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Cementation of biodegraded radioactive oils and organic waste

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Abstract Microbiological pre-treatment of the oil-containing organic liquid radioactive waste (LRW) before its solidification into cement matrix (CM) has been investigated and shown to be efficient. Biodegradation of the oil containing LRW is possible by using the microflora, which oxidize the organic components of the oil to carbon dioxide, water and different oxo-organic compounds, sorb radionuclides and cause emulsification of oil in cement slurry due to biogenic surface-active substances, improving the mixing ability of the LRWCM. Here we present the biotechnological parameters of biodegradation and cementation, and the physical–chemical properties of the final LRWCM.

Keywords Biodegradation · Cementation · Oils · Organic radioactive waste

Introduction

Liquid radioactive oil wastes conditioning is one of important problems of radioactive waste management. Different vacuum and transformer oils have been accumulated by nuclear plants, nuclear fleet and facilities of the nuclear fuel cycle. The reprocessing of oily radioactive waste reduces risks of its high inflammability during storage. Some reprocessing technologies have their drawbacks: the separation is complicated because of variability of composition (more than 50 different hydrocarbons, aromatic and heteroatomic components) presents while the thermal processing to gas products pose problems due to radioactive aerosols and toxic gaseous organic compounds like dioxins being formed [1, 2].

The wider used actual technology for oil LRW treatment is its inclusion into cement matrix (CM). The technological challenges on this way are allied to interfusion and delaminating of hydrophobic oil and cement aqueous solution, which leads to low percentage of oil inclusion in the matrix (5–7 wt%). The problem was resolved at the FSUE "RADON" by preliminary suspending with a specially selected composite material, which provided inclusion up to 15 wt% of oils in a block of cement [3]. Researchers of FSUE "PA"Mayak" developed methods that have let including as much of radioactive oils as up to 20 wt% into the cement [4], and 40 wt% in the polymer matrix [5], without deteriorating the properties of the final product according to State Standards GOST P 51883-2002. For the temporary storage of oil-LRW, a method enabling to incorporate up to 60 wt% of oil by impregnating the porous matrix of the prepared concrete was elaborated [6]. Further long-term field tests gave evidence [7] that the long-term storage of CM including radioactive oils under conditions of surface storage, the biogenic inorganic matrix degradation occurs due to the activity of bacteria. The surface bacteria oxidize readily available oil components inside the compound—aliphatic and unsaturated hydrocarbons, aromatic and low molecular heteroatomic compounds. Metabolites of such bacteria, mostly organic acids destroy inorganic matrix deteriorating its immobilization properties [8]. Addition of effective biocide was necessary to suppress

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the negative destructive microbiological processes in the CM [9].

The main idea of this work is to apply microbial degradation of organic LRW components before including into inorganic matrix in order to significantly reduce the volume and provide the conversion of hydrophobic oil to oxidized hydrophilic products compatible with the CM. Biological hydrocarbon oxidation by fungal and bacterial cultures was well demonstrated in the twentieth century. The activation mechanism of saturated hydrocarbons (open-chain and cyclic alkanes) that has been substantiated thus far is the monooxygenase reaction. Aromatic hydrocarbons are initially attacked by ferments of monooxygenases or dioxygenases groups, depending on the type of alkyl side chain or the type of microorganism [10]. Thus, bacteria use organic matter for cell respiration and for assimilation processes as carbon source.

Biodegradation of LRW organic phase to nonradioactive gaseous products (i.e. carbon dioxide) could reduce significantly the total volume of liquid waste to be conditioned, and also to get rid of the hydrophobic component, the latter being antagonistic to cement slurry. The positive effect of pre-biodegradation of oily LRW could be enhanced by formation of biogenic polymers and surfactants with emulsifying properties as part of the residual cell biomass. Dehydrated cells, which absorbs a vast amount of radionuclides could have some astringent properties that facilitate the inclusion into inorganic matrix.

The aim of this work is the estimation of the microbial efficiency for degradation the oily radioactive waste reducing their volume before curing. Chemical components of oily waste can act as a medium for a number of bacterial strains that were determined by special experimental tests previously [11].

Experimental technique

Oil biodegradation tests were conducted in 500 ml vessels with magnetic mixing system. The aerobic strains of oil destructor bacteria belonging to the genera *Pseudomonas*, *Flavobacterium*, *Acinetobacter*, *Aeromonas*, *Arthrobacter*, *Rhodococcus* were used. Strains of microorganisms were isolated from low-temperature oil reservoirs in Russia (Tatarstan, mine Romashkinskoye) and in China (Kondian deposit), as well as from the deep underground storage of liquid radioactive waste (LRW) of FSUE MCC. Based on the isolated cultures, three consortium (OD 2, 3, 4), were established including the most active oil-destructing bacteria with different individual characteristics of consumed hydrocarbons spectrum (Table 1). OD3 consortium was the most full—six different strains. OD 4 was a monoculture strain *Pseudomonas putida*.

Table 1 The consortiums composition

OD2	*Rhodococcus*, *Acinetobacter*, *Pseudomonas*
OD3	*Pseudomonas*, *Flavobacterium*, *Acinetobacter*, *Aeromonas*, *Arthrobacter*, *Rhodococcus*
OD4	Strain *Pseudomonas putida*

Bacteria were cultivated for 7–14 days in a substrate with the composition, g/dm^3 : $NaNO_3$—2; carbamide—0.5; Na_2CO_3—0.5; KH_2PO_4—0.6; K_2HPO_4—1; yeast extract −0.01; pH 7–7.2; and oil to substrate ratio = 1:10. At 3, 5, 7 and 10 days of biodegradation of the oil was extracted with 5 cm^3 of dichloromethane and then a gravimetric analysis of samples was provided to compare the oil samples weight before and after the cultivation.

Vacuum oil VM-4 and transformer oil grade GC were used in this work. The level of oil destruction was investigated by comparative gravimetric, gas chromatography–mass spectrometry, IR and UV spectrometry methods.

Spectrometer with detectors of ultra-pure Ge (Canberra Ind., Inc.) and Liquid-scintillation spectrometer TriCarb-2700 (Packard Ind.) were used for radiometry.

After 15 days of biodegradation some part of the formed biomass was dehydrated by evaporation at a temperature of 65 °C, and then mixed with cement slurry, prepared of portland cement M400 D0 with water–cement ratio W/C = 0.7, where W is the mass of water contained in the slurry and C-weight of portland cement, g. For comparison, the other part of the biomass sludge of similar composition was not dried and mixed with dry portland cement, with the same W/C = 0.7. Spreadability was determined in the resulting slurries using AzNII cone. Delamination was determined in dimensional cylindrical vessel with a capacity of 20 cm^3 for 1.5 h at rest. The cubes with the dimensions of $2 \times 2 \times 2$ cm^3 were prepared of cement slurries, using collapsible forms, heated in air and humid conditions up to 28 days, whereupon the compression strength was determined.

Results and discussion

Reduction of organic phase was estimated after cultivation consortiums OD 2, 3, 4 by gravimetric method. The results (Table 2) indicate that the mass of oil after biodegradation during 7–15 days decreased to 40–67 % of the original. Comparison of the mass of 1 cm^3 of oil samples without microorganisms with the original oil drop indicates the nature of microbiological changes. Biodegradation within 3–5 days is not flowing full, requires the further conduct of the process to achieve the claimed technical effect. The best results were achieved with microbial community OD2.

Table 2 Oil destruction after cultivation by gravimetric method

Microbial community	Weight of 1 cm^3 oil (g)				% of destructed oil at 15 day
	Before	After … days			
		3–5	7	15	
OD2	0.98	0.62	0.33	0.30	67.0
OD3		0.76	0.67	0.52	42.9
OD4		0.81	0.60	0.54	40.7
Without cells		0.98	0.97	0.95	–

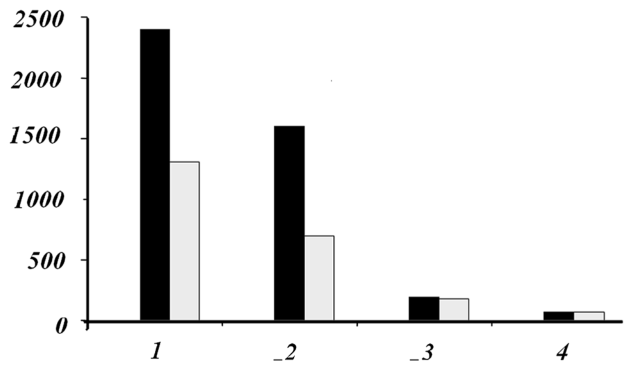

Fig. 1 Results of CMS analysis of main oil fractions before (*filled square*) and after (*grey square*) biodegradation: 1-alkanes, 2-olefines, 3-polyaromatic hydrocarbons, 4-resins

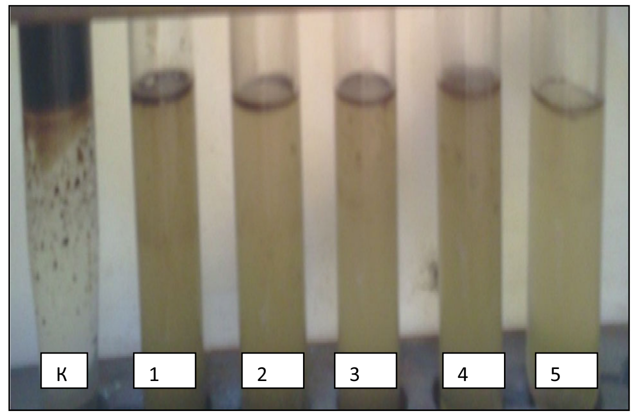

Fig. 2 Education biogenic surfactant emulsifiers after biodegradation of oily liquid radioactive waste: K-control formulation without biodegradation

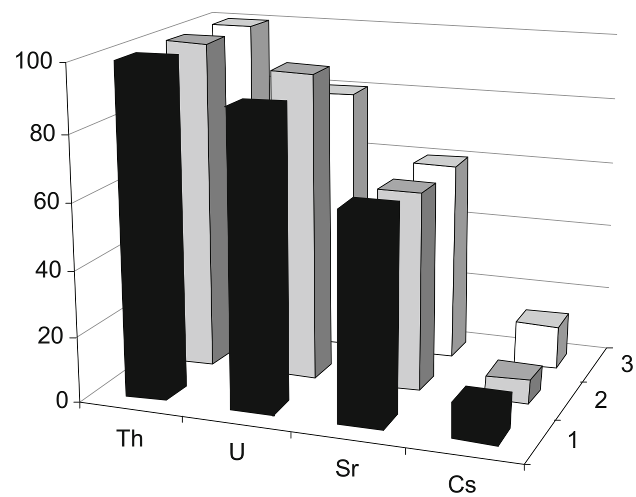

Fig. 3 Radionuclides sorption rate by different microorganisms. *open square*—OD2, *closed square*—OD3, *grey square*—OD4

Results of component analysis before and after the oil biodegradation analyzed by gas chromatography–mass spectrometry show a decrease in the proportion of the most easy-consumped fractions: *n*-alkane to 50 %, olefines 20–30 %, 40–60 % aromatic. Polyaromatic molecules and resins are resistant to biodegradation which ensures prevention of biodegradability LRW composed of oily compound during prolonged storage Polycyclic aromatic and resinous polymer fraction virtually undergone biodegradation, which is important from the viewpoint of safe storage of the final product conditioning (Fig. 1).

Foam formation was visually observed, while culturing all studied consortia with aeration and vigorous stirring. Foaming indicates release of biosurfactants, which has glycolipid nature. The formation of such substances in biomass will have a positive effect at following conditioning. According to [11], the ability of cells to produce such substance can be artificially stimulated by the introduction of specific additives to the medium, e.g. monosodium glutamate in order to improve the emulsifying properties of biomass, and accordingly, the properties of the biomass-based compound. After 15 days of biodegradation visually estimated the presence of the phase "oil:-water" in tubes with a control sample without bacteria (A) and in vitro microbial consortia with OD2 (tube No 1, No 2), OD3 (tube No 3, No 4), OD4 (tube No 5).

The results presented in Fig. 2 show that in the process of biodegradation of oily LRW biogenic emulsifying surfactants of glycolipid nature are formed. Because of its reaction medium becomes steady and the phase interface almost disappears.

In medium, containing transformer oil GC, were added radionuclides of thorium, uranium, cesium, strontium

Table 3 Properties of oil-containing LRW RSC (Kurchatovski Institute)

Appearance				Density (g/cm^3)	Dynamic viscosity (Pa s)
Oily dark-brown liquid				0.84	0.058
Radionuclide composition (Bk/kg)					
^{137}Cs	^{134}Cs	^{60}Co	^{241}Am	^{154}Eu	^{234}U
9.3×10^4	Not found	2.1×10^4	8.6×10^2	6×10^1	1.5×10^4

Table 4 Properties of hardened biomass with biodegraded oily LRW

Compound composition				Cement spreadability (mm)	Oil segregated from cement slurry, % from initial vol.	Compressive strength at 28 day, MPa
Biomass OD2 (g)	Cement (g)	Water (g)	W/C			
0	28.6	20.0	20/28.6 = 0.7	225	0	21.3
20.0[a]	28.6	20.0	20/28.6 = 0.7	125[b]	29.4	3.8[c]
20.0	28.6	–	20/28.6 = 0.7	190	0.2	14.6
2.4	26.2	20.0	20/(26.2 + 2.4) = 0.7	185	0	13.8

[a] Oily LRW, no biodegraded

[b] Slurry delamination

[c] Requirements of GOST R 51883-2002: compressive strength at 28 day 5.0 MPa

concentrations typical for oily LRW (^{137}Cs 1×10^3 Bq/dm^3, ^{90}Sr 1×10^3 Bk/dm^3, Th, ^{233}U 1×10^2 Bq/dm^3). After dehydration slag biomass rigging determined the content of radionuclides. The results (Fig. 3) show that the sorption of Th reached almost 100 %, U—85 %, Sr—50, Cs—10 % on average.

The properties of the initial oily liquid waste that has been not biodegradated are shown in Table 3. The results are shown in Table 4.

The data presented in Table 4, indicate that the formation of biogenic surfactant emulsifiers prevents cement slurry delamination during curing oily LRW under this process. Slurries based on biodegraded oily liquid waste, possess the required spreadability and compressive strength requirements of GOST R 51883-2002. Thus, the proposed method solves the technical problem to reduce the volume of the final product, and improve the parameters of oily LRW cementation (increase spreadability, cessation slurry delamination).

Conclusions

Oil containing LRW biodegradation was shown to be effective for the reduction of the LRW volume and important conversion of hydrophobic oil to oxidized hydrophilic products compatible with the CM. Microflora was able to oxidize up to 60 % of organic components of the oil to carbon dioxide and water. The process of emulsification of hydrophobic organic components due to biogenic surface-active substances formed by biodegradation of oil may follow the biological treatment of oil before solidification and greatly improve this processes. The biomass formed may be used as biosorbent for radionuclides. It could be included into the CM with good compressive strength properties.

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