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Thermodynamic Properties Of Alkali Species In Coal Based Combined Cycle Power Systems

Keywords: PPCC, Alkali Removal, Sorbent Material, Hot Gas Cleaning, Coal Ash Slag, Alkali Partial Pressure

Introduction

The limitation of fossil fuel resources and the necessity of reducing CO_2-emission require the increase of the efficiency of power plants by using combined cycle power systems (combination of gas and steam turbine process). Pressurized Pulverized Coal Combustion (PPCC) is a potential concepts to realize these objectives. The attainable efficiency for power plants is determined by the upper process temperature. This motivation has led to the development of combined cycle power systems. Up to now combined cycle power systems with

efficiencies in excess of 50 % can only be realized by using ash free fuels like natural gas or oil. Coal constitutes more then 80 % of the world's total fossil fuel resources. And up to now coal fired power plants only reach efficiencies below 50 %, therefore further developments are necessary.

The Pressurized Pulverized Coal Combustion (PPCC) is a coal fired combined cycle concept which is able to achieve efficiencies higher than 50 %. Figure 1 shows the flow diagram of the Pulverized Pressurized Coal Combustion. Combustion takes place at temperatures of nearly 1600 °C. The produced flue gas is routed through a column of ceramic balls as a liquid slag separation unit at an average temperature of 1450 °C. A separate alkali removal (T < 1400 °C) is the last clean up step before the flue gas enters the gas turbine. Gas cleaning related to fly ashes and alkali species is a necessary prerequisite for the direct use of combustion gas in gas turbines.

Using hot flue gas for powering a gas turbine requires a hot gas cleanup to protect the turbine blades from corrosion. One of the main problems in PPCC is the alkali release during the coal conversion process which produce a much higher alkali concentration in the flue gas than the specification of the turbine manufacturers allows.

Alkali metals are mainly bound in the mineral matter of a coal as salts and silicates. Whereas conversion processes of coal particles during gasification and combustion have been investigated and are well understood and many experiments dealing with the fate of mineral impurities in boilers have been published (Raask 1985), the knowledge of alkali metal release from coal and mineral matter during combustion and the resulting partial pressure of alkali species is small (Witthohn 1999).

This paper is dealing with problems of the control of alkali partial pressures in future Pressurized Pulverized Coal Combustion Systems. Partial pressures over coal ash slags and sorption materials were determined with and without additives. Further more a concept for successful sorption of alkalis is presented. These investigations accompany the modifications at a pilot plant built up by our industrial partners.

Objectives

Aim of this project is to support the development of a concept for a successful alkali removal. Two strategies are possible.

- Optimizing the alkali retention potential of the coal ash slag in the combustion chamber and the liquid slag separators
- separate alkali removal with solid sorbents (getters) at temperatures below 1450 °C.

Therefore in a first step the alkali partial pressure over coal ash slag should be determined in order to get information about the retention potential of the slag. The influence of additives on the retention potential of the slag should be investigated. The measurements should show if the alkali partial pressure over the slag is generally low enough in case of thermodynamic equilibrium. In case of too high alkali partial pressures a separate alkali removal is needed. Therefore in a second step commercial sorbent materials should be investigated concerning their sorption potential for alkalis. To get information about the influence of getter components on the sorption potential some mixtures of pure components, predicted by thermodynamic modeling to be most effective, should be investigated.

Approach

Alkali partial pressures over coal ash slags as well as over potential solid sorbents before and after annealing experiments were investigated by Knudsen Effusion Mass Spectrometry (KEMS). Complementing methods like DTA, DSC, XRD, SEM were used to support the results. Thermodynamic calculations with FACTSAGE accompanied all experiments.

The first part of this paper deals with the properties of a coal ash slag from a pilot plant (table 1), the valuation of its alkali retention potential and ways to improve this potential by additives. Coal ash slags can be regarded as silicate melts or glasses. A lot of work has been done in the field of properties of silicate melts and glasses (Mysen 1985). This has been taken into consideration for selecting additives. Network forming additives like SiO_2, TiO_2 and Al_2O_3 were selected in order to investigate the influence of an improved polymerization.

The homogeneous grinded coal ash slag from the pilot plant with and without additives was investigated to determine the partial pressures of alkali species in dependence on the bulk composition of the slag. Potential network forming agents were selected: SiO_2, TiO_2 and Al_2O_3. Two experimental series with a content of 5 and wt.-10 % additives were prepared.

Different potential solid sorbents, mullite, kaolinite, refractory brick and SiC (table 2), were mixed up with 5 wt.-% Na_2O and annealed for 50 h in a furnace at 1400 °C in order to determine the thermodynamic stable sodium containing phases. Afterwards 100 mg of each sample were measured by KEMS to determine the alkali partial pressures over these phases. From these measurements the alkali retention potential of each phase can be obtained. With respect to these results and thermodynamic calculations, aluminosilicate mixtures with different amounts of Na_2O (0.2, 1, 5 and 10 wt.-%) were prepared to prove if calculations and experimental results matched. These samples were annealed in a furnace at 1600 °C in closed platinum tubes.

The vapor pressure measurements of alkali species were carried out by Knudsen Effusion Mass Spectrometry (KEMS). Partial pressure measurements were made as a function of temperature and composition.

Figure 2 shows a scheme of the Knudsen cell mass spectrometer system which mainly consist of four principal units.

- Generation of a molecular beam in the Knudsen cell
- Ionization of the molecules in the ion source
- Mass separation in a quadrupole mass filter
- Ion detection in the detector system

The last three units form the analytic system supplied by Balzers (QMG 421). The whole experimental setup is kept under vacuum conditions ($< 10^3$ Pa).

The Knudsen cell is an iridium crucible with an orifice. This orifice is small enough for equilibrium to be approached in the cell under experimental conditions, but large enough to allow a representative portion of molecules to escape. These molecules represent the equilibrium composition of the gas phase over the sample. For all samples an iridium cell with a diameter of 7.5 mm, a volume of 1500 mm^3 and an orifice diameter of 0.03 mm was used. The cell is heated up by heat radiation and electron emission of a cathode (tungsten). A pyrometer and thermocouples were used to measure the temperature.

After electron impact ionization inside the ion source, via tungsten cathode, the molecular beam is directed into the quadrupole mass filter system and analyzed by the detector unit.

The main features of the KEMS system are:
- Identification of gaseous species

- Determination of partial pressures between 10^{-6} and 10 Pa
- Sample temperatures up to 2000 °C
- Determination of thermodynamic data (activities)

Isotopic distribution, studies of pure substances and fragmentation patterns were taken into account to determine the species and their partial pressures. To calculate the partial pressures p_i of the species I at the temperature T_i from the detector signals I_i [1/s] the linear relation

$$p_i = K \frac{I_i T_i}{a_i \sigma_i}$$

was used. The isotopic abundances a_i and the ionization cross sections σ_i are known from data bases (Mann 1967). The calibration constant K of the system was determined by a partial pressure measurement with pure silver as reference. All of these measurements are accompanied by thermodynamic equilibrium modeling performed with the FACTSAGE data base.

Some commercial materials and aluminosilicate mixtures which seemed to be best suitable for alkali removal were investigated on their alkali removal capacity by Knudsen Effusion mass spectrometric method. Modeling of the alkali sorption in the three component systems Al_2O_3-SiO_2-Na_2O was done.

Results

For the experiments with emphasis on the retention potential of coal ash slags a homogeneous grinded boiler slag from the pilot plant (table 1) was used. Two investigation series were performed. Both, with 5 wt.-% additives (SiO_2, TiO_2 and Al_2O_3) and with 10 wt.-% additives, were compared with the untreated slag. All Knudsen effusion mass spectrometric measurements were carried out with samples of 100 mg. Alkali partial pressures were determined in the temperature range from 1250 to 1450 °C. Preliminary measurements and thermodynamic calculations have shown that sodium and potassium are the dominating gaseous alkali species under experimental conditions.

Figure 3 and figure 4 show the results of the 5% series. The partial pressures of sodium and potassium are given as a function of the reciprocal temperature. The samples with additional SiO_2 and particular TiO_2 show a significant decrease of the alkali partial pressures. At 1400 °C the partial pressure of sodium is reduced from 0.6 Pa (untreated slag) to 0.42 Pa. This is a decrease of 30 %. Figure 4 shows very similar results. At 1400 °C the potassium vapor pressure is reduced from 0.59 Pa for the untreated slag down to 0.375 Pa for the sample with 5 wt.-% TiO_2. This is a decrease of 36 %. As expected, SiO_2 and TiO_2 react as network forming agents, which results in an increase of polymerization of the slag and better retention of alkalis. Figure 5 shows a silica melt and the influence of sodium oxide and calcium oxide on the structural units (Scholze 1988). Network modifier like alkalis break up the oxygen bridges between Si cations and this results in a depolymerization of the melt. The degree of polymerization of a slag has a direct influence on its alkali retention. In figure 3 and 4 aluminum seems to have less effect on alkali partial pressures. Aluminum can substitute silicon in silicate melts in four fold coordination by charge balancing with a cation in the vicinity. But it can also occur in six fold coordination (Mysen 1995, Neuville et al. 1996). In six fold coordination it is no longer a network former and this explains why aluminum shows only a small influence on alkali partial pressure.

Figure 6 and figure 7 show the measurements with 10 wt.-% additives. The diagrams show further improvement in reducing alkali partial pressures. The value for sodium is reduced

to 0.3 Pa at 1400 °C for the sample with 10 wt.-% SiO_2. This is a decrease of 50 % compared to the untreated slag. Potassium partial pressure shows a decrease in the same dimension.

The determined partial pressures are still to high for a combined cycle process. The addition of further network former increases the polymerization of the slag as well as the viscosity which endangers the liquid slag extraction of the boiler. These results show that in spite of the reached progresses a separated alkali removal is unavoidable.

Therefore, a set of potential commercial sorption materials was tested. Mullite, kaolinite, refractory brick and silicon carbide were mixed with 5 wt.-% Na_2O and annealed for 50 h in platinum tubes at 1400 °C. Afterwards 100 mg of each sample was measured by KEMS.

Figure 8 shows the sodium partial pressure as a function of the reciprocal temperature for the tested materials. The diagram reveals SiC to be absolutely unsuitable for alkali removal under these conditions. The partial pressures are orders of magnitude higher than the partial pressures over the tested slag or the other tested materials. All other tested materials showed a better performance. Sodium partial pressures at 1400 °C of mullite (7.5 Pa) and kaolinite (1.3 Pa) are higher compared with those of the slag measurements. The partial pressure of refractory brick is 0.56 Pa which is similar to the partial pressures of the slag measurements in spite of its higher sodium content. All aluminosilicates showed a melting phase. According to XRD and SEM/EDX investigations the Al_2O_3/SiO_2 ratio in the formed sodium containing phases seem to have an influence on the sodium partial pressure. Based on these results thermodynamic modeling was used to find the best mixture between SiO_2 and Al_2O_3 to reach the lowest alkali partial pressures at temperatures between 1250 and 1400 °C. Mixtures with ratios of Al_2O_3/SiO_2 in the region of 1/8 were found to be best suited for a successful alkali removal.

Referring to these results mixtures with this Al_2O_3/SiO_2 ratio of 1/8 were mixed up with different amounts of Na_2O. All samples were annealed for 3 h at 1600 °C in a furnace to get a homogeneous melt. Figure 9 shows the results of these measurements. The mixture with 0.2 wt.-% Na_2O shows higher sodium partial pressure than the mixture with 1 wt.-% Na_2O and is with 0.035 Pa at 1400 °C in the same region as the partial pressure over the sample with 5 wt.-%. The sample with 1 wt.-% Na_2O has at 1400 °C a sodium partial pressure 0.02 Pa which is the lowest measured partial pressure of all mixtures in this series. The sample with 10 wt.-% has a sodium partial pressures of 0.4 Pa at 1400 °C which is similar to the value measured over the slag.

To explain the correlation between sodium partial pressure and sodium amount of the mixture accompanying thermodynamic calculations were done. Figure 10 shows a calculated phase diagram of the system SiO_2-Al_2O_3-Na_2O at 1400 °C. In mixtures with low alkali content crystalline mullite and SiO_2 are stable beside a liquid phase. This is confirmed by XRD measurements of the samples with 0.2 and 1 wt.-% Na_2O. At higher Na_2O content of the mixture no crystalline phase is stable. This can be taken as explanation for the differences in sodium partial pressures obtained. In mixtures with low alkali content there is only little liquid phase with an accordingly high alkali concentration and therefore, a relatively high sodium partial pressure. By adding sodium the portion of the melt increases until the system is completely liquid. Because this liquid has a lower sodium content than the liquid which is formed at low sodium content of the mixture its sodium partial pressure is lower. This last series has shown thermodynamic calculations and experimental results match very well.

Future Activities

   A lot of work is still to be done to develop a successful concept for alkali removal. The experiments on coal ash slag have shown that a separate alkali removal is unavoidable. Results gained during the investigations show that the sorbent phase will be liquid. Therefore solid sorbents have to be found (on the basis of this work) which form in contact with alkali species a low melting phase with low alkali equilibrium vapor pressures which easily drops off the sorbent surface (similar to liquid slag extraction).

Beside this an experimental setup is under construction which will allow sorbents testing under simulated flue gas conditions.

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Figures and Tables
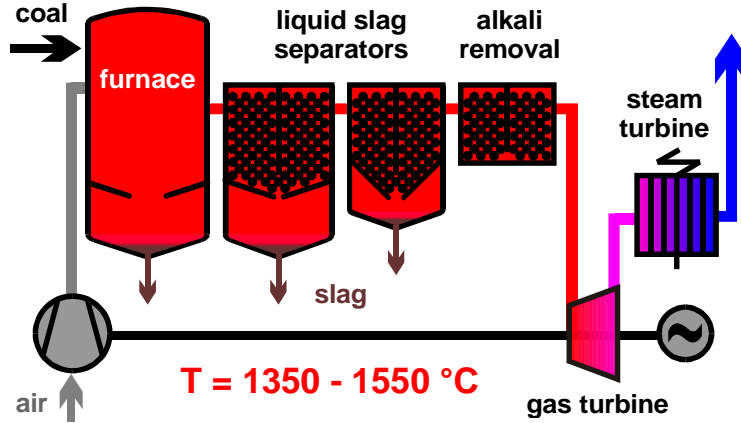
Figure 1: Flow diagram of Pressurized Pulverized Coal Combustion
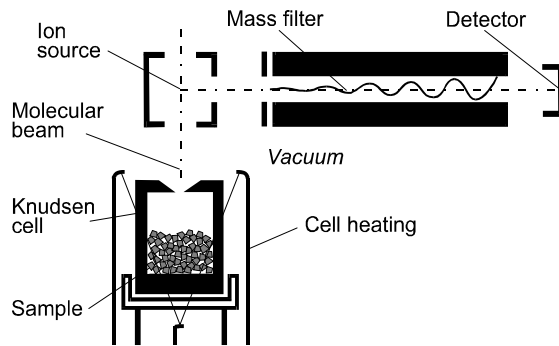
Figure 2: Principle of Knudsen Effusion Mass Spetrometry
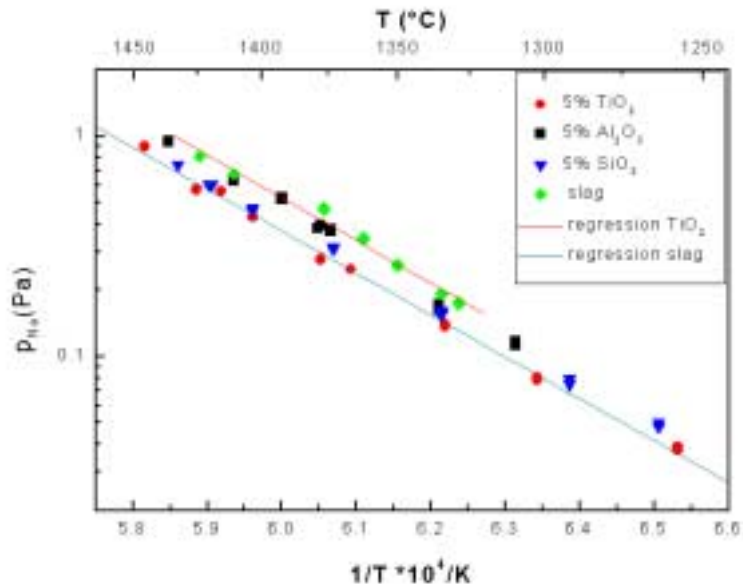
Figure 3: Sodium vapor pressures as a function of reciprocal temperature (5 wt.-% additives series)
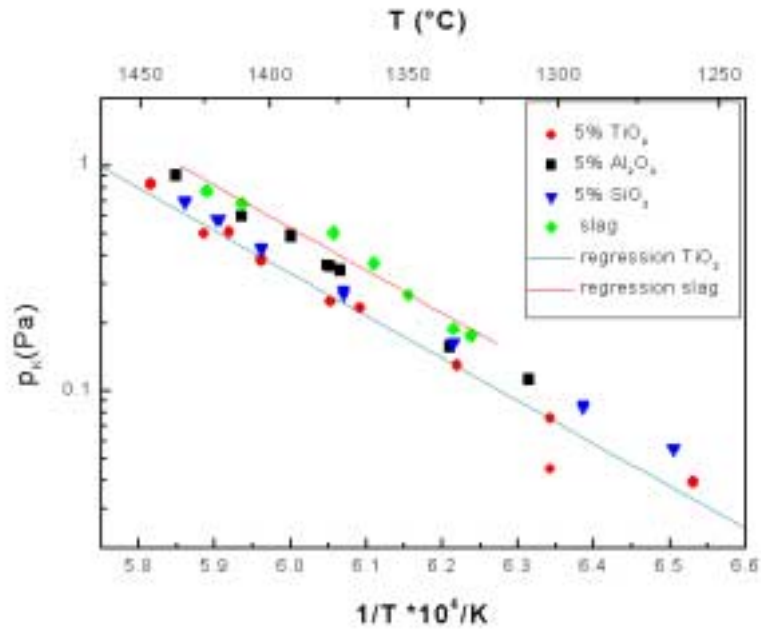
Figure 4: Potassium vapor pressures as a function of reciprocal temperature (5 wt.-% additives series)
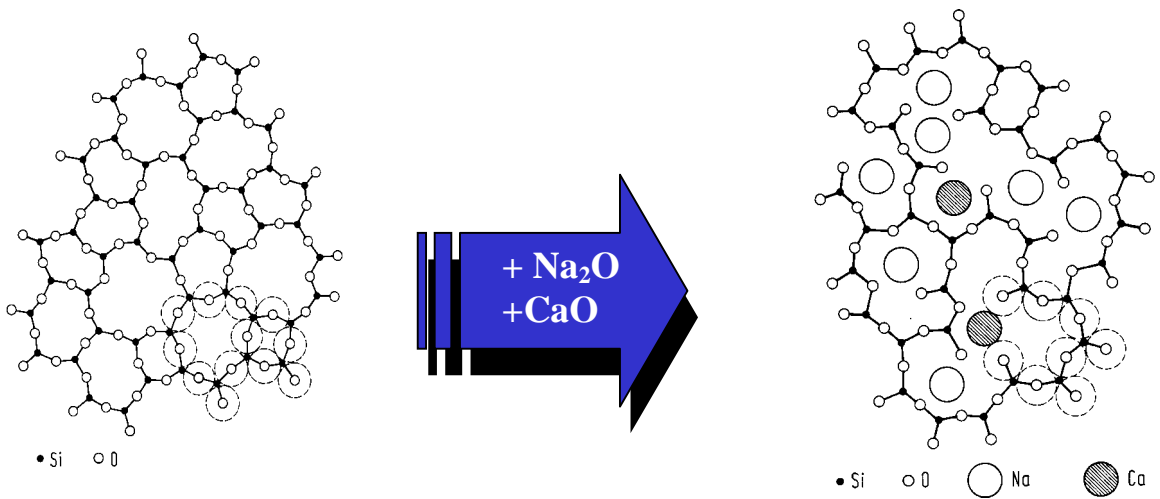

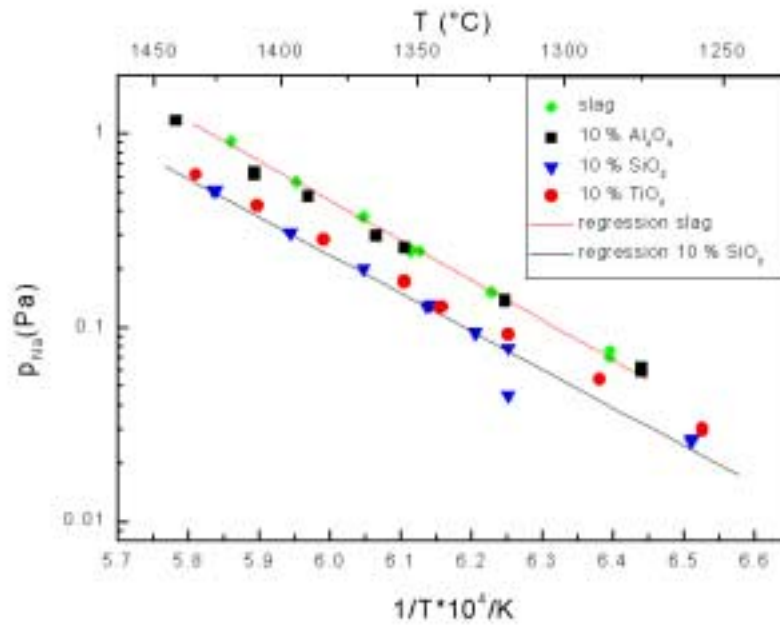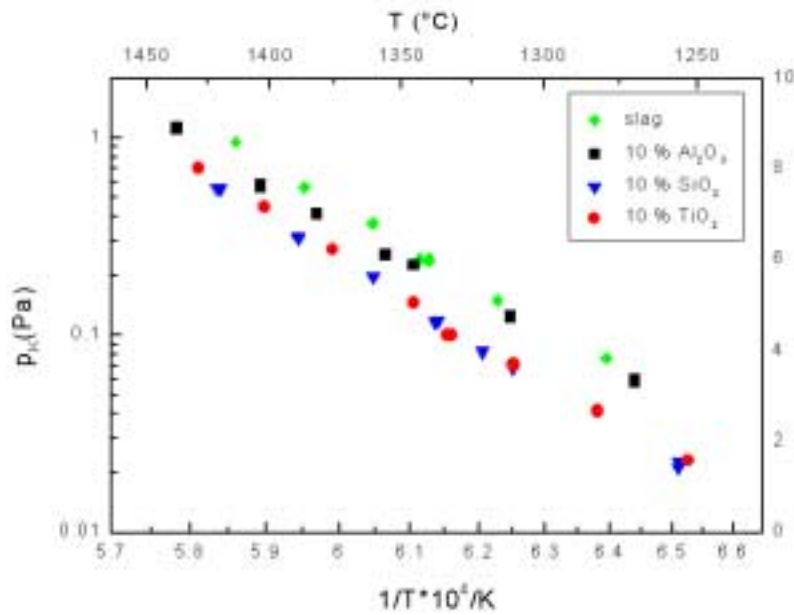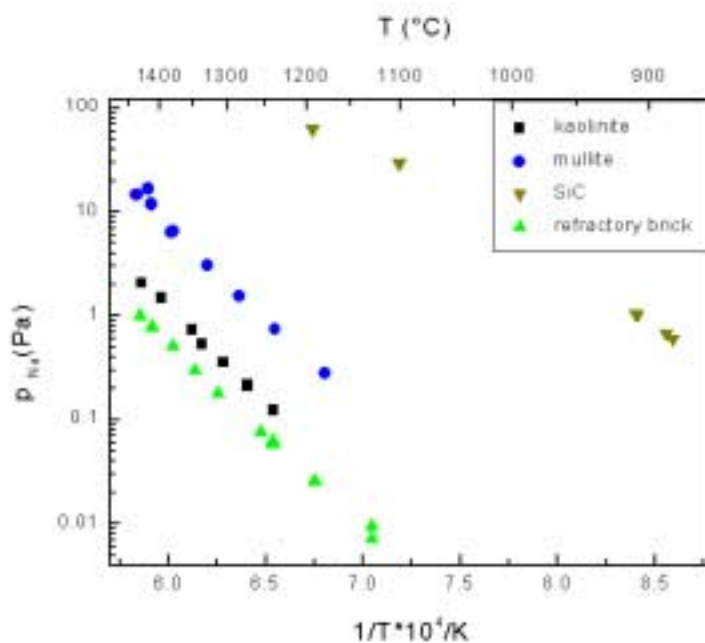Figure 5: Influence of sodium and calcium on silicate network

Figure 6: Sodium vapor pressures as a function of reciprocal temperature (10 wt.-% additives series)

Figure 7: Potassium vapor pressures as a function of reciprocal temperature (10 wt.-% additives series)

Figure 8: Sodium partial pressure over solid sorbents
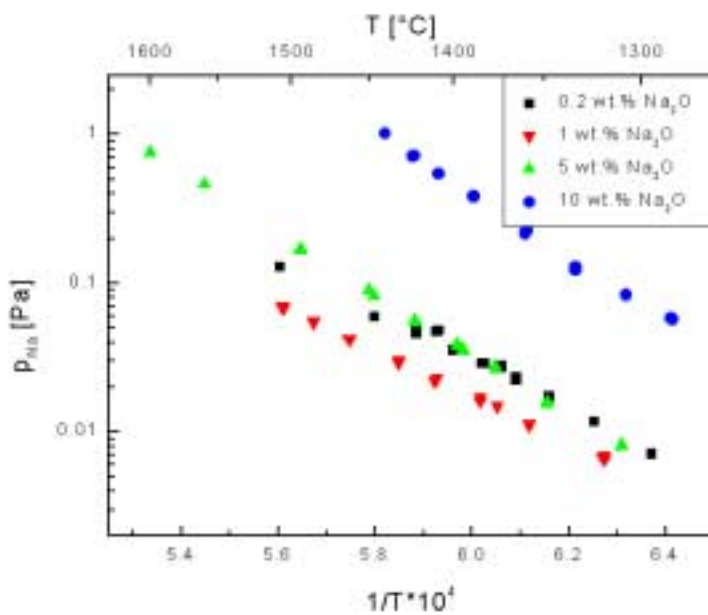
Figure 9: Sodium partial pressures over 1/8 molar mixtures of Al_2O_3 and SiO_2 with different amounts of Na_2O
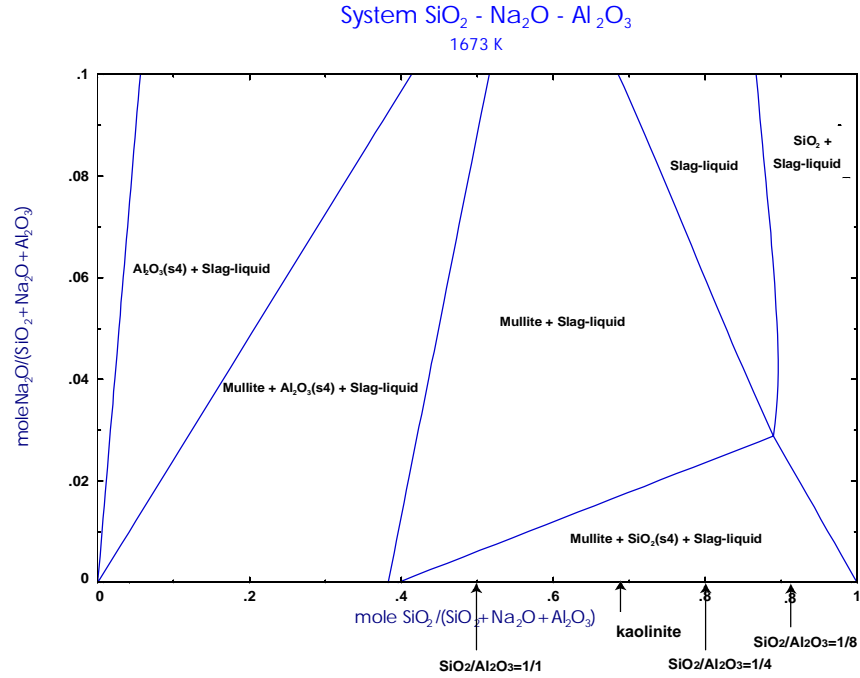
Figure 10: Part of the phase diagram SiO_2-Al_2O_3-Na_2O calculated with FACTSAGE

Table 1: Composition of the coal ash slag (wt.-%)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	CO_2	SO_3
Boiler slag	36,2	27,0	14,4	9,1	2,5	2,1	1,2	0,4	0,154	0,082

Table 2: Composition of tested sorbtion materials

sorption material	Al_2O_3 / wt.%	SiO_2 / wt.%	Fe_2O_3 / wt.%	TiO_2 / wt.%	Na_2O / wt.%	K_2O / wt.%	H_2O / wt.%
kaolinite	36,29	43,87	1,39	1,45	0,04	0,26	14,3
mullite	70,86	25,68	0,33	0,22	0,22	0,3	-
Refractory brick	58,4	36,38	1,03	2,59	0,04	0,08	-.
SiC	-	-	-	-	-	-	-