

MAGNESIUM IMMOBILIZATION MATRICES FOR LRW OF A COMPLEX CHEMICAL COMPOSITION

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The article considers magnesium matrix material that can be applied to immobilize liquid radioactive waste of a complex chemical composition. This material allows to contain high concentrations of radioactive salts in the solidified compound, which is provided by the use of certain salts contained in the liquid radioactive waste during magnesium binder mixing. The paper also considers the incorporation of organic compounds into the solidified compound.

Keywords: *radioactive waste, liquid radioactive waste, magnesium matrices, mixing liquid, still residue, degree of filling.*

To date, cementation has been considered a widely used industrial method providing low- and intermediate-level LRW immobilization with Portland cement introduced as a main binder consisting of tri- and dicalcium silicates, calcium aluminoferrites and tricalcium aluminate.

Cementation method is quite simple, well proven, and Portland cement is massively produced by the industry. However, this method has a number of important disadvantages with the key one seen in a relatively low degree of salt and organics inclusion and the presence of unbound water in the solidified compound. Due to a low filling degree with radioactive salts and organics, the volume of secondary solidified waste subject to disposal increases significantly as compared to the initial LRW volume.

To improve the immobilization efficiency in case of complex chemical LRW composition, magnesia materials are proposed instead of Portland cement: the binder is MgO and the mixing liquid are aqueous solutions of magnesium salts ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, etc.); the highest

strength is typical for compounds mixed with 30% solution of magnesium chloride $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (bischofite). Aqueous solutions of aluminum and zirconium hydrochlorides can be also used as a mixing liquid for magnesia binders [1].

The use of various mixing fluids can massively change the properties of the resulting composites. In this case, oxo-chlorides, oxosulfates, oxophosphates and other magnesium oxosalts are formed, which are stable compounds with large amounts of chemically bound water having different physical and chemical properties. For example, application of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution results in a compound with low hygroscopicity, whereas the application of H_3PO_4 provides a dramatic increase in the heat resistance and water resistance of the compound.

Various mineral and/or organic substances can be used as fillers to produce solid compounds. Application of various sealers and fillers results in a wide variety of materials, which, due to their composite structure, may have a number of favorable characteristics.

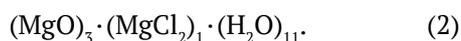
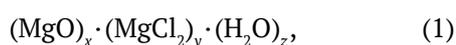
The main properties of magnesia compounds can be summarized as follows:

- long-term high mechanical strength;
- high adhesion to mineral and organic substances providing their compatibility with LRW components and a high degree of compound filling with waste;
- high thermal and frost resistance;
- low thermal expansion factor;
- resistance to radiation damage;
- resistance to bacteria and microorganisms;
- high chemical resistance to salts, alkalis, oils, organic solvents;
- high moisture resistance and water resistance;
- high content of chemically bound water ~ 40%.

Due to these properties, the use of magnesia matrix material for liquid radioactive and/or chemical waste immobilization purposes allows to include substances of various chemical compositions into magnesia compounds while meeting the regulatory requirements (GOST R 51883-2002, NP-019-15) set forth for solidified waste [2]

Caustic magnesite powders PMK-75, PMK-82, PMK-87, PMK-90 (GOST 1216-87), which differ in the magnesium oxide content, are used as magnesia binders. Bischofite is a natural mineral, whose deposits vary in its content. In the chemical industry, petrochemistry and other industries, technical bischofite purified from impurities is used according to GOST R 55067-2012.

During mixture hardening, a very dense polymeric inorganic substance is formed after a few hours — hydrated magnesium oxychloride (1), whereas, the material (2) has the highest strength:



It should be noted that the stability of the resulting compound depends on the MgO/MgCl₂ ratio with 4/1 seen as the optimal one (Table 1).

Table 1. Dependence of compound stability on MgO/MgCl₂ ratio

Nº	MgO	MgCl ₂	MgO/MgCl ₂	Sample stability
1	8.0	4.0	2/1	Fell apart after 1 day
2	8.6	3.4	2.5/1	Fell apart after 3 days
3	9.0	3.0	3/1	Lots of cracks
4	9.4	2.7	3.5/1	Separate cracks
5	9.6	2.4	4/1	Durable, no cracks

To produce magnesia compound, which was done to determine its characteristics, the following materials were used:

- binder — caustic magnesite powder PMK-82;
- mixing liquid — 30% bischofite solution;
- mineral filler — ash, metallurgical slag, etc.;
- catalytic additives-regulators.

Figure 1 presents magnesia compound specimens with their main characteristics given in Table 2.



Figure 1. Samples of magnesia compound

Table 2. Basic parameters of magnesia compound

Nº	Parameter	Value
1	Mechanical compressive strength, MPa (corresponds to concrete grade B60)	65 MPa
2	Radiation resistance (decrease in mechanical strength due to absorbed radiation dose of 10 ⁶ Gy)	5.7%
3	Water resistance (corresponds to the concrete grade W16)	Less than 1.6 MPa
4	Frost resistance (decrease in mechanical strength after being exposed to a temperature of -50 °C)	4%

The efficiency of magnesia matrix material application for LRW immobilization purposes is based on a process method [3] described below. In contrast to cementation method, when LRW is introduced into a cement paste, not a magnesium chloride solution, but a solid crystalline hydrate MgCl₂·6H₂O is used to form the mixing agent. Therefore, to produce the mixing liquid, water available in the LRW can be used as well as the crystallization water of the crystalline hydrate. For this reason, an increased content of radioactive salts and organic substances present in the waste is found in the hardened magnesia compound.

Various LRW streams contain chlorides, sulfates, phosphates and other compounds affecting the compound properties. As an example, Table 3 shows chemical composition of bottom residues from RBMK-1000 reactor units and the special laundry of the FSUE FEO's Leningrad Branch (North-Western department). If a magnesian matrix material is used to immobilize LRW of a complex chemical composition, the waste components are considered as additional mixing liquid and are included into the polymer structure of the compound, which also

increases its filling degree and reduces the volume of secondary solid radioactive waste (SRW) subject to disposal.

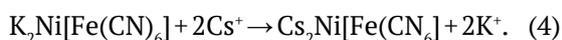
Table 3. Chemical composition of some LRW

Component	Contained substance	Concentration of the substance, g/l	
		BS from RBMK-1000	BS from special laundry
NH ₃	NH ₄ NO ₃	0.38	0.23
Fe ³⁺	FeCl ₃ ·6H ₂ O	0.39	–
Cl ⁻	NaCl	79.13	10.06
NO ₃ ⁻	NaNO ₃	212.47	2.06
SO ₄ ²⁻	Na ₂ SO ₄ ·10H ₂ O	60.37	23.48
PO ₄ ³⁻	Na ₃ PO ₄	5.40	1.88
SiO ₃ ²⁻	Na ₂ SiO ₃ ·9H ₂ O	40.11	1.61
C ₂ O ₄ ²⁻	Na ₂ C ₂ O ₄	1.37	1,203
CO ₃ ²⁻	Na ₂ CO ₃	–	116.60
SAS		1.00	1.2
Na(OH)	NaOH	0.4	0.004

Also, due to the bactericidal action of magnesium chloride compositions, organic fillers do not rot and do not decompose with gas releases, and therefore the solidified LRW meets the regulatory requirements (NP-019-15).

Adequate composition of magnesia compositions and appropriate physical, chemical and mechanical characteristics are provided through the use of various additives. Magnesia binder is fast-hardening: the setting starts in ~20 minutes after magnesia paste formation and ends no later than in two hours. Sufficient durability of magnesia mixture during its formation is maintained via setting retarders (tartaric, citric acid, etc.) introduced at a dosage of 0.01–0.2 % by binder weight.

Magnesia compositions cannot sorb cesium; therefore, to immobilize ¹³⁷Cs, it is necessary to introduce potassium ferrocyanide (K₄[Fe(CN)₆]) and nickel nitrate (Ni(NO₃)₂) solutions during their formation, which, upon being mixed according to reaction (3), form a sparingly soluble compound, nickel-potassium ferrocyanide (K₂Ni[Fe(CN)₆]) considered an effective selective cesium sorbent (reaction 4):



The complex salt Cs₂Ni[Fe(CN)₆] is insoluble in aqueous media at pH < 10; therefore, at all stages of compound formation, pH level should be monitored, and if pH level exceeds 10, hydrochloric

acid should be introduced into the mixture until pH is leveled to ~9–9.7. In the process of such mixture hardening, a polymer structure is formed involving products of magnesium oxide hydration, and after a few hours due to the hardening, a crystalline structure is formed containing no water-soluble compounds, which provides its water resistance.

To demonstrate the effectiveness of magnesia material application for LRW immobilization purposes, experiments were implemented to immobilize still residue from the LRW distillation unit operated at a special laundry. Its chemical composition was as follows: salt content of 600 g/l; organic substances content of 5.3·10⁷ Bq/l with 30 % of the activity being equally distributed between ¹³⁷Cs and ⁹⁰Sr and an insignificant fraction of ⁶⁰Co (1–2%). The matrix material involved:

- binder — caustic magnesite powder PMK-87 according to GOST 1216-87, 40 wt. %;
- sealant — industrial magnesium chloride according to GOST R 55067-2012, 10 wt. %;
- catalytic additive — shungite powder, 0.2 wt. % of the total reagent mass;
- cesium sorbent — 0.5 ml of a 14 % potassium ferrocyanide solution and 0.75 ml of a 13 % nickel nitrate solution, which upon mixing forms nickel-potassium ferrocyanide (NPFC) considered a sparingly soluble compound;
- to increase the filling degree of the compounds, calcium chloride was introduced to the composition to bind phosphates, oxalates and silicates resulting in sparingly soluble compounds.

The drying time of the samples in a room at 18–20 °C accounted for 10 days, while the exposure time in water amounted to 20 days. Compound properties were as follows:

- filling degree with dry radioactive salts — 37 %;
- mechanical strength — 5.5 MPa;
- ¹³⁷Cs retention, 95–97 %;
- volume increase — 1.4 times.

Since magnesia binder is a fast-hardening one, it can be used to immobilize spent ion-exchange resins, the density of which is far less than the density of magnesia paste. Due to a short setting time, the resins do not have time to float before the matrix hardening process is completed and are evenly distributed in the volume of the solidified compound (Figure 2).

Ash from SRW incineration is an inert filler of magnesia material, which affects only the strength characteristics of the compound, so its amount is limited only by the regulatory requirements on the mechanical strength. Table 4 summarizes the results of experiments on the inclusion of various RW types into magnesia compound.

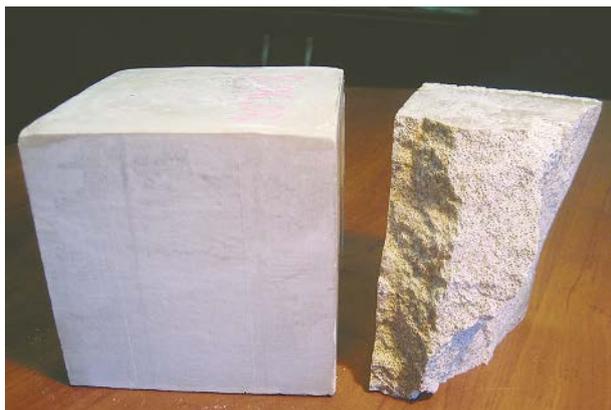


Figure 2. Magnesia compound sample with ion exchange resin inclusion

Thus, in contrast to Portland cements, magnesium matrix materials provide the inclusion of organics into the compound and also surpass them by far considering the degree of filling with waste and are comparable in this parameter with the bituminous

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Table 4. Mechanical strength of magnesia compound for various RW types

RW type and its contents in the compound	Mechanical strength of samples (MPa) during their hardening in a dry environment (numerator) and at 100 % humidity in a desiccator (denominator)		
	Holding time (days)		
	10	20	30
BR with salt content 400 g/l, 13 wt. %	7/6	9/7	10/8
IER, 14 wt. %	4/4	5/4.5	5.5/5
BR + IER + ash	7/6	8/6.5	9/7.5
ash	9/8	12/10	18/12

ones. However, unlike the latter ones, they are non-combustible and their volume is 2.5–3 times lower. Moreover, the described method is characterized by low power consumption, the immobilization process can be implemented at any positive temperatures.

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Bibliographic description

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