



Experimental study of mercury removal from exhaust gases



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HIGHLIGHTS

- Na-P1 and Na-X were derived from coal fly ash and after silver impregnation tested for Hg uptake.
- Na-X/Ag achieved higher breakthrough capacities than commercially available activated carbon.
- Material is thermally stable and can be regenerated.

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ABSTRACT

An initial study has been made of the use of synthetic zeolites for mercury capture from exhaust gases. Synthetic zeolites (Na-X and Na-P1), and for comparison a natural zeolite (clinoptilolite) and activated carbon with bromine (AC/Br) were tested for mercury uptake from a gaseous stream. The materials were subjected to mercury adsorption tests and their thermal stability was evaluated. The untreated synthetic zeolites had negligible mercury uptake, but after impregnation with silver, the adsorption of mercury was markedly improved. The synthetic zeolite Na-X impregnated with silver adsorbed significantly more mercury before breakthrough than the activated carbon impregnated with bromine, indicating the potential of zeolite derived from coal fly ash as a new sorbent for capture of mercury from flue gases.

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1. Introduction

Removal of mercury (Hg) from exhaust gases is becoming an increasingly important issue, especially in the context of a new United Nation's convention on reduction of mercury emissions and exposure on a global scale. Although mercury is released into the atmosphere from both natural and *anthropogenic* sources, fossil fuel burning (mainly coal combustion) is the second largest contributor [1]. During coal burning, mercury is released in its elemental form (Hg⁰). However due to various thermo-chemical reactions occurring in the flue gas, some of it can be oxidised (Hg²⁺) and/or be bonded to the particulate matter (Hg^p) [2]. Oxidised (which is water soluble) and particle-bonded mercury can be captured by conventional air pollution control devices (APCD) such as fabric filters, cold and hot electrostatic precipitators (ESP), wet and dry flue

gas desulphurization (FGD), and selective catalytic reduction (SCR). However, Hg⁰ (insoluble in water) is very difficult to capture by such systems [3]. As proportions of the emitted elemental, oxidised and particulate-bonded mercury vary within different coal plants, the performance of APCD as regards total capture of the mercury emitted also varies. To remove 100% of Hg, the available control technologies must be combined with sorbents, which are able to oxidise and capture elemental mercury [4].

Many materials have been considered and studied for their potential to remove mercury from flue gases. These include activated carbons (impregnated with iodine, bromine and sulphur) and carbon-based materials such as fly ash, metals such as copper, lead, gold, silver) and their oxides and sulphides, calcium species (lime) and zeolites [5–12]. However most of these sorbents are less effective at higher temperature, have low capacities, cannot be regenerated and are easily deactivated by flue gas components such as sulphur oxides (SOx) [13,14], which means that the search for the ideal mercury sorbent is far from over [15]. Synthetic zeolites derived from coal fly ash have been suggested to be potentially economically feasible and environmentally friendly mercury sorbents, and can be considered to be worthy of further investigation.

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It has been reported that the production of coal fly ash (CFA) is approximately 750 million tonnes per year, from which, on average, only 25% was utilised, the rest was disposed of as waste [16]. Although, the composition of CFA is complex and varies greatly [17], its utilisation has received a great deal of attention. Currently, fly ash is predominantly used as: a substitute material (e.g. as clinker) in the construction industry; a geotechnical material (e.g. asphalt filler, pavement base course) and soil stabiliser [16]. However, more interesting is its future possible application, as an adsorbent for various pollutants (including radioactive elements and heavy metals). It has been demonstrated that, manufacture of synthetic zeolites from CFA is a relatively straightforward procedure [18–22] and such materials have been found to be effective in the removal of various pollutants from different environments (water, soils, flue gases) [15,23–29]. A comparison with natural zeolites shows that synthetic zeolites are better for the removal of mercury compounds, due to the consistent size of the channels and chambers, in contrast to the microstructure of natural zeolites sizes which can be variable and often associated with a number of lattice defects [30]. Moreover, successful regeneration of these materials has been reported [15,31]. Hence, the research into zeolitic materials and their potential for Hg removal can be justified with the aim of solving the problems of both utilisation of a waste material and removal of a toxic emission.

The main aim of the work described in this paper was to carry out a preliminary examination of the performance, suitability and potential of synthetic zeolites derived from fly ash to remove elemental mercury from flue gases. To improve their Hg adsorption efficiencies, the zeolitic materials were thermally activated and also loaded with silver (Ag), as evidence from previous work indicated that Ag may improve mercury removal rates [15]. In addition, for comparison natural zeolite–clinoptilolite (thermally activated and Ag impregnated) and activated carbon loaded with bromine (AC/Br) were also tested for mercury uptake.

2. Experimental

2.1. Sorbent preparation

The synthetic zeolites have been synthesized in the hydrothermal reactions of fly ash, from hard coal combustion in Koziencie (Na-X) and Rybnik (Na-P1) Power Plants, Poland, with sodium hydroxide (NaOH). The two types of zeolite Na-X, Na-P1 were prepared using the following conditions:

- Na-X: 20 g of fly ash was mixed with 0.5 dm³ of NaOH at a concentration of 3 mol * dm⁻³ for 24 h at 75 °C.
- Na-P1: 20 g of fly ash was mixed with 0.5 dm³ of NaOH at a concentration of 3 mol * dm⁻³ for 24 h at 95 °C.

The preparation of the zeolites is on the quarter technical scale, and its repeatability has been confirmed in numerous experiments.

Prior to the Hg adsorption experiments, the samples were dried at 350 °C for 6 h to remove moisture. In order to improve the zeolite's adsorption capacity towards Hg, the synthetic zeolites were loaded with Ag using the ion exchange method. In addition, Na-P1 was also activated by melting with AgNO₃. For comparison, a natural zeolite a clinoptilolite, Sokyrnytsya deposit, Ukraine was examined under the same experimental conditions as the synthetic materials.

2.2. Morphology and textural characterisation

The mineral composition of the synthetic zeolites was determined by means of powder X-ray diffraction (XRD) using a Philips

X'pert APD diffractometer with the data being processed by Philips X'Pert and ClayLab ver. 1.0 software. Mineral phases were identified based on the PCPDFWIN ver. 1.30 database formalized by JCPDS-ICDD. The presence of zeolite phases analysed in individual products were determined based on the characteristic d-spacing, i.e. the Na-X ($d_{hkl} = 14.47, 3.81, 5.73, 8.85, 4.42, 7.54, 4.81$ and 3.94 \AA), the Na-P1 ($d_{hkl} = 7.10, 5.01, 4.10, 3.18 \text{ \AA}$), and for clinoptilolite ($d_{hkl} = 8.95, 7.91, 2.97, 3.16, 3.42, 5.11, 4.65, 3.97, 3.96, 3.95 \text{ \AA}$).

The morphology and chemical composition of the main mineral components of the zeolites were determined using an FEI Qanta 250 FEG scanning electron microscopy and energy dispersive spectroscopy (SEM/EDAX).

Textural properties of the zeolites, after degassing at 250 °C for 24 h. under reduced pressure (10^{-3} hPa), were examined on an ASAP 2020 Micromeritics Analyzer. The specific surface area, pore volume as well as pore size distribution were determined by nitrogen adsorption/desorption isotherms at $-196.15 \text{ }^\circ\text{C}$.

The specific surface area was determined based on the BET multilayer adsorption, where relative pressure (p/p_0) was between 0.01 and 0.16 giving positive BET constants. The total pore volume (V_p) was determined from the adsorbed nitrogen volume at $p/p_0 = 0.99$. Pore diameters (D_p) were calculated according to $D_p = 4V_p/S_{\text{BET}}$. The distribution of pore volume (R_p) was calculated by using a general isotherm equation based on BJH adsorption model at p/p_0 between 0.01 and 0.99 proposed by Barrett et al. [32] to calculate the percentage of micro, meso and macropore volumes respectively.

As investigated zeolites have different ion exchange capacities, their silver content was determined using inductively coupled plasma–mass spectrometry (ICP/MS) (Thermo-Fisher Scientific X-Series II).

2.3. Mercury adsorption tests

The mercury adsorption tests were performed in the rig shown in Fig. 1. The arrangement included: an elemental mercury generator in a water bath, a packed-bed Teflon tube reactor, containing 0.1 g of the sorbent, atomic fluorescence spectrometer (AFS) mercury detector (Millennium Merlin, PSA) and a data acquisition system. Mercury vapour was generated at 30 °C ($\pm 0.5 \text{ }^\circ\text{C}$) and introduced at a known and constant concentration (e.g. 0.00288 mg per 80 ml/min flow of N₂) into an accurately controlled stream of carrier gas (initially-nitrogen). This gas mixture was passed through a Teflon tube (0.47 cm id) packed with a known mass (0.1 g) of the sorbent to be evaluated. The gas leaving the tube was diluted further with nitrogen before being presented to the atomic fluorescence detector. The detector output was logged over time in order to find the point at which breakthrough of mercury occurs. Some tests were extended to allow the determination of the equilibrium mercury content of the sorbents.

2.4. Thermal stability of the sorbents

The thermal stability of the materials was investigated using a TGA Q500 (TA Instruments) instrument and approximately 20 mg of sorbent material. Analyses of spent materials provided evaluation of the quantity of Hg released, by monitoring the weight loss in the specified temperature range under a stream of inert gas. Samples were heated from ambient temperature to 110 °C, and then maintained for 20 min at this temperature to remove moisture. Following this pre-treatment, the temperature was raised from 110 to 800 °C at a ramp rate of 20 °C/min.

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