

## Abstract

Anthropogenic mercury emissions have been a significant threat to the environment for many years. Despite the fact that this problem is more and more noticed, and due to new legal regulations, further steps are taken to reduce emissions, new solutions are still being sought to reduce it effectively. The energy industry based on the processes of fossil fuels combustion, mainly coal, is one of the largest emitters of mercury. At the same time, it supplies materials in the form of coal combustion by-products - fly ash. Their specific properties, such as fine graining or an increased content of heavy metals, make their storage difficult and pose an environmental problem. Therefore, new directions for their management and utilization are still being sought. Due to some similarity of the chemical composition to natural rocks (tuffs and tuffites), which form deposits of zeolites in nature, it was proposed to use fly ash in the production of synthetic zeolites. The possibility of carrying out such a process, whether by the method of a single-stage hydrothermal synthesis or a two-stage procedure using thermal fusion and proper hydrothermal synthesis in an alkaline environment, is still a relatively new direction in the management of this type of waste.

In this work, two types of fly ash were selected for the syntheses of zeolites. The first was a product of hard coal combustion for energy purposes, while the second was brown coal combustion product. Based on the American standard ASTM C 618-89, which is one of the most frequently used in the Anglo-Saxon branch literature, it was found that the tested fly ashes belongs to F and C class, respectively. Both types of ashes were used as the main substrates in the synthesis of zeolites X (FAU type) and A (LTA type).

By manipulating a number of variables of the syntheses process, a new procedure was developed to convert C and F class fly ash into X and A type zeolites and their activated forms. The methodology of syntheses on a laboratory scale proposed in this work made it possible, in some cases, to convert these wastes into X and A zeolite materials of monomineral nature and a high degree of crystallinity. It was important to obtain a high degree of the fly ash conversion into zeolite phases. The quality ratio of the derived zeolite materials to the time of fusion and then proper hydrothermal synthesis was relatively high, which was an important cognitive aspect of the conducted research. The development of new syntheses procedures creates the prospect of reducing the amount of waste materials, but also developing efficient and economical technologies for the production of zeolites. The originality of the applied method is based on the simultaneous synthesis and activation of zeolite materials. This allowed for the

elimination of the additional modification stage, which may be of key importance in the context of possible commercialization of the proposed solution.

As part of the work carried out, apart from developing the procedures for obtaining activated zeolite materials, a prototype measuring installation was designed and built to test the effectiveness of  $\text{Hg}^0$  removal by solid sorbents from the inert gas stream (argon).

Using the SBPR-1 prototype installation, a number of tests were carried out on the sorbents obtained as part of this work. Both the substrates (fly ash) and the products obtained from them (raw and modified with silver and iron compounds) were tested. The reference material used in the work for comparative purposes was the commercial activated carbon WAD Hg 4S, dedicated to the processes of removing elemental mercury from gases. All silver activated samples obtained from the ash showed promising properties for the removal of  $\text{Hg}^0$  from the carrier gas stream. Among obtained materials, during the  $\text{Hg}^0$  removal experiment, the highest result of the actual mass of mercury removed was shown by silver-modified zeolite X derived from F class fly ash. Raw zeolites X and A obtained from both fly ashes, as well as samples activated with iron showed no sorption ability towards  $\text{Hg}^0$  - almost immediate breakthrough of the sorbent bed was observed.

The selected samples were then tested for the removal of gaseous forms of mercury on a prototype installation generating the flue gas environment. In this case, all tested samples showed at least a partial ability to remove gaseous mercury species from the carrier gas stream. The highest result of the actual mass of effectively removed gaseous forms of mercury was observed for the X zeolite sample obtained from C class fly ash and modified with silver.

**As part of this work, the following research goals were proposed:**

- 1) Analysis of the fly ash utilization as substrates in the syntheses of modified sorbents with a zeolite structure, effective in terms of mercury removal from exhaust gases.
- 2) Development of a new procedure for the two-stage syntheses of zeolites from fly ash and their modification in order to increase the sorption ability in relation to  $\text{Hg}^0$ .
- 3) Determination of the efficiency of  $\text{Hg}^0$  removal from an inert gas stream by the produced sorbents, using a prototype installation constructed for this purpose.
- 4) Determining the efficiency of capturing gaseous forms of mercury by selected sorbents on the basis of tests in the flue gas environment.

**The following research hypotheses were formulated in the thesis:**

- 1) F and C class fly ash can be used as a substrate in the syntheses of X and A zeolites with an appropriate level of purity and crystallinity, having a high potential for industrial and environmental applications as a substitute for commercially available equivalents.
- 2) The efficiency of  $\text{Hg}^0$  removal from the carrier gas stream by the obtained zeolite sorbents depends on:
  - a) the class of fly ash (F or C) used as starting material,
  - b) the structure of the obtained zeolite (X or A),
  - c) the type and amount of the zeolite structure activating reagent.
- 3) Modified sorbents, achieving high efficiency of elemental mercury removal in a neutral gas stream, have lower efficiency in the exhaust gas environment.

As a result of the work carried out, a detailed review of the literature was made, and a number of modified zeolite materials were produced as part of laboratory experiments. Using modern techniques of instrumental analysis, the characteristics of the starting materials and the obtained sorbents were made. In the further part of the work, a prototype SBPR-1 apparatus was built, which served as a tool to achieve the assumed goals and verify the hypotheses. The culmination of the research was the analysis of the effectiveness of the removal of gaseous forms of mercury by the modified zeolite materials obtained as part of the study with the use of an installation generating an exhaust gas environment similar to that observed in the power industry.

**Based on the analysis of the obtained research results, the following conclusions were made:**

- 1) The developed method of synthesis along with activation allows for obtaining FAU (X zeolite) and LTA (A zeolite) zeolites with a high degree of purity and crystallinity, using F and C class fly ash of as the main substrates. Simultaneous synthesis and activation of zeolites allow to avoid an additional stage of their modification, saving time and resources.
- 2) The lack of a significant decrease in sodium content in zeolites modified with silver and iron nitrates suggests that the incorporation of sodium and activating substances into the zeolite structure is not a highly competitive process.

- 3) The sorption capacity of the tested materials depended both on:
- fly ash class (F or C);
  - synthesized zeolite structure (FAU or LTA);
  - the type of activating substance, i.e.:  $\text{AgNO}_3$  or  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
- 4) Sorbents obtained from F class fly ash had higher sorption capacity in relation to  $\text{Hg}^0$  compared to their analogs obtained from C class fly ash. This is due to the higher content of amorphous aluminosilicate enamel in F class fly ash. The enamel is easier to dissolve in the alkaline synthesis medium, more effectively providing silicon and aluminum – the main building elements of PBU ( $\text{TO}_4$  tetrahedrons) that form zeolites. C class fly ash was characterized by a much more diverse chemical composition. The use of it as the main substrate reduces the efficiency of zeolite synthesis (compared to the efficiency of zeolite syntheses with the use of F class fly ash).
- 5) Activation with iron nitrate did not develop zeolites sorption ability towards  $\text{Hg}^0$  in an inert gas stream, but was effective for removing gaseous forms of mercury in the flue gas environment. This is probably due to the significant temperature difference in the mercury removal processes. Removal of  $\text{Hg}^0$  using the SBPR-1 installation was carried out at the temperature of  $\sim 24^\circ\text{C}$ , while the removal of gaseous forms of mercury in the flue gas environment was carried out in the temperature range from  $107$  to  $123^\circ\text{C}$ . At low temperatures, physical sorption processes dominate, while at high temperatures, chemical sorption – the boundary between these types of sorption is around  $110^\circ\text{C}$ .
- 6) Activation with silver nitrate developed in zeolites a sorption ability both for  $\text{Hg}^0$  in an inert gas stream and for the removal of gaseous forms of mercury in the flue gas environment. The mechanism responsible for binding mercury is probably amalgamation.
- 7) Values of  $\dot{S}_r$ ,  $\text{RM Hg}^0 U_c$  [ $\mu\text{g}$ ] (actual mass of mercury removed during 1 measurement cycle) and  $M \text{Hg}^0 U_{1g 150 \text{ minutes}}$  [ $\mu\text{g/g}$ ] (mass of mercury removed by a hypothetical 1 g of sorbent during 15 measurement cycles) for samples modified with silver nitrate were relatively stable and close. This allows the conclusion that the modification of zeolites X and A even with the use of the smallest amount of silver nitrate (1% by weight of  $\text{AgNO}_3$  in relation to the weight of the sinter after the thermal fusion stage during synthesis) allowed for the effective introduction of silver into zeolite structures and developed in them a high ability to removing  $\text{Hg}^0$  from an inert gas stream.

- 8) Among the tested samples, zeolite X (FAU type) derived from F class fly ash, activated with an intermediate (FFA-X Ag7,5%) and the highest (FFA-X Ag15%) dose of silver nitrate, achieved the highest value of the actual mass of elemental mercury removed . The test was carried out on the SBPR-1 installation.
- 9) Among the tested samples, zeolite X (FAU type) obtained from F class fly ash, activated with the highest dose of silver nitrate (FFA-X Ag15%), achieved the highest efficiency in removing gaseous forms of mercury in the exhaust gas environment.
- 10) Among the tested samples, zeolite X (FAU type) obtained from C class fly ash, activated with the highest dose of silver nitrate (CFA-X Ag15%), was characterized by the highest value of the actual mass of gaseous forms of mercury removed.

Based on the research, it can be concluded that the obtained zeolites could find commercial applications in flue gas purification technologies in the future.