

# SLAG ATLAS

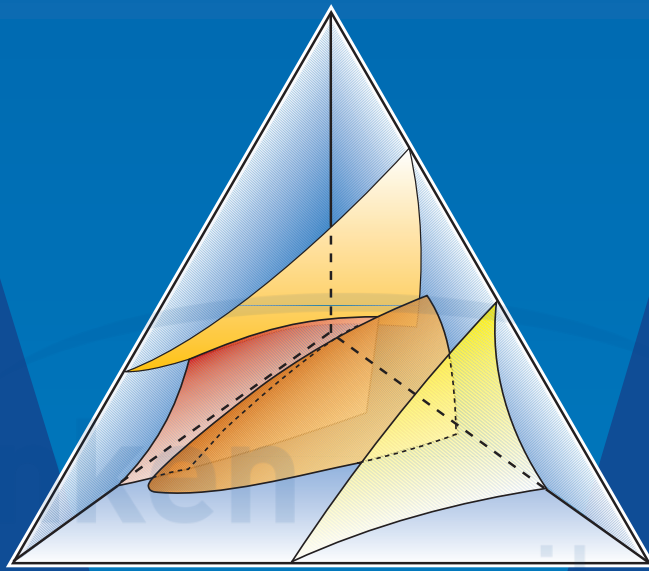
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# SLAG ATLAS



# **SLAG ATLAS**

**2nd Edition**

Edited by

Verein Deutscher Eisenhüttenleute (VDEh)



maenken  
kommunikation

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## Preface

In iron and steelmaking as well as in non-ferrous metal production and other refining technologies the use of slag is of essential importance. The refining reactions are controlled by metal/slag systems and nearly all process steps in iron and steel production, from hot metal production to special melting processes, as well as continuous casting, are closely related to the use of metallurgically effective slag. Knowledge of the properties of the slag used is needed to enable assessment of the various reactions and optimal process control.

As compared to metal melts, liquid slag display a greater variety of properties which can be varied over a wide range by changing compositions and temperatures. Complete and detailed information is needed to optimize the processes in iron and steelmaking; in particular, to optimize refining techniques in hot metal and in scrap-based steelmaking for lower contents of tramp elements and improved cleanness. In continuous casting processes the heat extraction, lubrication and surface quality have to be influenced in an optimal way by liquid casting slag.

The Committee on Metallurgical Fundamentals of the German Iron and Steel Institute (VDEh) therefore began already during the sixties with the compilation of slag data. The results were published in the first issue of the Slag Atlas, edited by VDEh with financial assistance of the European Coal and Steel Community (ECSC) in 1981.

But it was soon recognised that, without greater institutional efforts, a critical assessment of all data available was very difficult or even impossible due to incompleteness of the published data and because of the ever increasing amount of the data to be collected. Consequently, a critical selection was often not possible in the course of subsequent data compilation. Therefore in an international multi-partner research project of the ECSC (Project No. 7210-CF/107) a comprehensive review and evaluation of slag data was started in 1989 by co-working of VDEh, Max-Planck-Institut für Eisenforschung (MPI) and Lehrstuhl für Theoretische Hüttenkunde of RWTH Aachen in Germany, Institut de Recherches de la Sidérurgie Française (IRSID) and Institut National Polytechnique de Grenoble (INPG) in France as well as National Physical Laboratory (NPL) in the United Kingdom.

The research obtained significant results and improvements in the knowledge of slag properties. Furthermore, important data are now available on diffusion coefficients, heat conductivity, optical properties and sulphide and phosphate capacities. This information is particularly relevant due to the current efforts to reduce sulphur and phosphorous levels in steel, to control the kinetics of metal/slag reactions and the erosion of refractories and submerged entry nozzles, to precisely calculate thermal balance and heat transfer, and finally to contribute significantly to quality control in steel production.

The research project 7210-CF/107 was terminated with the production of a final report of over 2000 pages, presented in 15 volumes and compiled by the 6 partners. Due to the large amount of data reported, to the novel aspect of the work and to the active interest of researchers and production managers throughout the European steel industries, an action of valorization of the research results was desirable in order to adequately diffuse information to production, research and education establishments. So in the ECSC contract 7210-ZZ/608 the publication was prepared in this second issue of the Slag Atlas.

The editor is very grateful to all the authors listed up above for their comprehensive work and their engagement over many years. The editor thanks also Mrs. B. Schmitz and Dr.-Ing. J. A. Schmitz, Düsseldorf, for their excellent work in preparing this issue. Finally, special thanks are due to Dr. R. Tomellini, Brussels, for providing all the necessary support for publishing the results in this book.

We thank the European Commission for the financial assistance under the research promotion scheme by the ECSC.

Düsseldorf, September 1995

Verein Deutscher Eisenhüttenleute (VDEh)

Dr.-Ing. D. Springorum

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## 1.1 Introduction

The physico-chemical properties of metallurgical slags are controlled principally by their structures. Two theories have been put forward to account for the structure of liquid slags and their physico-chemical properties viz the molecular and the ionic theories.

The molecular theory assumes that a liquid slag is composed of individual oxides, fluorides etc. eg  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{CaO}$ ,  $\text{CaF}_2$  etc. and that these can combine to form  $\text{CaO}\cdot\text{SiO}_2$  etc. This proposition leads to use of the activity of a component eg  $\text{SiO}_2$  which allows the effects of additions of say  $\text{CaO}$  to be characterised. However, electrical conductivity studies have shown that the conduction mechanism in liquid slags is predominantly ionic and that electronic conduction only becomes important in slags containing more than 70%  $\text{FeO}$  or  $\text{MnO}$ . Thus the molten slag must be ionic in nature. Herasymenko [1] first put forward the theory that liquid slags consisted of (I) cations, such as  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$  etc., (II) anions such as  $\text{O}^{2-}$ ,  $\text{F}^{2-}$ ,  $\text{S}^{2-}$  and (III) anion complexes such as  $\text{SiO}_4^{4-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{AlO}_3^{3-}$ .

Zachariassen [2] and Warren [4] showed that the principal feature of X-ray results was that  $\text{SiO}_4^{4-}$  tetrahedra which inter-connected to form 3-dimensional networks. Most of the earlier work on the structure was deduced from interpretations of data for physical properties and phase of equilibria. However, such deductions require a knowledge the mechanism by which the structure affects the particular physical property. In more recent years, spectroscopic techniques have been used to provide both an independent determination of slag structure and an insight into the mechanism responsible for the structure-property relationship. Much of the recent advances in the field of slag structure have come from geological laboratories involved in the study of the structures of magmas and natural minerals. Furthermore, several excellent reviews of the structures of silicate liquids have emanated from these same sources [5, 6] in recent years and are recommended to the reader who requires more detail than that given in this review.

## 1.2 Methods used to determine structure

Several methods have been used to determine the structures of slags, these can be classified into the following categories:

- physical property measurements,
- chromatographic separation of various polymeric units,
- X-ray and spectroscopic techniques,
- development of "structural" thermodynamic models,
- molecular dynamics (MD) calculations.

The structural information which can be derived from these techniques are given in Tabs. 1.1 and 1.2. A full description of the techniques lies outside the scope of this review; further details for the relevant physical property measurements are given in the relevant chapters of the Slag Atlas but brief details of the molar refractivity, chromatographic separation and the X-ray and spectroscopic techniques are given below. For a full description of the X-ray and spectroscopic methods the reader is referred to the reviews of Fleet [7] and Wong and Angell [8]. In spectroscopic studies it has become a common practice to compare the spectra of a melt (or

quenched glass) with that obtained from its crystalline equivalent for which the structure is known (ie known bond lengths, and coordination eg whether a cation (eg  $\text{Fe}^{3+}$ ) has tetrahedral (IV) or octahedral (VI) coordination). This process is usually referred to as "fingerprinting".

### 1.2.1 X-ray, electron and neutron diffraction

Diffraction techniques are the only methods which will provide an overall image of melt structures. RDF functions, shown in Fig. 1.1 indicate the short- and intermediate-range order in the melt. The RDF's are a composite of the pairwise interactions for all atoms in the melt. Neutron diffraction has a distinct advantage over X-ray diffraction since scattering efficiencies are independent of atomic number.

### 1.2.2 Vibration spectroscopy

Vibration spectroscopy (Infra-red (IR), Ultra-violet (UV) and Raman have proved important tools in the determination of slag structures. Vibrational and rotational excitations in the sample are studied directly in the IR and microwave regions of the electromagnetic spectrum but in Raman these studies are transferred to the visible region where detection methods are well developed. It is for this reason that Raman spectroscopy has proved the most useful method to date for studying slag structure.

Molecular vibrations are classified into 3 modes viz symmetric stretching, asymmetric stretching and bending. Symmetric stretching leads to intense and partly polarised Raman lines whereas asymmetric bending leads to weak polarised lines. In crystalline materials the lattice vibrations are dominated by the silicate molecular units, and these produce well defined lines in the Raman spectrum (Fig. 1.2). However in melts (and quenched glasses) these are in the form of broad bands and must be deconvoluted (Fig. 1.3). Individual bands have been shown to be specific to certain anionic units eg  $\text{SiO}_2$ ,  $\text{Si}_2\text{O}_5^{2-}$  etc. and the concentrations of these species can be derived from areas under these peaks. More recently, Mysen [9] has suggested an alternative analytical treatment for the derivation of the concentrations of these anionic units which leads to values in closer agreement with those derived from NMR data.

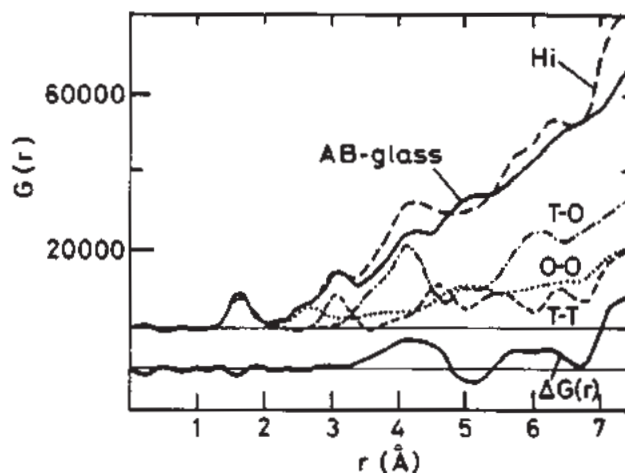


Fig. 1.1. Radial distribution function ( $G(r)$ ) for  $\text{NaAl Si}_3\text{O}_8$  quenched glass compared with contribution derived by pseudo crystalline model for  $\text{T-O}_n$ ,  $\text{O-O}_n$ , ...,  $\text{T-T}_n$ ; the lower curve  $\Delta G(r)$  represents the difference between experimental and pseudo crystalline model

**Tab. 1.1.** Structural information obtained from X-ray and spectroscopic methods

Method	Measurement	Information obtained
X-ray Neutron } Electron } Diffraction	RDF (Fingerprinting)	(I) Bond lengths eg T(Si-O) (II) Co-ordination numbers (III) Intertetrahedral angles, T-O-T (IV) Overall intermediate structure (V) Local O co-ordination around large cations
Spectroscopy Infra-red (IR) Raman Ultra-violet (UV)		(I) Bond lengths (II) Bond angles (III) Identification and concentrations of various anionic units
NMR Spectroscopy	Chemical shift (Fingerprinting)	(I) Identification of and concentrations of different anionic units (II) Bond lengths (III) Bond angles
Mössbauer	Isomer shift (IS)	(I) Valence state (II) Co-ordination of environment eg identification and concentration of Fe <sup>3+</sup> (IV) and Fe <sup>3+</sup> (VI) sites
	Quadrupole splitting (QS)	(I) Distortion of oxygen polyhedron (II) Oxidation state eg Fe <sup>2+</sup> or Fe <sup>3+</sup> (III) Co-ordination eg Fe <sup>3+</sup> (IV) or Fe <sup>3+</sup> (VI)
X-ray Absorption Spectroscopy	EXAFS XANES (Fingerprinting)	(I) Bond length (II) Bond angles (III) Co-ordination of specific atoms eg Al in NaAlO <sub>2</sub> + SiO <sub>2</sub> or Ti <sup>4+</sup> (IV) or Ti <sup>4+</sup> (VI)
X-ray Emission Spectroscopy (ESCA or XPS) ESR Spectroscopy	K <sub>α</sub> , K <sub>β</sub>	(I) Co-ordination of specific elements eg Al, Fe in anionic units (II) Changes in valence state
Luminescence Spectroscopy		(I) Co-ordination of Mn <sup>2+</sup> , Fe <sup>3+</sup> , Ti <sup>3+</sup> or S (viz or S <sup>2-</sup> or SO <sub>4</sub> <sup>2-</sup> in slag) Separate peaks for Fe <sup>3+</sup> (IV) and Fe <sup>3+</sup> (VI) co-ordination

**Tab. 1.2.** Structural information obtained from various measurements

Method	Information provided
Chromatography	Distribution of chain lengths of various polymeric units
Density	Packing and co-ordination
Molar Volumes	
Molar refractivity	Concentration of O <sup>0</sup> , O <sup>-</sup> , O <sup>2-</sup>
Viscosity	(I) Activation energies, related to bond strength (II) The effect of different cations
Enthalpy of mixing, solution	(I) Measure of bond strength (II) Effect of different cations including ordering of structure
Electrical conductivity	Indication of ionic or electronic conduction
Liquidus phase equilibria (depression of freezing point)	Gives γ <sub>SiO<sub>2</sub></sub> ; γ <sub>SiO<sub>2</sub></sub> → 1 indicates increased ordering eg formation of Ti complexes
MD calculations	(I) Bond lengths (II) T-O-T angles (III) Co-ordination eg Al in Na <sub>2</sub> O + Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub> is (IV) even when R* > 1
Structural thermodynamic models	Concentration of various anionic units present in the melt



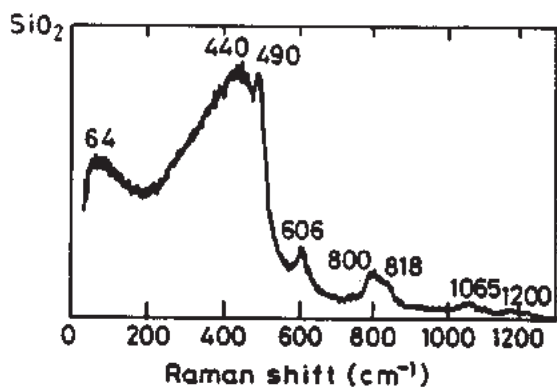


Fig. 1.2. Raman spectrum for vitreous SiO<sub>2</sub>

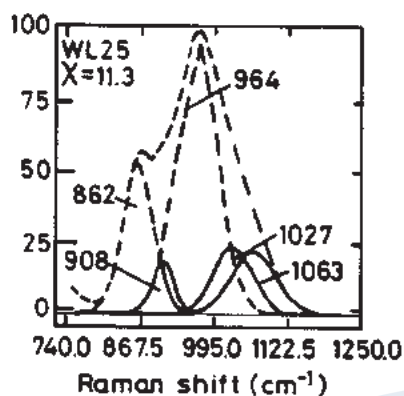


Fig. 1.3. Raman spectrum for a CaO + SiO<sub>2</sub> glass, showing deconvolution

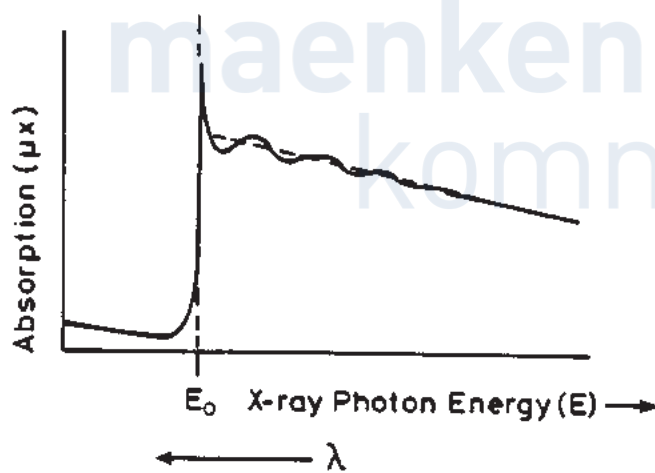


Fig. 1.4. Schematic representation of the fine structure in X-ray absorption profile; E is related to the wavelength,  $\lambda$

### 1.2.3 Nuclear magnetic resonance (NMR)

When a specimen is placed in a magnetic field there is a change in the energy state of the molecule or atom. This change is dependent upon the magnetic field, the internal field of the sample, the chemical bond and the molecular motion. The outer electrons shield the nucleus and there is a minute change in the resonant energy, which results in a chemical shift in the NMR absorption peak; structural data can be derived from the chemical shifts.

### 1.2.4 Electron spin resonance (ESR)

ESR is based on the resonant absorption of long wavelength microwave radiation by electrons with unpaired spins. It has

been used principally to determine the co-ordination of transition metals in the silicate network.

### 1.2.5 Mössbauer spectroscopy

Mössbauer (or nuclear resonance fluorescence) spectroscopy depends on the emission of  $\gamma$ -rays and their resonant absorption by atoms of the sample; this resonance is associated with allowable nuclear spin states. In practice, Mössbauer has been applied principally to slags containing Fe; the chemical isomer shift (IS) provides information on the valence state and the co-ordination environment of the atom (Fe) whereas the quadrupole splitting (QS) provides a measure of the distortion from cubic site symmetry. Mössbauer spectroscopy has proved particularly useful in differentiating between tetrahedral (IV) and octahedral (VI) co-ordination of Fe<sup>3+</sup> in silicates.

### 1.2.6 X-ray absorption spectroscopy

X-ray absorption spectroscopy exists in two forms viz X-ray absorption near edge spectroscopy (XANES) and Extended X-ray absorption fine structure (EXAFS). The threshold energy ( $E_0$ ) shown in Fig. 1.4, is associated with the energy required to eject a bound electron. XANES covers the range from  $E_0 = 0$  to 40 eV and EXAFS from 40 to 1000 eV. EXAFS provides a radial distribution function (RDF) and after Fourier transformation this yields information on bond lengths, bond angles (T-O-T) and coordination of specific atoms (cf RDF from diffraction which is a composite of all pairwise interactions). XANES tends to be more qualitative than EXAFS and is used particularly in the determination of the coordination geometry of the absorbing atom.

### 1.2.7 X-ray emission spectroscopy

The wavelength of X-ray lines vary slightly with the oxidation state of the atom and its coordination environment. The shifts in coordination geometry can be established from shifts in  $K_{\alpha}$  and  $K_{\beta}$  lines after careful calibration with crystalline silicates of known structure ("fingerprinting").

### 1.2.8 X-ray photon spectroscopy (XPS) or electron spectroscopy for chemical analyses (ESCA)

This technique is based on the fact that when X-ray, UV radiation or a charged particle strike the sample, electrons are emitted and the energy levels of molecules or atoms can be derived from energy measurements.

### 1.2.9 Chromatographic separation

The concentrations of the various anionic emits (eg SiO<sub>4</sub><sup>4-</sup>, Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>, Si<sub>3</sub>O<sub>10</sub><sup>8-</sup>) in quenched glasses were determined [10 - 14] by addition of trimethylsilyl (TMS) derivatives to aqueous solutions of the glass; the volatile products are separated by gas chromatography and the concentrations of the various anions determined; crystalline materials were used as standards to calibrate the method. However the method is not always quantitative and internally consistent. Furthermore the results reported for the concentrations of the anionic species differed from values obtained by Raman spectroscopy, however, values reported by Pasishnik et al [14] were in essential agreement with concentrations obtained spectroscopically.

### 1.2.10 Molar refractivity

Ionic refractivity can be related to the size of the ionic radius but small, highly-charged cations hardly contribute to the molar refractivity. Iwamoto et al [15] determined the concentrations of non-bridging ( $O^-$ ) bridging ( $O^-$ ) and free oxygens ( $O^{2-}$ ) in quenched glasses with this technique.

### 1.3 The structure of slags containing silica and/or other complex-forming constituents

Virtually all metallurgical slags contain silica and/or other complex-forming components. The structure of silicate is therefore of special interest for understanding the structure and behaviour of slags.

Silicate slags are built up of Si cations which are surrounded by 4 oxygen anions arranged in the form of a tetrahedron. These  $SiO_4^{4-}$  tetrahedra are joined together in chains or rings by bridging oxygens (BO), (Figs. 1.5 and 1.6). Cations such as  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$  tend to break these bonded oxygens and form non-bridging oxygens (NBO),  $O^-$ , and free oxygens,  $O^{2-}$ . The degree of depolymerisation of a silicate melt can be expressed by the ratio of (non-bridging oxygen atoms/number of tetrahedrally – coordinated atoms (eg Si)). This is usually denoted as the (NBO/T) ratio, and the physical properties, such as viscosity, thermal conductivity etc., are very dependent upon the (NBO/T) ratio.

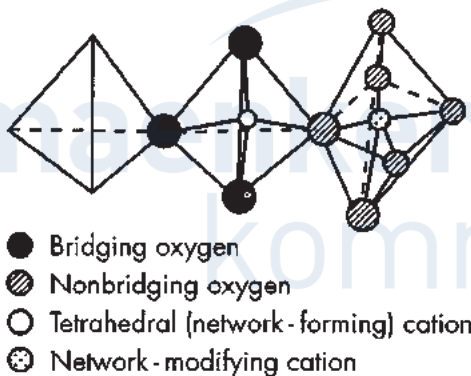


Fig. 1.5. Schematic representation of network of tetrahedra formed by Si etc. and oxygen atoms

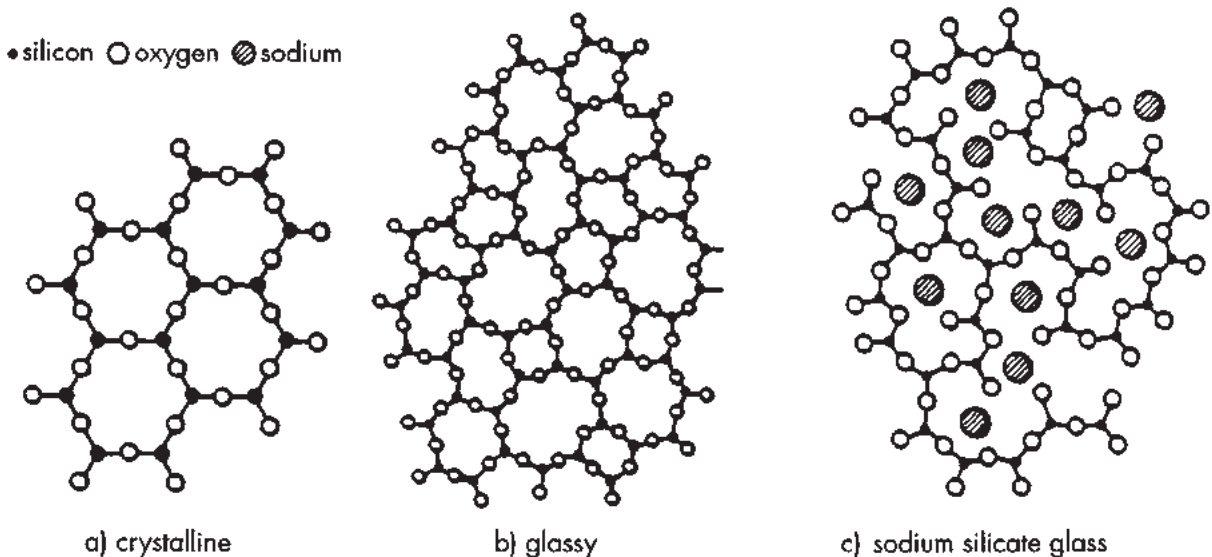


Fig. 1.6 a-c. Schematic representation in 2-dimensions of structure of (a) crystalline silica, (b) glassy silica and (c) sodium silicate glass

The silicate melts contain various 3-dimensionally, interconnected anion units such as  $SiO_2$ ,  $Si_2O_5^{2-}$ ,  $Si_2O_6^{4-}$ ,  $Si_2O_7^{2-}$ ,  $SiO_4^{4-}$  which coexist in the melt (Fig. 1.7). The nature of the cation affects the proportion of these anionic units but not the overall degree of depolymerisation ie the (NBO/T) ratio; the more extreme units  $SiO_2$  and  $SiO_4^{4-}$  are favoured by small cations of high valence eg  $Mg > Ca > Sr > Li > Na > K$ .

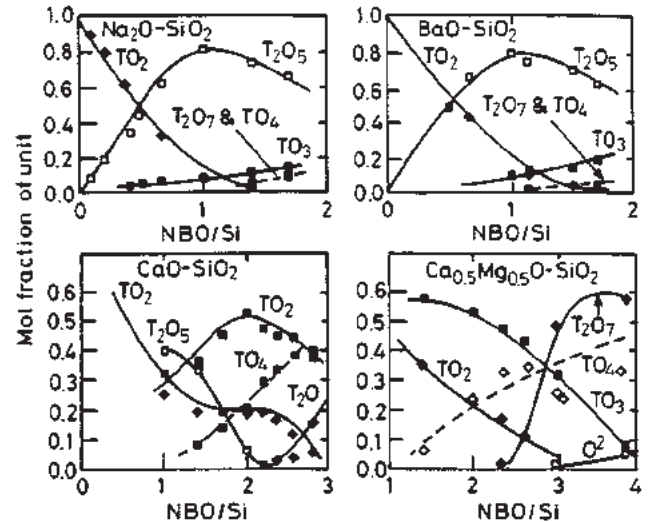


Fig. 1.7. Molar concentrations of various anionic units in binary  $SiO_2$  + metallic oxides as a function of (NBO/Si) for the bulk composition (5)

Other cations such as  $Ti^{4+}$ ,  $P^{5+}$ ,  $Al^{3+}$  and  $Fe^{3+}$  also form tetrahedra and can be incorporated into the silicate network eg  $TiO_4^{4-}$ ,  $PO_4^{3-}$ ,  $AlO_4^{5-}$  and  $FeO_4^{5-}$ . However it is important that electrical charge-balance be maintained and cations are needed for charge-balancing ( $Na^+AlO_4^{5-} = NaAlO_4^{4-}$ ). Divalent cations (eg  $Ca^{2+}$ ) must charge-balance two  $AlO_4^{5-}$  tetrahedra and this requires some ordering of the melt; these duties are easier for larger cations (eg  $Ba^{2+}$ ) than for small cations such as  $Mg^{2+}$  and this probably accounts for the cation effect mentioned above. There is evidence to suggest

that cations involved in charge-balancing duties do not participate in network-breaking. Thus  $\text{Al}_2\text{O}_3$  additions cause further polymerisation of the melt.

In slags containing iron oxides,  $\text{Fe}^{2+}$  ions tend to operate as network breakers but  $\text{Fe}^{3+}$  ions can function as both network formers and breakers. The tendency for network forming increases as the  $(\text{Fe}^{3+}/\text{Fe}^{3+} + \text{Fe}^{2+})$  ratio increases and since this ratio tends to be low in steelmaking operations it can be assumed that  $\text{Fe}^{3+}$  ions usually tend to act as network breakers in steelmaking slags.

$\text{P}_2\text{O}_5$  forms  $\text{PO}_4^{3-}$  tetrahedra, although there is some tendency to form P-O-Si bonds, usually  $\text{P}_2\text{O}_5$  tends to form phosphate complexes which result in increased polymerisation of the melt. Phosphate anions have a greater affinity for cations than silicate ions and this results in the creation of highly-polymerised silicate units eg  $\text{SiO}_2$  in the melt.

In slags containing  $\text{TiO}_2$ ,  $\text{Ti}^{4+}$  can act as both network breaker and former, however for the range 1 – 7%  $\text{TiO}_2$ , which covers most steelmaking slags,  $\text{TiO}_2$  operates as a network-former.

The addition of  $\text{CaF}_2$  to acidic, polymerised, silicate melts results in the depolymerisation of the melt but in basic melts, it only acts as a diluent.

The physical properties of slags can be estimated from a knowledge of the structural characteristics such as the (NBO/T) ratio and the valency and size of the cations (see appendix).

Readers who wish more detailed information on the structures of slags containing silica and/or other complex-forming constituents are asked to refer to the original publications (see below and reviews [5, 6, 129]).

Slags containing silica:	Ref. [16 – 64]
alumina:	[65 – 87]
iron oxide:	[88 – 94]
titanium oxide:	[95 – 106]
phosphorus oxide:	[107 – 111]
fluorides:	[112 – 128]

## 1.4 Appendix

### Calculation of (NBO/T)

The (NBO/T) ratio can be calculated in the following manner, a worked example is given below in **Tab. 1.3**.

1. Calculate mole fractions of various constituents eg  $X_{\text{SiO}_2}$ ,  $X_{\text{Al}_2\text{O}_3}$ ,  $X_{\text{CaO}}$ .

2. Since some molecules contain two cations eg  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3$  multiply these mole fractions by 2 eg  $2X_{\text{Al}_2\text{O}_3}$ ,  $2X_{\text{P}_2\text{O}_5}$

Sum network formers (T)

$$x_T = \sum X_{\text{SiO}_2} + 2X_{\text{Al}_2\text{O}_3} + 2X_{\text{Fe}_2\text{O}_3} + X_{\text{TiO}_2} + 2X_{\text{P}_2\text{O}_5}$$

3. Determine the fraction (f) of  $\text{Fe}^{3+}$  in (IV) coordination and that in VI coordination =  $(1 - f)$

In practice,  $f = 0$  for most iron and steelmaking slags.

4. Determine total charge on network-breaking cations eg  $\sum z_i x_i$

$$y_{\text{NB}}^{(1)} = \sum 2(X_{\text{CaO}} + X_{\text{MgO}} + X_{\text{FeO}} + X_{\text{MnO}} + X_{\text{Na}_2\text{O}} + X_{\text{K}_2\text{O}}) + 6(1 - f)X_{\text{Fe}_2\text{O}_3}$$

5. Calculate  $y_{\text{NB}}^{(2)}$  by allowing for the electrical charge balance of  $\text{AlO}_4^{4-}$ ,  $\text{FeO}_4^{4-}$  (IV)

$$y_{\text{NB}}^{(2)} = y_{\text{NB}}^{(1)} - 2X_{\text{Al}_2\text{O}_3} - 2fX_{\text{Fe}_2\text{O}_3}$$

6.  $(\text{NBO/T}) = y_{\text{NB}}^{(2)}/x_T$

**Tab. 1.3.** Calculation of (NBO/T) for a blast furnace slag

Oxide	Mass %	x	$x_T$	$y_{\text{NB}}^{(1)}$	$y_{\text{NB}}^{(2)}$	(NBO/T)
$\text{SiO}_2$	36.1	0.3591	0.3591			
$\text{TiO}_2$	0.46	0.0034	0.0034			
$\text{Al}_2\text{O}_3$	13.1	0.0768	0.1536			
$\text{Fe}_2\text{O}_3$	-	-			-0.1536	
$\text{P}_2\text{O}_5$	-	-				
CaO	40.9	0.4359		0.4359		
MgO	7.7	0.1142		0.1142		
FeO	0.40	0.0033		0.0033		
MnO	0.25	0.0021		0.0021		
$\text{Na}_2\text{O}$	0.20	0.0019		0.0019		
$\text{K}_2\text{O}$	0.50	0.0032		0.0032		
$\Sigma$			0.5161	1.1212		
					+1.1212	
					0.9676	
(NBO/T) = 1.87						1.87