Structural dependence of alkali oxide activity in coal ash slags

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The limitation of fossil fuel resources and the necessity of reducing CO_2 emission require an increase of the efficiency of power plants by using combined cycle power systems. Pressurized Pulverized Coal Combustion (PPCC) is a potential concept to realise these objectives. The direct use of hot flue gas for driving a gas turbine requires a hot gas cleanup to achieve corrosion prevention of the turbine blading. One of the main problems is the alkali release during the coal combustion process. Molten coal ash slag has a high potential for alkali retention which depends on the alkali oxide activity in the slag. Knudsen Effusion Mass Spectrometry (KEMS) was used to determine thermodynamic data of alkali gas species over molten coal ash slags and of alkali oxides in molten coal ash slags. The main interest of the investigations focused on the structural dependence of the thermodynamic properties of the alkalis. It was found that there is a strong correlation between the thermodynamic properties and the ratio of nonbridging oxygen to tetrahedral oxygen (NBO/T). An increase of the polymerization of the slag results in a decrease of the alkali oxide activity in the slag and thus a decrease of the alkali partial pressure over the slag.
Keywords: coal ash slag, structure, alkali oxide activity, alkali vapour pressure, PPCC, KEMS.

Introduction

The limitation of fossil fuel resources and the necessity of reducing CO_2 emission require an increase of the efficiency of power plants by using combined cycle power systems. Up to now efficiencies in excess of 50 per cent are only achievable by using ash free fuels, for example, natural gas or oil in gas and steam power stations. Coal constitutes 80 per cent of the world's total fossil fuel resources. Today coal is mostly fired in steam power stations. Even if supercritical steam parameters are used, these coal fired power plants only reach efficiencies below 50 per cent, so that further development is essential. The Pressurized Pulverized Coal Combustion (PPCC) is a coal fired combined cycle concept which is able to achieve efficiencies in excess of 50 per cent[1].

The direct use of the hot flue gas for driving a gas turbine requires a hot gas cleanup to achieve corrosion prevention of the turbine blading. One of the main problems is the alkali release during the coal combustion process. The alkali metals are mainly bond in the mineral matter of the coal as salts and silicates. The alkali release leads to an alkali concentration in the flue gas significantly higher than the specifications of the gas turbine manufacturers.

Molten coal ash slag has a high potential for alkali retention which depends on the alkali oxide activity in the slag. This paper deals with the structural dependence of the alkali oxide activity in the coal ash slag.

Experimental

The alkali oxide activities in and the alkali partial pressures over a molten coal ash slag with and without additives and several model slags were investigated by Knudsen Effusion Mass Spectrometry (KEMS)[2] in the temperature range from 1250 to 1450°C.

Figure 1 shows a scheme of the Knudsen cell mass spectrometer system which consist mainly 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 set-up 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 a cell with a diameter of 7.5 mm, a volume of 1500 mm^3 and an orifice diameter of 0.3 mm was used. The cell is heated up by heat radiation and electron emission of a tungsten cathode. A pyrometer and thermocouples were used to measure the temperature.

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

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 from the detector signals I_i the relation

$$p_i = c \frac{I_i T}{A_i \sigma_i} \quad [1]$$

was used. A_i is the isotopic abundances and σ_i is the ionization cross sections. A_i and σ_i are known from data bases[3]. The calibration constant c of the system was determined by a partial pressure measurement with pure silver as reference.

Ion source
Molecular beam
Knudsen cell
Sample
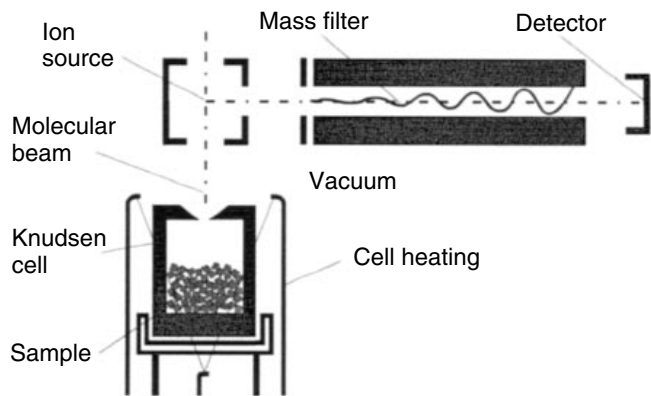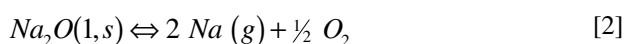Mass filter
Detector
Vacuum
Cell heating

Figure 1. Scheme of Knudsen effusion mass spectrometry

For the calculation of the alkali oxide activity in the slag stoichiometric vaporization of Na_2O according to Equation [2] and an ideal behaviour of the gas phase was assumed[4-5].

$$Na_2O(1,s) \Leftrightarrow 2\,Na\,(g) + \frac{1}{2}\,O_2 \qquad [2]$$

Dimers and monooxides are negligible, because their concentration in the gas phase is orders of magnitude lower than the concentration of Na and O_2. According to Equation [2] the partial pressure of O_2 is one fourth of the partial pressure of Na. Therefore, the alkali oxide activity was calculated according to Equation [3]:

$$a_{Na_2O} = \frac{p_{Na}^{2.5}}{2K_p} \qquad [3]$$

where a_i is the activity, p_i is the determined partial pressure, and K_p is the equilibrium constant of [2]. The data of the equilibrium constant were taken from the FACT database.

The first part of this paper deals with the properties of a coal ash slag from a pilot plant (Table I) and the influence of 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[6]. This has been taken into consideration for selecting the 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 second part of this paper deals with the properties of model slags (Table II). Pure oxides were mixed and annealed at 1500°C for two hours. The model slags have different ratios of base to acid according to Equation [4] and of nonbridging oxygen to tetrahedral oxygen (NBO/T) according to Equation [5] in order to investigate the influence of the structure of the slag.

$$\frac{base}{acid} = \frac{Na_2O + K_2O + FeO + MgO + CaO}{SiO_2 + TiO_2 + Fe_2O_3 + Al_2O_3} \qquad [4]$$

$$\frac{NBO}{T} = \frac{Na_2O + K_2O + FeO + MgO + CaO - \left(Fe_2O_3 + Al_2O_3\right)}{SiO_2 + TiO_2 + 2*\left(Fe_2O_3 + Al_2O_3\right)} \qquad [5]$$

Results and discussion

Figures 2 and 3 show the results of the series with boiler slag and five mass per cent additives. The activities of sodium oxide and the sodium partial pressure are given as a function of the reciprocal temperature. The behaviour of the potassium oxide activity in the slag and the potassium partial pressure over the slag is in principle the same. The samples with addition of SiO_2 and particular TiO_2 show a significant decrease of the alkali oxide activity in the slag and thus a significant decrease of the alkali partial pressure over the slag. At 1400°C the partial pressure of sodium is reduced from 0.6 Pa over the untreated boiler slag to 0.42 Pa over the boiler slag with 5 mass per cent TiO_2. This is a decrease of 30 per cent. At 1400°C the potassium vapour pressure is reduced from 0.59 Pa over the untreated slag down to 0.375 Pa over the sample with 5 mass per cent TiO_2. This is a decrease of 36 per cent. As expected, SiO_2 and TiO_2 react as network forming agents, which results in an increased polymerization of the slag. This increase of polymerization results in a decreased alkali oxide activity and thus a decreased alkali vapour pressure. Figure 4 shows a silica melt and the influence of sodium oxide and calcium oxide on the structural units[7]. Network modifiers like alkali oxides and alkaline earth oxides break up the oxygen bridges between Si cations and this results in a depolymerization of the melt. The degree of polymerisation of a slag has a direct influence on its alkali oxide activity. The addition of aluminium seems to have less effect on

Table I
Composition of the coal ash slag (mass per cent)

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O	P$_2$O$_5$	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 II
Composition (mass per cent) and structure of the model slags

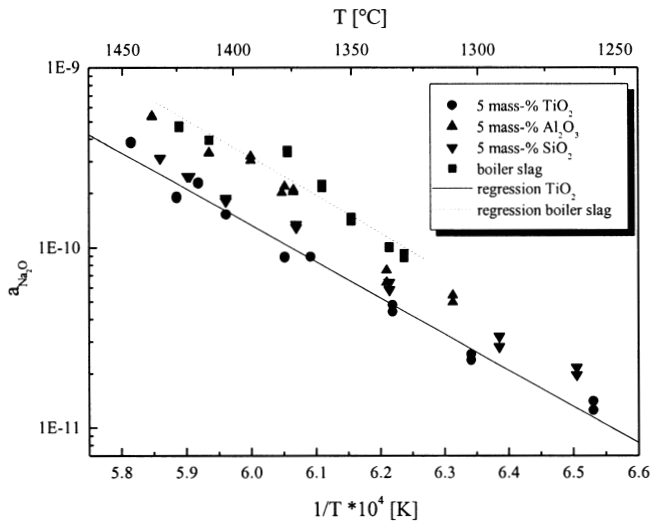|	M1	M2	M3	M4	Boiler slag red.	Boiler slag ox.
SiO$_2$	51.76	55.91	56.22	56.02		
Al$_2$O$_3$	28.20	19.64	24.00	29.46		
CaO	15.29	19.99	15.04	9.88		
Na$_2$O	4.74	4.46	4.75	4.63		
Base/acid	0.307	0.381	0.294	0.205	0.543	0.283
NBO/T	0.051	0.179	0.078	-0.025	0.182	-0.064

MOLTEN SLAGS FLUXES AND SALTS

Figure 2. Sodium oxide activities in a boiler slag with and without additives
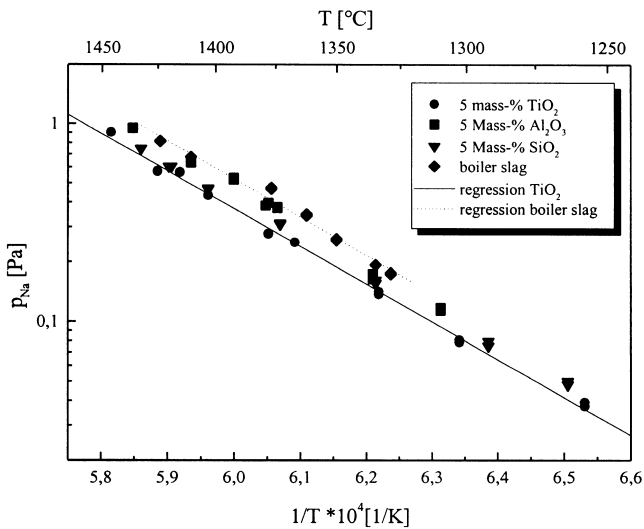
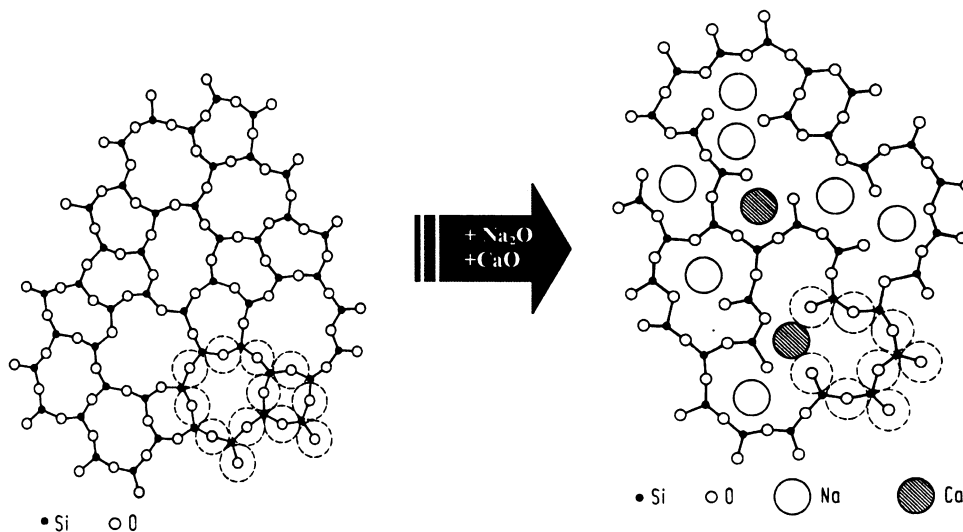**Figure 3. Sodium partial pressure over a boiler slag with and without additives**

alkali oxide activity. Aluminium is an intermediate in glass melts. It 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[8–9]. In six fold coordination it is no longer a network former and this explains why aluminium shows only a small influence on alkali oxide activity. This small effect is due only to dilution of the slag.

In the model slags the number of slag components was reduced to investigate the influence of the structure of the slag on the alkali oxide activity. The model slags consist only of SiO_2, Al_2O_3, CaO, and Na_2O (Table II). The Na_2O concentration is constant. The model slags have similar ratios of base to acid and NBO/T as the boiler slag under a reducing or an oxidizing atmosphere. Under oxidizing conditions the slag contains Fe_2O_3 which acts as an intermediate. Under reducing conditions it contains FeO which acts as a network modifier.

Figure 5 shows the sodium oxide activities in the model slags. Although the concentration of Na_2O in all model slags is nearly the same, there is a difference of more than one order of magnitude in the sodium oxide activities. Taking into account the structural data of the model slags (Table II) there is a strong correlation between the NBO/T ratio and the sodium oxide activity in the slag. A decrease of the NBO/T ratio, which means an increase of the polymerization of the slag, results in a decrease of the alkali oxide activity in the slag and thus a decrease of the alkali partial pressure over the slag.

Concerning its structure, the boiler slag is under the reducing conditions in the KEMS experiments very similar to the model slag M2. But the Na_2O concentration in the boiler slag is much lower. Therefore, the sodium oxide activities differ by a factor of about four. But the activities are in the same order of magnitude which indicates the structural similarity of the slags. Further on the structure of the slag cannot only be described by the NBO/T ratio. The structure is also influenced by the strength of the oxygen bond. According to Dietzel's[10] field strength criterion the Ca^{2+} in the model slags is a stronger network modifier than the Fe^{2+} in the boiler slag. This results in an increased alkali oxide activity in the slag at the same NBO/T ratio.

Figure 4. Influence of sodium and calcium on a silicate network

Figure 5. Sodium oxide activities in model slags

Conclusions

Knudsen Effusion Mass Spectrometry (KEMS) was used to determine alkali oxide activities in molten coal ash slags and vapour pressures of alkali gas species over molten coal ash slags. It was found that there is a strong correlation between the thermodynamic properties and the ratio of nonbridging oxygen to tetrahedral oxygen (NBO/T). An increase of the polymerization of the slag results in a decrease of the alkali oxide activity in the slag and thus a decrease of the alkali vapour pressure over the slag. Therefore, network forming agents like SiO_2 and TiO_2 are suitable additives to decrease the alkali oxide activity in coal slag and thus decrease the concentration of corrosive alkali species in the hot flue gas of a PPCC.

Acknowledgement

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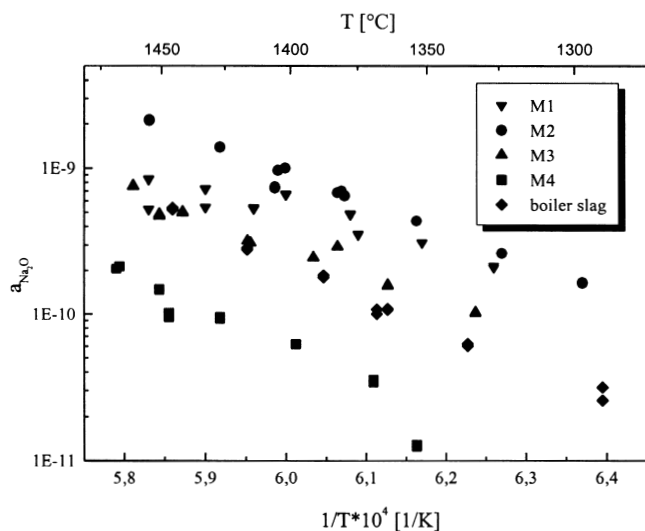10. Dietzel, A. Z. Elektrochem., vol. 48, 1942, pp. 9–23.