Alkali Removal at About 1400 °C for the Pressurized Pulverized Coal Combustion Combined Cycle. 1. Thermodynamics and Concept

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Received June 30, 2006. Revised Manuscript Received August 24, 2006

The limitation of fossil fuel resources and the necessity of reducing CO₂ emission require an increase of the efficiency of power plants by using combined cycle power systems. The pressurized pulverized coal combustion (PPCC) combined cycle is a coal fired combined cycle concept which is able to achieve efficiencies in excess of 53%. 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 release of alkalies during the coal combustion process. Therefore, the thermodynamic basics for the control of alkali vapor pressures in the hot flue gas of PPCC have been investigated by thermodynamic equilibrium calculations and Knudsen effusion mass spectrometric measurements on alkali oxide activities in and alkali partial pressures over coal ash slags with and without additives and alkali laden model sorbents. The obtained results reveal that the requirements of the gas turbine manufacturers regarding alkali concentration in the hot flue gas should be satisfiable by certain aluminosilicate sorbents. On the basis of these results, a concept for alkali vapor removal is proposed.

Introduction

The limitation of fossil fuel resources and the necessity of reducing CO₂ emission require an increase of the efficiency of power plants by using combined cycle power systems. Up to now, efficiencies in excess of 50% are only achievable by using ash free fuels, for example, natural gas or oil in combined cycle power plants. Coal constitutes 80% 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%, so that further development is essential, e.g., coal based combined cycle processes with the highest efficiency.

The pressurized pulverized coal combustion (PPCC) combined cycle (Figure 1) is one coal fired combined cycle concept which is able to achieve efficiencies in excess of 53%.1,2 Coal is burned in a slag-tap furnace at 1500–1700 °C and 15–20 bar. The hot flue gas is directly used for driving a gas turbine having a gas inlet temperature of ≥1200 °C (ISO) and a real flue gas temperature of ≥1400 °C, respectively. The residual thermal energy of the gas stream leaving the gas turbine is finally transferred to a steam cycle.

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. Beside the fly ash, which is molten because of the very high temperature, the main problem is the release of alkalies during the coal combustion process. The alkali metals are mainly bound 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 (<0.01 (mg Na + K)/Nm³). Therefore, the flue gas is routed through a column of ceramic balls as a slag separation unit and an alkali removal unit at an average temperature of 1450 °C before entering the gas turbine.

In the last twenty years, there have been several studies of sorbents for capturing alkalies, e.g., refs 3–8. According to these investigations, the most preferable method of alkali control is

![Figure 1. Schematic flow diagram of the pressurized pulverized coal combustion (PPCC) combined cycle process.](image)

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to pass the combustion gases through a fixed bed of nonvolatile inorganic solid sorbents. Possible sorbents should show high-temperature stability, fast sorption kinetics, and high loading capacity. Aluminosilicates like kaolin, bauxite, bentonite, and emathlilite have been identified as suitable sorbents for gas phase alkali capture at high temperatures. Depending on the composition of the sorbent, chemical fixation (high silica content) or physical adsorption (high alumina content) prevail. However, the past investigations were concerned with cleaning flue gases at temperatures below 1000 °C. Since the alkali removal in a PPCC occurs at about 1400 °C, the data and mechanisms found in the literature cannot simply be applied.

The objective of the present work was to investigate the thermodynamic basics for the control of alkali vapor pressures in the hot flue gas of PPCC. Thus, the principle possibility of a successful alkali removal should be examined. Subsequently, a concept for the alkali removal should be developed. Two possible strategies were taken into consideration: (i) optimizing the alkali retention potential of the coal ash slag present in the combustion chamber and the liquid slag separator and/or (ii) alkali removal with solid sorbents. For this reason, alkali oxide activities in and alkali partial pressures over coal ash slags with and without additives and model sorbents were determined by Knudsen effusion mass spectrometry (KEMS). The experiments were accompanied by thermodynamic equilibrium calculations.

### Experimental Section

#### Samples

In the first step, the retention potential for alkalies of an original boiler slag from the PPCC pilot plant in Dorsten, Germany, and its improvement by network forming additives was investigated. The composition of the slag is given in Table 1. Coal ash slags can be regarded as silicate melts or glasses. The properties of silicate melts depend on their structure.

The polymerization of the slag has a strong influence on the alkali oxide activity in the slag. Therefore, the network forming additives SiO₂, TiO₂, and Al₂O₃ were used. Next, 5 or 10 mass % of these additives were mixed into the boiler slag. The samples were annealed for 24 h at 1600 °C in closed platinum crucibles before the KEMS measurements.

In the second step, mixtures of pure SiO₂, Al₂O₃, MgO, Na₂O, and K₂O were investigated as alkali laden model sorbents. The investigated compositions are given in Table 2. Thus, the alkali oxide activities in the thermodynamic stable alkali containing phases were determined. The mixtures were annealed for 24 h at 1600 °C in closed platinum crucibles before the KEMS measurements.

#### Experimental Setup

The alkali oxide activities in and the alkali partial pressures over the slags and model sorbents were investigated by Knudsen effusion mass spectrometry (KEMS) in the temperature range from 1250 to 1450 °C.

### Table 1. Analysis of the Coal Ash Slag (mass %)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>36.2</td>
<td>27.0</td>
<td>14.4</td>
<td>9.1</td>
<td>2.5</td>
<td>2.1</td>
<td>1.2</td>
</tr>
</tbody>
</table>

### Table 2. Analysis of the Alkali Laden Model Sorbents (mass %)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSiNa5</td>
<td>34.57</td>
<td>60.29</td>
<td>5.14</td>
<td></td>
</tr>
<tr>
<td>AlSiNa5</td>
<td>66.01</td>
<td>28.96</td>
<td>5.03</td>
<td></td>
</tr>
<tr>
<td>AlSiNa5</td>
<td>77.16</td>
<td>17.76</td>
<td>5.07</td>
<td></td>
</tr>
<tr>
<td>AlSiNa05</td>
<td>77.47</td>
<td>22.04</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>AlSiNa1</td>
<td>81.12</td>
<td>17.67</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>AlSiNa4</td>
<td>78.72</td>
<td>17.15</td>
<td>4.13</td>
<td></td>
</tr>
<tr>
<td>AlSiNa9</td>
<td>73.23</td>
<td>17.59</td>
<td>9.19</td>
<td></td>
</tr>
<tr>
<td>AlSiK4</td>
<td>78.31</td>
<td>17.15</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>AlSiNa0K3</td>
<td>74.03</td>
<td>19.65</td>
<td>2.83</td>
<td>4.38</td>
</tr>
<tr>
<td>AlSiNa3Na03</td>
<td>78.53</td>
<td>17.67</td>
<td>3.47</td>
<td>0.31</td>
</tr>
<tr>
<td>AlSiNa5Na05</td>
<td>75.87</td>
<td>15.52</td>
<td>3.82</td>
<td>4.73</td>
</tr>
<tr>
<td>AlSiNa8Na1</td>
<td>71.02</td>
<td>15.87</td>
<td>8.30</td>
<td>4.45</td>
</tr>
<tr>
<td>AlSiNa8Na7</td>
<td>68.64</td>
<td>16.70</td>
<td>7.25</td>
<td>3.77</td>
</tr>
</tbody>
</table>

Figure 2 shows a scheme of the used Knudsen cell mass spectrometer system which mainly consists 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, and 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 (<10⁻¹³ 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 mm³, 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 in the ion source via a tungsten cathode, the ion beam is directed into the quadrupole mass filter system and analyzed 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 total pressure, the relation was used.

\[ p_i = \frac{I_i}{A_i \sigma_i} \]

where \( A_i \) is the isotopic abundance, and \( \sigma_i \) is the ionization cross section. \( A_i \) is known from databases, and \( \sigma_i \) is, in case of sodium, \( 3.9 \times 10^{-20} \text{ m}^2 \) at an ionization energy of 70 eV and \( 3.39 \times 10^{-20} \text{ m}^2 \) at 55 eV and, for potassium, \( 5.7 \times 10^{-20} \text{ m}^2 \) and \( 6.19 \times 10^{-20} \text{ m}^2 \), respectively. The calibration constant \( c \) of the system was determined by a partial pressure measurement with pure silver (\( \sigma = 4.59 \times 10^{-20} \text{ m}^2 \) and \( 4.85 \times 10^{-20} \text{ m}^2 \)) as reference.


For the calculation of the alkali oxide activity in the slag stoichiometric vaporization of Na₂O according to eq 2, ideal behavior of the gas phase was assumed.¹⁵,¹⁶

\[ \text{Na}_2\text{O}(l,s) \rightarrow 2\text{Na}(g) + \frac{1}{2}\text{O}_2 \]  

(2)

Dimers, monoxides, and atomic oxygen are negligible, because their concentration in the gas phase is orders of magnitude lower than the concentration of Na and O₂. According to eq 2, the partial pressure of O₂ is one-fourth of the partial pressure of Na. Therefore, the alkali oxide activity was calculated according to eq 3:

\[ a_{\text{Na}_2\text{O}} = \frac{p_{\text{Na}}^{2.5}}{2K_p} \]  

(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 pure substance database.¹⁷

**Thermodynamic Equilibrium Calculations.** To get a better understanding of the thermodynamics of the oxide systems, parallel with the experiments, thermodynamic equilibrium calculations were performed using the computer program FactSage and the FACT database.¹⁷ The calculation of the thermodynamic equilibrium is done in this program by minimizing the Gibbs free energy of chemical reaction systems. The amount and composition of compounds in complex chemical reaction systems can be calculated for a wide temperature and pressure range. However, investigations have shown that the available thermochemical databases are not sufficient to calculate the exact values of alkali oxide activities in and alkali vapor pressures over oxide mixtures and melts.¹⁸ Therefore, experiments are necessary, anyway.

**Results and Discussion**

**Alkali Retention by Coal Slag.** Figures 3 and 4 show the results of the measurements on a boiler slag with and without additives.

![Figure 3. Sodium oxide activity in a boiler slag with and without additives.](image)

![Figure 4. Potassium oxide activity in a boiler slag with and without additives.](image)

of the reciprocal temperature. The behavior of the sodium and potassium partial pressure over the slag are in principle the same. However, the absolute values of the partial pressures are different in the experiments and in the real plant, because these values depend upon other components of the flue gas, e.g., chlorine, sulfur, and water vapor, and especially on the oxygen partial pressure. Therefore, mainly the influence of network forming additives on the activity of alkali oxides is discussed. Furthermore, the oxidation state of iron may be different in the experiments and in the real plant because of the different oxygen partial pressures. The other main constituents of the slag should have the same oxidation state under both conditions. Since FeO is a weak network modifier and Fe₂O₃ is a weak network former or an intermediate, the absolute value of the alkali oxide activity is influenced by the oxidation state of iron. Therefore, alkali oxide activities are likely lower under PPCC conditions than under experimental conditions. However, the used additives tend to have the same effect under reducing and oxidizing conditions.

The samples with addition of SiO₂ and particularly TiO₂ show a significant decrease of the alkali oxide activity in the slag. At 1400 °C, the sodium oxide activity is reduced from about 3 × 10⁻¹⁰ in the untreated boiler slag to about 2 × 10⁻¹⁰ in the boiler slag with 5% SiO₂ or TiO₂. This is a decrease of 30%. It is decreased to about 6 × 10⁻¹¹ with 10% SiO₂ or TiO₂. This is a decrease of 80%. The potassium oxide activity is reduced from about 2.5 × 10⁻¹² in the untreated slag down to 1.2 × 10⁻¹² in the slag with 5% SiO₂ or TiO₂ and down to 5 × 10⁻¹³ in the slag with 10% SiO₂ or TiO₂. This is a decrease of 50% and 80%, respectively. In both cases, the effect of 5% TiO₂ is slightly stronger than that of 5% SiO₂ and the effect of 10% SiO₂ is slightly stronger than that of 10% TiO₂. As expected, both SiO₂ and TiO₂ 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. The addition of aluminum has less effect on the alkali oxide activity. Aluminum is an intermediate in glass melts. It can substitute silicon in silicate melts in 4-fold coordination by charge balancing with a cation in the vicinity. But, it can also occur in 6-fold coordination.¹⁹,²⁰ In 6-fold coordination, it is no longer a network former and this explains why aluminum

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show only a small influence on alkali oxide activity. This small effect is only due to the dilution of the slag.

The determined alkali partial pressures over the slag are reduced from about 0.6 Pa over the untreated slag down to about 0.3 Pa over the slag with 10% SiO$_2$. This is a decrease of 50%. These vapor pressures are still about 2 orders of magnitude higher than the specifications of the gas turbine manufacturers and, thus, much too high for driving a gas turbine without corrosion risk. Moreover, the vapor pressures in a real plant might be higher because of the composition of the flue gas, as mentioned before. The addition of further network forming additives would further increase the polymerization of the slag resulting not only in a further decreased alkali oxide activity in the slag but also in an increased viscosity of the slag, which complicates or even hinders the removal of liquid slag in the boiler and the liquid slag separator.

Between 1450 and 1350 °C, which will probably be the temperature range of interest in a future PPCC plant, the alkali oxide activity is decreased by up to 1 order of magnitude. Thus, a decrease in temperature by less than 100 K has the same effect as the addition of 10% SiO$_2$ or TiO$_2$. However, a colder slag has a higher viscosity resulting in the problems mentioned before. Further on, a reduced gas temperature results in a reduced efficiency of the process, so that one would rather increase the gas temperature. Anyway, the vapor pressures are too high. Therefore, a separate alkali removal unit is necessary to achieve alkali concentrations in the hot flue gas compatible with the specifications of the gas turbine manufacturers.

**Alkali Removal by Sorbents.** Thermodynamic equilibrium calculations and measurements on alkali oxide activities in alkali laden model sorbents (Table 2) were performed to determine the most suitable sorbent composition. From the literature, it is well-known that aluminosilicates are suitable sorbents for alkali capture at temperatures below 1000 °C. Therefore, the investigations focused on aluminosilicates.

The stoichiometric alkali aluminosilicates with the lowest alkali oxide activities, albite (NaAlSi$_3$O$_8$) and orthoclase (KAlSi$_3$O$_8$), which are formed during alkali sorption below 1000 °C, are not stable at 1400 °C because their melting points are too low. Beside carnegieite (NaAlSi$_3$O$_8$) and leucite (KAlSi$_3$O$_8$), only the liquid phase is as stable as the alkali containing phase at 1400 °C. The alkali partial pressures over both solid phases are already higher than the specifications of the turbine manufacturers at 750 °C and, thus, much higher at 1400 °C. Therefore, the alkali have to be bound in the liquid phase to fulfill the demands of the turbine manufacturers, if it is possible at all.

First of all, the alkali oxide activity in model sorbents was calculated for different alkali oxide concentrations depending on the Al$_2$O$_3$/SiO$_2$ molar ratio at 1400 °C to determine the optimum Al$_2$O$_3$/SiO$_2$ ratio of the sorbent. The results of the thermodynamic equilibrium calculations for sodium oxide are given in Figure 5. Apart from the absolute values, the activities of potassium oxide follow the same trend. It can be seen from Figure 5 that there is a minimum sodium oxide activity of about 1.8 $\times$ 10$^{-14}$, independent of the sodium oxide concentration in the system below ~3 mol % sodium oxide. At these lower sodium oxide concentrations, the solid phases like mullite and tridymite are stable beside a liquid solution phase. All sodium oxide is present in this liquid phase. However, the sodium oxide in this liquid phase is independent of the sodium oxide concentration in the system. Only the amount of liquid phase is influenced by the sodium oxide concentration. The amount of the different solid phases depends on the Al$_2$O$_3$/SiO$_2$ ratio. Therefore, the sodium oxide activity in this liquid phase is constant. At higher sodium oxide concentrations, the system forms one homogeneous liquid phase. Thus, the sodium oxide activity in the system depends on the sodium oxide concentration in the liquid phase/system. Moreover, at higher sodium oxide concentrations, the sodium oxide activity has a discrete minimum. The minimum shifts from an Al$_2$O$_3$/SiO$_2$ ratio of about 1/4 for 3 mol % sodium oxide to an Al$_2$O$_3$/SiO$_2$ ratio of about 1/4 for 10 mol % sodium oxide. This trend was expected, because alumina only acts as network former if its charge in 4-fold coordination is compensated by a cation, in this case sodium. The highest polymerization of the liquid phase and, thus, lowest sodium oxide activity in the liquid is obtained if alumina and sodium oxide balance each other. The polymerization of the liquid decreases and, thus, the sodium oxide activity increases if there is no balance. Since sodium oxide is a strong network modifier and alumina is only an intermediate, an excess of sodium oxide (lower alumina content) leads to a much steeper decrease of polymerization of the liquid phase and, thus, increase of sodium oxide activity in the liquid than a similar excess of alumina.

![Figure 5](image)

Figure 5. Calculated sodium oxide activity in the system Na$_2$O-SiO$_2$-Al$_2$O$_3$ at 1400 °C.

![Figure 6](image)

Figure 6. Sodium oxide activity in model sorbents with different Al$_2$O$_3$/SiO$_2$ ratios.
sodium oxide activity (Figure 6). In sorbents with more than 1% sodium oxide and an Al₂O₃/SiO₂ molar ratio of about 1/8, the sodium oxide activity increases with increasing sodium oxide content (Figure 7). In seeming disagreement with the thermodynamic equilibrium calculations, the mixture with about 0.5% sodium oxide (AlSi8Na05) shows a higher sodium oxide activity than the mixture with about 1% sodium oxide (AlSi8Na1). According to the calculations, it should show the same sodium oxide activity. The reason is the kinetic of melt formation. As visible observations and X-ray diffraction (XRD) analyses of the samples after the measurement show, no solid alkali containing phase was detectable in any mixture; the mixtures with high sodium content were completely molten, AlSi8Na1 was partly molten and contained mullite and cristobalite, and AlSi8Na05 was almost unmolten mainly consisting of mullite and cristobalite. Likely, the melt formation in AlSi8Na05 was not completed resulting in a higher sodium concentration in the liquid phase than expected for thermodynamic equilibrium conditions and thus leading to a higher sodium oxide activity in the mixture.

An important result of the measurements is that in relatively good agreement with the calculations the achievable sodium oxide activity is about 3 orders of magnitude lower than the lowest measured sodium oxide activity in the slag with additives. This should be sufficient to fulfill the requirements of the turbine manufacturers. Even at the highest measured temperature of 1450 °C, the activity should be sufficiently low. Measurements with mixtures containing potassium oxide or both sodium and potassium oxide (Figure 8) show that it should also be possible to sufficiently absorb potassium oxide. Although the potassium oxide concentration in the AlSi8Na3K3 mixture is about three times higher than in the slag, the potassium oxide activity is 2.5 orders of magnitude lower than the lowest measured potassium oxide activity in the slag with additives. Moreover, potassium oxide does not seem to influence the sodium oxide activity. According to the calculations, a mixture with 3% sodium oxide should show nearly the same sodium oxide activity as a mixture with 1% sodium oxide. Accordingly, the measured sodium oxide activities in AlSi8Na1 and AlSi8Na3K3 are nearly the same.

Although the achievable alkali oxide activities should be sufficient, the fact that sorbents with very low alkali oxide concentrations show higher alkali oxide activities could be a problem. If the formation of melt is too slow, a fresh sorbent should show in the beginning of alkali sorption too high alkali oxide activities until a certain amount of alkalies is absorbed.

To overcome this problem, network modifying additives like alkali or alkaline earth oxides which decrease the melting point and, thus, promote the melt formation can be added. However, the sorbent itself should be solid at 1400 °C for better handling. Therefore, the addition of alkaline earth oxides is more reasonable. Furthermore, in a real power plant, clay minerals will likely be used instead of synthetic mixtures. Therefore, the influence of magnesia as a network modifying additive on the sodium oxide activity was investigated. Figure 9 shows the measured alkali oxide activity in the alkali laden sorbents with different concentrations of magnesia and sodium oxide as a function of the reciprocal temperature. As expected, magnesia acts as a network modifier resulting in a depolymerization of the liquid and, thus, leading to an increased sodium oxide activity. For example, the sodium oxide activity in AlSi8Na1 is about 5 × 10⁻¹⁴ at 1400 °C whereas it is about 2 × 10⁻¹³ in AlSi8Mg8Na1. A higher concentration of magnesia results in a higher sodium oxide activity. The sodium oxide activity is about 2 times higher in AlSi8Mg8Na5 than in AlSi8Mg4Na5. In contrast to the mixtures without magnesia, the mixture with 0.3% sodium oxide shows a lower sodium oxide activity than the mixtures with higher sodium oxide concentration. The mixture was completely molten. However, the sodium oxide activity in AlSi8Mg4Na03 is in the same range as in AlSi8Na1. This means that, on one hand, a magnesia containing sorbent should sufficiently absorb alkalies from the beginning in contrast
Concept for Alkali Removal at about 1400 °C under PPCC Conditions and Outlook. On the basis of the obtained results, a concept of a so-called “drip-off getter” is proposed to sufficiently remove alkali metal vapors from the hot flue gas at about 1400 °C under PPCC conditions. The drip-off getter should be a high temperature and flow resistant aluminosilicate with a preferable Al$_2$O$_3$/SiO$_2$ ratio of about 1/8. In contact with gaseous alkali species, it should form a low melting phase at its surface with a low alkali oxide activity and, thus, a low alkali vapor pressure. This liquid should easily drip off from the sorbent surface. Thus, the absorbed alkalies can easily be removed out of the alkali removal unit with the formed liquid. In addition, the sorbent always has an unsaturated surface. The hot flue gas should flow countercurrent to the dripping off liquid. Thus, the liquid can absorb more alkalies resulting in a decreased viscosity and, thus, an easier removal. In addition, the effective capacity of the sorbent is increased, because the maximum alkali oxide concentration in the liquid depends on the alkali concentration of the hot flue gas at the inlet of the sorbent bed, which is much higher than the concentration at the outlet. Obviously, the sorption kinetic should be fast.

In future work, sorbents will be investigated with respect to efficiency, capacity, sorption kinetics, and relevant sorption mechanisms. Model systems and technical sorbent materials will be selected based on the results of the present work.

Conclusions

The thermodynamic basics for the control of alkali vapor pressures in the hot flue gas of PPCC have been investigated by Knudsen effusion mass spectrometric measurements on alkali oxide activities in and alkali partial pressures over coal ash slags with and without additives and alkali laden model sorbents. The experiments were accompanied by thermodynamic equilibrium calculations.

In a first step, the improvement of the alkali retention potential of the coal ash slag present in the combustion chamber and the liquid slag separator was investigated. The slag itself has a relatively high potential for alkali retention. This potential can be increased by network forming additives like SiO$_2$ and TiO$_2$. The addition of 10% of these additives decreases the alkali oxide activity in the slag by 80%. However, the achievable alkali vapor pressures are still about 2 orders of magnitude higher than the specifications of the gas turbine manufacturers. Therefore, a separate alkali removal unit employing sorbent materials is necessary.

In a second step, the thermodynamic behavior of alkali laden model sorbents was investigated to determine the most suitable sorbent composition. The lowest alkali oxide activities have been achieved with aluminosilicates having an Al$_2$O$_3$/SiO$_2$ ratio of about 1/8. The alkalies are bound in the liquid phase in these sorbents. At low alkali oxide concentrations (<1%) in the sorbent, the melt formation is kinetically limited, resulting in an increased alkali oxide activity. The addition of alkaline earth oxides like magnesia promotes the melt formation, leading to a low alkali oxide activity in the sorbent even at a very low alkali oxide concentrations, <1%. However, at higher alkali oxide concentrations (>1%), the alkali oxide activity is slightly increased in comparison with pure aluminosilicates. The calculated and measured alkali oxide activities of <10$^{-13}$ in the case of sodium oxide and <10$^{-14}$ in the case of potassium oxide should be sufficient to fulfill the requirements of the gas turbine manufacturers.

On the basis of the obtained results, the concept of a so-called “drip-off getter” is proposed to sufficiently remove alkali metal vapors from the hot flue gas at about 1400 °C under PPCC conditions.

Acknowledgment. This work is part of a project supported by the Bundesministerium für Wirtschaft und Technologie (BMWi) under contract number 0326844E. The authors thank M. Förster and D. Pavone (DKSF GbR) for kindly providing us with the original boiler slag of the PPCC test facility in Dorsten, H. Lippert (ZCH) for performing the chemical analysis, and P. Lersch for performing the XRD measurements.

EF060305K