

**TRANSFER AND FIXATION OF RADIONUCLIDES
BY NANOSIZED LATEXES CONTAINING POLYACRYLIC ACID**

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ABSTRACT

The present work is devoted to the possibilities of removal of dust-suppressor emulsions from solutions using different methods on model systems and liquid radioactive wastes from the ‘Shelter’ at Chernobyl Nuclear Power Plant (ChNPP). It is shown that the most efficient removal of dust suppressors (and transuranic (TRU) elements bound to them) was ensured by using cationic flocculants. Effects of salt and dispersed solids content, pH and emulsion concentration on efficacy of the wastewater treatment are discussed. It is also shown that functionalization of the latex emulsions with nanosized sorbents selective to radionuclides (transition metals ferrocyanides, barium/calcium sulfates) can yield selective colloidal stable sorbents, which can be used for decontamination of bulk materials (spent ion-exchange resins, corrosion-unstable metal structures, soil, and ground). These colloidal sorbents are capable of penetrating bulk (porous) materials without filtration and, further, can be easily separated from solutions, localizing radionuclides in a small volume of solid waste. Application of the nanosized sorbents selective for cesium and strontium to decontaminate zeolite and spent ion-exchange resins are demonstrated.

INTRODUCTION

Building polymer films on dust-generating surfaces using polymer latexes is an efficient method of reducing radioactive aerosols emission. Co-polymer emulsions of the ‘core-shell’ type containing a hydrophobic core (siloxane or polystyrene) surrounded by a hydrophilic polyacrylate shell have found an extensive application. For example, depositing siloxane-acrylate dust-suppressing films on the surfaces of structures and equipment of the destroyed 4th unit at the ChNPP (‘Shelter’) provided substantial reduction of radioactive dust and aerosols emission from the ‘Shelter’ [1]. The disadvantage of this technology is the accumulation of liquids containing the dust-suppressor emulsions inside the ‘Shelter’. Treating this liquid with evaporation processing equipment at ChNPP resulted in damage to the secondary evaporation heat-exchangers which were clogged with rubber-like deposits. In addition, the radionuclide carry-over from Shelter liquids (especially fuel composition and TRU) increased dramatically.

The present work is devoted to the possibilities of removal of dust-suppressor emulsions from solutions using different methods (oxidation, sorption and flocculation) on the examples of model systems and liquid radioactive wastes of the ‘Shelter’ at ChNPP. We also show that siloxane-acrylate latexes used as dust-suppressors can be functionalized with nanocrystals of sorbents selective to radionuclides and used for decontamination of solid materials and LRW treatment.

EXPERIMENTS

Siloxane-acrylate latex emulsion (dust-suppressor KE 13-36) was purchased from JSC ‘Astrochim’, Electrostal, Russia. Average particle size of the latex was 160 nm. Flocculant ‘Chitofloc’ based on soluble salts of aminopolysaccharide chitosan was produced in the Institute

of Chemistry, Vladivostok, Russia according to the technical conditions №2163-007-02698192-2005. All other reagents were of analytical grade.

Oxidation of dust suppressor KE 13-36 (solid content 0.05%) was performed by hydrogen peroxide solutions with concentrations 1-10% in the presence of 0.005M Fe(III) oxalate as a catalyst. Filtration of dust-suppressor emulsion through sorption and ion-exchange materials were performed in columns 8×100 mm with flow rate 1 ml/min. Dust suppressor concentration was monitored by measurements of optical density at $\lambda=500$ nm.

To obtain colloid stable sorbents based on dust-suppressor latexes and selective for cesium ions solutions of CoCl_2 and $\text{K}_4[\text{Fe}(\text{CN})_6]$ were consecutively added to the latex emulsion with solid content 0.1% to reach ferrocyanide concentration 14 mmol/L. Colloid stable sorbents selective for strontium ions were obtained by consecutive addition of $\text{BaCl}_2/\text{CaCl}_2$, and Na_2SO_4 solutions. The size and electrokinetic potential of particles were determined by means of photon-correlation spectroscopy and laser Doppler electrophoresis on the ZetaSizer Nano ZS (Malvern, UK) device. The AFM pictures were obtained with using the AFM-microscope produced by NT-MDT company (Zelenograd, Russia).

Static experiments on decontamination of solid materials were performed by contacting, at constant mixing, 1 g of ion-exchange resin KU2×8 with sorbed ^{137}Cs radionuclide and 50 ml of decontaminating solution (emulsion KE 13-36 with cobalt ferrocyanide nanoparticles containing 10 g/l KCl). Dynamic experiments on decontamination of zeolite (Chuguevka deposit, sample mass 1 g) with sorbed ^{137}Cs or ^{90}Sr - ^{90}Y radionuclides were performed in columns of a diameter 8 mm at decontamination solution (or polyacrylic acid solution with cobalt ferrocyanide nanoparticles) flow rate 0.5 ml/min. The KE 13-36 emulsion with potassium/barium sulfate nanoparticles was used for strontium removal. The activity of cesium and strontium radionuclides in liquid and solid phases after feeding the decontamination solution was determined on a gamma-spectrometer Aspect 1C and a beta-spectrometer Gamma+Progress, respectively.

The pH dependence of cesium ions uptake by dust-suppressor KE 13-36 and colloid-stable nanosized sorbents containing ferrocyanides of cobalt and nickel was studied in NaNO_3 solutions (25 g/L) with activity 85 Bq/ml (^{137}Cs). Sorption isotherms of cesium ions on colloid-stable sorbents containing ferrocyanides of cobalt and nickel was studied at pH 7.5 in NaNO_3 solutions (25 g/L) with initial concentrations of CsCl from $1\text{e-}6$ to $6\text{e-}5$ mol/L and constant amount of ^{137}Cs (85 Bq/ml) added. To measure the equilibrium cesium concentration after the sorption dust-suppressor or colloidal-stable sorbents were qualitatively precipitated with flocculant “Chitofloc” and filtrated.

Flocculation of dust-suppressor KE 13-36 from liquid radioactive wastes (LRW) of ChNPP were performed on samples of drainage waters, evaporator concentrates (solutions after special water treatment system SVO-4) and liquids from sumps. Fixed amount of flocculant “Chitofloc”, solution of NaOH (pH correction), Fe(III) chloride (inorganic coagulant) and CaCl_2 (free oxalate correction) were added to LRW. After filtration of solutions through paper filter “blue ribbon” optical density and alpha-activity of the solutions were determined.

RESULTS AND DISCUSSION

One problem with the dust-suppressor solutions in LRW of ChNPP is oxidation destruction of organic compounds present in Shelter liquids. Several variants of oxidizing organics in the above liquids are possible. Usually, the oxidizers which do not produce precipitate (a secondary SRW), are applied for this purpose. The examples of such treatment include the application of ozone (Kola NPP, Russia) and hydrogen peroxide (Tarapur, India) in LRW oxidation. To estimate the efficiency of oxidation of dust-suppressor by hydrogen peroxide we have performed model experiments with KE-13-36 emulsions with addition of iron oxalate

(Fenton reagent) and Co-EDTA complexes as catalysts. It was found that oxidation by hydrogen peroxide (1-10%) at small periods of oxidation does not yield substantial reduction of dust-suppressor concentration even at high peroxide levels. The reason is related to high colloid stability of emulsion particles due to ionized carboxyl groups of acryl polymers. Even significant oxidation of the emulsion surface does not result in essential destruction of emulsion particles. Besides, the emulsion oxidation process is interfacial and, therefore, the reagents feed and withdrawal rates are restricted. On the other hand, the emulsion oxidation for a long time period is hardly possible at significant LRW flow rates, since it requires a reactor that is too large.

The output curves for sorption of KE-13-36 emulsion on a number of sorbents and ion-exchange resins revealed that the retention volume of emulsion for all sorbents is very close to the column volume. Some reduction of the emulsion concentration was observed at filtration of solution through a layer of anion-exchange resin; however, even in this case the effect is insignificant.

Experiments on the behavior of dust-suppressor KE 13-36 under hydrothermal conditions revealed no optical density reduction up to 140°C while above this temperature significant reduction was observed but only at low flow rates (significant time of emulsion presence in high-temperature zone). Although there was no decomposition of the KE 13-36 under the studied conditions, with temperature increase up to 160-180°C significant reduction of optical density of dust-suppressor emulsion coming out of the hydrothermal reactor was observed due to complete emulsion polymerization with formation of rubber-like matter. These experiments confirm the assumption that polymerization of dust-suppressor used at ChNPP on heat exchangers walls overheated in SVO-4 secondary evaporators which significantly limits application of traditional LRW treatment at ChNPP.

Due to the high surface charge of the dust-suppressor determined by ionization of carboxylic groups attaining sufficiently complete coagulation requires addition of large amounts of acids (pH<1). This complicates management of TRU due to dissolution of most transuranics contained in LRW in addition to problems of handling acids. One of the most widely used methods of solutions purification from colloids is coagulation or co-precipitation on hydroxide precipitates. In our experiments we studied the described process of the emulsion KE-13-36 precipitation by iron hydroxide and found that the purification degree (decontamination factor) for emulsion solutions with solid phase content 40 mg/l was higher than 100 only at doses of Fe(III) above 150 mg/l. Therefore, the removal of dust-suppressor by co-precipitation with iron hydroxide results in formation of significant amounts of solid radioactive waste. In this case, the iron hydroxide precipitate belongs to the group of hard-to-filter precipitates (especially for the precipitates iron-KE-13-36 emulsions), and processing in large amounts would cause great problems requiring the use of special equipment.

An alternative solution would be application of cationic flocculants. Moreover, there exist a number of synthetic and natural cationic flocculants that selectively remove radionuclides from solutions. That makes it possible to combine the stages of emulsion and TRU removal into one process. It was found that dust-suppressors can be efficiently precipitated from solutions with “Chitofloc” at flocculant doses 3-5 mg/L and solid content of KE 13-36 down to 0.006%. When it is required to precipitate dust-suppressors from solutions with solid content below 0.006% combination of polymeric flocculant with inorganic flocculant (floculation composition) is recommended. However, compared to inorganic flocculants, doses of Fe(III) in floculation composition is at least 10 times lower which greatly improves LRW treatment reducing the volume of secondary solid wastes. Fig.1 gives some examples of usage “Chitofloc” flocculant for simultaneous removal of dust-suppressor (estimated as a reduction of

optical density) and TRU (estimated as a reduction of alpha-activity) from the original LRW samples.

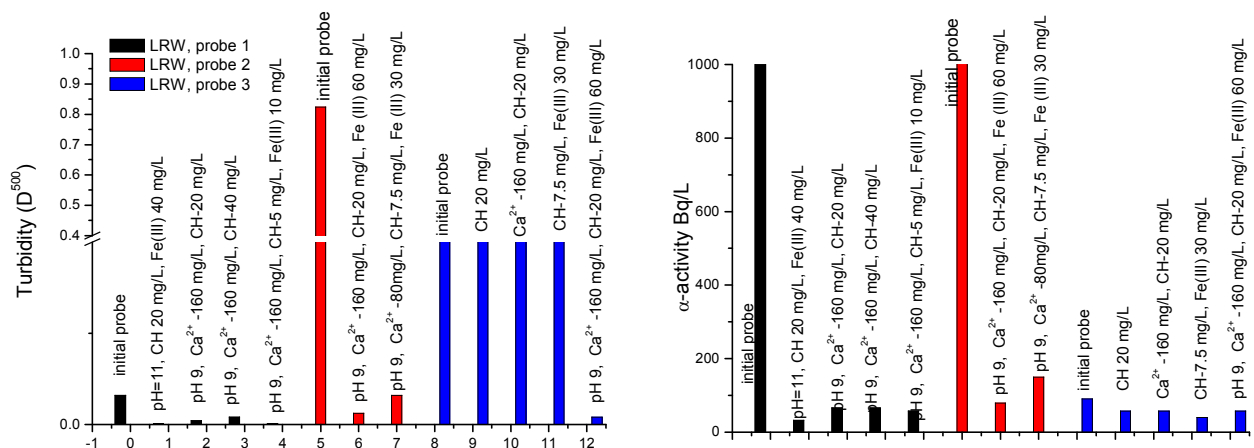


Fig.1. Reduction of turbidity and alpha-activity of dust-suppressor (KE 13-36) containing LRW at ChNPP by flocculation process with “Chitofloc” (CH)

The negative effect of dust-suppressor emulsions on LRW treatment process due to their high colloidal stability, small size and high cation-exchange capacity (which is responsible for transfer of cesium and strontium radionuclides) can be turned into benefits, if one consider possibilities of selective sorbents synthesis based on nanoparticles of dust-suppressors. The presence of anionic centers on the latex particle surfaces offers the possibility of binding to them ions of divalent metal-precursors of some well-known sorbents selective for radionuclides of cesium (ferrocyanides of transition metals) and strontium (sulfates of calcium/barium). At the second stage of synthesis the anion precursor is added into the latex emulsion, and nanosized colloid-stable selective sorbent is formed. The general scheme of such sorbents preparation is shown in Fig.2. With the added metal concentration increase one can observe the decrease of electrokinetic potential (by modulus) at invariable particle size, while the residual negative charge on the surface provides the system high colloid stability. To form nanoparticles of a selective sorbent, we limited the amount of ion introduced at the beginning of the plateau on the dependence of electrokinetic potential of the metal concentration in solution, since it was found that the addition of an excess amount of metal resulted in the formation of non-stabilized sorbent particles in solution. Further introduction of equivalent amount of the selective sorbent anion-precursor into solution does not cause a change in the emulsion particles size. This is accompanied by a reduction of the particles electrokinetic potential down to -30 mV for cobalt ferrocyanide immobilized in polystyrene-acrylate emulsion (PAE); -36 mV for siloxane-acrylate emulsion (KE 13-36) and -40 mV for calcium/barium sulfate immobilized in KE 13-36. One can see on the presented AFM-images (Fig. 2) that, as a result of introducing cobalt ferrocyanide nanoparticles, the initially spherical PAE particles transform into a cubic shape characteristic for ferrocyanide macrocrystals [2]. On the surface of the film formed by the siloxane-acrylate emulsion KE 13-36 with introduced calcium/barium sulfate, one can easily discern particles similar in shape to raspberries, while the initial emulsion spreading results in formation of a smooth film.

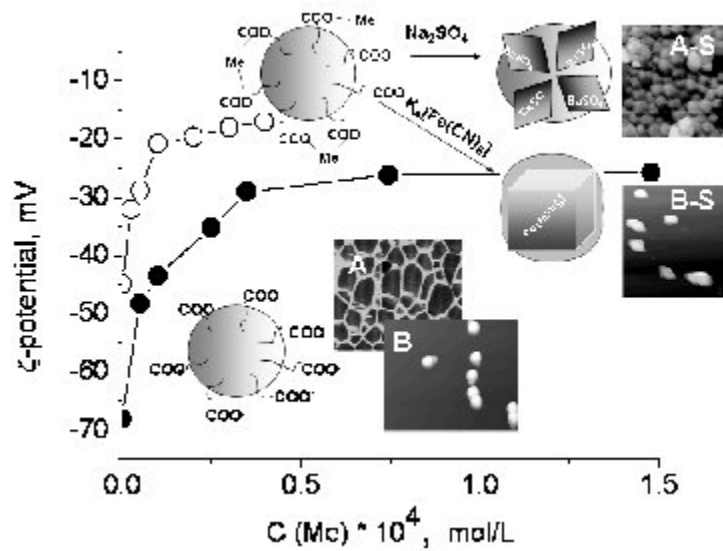


Fig.2. Scheme of formation of nanosized crystalline sorbents – barium sulfate in KE 13-36 emulsion and cobalt hexacyanoferrate in PAE emulsion, where A and B – AFM-images (2×2 micrometers) for initial emulsions KE 13-36 and PAE, respectively, A-S and B-S – for emulsions with introduced sorbent nanoparticles. Open symbols on the dependence of electrokinetic potential of latex particles on concentration of introduced metal ions (Me) correspond to PAE (solid content 0.1%), closed – to KE 13-36 (solid content 0.02%)

This type of sorbents is especially promising for decontamination of solid materials, since aside from high selectivity it is characterized by high penetration ability in porous media and easy separation after decontamination by flocculation/precipitation process. Due to immobilization into stable polymer colloids, the selective sorbent nanoparticles preserve high stability at filtration. After 50 filtration cycles of the emulsion KE 13-36 with immobilized nanoparticles of cobalt ferrocyanide through a layer of natural zeolite, the cobalt content in the emulsion and emulsion optical density remained constant.

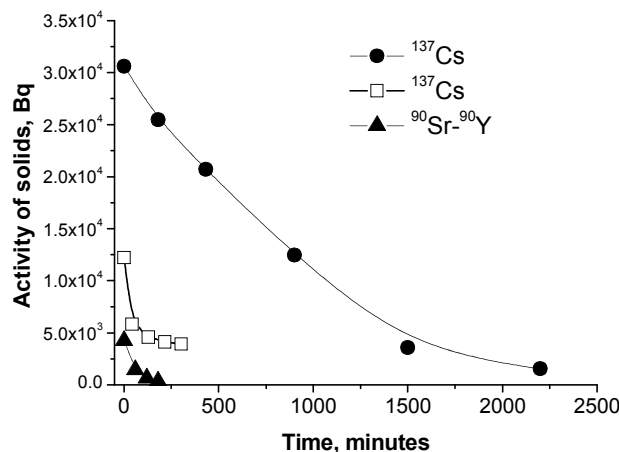


Fig. 3. Decontamination of zeolite (clinoptilolite of Chuguevka deposit) from cesium and strontium radionuclides by nanoparticles of selective sorbents (cobalt ferrocyanide and barium/calcium sulfate) immobilized in KE 13-36 emulsions

The combination of high selectivity nanosized sorbents immobilized into emulsions with the ease of their removal from solution enables one to recommend the developed schemes for different material decontamination. The example of decontamination of KU2×8 ion-exchange resin by KCl solution and the same solution containing emulsion with cobalt ferrocyanide immobilized in different ways confirms that use of emulsions with nanosized selective sorbents allows multifold increase of the efficiency of decontamination of ion-exchange resins and other ion-exchange materials. The possibility to decontaminate porous materials selectively binding radionuclides was also clearly demonstrated by the experiments of cesium and strontium removal from natural zeolite (clinoptilolite of the Chuguevka deposit, Primorsky Krai) using the suggested schemes – see Fig. 3.

One of the typical problems in application of transition metal ferrocyanides for cesium uptake is instability of ferrocyanides at alkaline media. Here we have investigated efficacy of colloid-stable selective sorbent based on KE 13-36 latex and cobalt ferrocyanide in NaNO₃ (25 g/L) at pH 3-10 and found that more than 99% percent of ¹³⁷Cs was efficiently removed after latex precipitation. Total activity of the solution was 2100 Bq and total cobalt ferrocyanide content in the probe was 2.2e-8 mol. Under the same experimental conditions non-functionalized KE 13-36 latex has shown an uptake of 10-11% of ¹³⁷Cs which confirms the role of the dust-suppressor in increasing mobility and transfer of radionuclides in ChNPP. To determine sorption capacity of cobalt and nickel ferrocyanides immobilized in KE 13-36 (colloid stable sorbents) sorption isotherms were obtained at pH 7.5 in NaNO₃ (25 g/L) solutions. As can be seen from Fig.4 nickel and cobalt ferrocyanides immobilized in KE 13-36 latex show comparable sorption capacities and can be efficiently used for decontamination of LRW and SRW.

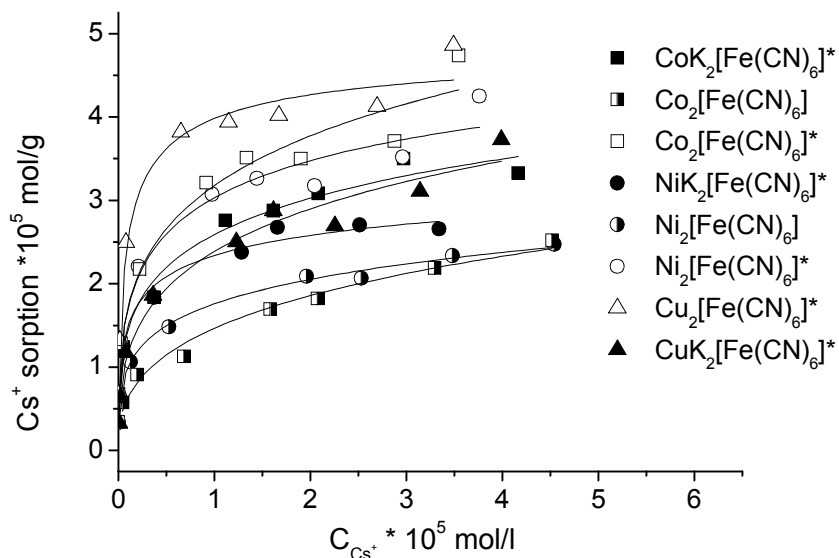


Fig.4. Sorption isotherms of cesium ions on KE 13-36 latexes functionalized with cobalt and nickel ferrocyanides (*-ferrocyanides content is 4e-5 mol per 1 g of the latex, systems without asterisk - 2e-5 mol per 1 g), NaNO₃ (25 g/L), pH 7.5

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