# GEOPOLYMER MATERIALS BASED ON MAGNESIA-IRON SLAGS FOR NORMALIZATION AND STORAGE OF RADIOACTIVE WASTES

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UDC 541.183:621.311

The development of safe and ecologically clean systems for handling radioactive wastes predetermines the sustained stability of geoecocenology.

The measures adopted in the nuclear power industry for improving the safety of nuclear power plants have produced conditions for developing nuclear power in the future. The Kola Peninsula lies in a territory of active use of atomic energy, which results in accumulation of liquid and solid radioactive wastes, requiring processing and utilization, in the Murmansk region. These problems can and must be effectively solved taking account of the specific nature of the region. The Kola region is rich in mineral resources and wastes from mining, which can serve as material for producing and obtaining cheap sorption-active and self-hardening compositions for storing radioactive substances.

Experience in preparing and handling radioactive wastes at nuclear power plants and other industrial plants associated with radioactive substances has shown that the most promising methods of immobilization and storage of liquid wastes is sorption on a solid-state adsorbent, sealing of the spent adsorbents in concrete blocks followed by vitrification and storage in underground or underwater repositories [1-5]. The subsequent arrangement of the spent adsorbents, elimination of contact with the surrounding medium or storage, impose definite requirements on the adsorbents:

the radionuclides must form with the adsorbent matrix insoluble stable compounds which guarantee that the adsorbents are radiochemically stable in the immobilization medium without secondary contamination;

the technical products must be convenient for subsequent operations: it must be possible to produce parts and blocks and to ensure shielding from radionuclides contained in the blocks formed;

the adsorbents must be cheap and the technology must be simple.

In turn, stringent requirements are imposed on the solidifying compositions (binder materials), which in geological formations contain the spent adsorbents:

stability of binders with respect to mineralizing solutions and brines in a wide range of pH and eH;

resistance to disintegration;

low micro- and mesoporosity;

closeness of the chemical and mineral compositions to that of the surrounding rock;

low coefficient of diffusion of ground-water components in the binder medium;

ability to strengthen the structure of the binder as a result of interaction of its components with the components of the geological immobilization medium; and,

radiation resistance of the mineral forms of the binder.

These requirements can be met by synthesizing technological materials using the technology of solidifying mineral dispersions (SMD materials) based on polymineral alumosilicate raw material [6-9]. These materials are based on the concept of synthesis of coagulation–condensation solidification structures in highly concentrated mineral dispersions. A highly concentrated mineral dispersion is a multiphase system containing a dispersed phase and a dispersion medium, which can interact with the formation of condensed phases and can self-harden. Such hardening mineral dispersions have found applications for synthesis of some technical materials: adsorbents and cements.

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Translated from Atomnaya Énergiya, Vol. 85, No. 1, pp. 78-82, July, 1998. Original article submitted May 29, 1998.


1063-4258/98/8501-0510$20.00 

TABLE 1. Sorption of Radioactive Isotopes from Model Solutions on Geopolymer Slag/alkaline Absorbents

| Purification factor | Number of volumes passed | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 27 | 80 | 134 | 187 | 241 | 295 | 349 | 1000 |
| Ruthenium | 2,6 | 2,5 | 2,4 | 2,4 | 2,4 | 2,2 | 2,2 | 2,2 |
| $^{137}Cs$ | 1800 | 1200 | 1000 | 800 | 600 | 500 | 450 | 350 |
| $^{60}Co$ | 2400 | 2400 | 2400 | 2400 | 2400 | 2400 | 2400 | 2400 |

TABLE 2. $^{137}Cs$ Desorption by Water as a Function of the Content Time of the Phases

| Eluate | Initial content in adsorbent, mg/g | Content time of the phases, h | Residual content in adsorbent, mg/g | Degree of stability, % |
|---|---|---|---|---|
| Water | 33 | 0,16 | 33 | 100 |
| | | 6 | 32,9 | 99,7 |
| | | 30 | 32 | 97 |

The possibility of obtaining and using multifunctional geopolymer SMD materials are due to the following:

the existence of sorption activity for products of solidification of a composition as a result of hydrate water bound with covalent and hydrogen bonds;

formation of insoluble compounds between the components of the solution being purified and the SMD materials;

strength of the structures determined by the dimensions of the initial particles of the mineral phase and the number of binding contacts per unit surface area;

stability of SMD materials in geocenology as a result of the closeness of the composition of the products of new formations, represented by layered and framework alumosilicates, hydroxides of iron, aluminum, silicon, with final products of wind erosion of most rocks:

| **Neogenesis** | **Products of metamorphism of rocks** |
|---|---|
| Silicon gel | Silicon gel |
| Alumosilicon gel | Alumosilicon gel |
| Iron hydroxides | Quartz |
| Aluminum hydroxides | Aluminum oxide |
| Metal oxyhydrosols | Iron, aluminum hydroxides |
| Swelling clay materials | Swelling clay materials |
| Metal hydrosilicates | Micas, garnets |
| Garnets, zeolites | Zeolites |

These properties make it possible to remove, in an ecologically clean manner, spent SMD adsorbents in formed parts from concrete based on geopolymer SMD binder, whose mineral and geochemical composition is analogous to that of the adsorbent being stored. The solid products are characterized by high resistance to wind erosion during epigenesis processes. The possibility of using mineral components of a local geoecosystem as the dispersed phase permits approaching to the maximum degree possible wind-erosion-resistant solid rocks of adsorbents.

One such solidifying mineral dispersion is a system based on magnesia–iron slag from the combine "Pechenganikel'" in the Murmansk region. The technology for obtaining slag-alkaline geopolymer SMD materials — adsorbents and binders — has been investigated [6-9].

Granular slags of ore-thermal and depleted charges of the combine "Pechenganikel'" are externally black sands with dense, shiny grains of irregular shape. The grain sizes do not exceed 5 mm, the main size being 0.6-3 mm. The density of slag is 3.12-3.24 g/cm$^3$, and the volume mass is 1.65-1.7 g/cm$^3$. The compounds $SiO_2$, FeO, MgO, and $Al_2O_3$ predominate in the chemical composition of the slag. In a period of several years the chemical composition of the slag fluctuates in a narrow range (mass %): $SiO_2$ 39–42, $Al_2O_3$ 7–9, FeO 32–35, CaO 2–3, MgO 6–8, S 0.6–0.8, $R_2O$ 1.6–1.7.

Slag glass can hydrate when the slag is granulated and processed with steam. It breaks up when processed with dilute solutions of hydrochloric and sulfuric acids and NaOH. It almost does not break up in $Na_2CO_3$ and water. On leaching with NaOH and heating, $SiO_2$, $Al_2O_3$, and other components leach out of the slags into solution. Slag glass breaks down when a mixture of finely ground slag and water or alkali is boiled for three hours.

Investigations show that as a result of selective dissolution of the ingredients of the glass-forming magnesia–iron alumosilicate (slag) in water solutions of alkali silicate, accompanied by transfer of silicon, aluminum, and iron into solution, adsorption-active compounds are synthesized: the clay mineral nontronite, limonite, zeolite, and some amorphous products. The polymineral composition of the phases formed predetermines the physicochemical and physicomechanical properties of the geopolymer binding adsorbents: high adsorption capacity, low porosity, high density and operating properties in corrosive media. The polymineral composition of the products of solidification of slag-alkaline geopolymer materials gives it polyfunctional properties as an adsorbent. The mechanism of adsorption of cations is determined by ion exchange and chemisorption due to formation of insoluble compounds. The adsorption properties are realized in full in the process of adsorption in a dynamical regime. The linear filtration rate of the solution being purified is 4-5 m/h, and the adsorbent-solution contact time is not less than 20 min at temperatures ranging from 0 to 50°C. The maximum sorption capacity of a geopolymer slag-alkaline SMD material with respect to cations is as follows:

| | mg·equiv/g | mg/g | mg/liter |
|---|---|---|---|
| Cs | 0,8 | 106,3 | 180,7 |
| Ca | 2,1 | 84,2 | 143,1 |
| Sr | 2 | 183,9 | 312,6 |
| Ni | 1,1 | 64,6 | 100,8 |
| Cu | 1,2 | 76,2 | 129,5 |
| Co | 1,1 | 64,8 | 110,2 |
| Fe | 1,6 | 89,3 | 151,8 |

The high efficiency of a geopolymer slag-alkaline SMD material has been noted in the process of removing radionuclides from multicomponent solutions. Sorption was performed in a dynamical regime with a linear filtration rate of the solution through the column of 6 m/h. In the investigations, three types of solutions simulating plant runoff were used (g/liter): 1) potassium bicarbonate 1, potassium nitrate 2.54, calcium nitrate 0.654, ruthenium 0.002, pH 4.06; 2) hexametaphosphate 1.17, sulfunol 0.5, sodium oxylate 2.48, cesium 0.004, pH 6.2; 3) potassium bicarbonate, cobalt 0.006, pH 5.5, the activity of the solution was 20 mBq/liter. The solution was analyzed before and after the column in an apparatus with a scintillation counter based on a NaI(Tl) crystal, which gave a counting rate of 350 counts/sec·ml and a statistical accuracy of measurement with relatively low exposure (100-300 sec) (Table 1).

To determine the degree of retainment of radionuclides in the sorbent matrix (ratio of material passed from sorbent into solution to the initial content), the desorption of $^{137}Cs$ from an adsorbent saturated with this cation by distilled water was studied. Desorption was conducted under static conditions with a solid-solution phase ratio of 1:100 and contact time ranging from 10 min up to 30 h (Table 2).

The adsorbents, saturated with radioactivity components, are used as fine-grain fill for concrete based on slag alkaline cement with composition similar to that of the adsorbent. We present the technical characteristics of alkaline-slag geopolymer cements. The physicotechnical properties of the geopolymer alkaline-slag adsorbents — binders and materials based on them — were determined in accordance with Russian law.

**Strength.** Geopolymer cement is a fast-hardening hydraulic binding material, capable of solidifying under normal conditions (20 ± 2°C), at low temperature (4°C), and under conditions of hydrothermal processing. The binder has a coupling strength with a steel armature of 5.08 MPa. The properties of the fine-grain concrete with normal solidification based on geopolymer cement of optimal composition (1:1) with a fill consisting of granular slag from the combine "Pechenganikel'" are as follows:

| | |
|---|---|
| Maximum strength, MPa: | |
| under compression | 80 |
| bending | 9 |
| tension | 4 |
| Dynamical elastic modulus, MPa | $3.5 \cdot 10^4$ |
| Bulk mass, kg/m$^3$ | 2700 |
| Cold resistance, number of cycles: | |
| laboratory tests | 300 |
| natural conditions | 1000 |
| Sulfate resistance, % | 100 |
| Water resistance during solidification in flowing water | 70 |
| Water impermeability, gauge atmospheres | 8 |
| Abradability, cm/(kg/cm$^2$·km) | 1.4 |
| Linear deformation, %: | |
| in dry air | −0.06 |
| at 95-100% humidity | −0.01 |
| in water | 03 |
| Working temperature of heat-resistant concrete, °C | 800 |
| Heat resistance at 800°C, number of cycles | 20 |
| Coefficient: | |
| linear expansion, 1/°C: | |
| at 20-300 | $0.82 \cdot 10^{-5}$ |
| at 20-60 | $0.67 \cdot 10^{-5}$ |
| thermal activity, kcal/(m·°C·h): | |
| wet concrete | 1.29 |
| dried at 150°C | 0.8 |
| diffusivity, m$^2$/h | $1.22 \cdot 10^{-7}$ |

**Cold Resistance.** The resistance of geopolymer cement to alternating freezing and thawing turned out to be high — 300 cycles, and in tests performed under natural conditions and sea water its resistance exceeded 1000 cycles.

**Water Impermeability.** Concrete based on 1:1 geopolymer cement, hardening in a wet medium, in water and under hydrothermal conditions corresponds to V-8 grade, which permits operation under conditions of hydrotechnical construction.

**Linear Deformation.** For samples solidifying in water, the linear deformation is 0.15% and for an autoclave sample the deformation is 0.19%.

Bench tests of geopolymer cement subjected to the corrosive action of sea water in a tidal zone, alternating freezing and thawing twice a day during the winter, alternating drying and wetting during the summer, and leaching and mechanical loads, showed high operating and technical properties. After 736 cycles of alternating freezing and thawing its strength increased to 106% under compression and 137% under bending. The dynamical elastic modulus increased to 141% compared with its monthly age. The samples retained their shape well. No indications of breakdown were found.

Geopolymer cement samples have a maximum rating of 10, concrete based on portland cement and puzzolana portland cement have ratings of only 5-6. Concrete based on geopolymer cement is noncorrodible in sea water and is recommended for use in systems for mobilizing radionuclides, including in strongly mineralized media.

**Heat Resistance.** Geopolymer cement with a composition of 1:1 is heat resistant at temperatures up to 800°C and is recommended for producing vitrified materials containing immobilized radionuclides.

**Acid Resistance.** The dispersed part of such concrete contains 90% magnesia−iron glass, which is a class 3 acid-resistant material. The products of solidification-neogenesis not only make the structure of the concrete more dense, but they increase the acid resistance. Concrete with a composition of 1:1 (ground slag, pulverized slag) remains stable when boiled in a solution of sulfuric acid with a density of 1.84 and a mixture of 89% $HNO_3$ and 7.5% $H_2SO_4$, it retains 95-96% of its mass and is acid-resistant. Resistance in hot (95-100°C) solutions of boric acid and alkaline solutions is 98-100%. It withstands heat cycling at 250-300°C for 1000 h with no change in compressive strength.

In summary, the adsorption and physicotechnical properties of geopolymer slag-alkaline SMD materials make it possible to recommend them for radiation-shielding barriers, immobilization and storage of liquid and solid radioactive wastes, instead of the currently used technology employing ion-exchange resins and high-grade aluminate portland cement.

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## OBTUARY

Vadim Pavlovich Mashkovich died suddenly at the age of 67 on July 16, 1998. He was a State prize laureate, Doctor of Engineering Sciences, Professor at the Moscow Engineering Physics Institute, well-known scientist in this country and abroad, author of more than 250 scientific works. A large number of works were published in our journal. Vadim Pavlovich was an irreplaceable organizer of all-union conferences on radiation protection, founder of a scientific school which prepared about twenty Candidates of Science. We express our deep sympathy to his family and close friends.