The Problems of Phosphogypsum Utilization in Lithuania

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Abstract
There are no mines in Lithuania but there are fertilizer waste dumps. For many years phosphor fertilizer has been made in Kedainiai chemical plant in the central part of Lithuania using apatite as a raw material which is brought from Kola peninsula. During the production of 1 t of phosphoric acid 4,5 t of phosphogypsum is produced. For many years phosphogypsum has been transported into the dump in which more than 8 mln tones of phosphogypsum have been accumulated. Phosphogypsum includes volatile fluor and phosphoric acid. Ecological polution of the waste materials is obvious, however, according to Lithuanian laws the plant does not pay any fee for the damage.

Institute of Architecture and Construction has prepared several technologies concerning the utilisation and remaking of the phosphogypsum wastes into building materials and products. The report is based on the problems of their characteristics and realization.

Keywords: Lithuania, phosphogypsum, utilization, waste.
Introduction

Lithuania lacks sources of natural gypsum. That’s why Latvian natural gypsum from Seuriese pit was used in the production of gypsum products. This pit has been exploited for a very long period of time in spite of comparatively low quality of gypsum.

However, in Lithuania we have large amounts of fertilizer production waste. For many years phosphorus fertilizers have been produced by Kedainiai chemical plant (today joint stock comp. “Lifosa”) which is in the central part of Lithuania. The main raw material used is apatite brought from Russia, Kola Peninsula.

With the production of one ton of phosphorus acid there form 4.5 ton waste material, i.e. phosphogypsum. For many years phosphogypsum has been transported into the so-called waste-hills in which more than 8 mln. tons have been accumulated.

Phosphogypsum includes volatile fluor, the remainders of phosphorus acid and other harmful materials. The pollution of the environment is obvious enough, but still, according to the present laws of Lithuanian Republic, the enterprise does not pay any fees. The Institute of Architecture and Construction has prepared some technologies concerning the utilization of these waste materials and the processing of phosphogypsum into building materials and products.

Technology of the utilization

Already in 1987 in Kedainiai near the chemical enterprise a plant for phosphogypsum processing into P-modification building gypsum was built according to the project made by the institute. The wasteless technology was based on the neutralization of phosphogypsum but not its washing with water.

The essence of the technology is as follows:

- phosphogypsum dehydrate in which there is no more than 1.3% of general $P_2O_5$ and 0.9% $P_2O_5$ which is water soluble is neutralized with lime cream and the pulp is filtered;
- filtrate is once again used for lime cream preparation;
- filtered phosphogypsum is dried;
- dried phosphogypsum is dehydrated;
- the product is cooled down;
- the product is ground;
- the product is stored and stabilized.

This technology of $\beta$-semihydrate gypsum production is distinguished itself by many advantages: there were no technological flowing waters, the process was continuous, and the product produced distinguished itself by stable properties: the beginning of binding – 13-15 min., the end – 20-24 min., strength under pressure after 2 h is 5-6 MPa, strength under pressure of dried products 12-13 MPa. Gypsum slabs, blocks, mixtures for finishing works have started to be produced of this building gypsum in Lithuania.

In 1990 with the restoration of Independence in Lithuania the economical situation changed. The amount of production diminished and the size of building material
The industry decreased about 80%. The phosphogypsum processing plant did not manage to adjust to new conditions and in 1993-94 \( \beta \)-phosphogypsum plant was finally closed. At present this product is no longer produced in Lithuania.

From 1997 the joint stock company “Lifosa” changed the technology of fertilizer production, and the waste material is no longer dehydrate phosphogypsum but semihydrate acid phosphogypsum. A very small amount of it the plant processes into a high-quality a-modification building gypsum. The main properties of this gypsum are:

- the beginning of binding: 16 min., the end: 32 min., strength under pressure after 2 h: 14.4 MPa;
- \( P_2O_5 \) general: 0.33%, \( P_2O_5 \) water soluble: 0%;
- fluor general: 0.25%, fluor water soluble: 0%.

However, today the amount of the production does not meet even the minimal demand of producers and consumers.

In 1997 the firm “Palamono keramika” using the technology invented by the Institute of Architecture and Construction produced the first experimental batch of a new building material – anhydrite cement. The raw material for this binding material – i.e. dehydrate acid phosphogypsum – has been taken from that part of phosphogypsum waste-hills where new waste materials were not transported in last years. The upper and the middle parts of the hills (2/3 of the height) have been thoroughly examined. The chemical tests showed that during many years rain and other natural factors considerably diminished the amount of harmful admixtures in the phosphogypsum – dehydrate waste. The average chemical compositions was as follows: \( R_2O_3: 2.03\% \); \( CaO: 31.63\% \); \( SO_3: 44.82\% \); F general: 0.2%; F water soluble: 0.04%; pH: 2.6-4.8%.

The essence of anhydrite cement production technology is the following: acid phosphogypsum – dehydrate is neutralized by lime cream in clay mixer, then clay and glass slime (the waste got during TV screen grinding) additives are introduced and the produced mixed material is burned in gyrator furnace. The approximate composition of materials is: 79.0-79.3% phosphogypsum; 16% clay; 4% glass slime; 0.5-1% lime. The production was carried out in a claydite shop of a plant “Liapor”. Anhydrite cement was burned at 850-900°C and the product produced in granulated shape. The chemical composition of the granulate is: \( SO_3: 36.45-41.05\% \); \( CaO: 32.0-33.27\% \); \( R_2O_3: 9.35-15.6\% \); \( P_2O_5 \) water-soluble: 0.03%; F general: 0.03-0.06%; F water soluble: 0%. The mechanical strength of the granules 1.5-2.0 MPa; volume mass 967-985 kg/m\(^3\).

In the next stage the granulate is ground and then we get anhydrite cement. The main physical-mechanical properties are these: the beginning of binding 1 h 20 min., the end: 2 h 15 min., the strength after 28 days under pressure is 20-30 MPa, under bending: 3-4.5 MPa.

This binding material can successfully replace the ordinary portlandcement in many building spheres. It should be also profitable from the economical point of view as anhydrite cement is burned at much lower temperature than portlandcement. Yet, its production size is still small.
Conclusions

In Lithuania, as well as in the former SU, gypsum materials and products took an insignificant place in the nomenclature of building materials. Because of extremely low prices of energetic resource cement was used nearly in all spheres.

With the change of both political and economic situation building materials made of gypsum have been widely used, especially for interior trim. In fact all these materials are being imported.

However, the amount of local phosphogypsum waste with the realization of technologies suggested by the Institute of Architecture and Construction, could ensure a long-term production of gypsum materials. At the same time, it would give the possibility of the gradual diminishing of accumulated phosphogypsum waste dumps.