The Removal of ^{106}Ru from Simulated Liquid Nuclear Wastes

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Co-ordinating copolymers, particularly those containing sulphur donor atoms, have been found useful for removing ^{106}Ru from simulated liquid nuclear wastes.

The use of nuclear fission as a source of energy produces the much publicised problem of ensuring that releases of radioactive fission products[1,2] to the environment are kept within internationally acceptable limits. Most published literature has been concerned with the fission products with medium term half lives *e.g.* ^{137}Cs ($t_{\frac{1}{2}}$ 30.1 years), ^{90}Sr/^{90}Y ($t_{\frac{1}{2}}$ 28.5 years), but another problem concerns short-lived fission product ^{106}Ru ($t_{\frac{1}{2}}$ 368 days). The annual ^{106}Ru discharges[1,3] to the North East Irish Sea from the BNFL (or BNF plc) Sellafield fuel reprocessing plant have been decreasing (1972, 31 kCi and 1979, 11 kCi). In 1968 the concentration[4] of ^{106}Ru in surface water was about 100 pCi l^{-1} in the vicinity of the pipeline but the corresponding figure for the radioisotope in silt from the sea bed was about 1000 pCi g^{-1} of dried material (September 1968). It has been estimated[2] that up to 95% of the ^{106}Ru is associated with the sea bed which acts as the ultimate sink and hitherto may have allowed decay to occur before long term release back to the water column. However, the discharge of large volumes of low-activity liquid wastes into the sea can result in three methods of human exposure: through edible seaweed (*Porphyra umbilicalis*) for laverbread,[4] marine fauna, and contaminated sediments on beaches. In addition ^{106}Ru has been found more than 150 km from the pipeline.[5] Consequently, it is highly desirable to reduce the ^{106}Ru level as much as possible.

It has been shown previously[6,7] that solid copolymers with covalently attached dithiocarbamate groups can concentrate platinum group metals such as rhodium and iridium. In addition a copolymer with thiadiazole groups was able to concentrate silver and cadmium.[8,9] This communication describes preliminary studies with these and other copolymers with simulated nuclear wastes. Previous tests using inorganic cation exchangers have shown that they are not particularly selective in ^{106}Ru removal because the species which contain ruthenium change from complex cations to uncharged or even anionic species.[10] However, most compounds[11] contain the Ru–N–O (ruthenium nitrosyl) group which, although itself not very labile, does not inhibit substitution of groups in other positions of the octahedral structure; the position opposite to the NO group is particularly labile. For example,[12] the complex $RuNOL_3$ ($L = Et_2NCS_2^-$) has been prepared and its crystal structure studied. Consequently, it was decided to investigate co-ordinating polymers.

Three simulated waste solutions were studied and their compositions are given in Table 1. The results of the extraction from these solutions are given in Table 2. The ^{106}Ru concentrations used were higher than those in real effluent but were fixed for the purposes of this preliminary study for convenience of analysis. Solution C approximates to 'pond water'. The distribution coefficients (K_D) were calculated for solid substances which included non-polymeric materials, commercial copolymers, new copolymers, and experimental resins. The solids (0.2 g) were contacted with the solutions (20 cm^3) for one week in poly(ethene) vials with constant stirring. Control solutions with no equilibrated solid phases were treated in the same way. ^{106}Ru was determined by Cerenkov counting *via* its Rh daughter. The K_D values were calculated[13] from equation (1), where A_O = initial activity of solution, A_F = final activity, V = solution volume (cm^3), W = mass of resin (g).

$$K_D = \frac{A_O - A_F}{A_F}\,\frac{V}{W} \tag{1}$$

Table 1. Composition of simulated waste solutions.

	Solution A	 B	 C
NaOH	—	—	0.005 M
Na_2CO_3	—	—	0.0028 M
HNO_3	0.15 M	0.08 M	—
$NaNO_3$	5 M	2.5 M	0.01 M
Ru-NO[a]	3.63×10^{-6} M	3.63×10^{-6} M	3.63×10^{-6} M

[a] Ru-NO signifies species which contain this group, ref. 10.

Some of the solid compounds showed signs of decomposition under the combined effects of one week of irradiation and chemical attack from the solution. With solutions A and B the copolymer with pyrrolidone groups formed a gel and that with dithiocarbamate groups (**8**) gave off hydrogen sulphide as did substance (**1**) (bismuthiol or 1,3,4-thiadiazole-2-5-dithiol) but this appeared satisfactory after filtration. The pyrrolidone copolymer was also unstable when in contact with solution C. All samples which were in the bead form were used as supplied and no attempt was made to limit the range of sizes. Although the K_D values above were reproducible to within 1%, the accuracy is probably nearer 10%.

Since a K_D value of greater than unity shows a selectivity for ^{106}Ru it can be seen that the dithiocarbamate copolymer (**8**) and amidinothiourea are of potential for use in pond water clean-up. These are less useful for the acidic solutions

Table 2. Extraction of ^{106}Ru with solid reagents. Apparent K_D values (cm^3 g^{-1}).

Sample (physical form)	Solution A	 B	 C
(**1**) 1,3,4-Thiadiazole-2,5-dithiol (powder)	800	80	10
(**2**) An aminophosphonic acid copolymer (beads)	100	100	36
(**3**) A thiol copolymer (beads)	800	530	70
(**4**) An iminodiacetate copolymer (beads)	480	300	1.1
(**5**) An amideoxime copolymer (beads)	70	95	103
(**6**) A pyrrolidone copolymer (powder)	65	1.5	—[c]
(**7**) Amidinothiourea (powder)	200	512	2 460
(**8**) A dithiocarbamate copolymer[a] powder	250	250	13 800
(**9**) A thiadiazole copolymer[b] (beads)	1550	260	16
(**10**) Zeolites – Na,X (beads)	<1	20	994
(**11**) – Na, clinoptilolite	<1	<1	334
(**12**) – Linde, A-51	—[c]	—[c]	1 762

[a] Refs. 6 and 7. [b] Refs. 8 and 9. [c] Not tested.

probably owing to decomposition. However, the thiadiazole-containing copolymer (**9**) and the lower molecular weight compound (**1**) were useful for the acidic solution A which had a large amount of added sodium nitrate. Compound (**1**) is *multifunctional* and the ^{106}Ru may act as a cross-linking agent and this may also be the case for amidinothiourea and solution C. The thiol containing copolymer (**3**) and amidinothiourea (**7**) appear to be the best of the reagents tested so far for solution B which had half the amounts of acid and nitrate contained in solution A. So far it appears that the co-ordinating reagents are more efficient than the zeolites and the sulphur reagents are better than the oxygen reagents. Zeolite A-51 shows the best figures of the inorganic compounds for the alkaline conditions representative of pond water.

These preliminary studies on ^{106}Ru species in solution are sufficiently encouraging to indicate that a process will be developed whereby releases of ^{106}Ru can be further reduced. Future work includes the screening of other organic copolymers, functionalised inorganic compounds for extraction, selectivity, resistance to leaching and to radiolytically induced degradation. The above materials resisted decomposition by radiolysis (except where indicated) for exposures of up to four weeks which would be sufficient for normal handling procedures. These comments concerning radiolysis apply strictly to low-level exposure to radiation damage. It is hoped that a material or materials will be found for use on a plant scale where multi-curie amounts of activity are present. Attention will be given to insoluble residues from the fuel elements.

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