

Fly ash as a new sorbent for CO₂ emissions reduction

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Abstract

The study is focused on reduction of anthropogenic carbon dioxide emissions from the atmosphere which are created mainly due to fossil fuels incineration. Removal of CO₂ by post-combustion process, realized via adsorption on a suitable solid material can be considered as promising way. A wide range of materials, both natural and synthetic, is tested for these purposes. In this study, fly ashes, collected from the ESPs of power and heating plants were chosen as an experimental material for CO₂ capture. Potential application of fly ashes as well as bottom ashes provides in fact no material costs, since these materials are usually disposed as wastes. Sorption properties were tested in two markedly different temperature ranges using two flow-through apparatuses and by static adsorption method. The aim of the study was to verify capacities of physical and chemical CO₂ sorption for each fly ash at different conditions.

Keywords: fly ash, surface characterization, CO₂ capture, high-temperature sorption

Introduction

Combustion of fossil fuels together with cement industry is considered as the main contributor to anthropogenic emissions of carbon dioxide to the Earth's atmosphere. These emissions are partly captured by ecosystems and oceans. However, the residual amount of CO₂ has probably a negative impact on global warming associated climate change¹. U.S. Energy Information Administration (EIA) predicts an increase of CO₂ emissions by ca. 3.3 billion metric tons between years 2012 and 2020. According to this trend, the global CO₂ emissions will reach 25.6 billion metric tons at 2020 and further growth is projected to exceed 43 billion metric tons till the year 2040. These predictions do not include those plans in the United States that will accomplish the goals of Clean Power Plan (CPP) regulation and will decrease CO₂ emissions by ca. 0.5 billion tons till the year 2040. However, large part of the emissions growth is attributed to developing countries which are not involved within Organisation for Economic Co-operation and Development (OECD). Developing countries have often no alternative to burning fossil fuels to satisfy high energy demands. According to EIA the emissions, generated by industry in developing countries, will increase by about 51 % between the years 2012 and 2040. This trend can be compared with the OECD member states, which assumed emissions growth is only 8 % within the same time interval. At present time global energy consumption is covered by fossil fuels from 84 %. In the case, the increase in usage of renewable sources and also nuclear power will meet the predictions the share of fossil fuels should decrease to approximately 78 %. Contribution of the individual fuels would therefore change proportionally. For instance the share of black coal and lignite in the energetic mix should decrease from 28 % (2012) to 22 % in the year 2040. During the same time period decrease in application of liquid fuels is expected in the range from 33 % to 30 %. Meanwhile the use of natural gas should increase by 3 %, which means the final percentage will be 26 %².

Based on these scenarios, fossil fuels will be still important for energy production and therefore CO₂ emissions will still represent the environmental risk for the next few decades. There is an ambition to develop such technologies, which would be able to decrease CO₂ emissions at industrial scale and will be economically acceptable. Adsorption of carbon dioxide on solid substrates is considered as one of the possible solutions. However, it is necessary to find a low-cost sorbent having high selectivity for CO₂ under specific conditions and being stable and reusable. Flue gases exiting the combustion chamber reach temperatures in the range of 400 – 600 °C. It is desirable to capture CO₂ at these temperatures to make the process more feasible and advantageous. Cooling down the flue gases before CO₂ sorption is not energetically preferable. A wide range of adsorbents are generally capable to separate CO₂, e.g. activated carbon, zeolites, CaO- or MgO-based sorbents, silica gel, various hydrotalcite-like compounds

etc. Based on the prediction that the significant part of energy production in two to three decades will be still covered by fossil fuels (mainly by coal), the possibility to use the wastes, generated by the power industry, is considered. The suitable waste should be primarily fly ash, which is stable at high temperatures and contains inert aluminosilicates³⁻⁵.

Nowadays, the most used technology for energy production is combustion of coal in pulverized form. Pulverized coal burners often incinerate medium to high quality bituminous coal. This technology has been in use for almost one century and therefore is well proven and optimized. However, in the last several years new coal burning technology has arisen: circulating fluidized-bed (CFB). Before combustion in the fluidized-bed reactors the coal must be ground to relatively large grain size 3 – 6 mm. Thus installation of the CFB combustors brings savings in the cost of time, energy and equipment compared to the conventional pulverized combustion (PC). The main difference between these two systems is that the CFB technology prolong the residence time of hot solid unburnt substances in a boiler due to recirculation of the particles in the system. This effect leads to better conversion of carbon and homogenous heat flow through the whole boiler and also in the recirculation system. Two advantages result from this. At first the ability of the system to combust wider range of fuels is enhanced and secondarily better tolerance to changes in the fuel quality during the incineration process is ensured⁶.

Indeed, both of these combustion technologies produce solid wastes. The solid waste, which utilisation is discussed within this study, is called fly ash (FA). FA is composed mostly of inorganic non-combustible compounds from coal and is captured from flue gas by electrostatic precipitators or baghouse filters. FA has a form of heterogeneous powder whose particles have spherical shape with diameter in the range from micro to millimetres. In some cases the particles can have high reactivity. The quality and physicochemical properties of fly ash are based on the quality of incineration and combustion technology. Fly ash coming from fluidized combustion contains a part of unreacted CaO. Calcium oxide is used for flue gas desulphurization (FGD) and in fluidized technology SO_x is captured directly in the combustion chamber. On the contrary, pulverized combustion uses FGD behind the combustion chamber, respectively behind the capture of solid particles and therefore fly ash from this type of process does not contain free CaO⁷⁻¹³.

Fly ash is usually disposed as waste, but recently it is more frequently used in various industrial sectors, which proportionally decreases its environmental impact. About 20 % of fly ashes is used in the building industry for concrete production, where is applied as low-cost binder. In addition to cement replacement for concrete production, fly ash has been used in the processes of water treatment or for zeolite synthesis. Portland cements and polymers syntheses or as a backfill after mining are examples of another FA utilization. In spite of its application in various sectors FA production is much higher than commercial demand. This negative fact leads to the problem that there is still large amount of fly ash, which has to be deposited as waste to lagoons, ponds or landfills. Due to declared tightening of requirements for landfilling reduction of possible areas for the future FA storage should be expected. On account of the above mentioned limitations it is necessary to develop new technologies for fly ash recycling⁹⁻¹¹. One of the possibilities is its application for carbon dioxide separation from flue gas. Adsorption of carbon dioxide occurs at the surface of ash particles, where strong interaction between CO₂ molecules and substances in fly ash takes place. For this purpose large specific surface of the sorbent is required. When CO₂ reacts with CaO present in fly ash CaCO₃ is formed and carbon dioxide is captured permanently. In this case CO₂ cannot be released to the air without dramatically changed conditions (pH, temperature). The important advantage is in lowering the CaO content in fly ash, which negatively affects properties of cement. Other applications of fly ash, which development is in progress, are in ceramic industry, catalysis, metal ions removal or hydrotalcite-like compounds synthesis^{7, 12-19}.

It is commonly assumed that the use of fly ashes in various industry sectors would increase in future. Moreover, growth of potential synergies in industry is expected. On the other hand, almost all of the above mentioned technologies are actually in the early stages of development. Commercialization of these methods therefore requires to be supported by research activities²⁰.

Materials and methods

Materials and their characterisation

Within the experiments, tests with three types of fly ash were performed. Essential data about the sample base are specified in table 1.

Table 1: Basic information about the samples

Sample identification	Technology of combustor	Type of combusted coal	Specification of facility
K31	Fluidised bed combustor K31, commissioned in 1996	Lignite, black coal, biomass	Alpiq Generation (CZ) s.r.o.; Zlín city heating plant
K32	Fluidised bed combustor K32, commissioned in 2002	Lignite, black coal, biomass	Alpiq Generation (CZ) s.r.o.; Zlín city heating plant
B6	Supercritical pulverized coal combustor B6, in trial regime	Lignite	ČEZ, a. s.; Ledvice power plant

The samples K31 and K32 came from the same technology but were generated at different thermodynamic conditions. K31 combustor is designed with higher nominal heat output (120 MW_t) and steam production (150 t·h⁻¹ at 9.6 MPa and 540 °C) than K32. It has nominal heat output 100 MW_t and steam production 125 t·h⁻¹ at 9.6 MPa and 535 °C. The sample B6 comes from a combustor, which has been in the testing regime since 2017. The unit has nominal heat output 1,286 MW_t and steam production 1,684 t·h⁻¹ at 28 MPa and 600 °C.

Testing methods

Wide range of instrumental methods, to which the sample base is subjected, can be divided into three categories. The first of them includes analyses, applied in order to provide basic characterisation of the materials. The specific methods within this category are as follows.

The elemental composition of samples was measured using the XRF analyser ARL 9400 XP+ (producer Thermo Fisher Scientific, United States) with evaluation software UniQuant 4. Evaluation of BET surface and pore size distribution was realized using the automatic analyser Coulter SA 3100 (producer Beckman Coulter, Inc., United States). This measurement is done by reversible adsorption of N₂ at 77 K and then evaluated mathematically using BET adsorption theory.

Thermogravimetry was used to detect if the samples undergo thermal decomposition and therefore they can be potentially used for high temperature sorption. The tests were provided under nitrogen atmosphere using the automated analyser TGA-2000 (producer Navas Instruments, United States). Tests performed via the TG analyser consisted of the following three consecutive steps. The procedure started with drying the samples up to 105 °C with heating rate of 12 °C·min⁻¹. The second step was calcination, realized by heating up to 400 °C with temperature ramp of 5 °C·min⁻¹. The purpose of this step was to determine whether the material releases crystal water, water inserted into the lattice structure, or any adsorbed gases, respectively. The third step was high temperature calcination, continuing to the temperature of 900 °C and using the same heating rate as applied for the second step.

Evaluation of sorption properties at low temperatures was provided by static adsorption method. Static adsorption was carried out in a desiccator (without any adsorbent at the bottom) connected with Tedlar gas sampling bag filled with pure CO₂. 10 g of each sample was weighed into a porcelain crucible and placed to the desiccator. Then the desiccator was heated up in a climate chamber to 200 °C under vacuum. After this preparatory phase the temperature was set down to the desired level, the gas sampling bag with CO₂ was connected with the desiccator and a valve was open to fill the whole desiccator with the gas. All tested samples were in contact with CO₂ until the constant weight was reached. The crucibles were weighed each three days. After each weighing the whole system was evacuated and subsequently filled with pure CO₂ before placing back to the climate chamber. Three

independent experiments were performed at different temperatures. The chosen temperatures were 30, 40 and 50 °C.

Sorption capacities at high temperatures were determined using self-constructed fluidized-bed and fixed-bed apparatuses in ten cycles of sorption/desorption. High temperature tests of sorption/desorption were performed in the two above mentioned independent apparatuses, where the principle of measurement was very similar. Thus the experimental procedure is described only once. First step was thermal decomposition of the sample (known as calcination). Calcination was carried out under nitrogen atmosphere up to 900 °C. When the desired temperature was reached, the measurement continued under isothermal conditions until zero content of CO₂ was detected by the IR analyser at the reactor output. Calcination phase was followed by cooling down under N₂ until reaching carbonation temperature 650 °C. Then the gas flow was switched from nitrogen to model gas mixture and carbonation started at isothermal conditions. Two model gas mixtures were used in order to simulate desulfurized flue gas from standard coal fired power plant. The two different mixtures were applied which composition was as follows: 14 mol. % CO₂ in N₂ or alternatively 12 mol. % CO₂ + 7 mol. % O₂ in N₂. Carbonation was carried out until establishing chemical equilibrium when the inlet and outlet CO₂ concentrations became identical.

Finally the furnace was switched off and the reactor cooled down to the ambient temperature spontaneously. Then the system was ready for the next cycle, beginning with new calcination step.

Correct evaluation of all experiments requests, among other things, recording of the time delay between switching on the gas input and displaying the corresponding response by the IR analyser. This delay that can be so called “dead volume” distorts the results because it represents unreal contribution to the sorption capacity. Measurements of blank were carried out at laboratory temperature and using the sample, which was previously completely saturated by CO₂. Then the apparatus was purged with nitrogen until zero CO₂ concentration was displayed. After that N₂ was replaced by the corresponding model gas mixture and the response of the IR analyser was recorded continuously until reaching the same CO₂ concentration at the apparatus inlet and outlet. The value of this apparent sorption capacity was deducted from the all values of capacities, measured within the same series.

Results and discussion

XRF analysis

No suitable calibration standard is available to fit completely the elemental composition of fly ashes. Therefore the measured values must be understood as semi-quantitative only. Due to commonly known limitations of the XRF method some elements, including carbon and oxygen, cannot be detected. The analytical data are thus normalized to 100 % of the sample weight and expressed as elements. Table 2 contains only selected elements which are the most significant and considered important for potential utilization of the material.

Table 2: Data from XRF analysis

Element	Content in the sample (% wt.)		
	K31	K32	B6
Na	0.993	0.717	0.285
Mg	2.130	1.380	0.601
Al	18.250	15.380	33.040
Si	17.420	14.490	46.470
P _x	0.205	0.123	0.196
S _x	6.000	8.930	0.268
Cl	0.046	0.185	<50 mg.kg ⁻¹
K	0.854	0.733	1.600
Ca	41.890	47.640	2.380
Ti	1.700	1.410	5.430
V	0.116	0.061	0.121

Mn	0.170	0.117	0.061
Fe	9.580	8.660	8.800
Sr	0.169	0.044	0.156
Ba	0.238	0.102	0.140

Based on these data it can be clearly said that there are two big differences between fly ashes from fluidization technology (K31 and K32) and pulverized combustion (B6). For fly ash B6 Al and Si are dominating elements, while K31 and K32 contain elevated concentrations of Ca. Due to the application of dry limestone FGD method meaningful part of Ca is present in the form of CaSO_4 . Below described TGA measurements, however, verified that relatively significant part of Ca is still remaining in reactive form of CaCO_3 . Thus it can be utilized for CO_2 capture. The sample B6 does not contain enough thermolabile carbonates and therefore is not favourable for high temperature CO_2 sorption. For this reason B6 was used only for low temperature static adsorption testing.

BET surface and pore size distribution

The sample from pulverized coal burner B6 exhibited very low specific surface as it can be seen in figure 1. Thus, no measurable capacity for physical adsorption could be expected. Moreover it contained no significant concentrations of thermolabile carbonates that could make it useable for high temperature chemisorption as stated above. Taking into account these facts the sample B6 was subjected to several chemical treatments in order to enhance its porosity. Summary of the modifications applied to the sample B6 is as follows:

Table 3: Summarization of chemical modifications of the fly ash B6

Sample identification	Method of sample treatment
B6	Fly ash B6 in its raw form (without any treatment)
B6 KS	B6 boiled in H_2SO_4 (40 % solution), then washed in distilled water and dried at 200 °C
B6 NaOH	B6 boiled in NaOH (40 % solution), then washed in distilled water and dried at 200 °C
B6 P	B6 calcined at 850 °C under nitrogen and then activated by steam at 350 °C
B6 SL	B6 calcined at 1,000 °C under air, then shock-chilled by dry ice
B6 V	B6 calcined at 1,000 °C under air, then shock-chilled by tap water and dried at 200 °C

BET surface as well as pore size distribution were determined for all of the modified forms of B6 and for the fly ashes K31 and K32. The obtained data are listed in figure 1 and figure 2.

From the first chart it can be seen that K31 shows the highest BET surface in comparison with others unmodified fly ashes. Boiling in NaOH increased the specific surface of B6 markedly. Other treatment procedures did not lead to useful increase in BET surface. On the contrary, some of them can even reduce it. Based on these measurements the samples B6 SL and B6 V were not tested for CO_2 sorption.

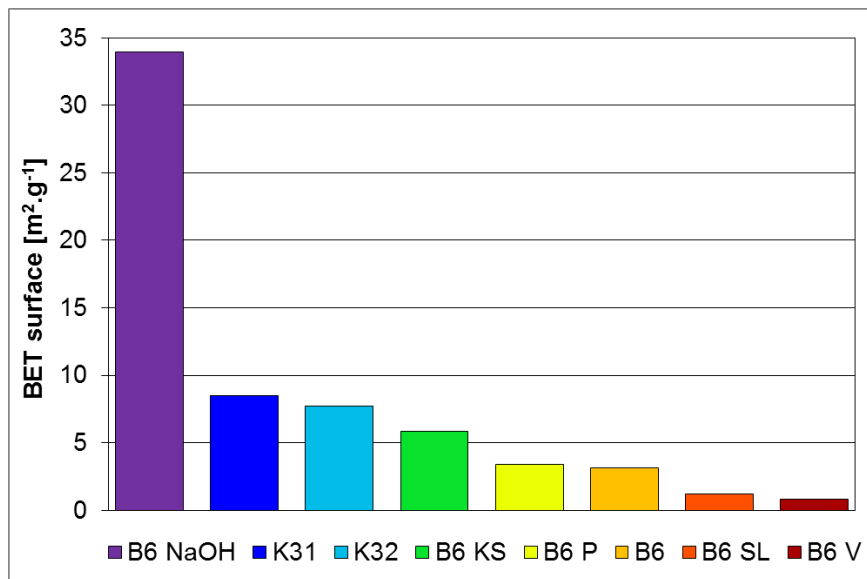


Figure 1: Comparison of BET surfaces of the overall sample base

The largest pore volumes were formed by the pores with the diameters in the range between 20 – 80 and over 80 nm. Fly ash B6, modified by NaOH exhibited the highest total pore volume almost in every pore diameter range. Based on these data the sample B6 was tested by static adsorption method, proposed for physical sorption of CO₂.

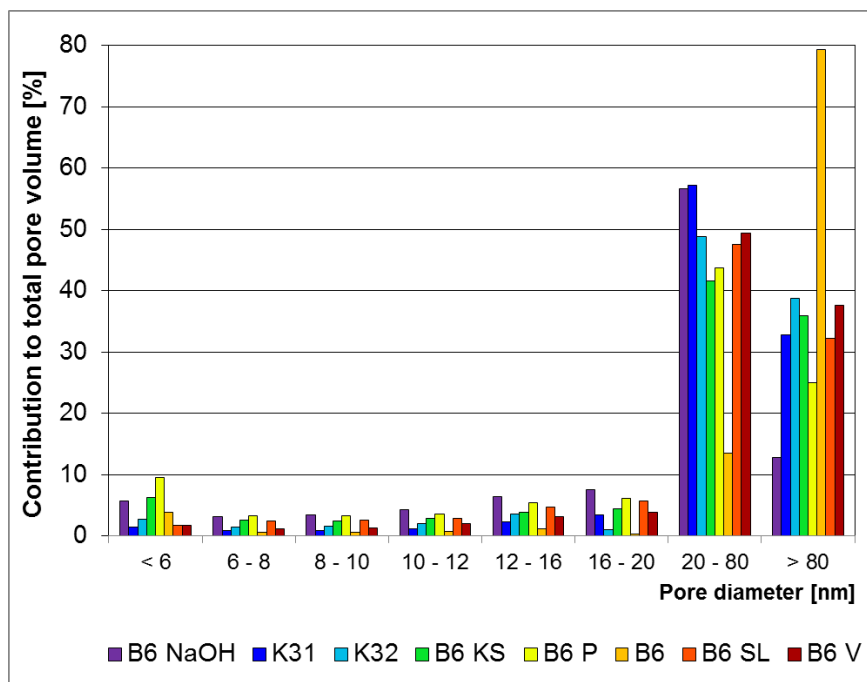


Figure 2: Comparison of pore size distribution of the modified and raw samples

TG analysis

This type of analysis was chosen only as additional, or supporting, method in order to obtain information if the samples can undergo thermal decomposition and so they can be used in high temperature process. The temperature range, within which the measurements were performed, started at laboratory temperature and finished at 900 °C. Results from this analysis are shown in figure 3. All values in the chart are expressed for dry sample. As one can see in the graph, a curve for B6 shows only minor downward trend in comparison with K31 and K32. It is obvious that B6 achieves weight change lower by order of magnitude than the two samples containing unreacted CaCO₃. However, the whole sample base

exhibits a similar pattern in the range between 450 – 600 °C, where the weight loss is clearly visible. This temperature is too low to correspond with decomposition of carbonates. For that reason, verification of applicability of reversible sorption within the discussed temperature range is planned for near future.

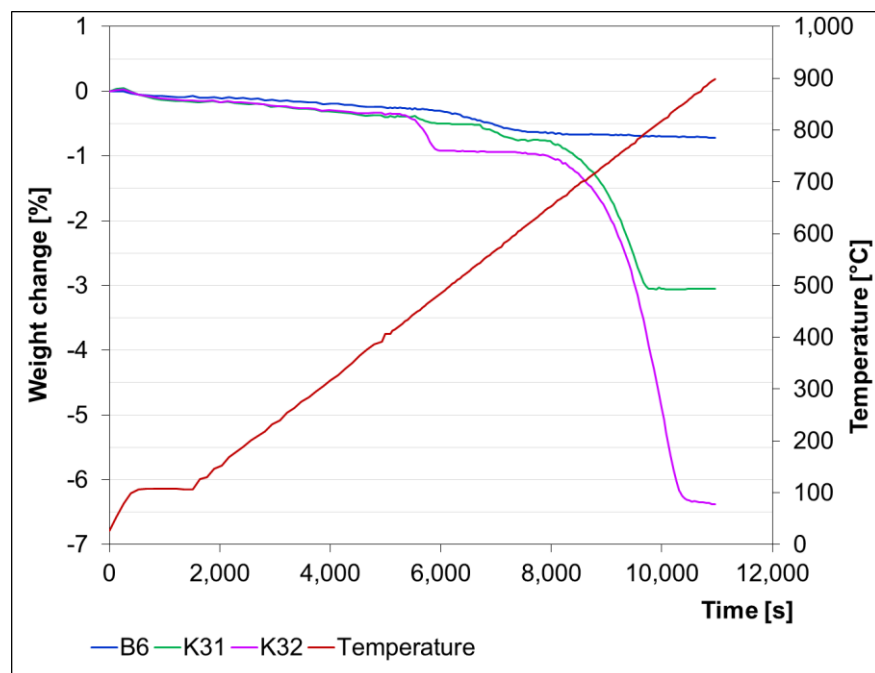


Figure 3: Recorded TGA curves (relative weight changes)

Static adsorption method

To evaluate the equilibrium adsorption capacities static adsorption method was chosen. The principle of this method is not complicated. The sample is placed into a suitable vessel and then exposed to CO₂ at isothermal conditions and atmospheric pressure. The term “static method” refers to a fact that CO₂ does not flow through the system but it is filled in a gas sampling bag, connected with the vessel via a hose. The aim was to test physical sorption of CO₂. Two modified samples (B6 V, B6 SL) from the sample base were not tested because they achieved even significantly lower surface area than unmodified sample B6. The evaluated data are summarized in graphic form in figure 4. The highest sorption capacity was reached by the sample B6 boiled in NaOH. Explanation of this effect is following. Hydroxide reacted with SiO₂, representing dominating substance in the ash particles. Removal of Si from the crystalline structure causes increase in pore volume as well as specific surface. B6 NaOH had the highest BET surface and therefore it was expected that the sample would provide high physical sorption capacity. The graph shows sorption capacities for temperature 30 °C because at this temperature the samples provided the highest values for CO₂ capture. Except the sample B6 NaOH, all the others do not give satisfactory sorption capacities for potential industrial application.

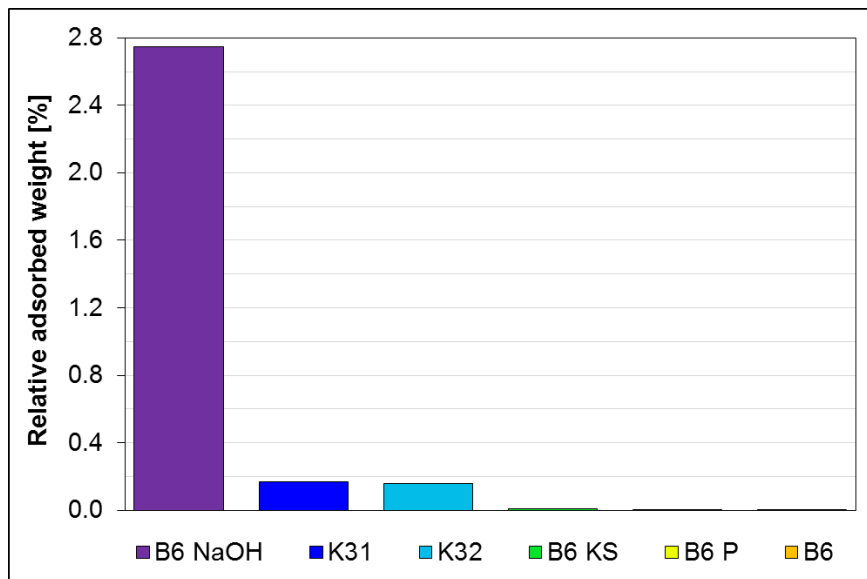


Figure 4: Sorption capacities for the whole sample base at 30 °C

High temperature tests in flow-through apparatus

The results presented above pointed out that only physical sorption of CO₂ does not provide sufficiently high sorption capacities to be applied in any industrial sector. Accordingly to this, experiments at high temperatures were performed to test both physical and chemical sorption. However, these conditions are only applicable on the fly ash containing elevated concentrations of unreacted CaCO₃, undergoing decomposition to CaO at high temperature. If this happens the material is suitable for the similar reversible capture process as described for natural limestones in previously published studies^{21, 22}.

For these experiments only two samples from the sample base were chosen (K31 and K32). They were tested in fixed-bed apparatus and fluidized-bed apparatus. One full set of cyclical measurements consisted of ten cycles of calcination/carbonation. Before starting the cyclical measurement, 100 g of the given sample was weighed and placed into the reactor. The reactor was kept closed during the whole one experiment. Achieved capacities from the experiments are shown in figure 5 and figure 6. These graphs demonstrate that two different reactors provide various physical conditions which have an impact on decline of the sorption properties. The corresponding behaviour was already observed during the same experiments with natural limestones²³. The effect, which is known as sintering, can be explained by SEM photos of the surface of materials exposed to a certain number of cycles. Sintering is a process where particles react together and create solid pieces which clogged pores. Furthermore, available literary sources report that fast heating has a negative impact on sintering and blockage of the pores, which affects sorption kinetics and capacity for CO₂ capture. This issue will appear more in the fluidized-bed reactor, where heat exchange and temperature raise during cycles is more intensive.

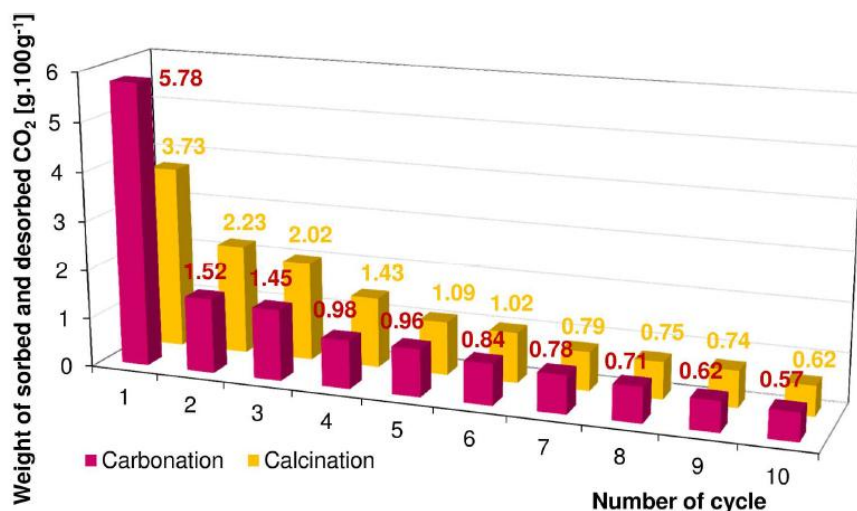


Figure 5: Evolution of sorption capacities at 650 °C, measured for the sample K32 using fluidized-bed apparatus

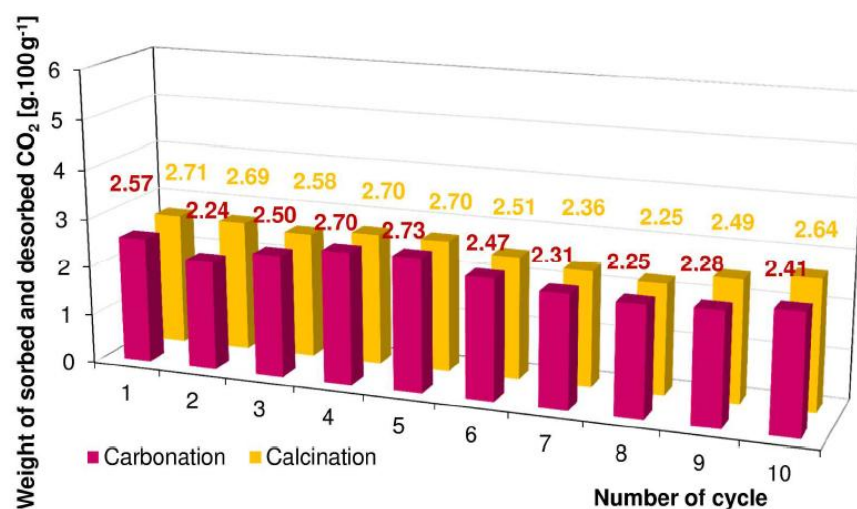


Figure 6: Evolution of sorption capacities at 650 °C, measured for the sample K31 using fluidized-bed apparatus

Conclusion

The sample base consisted of three samples from fluidized and pulverized technology of coal/lignite combustion. The sample B6, which was taken from the ESP of pulverized coal burner, contained low amount of thermolabile carbonates. This indicated negligible capacities available for high temperature CO₂ chemisorption. For that reason the B6 sample was subjected to some chemical modifications, which aim was increasing its sorption properties. Outcomes of testing under static sorption conditions show that only contribution of physical adsorption is not capable to meet requirements of industrial application. Treatment with boiling NaOH solution seems to be the only approach that theoretically leads to industrially promising capacities. For instance the sample B6 treated with NaOH reached at 30 °C the capacity almost 2.8 wt. %. The samples K31 and K32, collected from the fluidized bed combustor, contained elevated amounts of unreacted CaCO₃ or CaO, respectively, which allows preferentially chemical sorption at high temperatures. High temperature testing of fly ashes K31 and K32 offered good capacities for CO₂ capture, corresponding with standard conditions of the carbonate looping process. Based on the results presented in this study, fly ashes from fluidized incineration technology (equipped with the dry limestone FGD) are more appropriate than fly ashes from pulverized coal burners. The main reason is in the sufficient content of unreacted carbonates that allow capturing significantly higher amount of CO₂.

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