# EXPERIMENTAL SIMULATIONS OF PRIMARY SLAG FORMATION IN THE BLAST FURNACE

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Key Words: primary slag, experimental simulation, melting behaviour, viscosity, solidus, meltdown, FeO content, blast furnace

## Abstract

Synthetic $MgO-Al_2O_3-CaO-SiO_2$ slags with additions of FeO and/or FeS have been used for experimental simulation of primary slag formation in the blast furnace. Investigation include determinations of the melting behaviour and viscosities of slags by optical dilatometer, TGA-DTA and viscometer.

Results indicate the conclusive significance of FeO in the formation and nature of primary slags. However, the effect of FeO is fundamentally dependent on the chemical composition of the base slag. A clear effect of FeO is to lower the solidus and meltdown temperatures. The presence of FeS in the slag system facilitates even earlier slag formation. The viscosities are effectively lowered with increasing FeO content.

# INTRODUCTION

The formation of initial slags (melts) in the blast furnace, their evolution in composition, volume, density, viscosity and wettability into primary slags and the numerous variables affecting the process of primary slag formation are a complicated group of questions, which are only partly understood. One of the most interesting features includes the evolution of slag-forming components into liquids having abilities to mobile flow.

Knowledge about the mineralogical composition of burden materials at the cohesive zone and the composition of melts from the initial to dripping stages of melting is missing or quite limited, or at least miscellaneous /2/. This is, of course, easy to understand, because actual samples from a blast furnace are not easy to obtain. Information on mineral phases and initial melt compositions are published mainly from experimental tests done with different burden materials /3, 4, 5, etc. /. But in general, the validity of these analyses is variable, because there seems to exist some difficulties in realizing the position of numerous solid phases and melt participation in the melting process. The term 'slag' or 'slag phase' can mean everything from a total melt to one mineral species. Also, conditions of the tests can be different from the history of conditions the burden has experienced in the blast furnace.

Thermodynamic calculations of mineral and initial melts compositions are difficult, because bulk composition, composition of solids and gaseous phases and physical conditions are continuously changing and are not exactly known /2/.

The chemical (mineralogical) composition of the slag-forming components of burden materials at the initial stage of melting is the main controller of the melting behaviour of the

system. Keeping this in mind, experimental research with synthetic slags can be successfully used to simulate the formation of primary slags in the blast furnace process.

This paper summarises, at a general level, one part of the results achieved in the University of Oulu portion of an ECSC multi-partner project: "Investigations of chlorine and alkali behaviour in the blast furnace and optimisation of blast furnace slag with respect to alkali retention capacity. "

## EXPERIMENTAL PROCEDURE AND SAMPLE PREPARATION

Synthetic slags of a $CaO-SiO_2-MgO-Al_2O_3$ system have been used for laboratory-scale simulations of the melting behaviour and viscosity of primary slags of different blast furnace burden materials. The effects of FeO and sulphur additions on melting behaviour and viscosity of different slags have been investicated.

Primary slag is defined here as a total slag (melt) of the slag-forming components of a single burden material (sinter, pellet or lump ore). Base slag is defined to be composed of four main oxides (CaO, MgO, $Al_2O_3$, $SiO_2$) of an individual burden material.

To research the melting behaviour and viscosity of only the slag phase of each burden, the following basic frameworks were proposed. Firstly, reduction degree was assumed to be at wüstite/iron boundary, resembling the conditions generally assumed to exist at the cohesive zone of the blast furnace. Secondly, to avoid supersaturation of the systems with FeO, the content of FeO intended to be kept under the solubility limit of FeO into molten base slags.

The melting tests were carried out by optical dilatometer (Figure 1) and simultaneous thermogravimetric differentially thermal analyser (TGA-DTA). The maximum temperatures, restricted by the equipment used, were 1550 and 1500 °C, respectively. Tests were conducted in an argon atmosphere using corundum ($Al_2O_3$) sample plates and crucibles. Temperature calibrations for both equipment were made with pure Cu (99.99 %).

The viscosity measurements were made with a high temperature rotational viscometer (Figure 2) in molybdenum crucibles using an Ar atmosphere enriched with 1 % CO to prevent oxidation of the crucible. The maximum temperature for measurements was limited to 1530 °C by the viscometer furnace.

The slags for the viscosity measurements were melted directly from oxide mixtures while the viscometer furnace was heated up. The base slags for melting tests were prepared by melting pure oxides in platinum crucibles in ratios proportional to raw material analyses. After grinding, the base slags were hydraulically pressed into tablets and fired at least 14 hours close to their solidus temperatures to crystallize relevant equilibrium mineral assemblages. After firing, the slags were ground again to powders (Ø<0.05 mm). Cylinder-like samples for dilatometer were prepared by hydraulic press. The samples for the TGA-DTA were prepared by pressing the slag powder into a crucible by hand.

Additions of iron oxide and sulphur were made as solid mineral powders of wüstite (FeO) and pyrrhotite (FeS) or oldhamite (CaS), respectively. With one exception, the experiments were made for compositions, where the saturation level of FeO in the slag was not exceeded.

The solidus temperatures were determined from DTA curves. The meltdown temperatures were detected with an optical dilatometer. Meltdown illustrates the dynamic progression of melting of the sample for the first time into a lenss-haped form, having a surface coinciding with an arch of a circle.

# RESULTS

The compositions of five synthetic base slags, describing sinter, pellet and lump ore base slags, are expressed in Table 1. The composition points of FeO-enriched slags are presented on proper liquidus phase diagrams in Figures 3 and 4. In Figure 3, MgO and $Al_2O_3$ are added to CaO and $SiO_2$, respectively, while in Figure 4, CaO and MgO are ignored.

Although the liquidus temperature and outlines of melting behaviour for each slag can be roughly seen in those figures, one must remember that all the relevant slag components are not included and some mineral phases actually melting in the slag systems are lacking in these diagrams.

**Melting tests**

The main features of melting behaviour of different base slags as a function of FeO are compressed in Figures 5 to 9. Figures 5 to 8 show the softening and melting behaviour of four $CaO$-$SiO_2$-rich base slags with different basicities. An example of the melting behaviour of $Al_2O_3$ and $SiO_2$-rich base slag is shown in Figure 9.

The melting behaviour of the most basic base slag A, with FeO additions is seen in Figure 5. FeO addition at levels of 10, 20, 40 and 50 % lowers the solidus to temperatures near 1200 °C. The melt down temperature decreases with FeO addition, but remains at about 1300 °C even at the highest FeO level. From the phase diagram it is obvious that despite the meltdown, the slags should not be totally liquid at these temperatures without $Al_2O_3$ dissolution from the sample plate. Dicalcium-silicate ($\alpha$-$Ca_2SiO_4$) should remain only partially melted.

The base slag B (Figure 6) has a basicity of 0.61. The base slag melts down at 1254 °C, with quite a rapid collapse, as do all the FeO enriched slags. The meltdown temperature decreases slowly and the mushy zone is narrowed with progressive FeO addition until the minimum region is reached, actually between the levels 30 % and 45 % FeO. As FeO is added over the solubility limit, the meltdown temperature increases as the primary phase field of wüstite (60 % FeO) is reached.

The base slag C (Figure 7) has a basicity intermediate between that of slags B and D. The base slag can not be melted down at 1550 °C. Addition of FeO lowers the solidus below 1100 °C. Meltdown temperatures decrease steeply after levels of FeO over 15 %. Decreasing is rapid towards the olivine ($(Ca,Fe)_2SiO_4$) primary phase field, which is reached close to the 45 % FeO level. After that, the interval between solidus and meltdown temperatures is only about 50-60 °C.

Of the tested slags, the base slag D (Figure 8) was the most acid one. The solidus temperature of the slag decreased from 1200 °C to about 1160 °C with FeO addition. Meltdown is reached only at levels of 45 % and 60 % FeO. The mushy zone is effectively narrowed and the

meltdown temperature is steeply decreased towards the FeO level existing at the boundary between the fayalite ($Fe_2SiO_4$) and tridymite ($SiO_2$) primary phase fields.

An example of the tested $Al_2O_3$ and $SiO_2$ rich slags is given in Figure 9 as base slag E, which does not melt totally in the test furnaces used. Addition of FeO decreases the meltdown temperatures throughout the iron-cordierite ($Fe_2Si_5Al_4O_{18}$) field to the fayalite and hercynite ($FeAl_2O_4$) primary phase field boundary. The solidus temperature remains constant at about 1050 °C. A wide mushy zone at low FeO levels narrows as a function of the FeO content.

Additions of FeS (3-7 %) to the base slag A lower the solidus to 960 °C, deriving from the melting of the sulphide. The main melting stage seems to begin about 50-70 °C earlier with FeS additions than in the original base slag. CaS additions (2.5-6 %) lower the solidus 40 °C, but the meltdown temperature is increased by about 20 °C. Combined additions of FeO (20-50 %) and FeS (3-7 %) to base slag A incicate a solidus existing at 919°C. The main melting stage begins at 1212-1247 °C and is over before 1300 °C.

The meltdown temperatures of the last system were impossible to determine. This was due to the existence of two immiscible liquids, which were actually seen to exist separately. One apparently was a FeO-FeS-$SiO_2$ liquid and the other $Al_2O_3$-MgO-FeO-CaO-$SiO_2$ main liquid. The composition of the liquids was not verified by analysis.

**Viscosity measurements**

Excluding the base slag B, viscosity measurements were made only for FeO enriched slags. The addition of FeO enables viscosity measurements by decreasing the liquidus temperatures. However, for all compositions, measurements were taken partly or even entirely inside the mushy zone. Unfortunately, deviations in viscosity at values $\eta < 20$ P, originating from the geometry of the rotator and crucible, were so significant that the values below that level have been ignored.

The viscosity measurements of base slag A was taken with 50 % FeO. A lower FeO content did not reduce the liquidus temperature enough for the current viscosity measurement furnace ($T_{max} \approx 1530$°C). All the measurement points are from mushy zone, where the first solid phases, dicalsium-silicate and wüstite ($\alpha$-$Ca_2SiO_4$ and FeO) are crystallizing (Figure 10). The viscosity values at temperatures higher than about 1250 °C are too low to measure accurately.

Effect of FeO addition for on the base slag B was tested at levels of 5, 10, 45 % FeO. The viscosity of the base slag was also measureable. The results are visualised in Figure 11. The viscosity seems to be mainly affected by the decrease in liquidus temperature and the nature of the mushy zone, when FeO content is increased.

The viscosities of the base slag C were measured at levels of 15, 25, 45 and 60 % FeO (Figure 12). Variations in viscosity with increased FeO addition and with partial crystallization as a function of decreasing temperature of each FeO level can be seen. The effect of FeO content on viscosity is obvious, although the viscosities are very small in the liquid state at all FeO levels. For example, the case with 15 % FeO is partly solid (tridymite), even at the highest temperature. Viscosity increases quite steeply as solidification proceeds. Viscosity jumps steeply at about 1250 °C, when pseudowollastonite ($\beta$-$CaSiO_3$) starts to solidify with tridymite. The reason why viscosity can be measured that far in the mushy zone is possibly the greasing effect of the quite FeO-rich residual liquid. Apparently, the illogical order of the

FeO 60 % and 40 % FeO samples is explained by the fact that the former actually has a higher liquidus temperature.

The viscosities for the base slag D were measured at levels of 45 % and 60 % FeO (Figure 13). The viscosities of the 60 % FeO containing sample are much lower than at the level of 45 % FeO. Both samples have clear solidifying points, after which the viscosity increases rapidly inside the mushy zone.

For the base slag E, viscosities were measured at levels of 30 % and 40 % FeO (Figure 14). The former crystallizes tridymite after about 1350 °C. It also crystallizes iron-cordierite when the viscosity increase becomes steeper. The sample containing 40 % FeO falls to the iron cordierite primary phase field and crystallizes rapidly after about 1175 °C. Despite this, the increase of viscosity is relatively low, which can be taken as an argument for the good greasing properties of the residual FeO-rich silicate liquid.

# DISCUSSION

In this research, the philosophy of thinkingis based on the mineralogical and phase diagrammatic approach, although no mineral or slag (melt) analyses are expressed. Because some contamination of the tested systems with alumina plates and crucibles is apparent, the results can not have the status of scientific experimental research in a strict sense. However, the main features and trends of the melting behaviours are highly correct and clear.

Keeping in mind the principles of the blast furnace process, it is easy to realize that at the beginning stage of melting, both the chemical and the mineralogical composition of each burden material must be remarkably different from that, which was charged from the top.

From a scientific perspective, the composition of the initial melt of one burden evolves into a primary slag via a composition path dependent on the mineralogical composition. This is controlled by the history of evolution of the bulk chemistry and physical conditions before the solidus temperature. The different mineral assemblages at solid state in different burdens create varying melting behaviours. The changing characteristics include the solidus and liquidus temperatures and the evolution of the melt in composition, density, volume, viscosity and wetting properties during the melting process.

If we continue the principle of thinking to concider the mineralogy of burden at the beginning of the melting (cohesive zone), we can use the proper phase diagrams and make at least a good guess of the mineralogy. This is especially true, when only the main components are included and iron is fixed to exist as wüstite and metallic iron. At equal FeO contents, the difference in composition between different burdens creates a different mineralogical composition in their slag forming bulk. If the bulk compositions are still situated inside one compatibility triangle, the solidus temperatures are same, but the liquidus temperatures and the intervening melt paths change with a difference in composition. When the compositions are in different composition triangles, both the solidus and liquidus temperatures are different.

The melting experiments of the five different base slags with FeO additions led to five different melting behaviours. These can be considered as a direct consequence of the differences in mineralogical composition, both as a function of the base slag composition and the FeO content.

Both the most basic base slag A, and the acid C and D base slags, whose composition falls to the dicalcium-silicate and silica primary phase fields, respectively, have higher meltdown temperatures with respect to the intermediate base slag B (wollastonite field) at the same FeO content. The solidus temperatures of the slags B and C are quite equal, but certainly different from the slags A and D.

These results combined with the information of the CaO-FeO$_x$-SiO$_2$ phase diagram (only 3 of 5 components included), can lead to the impression that, instead of just the different primary phase these slags must also have a different mineral assemblage in the solid state. The slags B and C possibly have mostly the same mineralogy, but different amounts of the individual phases. The slags A and D should be markedly different in the mineral assemblage, both with respect to each other and also with respect to the slags B and C.

If we assume that the melting behaviours of synthetic systems used are comparable to the melting behaviour of each corresponding real burden bulk slag at the cohesive zone, we have here five different kinds of melting (cohesive) zones (Figures 5-9). Meltimg begins at the solidus temperature of each system. If there is enough wüstite left, all the slag phases can melt quite rapidly at the lowest meltdown temperature of each system. When the FeO content is limited (reduced to Fe), melting continues to the meltdown temperature of corresponding FeO levelt. The situation is a little bit different in an actual case, because of the more components, more phases, partial engaging of some slag-forming components (MgO, CaO) into the wüstite and the advancing reduction of FeO out of the melt.

Unfortunately, deviations in the viscosity measurements at values $\eta < 20P$ were so significant, that the values could not be included. All the measured totally liquid slags had very low viscosity above the liquidus. The crystallization begins with the CaO and SiO$_2$ (A and B slags), SiO$_2$ (C and D slags) or Al$_2$O$_3$ and SiO$_2$ (E slag) -rich phases, and the viscosity of the residual melt can be thought to remain low even down to the solidus temperatures, but volume of the melt is decreasing. The viscosities were usually measureable some extent inside the mushy zone, apparently because the FeO-enriched residual liquid acts as a lubricant between the crystals.

In the blast furnace process, the situation is reversed as melting begins with the FeO-rich initial slag with a low viscosity. The reduction of FeO out of the slag of course has the opposite reaction to viscosity. At which stage the viscosity, volume, density, wetting properties, etc. allow the liquid to flow downward is a fundamental question. In addition to the composition-related properties, the influence of physical properties (porosity, counterpressure, etc.) inside the burden should also be considered.


# SUMMARY

Experimental melting tests and viscosity measurements for a synthetic CaO-SiO$_2$-MgO-Al$_2$O$_3$ system with FeO and/or FeS additions have been made. Differences in the melting behaviours between the slags used, can be explained according to differences in the mineralogical composition of the slags at the beginning of the melting stage. The results are considered to be applied to the melting behaviours of corresponding slag phases of the actual burden materials in the blast furnace at a cohesive zone.

Both the melting tests and viscosity measurements conclusively indicate the significance of the FeO content in the melting behaviour and viscosity of different slags. Clear, but not simple or linear trends show a decrease in the solidus and melt down temperatures with increased FeO content. The examined base slags had a distinctly different melting behaviour as a function of FeO additions, indicatind that the mineralogical (chemical) composition of the base slags are the fundamental causes for differences in the melting process as a function of FeO addition.

The addition of sulphur as CaS had quite a limited effect on the melting behaviour of the basic base slag. The effect of FeS enrichment was more pronounced. The combined additions of FeO with FeS lowered the solidus to 919 °C, probably in a form of a $FeO-FeS-SiO_2$ liquid, immiscible to the rest of the slag.

The viscosities of different base slags were strongly decreased by the FeO content, even at quite low levels of FeO. The viscosities were very low at temperatures above the liquidus and increased rapidly just when the mushy zone was reached. The temperatures at which the mushy zones appeared were strongly dependent on the composition of the base slags and FeO content.

## ACKNOWLEDGEMENTS

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**Table 1:  Chemical composition and basicity of the base slags used**

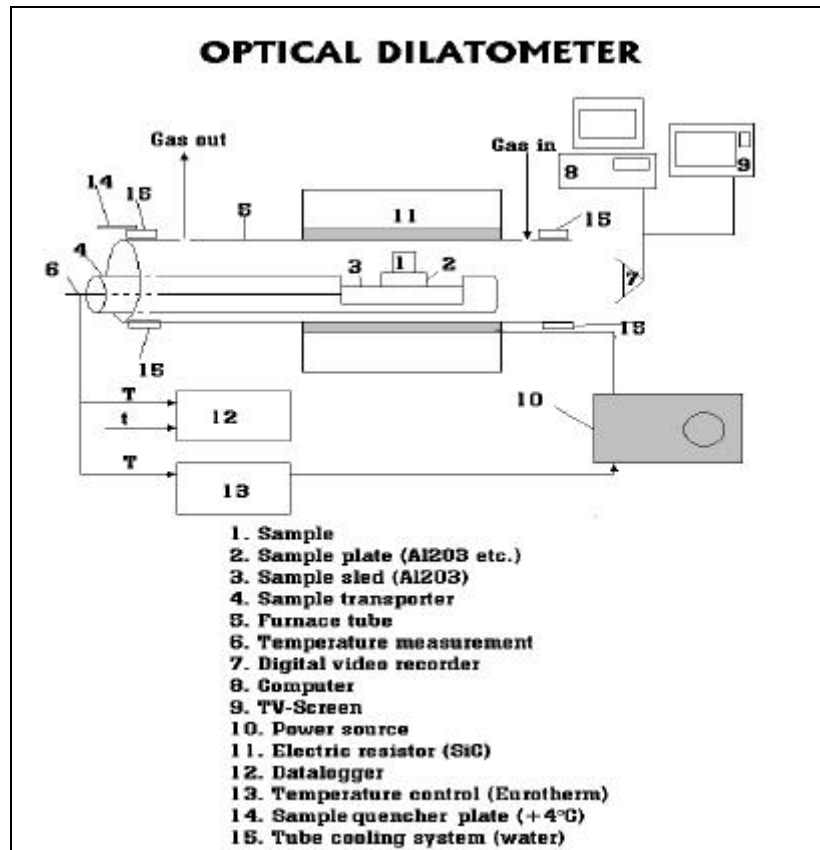| Base slag | SiO$_2$, % | Al$_2$O$_3$, % | CaO, % | MgO, % | B (CaO/SiO$_2$) |
|-----------|-----------|----------------|--------|--------|------------------|
| Sinter A | 33.3 | 7.4 | 50.0 | 9.3 | 1.50 |
| Pellet B | 45.8 | 12.9 | 38.1 | 3.3 | 0.61 |
| Pellet C | 75.2 | 3.9 | 16.1 | 4.8 | 0.21 |
| Pellet D | 90.9 | 3.8 | 3.1 | 2.2 | 0.03 |
| Lump ore E | 71.9 | 24.9 | 2.7 | 0.5 | 0.04 |



**OPTICAL DILATOMETER**

1. Sample
2. Sample plate (Al2O3 etc.)
3. Sample sled (Al2O3)
4. Sample transporter
5. Furnace tube
6. Temperature measurement
7. Digital video recorder
8. Computer
9. TV-Screen
10. Power source
11. Electric resistor (SiC)
12. Datalogger
13. Temperature control (Eurotherm)
14. Sample quencher plate (+4°C)
15. Tube cooling system (water)

Figure 1:   Schematic diagram of the construction of a high temperature optical dilatometer.

## ROTATIONAL VISCOMETER (Searlé)
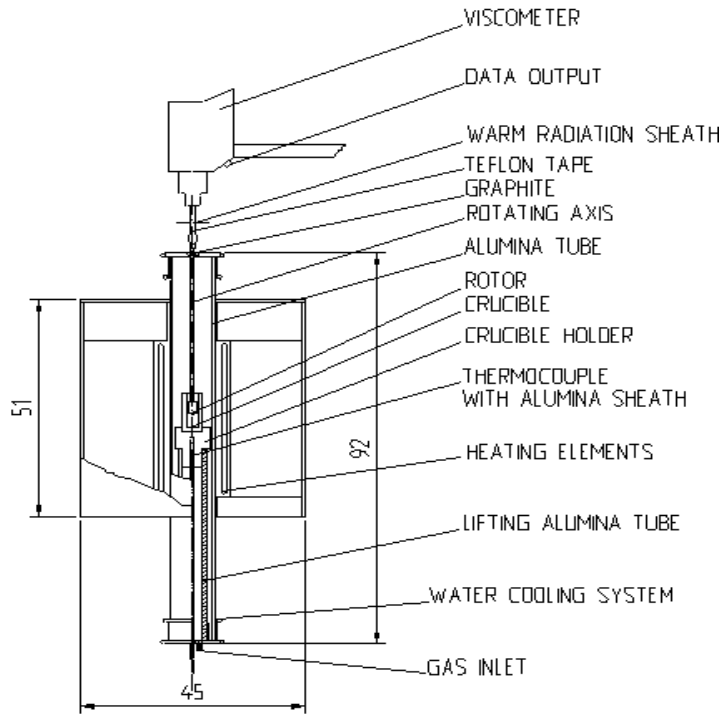


Figure 2: Schematic diagram of the construction of a high temperature viscometer.

**CaO-FeO$_x$-SiO$_2$**
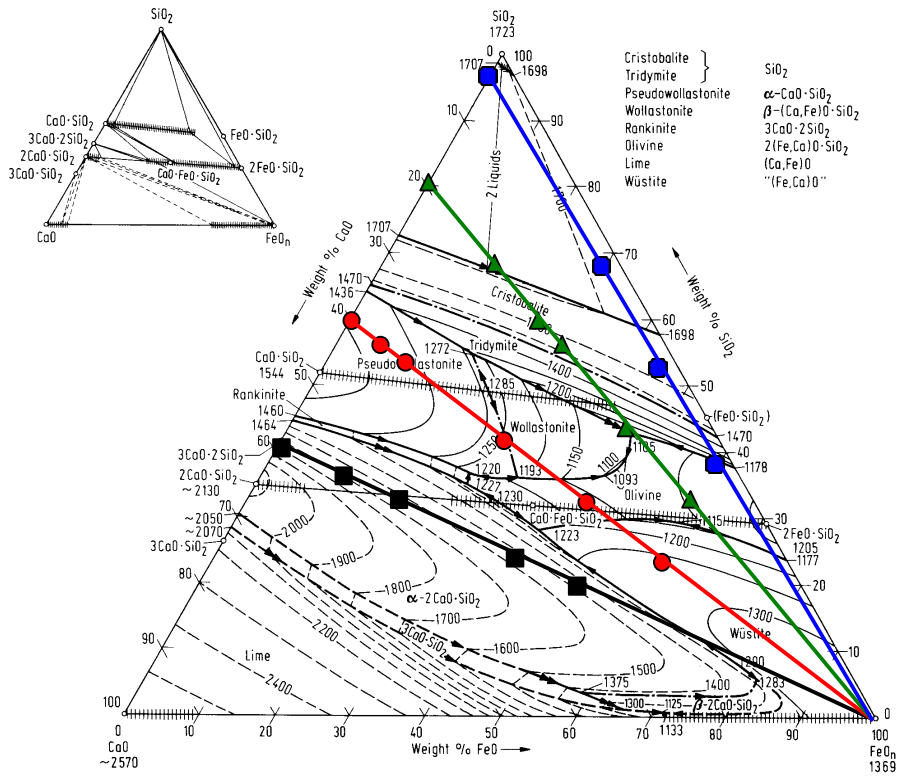


Figure 3: CaO-FeO$_x$-SiO$_2$ liquidus phase diagram /1/. Tested compositions of base slags  A:■, B: ● , C:▲  and D:■

**Al$_2$O$_3$-FeO$_x$-SiO$_2$**
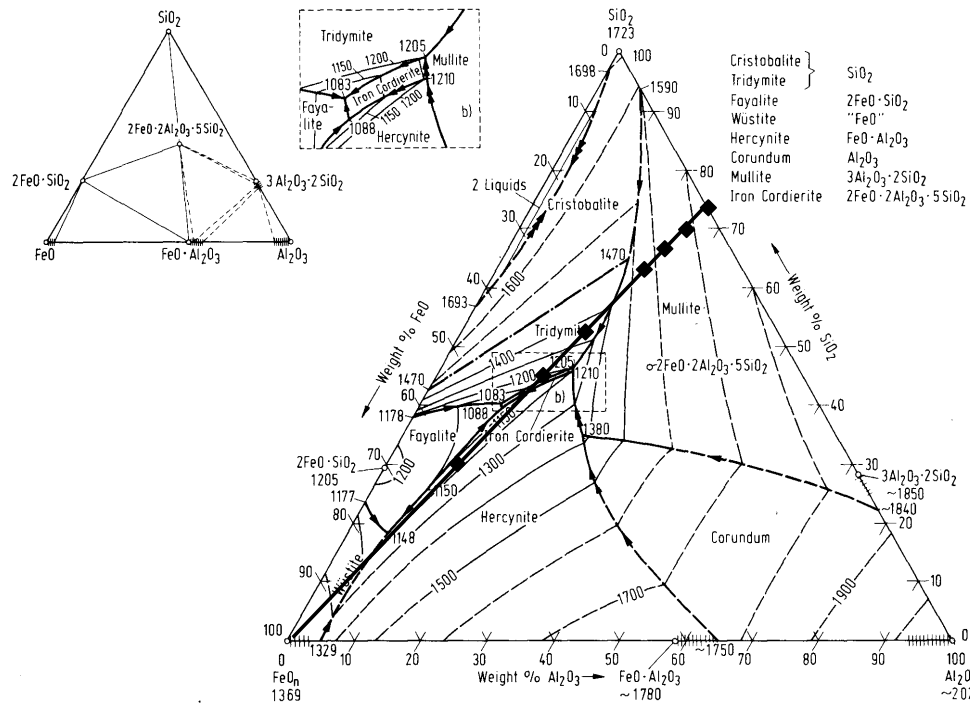


Figure 4: Al$_2$O$_3$ -FeO$_x$-SiO$_2$ liquidus phase diagram /1/. Tested compositions of base slag E:◆
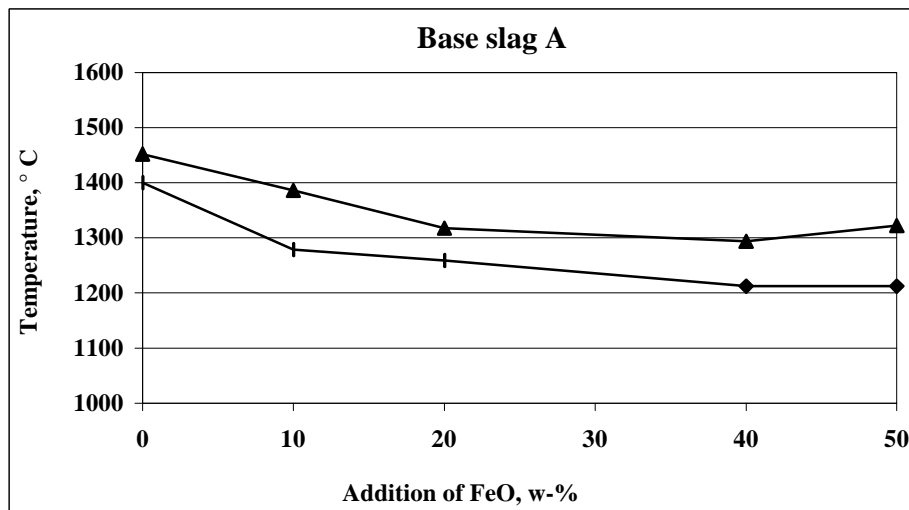


Figure 5: Melting behaviour of base slag A as a function of FeO.
◆ solidus, ▲ meltdown
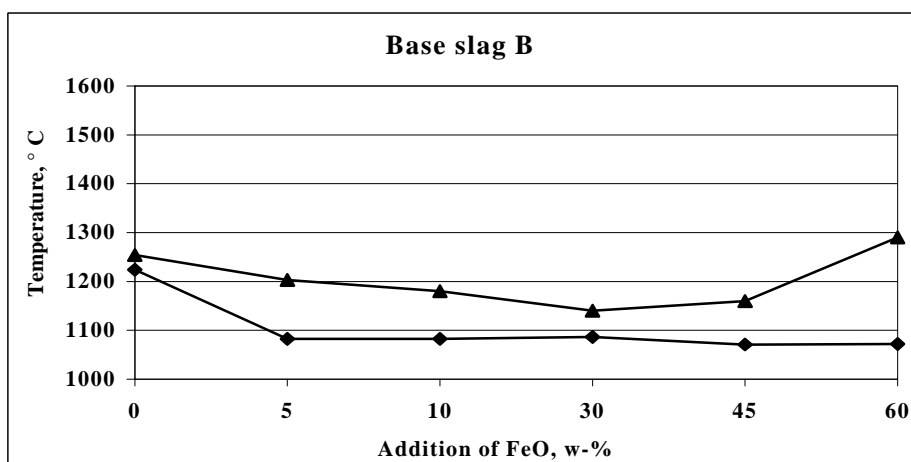
Figure 6: Melting behaviour of base slag B as a function of FeO.
solidus, meltdown
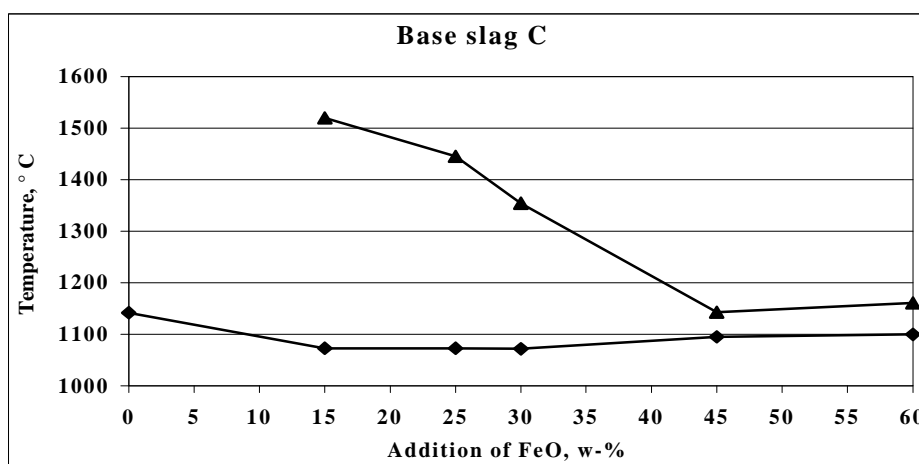


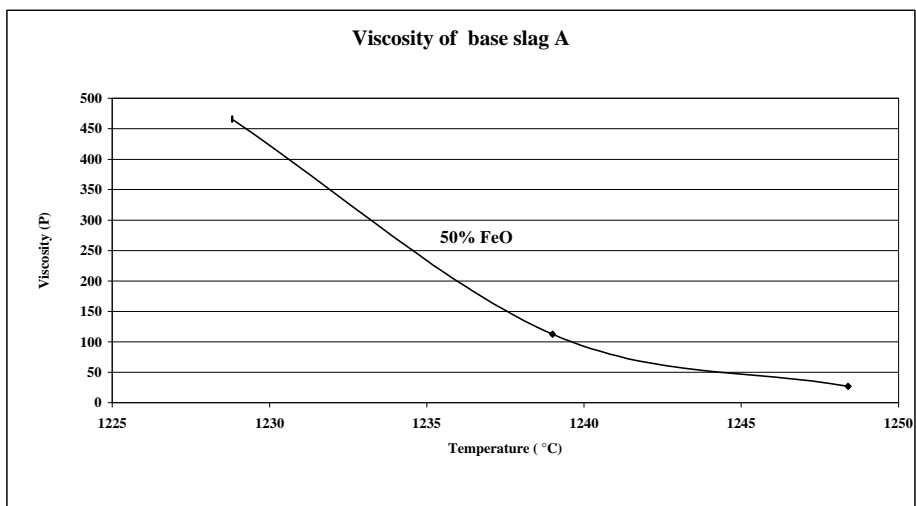Figure 7: Melting behaviour of base slag C as a function of FeO.
solidus, meltdown
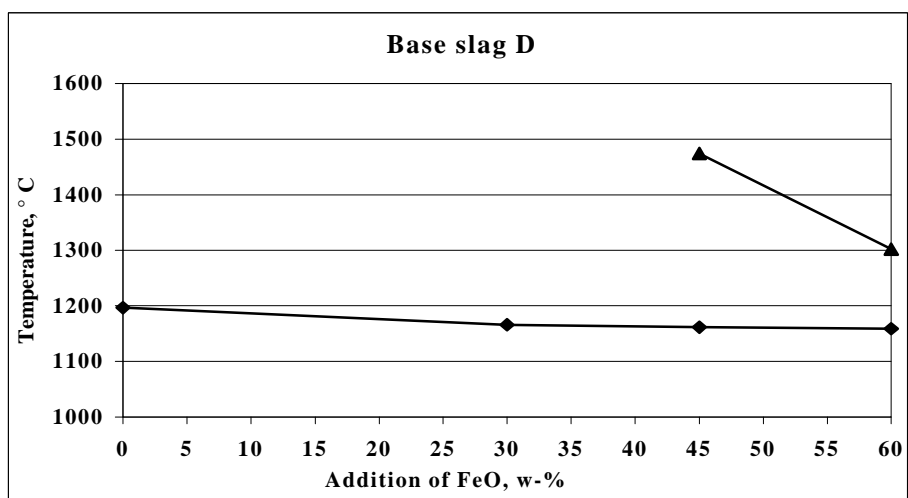


Figure 8: Melting behaviour of base slag D as a function of FeO.
solidus, meltdown
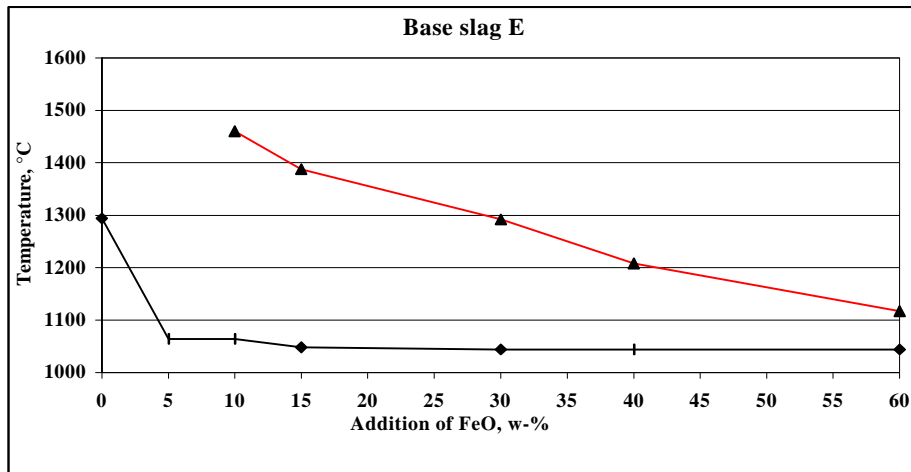
Figure 9:  Melting behaviour of base slag E as a function of FeO.
solidus, —▲— meltdown.
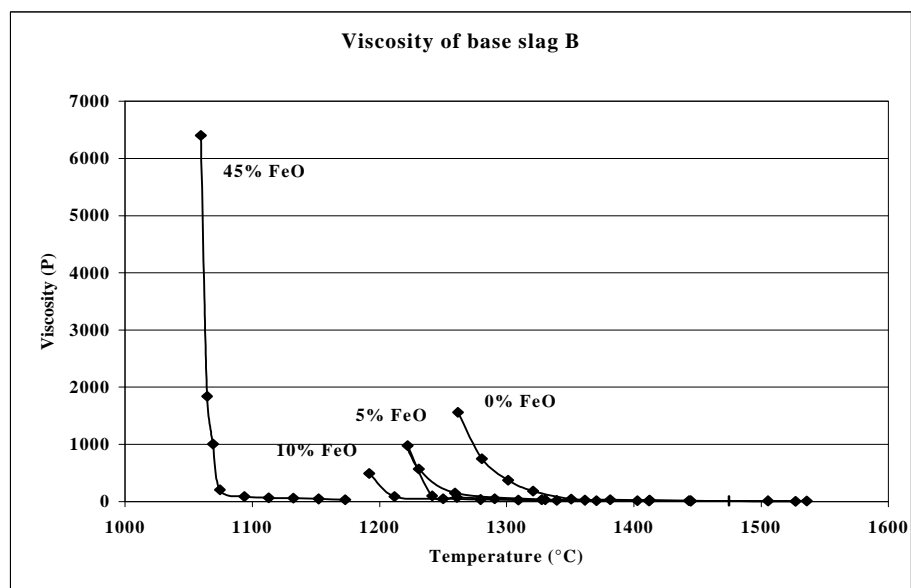


Figure 10:  Viscosity of  base slag A with 50% FeO.



Figure 11: Viscosity of base slag B with 0%, 5%, 10% and 45% FeO additions.
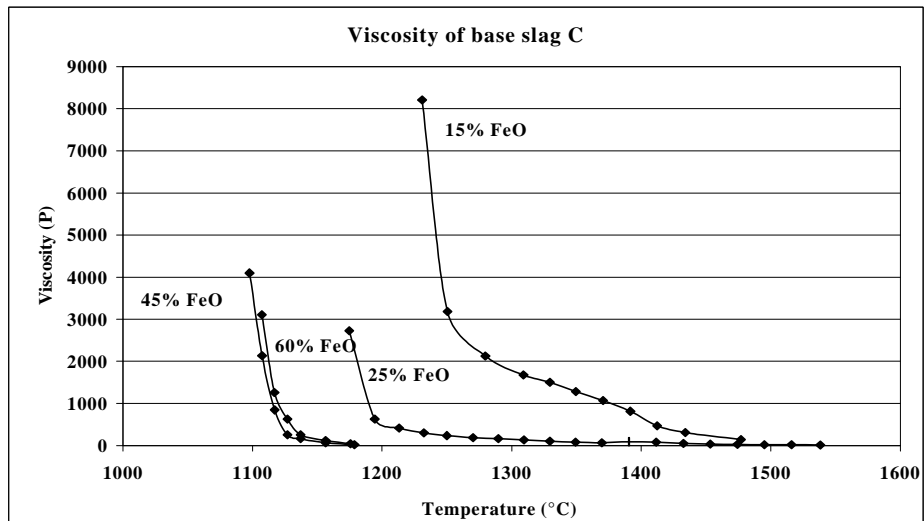
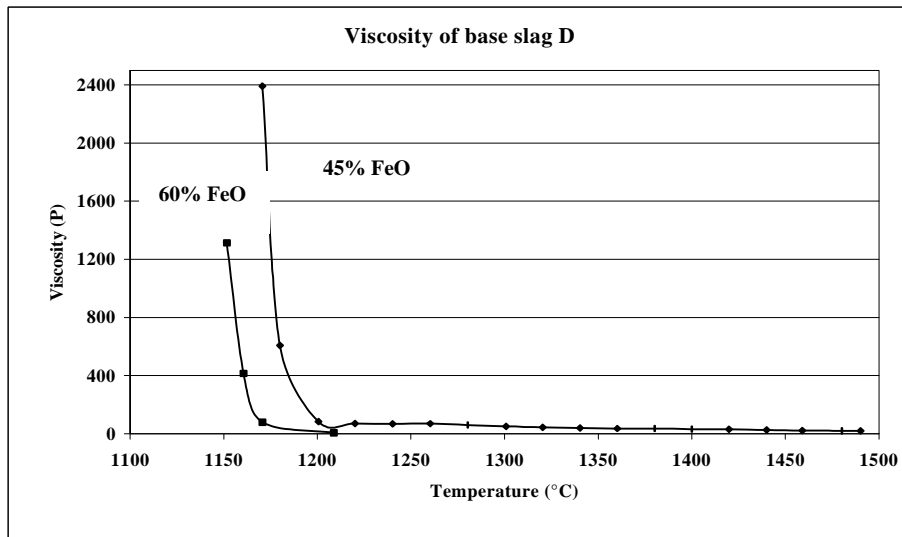Figure 12: Viscosity of base slag C with 15%, 25%, 45% and 60% FeO additions.



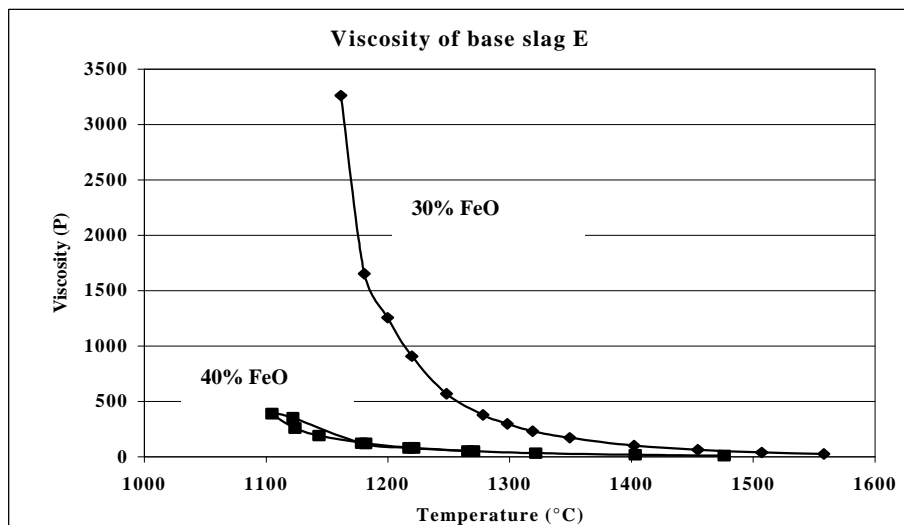Figure 13: Viscosity of base slag D with 45% and 60% FeO additions.



Figure 14: Viscosity of base slag E with 30% and 40% FeO additions.