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USE OF A CROSS-LINKED POLY(4-VINYLPYRIDINE) FOR NUCLEAR WASTE TREATMENT

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ABSTRACT

The nuclear fuel reprocessing currently used generates liquid wastes with a significant level of radioactivity that requires expensive and specific treatments. Therefore, in this study, an attempt has been made to develop another process that is more effective and produces less-active wastes by using a poly(4-vinylpyridine) resin as selective material for fixation of metal ions present at trace level, in particular of nonactive ruthenium and, ^{106}Ru, ^{95}Nb, ^{125}Sb, ^{144}(Ce + Pr), ^{241}Am, Pu, ^{244}Cm.

INTRODUCTION

Irradiation of nuclear fuel in power reactors leads to the production of many fission products, ranging in atomic mass from 70 to 160. These fission products generally constitute the radioactive wastes generated at the end of the nuclear fuel

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cycle. If nearly all of them are recovered and stocked at the first reprocessing cycle, the process generates, at all the stages, the forging of important waste volumes.

The liquid wastes impose a complex treatment composed of several steps of coprecipitations with various chemical reagents ($Ba(NO_3)_2$, $Fe(NO_3)_2$,...) to be tared, and, although satisfactory at the level of the rejection norms presently enforced, this method presents many disadvantages. Indeed, the method is not very selective and generates important amounts of low-activity solid waste which has to be managed for many centuries. In addition, it requires significant reagent volumes, such as NaOH, H_2SO_4, or $Ba(NO_3)_2$, so a potential decrease of the maximal rejection norms allowed risks to reintroduce the use of such a process. Therefore, an attempt has been made to develop another process that is more effective and produces less-active wastes. Among the radioactive elements present in traces in the liquid wastes, ruthenium is known to be the most difficult to eliminate.

The use of poly(4-vinylpyridine), P4VP, for the removal of heavy cations and transition metals has been demonstrated (1-2), but no detailed report has been found on the recovery of Ru, although considering the literature (3-4-5), the poly(4-vinylpyridine) structure can be proposed to complex the Ru.

This paper describes the sorption behavior of the ruthenium on a cross-linked poly(4-vinylpyridine) resin. In addition, the behavior of some γ and α, β emitters is studied.

EXPERIMENTAL PROCEDURE

Chemicals and Reagents

The P4VP examined was supplied by Reilly Industries Inc., Indianapolis, Indiana. The stock solutions of ruthenium were prepared by dissolving a salt of $RuCl_3$ in nitric acid at pHs 0; 1.05; 2; 3.02; 4.02, and 5.11. The required amounts of sodium and chloride were weighed with the ruthenium and dissolved in a solution with the desired concentration of nitric acid. In inactive medium, ruthenium, sodium and chloride concentrations were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a standard deviation of ± 2 %. The system used for this work was the PE 2000 ICP system from Perkin Elmer Corporation. The acidities were measured on a suntex 2000A pH meter. The concentrations of the radioelements, arising from real liquid wastes from COGEMA MARCOULE, were determined by γ, α spectrometry, β countage, after filtration and adjustment of the concentration of the nitric acid (0.1 mol L^{-1}).

Measurements of the Activity by γ-Ray Spectrometry (6)

The INTERTECHNIQUE equipment was composed of a high-purity semiconductor Ge detector, a preamplifier, an amplifier, a coder, an analyzer, and computer treatment. The concentrations were measured with a standard deviation of ± 5 %.

Measurements of the Activity by α Spectrometry (7)

These measurements required actinides separation from the fission products using dicyclohexano-18-crown-6 adsorbed on a FLORISIL (MgO/SiO_2 = 15,85) support (8).

The basic NUMELEC equipment was composed of an argon-methane ionization chamber, a preamplifier, a high-voltage drawer, and a multichannel analyzer. The efficiency analysis line standardization and the energy adjustment were effected from standard solutions. The concentrations were measured with a standard deviation of ± 5 to 10 %.

Measurements of the Activity by β Countage (9)

The strontium analysis were made using β countage, and these measurements necessitated the elimination of the other radioelements.

The NUMELEC equipment was composed of an argon-methane ionization chamber, a preamplifier, a high-voltage drawer, and a counter. The precision of the analyses was calculated from the variance and the deviation of the results obtained with 8 measurements (± 6 %).

ICP-AES Measurements in Active Medium (10)

The quantities of alkaline and alkaline earth elements were determined by ICP-AES using a JOBIN & YVON spectrometer. The measurements were based on the internal standardization method and the results were given with a standard deviation of ± 3 %.

Extraction Procedure in Inactive Medium

The extractions were carried out by shaking 10 mL of an aqueous nitric acid solution containing $Ru(NO_3)_3$ only or a mixture of various concentrations of $Ru(NO_3)_3$ and, $Na(NO_3)$ or NaCl with 0.2 g of P4VP resin.

Preliminary experiments have shown that the equilibrium of Ru extraction was reached, under our conditions of concentrations, after 1 h of horizontal shaking at room temperature. After filtration, the concentration of metals in the aqueous phase was measured, and their concentration sorbed on the resin was calculated by difference. No modification of ions concentrations in the initial solution was observed after filtration over a DURIEUX (No 111) filter paper (pore diameter: 6μm, thickness : 0.16 mm).

Extraction Procedure in Active Medium

Batch Procedure. The extractions concerning the study of the pH influence were carried out by shaking 3 mL of reprocessing liquid waste of known acidity containing ^{106}Ru, ^{125}Sb, ^{134}Cs, and ^{60}Co of known concentrations with 0.2 g of P4VP resin of a particule size of ca. 60 mesh. After 40 min of vertical shaking, the solution was filtered, and the concentrations of the nonsorbed elements in the aqueous phase were measured. The kinetics of extraction was studied by shaking 3 mL of reprocessing effluent at pH 1, containing ^{106}Ru, ^{54}Mn, ^{60}Co, $^{144}(Ce + Pr)$, ^{95}Nb, ^{134}Cs, and ^{125}Sb of known concentrations with 0.05 g of PVP resin. After 0 to 180 min of vertical shaking, the solution was filtered, and the concentrations of metals in the aqueous phase were measured to calculate, by difference, their concentrations sorbed on the resin.

Column Procedure. Column studies were conducted using a 0.8 x 22 cm glass tube packed with 1 g of P4VP of a particule size of ca. 60 mesh. Then 5 to 450 mL of effluent was allowed to pass through the column at a flow rate of 3 mL min^{-1}.

RESULTS AND DISCUSSION

The cross-linked P4VP resin is stable up to 260°C for an extended period, and its pyridine functional groups are highly resistant to attack by oxidizing and reducing agents, leading to longer resin life under harsh conditions (11). In addition, a published study (12) indicates that vinylpyridine resins are more stable to ionizing radiation than are other resin types. Radiation stability of polymeric styrene-divinylbenzene resins, when irradiated in the presence of water in acidic ($pH < 1$) or basic ($pH > 10$) conditions shows the following order of stability: pyridine exchangers > nuclear sulfonic and carboxyl cation exchangers > weakly basic anion exchangers of the primary, secondary and, the tertiary type > strongly basic anion exchangers of the quaternary ammonium base type (13)

Tests in Inactive Medium

Considering the manipulation difficulties of the experiments in radioactive medium, tests were first run on inactive solutions and later on radioactive wastes.

Extractions were done according to the procedure in Figure 1.

Effect of pH on Ruthenium Extraction. A typical pH-profile of the Ru sorption of P4VP is shown in Figure 2. The ruthenium concentration in the aqueous nitric phase was measured using ICP-AES, and its concentration sorbed on the resin was calculated by difference.

Maximum sorption of Ru is observed at pH 1 in aqueous nitric solution; the amount of sorption decreases with increasing pH. A decrease of the sorption of metal ions in chlorhydric medium has been observed by Sugii et al. (1), and this phenomenon has been explained by assuming that the resin becomes less hydrophilic above pH 5. A maximum is observed because the ruthenium species which gives the most stable complex with the P4VP is more abundant at pH 1.

Effect of Chloride anions on the ruthenium kinetics of extraction. Sorption kinetics of Ru on the P4VP from 1.38 mol L^{-1} nitric acid containing neutral salts has been examined and the results are shown in Figure 3.

Ruthenium shows a slow extraction, except when sodium chloride is present, where the extent and the kinetics of sorption are increasing appreciably, on the other hand the presence of nitrate ions has no influence. This suggests that chlorides contribute to the complex formation. In addition, the ruthenium capacity is found to be independent of the presence of high sodium and potassium concentrations ($[Na] = 50000 \times [Ru]$ and $[K] = 12 \times [Ru]$). This suggests that

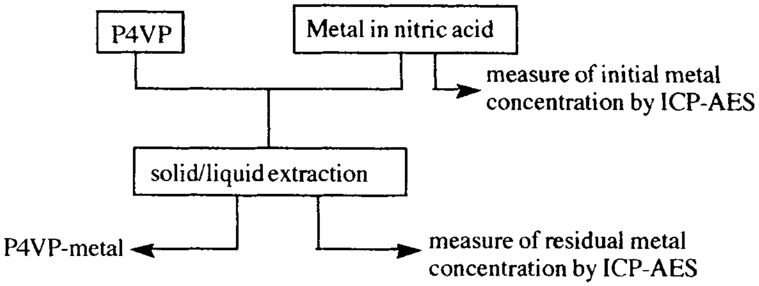

FIGURE 1. Process of solid/liquid extraction using a poly(4-vinylpyridine) resin for metals removal.

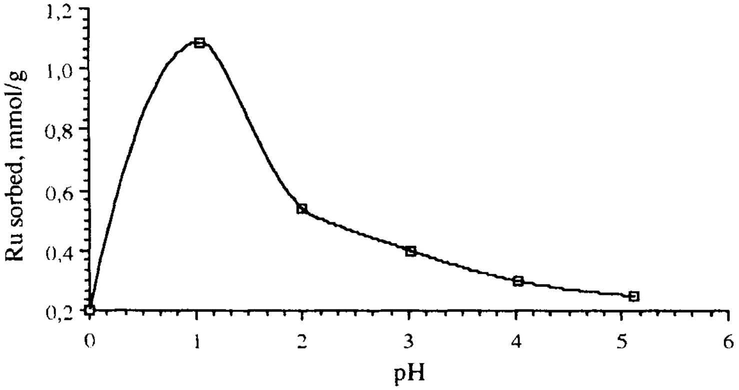

FIGURE 2. Sorption of ruthenium on P4VP from aqueous nitric solutions. Concentration of Ru : 0.5 mg L^{-1}

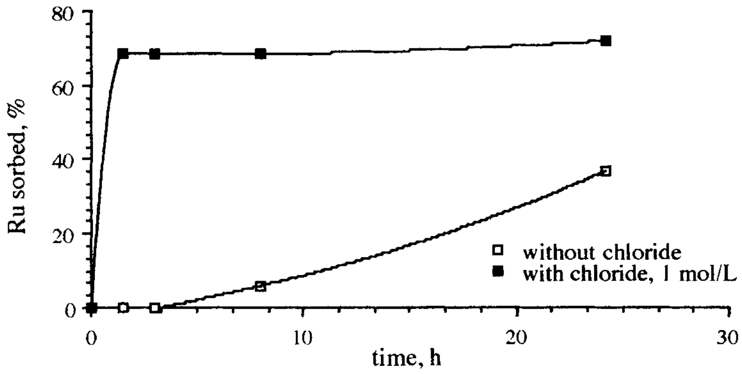

FIGURE 3. Influence of chloride anions on extraction kinetics of ruthenium in the presence of sodium and potassium chloride. Concentration of Ru : 0.5 mg L^{-1}, Na : 25 g L^{-1}, K : 6 mg L^{-1}

chloride ions may form chlorinated species of ruthenium which could be fast exchange on the resin or which induce a faster sorption by a complexation mechanism.

In light of the results obtained, the selective removal of ruthenium present in nitric solutions can be achieved by a crosslinked poly(4-vinylpyridine) resin by controlling the acidity, the time of contact and the presence of an amount of chloride ions in the aqueous solution.

Tests in Radioactive Medium

The wastes used are produced by all the industrial wholes of the spent nuclear fuel reprocessing plant of COGEMA MARCOULE. Their characteristics are summarized in Tables 1 and 2.

After the coprecipitations actually imposed on the liquid wastes and which permit to eliminate the major part of the radioactivity, ruthenium is responsible for 90% of the residual radioactivity.

Tests in Batch. Extractions were performed according to the procedure in Figure 1 and the initial and final metal concentrations were measured by γ spectrometry.

TABLE 1. CHEMICAL COMPOSITION OF THE EFFLUENTS

Ion	Ca^{2+}	Na^+	K^+	Mg^{2+}	Ba^{2+}	U
Concentration ($mg\ L^{-1}$)	40	7000	120	80	< 5	6
Ion	NO_2^-	NO_3^-	SO_4^{2-}	Cl^-	F^-	PO_4^{3-}
Concentration ($mg\ L^{-1}$)	120	20000	1300	20	8	10

Salts content, 10 $g\ L^{-1}$; acidity $< 0.5\ mol\ L^{-1}$

TABLE 2. RADIOCHEMICAL COMPOSITION OF THE LIQUID WASTES

Global β Activity ($GBq\ m^{-3}$)			Global α Activity ($GBq\ m^{-3}$)		
22			0.481		
β spectrum	Concentration ($\mu g\ m^{-3}$)	%	α spectrum	Concentration ($\mu g\ m^{-3}$)	%
^{106}Ru	57,9	33	$^{239\ to\ 242}Pu$	300	48
^{137}Cs	2100	31	^{241}Am	800	21
^{134}Cs	40,9	8	^{238}Pu	104	14
$^{144}(Ce+Pr)$	17,1	9	^{242}Cm	0,5	13
^{90}Sr	250	6	^{244}Cm	6,4	4

Influence of the pH on Ruthenium Extraction

Following the previous study in inactive medium, the influence of the acidity on Ru extraction from radioactive wastes has been evaluated, and ruthenium behavior in real effluents and in synthetic inactive solutions is similar. Indeed, maximum sorption of ^{106}Ru is observed at pH 1 in reprocessing aqueous nitric solution, and a decrease of the sorption takes place with increasing pH. Fortunately, this maximal efficiency of ruthenium extraction corresponds to the usual acidity of the MARCOULE liquid wastes.

Ruthenium Extraction Kinetics in Presence of the β, γ Emitters

Figure 4 shows the sorption kinetics of ^{106}Ru on the P4VP from nitric acid in the presence of ^{95}Nb, ^{137}Cs, and ^{125}Sb at pH 1. ^{137}Cs is not sorbed at all ; ^{95}Nb and ^{125}Sb are sorbed with the ^{106}Ru, with their maximum sorption being observed after 40 min of contact. After 75 min, the ^{106}Ru is partly released from the resin. This phenomenon may be ascribable to a competition between sorption of the ions studied and of several other ions including H^+ and/or, a modification of the metal species present in solution. This last transformation could be relatively low comparatly to ion exchange.

Tests in Column. In view of eventual industrial utilization, the P4VP resin has been studied by the continuous flow column method.

Efficiency of the P4VP in Relation to the β, γ Emitters

The P4VP has been applied to the sorption of ^{106}Ru, ^{125}Sb, ^{60}Co, ^{137}Cs, ^{54}Mn, and ^{144}(Ce+Pr) by column operation. The results are shown Figure 5.

^{106}Ru, ^{125}Sb, ^{54}Mn, ^{60}Co, and ^{144}(Ce+Pr) are retained on the resin by a mechanism that may not be based on ion exchange. Maximum sorption of metal ions is observed after 50 mL of effluent are passed through the column. An important decrease in sorption is observed above a 60-mL volume of effluent solution for ^{60}Co and ^{54}Mn and above a 360-mL volume of effluent solution for ^{106}Ru, ^{125}Sb and, ^{144}(Ce +Pr). This can be assigned to an efficiency decrease of the resin following a protonation of its functional groups. On the other hand, it has been

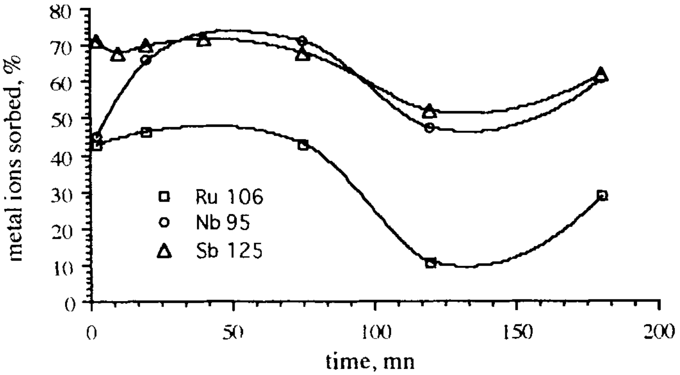

FIGURE 4. Kinetics of extraction of β , γ emitters on P4VP resin from aqueous nitric solution at pH 1.

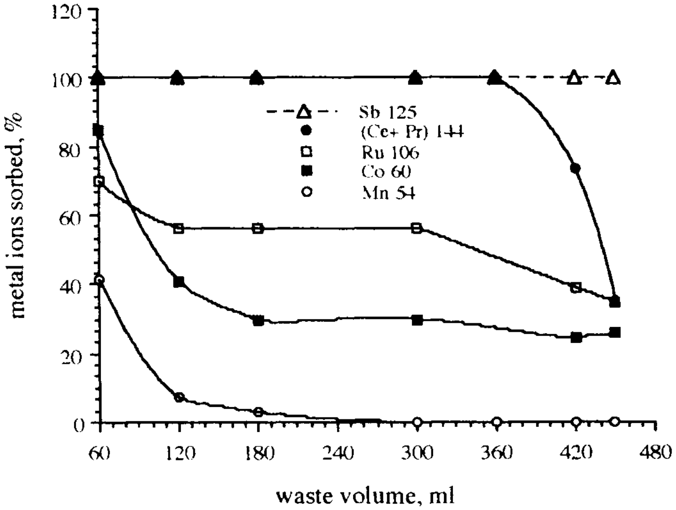

FIGURE 5. Retention of β , γ emitters on a P4VP column.

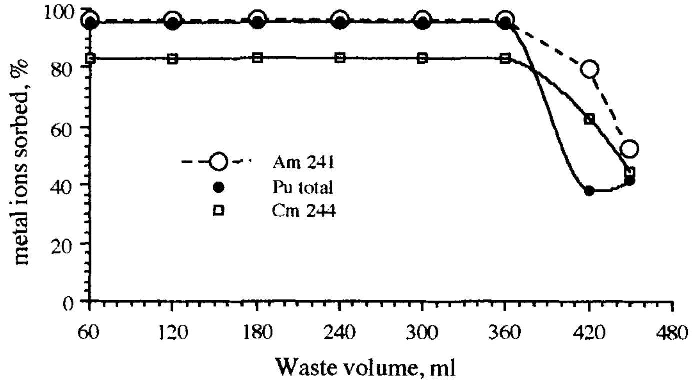

FIGURE 6. Sorption of α emitters on a P4VP by column operation.

observed that Na, K, Mg, Ca, and, in a general manner, all the alkaline and alkaline earth elements are not retained by the resin (14-15).

Efficiency of the P4VP in Relation to the α Emitters

The P4VP has been applied to the sorption of α emitters contained in a medium-activity liquid waste by column operation, and its extraction efficiency in relation to these elements is shown in Figure 6.

All the α emitters present are sorbed by the P4VP; nevertheless, in a medium-activity liquid waste, the concentration of α emitters is too low to allow saturation of the resin. After 360 mL of effluent solution are passed through the column; the efficiency of the resin decreases; and ^{241}Am, total Pu, ^{244}Cm are weakly retained by the resin.

Conclusions on Active Tests

The P4VP resin sorbs all the radioelements contained in medium-activity liquid waste except alkaline and alkaline earth elements. In addition, considering the good selectivity of the P4VP toward the alkaline and alkaline earth elements, in particular toward the sodium, and because of its chemical and radiochemical stability (13-14), the liquid waste treatment with the P4VP can be considered.

In a general manner, the decrease of the P4VP capacity for metal ions sorption may be ascribable to the acid-base interaction between the pyridine groups of the polymer and the protons of the nitric acid. Indeed, this efficiency decrease squares with the protonation of 50% of pyridine groups. Further details of proton interference in sorption mechanisms of metal ions on cross-linked poly(4-vinylpyridine) will be discussed somewhere in the near future.

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REFERENCES

1. A. Sugii, N. Ogawa, Y. Iinuma, and H. Yanamura, Talanta 28, 551 (1981).
2. D.C. Kennedy, Chemical Engineering, p.106 (1980).
3. A.D. Pomogailo and I.E. Uflyand, Platinum Met. Rev. 34, (4), 185 (1990).
4. G. Ciantelli, P. Legittimo, and F. Pontani, Anal. Chim. Acta. 53, 303 (1971).
5. T. Yamamoto, Z. H. Zhous, T. Kanbara, and T. Maruyama, Chem. Lett. 223 (1990).
6. COGEMA Marcoule 361-2-MA-49-08-Ind 0 (1984).
7. COGEMA Marcoule 361-2-MA-49-04-Ind 0 (1984).
8. M. Lemaire et al., E. Patent 90403575.5- (1991).
9. COGEMA Marcoule 361-2-MA-49-02-Ind 0 (1982/2).
10. COGEMA Marcoule 361-2-MA-48-09-Ind 0 (1985).

11. Reilly Chemicals, A New Family of Cross-linked Poly(vinylpyridines), Metal recovery, Reillex report 5 (1990).

12. T.E. Gangwer, M. Godstein and, K.K.S. Pillay, Radiation Effects on Ion Exchange Materials, BNL-50781, Brookhaven National Laboratory, Upton, New-York (1977).

13. K. K. S. Pillay, J. Radioanal. Nucl. Chem. 102,1 , 247 (1986).

14. J. Foos et al., F. Patent 9,202,514 (1992).

15. M. Lemaire et al., F. Patent 9,202,516 (1992).