

Evaluation of Phase Diagrams with Regard to Alkali Resistance of Calcium Aluminates at High Temperatures

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The paper is a critical view on calcium aluminates concerning their thermal stability and possibility of reaction with alkalis in regard to the evaluation of phase diagrams in subsolidus field but at temperatures of 1100 °C to 1200 °C. In this solid state the volume changes followed by density changes from original to the formatting compounds due to the alkali corrosion. The main topic is the calculation of type and amount of the formatting alkali compounds and the volume change of the solid phase mixture in each of the five calcium aluminates herein. Due to the CA_6 reaction with alkalis to β -alumina the linear expansion is about 14 % and the solid phase is destroyed as well. The other four calcium aluminates have linear expansion of maximal 2,6 % or shrinkage of maximal 3,7 % respectively. Therefore one can expect an alkali stability of these four calcium aluminates somewhat.

In the $CaO-Al_2O_3$ system the lowest eutectic melts at 1435 °C between C_3A and $C_{12}A_7$. So the densification by sintering can start nearly 200 to 300 K below the temperature of the first melt. Therefore porous calcium aluminate thermal insulating materials have a possible service temperature of 1100 to 1200 °C.

1 Introduction

Calcium aluminates are components of portland and aluminate cements [1] and of several abrasives [2]. They are binders of refractory concretes and mixtures [3].

Since decades our institute works on refractory concretes comprehensively, with aluminate cements [4], at the synthesis of cal-

cium aluminates [5] and especially with hibonite materials [6]. Hydrothermal hardened refractory concretes and thermal insulation lightweight materials, both on the basis of calcium aluminates, are in centre of our interest [7] and protected in several patent documents, e.g. [8–10]. In the last 22 years since the “fall of the Berlin wall” and the united Germany we had a strong

and successful cooperation with our colleagues in Germany and Europe [11, 12]. Since then beside other refractories also thermal insulating materials have been developed [13, 14], especially on the base of CA_6 [12, 15, 16].

With increasing usage of waste combustion more and more problems with corrosion of refractories, thermal insulating materials and steel elements of the kilns by alkali compounds occurred. Therefore the development of new alkali corrosion resistant materials is necessary. This paper presents the evaluation of phase diagrams with regard to the alkali corrosion resistance of calcium aluminates.

2 Phase equilibrium diagrams

2.1 Diagram $CaO-Al_2O_3$

The diagram has been published at first by *Shepherd et al.* in 1909. It exists in slightly different forms by other authors as well *Hallstedt* 1990 (Fig. 10349 in [17]) and *Ball* 1992 (Fig. 10350 in [17]) published this diagram calculated from thermodynamic data.

Tab. 1 Characteristics of calcium aluminates

Calcium Aluminate	C_3A	$C_{12}A_7$	CA	CA_2	CA_6
System of Crystallisation	cubic	cubic	monoclinic	monoclinic	hexagonal
Composition					
CaO [mass-%]	62,3	48,5	35,5	21,6	8,4
Al_2O_3 [mass-%]	37,7	51,5	64,5	78,4	91,6
Density [g/cm ³]	3,03	2,70	2,98	2,86	3,69
Melting point					
congruent [°C]		1449	1602	1778	
incongruent [°C]	1544				1883

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Tab. 2 Eutectics of system CaO–Al₂O₃

Ca-aluminat 1/ Ca-aluminat 2	C ₃ A/C ₁₂ A ₇ Humid	C ₁₂ A ₇ /CA Humid	CA/CA ₂	CA ₂ /CA ₆	C ₃ A/CA Dry
Composition					
CaO [mass-%]	51,6	46,8	34,1	20,3	49,4
Al ₂ O ₃ [mass-%]	48,4	53,2	65,9	79,7	50,6
Eutectic melting temperature [°C]	1435	1445	1600	1775	1365

It is verified by experimental data. According to this there are five calcium aluminates (Tab. 1). However the compound Ca₁₂Al₁₄O₃₃ (short C₁₂A₇, mineral name "mayenite") only exists in normally present atmosphere and not in complete dry conditions. C₁₂A₇ contains even at 950 °C OH-ions and is therefore specified as a hydrogarnet Ca₁₂Al₁₄O₃₂(OH)₂ [18]. Tab. 2 shows the eutectic compositions and temperatures of the phase diagram, which is earlier mentioned. Between five calcium aluminates four eutectics are existent under normal humid conditions. Partly they are located nearby the chemical compositions of calcium aluminates and therefore differenti-

ated hardly of the melting temperatures of pure compounds. In completely water free system CaO–Al₂O₃ without C₁₂A₇ the lowest eutectic point is situated between C₃A and CA and thus melts at 1365 °C, that is 70 K lower than between C₃A and C₁₂A₇. So the formation of C₁₂A₇ depends on the partial water pressure probably and explains different experimental results in this region of diagram CaO–Al₂O₃.

The equilibrium diagram CaO–Al₂O₃ gives reason to expect the following high temperature characteristics:

- The melting temperatures of CA₆ and CA₂ and their eutectics show possibilities for the application as refractory products. There are existent already refractories on CA₆ bases like e.g. products with the trade name SLA-92 [12, 15], BONITE [19] and CALUTHERM [16].
- For the CaO-richer and therefore more reasonable calcium aluminates C₃A, C₁₂A₇ and CA service temperatures of 1000 to 1200 °C can be expected. This is interesting for heat resistant insulation materials in this temperature range.

It should be taken under consideration that CA₂, CA, C₁₂A₇ and C₃A have hydraulic properties which may react with water and water vapour to hydrates.

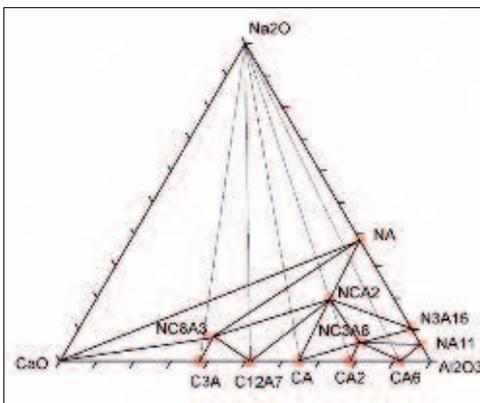


Fig. 1 Subsolidus cut at 1200 °C in the Na₂O–CaO–Al₂O₃ diagram [mass-%]

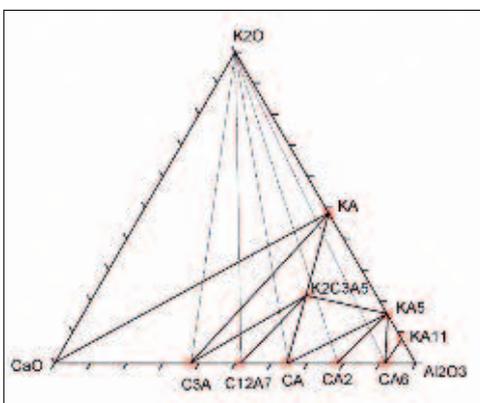


Fig. 2 Subsolidus cut at 1100 °C in the K₂O–CaO–Al₂O₃ diagram [mass-%]

lished a subsolidus equilibrium cut on the alumina-rich side at a temperature of 1200 °C (Fig. 10503 in [17]) in 1986, which means there are only solid phases. In this diagram the ternary compounds NC₃A₈ and NCA₂ are existent including their densities.

Fig. 1 shows a new designed diagram with three ternary compounds NC₃A₈ and NCA₂ by [22] and NC₈A₃ by Brownmiller [20], whereas the axis in mass-%, the marks of the chemical composition of the binary and ternary compounds, the conjugation lines between these compounds as thick lines and the reaction lane of every calcium aluminate to the Na₂O-corner as thin lines are outlined.

2.3 Diagram CaO – Al₂O₃ – K₂O

Similar to the Na₂O–CaO–Al₂O₃ diagram an older phase diagram K₂O–CaO–Al₂O₃ (Fig. 390 in [20]) exists by Brownmiller in 1935, which contains the lowest eutectic contains at 1395 °C in the binary composition CaO–Al₂O₃. In this system there is a subsolidus equilibrium cut at a temperature of 1100 °C by Van Hoek (Fig. 10457 in [17]). Only one ternary compound K₂C₃A₅ is existent.

Fig. 2 shows the diagram in mass-% and like Fig. 1 also the conjugation triangles and the reaction lanes from every calcium aluminate to K₂O. The compound C₁₂A₇ forms a solid solution with maximum 2,0 mol-% K₂O, that is 0,14 mass-% K₂O, which cannot be marked in Fig. 2.

It is important, that neither Na₂O nor K₂O lower the deepest eutectic melting temperature in both systems; it is in each case between C₃A and C₁₂A₇ (formerly C₅A₃) at 1395 °C.

3 Calculation of volume changes as a result of calcium aluminate reactions with alkali oxides in solid state

The resistance to alkali corrosion shall be theoretical judged on the phase diagrams. The first step is the calculation of type and amount of new compounds at the reaction of the calcium aluminates with Na₂O or K₂O. In Fig. 1 or 2 can be seen, that the reaction of calcium aluminates with Na₂O or K₂O runs to the 100 %-Na₂O/K₂O-corner on the thin line and cuts therefore the conjugation lines. From the cut points between conjugation and reaction line the type and amount of the coexisting phases result with the lever rule.

As simplest example Fig. 3 shows the reaction of K_2O with C_3A and the amount of the respective coexisting phases in regard to the K_2O concentration. At 25 mass-% K_2O C_3A is destroyed in CaO and KA completely. The lever rule calculates the amount of CaO and KA . At 25 % K_2O and 1100 °C only solid matter exists. These 100 % solid phase consists of 53,2 % KA and 46,8 % CaO . The K_2O content of more than 25 % is gaseous and reduces the content of the solids.

If the reaction line goes through several conjugation triangles and therefore cuts a few conjugation lines the situation is more complicated. Fig. 4 shows this situation as example at the CA reaction with Na_2O . CA is destroyed completely in 45 % $C_{12}A_7$ and 55 % NCA_2 at 9,5 % Na_2O . At higher Na_2O content NC_8A_3 , NA and CaO develop. Because of the presence of gaseous Na_2O the solid phases decreases at a Na_2O content of more than 28,2 %.

The second step consists of specific volumes calculation [cm^3/g] out of the known densities [g/cm^3]. For every calcium aluminate the starting point and the accompanying solid phase mixture as an end point of the alkali reaction is established. In that way the volume change (in linear dimension shrinkage or elongation) of the calcium aluminates can be ascertained. This method has been described in [23, 24] in detail.

Fig. 5 shows the linear changes like shrinkage and elongation calculated by the volume of the solid phase compound which forms due to the reaction of the respective calcium aluminate with Na_2O . CA_6 shows in that figure an increase in length by 14 % at 1200 °C. This theoretical indication has been verified by experimental basic fundamental research in the Al_2O_3 -rich corner of the equilibrium diagram Na_2O - CaO - Al_2O_3 by Verweij [22]: "It was observed that CA_6 reacted very readily with sodium containing compounds ... The grain-boundary reaction may destroy the coherence of the microstructure."

In Fig. 5 the less linear changes from the other calcium aluminates are shown. The compounds C_3A , CA_2 and CA reveal only very small expansions do have. The compound CA has already been used in float glass smelters as a tin bath bottom block and proofed its Na_2O -resistance justified by a phase diagram [25]. In Fig. 5 only $C_{12}A_7$ shows a shrinkage by 3 %.

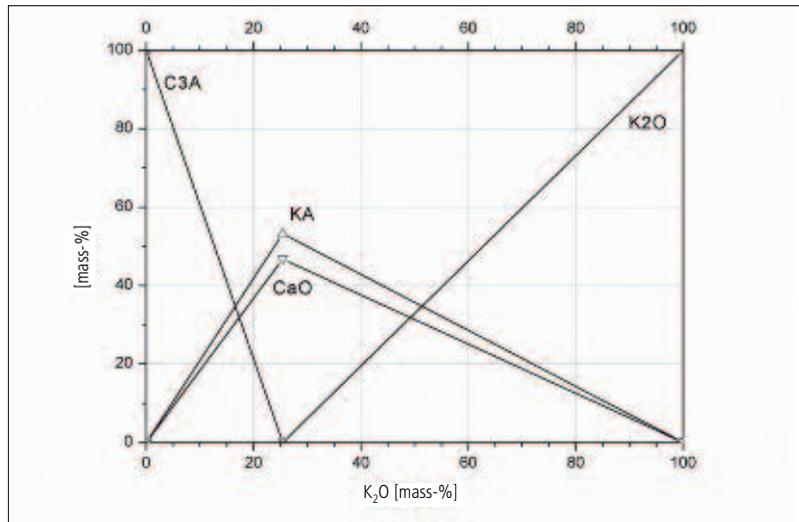


Fig. 3 C_3A reaction with K_2O at 1100 °C

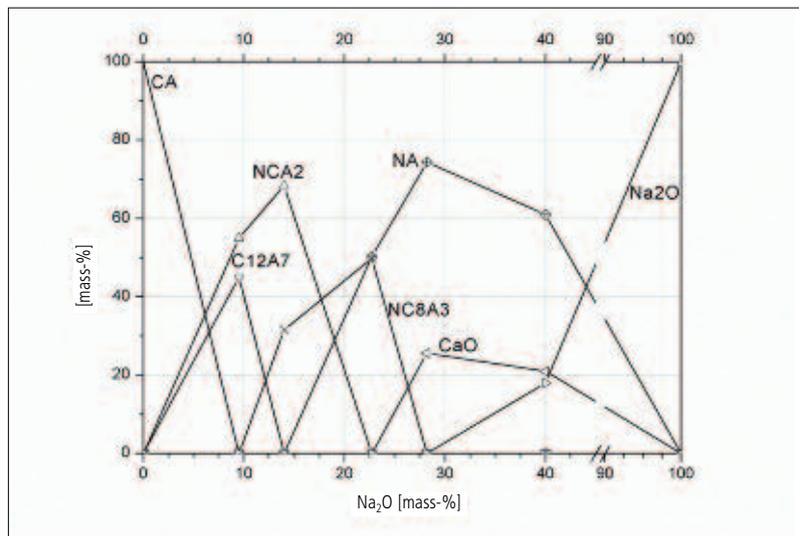


Fig. 4 CA reaction with Na_2O at 1200 °C

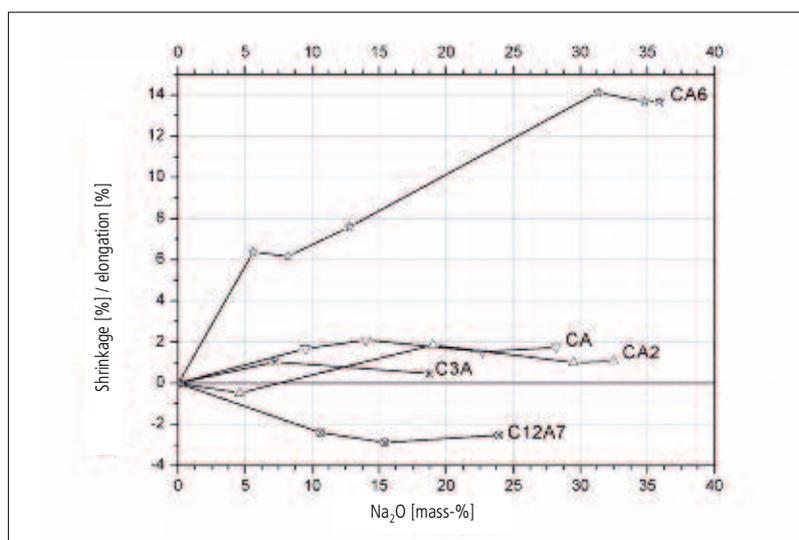


Fig. 5 Calculated linear changes of calcium aluminates in reaction with Na_2O at 1200 °C

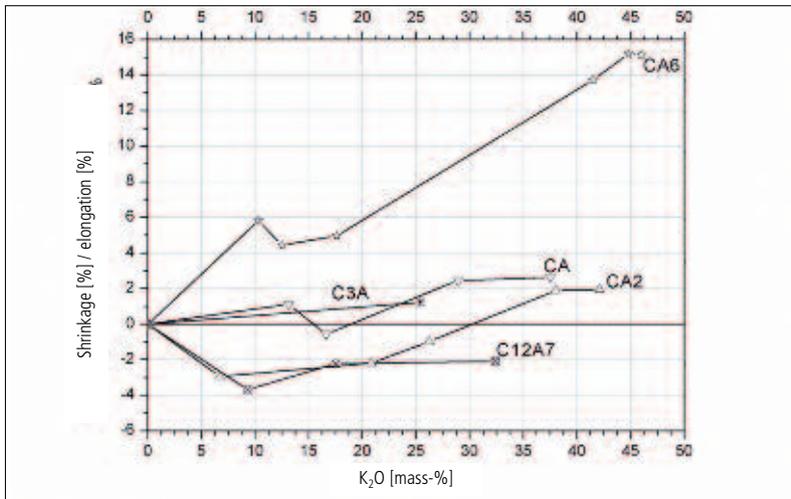


Fig. 6 Calculated linear changes of calcium aluminates in reaction with K₂O at 1100 °C

The compound CA₆ has also in reaction with K₂O the most increase in length by 15 % at 1100 °C as seen in Fig. 6. Other calcium aluminates show once more considerably less length changes once more. In particular C₃A and CA do have a minor expansion up to 2 %. However C₁₂A₇ and CA₂ have a shrinkage up to 3–4 % especially with a relative low K₂O-content.

The lines in Fig. 5 and 6 ended at an alkali oxide content where more alkali begins to be gaseous and thus does not change the linear dimensions of the solid phase compound anymore.

The reaction of CA₆ with a relatively large density of 3,69 g/cm³ leads to alkali compounds with lower densities and causes the large expansion of CA₆. At this reaction the following compounds develop: ternary alkali compounds (2,71–3,03 g/cm³), CA₂ (2,86 g/cm³), CA (2,98 g/cm³) and ultimately at highest alkali oxide content KA (2,63 g/cm³) or NA (2,69 g/cm³). C₃A (3,00 g/cm³), CA₂ and CA compared to CA₆ have densities near their alkali reaction products and therefore small length variations.

A shrinkage occurs with the low density of C₁₂A₇ (2,70 g/cm³).

The calculation of the changes in volume or length of the calcium aluminates allows the following assessment about their alkali resistance in temperature range 1100 to 1200 °C:

- CA₆ has oversized expansion and therefore it is not alkali resistant
- C₃A and CA show a small expansion and therefore they are alkali resistant
- C₁₂A₇ and CA₂ shrink a little. By that the possibility of crack development occurs, but also suitability as an alkali resistant material.

4 Experimental inspection of the calcium aluminate length changes at their reactions with alkalis

For an experimental inspection the synthesis of calcium aluminates occurs at 1200 °C, a mixture with 10 mass-% K₂CO₃, KCl and K₂SO₄ respectively and 70 mass-% of calcium aluminate, a press forming to tablets with a diameter of 51 mm and firing at 1100 °C and 50 h long follow. The change of diameter of the tablets is an indication of the alkali resistance. This procedure is the so called tablet method [26]. Tab. 3 compares the experimental measured diameter

Tab. 3 Comparison of the diameter changes L of calcium aluminate disks after their reaction with alkalis with the calculated amounts (+Δ L = elongation, –Δ L = shortening)

Δ L [%]	C ₃ A	C ₁₂ A ₇	CA	CA ₂	CA ₆
Calculated					
Na ₂ O at 1200 °C	+1,0	–2,8	+1,9	+1,8	+14,1
K ₂ O at 1100 °C	+1,2	–3,7	+2,6	–2,8	+15,1
Measured at 1100 °C	+2,0	+1,1	+4,3	+4,0	+11,2

changes with the calculated (in Figs. 5 and 6 the maximal amounts) length variations of the calcium aluminates.

A comparison of the calculated with the measured length variations shows, that the experiment confirms the calculation from the phase diagrams in a satisfactory way. Indeed the absolute values of the length changes are different, but relatively they blend: CA₆ has the greatest expansion however, C₁₂A₇ has the smallest.

References

- [1] Company Profiles: KERNEOS – Calcium aluminate energy to fuel refractory performance. refractories WORLDFORUM 1 (2009) [1] 26–29
- [2] Hinz, W.: Silikate. Berlin 1963
- [3] Petzold, A.; Ulbricht, J.: Feuerbeton. Leipzig, Stuttgart 1994
- [4] Seifert, H.; Schlegel, E.; Sonntag, F.: Hochtemperaturreaktionen tonerdehaltiger Feuerbetone. Silikatechnik 26 (1976) [8] 269–270
- [5] Schlegel, E.: Die Bildung von Calciumdialuminat CA₂ durch Festkörperreaktion. In: Hochschule für Architektur und Bauwesen Weimar, 5. Int. Baustoff- und Silikattagung Weimar, 17.–23. Sept. 1973, Proc. section 2, part 2; 1973, 451–462
- [6] Boldt, R.: Der Wärmetransport in hochporösen Werkstoffen auf der Basis von Wollastonit, Hibanit und Mullit. Dissertation Bergakademie Freiberg 1985
- [7] Seifert, H.; Schlegel, E.: Hydrothermale Härtung zur Herstellung ungebrannter, hitzebeständiger und feuerfester Baustoffe. Silikatechnik 36 (1985) [7] 209–210
- [8] Schlegel, E.; Seifert, H.: Verfahren zur Herstellung eines Ofenleichtbaustoffs. DD PS 206 142, AZ: WP C 04 B/ 2412 287, 30.06.1982
- [9] Schlegel, E.; Seifert, H.: Verfahren zur Herstellung keramischer und feuerfester Werkstoffe. DD PS 206 145, AZ: C 04 B/ 2412 270, 30.06.1982
- [10] Schlegel, E.; Seifert, H.; Weißbach, H.: Feuerfeste und keramische Werkstoffe. DD PS 206 146, AZ: WP C 04 B/ 2412 262, 30.06.1982
- [11] Criado, E.; De Anza, S.: Calcium hexaaluminate as refractory material. UNITECR'91, Aachen/Germany, Proc. 403–407
- [12] Van Garsel, D. et al.: New insulating raw material for high temperature applications. 41th Int. Coll. on Refractories Aachen, 29./30. Sep 1998, Düsseldorf 1998, 122–128
- [13] Schlegel, E.; Schaarschmidt, G.: Mikroporöse Wärmedämmstoffe auf der Basis von Calciumsilicaten und -aluminaten. Die Feuerfest-

- keramik (1990) [2] 18–20
- [14] Petzold, A.: Anorganisch-nichtmetallische Werkstoffe. Charakteristik, Eigenschaften, Anwendungsverhalten. 3rd ed., Leipzig 1992
- [15] Kockekey-Lorenz, R.; Buhr, A.; Racher, A.P.: Industrial application experiences with micro-porous calcium hexa-aluminate insulating material SLA-92. 48th Int. Coll. on Refractories, Aachen/Germany; 8./9. Sept. 2005, Düsseldorf 2005, 66–70
- [16] Hölscher, T. et al.: CALUTHERM® – A hydrothermal cured thermal insulation material based on hibonite for temperatures up to 1600 °C. *Interceram* **57** (2008) [5] 330–334
- [17] Roth, R.S.: ACerS-NIST Phase equilibria diagrams, Vol. XIII. Westerville/Ohio 2001
- [18] Nurse, R.W.; Welch, J.H.; Majumdar, A.J.: The $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ phase in the $\text{CaO}\text{--}\text{Al}_2\text{O}_3$ system. *Trans. Brit. Ceram. Soc.* **64** (1965) [9] 323–332
- [19] Buhr, A.; et al.: Bonite – A new raw material alternative for refractory innovations. 47th Int. Coll. on Refractories, Aachen/Germany 13./14. Oct. 2004; Düsseldorf 2004, 205–210
- [20] Levin, E.M.; Robbins, C.R.; McMurdie, H.F.: Phase diagrams for ceramists. Columbus/Ohio 1964
- [21] Roth, R.S.: Phase equilibrium diagrams for ceramists, Vol. XI. Westerville/Ohio 1995
- [22] Verweij, H.; Saris, C.M.P.M.: Phase formation in the system $\text{Na}_2\text{O}\text{--}\text{Al}_2\text{O}_3\text{--}\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--}\text{Al}_2\text{O}_3$ at 1200 °C in air. *J. Amer. Ceram. Soc.* **69** (1986) [2] 94–98
- [23] Schlegel, E.: Evaluation of phase diagrams with regard to the alkali corrosion of Refractories. Proc. XVIth Int. Conf. on Refractories Prague/Czech Republic, 14./15. May 2008, Praha 2008, 23–30
- [24] Schlegel, E.: Auswertung von Phasendiagrammen hinsichtlich der Alkalikorrosionsbeständigkeit feuerfester Baustoffe. *Keram. Z.* **61** (2009) [2–3] 94–97 and [5] 266–271
- [25] Boymanns, G.; Gebhardt, F.; Schilling, M.: Tin bath bottom blocks – a comparison of refractories of the systems $\text{SiO}_2\text{--}\text{Al}_2\text{O}_3$ and $\text{CaO}\text{--}\text{Al}_2\text{O}_3$. *refractories WORLDFORUM* **1** (2009) [1] 77–80
- [26] Schlegel, E.; Aneziris, C.G.; Fischer, U.: Alkali corrosion of refractory installations in cement kilns – comparison of theory, laboratory tests and practice. Proc. 52th Int. Coll. on Refractories, Aachen/Germany, 23/24. Sept. 2009, Bonn 2009