EVALUATION OF PHYSICOCHEMICAL ASPECTS AND OPTIMIZATION OF SLAG PRACTICE IN THE REFINING PROCEDURES OF GRAIN ORIENTED SILICON STEELS AND ULTRA LOW CARBON STEELS IN SOME OF THE STEEL PLANTS IN BRAZIL

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ABSTRACT

In this work, optimization of slag practice in the refining of grain oriented silicon steels and ultra-low carbon steels, as adopted in some of the steel plants in Brazil, has been described. The influence of physicochemical characteristics of the slag for obtaining desired results, in terms of quality of steel produced, has been highlighted.

1 - Introduction

It is well known that optimization of process variables in any industrial operation is very essential to obtain quality product with high productivity. In fact, due to stringent requirements in respect of quality and global competition it is all the more important that the an understanding of the various physicochemical parameters affecting the process are controlled rigorously to attain this goal. Besides technical economical and commercial considerations, in the present times, the environmental aspects also have to be considered to comply with the standards for emissions rejects etc. from the process..
The procedures for optimizing the process parameters vary from plant to plant depending on the raw material quality and the type of equipment and infrastructure. Even under limitations with respect to these it is possible to optimize the parameters to obtain good results. .In the process of steel making there is the primary stage where using the raw materials available one is in a position to optimize the variables to produce steel say through blast furnace and LD routes. ,However the task of achieving the final quality/specification of the product depends essentially on secondary refining. It should be remembered that this stage is fairly complex as there is a great a range of products and specifications, requiring diverse facilities and operation procedures , as we have to deal with complex multiphase multi component systems Control and varying the process parameters would naturally depend upon the melt shop facilities and monitoring and sampling procedures for various parameters in addition to the experience of the operator, which is also very important.

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Actual melt shop facilities would define the type of steel grades that can be produced. For example with a RH degassing facility there is a possibility to produce ultra low carbon steel without much difficulty. In addition, .heating capacities, vacuum levels etc. also are parameters determining the type and grades of steel that can be produced. Even if one has sophisticated analysis and monitoring procedures sampling at the wrong moment is not likely to give good results. Too early sampling will lead to unreliable values representing intermediate non-equilibrium state in the system. On the other hand late sampling may result in delays complicating the schedule of production

The more common measured data available to the operator, are the steel temperature and composition and the dissolved oxygen . In vacuum treatments the vacuum levels and the outlet gas composition are known from which it is possible to predict carbon levels .
Reliability of the slag data obtained from samples would depend upon how the samples have been taken from the melt. For example in ladle furnace or RH degassing ladle, it is necessary to see that the sampling method does not pick up only the liquid fraction as this will lead to erroneous results in the case of essentially foaming slags.. The slag height is also dynamic and it is advisable to get samples at different levels to get more reliable data in respect of chemical composition. However slag properties ,such as activities of components, viscosity among others, cannot be evaluated in the short time interval for the refining process. Here comes the experience of the operator handy. With experience it is possible to evaluate some of the process conditions, like slag fluidity, slag thickness, steel motion intensity and patterns. Besides , based on historical data of similar heats, he can roughly estimate properties and foresee results, like, alloy yields, inclusions removal rates, lining wear, etc. Although these personal inputs in many cases are able to achieve acceptable results presently market conditions are exigent about stringent quality control, more precise inputs and efficient tools are needed to obtain optimum results. .The effectiveness of any optimizing

condition is the reproducibility of results under those conditions. This can be achieved by modeling and optimizing the slag practice employing principles of thermodynamics and data on physicochemical characteristics of the slag..

2 - Process analysis

Figures 1 and 2 shows both the model operation scheme and the links between processing steps. .Various thermodynamic, kinetic as well as heat and mass transfer and fluid dynamic together with empirical and physical modeling data, concepts and correlations in respect of the secondary refining process were collected on the basis of an extensive literature survey were collected and used to develop a computer algorithm for the optimization of slag characteristics for refining procedures for different steel grades.[1-12]

The optimizing operation is carried out on in two stages.. The first one involves a preliminary determination of a synthetic slag to be used as starting reference. For that the inputs about steel specifications and actual values were taken from available data on heats over a period of time (current standard practice). From the final desired steel composition, the correspondent final slag composition is estimated. considering only its main components, namely CaO, SiO2, Al_2O_3 and MgO . The pseudo ternary and quaternary systems are established with the help of available diagrams. Phase diagrams are always employed and also others having activity viscosity sulphide capacity data depending upon the type of application and main requirements of the product. Should sulfur level is the main concern, Cs diagrams would be helpful. If inclusion removal is aimed, activities diagrams are considered and so on. .All the data for the diagrams are stored in the computer. Once this slag is established, components corresponding to deoxidation products, carryover slag and lining material are adjusted to get the composition of the initial synthetic slag. The adjustment involves removal in the inverse order of the normal sequence of the process. The model recalculates the slag by simple mass.balance. The, composition and the amount, thus obtained, are included in the initial data .In the operation of the main model, the process is divided in stages, that are selected so that, each one, includes well defined steps of actions.as given in table 1

From the simulation trials for the above stages in the case of a medium carbon, aluminium killed steel, different characteristics of the slags resulting in the 4 stages can be correlated .Figs 3-6 give an idea about the variation of different characteristics of the slag during the above 4 stages C1,C2,C3,C 4.

The variation of relative composition of $CaO-SiO_2-Al_2O_3$ components only constituting about 77%of the total slag is given in Fig.3 . It can be seen that alumina activity steadily increases through the stages C1-C4 due to absorption of inclusions formed during the deoxidation of the melt with aluminum and correspondingly there is a decrease in the CaO activities. In Fig 4 a variation of Oxygen content of the metal with molfraction of FeO is represented. It can be noted that there is a gradual decrease in the oxygen content of the metal from initial to the final stages., whereas from Fig 4 b it is evident that with the decreasing oxygen content, the interfacial tension between the slag and metal increases ,facilitating elimination of inclusions and their absorption in the top slag. Fig.4c gives the variation of water capacity (C_{H2O}) with coefficient for hydrogen partition (L_H). L_H continuously decreases during the 4 stages. This implies that the hydrogen content of the metal may increase. However this is not the main concern in this type of steel. From Fig.4 d, it can be seen that the sulphide capacity of the slag in the C1 stage is low and with the addition of the synthetic slag this increases but decreases again in the C3 and C4 stages, when Sulphur and Al_2O_3 get absorbed in the slag.

Fig 4 e gives the relation between corrected optical basicity(Λ) and viscosity of the slags at the melting temperature(η_m). Viscosity increases from C1 to C4 due to absorption of Al_2O_3. The efficiency of desulfurization relative to the original sulfur content of the metal is plotted as a function of thermodynamic and kinetic factors [3] namely , λ(product of the equilibrium sulfur partition coefficient and slag specific consumption – kg/kg) and B(product of kinetic parameter defined by ks and contact area of slag metal interface per unit volume of metal) for all the 4 cases, in fig 5 a . There is an increasing tendency from C1 to C4 ,although there is a discrepancy with respect of C2 and C3, which might have been caused by stirring effects. Fig 5 b shows the variation of the metal slag wetting angle which confirms the improvement inclusion absorption ability of the slag from C1 to C4 The Fig 6 gives an idea about the melting points of theses slags, showing an increasing tendency from C1 through C4. This is to be expected due to the absorption of the Alumina resulting from deoxidation, by the slag. Fig.7 gives an estimate of inclusion size computed at a certain point of time as a function of height of ladle using Stokes equation for the case C4. Large inclusion sizes get removed rapidly and tend to accumulate near the top of the ladle

The computer code developed is in a position to consider other kinds of inputs at the control desk and the nature of the possible actions. For this purpose, "windows", i.e., entrances to the model are provided. For example, the amount of solidified slag, calculated with the help of the "thermal model" can be manually removed from the system and the residual liquid slag is automatically recalculated (amount and composition)

3 - Case Studies

Procedure above described for the medium carbon steel can also be applied to refining of other grades of steel such as ultra low carbon steel and silicon added grain oriented steels. In the following some of the aspects of refining of theses grades are described. .

a) Grain Oriented Silicon Steel

The main steps, from teeming up to the end of the ladle furnace process, are shown in figure 8 The main aspects that must be controlled and adjusted are silicon, carbon, sulfur, manganese and aluminum levels .Depending on the steel grade the silicon content ranges from 0,8 to 4,8%.The sulfur must be maintained into a narrow range and neither too low nor too high level can be surpassed. The carbon content is below 0,05% and the aluminum and manganese contents must be maintained at very low levels. Besides that, the cleanliness must be high .All these constraints are due to the required magnetic characteristics. One of the problems which differentiates this steel grade is the high activity of silicon in metal due to which both Al and Mn are very easily reduced and hence the content of aluminum and manganese species in slag must be maintained as low as possible. Another concern is the ability of the above slag to desulfurize, as far as it is conditioned to absorb inclusions. When the synthetic slag is mixed with the BOF carry over slag and other slag formers the resulting slag should satisfy these requirements. Another important aspect is the moment of synthetic slag addition. All other conditions are same as in the normal practice described before.

Some relevant results of optimization are shown in figure 9. There is a substantial improvement in the process in respect of sulphur range , sulphur yield combined with lower Carbon , Aluminum and Titanium. Hence the proposed procedure on the basis of simulation is being adopted in the current practice.

Some of the properties as in the case of medium carbon steel described above are highlighted in table 2, for each step of the process, although some of the parameters listed do not have direct significance to the process. For evaluation of some of the parameters such as interfacial tension or sulphide capacity more than one equation was used for different ranges of compositions and this resulted in a variation in values .Equations used for calculating the parameters were taken from the respective references. However representative values had to be chosen applicable in a particular range.

b) Ultra low carbon steels (IF)

The sequence of IF steel ladle treatment and a comparison between the actual values obtained and results of simulation are represented in figure 10. Actual composition values (for C1 and C4 only) are in good agreement with the predicted values.

.The main concerns for achieving the aimed properties in the product are besides the very low levels of carbon and nitrogen, the low levels of residuals and non-metallic inclusions.
From the slag side, this means, properties that prevent the pick up of carbon and nitrogen and an excellent ability of absorbing inclusions. The inclusion level in steel must be below 50ppm (O_T) and its size below 50µ .As the metal is Al deoxidized , the main inclusion type is alumina. In principle, the process conditions do not favor inclusion removal. The stirring time after aluminum addition is short, and the motion patterns are a consequence of the circulation in the RH vessel and does not take into account the inclusion flotation factor. In other words, one has to take advantage of the available motion, independent of whether it is good or not for promoting slag-inclusion contact. To counteract that, the slag characteristics must be highly favorable for absorbing inclusions. This means a sufficiently fluid slag, with a suitable melting point, low alumina activity, with high metal-slag interfacial tension, with low FeO. This slag must be formed as early as possible, i. e., it must be ready at the very beginning of the vacuum treatment. In other to achieve these goals, a synthetic slag was designed with the help of the model, and also the right moment for addition of the same to achieve satisfactory results. The industrial trials are in progress. Slag composition obtained through application of theoretical principles, are fitting well with the actual slags as well as the inclusions levels. This means that both the optimization procedures with the help of the computer code as described earlier is reliable . Some of the properties as in the previous case described above are highlighted in table 3, for each step of the process, although some of the parameters listed do not have direct significance to the process. In some cases such as evaluation of interfacial tension different equations were used due to changing compositions of the slags and the validity range of the equations. Equations utilized for the calculations were taken from the respective references. Contact angles for the slag compositions C1-C4 are also given .In figure 11 fusion temperature of theses slags are represented. In figure 12 a comparison of inclusion contents in the old practice (Avg.2#) , the present practice (Avg1#) and the prediction of model optimization(Test) are given. The latter is close to the present practice and it is intended to make more runs and improve this further.
The work being developed hereafter has the objective to achieve inclusion levels below the actual levels attainable at present. As mentioned before, this search is not limited to slag practice only but in all other procedures to ensure production of a clean steel.

4 - Conclusions

The results obtained in relatively complex steel treatments suggest that simulation based on the computer code developed is a reliable procedure for optimizing the characteristics of the slag in refining operations .Fundamental data and research work carried out in evaluating the physicochemical characteristics of the slag over the years can be used with advantage for control and optimizing operations in secondary steel making of the slags Slag optimization during refining process is an evolutionary operation aimed at producing clean steel maintaining the composition limits for the steel.

5 - Acknowledgements

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6 - References

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Table 1.Typical steps involved in the secondary refining in the ladle furnace

	1st Step –C1	2nd Step -C2	3rd Step-C3	4th Step-C4
Characterization	Teeming	Preliminary. refining	Ladle furnace 1	Ladle furnace 2
Period	Beginning to end	End of teeming upto entry in the ladle furnace.	Entry into the ladle furnace upto end of additions	End of the additions upto end of refining.
Unitary operations	Deoxidation Adjustment of composition , Conditioning of slag	Deoxidation, Adjustment of composition , Conditioning of slag ,Flotation of inclusions	Deoxidation, Adjustment of composition , Conditioning of slag, flotation of inclusions desulfurization	Flotation of inclusions homogenization Adjustment of temperature
Entrance data (measured and estimated)	Compositions of slag and steel at the end of blow Temperature , pouring time Volume of carryover slag Ladle conditions	Compositions of steel and slag Steel Temperature SlagThickness and appearance Time	Compositions of steel and slag, Steel Temperature Slag Thickness and appearance Time	Compositions of steel and slag Steel Temperature Slag Thickness and appearance Time
Operator Responsibilities.	Addition of Deoxidants, alloying elements and conditioning agents to the slag Sequence of additions Interruption of the leak Measurement and sampling	Addition of Deoxidants alloying elements and conditioning agents to the slag Sequence of additions Duration and intensity of the gas bubbling Measurement and sampling	Addition of Deoxidants, alloying elements desulfurizing agents and conditioning agents to the slag Sequence of additions Duration and intensity of gas bubbling and heating Measurement and sampling	Duration and intensity of the gas bubbling and heating Measurement and sampling

Table 2- Physico-chemical characteristics of refining slags for grain oriented steel

PARAMETERS SLAG /METAL		C1	C2	C3	C4
Dissolved Oxygen - ppm [O]		474,00	148,00	47,00	28,00
Total Oxygen - ppm $[O]_T$		4250,00	881,00	413,00	82,00
Sulfur capacity - logCs					
	Ref(11)	-1,97	-4,00	-3,28	-3,10
	Ref(12)	-3,43	-3,43	-2,95	-2,84
Sulfur partition - (S)/[S]					
	Ref(11)	1,81	0,05	0,88	2,21
	Ref(12)	0,89	0,03	0,29	0,63
Phosphorus capacity - $\log C_P$					
	Ref(11)	18,82	16,78	17,52	17,62
	Ref(13)	4,67	3,51	3,94	3,83
$\log C_{PM}$	Ref(14)	5,12	3,25	3,91	3,83
Phosphorus partition - (P)/[P]					
	Ref(15)	893,00	43,00	7,00	1,32
	Ref(13)	526,00	17,71	3,47	0,76
Water capacity - $\log C_{H2O}$	Ref(16)	3,16	2,81	2,88	2,89
Water partition (H)/[H]	Ref(16)	2,11	0,68	0,41	0,30
Carbonate capacity-$\log C_{CO}$	Ref(11)	2,08	0,07	0,64	0,72
Viscosity(poise)	Ref(17)	0,34	1,28	0,60	0,57
Surface tension(dyn/cm)	Ref(18)	589,00	425,00	457,00	461,00
Interfacial tension(N/m)					
	Ref(1)	574,00	486,00	631,00	668,00
	Ref(12)	688,00	932,00	1170,00	1276,00
	Ref(19)	671,00	975,00	1318,00	1395,00

Table 3- Physico-chemical characteristics of refining slags for ultra-low carbon steel

PARAMETERS OF SLAG		C1	C2	C3	C4
Sulfur capacity - $\log C_s$					
	Ref(11)	-2,25	-2,53	-2,58	-2,63
	Ref(12)	-2,02	-2,29	-2,34	-2,43
Sulfur partition - (S)/[S]					
	Ref(11)	3,12	2,50	1,59	2,09
	Ref(12)	1,11	0,92	0,65	0,77
Phosphorus capacity - $\log C_P$					
	Ref(11)	18,84	18,69	18,62	18,62
	Ref(13)	4,40	4,40	4,35	4,37
$\log C_{PM}$	Ref(14)	5,69	5,78	5,70	5,80
Phosphorus partition - (P)/[P]					
	Ref(15)	115,98	39,78	51,74	20,68
	Ref(13)	5,42	1,16	1,95	0,65
Water capacity - $\log C_{H2O}$	Ref(16)	3,16	3,12	3,10	3,10
Water partition (H)/[H]	Ref(16)	1,44	1,16	1,31	1,12
Carbonate capacity-$\log C_{CO}$	Ref(11)	2,01	1,81	1,75	1,74
Viscosity(poise)	Ref(17)	0,36	0,46	0,48	0,51
Surface tension(dyn/cm)	Ref(18)	1070,66	1154,19	1151,10	1176,06
Interfacial tension(N/m)					
	Ref(1)	783,98	816,74	751,92	817,34
	Ref(12)	940,40	1032,73	963,97	1046,46
	Ref(19)	790,36	768,48	657,37	664,94

Contact angles - slag-metal

(see figure 5)

Process Step	α	β	θ	Reference colours
C1	21	20	41°	
C2	24	23	47°	
C3	24	25	49°	
C4	30	37	67°	

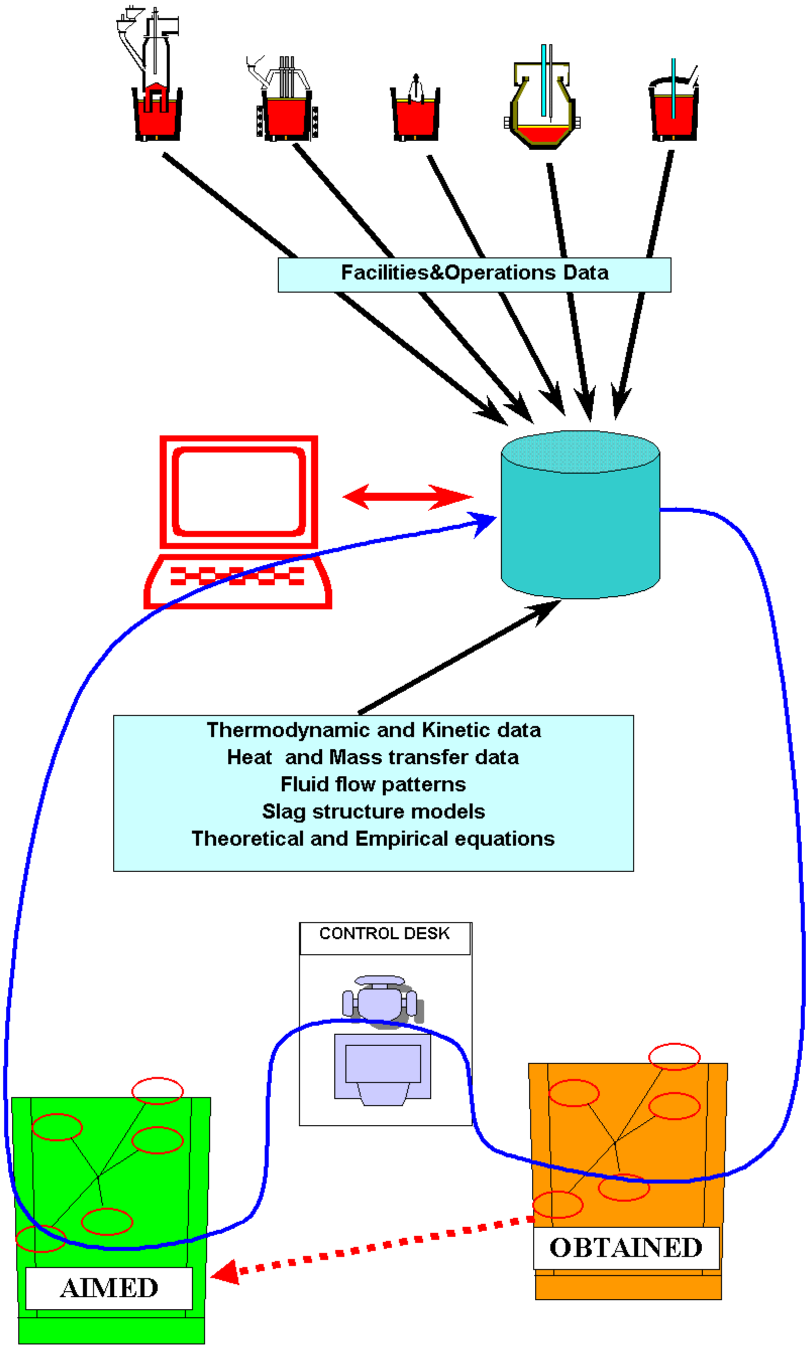


Figure 1 - Model operations Scheme - General

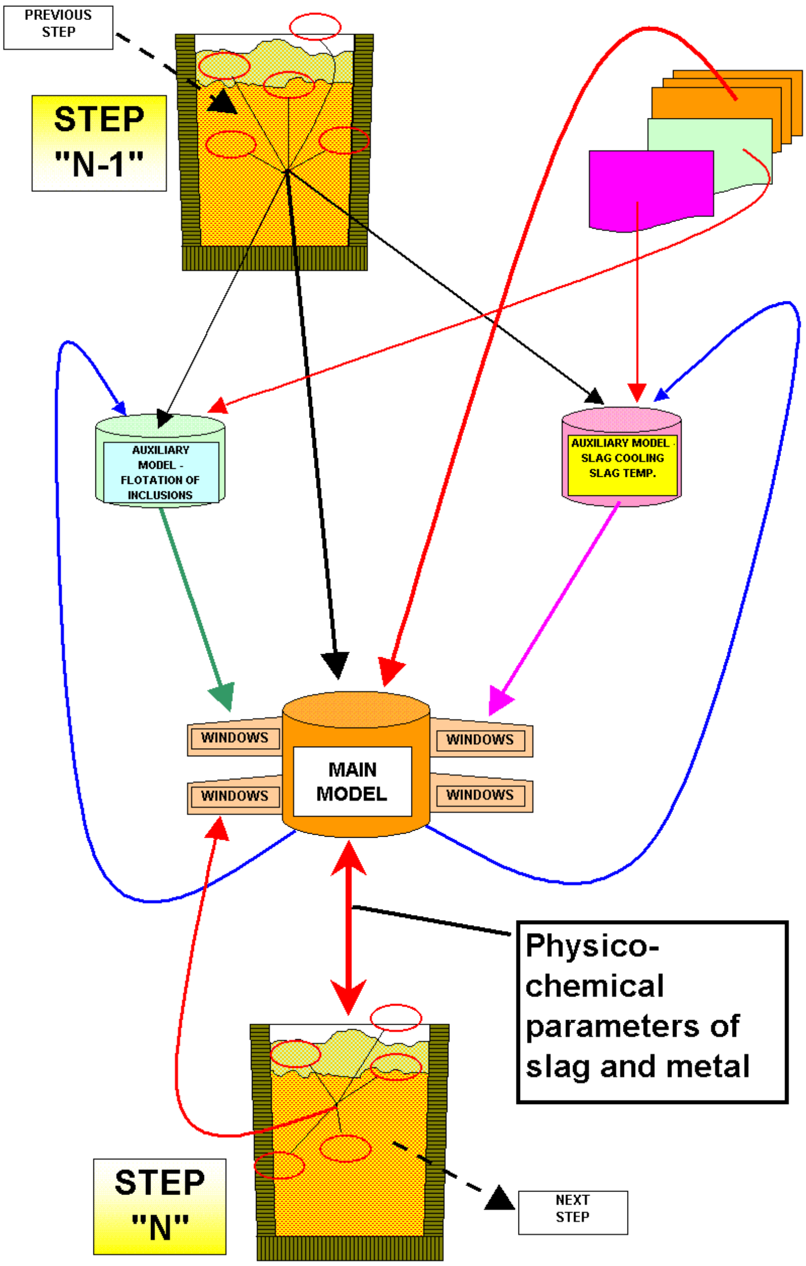
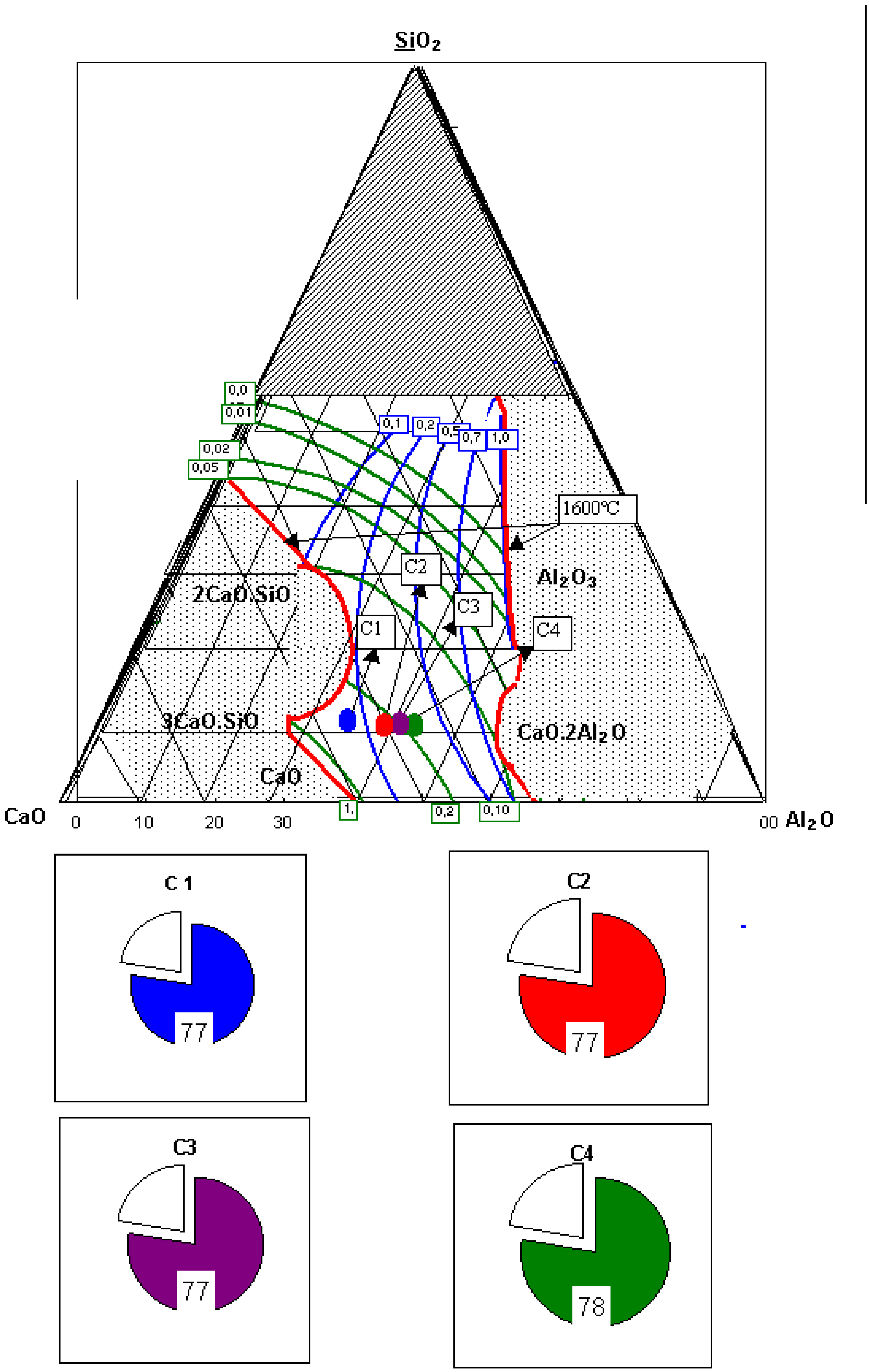


Figure 2 - Model operations scheme - links between staps



% of CaO+SiO$_2$+Al$_2$O$_3$ in slag

Figure 3 -Variation of CaO and Al$_2$O$_3$ activities during the 4 stages

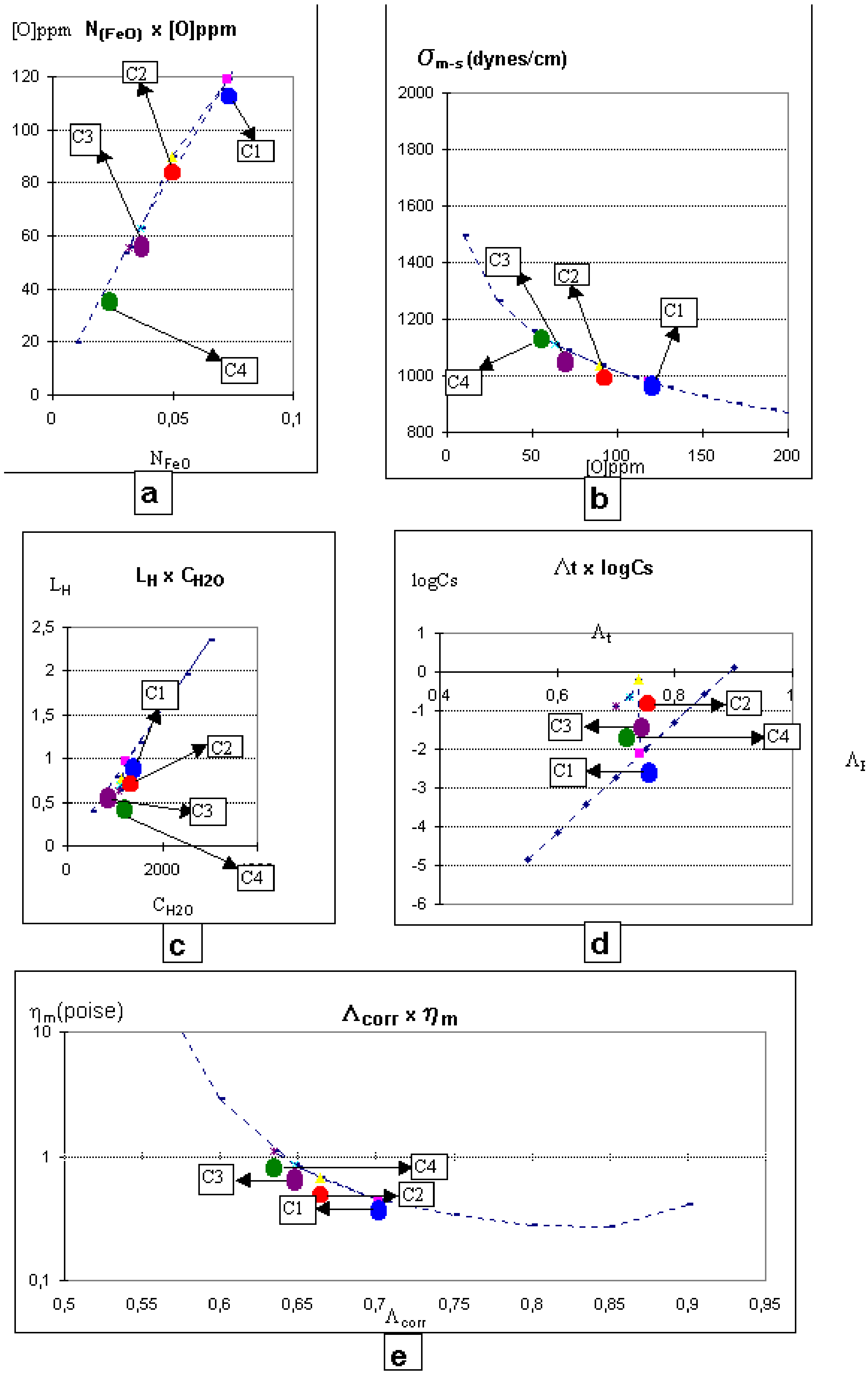


Figure 4 - Variation of selected parameters/properties

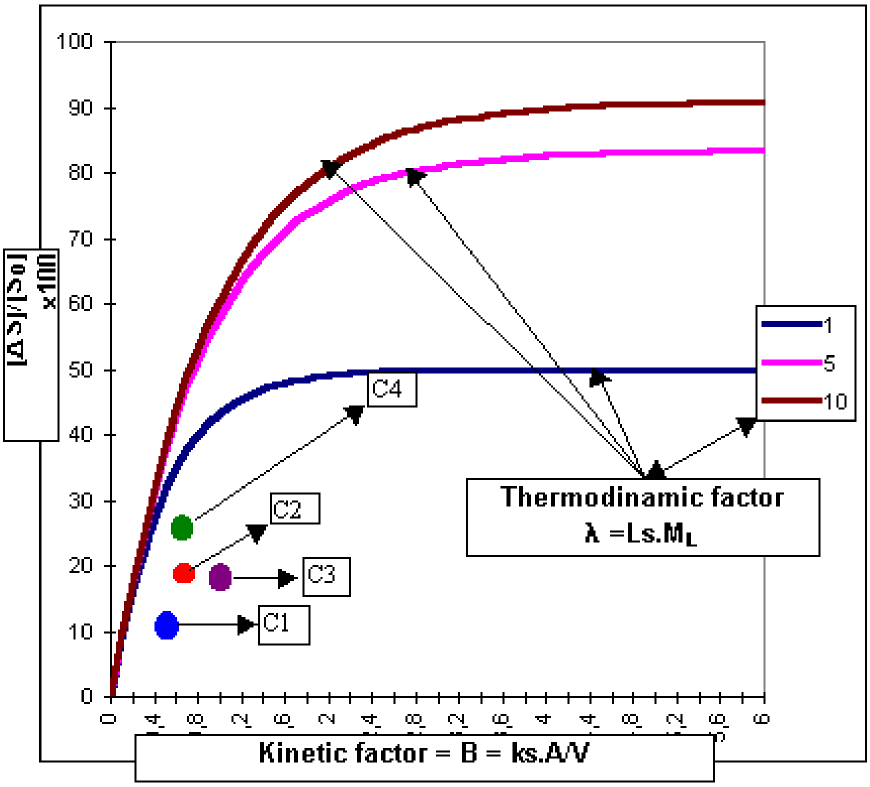
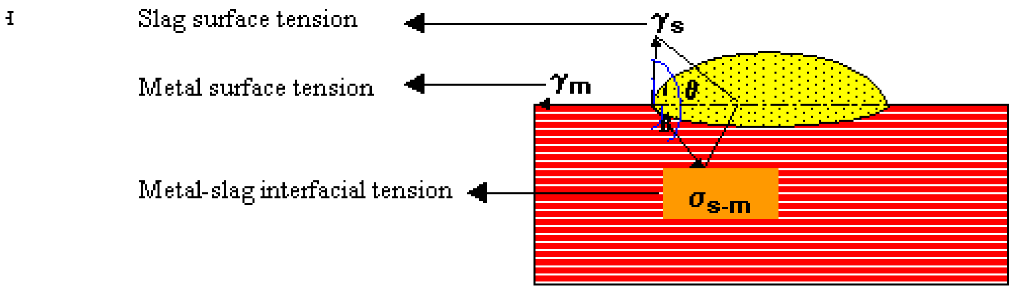


Figure 5a - Influence of thermodynamic and kinetic factors on dessulfurization

Wetting angle - two liquid phases - conception



Simulated condition	α	β	θ	Reference colour
C1	21	20	41°	
C2	24	23	47°	
C3	24	25	49°	
C4	30	37	67°	

Figure 5b Wetting angle - metal-slag

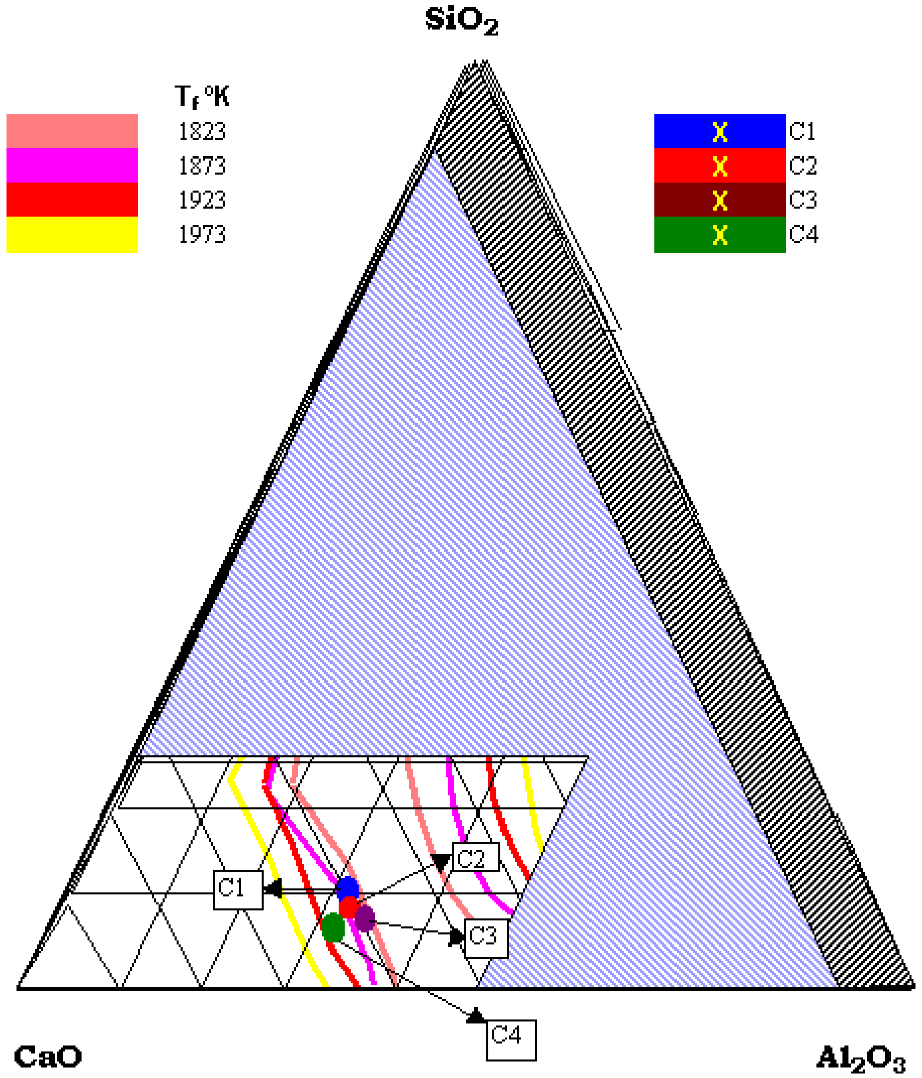


Figure 6 - Fusion Temperature of Slags

System CaO - SiO2 - Al2O3 - 10% MgO

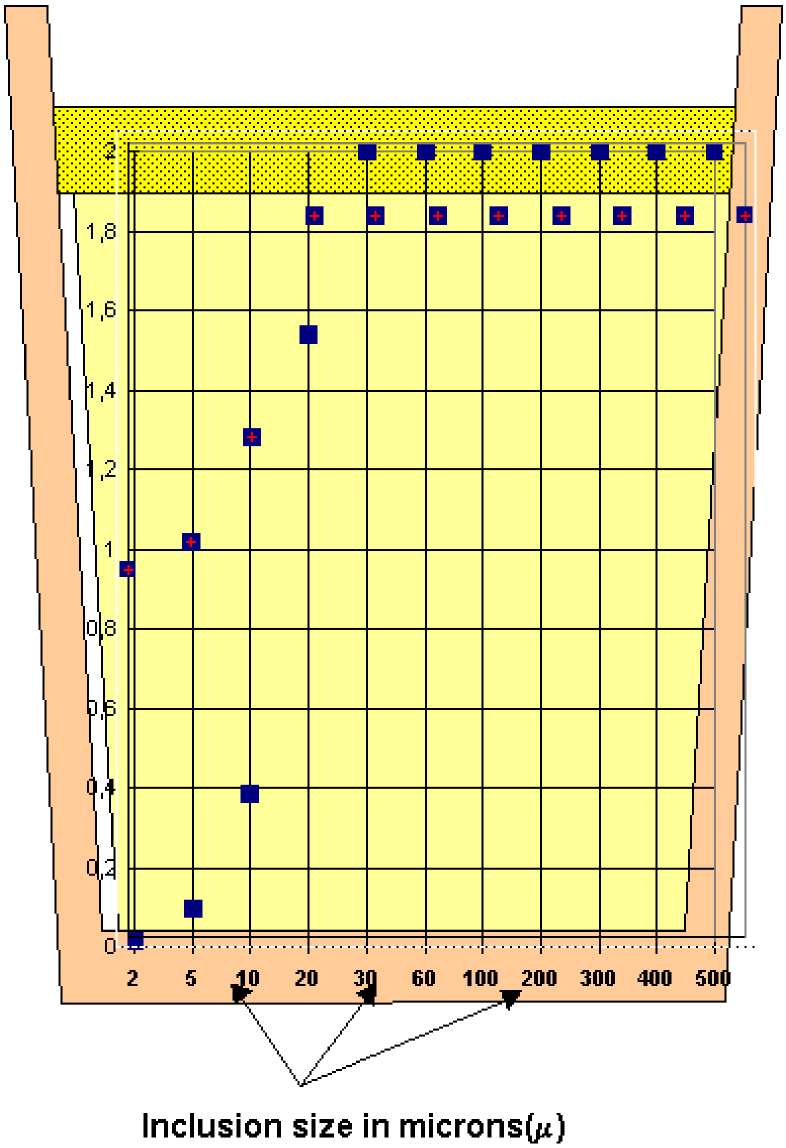


Figure 7 - Estimated position of inclusions in the as a function of their size