MULTI-VARIATION ANALYSIS AND OPTIMISATION OF ELECTRICAL CONDUCTIVITY OF MnO-SiO_2-CaO SLAGS

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ABSTRACT

Physical properties of slags and their dependence on temperature and composition are of vital importance for ferroalloys processing. For electrical conductivity, viscosity, etc. several phenomenological and thermodynamic models have been earlier developed based on different approaches, such as optical basicity and others. In this work a model-free mathematical analysis is used for treatment of available experimental data for the MnO-SiO_2-CaO system for the whole composition range. Many fields in sciences and technologies make extensive use of high-dimensionality data, which are presented in the form of numerical tables. Visualizing these data through 2-D maps is an efficient way to discover regularities and extract valuable information. It is shown that using a multi-objective optimisation and response surface methodology (metamodelling) it is possible to approximate such experimental data adequately to be applied in ferroalloys making engineering practice.

1 INTRODUCTION

Electrical conductivity of molten slags is very critical for correct selection of ferroalloys furnaces operation. It is well known that dependence of electrical conductivity (and viscosity) on temperature is largely non-linear. There are different theoretical models of electrical conductivity of slags, based either on their treatments as ionic liquids (electrolytes) or more simplified phenomenological correlations such as approximation using Stockes-Einstein-Nernst equations

$$\eta \chi \sim aT^b \tag{1}$$

where η is dynamic viscosity,
χ is specific electrical conductivity.

This equation is based on relating Stockes-Einstein diffusion coefficient (mobility) to the same obtained by Nernst equation. It is self-evident that product of two exponential functions will depend on temperature in the similar fashion. However, in complex ionic melts it is difficult to assign specific values to parameters like “particle radius” or “number of particles per unit volume with specific charge”. Many silicate slags exhibit complicated oligomerisation of silicate networks where the “particle” definition makes little sense. It does not restrict equation (1) to provide good correlations for selected slags in some cases, but such correlations remain mostly artificial. The concept of optical basicity was intensively applied earlier, but as it was stated it is not scientifically justified for slags with transition metals.

In this work, another approach was applied to analyse experimental data on electrical conductivity of the liquid slags of the MnO-SiO_2-CaO system. The idea of the analysis is very simple – in most of the cases furnace maker and process developer do not need to know the science behind one or another model neither evaluate to which extent this or that model will be suitable for a particular ferroalloys manufacturing process. It would be very sufficient to know and predict the real values of electrical conductivity and its dependence on temperature and slag composition within the approved tolerances. The original set of data was taken from [1],[2] measured by a four-probe method at different temperatures within a wide composition range. Here the subset of these data is treated which is relevant to manufacturing of manganese ferroalloys (silicon-manganese, metallic manganese, high-

grade low-carbon ferromanganese). The data have been processed without any phenomenological or thermodynamic modelling restrictions.

2 EXPERIMENTAL DATA PRE-PROCESSING

Authors [1],[2] have calculated apparent activation energies of electrical conductivity using experimental dependence of conductivity vs. temperature. However, in [2] measured specific electrical conductivity χ was recalculated into equivalent conductivity Λ:

$$\Lambda = \frac{\chi V_m}{2(1 - N_{SiO_2})}, \tag{2}$$

where: V_m – liquid slag molar volume, m^3/mol,
N_{SiO2} – molar fraction of SiO_2.

Application of equation (2) was based on the assumption that electrical conductivity of slags of this system is ruled mostly by Ca^{2+} and Mn^{2+}, hence is the valence number 2 in equation (2). Silica was assumed to exist in more complex forms like SiO_4^{4-}, $Si_2O_7^{6-}$ etc. and its effect of electrical transport was neglected. The Λ data shown in [2] exhibits significant non-linearity vs. SiO_2 concentration or vs. the "manganese module" $t = N_{MnO}/(N_{MnO}+N_{CaO}) = N_{MnO}/(1 - N_{SiO2})$. Later analysis of these data [1] did not reveal such correlations of these plots with thermodynamic properties of these slags neither did show a clear dependence of the composition. It was also questioned, to which extent the assumption of basic +2 charge carriers only is valid within the whole composition range and temperatures studied. The charge transfer in electrolytes must obey electro-neutrality even if partial charge transfer numbers might be different for different cations and anions.

The CaO-MnO-SiO_2 system is known to have different solid phases in the practical temperature range. Fig. 1 shows an example of calculated cross-section at 1500°C where liquid state is shown in grey. One may see that use of "manganese module" *t* might be justified because its variation from 0 to 1 covers the whole liquid phase region within 45-65% SiO_2. However, if silica fraction would be fixed and *t* varied, the application of equation (2) would not be so evident.

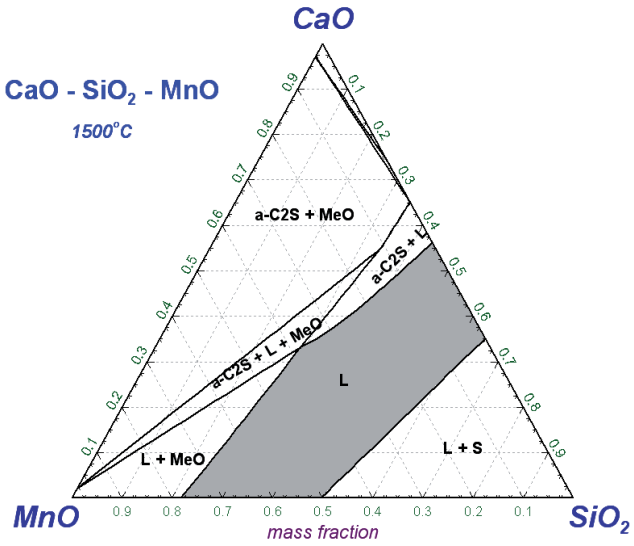

Figure 1: Cross-section of the system at 1500°C (FactSage 5.4.1, oxide slag database).

In this work the standard exponential dependence of electrical conductivity with temperature ($\ln(\chi) = \ln(A) - E/RT$) was assumed, with activation energy (E) and the pre-factor ($\ln(A)$). The original experimental data were plotted first as a cross-correlation matrix (Fig. 2) between percent concentrations of oxides components. The correlation between oxide constituents themselves was

not analysed because %MnO = 100 - %SiO_2 -%CaO by definition. Regression lines of E and ln(A) vs. components and vs. each other are shown on the upright part of Fig. 2 and respective correlation coefficients on the left down side of the diagonal.

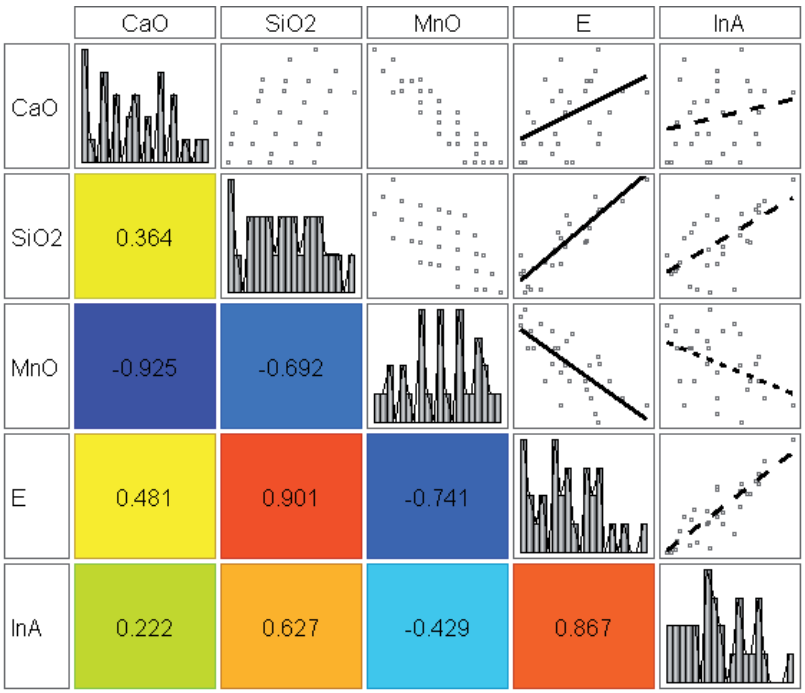

Figure 2: Cross-correlations matrix of the slag composition, activation energy and pre-factor (see text for details).

It can be seen that activation energy values have the highest correlation with silica content and than with MnO, whereas pre-factor correlation is weaker. An interesting feature is a strong autocorrelation (+0.867) between the E and ln(A) values which is larger than any other cross-correlation with composition. The existence of autocorrelation in any set of data is normally an indication of a strong relationship between the variables, but this effect analysis is outside of the scope of this work. This feature is shown more clearly in Fig. 3, which also reveals outliers – statistically "misplaced" points – in grey. It is difficult to justify the reason of this scatter; it may be due to experimental error.

To check this, a special statistical procedure [3,4] known as SMACOF (Scaling by Majorizing a Complicated Function) has been applied to original electrical conductivity data. It is a widely used method to solve the classical multidimensional scaling problem of minimizing the squared-error stress function. The principle of such relational perspective mapping, RPM [4], is schematically shown in Fig. 4. This method is very useful when dealing with new types of data where conventional analysis tools such as statistical modeling have difficulties because of lack of initial models. Data visualization, on the other hand, presents data directly to the human eyes, whose extremely high capability of pattern recognition is still unmatched by other analytical techniques [4]. Figure 5 suggests that indeed three experimental data points are located farther from the main dataset.

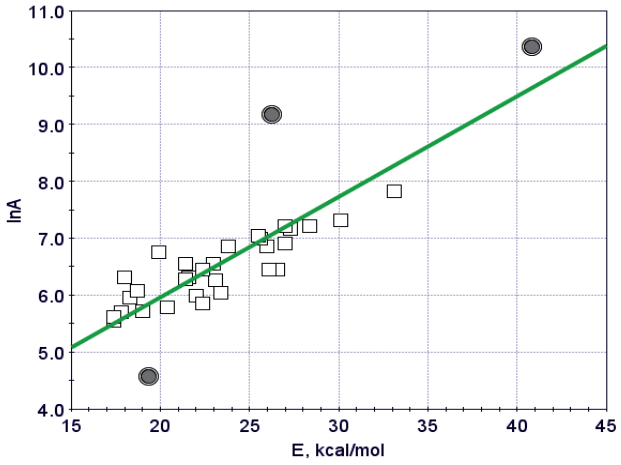

Figure 3: Correlation of the activation energy and pre-factor. “Outliers” points shown in grey.

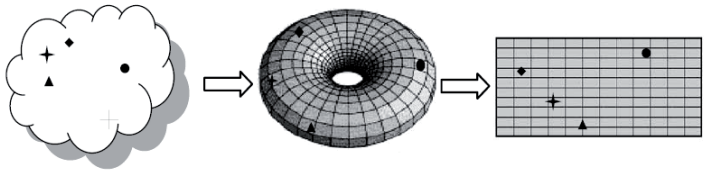

Figure 4: The principle of transformation of experimental dataset into a 2D map [4]: data are relocated on the binding surface and then projected onto 2D plot.

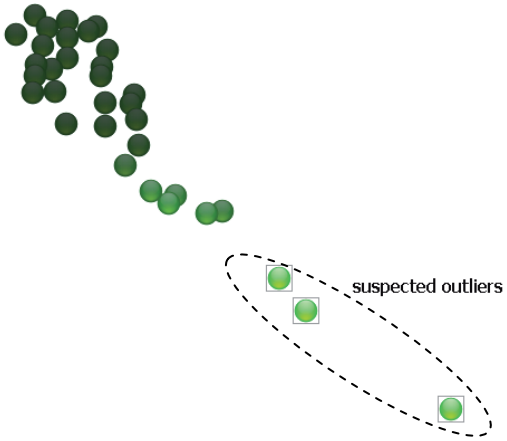

Figure 5: SMACOF plot of the original conductivity data (PRM algorithm uses Euclidean distances and there is no defined X-Y coordinate axes).

3 MULTI-VARIATE DATA ANALYSIS

The main interest in post-processing of the data is in revealing of possible correlations with slag composition. Figure 6 shows activation energy plotted in 4D also as function of slag composition as %MnO (diameter of the circles) and %SiO_2 (colour value). It may be seen that larger values of activation energy tends to group at low MnO and high silica slags.

Figure 6 gives rather clear indication that blue (low silica) and larger (high MnO) points represent slags with both lower activation energy and the pre-factor. It is important that no any modelling

assumption has been done – all these data are extracted directly from experimental measurements (which, of course, are further assumed to be free of any essential systematic error or deviation).

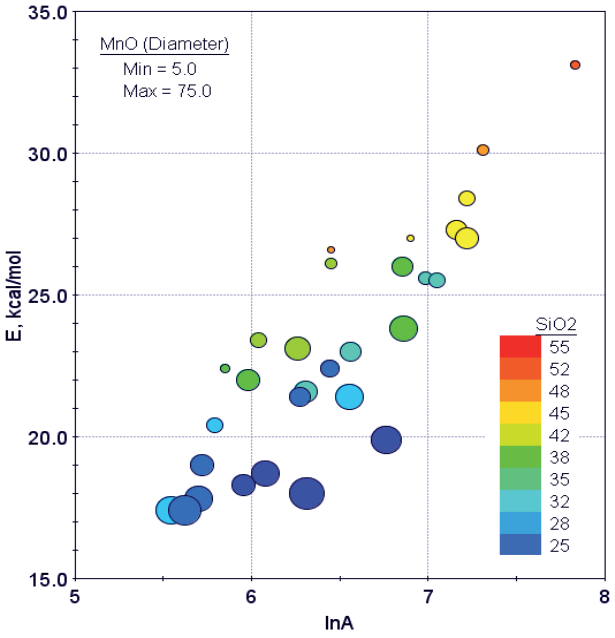

Figure 6: Correlation trend of activation energy, pre-factor and slag composition.

If a reliable functional dependence of activation energy from composition would be obtained, electrical conductivity of these slags could be thus reasonably approximated by equation:

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

where activation energy is expressed in kcal/mol. However, due to clear non-linearity, conventional polynomial or multi-function fitting of E to composition inputs does not result in reasonable fit (even when weighted residuals are small, extrapolation of such fits usually result in non-physical values such as negative E at higher CaO contents).

In this work, another approach - a response surface method (RSM), also known as metamodelling - was used to assess the E dependence on slag concentration. The RSM was performed on the experimental data set with a dedicated software. Several methods were exploited and finally a rather good fit was obtained using Kriging method [5]. The Kriging behaviour is controlled by a covariance function, called a variogram, which rules how varies the correlation between the values of the function at different points. A function can be of different roughness or it can exhibit different ranges of variation, affected by noise - all these features can be resumed in a variogram model [5].

The variogram range of the covariance function corresponds to a characteristic scale of the problem. If the distance between two points is larger than the range, the corresponding outcomes should not influence each other (completely uncorrelated). Range is inversely related to the number of oscillations of the function. Small ranges mean sudden variations, while large ranges mean very regular trends, with very few oscillations. The variogram sill corresponds to the overall variability of the function. The gap between the values of very distant points should be of the same scale of magnitude of the sill [5]. This seems particularly advantageous on dataset with unknown errors, because all the points validity and deviations from the real values cannot often be completely justified. In the calculations input variables (%SiO_2 and %CaO) were not normalised, and the strategy used was to perform auto-fitting minimising leaving-one-out error with automatic variogram type. Traditional fitting procedures, which rely on Gaussian method, in many cases might lead to wrong forecasting because Gaussian functions are infinitely many times differentiable. This results in “oversmoothing” of

the objective function. To avoid oversmoothing, a metamodel with Matèrn variograms of type 5/2 was applied. It has an intermediate smoothness between Gaussians and pure exponential - Matèrn 5/2 model is twice differentiable [5] and is based on the “gold sectioning” of the data range with Euclidean distances relative to the mean values.

The results are shown in Fig. 7 together with experimental points. As one may see this RSM provides an adequate description of behaviour of E over the compositional range of interest and it does not fail when being extrapolated to other compositions.

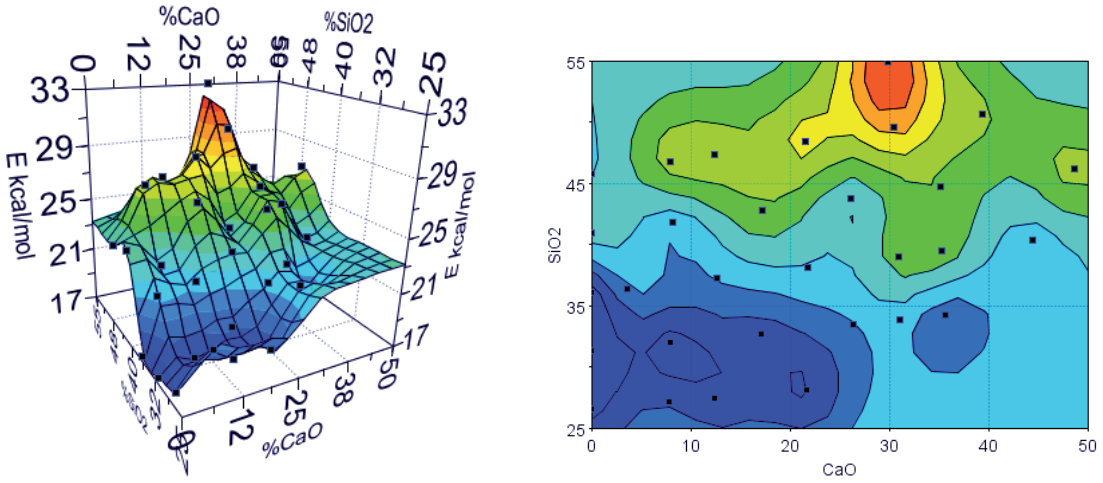

Figure 7: Kriging RSM fitting of activation energy to slag composition (squares are experimental points), right picture represents the top view of the 3D plot.

For the activation energy dependence, a principal component analysis (PCA) was performed using the same software [6]. This plots projections in the reduced 2D space defined by the first two principal components (eigenvalues) marked as PC1 and PC2 respectively, Fig. 8. In this case PC1 = $0.953 \cdot X_1 + 0.257 \cdot X_2 + 0.163 \cdot X_3 + 0.0126 \cdot X_4$ and PC2 = $-0.302 \cdot X_1 + 0.859 \cdot X_2 + 0.389 \cdot X_3 + 0.0481 \cdot X_4$, where X_1 - %CaO, X_2 - %SiO_2, X_3 – E, and X_4 – ln(A), with all variables scaled from 0 to 1 by the range.

The arrows show the relative contribution of the original variables to the variability – the longer is the arrow, the higher is the strength of the contribution. Arrow collinear to the PC1 or PC2 axes contributes mostly to that variable only. From Fig. 8 it is seen that arrow of activation energy (E) is more collinear with SiO_2 than with CaO and thus SiO_2 additions provides the most contribution to activation energy.

4 ANALYSIS OF ELECTRICAL CONDUCTIVITY

The data of electrical conductivity analysed in this study were collected for 1673 K. These points were plotted as function of slag composition, Fig. 9 in 3D and as a normalised bubble plot, Fig. 10. The area beyond the line of 0% CaO is a pure visual mathematical extrapolation and should not be considered. These data can be compared with similar dependence of activation energy (Fig. 7). Here the higher electrical conductivity is obtained at low silica, low CaO slags (approaching ~75% MnO). This corresponds to the lowest values of activation energy and average values of the pre-factor (Fig. 7).
The conductivity remains high in all slags with >60% MnO irrespectively of CaO/SiO_2 ratio, Fig. 10. It is noteworthy that these data are again purely experimental and no any assumptions about the mechanism of electrical charge transfer have been imposed. The similar analysis made on the electrical conductivity dataset allows getting reasonable predictions with RSM (Fig. 11).

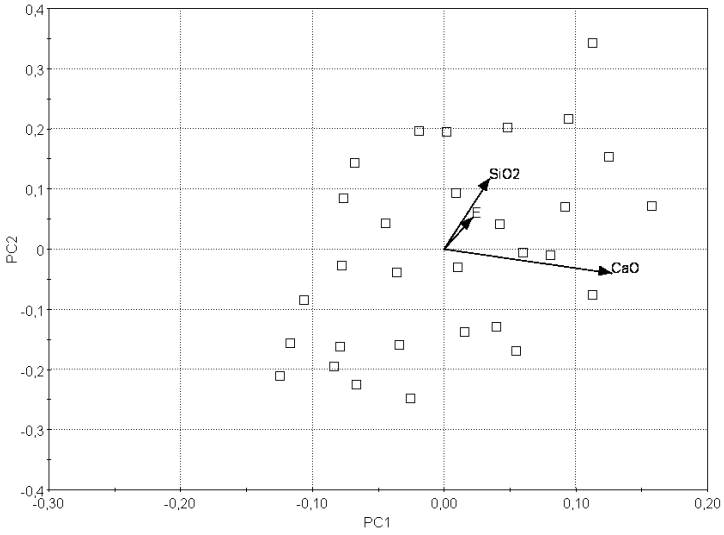

Figure 8: Principal component analysis (PCA) of the activation energy variation (see text for details).

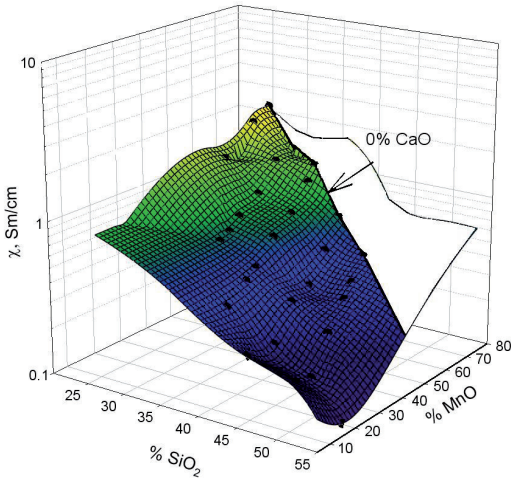

Figure 9: Measured and approximated electrical conductivity at 1673 K

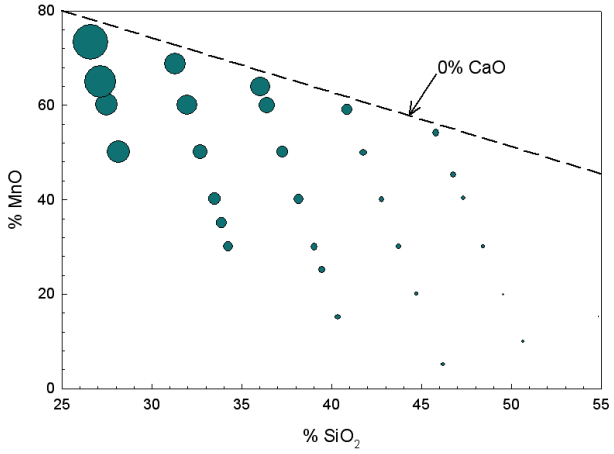

Figure 10: Normalised electrical conductivity (maximal size = 1) at 1673 K (see text)

The data could be displayed also in the standard triangular plot (Fig. 12) for the range of compositions of interest. Here experimental points (squares) are normalised in the respect to the largest one (as for Fig. 10) and the respective RSM function is categorised as grey value (lightest values correspond to largest electrical conductivity). Eventually iso-conductivity lines could be constructed, but this is not needed for RSM application because the objective function is already digitized (in this example it was exported as an Excel VBA function which might be embedded in the worksheet).

For engineering and research practice application of the algorithm shown might give valuable additional information about the experimental data structure, hidden cross-correlations, proper higher-dimensionality links and finally provide a model for qualitative prediction of the parameters of interest beyond experimental field. This task is getting more challenging when number of variables is large and the data mining approach is not evident.

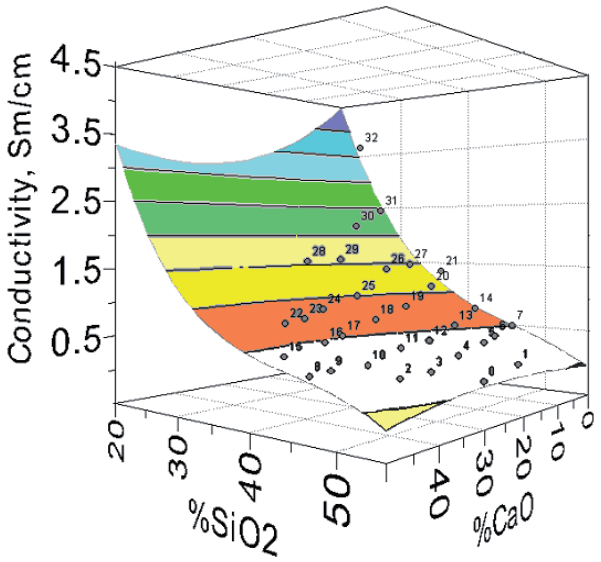

Figure 11: Experimental (numbered points) and RSM predicted electrical conductivity of slags at 1673 K.

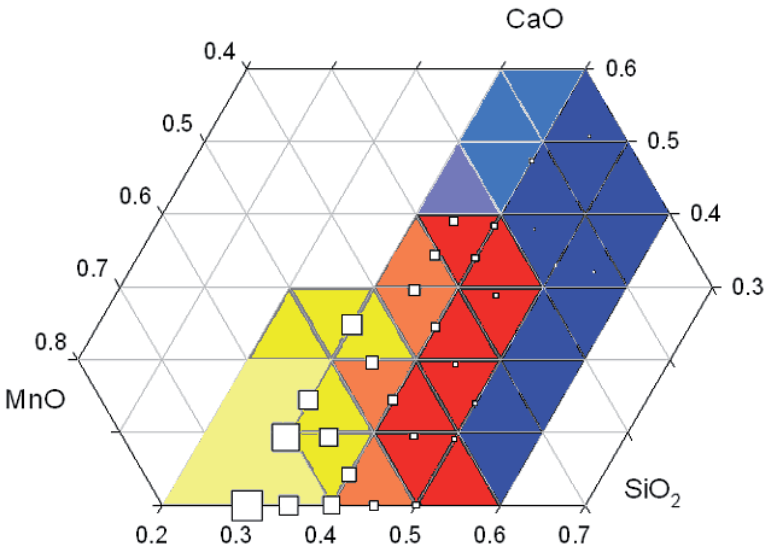

Figure 12: Experimental (normalised squares; maximal = 1) and RSM predicted electrical conductivity categories for slags at 1673 K vs. molar compositions. Colour reflects respective conductivity range.

5 CONCLUSIONS

In this work, new computational mathematical methods were applied to post-processing of the experimental data set of electrical conductivity of the liquid slag of the MnO-SiO_2-CaO system. It was shown that such methods are able to discover hidden correlations between parameters and to evaluate experimental data critically in respect to outliers and possible errors. This analysis is model-free i.e. does not postulate any slag model neither require any fitting parameters to provide interpolation and extrapolation. It is important that experimental data re pre-processed using proper visualization to examine possible errors and to estimate possible data structure. This is particularly

needed where there is limited knowledge about the experiments themselves. Analysis of multi-dimensional data requires some mathematical skills and experience but this is generally achievable with existing dedicated software.

It was shown that with a multi-variation analysis, principal components analysis (PCA) and the response surface method (RSM metamodelling) it is possible to approximate such experimental data adequately to be applied in ferroalloys making engineering practice. This has been demonstrated for electrical conductivity, but it eventually applies to any other property or their combinations. It is however very important to generate correct and consistent set of experimental data with proper design of experiment strategy. One may use limited number of tests to get a basic set of data which could be metamodelled into a field of virtual experiments, and these predictions might be used for making key measurements for both RSM validation and for narrowing search field for optimal slag properties and process conditions.

6 REFERENCES

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