

CONDENSED-STATE PHYSICS

CEMENT-BASED GROUTING TECHNOLOGIES FOR RADWASTE AND TOXIC WASTE STORAGE

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The cement-based technologies for immobilization of the toxic and medium-activity liquid radwastes, whose cations are adsorbed on the cation ion-exchange resin, are proposed. Two types of bonding agents are used as the insulating matrix: oilwell Portland cement and elemental sulfur modified with chemical additives. It is shown that an introduction of nanodisperse calcium hydroxide into the cement matrix improves the performance characteristics of the resulting compound, while an optimal result is achieved by adding a micron-sized additive into the sulfur binder. A mechanism for improving the strength of the sulfur compound is proposed and probable chemical reactions underlying the formation of its structure are discussed.

Keywords: LRW, toxic waste, sorption, cementation, ion-exchange resin, compound.

INTRODUCTION

The advances in nuclear power engineering and chemical industry are accompanied by a buildup of abundant wastes differing in their radioactivity, toxicity, compositions, and aggregate states. Ion-exchange resins are among these wastes, which are extensively used for water purification from radioactive and toxic pollutants. These sorbents are hazardous wastes requiring reliable immobilization to ensure their stability in storage, transportation, and final burial in the form of monolithic blocks. The technologies available for their treatment and disposal involve two types of immobilization: direct and indirect [1]. The former processes consist in solidification using cement, bitumen, or polymer compositions [2–6]; the latter involves vitrification at 1100–3000°C. [7]. Recently, there has been an active development of the technologies for dissolving, decomposing and mineralizing the waste resins by the Fenton method [8, 9]. Indirect technologies are, however, quite costly and are applied for the disposal of high-level radioactive wastes. Therefore today the direct technologies are in the greatest demand for the disposal of large-tonnage low- and medium-level radioactive and toxic wastes. The principal research efforts are focused on increasing the filling ratio of the waste resins, reducing the leaching level, and improving the binder matrix stability.

An effective method for burying the low- and medium-activity radioactive and toxic wastes consists in grouting them into inorganic-binder matrices. The conventional technologies have widely used the matrices based on Portland cement with certain chemical additives, such as fast-hardening aluminous cement, betonite, calcium aluminite, etc. [10–14]. An introduction of such additives considerably improves the service characteristics of the resulting compound. The volumes of liquid wastes have been reduced by the method of their concentration via sorption on the cationic and anionic ion-exchange resins. A treatment of liquid radioactive wastes using ion-exchange resins (IERS) commonly involves their high-temperature pre-processing at 400°C, until they lose their water regain capacity, and their mixing with Portland cement. This process yields the gas-vapor products, whose condensation and disposal require additional

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TABLE 1. Characteristics of CTI-50 Oilwell Cement and Elemental Sulfur

Oilwell cement	Value	Elemental sulfur	Value
Density, g/cm ³	1.8	Density, g/cm ³	2.07
Grain size, μm	5–80	Grain size, μm	20–80
Spreadability, mm	185	Melting temperature, °C	112.8°C
Compressive strength on 28-th day, MPa	42.8–66	Compressive strength in casting, MPa	12.4
Thickening time, min	28	Boiling temperature, °C	444.6
Threshold dose, mGy	100	Threshold dose, mGy	1

TABLE 2. Technical Characteristics of KU-2-8 Cation-exchanger Resin

Parameter	Value
Grain-size composition:	KU-2-8
– grain size, mm	0.315 – 1.25
– volume of the effective-size fraction, %, minimum	96
– effective grain size, mm	0.40 – 0.55
Moisture fraction, %	43 – 53
Full statistical exchange capacity, mmol/cm ³ (mg-eq/cm ³), minimum	1.9
Osmotic stability, %, minimum	94.5
Apparent density of ion exchanger, g/dm ³	0.80
Threshold dose, mGy	1.0

technological and ecological solutions. When the IERs are immediately introduced into the cement compositions, the sorbent is primarily dried up to a 50 wt.% moisture content and treated with water-repellent compositions in the amount of up to 33% of the dry IER weight. Notwithstanding these manipulations, the filling capacity of the cement compounds, calculated per dry sorbent, is commonly in the range of 10–20 wt.% only, which still yields quite a large amount of wastes.

A promising avenue of research into immobilization of radioactive and toxic wastes is a search for novel inorganic binders. From our perspective, here belongs elemental sulfur. It possesses a number of useful physical-chemical properties [15]. Sulfur is highly competitive with the conventional types of binders used for the production of radiation-safety materials and in its protective properties is intermediate between the cement brick and solid epoxy, and demonstrates high radiation stability [16]. It is capable of absorbing the radiation energy and scattering it as heat, without any considerable changes. Sulfur is an inorganic polymer. It forms low-solubility crystalline residues of metal sulfides with practically all toxic elements. These properties make sulfur a material of choice to be used as a binder matrix for the disposal of radioactive and toxic wastes.

MATERIALS AND EXPERIMENTAL METHODS

The cementation matrix used in this study was a CTI-50 oil-well cement and powdered elemental sulfur – petroleum industry waste products, whose basic characteristics are listed in Table 1.

The choice of oilwell cement was dictated by the fact that it does not lose its properties at high or low temperatures and pressures and in some aggressive media, and it does not shrink when transformed into a rock-like state. All these features taken together create an additional advantage in the cases of long-term storage of radioactive cement-based polymer-bearing compounds. The performance characteristics of the initial ion-exchange resin are given in Table 2. Water solutions of copper, cobalt and nickel chlorides were added to some portions of the sorbent, and Co⁺², Cu⁺² and Ni⁺² cations were sorbed under static conditions. It is well known that the completeness of extraction of these ions approximates the values of a complete ion exchanger capacity (1.9 mmol/cm³, Table 2). Then some of the ion-

TABLE 3. Main Characteristic of Compounds

Name	Value
Leaching rate (with respect to Cs-137), g/cm ² ·day, maximum	1·10 ⁻³
Mechanical strength (compressive yield strength), MPa	minimum 4.9
Radiation resistance, Gy	1·10 ⁶
Frost resistance (number of freezing/thawing cycles)	minimum 30
Stability to long-term water detention, days	90

exchanger portions were mixed in equal proportions and the resulting mixtures were introduced into the insulating matrix.

The compressive strength was determined on the cubic samples measuring 70.7×70.7×70.7 mm. Six samples were fabricated for every period of testing. The box-forms filled with the mortar mix based on a hydraulic binding agent were kept until removal of the form-work in a normal-storage chamber at a temperature of (20±2)°C and a relative air humidity of 95–100%. The samples were removed from the forms in (24±2) hrs and kept at a temperature of (20±2)°C. In so doing, the following conditions were fulfilled: during the first three days the samples from the solutions prepared using hydraulic binders were stored in a normal storage chamber at a relative air humidity of 95–100% (dry state), and the rest of the time – in water (water saturated state).

The corrosion processes were estimated in the cement brick by determining the calcium ion concentration in the water solution after the distilled water contact with the cement brick by the titrimetry method. From our perspective, leaching in terms of Ca²⁺ is the most informative index of the compound corrosion, since calcium is the major chemical element in the cement brick. Its content (in an oxide form, CaO) accounts for up to 60 wt.% of the total content of all oxides. Furthermore, calcium is present in all four main minerals of the cement. Therefore its washing out during the contact of cement samples with distilled water or aggressive liquid medium provides a most objective estimate of the corrosion processes of the cement brick.

The technique for measuring the weight concentration of calcium in the water-bearing media by the method of titrimetry allows determining its concentration to a high accuracy in the range from 1.0 to 200.0 mg/dm³. For the analysis, we used 10 cm³ of water solution, added 0.2 cm³ of 8-% solution of calcium hydroxide, 20–30 mg of the murexide indicator and titrated against a Trilon B solution until the pink-to-red-violet discoloring.

The molar concentration of calcium in the analyzed water sample was found via the following formula:

$$X_m = \frac{C_{Tr} \cdot V_{Tr} \cdot 1000}{V},$$

where C_{Tr} is the molar concentration of a Trilon B solution, mol/dm³; V_{Tr} is the volume of the Trilon B solution used for titration of the sample, cm³; V is the water volume taken for titration, cm³.

In order to determine the phase composition of the samples we used a SHIMADZU XRD-6000 polycrystalline diffractometer capable of recording in the Bragg–Bretano geometry equipped with a PN-305-20131-01 focusing pyrographite crystal-monochromator using a secondary gamma-quanta beam. The analytical results were verified using the XRD powder diffraction computer databases PDF2 or PDF4 of the International Center for Diffraction Data (ICDD, Denver, USA), FPL D 070 1 89-5289.

The chemical elements in the sample were identified using a SHIMADZU XRF 1800 fluorescent spectrometer capable of determining the concentrations of 88 elements in the range from 10⁻⁴ to 100%.

EXPERIMENTAL RESULTS AND DISCUSSION

According to the RF State Standards, the cement-based compounds have to comply with the characteristics given in Table 3.

TABLE 4. Supply of Components and Results of Compressive Strength Tests in Dry and Water-Saturated States vs. Reference Samples

Number of components, wt.% Reference Sample			
Ion-exchange resin (KU-2-8)	Calcium hydroxide Ca(OH) ₂	Cement	Water
Ion-exchange resin (KU-2-8)	Chemical additive	Cement	Water
0	0	100	Up to a mixture pourability of 10–12 cm
30	3.75	66.25	Up to a mixture pourability of 10–12 cm
Characteristics			
Moisture, wt.%	Density, kg/m ³	Compressive yield strength, MPa	
		Dry state	Water-saturated state (90 days)
12	2040	42.8	46.3
Number of components, wt.% With calcium hydroxide			
Ion-exchange resin (KU-2-8)	Calcium hydroxide Ca(OH) ₂	Cement	Water
30	3.75	66.25	Up to a pourability of 10–12 cm
Characteristics			
Moisture, wt.%	Density, kg/m ³	Compressive yield strength, MPa	
		Dry state	Water-saturated state (90 days)
19.5	1360	12.5	15.0

A peculiarity of cementing the sorption-localized radioactive and toxic elements on the ion-exchange resins is their capacity to absorb water in the amount of more than 50 wt.% (Table 1) and retain it in the pores of the matrix, which gives rise to swelling of the polymer grains, an increase in its volume, a generation of internal stresses and, eventually, to a considerable strength reduction. The solvent absorption process could be stabilized by an introduction of chemical additives binding the excessive water in the pores of the sorbent.

In this work we study the influence of various chemical additives, such as potassium silicate and calcium oxide, hydroxide and chloride, on the performance of compositions based on the oilwell cement and ion-exchanger resins. These chemical additives have been selected due to their physical-chemical compatibility with the cement brick structures. According to the preliminary experimental results, an addition of potassium silicate causes a self-destruction of the samples as early as 7 days after their saturation with water even at a low-level filling of the cement brick with ion-exchange resin in the amount of 15 wt.%. The best compressive strength characteristics were achieved in the dry and water-saturated states, and the best filling ratios of the cement matrix with the polymer sorbents were observed via a preliminary treatment of the ion-exchange resin grains with chemical additives of nanodisperse calcium oxide with a weight fraction of CaO or calcium hydroxide (Ca(OH)₂) of at least 96 wt.%. To this end, a required amount of calcium oxide or hydrated lime were dissolved in part of the mixing water and stirred together with the polymer sorbent. The resulting mixture was poured into a vessel with a tight cover and held for at least 10–12 hrs to provide diffusion of the calcium ions into the ion-exchanger pores. The resulting mixture was then mixed with cement, adding water in the amount necessary to achieve a mixture pourability of 10–12 cm. Table 4 presents the experimental results.

The achievement of a considerably high strength of the samples at a high sorbent-filling degree (30 wt.%) can be attributed to the excessive water binding by the calcium-bearing products, their sorption on the ion-exchanger surface and in its pores, and the formation of strong bonds with the hydration and solidification products of the cement brick. This is indirectly supported by the micrographs from the bulk of the samples after their strength tests, where most of the sorbent grains are enveloped by a nanodisperse calcium hydroxide film (Fig. 1).

The cement compound consists of four main phases (Fig. 2).

The results of a chemical analysis of the sample surfaces demonstrate the absence of a diffusion-induced removal of the cations of toxic copper, cobalt and nickel elements (Fig. 3).

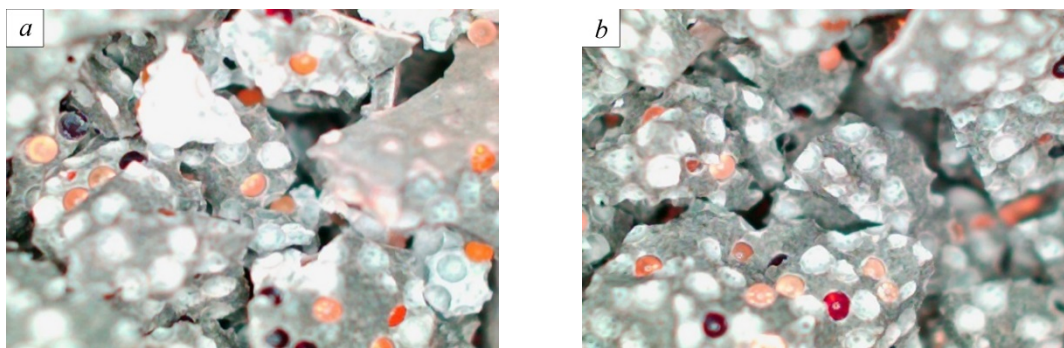


Fig. 1. Micrographs from decomposed samples of the compound (Magnification $\times 40$).

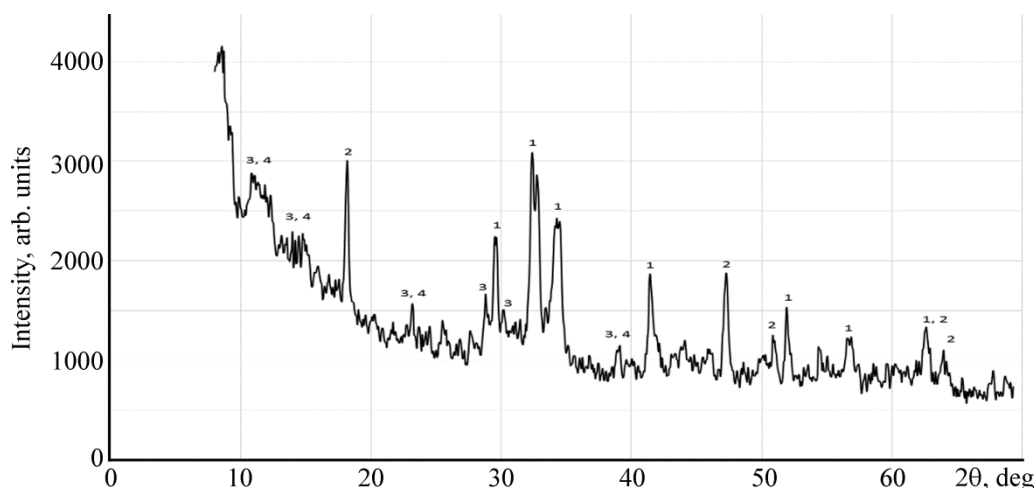


Fig. 2. Diffraction pattern from a cement compound sample: 1 – portlandite, 2 – alite, 3 – hydrated calcium silicate, 4 – calcium aluminat.

There are none of them in the solution volume either. Their presence was determined by performing high-quality analytical reactions. A cobalt cation provides blue coloring with a rhodanide ion; nickel cations in an ammoniac medium with dimethylglyoxim form a complex salt residue of a poppy-red color; an excessive addition of ammonium hydroxide in the presence of copper ions results in the formation of a solvable complex compound of a cornflower blue color. The data obtained imply a reliable insulation of toxic cations in the cement matrix.

The experiments have shown that the most active leaching in terms of calcium ions is observed in the first day of the compound contact with the liquid, following which it becomes slower and the maximum values (≈ 20 mmol/l or, considering the sample surface area – $5.8 \cdot 10^{-5}$ g/cm²) do not exceed the recommended leaching values in terms of the Cs-137 ions (Table 3). The kinetic curves of variation in the calcium ion concentration and electrical conductivity demonstrate a symbiotic character. This indirectly validates the principal role of Ca²⁺ in the corrosion processes.

We have also studied the use of elemental sulfur as an insulating matrix. Its advantages include: low value of dynamic viscosity (on the order of $8 \cdot 10^{-3}$ Pa·s) in the region of the melting temperature, which allows to solve a technological task of homogeneous stirring of the binder with the sorbent; the melting temperature is lower than that of decomposition of the KU-2-8 ion exchanger, which rules out the formation of gaseous products and retains the native structure of the ion exchanger grains; sufficiently high compressive strength; chemical inertness with respect to most of the aggressive factors of the surrounding medium; low water absorption rates and high frost resistance; ability of being modified to achieve much better performance characteristics of the compound: availability of cheap large-tonnage supply of the initial raw materials in the form of petroleum industry wastes. The main disadvantage is a low resistance

TABLE 5. Physical and Service Properties of Compounds

Parameter	Degree of sulfur matrix filling with sorbent pre-treated with calcium hydroxide, wt.%				
	0	20	30	40	50
Compressive strength, MPa	18.2	27.4	24.3	8.8	4.2
Water absorption, %	0.8	1.2	1.9	3.4	9.6
Density, g/cm ³	2.07	2.1	1.9	1.7	1.1
Frost resistance, number of thawing / freezing cycles	60	49	42	35	29
Thermal stability, °C	120	210	200	160	124
Calcium ion leaching, g/cm ²	0	$5.1 \cdot 10^{-7}$	$3.2 \cdot 10^{-7}$	$2.7 \cdot 10^{-7}$	$1.9 \cdot 10^{-7}$

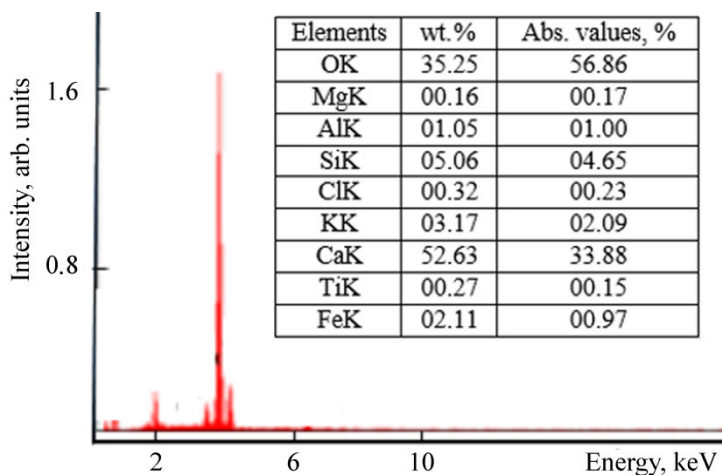


Fig. 3. Chemical analysis of the compound surface after its saturation in distilled water for 48 hrs.

to heat impact. For the cement-based systems it is 250–300°C, while for the sulfur compounds – not higher than 200°C. Moreover, due to a large density difference between the filler and the sulfur melt, the phases are observed to separate during mixing of the ingredients, and the density of compounds sharply decreases.

In order to rule out separation of the mixture components, the ion-exchange resin-simulator with the sorbed Co^{+2} , Cu^{+2} and Ni^{+2} cations was pre-treated with a calcium hydroxide suspension with micron-sized particles and then dried to a constant mass at a temperature of 70–80°C. The resulting dehydrated mixture was fed into the sulfur melt heated to 120°C, thoroughly mixed to a homogeneous mass and then cooled. Given these conditions, no separation of the mixture components was observed.

Table 5 presents certain physical and performance characteristics of sulfur compounds with different degrees of the sulfur-matrix filling with the KU-2-8 sorbent pre-treated with a calcium hydroxide suspension.

Table 5 implies that the experimental sulfur compounds meet the main requirements on the radwaste (Table 3) and toxic waste immobilization in binder matrices and allow achieving a high filling degree, exceeding the available literature data. It should be underlined that the compressive strength of the samples, in the cases where we used a sorbent treated with calcium hydroxide, was higher compared to pure elemental cast sulfur (Table 5).

We believe the most probable mechanism of the sample strength improvement seems to be due to the following reactions.

1. Calcium hydroxide ensures binding of the sulfur dioxide gases and hydrogen sulfide released during sulfur heating, which decreases the probability of pore formation reducing the compound strength

TABLE 6. Calculated Parameters (on the example of an S:KU-2-8 resin:Ca(OH)₂ = 75:20:5 film) of Adhesion to the Cement Brick Surface. Limiting Wetting Angle – 70°. Film thickness 9·10⁻⁴ m. Film surface area – 4·10⁻⁴ m²

Parameters	F _{tear.} , N	W _{adh.} ·10 ³ , J/m ²	W _A ·10 ⁴ , J/m ²	W _{coh.} ·10 ³ , J/m ²	f, J/m ²
Values	490	1.1	1.61	2.4	-1.3

Note: $F_{tear.} = ma$ – tearing force, $W_{adh.} = h \cdot F_{tear.} / S$ – adhesive strength, $W_A = F_{tear.} (1 - \cos \Theta) / b$ – work of adhesion, $W_{coh.} = 2W_{adh.} / (1 + \cos \Theta)$ – work of cohesion, $f = (W_{adh.} - W_{coh.})$ – droplet spreading coefficient, h – film thickness, m, S – film surface area, m², b – film width, m, Θ – wetting angle, deg.

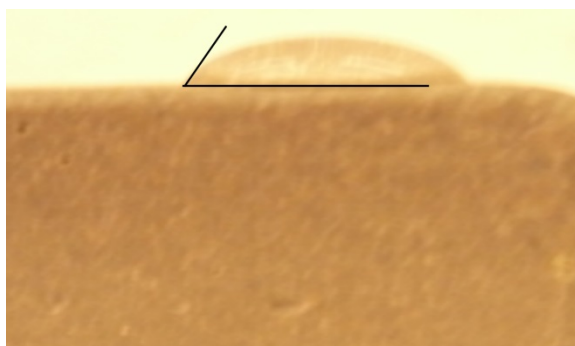
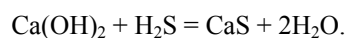
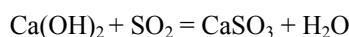
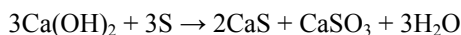


Fig. 4. Photo of a sulfur-based compound and the wetting angle 5 minutes after application of the composition (on the example of a sulfur:KU-2-8 resin:Ca(OH)₂ = 40:50:10 composition) on the compound surface.



According to the thermodynamic calculations, the Gibbs energy for these reaction is negative already at room temperature.

2. Calcium hydroxide interacts with elemental sulfur to form calcium polysulfide, CaS



It is well known that the compounds synthesized using elemental sulfur, where the sulfur component is found in a polymer state, have much better physical-mechanical and performance characteristics [16].

In order to additionally improve the protective properties of the elemental-sulfur compounds we propose to embed them into a cement matrix.

We have experimentally revealed that the limiting wetting angles for the compounds with a filler fractions from 10 to 50 wt.% lie in the range of 82–58° (Fig. 4). According to the calculations of the adhesion parameters using the limiting wetting angles [17, 18], the work of adhesion and cohesion in the two experimental matrices is observed to be high (Table 6). This fact verifies the technical decision made in this study.

The negative value of the droplet spreading coefficient (Harting coefficient) indicates high adhesive characteristics of the contact surfaces of the cement and sulfur compositions, which makes it technologically reasonable to introduce the molten sulfur compound mass into a container made of cement brick or concrete.

CONCLUSIONS

The principal characteristics of the protective properties of matrices, based on oilwell cement and sulfur, applied in radioactive and toxic waste immobilization, have been determined. It has been demonstrated that in order to provide a more reliable protection of the compounds, involving the ion-exchange resins and binding matrices, from the environmental factors the sorbent is pre-treated with calcium oxide or hydroxide. The most promising technology is a combination of both experimental compound types.

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