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THERMAL DECOMPOSITION OF SELECTED CHLORINATED ALIPHATIC HYDROCARBONS IN THE FLUIDIZED BED REACTOR WITH CHEMICALLY ACTIVE BED MATERIAL

TERMICZNY ROZKŁAD WYBRANYCH CHLOROWCOPOCHODNYCH WĘGLOWODORÓW ALIFATYCZNYCH W REAKTORZE FLUIDYZACYJNYM Z CHEMICZNIE AKTYWNYM MATERIAŁEM ZŁOŻA

Abstract: Combustion of fuels, including renewable fuels, is associated with emissions of various gaseous compounds containing chlorine. The reversible sorption / desorption of hydrogen chloride, in a fluidized bed reactor, while combustion of Cl-containing substances, was carried out. Dichloromethane (DCM) was used as the source of chlorine. DCM thermal decomposition in a sand bed and then in a fluidized bed containing hydroxyapatite was investigated. In both series: process temperature was 930ºC, the air excess 1.3, the concentration of DCM 2900 ppm. The concentration of components containing chlorine such as HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$ in the flue gases were monitored by FTIR analyzer. The main chlorine product was HCl. Samples of the hydroxyapatite before the process of thermal decomposition of DCM, taken from the bed during the process, and after the thermal decomposition of chlorapatite at 1050°C were analyzed by X-ray diffraction (XRD). The content of chlorapatite in the analyzed samples was respectively 10, 53 and 18%. X-ray fluorescence (XRF) analysis showed the molar ratio of Ca:P:Cl was: 1.12:0.41:0.01, 1.01:0.36:0.09, 1.10:0.40:0.05 respectively. The hydroxyapatite can be used as an absorbent of the $HCl_{(g)}$ during combustion of materials containing chlorine.

Keywords: chlorine, chemically active fluidized bed, hydroxyapatite

The chlorine content in coals varies and is dependent on where coal seams were formed and its degree of coalification. Mass fraction of chlorine in lignite is < 0.005-0.029%, and in bituminous coal 0.02-0.159%. In biomass used as additive to conventional fuels content of chlorine is also various, woody material contains less (less than 0.05% chlorine), a material derived from annual plants more (> 1%) of this element [1]. The most chlorine is included in the wastes and its proportion in total weight of the wastes is difficult to define. Textiles contain only 0.02% of the chlorine while PVC pipe scraps 46% of this element [2]. All of these substances are the source of chemical energy and can be converted into energy in power plants. Chlorine is mainly released as HCl, but the chloride emission standards are limited only for incinerators of waste [3]. The presence of chlorine in the combustion zone may be the source of not only HCl but also polychlorinated dibenzo-para-dioxins and dibenzofurans [4, 5], as well as leads to intensification of high-temperature chlorine corrosion of the superheater tubes [6, 7]. The source of molecular chlorine required to initiate corrosion may be chlorides present in the exhaust gas, or settling on the boiler's walls in the form of sodium and potassium chloride [8]. Chlorine compounds are undesirable substances not only in power plants, but also as

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a product of combustion in the environment [9]. It seems appropriate to search for methods to reduce the formation of the chlorine compounds in the combustion chamber and transform them into possible least environmentally harmful substances.

The processes of thermal decomposition of DCM and chlorobenzene in a reactor with a fluidized bed of sand have been described at work by Olek et al [10]. It has been shown that in the bubbling fluidized bed degradation of total chlorine takes place in the bubbles flowing through the bed, in which the temperature of combusted gaseous mixture (LPG or propane with air) exceeds 1200°C, while the mean fluidized bed temperature is about 850°C. It was also found that the Cl introduced into the reactor in the form of DCM or chlorobenzene, leaving it in the form of HCl.

HCl emissions can be reduced by sorption to the gaseous products on calcium carbonate, hydroxide or calcium acetate. The product of this reaction is calcium chloride, however, efficiency of the method decreases with increasing temperature [11]. Zhang et al found that for the most effective calcium acetate process efficiency drops greatly from 99% to 13.52% with the increase of temperature from 200 to 1000°C [12]. Fujita et al investigate the possibility of high temperature HCl removal by using hydrogrossular $Ca_3Al_2(SiO_4)(OH)_8$ [13]. Hydrogrossular is effective for HCl sorption in temperature from 400 to 1000°C. Tanahashi et al used dry-sorbent based on coal fly ash with slaked lime to remove HCl during pyrolysis of PVC [14]. They achieved 99.8% efficiency of HCl sorption in pilot scale reactor under pyrolysis conditions.

In this work an attempt is undertaken to determine the possibility of carry out a reversible sorption/desorption of hydrogen chloride in a stationary fluidized bed, during the thermal decomposition of substances containing chlorine. The possibility of use of hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) as a sorbent for HCl removal has been proven. Methods of the preparation of synthetic hydroxyapatite and possibility of replacement the hydroxyl group by chlorine are known. Kannan et al reported the results of studies on the preparation chloroapatites through aqueous precipitation method [15]. Thermal stability of chloroapatite is up to 1200°C.

HAp is decomposed in two stages. In the temperature range 900-1360ºC undergoes dehydroxylation, that is, removal of the hydroxyl groups without loss of crystal structure of mineral [16]. At temperature above 1430ºC mineral loses thermal stability and decomposes into calcium phosphates. The conditions for dehydroxylation of HAp have been created in the stationary fluidized bed of sand. The average temperature of the bed of quartz sand should not exceed 1100°C, but inside the bubble temperature reaches value about 400ºC higher than the average temperature of the bed material [17]. Under conditions formed in the fluidized bed, in the atmosphere enriched in chlorine, the OH groups in hydroxyapatite may be substituted by chloride atoms to form chloroapatite.

The aim of present work is to determine the chemical composition of gases produced from the decomposition of chlorinated hydrocarbons in a fluidized bed made of sand and supplemented by chemically active substance (hydroxyapatite). The effect of adding chlorine and hydroxyapatite on the combustion process is monitored by measurement of the concentration of CO_2, CO and NO_x in the flue gases. Special attention is paid to the chlorine compounds such as HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$.

In order to verify the transformation of HAp into the chloroapatite: for the starting material, received from the bed during the process and after the process, the elemental

composition and phase composition were specified. In order to detect the physical changes undergone in the material during the thermal treatment SEM scans and porosimetric analysis were carried out.

Experimental

Materials and apparatus

The bed material was quartz sand (200 g, particle size 0.3 to 0.385 mm). Initially sand was fluidizing by air, then by a LPG and air mixed in plenum chamber. Dichloromethane (DCM) - technical grade - was chosen as sources of chlorine. Sorbent material was hydroxyapatite in the form of feedstock bone (100 g, particle size 0.6 to 0.75 mm). The bone material was obtained in the process of mineralization of solid waste from meat and bone meal in a fluidized bed reactor at a temperature of 1000°C [18].

The observations were made using a laboratory with a stationary fluidized bed of a solid material. The 5-20 kW fluidized bed reactor with the set of analyzers has been described in detail before [10]. From the set of analyzers two of them were used. Concentration of O_2, CO, CO_2 and NO_x was controlled by Horiba PG250 analyzer. Concentration of O_2 was measured by electrochemical sensor (EC), CO and CO_2 by the non-dispersive infrared detectors (NDIR), NO_x by chemiluminescence detector (CLA). Standard library of IR spectra of FTIR analyzer (Gasmet DX-4000) was extend to include selected gaseous components. The concentration of the substances characterizing the combustion process, CH_4, C_2H_6, C_3H_8, C_2H_4, C_6H_6, C_2H_2, C_6H_5OH, CH_3OH, C_2H_5OH, CHOH, C_3H_4O and chlorine compounds HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$ were controlled. Concentration measurements were accurate to no less than 2 ppm_v.

The chemical composition of solid products was analyzed by X-ray fluorescence (XRF). The phase composition was studied by X-ray diffraction. The porosimetric analysis was determined by the BET method, based on isotherms of nitrogen sorption obtained by the Micromeritics analyzer, model ASAP2020. Microscopic examination of surface structure was done by using SEM TM3000 Tabletop Microscope.

Research methodology

The experiment was initiated by fluidizing sand bed by air at temperature of 20ºC, then to the air LPG was added and ignition was initiated. The tests were carried out at an air excess ratio of $\lambda = 1.3$. The bed was gradually heated to 930°C at rate ~1.5 K/s. After the bed temperature reached 930ºC dosage of 2900 ppm_v of DCM to the fuel-air mixture was started. After stabilization the flow of DCM, 100 g of bone material was added to the reactor (Fig. 1), which caused rapid decrease of HCl at the outlet of reactor. Process was carried out until HCl achieved level before hydroxyapatite was added to the bed. Then DCM was turned off.

The possibility of desorption of chlorine from chloroapatite was investigated by the raise of the bed temperature to about 1050ºC, for a period of time. The samples of the sorbent before dosing into the reactor (P1), at the end of the sorption process (P2), and after the process of thermal decomposition of chloroapatitie at 1050°C (P3) were analyzed.

Results and discussion

As expected, in presence of Cl radicals the combustion process of hydrocarbons fuel has been partially inhibited. However, this was not apparent in changes in the bed temperature (Fig. 1a). An increase of the concentration of CO from 17 to 120 ppm_v is the characteristic phenomena of inhibitory effect of Cl radicals. Concentration of NO_x did not change and was not more than 15 ppm (Fig. 1b). Detailed explanation of the phenomena associated with the introduction of both DCM and chlorobenzene to the mix air + LPG combusted in the fluidized sand has been presented by the authors in an earlier work [10]. After injection of the hydroxyapatite to the reactor temporary decrease of mean bed temperature was observed (due to ambient temperature of added material) followed by decrease in the concentration of CO_2 and increased concentrations of CO and NO_x. Along with the addition of hydroxyapatite new equilibrium was settled down in the reactor, the CO concentration was stabilized at a higher level of 350 ppm_v. Over time, the concentration of NO_x was lowered to 15 ppm_v, and after turning off the dosage of DCM decreased to 13 ppm_v.

Hydroxyapatite particles compared to the sand have greater specific surface area. The introduction into the combustion chamber the substances with strongly developed surface area promotes recombination reactions of radicals OH and HO_2 occurring mainly on the surface of a solid. The effect was to inhibit the oxidation of CO to CO_2, wherein the radicals OH and HO_2 play a crucial role.

Throughout the whole combustion process DCM was detected in the flue gases (Fig. 1c), the mean concentration was 32 ppm_v, the background level was 17 ppm_v. A 99.5% level of thermal decomposition of DCM was obtained, which is consistent with previous studies [10]. During the combustion of LPG with DCM the main gaseous product containing chlorine was hydrogen chloride. Concentration of HCl was 5700 ppm_v. After introduction of HAp rapid and significant decrease in the concentration of HCl (Fig. 1c) to 950 ppm was observed and not more than 20 ppm_v increase in the concentration of chloromethane (Fig. 1c, gray line). The achieved degree of reduction of HCl concentration in the flue gases was 33%. The presence of chloromethane in the flue gases after the introduction of hydroxyapatite is related with a temporary increase in concentration of CH_4 from 0 to 160 ppm_v. As a consequence methyl radical may recombine with chlorine to form methyl chloride:

$$CH_3 + Cl + M \rightarrow CH_3Cl + M \qquad (1)$$
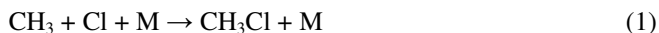
After saturation of whole hydroxyapatite introduced in to reactor by chlorine, the mean concentration of HCl has returned to the level of 5700 ppm_v. Due to the delays in the analytical sensors, measured concentration of HCl did not reach the background concentration immediately after switching off the supply of DCM. The increase of the bed temperature from 930 to 1050°C caused an increase in concentration of HCl from 240 to 330 ppm_v. The concentration of phosgene, $CHCl_3$ and CCl_2 did not exceed 2 ppm_v, these compounds were omitted in the graphs.

Figure 2-4 show the microscopic (SEM) images of bone material taken from the reactor at different stages of the process of thermal decomposition of DCM.
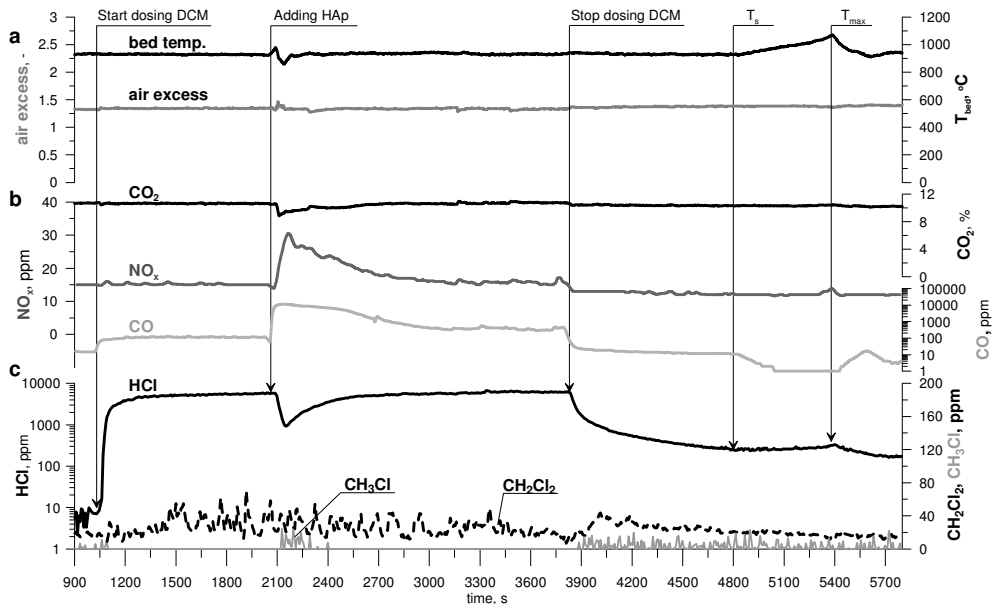
Fig. 1. Selected parameters of the process of thermal decomposition of DCM in bed material enriched by hydroxyapatite, the concentration of NO_x, CO and CO_2, and the concentration of chlorine products of decomposition process mixture of DCM + LPG
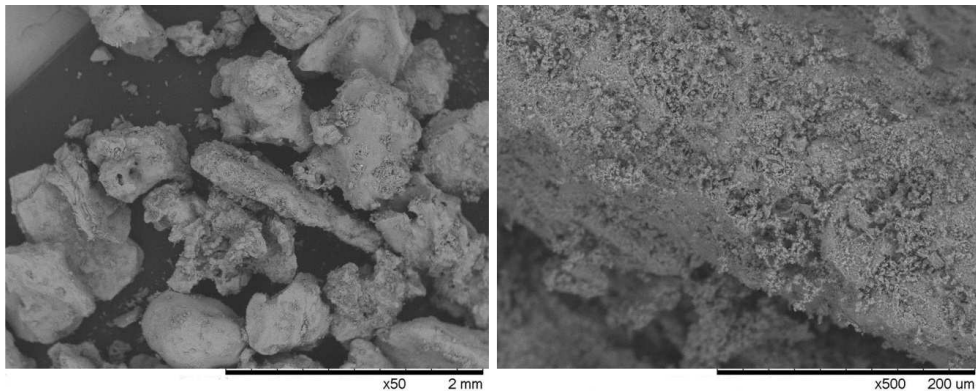

Fig. 2. Microscopic images of HAp from the sample P1

Low magnification (x50) makes it possible to show the shape of the grains. The oval-shaped granules form the dominant fraction. Along with the lengthen the residence time of HAp in the fluidized bed gradual changes can be seen as 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 0.6 to 0.75 mm, 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 the sample P3 which has the longest residence time in the reactor undergone a process of chlorine desorption (above 1000°C) consequently there a tendency to detachment the flat blades of the material from the mineral surface was observed.
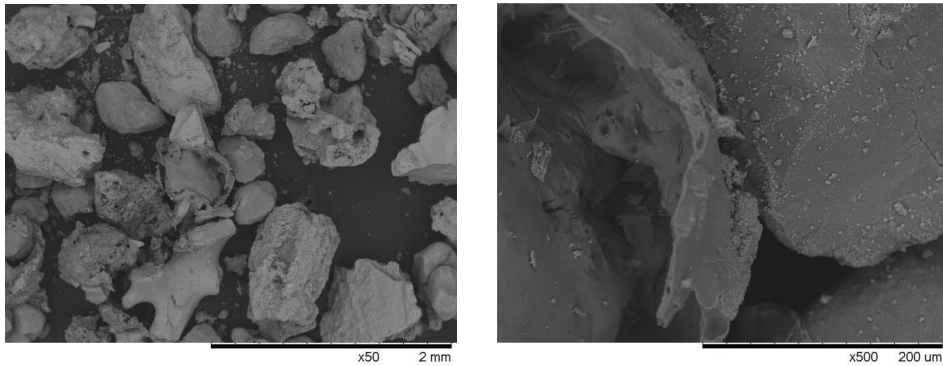

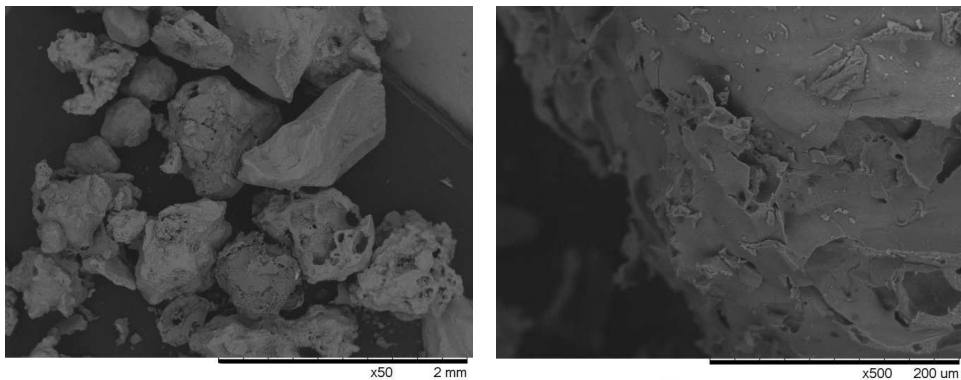Fig. 3. Microscopic images of the HAp from sample P2

Fig. 4. Microscopic images of the HAp from sample P3

As a result of progress of sorption and desorption processes, surface area and pores size of the sorbent were decreased. As demonstrated in the work [19] after the process of calcination at 600°C BET surface area is 21.75 m^2/g, but if calcination temperature was increased to 950°C the surface area is reduced to less than 7 m^2/g. Material P1 was earlier calcined in a rotary kiln, then mineralized at 900°C in a fluidized bed incinerator, so the value of 3 m^2/g of BET surface area it was not surprising. The porous material can be obtained at a temperature not higher than 900°C, above it the sintering process is observed [20], 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 the sample P3 in comparison to sample P1.

Table 1

Porosimetry analysis of samples of materials before introduction into the reactor (P1), received from the bed during the adsorption process (P2), sifted from the bed after decomposition process of chloroapatite (P3)

	The specific surface [m^2/g]	The average pore volume [cm^3/g]	Average pore diameter [Å]
P1	3	0.024	547
P2	2.5	0.025	508
P3	1.3	0.003	132

In Table 2 the mass fractions of elements in samples P1, P2 and P3 was shown. Base chlorine content in the analyzed material was 0.45%, which is three times higher than the literature data indicate 0.13-0.15% [21]. The share of chlorine 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 still higher than in the material P1, only a part of the chlorine has been desorbed. Increased level of calcium in sample P2, in comparison of other samples, can be noticed. This is due to slightly contamination of the analyzed sample by bed material (SiO_2) in the sample P2. For this reason, the actual content of chlorine in the sample P2 may be slightly higher than the measured 3.26%.

Table 2

Elemental composition of samples P1 (before introduction into bed), P2 (material extracted during the process), P3 (sifted from the field after the completion of the decomposition of chloroapatite)

Element	Ca	O	P	Si	Na	Fe	Mg	Cl	K
	Conc. [%]								
P1	44.8	37.5	12.6	1.39	1.05	0.77	0.50	**0.45**	0.43
P2	40.3	37.8	11.2	5.01	0.48	0.91	0.37	**3.26**	0.12
P3	43.9	37.5	12.4	2.37	0.42	1.07	0.36	**1.65**	0.06

Table 3

Phase composition of the sample before introduction into the reactor (P1) received from the bed during the adsorption process (P2), sifted from the bed after completion of the decomposition process of chloroapatite (P3)

	Hydroxyapatite	Orthophosphate(V) calcium	Chloroapatite	Calcium oxide
	Weight fraction [%]			
P1	**74.5**	13.6	10.6	1.3
P2	31.4	16.0	**52.6**	0
P3	**62.1**	19.4	18.5	0

The X-ray analysis showed that the main crystalline phase in samples P1 and P3 was HAp (Table 3). In the sample P2 decreased share of HAp was determined, the dominant component was chloroapatite. The content of this mineral was 52.6% compared to 10.6% in the sample P1 and 18.5% in the sample P3. This shows that carrying out the sorption of HCl in bed material in the presence of HAp is possible. Due to the HAp being at a temperature ~1000°C (emulsion), and as shown in previous works [17] temporarily at higher temperatures (bubbles) increased content of orthophosphate(V) calcium was observed. Calcium phosphates were produced by partial disintegration of HAp.

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

Conclusions

The study confirmed the possibility of carrying out the process of thermal decomposition of dichloromethane in fluidized bed reactor. Degree of DCM decomposition was 99%. The main chlorine component of the process 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 the concentration of CO occurred after introduction of hydroxyapatite into the bed. However, under conditions of an excess of oxidant, while residence time will be appropriate, *eg* 2 s, CO should be burnt out in the freeboard.

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

This method could be used in installations of thermal treatment or incineration, where wet flue gas cleaning systems would not be reasonable due to high costs. Chlorine is bound in a product which is stable at ambient temperature. Obtained chloroapatite may be used in the industry. Sorption process can also be partially reversed at a temperature above 1000°C, although the process is accompanied by cracking of the mineral surface (Fig. 4) and material sintering. Theoretical calculations show that with HAp amounts of used in this research, the retained mass of chlorine may be higher - hydroxyapatite sorption capacity is not utilized in 100%.

Acknowledgement

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Abstrakt: Spalanie paliw, w tym paliw ze źródeł odnawialnych, związane jest z emisją gazowych związków zawierających chlor. Wykonano badania sprawdzające możliwość odwracalnego procesu sorpcji/desorpcji chlorowodoru w stacjonarnym złożu fluidalnym podczas spalania substancji zawierających chlor. Jako źródło chloru zastosowano dichlorometan. Proces termicznego rozkładu DCM przeprowadzono w złożu piaskowym, a następnie w złożu piaskowym z dodatkiem biohydroksyapatytu. W obu seriach pomiarowych temperatura procesu wynosiła 930ºC, współczynnik nadmiaru powietrza 1,3, a stężenie DCM 2900 ppm. Za pomocą analizatora FTIR monitorowano stężenia następujących związków chloru w gazach poprocesowych: HCl, CH_2Cl_2, CH_3Cl, $CHCl_3$, CCl_4, $COCl_2$. Dominującym związkiem chloru w gazach był HCl. Metodą XRD przeanalizowano biohydroksyapatyt przed procesem termicznej dekompozycji DCM, odebrany ze złoża w trakcie procesu, oraz po zakończeniu dozowania DCM i procesu termicznej dekompozycji chloroapatytu w 1050°C. Zawartość chloroapatytu w analizowanych próbkach wynosiła odpowiednio 10, 53 oraz 18%. Analiza XRF wykazała następujące stosunki molowe Ca:P:Cl w próbkach: 1,12:0,41:0,01, 1,01:0,36:0,09, 1,10:0,40:0,05. Przeprowadzone badania wykazały możliwość wykorzystania biohydroksyapatytu jako materiału sorpcyjnego w stosunku do gazowego chlorowodoru powstającego w gazach spalinowych podczas utylizacji materiałów organicznych zawierających chlor.

Słowa kluczowe: chlor, chemicznie aktywne złoże fluidalne, hydroksyapatyt