Journal of Cleaner Production 137 (2016) 150–156

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Effects of waste fluid catalytic cracking on the properties of semi-hydrate phosphogypsum

D. Nizevičienė [a, *], D. Vaičiukynienė [b], V. Vaitkevičius [b], Ž. Rudžionis [b]

[a] Kaunas University of Technology, Faculty of Electrical and Electronics Engineering, Studentu st. 48, LT-51367, Kaunas, Lithuania
[b] Kaunas University of Technology, Faculty of Civil Engineering and Architecture, Studentu st. 48, LT-51367, Kaunas, Lithuania

ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form
14 June 2016
Accepted 6 July 2016
Available online 15 July 2016

Keywords:
Semi-hydrate gypsum
Phosphogypsum
Zeolite
Waste fluid catalytic cracking

ABSTRACT

Phosphogypsum poses environmental problems; therefore, this research paper examines and discusses the possibilities of effective utilization of phosphogypsum as a binding material. However, water-soluble primary calcium phosphate and fluoride, while remaining in phosphogypsum as unwanted impurities, makes it unsuitable for the production of gypsum-based products. This paper describes the process of adsorbing hazardous phosphogypsum impurities by zeolite. The waste fluid catalytic cracking (FCC) process catalyst based on synthetic zeolite Y was used in the experimental research described in this paper. In order to improve the properties of the binding material from phosphogypsum the ultrasound treatment of phosphogypsum paste was used. The samples were characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectrometer (EDS), the compressive strength of phosphogypsum specimens. The results showed, that the compressive strength increased about four times while using ultrasound treatment and waste FCC catalyst (zeolite Y) addition from 0.5 until 10% compared with specimens without zeolite and sonication. With the increase of zeolite by more than 10%, compressive strength decreased additionally. It was also determined that phosphogypsum paste used with waste FCC catalyst (zeolite Y), which was treated with ultrasound was an effective additive for neutralizing the acidic phosphogypsum medium. It neutralized the acidic admixtures, regulated the phosphogypsum hydration and the time setting duration as well. Additives modified the microstructure of hardened gypsum and increase its strength.

1. Introduction

A large amount of waste material phosphogypsum is generated by phosphorus fertilizer industry. Industrial by-products pose environmental problems. Currently, there is a great interest in using purified phosphogypsum as an alternative raw material for many applications. In this research, the paper examines and discusses the possibilities of effective utilization of phosphogypsum as a binding material. However, water-soluble primary calcium phosphate and fluoride, remaining in phosphogypsum as unwanted impurities, render it unsuitable for the production of gypsum-based products. The soluble phosphate impurities in phosphogypsum impede its utilization indirectly producing binding material.

In order to make phosphogypsum harmless and suitable for later applications, numerous researchers have proposed different methods of phosphogypsum utilization: converting phosphogypsum into gypsum-based binding materials, preparing it to sorbents or converting it to cementitious binder, sulfuric acid leaching, extracting of rare earth elements and thermal treating. Kadirova et al. (2014) suggested the study related to utilization of phosphogypsum, in order to reduce its negative impact, for the preparation of sorbents. Sorption materials were prepared from phosphogypsum and kaolin. Kaziliunas et al. (2006) developed some technologies for converting phosphogypsum into gypsum-based binding materials. Under hydrothermal conditions the harmful soluble phosphorus and flour compounds were neutralized in lime suspension. Different utilization method of phosphogypsum was used by combining a percolation sulfuric acid leaching of phosphogypsum. In this way, it is possible to obtain high-quality raw gypsum materials (Lokshin and Tareeva, 2015). Liu et al. (2015)

* Corresponding author. Tel.: +370167122485.
E-mail address: dalia.nizeviciene@ktu.lt (D. Nizevičienė).

http://dx.doi.org/10.1016/j.jclepro.2016.07.037

studied the cementitious binder of phosphogypsum like eco-friendly building products. The compressive strength of this binder reached up to 41 MPa and the compressive strength of bricks with this binder and river sand was approximately 21 MPa Valkov et al. (2014) has proposed a method for reprocessing of phosphogypsum with the extraction of rare earth elements, which allows obtaining environmentally friendly phosphogypsum. The results of the fast firing showed that the soluble phosphate content decreased considerably but it did not change the total phosphate content in phosphogypsum. The hemihydrate gypsum appeared and the pH value increased after fast firing.

In the gypsum industry, the main fields of phosphogypsum utilization are the conversion of phosphogypsum to plaster and plaster products. Singh (2005) studied the impact of phosphogypsum impurities on strength and microstructure of selenite plaster. He concluded that the formation of prismatic, rhombic and lathe like crystals retards the normal setting and strength development of selenite gypsum plaster. Garg et al. (2009) suggested making high strength alpha plaster from phosphogypsum. It was found that with small quantity of chemical admixture, alpha plaster of high strength could be produced. The industrial application of the new type of bricks (instead of clay bricks) could help to reduce the environmental impact of waste phosphogypsum significantly.

The impurities of phosphogypsum affect the quality of building materials. Phosphogypsum was used as raw material for the preparation of non-autoclaved aerated concrete. The results showed that phosphogypsum was not only important as filler but as well as an activator (Yang et al., 2013). Cuadri et al. (2014) proposed a novel application for phosphogypsum waste, as a modifier of bitumen for flexible road pavements. In previous studies (Zhou et al., 2012) an innovative Hydration-Recrystallization process for preparing non-fired bricks from waste phosphogypsum was proposed. In this way, it is possible to obtain non-fired bricks prepared from waste phosphogypsum.

There are many researches describing the use of phosphogypsum in cement industry as raw material in the raw mix of cement and as cement setting regulator. Yang et al. (2013a) studied the manufacturing technique for producing belite–ferroaluminate cement utilizing of phosphate fertilizer industry waste products as raw materials. Effect of phosphogypsum content on performances of cement was investigated. Experimental results (Shen et al., 2014) indicated that phosphogypsum can be utilized to produce calcium sulphoaluminate cement, and the suitable firing temperature was between 1250 and 1300 °C. In another scientific research it was investigate the utilization of phosphogypsum in calcium sulphoaluminate cement. The decomposition of phosphogypsum had a significant effect on the formation of calcium sulphoaluminate, and decreased compressive strengths of calcium sulphoaluminate cement (Shen et al., 2014). Shen et al. (2015) suggested the new synthesis method for belite sulfoaluminate-ternesite cement. Potgieter et al. (2003) suggested a combined treatment of wet milling phosphogypsum with the lime slurry in a ball mill. Altun and Sert (2004) found that phosphogypsum could be used instead of natural gypsum for Portland cement. The highest 28-day compressive strength was found in the sample with 3 wt% phosphogypsum.

Some research suggested the methods of phosphogypsum utilization with fly ash. Rashad (2015) reported that it is possible to recycle phosphogypsum in alkali-activated fly ash system similar to traditional Portland cement system. By replacing fly ash with 5% or 10% calcined phosphogypsum increased the strength before and after firing. Değirmenci (2008) investigated the potential utilization of phosphogypsum with fly ash and lime in the construction industry. He determined that the obtained cementitious binder could be used for the production of interior wall materials such as bricks and blocks. Zieliński (2015) presented a study of the effect of constant magnetic field on composites (cement–fly ash–phosphogypsum) used in building industry.

This paper describes the process of adsorbing hazardous phosphate and fluoride impurities by zeolite. Zeolites are porous crystalline aluminosilicates, which comprise the assemblies of SiO_4 and AlO_4 tetrahedra joined together through the sharing of oxygen atoms. Zeolites with well-defined pore structure are widely used as sorbents. The waste fluid catalytic cracking (FCC) process catalyst based on synthetic zeolite Y was used in the experimental research described in this paper. This zeolite was polluted with oil products and subsequently became waste. The quantity of this waste inevitably rises because of rapidly expanding oil industry. Earlier studies have shown that this residue exhibits good adsorption properties for chromium removal (Gonzalez et al., 2013) and encapsulation of heavy metals (Sun et al., 1998). The aim of this paper is to determine the properties of phosphogypsum obtained from Kovdor apatite mine and find out the possibilities of producing binding material from phosphogypsum and zeolite waste (FCC catalyst). The acid impurities are adsorbed using waste FCC catalyst. The use of two types of production waste to obtain binding material makes a more positive effect on the environment.

2. Experimental

2.1. Experimental techniques

A chemical composition of phosphogypsum was determined by classical methods of chemical analysis according to the standards (EN 196-2). Methods of testing cement - Part 2: Chemical analysis of cement; GOST 20851.2–75 Mineral fertilizers. Methods of determination of phosphorus content (in Russian). The chemical composition of waste FCC catalyst was determined according to EDS.

The X-ray diffraction analysis of the materials was performed using the X-ray diffractometer DRON-6. CuKα radiation and Ni filter were used. The power X-ray diffraction patterns were identified with references available in PDF-2 date base (PDF–2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA, 19073-3273 USA).

The pH measurements of water suspensions were conducted by pH-meter EDGE, 230 V, when the ratio of water (W) and solid material (S) W/S was 10.

The structures of fresh phosphogypsum and hardened phosphogypsum with FCC waste were studied by scanning electron microscope. A high resolution scanning electron microscope FEI Quanta 200 FEG with a Schottky field emission gun (*FEG*) was used for the research. Chemical compositions of FCC waste were investigated by an energy-dispersive X-ray spectrometer (EDS) with silicon type drift droplet detector.

The hydration water in gypsum (loss on ignition, %) was calculated after heating the material at the temperature of 400 °C.

Ultrasonic treatment was carried out by BANDELIN Electronic ultrasonic converter UW3400 of 200 W power and 20 kHz frequency. Treatment duration was 0.5 min.

The phosphogypsum paste hydration temperature measurements were performed with 8-channel USB TC-08 Thermocouple Data Logger (temperature measurement range from −270 to +1820 °C).

In order to find out the mechanical characteristics of the phosphogypsum, 2 × 2 × 2 cm cubes were formed from phosphogypsum paste of normal consistency. The water/phosphogypsum ratio and the setting time of the mixture (normal consistence) were determined according to the standard EN 196-3. The cubes were compressed with the press ELE AutoTest. The compressive strength