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Highly porous calcium hydroxyapatite–based composites for air pollution control

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Abstract

The control of emission gas from incinerators appears as a key issue for the improvement of the incineration technology. In this paper, we developed new sorbent materials based on calcium hydroxyapatite (Ca–HA) matrix. Using gelatine and bio–glass as porous and structural agents, which are largely available and have reasonable costs, powder of Ca–HA could be easily formulated into desired morphologies. As an example, a Ca–HA based accumulator having good porosity and mechanical stability was obtained by mixing Ca–HA powder with gelatine, bio–glass and water, followed by molding, then calcination steps. This accumulator showed an interesting capacity for the collection and tracing of Cd used as single model heavy metal in gas phase.

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Keywords: Calcium hydroxyapatite, composite, porosity, fumes, heavy metals, cadmium.

1. Introduction

Municipal and industrial solid wastes are increasingly produced worldwide [1]. Landfill and incineration are the most used techniques for the management of municipal and industrial wastes. But with the limit in landfill sites and the growing amount of wastes, incineration is becoming more advantageous, because it allows (i) a high reduction of waste volume up to 90% or waste weight up to 70%; (ii) an effective destruction of pathogens and other organic toxic compounds; (iii) the recovery of energy from organic wastes [2, 3]. However, emissions of pollutants from incinerator flue gases are currently of great environmental concern because of their toxicity. The emission of heavy metals takes place during the combustion of wastes, wherein heavy metals are vaporized by the thermal effect of combustion and then emitted with exhaust gases despite filtration of smoke particles [4]. Thus, the control of incinerator gas emission, in particular heavy metal emission, is an important factor for the improvement of the efficiency and acceptability of the incineration technology.

Calcium hydroxyapatite (Ca–HA, chemical formula: $Ca_{10}(PO_4)_6(OH)_2$) belongs to the family of apatitic compounds [5]. Ca–HA is known as a versatile material for different domains of applications, in particular environmental purposes, thank to its intrinsic physico–chemical properties: high specific surface area, very low solubility in water, high thermal stability, high ionic exchange capacity for several cations and anions [5, 6]. However, most of developments of Ca–HA based materials in environmental field are limited to the liquid phase for the removal of fluoride [7, 8]; organic pollutants [9–12]; metals and heavy metals [13–15] etc.

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For such applications, powder Ca–HA is usually used because of its easy production by conventional precipitation or acid–base reaction in an aqueous solution. To our knowledge, no work has been done on the development of porous Ca–HA based composite for the treatment of pollutants in gas phase, in particular the collection and tracing of metals present in incinerator fume.

The objectives of this work are threefold: (i) the formulation of Ca–HA powder composite (accumulator); (ii) the physical, chemical and thermal characterizations of the materials; (iii) and the determination of their reactivity and implantation of the collection and tracing of metal pollutants in gas phase.

The characterization of the composite has been carried out using a combination of various techniques such as SEM-EDS, XRD, BET, adsorption–desorption isotherm, ICP–AES etc). The efficiency and the reactivity of the composite showed that significant amounts of vaporized heavy metals were accumulated at the surface of the solids while a smaller amount of metals diffused in the pores of the solids without destroying the composite. In fact, the composites were obtained in severe experiment conditions (high temperature, high acidity and high humidity) and thus were chemically and thermally stable, and showed good reactivity for the collection of cadmium in gas phase.

2. Materials and methods

All chemical products used in this work were purchased from commercial suppliers (Table 1).

Table 1. Chemical products used in this work.

Name	Principal components	Purity, wt%	Supplier
Calcite	$CaCO_3$	98	Fisher Scientific
Ammonium dihydrogen orthophosphate	$NH_4H_2PO_4$	99	Fisher Scientific
Gelatine	Protein	86 (in water)	Weishardt
Bio–glass	SiO_2, Na_2O, K_2O, MgO, CaO, P_2O_5, B_2O_3	99	Medical Calcium Phosphates
Cadmium chloride	$CdCl_2$	99	Fisher Scientific

2.1. Synthesis of calcium hydroxyapatite (Ca–HA)

Ca–HA was synthesized according to the previous studies [16, 17]. Briefly, 66.7 mmol of $NH_4H_2PO_4$ and 400 mL of permuted water were introduced in a 1.2 litre (L) U-form glass reactor (i.d.: 10 cm, length: 15 cm), equipped with a vertical stirrer. Then, 100 mmol of calcite powder were gradually added in the solution of $NH_4H_2PO_4$ under stirring (400 rpm). The reaction mixture was kept at 80 °C for 24 h. During the reaction, samples withdrawn from the reactor was filtered, washed several times with permuted water on 0.45 µm filtration paper and dried overnight at 105 °C prior to all analysis. Powder product obtained after 24 h of reaction was finally sieved to eliminate particles larger than 45 µm before the formulation step.

2.2. Formulation of Ca–HA composite

This formulation step was dedicated to the transformation of Ca–HA powder into Ca–HA granulates with controlled porosity and thermal/thermo–mechanical stability. A mixture containing Ca–HA powder, bio–glass (8 wt%), gelatine (10 wt%) and water was prepared. The quantity of water was calculated to obtain a doughy mixture by minimizing water content. Gelatine was used as porous agent, which could be thermally decomposed to create new porosity by release of gas molecules. Bio–glass is used as a structural agent, which is chemically inert and enhances the cohesion of apatitic particles. The moulding was carried out with a plastic cylinder (i.d. of 10 mm, length of 20 mm). This granulate was freely dried under atmospheric conditions until the total removal of water before the calcination at 1000 °C with heating rate of 2 °C min^{-1} and 15 min of plateau time at 1000 °C. The resulting cylindrical Ca–HA based product is called thereafter accumulator.

2.3. Collection of heavy metals in gas phase

Fig. 1 illustrates the experimental apparatus used for the collection of heavy metal by accumulator at high temperature. The horizontal reactor was composed by a ceramic cylindrical tube (i.d. of 20 mm, length of 100 cm), which can be heated electrically up to 1000 °C by a furnace. The accumulator in cylindrical form (20 mm x 10 mm) was set at one extremity of the furnace where the temperature was well controlled. The reactor was heated to 650 °C which is close to the temperature of incinerator fumes and is above the melting point of $CdCl_2$ used as source of Cd [18]. After reaching this temperature, a ceramic crucible containing a quantity of approximately 110 mg (exactly weighed) of cadmium under $CdCl_2$ form was rapidly pushed at the centre of the ceramic tube. An air circulation with controlled flow rate of 1 L h^{-1} passed through the tube in order to orient the movement of the polluted

gas over the accumulator. A moderate evaporation of $CdCl_2$ is expected in these conditions. Gas from the outlet of the ceramic tube was washed twice with 5 wt% nitric acid solution. The smaller diameter of the accumulator compared to the internal diameter of the reactor facilitates the metal gas flow. Thus, an accumulation of cadmium on the surface of the accumulator was expected.

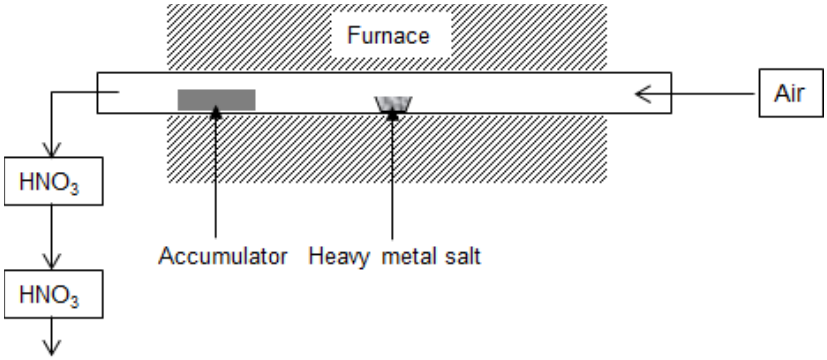

Fig. 1. Experimental setup for accumulator testing.

2.4. Analysis and characterization

Elemental analysis was carried out using ICP–AES technique (HORIBA Jobin Yvon Ultima 2). Powder sample was mineralized with mixture of concentrated nitric and hydrochloric acids before analysis. X–ray diffraction (XRD) of the solids was performed using a Phillips Panalytical X'pert Pro MPD diffractometer with a Cu Kα (1.543 Å) radiation source. Thermogravimetry (TG) was performed in a TA Instruments SDTQ600 analyzer with a heating rate of 5 °C min−1 under air flux (100 mL min−1). Infrared spectroscopy (IR) was recorded on a Shimadzu FTIR 8400S spectrometer with a direct measure of solid powders. Mercury porosimetry was performed on an Autopore III 9410 Micromeritics. Scanning electron microscopy coupled with energy dispersive X–ray spectroscopy (SEM–EDS) was measured on a Philips XL30 ESEM apparatus (FEI Company). The mechanical resistance was measured usingLRX Plus apparatus (Lloyd Instruments).

3. Results

3.1. Synthesis of Ca–HA

The use of calcium carbonate as starting reactant for calcium source has advantages related to its lower cost and availability compared to soluble calcium salt.

Fig. 2 shows an example of TG analysis of the sample withdrawn from the reactor after 30 min of synthesis. Different weight losses were observed and were already discussed in our previous study [16]. Free water was removed below 100 °C. The second weight loss with the maximum of DTG signal (DTG_{max}) at 108 °C could be attributed to the dehydration of mono-calcium phosphate monohydrate (MCPM, $Ca(H_2PO_4)_2{\cdot}H_2O$). The net DTG signal with DTG_{max} at 185 °C was attributed to the dehydration of dicalcium phosphate dihydrate (DCPD, $CaHPO_4{\cdot}2H_2O$) or brushite as the main intermediate. A small weight loss around 430 °C could be due to the dehydration of monetite ($CaHPO_4$) to form calcium pyrophosphate ($Ca_2P_2O_7$). Finally, remaining calcite decomposed in the temperature range of 610 to 730 °C.

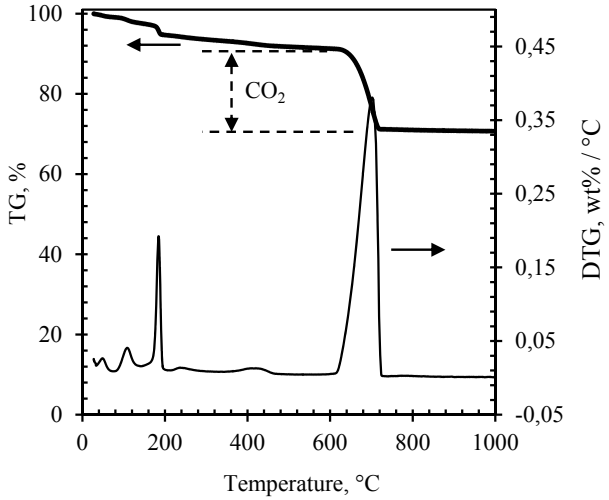

Fig. 2. Example of TG analysis of the solid powder obtained after 30 min of reaction between $CaCO_3$ and $NH_4H_2PO_4$ at 80 °C.

From TG curves, the content of calcite remained in the solid powder can be easily calculated, according to the equation of decomposition of calcite (Eq. (1)), where the weight loss corresponds to the formation of CO_2 as exaust gas.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

Fig. 3 present the evolution of the content of calcite remaining in the solid products at different reaction time of synthesis. Most of the calcite was decomposed within the first two hour of reaction, as observed by the violent release of carbonic gas. The decomposition reached up to 99.4 % after 24 h of reaction, indicated the complete decomposition of calcite particles.

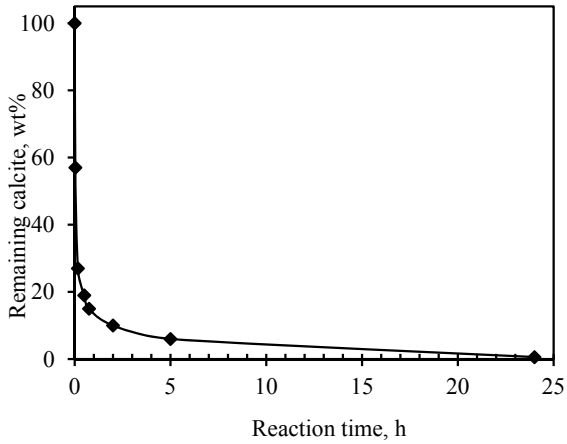

Fig. 3. Evolution of the content of remaining calcite in the solid powders obtained from the reaction of $CaCO_3$ and $NH_4H_2PO_4$ at 80 °C.

XRD pattern of the final solid powder obtained after 24 h of synthesis at 80 °C is shown in Fig. 4. As expected, there was only a very weak signal of the principal diffraction peak of calcite at 2 θ of 29.4 degrees. Ca–HA of low–crystallinity was formed as the main phase. This low–crystallinity must be explained by the moderate temperature of synthesis [15, 16].

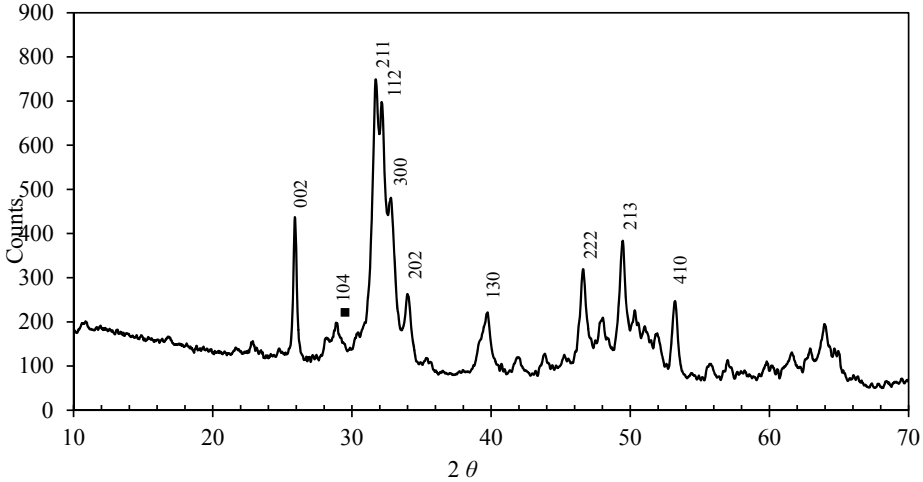

Fig. 4. XRD pattern of the solid powders obtained from the reaction of $CaCO_3$ and $NH_4H_2PO_4$ at 80 °C for 24 h; (■) calcite (JCPDS standard N° 01–086–2334); other peaks: Ca–HA (JCPDS standard N° 01–072–1243).

3.2. Characterization of accumulator

The thermal analysis (TG) of the initial Ca–HA and the dried accumulator is shown in Fig. 5. For Ca–HA (Fig. 5 (a)), a continuous weight lost in the studied temperature range was observed which was explained by the removal of lattice molecular water [19, 20]. For the dried accumulator, a removal of surface moisture was observed at the temperatures below 100 °C. Then, different weight losses in the temperature range of 114–670 °C were observed which could be all attributed to the complex decomposition of gelatine. This included generally the protein chain breakage and peptide bond rupture [21–23]. No weight loss was observed above 670 °C indicating that the calcination at 1000 °C allowed the total decomposition of gelatine in the dried accumulator.

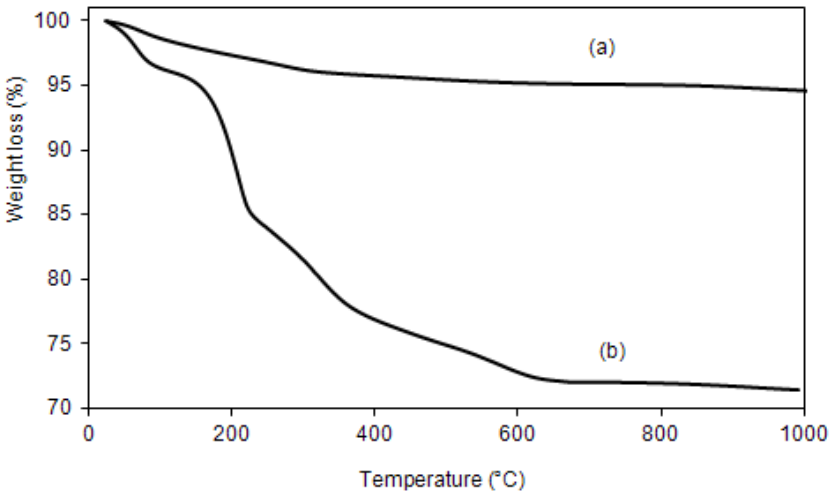

Fig. 5. TG analysis of the initial Ca–HA (a) and the dried accumulator (b) in the temperature range of 20–800 °C under air atmosphere.

SEM images of the accumulator calcined at 1000 °C for 15 min are showed in Fig. 6. In the left–hand side, Ca–HA particles of sizes varying in a large range from hundreds of nm to hundreds of µm were observed. Big particles of Ca–HA seemed to be formed by agglomeration of small particles as suggested by images at high magnifications [16].

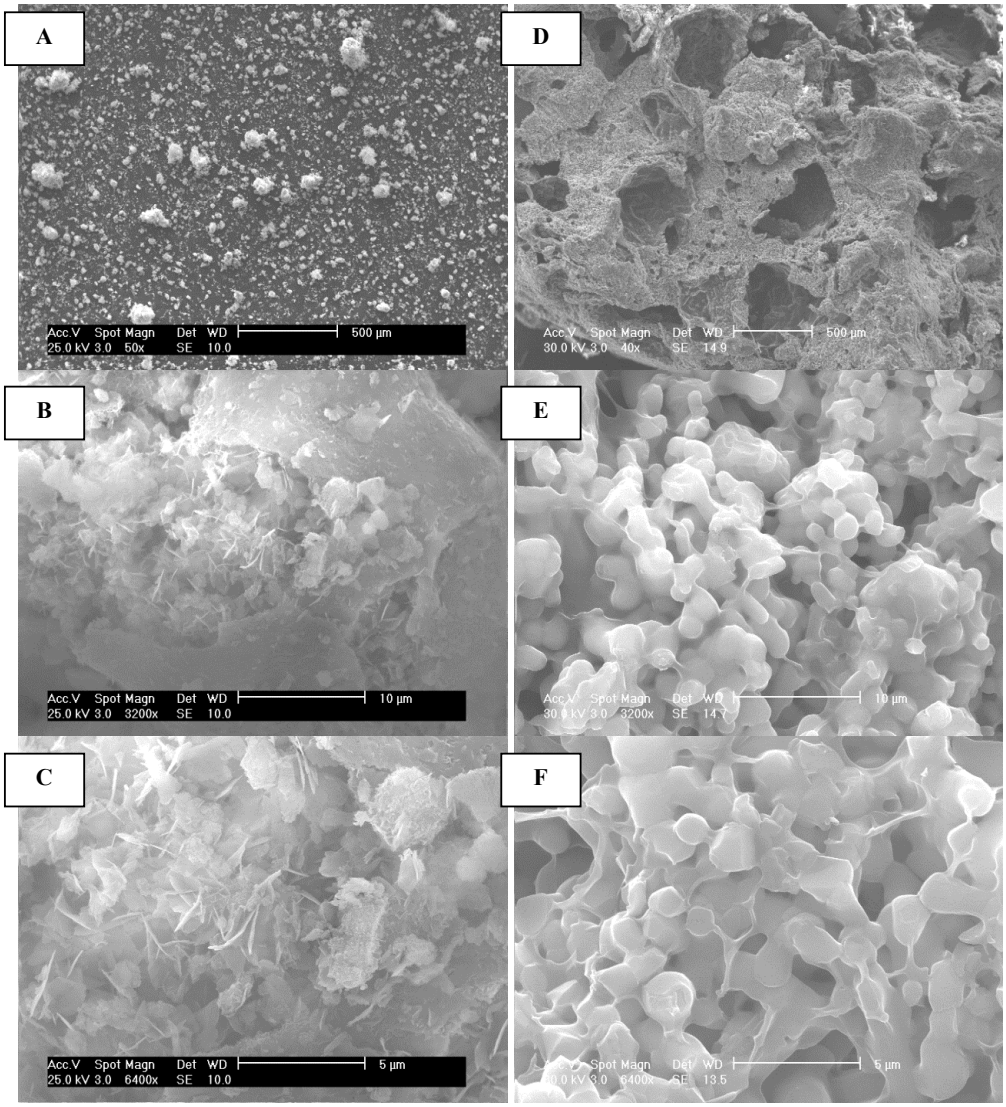

Fig. 6. SEM images of Ca–HA powder dried at 105 °C (A, B, C), and of the accumulator calcined at 1000 °C (D, E, F).

On the right–hand side, the morphology of Ca–HA particles changed completely. Thermal sintering took place with the formation of contacts between adjacent particles. In contrast to the classical thermal sintering of Ca–HA where particles lost their porosity, the accumulator was highly porous and its macropores could be easily observed at different magnifications.

In order to better evaluate the porosity of the calcined accumulator, mercury porosimetry was performed and the result is shown in Fig. 7. Pore distribution extended from about 0.1 µm up to 352 µm could be obtained. Pore sizes around 1 and 150 µm were observed, which confirmed again the observation in Fig. 6. This porosity was probably created by the release of gas molecules during the thermal decomposition of gelatine. The porosity of 62% could also be calculated for this calcined accumulator.

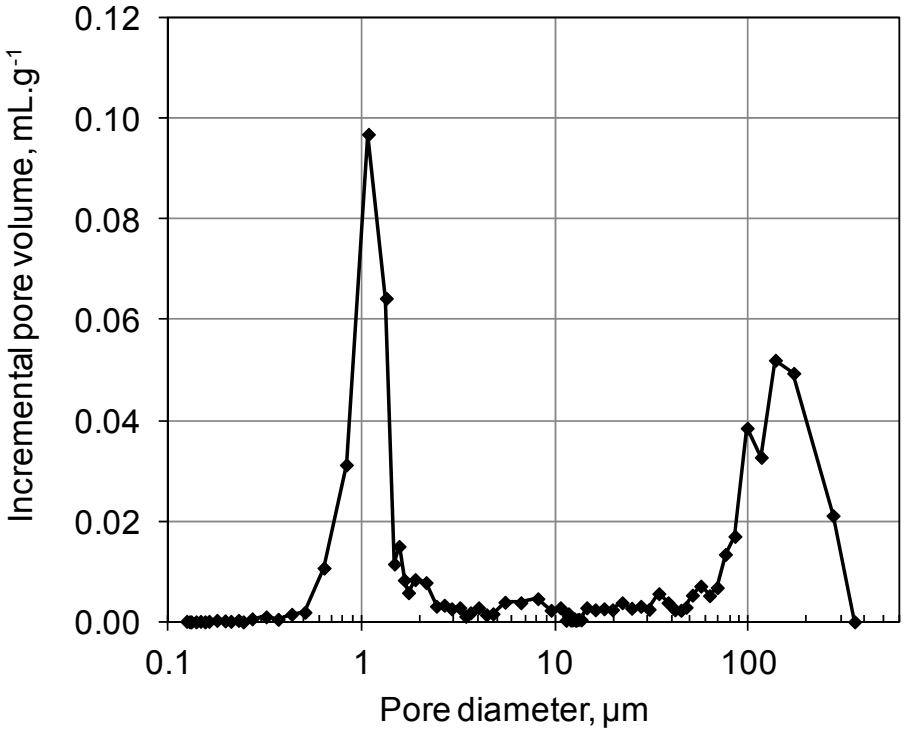

Fig. 7. Pore distribution of the accumulator calcined at 1000 °C obtained from mercury porosimetry; pore diameter is in base 10 logarithmic scale.

The mechanical resistance of the accumulator before and after calcination was also measured and the results obtained are shown in Table 2. The calcination led to the formation of porous material as illustrated above. Thus, the mechanical strength of the accumulator was dramatically reduced from 12.3 to 2.4 MPa. However, the calcined accumulator sustained the mechanical stress well enough for the application considered.

Table 2. Mechanical resistance of the accumulator before and after calcinations.

Accumulator	Height, mm	Diameter, mm	Stress (MPa)
Before calcinations	20	10	12.3
After calcination	20	10	2.4

3.3. Accumulation of heavy metals

The experiment of collection of cadmium was repeated three times in order to check the reproducibility of the procedure. After the collection, the accumulator was carefully recovered and completely mineralized before ICP–AES analysis. Fig. 8 presents the results obtained.

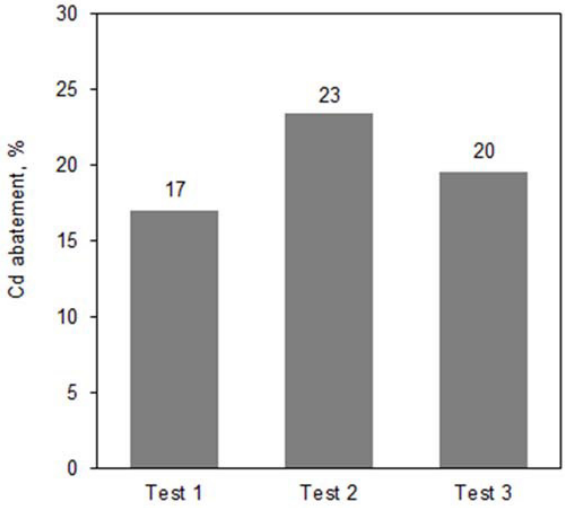

Fig. 8. Cd abatement by the accumulator during the collection test.

For the reactor set-up used (Fig. 1), the stream of polluted gas is expected to pass over the external surface of the accumulator which must not favor the contact of Cd with the surface of the whole accumulator. However, an important abatement of Cd varying in the range of 17–23% was obtained which demonstrated that the accumulator had an interesting reactivity for the collection of Cd.

In order to localize the Cd sequestrated in the matrix of the accumulator, SEM–EDS analysis was performed which allows the determination of the elemental distribution within the accumulator. Fig. 9 presents an example of SEM–EDS analysis.

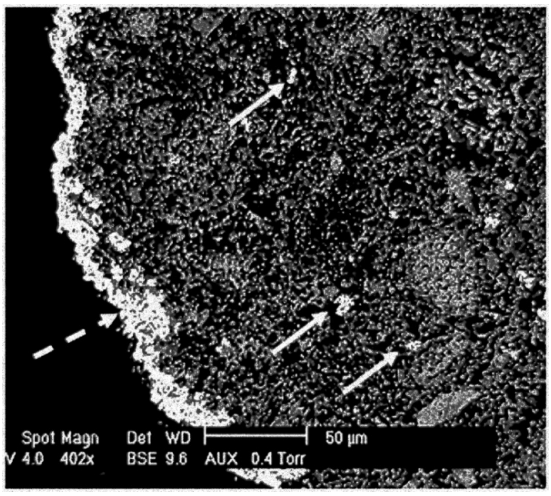

Fig. 9. Example of SEM–EDS analysis of the accumulator after the collection of Cd.

On Fig. 9, the presence of Cd is characterized by bright regions. Cd was clearly observed on the border of the accumulator (dotted arrow). In the middle of the accumulator, some agglomerates of Cd were also observed (continuous arrows). This could be explained by the diffusion and agglomeration of Cd within the pores of Ca–HA composite matrix which may be also considered. Supplementary analysis by the X–ray map of Cd confirmed again the high presence of Cd on the surface of the accumulator (results not shown here).

4. Conclusions

New sorbent materials (accumulator) based on Ca–HA matrix for the treatment of heavy metal in gas phase has been successfully developed using a simple moulding technique. The calcination at 1000 °C allowed the thermal stabilisation of the

accumulator. Thus it can be used in high temperature processes avoiding the classical thermal sintering and loss of reactivity of Ca–HA based materials. The use of gelatine and bio–glass as porous and structural agents allowed the accumulator to have satisfactory porosity and mechanical stability.

In contact with a gas stream containing Cd as model heavy metal at high temperature (650 °C), the prepared accumulator showed an interesting reactivity for the collection of Cd. The Cd abatement reached around 20% in the experimental conditions used. The accumulation of Cd was especially observed at the surface of the accumulator.

Acknowledgements

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