A METHOD FOR REGENERATION OF SPENT ELECTROCHEMICAL DECONTAMINATION SOLUTION AND ITS TREATMENT FOR FINAL DISPOSAL

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ABSTRACT

This paper describes the method of regeneration of spent electrochemical decontamination solution. The proposed method allows separation of radionuclides and stable metals from spent decontamination solution in a form suitable for final disposal and repeated use of the remaining solution for electrochemical decontamination. Development of this method was based on the results of the speciation studies which showed that Fe(III) can be precipitated in the presence of organic complexing agents, in a form of iron hydroxide, and Ag-110m, Co-60, Mn-54 radionuclides can be co-precipitated on it.

In order to verify the conclusions made as a result of the speciation studies, the experiments with electrochemically prepared simulant solution and real solution were carried out. The test results proved that the proposed method can be applied in practice.

Treatment of the ultimately spent decontamination solutions can be also made applying iron precipitation, which allows for removal of the bulk amount of contaminants, as the first step. Then, if necessary the remaining radionuclides can be removed by sorption. A series of novel absorbers has been tested for their potential for the sorption removal of the remaining radionuclides from the supernate. The test results showed that most of them were more effective in neutral or alkaline range of pH, however, the high efficiency of the sorption removal can be achieved only after the removal of the oxalic and citric acids from solution.

INTRODUCTION

The current research concerns the problem of treatment of liquid radioactive waste containing organic complexing agents. A considerable volume of such a waste is generated across the European countries. These solutions are complex mixtures, which apart from organic complexants and radionuclides can include non-radioactive inorganic substances. The main source of such waste streams is decontamination of the Nuclear Power Plants (NPP) primary circuit equipment during standard operation or decommissioning of the NPPs. The complexity of such a waste makes its treatment for disposal a difficult task. Also, the presence of organic complexants in solidified wastes represents an additional risk to the environment, due to an increased leachability of radionuclides.

In the Slovak and Czech VVER-440 type NPPs, the greatest volumes of secondary wastes arise from the „in situ“ electrolytic decontamination of the main circulating pump and the main gate valve casings. This method is based on the anodic dissolution of contaminated surface layers of the treated metal. In the NPPs Jaslovské Bohunice (Slovakia) and Dukovany (Czech Republic) the modification of this process is applied which is characterised by using the electrolyte composed of the oxalic (up to 10 g/dm^{-3}) and citric acids (5 g/dm^{-3}) and current densities 100 – 130 $mA.cm^{-2}$. Typically, composition of such a solution, after several cycles of electrochemical decontamination (spent solution), apart from remaining complexing agents includes stable metals (Fe, Cr, Ni; total concentration up to $5 \cdot 10^{-2}$ Mol/L with approximate ratio 72 : 19 : 9) and radionuclides (total activity in the half course of electrolyte working capacity, according to gamma spectrometric analysis of solution – $1 \cdot 10^{5}$ Bq/L; Ag–110m - 9,4 %; Co–58 - 42,8 %; Co–60 -34,5 %; Fe–59 - 1,4 %; Mn–54 -10,5 %;).

This paper describes the method of regeneration of such a spent decontamination solution that has been developed in the frame of European INCO-Copernicus project ERB IC15-CT98-0202 "Highly versatile but sustainable processes for the removal of radionuclides from radioactive waste (SUSRAD)". The proposed method allows separation of radionuclides and stable metals from the spent decontamination solution in a form suitable for final disposal and repeated use of the remaining solution for electrochemical decontamination.

EXPERIMENTAL

All solutions were prepared by dissolution of a certain amount of high purity salts in distilled water. After adjusting pH with an aqueous solution of ammonium, the solutions were stored for 2-5 days before the beginning of experiments to establish equilibrium in the soluti on. The experiments were carried out at the ambient temperature, approximately 20°C.

Sedimentation of iron(III) hydroxide and radionuclides co-precipitation with it was studied by centrifugation method. A laboratory centrifuge was used for the experiments; the phases were separated by 30 minutes centrifugation at 8000 rpm. The results were presented as "centrifugation precipitation percent".

The total concentration of oxalic and citric acids was determined applying the method of chemical oxygen demand [1]. Concentrations of radionuclides and stable iron were determined using the radioactive isotopes: ^{60}Co, ^{59}Fe and ^{54}Mn. The measurements were taken by γ-spectrometers – "Aspect", Gamma-1C with NaI(T1) scintillation detector and multichannel spectroanalyser Canbera-Paccard, System-100 with germanium semiconductor detector (DGDK 63 B). In order to minimise the loss of the radionuclides due to the sorption on the walls of the experimental vessels they were preliminary saturated with the radionuclides. Concentration of H^+ ions in solution was measured by a pH meter – "ZIP", EV-74 with a glass electrode. The pH meter has been standardised according to a common technique which demands the use of alkali, acid and neutral buffer solutions. The experimental solution contained no other ions that, according to the manual, could affect reading the pH.

Simulant electrochemical decontamination solution was prepared by electolysis of stainless steal in solution of citric and oxalic acids under the same conditions which were used for the full scale decontamination process. Radionuclides were introduced into solution immediately after electrolysis and the solution was allowed to equilibrate for half an hour, and then the measurements of initial concentration (before iron hydroxide precipitation) of all the solution components were taken. All the values presented on Fig.3. are the percent of a component left in solution.

The precipitation in real spent solution was performed by addition of the required volume of NaOH solution to the electrolysate solution under gentle mixing. The solution was allowed to equilibrate for 22 hours, then the iron hydroxide precipitate was separated by successive centrifugation for 15 minutes at 7.000 rpm and filtration through a Synpor 6 membrane filter (Labora Praha, Czech Republic; pore diameter 0.40 mm).

Desalination / sodium separation of the resulting solution was performed by passing the treated solution through a column of Amberlite IRN77 strongly acidic cation exchanger.

The sorption value was presented as distribution coefficient (1):

$$K_d = \frac{A_0 - A}{A} \; \frac{V}{m} \qquad (1)$$

Where A_0 and A - activity of radionuclides in solution before and after sorption accordingly; V – volume of solution; m – weight of absorber.

All the results presented are an average value of 2-3 independent experiments.

SPECIATION OF THE RADIONUCLIDE AND STABLE METALS IN SOLUTION

The subject of speciation studies within the current research was determined by composition of the target solution, which included radionuclides, stable metals and complexing compounds. Since the electrochemical decontamination waste contained Fe(III) at high concentration, its precipitation, in a form of iron hydroxide, was suggested as a first step of the solution treatment. Hence, the subject of speciation studies was mainly concentrated on the hydrolysis reactions of Fe(III) and the radionuclides with increase of pH and effect of complexing anions on this process.

From the Fig.1 it is seen that the presence of a complexing anion at high concentrations in aqueous solution hinder formation of iron hydroxide and shifts the beginning of its formation into a range of higher pH.

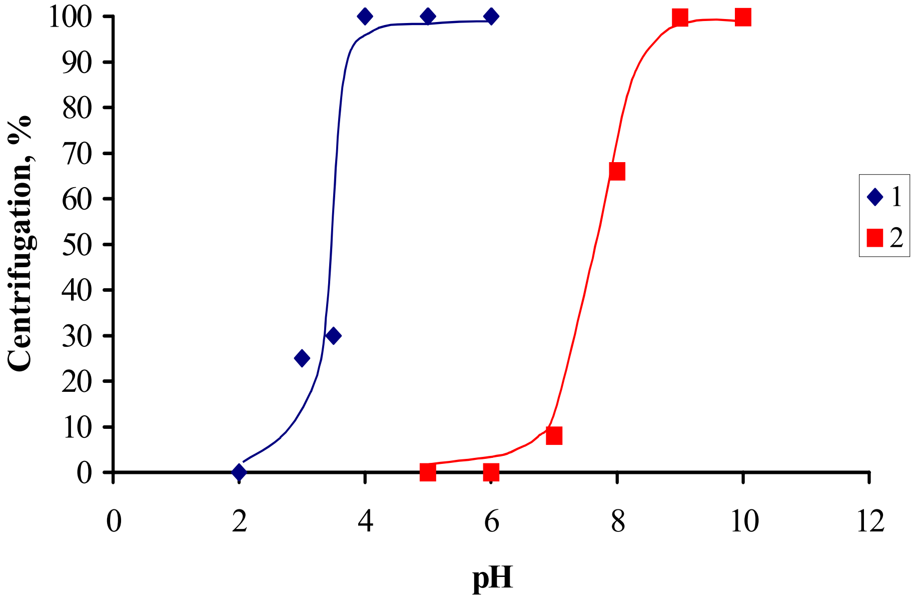

Fig. 1. Effect of oxalate anion on precipitation of iron hydroxide. Iron(III) concentration - 10^{-2} Mol/L; Concentration of oxalic acid: 1 - 0 Mol/L; 2 - 10^{-1} Mol/L

From the Fig.2 (curve 1) it is seen that co-precipitation of the radionuclides with iron hydroxide strongly depends on pH of solution. The increase of pH from 6 to 8 and higher changes percent of co-precipitation from marginal to nearly full removal of the radionuclides from solution. So, at pH higher than 8 activity of solution is reduced to background values after sedimentation of iron hydroxide. (The same effect was also observed for ^{54}Mn). Formation of Co(II) and Mn(II) first hydroxocomplexes proceeds also in that field of pH. So, it seems to be a correlation between the presence of OH-groups in co-ordination sphere of the radionuclides and their enhanced sorption on iron hydroxide, which is also in a good agreement with literature data [2].

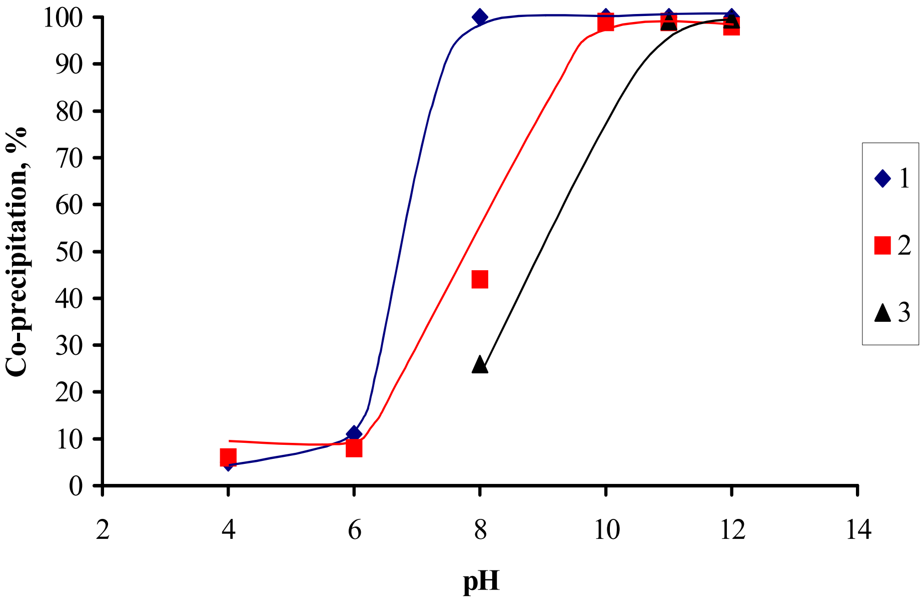

Fig.2. Effect of oxalic acid on co-precipitation of ^{60}Co with iron hydroxide. Iron concentration - 10^{-2} Mol/L. Concentration of oxalate: 1 - 0 Mol/L; 2 - 10^{-2} Mol/L; 3 - 10^{-1} Mol/L

The presence of complexing anion in solution shifts the beginning of the radionuclides co-precipitation into a field of higher pH and the higher the concentration of complexing anion is in solution the higher pH is needed for co-precipitation of the radionuclides (Fig.2, curves 2 and 3). This can be explained by the competition of the organic complexant and OH-anions in co-ordination sphere of Co(II) and Mn(II) cations.

So, the results of speciation studies show that iron can be precipitated in the presence of organic complexing agents, in a form of iron hydroxide, and the radionuclides can be either co-precipitated or not depending on pH. This suggests a possible way for regeneration or treatment of the target solution – that is alkalization of solution, which will remove metal-ions and radionuclides leaving the organics in solution.

EXPERIMENTS WITH ELECTROCHEMICALLY PREPARED SIMULANT SOLUTION

In order to verify the conclusions made as a result of the speciation studies, the experiments with electrochemically prepared simulant solution were carried out. The proposed treatment of the solution consisted of alkalisation of the solution by addition of NaOH and separation of iron hydroxide sediment by centrifugation.

The results of the experiments show that at pH higher than 10.5 it is possible to remove more than 94 % of iron from solution and to reduce activity of solution down to background values, due to co-precipitation of the radionuclides with iron hydroxide flocks (Fig.3). At the same time, nearly all the organics are left in solution after iron hydroxide precipitation. If one removes the excessive NaOH from the solution it can, in principal, be used repeatedly. The solution after treatment can be acidified by passing through a column loaded with cation-exchange resin in H^+- form.

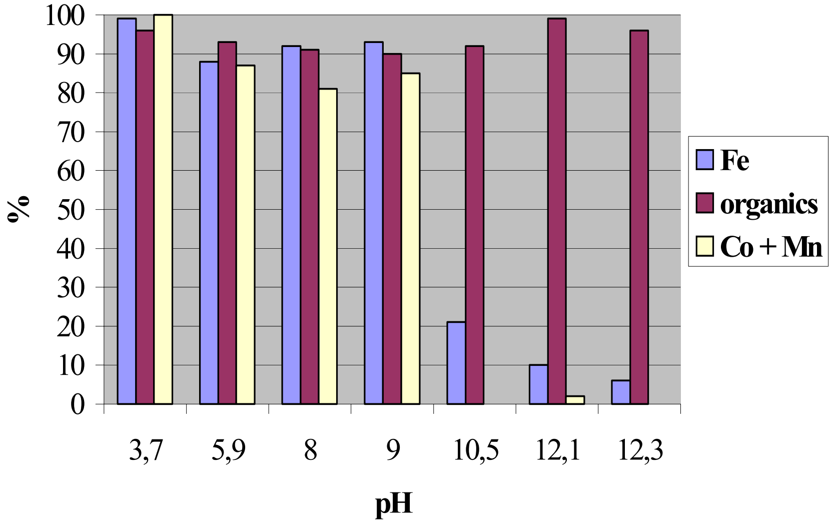

Fig.3. Effect of pH on composition of electrochemically prepared simulant solution

TEST OF THE METHOD ON REAL SOLUTION

The proposed method for regeneration of spent electrolyte solution has also been tested on real solutions (the composition is given in introduction). The test results are presented in Table I.

Table I. Behaviour of radionuclides, macroelements and complexants in regeneration process

Nuclide	**10^3 cps**		
	Spent solution	**After precipitation**	**After desalination**
Ag-110m	65.1	0.0	0.0
Cs-137	21.0	14.0	0.0
Co-58	208.6	7.9	3.7
Co-60	1380.2	103.0	71.7
Mn-54	1459.7	139.0	102.7
	c, [mg/L]		
Metal	**Spent solution**	**After precipitation**	**After desalination**
Fe	6.8	0.7	0.6
Ni	0.9	0.1	0.1
Cr	2.5	1	0.9
	c, [mg/L]		
Complexant	**Spent solution**	**After precipitation**	**After desalination**
Oxalic acid	3.9	4.9	3.1
Citric acid	3.2	3.2	3.2
	Spent solution	**After precipitation**	**After desalination**
pH	1.8	10.2	3.4

From these data the following conclusion may be drawn:

- Some 90 % of the macroelements (Fe, Ni, Cr) are removed during the precipitation step
- Significant amount of the oxalic acid is lost in the desalination / sodium removal step
- The activity of the major contributors to the total activity of the spent solution (radiocobalt, 54 Mn, 110m Ag) is decreased by 90–100 % in the precipitation step, it is not further significantly reduced in the sorption desalination / sodium removal step.
- 137 Cs is not significantly removed by precipitation while it is quantitatively removed in the desalination / sodium removal step.

After the desalination / sodium removal step, the efficiency of the resulting solution for the electrochemical decontamination was tested and compared with that of a fresh solution in a series of standard decontamination runs. The concentration of the oxalic and citric acids in the regenerate was adjusted to its original values in the fresh electrolyte. The decontamination efficiency of the regenerated electrolyte was compared to that of the fresh electrolyte in a series of tests. From the results obtained (Fig. 4) it can be seen that the performance of the fresh and regenerated electrolytes is practically the same - from three out of the total of four samples all the activity was removed within 13 minutes of the test decontamination run.

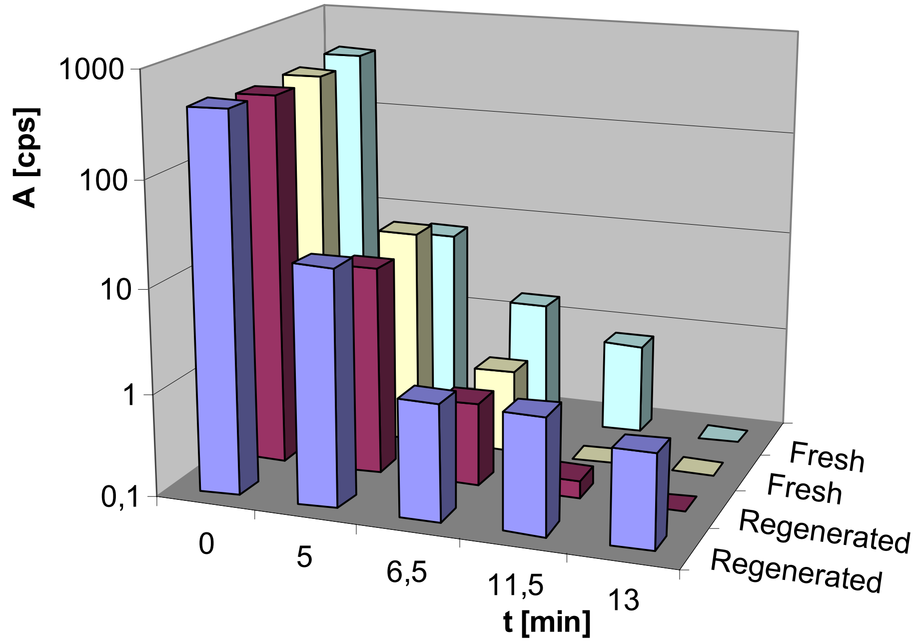

Fig.4. Comparison of the performance of the fresh and regenerated electrolytes

So, the results of verification of the process designed for the regeneration of the spent electrolyte from electrochemical decontamination were rather promising. No difference in the performance of fresh and regenerated electrolytes was found in the first experiments.

TREATMENT OF THE ULTIMATELY SPENT SOLUTIONS FOR FINAL DISPOSAL

After several regeneration cycles, the solutions can not be longer used in electrochemical decontamination process. Treatment of such solutions can be made applying iron precipitation, which allows for removal of the bulk amount of contaminants, as the first step. Then, if necessary, the remaining radionuclides can be removed by sorption. A series of novel absorbers, synthesised in the University of Reading and Czech Technical University, has been tested for their potential for the sorption removal of the remaining radionuclides from the supernate.

Samples

JP33W:	This material is formed by dropping the feed solution into a bath of hexanol saturated with hydrochloric acid. The feed solution is composed of sodium tungstate and GLASCOL (10% solution of polyacrylic acid in water) in a 1:1 ratio (prepared at the Reading University).
JP35WP:	This material s formed by dropping the feed solution into a bath of hydrochloric and phosphoric acids dissolved in hexanol. The feed solution is the same as above (prepared at the Reading University).
W-MCM-41:	Highly ordered silica materials of the MCM type modified with tungsten (prepared at the Reading University).
V-MCM-41:	Highly ordered silica materials of the MCM type modified with tungsten (prepared at the Reading University).

NaTiO: sodium titanate, prepared from TiO (prepared at the Czech Technical University).
NiFC: sodium-nickel hexacyanoferrate – $Na_{0,32}Ni_{1,84}[Fe(CN)_6]$ (prepared at the Czech Technical University).
ZrO: zirconium oxide (Grade XZ 0632/03) –MEL Chemicals, UK

The test results are summarised in Tab.II.

Table II. Absobers test results.

Absorber	**pH**	**K_d**			
		^{60}Co	**^{54}Mn**	**^{59}Fe**	**^{110m}Ag**
V-MCM -41	1.15	83	62	-	-
	5.4	87	88	-	-
	11.7	6012	11777	-	-
W-MCM-41	1.12	98	93	-	-
	5.5	166	220	-	-
	11.8	5528	25347	-	-
JP33W	1.1	59	53	-	-
	3.15	17	-	-	-
	7.0	36	96	-	-
	11.9	4300	6123	-	-
JP35WP	1.1	134	142	-	-
	2.25	25	-	-	-
	12.3	69	73	-	-
NaTiO	1.4	*absorber dissolves*			
	3.6	<1	17	<1	10058
	7.1	2208	955	41	5613
NiFC	1.4	1760	158	906	6.9×10^5
	3.6	395	211	1	4.3×10^5
	7.1	100	42	60	4.8×10^5
ZrO	1.4	176	184	44	6.9×10^5
	3.6	<1	<1	<1	2859
	7.1	37	142	6	2690

From the data obtained it is seen that sorption of the radionuclides on these absorbers is high and all of them can be made use of for treatment of the radioactive waste. However, their efficiency is pH dependent and, moreover, for some absorbers - JP33W, W-MCM-41, V-MCM-41, NaTiO - it increases with increase of pH, and for the rest of the absorbers on the contrary.

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REFERENCES

[1] L.A.Kolsky “Spravochnik” / Kiev “Navukova dumka” – V.1,2. – 1980

[2] V.I.Grebenschikova, A.F. Prokudina in “Coprecipitation and adsorbtion of radioactive elements” / Moscow-Leningrad, “Nauka” - P .103 - 1965