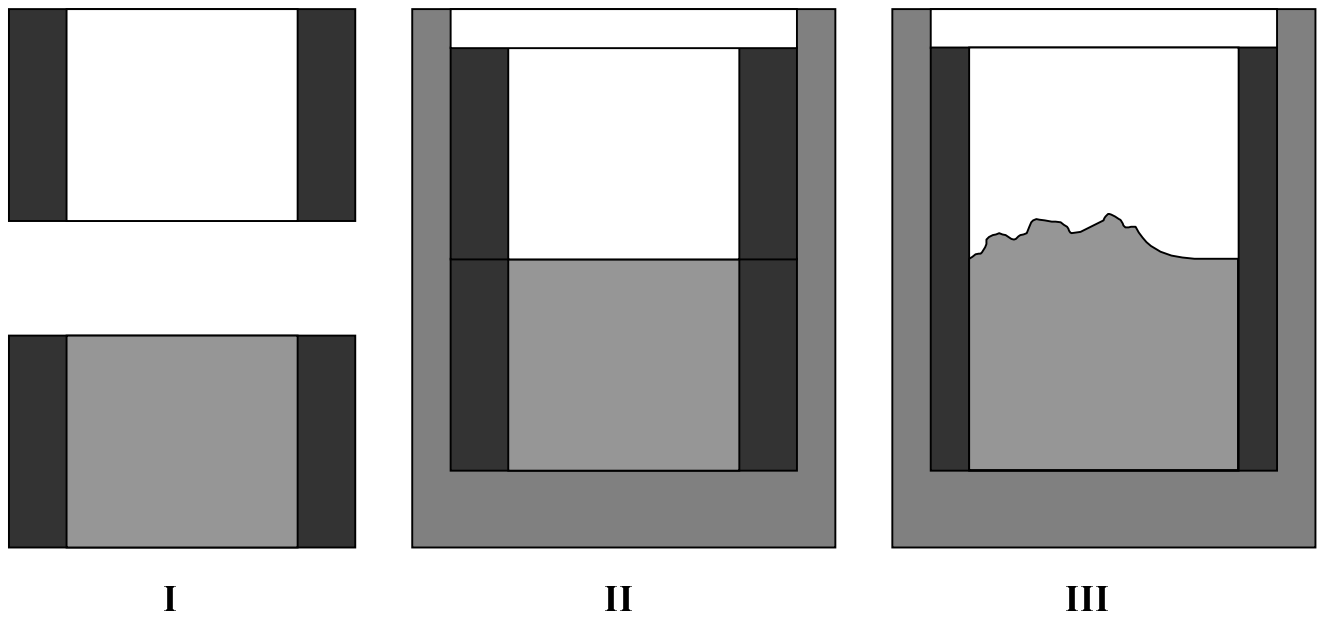
Fig.3: Schematic representation of the diffusion couples made from slices of metal and slag contained in a graphite tubing(I), that were assembled inside a graphite crucible (II). The slag is white and the ferro-silicon is gray on this figure. The initially flat interface was found deformed after melting and quenching (III).

FERRO SILICON

Bulk Slag

Primary Silicon

Anorthite needles

Silicon-rich metal droplets
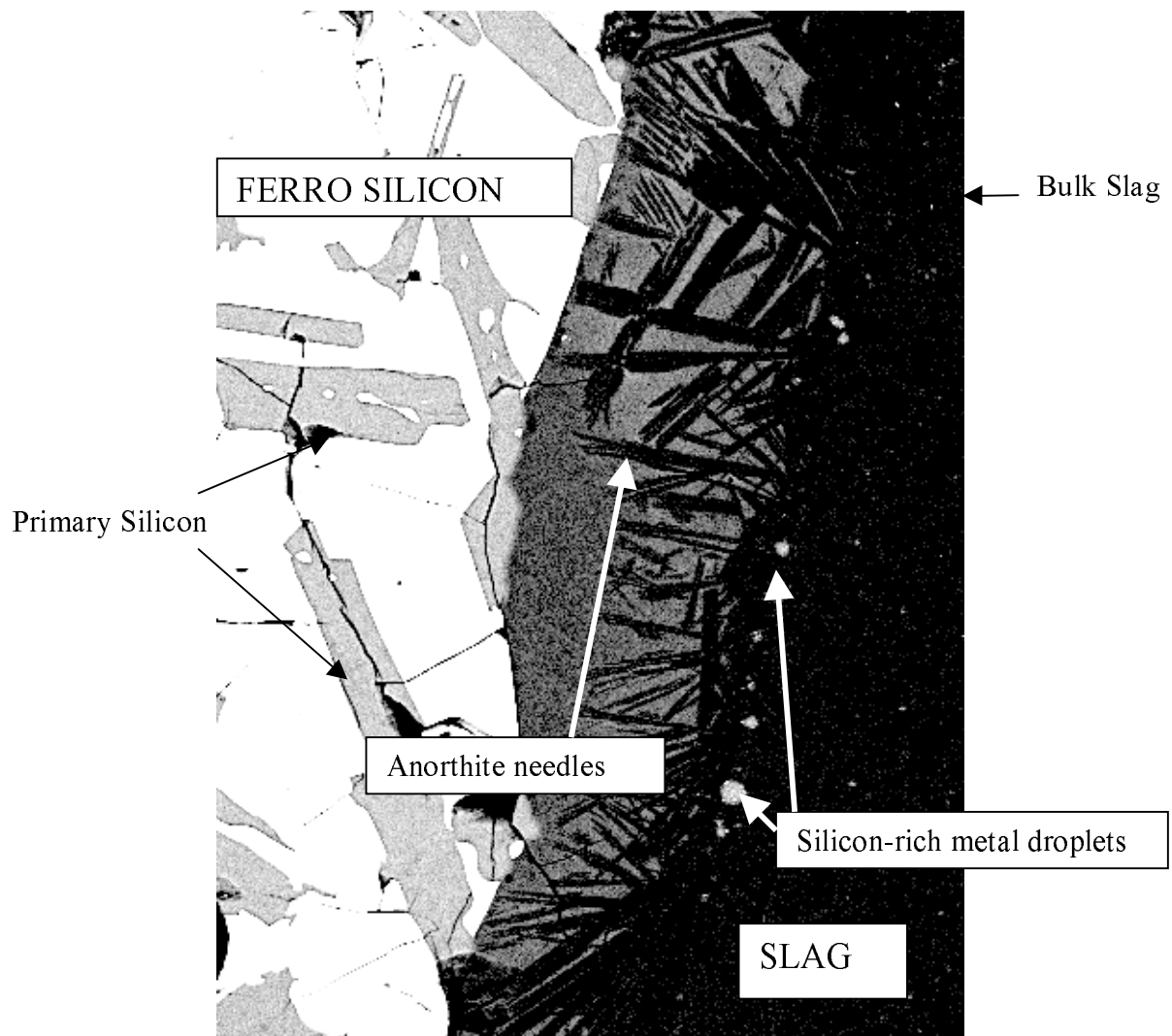
SLAG

Fig 4: Cross section of the interface between a FeSi65 (0.2% Al and 0.2% Ca) and a slag (22% Al2O3, 14% CaO, 64%SiO2) after 1h of contact at 1450°C. The metal and the slag are separated by an alumina-rich layer saturated with anorthite. Silicon-rich metallic droplets appeared stranded on the slag side of the interfacial layer.
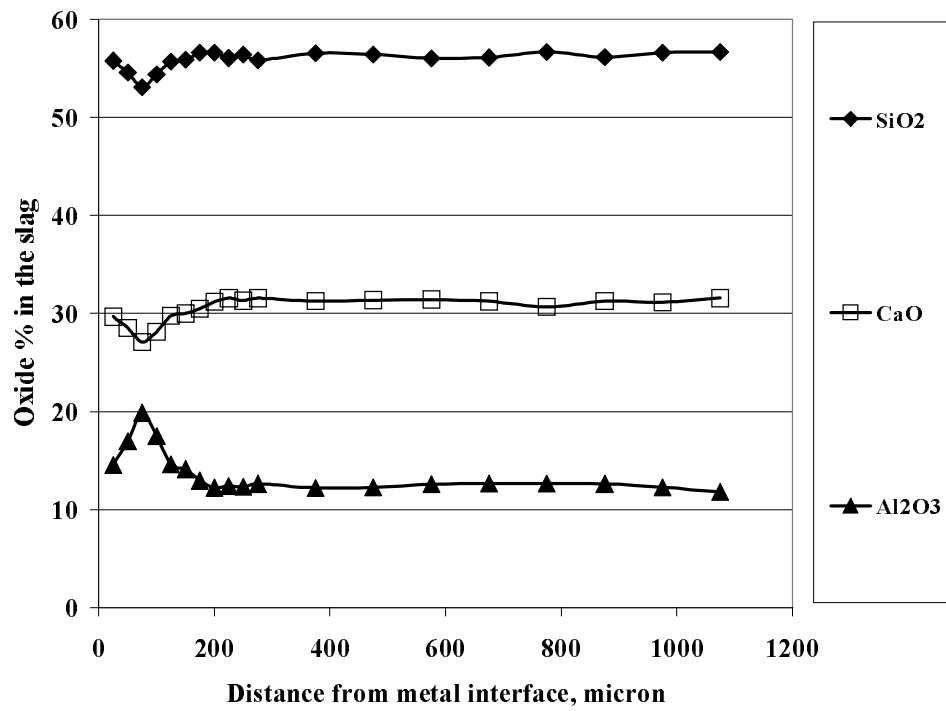
Fig 5 : Concentration profiles after 2h at 1450°C for an FeSi65 alloy with 0.2%Al and 0.2%Ca in contact with a 10%Al_2O_3-30%CaO-60%SiO_2 slag. Composition gradients are more accentuated for Al_2O_3 than for the other components.
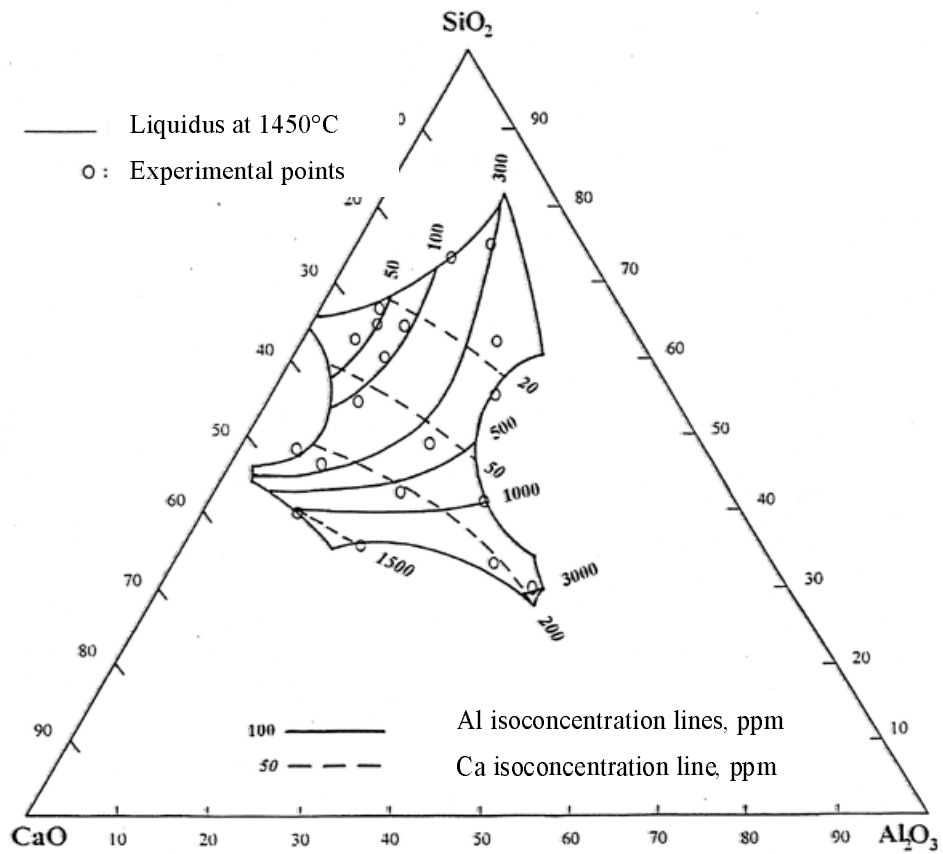
Fig.6: Isoconcentration lines for Al and Ca in a FeSi65 alloy at 1450°C, deduced from the measured equilibrium values for the slag compositions (in wt%) represented by hollow dots.
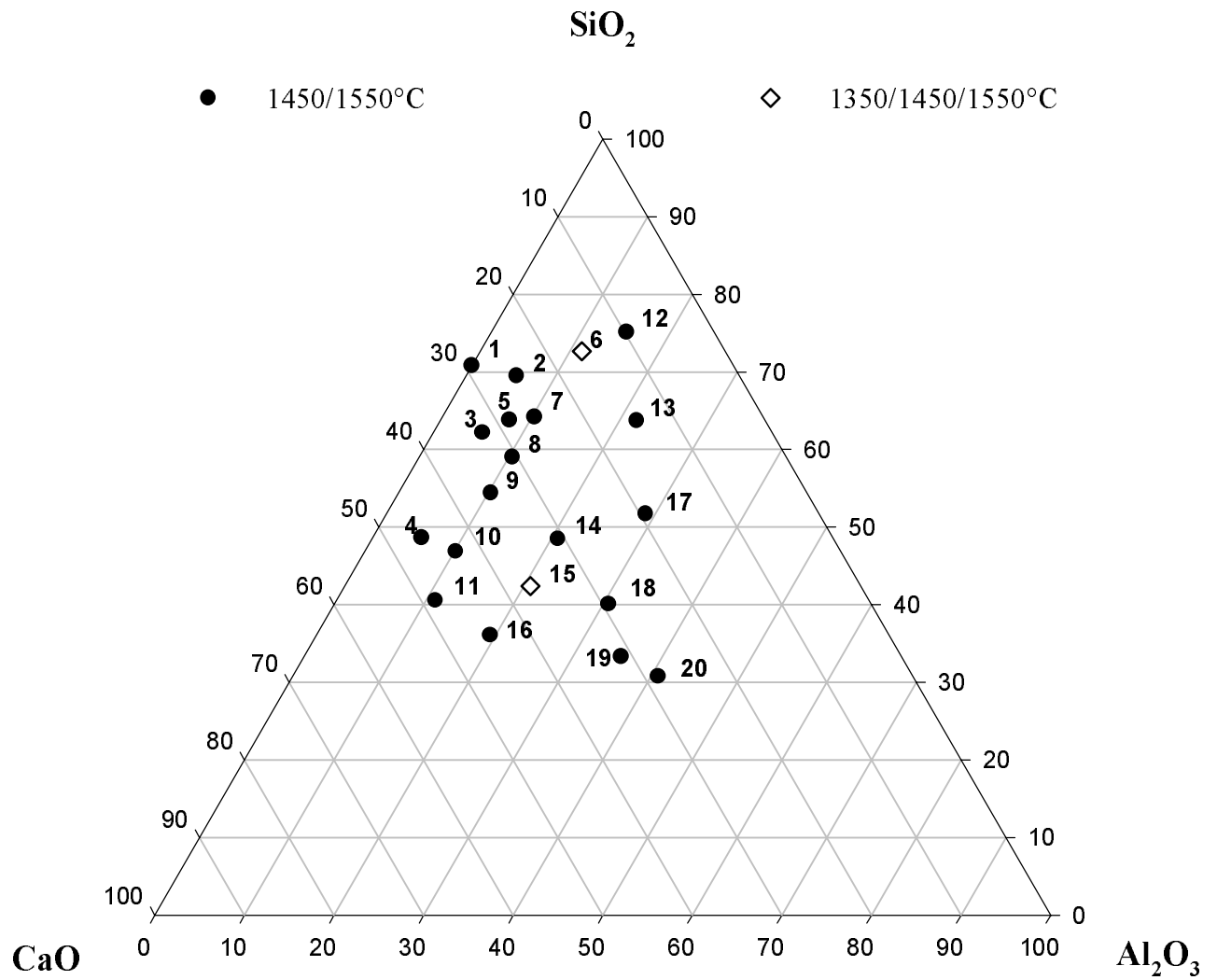
Fig.7: Experimental compositions for which equilibrium measurements were carried out at 1450 and 1550°C (full dots) and also at 1350°C (diamonds). The slag sample numbers are those used in Fig.8 and 9.
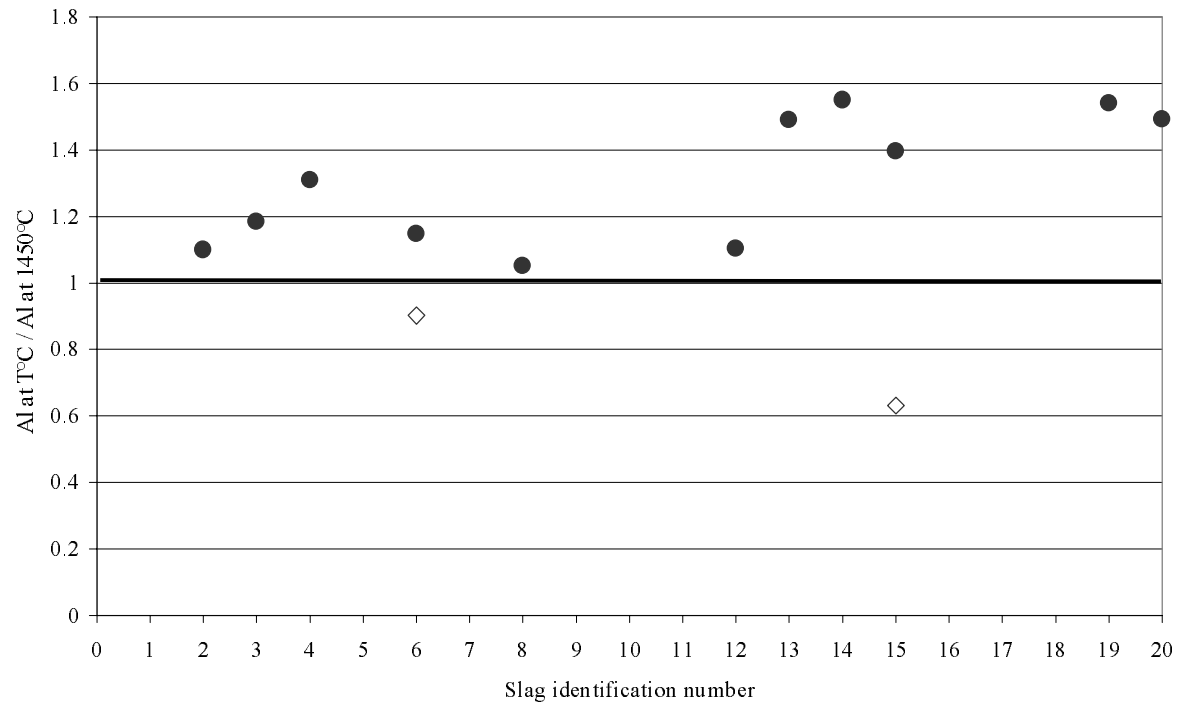
Fig.8: Ratio of Al content at equilibrium at 1550°C to Al content at 1450°C (full dots) or Al at 1350°C to Al at 1450°C (diamonds). The numbering of slags correspond to an overall increase of alumina content (See Fig 7).
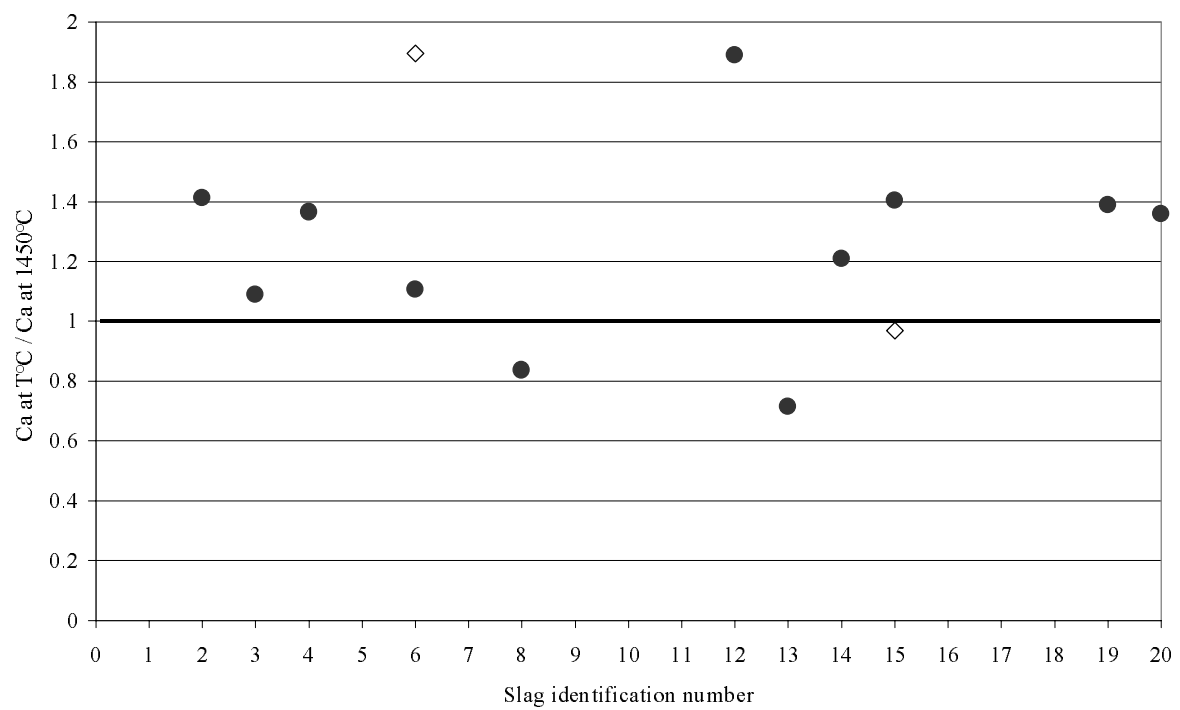
Fig 9: : Ratio of Ca content at equilibrium at 1550°C to Ca content at 1450°C (full dots) or Ca at 1350°C to Ca at 1450°C (diamonds).
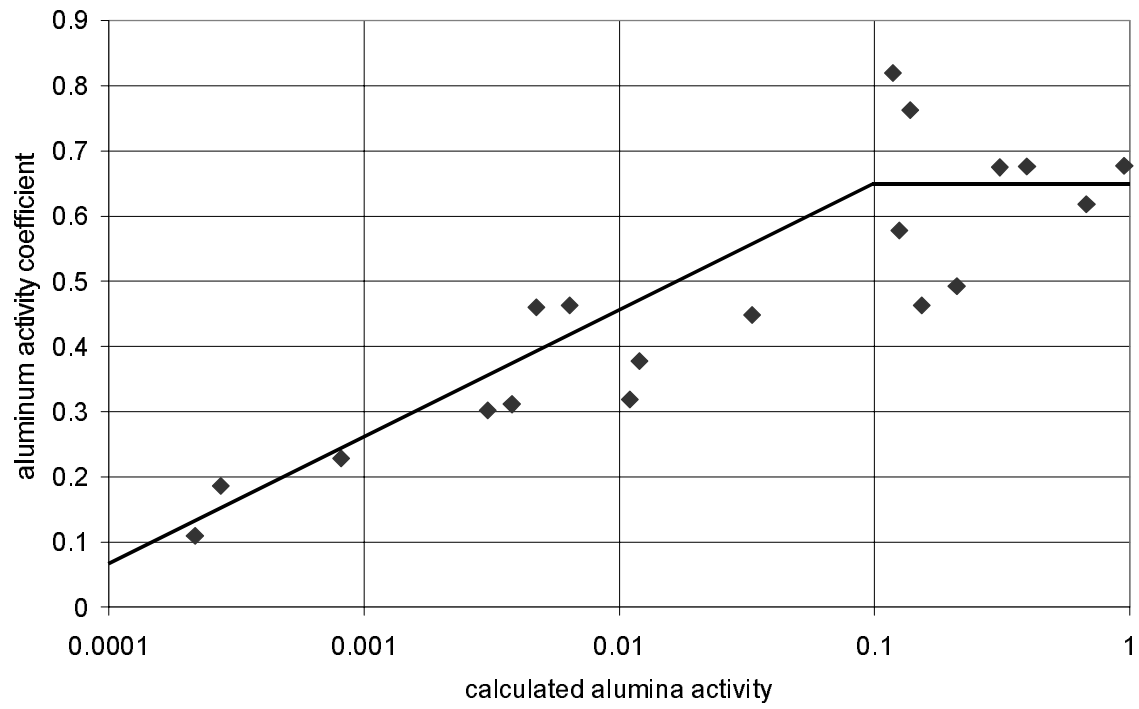
Fig.10: Calculated Al activity coefficient in the metal versus calculated alumina activity in the slag showing a anomalous dependence behavior at alumina activities below 0.1.