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CONDITIONING OF SOILS AND SILT BOTTOM SEDIMENTS CONTAINING RADIOACTIVE MATERIALS

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The paper presents some proposals on the use of radioactively contaminated materials generated from nuclear decommissioning and remediation of radioactively contaminated sites as initial components for radioactive waste immobilization. It provides results of previous research on the development of processing and conditioning methods for solid radioactive waste present in the form of soils and silt bottom sediments in water bodies. The paper discusses the feasibility of applying certain composition of the initial mixtures and the characteristics of the obtained products, technological parameters of the binding materials synthesis. It overviews the studies on the phase formation under calcination of raw mixtures and hydration of produced materials. Considered are the key technological parameters of the process, the results of grand waste lots processing using a stand installation. Properties of conditioned waste have been studied as well.

Key words: *radioactive waste, silt bottom sediments, soils, soil processing, co-processing of radioactive waste.*

Federal Target Program "Nuclear and Radiation Safety in 2016—2030" stipulates a list of activities to be implemented under its framework, the major part of which are associated with nuclear decommissioning, as well as nuclear cleanup and remediation of radioactively contaminated sites. Considering the total RW inventory generated as the result of the abovementioned operations, low-level (LLW) and very low-level waste (VLLW) make up a significant portion of the waste produced amounting to up to 70—80%. Typically, these are construction waste, contaminated soil and silt bottom sediments [1]. Given the intensification of nuclear decommissioning operations, mainly focused on nuclear legacy cleanup, the amount of such waste can be basically estimated at hundreds of thousands of cubic meters. It should be noted that the generated RW belongs to different RW classes with different requirements imposed on its conditioning to ensure its compliance with waste acceptance criteria for disposal [2].

If the waste is assigned to RW class 3 according to retrievable RW classification system [3], a requirement should be met stating that the waste should be disposal of in a stable form, i.e. should be enclosed into a monolith matrix using certain matrix materials and technologies. Currently, a cement matrix is most commonly used for these purposes offering a number of technological advantages (versatility of application, ease of preparation, etc.) and having relatively low cost of its components [4].

Radioactive waste involving contaminated soils, rocks and bottom sediments is very common and quite difficult to condition. Currently, several methods are used for its treatment:

- separation allowing to segregate the portion of waste with maximum contaminant content [5, 6];

- inclusion into various types of matrix materials with cement materials being most commonly applied as such [4].

Practice showed [5—7] that separation-based methods are most effective with respect to radioactively contaminated sandy soils with a low content of finely dispersed fraction and if the contaminant is present in a liquid phase. It should be noted that after processing, part of the radioactive contamination remains on the material being processed, which may require some particular measures for its further treatment.

When this type of waste is incorporated into a cement compound, the volume of conditioned RW increases significantly (by 1.5 – 2 times). Moreover, the increase in conditioned RW amounts at decommissioned facilities results from the necessary solidification of accumulated and newly generated liquid radioactive waste (LRW), usually using the cementing method.

Based on these assumptions, a set of studies was previously carried out to develop methods enabling joint processing of pre-treated sludge or soil containing radioactive or toxic substances and low-level LRW [8–12]. These methods are based on preliminary calcination of the materials allowing to reduce the amount of RW subject to disposal. The reduced volume of sludge or soils is achieved due to the burning of their organic component resulting in the formation of removable volatile components. At the same time, after being calcinated and grinded, their mineral part forms a binding material having a hardening ability when mixed with aqueous solutions. This process results in cement stone formation.

Under this research some laboratory studies were performed involving the processing of enlarged batches of radioactive waste at a stand unit.

The laboratory studies were performed to investigate the composition and characteristics of sludges that required processing. Sludges of different origin and chemical composition were used. These were also characterized with different levels of contamination and radionuclide composition of the contaminants [9, 10]:

- sludge taken from process settling pools (sludge No. 1 and No. 2);
- sludge from the filtration fields of industrial plant's active drains containing radioactive and toxic substances (sludge No. 3).

The silt bottom sediments had the following characteristics [10]:

- the content of organic components in the processed sludge amounted to 8—25 % wt;
- the water content in the treated sludge after vacuum dehydration accounted for 15—20 %;
- the residual mass of samples after calcination at 1,000 °C and dehydrated sludges No. 1 and No. 2 amounted to 52.5—55.0 %, for sludge No. 3 — 30—32.5 %;
- the specific activity of sludges No. 1 and No. 2 amounted to $(1.8—9.5)\cdot10^4$ Bq/kg for β-emitters, $(9.6–55.0)\cdot10^3$ Bq/kg — for α-emitters, and $1.2\cdot10^3$ and $1.0\cdot10^3$ Bq/kg for sludge No. 3;
- Table 1 presents the chemical composition of the processed sludge.

Table 1. Chemical composition of the sludges, % wt

Sample	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	PbO	HgO	Cr_2O_3	NiO	MnO_2	Residue
№ 1, № 2	10–12	60–62	11–13	8–10	2–4	2–3	2–4	Not determined					1.0–1.5
№ 3	4–6	65–70	11–13	8–10	2–4	1–2	3–5	0.10–0.15	$1.5\cdot10^{-3}$	0.1–0.2	0.01	0.05–0.10	1.5–2.2

The potential of producing an inorganic binder based on these sludges capable of hardening after its interaction with water and aqueous solutions was evaluated given the composition and characteristics of the waste subject to processing. Qualitative and quantitative indicators set in accordance with relevant regulatory provisions were adopted as the requirements for the final product [13, 14].

Therefore, in [9—12] two methods of sludge processing were considered. These differ from each other by the composition of the mixture transferred to heat treatment unit. The first method (calcination method) suggests that sludges containing radioactive or toxic substances were calcinated with the resulting product being grinded, mixed with Portland cement and gaged with water to form a monolithic compound.

The studies demonstrated that the temperature range from 700 to 1,000 °C should be considered as an optimal one allowing to obtain a product with the required properties. At this temperature, free and chemically bound water, as well as volatile organic components, are completely removed from the treated sludge. The calcined product was grinded to a powder with a specific surface area of 1,500—2,500 cm^2/g. To produce the samples, the grinded material was mixed with Portland cement at a product/Portland cement ratio of 1:1, 2:1, 3:1, 5:1, 10:1 and 20:1. Distilled water was added to the resulting mixture at a water/(cement+product) ratio

Table 2. Properties of cement sludge-based compounds after its calcination with water/(calcined sludge + Portland cement) ratio being equal to 0.4

Sludge mass after calcination (as a percentage of the original mass)*	Calcination temperature °C	Calcined sludge/ Portland cement ratio	Setting time, min		Compressive strength of the product (compound) after hardening, MPa				Ratio of the original sludge** volume to the volume of the solidified product
			Start	Finish	After 7 days	After 14 days	After 28 days	After 56 days	
35.7	700	1	23.27	27.53	21.0	24.8	26.1	28.0	0.63
47.6	700	2	9.53	21.21	18.2	16.9	24.1	29.2	0.84
53.6	700	3	16.35	22.30	13.9	13.7	18.5	17.3	0.95
59.5	700	5	19.50	21.17	2.8	1.3	6.8	7.9	1.05
53.6	800	3	110.20	117.18	10.1	16.6	21.7	22.6	0.95
53.6	900	3	39.55	41.12	9.5	16.4	24.6	25.7	0.95
65.0	900	10	58.20	72.15	4.2	7.2	9.0	13.3	1.19
53.6	1000	3	36.40	38.40	11.1	12.2	24.0	23.6	0.99
59.5	1000	5	94.30	105.15	6.2	9.7	17.1	18.7	1.10

* Initial mass of the sludge after vacuum dehydration.
** Initial volume of the sludge after vacuum dehydration.

of 0.4—0.5 by weight. Table 2 presents the properties of the final products obtained using this processing method.

Given the above data, a cement compound complying with the requirements set for its strength characteristics (at least 5 MPa after 28 days of hardening) was produced at a sludge/Portland cement ratio of 10 or lower. At sludge/Portland cement ratio over 10, the strength characteristics of the obtained compounds did not meet the requirements.

To assess the feasibility of applying such a material for LRW immobilization purposes, experiments were performed on cement compounds production. Materials simulating sodium nitrate-based LRW with a salinity of 100, 300, 500, and 700 g/l were used in the experiments. Solution/binder ratio for the cement compounds obtained varied in the range from 0.4 to 0.8. Compressive strength index was selected as the criterion demonstrating the acceptability of the product. Figures 1a, b, c demonstrate the experimental results obtained. The indicated data shows that 20% of cement added to the mixture can be used to immobilize LRW with salinity of up to 300—500 g/l and solution/binder ratio of 0.4—0.6.

The second method (synthesis method) involved the synthesis of alkaline binder material (ABM) using sludge as one of its components.

The raw mix for ABM synthesis involved two components: salt and mineral. Dry LRW residue from nuclear power plants was used as the former one (Table 3), and the processed sludge was used as the latter one.

Under laboratory conditions, radioactive sludge-based ABM was synthesized as follows. The sludge

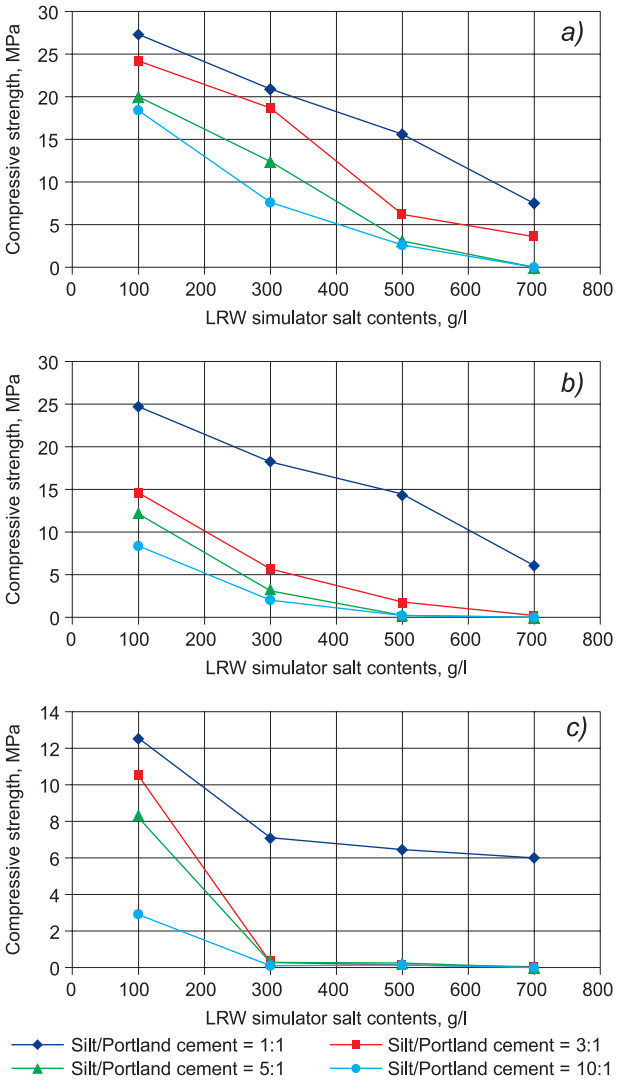

Figure 1. Strength characteristics of cement compounds on the 28th day of hardening obtained for different Solution/Binder ratios: a) S/B = 0.4; b) S/B = 0.6; c) S/B = 0.8

Table 3. Average content of the main components in the dry LRW residue (% wt)

Site of generation	Component content								
	Na^+	K^+	Ca^{+2}	Fe^{+3}	H_3BO_3	SO_4^{2-}	SO_4^{2-}	CO_3^{2-}	Cl^-
Kursk NPP	27.0	0.7	0.3	–	–	67.4	2.7	1.9	-
Moscow Research and Production Association Radon	20.4	–	5.8	2.7	–	62.0	4.4	2.3	5.4
Novovoronezh NPP	16.0	2.9	–	–	32.7	47.7	–	–	–

was mixed with LRW simulator and aluminum oxide (Al_2O_3). LRW simulator was used as a salt component, whereas, sludge and Al_2O_3 were used as additives containing oxides (SiO_2 and Al_2O_3) required for ABM synthesis. The mixture was calcinated at a temperature of 850 °C (isothermal exposure time at a maximum temperature accounted for 1 hour). The calcined product was grinded to a powder with a specific surface of 2,500—3,000 cm^2/g. To produce compound samples the resulting cement was mixed with water at a solution/binder (S/B) ratio of 0.3—0.6.

Standardized compressive strength index [12] was considered as a suitability criterion during the studies aimed at determining the composition of the initial raw material mixture and the conditions for ABM synthesis.

The studies showed that the salt component content in the initial mixture produced for ABM synthesis should vary between 65—80 % wt. As for optimal thermal parameters of the process indicating the completeness of mineral formation process (synthesis temperature and isothermal exposure time at a maximum temperature), the temperature should amount to some 900 °C accounting for 1 hour of exposure. It has been demonstrated that two areas associated with the chemical composition of raw mixes exist in which the strength of the cement stone obtained by means of synthesized ABM solidification satisfies the requirements for cement compounds with radioactive waste. The raw mix in the first area had the following composition: 64—80 % wt. — LRW salts, 14—15 % wt. — SiO_2 and 6—22 % wt. — Al_2O_3; in the second area, the content of these components was as follows: 68—74, 20—25 and 6—8 % wt., respectively.

X-ray phase and petrographic analyzes performed showed that, the main mineral phases in these areas were calcium orthosilicate $2CaO{\cdot}SiO_2$ in various polymorphic forms, namely: α_m-C_2S — bredigite and β-C_2S — belit (larnite) being present in large quantities. The following substances were discovered as well: $Na_2O{\cdot}CaO{\cdot}SiO_2$ — sodium-calcium silicate; $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2$ — cornehyite; $2CaO{\cdot}Fe_2O_3$ — C_2F — dicalcium ferrite with Fe atoms being replaced by Al atoms forming a number of solid solutions. $2Na_2O{\cdot}3CaO{\cdot}3SiO_2$ was also present in minor quantities.

ABM hydration products were studied as well. It was shown that at the initial stage of hardening (up to 1 year), zeolite structures such as hydrate-nepheline $Na_2Al_2Si_2O_8{\cdot}(4—6)H_2O$, chabazite $(Ca,Na)[AlSi_2O_6]_2{\cdot}6H_2O$ are formed. Upon further hydration under normal conditions after 1 year of exposure, interaction products of analcime $Na[AlSi_2O_6]{\cdot}H_2O$ type were discovered in the cement stone, as well as an increase in $NaCa_2Al_6Si_{32}{\cdot}13H_2O$ amount (chabazite-type aluminosilicate).

To finalize the laboratory studies, pilot sludge processing was carried out at a pilot industrial installation. The installation consisted of a tunnel muffle electric furnace, loading and unloading units and a gas cleaning system.

Sludge was processed as follows:

- during processing by the calcination method, 0.5—1.0 kg portions of sludge were placed on pallets being transferred on a conveyor belt of a tunnel muffle electric furnace. Moving along the length of the furnace, the material was calcinated at a temperature of 800—900 °C for 10—15 minutes with subsequent grinding in a ball mill. The grinded product was transferred to a cementing unit, where it was mixed with cement and water at a product/Portland cement ratio of 5/1 and water/(cement + product) ratio of 2/5. The processing rate amounted to 25 kg/h.
- during processing by the synthesis method, radioactive sludge was mixed with additives in a compact cementing unit. The resulting raw mix was placed by 0.5—1.0 kg portions on a conveyor belt of a tunnel muffle electric furnace in pallets. Moving along the length of the furnace, the material was heated to a temperature of 1,000 °C and calcinated at a given temperature for 20—40 minutes. Then, the calcined material was grinded in a ball mill to a powder with a specific surface of 2,500—3,000 cm^2/g. The synthesized cement was mixed with water in a cementing unit with a water-cement ratio of 0.3. The processing rate amounted to 25 kg/h. The synthesis parameters were chosen based on the studies of the optimal composition ranges for raw mixes. Figure 2 presents the results of these studies.

Based on the studies performed, it has been demonstrated that the optimal range of raw mix compositions for alkaline material synthesis based on cement compounds satisfying the established quality criteria [3, 13, 14], accounts for the area, the

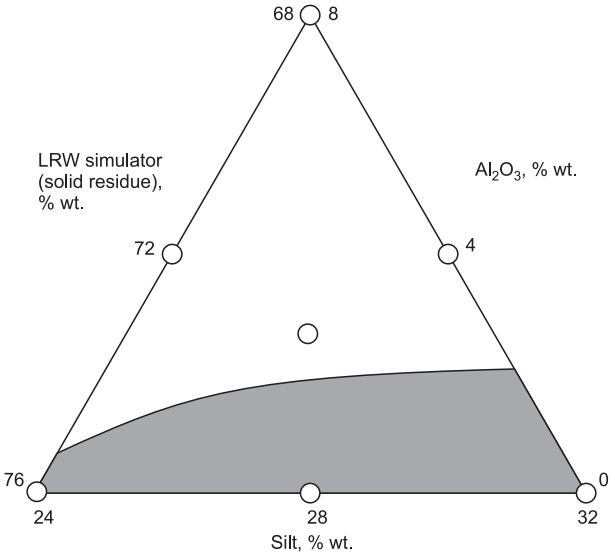

Figure 2. Areas of raw mix compositions for cement compound production

content of the main components in which by % wt. is as follows: LRW simulator — 68—76, sludge — 24—32, Al_2O_3 — 0—2 (Figure 2)

During processing, the composition of the exhaust gases (from the furnace) and the amounts of aerosols during grinding of the calcined product were monitored. Radionuclide losses during calcination were found to be as follows: ^{137}Cs — less than 1 %, ^{238}Pu — less than 1.4 %, aerosols — less than 0.01 %. CO concentration in the exhaust gas was up to 2,500 mg/m^3, concentrations of NO_x, HCl and NH_3 were found to be insignificant. Radionuclide concentrations found in the condensate of the gas treatment system and in the air when grinding the calcined product appeared below the threshold level.

920 kg (0.613 m^3) of sludge No. 1 and 30 kg (0.023 m^3) of sludge No. 3 was processed by the calcination method, 30 kg (0.02 m^3) and 20 kg (0.015 m^3) — using the synthesis method. A total of 0.671 m^3 of sludge was processed. As a result of processing, 0.37 m^3 of cement monolith was produced resulting in 1.8-time reduction in the volume of the final product compared to the one of the initial sludge.

The resulting cement materials were tested to compare their properties with threshold limits set forth in relevant quality criteria for:

- mechanical strength (compressive strength);
- water resistance (leaching rate for radionuclides based on ^{137}Cs);
- resistance to thermal cycles (frost resistance);
- waterproofness (resistance to prolonged stay in water);
- radiation resistance.

To reduce the leaching rate of cesium, bentonite (3 % wt) was added to the mixture. Table 4 summarizes the main results of the tests performed.

Table 4. Properties of cement compounds resulted from pilot processing of sludge

Treatment method	Bentonite additive, % wt	Setting time (start-finish), min	Compressive strength, MPa			Leakage rate, g/cm^2·day	
			After 7 days	After 28 days	After 56 days	After 7 days	After 56 days
1	0	24—33	10.3	19.9	23.3	$3.6 \cdot 10^{-4}$	$5.0 \cdot 10^{-5}$
1	3	35—46	8.8	12.3	19.6	$1.5 \cdot 10^{-4}$	$1.7 \cdot 10^{-5}$
2	0	26—30	15.4	22.7	29.2	$7.3 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$
2	3	45—56	11.6	18.5	24.5	$2.9 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$

Conclusions

Research performed enabled the development of processing methods for soils and silt bottom sediments with the characteristics of the final solid product (cement compound) being consistent with relevant regulatory requirements. Moreover, the volume of the processed products is less than or at least does not exceed the initial RW volume resulting in a 2—3-fold reduction in the waste amounts subject to disposal. ABM synthesis method enables to obtain a product that binds the radionuclides present in the raw material and can be used for conditioning purposes instead of Portland cement for various SRW and LRW. Its application allows a 10-fold increase in the volume reduction coefficient.

Summarizing the above, it can be stated that the joint RW processing method at centralized sites and during NPP decommissioning, when all the components required for alkaline binder material synthesis are available in one place, has a great practical benefit.

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