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APPLICATION OF ULTRAFILTRATION AND COMPLEXATION TO THE TREATMENT OF LOW-LEVEL RADIOACTIVE EFFLUENTS

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ABSTRACT

This paper addresses certain aspects of the design and development process aiming at reducing the radioactivity of liquid low-level waste streams (LLLW) to a very low level. Two types of membrane processes are being examined: ultrafiltration (UF) and seeded ultrafiltration (SUF). The UF membrane enables the removal of very fine particles of solid material from liquid radioactive waste. Only the particles with molecular weight above the cut-off of the UF membrane are retained. Much greater radioactivity removal may be achieved if the effluent is treated with high-molecular-weight ligands that form complexes with radioactive ions or small-sized radioactive molecules. This paper presents results of experiments consisting of decontamination of model radioactive effluents, simulated waste, and original LLLW by using several ligands for binding the radioactive ions of Cr, Co and Cs.

INTRODUCTION

Nuclear reactors, isotope laboratories, and nuclear medicine centers, as well as laundries washing clothes contaminated by radioactive substances, produce various nuclear waste. Liquid low-level waste (LLLW), produced in Poland at the rate of 800-1000 m^3/year, has become a subject of our interest. The waste contains particles of solids, emulsions, and detergents. The concentration of salts of alkaline metals is about 0.5-2 5 g/L. The LLLW appears as a result of decontamination of rooms, laboratory glass as well as remains of solutions used in experiments, production and distribution of radioisotopes, and as effluents from laundries washing contaminated clothes. Most frequently, they contain the radioisotopes: ^{32}P, ^{35}S, ^{51}Cr, ^{60}Co, ^{65}Zn, $^{85+89}$Sr, ^{90}Y, ^{121}Te, ^{131}I, and ^{137}Cs. The total specific activity of β and γ emitters in LLLW was about 3.1×10^{3} to 7.5×10^{4} Bq/L from 1985 to 1992.

The process of LLLW decontamination should result in elimination of radioisotopes from the waste, volume reduction of the concentrate containing isotopes, and fossilization of the isotopes in glass, asphalt, or concrete. The concentration of the radioactive components in the water regenerated should be reduced to the level at which the specific activity of each radioisotope would not be highe than the maximal value set by the sanitary standard for communal sewage or water utilized in industry - depending on the purpose with which the regenerated water is to be used.

Achievement of the aims sketched above is possible by applying different methods (i.e., sorption, thermal, and membrane) of separation of suspensions and solutions to a multistage process of the LLLW treatment. Sorption and thermal methods are similar in appearance and the fact that they each introduce a new phase: steam in the thermal method and a solid substance in the sorption method. Radioisotopes are accumulated in one of the phases: the liquid phase in the case of evaporation, whereas the solid phase in the case of sorption. In the membrane methods belonging to the group of pressure filtration, ultrafitration (UF), nanofiltration (NF), and reverse osmosis (RO), the separation takes place without a new phase, and its efficiency depends on retention coefficient of the membrane for soluble substances occurring in the solution.

Analysis of the LLLW samples taken from the storage tanks located in the Institute of Atomic Energy, Świerk (IAE) and Institute of Nuclear Chemistry and Technology, Warsaw (INCT) has shown that radioactive substances occur in forms of small-sized molecules and free ions, and 60-75 % of their specific activity comes from ^{51}Cr, ^{60}Co, and ^{137}Cs. These radionuclides occur as ions $^{51}Cr^{3+}$, $H^{51}CrO_4^{-}$, $^{60}Co^{2+}$, and $^{137}Cs^{+}$; therefore, they pass through the UF membranes for which the smallest cut-off value is of the order of 2000 mol.wt. Therefore, at the stage of initial purification of LLLW (precipitation, sedimentation, filtration by net filter, ultrafiltration), one achieves less than a tenfold lowering of the specific activity of LLLW. With the purpose of better decontamination by the UF process, one has to bind the radioactive ions having masses higher than the cut-off of the UF membrane used at this stage of the treatment of the LLLW.

EXPERIMENTAL

Macromolecular Ligands Used for Complexation of Ions: Cr^{3+}, $HCrO_4^-$, Co^{2+}, and Cs^+.

The UF membrane retains molecules whose sizes are larger than the sizes of its largest pores - they remain in the retentate, whereas particles having smaller sizes and ions penetrate through the mem brane to the permeate. The seeded ultrafiltration (SUF) method enables retaining part of effluent components that previously moved to the permeate because now they are binded with ligands. The SUF process identified in the title as "complexation" encompasses all the processes of binding macromolecular ligands with ions and molecules occurring in effluents in very small concentrations.

Preparation of radioactive solutions, simulated waste, and LLLW for separation using the SUF method demands conditions affording an oportunity for the appearance of complexes of macromolecule + ion(molecule) or particle-of-suspension + ion(molecule) attaching radioactive ions or molecules that, subsequently, remain in the retentate in the following UF process. Ligands having those properties may be identified with certain components of the LLLW (e.g., detergents and other surface-active substances). The ability to attach one or not more than several kinds of ions or particles (selectivity) constitutes the characteristic feature of the majority of ligands. This means that removal of a radioactive component by using the SUF method requires selection of the appropriate ligand. The LLLW contains a number of radioactive substances, and the SUF method enables removal of some of them subsequently (UF following addition of each ligand) or simultaneously (UF following addition of the ligand mixture).

In the course of the search for ligands attaching ions of Cr, Co, and Cs, we have paid attention to synthetic soluble polymers used to extract metals occurring in the effluents in trace amounts [1-6], as well as to suspensions of cyanoferrates sorbing ions of Cs^+ [7-10] and chitosan obtained asa result of chitin deacetylation [11-14]; the last ligand is able to attach ions of certain metals from very dilute solutions despite much higher concentration of ions of alkaline metals.

<u>Apparatus and Experimental Procedure</u>

The process of binding of ions of Cr^{3+}, $HCrO_4^-$, Co^{2+}, and Cs^+ with various ligands as well as removing the complexes that appear astheresult of UF were investigated on a laboratory scale using the small rig unit shown in Fig.1. The model solution, simulated waste, or samples of the original LLLW were poured into the reactor (a 3-L vessel with mixer), ligand was added, and the pH level was adjusted to the value required. The solution was mixed for several hours; subsequently, it remained at rest for 10-20 h (seasoning) with the purpose of establishing the state of equilibrium. Mixing and seasoning periods were established experimentally for each ligand and the radioactive ions attached by this ligand - the periods were accepted when their elongation did not result in diminishing of the specific activity of the permeate obtained by UF of the "seeded" solution.

With this purpose in mind, the UF module having an active surface of 0.01 m^2 built of 17 polysulphone capillaries (cut-off 3000 mol.wt) was used. The initial volume of solution, V_0, was 2 L during each test; the solution was furnished to the module with the help of a peristaltic micropump under a pressure of 0.1 MPa, and the retentate flow was kept at a level of 20 L/h. These operating conditions of the laboratory unit prevented sedimentation on the membrane surface (fouling layer) and guaranteed the permeate flow from 0.6 to 0.9 L/h. Location of the feed vessel within the thermostat afforded an opportunity for performing tests at a constant temperature. The dead space of the unit was 0.06 L and enabled conducting the UF

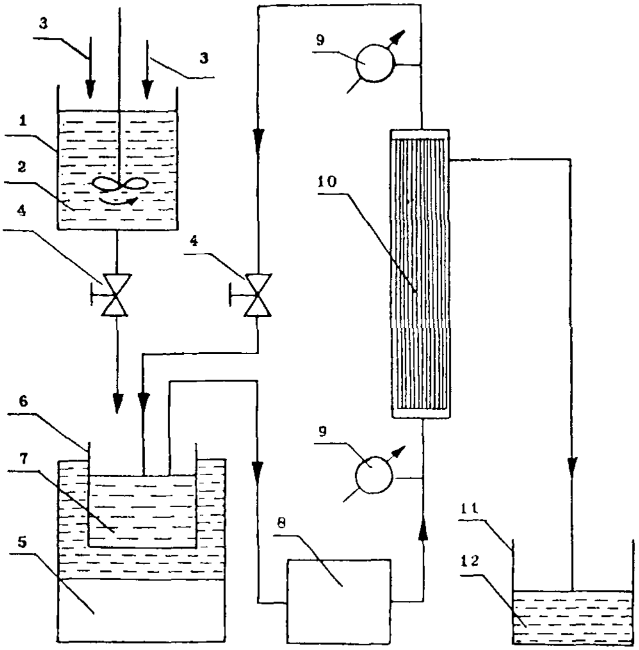

FIGURE 1. Schematic diagram of laboratory unit used for SUF tests.

1 - reactor vessel; 2 - model solution, simulated waste or real LLLW; 3 - macromolecular ligands; 4 - taps; 5 - thermostat; 6 - feed vessel; 7 - "seeded" solution; 8 - peristaltic pump; 9 - pressure gauges; 10 - UF capillary module, 11 - permeate reservoir; 12 - permeate.

to a moment when the retentate volume, V_r, was 20 times smaller than the volume of the initial solution, V_0 (V_0/V_r = VRC = 20 ; VRC - volume reduction coefficient).

At particular stages of the CUF process, samples of the solutions were taken and the total concentrations of Cr, Co, and Cs were determined using an atomic absorption spectrometer Perkin-Elmer 5000. Measurement of specific activity of the model solutions (one kind of radioisotope in the solution) and total activity (this resulted from all the β and γ emitters occurring in the solution) was conducted at standard system counting the pulses generated by the probe with a NaI/Tl scintillation crystal. In the case of simultaneous occurrence of several radioisotopes in the solution (simulated waste, real LLLW from IAE and INCT), the 800-channel analyzer DIDAC with the spectrometric probe SCINTILBLOC (Intertechnique, France) and standards with specific activity known (^{51}Cr, ^{60}Co, ^{137}Cs) have been used.

Tests with Model Solutions

Analysis of LLLW samples from storage tanks of IEA and INCT has shown that concentrations of salts of alkaline metals are not higher than 2.5 g/L and average weight ratios of Na:K:Mg:Ca are 120:1:4:40. This has been taken into account while preparing the base medium for model solutions, a mixture of easy soluble salts of these alkaline metals, in which the weight proportion has been kept, has been added to the distilled water. Concentration of the mixture, c_m, was 0.5 g/L in all tests performed with those solutions at c_m = const. The mixture concentration was changed from 0.005 to 2.5 g/L in the tests conducted with the purpose of determining the dependence of the decontamination factor DF (DF = A_0/A_p ; A_0, A_p - specific activity of the feed solution and the permeate) on the concentration oft the salts mixture in seeded solution.

The base medium has been used to prepare solutions containing, for one of the following salts: $CrCl_3$, Na_2CrO_4, $CoCl_2$ and CsCl. Masses of the salts added were adjusted to obtain a concentration of 0.005 g/L of ions: Cr^{3+}, $HCrO_4^-$, Co^{2+}, and Cs^+ in solutions. Those solutions were supplemented with small amounts (0.2-1.0 mL) of solutions of the same salts containing ^{51}Cr, ^{60}Co, and ^{137}Cs, respectively. Amounts of Cr, Co, and Cs introduced to solutions as a result of that operation may be neglected because they are of the order 10^{-8} to 10^{-12} g. Radioactive solutions were added until specific activity of each portion of the model solution had achieved the value $A_0 = 10^4$ Bq/L.

Each of the model solutions has been distributed into several 2-L portions. Ligands able to create complexes with ions Cr^{3+}, $HCrO_4^-$, Co^{2+}, and Cs^+ or attach them in the way of absorption have been added to the portions. In result following seeded model solutions have been obtained:

1. Cr^{3+} + PEI , 2. Cr^{3+} + PAA , 3. Cr^{3+} + PVP , 4. $HCrO_4^-$ + MCH,
5. Co^{2+} + PEI , 6. Co^{2+} + PAA , 7. Cs^+ + CuFC , 8. Cs^+ + CoFC.

Here: PEI - polyethylenoimine, PAA - polyacrylic acid, PVP - polyvinylpyrolidone, MCH - microcrystalline chitosan , CuCF and CoCF - suspensions of cupric and cobaltic cyanoferrates, respectively.

For each of the eight solutions, three series of tests have been performed at the temperature 20 ^{0}C and pH = 7. One has assigned for one of the following variable parameters, respectively, to subsequent tests in the series: mixing period, seasoning period and relative ligand concentration c_{lig}/c_{ion} (c_{lig} , c_{ion} - respectively, the ligand concentration and concentration of ions creating complex with the ligand molecule or being absorbed by the ligand suspension).

These tests have shown that under conditions of the experiment which were presented above, the periods of 4 h of mixing and 16 h of seasoning are sufficient and ligand concentration should be from 5 to 20 times as high as total concentration of ions bound by this ligand.

Two consecutive series of tests have been performed utilizing the results obtained previously and presented above. Then, the following conditions have remained: mixing for 4 h, seasoning for 16 h, c_{ion} = 0.005 g/L, c_{lig}/c_{ion} = 20, T = 20 ^{0}C. The following values have been considered as consecutive variable parameters:

pH = 4 to 11 (c_m = 0.5 g/L) and c_m = 0.001 to 2.5 g/L (pH = 7).

It has been established (Fig. 2) that the best conditions under which ions Cr^{3+} and Co^{2+} can be bound with macromolecules PEI, PAA, and PVP occur are pH = 6.5 to 8.5 whereas binding the ions $HCrO_4^-$ with MCH processes best at pH = 4 to 6. The most efficient absorption of ions Cs^+ by the suspension CuCF or CoCF may be realized at pH = 9.5 to 10.5. Growth of the value c_m within the range noticed above results in diminishing of the value DF for several percent.

Tests with Simulated Radioactive Waste and Original LLLW

The simulated sewage has been composed in a way as to contain all of the radioactive ions: $^{51}Cr^{3+}$ (or $H^{51}CrO_4^-$), $^{60}Co^{2+}$, and $^{137}Cs^+$. Analogously to tests with

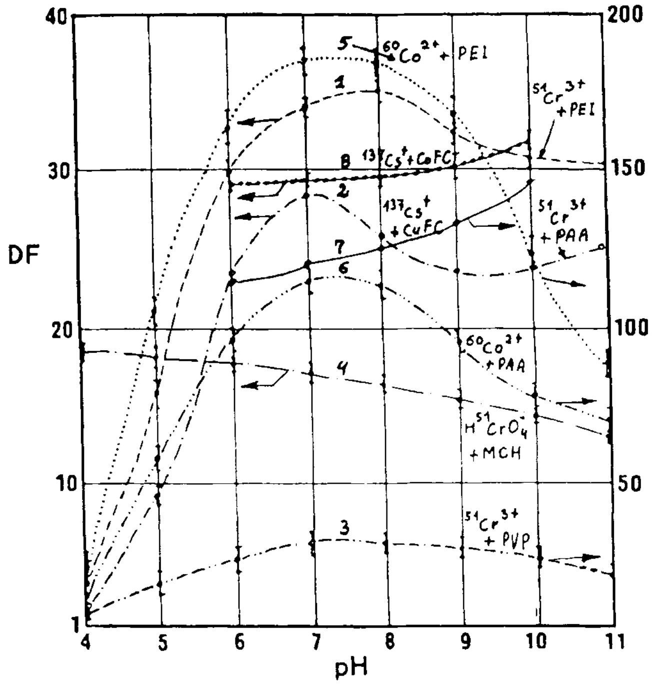

FIGURE 2. Changes of the decontamination factors DF with pH of "seeded" model low-level radioactive solutions

$c_{ion} = 0.005$ g/L ; $c_{hg} = 0.1$ g/L ; $c_{m} = 0.5$ g/L .

model solutions, one has prepared four portions of base media for 2 L each characterized by concentration of the alkaline metal salts $c_m = 0.3$, 0.7 , 1.2 , and 2.5 g/L, and one has added appropriate portions of diluted solutions of the radioactive salts: $^{51}CrCl_3$ (or $Na_2{}^{51}CrO_4$), $^{60}CoCl_2$, and $^{137}CsCl$. Total specific activity of each of the four portions of sewage was $3 \cdot 10^4$ Bq/L, whereas the characteristic of the particular radioisotopes was 10^4 Bq/L. Concentrations of Cr, Co, and Cs were below 10^{-7} g/L, thus they did not exceed the level admitted under Polish sanitary regulations concerning water used in industry.

Composition of the simulated sewage was as follows:

S-1 : $^{51}CrCl_3$ + $^{60}CoCl_2$ + $^{137}CsCl$; c_m = 0.3 g/L ,
S-2 : " " " ; 0.7 g/L ,
S-3 : $Na_2{}^{51}CrO_4$ + $^{60}CoCl_2$ + $^{137}CsCl$; 1.2 g/L ,
S-4 : " " " ; 2.5 g/L .

Portions containing 0.020 g of the ligands applied previously - PEI, MCH, and CuCF (suspension) - have been added simultaneously to the portions of each kind of the simulated sewage. Each portion has been mixed (4 h) and after seasoning (16 h) it has been ultrafiltrated (all the operations at pH = 7 and T = 20 °C); as a result, 1.9-L volumes of permeate and 0.1 L of retentate (VRC = 20) have been obtained. The values of DF obtained for the permeate are presented in Table 1.

The SUF process has been applied to the samples of low-level radioactive waste (LLLW) from IAE and INCT storage tanks with the help of the same method as in the case of simulated sewage.

The samples had the following characteristics:

R-1 (IEA): total concentrations of Cr, Co, and Cs - below 10^{-7} g/L ;
$A_0 = 4.7\times10^3$ Bq/L ; (^{51}Cr - 48 % , $^{134+137}$Cs - 27 % , ^{60}Co - 17 %, othe β and γ emiters - 8 %) ; c_m = 0.76 g/L.

R-2 (INCT): total concentrations of Cr, Co, and Cs - below 10^{-7} g/L ;
$A_0 = 9.2\times10^3$ Bq/L ; (^{51}Cr - 5 % , $^{134+137}$Cs - 56 % , ^{60}Co - 27 %, other β and γ emiters - 12 %) ; c_m = 1.64 g/L.

The DF values obtained at VRC = 20 are presented in Table 1.

Tests at Industrial Pilot Plant

One has prepared 200-L portions of the simulated sewage and LLLW used for laboratory-scale tests. Distribution of each portion into 190 L of permeate and 10 L of retentate with the help of SUF method has been performed under the same conditions as in the case of laboratory tests. The DF values are presented in Table 1.

TABLE 1. DECONTAMINATION FACTORS OF SIMULATED RADIOACTIVE AND ORIGINAL LLLW OBTAINED BY USING SUF METHOD

Effluent	S-1	S-2	S-3	S-4	R-1	R-2
DF for laboratory unit	68	64	65	58	56	52
DF for pilot plant [a)]	59	62	52	46	37	40

[a)] $V_0 = 200$ L, VRC = 20 ($V_p = 190$ L, $V_r = 10$ L).

UF module : AMICON H26P30-43, capillary type, cut-off $3 \cdot 10^4$ mol.wt, membrane surface area 2.5 m^2.

RESULTS AND DISCUSSION

One has obtained the following DF values for particular radioactive ions: $^{51}Cr^{3+}$ - 93 to 128, $^{60}Co^{2+}$ - 102 to 135, $H^{51}CrO_4^-$ - 56 to 75, ^{137}Cs - 32 to 45.

They have been obtained as a result of laboratory tests in the course of which various macromolecular ligands are employed to create complexes or absorb ions: Cr^{3+}, $HCrO_4^-$, Co^{2+}, and Cs^+. The values DF = 52 to 68 in laboratory tests and DF = 37 to 62 at the pilot plant have been obtained while employing the mixture of three ligands: polyethylenoimine, microcrystalline chitosan, and suspension of cupric cyanoferrate, which have the most efficiency to create complexes or absorb the ions mentioned under the conditions maintained during SUF experiments with simulated radioactive waste and real LLLW.

Utilizing the mixture of certain ligands in the SUF process is possible in the case when all components of the mixture have a high efficiency to bind radioactive substances in the solution when values of pH, temperature, and concentration of alkaline metal salts remained the same for all the ligands. In other case, particular radioactive substances are to be removed subsequently: the solution or LLLW is seeded by additon of one ligand and ultrafiltrated.

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