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Study on the possibilities of treatment of combustion by-products from fluidized bed boilers into a product devoid of free calcium oxide^{\star}



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ARTICLE INFO

Article history: Received 22 September 2015 Received in revised form 11 December 2015 Accepted 14 December 2015 Available online 22 December 2015

Keywords: Fly ash Bottom ash Calcium oxide Combustion by-products

ABSTRACT

The purpose of this paper is to examine the possibility of reduction of free calcium oxide content in waste from fluidized bed boilers by treating them with carbon dioxide under various conditions. The primary examination concerning the possibilities of reducing the content of free calcium oxide in waste included carbonation process in a laboratory, taking into account various parameters of the process. The primary examination has been carried out in a fluidized bed reactor, rotary reactor and a ball mill reactor.

Depending on the reaction process, the variables in the examined processes included: reaction time, temperature, amount of the catalyst (water), application of an abrasive material. After completion of the process, the treated material was tested with regard to the content of free calcium oxide. Thus, it was possible to determine the most optimal conditions for treatment of combustion products from fluidized bed boilers, that is the conditions which will ensure reduction of the content of free calcium oxide at an appropriate level, under the physical conditions most similar to normal conditions and in the shortest possible time.

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1. Introduction

The continuous tightening of standards concerning emission to the atmosphere of pollutants from combustion of fuels in power plants, has forced the energy industry to start a series of actions, the aim of which is to change the combustion technology in order to keep these standards without the need to construct new, separate installations for purifying exhaust gases. The analysis of combustion technologies showed that the technology of fuel combustion in a fluidized bed constitutes very effective method of combining the combustion process with the simultaneous purification of exhaust gases (Brożyna & Mazurkiewicz, 2000; Pyssa, 2005; Stańczyk &

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http://dx.doi.org/10.1016/j.jsm.2015.12.002

^{*} The article was developed based on work titled "Study on the possibilities of treatment of combustion products from fluidized bed boilers into a product devoid of free calcium oxide" and developed in the Central Mining Institute at the request of TAURON Wytwarzanie S.A.

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Peer review under responsibility of Central Mining Institute in Katowice.

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Bieniecki, 2007). Therefore, the number of power units which operates based on combustion in fluidized bed boilers is steadily growing in Poland (Niesler, 2011), and it results in a continuous increase in the amount of combustion products from fluidized bed boilers, which, due to low temperature in the fluidized bed (ca. 850 °C) and because of fuels used, significantly differ (mainly in phase composition and considerably higher amount of free calcium oxide CaO_w) from waste produced during combustion in dust boilers (Gawlicki & Roszczynialski, 2000; Jarema-Suchorowska & Kuczak, 2010; Zapotoczna-Sytek, Łaskawiec, Gembarowski, Małolepszy, & Szymczak, 2012).

According to the Act on Waste of December 14, 2012 (WA, 2012) and the Regulation of the Minister of Environment of December 9, 2014 on waste catalogue (RME, 2014), waste from fluidized bed boilers are classified under the following codes:

- 10 01 24 sands from fluidized beds (with the exception of 10 01 82),
- 10 01 82 a mixture of fly ash and solid waste with calcium-based flue gas desulphurization (dry and semi-dry methods of desulphurization and fluidized bed combustion.

In the light of applicable laws, wastes from fluidized bed boilers are not classified as hazardous waste. Nevertheless, according to the representatives of the power and waste management industry, the planned changes to the regulations concerning substances and mixtures may result in the classification of waste from fluidized bed boilers as hazardous waste (Jacak, 2013; Paluch, 2013). According to the above, waste from fluidized bed boilers are characterized by their composition, that is, they include much more free calcium oxide CaO_w compared to waste from ash boilers. The amount of free calcium oxide CaO_w in this type of waste may be up to 10% of weight or it may even exceed this value (Jarema-Suchorowska & Kuczak, 2010; Zapotoczna-Sytek et al., 2012). Pursuant to the criteria specified in the Regulation (EC) No 1272/2008 of the European Parliament and of the Council of December 16, 2008 on classification, labelling and packaging of substances and mixtures (RPE, 2008), amending and repealing Directive 67/548/EEC, 1999/45/EC and amending the Regulation (EC) no. 1907/2006, calcium oxide CaO is classified as a substance having irritating properties and it is labelled as H315 and H318. According to the draft Decision of the European Commission amending Decision 2000/532/EC of May 3, 2000 (DKE, 2000), if waste contains one or more substances in the amount exceeding the limit values, which are classified by one of the following hazard categories and hazard codes - H314, H315, H318, H319 and when one or more acceptable concentrations are reached or exceeded, the waste has to be classified as hazardous, however, the limit value to consider that the particular waste is hazardous due to the irritant properties is 1.0%. It means that since the provisions of Decision of the European Commission amending Decision 2000/532/EC started to apply in Poland, waste from fluidized bed boilers containing more than 1.0% of weight of free calcium oxide CaOw (and generally, it is 100% of such waste), will have to be classified as hazardous waste (Jacak, 2013; Paluch, 2013).

The waste having high content of alkali oxides (inclusive of calcium oxide) show good capacity to bind carbon dioxide in the form of carbonates (IPCC, 2005; Muduli, Nabak, Dhal, & Mishra, 2014; Uliasz-Bocheńczyk, 2007). On this basis, the study has been focused on optimizing the parameters of the carbonation process of calcium oxide contained in waste from fluidized bed boilers.

2. Methodology

The principal purpose of the studies on the possibilities of treatment of waste from fluidized bed boilers into a product devoid of free calcium oxide was to determine the possibility of reduction of free calcium oxide content in such waste by treating them with carbon dioxide under various conditions.

The tests were carried out on waste from the fluidized bed boiler. The adopted research methodology consisted of two stages:

- preliminary research on waste and
- principal research on the possibilities of reduction of the content of free calcium oxide in waste.

The purpose of the preliminary research was to determine the basic physical and chemical properties of waste as well as their potential in terms of the possibility of binding carbon dioxide by free calcium oxide. The preliminary research consisted in the determination of the content of calcium oxide CaO_w in accordance with the standard PN-S-96035:1997P Road. Fly ash (PN, 1997).

The principal research concerning the possibilities of reducing the content of free calcium oxide in waste included carbonation process in a laboratory, taking into account various parameters of the process. The principal research was carried out in the following systems:

- fluidized bed reactor,
- rotary reactor,
- ball mill reactor.

Depending on the reaction process, the variables in the examined processes included: reaction time, temperature, amount of the catalyst (water), application of abrasive material. After completion of the process, the treated material was tested with regard to the content of free calcium oxide. Thus, it was possible to determine the most optimal conditions for treatment of fly ash from fluidized bed boilers, that is the conditions which will ensure reduction of the content of free calcium oxide at an appropriate level, under the physical conditions most similar to normal conditions and in the shortest possible time.

3. Characteristics of the tested material

The following wastes were subject to tests:

• bottom ash, with the code 10 01 24 as specified in the Regulation of the Minister of Environment on the waste

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