

Investigation of the sorption of mercury vapour from exhaust gas by an Ag-X zeolite

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ABSTRACT: The removal of gaseous mercury from flue gases from coal-fired power plants is currently an environmental challenge under investigation. Therefore, the main aim of this paper was to evaluate the suitability of faujasite group zeolites (Na-X) to adsorb mercury compounds. Previous, initial tests showed negligible Hg⁰ uptake by Na-X zeolite, but silver impregnation improved adsorption markedly. Therefore, the testing of mercury adsorption from flue gases into Ag⁺-impregnated Na-X synthetic zeolite (Ag-X zeolite) derived from coal fly ash was carried out. This material was characterized by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy, X-ray fluorescence and nitrogen adsorption/desorption before being evaluated for mercury removal from exhaust gas. After preliminary mercury adsorption tests (fixed bed) under a nitrogen atmosphere, the adsorbent was examined with a simulated flue gas composition under various conditions, i.e. weight of zeolite, temperature of experiment and zeolite in powder and granulated forms. The removal of mercury was shown to depend on the sorbent texture (powder or granulate), exhaust gas flow rate and contact time, as well as the temperature of the experiment. The Ag-X zeolite tested reduced the level of mercury in the flue gas and, depending on the experimental conditions, long-time mercury breakthrough ranges from 15 to 40% were obtained. The best results for mercury capture were obtained for granulated material.

KEYWORDS: mercury uptake, flue gas, Na-X zeolite, fly ash, Ag impregnation.

Mercury (Hg) is one of the most important environmental contaminants and has received special attention because of its high volatility together with high toxicity and bioaccumulation ability. In the atmosphere mercury derives from both human (as anthropogenic) and natural (i.e. volcanic activity) sources, with anthropogenic emissions far exceeding those from natural

sources. The amount of mercury in Earth's biosphere is increasing gradually (Pirrone *et al.*, 2010). The World Health Organization (WHO) and the European Union (EU) have set strict limits on mercury concentrations due to its impacts on both drinking water and the environment (WHO, 2011; revised Directive, 98/83/EC; Tomaszewska, 2011). The current EU recommendations and national standards set the maximum mercury concentration in drinking water and in water discharged into surface watercourses or to the ground at 0.001 mg/dm³. Coal combustion is considered to be the main source of mercury emissions to the atmosphere

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accounting for 60%, or even more, of the total mercury emissions (Pacyna *et al.*, 2006) to low concentrations of mercury in both environmental samples and coal, analyses are normally conducted at the ppm or even at ppb level or between several ng/m^3 in the air and $\mu\text{g/m}^3$ in the process gases (Macherzyński *et al.*, 2014). Recent studies have been focused on the removal of mercury from flue gases, as this is one of the main targets of the Minamata Convention, 9–11 October 2013 (Minamata Convention, 2013). Mercury vapour in power plant flue gases contains both elemental (Hg^0) and oxidized mercury, mainly as HgCl_2 , but in some cases HgO forms (Gerasimov, 2005). Elemental mercury is predominant at higher temperatures and in exhaust gases that contain only small amounts of HCl (Hall *et al.*, 1991; Morency *et al.*, 2000). Generally, HgCl_2 can be removed from the flue gases more efficiently than Hg^0 by adsorption on fly ash, wet scrubbing, dry injection or on a fixed bed of an activated carbon. Removal of Hg^0 is more difficult, because it is practically insoluble in water, but it can be removed to a certain extent with treated activated carbon, which is expensive (Morency *et al.*, 2000).

Mercury chemistry in flue gas is complex, because mercury interacts with other acidic gases (e.g., HCl, SOx) as well as with unburned carbon in the ash. The composition of the coals that are burned in power plant boilers varies, resulting to a range of compositions of flue gas. Thus, there is not a technology of “one size fits all” for mercury-emissions control and solutions must be tailored to a given boiler (Macherzyński *et al.*, 2011). Hence, there is a need to develop new, efficient and economical methods for capturing mercury from exhaust gases, especially from coal-fired power plants (Feeley *et al.*, 2003).

Previous studies have shown that the most effective adsorbents of Hg from flue gas are activated carbons. However, the mercury capacity, cost and availability of the carbon sorbent play an important role in the feasibility of the proposed carbon injection technology (Maroto-Valer *et al.*, 2005). Therefore, research is underway on the development of new types of high-selectivity sorbents for removal of mercury from flue gas, in order to reduce the cost of uptake of the technology.

An additional problem related to the use of activated carbon as a mercury sorbent in coal-fired utility boilers, is the deterioration of the quality of the fly ash that has a potential commercial value in

cement making and for the plastics industry. Limits of carbon content in the fly ash are imposed to prevent degradation of the final products. For example, the excess carbon in the fly ash used in cement manufacture actually absorbs the air, which produces a less durable material (Morency *et al.*, 2000).

Other potential sorbents for mercury-pollutant uptake might be synthetic zeolites, which usually have natural analogues, derived from the fly ash. Fly ash can be converted into different zeolite structures, including, among others analcime (Adamczyk & Białecka 2005; Wang *et al.*, 2003; Querol *et al.*, 1997), chabazite (Wang *et al.*, 2003), cancrinite, gmelinite, Na-P1 (Holloman *et al.*, 1999; Wang *et al.*, 2003; Adamczyk & Białecka, 2005; Inada *et al.*, 2005; Moutsatsou *et al.*, 2006; Querol *et al.*, 2007), ZSM-5 (Mohamed *et al.*, 2008), ZSM-28 (Wang *et al.*, 1998), Na-X (Shigemoto *et al.*, 1993; Querol *et al.*, 1997; Tanaka *et al.*, 2002; Franus *et al.*, 2014; Wdowin *et al.*, 2014), Na-Y (Ojha *et al.*, 2004), phillipsite (Querol *et al.*, 1997) and sodalite (Musyoka *et al.*, 2011). The use of zeolitic materials based on waste (fly ash) seems to be promising and economically justified (Morency *et al.*, 2000) and zeolites derived from fly ash are commonly used in the removal of environmental pollutants such as ammonium ions (Franus & Wdowin, 2010; Liu *et al.*, 2012) or heavy metals from natural waters and wastewater (Wang *et al.*, 2009; Koukouzas *et al.*, 2010; Merrikhpour & Jalali, 2013); radionuclides from mine waters (Chałupnik *et al.*, 2013, Zhu *et al.*, 2013); benzene, toluene and xylenes (BTX) from aqueous solutions (Szala *et al.*, 2015) and separation/adsorption of gases such as CO_2 (Walton *et al.*, 2006; Wdowin *et al.*, 2012), SO_2 (Yi *et al.*, 2012) or mercury (Wdowin *et al.*, 2014b).

The present paper examines mercury uptake from exhaust gases onto silver-impregnated Na-X zeolite, which has the zeolite, faujasite, as a natural analogue. The zeolite tested, was loaded with silver (Ag), as previous work has indicated that Ag may improve mercury removal rates (Barrer & Whatman, 1967; Herron & Corbin, 1995) and that such materials may compete even with activated carbon loaded with bromine (AC/Br) (Liu *et al.*, 2010; Wdowin *et al.*, 2014b).

The main aim of this work was to examine the removal of mercury gas from flue gases onto silver-impregnated Na-X zeolite (Ag-X). Preliminary results carried out by Wdowin *et al.* (2014b) have

shown that among other zeolites, Ag-X provided very promising results in the removal of elemental mercury from flue gases. Therefore, this paper is the next step in the evaluation of the suitability of this zeolite for the removal of mercury from flue gas.

MATERIALS AND METHODS

Preparation of the Ag-X zeolite from fly ash

Synthetic zeolite type X (faujasite group, second building unit - D6R), was obtained by hydrothermal synthesis from fly ash (from hard coal combustion in Koźienice Power Plant, Poland) with aqueous NaOH solution (Franus, 2012). Fly ash (20 g) was heated with strong NaOH solution (0.5 dm^{-3} , 3 mol dm^{-3}) for 24 h at 75°C . The X-ray diffraction (XRD) analysis of the washed and dried solid showed 63 wt.% Na-X zeolite, with the remainder consisting of quartz and mullite. The impure Na-X zeolite (100 g) was ion exchanged with silver by shaking (speed 180 rpm) in the dark for 24 h at room temperature with silver nitrate solution (0.5 dm^{-3} , 0.5 mol dm^{-3}) The washed sample was air-dried in the dark and the Ag-loaded zeolite was characterized as follows.

Chemical, mineralogical and textural analysis

The chemical composition of the Ag-X zeolite ions was determined by X-ray fluorescence (XRF) analysis with a Philips PW 1404 XRF spectrometer equipped with a dual Cr-Au anode X-ray tube with a maximum power of 3 kW. The mineralogical composition of the Ag-loaded zeolite was determined by powder XRD using a Philips X'pert APD diffractometer and the data were processed with Philips X'Pert and ClayLab ver. 1.0 software. The mineral phases were identified based on the PCPDFWIN ver. 1.30 database formalized by JCPDS-ICDD. The morphology and chemical composition of the main mineral components of the zeolite were determined by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) (FEI Qanta 250 FEG SEM).

Textural properties of the zeolite were examined with an ASAP 2020 Analyzer (Micromeritics). The BET specific surface area and pore size and radius were determined from the shape of the vapour nitrogen adsorption/desorption isotherm at -196.15°C . Prior to analysis, the samples were

degassed under strictly controlled conditions of high temperature (250°C , for 24 h) and reduced pressure (10^{-3} hPa). The specific surface area was determined according to the BET multi-layer adsorption theory at p/p_0 ratios between 0.06 and 0.3. The pore volume (V_p) was determined from the volume of adsorbed nitrogen at pressure $p/p_0 = 0.98$. Pore diameters (D_p) were calculated according to the formula: $D_p = 4V_p/S_{\text{BET}}$, where S_{BET} is the BET surface area. The distribution of pore volume (R_p) was calculated using a general isotherm equation based on the BJH adsorption model at p/p_0 0.01–0.99 (Barrett *et al.*, 1951), which calculates the percentage of micro-, meso- and macropore volumes.

An Automated Mercury Analyzer MA-3000 (Nippon Instruments Corporation) was used to determine the total mercury in the zeolites (50–60 mg samples). The method was tested successfully with standard or certified reference materials: 2692c and 2693 (NIST, USA), 502-680 (LECO Corporation, USA) and BCR-038 (LGS Standards, UK).

Mercury removal from exhaust gases

The sorption properties of the materials were investigated with a dedicated-designed system (AGH-UST), which enables contact of sorbents with real flue gases enriched in elemental mercury vapour. The system consists of:

- a hard coal combusting furnace (900°C),
- an external elemental mercury source with a load ranging from 10 to $20 \mu\text{gHg/h}$. Preliminary experiments in hot air used $3 \mu\text{gHg/h}$,
- a heated coal fly ash filter,
- a thermostatic oven with glass vessels equipped with sorbent cells (traps); a reference vessel (C_{HgRef}) with empty traps was also used to determine mercury concentration in the bypass gases,
- a heated flue gas and mercury gas lines.

Finally, a mercury gas analyser EMP-2 (Nippon Instruments Corp.) equipped with cooled scrubbers containing 10% KOH was used for on-line determination of elemental mercury concentration in the outgoing gases. Gas transfers were performed using Teflon tubes. Test temperatures were 110 and 150°C , as in most of the experiments the gas flow was $85 \text{ dm}^3/\text{h}$. Further comprehensive study on the system is continuing. The furnace was adapted for

TABLE 1. Chemical composition and technical parameters of the hard-coal loads used in the experiments.

Sample	Hg _t (ppb)	C _t (%)	H _t (%)	S _t (%)	Cl _t (mg/kg)	Ash (%)	Volatile matter
Hard coal	31	58.6	4.3%	1.7	700	15.4	30%

combustion of pulverized coal (coal loading ~6 g/h). The same coal is used in pulverized-coal boiler power plants (Table 1).

Two types of tests were carried out in this work. The first was performed to confirm the efficiency of Ag-X zeolite towards elemental mercury removal from the hot air stream. Then, long-term experiments of Hg uptake by zeolites were carried out using three systems:

1.5 g of powdered zeolite placed between glass wool at 150°C.

3 g of powdered zeolite placed between glass wool at 150°C.

3 g of granulated zeolite placed in the bed at 110°C.

Before each experiment, zeolite samples were dried at 160°C to constant weight; 10–12 wt.% of water was removed from the zeolite in this process. Afterwards, the zeolites were placed directly into the sorbent traps.

The composition of exhaust gases was controlled during the tests. The furnace works under forced suction of exhaust gases generated by the mercury analyser and an additional pump. Hence, the gas concentrations were determined by the established gas flow. At a flow rate of 85 dm³/h, the approximate composition of the exhaust gases for an oxygen concentration of 4–8% was: CO₂ =

11–17%, CO = 20–50 ppm, with very large temporary fluctuations, NO = 70–100 ppm, SO₂ = 650–1000 ppm, also with temporary high growths. The coefficient λ was 1.6–1.7 for 85 dm³/h and 1.2–1.3 for 60 dm³/h (standard flow through a gas analyser). The flue gas was passed through a heated filter where the finest fly ash was collected. After mixing with an additional elemental mercury stream the gas was transferred through a bed of sorbent placed in a trap, which was part of a glass vessel heated inside the thermostatic oven. Glass wool was used to immobilize powdered zeolites as granulated zeolites created a stationary bed at the flow rate of 85 dm³/h. The long-term experiments were performed for at least 2 h.

RESULTS AND DISCUSSION

XRD and SEM analysis

The presence of the Ag-X phase, which appeared to be identical to Na-X (except for the peak at 6.25 Å) (Fig. 1), was identified by XRD from the characteristic diffraction maxima at 14.47, 8.85, 7.54, 6.25, 5.73, 4.81, 4.42, 3.81 and 3.94 Å. In addition to zeolite-X, minor amounts of mullite, quartz and carbonates were also detected.

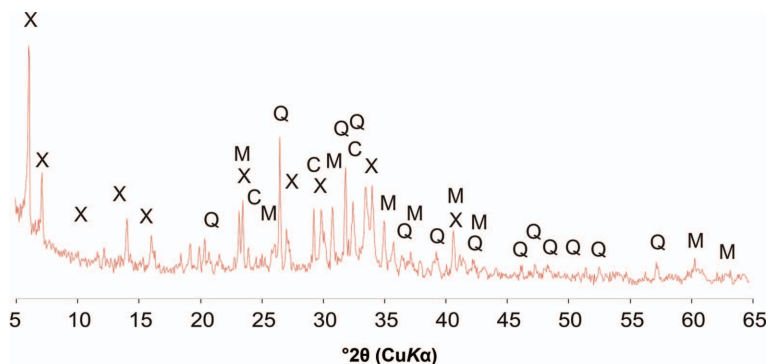


FIG. 1. XRD pattern of the zeolite prepared; X = Ag-X zeolite, Q = quartz, M = mullite, C = carbonates.

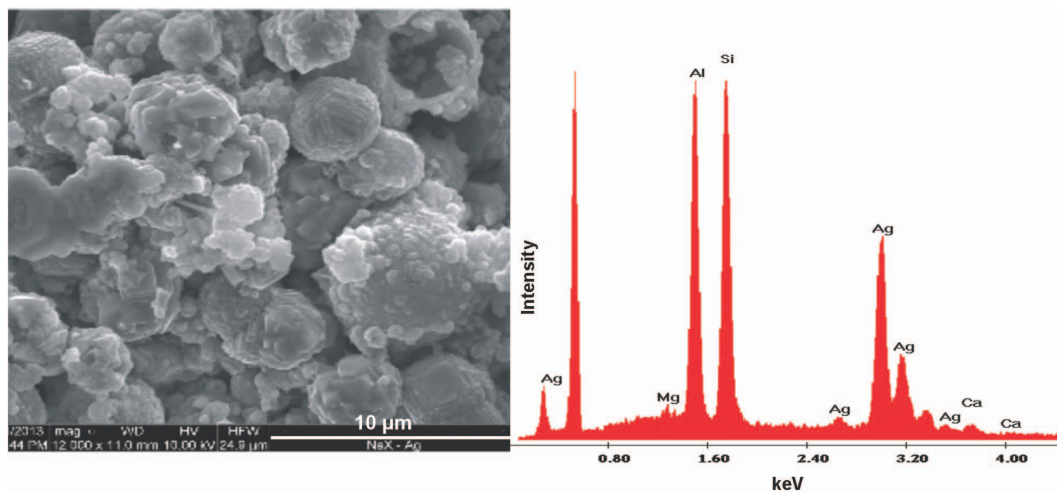


FIG. 2. SEM image and EDS analysis of zeolite Ag-X.

Analysis by SEM-EDS (Fig. 2) showed that the Na-X zeolite and Ag-X zeolite crystals appear to have cubic and octahedral morphologies. Ag was not present in separate crystals on the zeolite surface, suggesting that the Ag occurs in extra-framework sites as a result of ion exchange of Ag^+ for Na^+ .

Chemical analysis

The chemical composition (wt.%) of the initial zeolite bulk material (Na-X) was: SiO_2 : 40.20, TiO_2 : 1.61, Al_2O_3 : 28.20, Fe_2O_3 : 8.31, MnO : 0.17, MgO : 2.98, CaO : 10.40, Na_2O : 6.22, K_2O : 0.64, P_2O_5 : 0.40, SO_3 : 0.18, NiO : 0.03, CuO : 0.03, ZnO : 0.04, SrO : 0.25, ZrO_2 : 0.04, Nb_2O_5 : 0.01 and PbO : 0.02. The chemical composition of the Ag-X zeolite before the Hg-uptake tests was as follows (wt.%): SiO_2 : 22.9, TiO_2 : 2.49, Al_2O_3 : 14.5, Fe_2O_3 : 13.7, MnO : 0.243, MgO : 0.768, CaO : 7.89, Na_2O : 0.0175, K_2O : 0.343, P_2O_5 : 0.175, SO_3 : 0.0724, Cr_2O_3 : 0.113, NiO : 0.0582, CuO : 0.0592, ZnO : 0.0897, SrO : 0.161, ZrO_2 : 0.0158, Nb_2O_5 : 0.0126, Ag_2O : 36.4 and PbO : 0.0314. Although the zeolite contains abundant Fe, iron-bearing minerals were not detected by XRD analysis. This is due to the fact that Fe is present in amorphous phases as indicated by a high background to the XRD pattern.

The chemical analysis of the zeolite-X before and after Ag treatment shows that essentially all of the Na^+ had been replaced by Ag^+ . The main chemical elements in the Ag-X zeolite are Ag^+ , Si^{4+} and Al^{3+} and to a lesser degree Ca^{2+} and Fe^{3+} .

Textural characteristics

The Ag-X zeolite has a porous structure consisting of 37% micropores, 49% mesopores and 14% macropores. The pore-size distribution analysis (Fig. 3) indicates that the predominant pore diameters are 2–7 nm. The specific surface area of the tested zeolite is $178 \text{ m}^2/\text{g}$. The adsorption isotherms showed a characteristic hysteresis loop, which is associated with capillary condensation in mesopores (Fig. 4). However, the shape of the hysteresis loop indicates II/III type isotherms according to the IUPAC classification or E type isotherms according to the de Boer classification (1958) indicating the presence of “ink bottle” shaped and spherical-shaped pores.

Mercury removal from exhaust gases

The efficiency of Ag-X zeolite in the removal of elemental mercury from the hot air stream is depicted in Fig. 5. Introduction of two traps containing Ag-X zeolite ($2 \times 2 \text{ g}$) in the stream of hot air rich in Hg^0 vapours showed more than 98% removal of the Hg^0 . The longer time to stabilization of the mercury concentration is related to the dead volume and the “memory” of the system, through which the reference stream of $130 \mu\text{g Hg}^0/\text{Nm}^3$ had been passed.

Subsequently, a series of tests of Hg uptake from flue gases was performed in order to establish standard conditions for testing of the zeolite materials with simultaneous estimation of the

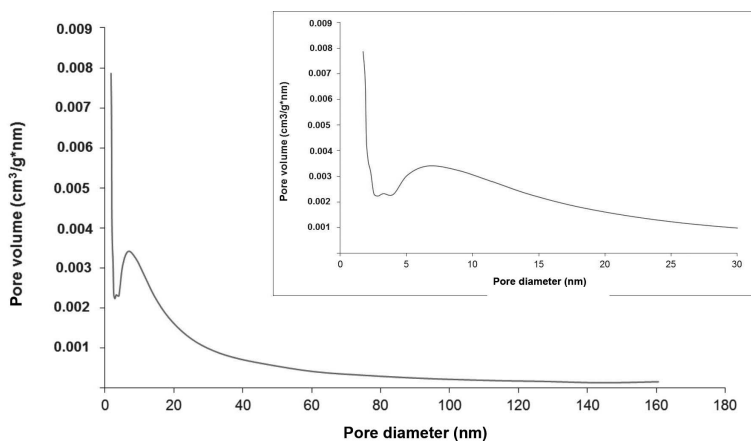


FIG. 3. Pore-size distribution of the prepared Ag-X zeolite.

amount of mercury passing through the sorbent without being removed by the zeolite. The results of these long-term experiments are summarized in Table 2. The ratio between mercury concentration after a sorbent trap and after a reference cell ($C_{\text{Hg}}/C_{\text{HgRef}}$) was used as a mercury capture indicator.

The total mercury concentration in Ag-X zeolite is 159 ppb (SD = 0.7%) and is attributed to the origin of this material, which was synthesized from fly ash. This mercury was not released at the beginning of each experiment when pure hot air flowed through the bed. Introduction of Hg^0 into the stream of clean hot air caused the appearance of Hg and a small increase in the $C_{\text{Hg}}/C_{\text{HgRef}}$ rate was obtained. The maximum value of the ratio (6.5%) was observed for 1.5 g of sorbent and a relatively

large Hg loading, 19.5 $\mu\text{g}/\text{h}$. In other cases the ratio did not exceed 3%. The effects of introducing exhaust gases to the stream was noticeable from the onset of the experiments and caused a significant growth of the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio in the beds tested. In powders the increase of the ratio was rapid and reached a plateau after several minutes, whereas in the granular form the increase of the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio was relatively slow and plateaued at 13.5% after 30 min. The mean values of the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio calculated after 2 h shows the advantage of using the granular form over the powder form. The granular form was tested at lower temperature, which could be responsible for the observed increase in physical sorption. Comparison between experiments using different amounts of the powders at different loadings of Hg yielded unexpected

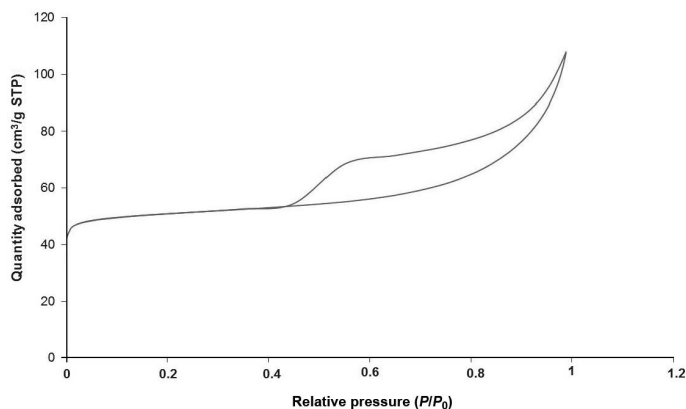


FIG. 4. Nitrogen adsorption/desorption isotherm of zeolite Ag-X.

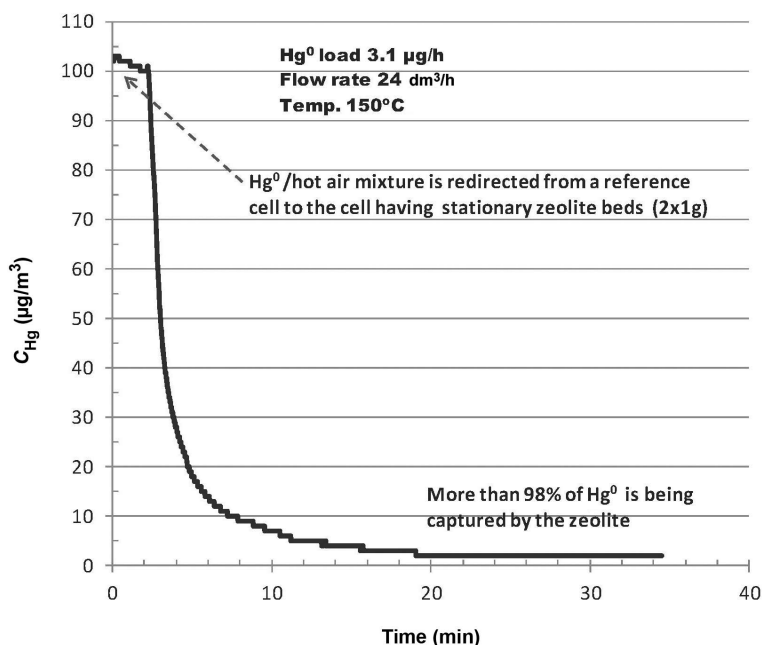


Fig. 5. Performance of the Ag-X zeolite in hot Hg⁰ vapour/air mixtures.

results. Relatively high breakthrough values using 3 g of powder samples may indicate that the material was not effective throughout its whole volume and only contact with exhaust gases was occurring within micro-tunnels made by the gas. The 3 g bed of powder was twice the thickness of the granular bed and yielded higher flow resistance, which caused the micro-tunnels to run in parallel.

Figure 6 represents a long-term mercury removal experiment using the granulated bed (3 g Ag-X). The curve of residual mercury not removed was included (solid line), indicating that in a 2 h

experiment up to 87% of the total mercury was retained by the granular zeolite bed. In addition, on switching off the furnace (twice) the amount of mercury passing through the sorbent without being captured, decreased immediately. The influence of exhaust gases on the value of the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio is unambiguous in all the studied cases and the influence is definitely smaller for the granular form. Gases present in the exhaust fumes (predominantly SO₂ and CO₂) may either be blocking active sites in the Ag-X zeolite or may be competing with Hg (HCl, HF and SO_x may react rapidly with Ag),

TABLE 2. Performance of Ag-X zeolite during retention of Hg.

	Sorbent bed	Hg load (µg/h)	Temp. (°C)	$C_{\text{Hg}}/C_{\text{HgRef}}$ (%) in a hot Hg ⁰ vapour/air mixture	$C_{\text{Hg}}/C_{\text{HgRef}}$ (%) increase Hg ⁰ in a flue gas until stabilization	Mean Hg $C_{\text{Hg}}/C_{\text{HgRef}}$ in a long-term experiment (2 h)
1	Ag-X powder 1.5 g	19.5	150	up to 6.5% in 20 min – increasing	14% in 5 min	31.0%
2	Ag-X powder 3 g	11.3	150	up to 1.7% in 33 min – stable	31.5% in 3 min	31.5%
3	Ag-X granulate 3 g	10.1	110	up to 3% in 13 min – increasing	13.5% in 32 min	15.5%

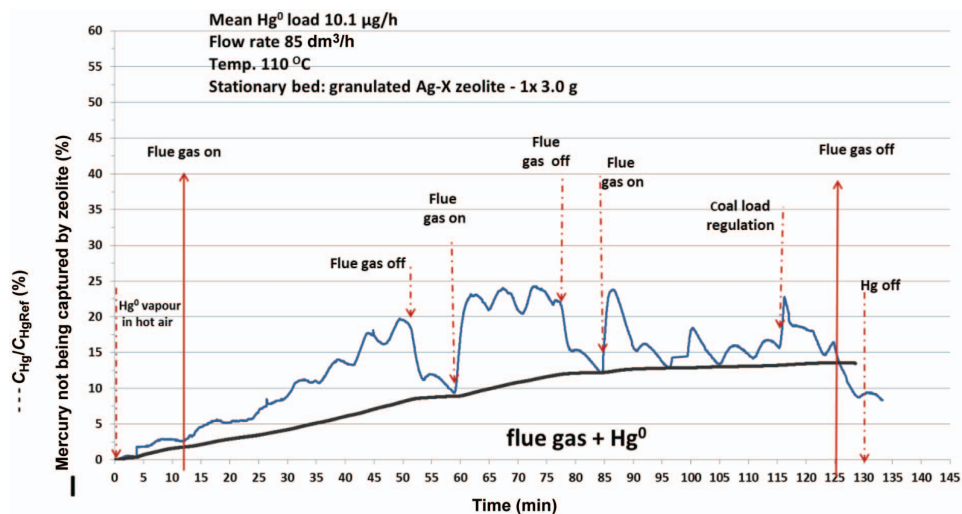


FIG. 6. $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio (dashed line) and mercury passing through granular Ag-X zeolite sorbent without being captured (solid line) in a long-term experiment.

lowering the affinity of the zeolite for Hg. Moreover, such gaseous species can cause significant changes in speciation of mercury (Grzywacz *et al.*, 2014). Considerable increase of the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio was observed when the furnace was turned off temporarily (coal was not loaded). Some of the negative effects mentioned before are irreversible, because after turning the furnace off, the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio did not regain its low initial values.

In summary, the simple Ag-Hg amalgamation, multilayer Hg sorption and redox sorption mechanisms on Ag-X zeolites, suggested previously for the dry N_2 -Hg gas system (Barrer & Whiteman 1961; Abrams & Corbin 1995; Wdowin *et al.*, 2014), are not the prevalent Hg uptake mechanisms in the studied system. The presence of SO_x and H_2O in flue gas inhibits Hg^0 removal by zeolites (Fan *et al.*, 2012), whereas O_2 in the flue gas has a positive effect on Hg^0 removal. Similar phenomena might occur in the Ag-X zeolite; thus additional experiments should be carried out after desulfurization and CO_2 capture treatment of the exhaust gases. The lower uptake of mercury in flue gases by zeolites observed in other studies, suggests that physisorption might not be enough to capture highly volatile mercury vapour (*c.f.* Jurng *et al.*, 2002). In this study a range of complex reactions both in the flowing exhaust gas and subsequent sorption or chemical reactions on the interface between the gas phase and the Ag-X zeolites, need

to be considered. Additional structural studies of zeolite samples taken after different time periods, followed by speciation analysis of the mercury and direct studies of the composition of the exhaust gases might provide information explaining the amount of mercury captured by the zeolite beds studied.

CONCLUSIONS

A zeolite Na-X synthesized from fly ash was converted to Ag-X through ion exchange after Ag treatment. The Ag-X zeolite has extensive micro- and meso-porosity and a large specific surface area ($178 \text{ m}^2/\text{g}$) that allows the classification of such materials as sorbents. The sorption of Hg by Ag-X in the presence of other gases (i.e. SO_x , NO_x , CO_2 , HCl, HF and CO) was lower compared to previous studies that used only pure Hg^0 . The long-time mercury breakthrough ranges were better for granulated materials (15%) than for powder (40%). With the powders the increase in the $C_{\text{Hg}}/C_{\text{HgRef}}$ ratio was rapid and reached a plateau after several minutes, whereas in the granular form the increase in the ratio was relatively slow and a plateau was observed at 13.5% after 30 min.

The experiments involve mixtures of flue-gas reactions that might affect the speciation of the mercury, which may explain the lower adsorption of mercury compounds by this material. Future work would include a speciation study of mercury

compounds occurring in the flue-gas mixture used for the tests, before and after contact with the sorbent bed, as well as X-ray photoelectron spectroscopic analysis of the mercury species formed on the Ag-X zeolite. Research into Ag-X zeolites derived from fly ash as potential materials for Hg removal are justified because they may contribute to solving the problems of amelioration of a toxic emission and utilization of a waste material in the preparation of low cost, basic adsorbents.

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