Influence of Mineral Additives on the Technological Properties of Sealing Slurries for Geoengineering Works.

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Vplyv minerálnych prísad na technologické vlastnosti tesniacich zmesív pre geoinžinierske práce

One of the most important factors influencing the efficiency of sealing and reinforcing the ground and rock mass with geoengineering methods is a proper selection of respective technological parameters in view of existing hydrogeological and geotechnical conditions.

Selected mineral additives increase the sealing properties of fresh and set slurries. They also decrease the cost of the slurry, provide a method for utilizing the stored materials (additives), and consequently, lessen the risk of environmental pollution.

The results of laboratory tests on the influence of selected mineral additives on technological properties of sealing slurries are presented in the paper.

Key words: *Mineral Additives, Sealing Slurries, technological properties*

Introduction

With the development of cementing technology applied for sealing casing and reservoir horizons, as well as for geoengineering works, a number of new difficulties is encountered, for which new recipes are being worked out.

Slurries by no means can be selected at random or as a result of incomplete laboratory analyses. Correct cementing operations precondition further drilling works, and so a good operation and exploitation of the well.

For sealing and reinforcing ground and rock mass as well as for cementing of casing special cements are used. Their activity, technological and strength parameters should be adjusted to extreme geological conditions and resistant to the aggressive influence of formation fluids.

A proper selection of hydraulic binders should ensure that the produced sealing slurry has the following properties, e.g. [5]:

- proper rheological parameters,
- strictly defined consistency after making,
- complex time of re-pumpability,
- proper time of bonding and setting,
- good co-operation with sealed medium of varying lithology, including clayey-type minerals,
- minimal expansion of changes of the set slurry volume,
- high resistance to highly mineralized formation waters,
- low sedimentation and low filtration,
- relatively low cost in reference to the purpose it should perform in the sealed rock mass.

The meeting of these requirements is very important for obtaining an efficient sealing effect of ground and rock mass. On the other hand, the specific conditions in the rock mass should give a priority to some parameters, even at expense of others.

Laboratory experiments on determining the influence of some mineral additives on technological properties of fresh and set cement slurries are made to increase the efficiency of sealing operations on the ground and the rock mass.

Cement additives

Sealing slurries based on the Portland cement have a number of disadvantages, e.g.: a long time of bonding and bad rheological properties. However, they can be significantly improved by mineral additives.

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The additives can be classified as follows [1, 2, 4]:
- hydraulic materials,
- puzzolana materials,
- filling material.

Among the hydraulic materials prevail ground blast-furnace granulated slags. Activated, they bond and set under water, similar to the Portland cement. In reaction with water, the same phases are produced as in the case of Portland cement. The following activators can be used:
- basic compounds, e.g. $Ca(OH)_2$, NaOH, Na_2SiO_3,
- weakly acidic materials: $CaSO_4$, $Al_2(SO_4)_3$,
- physically acidic factors: $CaSO_4$, $Al_2(SO_4)_3$.

The basic physical component of set ground blast-furnace granulated slag slurry of CSH. Moreover, lower quantities of Portland cement and hydrated calcium aluminate which are resistant to the chemical corrosion are present. A new phase also appears, i.e. hydrogelena (C_2ASH_8), which increases the resistance to the chemical corrosion. The morphology of hydration products has an influence on the pore structure: the number of gel pores increases and the number of capillary pores decreases [4, 5].

One of puzzolana additives is active silica, which reacts with calcium hydroxide in water conditions at the room temperature. In the course of this reaction, compounds having hydraulic properties are produced. Opposite to blast-furnace slags, puzzolana materials contain small quantities of calcium. Therefore, to have them set, an admixture of Ca(OH)2 or cement are needed for separating calcium hydroxide in the course of hydrolysis.

Natural puzzolana additives can be found in rocks:
- volcanic,
- organic.

The first group consists of pyroclastic rocks forming loose sediments or compact rocks, formed in the course of diagenetic cementation processes. Pyroclastic rocks are acidic and contain much glass or zeolites. They have puzzolana properties. Glasses, opal forms of silica and zeolites are active components of the natural puzzolana reactive with calcium hydroxide. Puzzolana also contain variable amounts of neutral material, e.g. crystalline phases: quartz, feldspar, dolomite, magnetite, pyroxene, calcite. The natural puzzolana may also contain components hazardous for the fresh and set slurry, e.g. the organic matter and swelling clays (montmorillonite).

Fly ashes and the silica dust are very important additives of the artificial puzzolana group.

The grain composition of ashes varies, and their specific surface area ranges between 2000 and 4500 $cm^2 g^{-1}$

The puzzolana properties are connected with the glass phase. Its increased content and fineness in ashes improve the puzzolana properties. The high quality of ashes is determined by:
- low carbon content,
- high glass content,
- low alkalies content,
- fineness.

The higher is the degree of comminution of coal combusted in furnaces, the higher is the glass content in the ashes and finer are the grains (and thus, the better are the puzzolana properties!),. However, the ash properties may considerably vary, even for the same coal.

The introduction of fly ashes in to the cement modifies a number of its properties. The bonding time of ash cement is much longer than for the Portland cement. The scale of time elongation increases with the quantity of admixed fly ash.. It should be stressed that the bonding time is also significantly influenced by the temperature of bonding and setting.

The strength of the fly ash-based cement increases slowly at the initial stage of setting. This is connected with the relatively slow puzzolana reaction and its influence on the mechanical properties of the set cements. During a long time of maturation, the strength of ash-based cement exceeds the compressive strength of Portland cement of the same strength category.

The period of low increase of compressive strength of ash-based cement at the initial stage of setting is accompanied by the moderate kinetics of heat generation in the process of bonding and setting. Among the properties of fly ash-based cements are also a high resistance to the chemical corrosion, a high water-tightness and a limited shrinkability [1, 2, 3] .

Silica dust is generated during the production of metallic silicon or silicon and iron alloys (ferrosilicon) and other metals in arc furnaces. Owing to a large specific surface (7000 cm^2/g) and glass content, silica ashes have good puzzolana properties. Of great importance is the form of dust grains, i.e. glass balls 0.1 to 0.2 mm in size. They can be easily agglomerated, when the power energy of mixing is employed. In these conditions the balls are evenly distributed among the cement grains and play the role of a fillers. Moreover, as a result of a high puzzolana activity, the reaction with calcium can be observed after one day. The increase in the strength of the set slurry with fly ashes as ashes admixture is observed after ten days, and a favourable content is 5 to 15 %.

Owing to their physical properties and a considerable comminution, the fillers are used for improving the managability and the consistency of the slurry, increasing the content, and so lowering the permeability of the set slurry, mainly through decreasing the number of capillary pores, lowering the trend of the microcracks formation. It should be born in mind that fillers are not all neutral, and their influence on the properties of a slurry can be reduced to three mechanisms:

- the filler causes dispersion of klinker nuclei and filling free spaces between them,
- expitaxial influence on crystallization of CSH,
- chemical reaction with aluminates and production of hydrated aluminate-carbonates.

Geopolymer slurries

Goepolymer slurries are exclusively based on inorganic components. They are obtained by modifying prepared slurries based on common multicomponent cements or granulated furnace-slag slurries with puzzolana additives [3, 5, 6].

Among artificial puzzolana materials are also dehydrated clayey minerals. They acquire puzzolana properties in the course of thermal activation. Among all minerals, the properties and structure of kaolinite is best recognized. After roasting kaolinite at 450 ÷ 700°C, a highly reactive metakalinite is obtained. It has puzzolana properties. Metakaolinite in the slag-alkaline slurries significantly modifies the microstructure and texture of set geopolymer slags [1, 7].

The metakaolinite admixture of the slag-alkaline binder modifies its chemical composition, increasing the aluminium content. Among the slag binder hydration products no free $Al(OH)_3$ is observed; however, most of Al^{3+} is present in CSH. The capability of gel CSH to admit aluminium ions increases with the decreasing molar ratio C/S. A crystalline product formed after 90 days of maturation processes is $CaAl_2Si_2O_8 \cdot 4H_2O$, known as gismondite. Being a zeolite and having a considerable immobilization potential, gismondite is very important in hydration processes. This material can be used for stopping ions, the size of which does not exceed that of water molecules.

Apart from the phase composition, metakolinite in the slag-alkaline binder also modifies the microstructure of hydration products, which modifies the strength parameters of the set slurries. Then, the porosity lowers the structure changes and the number of gel pores increases. As a result, the set slurries reveal an increased resistance to the chemical corrosion as well as a higher initial and end strengths [1, 2].

Conclusions

Mineral additives significantly influence technological parameters of fresh and set sealing slurries.
Selection of type and concentration of sealing slurry additives depends on geological-technical conditions in which sealing and reinforcement operations are performed on the ground and rock mass.
Geopolymer slurries based on ground blast-furnace slag grains and properly selected puzzolana additives show a number of useful properties, e.g. proper rheological parameters as well as a resistance to the physical and the chemical corrosion.

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