Commission of the European Communities

technical steel research

Steelmaking

FUNDAMENTAL RESEARCH IN THE ECSC: REVIEW OF PREVIOUS WORK AND FUTURE NEEDS

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FUNDAMENTAL RESEARCH IN THE ECSC: REVIEW OF PREVIOUS WORK AND FUTURE NEEDS

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1. INTRODUCTION

The objectives of this study is an appraisal and a critical analysis of ECSC financed work in the field of "Theoretical Metallurgy", and some proposals of selection criteria for future work in that field.

ECSC devotes part of its research funds to more fundamental topics in the field of iron and steelmaking, i.e. thermodynamics, kinetics, hydrodynamics and reactions mechanisms.

This programm has been developed in 15 laboratories in the European Community. The total approximate budget for the last ten years has been 3,1 M. ECU. This represents about 1.5 % of total each year ECSC research fund.

The sound use of these funds requires a rigorous and difficult choice among the proposals: they should fulfill the expectations derived from the definition of "practical oriented fundamental research": on its rsults one should be able to build new developments in a given industry. Therefore such a work should allow

- to strengthen and improve existing processes by bringing new data, basic interpretation of their mechanisms and lead to their optimization,

- to build new processes that will be competitive in the coming years.

In a first part, the main results of the studies completed in the past ten years are presented. A very large amount of scientific work has been achieved and many industrial processes could benefit from a more extensive use of the collected data. This text could then be used as an advertisement for some very useful parts of final reports that may not have received enough publicity at the time of their publication.

The second part of this study present the topics corresponding to urgent needs for further research, and some suggestions for the priorities in the fields of application.

In the appendix, the results of each individual research contracts are briefly presented and appraised.

2. MAIN RESULTS FROM THE PAST PROGRAMME

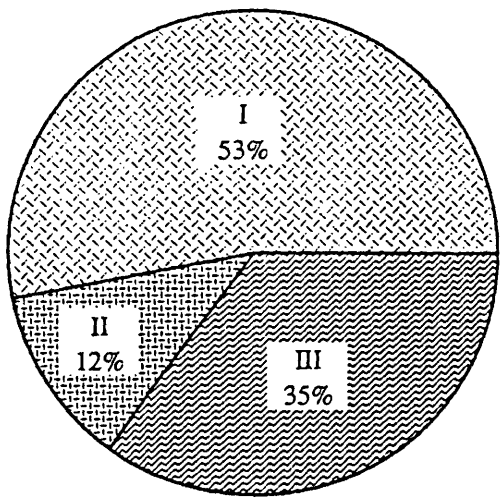
2.1 Orientation of the research topics

This programm is aimed at providing a fundamental approach for the optimization of iron - and steelmaking processes and for the development of new processes. During the last ten years an evolution can be observed in the distribution of the selected research topics among the three categories:

I Physical and thermo-chemical equilibrium properties.
II Reaction kinetics.
III Process mechanisms and process modelling.

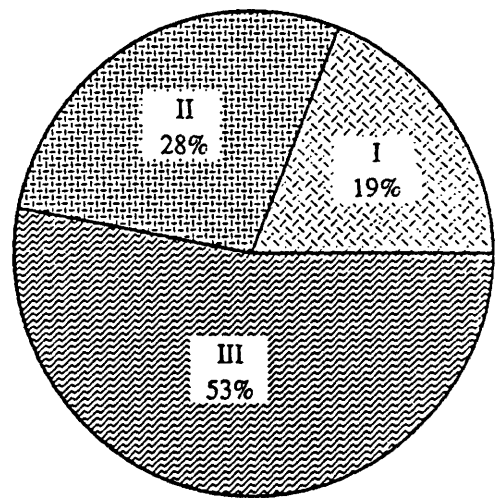
The efficient compilations and determinations done in the first research contracts allowed progress towards more directly applicable work.

1976 - 1982



(Funds for 14 projects)

1983 - 1988



(Funds for 14 projects)

The selection of these topics can be closely associated with the steps taken during the study of steelmaking reactions, starting from equilibrium properties, then considering kinetics of individual reactions and aiming at a complete process modelling.

2.2 Physical, thermal and thermo-chemical properties

Any quantitative process analysis requires a large set of physical and thermal data. Surveying them constitutes the necessary first step of most technical advances. Extensive critical compilations were undertaken in several laboratories and missing or uncertain data were experimentally determined. Such a task that requires the best scientific experts is quite time consuming and often considered as unrewarding. Remarkable work was performed and the results provide reliable values on which all European experts have agreed and which can be universally used; this ensures that when comparing figures derived from industrial measurements in different plants, the same set of properties data has been used: this common language allows diffusion of technical advances among Community members.

2.2.1 Metal phases properties

Thermo-chemical evaluations including heats of formation, standard entropies and heat capacities were carried out for a large number of iron-based systems /1/:

Fe + [O, C, H, N, P, Al, B, Ca, Ce, Cr, Mn, Nb, Ni, Si, W, N]

All binary phase diagrams of iron with the elements of the periodic table have been critically compiled, redrawn and gathered in a single book. The iron-oxygen system, that has been particularly reviewed /2/ is shown as an example on figure 1 /1/.

A very extensive set of interaction coefficients in iron based alloys has been compiled /3/.

For all the systems studied, evaluation methods providing consistency between thermodynamic properties and phase boundaries were used. Models allowing an estimation by interpolation in multicomponent systems have been developed concerning thermodynamic

data. An empirical method for estimation of the Henrian constants of dilute metallic solution has been proposed, which is intended to replace the regular solution concept for dilute solutions /4,5/.

A number of missing data were determined experimentally:

- Activities in liquid and solid Fe-Ni and Fe-V alloys /6/.

- Thermodynamic data for ternary systems Fe-Co-Cr, Fe-Co-Mo, Fe-Ni-Mo, Ni-Co-Cr, Ni-Co-Mo and Ni-Co-Cr /4,6/.

- Special attention was given to thermodynamic studies of calcium in steel melts: calcium solubility of steel melts in equilibrium with CaO saturated slags was measured depending on temperature and contents of different alloying elements /7,8/.

For pure iron solubility of Ca is 0,03 % at 1 600 °C. Carbon contents lead to a higher solubility till at contents of 0,9 % C and 0,048 % Ca, when double saturation with calcium carbide and calcium is reached. Al, Si and Ni increase the Ca solubility whereas Cr has a reverse effect. For melts of stainless steel with 18 % Cr and 8 % Ni, a Ca solubility of 0.022 was measured.

2.2.2 Physical properties of iron oxide bearing slags (converters or electric furnace slags)

Physical properties of molten slags were collated and evaluated in view of providing recommended values for use in computer modelling of the process. The slags studied belong to binary, ternary or quaternary systems incorporating the major constituants of converter or electric arc furnace slags:

CaO, SiO_2, FeO, Fe_2O_3, MnO and MgO.

The influence of some of the minor constituants P_2O_5, Al_2O_3, K_2O and Cr_2O_3 was also studied.

The following properties were critically reviewed:

- density, (figure 2),
- viscosity, (figure 3),
- electrical conductivity,
- thermal properties.

In addition, models for calculating physicochemical and thermal properties of liquid slags have been appraised: they provide a rapid estimation of the effects of changes in composition and temperature on the respective properties. Such models are particularly useful for those systems for which there is a limited amount of measured data; they are essential for the complex, multicomponent slags found in industrial applications.

The printed published report constitute a reference book for engineers in the field of steel refining /9/.

Data from various sources have been gathered, compared, and critically compiled: most publications in that field had merely proposed new data enhancing only the discrepancies with previous work: this compilation tends to reconcile the various sources and proposes the most reasonnable choice for each property as a function of temperature and composition. While most experimental determinations are made in a purely scientific scope to understand the structure of liquid silicates, here the main point is to provide the steelmaker with the best possible evaluation for the very complex slags found in industrial conditions.

2.2.3 Heat transfer properties for calcium fluoride based slags

Thermal properties data have been determined to allow reliable mathematical models to be developped for the slags used in steel melting and refining processes, ESR, electric arc furnaces and converters /10/.

- Some properties showed a relatively small dependance upon composition:

  - all the molten slags were opaque to I.R. radiation,
  - total normal emissivity was around 0.9.

- Confirmation was obtained that some very simple models could be used for the prediction of heat capacity and of thermal expansion for multicomponent systems by using data for single components or compounds.

- Thermal diffusivity of solid ESR slags were considerably affected by the presence of pores and microcracks in samples and by the nature of the gas contained in these microcracks.

- Thermal expansion of ESR slags decreased with decreasing CaF_2 content.

Absorption of water during storage lead to a decrease of thermal diffusivity of ESR slags.

These laboratory measurements on synthetic and industrial slags lead to a valuable set of values of the thermal properties: this is important for the selection of suitable slag compositions for ESR operation. This can be used to improve the predictability, control and efficiency of the process.

2.2.4 Thermochemical properties of oxide phases and complex slags

Thermodynamic data for inorganic compounds which are of interest in steelmaking were critically compiled: the heats of information, fusion evaporation, the standard entropies and the heat capacities were gathered for more than 70 compounds, mainly oxides but also carbides, nitrides and borides.

Extensive compilations of phase diagrams and of thermodynamic activity of components were performed for binary, ternary and quaternary systems /3/ belonging to:

- CaO - FeO- Fe_2O - SiO_2 + (MnO or MgO)
- CaO - P_2O_5 - FeO + (SiO_2 or MnO)
- CaO - CaF_2 + (SiO_2, Al_2O_3, CaS or FeO) (with CaO or CaF_2 as major constituant)
- CaO - Al_2O_3 - SiO_2 + (MnO or MgO)

Experimental determinations were made for:

- the heat of formation of MgO-NiO solid solutions /4/,
- the components activities, in the binary systems K_2O-SiO_2, and for CaO - Al_2O_3 + (CaF_2, MgO or Cr_2O_3) and CaO - Ti_2O_3 - TiO_2 systems /3/,
- the solubility of water in calcium fluoride containing slags /10/.

The CaO-Al_2O_3 system is of special interest for inclusion formation. Activity data measured by mass spectrometry are presented in figure 4 /3/.

Special attention was given to the thermodynamic properties of the Fe-O-Cd system in order to understand the behaviour of cadmium in iron bearing materials. Partial pressure of cadmium in equilibrium with the various phases of this system has been evaluated. Around 1 000 °C, only Cd and O_2 are present in the gas phase in equili-

brium with CdO and $CdFeO_4$. It has been shown that small cadmium contents in association with iron oxide form stable solid solutions under oxidizing conditions /11/. This fixation is important for technical systems when considering a possible pollution of the environment.

Diffusion data have been systematically compiled for a large number of elements in solid and in liquid iron /6/.

2.2.5 Slag thermodynamic models

In the case of industrial slags, the very large number of components that are present in appreciable proportions imposes the development of evaluation methods for predicting the equilibrium state and thermodynamic properties. Several types of models have been developed.

- An analytical description of liquidus surfaces in quaternary systems has allowed the computer reading of phase diagrams /3/: CaO - SiO_2 - Al_2O_3 - MgO; CaO - SiO_2 - FeO - MgO and CaO - P_2O_5 - SiO_2 - FeO.

- Flood-Grjotheim model has been developed for description of thermodynamic activities of constituants in the basic part of the refining slags containing CaO - SiO_2 - P_2O_5 - MgO - MnO - iron oxides as main constituants with low contents of Al_2O_3, CaF_2 and Na_2O /3/. It can provide equilibrium partition between metal and slag for oxygen, manganese, phosphorus and sulfur.

- The concepts of statistical thermodynamics and Monte Carlo calculation technique have also been used to estimate thermodynamic properties of slags /12,13/. Applications have been made for a number of compositions of the SiO_2 - Al_2O_3 - CaO and SiO_2 - CaO - FeO. However the too long computer time required are still an obstacle to the full development of this powerful method.

- A method derived from Kapoor-Frohberg's model has been particularly successful for describing both phase diagrams and thermodynamic activities in multicomponent slags /14,15/. It is based on a statistical thermodynamics model: the liquid mixture of oxides is described in terms if cells composed of an oxygen anion linked to two cations. It makes use of only binary parameters (two to four per couple of components).

The model allows the calculation of:

a) the free energy, enthalpy and entropy as well as liquid slag component activities,

b) the phase diagram in various situations: liquid miscibility gaps, equilibrium of liquid with stoichiometric compounds of ideal solutions of stoichiometric compounds.

Extensive tests with experimental data have been made for systems containing up to six components chosen among

$$SiO_2 - Al_2O_3 - Fe_2O - CaO - FeO - MgO - MnO \quad .$$

There is a fair aggreement on both component activities and phase diagram over large temperature and composition domains (including basic and acid slags), (figure 5).

Computation times are quite short and allow direct use of the model in multiphase equilibria calculations.

The slag model's main features,

- adequate representation of complex slags over large composition domains,

- combined representation of phase diagram and component activities,

- use of only binary parameters, which allows predictions in unexplored composition domains,

- short computation times,

make it a powerful tool which has since been widely used for the description of slag-metal reactions and inclusions formation in iron and steelmaking.

2.2.6 Surface tension and metal-slag interfacial properties

Most important iron and steelmaking reactions occur at interfaces: interfacial properties are therefore essential in understanding their reactions mechanisms. Surface tension and interfacial tension between metal and slag were critically reviewed for iron oxide bearing slags.

Contact angle between liquid metal and solid oxides is the key parameter to predict the possible formation of oxide inclusions cluster: this occurs when the angle is larger than 90 degrees. Such clusters are favorable for inclusions decantation and metal cleanness, but can be troublesome when contributing to nozzle clogging.

Contact angle measurements /14/ were performed by sessile drop method in the systems,

- liquid iron-oxygen alloys in contact with solid alumina or solid $FeO-Al_2O_3$,

- liquid iron-manganese-oxygen alloys with Al_2O_3 or $(Fe-Mn)O \cdot Al_2O_3$ spinel.

The most influent parameter is the oxygen partial pressure. Contact angle is larger than 90 degrees at low oxygen potential. It decreases when P_{O_2} increases and reaches values below 90 degrees

at a level of oxygen content, (0.12 % O without Mn) which decreases when the Mn content increases.

Other measurements concerned solid inclusions formed in calcium treated melts: liquid iron containing very low oxygen contents, in contact with calcium aluminates $CaO \cdot 2Al_2O_3$ or $CaO \cdot 6Al_2O_3$, or iron-sulfur melt in contact with calcium sulfide; in all cases, contact angle is larger than 90 degrees.

The conclusion from these studies is that whereas inclusion cluster formation is always possible in well deoxidized metal; it may not be possible in zones which have been locally contaminated by reoxidations, in particular at high manganese contents, when the contact angle decreases below 90°.

Figure 6 illustrates the contact angles between iron-oxygen melts and solid Al_2O_3 or $FeO \cdot Al_2O_3$ inclusions. Figure 7 shows the additional effect of manganese on contact angle /14/.

2.3 Reaction kinetics and EMF measurements

In the control of steelmaking reactions, the remarkable change that occurred in the last ten years, is the progress towards mathematical description of actual reactions kinetics. Thermodynamic data are used not only to predict the feasibility of a reaction in a qualitative way, (depending upon the free enthalpy change is positive or negative), but also to define accurately the equilibrium state.

The frequent case of a mass transfer at an interface can be chosen as an example. The rate of change of the contents of an element X can generally be expressed by a function:

$$\frac{d\ \%X_t}{dt} = k\ \frac{A}{V}\ (\%X_t - \%X_{equilibirum})$$

where $\%X_t$ is the content at time t.

This type of equation can be used to list the needed data:

- k, the kinetic factor is a function of physical properties of metal and slag phases: density, diffusivity, viscosity and interfacial tension.

- A/V represents the relative interface area, A, for the metal volume V. This interface A is strongly dependant upon interfacial tension and of stirring conditions, (i.e. gas injection, electromagnetic stirring, etc.).

- $\%X_{equilibrium}$, the dissolved element content at equilibrium is one of the key data for the prediction of this reaction rate for multicomponent systems, improvement in the precision of its evaluation remains a major objective.

2.3.1 Slag compositions for dephosphorization of steel melts

The question of very low phosphorus contents in steel may rise to greater importance in future steelmaking processes. Experimental research work has been carried out to optimize slag compositions for obtaining low phosphorus contents during steel ladle treatments, in oxidizing or in reducing conditions.

With iron oxide bearing slags belonging to the CaO - FeO_n + (SiO_2, Al_2O_3 or CaF_2) systems, more favourable values of phosphorus distribution are obtained with the lime saturated slags. In detail, the following results have been obtained /11/:

- for lime silicate slags (CaO-FeO_n-SiO_2),

  the largest P distribution ratios were obtained for lime saturation close to the double saturation of CaO and 3 CaO·SiO_2, (figure 8a),

- for lime aluminate slags (CaO-FeO_n-Al_2O_3),

  the P distribution for lime saturation rises with increasing FeO_n-contents and reaches the highest values in the lime saturated binary system CaO-FeO_n, (figure 8b).

- for lime fluorspar slags (CaO-FeO_n-CaF_2),

  a maximum in the P distribution is reached with lime-saturated fluorspar slags at 50 % CaO, 20 % FeO_n and 30 % CaF_2, (figure 9).

For the desulphurization examined at the same time, a noticeable refining effect was only achieved on treatment with soda slags (Na_2CO_3-FeO-SiO_2).

These laboratory results indicate that, with the best iron oxide bearing slags, very high partition ratio $\%P_2O_5/\%[P]$, (of 1000 or

more) can be reached, and correspondingly phosphorus contents lower than 10 ppm could be obtained.

In reducing conditions, the thermodynamic of calcium treatments have been studied /7,16/. Laboratory experiments for dephosphorization of steel melts confirm the assumption that for reducing conditions in a Fe-P-Ca-CaO-CaF_2 ($CaCl_2$) system dephosphorization reaction is based on the formation of Ca_3P_2 which is then dissolved in the slag. The refining effect is essentially determined by calcium content, (figure 10).

It is shown that dephosphorization under reducing conditions is a promising method to dephosphorize chromium-alloyed steel melts. Calcium halide slags containing dissolved metallic calcium are able to serve as useful fluxes for the calcium treatment.

From these studies, optimal conditions can be selected for phosphorus removal from steel melts. Feasability of either method on industrial scale will be strongly dependant on the economics of slag formation, and slag removal and handling.

2.3.2 Continuous measurement of dissolved oxygen in steel melts

Short-time immersion measurement with solid-electrolyte tube probes for direct determination of oxygen activity in steel melts has been developed to the stage of technical maturity and are currently employed in steel works. However it has so far not been possible to develop a method for the continuous measurement of oxygen in steel melts with an immersion probe to the same stage.

A continuous oxygen measurement in steel melts would enable a better process control in refining and casting processes. Oxygen absorption by reoxidation of the steel melt can be detected immediatly. Such a development would then be a further progress in developing advanced techniques for clean steel production.

It was shown that continuous oxygen measurement with thinwalled tubeprobes and metal/metal-oxide reference is only possible in exceptional cases i.e. when the partial oxygen pressure of the steel melt is approximately equal to the oxygen equilibrium pressure of the reference mixture used /17,18/.

The field of application of the probes can be extended to oxygen activities of about 0.0002 to 0.1 by using a Pt-Rh contact wire flushed with air as an internal reference; the probe section intended for immersion was externally coated with a porous $ZrO_2(CaO)$ or $ThO_2(Y_2O_3)$ material. Accurate and reproducible EMF and temperature recordings remained stable for up to two hours, (figure 11) /17/.

Further applied work using these results lead to trials of a probe in industrial tundish of various continuous casting plants. For low oxygen activities, in aluminium killed steels and in high alloys steels, a plug type electrode with $Cr-Cr_2O_3$ reference was built (figure 12), it allowed reliable measurements during periods over two hours /19/.

In spite of these good metallurgical results, commercial scale production of a continuous oxygen probe has still not been undertaken by an industrial manufactures.

2.4 Reaction mechanisms and process modelling

Global reaction kinetics for a given industrial process is the most demanding part, and theoretical treatment should be adapted to each reactor type. Recent work has concerned reaction mechanisms in individual reactors, lower part of the blast furnace, and liquid steel ladles. These studies should of course be closely linked with parallel fundamental work done in other committees.

2.4.1 Silicon transfer in the blast furnace

The objective was to analyse the physicochemical aspects of silicon transfer in the blast furnace and to define the operating conditions promoting the production of consistent hot metal, with low and regular silicon content, (figure 13) /20/.

- A thermodynamic model of Si equilibrium between slag and metal has been developed. The thermochemical description of the activities of components in the slag and metal phases relies on the results of the above mentionned ECSC research programs.

  It is shown that, at the tuyere level, the equilibrium silicon content should be high, whereas under hearth conditions a potential desiliconization capacity exists: in order to take advantage of this capacity, some oxygen would have to be fed at the reaction interface.

- The role of gaseous SiO in the process of silicon transfer has been studied under laboratory conditions: the generation of SiO from coke ash reduction may lead to a SiO partial pressure close to 10^{-2} bar, under tuyere conditions, the most important parameter being the temperature /21/.

  The kinetics of SiO absorption into slag or metal have been determined; transfer into slag increases with the oxygen poten-

tial, whereas transfer into metal is improved by a high carbon content in the metal.

- The flow of liquids (metal and slag) in the hearth of the blast furnace has been investigated by radioactive tracer techniques on industrial furnaces, and by experiments on a small scale hydraulic model. The radiotracer results show that the hearth is far from a well mixed reactor, explaining thus the large chemical and thermal heterogeneities of liquids that are observed and that may affect hot metal quality, (figure 14). The cold model experiments point out the permeability pattern in the hearth as a key factor acting on the flow behaviour of liquids /20/.

The silicon equilibrium model between slag and metal is now used in several plants as a process control tool to characterize the performance of the furnace regarding hot metal quality /22,23/.

According to the present analysis, the oxygen potential and the availability of oxygen at slag metal interface appear as determinant parameters to control silicon transfer. This concept has led to industrial trials consisting in injection of pulverized iron oxides at the tuyeres of the blast furnace. The successful results were entirely consistent with the present analysis, and confirmed its validity, (figure 15) /24/.

2.4.2 Slag entrainment while emptying metallurgical vessels

Slag carry-over from BOF, ladle or tundish can be a great disadvantage in secondary steelmaking operations and in continuous casting practice. Therefore a deeper understanding of flow phenomena during drainage of metallurgical vessels was needed to derive measures preventing slag carry-over. Model trials and plant trials were carried out to clarify the flow characteristics /25,26/.

Slag carry over can be caused by three types of phenomena, a metal slag emulsification, the formation of a vortex sink (figure 16a) or of a "drain sink" (figure 16b), phenomenon, much less studied up to now, observed toward the end of tapping /27/.

The occurrence of vortex sinks depends to a great extent on an already existing angular momentum in the melt during tapping of teeming. An eccentric nozzle delays the formation of a vortex when the slag passes through the nozzle (figure 17a) /28,29,30/.

A drain sink occurs at the end of the draining process, when the volume flow is smaller than the possible nozzle capacity (figure 17b). For a rough estimation the general rule applies: a drain sink will occur when the rest height of the liquids is equal to the nozzle diameter /27/.

A number of important pratical consequences can be derived from this study:

- In converter tapping, the injection of gas too close to the nozzle can lead to higher slag carry-over due to an emulsification.

- During the drainage of teeming ladles, top slag is carried over towards the end of teeming. Emulsified slag carried over to the tundish leads to an uncontrollable decrease of oxidic cleanness in the product; the rest steel method generally used as countermeasure results in a substantial reduction of steel yield.

- The last draining stages of teeming ladles are dominated by the flow phenomenon "drain sink". This phenomenon results in a decrease of the casting rate and in a sharp increase of casting rate delay. "Vortex sinks" are only of secondary importance in ladle drainage. Flow breakers, which prevent the development of vortex sinks, would be virtually ineffective as countermeasure against predominent drain sinks.

A countermeasure to be considered in this respect is the tilting of the ladle with the nozzle arranged close to the ladle wall and the slanted lining or stepping of the ladle bottom. In the presence of a drain sink this measure improves phase separation during casting.

Measurements made at the revolving turret scales of a continuous casting plant confirm the possibility of detecting the delay in casting rate at slag carry-over. To this end, the measuring signals have to be conditioned in a process computer. This measuring method is being further improved at present, (figure 18).

- During tundish to mold casting, a vortex sink can be of great importance for slag carry-over. Under steady conditions, slag carry-over can be prevented by a correspondingly high filling level of the tundish. Further investigations will be necessary for the detection of non-steady conditions, which can lead to slag/metal emulsification.

  The provision of a dam/weir combination in the tundish can prevent the wide spreading of disperse phase in the tundish.

This wide scope has brought a new understanding of flow phenomena during drainage of metallurgical vessels: it points out the consequences that should be drawn in order to prevent slag carry over and to obtain a better steel cleanness.

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2.6 Figures

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Fig. 2: Influence of Fe_xO content on the density (g/cm^3) of $CaO-Fe_xO-SiO_2$ slag melts at 1 400 °C /9/

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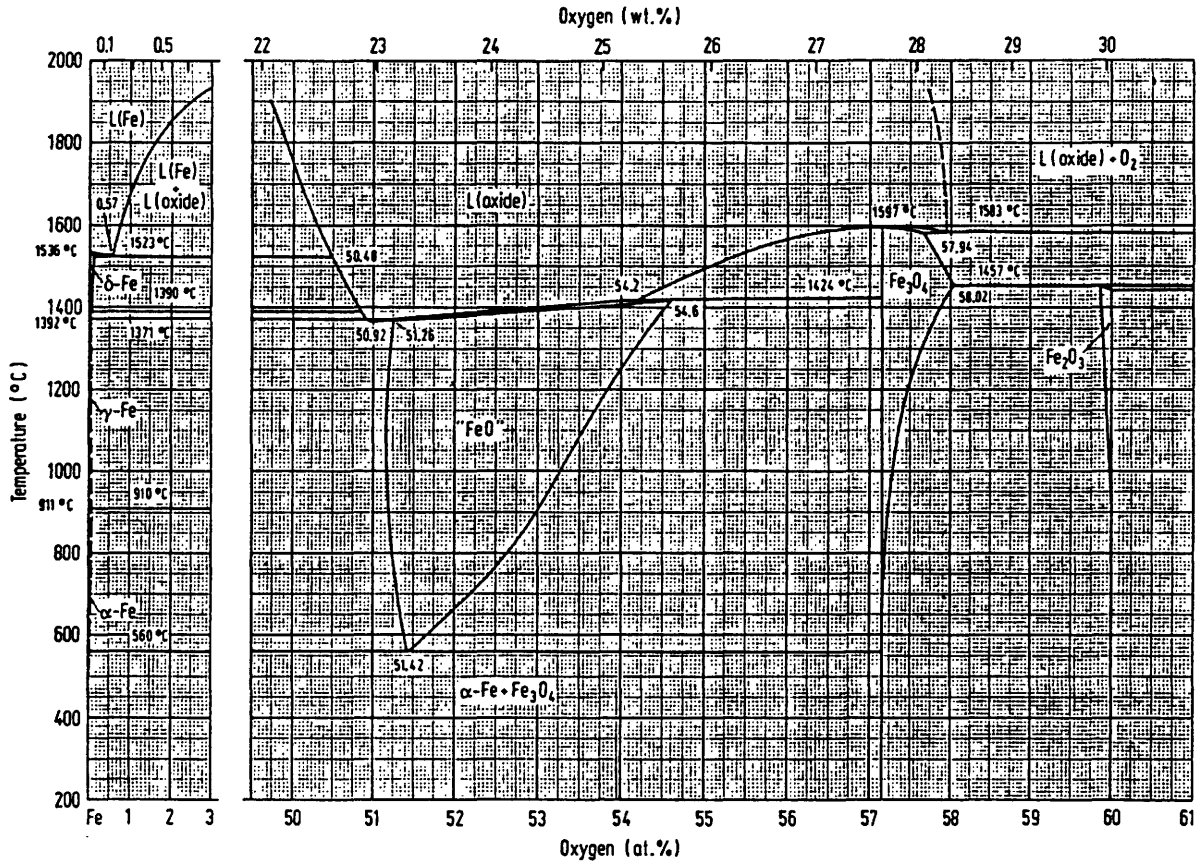

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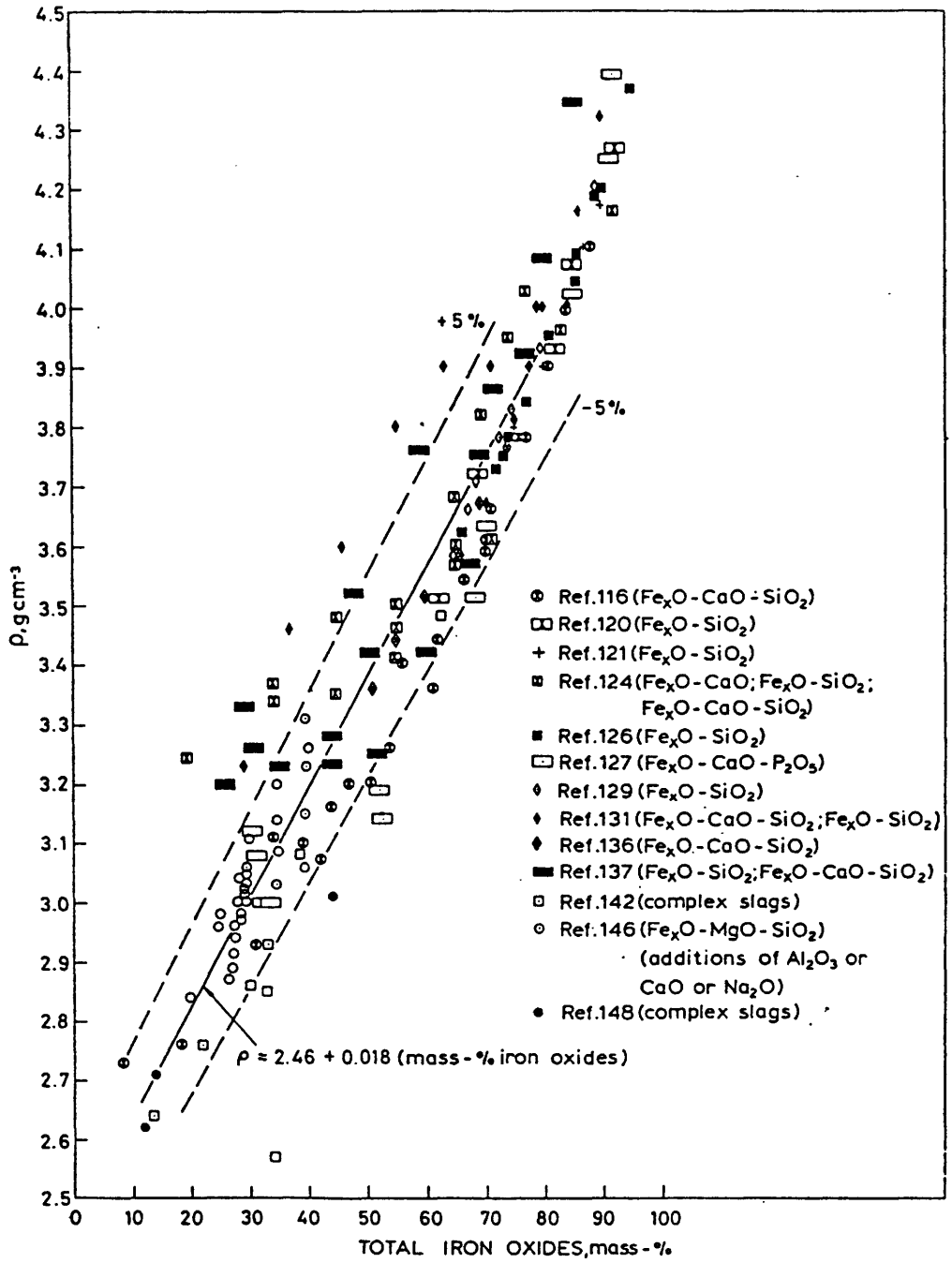

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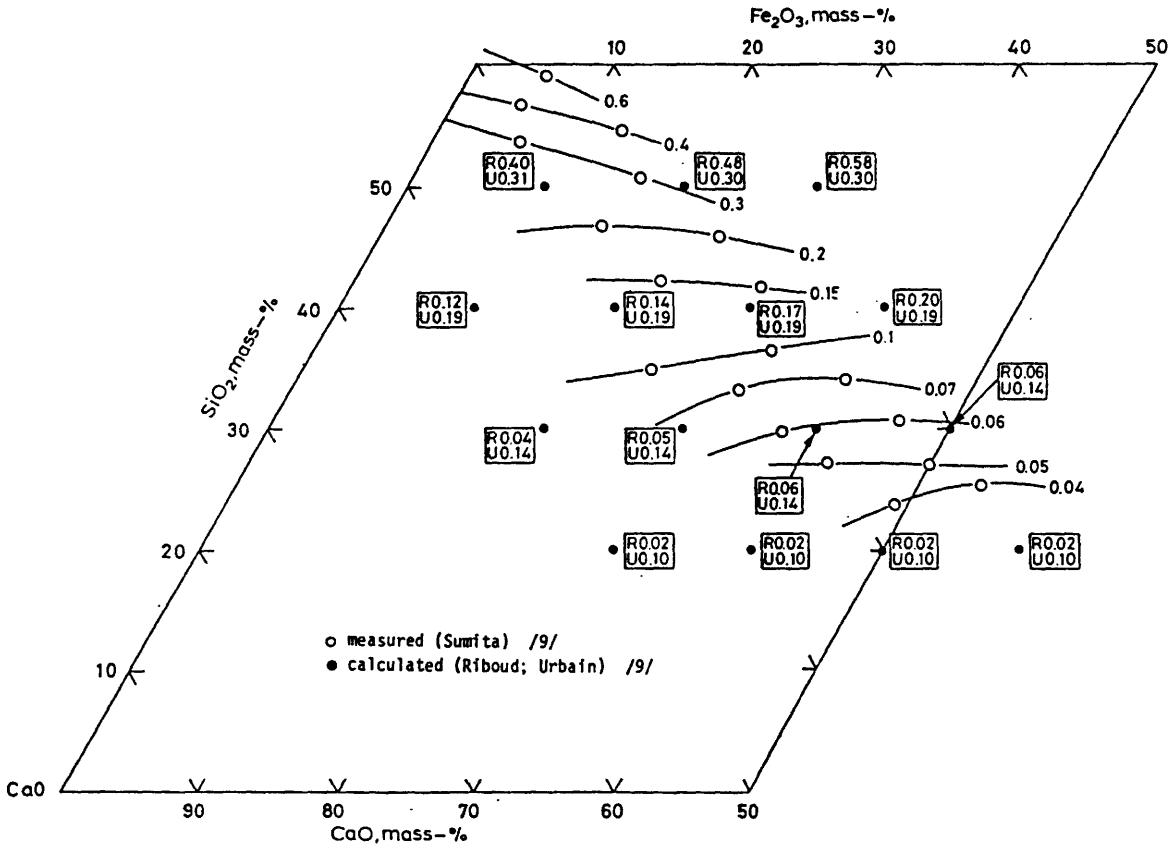

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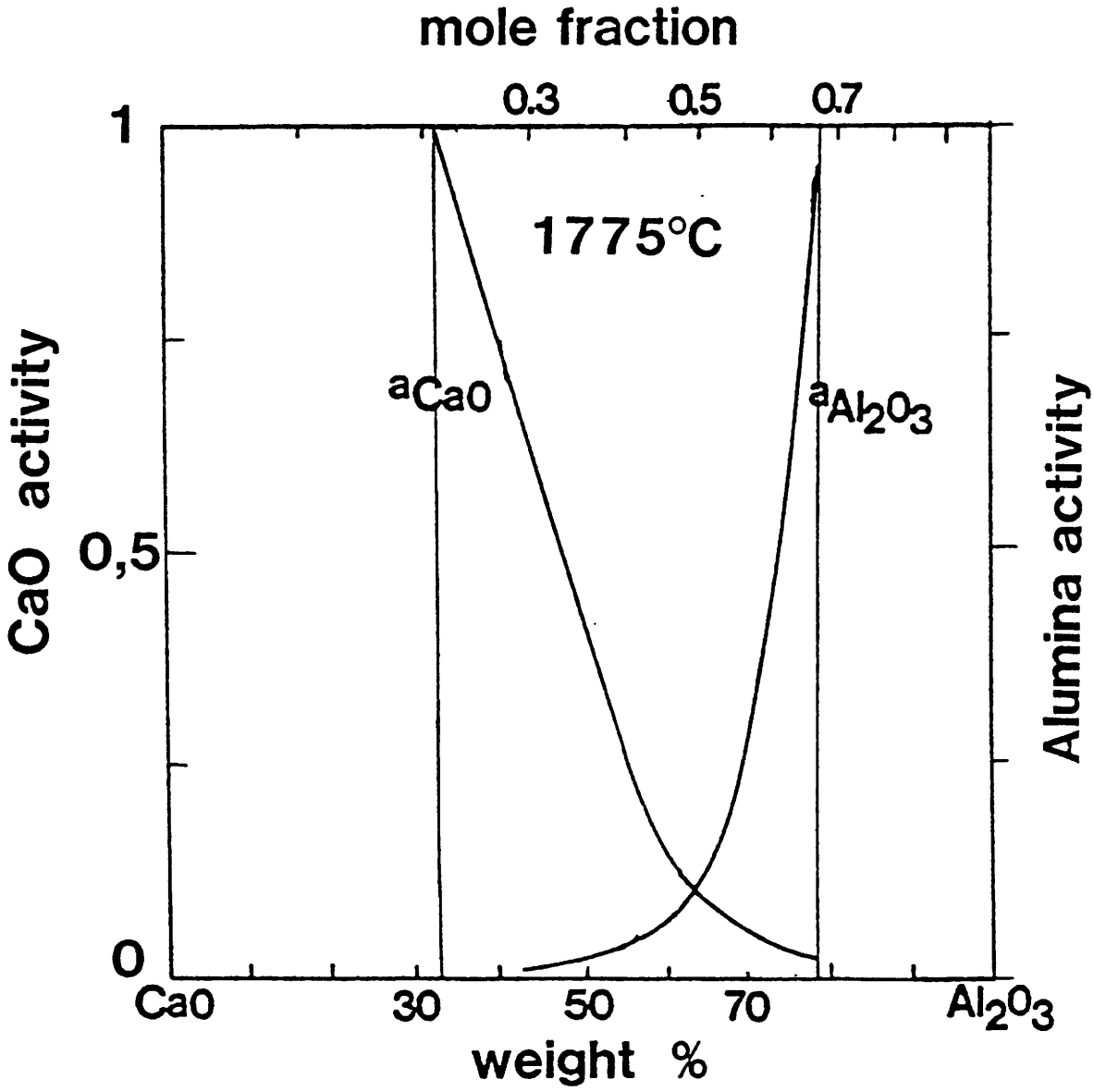

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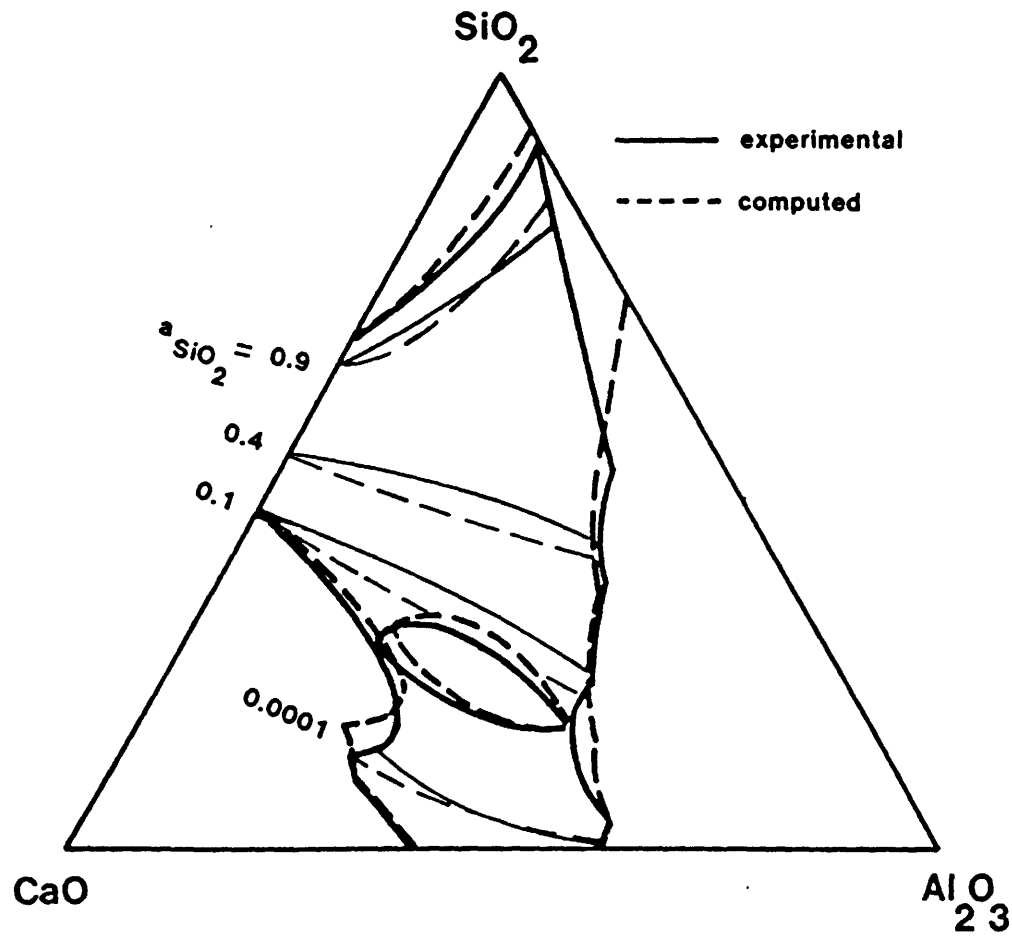

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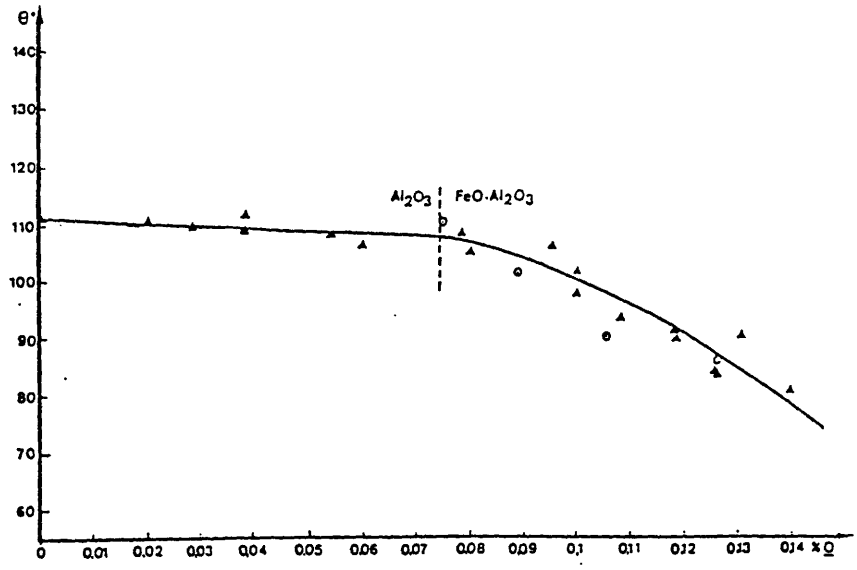

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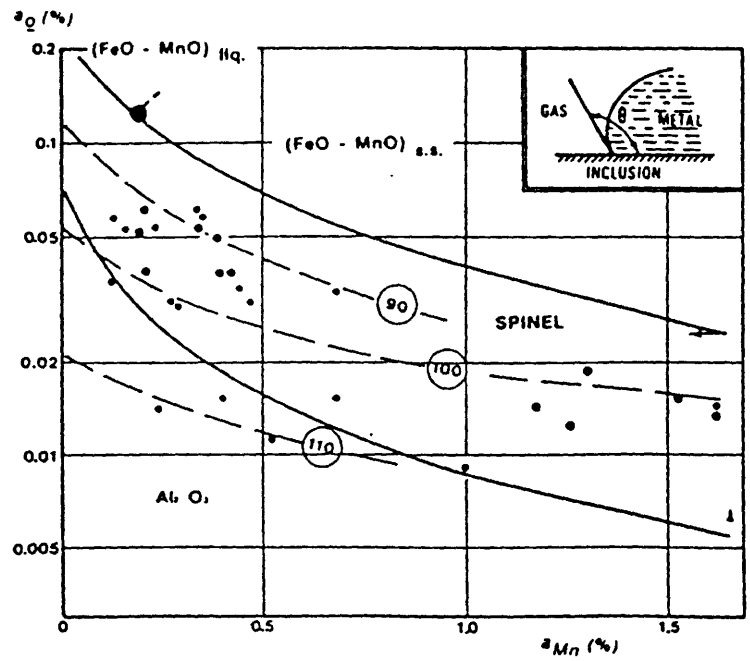

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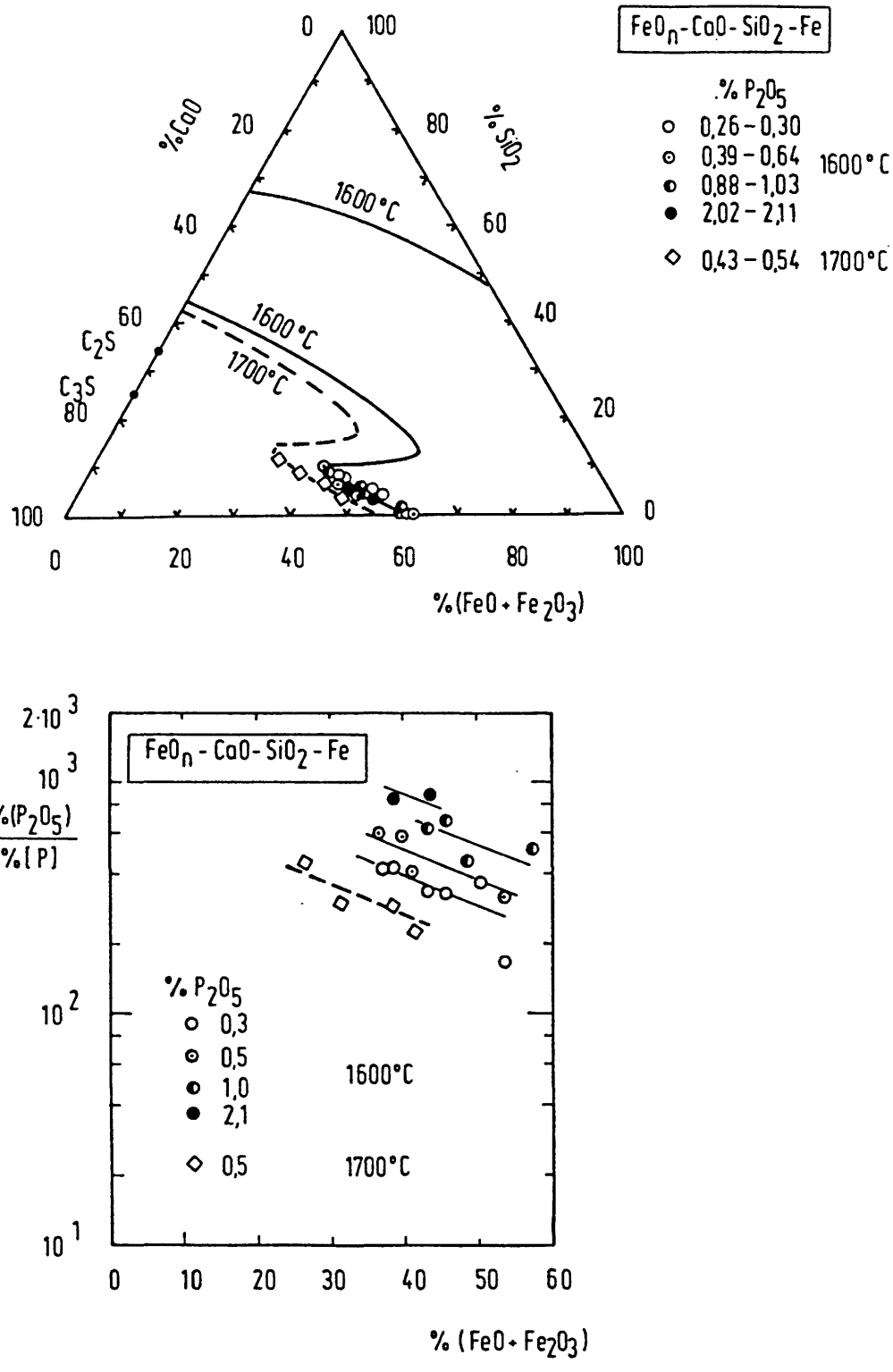


Fig. 8: Phosphorus partition between liquid steel and lime saturated slags /11/

a) $CaO-FeO_n-SiO_2$ slags at 1600 °C

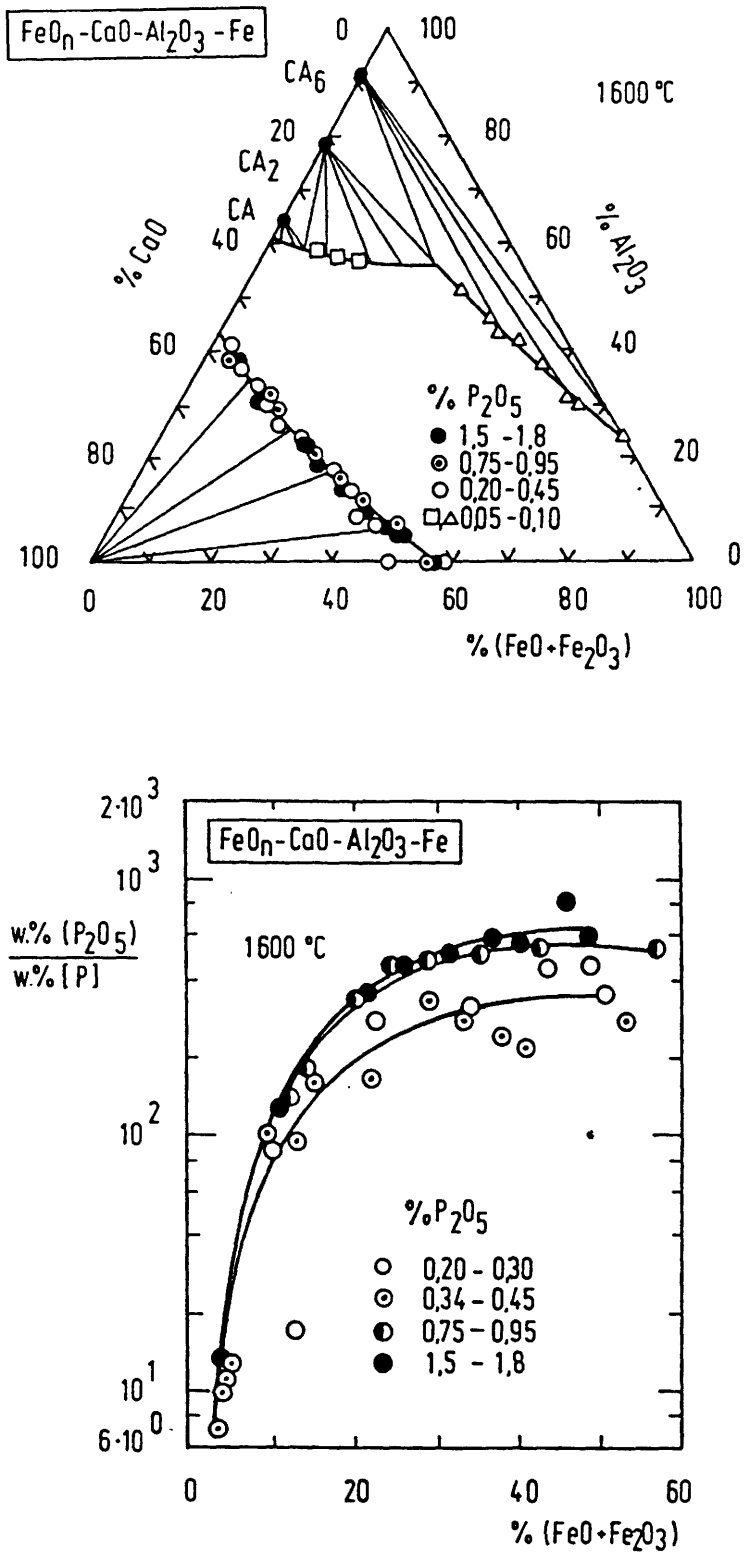
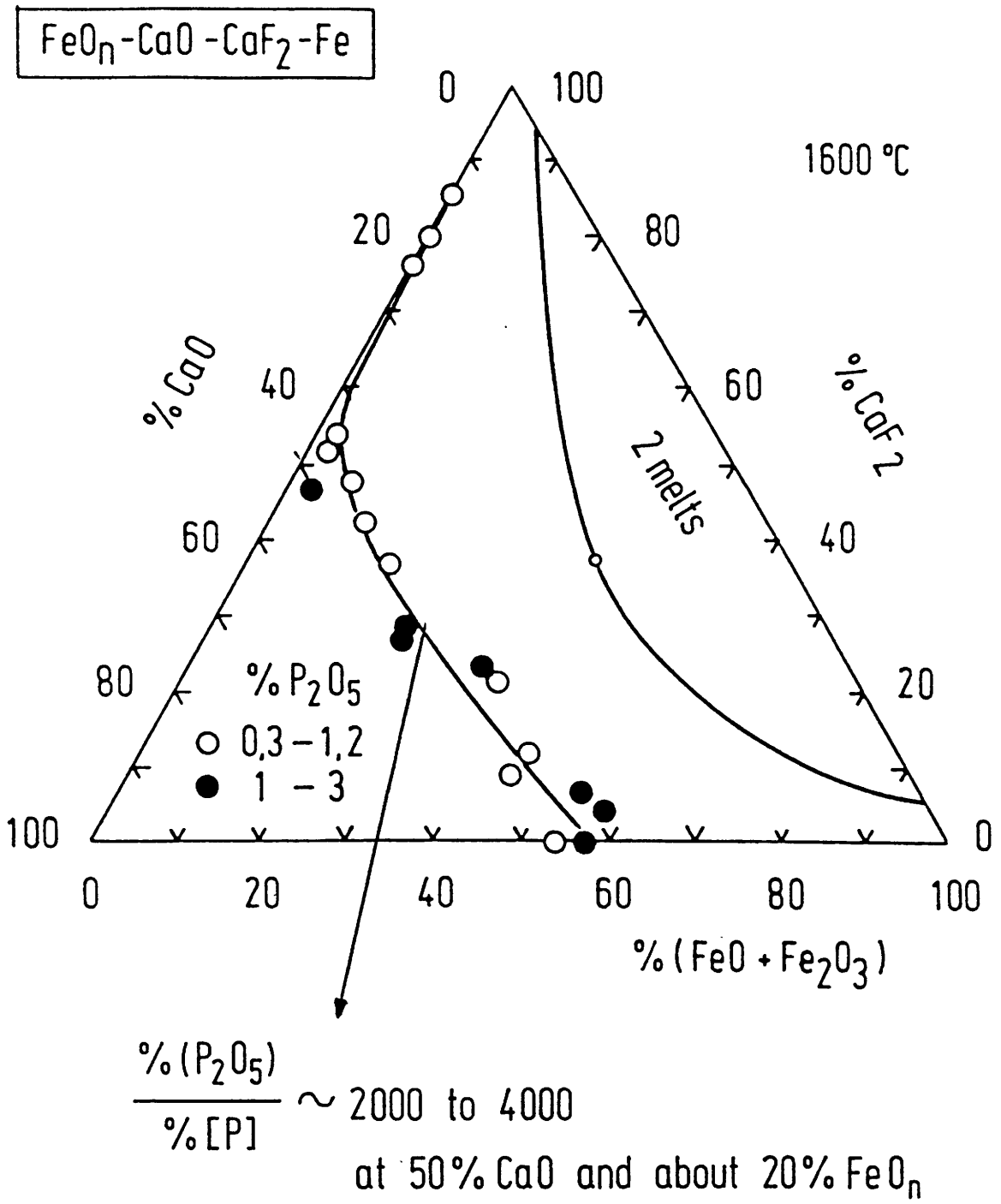


Fig. 8: Phosphorus partition between liquid steel and lime saturated slags /11/

b) $CaO-FeO_n-Al_2O_3$ slags at 1 600 °C



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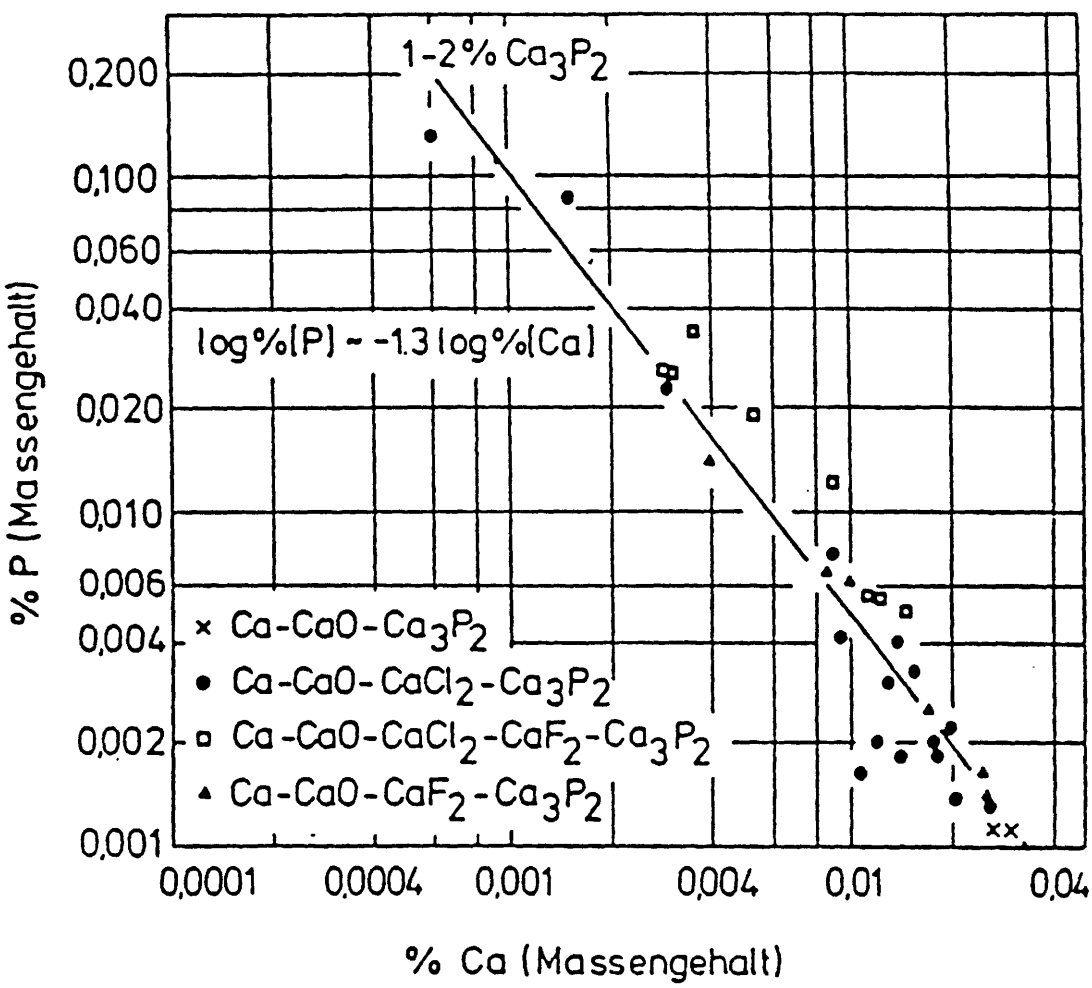

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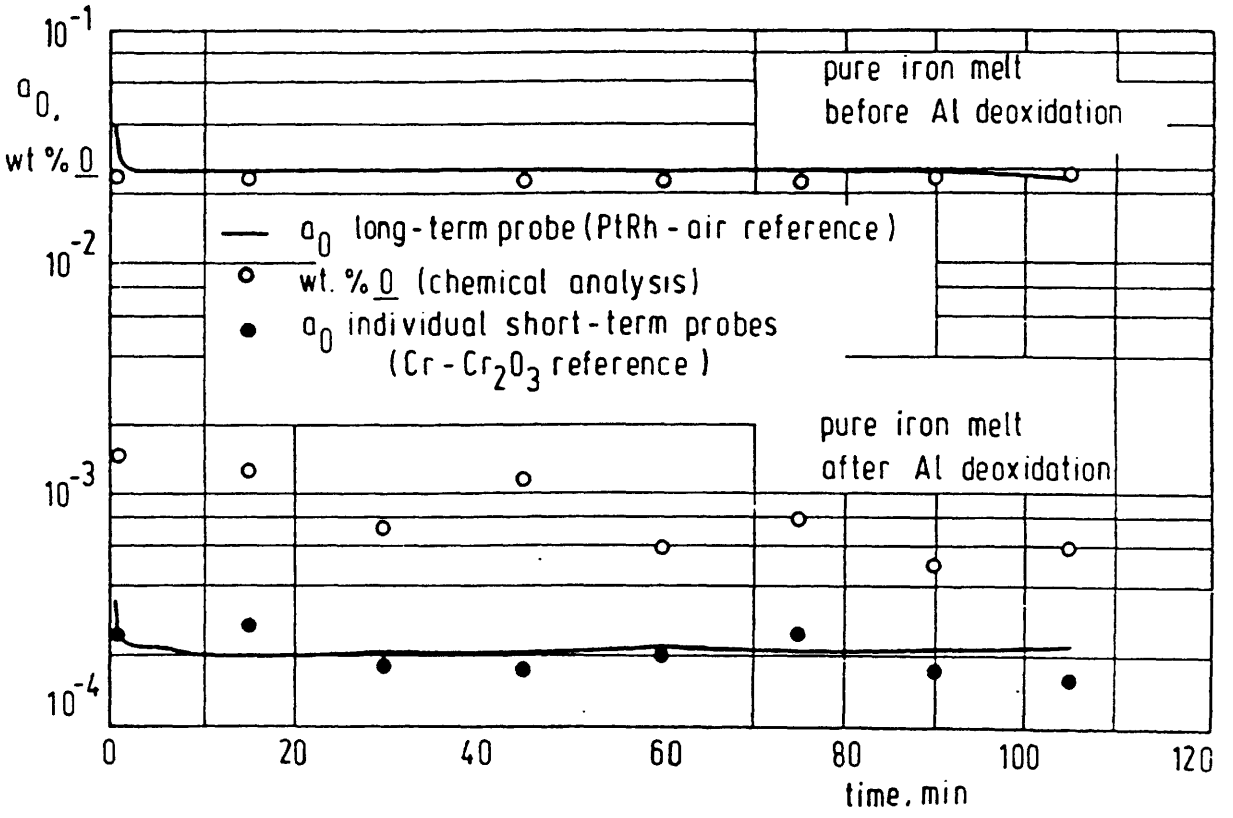


Fig. 11: Results of continuous EMF measurements of oxygen in steel melts /17/

Examples of results of continuous oxygen activity measurements with a cell : Pt-Rh/air/ZrO_2(CaO)/ThO_2(Y_2O_3)/Fe_{liq}.

- Comparison with chemical analysis in a melt before deoxidation (upper part of figure).
- Comparison with the usual short term probes in an aluminium deoxidized steel melt ; (in that case samples used for chemical analysis are strongly influenced by oxide inclusions).

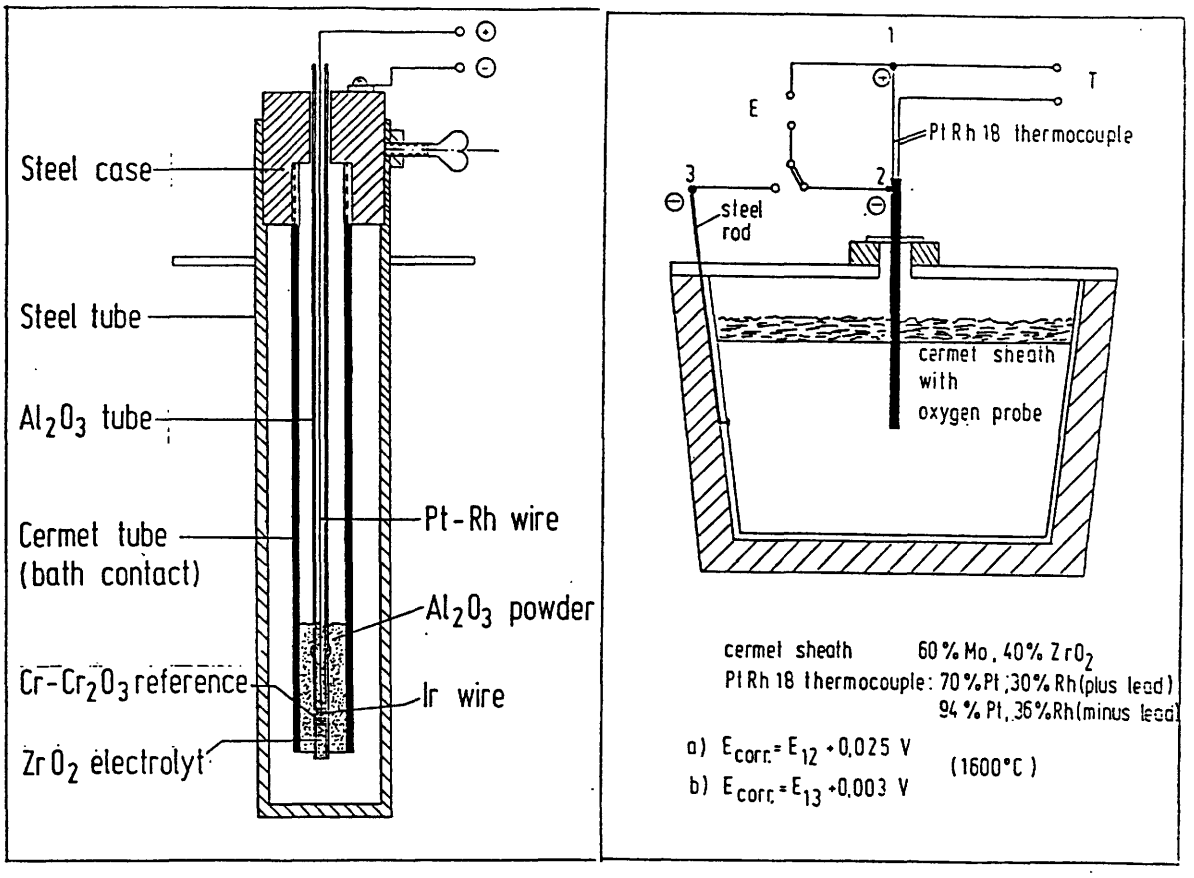


Fig. 12: Plug type EMF probe for continuous measurement of oxygen in steel melts in a tundish /19/

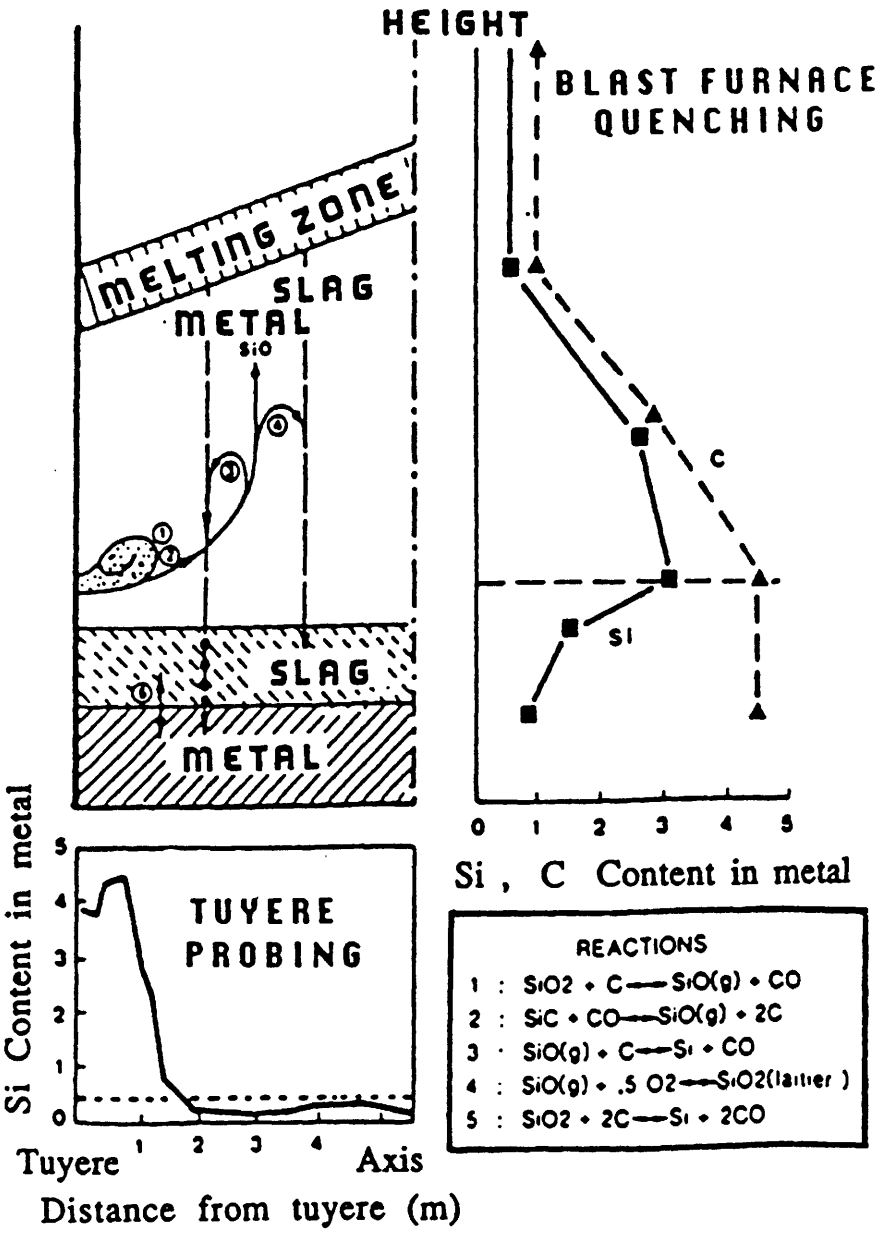


Fig. 13: Schematic representation of silicium transport phenomena in the blast furnace /24/

RESIDENCE TIME DISTRIBUTION

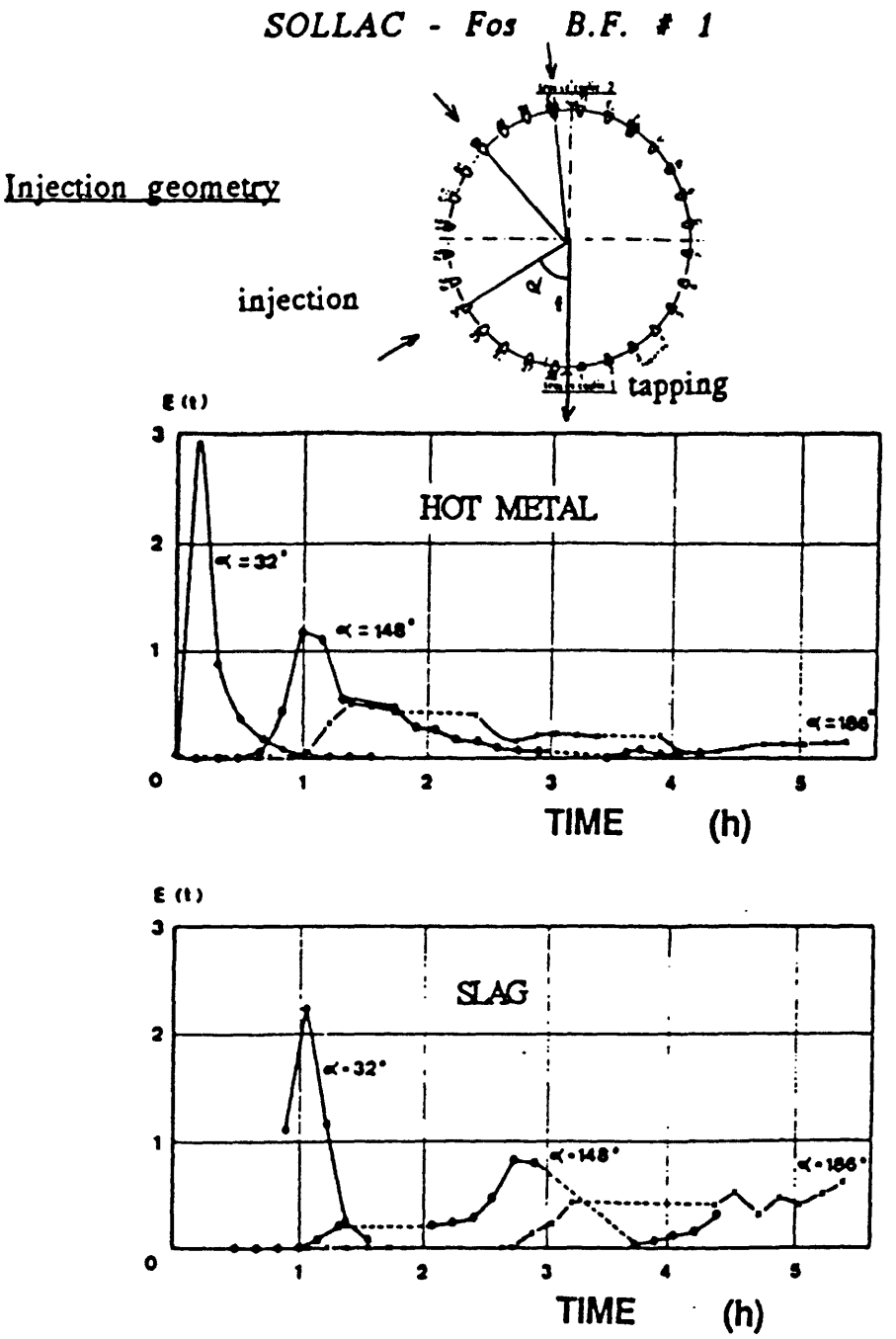


Fig. 14: Residence time distribution $E(t)$ of metal and slag in the hearth of Solmer BF 1 /20/

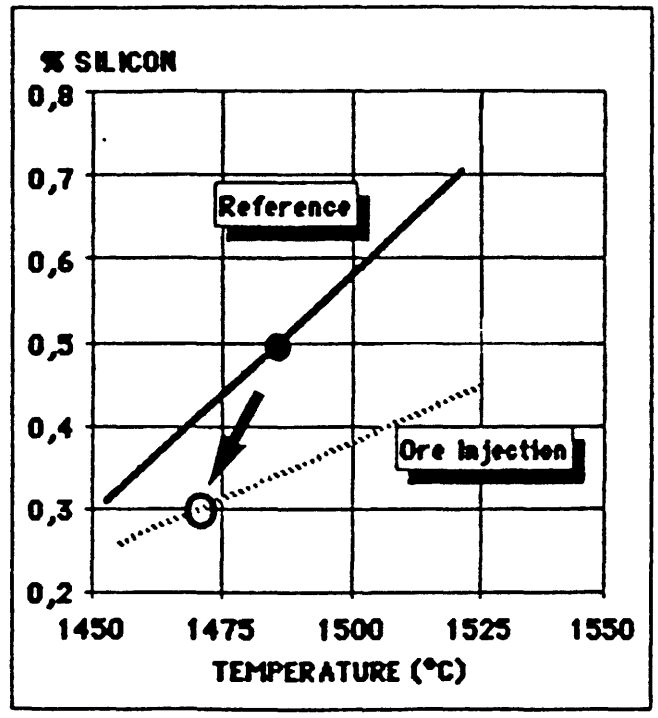
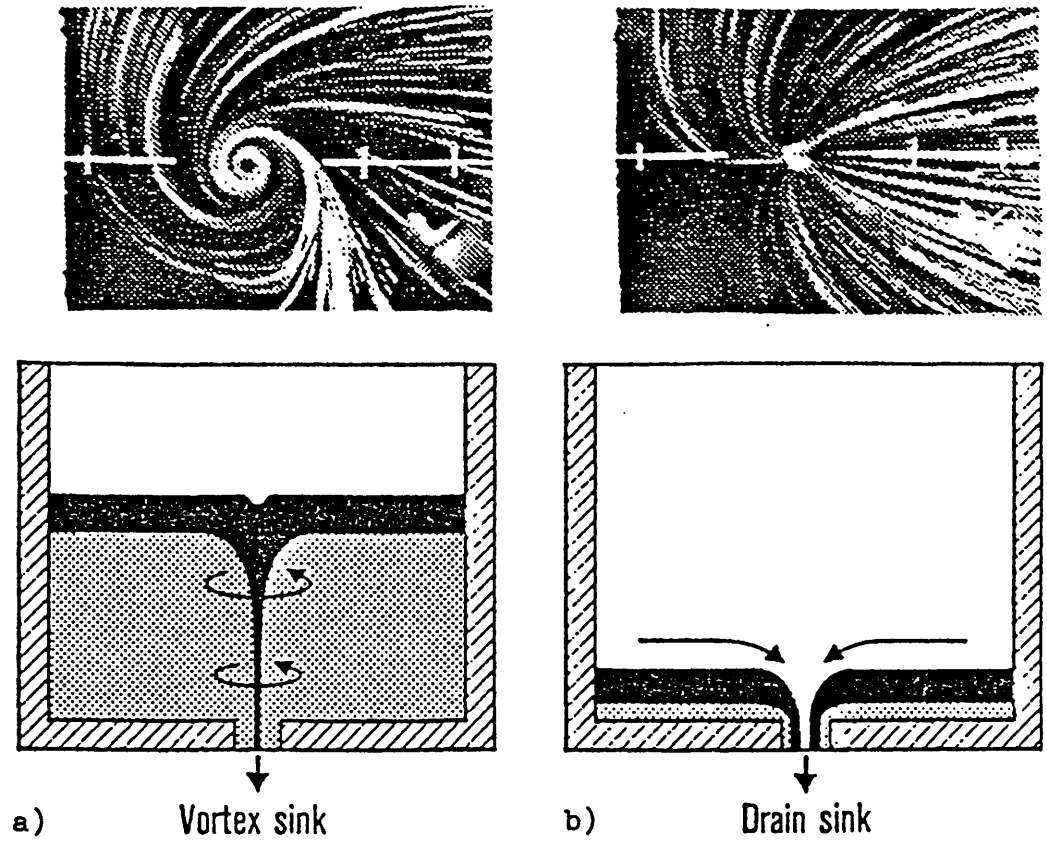


Fig. 15: Effect of an ore injection upon the silicon content-temperature relationship ; injection of 20 kg/ton hot metal of a slurry, 15 % water - 85 % iron ore.



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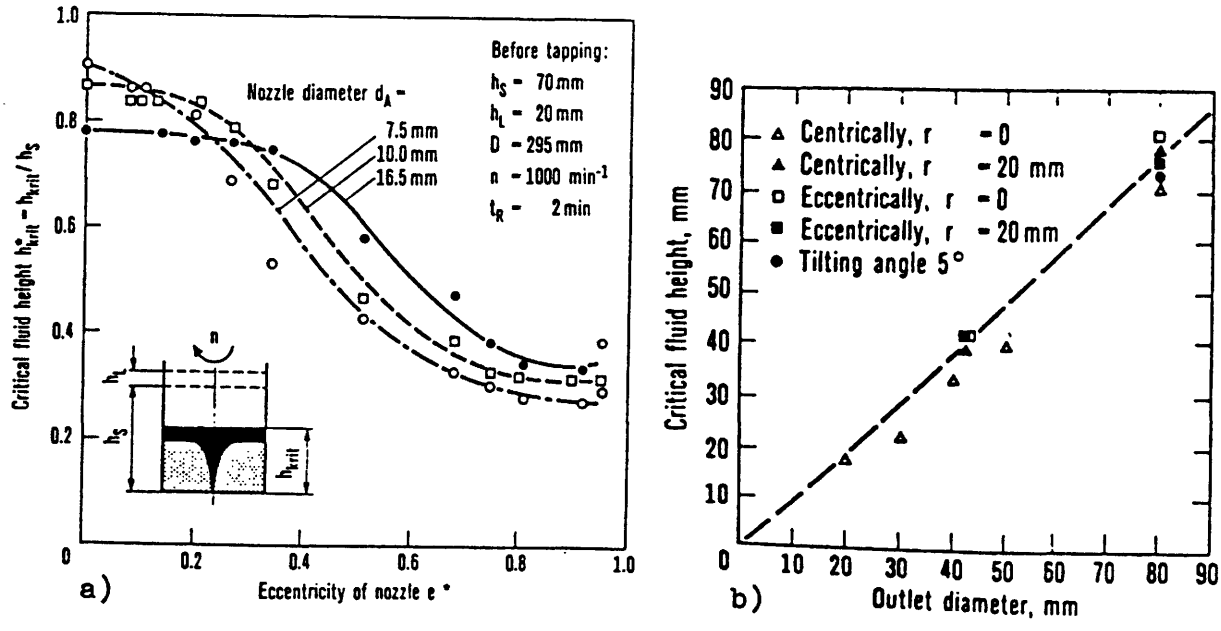

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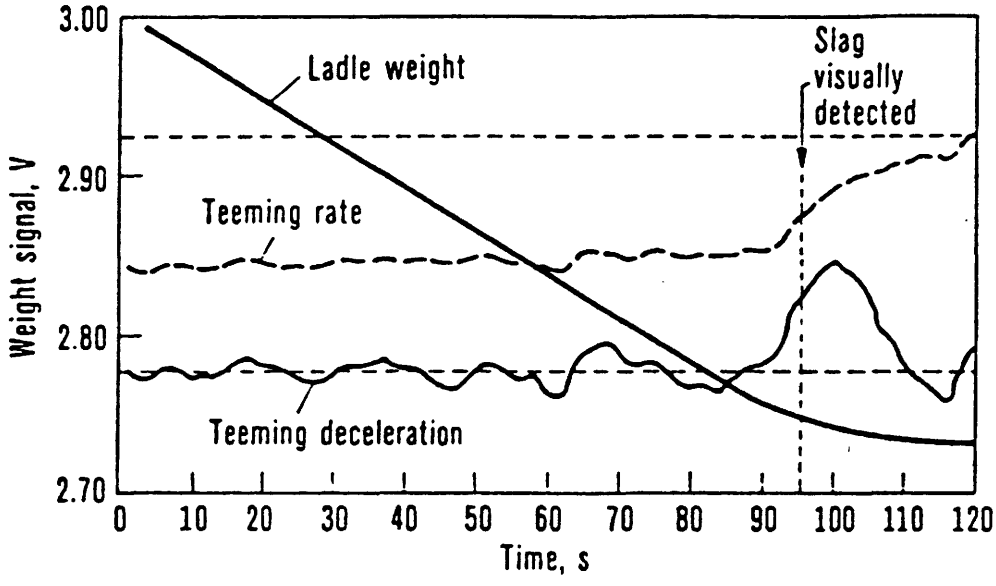

Fig. 18: Measuring method for slag carryover by detecting the delay in casting rate /27/

3. LIST OF PAST AND RUNNING CONTRACTS

3.1 List of past contracts

A) Data programme in the field of metallurgical thermochemistry (Contract no. 6210 CA-1/107; VDEh, Düsseldorf)

B) Critical assessment of the chemical metallurgical data of compounds and alloys pertinent to iron and steelmaking (Contract no. 7210 CA/130; RWTH Aachen)

C) Review and compilation of thermochemical data (Contract no. 7210 CA-3/303; IRSID, Maiziéres-lés-Metz)

D) Thermochemical and kinetic data on steelmaking related materials (Contract no. 7210 CF/301; IRSID, Maiziéres-lés-Metz)

E) Calculation of thermodynamic properties of slags by Monte-Carlo method (Contract No. 7210 CA/406; CSM, Rome)

F) Thermodynamic properties of slags for secondary metallurgy processes and of waste materials (Contract no. 7210 CF/102; VDEh, Düsseldorf)

G) Physical properties of B.O.S. slags (Contract no. 7210 CB/803; NPL, Teddington)

H) Physical properties of slags (Contract no. 7210 CA/806; NPL, Teddington)

I) Continuous measurement of dissolved oxygen in steel melts using EMF probes (Contract no. 7210 GA/110; MPI, Düsseldorf)

K) Measurement of oxygen potentials in slags (Contract no. 7210 GA/403; CSM, Rome)

L) Silicon transfer in the blast furnace
(Contract no. 7210 AA/310; IRSID, Maiziéres-lés-Metz)

M) Thermodynamic behaviour of complex deoxidizers
(Contract no. 7210 CA/412; CSM, Rome)

N) Electrochemical deoxidation and desulfurisation in a semi-industrial scale (Contract no. 6210 CA-3/301; IRSID, Maiziéres-lés-Metz)

O) Fundamental thermodynamic studies on calcium treatment of steel melts (Contract no. 7210 CF/101; MPI, Düsseldorf)

P) Fluid flow phenomena of metal and slag during drainage of metallurgical vessels (Contract no. 7210 CB/103; VDEh, Düsseldorf)

3.2 List of running contracts

R) Nitrogen contents in iron and steelmaking
(Contact no. 7210 CB/107; VDEh, Düsseldorf)

S) Use of optical basicity concept for determining phosphorus and sulphur slag/metal partitions
(Contract no. 7210 CF/802; BSC, Rotherham)

T) Refining of steel melts with alkaline earth metals
(Contract no. 7210 CF/103; MPI, Düsseldorf)

U) Plasma ladle furnace metallurgy (Contract no. 7210 CF/104; Krupp Stahl AG, Bochum)

V) Hydrodynamics concerning continuous casting
(Contract no. 7210 CA/417; CSM, Rome)

W) Segregation and phase distribution during solidification of carbon, alloy and stainless steels (Contract no. 7210 CF/801; BSC, Rotherham)

X) Study about new electrochemical sensors for direct measurement of dissolved elements in steel melts
(Contract no. 7210 GD/403; CSM, Rome)

Y) Development of electrochemical sensors for direct measurement of dissolved Al, Ti, Si, Mn and Cr in iron and steel melts
(Contract no. 7210 GD/103; MPI, Düsseldorf)

Z) Investigation of the behavior of zinc and lead in steelmaking processes (Contract no. 7210 CF/105; MPI, Düsseldorf)

The following projects are awaited to start in autumm 1988:

- Fundamental study of the mechanism of skull formation in metallurgical aggregates
(P 2205; CRM)

- Fundamental studies related to the mechanismus of inclusion removal from steel
(P 2285; BSC + NPL)

- Fundamental study about the mechanisms of filtration of steel melts
(P 2294; MPI)

- Evaluation and critical compilation of thermochemical data and physical property values of slags for iron and steelmaking (Slag Atlas)
(P 2319; VDEh + MPI + RWTH Aachen + IRSID + Univ. Grenoble + NPL joint project)

4. CONCLUSIONS FROM PAST AND PRESENT CONTRACTS

The usefulness of thermodynamic and kinetic data

- for the assessment of practical problems of iron- and steel production, i.e., refining, metal-slag-refractory interactions,
- for calculations of equilibrium data to estimate the possible yield of metallurgical reactions, or,
- for calculations of reaction paths and reaction rates,

was being increasingly realized since the middle of the 70 th. Thus, in the beginning of a closer co-working in the European Coal and Steel Community in the field of theoretical metallurgy, in 1975, research was characterized by evaluation and compilation of thermochemical data of iron systems.

The value of these first compilations is to be seen in a now available unique set of consistent thermochemical data of iron-based systems, presently used in European data banks like "Therdas" in Aachen, Grenoble or Teddington.

Further research work was then related more and more to specific fundamental questions of iron and steelmaking. Thermodynamics and physical properties of B.O.S. slags and of E.S.R. fluxes were reviewed. To come to a deeper knowledge about deoxidation and calcium treatment of steel, measurements and model developments were performed as well as research work about the fundamentals of electrochemical reaction or electrochemical measuring methods in steel and slag melts.

The most recently completed projects and some projects just started were shifted to special problems, of iron or steelmaking reactions, and of process techniques, with emphasis on kinetics and hydrodynamics rather than thermodynamics. These studies such as silicon transfer in ironmaking or kinetics in plasma furnace me-

tallurgy are related to important operational tasks of optimizing energy consumption. Another important aim is quality improvement of steel; main contributions are studies such as

- fluid flow phenomena during drainage of metallurgical vessels,
- filtering of steel melts,
- mechanisms of inclusion removal combined with more knowledge about hydrodynamics, and
- segregation control during solidification.

Summing up the results of the past contracts which effected a real "spin off" in iron and steelmaking it can be stated that,

- thermochemical data compilations have enabled working with consistent data sets for calculating metallurgical processes,
- fundamentals especially about Ca metallurgy and optimal slag compositions contributed to clean steel production with low levels of dissolved elements,
- detailed knowledge about fluid flow phenomena of steel melt and slag during drainage of vessels, ladles and tundishes led to measures to avoid slag carry over and to improve steel cleanness.

5. FUTURE NEEDS OF FUNDAMENTAL RESEARCH FOR IRON AND STEELMAKING

5.1 Most important needs

From an enquiry among ECSC research and development organizations, the most important needs of fundamental data have been listed. They can be classified into

- metal and slag properties,
- mass transfer kinetics,
- process mechanisms and process modelization.

5.1.1 Metal and slag properties

a) General metal properties

- Mechanical properties of steel:
  - high temperature properties and improvement of models of strand shell behaviour in continuous casting,
  - improvement of subsolidus viscoplastic models used in rolling studies.
- Thermal and electrical conductivity of liquid metals.
- Phase diagrams for high alloys steels (i.e. Fe-Ni-Co-Si-Al system used for high temperature applications).
- Measurements of interaction coefficients in liquid high alloys steels.

b) Slag properties

- Physical properties measurements for missing data in slag melts.

- Activity measurements in liquid oxide mixtures and solubility limits of S, P, N, etc ..

- Development of models for the description of thermodynamic properties and equilibria between phases:

  - checking the consistency of existing models of solid and liquid phases in oxide systems,

  - extension of models to sulfides, fluorides, phosphates, etc. ...

- Equilibrium partition between metal and slag;
  example: lime saturated slags in equilibrium with high purity steel.

5.1.2 Mass transfer kinetics

- Kinetics of slag formation.

- Kinetics of liquid iron oxide reduction by reducing solids (i.e. carbon), or gases (i.e. CO, H_2, etc. ...).

- Hydrodynamics of multi-phases mixtures, gas-liquid-solids; gas and powder injections; properties of buoyant plume; dissolution of solid particles (alloys, scraps, powders).

- Metal-slag mass transfer in various conditions:

  - simple slag cover with stirring in steel only; (convection, electromagnetic stirring, etc.); influence of interfacial turbulence, composition change in layers close to the interface ...

  - gas stirring of the metal-slag interface,
  - reactions with suspended particles.

- Kinetics of tramp and trace elements removal in high chromium steels, ferroalloys, and special alloys.

- Condensation of vaporized species in view of understanding fume formation in metallurgical processes.

- Calculation of composition surface depletion during metal processing.

5.1.3 Process mechanisms and process modelling

a) Reduction in solid state

- Sticking phenomena during reduction of fine ores.

b) Liquid iron and steel treatments

- Reactor theory: modelling of multiphase systems for the optimization of metalurgical processes, with regard to mass transfer, energy consumption and environmental aspects.

- Modelling of turbulent fluid flow.

- Energy input in converter type reactors, smelting reduction or oxygen steelmaking: heat and mass transfer studies

  - assimilation of particulate matter (i.e. coal) in the jet cavity,

  - post combustion of CO; lance design, aerodynamics and hydrodynamics,

  - foaming in converters and electric furnaces, more particularly during carbon addition (detrimental, or favorable aspects),

- Heat and mass transfer in plasma furnaces: melting furnaces ladles and tundishes.

- High purity steelmaking:

  - Control of very low contents of dissolved elements.

  - Interactions of non-metallic inclusions with fluid flow patterns; refractory materials and slag absorption; influence of inclusions morphology,

  - Filtering of carbon steels by ceramic foams and deep bed filters,

  - Refractories for high purity steel.

- Fundamental study of the mechanisms of skull formation on water cooled lances, refractory linings, hoods, etc., of metallurgical vessels (torpedo cars, charging of casting ladles, converters, furnaces, vacuum installations; wetting and heat transfer properties, (beneficial and detrimental aspects).

- Metal losses during oxygen blowing; (case of low slag formation).

c) Casting and solidification; rapid solidification processes

Studies concerning rapid solidification would be very important for the various types of application:

- near net shape casting processes,

- new alloys preparation by rapid solidification, and

- the formation of the very first steps of shell formation in thicker more conventional products.

- Calculation of liquidus and solidus temperatures for equilibrium and rapid solidification conditions, based on more precise data,

- Grain boundary segregation and dendrite arm spacing during rapid solidification; consequences on liquid steel purity requirements.

- Thermodynamic calculations of metastable phases separation from hot metal and steel and their stabilization (i.e. carbides, nitrides ...).

- Influence of rapid solidification on size and distribution of inclusions.

- Mechanisms of first shell formation, role of surface phenomena.

- Fundamental aspects of spray casting.

- Fundamental aspects of slurry casting: rheological behaviour of partly liquid steels.

- Thermodynamic prediction of amorphous phases formation.

Efforts should be maintained concerning improvement and innovation in more conventional casting processes:

- Consequences of solidification conditions upon microstructure and microsegregation in high alloys steels.

- Theory of microsegregation formation during solidification of peritectic steels.

- Inclusions control through liquid steel treatments and solidification in the system Fe-O-S-Al-Ca; deformation behaviour of inclusions.

- Development of non oxidizing slag covers and casting fluxes.

d) Other processes and new products

Fundamental aspects of

- surface treatments: galvanazing, electrochemical deposition, vapour deposition, ion implantation, plasma treatments, laser treatments ...
- layered materials production by casting or by rolling,
- development of composites with steel matrix.

e) Waste materials recycling and pollution control

- Fundamental aspects of dusts and sludges treatments:
  - Zn bearing materials,
  - Sn bearing materials,
  - Cr^{6+} containing dusts and slags.
- Volatilisation and condensation of contaminants.
- Binding state of special elements in solid slags and dusts regarding further treatments or deposits behaviour.
- Basic steps of processing by mechanical, phyrometallurgical, or hydrometallurgical treatments.

f) Measuring techniques

- Development of direct liquid steel analysis techniques:
  - Electrochemical sensors.

- Signal formation in direct spectroscopic methods: mechanisms at the liquid metal spot of energy impacts.

5.2 Proposed Priorities

Results are strongly needed for all of the above listed topics: they are important contributions to the quality and cost competitiveness in the production and processing of steel. They would lead to better control in the optimization of conventional processes, or are necessary fundamentals in developing new processes. Should priorities be given the most demanding fields of application concern,

- in conventional processes:

  - high purity steelmaking and processing,
  - energy input and optimization in converter type processes,
  - segregation and inclusion control in continuous casting,
  - direct liquid steel analysis,
  - pollution control and waste product recycling,

- in new processes:

  - smelting reduction developments,
  - near net shape casting,

- in product oriented studies:

  - new products by rapid solidification,

  - inclusions and high temperature precipitates control for products properties,

  - fundamentals of surface treatments.

Il should be pointed out that one modern tool for optimizing and developing processes should be mathematical models based on physi-

co-chemical mechanisms , with the help of other simulation models.

Within the proposed priorities the topics

- high purity steelmaking and
- segregation and inclusion control in continuous casting

were mentioned as the most important tasks in fundamental research of iron and steelmaking.

6. GENERAL CONCLUSIONS

Priority in the research objectives of the EC should be given to projects aimed at developping steel products with higher quality and at broadening the use of steel products. Both measures will prove the international competitiveness of the steel industry of the community.

In this context, although basic research is only a small part in the whole field of efforts to meet the challenge of the future, it should never be neclected.

Limits between basic and applied research are in any case overlapping: projects that are listed and discussed above are those for which the Executive Committee C 6 "Theoretical Metallurgy" of the ECSC is responsible; other projects with "fundamental nature" are also discussed in other committees.

The common basic research of the community has enabled

- a good collaboration of the European fundamental research institutions in areas of common interest,
  - by providing a common "language" and a coherent set of data, and
  - unifying the level of knowledge,
- the possibility of joint research programs in cases of limited national research capacities,
- a co-ordination of activities and
- the transfer of results to all those concerned within the community.

The main tasks of basic research in the future should remain,

- the optimization of the existent processes regarding quality of steel products,

- the modification of processes regarding energy input and environmental questions,

- the development of advanced new processes and new products,

- a further development of process control.

Referring to these topics, chapter 5 of this study recommends a detailed list of important objectives of further research items and proposes priorities. The trends in this compilation should go in following directions:

- regarding production processes: a strengthening of development and use of process models,

- regarding products: a stronger engagement with high alloyed steels and near net shape products while securing clean steel properties.

In view if an efficiency improvement, in theoretical metallurgy research itself, and in the transfer of its results, the following suggestions are proposed:

- the time - now more than 1 year - between proposal of a project and contract signature should be shortened also for basic research,

- the capacities for basic research in the steelworks has been reduced in the last years. More international co-working in common tasks of basic research could compensate this, especi-

ally regarding the fact that competition in this field is not as strong as in those concerning final products,

- a periodic updating of results and synthetic reports should be encouraged for knowledge-transfer on specific research topics which have involved several research groups for some years,

- final reports should point out the relevance of the results for practical applications.

- final reports should be discussed also in other executive committees if special points of contact are given,

- presentation of results in international conferences should be funded by the ECSC,

- the executive committee "Theoretical Metallurgy" should be engaged not only in discussing running research projects but also in pre-discussion of proposed projects. The committee should also recommend new areas or special research projects which seem to be important for the future.

Taking this into account, the ECSC research organisation would improve substantially the efficiency of current R & D structure of the community.

7. APPENDIX 61

7.1 Results and appraisal of individual contracts completed in the last ten years
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7.1 Results and appraisal of individual contracts completed in the last ten years

(see chapter 3.1: Past contracts)

A) DATA PROGRAM IN THE FIELD OF METALLURGICAL THERMOCHEMISTRY

- Contract n° 6210 CA/1/107 - VDEh, Düsseldorf, 1975 - 1978

  In co-operation with subcontractor:
  Lehrstuhl für Theoretische Hüttenkunde und Metallurgie der Kernbrennstoffe, RWTH Aachen

Objectives:

Compilation of evaluated thermochemical data for iron systems employing, where necessary, of methods to estimate standard entropies, heats of formation and heat capacities.

Results:

Thermochemical evaluations, including heats of formation, standard entropies and heat capacities were carried out for 14 iron - non metal systems and 19 iron-metal systems, including Fe-O, Fe-H, Fe-N, Fe-B, Fe-P, Fe-O-C as well as Fe-Al, Fe-Cr, Fe-Ni, Fe-Nb, Fe-V, Fe-W and Fe-rare earth metals.

Missing data for the systems Fe-Co-Cr and Ni-Co-Cr were measured by high temperature calorimetry.

A review of diffusion data for elements in solid and liquid iron is presented.

Appraisal:

In the application of thermochemical data and principles, essential experimental data are often missing. In this context, methods developed by O. Kubaschewski to estimate data are very helpful, because the experimental acquisition of data is a slow process.

Special attention should be given to the review paper on the system Fe-O. This system has been the subject of a very great number of studies. However, it is necessary to achieve consistency of thermodynamic values between all phases of the system and the different equilibria between hematite, magnetite, wüstite and iron (s, l) should not be considered independently of each other. In the present assessment, solid wüstite has been chosen as the most suitable reference phase for the entire system because considerably more experimental data are available for this phase than for any other. A complete phase diagram for the iron-oxygen system constructed on the basis of self-consistent thermochemical data is presented.

For all the systems studied, evaluation methods providing consistency between thermodynamic properties and phase boundaries were used.

Publications: see A 1 to A 5

B) CRITICAL ASSESSMENT OF THE CHEMICAL METALLURGICAL DATA OF COMPOUNDS AND ALLOYS PERTINENT TO IRON AND STEELMAKING

- Contract n° 7210 CA/130 - Lehrstuhl für Theoretische Hüttenkunde und Metallurgie der Kernbrennstoffe, RWTH Aachen, 1979 - 1982

Objectives:

The work was concerned with four major themes - namely:

1. Critical compilation of all binary phase diagrams of iron with the elements of the Periodic Table, in so far as experimental information is available.

2. Critical compilation of new thermochemical data for dilute solutions of elements in iron and of new or up-dated thermochemical values for compounds such as carbides, nitrides, oxides, silicides, borides, etc., which can play a role in steelmaking.

3. Calorimetric measurements for alloy systems formed from Fe, Ni, Co, Mo and Cr and for simple oxide systems with wide homogeneity ranges which are components of slag systems.

4. Compilation of diffusion data for selected oxide systems relevant to slags and furnace linings.

Results:

1. The critical compilation of all binary phase diagrams of iron has appeared in book-form under the title "Iron-Binary Phase Diagrams". The assessments are critical, based on an extensive collection of references well into 1981.

2. A critical compilation resulted in tabulated thermodynamic data for inorganic compounds which are of interest in steelmaking. The heats of formation, fusion and evaporation as well as the standard entropies and heat capacities are given for more than 70 compounds, mainly oxides, but also carbides, nitrides and borides. In addition, a thorough evaluation of the thermodynamic properties of the system titanium-oxygen is presented.

   An empirical method for estimation of the Henrian constants of dilute metallic solution is proposed which is intended to replace the regular solution concept for dilute solutions.

3. With regard to measurements for alloy and oxide systems, new results are presented for

   - activities in liquid and solid Fe-Ni and Fe-V alloys
   - heat capacities of Ni between 430 and 1 240 °C
   - heats of formation in the system Fe-Co-Cr together with a thermodynamic evaluation of this system
   - heats of formation and of transformation in the systems Fe-Co-Mo, Fe-Ni-Mo, Ni-Co-Mo and Ni-Co-Cr
   - heats of formation of MgO-NiO solid solutions between 700 and 1 300 °C.

4. This part of the report presents diffusion rates in simple and multicomponent oxides, solid and liquid, as far as they might be pertinent to slag and furnace lining reactions. The available data have been sifted and tabulated. Representation is mostly in the form of the constants D_0 and Q of the Arrhenius equation.

Appraisal:

The critical compilation of thermodynamic and diffusion data is necessary for reliable calculation, interpretation and optimisation of metallurgical processes.

Part 1, together with the publication in 1982 of "Iron - binary phase diagrams", represents the most up-to-date information of this type available, subsequent to the edition of "Hansen & Anderko" in 1958 and the supplements by Elliott and by Shunk in 1965 and 1969 respectively.

The present work will in future allow the systematic computer evaluation and storage of thermodynamic data for alloy and slag systems, as begun, for example, in parts 2 and 3 of this study. Areas where data are lacking will be revealed and badly-needed self-consistent thermodynamic and phase diagram descriptions for slag systems will be produced.

Part 4 of this study represents the first attempt to compile available diffusion data for single and multicomponent oxide phases. The knowledge about diffusion data especially for liquid slags is very unsufficient till today, but these informations are important for calculations of metal-slag-gas mass transfer in refining operations. So there should be put some attention on further research work in this field.

Publications: see B 1 to B 5.

C) REVIEW AND COMPILATION OF THERMOCHEMICAL DATA

- Contract n° 7210-CA/3/303 - IRSID, 1976-1980
  In cooperation with - NPL, Teddington
  - LPTCM, Grenoble
  - AERE, Harwell

Objectives:

The aim of this study involving 4 laboratories was a critical review of thermochemical data concerning the steel industry. The field covered included binary alloys, iron based ternary systems, and oxides systems with two to four components. Some new experimental data were to be obtained concerning the thermodynamic activity of components in the K_2O - SiO_2 and some lime based slags systems.

Results:

Phase diagrams and thermodynamic activity were critically compiled for

- Binary systems
  Fe + (Al, Mn, Ce, Ca, Si or B), B + (Mn, Cr, or Ni), O + (Ce, Cr, Mn, Ni, or V).
  Ternary interaction coefficients in iron based alloys.

- Oxides systems binary, ternary or quaternary data on
  - $CaO - FeO - Fe_2O_3 - SiO_2$; $CaO-P_2O_5 - FeO + (SiO_2$ or $MnO)$
  - $CaO - CaF_2 + (SiO_2$, CaS, or $FeO)$
  - $CaO - Al_2O_3 - SiO_2 + (MnO$, or $MgO)$.

Models allowing an estimation by interpolation in multicomponent systems have been developed concerning thermodynamic data, for

- iron rich melts,
- oxides systems based on Flood's model and also on Kapoor-Frohberg type model.

Computer reading of phase diagrams has been presented for the systems

$CaO - SiO_2 - Al_2O_3 - MgO$; $CaO - SiO_2 - FeO - MgO$, and

$CaO - P_2O_5 - SiO_2 - FeO$.

Experimental determinations of components activities were made

- in the system $K_2O - SiO_2$, by a gas transport and thermogravity method,

- in $CaO - Al_2O_3 + (CaF_2, MgO, \text{or } Cr_2O_3)$ and $CaO - Ti_2O_3 - TiO_2$ system by mass spectroscopy.

Appraisal:

This work was made by experts from four specialized laboratories in Great Britain and France. Its conclusions and choices have been unanimously accepted by the other ECSC experts.

Such a critical compilation of data is essential

- for all interpretations of trials or of industrial results,
- for the optimization of processes, and
- for the theoretical development of new processes.

Indeed, thermochemical data constitutes the basis of process metallurgy. The choice of the best established values or diagrams should be made in an international way in order to allow comparison and uniform interpretation of results obtained in the various plants. This common language is certainly one of the major contributions of the ECSC.

Publications: see C 1 to C 3.

D) THERMOCHEMICAL AND KINETIC DATA ON STEELMAKING-RELATED MATERIALS

- Contract n° 7210-CF/301 - IRSID, 1980-1983

Objectives:

The aim of this study was twofold:

- evaluation of the thermodynamic properties of complex iron and steelmaking slags (4 components and over), and development of a model allowing calculation of both phase diagram and component activities for these systems.

- measurement of interfacial properties (contact angle) between liquid metal and various solid oxides and sulphides.

Results:

1) Modelling of slag thermodynamic properties.

A statistical thermodynamics model has been developed to describe the properties of multicomponent slag systems. The liquid mixture of oxides is described in terms of cells composed of an oxygen anion linked to two cations. It makes use of only binary parameters (two to four per couple of components).

The model allows the calculation of:

a) the free energy, enthalpy and entropy as well as liquid slag component activities

b) the phase diagram in various situations: liquid miscibility gaps, equilibrium of liquid with stoichiometric compounds or ideal solutions of stoichiometric compounds.

Extensive tests with experimental data have been made for systems containing up to six components chosen among

SiO_2 - Al_2O_3 - Fe_2O_3 - CaO - FeO - MgO - MnO.

There is a fair agreement on both component activities and phase diagram over large temperature and composition domains (including basic and acid slags).

Computation times are quite short and allow direct use of the model in multiphase equilibria calculations.

2) Liquid alloys / solid oxides interfacial properties

Measurements of contact angle and liquid metal surface tension have been made by the sessile drop method:

- as a function of oxygen potential for the systems Fe - O/Al_2O_3

  or FeO - Al_2O_3 and Fe - Mn - O/Al_2O_3 or (Fe - Mn) O - Al_2O_3

- at low oxygen potential for the systems Fe - O / CaO . 2 Al_2O_3,

  FeO / CaO . 6 Al_2O_3, Fe - S / CaS.

For the first two systems, the contact angle is larger than 90° at low oxygen potential and decreases below 90° at a level of oxygen (0,12 %0 without Mn) which decreases at the Mn content is increased. For the last three systems, the contact angle at low oxygen potential is larger than 90°.

Appraisal:

The slag model's main features:

- adequate representation of complex slags over large composition domains

- combined representation of phase diagram and component activities

- use of only binary parameters, which allows realistic predictions in unexplored composition domains

- short computation times

make it a powerful tool which has since been widely used for the description of slag-metal reactions and inclusions formation in iron and steelmaking.

The very careful laboratory measurements on contact angle between liquid metal and solid aluminates, in particular the effect of oxygen content, has shed a new light on the possibility of Al_2O_3 cluster formation (and hence favorable conditions for decantation). Whereas cluster formation is always possible in well deoxidized metal, it may not be possible in zones which have been locally contaminated by reoxidations, in particular at high manganese contents.

Publications: see D 2 to D 5.

E) CALCULATION OF THERMODYNAMIC PROPERTIES OF SLAGS BY MONTE CARLO METHOD

- Contract n° 7210-CA/406 - CSM, Roma, 1977 - 1978

Objectives:

The aim of this study was to develop a method of estimation of thermodynamic properties of slags by applying the concepts of statistical thermodynamics and the Monte Carlo calculation technique.

Solid or liquid silicates are represented with a lattice model similar to the lattice of pure solid silica: the arrangements of the various cations in the lattice are described with a statistical thermodynamics method, in order to calculate the canonical ensemble partition function.

Results:

The development of the calculation method has been achieved. Applications have been made for a number of compositions of the SiO_2 - Al_2O_3 - CaO and SiO_2 - CaO - FeO systems.

Appraisal:

The use of this Monte Carlo method for silicate systems is quite original: it constitutes the first attempt ever reported. Such a calculation method is very promising for estimating properties of multicomponent systems.

This short study was only exploratory and has shown good agreement with the experimental results for a number of compositions investigated in the two ternary systems, but rather large discrepancies in some others, particularly in the FeO-rich corner of the ternary CaO - SiO_2 - FeO system.

From this exploratory use of Monte Carlo method, some conclusions can be drawn:

- its requires a very careful examination of the parameters used in the model. Furthermore, in some systems, mathematical difficulties may arise in the handling of the direct output of the calculation (that is the free energy of the system), in order to compute the activities of the components;

- further developments should require an improvement of the slag structure model concerning particularly the repartition of some of the cations (Al^{3+}, Fe^{3+}).

Required computer time was, at the time of this study, (and, is still probably now), too costly to allow the necessary adjustments of parameters. Adequate treatments of more than three components systems, for which such an estimation method would be useful, would require much longer computation time.

Publications: see E1, E2.

F) THERMODYNAMIC PROPERTIES OF SLAGS FOR SECONDARY METALLURGY PROCESSES AND OF WASTE MATERIALS

- Contract n° 7210 CF/102 - VDEh, Düsseldorf, 1982 - 1986

In co-operation with the subcontractors:

- Lehrstuhl für Theoretische Hüttenkunde, RWTH Aachen;
- Institut für Allgemeine Metallurgie, TU Clausthal;
- Max-Planck-Institut für Eisenforschung, Düsseldorf

Objectives:

Research work has been carried out in two areas:

- optimisation of the composition of slags for the ladle treatment of steel melts for dephosphorisation

- evaluation of thermodynamic data for waste materials from iron and steel production, in particular containing Cd, Zn, Pb and other unwanted elements.

Results:

Slag compositions for dephosphorisation of steel melts

The following results can be derived regarding optimal slag composition for obtaining low phosphorus contents in the steel:

1. The phosphorus contents of the slags should be as low as possible.

2. Generally more favourable values for phosphorus distribution are obtained with the lime saturated slags. In detail, the following results have been shown for the examined slag systems:

   - Lime silicate slags ($CaO-FeO_n-SiO_2$):

     The largest P distribution ratios were obtained for lime saturation close to the double saturation of CaO and $3\ CaO \cdot SiO_2$.

- Lime aluminate slags ($CaO-FeO_n-Al_2O_3$):

  The P distribution for lime saturation rises with increasing FeO_n-contents and reaches the highest values in the lime saturated binary system $CaO-FeO_n$.

- Lime fluorspar slags ($Ca-FeO_n-CaF_2$):

  A maximum in the P distribution is reached with lime-saturated fluorspar slags at 55 % CaO, 20 % FeO_n and 25 % CaF_2.

3. For the desulphurisation examined at the same time, a noticeable refining effect was only achieved on treatment with soda slags (Na_2CO_3- $FeO-SiO_2$).

Thermodynamic data for waste materials

Evaluations were carried out of the systems Fe-O-X with X = Cd, K, Na, Pb, Sb, Sn and Zn. Special emphasis was placed on the systems Fe-O-Zn and Fe-O-Cd, the former because of the growing importance of scrap containing Zn, the latter because the data could be important in connection with the processing of steelworks dust containing Cd from scrap-input.

For the Fe-Zn-O system, calculated isothermal sections at 500, 700 and 900 °C and Zn-partial pressures corresponding to the different phase equilibria at these temperatures are presented.

The phases in which cadmium is present in dusts and sludges, as well as in emissions, are determined by, among other things, the reactions in the Fe-Cd-O system. Extensive thermodynamic investigations of the Fe-Cd-O system were carried out. In the ternary system only one compound is formed - between CdO and Fe_2O_3. The $CdFe_2O_4$ and Fe_3O_4 form a complete range of solid solutions. The Gibbs energy of formation of the spinel $CdFe_2O_4$ at 1173 and 1273 K was determined. Furthermore, the 3-phase equilibrium of spinel solid solution-CdO-Cd and spinel solid solution-FeO_n-Cd, as well as the partial pressure of cadmium for a given oxygen partial

pressure were discussed. Measurements confirmed that only Cd and O_2 are present as components of the equilibrium gas phase over CdO and $CdFe_2O_4$.

The conclusion drawn from the investigations, that small Cd-contents in association with iron oxide form stable solid solutions under oxidising conditions, is important for technical systems.

In connection with the sintering of iron ore, the question of the equilibrium gas species and their concentrations was examined. This is important from the environmental viewpoint.

Appraisal:

Slag composition for dephosphorisation

The question of very low phosphorus contents in steel may rise to great importance for future steelmaking processes, today low phosphorus contents are necessary for few steel qualities speaking about P contents lower than 100 ppm. Fundamental research work with further results that make clear the dependences between very low P contents and steel properties are still missing.

The laboratory results of the present metallurgical research indicated that also under technical conditions it should be feasible to reach high distribution rates $(P_2O_5)/[P]$ of 1 000 and more and correspondingly phosphorus contents in steel lower than 10 ppm. But to meet these favourable conditions in the steelworks a great expense regarding selection of slags, fluxes, refractory is to be considered, which results in high production costs.

Thermodynamic data for waste materials

The evaluation of thermodynamic data for iron and steelmaking dusts and sludges has as background the fact that on the one hand the present processes must be carried out in such a way as to keep the pollution of the environment through residual and waste materials (dust, sludges, slags) as low as possible, and on the other hand that suitable processes must be found for the recycling of these materials.

No fundamental thermodynamic data for the oxide systems of iron which are necessary for the precalculation and appraisal of possible mass reactions for recycling processes were available. Thus, data for thermodynamic calculations in the systems Fe-O-X at higher temperatures, are needed for future postulation of effective recycling processes. Systems containing Zn and Sn are of special importance in connection with scrap melting in steelmaking processes.

The steel industry also acquires cadmium is present as a tramp element in ores, in coal and in scrap. This can lead to emissions into air and water during metallurgical processes and during the cleaning of waste gases. Cadmium can also be present in the dusts and sludges that are retained. The steel industry and the authorities concerned are anxious to decrease the emissions into air and water further. Moreover, considerable efforts are continuously being made to increase the proportion of utilised dust and sludges.

Thus it is especially important to deepen available knowledge of the composition of the dusts with respect to the distribution of the elements and the phases. The following investigations are also necessary in future:

- appraisal of the behaviour of volatile elements during conventional metallurgical processes and

- assessment of the possibilities of applying new processes to the preparation of dusts and sludges.

Publication: see F1.

G) PHYSICAL PROPERTIES OF B.O.S. SLAGS

- Contract 7210-CB/803 - National Physical Laboratory (N.P.L.), Teddington, 1981 - 1984

Obectives:

The objective of this work is to collate, and where possible, evaluate the relevant physical properties of molten BOS slags, with a view of providing recommended values for use in computer modelling of the process. The slags studied belong to binary, ternary or quaternary systems incorporating the major constituants of BOS slags: CaO, SiO_2, FeO, Fe_2O_3, MnO and MgO. The influence of some of the minor constituants P_2O, Al_2O_3, K_2O and Cr_2O_3 is also studied.

Results:

The following properties were critically reviewed:

- phase diagrams
- viscosity
- density
- electrical conductivity
- surface tension and interfacial tension between metal and slag
- thermal properties.

In addition models for calculating physicochemical and thermal properties of liquid slags have been appraised: they provide a rapid estimation of the effects of changes in composition and temperature on the respective properties. Such models are particularly useful for those systems for which there is a limited amount of measured data; they are essential for the complex, multicomponent slags found in industrial applications.

Appraisal:

This wide scope and comprehensive study is a very appreciated contribution to the steelmaking industry: the 120 pages of the prin-

ted published report constitute a reference book for engineers in the field of steel refining.

Data from various sources have been gathered, compared, and critically compiled: most publications in that field had merely proposed new data enhancing only the discrepancies with previous work: this compilation tends to reconcile the various sources and proposes the most reasonable choice for each property as a function of temperature and composition. While most experimental determination are made in a purely scientific scope to understand the structure of liquid silicates, here the main point is to provide the steelmaker with the best possible evaluation for the very complex slags found in the industrial situation.

Publication: see G1.

H) PHYSICAL PROPERTIES OF SLAGS

- Contract n° 7210-CA/806 - National Physical Laboratory (N.P.L.) Teddington, 1976 - 1979

Objectives:

The aim was to measure the physical properties of slags used in electroslag refinig (ESR), and in steelmaking processes.

Slags belonging to the CaF_2 - CaO - Al_2O_3 + (MgO, SiO_2) system and some industrial BOS slags were concerned, for measurements of total normal emissivity, thermal diffusivity, enthalpy, thermal expansion, and solubility of H_2O.

Results:

Thermal properties data have been determined to allow reliable mathematical models of the ESR process to be developped. In addition, a limited number of measurements were made on casting powders and BOS slags.

- Some properties showed a relatively small dependance upon composition:
  - all the molten slags were opaque to I.R. radiation,
  - total normal emissivity was around 0.9.
- Confirmation was obtained that some very simple models could be used for the prediction of heat capacity and of thermal expansion for multicomponent systems by using data for single components or compounds.
- Thermal diffusivity of solid ESR slags were considerably affected by the presence of pores and microcracks in samples and by the nature of the gas contained in these microcracks.
- Thermal expansion of ESR slags decreased with decreasing CaF_2 content.

- Equilibrium water content of slags increased with increasing CaF_2 and CaO contents. Absorption of water during storage lead to a decrease of thermal diffusivity of ESR slags.

Appraisal:

These very careful laboratory measurements on systhetic and industrial slags lead to a valuable set of values of the thermal properties: this is essential for the selection of suitable slag compositions for ESR operation and for the use of theoretical models. This can be used to improve the predictability, control and efficiency of the process.

The scope of this study was large enough, starting with some basic systems (one or two constituants) so that some general laws could be detected. Indeed, as for any type of physical property measurement, it is essential to analyze what are the most influent factors, and at least as important to detect what are the properties that remain relatively constant in the whole range of compositions, and those that can be predicted with the help of simple models, (i.e. addivity for heat capacity for mixtures or compounds).

These very expensive measurements can be performed correctly in only a small number of laboratories. When needed primarily by a single industry, cooperative financing is the adequate solution.

Publication: see H1.

I) CONTINUOUS MEASUREMENT OF DISSOLVED OXYGEN IN STEEL MELTS USING EMF PROBES

- Contract n^{o} 7210 GA/110 - MPI, Düsseldorf, 1976 - 1981

Objectives:

The objectives of this comprehensive study was to examine all decisive fundamental preconditions to enable the construction of an oxygen probe for continuous measurement in steel melts. That means research work to overcome the difficulties arising from long-term chemical and thermochemical stresses on the probes and in particular from the time-behaviour of the oxygen potential of the reference electrode.

Results:

The decisive parameters influencing the electromotive force EMF were studied first of all using thin-walled tube probes of MgO-partially stabilized ZrO_2 and solid metal/metal oxide reference mixtures under defined laboratory conditions. Results are given on the influences of

- various metal/metal oxide systems as references (Cr-Cr_2O_3, Nb-NbO, Ta-Ta_2O_5, V-VO, Zr-ZrO_2),
- various proportions of metal and metal oxide in the reference mixture,
- moisture content of the reference mixture,
- solid-state reaction at the electrolyte/reference interface,
- composition, purity and porosity of the electrolyte materials,
- deposition of precipitated alumina on the electrolyte surface.

Solid electrolytes of a high degree of purity were manufactured by means of isostatic compression and high-temperature sintering from

ZrO_2 powders, for which a special purification process was developed in the "Institut für Gesteinshüttenkunde" at the RWTH Aachen.

The test measurements in pure iron melts, with and without aluminium additives, were checked by means of comparative probes with a Pt-air reference, through chemical analyses of the oxygen content of the melts and on the basis of the O - Al equilibrium relationship.

These results show that continuous oxygen measurement with thin-walled tube-probes is only possible in exceptional cases when a metal/metal-oxide reference is used. Such cases occur when the partial oxygen pressure of the steel melt is approximately equal to the oxygen equilibrium pressure of the reference mixture used.

In view of this considerable limitation, the proposal was made for an other probe construction based again on a thin-walled tube-probe. In this probe a Pt-Rh contact wire flushed with air served as an internal reference and the probe section intended for immersion was externally coated with a porous $ZrO_2(CaO)$ or $ThO_2(Y_2O_3)$ material.

The test measurements provided the following results:

- sufficiently accurate and satisfactorily reproducible recordings values,

- measured values that remained stable with time (testing for up to two hours; longer measurement duration is possible),

- field of application of the probes can be extended to oxygen activities of about 0.0002 to 0.1,

- simultaneous temperature measurement by means of the probe is possible,

- immersion procedure with or without probe prewarming according to electrolyte composition; response time without prewarming about 75 seconds.

An oxygen- and temperature-measuring head was proposed for in-plant measurements.

Appraisal:

Short-time immersion measurement with solid-electrolyte tube probes for direct determination of oxygen activity in steel melts has been developed to the stage of technical maturity and is being employed in steel works (single measurement, duration 15 - 20 seconds). On the other hand, it has so far not been possible to develop a method for the continuous measurement of oxygen in steel melts with an immersion probe to the same stage.

A continuous oxygen measurement in steel melts should enable a better process control in refining and casting processes. Oxygen absorption by reoxidation of the steel melt can be detected immediatly. Therefore the development of a probe for continuous in-plant measurements of oxygen activity in steel melts is a further progress in developing advanced techniques for clean steel production.

A later, more applied research project of MPI within ECSC contract n° 7210-CA/135 of VDEh showed very clearly the importance of the results previously discussed. Because of the difficult handling of the thin-walled air reference probe, this design was replaced by a plug-type probe where a $Cr-Cr_2O_3$ reference could be used for long term measurements. This probe was tested in the tundish of various continuous casting plants of Krupp Stahl AG with different steel grades. In aluminium-killed steels, the expected level of 2 to 5 ppm was maintained over a measuring period of 2 h. Measurements on high-alloy melts resulted in reliable records, the values obtained being consistent with those from single immersion tests. Measuring errors were due to a contamination of the probes by slag and, occasionally, to the insufficient contacting of the reference electrode.

In spite of the good metallurgical results the break-through for a commercial scale production by an industrial probe manufacturer is still standing out in view of the continuous measuring of oxygen activities in steel melts.

Publications: see I 1 and I 2

K) MEASUREMENT OF OXYGEN POTENTIALS IN SLAGS

- Contract n^0 7210 GA/403 - CSM, Rome, 1977 - 1979

Objectives:

The feasibility of determining the oxygen potential of slags should be examined by experimental work using different cell types for measuring the EMF.

Results:

The results can be summarized as follows:

The measurements in $CaO-Al_2O_3-SiO_2$ slags with cell (A)

- Mo, slag/stabilized $ZrO_2/Cr-Cr_2O_3$, Mo -

at 1.600 °C seemed to be unsuitable for the measurement of the oxygen potential of molten slag.

The measurements with cell (B)

- $Fe_{sol.}$-FeO (in slag)/stabilized $ZrO_2/Cr-Cr_2O_3$, Mo -

for $CaO-SiO_2$-FeO slags with 5 and 10 % FeO at 1.500 °C showed that corrosion of the electrolyte was too rapid to permit stable values of the EMF to be attained.

A model has been developed to explain the behaviour of a concentraton cell (C)

- Pt, O_2 (0,98 bar)/slag I // slag II/O_2 (0,98 bar), Pt -

in which a diffusion potential has to be considered in addition to the potential of the electrodes. No experiments were made.

Appraisal:

Refering to C. Wagner[1]) a direct measurement of the activity of oxygen ions in slags from EMF measurements is not possible. According to the concentration cell (C) the assumption of constant activities of the cations in non-ideal solution behaviour slag systems is not valid and therefore the equation

$$\frac{a''_{O^{2-}}}{a'_{O^{2-}}} = \exp \frac{-2EF}{RT}$$

is not correct.

Regarding the EMF measurements with submerged $ZrO_2(MgO)$-electrolytes in slags - cell (A) and (B) - meantime Japanese results are published which show the feasibility of such measurements in blast furnace slags[2]) and steelmaking slags[3]). A further developed experimental technique and improved EMF probes taking into account a reference oxygen potential closer to the figure to be measured may avoid polarisation due to reactions between solid electrolyte and slag or reference material respectively.

For the interpretation of the EMF signal from measurements in liquid slags it should be ensured that a fixed oxygen potential is established.

The oxygen potential in slags containing iron can be defined by the Fe^{2+}/Fe^{3+} ratio for the reaction $2\,(FeO) + \frac{1}{2}\,O_2 = (Fe_2O_3)$.

Publications:

1. Wagner, C.: Metallurgical Trans. B 6 (1975) pp. 405/409.

2. Nagata, K.; Tsuchiya, N.; Urata, K.; Matsuoka, M.; Goto, K.S.: Tetsu to Hagané 71 (1985) No. 2, pp. 183/188.

3. Goto, K. S.; Yamaguchi, S.; Nagata, K.: Tetsu to Hagané 71 (1985) No. 8, pp. 958/964.

L) SILICON TRANSFER IN THE BLAST FURNACE

- Contract n° 7210-AA/310 - IRSID, 1982 - 1986

Objective:

The objective of the research was to analyse the physicochemical aspects of silicon transfer in the blast furnace and to define the operating conditions promoting the production of consistent hot metal, with low and regular silicon content. The study was carried out at different levels:

- thermochemical analysis of silicon transfer reactions and modelling of slag-metal equilibrium
- laboratory experiments to determine the kinetics of silicon transfer reactions involving gaseous SiO
- cold model experiments to simulate the flow behaviour of liquids (metal, slag) in the hearth of the blast furnace
- industrial trials on operating blast furnaces.

Results:

- A thermodynamic model of Si equilibrium between slag and metal has been developed. The thermochemical description of the activities of components in the slag and metal phases relies on the results of previous ECSC research programs (7210-CF/301 and 7210-CA/303).

It is shown that, at the tuyere level, the equilibrium silicon content should be high, whereas under hearth conditions a potential desiliconization capacity exists: to take advantage of this capacity it is necessary to feed some oxygen at the reaction interface.

- The role of gaseous SiO in the process of silicon transfer has been studied under laboratory conditions (work carried out in cooperation with A. Rist, Ecole Centrale de Paris). The generation of SiO from coke ash reduction may lead to a SiO partial pressure close to 10^{-2} bar, under tuyere conditions, the most important parameter being the temperature.

The kinetics of SiO absorption into slag or metal have been determined; transfer into slag increases with the oxygen potential, whereas transfer into metal is improved by a high carbon content in the metal.

- The flow of liquids (metal and slag) in the hearth of the blast furnace has been investigated by radioactive tracer techniques on industrial furnaces, and by experiments on a small scale hydraulic model. The radiotracer results show that the hearth is far from a well mixed reactor, explaining thus the large chemical and thermal heterogeneities of liquids that are observed and that may affect hot metal quality. The cold model experiments point out the permeability pattern in the hearth as a key factor acting on the flow behaviour of liquids.

Appraisal:

The work carried out during the contract gives a comprehensive description of the mechanism of silicon transfer in the blast furnace, from which the basic concepts of low silicon operation can be derived. The most important parameters acting on silicon transfer are identified, some of them are quantified.

The silicon equilibrium model between slag and metal is now used in different French plants as a process control tool to characterize the performance of the furnace regarding hot metal quality.

According to the present analysis, the oxygen potential and the availability of oxygen at slag metal interface appear as determinant parameters to control silicon transfer. This concept has led to industrial trials (7210-AB/312) consisting in injection of pulverized iron oxides at the tuyeres of the blast furnace. The successful results were entirely consistent with the present analysis, and confirmed its validity.

Publications: see L 1 to L 5.

M) THERMODYNAMIC BEHAVIOUR OF COMPLEX DEOXIDIZERS

- Contract 7210-CA/412 - CSM, Roma, 1979 - 1982
  In cooperation with Royal Institute of Technology (R.I.T.), Stockholm

Objectives:

The objective of this study was to obtain a better knowledge of the behaviour of calcium associated with aluminium and silicon during steel deoxidation. The purpose of the laboratory experiments was more particularly to determine the sequence of inclusion formation after the addition of deoxidizers and to compare the final state with equilibrium diagrams.

Results:

1 C.S.M. results consist of two main parts.

- The theoretical part concerns the calculation of stability of the various oxide mixtures of the system CaO - Al_2O_3 - SiO_2 in equilibrium with liquid iron. Monte Carlo method has been used for the thermodynamic activities calculation.

- In the experimental part, at laboratory scale (10 kg), the transformation of aluminia inclusions has been studied at various times after calcium addition in aluminium deoxidized steels (initial sulfur content: 0,0095 %). Microprobe analyses show that after the addition of Ca - Si alloy, the initial Al_2O_3 inclusions are transformed rapidly into inclusions of the CaO - Al_2O_3 - SiO_2 systems; during the initial 15-20 minutes, the latter are distributed within a large range of composition. Calcium sulfide (CaS) was formed when sufficient quantity of calcium was dissolved.

After a while, the range of inclusions composition became narrower, but a stable state was not reached due to calcium evolution and oxygen enrichment, during the experiment (pollution from atmosphere and refractories). Then calcium sulfide decomposed, and a large part of precipitated sulfur returned to the bath. Therefore, quantitative conclusions concerning solubility products could not be drawn.

2 Royal Institute of Technology results concern equilibrium data on Fe - Ca - O and Fe - Ca - S systems at 1600 °C.

Interactions between Ca - O and between Ca - S are very strong and the usual interaction coefficient e_O^{Ca} and e_S^{Ca} should be used with great care and only in connection with a given set of solubility products for CaO and CaS. It should be noted that the experimentally determined solubility products are 2 to 3 orders of magnitude larger than those previously proposed from thermodynamic calculations (based on data concerning standard free enthalpy of formation of pure solid compounds, and of dissolution of the pure elements in iron). It should however be noted that oxygen analysis concerned only total oxygen content, and included some contained in inclusions.

Appraisal:

Experimental work in Roma and Stockholm have lead to a better understanding of aluminia inclusions transformation. Despite some bias due to lack of direct oxygen activity measurements, these studies have shown that the calcium and oxygen, (or, calcium and sulfur) that can remain together dissolved in liquid steel (i.e. solubility product) are much higher than previously estimated. The range of magnitude obtained has been confirmed since that time, but differences to thermodynamic data still remain.

Fundamental studies remain to be done in order to reconcile

- the results from calculations made using free enthalpy data for the reaction between pure calcium and pure oxygen, and data on the behaviour of each one of these elements in their binary solution in iron at infinite dilution, with

- the direct experimental evaluation, (even using EMF), of solubility products for the measurable concentration range used in industry and in laboratory: despite their relatively low contents in calcium and oxygen, such alloys should probably be treated as concentrated solutions.

Monte Carlo calculations required so long computing time that optimization of the method and fitting of the coefficients has not been possible. The preliminary results of phase diagrams obtained during this contract can hardly be compared, even qualitatively, with the relatively well established experimental data. Development of new computer generations should be a requirement for new attempts in using this potentially powerful method.

Publications: see M 1 to M 2.

N) ELECTROCHEMICAL DEOXIDATION AND DESULFURIZATION ON A SEMI-INDUSTRIAL SCALE

- Contract n° 6210-CA/3/301 - IRSID, 1976 - 1978

Objectives:

This study aimed at evaluating the possibility to deoxydize and desulfurize steel melts by electrochemical means.

A previous laboratory study financed by ECSC (6210-72/3/031) had shown that part of oxygen and sulfur dissolved in a liquid metal could be removed by an electrochemical process. Best results were obtained with electrolytes containing Ca^{++}ions: CaO - CaF_2 - Al_2O_3 slags or solid CaO (or MgO) containing small quantities of CaF_2.

Results:

Trials were made on a 3 to 6 tons scale with basic lime-based slag as electrolyte. D.C. current of 10 kA intensity under 30 V, was running from a positive graphite electrode immersed in the electrolyte to the liquid killed steel. It was found that oxygen and sulfur transfer from metal to slag did occur, but that the kinetics during electrolysis (and quiet bath), were much slower than those observed by intense metal-slag stirring. From the best experimental results concerning electrolysis efficiency, one could deduce that, removal of 0.01 % sulfur required around 35 kWh per ton of steel.

Appraisal:

Removing oxygen and sulfur by electrolysis would have been a very attractive process since it did not involve the formation of indigenous inclusions or slag entrapment. This study on semi-industrial scale has led to the conclusion that it could not be extra-

polated at industrial size; the efficiency was too low as compared to the ladle processes that were being developed at that time: acceleration of transfer through the interface by electrolysis is not as efficient as the interface renewal obtained by intense metal-slag stirring. Further developments of deoxidation or desulfurization, by the proposed electrochemical process aimed at mass production, should be discarded.

Publication: see N 1.

0) FUNDAMENTAL THERMODYNAMIC STUDIES ON CALCIUM TREATMENT OF STEEL MELTS

- Contract n° 7210 CF/101 - MPI, Düsseldorf, 1981 - 1984

Objectives:

The study comprises three items:

- Experimental determination of calcium solubility in binary Fe-Ca and ternary Fe-Ca-X_i melts using pure CaO crucibles at an argon excess pressure of 10 bar (X_i = Si, Al, Ni, Mn, Cr and C).

- Investigation of CaO solubility in CaO-saturated calcium melts and of the CaO saturation line for CaO-$CaCl_2$ slags.

- The dephosphorization of steel melts with calcium for reducing conditions.

Results:

- The calcium solubility of steel melts in equilibrium with CaO saturated slags was measured depending on temperature and contents of different alloying elements.

  For pure iron the solubility of Ca is 0,03 % at 1 600 °C. Carbon contents lead to a higher solubility till at contents of 0,9 % C and 0,048 % Ca double saturation with calcium CaC_2 carbide and calcium is reached. Al, Si and Ni increase the Ca solubility whereas Cr has a reverse effect. For melts of stainless steel with 18 % Cr and 8 % Ni a Ca solubility of 0.022 was measured.

- In the binary system Ca-CaO activity of a Ca of a CaO-saturated calcium melt at 1 600 °C is about 0.8 following Raoult's law. In the system Ca-$CaCl_2$, the wide miscibility gap is closed at

1 350 °C. The temperature influence on CaO saturation in the system $CaO-CaCl_2$ was investigated; at 1 600 °C a maximum solubility of 16 % CaO in $CaCl_2$ was measured.

- Laboratory experiments for dephosphorization of steel melts confirm the assumption that for reducing conditions in a Fe-P-Ca-CaO-CaF_2($CaCl_2$) system dephosphorization reaction is based on the formation of Ca_3P_2 which is then dissolved in the slag. The refining effect is essentially determined by calcium activity.

Appraisal:

Calcium treatment of steel is a modern but common technique for secondary metallurgy treatment producing clean steel. But exact data about the influence of alloying elements on the solubility of Ca in steel were not available till now because of difficulties in the experiments due to the high vapor pressure of calcium. It has to be clarified now whether the remaining contents of soluble calcium in the steel which have been pointed out may influence steel properties.

An other aspect of this work is the dephosphorization under reducing conditions which is a promising method to dephosphorize chromium-alloyed steel melts. Calcium halide slags containing dissolved metallic calcium are able to serve as useful fluxes for the calcium treatment. Transfering these results to practical operation for dephosphorisation of high chromium stainless steel melts, costs and slag handling have to be judged.

Publications: see 0 1 to 0 3

P) FLUID FLOW PHENOMENA OF METAL AND SLAG DURING DRAINAGE OF METALLURGICAL VESSELS

- Contract n^{o} 7210 CB/103 - VDEh, Düsseldorf, 1983 - 1986

In co-operation with the subcontractors:

- Institut für Allgemeine Metallurgie, TU Clausthal,
- Betriebsforschungsinstitut (BFI) of VDEh, Düsseldorf,
- Hoesch Stahl AG, Dortmund,
- Krupp Stahl AG, Bochum

Objectives:

Aim of this joint research which was done in laboratory and industrial scale was to clear the influences of flow phenomena of metal and slag during drainage of metallurgical vessels. From the results measures should be derived preventing slag carry-over from converter, ladle and tundish.

Results:

The flow phenomena causing slag carry-over are the vortex sink, the drain sink and emulsification.

The occurrence of vortex sinks depends to a great extent on an already existing angular momentum in the melt during tapping or teeming. An eccentric nozzle delays the formation of a vortex when the slag passes through the nozzle.

A drain sink occurs at the end of the draining process, when the volume flow is smaller than the possible nozzle capacity. For a rough estimation the general rule applies: a drain sink will occur when the rest height of the liquid is equal to the nozzle diameter.

Following results have been derived for steelmaking processes:

- In converter tapping, the injection of gas close to the nozzle led to higher slag carry-over because of emulsification.

- During the drainage of teeming ladles, top slag is carried over towards the end of teeming. Emulsified slag carried over to the tundish leads to an uncontrollable decrease of oxidic cleanness in synchronously strand-cast bars; the rest steel method generally used as countermeasure results in a substantial reduction of steel yield.

- The last draining stages of teeming ladles are dominated by the flow phenomenon "drain sink". This phenomenon results in a decrease of the casting rate and in a sharp increase of casting rate delay. "Vortex sinks" are only of secondary importance in ladle drainage.

- In view of this state of things it is fair to assume that flow breakers, which prevent the development of vortex sinks, would be virtually ineffective as countermeasure against drain sinks.

- A countermeasure to be considered in this respect is the tilting of the ladle with the nozzle arranged close to the ladle wall and the slanted lining or stepping of the ladle bottom. In the presence of a drain sink this measure improves phase separation during casting; in case of a vortex sink it would be, however, useless.

- Measurements made at the revolving turret scales of a continuous casting plant confirm the possibility of detecting the delay in casting rate at slag carry-over. To this end, the measuring signals have to be conditioned in a process computer. This measuring method is being further improved at present.

- In continuous casting, a vortex sink can be of great importance for slag carry-over from the tundish to the mould. Under steady

conditions, slag carry-over can be prevented by a correspondingly high filling level of the tundish. Further investigations will be necessary for the detection of non-steady conditions, which can lead to slag/metal emulsification.

- The provision of a dam/weir combination in the tundish can prevent the wide spreading of disperse phases in the tundish.

Appraisal:

Slag carry-over from BOF, ladle or tundish can be a great disadvantage in secondary steelmaking operations and in continuous casting practice. Therefore a deeper understanding of flow phenomena during drainage of metallurgical vessels was needed to derive measures preventing slag carry-over. Model trials and plant trials of this study clarified the influences of the flow phenomena "vortex sink" and "drain sink" on slag carry-over. Thus measures could be discussed under theoretical and practical point of view to prevent vortex and drain sink. A gravimetric method was developed to detect slag flow during ladle teeming which shows good results during plant operation.

It can be stated out that this was the first study - looking world- wide - that examined the influences of fluid flow phenomena during drainage of metallurgical vessels. These phenomena are now understood and the consequences for preventing slag carry-over and for a better cleanness of steel are pointed out.

Publications: see P 1 to P 6

7.2 Publications

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