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Use of phosphogypsum in road construction

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The paper presents practical utilisation in the construction of a parking lot of compositions based on waste (phosphogypsum) from the wet process of orthophosphoric acid manufacture. The results of strength tests performed after half a year and after one and a half year of parking lot operation confirmed the feasibility, established earlier in laboratory tests, of utilising phosphogypsum mixes with fly ash and stabilising binder.

Keywords: Waste, phosphogypsum, road engineering.

INTRODUCTION

The wet process of the manufacture of orthophosphoric acid, which is the basic raw material in the production of high-quality phosphate fertilizers and other phosphorus compounds, entails the generation of phosphogypsum waste. At the beginning of the 21st century in Poland there were three plants producing wet process orthophosphoric acid, and consequently phosphogypsum. The economic situation, along with the growing environmental requirements, have conduced to changes in the production and to the shutting down of some of the plants. Now, the only plant in Poland, where phosphogypsum is still generated are the Zakłady Chemiczne "Police" SA. There most of the phosphogypsum waste is stockpiled in a stack, which is a common way of handling the waste worldwide. The changes in and stopping of wet process orthophosphoric acid production did not solve the problem of utilising the phosphogypsum waste already disposed of in stacks. Of the existing three phosphogypsum stacks, only the one in Police is still operating. The stack in Wiślinka of the Gdańskie Zakłady Nawozów Fosforowych "Fosfory" Sp. z o.o. has been shut down and reclaimed. The third phosphogypsum stack belonged to the now dissolved Zakłady Chemiczne "Wizów" SA near Bolesławiec. That stack is particularly interesting due to apatite as the phosphate raw material used. The problem with industrial utilisation of phosphogypsum is its huge amounts, resulting from the high capacities of wet process orthophosphoric acid plants. Another problem is the public belief that phosphogypsum is detrimental to human health and the environment. In recent years there has been a growing tendency to look upon phosphogypsum as a valuable resource. Hence the attempts made worldwide to change the attitude towards this waste[1, 2, 3].

In Poland, the annual production of phosphogypsum amounted in recent years to 2.3 – 2.5 million metric tons, whereas in 2009 it fell below 1.0 million tons. Of industrial significance can only be those solutions, where large quantities of phosphogypsum are used. Chances of industrial-scale utilisation of phosphogypsum might be sought in road engineering, where materials are used in large quantities.

First attempts to use phosphogypsum in road engineering were made in the USA in the 1980's. Trials were conducted in Florida[1, 4] to use phosphogypsum in construction of roads for light traffic, and it was found that this material, when mixed with non-cohesive soil, forms a stable base for bituminous pavement.

Extensive studies of using phosphogypsum in road engineering were also conducted in Finland between 1998 and 2002[5]. Phosphogypsum was supplied from a chemical plant in Siilinjärvi (Kemira Phosphates), where apatite was used as the phosphate raw material. The phosphogypsum contained two forms of calcium sulphate: $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$. Mixtures containing 90% phosphogypsum and 10% fly ash (dry matter basis) were prepared, followed by adding 6% of binder material. The alternative binders were cement, admixtures of pulverised blast-furnace slag with cement (proportions 1:1 and 7:3), or lime and blast-furnace slag alone. In total, 7,600 m of gravel road was built using these mixtures in various mutilayer pavement structures. Traffic loading of the road during a period of two years did not change its functional properties, and the highest bearing capacity was attained by that section of the road, where phosphogypsum mixed with blast-furnace slag and cement was used.

In Poland, studies on phosphogypsum utilisation have been conducted since the 1970's. They were focused mainly on the use of phosphogypsum in the manufacture of binders, construction materials and fillers. Research on the use of phosphogypsum in road engineering was conducted in the years 2007–2009 as part of a special project implemented by the Institute of Inorganic Chemistry in Gliwice (nowadays Fertilizers Research Institute, Inorganic Chemistry Division "IChN") in collaboration with the Road and Bridge Research Institute in Warsaw.

Phosphogypsum obtained during the wet process of orthophosphoric acid manufacture, consists mainly of hydrated calcium sulphate with contaminants, such as heavy metals, fluorine. High acidity of phosphogypsum precludes its application in road engineering (required pH is 6–9). 10% suspension of phosphogypsum has pH of about 2, what is the result of a presence of a small residues of orthophosphoric acid. It also increases the leachability of heavy metal compounds and fluorine compounds present in phosphogypsum. These drawbacks can be eliminated by immobilising effected by neutralising phosphogypsum. Neutralisation may be carried out by adding an alkaline material, e.g. fly ash, to phosphogypsum. Fly ash contains water soluble alkaline compounds, i.e. $Ca(OH)_2$, $Mg(OH)_2$, NaOH and KOH. As proved in geotechnical tests[6, 7], the properties of phosphogypsum neutralised with fly ash allow for its use only in the construction of bottom layers of road embankments. Addition to the mix of a binding material in the form of a stabilising binder and water and thickening thereof induces chemical reactions, that lead to solidification, which resembles the process of cement setting. The processes that occur have an effect on some physicochemical and geotechnical properties, such as bearing capacity, strength and resistance to frost upon addition of stabilising binders. The results of laboratory tests have proved the suitability of the mixes studied for their use in the construction of upper layers of road embankments and parking lot pavements. These results were verified on a real-world object, i.e. part of a parking lot constructed at the Institute's premises in Gliwice.

EXPERIMENTAL

The research project included preliminary studies, which covered all types of phosphogypsum produced in Poland during project duration, and principal studies, where two types of phosphogypsum were investigated: one produced at the GZNF "Fosfory", and the other stockpiled in the stack of the shut down Zakłady Chemiczne "Wizów" SA. The preliminary studies included geotechnical examination of phosphogypsum and selected ashes and establishing the component weight ratios of the mixes composed therefrom. The best results for the phosphogypsum - ash mixes in the proportions of 50:50 or 60:40 were obtained. In order to improve strength, binding agents in the form of cement CEM 32.5 or road binders: SILMENT CQ 25 or SOLITEX in the proportions from 4:100 to 8:100 respectively were added to the mixes.

Satisfying results were achieved when the binder was added to the phosphogypsum -ash mixes in the proportion of 6:100. The strengths of the mixes examined were sufficient to allow their use in the construction of upper layers of road embankments and sub-bases of pavements loaded light traffic.

The laboratory test results were verified in field tests on a part of a parking lot (30 m^2 surface area) made using phosphogypsum from the GZNF "Fosfory" ash from GDF SUEZ Energia Polska S.A. near Połaniec, and SILMENT CQ25 binder, blended in the proportion of 60:40:8.

Table 1. Chemical analysis of phosphogypsum from the GZNF "Fosfory"

Components	Content, % d.m.
phosphates ($P_2O_{5\ total}$)	1.24
phosphates ($P_2O_{5\ water}$)	0.44
calcium (CaO)	25.5
sulphates (SO_4)	53.3
fluorides (F)	1.06

d. m. – determined on dry matter basis

Table 2. Chemical analysis of ash from GDF SUEZ Energia Polska S.A.

Components	Content, % d.m.
silicates SiO_2	50.85
calcium CaO	3.08
calcium CaO_{free}	0.06
aluminates Al_2O_3	27.9
magnesium MgO	2.18
potassium K_2O	2.71
sodium Na_2O	0.75

d. m. – determined on dry matter basis

The basic constituents of the SILMENT CQ 25 binder include: SiO_2 – 40%, Al_2O_3 – 6%, Fe_2O_3 – 4%, CaO – 41%, MgO – 1%, SO_3 – 2.5% (manufacturer data).

The experimental parking lot pavement consisted of several layers of materials, the main layer comprising phosphogypsum-ash-binder mixture, separated from the remaining part of the parking lot with a waterproofing membrane. A perforated tube for sampling water effluent was inserted at the parking lot.

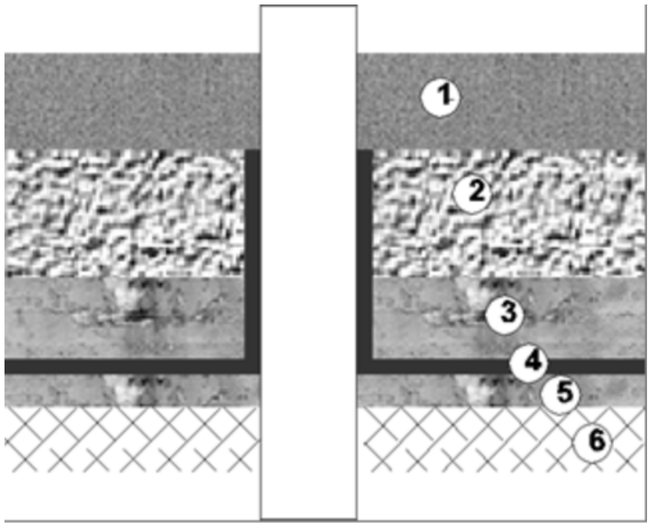

Figure 1. Layers of experimental parking lot pavement, 1 – slag pavement ~20 cm, 2 – ash-phosphogypsum base ~25 cm, 3 – filtration layer of sand ~10–15 cm, 4 – waterproofing membrane (road type), 5 – sand bed -5 cm, 6 – soil subgrade

The field tests included evaluation of the strength of the applied mix after a period of use and analysis of effluent sampled from the piezometer. Samples were cut out from the phosphogypsum-ash-binder layer of the parking lot base after 7 and after 16 months of trafficking. During that time the base was exposed to adverse weather conditions, particularly during the winter season. Cylindrical test samples (h=d=80 mm) were cut out for strength measurements. These samples were subjected to the action of destructive force on a testing press. The results were compared with those obtained in laboratory tests performed on cylindrical samples after a curing period. The conditions adopted for sample curing differed from those specified in the PN-S-06103 standard. The adopted curing times were longer: 180 and 360 days, with optimum humidity maintained and with no water access. During frost resistance tests, the cured samples were subjected to 14 freeze-thaw cycles within the temperature range of -20 to +20°C.

The environmental impact of the mixes was assessed by analysing contaminants in the water effluent collected in the piezometer. Effluent samples were analysed for the content of heavy metals, such as: barium, cadmium, chromium, copper, nickel, lead, molybdenum, zinc (optical emission spectrometry), arsenic (spectrophotometric method using silver diethyldithiocarbamate) and anions: chlorides (volumetric Volhard method), sulphates (gravimetric method using barium chloride), fluorides (potentiometric method using a fluoride electrode), phosphates (spectrophotometric method), total dissolved solids TDS (gravimetric method), and pH (electrometric method).

Besides required geotechnical and physicochemical properties, phosphogypsum designed for road construction must have their natural radioactivity level below the limit specified in The Regulation of the Council of Ministers of January 2007 on the requirements concerning the content of natural radioactive isotopes of potassium K-40, radium Ra-226, thorium Th-228 in raw materials and materials used in buildings designed to accommodate people and livestock, as well as in industrial waste used in construction industry, and the procedure for controlling the content of these isotopes (Dz.U. 2007.4.29). Natural radioactivity measurements were conducted by a certified laboratory using the method of comparative analysis of gamma radiation spectrum compliant with the procedure PB/ZO-OU/05 of 25.01.2007 and with the ITB (Building Research Institute) Instruction no. 234/2003 "Guidelines for measuring natural radioactivity of construction materials".

RESULTS AND DISCUSSION

The results of strength and frost resistance measurements obtained in field tests were much better than the laboratory test results (Table 3).

Table 3. Compressive strength comparison

Kind of investigations	Days	R (MPa)	R^{z-o} (MPa)
laboratory	180	1.26	0.38
	360	1.36	0.94
experimental parking	200	1.7	
	490	5.1	

where: R – strength expressed in MPa after *n* days of sample curing at room temperature under conditions protecting against moisture loss, R^{z-o} – strength expressed in MPa after *n* days of sample curing at room temperature under conditions protecting against moisture loss, 14 freeze – thaw cycles under optimum humidity conditions

The compressive strength measured in laboratory tests after 180 and 360 days of sample curing under conditions protecting against moisture loss and after 14 days of complete immersion in water (1.26 and 1.36 MPa, respectively) was comparable to the strength of a sample cut from the experimental parking lot base (1.7 MPa) after 200 days of its use. There was a much larger difference in strengths determined in frost resistance tests. Despite large temperature differences that occurred during the experiment duration (autumn-winter-spring season), frequent crossing of the freezing point and atmospheric precipitation, the strength measured was much higher than that determined in laboratory tests of frost resistance (0.38 MPa). The subsequent winter-spring season has not caused strength reduction. In fact it was quite the opposite: after 490 days the strength increased to 5.1 MPa, which was exactly 3 times more than the strength measured after 200 days of using the parking lot.

The environmental impact of the mixes used for the construction of the experimental parking lot was assessed by analysing contaminants in the water effluent. The presence of contaminants resulted from the leaching of water soluble substances by precipitation water not only from the layer that contained phosphogypsum, but also from other materials used for the construction of the parking lot. The analysis results of the contaminants monitored indicated that limits specified in Annex no. 1 to Regulation of the Minister of Environment of 28 January 2009 on the conditions of discharging wastewater to waters and soil and on substances particularly harmful to the environment, were exceeded only for chromium, sulphates and pH values (Dz.U. 2009.27.169).

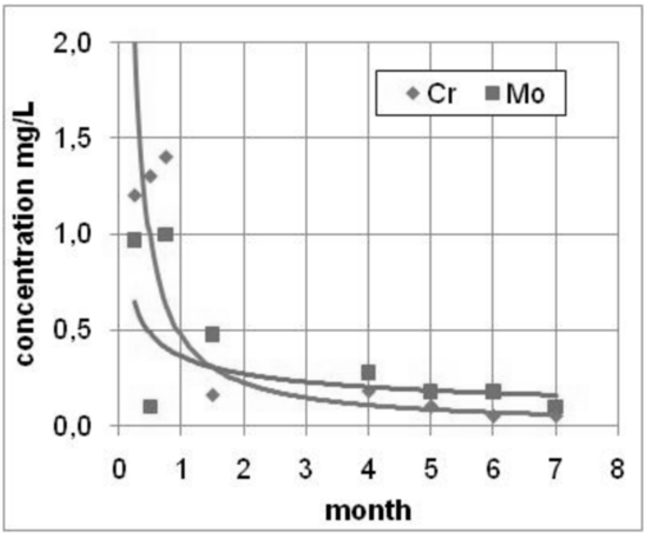

Figure 2. Change of chromium and molybdenum concentration in effluent

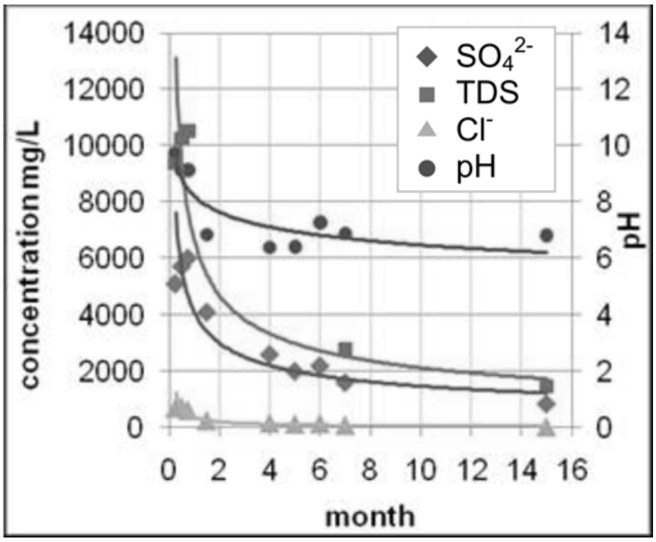

Figure 3. Change of sulphate and chloride concentration, pH and TDS in effluent

The excessive chromium concentration (limit exceeded by 0.9 mg/L) and excessive alkalinity (pH limit exceeded by 0.75) observed during the initial period of monitoring, receded in the fourth week: chromium concentration and pH fell below the maximum permissible limit. The exceedance of the limits was probably caused by the fact that neutralisation of mixture components was incomplete and the curing reactions were still proceeding and the products thereof have not formed a sufficiently compact structure, the evidence of which was also the low strength of the mix determined in laboratory tests after 14 days of curing.

Of all the contaminants monitored during experiment duration, only the concentration of sulphates exceeded the limit (500 mg/L) specified in the Ordinance. Similar results were obtained in laboratory tests, which is related to the solubility of calcium sulphate (1600 mg SO_4^{2-}/L). The high concentration of sulphates (above 5100 mg/L) observed during the initial six weeks, was much higher than the solubility value. After 6 months of the experiment duration the concentration of sulphates in the effluent collected decreased to a value corresponding to calcium sulphate solubility in the water. The increased solubility of calcium sulphate was due to the presence of other water-soluble salts, which affected the thermodynamic equilibrium – a well-known phenomenon[8, 9]. According to the studies described in the literature, calcium sulphate solubility is affected not only by temperature change and total dissolved solids (TDS), but also by the nature of ions present. The effect of chlorides, notably of sodium and magnesium chlorides, is particularly profound. The concentration of sulphates in eluates obtained in leachability tests of the mixes carried out in laboratory did not exceed the value of calcium sulphate solubility, the reason of this being the low concentration of chlorides in mix components used and the high dilution of the eluate (1 kg of mixture in 10 L of water). Higher concentration of chlorides in effluent determined during field tests was caused mainly by much lower quantities of the water (atmospheric precipitation). With the decrease in chloride concentration in the effluents analysed from 700 mg/L to less than 10 mg/L, and decrease in TDS from 10500 mg/L to 1460 mg/L, the concentration of sulphates also decreased from 6000 to 1600 mg/L.

The high concentration of sulphates in the effluent formed under direct action of water may be an issue when using phosphogypsum-based mixes in road construction on an industrial scale. However, it must be remembered, that these mixes will not be exposed to the direct impact of atmospheric precipitation. The inclusion thereof in the form of road embankments reduces water contact with them. It is not the only material used for road embankment construction, and the effluent removed therefrom by the drainage system contains precipitation water from the road surface, road shoulder, seen over slopes and partly from earthen structures. Therefore, when assessing the mixes from the environmental point of view, the actual concentration of sulphates occurring when phosphogypsum is used, should be taken into account.

The measurements of natural radioactivity of the mix used for the construction of the parking lot and of the material cut out from the parking lot pavement after 7 months, showed that radioactivity was below the permissible threshold and that there were no contraindications for using these composites for: road construction, building of upper and lower layers of embankments[6]. The obtained results are shown in the table below. Values of active indexes f_1 and f_2 have been determined in accordance with equations set out in regulation (Dz.U. 2007.4.29).

$$f_1 = \frac{S_K}{3000\ \text{Bq/kg}} + \frac{S_{Ra}}{300\ \text{Bq/kg}} + \frac{S_{Th}}{200\ \text{Bq/kg}}$$

$$f_2 = S_{Ra}$$

In conformity with the national regulations, industrial wastes with values of indices: f_1<4,2 and f_2<1200 Bq/kg can be used in the buildings situated on the ground foreseen for development in the local site planning and in the underground parts. During the construction of the roads, the absorbed dose rate at the rate of 1m over the surface area, could not exceed the value of 0.3 μGy/h in particular by laying and additional layer of some other material.

CONCLUSIONS

Field tests performed on a separated part of a parking lot have fully confirmed the suitability of three-component phosphogypsum-ash-binder mixes for use in road construction, both in terms of geotechnical and physicochemical parameters.

The geotechnical and strength tests carried out in laboratory also indicate that these mixes (composites) can be used in the construction of upper layers of road embankments and sub-bases of pavements loaded light traffic, that they meet the requirements set of required construction standards for mixes included in the upper layers of road embankments and sub-bases of pavements loaded light traffic, whereas phosphogypsum-ash mixes with no binder added can be used in the construction of lower layers of road embankments, because they meet the requirements set for materials for the construction of road embankments below the frost penetration zone.

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Table 4. Compressive strength comparison

Exploitation time [months]	Radioactive concentrations of isotopes „S" Bq/kg			Activity indices		Dose rate μGy/h
	K-40	Ra-226	Th-228	f_1	f_2 [Bq/kg]	
0	305.72±44.82	614.67±33.60	45.22±4.07	2.35	614.67	0.343
7	264.64±83.23	554.55±38.82	42.80±6.71	2.13	554.55	0.314
National regulations				< 4.2	< 1200	

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