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Effect of high alkali content in ferrosilicomanganese smelting slags on slag properties and on the destruction of furnace lining

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Abstract – Recovery of manganese from metallurgical wastes adds important value to the environment and sustainable economy. Here industrial experience of re-use of tailings from gas-cleaning units of ferrosilicomanganese smelting is presented, and the results and challenges are discussed. One of the most important issues is the very high alkali content (up to 20–23% Na₂O + K₂O) in the tailings. Despite the positive effect of alkalis on slag viscosity, especially at low temperatures, they nevertheless play a destructive role in the furnace lining. This limits the share of these tailings in the charge composition.

We have experimentally processed viscosity data for different slag compositions and temperatures, especially for variable alumina and alkali concentrations. The pre-exponential factor of the Arrhenius equation was found to be highly dependent on the activation energy values. For the first time for these slag compositions, it is shown that their viscosity can be estimated based on temperature and composition, by applying the Meyer-Neldel rule. The activation energy is shown to correlate mainly with two parameters, namely alumina content and the mass ratio of alkalis to alumina. These practical correlations can be used to optimize slag properties for viscosity and its reactivity towards the lining.

Keywords: ferrosilicomanganese, slag, viscosity, alkali, activation energy, lining

INTRODUCTION

Slags play an important part in the processing of ferro-alloys, as they are an important part of any pyrometallurgical process. They usually contain SiO₂, ferro-alloy metal oxides (MeO_x – where Me is process dependent, *e.g.*, Mn or Cr), and other oxides and compounds (CaO, MgO, FeO, alkalis, Al₂O₃, P₂O₅, S). Silica in slag melts is presented in the tetrahedral units based on the [SiO₄]⁴⁻ anion. There are five possible forms on silica tetrahedrons – the base tetrahedron [SiO₄]⁴⁻ and four other types [SiO₄]_n^{m-}, where n = 1...4 is the number of joint apexes, and m = 4 - n is the charge (Gasik *et al.*, 2009; Urbain *et al.*, 1982). The molar ratio of SiO₂ to the sum of metal oxides indicates the degree of polymerization (oligomerisation, or short-chains formation). Each metal oxide is considered as acting to break a bond of the network of tetrahedral units by supplying an additional oxygen, and charge compensating the electron at the broken bond with the cation (Sridhar, 2002). When this ratio is equal to two, each tetrahedral unit has one unshared corner, leading to the network structure resembling that of an endless sheet. When the ratio decreases toward unity, the structure turns into endless chains (Sridhar, 2002; Urbain *et al.*, 1982). In complex silicates, alumina, as an amphoteric oxide, accommodates itself in the silica network in silica-rich melts as AlO₄⁵⁻, but changes its role to that of a network breaker in low-silica melts. Besides the ratio of silica to metal oxides, the metal cation charge and size also plays a role; smaller size (Na⁺, K⁺, Fe²⁺, Mg²⁺) and higher charge (Fe³⁺, Al³⁺) promote the formation of (di)orthosilicates. These complex relations make it very challenging to establish

correlations between slag composition and physical properties, which are of paramount importance to the ferro-alloys smelting operations, slag tapping, processing, and recycling. There is a clear theoretical and practical interest in model-free mathematical analysis of experimental viscosity data for liquid slags having a wide range of composition. In many cases, experimental data are of high dimensionality (affected by many variables) and are presented in a tabulated form. From the tables, it is not easy to visually observe correlations between variables, and to evaluate the impact of different factors.

An analysis of experimental data on viscosity of liquid slags of ferrosiliconmanganese production was carried out for compositions having different alkali contents. The practical relevance of very high alkali presence is due to the recycling of tailings from gas-cleaning units (up to 20–23% Na₂O + K₂O might be present there). Whereas alkalis are usually considered to have a positive effect on slag viscosity, especially at low temperatures, they also play a role that is destructive to the furnace lining. This limits the permissible share of these tailings in the charge composition.

ANALYSIS OF SLAG VISCOSITY

Viscosity description

The flow behaviour of slags is an important factor in many metallurgical systems, influencing the efficiency of separation of slag from metal and matte phases, the extent of slag foaming, and the kinetics of metal smelting and refining reactions (Kondratiev, Jak, & Hayes, 2002). Dynamic viscosity (η , Pa·s) is a measure of the ability of a fluid to sustain shear stresses, and, in most cases, viscosities are independent of the shear rate (Newtonian fluids, described by the incompressible Navier-Stokes equation). The viscosity links the shear stress and the fluid velocity gradient normal to the shear stress vector (Sridhar, 2002). Shearing of layers of a fluid involves the breaking of bonds, and thus viscosity is a thermally activated process, often expressed as an Arrhenius-type relationship characterised by a pre-exponential factor A and an activation energy E :

$$\ln \eta = \ln A + \frac{E}{RT} \quad [1]$$

The range of viscosity that is typically encountered in metallurgical systems includes 10^{-3} – 10^{-2} Pa·s for liquid metals, and 10^{-2} – 10^{10} Pa·s for slags. If the slag needs to be tapped from the furnace, its viscosity should be lower than 15–25 Pa·s for free flow. Experimental methods for the determination of viscosity and other thermophysical properties of slags and metals have been reviewed by Aune *et al.* (2002) and Seetharaman & Sichen (1994), as well as in many other publications. Whereas the Arrhenius equation usually provides a satisfactory description of experimental data, it does not answer the question why melts of one or another composition has such or another activation energy (Iida, Morita, & Mizobuchi, 1988; Urbain *et al.*, 1982). Therefore, the Arrhenius equation in the form of Equation [1] is not in general very suitable for the prediction of melt viscosity for an arbitrary composition.

Authors have previously reported experimental observation of a linear correlation of E and $\ln(A)$ parameters for the MnO-CaO-SiO₂ system (Gasik & Gasik, 2010), and also for a wide range of metallurgical slags (Gasik, Kutsyn, & Gasik, 2011; Gasik & Gasik, 2013; Gasik *et al.*, 2014). The effect of a linear correlation of $\ln(A)$ versus E for transport processes was discovered first in semiconductors and was named as the Meyer-Neldel rule (MNR), reported first by Meyer & Neldel (1937) and reviewed by Dyre (1986). Later this rule was found to hold in many processes in physics, biology, chemistry, and electronics. MNR has been confirmed in such thermally activated processes as

diffusion in solid-state crystals and polymers, dielectric relaxation in polymers, electron conductivity in amorphous semiconductors, *etc.* (Dyre, 1986). For example, MNR was experimentally validated for diffusion in nickel and silver (Swalin, 1956). In his work, Dyre (1986) has especially analysed general application of MNR, and possible mechanisms behind this phenomenon. It was noticed that, for conductivity, all types of conductors (electron, polaron, ionic) follow MNR dependency. The general mechanism of all these charge transport phenomena is the activated “jump” of a localised quasi-particle (charge carriers). In slag melts, such carriers are especially ions and ionic oligomers. The second important feature of MNR is a requirement of some degree of disorder of the substance (Dyre, 1986), as no activation jumps are theoretically possible in ideal crystal lattice. The key variable in all these processes is the probability density of residence time of the particle in some location. It is evident that jump of the ionized particle in the melt from one place to another (*i.e.*, also viscous flow) leads to simultaneous transfer of charge, mass, and momentum, and none of the well-known viscosity models has a solid integration of these acting forces. Thus, when MNR is observed for one phenomenon (*e.g.*, electric conductivity), it should also be observed for another associated transport phenomenon (*e.g.*, viscosity, diffusion). The pre-exponential factor A in the Arrhenius equation [1] is not a constant, but it should follow the MNR (Meyer & Neldel, 1937), leading to a modified equation

$$\ln \eta = a_0 - \frac{E}{RT_0} + \frac{E}{RT} = a_0 + \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad [2]$$

where a_0 is the true constant, and T_0 is the characteristic Meyer-Neldel temperature (known as the isokinetic temperature), when viscosity in this case is independent of the activation energy. Both a_0 and T_0 are invariants, which are not dependent on slag compositions or temperature. This was shown to be valid even for slags that do not have silicates (Gasik *et al.*, 2014). Therefore, in this way, activation energies and pre-factors for viscosity of molten slags are described by the single fundamental equation. This allows calculation of such properties for any homogeneous melt, if the activation energy is known. As the activation energy has a very complex dependency on slag composition, it is not generally possible to approximate it with some simple functions, such as of basicity, even for relatively “simple” systems (Gasik & Gasik, 2010).

Experimental data

In this analysis, the authors have used data obtained from the viscosity measurements of experimental slags from Fe-Si-Mn production (Table I, Figure 1), where addition of alkalis, such as via pegmatite introduction, was tested in the Nikopol ferro-alloy plant (Ukraine). The details of the measurements, viscosity data, and the conditions have been reported earlier in more detail (Gasik, 1992; Gasik & Gavrilov, 2001). The earlier studies, however, focused mainly on the viscosity changes and their effect on the productivity of the smelting furnace and the alloy quality. Within limited experimental campaigns, the positive effect of lower slag viscosity with increased alkalis was well documented and acknowledged. The problems with lining stability were recognised much later, when more recycled materials such as tailings of furnace gas-cleaning units started to be utilised. These tailings may have up to 20–23% $\text{Na}_2\text{O} + \text{K}_2\text{O}$ present, and thus, even in minor amounts, might affect not only slag viscosity, but also their reactivity towards the lining, especially in the area of tap-holes.

The Arrhenius equation [1] was fitted to the viscosity data for the 1400–1600°C range (Figure 1) for every slag composition, with a very good correlation (0.995 ± 0.004), and the values for activation energy and pre-exponential factor A are shown in Table II. The plot of $\ln A$ versus E in Figure 2 clearly demonstrates excellent linear dependence between these parameters for all these slags.

Table I: Composition of slags (wt %) of ferrosilicomanganese smelting (Gasik, 1992; Gasik & Gavrilov, 2001). All slags have 49–50% wt. SiO₂, 16–17% MnO, 12–15% CaO, 2–3% MgO. Ratios are calculated using weight percentages.

Slag №	%Al ₂ O ₃	%Na ₂ O	%K ₂ O	%(Na+K) ₂ O	Na ₂ O/K ₂ O	(Na+K) ₂ O/Al ₂ O ₃
1	9	1.4	3.3	4.7	0.424	0.522
2	9.1	2.9	2.8	5.7	1.036	0.626
3	8.9	3.7	3.7	7.4	1.000	0.831
4	8.1	6.7	6.8	13.5	0.985	1.667
5	8.1	7.5	7.6	15.1	0.987	1.864
6	12.9	1.4	3.2	4.6	0.438	0.357
7	12.4	3	4.5	7.5	0.667	0.605
9	10.4	2.2	2.3	4.5	0.957	0.433
10	11.4	1.3	3.1	4.4	0.419	0.386
11	8.7	2.4	4.2	6.6	0.571	0.759

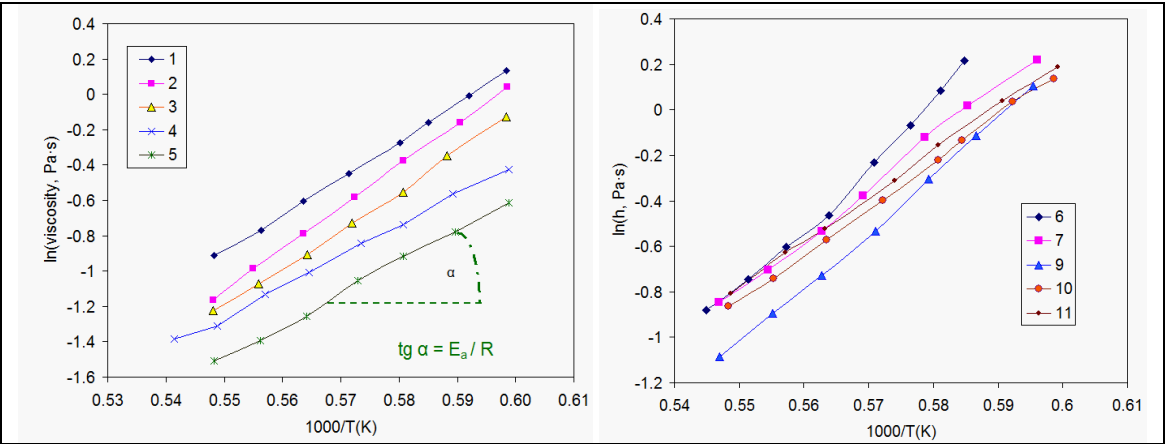


Figure 1: Viscosity of experimental slags (numbers of the curves) of Table I.

Table II: Parameters of Arrhenius equation for viscosity [1] of experimental slags

№	1	2	3	4	5	6	7	9	10	11
E, kJ/mol	174.5	197.7	182.5	143.5	150.0	229.3	186.2	205.6	169.0	164.9
ln A	-12.44	-14.19	-13.27	-10.76	-11.41	-15.96	-13.11	-14.63	-12.02	-11.69

For Figure 2, data (converting fitting coefficients into $T_0 = -1/R/\text{slope}$, and rearranging as for Equation [2]), a very good approximation can be obtained:

$$\eta = \eta_0 \exp\left(\frac{E}{RT} - \frac{E}{RT_0}\right) = 0.1612 \exp\left(\frac{E}{R} \left(\frac{1}{T} - \frac{1}{1950}\right)\right) \quad [3]$$

where activation energy E is composition-dependent, but not temperature-dependent. The value of $T_0 = 1950$ K represents the iso-kinetic temperature of all these slags when their viscosity is nearly the same and equal to ~ 0.16 Pa·s (despite composition differences), assuming that the slag is still homogeneous at that temperature.

This analysis shows that the fundamental MNR equation [2] is able to describe viscosity of liquid homogeneous slags. Furthermore, only the knowledge of the activation energy E is sufficient to calculate viscosity at any temperature. The remaining challenge is to find out how activation energy E is linked with the slag composition. In a general case, a special mathematical approach is required (Gasik & Gasik, 2010), but, for these slags, a simple correlation was found, indicating that the ratio of alkalis to alumina $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ might be the parameter to monitor (see Figure 3).

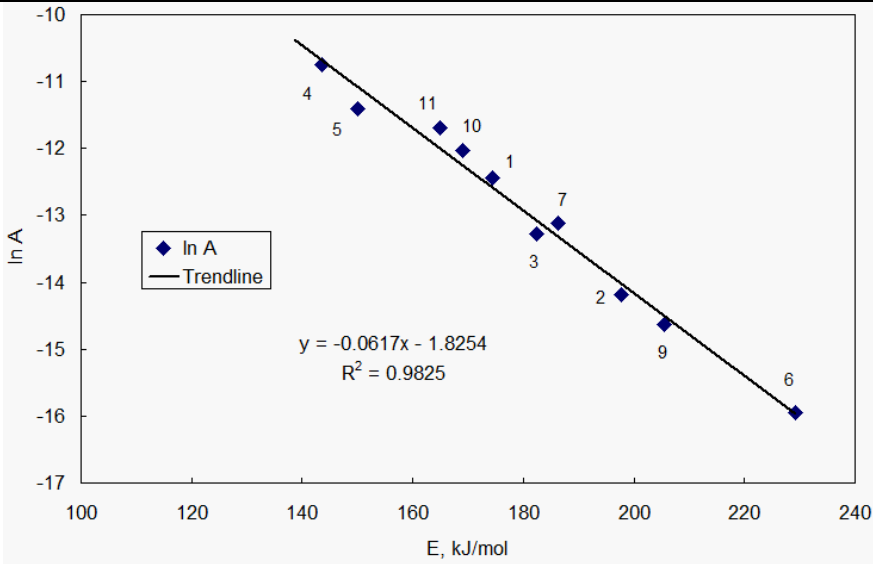


Figure 2: Dependence of pre-exponential factor ($\ln A$) on activation energy E (Table II) for viscosity of experimental slags of Table I

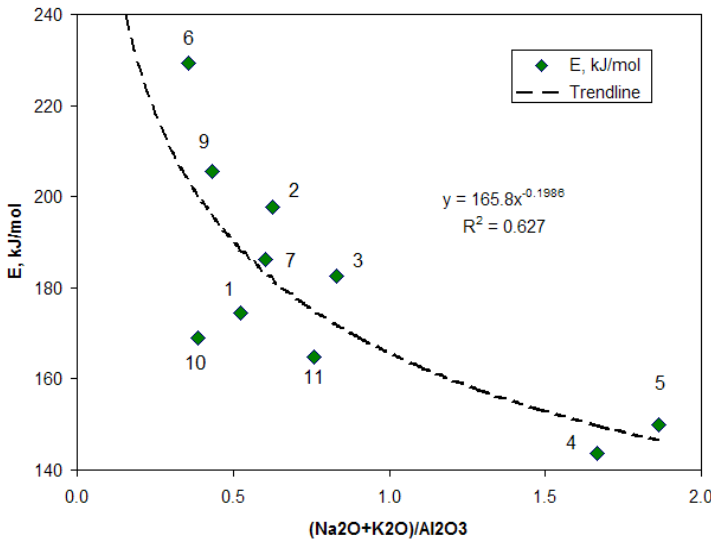


Figure 3: Dependence of activation energy E (Table II) for viscosity versus mass ratio of $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ in experimental slags of Table I (numbers near the points)

Therefore, an increase in the ratio $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ at all other constant conditions leads to a decrease in activation energy of viscous flow for these slags. This does not automatically mean a lower viscosity (which is temperature-affected), but it shows a lower (weaker) dependence of viscosity on temperature changes. The fitted equation of Figure 3 might be converted and approximated for the estimation of FeSiMn slag viscosity, when its main composition (alkalis and alumina content) and temperature are known:

$$\eta \approx 0.16 \exp\left(\frac{165.8}{R} \cdot \left(\frac{\%(\text{Na}_2\text{O} + \text{K}_2\text{O})}{\%\text{Al}_2\text{O}_3}\right)^{-0.2} \cdot \left(\frac{1}{T} - \frac{1}{1950}\right)\right) \quad [4]$$

As there is a non-uniform temperature distribution in the furnace, there will also be a variation of viscosity (and, consequently, of reactivity of the slag vis-à-vis the lining near the tap-holes). High-alkali-ratio slags will thus be more lining-aggressive over a wider temperature range.

CONCLUSIONS

In this work, the dependence of activation energy versus the pre-factor in the Arrhenius equation for viscosity and electrical conductivity was analysed, and the fundamental applicability of the Meyer-Neldel rule (MNR) was shown. All primary data used for analysis were experimental, and no modelling assumptions (about slag structure or ionic state) have been imposed. The results show that the Meyer-Neldel rule allows prediction of transport phenomena when the activation energy of one process is obtained from experiments or assessed via other correlations. For FeSiMn slags, the ratio $(\text{Na}_2\text{O} + \text{K}_2\text{O}) / \text{Al}_2\text{O}_3$ was shown to be the most important to evaluate activation energy and viscosity of liquid slags. This has practical importance for monitoring of, e.g., slag reactivity towards the lining, when using a higher share of recycled materials such as tailings of gas-cleaning units of a ferro-alloy plant.

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