Influence of the basicity on the redox equilibrium in the CaO—FeO—Fe$_2$O$_3$—SiO$_2$ system

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The redox Fe(III)/Fe(II) ratio in the CaO—FeO—Fe$_2$O$_3$—SiO$_2$ melts in equilibrium with air at the temperatures of 1400 °C, 1500 °C, and 1600 °C was measured. For the dependence of the redox ratio j on the temperature and the composition the following equation was derived

$$j = 1.6736 - 6.922 \times 10^{-4}\, T + 0.2927\, k - 6.181 \times 10^{-3}\, x'(\text{Fe}_2\text{O}_3)$$

The activity coefficients $\gamma(\text{FeO})$ and $\gamma(\text{FeO}_{1.5})$ were calculated using the model of the regular solutions. The dependence of the $a(\text{FeO}_{1.5})/a(\text{FeO})$ activity ratio on the basicity shows a minimum at the ratio $x(\text{CaO})/x(\text{SiO}_2) \approx 1$. Such course of this dependence is explained by the amphoteric behaviour of the iron(III) oxide.

Измерено ред-окс соотношение Fe(III)/Fe(II) в расплавах CaO—FeO—Fe$_2$O$_3$—SiO$_2$ в условиях равновесия на воздухе при температурах 1400 °C, 1500 °C и 1600 °C. Для зависимости ред-окс соотношения j от температуры и состава расплава было предложено следующее уравнение

$$j = 1,6736 - 6,922 \quad 10^{-4}\, T + 0,2927\, k - 6,181 \quad 10^{-3}\, x'(\text{Fe}_2\text{O}_3)$$

Коэффициенты активности $\gamma(\text{FeO})$ и $\gamma(\text{FeO}_{1,5})$ были рассчитаны с использованием модели регулярных растворов. Зависимость отношения активностей $a(\text{FeO}_{1,5})/a(\text{FeO})$ от основности имеет минимум при значении отношения $x(\text{CaO})/x(\text{SiO}_2) \approx 1$. Такой ход этой зависимости объясняется амфотерным характером окиси железа(III).

The oxidation ability and the basicity of an oxide melt are two most important parameters determining the distribution of the components in the molten metal—slag system. The oxidation ability of the slag may be defined as the partial pressure of the oxygen $p(\text{O}_2)$ in the melt, which is determined by the following reaction
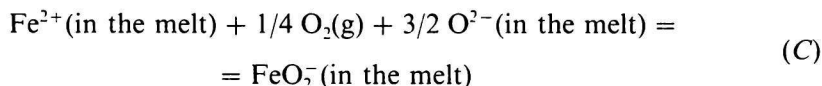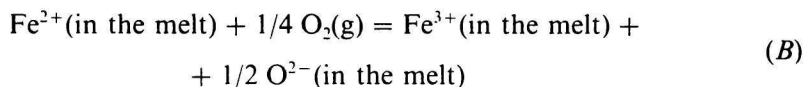
$$\text{FeO(in the melt)} + 1/4\ \text{O}_2(g) = \text{FeO}_{1.5}(\text{in the melt}) \qquad (A)$$
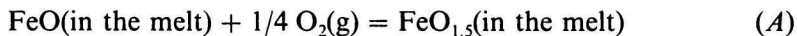
the equilibrium constant of which is given by the relation

$$K = \frac{\gamma(\text{FeO}_{1.5})\, x(\text{FeO}_{1.5})}{\gamma(\text{FeO})\, x(\text{FeO})} \frac{1}{(p(\text{O}_2)/p^\circ)^{1/4}} \qquad (1)$$

where γ are the activity coefficients, x are the mole fractions, and p^o is the standard pressure (101 325 Pa). As the values of the activity coefficients are hardly determinable in the practice, the apparent equilibrium constant K' is used only. It should be noted that also the ratio $x(FeO_{1.5})/(x(FeO_{1.5}) + x(FeO))$ for expressing the redox ratio does not enable us either to estimate the course of the oxidation-reduction reaction in the melt or to assume the ideal behaviour of the system.

Beside the partial pressure of the oxygen the redox equilibrium is affected by the acid-base character of the melt. The exact thermodynamic measure of the basicity is expressed as the activity of the O^{2-} ions. In practice the basicity is expressed as the ratio $x(CaO)/x(SiO_2)$. This measure is used also in the polycomponent systems. However, only in systems, in which CaO and SiO_2 are the only basic (donor O^{2-}) and acidic oxides (acceptor O^{2-}), respectively, there may be assumed that this ratio is proportional to the activity of the O^{2-} ions.

In the ionic form eqn (A) may be expressed by means of two reaction mechanisms

$$Fe^{2+}(\text{in the melt}) + 1/4\ O_2(g) = Fe^{3+}(\text{in the melt}) +$$
$$+ 1/2\ O^{2-}(\text{in the melt}) \qquad (B)$$

$$Fe^{2+}(\text{in the melt}) + 1/4\ O_2(g) + 3/2\ O^{2-}(\text{in the melt}) =$$
$$= FeO_2^-(\text{in the melt}) \qquad (C)$$

The Fe^{3+} ion is present in the melt either in the form according to eqn (B) or in the complex form according to eqn (C). Besides the FeO_2^- ions the presence of other complex particles, $e.\,g.$ FeO_4^{5-} $Fe_2O_5^{4-}$, may be assumed.

From the reaction (B) it is obvious that with the increasing basicity the $x(Fe^{3+})/x(Fe^{2+})$ ratio is decreased, while according to eqn (C) this ratio is increased. On the basis of the apparent equilibrium constants it is assumed [1] that the equilibrium (B) constitutes in the acidic melts (CaO—P_2O_5, $x(CaO) = 0.4$—0.6) and the equilibrium (C) constitutes in alkaline melts (Na_2O—P_2O_5, $x(Na_2O) = 0.3$—0.5). The experimental results of the redox equilibria [2, 3] are mostly interpreted by means of the mechanism (C). This fact is supported also by the structural observations, from which it follows that Fe(III) is present in the melts predominantly in the tetrahedral coordination [3].

The expression of the oxidation-reduction equilibrium by means of the apparent equilibrium constant is not thermodynamically exact [4, 5], therefore it is necessary to introduce the activity of the components. In the concentrated ionic solutions, such as the melts are, there is not possible to determine the activity of the ions according to the reactions (B) and (C). Therefore the subsequent considerations are based on the thermodynamic approach to the redox equilibrium according to the reaction (A).

The aim of this work was to study the influence of the basicity on the redox equilibrium Fe(III)/Fe(II) in the CaO—FeO—Fe_2O_3—SiO_2 system in air and the application of the model of the regular solution to the determination of the activity of the components. The dependence of the redox equilibrium on the partial pressure of oxygen was studied in [6, 7]. The physicochemical properties of this system in equilibrium with air were measured in detail in [8—11].

Experimental

For the preparation of the model slags the anal. grade Fe_2O_3, CaO, and SiO_2 were used. The oxides were mixed in the required stoichiometric ratio and homogenized. 20 g of a mixture prepared in such a way were heated in a platinum crucible in air in a furnace of the SF 2 type with a homogeneous temperature field according to the desired regime. By preliminary experiments it was found that at the given mass of the sample the redox equilibrium was attained approximately after 60 to 90 min. Therefore the melt was kept at the required working temperature (1400 °C, 1500 °C, and 1600 °C) for 2 h with the accuracy of ± 2 °C.

After the equilibrium was attained the sample was quenched in water. After drying the quenched melt was ground in an agate mill and homogenized. The content of the iron redox components was determined by means of the bichromate method with the N--phenylanthranilic acid as indicator. The content of the other components of the sample was determined by means of the atomic absorption spectroscopic method.

For the proper experiments the figurative points in three intersections of the concentration triangle of the model CaO—Fe_2O_3—SiO_2 system were chosen (Fig. 1). In the intersection A the constant ratio of the mole fractions $x(CaO)/x(Fe_2O_3) = 4$ and in the
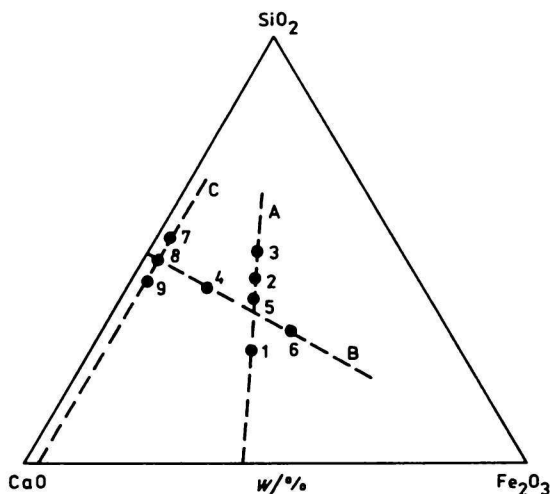

Fig. 1. The chosen intersections in the CaO—Fe_2O_3—SiO_2 system.

intersection B the constant ratio of the mole fractions $x(\text{CaO})/x(\text{SiO}_2) = 1$, respectively, were chosen. In the intersection C the constant content of 1 mole % Fe_2O_3 was maintained. The composition of the figurative points relates to the change of the composition of the converter slag during the steelmaking process.

Results and discussion

In the system with the starting components CaO, Fe_2O_3, and SiO_2 the oxidation-reduction equilibrium at the $p(\text{O}_2)/p° = 0.21$ and the temperatures of 1400 to 1600 °C was constituted. The equilibrium composition of the system is given in Table 1. The formal oxide content of Fe(III) is expressed as $x(\text{Fe}_2\text{O}_3)$ in order to be possible to compare it with the data in [6, 7, 9]. In the next considerations, however, the content of Fe(III) will be expressed as $x(\text{FeO}_{1.5})$, which is necessary for the use of the regular solutions model.

Table 1

Equilibrium composition of the investigated melts in the CaO—FeO—Fe_2O_3—SiO_2 system

Point	$t/°C$	$x(\text{CaO})$	$x(\text{SiO}_2)$	$x(\text{FeO})$	$x(\text{Fe}_2\text{O}_3)$
1	1400	0.523	0.328	0.019	0.130
2		0.388	0.489	0.036	0.086
5		0.451	0.412	0.031	0.105
1	1500	0.521	0.326	0.027	0.125
2		0.386	0.486	0.050	0.078
3		0.327	0.560	0.047	0.065
5		0.435	0.420	0.044	0.101
1	1600	0.518	0.325	0.036	0.120
2		0.383	0.482	0.063	0.071
3		0.325	0.555	0.062	0.057
4		0.451	0.470	0.031	0.049
5		0.431	0.417	0.060	0.092
6		0.400	0.380	0.085	0.135
7		0.403	0.583	0.006	0.008
8		0.483	0.503	0.005	0.009
9		0.538	0.452	0.003	0.008

On the basis of the data in Table 1 and by means of the regression analysis the dependence of the redox ratio on the temperature and the composition was determined

$$j = 1.6736 - 6.922 \times 10^{-4}\,T + 0.2927\,k - 6.181 \times 10^{-3}\,x'(\text{Fe}_2\text{O}_3) \qquad (2)$$

where $j = x(Fe_2O_3)/(x(Fe_2O_3) + x(FeO))$, $k = x(CaO)/x(SiO_2)$, T is the temperature (K) and $x'(Fe_2O_3)$ is the mole fraction of the iron(III) oxide in the original weighed-in mixture.

Eqn (2) is in accordance with the relation given in [9], which was derived on the basis of the experimental data [6, 7] for the ratio $p(O_2)/p^\circ = 0.05$, 0.1, and 1 by interpolation for $p(O_2)/p^\circ = 0.21$. Even if eqn (2) shows relatively high value of the correlation coefficient it is not stable. Only the coefficient for the variable k is statistically important, representing the empirical measure for the basicity of the slags used in the practice.

The enthalpy of oxidation for the oxidation-reduction equilibrium (A) was determined according to the relation

$$\log \frac{x(FeO_{1.5})}{x(FeO)} = -\frac{\Delta H}{2.303\ R}\frac{1}{T} + b \qquad (3)$$

where the redox ratio represents the apparent equilibrium constant, R is the gas constant (J mol⁻¹ K⁻¹), ΔH is the change of enthalpy of oxidation (J mol⁻¹) and b is a term which includes the partial pressure of oxygen and the influence of the composition.

Even though eqn (3) is a rough approximation only, the enthalpy of oxidation in the system under investigation for the given oxygen partial pressure $(p(O_2)/p^\circ = 0.21)$ and for the ratio $x(CaO)/x(SiO_2) = 0.79$, 1.03, and 1.59 was determined from the slope of eqn (3). The values $\Delta H = -91\ 700$ J mol⁻¹, $\Delta H = -104\ 600$ J mol⁻¹, and $\Delta H = -84\ 600$ J mol⁻¹, respectively, were found. The results are in a good accordance with the results in [12], where for the same system the value $\Delta H = -108\ 000$ J mol⁻¹ was found.

The linear dependence of $\log (x(FeO_{1.5})/x(FeO))$ on $1/T$ showed that the influence of the temperature on the $\gamma(FeO_{1.5})/\gamma(FeO)$ ratio is not too important. As it will be shown later, the influence of the composition is very important, especially on $\gamma(FeO_{1.5})$.

In Fig. 2 the dependence of the $x(FeO_{1.5})/x(FeO)$ ratio on the $x(CaO)/x(SiO_2)$ ratio is shown. With the increasing basicity the redox ratio Fe(III)/Fe(II) in the intersection A and C increases. In the intersection B, where the basicity is constant, no important influence of the redox equilibrium was found (cf. Table 1). From the course of the curve in Fig. 2 it could be supposed that the increasing basicity stabilizes the third oxidation stage of iron in the whole composition interval and that the mechanism according to eqn (C) is valid.

Let us assume that the system under investigation, CaO—FeO—Fe₂O₃—SiO₂, behaves regularly. Then for the calculation of the activity coefficients of the components $FeO_{1.5}$ and FeO the model of the regular solutions [13] may be used. In such a case for the system with an arbitrary number of components the following equation is valid
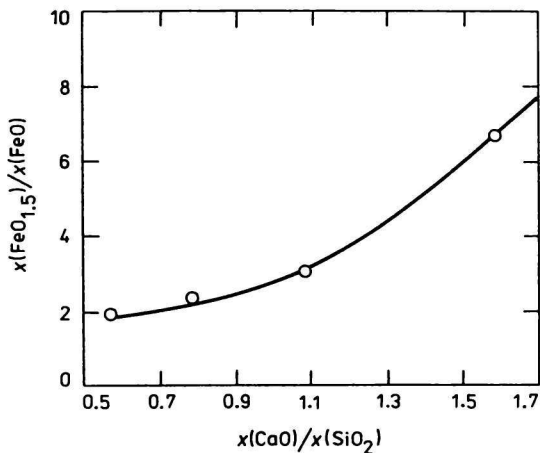
Fig. 2. The dependence of the content of the redox components on the basicity in the section A of the investigated system at 1600 °C.

$$RT \ln \gamma_i = \sum_j \alpha_{ij} x_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) x_j x_k \qquad (4)$$

where x is the mole fraction of the given oxide in the slag, α is the interaction energy between the cations. The interaction parameters are related to the interactions cation—cation only. The values of the interaction energies for the studied system are taken from [14] and given in Table 2.

Table 2

Interaction energy between ions for the CaO—FeO—Fe$_2$O$_3$—SiO$_2$ system [14]

Ion—Ion	$\dfrac{\alpha_{i,j}}{\text{J mol}^{-1}}$
Fe^{2+}—Fe^{3+}	-18660
Fe^{2+}—Ca^{2+}	-50210
Fe^{2+}—Si^{4+}	-41840
Fe^{3+}—Ca^{2+}	-114650
Fe^{3+}—Si^{4+}	32640
Ca^{2+}—Si^{4+}	-272000

In Fig. 3 the dependences of the $a(\text{FeO}_{1.5})/a(\text{FeO})$ and $\gamma(\text{FeO}_{1.5})/\gamma(\text{FeO})$ ratios on the $x(\text{CaO})/x(\text{SiO}_2)$ ratio in the intersection A at the temperatures of 1400 °C, 1500 °C, and 1600 °C are shown. The dependence of the activity ratio on the basicity shows a minimum for $x(\text{CaO})/x(\text{SiO}_2) \approx 1$—1.1. The dependence
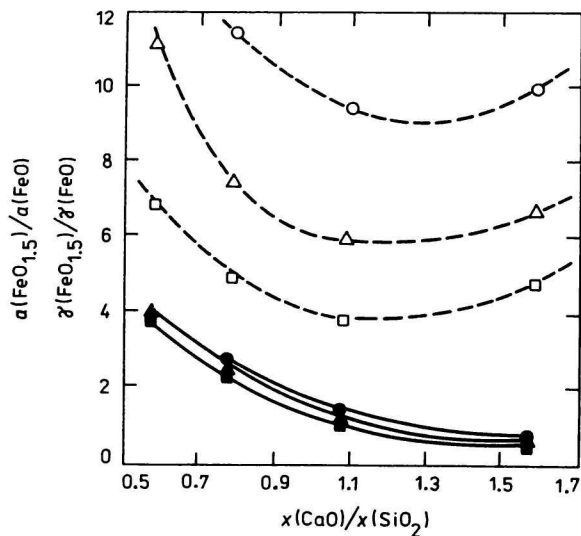
Fig. 3. The dependence of the activities ratio and the activity coefficients ratio of the components on the basicity in the section A of the investigated system.
○, ● 1400 °C, △, ▲ 1500 °C, □, ■ 1600 °C, —— the γ ratio, – – – the activity ratio.

of the solubility of H_2O (which is an acid-base reaction, too) on the basicity in the system CaO—SiO_2 with a minimum at $x(CaO)/x(SiO_2) = 1$ [15] shows a similar course, too.

From Figs. 2 and 3 it is obvious that the different course of the dependences of the mole fractions ratio and the activities ratio on the composition is due to the decrease of the activity coefficient ratio with the increasing basicity. Consequently, the conclusions on the mechanism of the acid-base reactions (eqns (*B*) and (*C*)) by means of the mole fractions may not be fully exact. From Fig. 3 it can be assumed that up to the basicity at $x(CaO)/x(SiO_2) \approx 1$ the equilibrium according to eqn (*B*) constitutes, while at higher values of the basicity the equilibrium according to eqn (*C*) takes place.

In Fig. 4 the dependence of the $\gamma(FeO_{1.5})$ and $\gamma(FeO)$ on the basicity is shown. It is evident that $\gamma(FeO_{1.5})$ decreases markedly with the increasing basicity, while the $\gamma(FeO)$ values remain nearly constant. From the course of this dependence it follows that the change in $\gamma(FeO_{1.5})$ gives rise to the minimum. This minimum may be explained by the amphoteric behaviour of iron in the third oxidation stage. Up to the ratio $x(CaO)/x(SiO_2) \approx 1$ $FeO_{1.5}$ is the donor for the O^{2-} ions and eqn (*B*) is valid. For higher values of the basicity $FeO_{1.5}$ is the acceptor for the O^{2-} ions and eqn (*C*) holds. The minimum on the curve of solubility of water vapour at the temperature of 1600 °C may be also explained by the change of the acid-base character of H_2O in the CaO—SiO_2 melt.
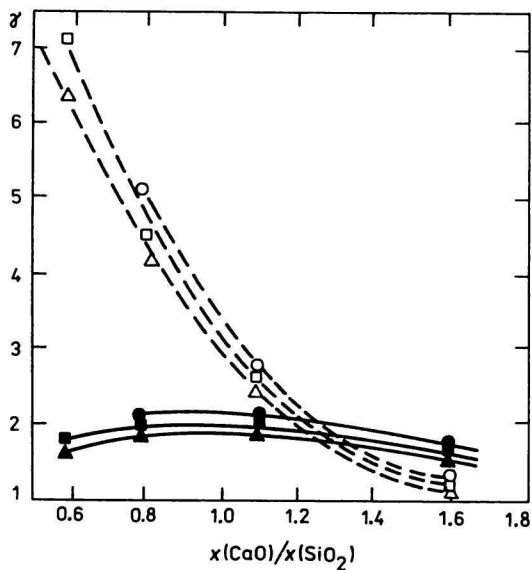
Fig. 4. The dependence of $\gamma(FeO)$ and $\gamma(FeO_{1.5})$ on the basicity in the section A of the investigated system.

○, ● 1400 °C, □, ■ 1500 °C, △, ▲ 1600 °C, —— $\gamma(FeO)$, --- $\gamma(FeO_{1.5})$.
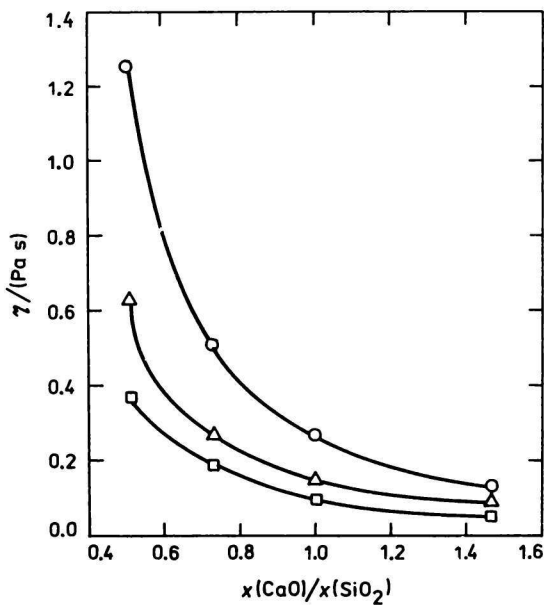

Fig. 5. The dependence of the viscosity [10] on the basicity in the section A of the investigated system.
○ 1400 °C, △ 1500 °C, □ 1600 °C.

In [10] the viscosity of the melts in the intersection A of the $CaO-Fe_2O_3-SiO_2$ system in equilibrium with air was measured. From the structural standpoint it was assumed [10] that Fe(III) forms complex anions such as FeO_4^{5-}, resp. $Fe_2O_5^{4-}$, which do not increase the viscosity of the melt. If the dependence of the viscosity [10] on the basicity is constructed (Fig. 5) a similar dependence as represents the curve in Fig. 4 for the activity coefficient $\gamma(FeO_{1.5})$ is obtained. With increasing basicity the viscosity decreases due to the depolymerization of the melt as well as the activity coefficient $\gamma(FeO_{1.5})$ due to the formation of the complex ions. The fact that the formation of the Fe(III) complex does not affect the viscosity of the melt is consistent with the results of the thermodynamic analysis from which it follows that it is only formed over the basicity $x(CaO)/x(SiO_2) \approx 1$.

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