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Arsenic stabilization in coal fly ash through the employment of waste materials

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ABSTRACT

Coal fly ash can be considered either as an industrial waste material or as a valuable raw material. This is due to the fact that the main problem in recycling this ash is the possible presence of heavy toxic metals and the necessary reliable treatment to avoid their leaching into the environment. In this paper fluidized bed combustion (FBC) fly ash containing leachable arsenic (As) and vanadium (V) is stabilized with a new proposed technology, based on waste or by-product materials.

In particular, silica fume, that is a by-product of the smelting process in the silicon and ferrosilicon industry [1], is the main stabilizing agent used in this work. It is employed here, for the first time, for stabilization of arsenic. Also other ash, containing calcium hydroxide, is employed in the stabilization process.

The starting fly ashes and stabilized materials have been characterized. The results of leaching tests show that, despite the lower leachability of vanadium in respect to arsenic, the proposed method results effective in the entrapment of both elements. Based on the results of characterization a different stabilization mechanism is proposed for the two elements: vanadium seems to be stabilized by silica; concerning arsenic, it appears that calcium hydroxide acts as stabilizing agent for this element, probably due to formation of more stable phases.

Introduction

Despite the current economic crisis, energy demand has strongly increased in recent years and it is forecast to continue growing in the future. This implies an increase in the consumption of fossil fuels, of which coal is expected to show the largest growth in demand [2]. Therefore an increase in coal combustion by-products is also expected. Fly ash, for example, generated as a consequence of the combustion processes, is composed of fine-grained particles that have variable morphology and consist primarily of an amorphous glassy material. Due to the high calcium content, currently the market for coal fly ash is focused on soil stabilization and gypsum replacement [2]. Moreover, coal fly ash shows interesting properties for agricultural purposes because it is also rich in many macro and micro plant nutrients [3].

Fluidized bed combustion (FBC) technology for coal power plants is one of the most widely used technologies for the combustion of solid fuels, mainly thanks to its lower environmental impact (the most significant advantage of this technology is to minimize the emissions of sulfur dioxide and nitrogen oxides) [4]. As a consequence, global generation of FBC-derived coal fly ash has steadily increased [5].

The elemental composition of fly ash is highly variable [3] and it is most affected by chemical properties and variations in parent coal and the operation of advanced air pollution control technologies.

The reuse of coal fly ash may offer some cost savings for several industrial sectors due to a reduction in disposal and transport costs and saving of natural resources.

For this reason coal fly ash is considered either as a valuable raw material or as an industrial waste material. The main problem in recycling this ash is the possible presence of heavy toxic metals and the necessary reliable treatment to avoid their release in the environment. According to the U.S. Environmental Protection Agency [6], one of major trace element of most concern regarding exposure of ecological receptors to fly ash is As [6]. Increasing release of this element has caused a serious damage to the environment and human health [7]. Today, coal combustion in power plants for electricity generation is recognized as the major anthropogenic emission source of As [8].

In fly ash As is generally concentrated in finer particles (normally referred to as those particles whose aerodynamic diameter is less than 10 μm), which may escape from particulate control systems [9].

Few studies are published about As in fly ash from fluidized bed [5,10], and most of them are focused on As quantification [8,9]. Recent research [11] shows that As is a leachable element that can also be found in fly ash derived from direct combustion of biomass for energy derived from circulating fluidized bed technology.

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Consequently, research on the stabilization of dangerous elements (e.g. As) is of particular relevance, especially taking into account the expected increased coal demand in the forthcoming years.

Different treatments and stabilization processes of fly ash have been proposed by the scientific community.

In order to stabilize waste and reduce the heavy metals leachability, the available processes are divided into three main categories: separation processes, that include all techniques that allow the extraction of some species from the fly ash; solidification/stabilization (S/S), that utilizes chemically reactive formulations, together with the water and other components in sludges form stable solids; and thermal methods, that include vitrification, melting, sintering, and microwave employment. For a recent comprehensive review of these technique see Ref. [3].

Moreover at this time none represents a sustainable solution for the management of this fly ash and for As leachability.

Recently a new room temperature process to stabilize fly ashes has been developed and optimized [12,13]. The advantage of this new technology is that it can be used for stabilization using other waste sources containing silica. In this work this technology was adapted to use silica fume as source of silica.

Silica fume or microsilica is very fine non-crystalline silica produced in electric arc furnaces as a by-product of the production of elemental silicon or alloys containing silicon[1].

Silica fume particles are very small, with more than 95% of the particles being less than 1 μm. Most particles are in spherical shape with a mean diameter of 0.2 μm. As a consequence silica fume particles show high surface area and high reactivity. The chemical composition of silica fume is related to the composition of raw materials used in the furnace. The SiO_2 content of silica fume is generally higher than 80%. Other oxides such as CaO, Al_2O_3, Fe_2O_3 and alkali contents of silica fume are relatively low [14].

Despite that today silica fume is still landfilled and large quantities of this material are recovered as pozzolanic material in concrete and cementitious products.

Moreover, the financial crisis has also impacted on global cement industry production. As a consequence, new applications markets for silica fume are expected to be developed.

In the present research we propose for the first time the stabilization of fly ash from fluidized bed coal combustion. The ash, collected from a power plant in Slovakia, is characterized by a significant amount of As, thus requiring stabilization before the use and/or landfilling. A stabilization process made by employing waste and by-product materials and a technology realized at room temperature has several positive implications, as for example low costs and technological simplicity.

Experimental procedures

Fluidized bed coal combustion fly ash employed in this study was collected from a thermal power plant in Slovakia. The samples were not subject to any preparatory operation at the plant.

Due to poor adsorption properties of the silica fume, it cannot be employed as-well as metal stabilizer [15]. In view of the good obtained results by employing colloidal silica [16] and rice husk ash [17] as metals stabilizers, the same patented procedure, described in these papers, was applied with silica fume.

The stabilization procedure used here was as follows: silica fume was mixed with three different types of fly ash: (i) fly ash from fluidized bed coal combustion (FBC); (ii) flue gas desulfurization residues (FGD); and (iii) coal fly ash (C), at weight percentages of 65%, 20% and 15%, respectively [13]. FGD and coal fly ashes were provided by power plants located in northern Italy. The silica fume quantity was 10 wt% of fly ashes mass.

The mixture was wetted with water, and mixed for 1 h. Water is necessary to stabilization process, but its quantity can be variable. A liquid/solid ratio of about 0.2–0.3 is generally reached. The sample rested in air for 48 h, then the leaching test was performed, to verify the heavy metals stability.

The FBC ash and the stabilized material were digested in acid solution by means of CEM Discover Microwave to obtain chemical composition. Samples were prepared using 0.3 g of powder sample in a solution of 2 ml HNO_3 (65 vol.%), 2 ml HF (47 vol.%) and 2 ml HCl (37 vol.%). The instrumental parameters of the digestion procedure are the following: temperature 210 °C, time 8 min, power 300 W and medium stirring.

Leaching tests on as-received fly ash from fluidized bed coal combustion and treated sample made by using silica fume were performed according to the CEN normative (CEN EN 12457-2:2002). The contact time of materials and aqueous solution was 2 h. Leaching tests on stabilized powders were carried out 2 days after the stabilization.

Chemical analysis was done by means of total reflection X-ray fluorescence technique (TXRF). TXRF analysis were made using a Bruker TXRF system S2 Picofox (air cooled, Mo tube, Silicon-Drift Detector), with operating values of 50 kV and 750 μA using an acquisition time of 600 s. TXRF quantitative analysis of the suspended samples was performed by the internal standard procedure. An appropriate amount of gallium, used as an internal standard element, was added [18].

XRD measurements of powder samples were performed using Cu Kα radiation between 5 and 75° (2θ) with a Panalytical X′Pert Pro diffractometer running at an acceleration voltage of 40 kV and current of 40 mA. Diffraction patterns were indexed using the instrumental software package.

Infrared measurements were performed by means of FT-IR spectrometer Bruker, Equinox 55, on transmission mode diluting the samples with KBr tablets.

Scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM-EDS) technique was used to determine morphology of the ash and the corresponding stabilized material. SEM images were obtained using a Nova NanoSEM operating at an acceleration voltage of 20 keV with a working distance of 5.3 mm fitted with an Oxford instruments energy dispersive X-ray spectroscopy (EDS) system operating with INCA software. Images and elemental maps were captured in scanning electron imaging (SEI) and backscattered electron imaging (BEI) as appropriate.

Results and discussion

Table 1 shows the chemical composition of the FBC fly ash and corresponding stabilized material.

Considering quantifiable elements, it is possible to deduce that FBC fly ash is mainly composed of Fe, K, Ca, Al, S and Ti. Minor elements are Mn, V, As, and Zn.

The amount of arsenic in world coals is in the range of 0.5–80 mg/kg [19], then it is evident that the present FBC fly ash shows not so high As concentration.

The corresponding stabilized material has a different composition, with a decrease in concentration of metals (like for example Ca, Ti, Cr, Mn, Fe, Al, Pb and As), due to the dilution of FBC fly ash with other powders. On the contrary, the quantity of other elements increases or is approximately the same (as for example K, Ni, Cu, Zn and V) due to the presence of these elements also in the ashes employed for the stabilization procedure. It is very interesting to notice that As and V concentration is comparable in the FBC fly ash and in the final stabilized material. On the contrary, the concentration of Se is increased in the final material, due to its presence in the other ashes employed in the process. It is evident that the stabilization process does not imply the removal of these elements.

Moreover, the most interesting chemical analysis are devoted to the results of leaching tests, reported in Table 2, and are discussed in the following.