Immobilization of Liquid Organic and Aqueous Radioactive Waste Decommissioning in Porous Cement Matrix – 14405

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ABSTRACT

During decommissioning of nuclear facilities such as A. A. Bochvar Research Institute of Inorganic Materials in Moscow, there arises the requirement to solidify of small quantities of various organic liquids and aqueous solutions containing alpha-active isotopes. Solidification technology of such waste in the special cement matrix has been developed at A. A. Bochvar Research Institute. The technology involves the preparation of a cement matrix with porosity of up to 70 % of volume and average pore size of 0.01-0.05 mm with high-speed foam generator and standard mixer. The cement matrix is a mix of Portland cement and additives. The cement composition provides for obtaining matrixes with strength of up to 5 MPa. Compressive strength of the matrix after impregnation does not lower. Then porous cement matrix is placed into the container with volume of 100 or 200 l with feeding device. The matrix hardens in the container and develops compressive strength of over 5 MPa. At the period of hardening not less than 28 days, when hydration processes of cement are over, liquid waste is pumped into porous space of the matrix through the feeding device. Hardened porous matrix is being impregnated by waste. During the industrial test the matrix was impregnated in metal container with volume of 200 l. The liquid waste used for the test included acid aqueous solutions, synthin solution of tributyl phosphate, spent oil, and liquid scintillator. Feeding of organic waste into bottom part of the container was conducted through the feeding device by the plunger pump. Filling rate of the cement matrix depended on the type of waste. At this filling rate the necessary impregnation pressure was up to 0.2 MPa. Filling rate of the final product reached 70 % of the volume. Properties of the final compound meet the regulated requirements. The technology has the advantages of waste filling rate up to 70 % of volume, elimination of waste components effect on the process of hardening of cement compound, simplicity of technological process and equipment, and possibility of immobilization of waste directly on site of its generation that allows transporting solidified waste into storage facility. Increase of the industrial solidification unit capacity is possible in case of simultaneous conducting of impregnation of several containers with porous matrix.

INTRODUCTION

During decommissioning nuclear facilities such as A. A. Bochvar Research Institute of Inorganic Materials in Moscow there arises the requirement to solidify small quantities of various liquid organic and aqueous solutions containing alpha-active isotopes. Several methods are available for the processing of organic liquid radioactive waste – incineration, pyrolysis, chemical and electrochemical oxidation, dissolution in acid and others [1- 4]. All these methods require complex equipment and highly-qualified personnel. During waste processing secondary radioactive waste (in certain cases chemically toxic) is formed. The majority of the methods can be used only to process organic liquid radioactive waste (RW) of particular composition.

In case where relatively small volumes of organic liquid RW is produced, it may be more effective to use less complex processes that would guarantee the required solidified volume of final product. One of such methods is cementation. However, conventional cementation has several disadvantages. Large volumes of cemented waste products are formed due to the inability to include significant amount of liquid RW into the cement matrix. In particular, the maximum permissible filling capacity of cement compound with organic waste must not exceed 4-5% of its mass without preliminary preparation [5,6]. In case preliminary preparation is conducted (emulsification or adsorption of organic components on solid materials) permissible level of filling capacity is 15-30% of its mass. In case these values are exceeded, the quality of the cement compound deteriorates. There is a known method of immobilization of aqueous saline liquid RW in porous ceramic matrixes by using repeated cycles of impregnation followed by drying. This method appears to have potential for the immobilization of organic liquid RW as well. This work was aimed at developing an effective technology for the immobilization of organic and aqueous liquid RW of various kinds by impregnation of porous cement matrix located in a container that serves as the final packaging for the transportation and storage [7].

DESCRIPTION

The following kinds of liquid RW were used in this study: solution of tributylphosphate (TBP) in synthene, liquid scintillant, petroleum oil and low acidic aqueous solutions. Radionuclide composition of liquid RW is given in Table I.

Table I. Radionuclide composition of liquid RW

Type of liquid RW	**Radionuclide specific activity, Bq/l**		
Solution of TBP in Synthin	U-238	U-235	Th-234+Pa-234m
	2.00E+5	2.00E+5	2.00E+5
Scintillator	Am-241	Cs-137	Pu-239
	2.40E+3	1.10E+6	2.10E+3
Petroleum Oil	U-238	U-235	U-234
	9.00E+3	1.30E+3	1.50E+4
Aqueous Solution	U-238	U-235	–
	2.00E+5	2.00E+5	–

Defining optimal composition of porous cement matrix

First task of the research was to define the composition of cement matrix that would satisfy the following requirements:

- compressive strength – more than 5 MPa after 28 days of hardening;
- porosity – 70%;
- size of pores - $(1\text{-}5)\cdot10^{-5}$ m.

Cement matrix was prepared by mixing foam with cementitious material. Characteristics of the cement matrix were varied by changing the proportion of its components. Fine-ground Portland cement (specific surface area 1210 m^2/kg, average particles size 4 micro meters) and regular Portland cement in the ratio from 0,2 to 1 were used as foundation for the cement matrix.

Concentration of foam generating agent was 0.1-0.6 % by mass, cement-water ratio ranged from 0.4 to 1.

The following modifying additives were put into the prepared cement matrix:

- agent of foam mineralization (fine powder of iron oxide, magnesium oxide and quartz sand in the amount of 0.5-3% by mass);
- setting accelerators (calcium carbonate, sodium silicate and calcium chloride in the amount of 1-5% by mass);
- sorbent additive (bentonite in the amount of 3.5-10% by mass).

After reviewing the results of the tests, it was determined that the optimal composition of porous cement matrix of the required quality should have the following characteristics:

- ratio of fine and regular Portland cement – 1:3;
- fine powder of iron oxide – 1.5% by mass;
- calcium carbonate – 3% by mass;
- bentonite powder – 10% by mass;
- foam generating agent - 0.2-0.5% by mass;
- cement-water ratio – 0.5-0.6.

Defining optimal parameters for impregnation of the cement porous matrix

The following parameters of the process of the impregnation of the cement porous matrix with liquid waste were defined – the degree of impregnation, the speed of impregnation and hydraulic resistance of the matrix. The parameters were defined at the laboratory facility. The testing was performed on 1/10 scale models of standard 200 l barrels (height of matrix 0.084m). The values of the parameters are presented at Table II.

It was assumed that the effective degree of impregnation (ratio of the degree of filling of the cement matrix with liquid RW and its porosity) must be between 80-90% of the volume of pores in the cement matrix.

The range of parameters for the speed of impregnation was adopted according to the following notions. The minimal speed of impregnation of 0.2 cm per minute allows to impregnate a cement matrix in a barrel with a capacity of 200 liters in 8 hours, which is in one working shift, which can be considered rational as far as operation is concerned.

The degree of impregnation of cement matrix with varying of the parameters of the impregnation in the intervals given in Table II amounted to 0.8-0.9, with the filling of the cement matrix with waste to 64% of volume and 52% of mass.

Table II. Results of the laboratory test

Parameters of impregnation	Solution of TBP in Synthin	Scintillator	Petroleum Oil	Aqueous Solution
Speed of impregnation, cm/min	0.2–9.9	0.2–3.9	0.2–0.9	0.2–9.0
Actual performance hydraulic resistance, 10^{-2} MPa	0.1–5.0	0.3–5.0	2.0–5.0	0.1–5.0

Cement matrix with liquid RW characteristics determination

Samples of cement matrix before and after impregnation were tested for hydraulic resistance, frost resistance, water resistance, and leachability of Cs-137 and U-238. For organic waste, fire and explosion hazard factors (flash and ignition temperature) before and after impregnation of cement matrix and reliability of waste fixation in the matrix by centrifuging samples of volumes up to 120 cm^3 for 1.5 hours were also investigated.

The results show that the compressive strength of the matrix before and after impregnation on the 28th day does not change and equals approximately 5.5 MPa with the porousness of approximately 70%. Matrix compressive strength after water and frost resistance tests with and without liquid RW impregnation does not lower considerably and also equals approximately 5.5 MPa with the porousness of approximately 70%. The leachability of Cs-137 and U-238 from the matrix containing organic liquid RW was between $(8\text{-}9)\cdot10^{-4}$ and $(3\text{-}7)\cdot10^{-4}$ $g/(cm^2\cdot day)$ respectively on the 28th day. The leachability of organic components on the 56th day equals approximately 10^{-6} $g/(cm^2\cdot day)$. Results shows that organic liquid RW bears no influence on solidified cement matrix.

It was established that organic liquid RW was securely fixed in the cement matrix – after centrifuging samples (post impregnation) for 1.5 hours with the relative centrifugal force of up to 90 m/s^2 (≈9g) no liquid waste was released from the samples.

Organic liquid RW fire and explosion hazard in the end product compared to the output state is lowered. Flash and ignition temperature of the output solution of tributyl phosphate in synthene equals 89 and 118 ^oC, after impregnation the flash and ignition temperature equals 128 and 140 ^oC respectively.

Trial plant experiments

Special equipment was designed to impregnate cement matrix in a 200 l barrel (Figure 1). Impregnation technology was tested on the following types of liquid RW: solution of tributyl phosphate in synthene (impregnation volume speed - 17-90 l/h) liquid scintillant (30 l/h) petroleum oil (21 l/h), low acidic aqueous solutions (20-90 l/h).

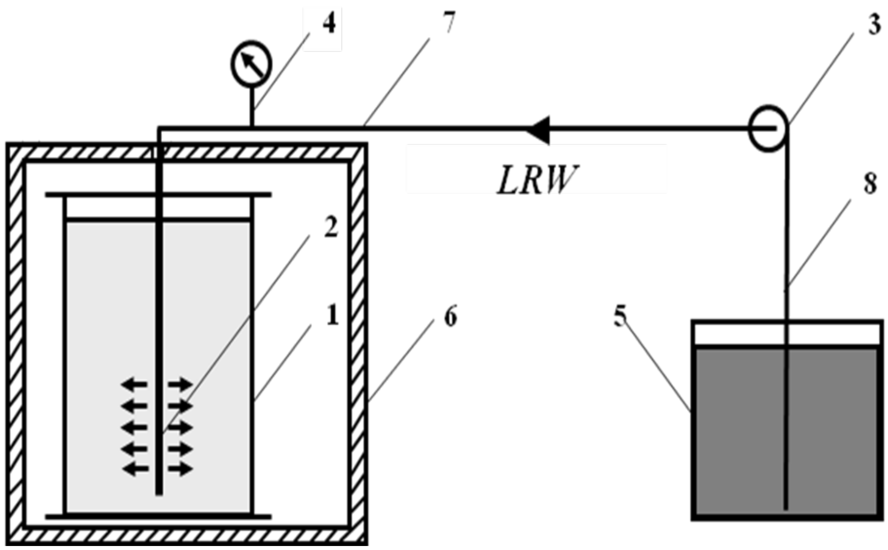

Fig. 1. Scheme of the experimental plant
1- drum with porous concrete; 2- feed tube; 3- plunger metering tube; 4- manometer; 5- storage tank for LRW; 6- shield box; 7,8-pipe.

Cement matrix impregnation in the 200 l barrel showed that at the effective impregnation speed of 0.2-1.1 cm/min and the degree of impregnation of 0.8-0.9 the cement matrix hydraulic resistance varied in the effective interval of 0.01-0.2 MPa. Degree of waste loading capacity of the cement matrix equaled up to 64% in volume and 52% in mass.

Radionuclides distribution by height of the cement matrix placed in a 200 l barrel was estimated. Activity levels were measured with a mobile gamma spectrometer ISOCS. The measurement data shown in Table III is consistent with the estimated laboratory data. Activity levels of the cement matrix sites on Cs-137 and U-238 in the 200 l barrel after a year have not significantly changed.

Table III. Radionuclide's distribution by height of the cement matrix in a 200 l barrel

Height of cement layer, m	**Activity of cement layer, Bq**	
	U-238	**Cs-137**
0.24	8.00E+6	6.00E+7
0.48	1.60E+7	9.00E+7
0.72	1.90E+7	1.10E+8

CONCLUSIONS

The developed technology allows effective immobilization of organic and water liquid RW of different make up by impregnating porous cement matrix. The technology has the following advantages: waste loading capacity of cement compound up to 70 % of volume, elimination of waste components effect on the process of hardening of cement compound, simplicity of technological process and equipment, possibility of immobilization of waste directly on site of its generation that allows transporting solidified waste into storage facility.

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