Predicting Oxide Activities in CaO-Al$_2$O$_3$-SiO$_2$ System by Computer Model

Napovedovanje aktivnosti oksidov v sistemu CaO-Al$_2$O$_3$-SiO$_2$ z računalniškim modelom

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The most important metallurgical effects of ladle treatment of aluminium - killed steels with calcium, are associated with the modification of alumina inclusions. For the development of the deoxidation - control model for inclusions, the thermodynamic slag model, based on the Gibbs energy minimization and modelling approaches postulated from Hastie et al., was used to calculate component oxide activities in the system CaO-Al$_2$O$_3$ and part of the system 3CaO.Al$_2$O$_3$-SiO$_2$, 12CaO.7Al$_2$O$_3$-SiO$_2$ and CaO.Al$_2$O$_3$-SiO$_2$ at 1500°C and 1600°C.
Key words: Slag activities, model computations, Gibbs energy minimization

Najpomembnejši metalurški učinki pri uporabi kalcija za obdelavo jekel pomirjenih z aluminijem so povezani z modifikacijo aluminatnih vključkov. Pri razvoju modela za kontrolo vključkov smo uporabili termodinamični model, ki sloni na Gibbsovem modelu minimizacije energije in postulatu, ki ga je postavil Hastie et al. Izračunavanja aktivnosti oksidnih komponent smo izvršili za sistem 3CaO.Al$_2$O$_3$-SiO$_2$, 12CaO.7Al$_2$O$_3$-SiO$_2$ in CaO.Al$_2$O$_3$-SiO$_2$ pri temperaturi 1500°C in 1600°C.
Ključne besede: aktivnosti žlinder, modelna izračunavanja, Gibbsova energija minimizacije.

1. Introduction

In last two decades calcium-based additions are made to molten steel not only for deoxidation and/or desulfurisation proposes, but also for the control of inclusion composition and morphology. The ladle metallurgy offers today excellent possibilities to control of the cleanness and quality of steels. The most important metallurgical effects of ladle treatment of aluminium-killed steels with calcium, are associated with the modification of alumina inclusions preventing his precipitation during the continuously casting known as *nozzle clogging process*. Also the role of the syntetic slags CaO-Al$_2$O$_3$-SiO$_2$ for the secondary refining of steel is growing dramatically because of it's excellent refining capabilities. In order to put inclusion engineering into practice, it is essential that the equilibrium relationship between the liquid steel and the corresponding inclusion should be determined. With suitable selection of the deoxidation practice (changing ratio Ca/Al) is possible to avoid nozzle clogging, ensuring inclusions with melting points lower than the steel melt temperature.

In this paper are presented equilibrium thermodynamic activity of the Al$_2$O$_3$, CaO, and SiO$_2$ in system CaO-Al$_2$O$_3$-SiO$_2$, determined with new **Gibbs Energy Minimization Model - GEMM** (The equilibrium calculation in the GEMM program is a minimization of the integral Gibbs free energy using a Langrangian multiplier method for the constraints) and discussed in relation to their use in deoxidation and calcium treatment control.

2. Thermodynamic model of oxide phase equilibria – GEMM

Many thermodynamical models are developed in last two decades for the investigation of multiphase equilibria and for thermodynamic predictions of multicomponent high-temperature oxide systems[1-3]. Calculations involving thermodynamic equilibria in multi-phase oxide systems are extremely time consuming, even in the systems with relatively few components. In recent years, there has been rapid progress in the use of thermodynamic models achieving better understanding of many metallurgical, ceramical and chemical systems of commerical significance.

This progress has been made possible largely by developments in computer software technology as well as the increasing availability of reliable and comprehensive thermodynamic values compared with *"hand"* calculations which have traditionally been assigned to specialists.

A new modelling approach for thermodynamic predictions of multiphase high-temperature oxide systems developed by J.W. Hastie and D.W. Bonnell[3] has been extended and applied for the investigation of the binary and ternary systems CaO-Al$_2$O$_3$ and CaO-Al$_2$O$_3$-SiO$_2$. Well-known examples of solution models in current use include, ideal, regular, and the molecular-level associated liquid or cluster models[4-7]. The basic approach used in the GEMM prediction model is a description of non-ideal mixture and the formation of complex liquids and solids as mixing componenets. This model has a thermodynamic basis and does not rely on assumed molecular or ionic entities in the liquid phase. The liquid components are not independent molecular species, but are essentially subphases that serve as models for the local associative order-an idea that Schenk himself greatly expanded some 50 years ago[3].

Although the components are included individualy, it is assumed that in most cases, the components form short range order, and do not necessarily represent discrete molecular, ionic or other structural entities. The component and complex-component oxides formed are assumed to mix ideally, in accordance

with Raoult' law. Hence, thermodynamic activities and apparent mole fractions (X^*) are equivalent quantities for this model.

In the GEMM-prediction model, the thermodynamic activity of oxides CaO, Al₂O₃, and SiO₂ can be calculated from the corresponding thermodynamic functions. The modelling approach has been validated by comparison with experimental activity data, obtained from Taylor[8], Kay[9], and recently published data from Fujisawa[10], and Nagata[11]. While the thermodynamic data are incomplete they are still sufficiently extensive to allow their use in the performance of common thermodynamical calculations for many high-temperature slags and other systems. Good agreement between the model predictions and experimental activity data is obtained. The utility of even sparse experimental data can, in principle, be greatly enhanced by GEMM optimization techniques.

3. Thermodynamic data bases

Before actual calculations can begin, the necessary thermodynamic data must be collected. For most oxide systems relevant to industrial steelmaking practice, the experimental thermodynamic data base are often a variety of somewhat obscure sources or are incomplete.

The CaO-Al₂O₃ and CaO-Al₂O₃-SiO₂ systems are an exception, in that there is an adequate thermodynamic data base which can be applied to test the model computations. Such a thermodynamical optimization technique offers the important benefit that it can drastically reduce the need to conduct costly experiments. The Gibbs free energy data for the corresponding oxide phase at 1600°C are given in **table 1**.

Table 1: Compounds Gibbs energy of formation, negative (kJ/mol) (s)=solid, (l)=liquid

Tabela 1: Prosta tvorbena energija nekaterih oksidov, minus (kJ/mol)

Components	1873 K(s)	1873 K(l)
Al₂O₃	1089.81	1065.70
CaO	431.08	427.47
SiO₂	578.50	–
3CaOAl₂O₃	2454.77	–
12CaO7Al₂O₃	13222.86	13280.00
CaOAl₂O₃	1564.62	1564.33
CaO2Al₂O₃	2693.83	2688.12
CaO6Al₂O₃	7063.18	7051.92

The GEMM-computer program used for calculation of the equilibrium composition, and hence activities, utilizes a data base made up of Gibbs energies of formation $\Delta(G_f)$ as a funciton of temperature (T). The free energies of formation $\Delta (G_f)$ are either known or can be estimated for these complex component liquids and solids.

The data for most oxides were obtained mainly from data base made by J. Hastie and Bonnell[12]. In a few instances, the coefficients to the $\Delta (G_f)$ equation have been re-evaluted using new thermodynamic data obtained in the literature.

4. Results

CaO-Al2O3 System

The CaO-Al₂O₃ system is one of the fundamental systems of the calcium-based slags and non-metallic inclusions, and there have been many reports on the thermodynamics of this system.

Much of the published information on the thermodynamic properties for some binary aluminates has been based on work

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conducted and published in 1960's. Extrapolation of these data to steelmaking temperatures may introduce large errors, especially for a particular composition range.

The CaO and Al₂O₃ activity data shown in **figure 1** are consistent with the bulk of literature experimental data at T=1600°C. Electromotive force (emf) and cell-activity data have recently been obtained by Fujisawa et al[10] covering a wide range of compositions. Our model activity data at T = 1500°C have been compared with recently published data by Nagata et al[11] and as is shown in **figure 2**. Good agreement between the model prediction and experimental activity data for a wide range of composition is demonstrated.
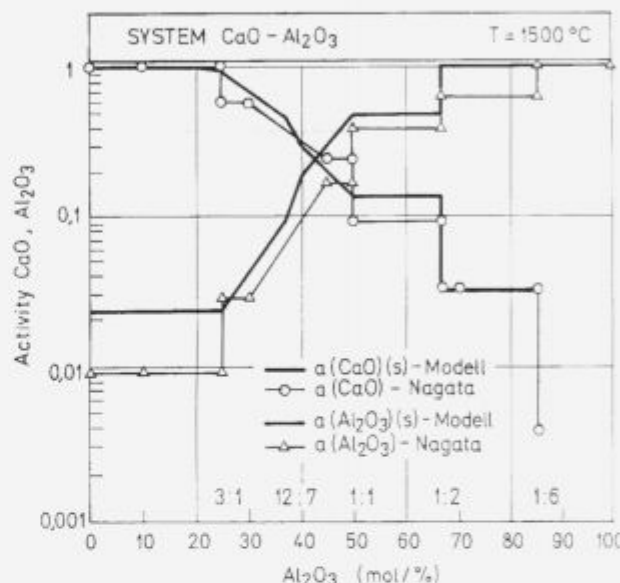

Figure 1: Model dependance of computed activity data in CaO-Al₂O₃ at T=1500°C.

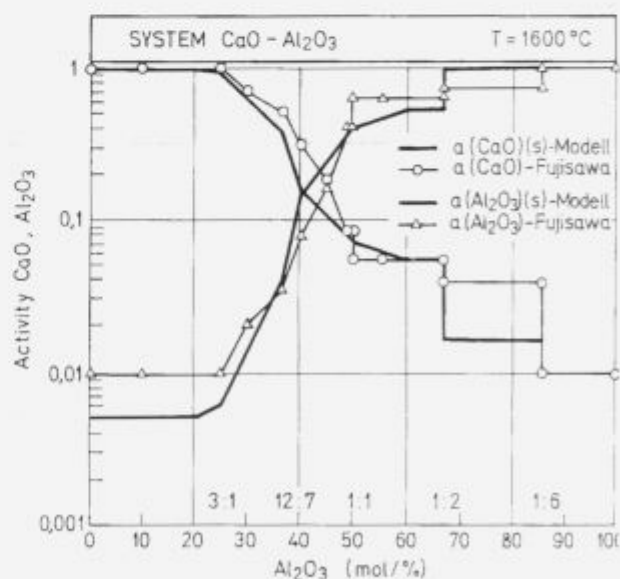**Slika 1:** Modelna izračunavanja aktivnosti oksidov v sistemu CaO-Al₂O₃ pri T=1500°C

Figure 2: Model dependance of computed activity data in CaO-Al₂O₃ at T=1600°C

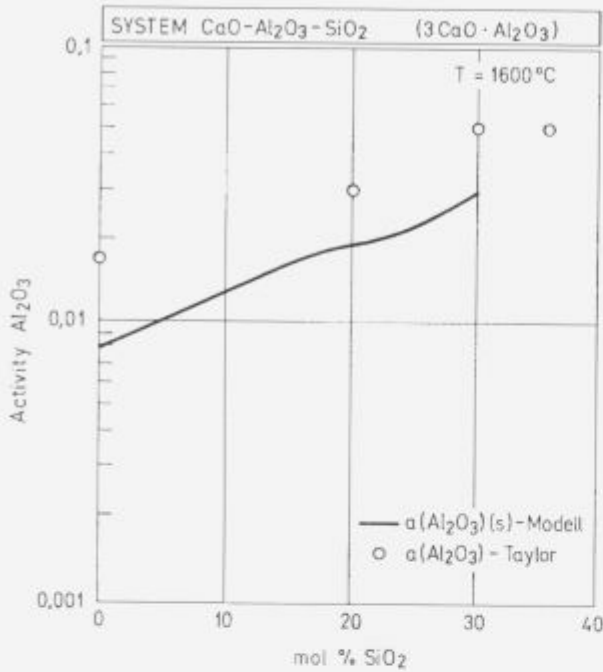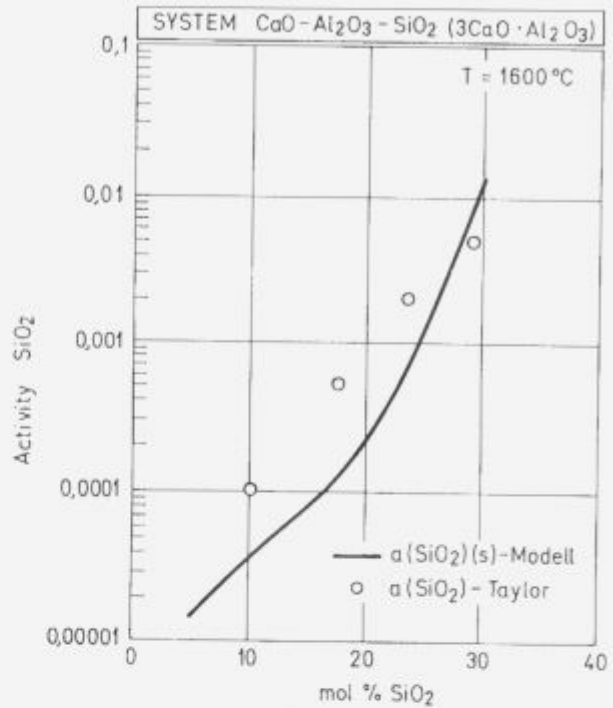**Slika 2:** Modelna izračunavanja aktivnosti oksidov v sistemu CaO-Al₂O₃ pri T=1600°C

Fig. 3a

Fig. 3c

Figure 3: Model computed data of CaO, Al₂O₃ and SiO₂ in CaO-Al₂O₃-SiO₂ system for 3CaO.Al₂O₃ composition and T=1600°C

Slika 3: Modelna izračunavanja CaO, Al₂O₃ in SiO₂ v sistemu CaO-Al₂O₃-SiO₂ za sestavo 3CaO.Al₂O₃ pri T=1600°C
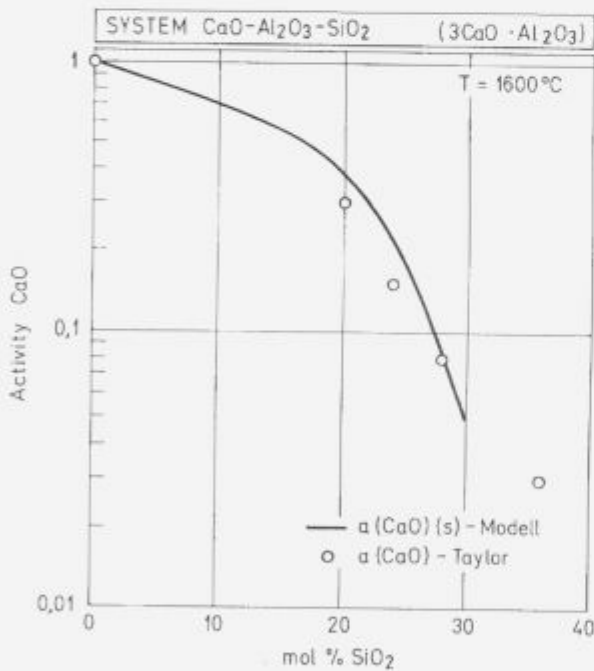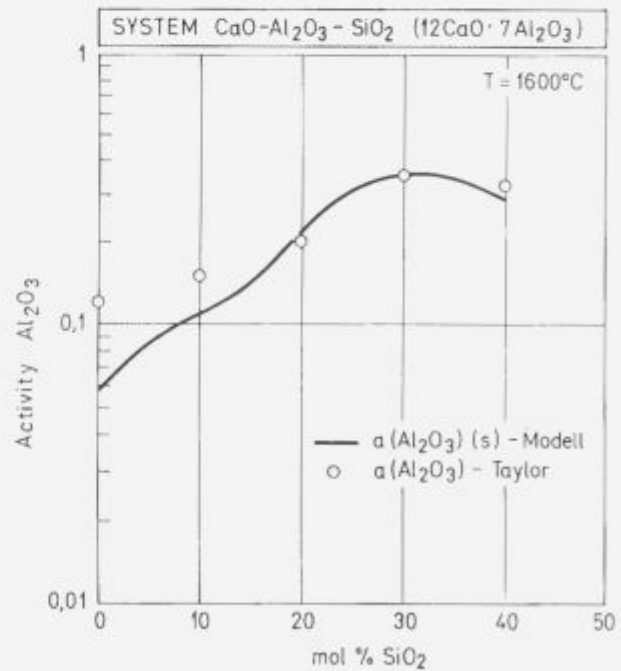

Fig. 3b

Fig. 4a

CaO-Al2O3-SiO2 System

The control and prevention of multiphase in CaO-Al₂O₃-SiO₂ and a suitable deoxidation practice should be applied to avoid undesirable alumina inclusions, they are not deformable and, besides, provoke tundish nozzle blockage problems. In order to determine oxygen und sulphur contents in molten steel and the conditions for aluminate and solid sulphide coprecipitation during casting, the knowledge of the activity of CaO, Al₂O₃ and SiO₂ in molten slag and inclusions is important. One of the main advantages in the used model is the treatment as a high order system at high temperatures where extrapolation of thermodynamic data may introduce large errors. For CaO-Al₂O₃-SiO₂ system, several experimental studies of activity measurement and phase - diagram determination are reported in the literature[8]. But, because of experimental difficulties, large discrepancies are observed between different experimental works. Tha activity of
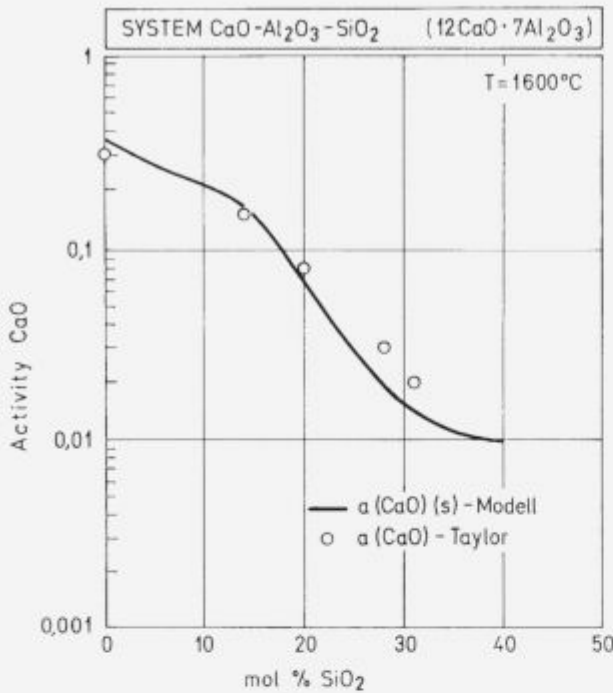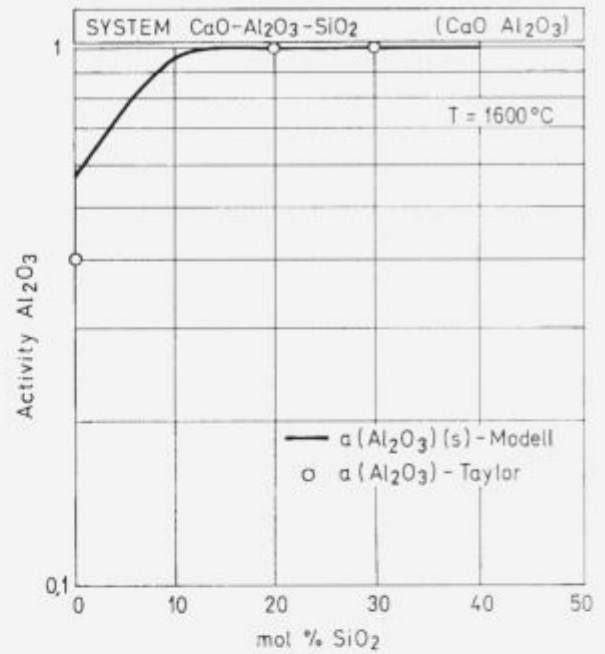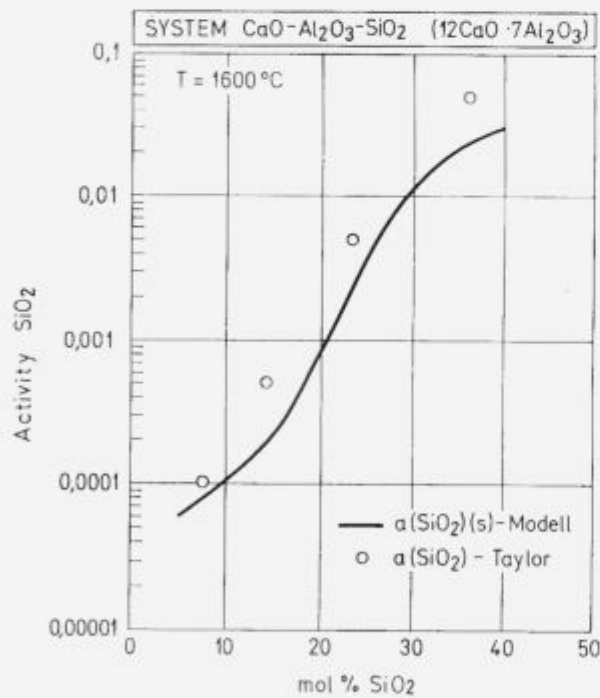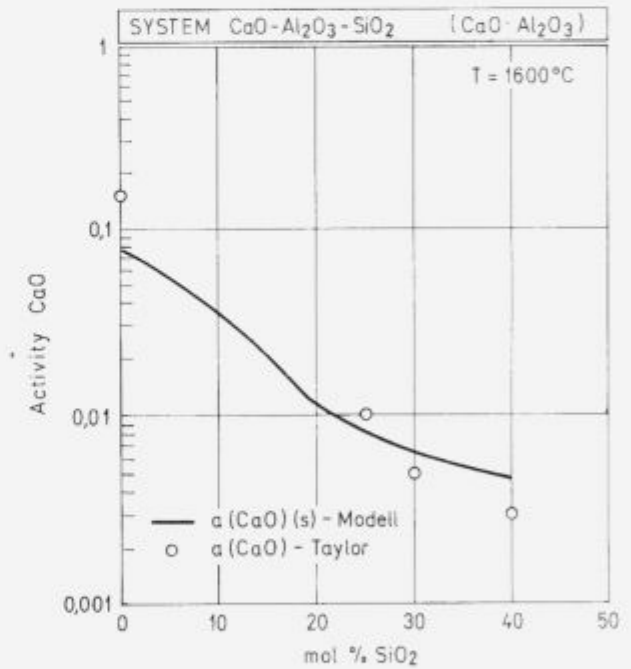
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Fig. 4b

Fig. 5a

Fig. 4c

Fig. 5b

Figure 4: Model computed data of CaO, Al₂O₃ and SiO₂ in CaO-Al₂O₃-SiO₂ system for 12CaO.7Al₂O₃ composition and T=1600°C

Slika 4: Modelna izračunavanja CaO, Al₂O₃ in SiO₂ v sistemu CaO-Al₂O₃-SiO₂ za sestavo 12CaO.7Al₂O₃ pri T=1600°C

CaO, Al₂O₃, and SiO₂ in CaO-Al₂O₃-SiO₂ molten slag at 1500°C was measured by Rein and Chipman in 1963 and 1965[13]. The activity data determined the activity of silica by equilibrium with a metallic phase, of carbon - saturated iron with silicon in solution. By integration of the Gibbs - Duhem law, the activities of lime

and alumina were calculated in all of liquidus domains. The compositions are expressed in mole fractions of CaO, AlO₁.₅ and SiO₂. The reason for choosing AlO₁.₅ rather then Al₂O₃ is because in the basic melts, Al₂O₃ give rise to two foreign ions AlO²⁻, wheres SiO₂ gives rise only to one SiO⁴⁺. Thermodynamic activities calculated using Gemm - computer program are shown in **figures 3 - 5**. Experimental activity data for the CaO-Al₂O₃-SiO₂ system is particularly sparse and disparate[8,13,14]. Very good agreement between the model and experiment data for the silica-
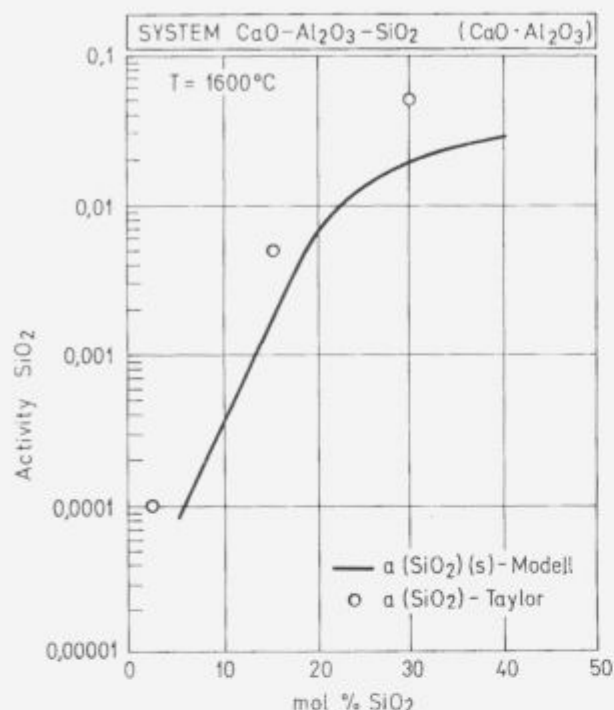
Fig. 5c

Figure 5: Model computed data of CaO, Al₂O₃ and SiO₂ in CaO-Al₂O₃-SiO₂ system for CaO.Al₂O₃ composition and T=1600°C

Slika 5: Modelna izračunavanja CaO, Al₂O₃ in SiO₂ v sistemu CaO-Al₂O₃-SiO₂ za sestavo CaO.Al₂O₃ pri T=1600°C

activities and computed thermodynamic activity data for Al₂O₃ and CaO at 1600°C is demonstrated.

5. Conclusion

The Gibbs energy minimization model (**GEMM**) is used with the corresponding thermodynamical data base to calculate the predicted composition of solids, liquids (non-ideal solutions), and the vapour phase.

The calculated composition of the CaO, Al₂O₃, and SiO₂ are taken as the activity. Numerous comparisons between model and the experimental activities in the systems CaO-Al₂O₃ and CaO-Al₂O₃-SiO₂ at different temperatures have confirmed the realiability of this approximation.

Considering the large number of the data base components, and the cumulative errors in the thermodynamic functions, the possibility exists that the present data base is not unique.

However, as has been pointed out by J. Hastie and D. Bonnell[3], the author expects that some future modifications of the data base will be relatively minor.

6. References

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