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The treatment of phosphogypsum with zeolite to use it in binding material

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HIGHLIGHTS

- Hydrosodalite allows regulating the phosphogypsum hydration and setting time.
- The positive effect of sonication and of hydrosodalite additive is combined.
- The content of radioactivity in PG does not exceed significantly average concentration.
- The total mass of a PG final product natural radioactivity does not create any problem.

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ABSTRACT

In Lithuania, there are accumulated large amounts of fertilizer by-product – phosphogypsum and there is a lack of sources of natural gypsum. Recycling of by-product is one of the effective solutions of its disposal problem. The paper describes an investigation of the hydration behavior of a phosphogypsum with zeolite (hydrosodalite) addition using ultrasound treatment. Two ultrasound treatment durations: 0.5 min and 2 min were used. It was found that hydrosodalite is an effective adsorption additive for acidic contaminants (solvable P_2O_5 and F) present in phosphogypsum, which allows regulating the phosphogypsum hydration and setting time. The compressive strength of samples containing 5% hydrosodalite and with 2 min sonication is 35% higher, than the compressive strength of samples without additive and sonication. In this case, the positive effect of sonication and of hydrosodalite additive is combined. Phosphogypsum as a residue from the phosphate fertilizer industry is classified as a Naturally Occurring Radioactive Material (NORM). Therefore, when it is used as an additive component to building materials radioactivity content must be checked. The different amount of the various radionuclides within the natural radioactive decay series, such as that of ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K, and ^{210}Pb were measured by high resolution gamma spectrometry. The results showed that activity concentration of natural radionuclides as ^{226}Ra, ^{228}Ra, ^{228}Th, ^{40}K are below the clearance limit and activity concentration indices calculated for all materials used for experiments met the existing criteria allowing to use them for construction purposes.

1. Introduction

Phosphogypsum (PG) is an acidic by-product of the phosphate fertilizer industry. Large quantities of the phosphogypsum are produced world-wide and it is estimated that more than 250 million tons will be produced annually [1]. Although phosphogypsum is mainly $CaSO_4{\cdot}2H_2O$, it contains elevated levels of impurities such as H_3PO_4, $Ca(H_2PO_4){\cdot}2H_2O$, $CaHPO_4{\cdot}2H_2O$ and $Ca_3(PO_4)_2$, residual acids, fluorides (NaF, Na_2SiF_6, Na_3AlF_6, Na_3FeF_6 and CaF_2), sulphate ions, trace metals and organic matter as well as natural radionuclides.

PG could be recycled as building material. There are many researches describing the use of PG in cement industry as a setting regulator. Potgieter et al. [2] suggested a combined treatment of wet milling phosphogypsum with lime slurry in a ball mill. Altun and Sert [3] investigated the usability of weathered PG from residue areas as set retarder in Portland cement. It was found that PG can be used in place of natural gypsum for Portland cement and the highest 28-day compressive strength was found in the

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sample with 3 wt% of PG. Yilmaz and Isildak [4] used set accelerators and concluded that addition of set accelerators — calcium formiate, calcium nitrate and sodium molybdate — improved the hydration characteristics of OPC (ordinary Portland cement) containing phosphogypsum. Calcium nitrate was found to be the most effective set accelerator.

Phosphogypsum can be also used for gypsum plasters production; however, it is known that PG impurities affect its. Phosphogypsum could change the microstructure of selenite plaster. Different morphology affects the normal setting and strength characteristics of selenite gypsum plaster to a great extent [5]. Singh et al. [6] deals with an investigation of the production of high strength plaster from the phosphogypsum and its use in making flooring tiles. To achieve this objective, phosphogypsum was calcined at 900–1000 °C to anhydrite which was mixed with suitable chemical activators and finely ground to achieve high compressive strength (36–37 MPa). Flash-calcination of gypsum by a new patented process produces a particular type of plaster [7]. It appears as a stable mixture of hemihydrate and of γ-anhydrite. It reveals that even after several months of exposition under moist atmosphere, γ-anhydrite is still present in the sample. A model of composite particle of plaster is proposed for explaining this unusual behavior.

Besides these afore mentioned, it is possible use of PG in ash-lime-phosphogypsum composites materials. Kumar [8] presented a study based on fly ash-lime-phosphogypsum (FaL-G) hollow blocks, which are light in weight and being hollow, impart thermal insulation to the buildings. It is observed that FaL-G hollow blocks have sufficient strength for their use in general building construction. Shen et al. [9] reported that a new type of lime-fly ash-phosphogypsum binder was prepared to improve the performances of lime-fly ash binder which was a typical semi-rigid road base material binder. Garg et al. [10] investigated the effect of curing temperature on the durability of a cementitious binder based on calcined PG, fly ash and lime. The results indicate that the strength of the binder decreased and loss in weight increased with increases in cycles and exposure temperature.

Looking at all the studies taken together, nowadays there is a great interest in using phosphogypsum as an alternative raw material for the applications in building industry. For this reason, it is needed to eliminate harmless impurities of phosphogypsum. Researchers have suggested different phosphogypsum purification methods: washing, wet sieving, neutralization with lime, with aqueous citric acid solution and treatment with hot aqueous ammonium sulphate solutions [11–16].

Relatively high content of natural radionuclides in rock phosphate ore results in that its processing and then disposal of residues – phosphogypsum – may contribute to enhanced levels of natural radionuclides in the environment. However, Haridasan et al. [17,18] present the results of the dissolution characteristics of ^{226}Ra from phosphogypsum and indicated that leaching of radium may be slow in field conditions near the PG stock piles. Shweikani et al. [19] investigated radiation dose assessment due to the presence of phosphogypsum in cement. Results showed that the extra dose to the public due to this addition was within the acceptable levels. The results of these studies support the safe use of phosphogypsum in construction materials.

In this paper, synthetic hydrosodalite made from microsilica, was used as neutralizing agent of PG properties constricting it use. Hydrosodalite has been chosen since it is microporous, aluminosilicate mineral commonly used as commercial adsorbent. The objective of the study is to investigate the effect of zeolite-like materials made from microsilica on the performance of phosphogypsum system. The evaluation of phosphogypsum's radioactivity was performed as well.

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 specific (particle) density of formed materials was determined by using the Pycnometer method. The air permeability method (Blaine method) was used for specific surface area evaluation according to standard EN 196-6.

The X-ray diffraction analysis of the materials was performed using the X-ray diffractometer DRON-6. CuK_α radiation and Ni filter were used. The power X-ray diffraction patterns were identified with references available in PDF-2 data 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 microstructures of hardened phosphogypsum with hydrosodalite were studied by scanning electron microscope. A high resolution scanning electron microscope ZEISS EVO MA10 was used for the research. Chemical compositions of hydrosodalite 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. The duration of sonication was chosen 0.5 and 2 min.

The phosphogypsum paste hydration temperature measurements were performed with 8-channel USB TC-08 Thermocouple Data Logger (temperature measurement range from −270 to +820 °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/solid material 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 Auto Test. The density of samples was determined according to EN 12390-7.

The activity concentrations of ^{226}Ra, ^{228}Ra, ^{228}Th, and ^{40}K, in samples were determined by mean of high-resolution gamma-ray spectrometry with high purity germanium detector broad energy type with 50% of the relative efficiency. All results reported were calculated for samples dried to stable mass (air-dry state). The activity concentration of radionuclides – radium ^{226}Ra, ^{228}Ra, thorium ^{228}Th, lead ^{210}Pb, and potassium ^{40}K were determined by use of gamma-ray spectrometry method. The spectrometric system consists of hyper pure germanium detector (HPGe), broad energy type (useful for low energy gamma emissions detection), with relative with relative efficiency 50%, cooled by liquid nitrogen (LN_2), amplifier, AD converter, multichannel analyzer and PC with software for spectra analysis. The energy calibration was performed by use of multi-gamma source which contains isotopes emitting gamma lines in wide range (46 – 2600 keV). The efficiency calibration was performed by use of measurement standards prepared from certified reference materials (CRM) with similar matrix and density provided by International Atomic Energy Agency (RGU-1 and RGTh-1 reference materials which contain uranium and thorium decay series in secular equilibrium and RGK-1 containing potassium isotope K-40 [20]. The measurement