

Mathematical Analysis of Experimental Data on MnO-SiO₂-CaO System Molten Slag Electric Conductivity in Manganese Ferroalloy Production

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The mathematical analysis results of experimental data on the electric conductivity of MnO-SiO₂-CaO molten slag compositions homogeneous for predetermined temperature are presented. It is determined that experimental data can be estimated more adequately with application of multitask optimization and yield surface (metamodeling). Also change of slag properties can be predicted more reliable without hypothesis and assumptions about molten oxide slag structure.

Keywords: MnO-SiO₂-CaO SYSTEM MOLTEN SLAG, ELECTRIC CONDUCTIVITY, EXPERIMENTAL DATA, MATHEMATICAL ANALYSIS, MULTITASK OPTIMIZATION, YIELD SURFACE OF SLAG PROPERTIES PREDICTION

Introduction

Physical properties of MnO-SiO₂-Ca slags and their dependence on the temperature and composition are the most important parameters in manganese ferroalloy production. Various models and approaches, for example, slag optical basicity concept, are suggested for electric conductivity, viscosity and other properties estimation. Model-free mathematical analysis of experimental data for MnO-SiO₂-CaO molten slag in the wide range of concentrations, corresponding to slags of smelting carbonaceous ferromanganese, ferrosilicon manganese and metallic manganese by silicothermal production method, is of theoretical and practical interest [1].

In many cases experimental and model data have high dimension and are presented in the tabular style. In this particular case, it is not easy to find out visually interdependence between parameters and estimate the effect of different factors. The usage of multitask optimization and yield surface (metamodeling) enables to estimate the experimental data more adequately and predict

behavior of slag properties without hypothesis about molten slag dstructure and their interaction.

Electrical conductivity of molten slag is critical for proper ferroalloy production process. It is known that electric conductivity, viscosity and other similar properties of liquid-alloy depend nonlinearly on the temperature. In due time, various theoretical models were suggested for description of slag electric conductivity. Particularly, they are based on the conception of slag as an ionic liquid (electrolyte) or on the simplified phenomenological ratios. In the model range the presence of some ionic radius and definite valences is postulated, but it does not always have experimental confirmation. Slags are often represented by silicate melts which tend to form silicate networks with different oligomerization degree, that is why it is difficult to introduce the idea of "intermediate particle" for them.

In this work another approach to slag electric conductivity analysis without using initially postulated patterns and preconditions is reviewed. The practical importance of such approach for

ferroalloy process consists in the necessity of final result adequate estimation (electric conductivity value) as a function of slag composition and temperature, but without involvement of any intermediate hypothesis. It can be achieved if there is sufficient amount of tabulated experimental

data which can be processed with the new mathematical methods.

In this case, experimental data of slag electric conductivity for MnO-SiO₂-CaO system measured with four-point probe method are used (**Table 1**) [2].

Table 1. Summary data of experiments on electric conductivity χ of CaO-SiO₂-MnO system liquid-alloys at 1500°C [2]

Number of series	Molar composition, %			t*	T _L , °C	lnA**	E, Kcal/mol	$\chi(1500^\circ\text{C})$ $\Omega^{-1}\text{cm}^{-1}$
	N _{SiO₂}	N _{CaO}	N _{MnO}					
I	0.55	0.321	0.129	0.286	1370	7.828	33.1	0.21
	0.55	0.186	0.264	0.586	1300	10.374	40.8	0.29
	0.50	0.417	0.083	0.166	1475	6.447	26.6	0.32
	0.50	0.330	0.170	0.340	1380	7.309	30.1	0.28
II	0.50	0.238	0.262	0.524	1300	7.216	28.4	0.42
	0.50	0.140	0.360	0.720	1280	7.159	27.3	0.54
	0.50	0.091	0.409	0.818	1290	7.217	27.0	0.63
	0.50	0	0.50	1	1450	6.259	23.1	0.75
	0.45	0.508	0.042	0.076	1450	6.897	27.0	0.45
	0.45	0.466	0.084	0.152	1410	4.570	19.3	0.40
	0.45	0.379	0.171	0.311	1360	6.447	26.1	0.37
III	0.45	0.288	0.262	0.476	1290	6.038	23.4	0.54
	0.45	0.194	0.356	0.647	1240	6.854	26.0	0.58
	0.45	0.095	0.455	0.827	1210	5.980	22.0	0.75
	0.45	0	0.55	1	1260	6.860	23.8	1.09
	0.40	0.473	0.127	0.211	1400	5.851	22.4	0.60
	0.40	0.384	0.216	0.360	1280	6.984	25.6	0.74
	0.40	0.340	0.260	0.433	1250	7.047	25.5	0.81
IV	0.40	0.245	0.355	0.591	1250	6.557	23.0	1.01
	0.40	0.145	0.455	0.758	1220	6.307	21.6	1.24
	0.40	0.042	0.558	0.930	1270	6.552	21.4	1.58
	0.40	0	0.60	1	1300	5.542	17.4	1.80
	0.35	0.390	0.260	0.400	1400	5.786	20.4	0.98
	0.35	0.344	0.306	0.470	1380	6.440	22.4	1.07
	0.35	0.295	0.355	0.546	1310	6.271	21.4	1.19
V	0.35	0.196	0.454	0.698	1250	5.717	19.0	1.36
	0.35	0.094	0.556	0.855	1280	5.700	17.8	1.88
	0.35	0	0.65	1	1340	5.620	17.4	1.95
	0.30	0.248	0.452	0.645	1400	5.950	18.3	2.10
	0.30	0.145	0.555	0.792	1400	6.077	18.7	2.13
VI	0.30	0.093	0.607	0.867	1300	6.758	19.9	3.00
	0.30	0	0.70	1	1315	6.314	18.0	3.29
	0.263	0	0.737	1	1450	9.181	26.2	5.61

*t – “manganese” module;

$$t = N_{\text{MnO}} / (N_{\text{MnO}} + N_{\text{CaO}}) = N_{\text{MnO}} / (1 - N_{\text{SiO}_2})$$

**A – pre-exponential factor

Electric conductivity activation energy values (E) depending on temperature are defined, and also there is made an effort to correlate measured values of electric conductivity χ with equivalent electric conductivity Λ :

$$\Lambda = \frac{\chi V_m}{2(1 - N_{SiO_2})}, \quad (\text{Eq. 1})$$

where V_m - molar volume of molten slag, m^3/mol , N_{SiO_2} - mole fraction of SiO_2 . The usage of this equation is based on the assumption that electric conductivity of this system is defined basically by Ca^{2+} и Mn^{2+} cations. Silicone oxide is supposed to be present in the form of complex forms SiO_4^{4-} , $\text{Si}_2\text{O}_7^{6-}$ and others, and their effect on the electric conductivity is excluded without detailed explanations. Values Λ shown in work [2] have essential nonlinearity on SiO_2 content or on so called "manganese module" $t = N_{\text{MnO}}/(N_{\text{MnO}} + N_{\text{CaO}}) = N_{\text{MnO}}/(1 - N_{\text{SiO}_2})$. However, further analysis [1] did not confirm such electric conductivity dependences on either concentration, or liquid-alloy thermodynamic functions. Also it is still unknown how much the supposition about the effective valence of cations Me^{2+} meets reality in the whole range of researched concentrations and temperatures. Effective charges and transport numbers in electrolytes are known to have different values under environment electric neutrality condition. System $\text{MnO}-\text{SiO}_2-\text{CaO}$ has various solid phases. **Figure 1** shows the calculated section (triangulation) at 1500°C , where liquidus (homogeneous liquid-alloy composition) is grey colored. It follows from this diagram that

application of above-mentioned "manganese module" t is justified when it changes from 0 to 1 within the whole range of liquid phase stability at 45-65% of SiO_2 . However, the varieties of manganese module will be ambiguous under fixed oxide concentration as the denominator of the equation (1) is a constant.

Results and Discussion

Mathematic modeling and analysis of results

In this work we assumed the standard exponential dependence of electrical conductivity on inverse temperature ($\ln(\chi) = \ln(A) - E/RT$) defined by the energy of conductivity activation (E) and pre-exponential factor (A). Firstly, the experimental data are presented as correlation matrix (**Figure 2**) – correlation between slag components is not considered as $\% \text{MnO} = 100 - \% \text{SiO}_2 - \% \text{CaO}$ by definition. Lines of regression E and $\ln(A)$ with the slag components and on each other are shown in the right part of **Figure 2**, and corresponding correlation coefficients are in the left from the main diagonal.

It can be noted that activation energy correlates the best with silicon oxide content and then with manganese oxide while the factor dependence is weaker. It is interesting to observe the mutual dependence of conductivity activation energy with the factor (correlation coefficient +0.866) which is more than any other correlation with slag content. The presence of significant autocorrelation in any data set indicates about their strong mutual interdependence, that is why they cannot be considered as independent variables [3, 4].

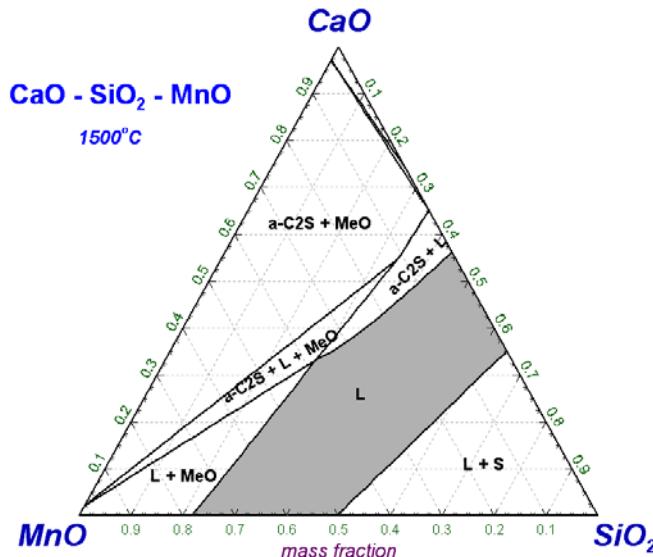


Figure 1. Isothermal section of phase diagram $\text{MnO}-\text{SiO}_2-\text{CaO}$ at 1500°C (thermodynamic database of oxide systems FactSage 5.4.1)

Figure 3 illustrates 4-dimensional diagram of activation energy dependence on pre-exponential factor, content of MnO (point diameter) and SiO₂ (point color). Higher values of activation energy tend to associate with low content of manganese oxide and high content of SiO₂. Large (high MnO content) dark blue (low SiO₂ content) points represent slags with low activation energy and pre-factor on the diagram 3. It should be noted that no patterns or hypothesis about slag composition are used in this analysis; all the data are taken directly from the experiments.

Due to high autocorrelation of pre-exponential factor and activation energy, the former can be excluded from the further analysis, and slag conductivity is expressed by equation 3

$$\ln(\chi) = 3.566 + E(SiO_2, CaO) \left(0.125 - \frac{1}{1.987 \cdot 10^{-3} \cdot T} \right) \quad (\text{Eq. 3})$$

where activation energy is (yet unknown) function of slag content and expressed in kcal/mol for convenient comparison with initial experimental data.

In this case, E dependence on slag content is hard to describe with polynomial or another approximation with satisfying result (even at good correlation the traditional regression functions give non-physical (negative) E values with extrapolation on higher calcium oxide content).

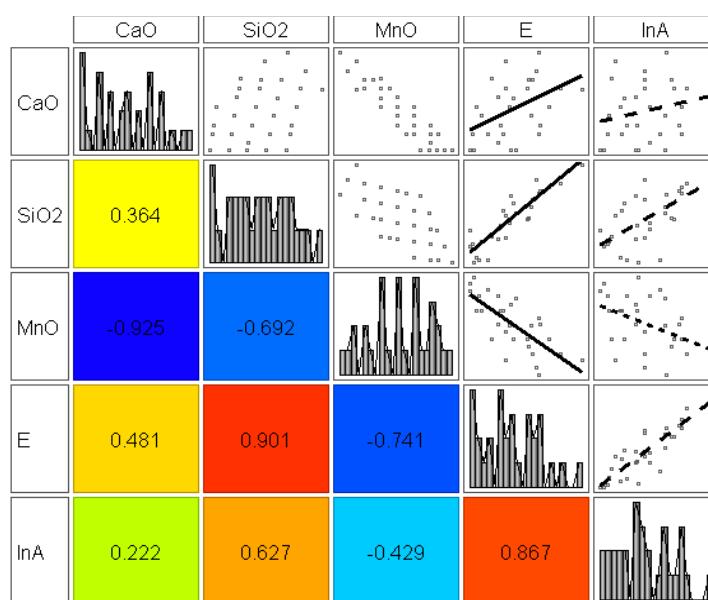


Figure 2. Correlation matrix of slag composition, activation energy and pre-factor (explanations in the text)

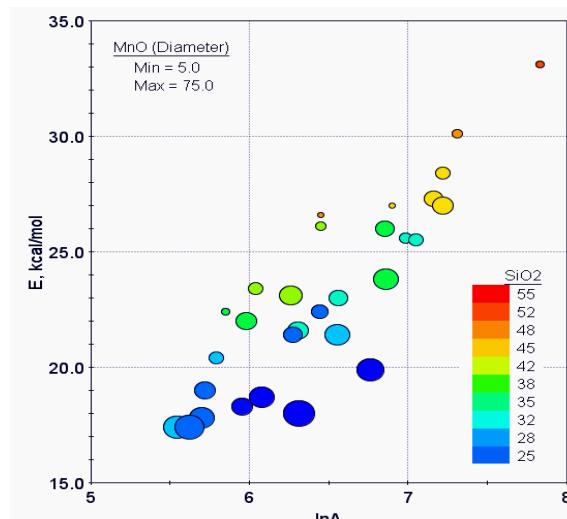


Figure 3. Dependence between activation energy, logarithm of factor, silicon (color) and manganese (diameter) oxide content in molten slag

In this work another approach, namely yield surface method also known as metamodeling [3, 4] is used for estimation of conductivity activation energy dependence on concentration. After testing some algorithms, we obtained good description by Kriging's method [5]. This method is based on the control of data co-variation function, the so called

$C(x_{ij}) = \sigma^2 \rho(x_{ij})$, which defines how correlation of $\rho(x)$ changes between values of function in the points i and j divided by the distance x_{ji} with variation parameter σ^2 . The variogram can have various profile or different variation ranges determined by "noise" level in the initial data [5]. If the distance between two points is more than variogram range, the corresponding function response should not affect each other (not fully correlated). The range is inversely proportional to the quantity of function oscillations so as small ranges mean sudden changes while big ranges indicate the presence of regular trends (with small quantity of oscillations). This is especially important during the analysis of data with unknown part of mistakes when it is impossible to check the correctness of all results and deviation of predicted values from the real ones cannot be defined (in opposite to standard regression analysis).

In this analysis the input values (percentage of components in the slag) are not normalized. The analysis strategy is to combine the metamodel with mistake minimization excluding the points one by one. In such cases, the traditional methods of regression based on Gaussian distribution can lead to incorrect prediction since Gaussian functions (4) can differentiate unlimitedly. This results in objective function "extrasmoothing". Matern variograms [5,6] are used instead of Gaussian

functions as Matern function (5) differentiates twice and it is based on the "golden ratio" of data set with Euclidian spaces concerning to average values:

$$\rho(x_{ij}) = \exp\left(-\left(\frac{x_{ij}}{\varphi}\right)^2\right) \quad (\text{Eq. 4})$$

$$\rho(x_{ij}) = \frac{1}{2^{\kappa-1} \Gamma(\kappa)} \left(\frac{x_{ij}}{\varphi}\right)^\kappa K_\kappa\left(\frac{x_{ij}}{\varphi}\right) \quad (\text{Eq. 5})$$

where $\varphi > 0$ - parameter of function range, $\kappa > 0$ - smoothing parameter, $\Gamma(\kappa)$ - gamma-function, $K_\kappa(x) = J_\kappa(x) \pm iY_\kappa(x)$ - Bessel function of the third kind. **Figure 4** shows the result of metamodeling with experimental points. It can be seen that metamodel gives adequate description of E dependence on slag composition, including that with extrapolation on other compositions. In spite of complex functional expression for activation energy this dependence is easy to represent as the algorithm for numeric computation.

In this work the data at 1500°C shown in **Figure 5** are used for computation of electric conductivity (the area behind the line with zero calcium oxide content is mathematical extrapolation and not considered). It is seen that high values of electric conductivity associate with low silicon and calcium oxide content. This corresponds to low values of activation energy and pre-factor (**Figure 3, 4**).

Electric conductivity remains high in all slags with MnO content >60% regardless of CaO/SiO₂ relation. These experimental data are compared to equation calculation (3) where metamodel was used for activation energy (**Figure 4**).

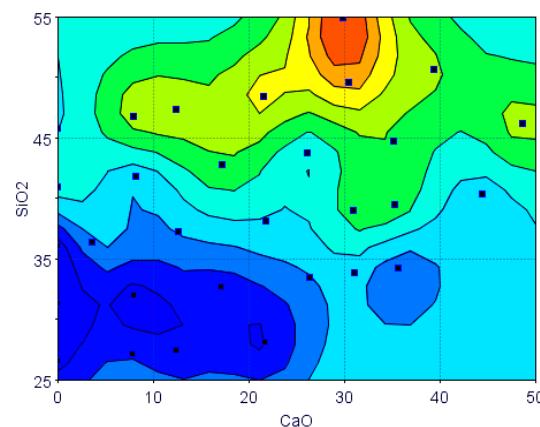
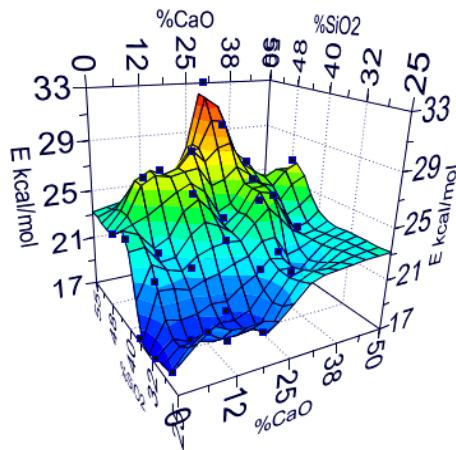


Figure 4. Metamodel of electric conductivity activation energy depending on slag composition (points are experimental data), view of three-dimensional graph projection is shown from above on the right side

The results are shown in **Figure 6** where the experimental points are marked on the plane determined by metamodel. Satisfactory accordance of results and predictions enables to use obtained dependence for electric conductivity estimation of any molten slag compositions and at other temperatures. It should be accentuated that all the data are experimental and no assumptions about slag liquid-alloys structure or nature of electric charges transfer in them are used.

For engineering practice the application of such algorithm can give immediate information about experimental data structure, unobvious correlations, and probable relations of higher order and may quantitatively predict the behavior of parameters, including that beyond of experimentally defined data limits.

In this work we considered only slag electric conductivity, however the suggested pattern will be even more effective if simultaneous determination of other parameters behavior is required. Anyway, the analysis is carried out without any pattern conceptions about slag composition or parameters.

It should be noticed that such analysis supposes high level of experimental data accuracy where the possible measure mistakes are excluded at high degree.

The usage of metamodeling enables to obtain engineer dependences of parameters with high enough accuracy for practical usage in ferroalloy production. Considering the interconnection of electric conductivity and dynamic viscosity of slag liquid - alloys $\chi\eta = (\alpha + \beta T)T^2$ [7],

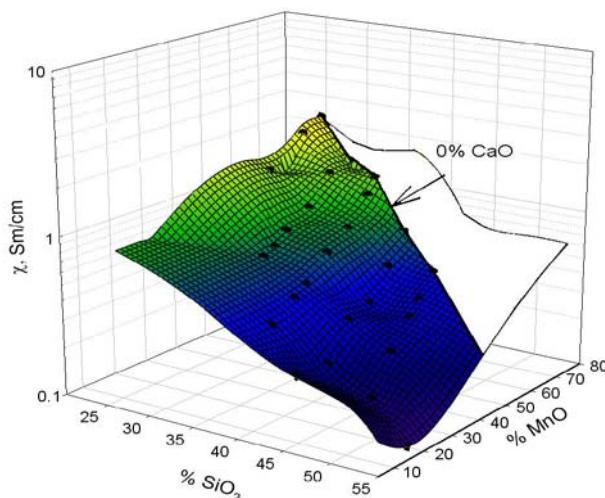


Figure 5. Measured values (points) of slag electric conductivity at 1500°C

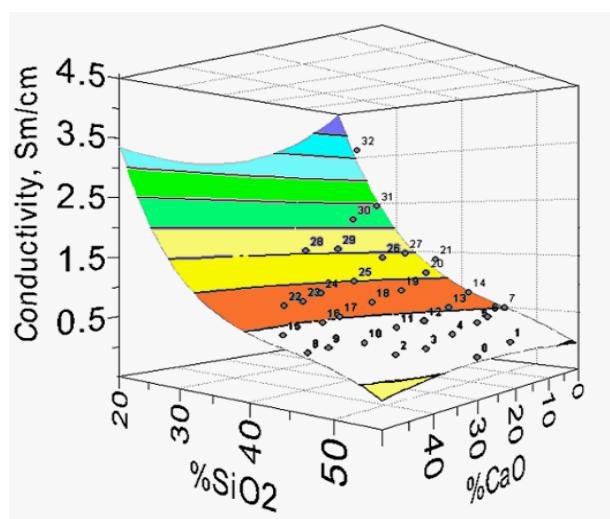


Figure 6. Measured values (points) of slag electric conductivity at 1500°C and predicted electric conductivity behavior (surface) calculated by equation (3) and metamodel

the authors are planning to apply the developed method of mathematic analysis for processing experimental data on viscosity of slag liquid-alloys in manganese ferroalloy production and estimation of result reliability. Mathematical expression of electric conductivity multiplied by dynamic viscosity can be received on the finishing stage. This is of interest for engineering computations of slag properties in manganese ferroalloy production.

Conclusions

1. Model-free mathematical analysis of experimental data on electrical conductivity of oxide (slag) liquid alloys of system MnO-SiO₂-CaO is carried out; conductivity as a function of chemical composition and temperature without involving any intermediate hypotheses, for example, determining the value of conductivity of cations Ca²⁺, Mn²⁺ and anticipated impact of anions - components SiO₄⁴⁻, Si₂O₇⁶⁻ is defined.

2. The standard exponential dependence of electrical conductivity of MnO-SiO₂-CaO system liquid-alloys on inverse temperature ($\ln(\chi) = \ln A - E / RT$) is computed; the results are presented in the form of correlation matrix with the corresponding correlation coefficients.

3. Interdependence of activation energy (E) and preexponential factor (A) is established. This correlation coefficient (+0.866) is more than that for any other correlation, for example, with chemical composition. Strong autocorrelation indicates significant relationship of E and A, and therefore they can not be considered as independent variables.

4. Four-dimensional graph of activation energy (E) dependence on the pre-exponential factor (A), MnO and SiO₂ content in the liquid-alloy is computed and presented; high activation energy values tend to associate with low MnO concentrations and high SiO₂ concentrations.

5. The method of yield surface (metamodelling) by Kriging is developed and implemented for description of dependence of electric conductivity activation energy on slag liquid-alloys. Expression for determination of oxide (slag) liquid-alloy electrical conductivity of system MnO-SiO₂-CaO is obtained.

6. It is determined that high values of slag melt electrical conductivity associate with low silicon and calcium oxide content, which corresponds to small values of activation energy and pre-exponential factor; electrical conductivity is independent in all slag liquid-alloys containing MnO more than 60% on relationship (bacytis) of

SaO/SiO₂.

7. Satisfactory conformity of the results with predicted data enables to use the obtained dependence for determination of slag liquid-alloys electric conductivity in the concentration areas of homogeneous compositions.

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Математический анализ экспериментальных данных электропроводности шлаковых расплавов системы MnO-SiO₂-CaO производства марганцевых ферросплавов

М.М.Гасик, В.С.Куцин, М.И.Гасик

Представлены результаты математического анализа экспериментальных данных об электропроводности гомогенных для заданной температуры составов шлаковых расплавов системы MnO-SiO₂-CaO. Установлено, что, применив многозадачную оптимизацию и поверхности отклика (метамоделирование), можно оценивать экспериментальные данные более адекватно и с большей достоверностью прогнозировать изменение свойств шлаков без участия гипотез и допущений о строении оксидных шлаковых расплавов.