

THERMODYNAMIC ACTIVITIES OF Na AND K IN COAL SLAGS AND THEIR VAPORISATION

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Abstract

Released gaseous alkali metal compounds cause high temperature corrosion especially at the gas turbine blading of coal-fired combined cycle power plants. Experimental and theoretical basic investigations are presented, which contribute to the understanding of the release and sorption of these contaminants. Knudsen effusion mass spectrometry (KEMS) was used to study the vaporisation of coal ashes and slags at temperatures between 200 and 1800 °C and to determine the released alkali species and their partial pressures. The data base system FACT and the modified quasi-chemical model for non-ideal solutions were applied to predict the thermodynamic behaviour of model systems for coal slags and to determine material compositions of maximum alkali sorption capacity.

INTRODUCTION

Modern coal fired power plants with combined cycle using high pressures and high temperatures will increase the efficiency in coal conversion. The PFBC (Pressurised Fluidised Bed Combustion) and the PPCC (Pressurised Pulverised Coal Combustion) are operating at temperatures between 750 and 1000 °C (PFBC) or 1350-1550 °C in case of PPCC. In this temperature range the mineral components of the coal are liberated and gaseous alkali metal species vaporise into the flue gas. These released gaseous alkali metal species in the hot flue gas cause high temperature corrosion (“hot corrosion”) especially at the gas turbine blading, so that these gaseous alkali metal species have to be removed from the flue gas before it is entering the gas turbine. With increasing process temperature in advanced plants with high efficiency, both the alkali partial pressures and the corrosion rate rise. Apart from improvements on the materials side, it is a key issue for the realisation or improvement of boilers with enhanced steam parameters and of directly coal-fired gas turbine systems to control the alkali concentration in the hot gas. The upper limit for the total content of the

alkali metal-containing species in the hot gas demanded by the gas turbine manufacturers differs considerably. This reflects the lack of operating experience with coal-fired turbines and the uncertainty in assessing the corrosion effect of coal flue gases.

Compared with conventional gas turbine fuels, natural gas and fuel oil, coal is a highly impure fuel. The mineral matter content of dried coals is typically between 5 and 15% by mass. Given as Na_2O and K_2O , the total mass fraction of the alkali metals in the ash of most coals is between 0.5 and 5%. Since cleaning of the raw coal to the extent necessary to fulfil the alkali concentration limit is not realistic, measures during or after combustion or gasification are required. The conditions for the alkali removal can be very different. The maximum temperatures in plants range from about 850 to 900 °C in pressurised fluidised-bed combustors, 1000 to 1700 °C in pulverised coal flames up to 1800 °C in entrained flow gasifiers. The pressures lie between about 1 bar in conventional boilers and 16 to 30 bar in industrial gas turbines.

Except for a restriction of the process temperature, which is for efficiency reasons not desired, a liquid or solid sorbent absorbing the alkali-containing species physically or chemically is necessary to reduce the alkali partial pressures. The sorbent can be used in principle by the following means: as additive supplied together with the coal; injected into the gas stream directly before the ash removal; in a separate granular bed filter; as component of the particle filter; or, if the (blended) coal slag is used as sorbent, during removal of the liquid slag. As can be seen in various contributions in Schmidt (1996), many alkali-absorbing getter materials have been investigated in the recent years. The most promising are aluminium-containing layer silicates (e.g. kaolinites) and aluminosilicates (e.g. micas), framework aluminosilicates (e.g. feldspars) and, especially desirable, power plant ash and slag itself.

This work.

Whereas conversion of a coal particle during gasification and combustion is fairly well understood and many experiences exist in the alteration of the mineral matter in boilers, see for example the books of Smoot and Smith (1985) and of Raask (1985), the knowledge of the alkali metal release from coal and mineral matter during these complex processes is very meagre. The alkali hot gas concentration cannot be predicted, and the requirements to be met by the removal technique are unclear. Factors influencing the alkali release during coal conversion are: temperature, pressure, gas composition (especially O_2 , H_2O , HCl , H_2 , CO ,

SO_x), residence time and morphology, composition and mineral phases of the mineral matter. The alkali metals in coal can be present as organometal compounds, chlorides, carbonates, sulphates and silicates. It is common knowledge that potassium for the most part is strongly bound in clay minerals, such as illite. However, the mode of occurrence of sodium is less clear. In brown coal and sub-bituminous coals, as in the coal of the German mining area in the Rheinland, sodium occurs largely in the organic matter, as relatively volatile humate (Köthen, 1993).

Almost all experimental investigations on release of alkali metals from coals and coal ashes have been done indirectly: the effect of different parameters (temperature, additive, atmosphere) on the alkali concentration at the outlet of various laboratory or semi-technical reactors (fixed and fluidised-bed, entrained flow) has been studied and the gas was analysed species-unspecifically, after aqueous sampling or, recently, on-line with excimer laser-induced fragmentation fluorescence by Hartinger et al. (1994). To distinguish among different alkali species, Krishnan et al. (1996) used a molecular-beam mass spectrometer. A direct approach was established by Hastie, Plante and Bonnell (1982), who applied mass spectrometry to measure the equilibrium partial pressures of alkali species over MHD slags. Krishnan et al. (1996) applied this method to laboratory ashed coals.

The first part of this paper is also based on high temperature mass spectrometry (Knudsen effusion method). Various coal ashes and plant slags were heated up in a Knudsen cell to determine the gaseous species and their partial pressures over a temperature range from 200 to 1800 °C. The temperature at which the ash from raw coal is produced may have a significant effect on chemistry of the ash. This is still the subject of current investigations with varied ashing temperatures, the lowest at about 150 °C in oxygen plasma. And in a further step the experimental set-up will be modified to study the influence of certain, above mentioned gaseous species on the alkali release.

The second part of this paper deals with thermodynamic equilibrium modelling performed with the data base system FACT. Computational thermodynamic modelling is widely used and enables easy variation of different parameters, such as the sorbent material composition, or consideration of the gas atmosphere resulting from conversion of the organic matter of the coal. Since coal slags are complex multi-component systems, in which numerous solid and liquid phases can occur, it is in a first step advisable to check the capability of the selected program. This has been done step by step for the coal ash-relevant oxidic systems through comparison with published experimental data. Since coal ashes and potential alkali sorbents have the same main constituents, these tests are valid for both. Where experimental results are

not available, samples will be prepared and investigated by mass spectrometry. Although it is unclear, how near the ash in a power plant is to chemical equilibrium, thermodynamic considerations are reasonable: they provide information about the final state, which the real (kinetic) process approaches, and an alternative, a kinetic treatment, is at present not possible. The main aims of the current basic investigations are: to improve the understanding of the alkali release from coal ashes, so that this process can be influenced; and to determine thermodynamically favourable sorbent materials that should be tested in kinetic experiments.

VAPORISATION STUDIES ON COAL ASHES

Experimental

Figure 1 shows a principle sketch of the Knudsen cell mass spectrometer system, which is composed of four principal units: generation of a molecular beam in the Knudsen cell, ionization of the molecules in the ion source, mass separation in the mass filter and ion detection in the detector system. The last three units form the analyser supplied by Balzers (QMG 421), the whole is arranged in a vacuum chamber ($<10^{-3}$ Pa).

The Knudsen cell is a crucible with an effusion orifice. The orifice is small enough for equilibrium to be approached in the cell, but large enough to allow a sufficient portion of molecules representing the gas composition over the sample to escape. For all samples pure iridium cells with a diameter of 7.5 mm, a volume of 1500 mm³ and an orifice diameter of 0.3 mm were used. The cell is heated up by heat radiation and electron emission of a cathode. A thermocouple and a pyrometer are used to measure the temperature.

After ionisation by electron impact in the ion source, which has a tungsten cathode, the molecular beam is directed into the quadrupole mass filter and finally analysed by two detector units: Faraday cup plus electrometer as well as SEM plus ion counter.

The main features of the 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 and kinetic data

Isotopic distributions, studies of pure substances and fragmentation patterns were taken into account to determine the species and their partial pressures. To calculate the partial pressure p_i [Pa] of the species i at the temperature T_i [K] from the detector signal I_i [1/s or A], the linear relation

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

was used as a good approach. The isotopic abundance a_i [-] and the ionisation cross-section σ_i [m²] are known from data collections, and the calibration constant K of the system was determined with pure silver as a reference.

In all experiments the samples were heated up in steps of about 50 K, each followed by a signal registration. Supporting the interpretation of the alkali signals, altogether 40 gaseous species could be identified over a range from 200 to 1800 °C.

Ash and slag samples

Table 1 gives the data of the 7 investigated ash and slag samples from 5 raw coals: 4 lignites and 1 hard coal. The samples A to E were produced by ashing of each raw coal in the laboratory, and the samples F and G are combustion residues of a plant.

All lignite ashes belong to coals from the German open-cast mining area in the Rheinland. The samples A, B and C are from coals, which are supplied to the boilers of three power plants. The coals come from different mines and are in part blended products. In contrast to these boiler coal ashes, sample D belongs to a coal, which is used for refining, e.g. briquette production.

The hard coal ash and the slags have their origin in a high volatile bituminous A coal from Ens Dorf at the Saar, Germany. This coal is fired in a pressurised pulverised combustion test plant with liquid slag removal. Operated at a combustor pressure of 16 bar, the DKSF plant in Dorsten, Germany, has a thermal power of 1 MW. Sample E is the laboratory ash produced from the pulverised coal, and the samples F and G are slags from the two successive slag removal devices of the plant. The first slag removal takes place at the bottom of the combustor, the second in a granular bed. In both the liquid slag is quenched in a water reservoir. The slag temperature in the combustor is up to about 1500 °C and about 1400 °C in the granular bed.

The laboratory ashes were produced in a muffle oven, where the coal is combusted in air. The oven temperature was increased with a heating rate of 2 K/min from ambient temperature up to the given ashing temperature.

The sample masses in the Knudsen cell were between 45 mg for the ashes of the refinement lignite (D) and the hard coal (E), 100 mg for the boiler lignite ashes (A to C) as well as 200 and 280 mg for the plant slags (F, G).

Alkali release from lignite ashes

Figure 2 shows on a logarithmic scale the alkali partial pressures measured over the laboratory ashes from three boiler lignites (samples A, B, C) and a refinement lignite (D) during heat-up from 200 to 1800 °C. The left diagram contains the data for the sodium species, the right diagram has the same axes and gives the corresponding plots for potassium. The measurement points are marked with symbols.

As can be seen from Fig. 2, the alkali release from the three boiler coal ashes takes place qualitatively very similarly. Three partly overlapping temperature ranges may be distinguished: a first between about 500 and 900 °C, a second between 900 and 1100 and a third above 1100 °C. Especially sample A and the refinement coal ash, sample D, which exhibit markedly lower or negligible alkali partial pressures above 1100 °C, indicate differentiation between the second and the third range.

In the range between about 500 and 900 °C the alkali metals are released exclusively as NaCl and KCl. Except for sample C, HCl is identified as further chlorine compound in this range, with a partial pressure comparable to that of the alkali chlorides. The compounds from which the alkali metals are released, cannot be determined by the analysis of the gas phase only. In agreement with common knowledge about the mineral phases in coal, it can be excluded that sylvite (KCl) is present in any sample, because all measured KCl partial pressures are clearly below the corresponding values over pure sylvite. With the exception of the sodium-rich sample C, where the NaCl pressures between 500 and 600 °C agree fairly well with the corresponding values over pure halite (NaCl), gaseous NaCl cannot originate from the salt, but forms from Na and Cl of other phases.

At temperatures between about 900 and 1100 °C the alkali metals are released as elements, with peak partial pressures, which are close to or higher than the corresponding maximum values of the chlorides in the preceding range. The alkali release in this range may be due to

the decomposition of carbonates or sulphates. Currently performed phase analyses can possibly contribute to a clarification.

Above 1100 °C the alkali metals vaporise also in elementary form. Figure 2 shows that the partial pressures increase strongly with the temperature. Except for sample A, which has a very low sodium content, the peak values are about an order of magnitude higher than in the preceding range. Since other alkali-containing compounds, such as carbonates or sulphates, are not stable up to 1100 °C, the alkali release in the third range can only be due to silicates or aluminosilicates. This is confirmed by the vaporisation behaviour of the ash of refinement lignite, sample D, which has a SiO₂ mass fraction of about a third that of the boiler ashes (Table 1). Figure 2 shows that above 1100 °C practically no gaseous alkali species occur over this sample and thus the alkali concentration in the sample must be very low at these temperatures. As alkali-containing mineral phase in sample A, a potassium feldspar, K[AlSi₃O₈], could be detected by XRD.

A comparison of the four samples shows that sodium and potassium behave very similarly, and the partial pressures increase with increasing alkali content.

Since the experiment lasts for about 10 hours, at high temperatures, where the samples are molten, a depletion in the more volatile species, such as the alkali metals, is unavoidable. Thus the partial pressures can decrease despite increasing temperatures. The plots in Fig. 2 show this behaviour at temperatures above about 1500 °C. A further phenomenon is encountered between 1150 and 1350 °C, where the partial pressures first decrease strongly and then again increase. This agrees very well with the initial softening (1120 to 1160 °C) and fluid temperatures (1260 to 1320 °C) of the ashes determined in accordance with DIN 51730 and can be explained by a successive dilution of a molten alkali-rich phase with melting phases low in alkali content.

Alkali release from hard coal ash and plant slags

As opposed to the lignite ashes, sodium and potassium are released in a similar manner exclusively as elements in two ranges from the investigated hard coal laboratory ash: with low partial pressures between about 700 and 1050 °C and with strongly increasing pressures above about 1100 °C (Fig. 3, sample E). The characteristic difference to the lignite ashes is that no alkali chlorides occur, although chlorine is detected in the gas phase as HCl at temperatures above 500 °C.

Compared to the boiler lignite ashes (Fig. 2, samples A, B, C), the alkali release between about 700 and 1050 °C takes place at low partial pressures. The phases from which the species vaporise in this range may be carbonates and sulphates. However, for the most part they are not stable at the high temperatures in the DKSF plant, since the slags from the plant (Fig. 3, samples F, G) do not show any alkali release in this range up to almost 1000 °C. It is conceivable that the difference to the lignite ashes in this range is associated with the higher ashing temperature. But varying the ashing temperature between 150 and 1175 °C did not result in any significant change of the alkali concentration over the whole range or in a detectable alteration of the alkali-containing phases in the ash of the hard coal up to 775 °C. Further clarification is expected from the mass spectrometric investigation of the sample ashed in oxygen plasma at 150 °C.

The alkali release in the range above about 1100 °C is qualitatively and quantitatively similar to that of the boiler lignite ashes at corresponding temperatures and must be explained again by alkali-containing silicates and aluminosilicates. As an example muscovite, $\text{KAl}_2[(\text{OH},\text{F})_2\text{AlSi}_3\text{O}_{10}]$, was detected in the raw coal. Naturally this phase undergoes a transition during heat-up.

The alkali releases from the two DKSF plant slags (samples F, G) do not differ substantially. With regard to the very similar compositions, this is not a surprising result. An exception is the range between about 400 and 600 °C, where Na and K are detected with relatively low partial pressure over the combustor slag. Whether this is a typical phenomenon or should be assigned to a sample impurity has to be clarified by a repeated measurement. Except for the relatively low partial pressures up to temperatures of almost 1000 °C, the plant slags show an alkali release that is quite similar to that of the laboratory ash (sample E). Since the alkali contents –corrected by the S and C content– in the three samples are very similar, it must be concluded that the by far greatest fraction of the alkali metals is strongly bound in or can be absorbed by silicates in the mineral matter and resists release under the conditions in the plant (temperatures up to 1500 °C). Only a small amount is vaporised at temperatures up to about 1000 °C. Above 1500 °C the laboratory ash shows a larger alkali partial pressure decrease than the plant slags. This must be due to the lower sample mass (45 mg as opposed to 200 and 280 mg for the slags) and thus stronger effect of the above explained sample depletion.

THERMODYNAMIC MODELLING OF COAL SLAGS

Procedure

Besides the experimental work, computational phase equilibrium modelling has been used to understand and predict the alkali metal release and absorption of coal slags and sorbent materials. The results are presented in form of chemical activities for the alkali metal oxides (Na_2O , K_2O), since this expresses the extent to which a material releases or incorporates the alkali metals. The chemical activity a_i of the component i in a mixture is defined as the relation of the partial pressure p_i of the component over the mixture to the vapour pressure p_i^0 of the pure component, i.e.

$$a_i = \frac{p_i}{p_i^0}.$$

Thus, the smaller the activity, the smaller the tendency of the mixture to release the component as gaseous species.

The mineral matter of coal is an oxidic multicomponent system, which varies strongly in composition. Usually the composition of a coal ash is specified by the mass fraction of the ten most abundant elements in form of their oxides: SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , SO_3 , Na_2O , K_2O , TiO_2 and P_2O_5 . In order to check the capability of the used data base program, all these components are not considered at once, but step by step in appropriate model systems. Besides the problem species, the alkali metals, reasonable model systems must contain the components that form the major constituents of coal ashes and that have the major effect on the alkali release. Thus, the following model systems were chosen ($A=\text{Na}$, K):

- $A_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$
- $A_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3$
- $A_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{CaO}$
- $A_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{CaO}-\text{SO}_3$
- $A_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{CaO}-\text{MgO}-\text{SO}_3$

The four-component system is the target system for hard coal ashes, the seven-component system is the target system for lignite ashes. For most hard and brown, at least 90% of the ash constituents are considered with these target systems, which should describe the thermochemical behaviour of the real ashes to a good approximation. The capability of the data base program is tested by comparison of calculation results with published experimental

data; this includes also quasi-binary and quasi-ternary systems that are part of the listed model systems.

Phase equilibrium modelling

First of all, phase equilibrium modelling is based on thermodynamic data, e.g. Gibbs energies of the components, compounds and solutions. Thermodynamic data for the components and compounds are listed in numerous data collections, whereas data for solutions are less accessible. Multicomponent oxide solutions, such as liquid slags, exhibit large deviations from ideal mixing behaviour. This deviation is expressed by an excess Gibbs energy and is considered in models for non-ideal solutions. Since the solution data are associated with the solution model by a particular parameter set, data bases are not in general compatible with every model. For the description of liquid oxide mixtures three solution models are principally appropriate: the modified quasi-chemical model by Pelton and Blander (Pelton and Blander 1984, 1986); the cell formalism by Gaye and Welfringer (1984) and Kapoor and Froberg (1973); and the approximation of ideal mixing of complex components by Hastie and Bonnell (Bonnell and Hastie, 1990).

The equilibrium state of a system is calculated by minimising the Gibbs energy of mixing of the system, which is done by a mathematical routine, the so-called ΔG -minimiser.

For the results presented here, the data base system FACT 2.1 by Bale et al. (1996), the modified quasi-chemical model for non-ideal solutions and the ΔG -minimiser ChemSage were used. The FACT slag data base is coupled with the modified quasi-chemical model and was chosen because it has been developed especially for coal slags and is the most extensive.

Comparison of calculated and experimental literature data

The comparison between calculated chemical activities and experimental data from the literature has been carried out for 8 quasi-binary and 3 quasi-ternary oxide mixtures of the components Na_2O , K_2O , SiO_2 , Al_2O_3 , FeO and CaO . As an example, the results for one quasi-binary and one quasi-ternary system are presented.

Figure 4 shows on a logarithmic scale the Na_2O activity in the quasi-binary system Na_2O – SiO_2 at temperatures from 1273 K to 1673 K as a function of the Na_2O mole fraction. The experimental data marked with symbols are results of emf measurements by Neudorf and Elliott (1980) and Yamaguchi et al. (1982), of transpiration measurements by Rego et al.

(1985) and of chemical equilibration by Tsukihashi and Sano (1985). The Na_2O activities calculated with FACT are shown as lines. Obviously there is a good qualitative and quantitative agreement between the calculated data and the values measured with three different methods. The calculated activities differ by no more than a factor of three from the experimental values.

Figure 5 presents the Na_2O activity in the quasi-ternary system $\text{Na}_2\text{O}\text{--SiO}_2\text{--CaO}$ at 1343 K as a function of the amount of CaO added to $\text{Na}_2\text{O}\text{--SiO}_2$ systems with three different $\text{Na}_2\text{O}/\text{SiO}_2$ ratios. The experimental data are results of emf measurements by Neudorf and Elliott (1980). Again a good agreement between the experimental and calculated results can be stated. The calculated Na_2O activity values differ by no more than a factor of two from the experimental values.

The comparison of calculated and experimental data for the other 7 quasi-binary and 2 quasi-ternary systems resulted in a similar good agreement. Thus, modelling was extended to the listed model systems.

Application to coal slag model systems

The quasi-ternary system $\text{K}_2\text{O}\text{--SiO}_2\text{--Al}_2\text{O}_3$ represents the simplest model system for a hard coal slag. For two different K_2O mole fractions, 0.02 and 0.10, the K_2O activity in this system was calculated for temperatures between 1273 and 2073 K as a function of the SiO_2 mole fraction. The result of the calculations with the data base system FACT is presented in Fig. 6, the thin lines for a K_2O concentration of 0.02 and the thick lines for 0.10.

The regions of constant K_2O activity with varying SiO_2 mole fraction are the result of equilibria between three coexisting phases. At constant composition an increase of the temperature results in an increase in the K_2O activity for every $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in this system. The addition of SiO_2 and Al_2O_3 to the systems $\text{K}_2\text{O}\text{--Al}_2\text{O}_3$ and $\text{K}_2\text{O}\text{--SiO}_2$ respectively results in a decrease of the activity for all temperatures. At constant temperature, minimal K_2O activities can be detected on the SiO_2 -rich side of the $\text{SiO}_2\text{--Al}_2\text{O}_3$ mixture. Starting from the system $\text{K}_2\text{O}\text{--SiO}_2$, these minima are achieved through addition of small amounts of Al_2O_3 , (between about 2 and 10 mol%). At temperatures up to 1673 K extended regions of minimum K_2O activities can be observed. With about 0.02/0.76/0.22, the $\text{K}_2\text{O}/\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the experimentally studied hard coal ash (Table 1, sample E) lies within this region. At temperatures above 1673 K an increase of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio results in a decrease of the K_2O activity up to an order of magnitude for this $\text{K}_2\text{O}/\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio.

The main effect of the increase of the K_2O mole fraction from 0.02 to 0.10 is the considerable reduction of the ranges of minimal K_2O activity on the SiO_2 -rich side. For temperatures to 1373 K the minimum K_2O activity does not change, i.e. although the incorporated amount of K_2O is increased by a factor of 5, the K_2O partial pressure remains constant. For temperatures above 1373 K the activity increases by up to 3 orders of magnitude compared to the system with a mole fraction of 0.02.

If SiO_2 – Al_2O_3 mixtures are used as a sorbent material for potassium at temperatures up to 1673 K, and a K_2O enrichment up to 10 mol% should be achieved, a SiO_2/Al_2O_3 ratio between 0.59/0.31 and 0.70/0.20 results in minimum K_2O activity and thus maximum sorption capacity for potassium. Kinetic tests must show how near this thermodynamic result can be approached in reality.

CONCLUSIONS

In the experimental part of the paper it was demonstrated that mass spectrometric vaporisation studies on coal ashes and slags allow new insight into the alkali metal release from these materials. The alkali metals were detected as Na, NaCl, K and KCl in the gas phase with partial pressures up to about 10 Pa at temperatures from about 400 to 1800 °C. For the ashes of a series of lignite samples from the same mining area, a characteristic alkali release pattern with three temperature ranges was observed. Studies on a hard coal ash and the accompanying power plant slags showed that by far the greatest fraction of the alkali metals is strongly bound in or absorbed by silicates in the mineral matter of this coal and is not released during conversion in the plant.

In the theoretical part of the paper it was shown that the results of calculations using the thermodynamic data base system FACT and the modified quasi-chemical model for non-ideal solutions agree well with published experimental data for quasi-binary and quasi-ternary coal slag-relevant model systems. Thus modelling should be able to predict the thermodynamic behaviour of more complex, real coal slags. Calculations for the system K_2O plus SiO_2 – Al_2O_3 , the latter forming the major constituent of many hard coal ashes, confirmed the strong absorption capacity of silicates for alkali metals and enabled the determination of compositions for maximum alkali retention. This provides information for coal blending, if the slag is used as an alkali getter material.

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TABLES

Table 1 Chemical composition of coal slags and ashes.

Sample	Lignites (Rheinland)					Hard coal (Saar)	
	A	B	C	D	E	F	G
	laboratory ashes					plant slags	
Temperature	450 °C	450 °C	450 °C	550 °C	575 °C	≈1500 °C	≈1400 °C
Ash content ²⁾	ad 9.6	ad 12.6	ad 9.9	ad 6.2	ad 8.4	—	—
SiO ₂ ²⁾	42.4	46.7	36.4	12.7	38.3	42.0	40.9
Al ₂ O ₃	2.8	3.1	4.2	2.1	18.3	24.3	24.3
Fe ₂ O ₃	8.9	7.0	10.2	11.1	11.4	14.9	11.2
CaO	19.3	15.5	17.4	38.1	8.5	9.4	9.7
MgO	3.0	4.3	7.6	3.5	2.8	2.6	3.0
Na ₂ O	<0.1	0.5	1.5	0.3	1.1	1.2	1.5
K ₂ O	0.3	0.4	0.5	0.1	1.7	1.7	1.7
SO ₃	12.5	15.0	11.6	14.4	9.2	<0.1	<0.1
P ₂ O ₅	<0.1	<0.1	<0.1	0.1	0.2	0.3	0.3
CO ₂	5.9	3.0	5.1	³⁾ —	12.5	<0.1	<0.1
Cl	0.3	0.1	0.3	0.5	<0.1	—	—
Rest ⁴⁾	1.8	0.8	1.2	0.5	2.8	1.4	2.1
Sum	97.2	96.4	96.0	83.4	106.8	97.8	94.7

K11.10/12.10/14.10/4.1/7.5/7.2/7.3

1) ashing or local maximum particle temperature 2) mass fraction [%] 3) not analyzed 4) TiO₂, BaO, SrO, MnO

FIGURES

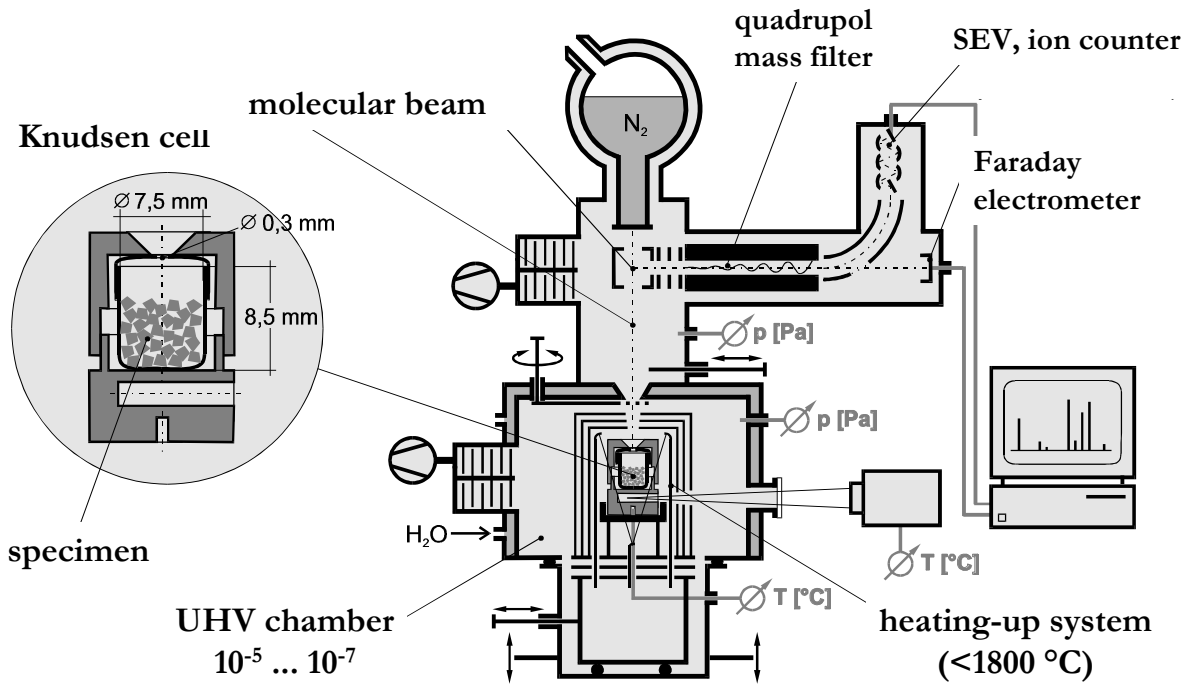


Fig. 1: Principle of Knudsen effusion mass spectrometry.

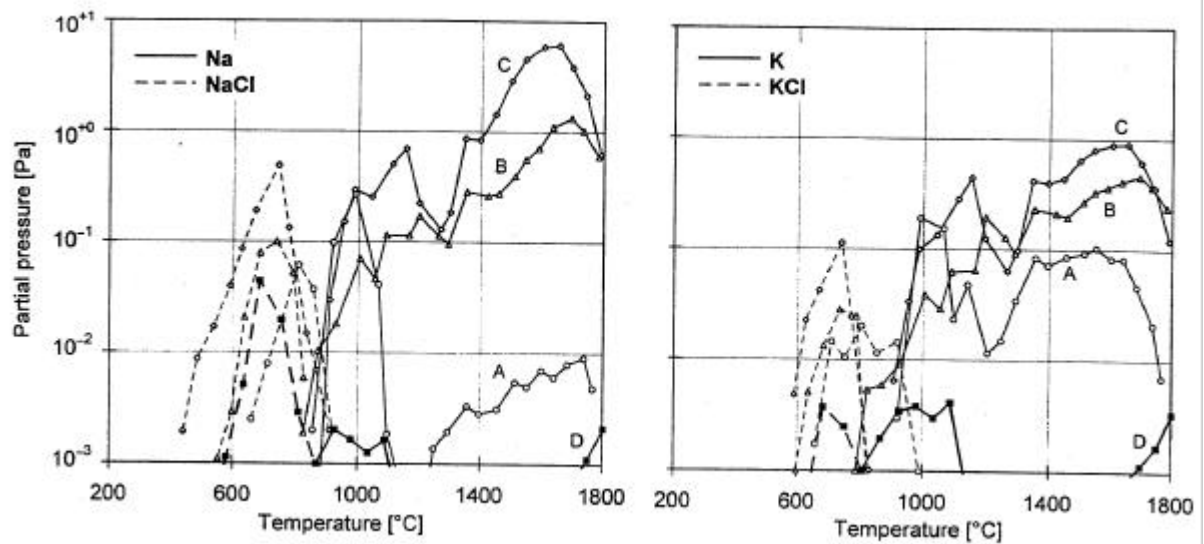


Fig. 2: Alkali release from laboratory ashes of different boiler lignites (A, B, C) and refinement lignite (D).

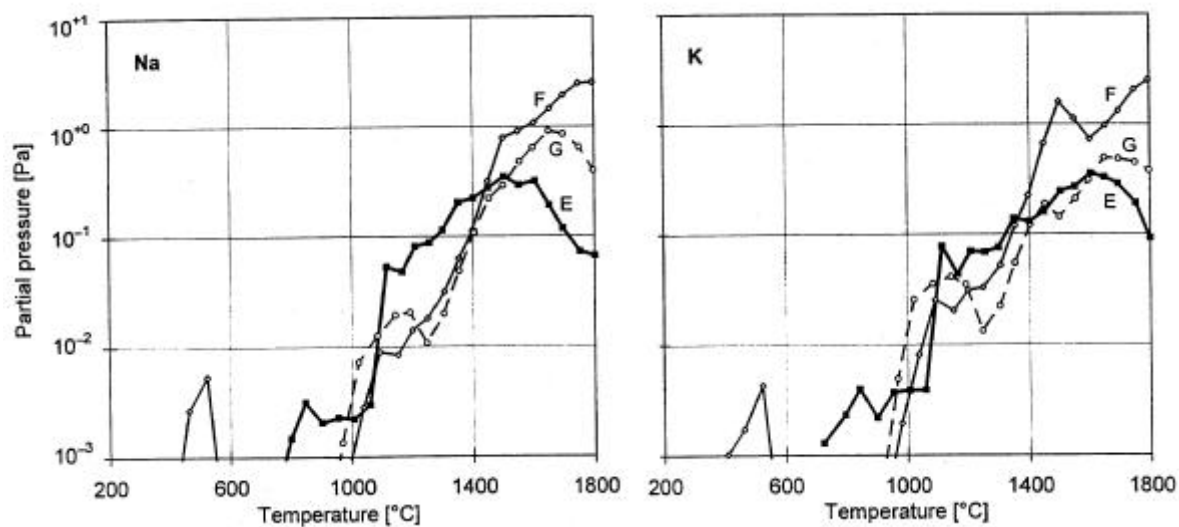


Fig. 3: Alkali release from a hard coal laboratory ash (E) and accompanying plant slags (F, G)

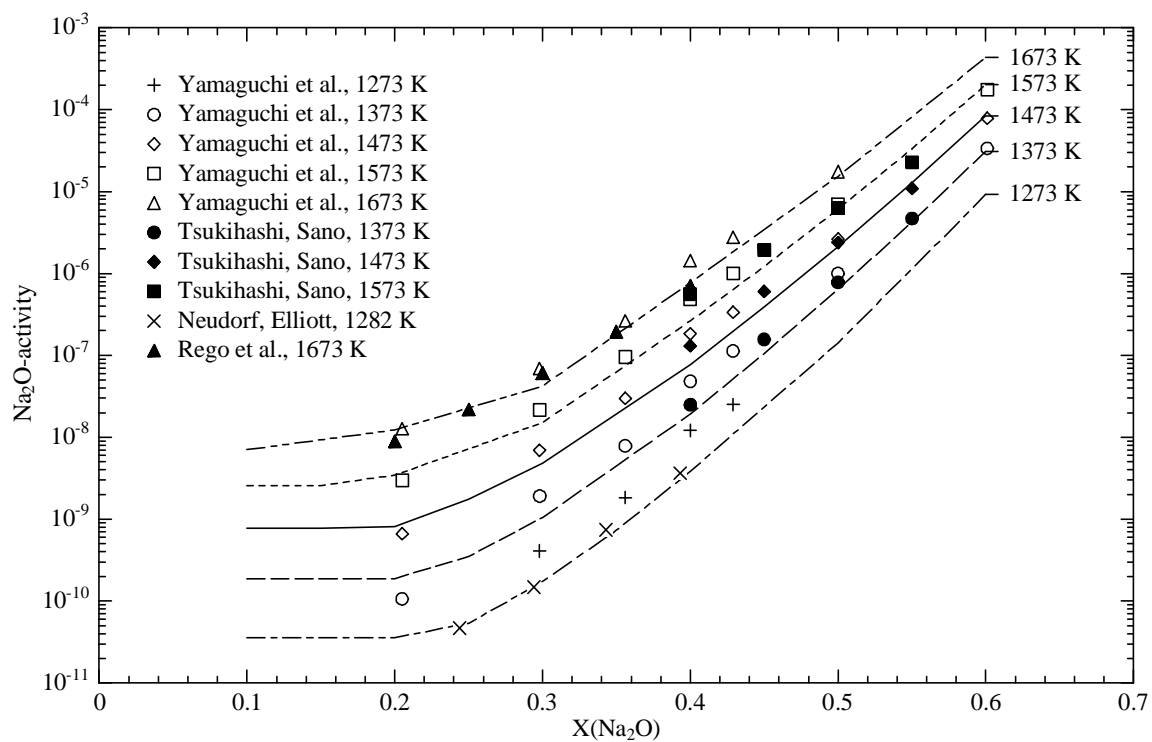


Fig. 4: Comparison of calculated and experimental Na_2O activities for the system $\text{Na}_2\text{O} \cdot \text{SiO}_2$.

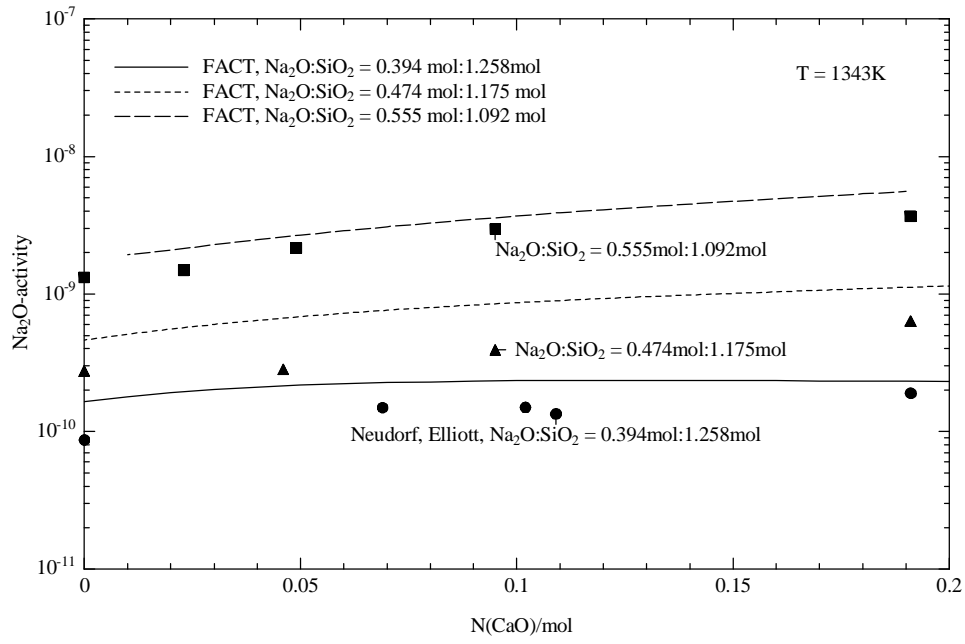


Fig. 5: Comparison of calculated and experimental Na_2O activities for the system $\text{Na}_2\text{O}*\text{SiO}_2*\text{CaO}$.

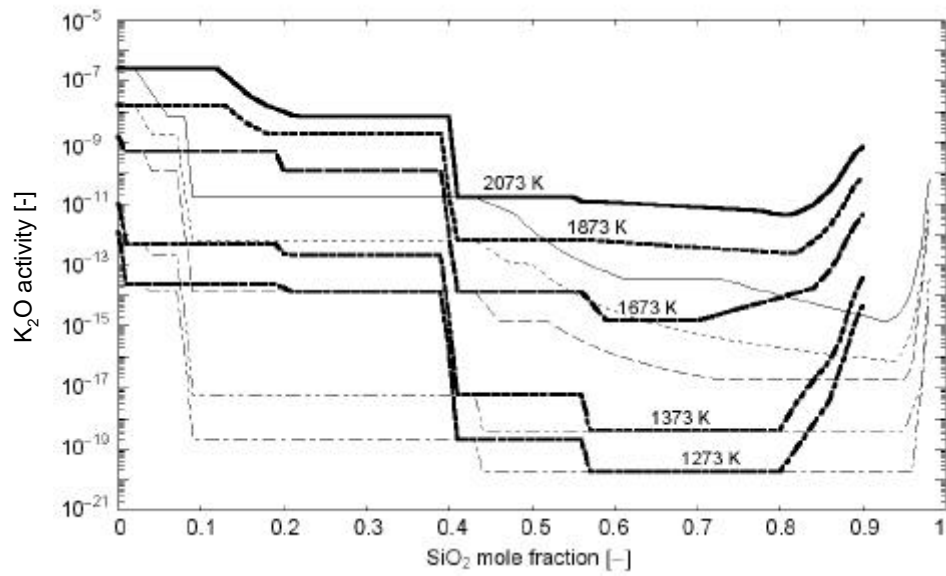


Fig. 6: K_2O activity in the system $\text{K}_2\text{O}*\text{SiO}_2*\text{Al}_2\text{O}_3$ for K_2O mole fractions of 0.02 (thin) and 0.10 (thick lines)