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Investigation of alkali corrosion resistance of potassium aluminosilicates using statistical techniques

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Abstract

Alkali aluminosilicates are potential materials for high temperature applications under alkali load. This study investigated the alkali corrosion behaviour of alkali aluminosilicates originating from the system K_2O-Al_2O_3-SiO_2 using mixture designs. The aim was to identify compositional regions showing alkali corrosion resistance and to establish a model for predicting the corrosion behaviour of alkali aluminosilicates under alkali corrosive conditions. Such a model is useful to predict the corrosion behaviour for example due to compositional variations in the raw materials and is important for a potential industrial production process. The mathematical results were optimized by augmenting the number of points in the lattice and dividing the experimental region into two areas. Finally, an established model can be used to predict the corrosion behaviour in a sub region of the ternary system K_2O-Al_2O_3-SiO_2.

Keywords: E. Refractories; Alkali corrosion; Alkali aluminosilicates; Design of experiments; $KAlSiO_4$

1. Introduction

High temperature processes need specific materials to meet the requirements in different industrial aggregates. One of the problems in these aggregates is alkali corrosion of refractory materials. The alkali compounds originate from energy carriers and raw materials used in the production process [1–3]. The consequences are either chemical reactions between the furnace lining and the alkali compounds leading to spalling due to the lower density of the reaction products or the formation of melts caused by the fluxing effect of alkali compounds [4,5]. Consequently, both effects deteriorate continuously the lining. This severe corrosion behaviour started to occur dramatically often when secondary fuels with higher alkali content substituted conventional fuels [6,7]. Therefore, there is an urgent need for the development of new materials with higher alkali corrosion resistance.

One approach is to use the crystalline reaction products formed during the corrosion process as refractory materials [8,9]. Common reaction products are ternary alkali aluminosilicates such as feldspars, feldspathoids, compounds of the stoichiometry $KAlSiO_4$ or modifications of the nepheline-group [4]. These compounds form under high temperature conditions with high alkali contents and are thus considered to be stable at elevated temperatures. Furthermore, some of these compounds have remarkably high melting points [10]. Therefore, they are considered to provide sufficient refractoriness in an alkali corrosive atmosphere. Previous studies showed that materials following this approach resulted in the desired alkali corrosion resistance and were recommended as worthwhile for further inquiries [8,9]. A previous study concentrated on materials with the stoichiometric composition of $KAlSiO_4$ and deviations thereof [9]. Alkali corrosion was tested using a simple test method by simulating alkali attack with alkali salts at elevated temperatures. An optimized material with a lower K_2O content compared to $KAlSiO_4$ yielded the best alkali corrosion behaviour. It was chosen for upscaling to produce formed samples for basic characterizations. An analysis of

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variance (ANOVA) [11,12] revealed that the chemical composition of the material determined the alkali corrosion behaviour.

Designed experiments are useful to identify such cause-and-effect relationships between a response variable (e.g. the corrosions resistance) and one or several controllable variables called factors (e.g. the chemical composition) [11,12]. In a first step the systematic change of the factors allows to separate their effects. Secondly, an empirical model can be established based on the experimental data using multiple regression analysis to describe the response surface and to predict values of the response variable within the investigated experimental region [12].

Mixture designs are a special method of designed experiments when the response variable depends solely on the fractions x of the components within the system [13], i.e. $x_1+x_2+\ldots+x_n=1$, where n is the number of components in the system. There are numerous examples in the literature using this technique for a successful optimization of various problems [14–16].

The investigations are based on a certain number of points positioned regularly in the examined experimental region [13]. This array of points is called a "lattice". The chosen lattice design depends on the purpose of the study and the maximum degree of the final model. A typical approach to describe empirically the relationship between factors and a response variable are multiple linear regression models based on polynomials. The number of terms in the polynomial is a function of the number of investigated components and the degree of the equation. First degree terms $\beta_i x_i$ express the effect of pure components i on the response variable, summarized in Eq. (1) (linear model). When the response to the components is not strictly linear, additional terms $\beta_{ij}x_i x_j$ describing the effect of the binary blends are added. The resulting model is called the second degree model (Eq. (2)). Furthermore, a third degree term $\beta_{ijk}x_i x_j x_k$ can be introduced in the model to describe the influence of ternary blending (special cubic model, Eq. (3)). A more precise description of binary blend effects is possible by adding terms of the structure $\delta_{ij}x_i x_j(x_i-x_j)$ resulting in the full cubic model (Eq. (4)). Models with terms of even higher degree can be applied to describe complex problems [13].

$$f=\sum_{i=1}^{n}\beta_i x_i \tag{1}$$

$$f=\sum_{i=1}^{n}\beta_i x_i+\sum_{i<j}\sum_{j=2}^{n}\beta_{ij}x_i x_j \tag{2}$$

$$f=\sum_{i=1}^{n}\beta_i x_i+\sum_{i<j}\sum_{j=2}^{n}\beta_{ij}x_i x_j+\sum_{i<j}\sum_{j<k}\sum_{k=3}^{n}\beta_{ijk}x_i x_j x_k \tag{3}$$

$$f=\sum_{i=1}^{n}\beta_i x_i+\sum_{i<j}\sum_{j=2}^{n}\beta_{ij}x_i x_j+\sum_{i<j}\sum_{j=2}^{n}\delta_{ij}x_i x_j(x_i-x_j)+\sum_{i<j}\sum_{j<k}\sum_{k=3}^{n}\beta_{ijk}x_i x_j x_k \tag{4}$$

The regression coefficients β_i, β_{ij}, δ_{ij} and β_{ijk} are estimated by the method of least squares which minimizes the sum of squares of the deviations of the observations y_u from the value $\hat{y}_u$ which is predicted by the chosen regression model f (Eq. (5)) [12,17]. u refers to the individual observations with $u=1\ldots U$, where U is the total number of observations. By minimizing the sum of least squares according to Eq. (5) the estimates of the regression coefficients for each (or for a certain) regression model can then be calculated.

$$\sum_{u=1}^{U}(y_u-\hat{y}_u)^2\rightarrow Min \tag{5}$$

In the next step the available models are evaluated by analysis of variance (ANOVA). The ANOVA separates the deviation of the observed values y_u of a response variable from the overall mean $\bar{y}$ into two parts [11–13,17]: the regression sum of squares (SSR) and the error sum of squares (SSE). The SSR describes the deviation of the predicted value $\hat{y}_u$ of the model from the overall mean. The SSE then describes the deviation of the observed value y_u from the predicted value $\hat{y}_u$ of the model (Eqs. (6) and (7)).

$$SSR=\sum_{u=1}^{U}(\hat{y}_u-\bar{y})^2 \tag{6}$$

$$SSE=\sum_{u=1}^{U}(y_u-\hat{y}_u)^2 \tag{7}$$

From these sums of deviations the mean regression sum of squares (MSR) and the mean error sum of squares (MSE) are calculated using the related degrees of freedom. The degrees of freedom describe the number of deviations which can vary. The remaining deviations are automatically determined due to the estimates of the specific parameters (overall mean $\bar{y}$, regression coefficients in the model evaluated). Then, the mean regression sum of squares MSR is determined by MSR=SSR/(p–1) and the mean error sum of squares MSE is calculated by MSE=SSE/(U–p) with p as the number of regression coefficients in the evaluated model. Finally, MSE and MSR are used to formulate a test statistic F_o (Eq. (8)) for testing the statistical significance of the regression model and for testing the description of the response variable.

$$F_0=\frac{MSR}{MSE} \tag{8}$$

The comparison of the resulting test statistic F_o to the tabled values for $F_{(p-1,U-p,\alpha)}$ of the F-distribution shows the significance of the regression model at a level of significance of α.

In case when several models are considered to be statistically significant they can be tested on their ability to explain the development of the response variable in the investigated experimental region. The coefficient of determination R^2 (Eq. (9)) measures the proportion of the variability of the response variable explained by the regression model using the error sum of squares (SSE) and the total sum of squares (SST) [12].

$$R^2=1-\frac{\sum_{u=1}^{U}\left(y_u-\hat{y}_u\right)^2}{\sum_{u=1}^{U}\left(y_u-\bar{y}_u\right)^2}=1-\frac{SSE}{SST} \tag{9}$$

Furthermore, an adjusted coefficient of multiple determination R_A^2 is used to evaluate the goodness of fit of a regression model. It describes the reduction of the estimated error variance of a