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Studies of Alkali Sorption Kinetics for Pressurized Fluidized Bed Combustion by High Pressure Mass Spectrometry

Keywords : Alkali Sorption, Kinetics, PFBC, High Pressure Mass Spectrometry (HPMS)

Introduction

Economic and environmental considerations require an increase of efficiency of coal fired power plants. These requirements initiated the development of combined cycle power generation systems such as Pressurized Fluidized Bed Combustion (PFBC), in which coal derived pressurized combustion gases are used to directly power a gas turbine. The temperature of the combustion process of common PFBC's has to be kept below 900 °C in order to prevent slagging inside the fluidized bed. This limits turbine gas entrance temperatures to about 850 °C. The PFBC Combined Cycle technique offers an increased efficiency, reduced emissions, lower costs and better flexibility concerning fuel types. However, several problems occur. Coal contains some amounts of sodium and potassium compounds in different chemical forms like salts or clay minerals. These alkali metals are released during the combustion process and can cause high temperature corrosion of the turbine blading at operating temperatures above 600 °C. For this reason, the alkali removal from hot PFBC flue gases at temperatures between 800-900 °C has been a major issue within the past 20 years.

Arising from the revealed problems related to hot gas cleanup of ordinary PFBC systems due to the high temperatures and the demand for even higher efficiencies a Second Generation Pulverised Fluidized Bed Combustion Combined Cycle (2nd Gen. PFBC) system has been developed (figure 1). This system mainly consists of a two-staged combustion operating at 10-16 bar pressure. In a first stage the coal is gasified under reducing conditions ($\lambda < 1$) at temperatures of 650-750 °C. Leaving the first stage the combustion gases pass a complex gas

cleanup section, consisting of ceramic filters for ash removal and an alkali sorption unit. The cleaned up gas is then mixed with a secondary air stream and either burned in a second combustion chamber or directly inside the gas turbine, in both cases at $\lambda > 1$. The residual thermal energy of the gas stream leaving the turbine is finally heat transferred to a steam cycle. The 2nd Gen. PFBC has two main advantages over the ordinary PFBC system. Resulting from the two stage combustion the gas turbine's gas entrance temperatures can be raised up to 1250 °C and therefore increase the system's total efficiency. On the other hand, the positioning of the gas cleanup section into a region of lower temperatures offers new possibilities for improved ash and alkali removal.

However, although operating at lower temperatures, the problems of 2nd Gen. PFBC concerning efficient alkali removal from the combustion gases yet have to be solved to fulfil the demands of the gas turbine manufacturers, leading to maximum amounts of gas phase sodium and potassium species in the flue gas entering the gas turbine lower than 50 ppbw (Punjak et al. 1988)

Objectives

Among the direct insertion of sorbent materials into the fluidized bed the most preferable method of controlling alkali vapor is to lead the combustion gases through a fixed bed of inorganic solid sorbents. Possible sorbents (getters) should show high temperature stability, fast adsorption kinetics, high loading capacity and irreversible adsorption to prevent alkali desorption during process fluctuations. Thermodynamic calculations and earlier investigations by other authors have revealed aluminosilicates as suitable sorbent materials to fulfil this task.

Most of the past investigations on alkali removal were concerned with cleaning high temperature (800-900 °C) flue gases from ordinary pressurized fluidized bed combustors (Lee et al. 1980, Punjak et al. 1988). For this reason, the major part of the past research focused on removing alkali species, such as chlorides and sulfates, from simulated flue gases (SFG) under oxidizing conditions.

In contrast, the influence of reducing atmospheres on alkali removal by solid sorbents has been investigated to a much lower extent. Experiments concerning this field were either performed under much higher temperatures of 850-900 °C using mixtures of N₂/H₂ or simulated flue gases (Bachovchin et al. 1986) in respect to coal gasification systems (11 atm), or for the control of alkali species in biomass gasification systems at temperatures between 660-725 °C (Turn, Kinoshita et al. 1999). The disadvantage of the latter investigation is the use of biomass gasifier gas, which makes the evaluation of the results much more complicated.

However, laboratory experiments of alkali uptake by aluminosilicate sorbents in a reducing environment at 750 °C have not been established so far. Data upon adsorption kinetics and the rate of alkali uptake has yet to be achieved. The adsorption mechanism responsible for alkali uptake is of great concern, either chemisorption or physisorption, and has yet to be determined under these conditions. In this context, the influence of water on the alkali uptake has to be investigated as well.

Along thermogravimetric investigations in which the alkali capture measured as the weight gain of a small collection of particles or pellets as a function of time was monitored (Uberoi et al. 1990, Punjak et al. 1989), the packed bed method was the most favoured experimental approach. In fact, the latter one was the only method to provide data concerning the degree of purification of a gas stream from alkali species. Packed bed methods can be used to examine the influence of superficial gas velocity and gas hourly space velocity, carrier gas composition and moisture

content, sorbent bed temperature and elapsed time. In most cases, a solid source of alkalichloride was used.

In packed bed methods the alkali capture was either determined by monitoring the alkali content of the gas exiting the packed bed or by analyzing the getter material after the completion of the test. Determining the alkali content of the gas downstream the sorbent bed has been, in most cases, performed by quenching the gas stream after the getter bed and analyzing the condensate for alkalis (Uberoi et al.1990). This was mainly done by acid solubilization of the condensate and atomic absorption (K) or atomic emission (Na) spectroscopy. The amount of alkali collected in the condensate was subtracted from the known amount of alkali released from the source and the total amount of alkali passing the bed quantified in this way.

In contrast to this batch sampling technique several on-line methods for alkali quantification have been developed. On-line methods are most suitable for measuring alkali vapor levels providing instantaneous results allowing time dependent changes and process perturbations to be quantified.

Among others, Flame Atomic Emission Spectroscopy (FAES) (Daijou, et al. 1996) and Plasma Excited Alkali Resonance Line Spectroscopy (Pearl) (Häyrynen et al 1996) have been used in most of the experiments. With these methods, sodium and potassium levels in the ppb to ppm range have been measured.

However, none of the previous mentioned setups can provide on-line measurement and determination of the alkali species in the gas stream at the same time. For this reason a new sampling method had to be found, being able to dedicate both aspects. This work describes the first approach to use High Pressure Mass Spectrometry (HPMS) for the quantification and analysis of alkali species in a gas stream downstream a sorbent bed of different tested aluminosilicates.

Approach

High Pressure Mass Spectrometry is a highly suitable method used for hot gas analysis in the range from room temperature to 1500 °C at atmospheric pressure. The HPMS technique can deliver realtime-, on-line analysis and specification of detected alkali metal vapors. For this reason, the HPMS technique is ideally suited for determining the alkali species downstream a sorbent bed. The integrity of the sampled high temperature alkali- laden gases is preserved during the free-jet expansion since chemical reactions are effectively quenched and condensation is prohibited. The nonequilibrium nature of the free-jet expansion and the subsequent formation of a molecular beam allows reactive and condensable species to remain in the gas phase at temperatures far below their condensation point for long periods of time in comparison to reaction rates (Dayton, 1995). Using the mass spectrometer comprehensive detection of all gas phase species can be fulfilled. The general setup for a HPMS system has been described in literature (Evans, Milne, 1987), therefore only additional information concerning the HPMS used in this study is given.

All alkali sorption experiments presented in this work were performed as packed bed studies (figure 2). The setup mainly consists of a heated flow channel housed in a furnace with 6 independent heating zones. For the channel, a one inch (25 mm), 850 mm long high density aluminumoxide tube was used to prevent reaction of the tube walls with the gas phase alkalis. The sorbent bed could be varied in length from 10-150 mm and was inserted into the tube between two bounds of high temperature (1800 °C) Al₂O₃-insulation drilled with several holes (ø 1 mm) for enabling the gas stream to pass through. The alkali source (NaCl) was positioned

15 mm upstream the sorbent bed and consisted of a high density Al_2O_3 -boat, surface area 10 cm^2 . For all experiments a mixture of 4 l/min $\text{He}/\text{H}_2(3\%)/\text{H}_2\text{O}(3\%)$ was used. The gas stream was directed through a nebulizer to provide the demanded moisture. Due to the six available independent heating zones of the furnace, all parts of the reactor downstream the alkali source were kept at elevated temperatures related to the source. This prevented alkalis from condensing on the tube walls downstream the source. The last heating zone (150 mm) inside the furnace was kept at a constant temperature of $850\text{ }^\circ\text{C}$ due to the expected heat transfer induced drop in temperature towards the flow channel exit. However, the hydrogen in the gas stream led to a flame formed by the reaction of H_2 with O_2 deriving from the ambient air at the reactor outlet, which kept the tube walls at the flow channel exit at temperatures above $750\text{ }^\circ\text{C}$. For investigations on the gas stream composition leaving the sorbent bed, this flow channel reactor was coupled to the HPMS system.

A stainless steel cone, 35 mm high with a 108° interior angle and an orifice diameter of 0.3 mm was used for molecular beam sampling. This cone was fitted to a water-cooled stainless steel flange connecting HPMS recipient and cone. This front orifice was connected with the flow channel tube by moving the furnace towards the HPMS and sealing the small circular gap between tube and cone with a small layer of high temperature insulation. The theoretical gas flow through the orifice at the given temperature and gas composition was calculated and the flow reactor operated with some excess gas flow to the calculated value to prevent ambient air from entering the gas stream. The protrusion of the orifice into the flow reactor prevented condensation on the sampling cone and excluded interactions between gas stream and orifice.

The HPMS system consists of a three-stage differentially pumped vacuum system (figure 3). Sampled gases entering the system undergo a free-jet expansion. The core of the expanded gases is extracted by a conical skimmer ($\varnothing\ 1\text{ mm}$) at the entrance to stage two forming a molecular beam. For better beam performance, this skimmer is constructed to be moveable along the recipient's main axis. A shutter positioned upstream the stage three entrance is installed to have the possibility of blocking the beam for background scanning. The molecular beam then enters the ionization region inside the third stage by passing another small hole ($\varnothing\ 1.5\text{ mm}$). Ions are formed by electron impact ionization. The ionization energy for the sorption experiments was 30 eV. The ions are filtered with a quadrupole analyzer (ABB Extrel) and detected with an off-axis channeltron electron multiplier. Control of scanning parameters and collecting the multiplier signal as a function of time and mass to charge ratio was performed by a complete computer and software package.

Quantification of NaCl with HPMS

Due to the complex properties of a free jet expansion inside the first stage of the HPMS system an exact quantification of different gas species is very difficult (Stearns et al. 1979). For instance, the analysis of a small amount of gas species in He used as carrier gas will lead to different intensities in the mass spectra than the same amount of species carried in a different gas like ambient air. By diluting some heavy molecules in a light gas the heavy molecules tend to concentrate in the centre of the expansion, leading to much higher molecular beam signals than diluting them into gas with high molecular weight (Miller, 1988). This leads to difficulties in quantification of gas mixtures with several components especially if the carrier gas is changed. Therefore HPMS systems have most often been used for qualitative analysis or rather semi-quantitative analysis.

In case of the sorption experiments presented in this study, the carrier gas remained a constant mixture of He/H₂/H₂O. Therefore, amounts of sodium chloride in the range of 0-100 ppmv do not significantly change the properties of the expansion and can definitely be quantified with this method. Thus, quantification was done by comparing the intensity of a known amount of NaCl in the carrier gas in several preliminary blank tests with the intensities of the NaCl peaks in the mass spectra during the experiments.

Quantification of NaCl was performed in a few simple steps. First, the furnace was heated up and as soon as the desired temperature was reached the NaCl source was inserted into the tube and the carrier gas flow (similar to later adsorption experiments) was turned on. After 50 hours, a long duration to exclude any problems in determining the correct value of the source's weight change, the source was removed. The alkali loss of the source was then determined by comparing the weight of the source before and after the experiment. Considering the total gas flow during the 50 hours, the total amount of NaCl in the gas phase could be calculated. In this way, a constant gas stream with a known concentration of NaCl could be produced.

Observing the mass spectrum during the blank tests revealed the NaCl peak on 58 and the Na₂Cl ((NaCl)₂ fragment) peak on mass 81 to be sufficient to give an image of the NaCl concentration of the gas stream. The NaCl peak on 60 and the Na₂Cl peak on 83 were neglected because of the constant relation to the ones before of 1:3 (ratio due to existence of chlorine isotopes 35/37 in the ratio of 3:1). Considering the ionization cross sections at 30 eV, the Na₂Cl peak was weighted by a factor of 1.33. The total amount of NaCl was taken as the sum of mass 58 peak and the weighted mass 81 peak. For sampling the gas stream, the HPMS and the furnace were connected as described above for a maximum of 5 minutes to reduce corrosion on the stainless steel sampling cone. The first two minutes the cone was exposed to the hot gas to heat up at the edge, then the gas was sampled for one minute and the signal averaged. According to the spectra the source was delivering a constant NaCl concentration into the gas stream. Several blank tests with NaCl concentrations of 2, 5, 10 ppm showed that there was a linear relation between the total amount of NaCl concentration in the gas and the total amount of NaCl detected with the HPMS, revealing a relative error of about 5 %. Sampling 65 ppm of Sodium Chloride in the same carrier gas led to almost the same result (error 7 % compared to 2 ppm and 5 ppm experiment).

Therefore, a linear relation between the NaCl concentration in the gas and the HPMS total NaCl signal could be found and this way a scale was established for determining the NaCl content in the gas downstream the sorbent bed during the packed bed studies.

The total error for quantification of NaCl with the HPMS system calibrated in the way described above is estimated to be < 10 % in the ppm range and < 30 % for NaCl contents of 50 – 100 ppb.

Results

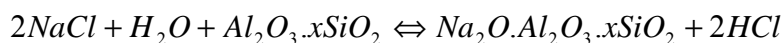
All of the sorbent testing presented in this paper was done using the flow channel reactor setup (figure 2). The investigation of four different sorbents is presented (table 1). Activated bauxite has been tested and characterized by other authors before and found to be a suitable sorbent for alkalis under oxidizing atmospheres. Mullite has been chosen for its high ratio of SiO₂/Al₂O₃, silica for testing the influence of alkali on pure SiO₂. The fourth presented sorbent is merchandized as cat litter and, as detailed analysis reveals, comes close to previous tested sorbents like emathlite or Fuller's earth, due to its high CaO content and high porosity.

Two kinds of experiments were performed. First, several packed bed experiments with a short sorbent bed and high alkali load in the gas stream to gain detailed information on the maximum uptake of the tested sorbents. During these screening tests, general information like the influence

of water on the alkali uptake and related to that the kind of sorption, either chemisorption or physisorption, could be gained. Second, packed bed studies with lower alkali content in the carrier gas and longer sorbent beds for investigations on the maximum capability of gas cleaning by quantitative analysis of the gas exiting the flow channel with HPMS. All tested sorbents were heat treated for 10 hours at 750°C under a reducing atmosphere to disable distortions of later results.

For the screening experiments the diameter of the reactor tube was 20 mm, the length of the sorbent bed 12 mm. This led to a total bed volume of 3.14 cm³ and was responsible for shorter duration of the experiments. A total gas flow of 3 l/min carrier gas was used resulting in a very short space time for the sorbent bed of 0.02 s. In addition, alkali load of sorbent at the beginning and the end of the bed that way was almost the same at the end of the experiment, leading to easier evaluation of the chemical analysis. The duration of the experiments varied from 52 to 192 hours. For better comparison, all sorbents were sized between 1.5-3 mm, except silica with 3-4mm. These preliminary experiments showed that the highest alkali uptake after 52 hours was reached by activated bauxite (54 mg/g) and cat litter (60 mg/g) (table 2). This was mainly due to their high porosity. In contrast, the high density of mullite led to much lower values because of reduced diffusion of Na into the center of the sorbent corns. In case of silica, the formation of a glassy layer on the surface strongly inhibited further alkali uptake.

During the screening experiments, the flow channel was connected with the HPMS (figure 2) from time to time to get information on the gas composition and to draw conclusions concerning the occurring reactions inside the getter bed. Figure 4 shows the involved species in the alkali uptake reaction and their intensities over the duration of the experiment using silica as a sorbent. Related to the uptake only HCl, NaCl and Na₂Cl ((NaCl)₂-fragment) could be spotted. The same behaviour could be found for all other tested sorbents. This led to the conclusion that sodium is mainly absorbed by a chemisorption due to the following reaction :



This result was supported by chemical analysis of the sorbents after the experiment, in which only negligible amounts of chlorine could be found, which shows that in these experiments chemisorption strongly dominates physisorption. The trend of the HCl curve can therefore be taken as an indicator that the rate of alkali uptake is very high at the beginning and decreases towards the end of the experiment. The hesitation of the HCl intensity at 2000 shows on the other hand, that the alkali uptake still had not finished when the experiment was stopped. This result is underlined by chemical analysis comparing the Na amount of bauxite and cat litter after the 52 h and 192 h experiments. The total uptake in the 192 h experiments for bauxite was determined to be 77 mg/g sorbent. The total amount of Na sorbed by cat litter was even higher (114 mg/g sorbent). The higher value for cat litter is probably due to its high silica content.

The reaction described earlier shows that water is necessary for chemical sorption to take place. To demonstrate the strong influence of H₂O on the alkali uptake, one sorption test was performed in the way described above with the standard He/H₂/H₂O -gas mixture and after several hours of the experiment the water was turned off. The influence of the water missing was severe (figure 5). While when using the standard carrier gas HCl was the major species and only a little NaCl could be measured, in absence of water only a little HCl could be observed and NaCl (also Na as fragment of NaCl) was the main peak. This shows clearly that chemisorption directly came

to an end after turning off the water. The residual production of HCl is probably due to moisture of the used laboratory gases.

For the main experiments, a larger tube (\varnothing 25 mm) was used to increase the amount of sorbent fitting into the tube. The length of the sorbent bed was 50 mm, leading to a total bed volume of 24,5 cm³. Using the same gas mixture as in the screening experiments, the gas flow was set to 4 l/min. The resulting space time over the sorbent bed was 0.1 s. The source delivered a constant NaCl load of 65 ppm into the gas stream. The HPMS system was calibrated for NaCl quantification as described above. By connecting the HPMS to the flow channel reactor (figure 2), the total NaCl content of the gas stream exiting the reactor could be determined. This way, quantification of NaCl downstream the sorbent bed was done for activated bauxite, cat litter and mullite over time (figure 6). The experiments clearly show that the capability of mullite to successfully remove NaCl from the gas stream is weak. As soon as five hours after the beginning of the experiment, the total amount of NaCl detected with the HPMS was above 10 ppm showing that using mullite can not be considered as a sufficient way of alkali control.

In opposition, activated bauxite and cat litter were able to reduce the NaCl content of the gas to values lower than 100 ppb. Measured values for cat litter (\sim 40 ppb) tend to be a little lower than for bauxite (\sim 80 ppb). The sufficient capability of these two sorbents to lower the alkali content of the gas is mainly due to their high porosity, which leads to high diffusion rates into the sorbent core. XRD Analysis of the sorbent after the experiment revealed the formation of albite (NaAlSi₃O₈), the most stable aluminosilicate phase, to be responsible for the good performance of these sorbents during the first 10 hours of the experiment (figure 6). After 15 hours, the formation of nepheline (NaAlSiO₄) becomes dominant. The beginning of the formation of this phase is the reason for the change of the curves for bauxite and cat litter to a higher level after 15 hours of the experiment.

In the last series of experiments, the influence of the sorbent bed length on the NaCl removing capability of bauxite was investigated (figure 7). The NaCl content of the gas stream exiting the flow channel reactor was measured by HPMS varying the length of the sorbent bed from 20-100 mm. The measured values for the short bed (20 mm) were about 320 ppb, indicating that the contact time between gas and sorbent was too low. Probably not all of the NaCl molecules did get in contact with the sorbent surface. On the other hand raising the bed length over 50 mm did not further reduce the alkali content of the gas stream. This leads to the conclusion that, once a certain length is exceeded, the alkali loaded gas comes to an equilibrium with the sorbent material. From that point, a further increase of the bed length becomes useless.

Finally, the partial pressures over nepheline and albite were calculated with the Factsage database considering the reducing atmosphere in the experiment. The calculated gas composition was close to the one obtained in the experiment.

Application

The studies presented in this paper show clearly the possibility of sufficient alkali removal from a hot gas stream under reducing atmospheres at 750 °C by solid sorbents. The gas concentration of NaCl could be reduced to values below 100 ppb in laboratory tests by passing the alkali loaded gas stream through a packed bed of aluminosilicates at ambient pressure. Considering the ten times higher pressure and the thinning of the combustion gas by a secondary air stream after the gas cleaning section, this will offer the opportunity to lower the alkali content at the gas turbine entrance to values lower than 24 ppb in future built 2nd Generation PFBC power plants.

Future Activities

The activities presented in this work were exclusively dealing with the removal of alkalis from a hot gas related to coal combustion, in which sodium plays the major role. Latterly, much attention has been focused on renewable energy sources to address the impacts of global warming. Biomass, the most common form of renewable energy, most often contains very high amounts of potassium. Therefore, high efficient power plants for biomass combustion will, concerning the need for alkali removal, face quite similar problems as coal power plants today. For that reason, future investigations will concentrate on experiments concerning potassium removal and quantification of potassium contents of gas streams downstream sorbent beds by high pressure mass spectrometry.

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Figures and Tables

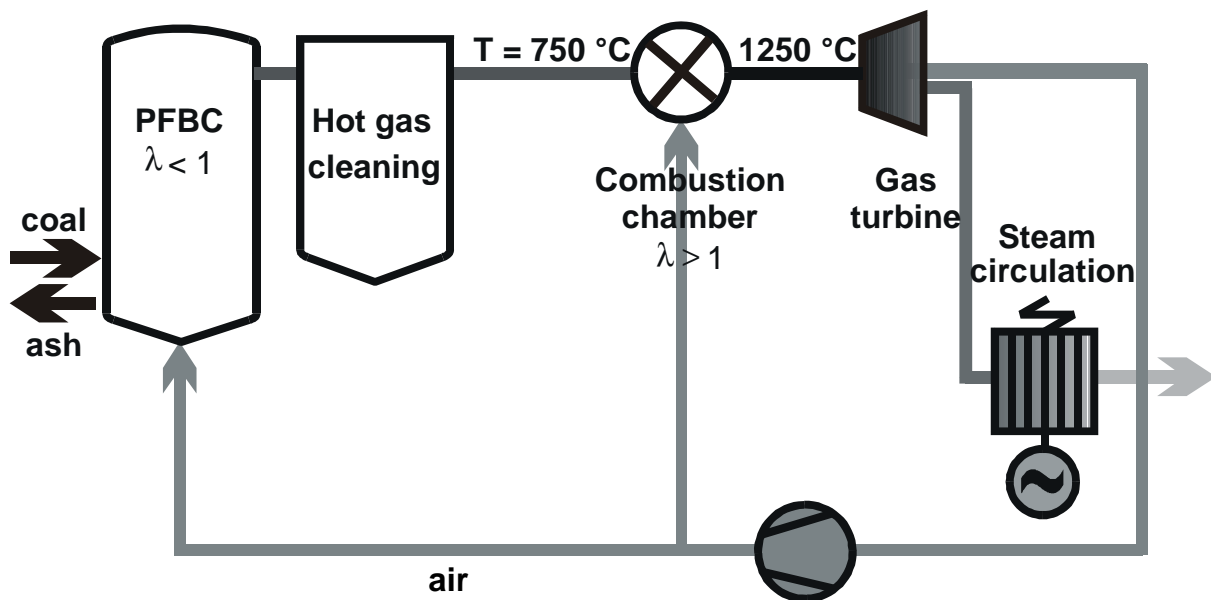


Figure 1 : Flow diagram of the PFBC Combined Cycle process

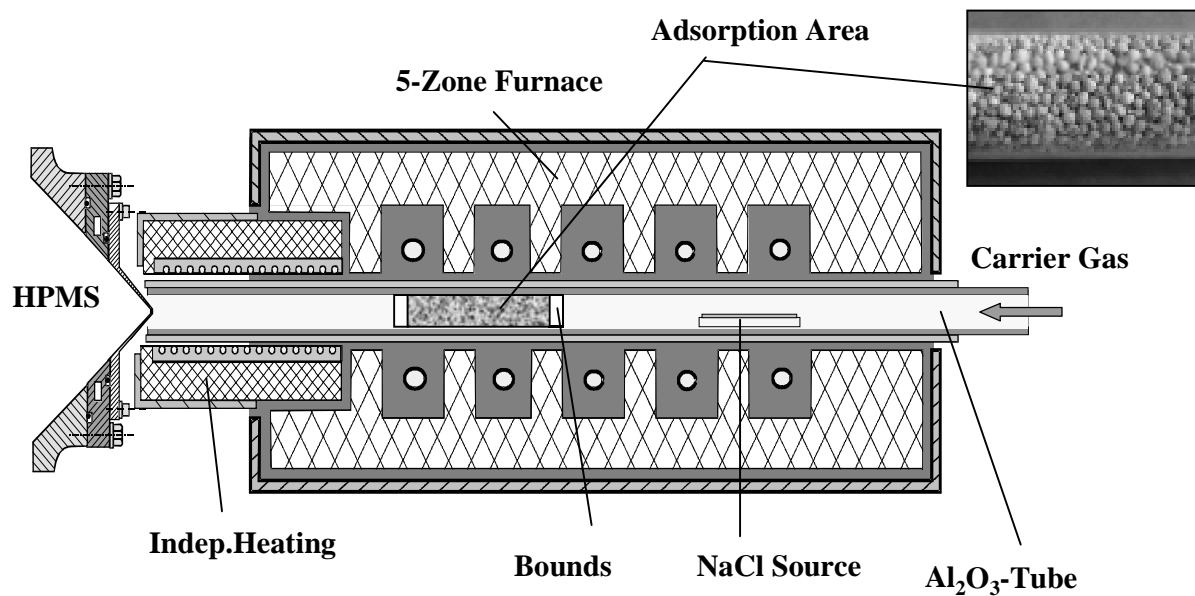


Figure 2. Schematic Representation of the High Temperature Reactor used for Alkali Sorption Experiments

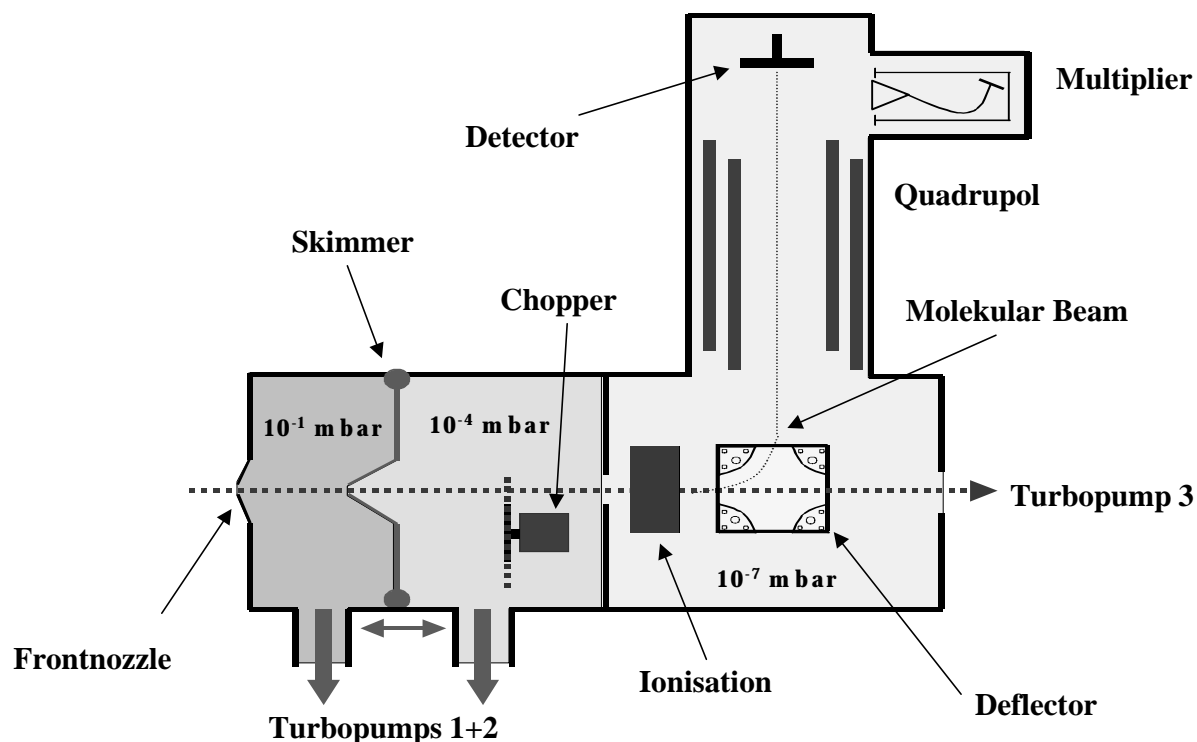


Figure 3. Schematic Representation of the High Pressure Mass Spectrometer system

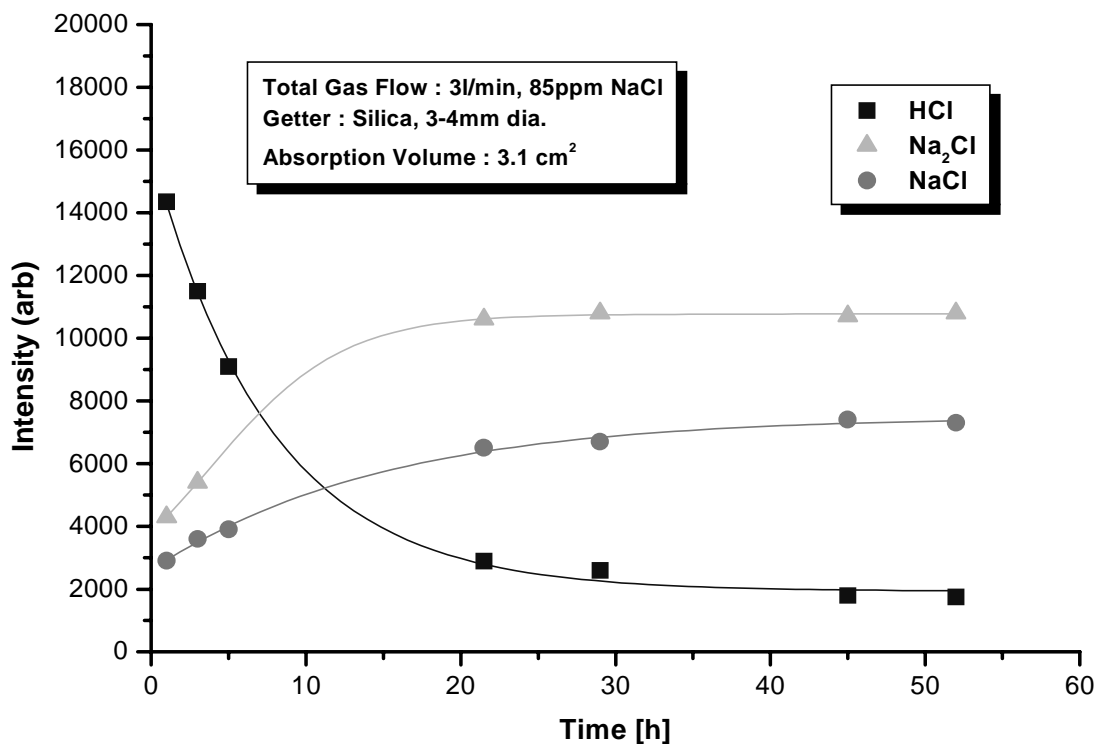


Figure 4. Intensity of Involved Species During Sorption Experiments over Time measured Downstream the Sorbent Bed (Silica) by High Pressure Mass Spectrometry

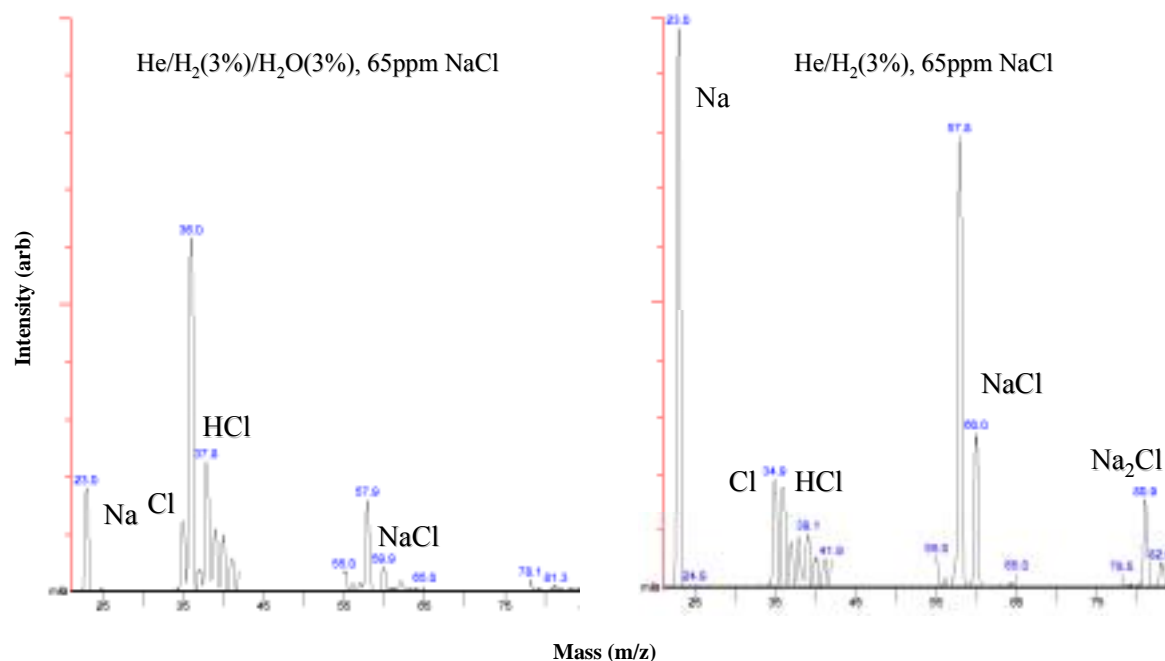


Figure 5. Mass Spectra of NaCl loaded Gas downstream the Sorbent Bed (Silica) after Several Hours of Experiment (He/H₂(3%)/H₂O(3%)), Influence of Removing the H₂O Source

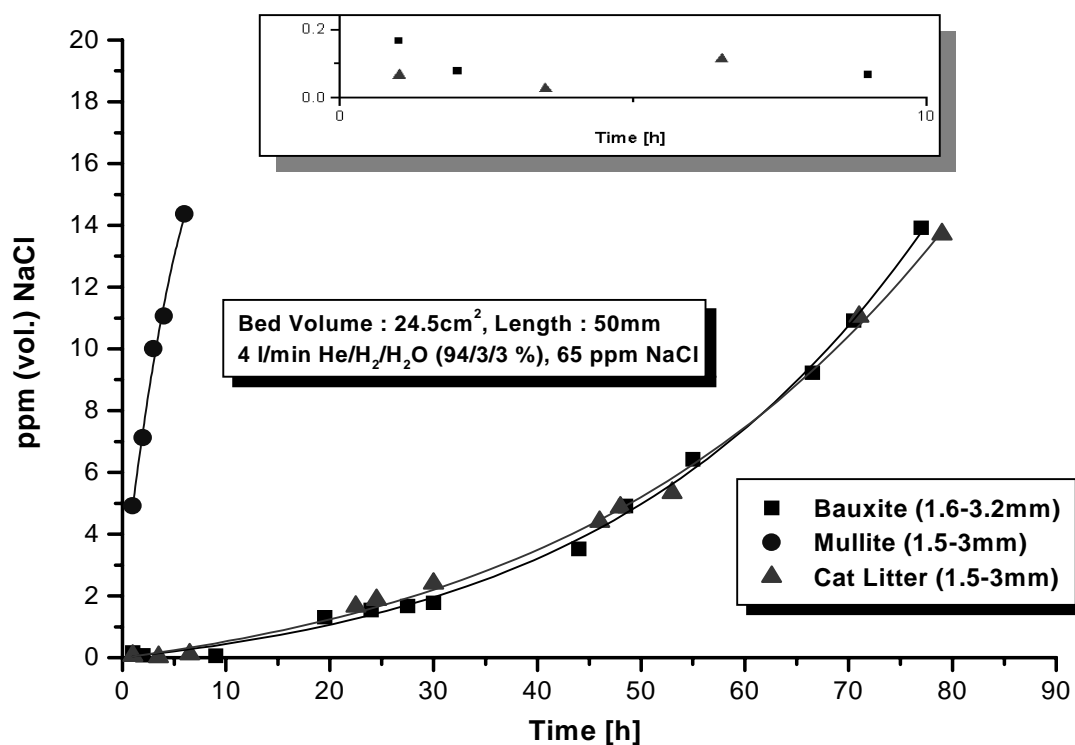


Figure 6. NaCl Concentration over Time Downstream the Sorbent Bed Measured by HPMS for Different Sorbents

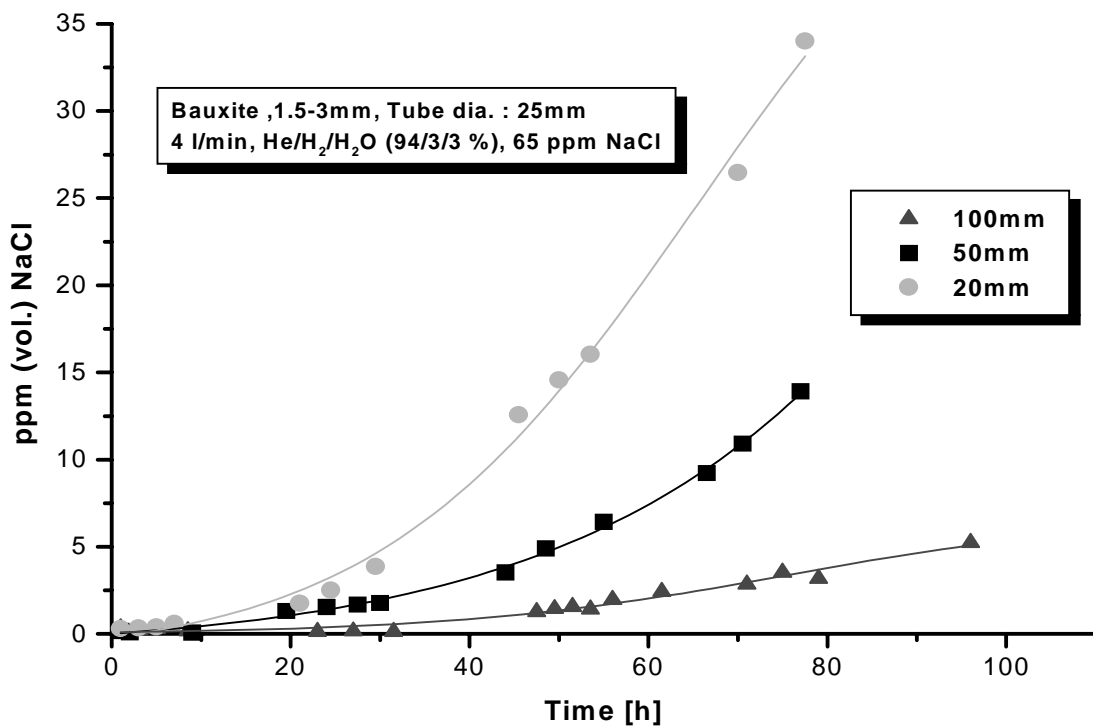


Figure 7. NaCl Dependence of Cleaned Gas on Sorbent Bed Length for Bauxite

Table 1. Chemical Analysis of Tested Sorbents before the Experiments

	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Liquid Loss
Bauxite	56,9	4,75	5,42	2,39	0,01	0,02	-	-	24,6
Mullite	64,64	28,25	0,19	0,17	<0,01	0,36	0,05	0,04	-
Cat Litter	13,42	50,72	4,29	0,74	1,49	1,08	2,94	3,49	-
Silica	< 0,2	89,24	0,2	0,17	0,22	0,12	0,18	0,04	13,1

Table 2. Na Concentration of Tested Sorbents after the Experiments

	Na (mass-%)	Cl ₂ (mass-%)
Bauxite (52/192 h)	5,4/7,7	0,8/-
Mullite	0,5	-
Cat Litter (52/192 h)	6,0/11,4	-/-
Silica	3,0	-