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SORPTION OF HYDROGEN CHLORIDE IN THE FLUIDIZED BED REACTOR

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Abstract: Combustion of fuels, including renewable fuels and thermal treatment of waste (CFCs, pesticides), is associated with emissions of pollutants including halogens. The reversible process of sorption/desorption of HCl, in a fluidized (bubbling) bed reactor (BFB), during co-combustion of Cl-materials, was carried out. The thermal decomposition of methylene chloride (DCM, CH₂Cl₂) in an inert sand bed with the addition of the hydroxyapatite sorbent (HAp, Ca₅(PO₄)₃(OH)) was investigated. The process parameters were as follows: temperature - 930 °C, the air excess - 1.3, stream rate of CH₂Cl₂ - 50 cm³/h. The concentration of HCl, CCl₄, CHCl₃, CH₂Cl₂, CH₃Cl, COCl₂ in the exhaust gases were monitored online with FTIR spectroscopy. The main chlorine product was hydrogen chloride. Samples of unprocessed HAp, taken from the bed during the process, and solid apatite residues were analyzed by X-ray diffraction (XRD). The content of chlorapatite (Ca₅(PO₄)₃Cl) in the analyzed samples was respectively 11, 53 and 19 %. X-ray fluorescence (XRF) analysis showed the molar ratio of Ca:P:Cl was: 1.00:0.36:0.01, 1.00:0.36:0.09, 1.00:0.37:0.04 respectively. The HAp could be used as an sorbent of the HCl_(g) during combustion of materials containing chlorine.

Keywords: chlorine, fluidized bed combustion, hydroxyapatite, sorption

Introduction

The chlorine is a component of a large group of combustible substances. Its amount in coals is varied and dependent on where coal seams were formed and its degree of coalification. The amount of chlorine in coals varies from 0.005 to 1 wt.% [1-3]. Predominantly its amount in coals is negligible, only coals formed in the saline waters have more than 1 wt.%. In biomass, chlorine content is also highly variable. The woody materials contain less than 0.1 wt.%, while the annual plants up to 0.72 wt.% [4, 5]. The chlorine included in total weight of the wastes is difficult to define. The source of Cl-waste can be a lots of solid (synthetic polymer, paper, textile, food), liquid (oils containing polychlorinated biphenyls (PCBs), dichloromethane, chloroform) or gas (chlorofluorocarbons - CFCs) substances. Textiles contain 0.4 wt.% of the chlorine while

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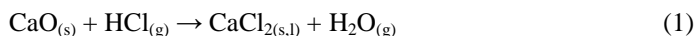
polyvinyl chloride (PVC) 56.7 wt.% of this element [6]. Furthermore, the use of toxic pesticides to manage pest problems, CFCs in refrigeration systems or PCBs in transformers creates a problem with the management of obsolete pesticides, phased out chlorofluorocarbons (CFCs) or worn-out transformers. These substances are classified as persistent organic pollutants (POPs). The lifespan of dichlorodiphenyltrichloroethane (DDT) in pedosphere is 5-30 years and CFCs in troposphere from 60 to more than 500 years [7, 8].

The higher heating values of coal, biomass, or refuse derived fuels (RDF) are not less than 15 MJ/kg [9]. All of these substances can be used as a source of chemical energy to produce heat or electricity in power plants or waste incineration plants. In the case of pesticides and CFCs, processes of thermal decomposition more and more persistent substances could be the best solution, which allows neutralize this substances.

Under controlled conditions, the main product of the combustion of Cl-containing substances at a temperature above 900 °C is HCl. Despite the fact that HCl is formed during combustion of coal or biomass currently the chloride emission standards are limited only for incinerators of waste [10]. Chlorine products of combustion, such as HCl or toxic polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [11-13] could be emitted into the atmosphere, where they may pose a risk for human health and the environment (acid rain) [14]. In addition molecular chlorine presence in the combustion chamber leads to intensification of chlorine corrosion of the superheater tubes [15-18]. The capture of chlorine in-situ in the combustion chamber and its transformation into environmentally safe substances seems to be very important environmental problem.

Hydrogen chloride can be removed by in-situ methods as well as end-of-pipe. In both groups of methods the calcium-based materials are important. Hydrogen chloride is characterized by a very good solubility in water, and at a temperature less than 782 °C with calcium-based sorbent forms a thermally stable calcium chloride [19]. There is a large group of techniques which use these properties to remove HCl in the exhaust gases by post-combustion devices such as dry or wet scrubber conjugated with Ca-sorbent injection. The halogen emissions can be reduced in wet FGD system (flue-gas desulfurization) with efficiency ranges from 95 to 99 % [20]. Unfortunately the end-of-pipe technology does not solve the problem, inter alia, corrosion of steel boiler elements.

There is little information about sorbents which allow bonding of chlorine in situ in the combustion chamber. Most researchers investigated the efficiencies of sorbents such as calcium and magnesium compounds as additive to the combustion chamber. HCl emission can be limited in the chemisorption process and calcium carbonate, hydroxide or calcium acetate can be used as sorbents. The product of this reaction is also calcium chloride, so the method's efficiency depends on the molten phase formation temperature [21]



Zhang et al. suggested that calcium acetate ((CH₃COO)₂Ca) is the most effective sorbent of hydrogen chloride. At 200 and 1000 °C the process efficiency is 99 % and nearly 14 % respectively [22]. Wey et al. reported that calcium additives reduced emission of HCl and Cl₂ better than magnesium-based sorbent [23]. Fujita et al. investigate the possibility of high temperature HCl removal by using hydrogrossular (Ca₃Al₂(SiO₄)(OH)₈) [24]. This mineral may be used at a temperature from 400 to 1000 °C.

In present research the HCl adsorption/desorption reversibility in a fluidized bed, during the co-combustion of substances containing Cl was determined. Homogeneous, exothermic reaction of combustion of gaseous fuel and the process of thermal destruction of gaseous chlorine compounds are utilized in BFB technology. Some elementary reactions may occur on the solids surface as heterogeneous reactions, which may result in a significant process change, such as flameless gaseous fuels combustion. Parallel processes, autocatalytic combustion and thermal destruction of halogenated derivatives (some are used as extinguishing agents) can be conducted with the greatest efficiency in the reactors, in which particles of solids material creates fluidized bed at relatively low temperature. Fluidization process enables countercurrent heat and mass transport in BFB significantly increasing their efficiency. Additionally the system is complicated when some products can interact with the particles of the fluidized bed, which modifies its properties.

The decomposition of organochlorine compounds in a reactor with BFB of inert material (sand) was discussed by Olek et al. [25]. It has been shown that in BFB combustion technology degradation of chlorine occurs in the bubbles flowing through the bed, in which the temperature of combusted gaseous fuels is higher than the average temperature of fluidized solid material. At the temperature above 900 °C, it has been acknowledged the inhibitory effect of chlorine on the CO oxidation. For the DCM flows of 0, 50, 100 cm³/h obtained the concentration of CO at 30, 70, 160 mg/m³, respectively.

In this work an attempt is undertaken to verification the capability of use the hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) as a sorbent for HCl removal. The calcination process of HAp takes place in two stages. At the temperature in the range from 900 to 1360 °C undergoes dehydroxylation, that is, removal of the hydroxyl groups without loss of the crystal structure of mineral [26]. At temperature above 1430 °C mineral loses thermal stability and decomposes into calcium phosphates. The conditions for dehydroxylation of HAp could be created in BFB of quartz sand. As shown in the earlier works dense phase of fluidized bed is made up with gaseous bubbles and an emulsion phase which contains almost the entire amount of bed material [27, 28]. The average temperature of the bed of quartz sand should not exceed 1100 °C, but inside the bubble temperature reaches value about 700 °C higher than the average temperature of the solid bed material [29].

The aim of this research was to verify interaction between chlorinated products and HAp under conditions created by co-combustion of LPG & DCM in the hot fluidized inert material (sand) and chemically active HAp. Whether in these conditions, OH groups in hydroxyapatite may be substituted with chlorine atoms to form chloroapatite. The effect of adding chlorine and hydroxyapatite on the combustion was monitored by measurement of the concentration of CO₂, CO, C_xH_y and NO_x in the exhaust gases. Furthermore the concentrations of compounds such as CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, COCl₂, HCl, were analyzed.

In order to verify the transformation of HAp into the chloroapatite: for the raw sorbent, received from the bed during the process and for residuals after the process, the chemical composition and phase composition were specified. In order to detect the physical changes that occurred in the material during the thermal treatment, SEM scans and porosimetric analysis were carried out.

Experimental

Materials and apparatus

The bed material and sorbent properties are given in Table 1. The sorbent material was bio-hydroxyapatite come from the animal wastes. It was obtained from the mineralization meat and bone meal in a BFB reactor at 900 °C. The theoretical sorption capacity of hydroxyapatite was 0.07 g_{Cl}/g_{HAP}.

Table 1

The material properties and process parameters

Items	Material	
Inert bed material	Quartz sand	Mass: 200 g; particle size: 300-385 µm
Sorbent	Hydroxyapatite	Mass: 100 g; particle size: 600-750 µm
Source of chlorine	Dichloromethane - technical grade	Flow rate: 0.014 cm ³ /s
Fuel	LPG	

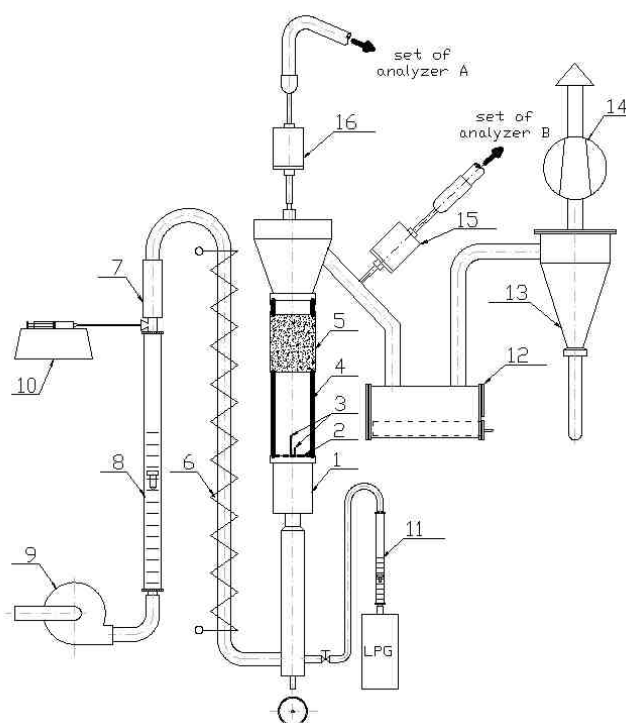


Fig. 1. Schematic of laboratory stand used in the present study: 1 - plenum chamber, 2 - perforated plate (distributor), 3 - two thermocouples, 4 - quartz pipe, 5 - insulating shield, 6, 7 - electric heater, 8 - air rotameter, 9 - blower, for fluidizing air, 10 - infusion pump, 11 - LPG rotameter, 12 - gravity settling chamber, 13 - cyclone, 14 - exhaust gases fan, 15, 16 - probe (heated)

The observations were conducted using a laboratory stand (Fig. 1) with bubbling atmospheric fluidized reactor (5-20 kW). The reactor was a quartz tube with an internal diameter of 96 mm and height of 500 mm (4) mounted on the plate (2), which was

a distributor of fluidizing medium and was placed on the plenum chamber (1). A movable shield (5) and blower, allowed temperature regulation with unchanging the air-fuel ratio. The exhaust gases were cleaned in gravity settling chamber (13) and cyclone (14). During the experiments the bed temperature was measured by set of thermocouples placed at 20 and 50 mm above the distributor (3). The DCM was injected by infusion pump (11) to the evaporator system (7, 8) and then to the fluidizing air.

The two groups of analyzers A and B were used. Samples of the exhaust gases were collected from two locations of the laboratory stand; directly from freeboard (about 400 mm above the distributor), and from the pipeline before the gravity settling chamber.

The oxygen content was monitored by electrochemical cell (EC), CO and CO₂ by the non-dispersive infrared detectors (NDIR), NO_x by chemiluminescence detector (CLA), total hydrocarbon by flame ionization detector (FID). The selected substances concentrations characterizing the combustion process: CH₄, C₂H₆, C₃H₈, C₂H₄, C₆H₆, C₂H₂, C₆H₅OH, CH₃OH, C₂H₅OH, CH₂O, C₃H₄O, nitrogen compounds: N₂O, NH₃, CHN and chlorine compounds: HCl, CHCl₃, CH₂Cl₂, CH₃Cl, CCl₄, COCl₂ were controlled by Fourier transform infrared spectroscopy (FTIR). Concentration measurements were accurate to no less than 2 ppm.

The solid materials elemental composition was analyzed by X-ray fluorescence (XRF). The phase composition was analyzed by X-ray diffraction (XRD). The porosimetric analysis was determined by the BET method, using the Micromeritics ASAP2020 analyzer. A scanning electron microscopy (SEM), TM-3000 Hitachi-Hightech Tabletop Microscope, was used for surface morphology characterization.

Research methodology

The sand bed was gradually heated by air/LPG mixture from ambient temperature to 930 °C, at rate ~1.5 °C/s. The measurements were conducted at an air excess coefficient of 1.3. A source of chlorine, DCM with a flow rate of 0.014 cm³/s was dosage by an infusion pump. The fluid was introduced into the preheater (80 °C), then as a gas to the fluidizing air. When HCl amount stabilized, HAp (100 g) was added to the combustion chamber (Fig. 1). It entails rapid reduction of HCl concentration. Process was kept until concentration of HCl returned to level before HAp injection. Then flow of DCM was stopped. The possibility of desorption of chlorine from chlorapatite was checked by increase the process temperature to about 1050 °C, for a period of time.

The process was controlled by monitoring the composition of the exhaust gases. The gases concentration collected from freeboard were controlled continuously by Horiba PG250 analyzer (O₂, CO, CO₂ and NO_x) and J.U.M. Model 3-200 analyzer (total hydrocarbon) (set of analyzer A, Fig. 1) and collected before the gravity settling chamber were continuously analyzed by VarioPlus analyzer (O₂, CO₂, CO) and periodically by analyzer Gasmeter DX-4000 (hydrocarbons, chlorocarbons, N₂O, NH₃, CHN). The sampling period was 5 s (set of analyzer B, Fig. 1).

The samples of unprocessed raw sorbent (P1), HAp taken out from the reactor directly before stopping of dosing DCM (P2) and sorbent after whole process (P3) were analyzed.

Results and discussion

The combustion of hydrocarbons has been partially inhibited by Cl radicals. However, this was not apparent in changes in the bed temperature (Fig. 2). An increase of CO

concentration is the characteristic phenomena of Cl radicals inhibitory effect. The average concentration of CO before and after the addition of DCM was 50 and 200 mg/m³. The higher concentration of CO, than those described in [25] was result from the use of a fine fraction of the bed.

The concentration of NO_x did not change and was not more than 30 mg/m³ and after turning off the dosage of DCM decreased to 25 mg/m³ (Fig. 2).

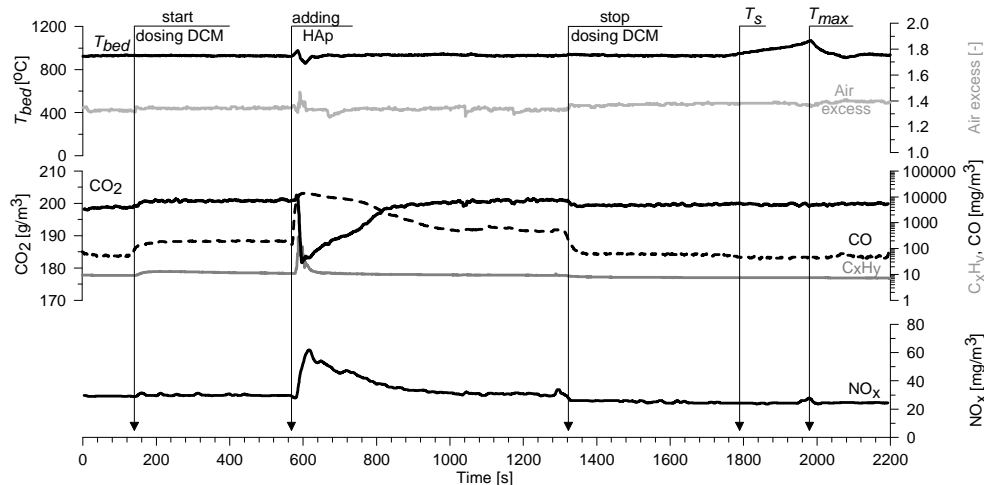
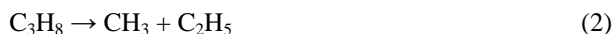


Fig. 2. Selected parameters and the concentration of NO_x, CO, CO₂ and C_xH_y (concentrations standardized to 6 % oxygen in the exhaust flue gases) (T_{max} - maximum process temperature, T_s - average process temperature, T_{bed} - fluid bed temperature)

Due to the ambient temperature of added HAp, after his introduce to the bed temporary decrease of average bed temperature was observed, followed by decrease in the concentration of CO₂ and increased concentrations of CO and NO_x. Along with HAp addition new equilibrium was settled down in the reactor, the CO concentration was stabilized at a higher level of 530 mg/m³. HAp particles compared to the sand have higher specific surface area. The injection into the reactor the substances with strongly developed surface area promotes recombination reactions of radicals OH and HO₂ occurring mainly on the solid particles surface. The effect was to inhibit CO to CO₂ oxidation, wherein the radicals OH and HO₂ play a crucial role.

The combustion of LPG with the addition of chlorine compounds also provides presence of unburned organic compounds from the group of alcohols and aldehydes. After chlorine introduction, concentration of ethanol has increased from 13 to 20 mg/m³ (Fig. 3). The appearance of alcohol in the combustion products indicates the deterioration of the hydrocarbons oxidation process. Following HAp introduction, a part of the chlorine has been eliminated and C₂H₅OH concentration decreases to the background level. At the same time CH₄ and C₂H₆ appeared in exhaust gases. This may indicate a large amount of methyl radicals presence, which partially recombine to form ethane:



While decreasing CH_4 and C_2H_6 concentrations subsequent increase in concentrations of ethanol was observed. When DCM dosage was turned off, ethanol concentration was reduced to 13 mg/m^3 and trace quantities of C_2H_6 appeared.

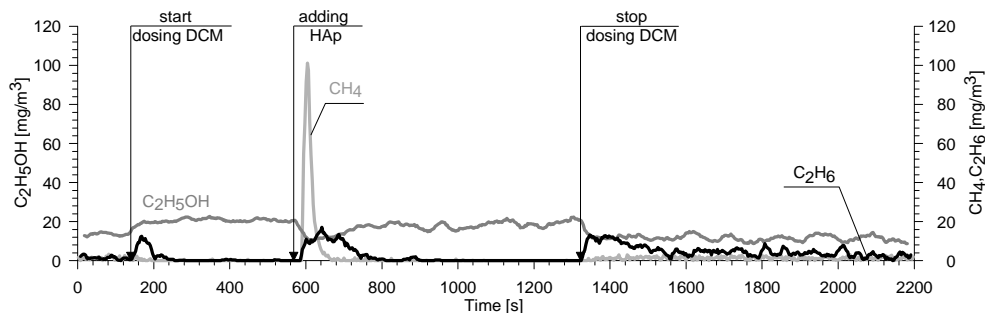


Fig. 3. The concentration of carbon products (concentrations standardized to 6 % oxygen in the exhaust flue gases)

Other monitored hydrocarbons, aldehydes, ketones, alcohols did not exceed 2 ppm_v, these compounds were omitted in the graphs.

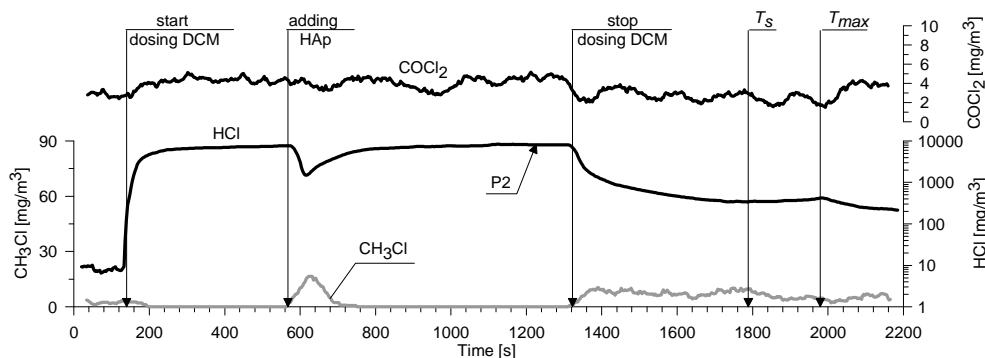


Fig. 4. The concentration of chlorine products, P2 - sampling of HAp during the process (concentrations standardized to 6 % oxygen in the exhaust flue gases)

Throughout the whole combustion process DCM was monitored. In the exhaust flue gases the mean concentration of DCM was 96 mg/m^3 , the background level was 62 mg/m^3 . The efficiency of 99.5 % of thermal DCM decomposition was obtained, which was consistent with earlier studies [25]. During LPG combustion with DCM the main gaseous product containing chlorine was hydrogen chloride ($C_{\text{HCl}} = 9276 \text{ mg/m}^3$) (Fig. 4). After injection of HAp rapid and essential drop in the HCl concentration (Fig. 4) to 1500 mg/m^3 was observed and not more than 16 mg/m^3 increase of methyl chloride (Fig. 4). The achieved HCl concentration reduction efficiency in the exhaust gases at temperature 950°C was 44 %, at a mass ratio sorbent to bed as 1:2.

The presence of chloromethane in the exhaust gases after the addition of hydroxyapatite is related with a temporary increase in concentration of CH_4 from 0 to

100 mg/m³. As a consequence methyl radical may recombine with chlorine radical to form methyl chloride:



When all HAp introduced in to reactor was saturated with chlorine, the average concentration of HCl has returned to the level of 9276 mg/m³.

Due to the long response time of the HCl sensor, its concentration did not reach the background level immediately after cutting off the supply of DCM. In addition, a slow process of desorption of chlorine was occurred. The desorption process can be speeded up by changing the temperature. The increase of the bed temperature from $T_s = 930$ °C to $T_{max} = 1050$ °C caused an increase in HCl concentration from 390 to 530 mg/m³ (Fig. 4). The decrease of the bed temperature to $T_s = 930$ °C caused a reversion of gradient of decrease of the HCl concentration to a value before the temperature change, concentration of HCl reached 230 mg/m³. The increase of the bed temperature accelerates desorption process, although for the selected parameters desorption efficiency was 1 %.

The CHCl₃ and CH₂Cl₂ concentrations did not exceed 2 ppm_v, these compounds were omitted in the graphs.

Figure 5 show the microscopic (SEM) images of unprocessed bone material (P1), taken during (P2) and after (P3) thermal DCM decomposition.

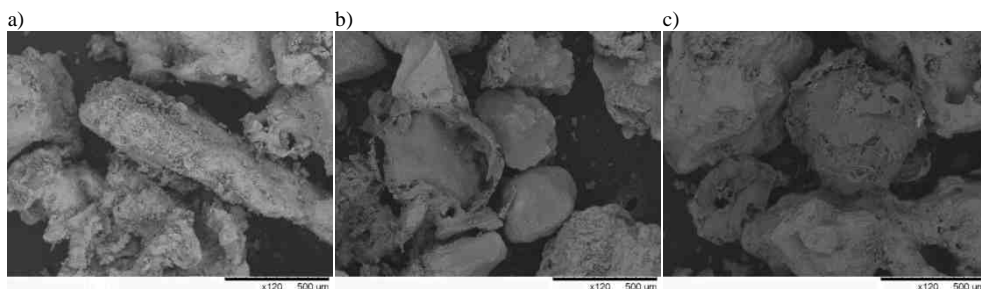


Fig. 5. a) SEM images of sample P1 - unprocessed HAp; b) sample P2 - HAp take from reactor during sorption process; c) sample P3 - HAp sieved from the sand bed after finish process and cooling bed material

At a 120-times magnification it possible to see the sorbent's shape. The oval-shaped granules forms are the dominant fraction. With lengthen residence time of HAp in BFB the changes in particles shape can be seen. It is the influence of hydrodynamic effects of the bed. The erosion of the material was seen, as smoothing and rounding of the edges of the particles were observed. In the sample P1 predominate in narrow range of particles size from 600 to 750 μm, while for the samples P2 and P3 wider range of particle size was observed. The surface of grains in the P1 sample was covered with small particles. In the sample P2 small particles were uncommon, it could be seen a smooth homogeneous surface. In case of P3 sample which has the longest residence time in the reactor undergone a process of chlorine desorption (above 1000 °C) consequently a tendency to detachment the flat badges of the material from the mineral surface was observed.

As a result of sorption and desorption processes, surface area and pores size of the sorbent were decreased. As demonstrated in the work [30] after the calcination at 550 °C surface area is 18 m²/g, but if calcination temperature increased to 1000 °C the surface area

would be reduced to less than $2 \text{ m}^2/\text{g}$. The raw material P1 before it mineralized at 900°C in BFB, had been earlier calcined in a rotary kiln, so the value of $3 \text{ m}^2/\text{g}$ of BET surface area it was not a surprise. The porous material can be obtained at a temperature not higher than 900°C , above it the sintering process is observed [31], which is confirmed by the analysis of samples of P2 and P3. The process of desorption at a temperature above 1000°C resulted in sintering of the bone material and decrease in the size of surface area as well as the pore diameter of P3 sample, in comparison to sample P1.

Table 2
Porosimetry analysis of samples of unprocessed HAp material (P1), apatite received from the bed during the adsorption process (P2), post process apatite material (P3)

	The specific surface	The average pore volume	The average pore diameter
	$[\text{m}^2/\text{g}]$	$[\text{cm}^3/\text{g}]$	$[\text{\AA}]$
P1	3.0	0.024	547
P2	2.5	0.025	508
P3	1.3	0.003	132

In Table 3 the mass fractions of elements in P1, P2 and P3 samples was shown. Content of chlorine in unprocessed material (P1) was 0.46 %, which is consistent with the literature data indicate 0.26-1.10 % (wt, dry base) [32]. The chlorine mass fraction in the sample P2 in relation to P1 increased more than 7 times, which indicates the inclusion of chlorine in the structure of HAp. In the sample P3 amount of the chlorine was higher than in the P1, only a portion of the chlorine has been desorbed. Increased level of calcium in sample P2, in comparison of other samples, can be noticed.

Table 3
Elemental composition of samples P1, P2, P3

Element	Ca	O	P	Na	Fe	Mg	Cl	K	Other
Concentration [%]									
P1	45.4	38.0	12.8	1.06	0.78	0.51	0.46	0.44	0.52
P2	42.4	39.8	11.8	0.51	0.96	0.39	3.43	0.13	0.58
P3	45.0	38.4	12.7	0.43	1.10	0.37	1.69	0.06	0.28

The X-ray analysis showed that the dominant crystalline phase in samples P1 and P3 was the hydroxyapatite (Fig. 8). In the sample P2 decreased quantity of HAp was determined, the main component was chlorapatite. The content of this mineral was 53 % compared to 10 % in sample P1 and 18 % in the sample P3. The sorption of HCl in situ in BFB in the presence of HAp is possible.

At above 1360°C HAp decomposed into tetracalcium phosphate (TTCP, $\text{Ca}_4(\text{PO}_4)_2\text{O}$), and tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$) [33, 34]. During the tests the bed has reached temperature of 1050°C (emulsion), and periodically, in bubbles, even 700°C higher temperature. So there is a high probability that part of the bed particles a passing by the bubbles could disintegrated into TCP and TTCP. Content of TCP in the sample P2 and P3 was 16 and 19 % respectively. The second products of degradation HAp is unstable TTCP and in $\text{H}_2\text{O}_{(\text{g})}$ presence could reproduced HAp at $1000\text{-}1200^\circ\text{C}$ [35].

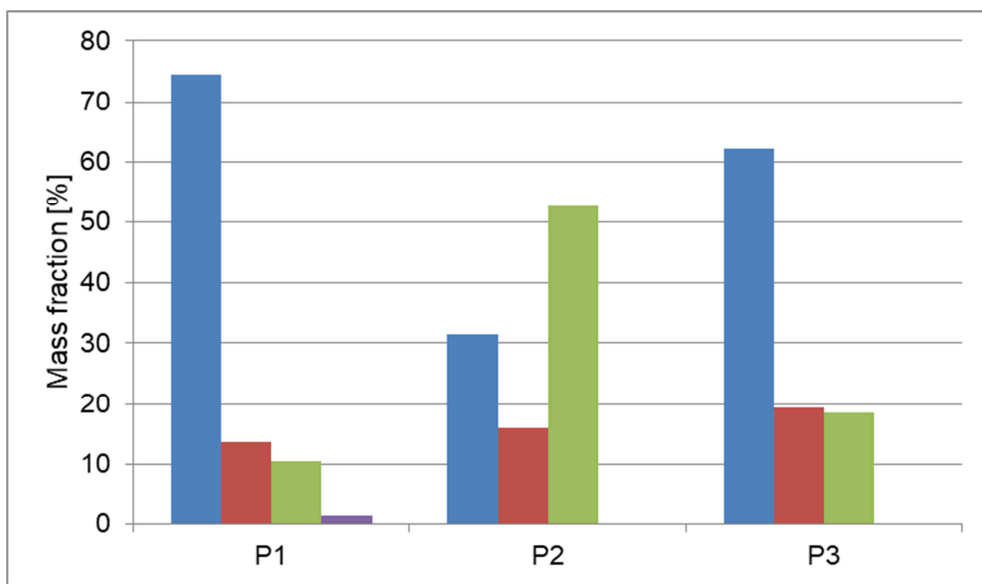


Fig. 8. Phase composition of the raw sample (P1) received from the bed during the adsorption process (P2), sifted from the bed after process (P3) (■ - hydroxyapatite, ■ - tricalcium phosphate, ■ - chlorapatite, ■ - calcium oxide)

The XRD and XRF analysis of samples P2 and P3 showed that desorption of chlorine from the chlorapatite was approximately 50 %.

Conclusions

The process of decomposition of DCM in heated fluidized bed is very effective. Degree of DCM decomposition was more than 99 %. The main chlorine component of the flue gases was gaseous HCl. Thermal degradation of DCM produces the Cl radicals which leads to the radical processes with the participation of OH radicals. As a result an increase of CO was observed. Also some increase in CO concentration occurred after addition of hydroxyapatite into the bed. However, under oxidizing conditions, while residence time will be appropriate, e.g., 2 s, CO should be burnt out in the freeboard.

The results showed that HCl released during DCM thermal decomposition is adsorbed by hydroxyapatite at the bed temperature of 930 °C. This dechlorination process occurring in the FB is analogous to dry desulphurization process, which also can be achieved in the FB using calcium carbonate.

This method could be used in installations of thermal treatment or incineration, where wet exhaust gas cleaning systems would not be reasonable due to high costs. Chlorine is bound in a chlorapatite which is stable at temperature ~1000 °C.

The sorption process can also be partially reversed above 1000 °C, although the combustion is accompanied by cracking of the mineral surface (Fig. 5) and material sintering. Theoretical calculations show that with HAP amount of used in this research, the adsorbed mass of chlorine may be higher - hydroxyapatite sorption capacity is not utilized in 100 %.

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