

Extraction of ^{106}Ru from Simulated Liquid Nuclear Wastes using Inorganic Phases with Covalently-bound Sulphur Ligands and Inorganic Sulphides

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Inorganic-based materials with pendant dithiocarbamate groups have acceptable affinities for ^{106}Ru and the loaded materials have some resistance to radiolysis even at high dosages; inorganic sulphides are also capable of extracting ruthenium.

Previously¹ we indicated that organic copolymers with covalently bound dithiocarbamate groups can be used to extract ruthenium from simulated liquid nuclear wastes. There is concern that these materials may have a low resistance to radiolysis and so further materials have been sought. It is well known that inorganic materials² have a greater resistance to radiolysis than organic materials, and as it is necessary to store the loaded materials particular attention has been paid to functionalised inorganic materials and to metal sulphides. Inorganic-based materials are expected to be compatible with the cements and concretes which the materials may be incorporated into for subsequent storage.

The silica support used was silica gel 60 (0.06 mm; Merck) and the zeolite support was 13X (Laporte Industries, Widnes). These were dried at 110 °C for 48 h in sodium-dried toluene and refluxed for 6 h with the silylating reagent until no more alcohol was evolved. The preparation of the derivatives is outlined in the footnotes to Table 2. The results in Table 2 indicate that covalently bound dithiocarbamate groups when bound to silica or to the zeolite are effective at taking up ruthenium. The K_D values[†] are particularly encouraging for solution 3, which is the simulated pond water. It appears that the dithiocarbamates derived from primary and secondary amines are effective at extracting ruthenium. The preliminary

[†] $K_D = \{(A_0 - A_F)/A_F\} \cdot (V/W) \text{ cm}^3 \text{ g}^{-1}$ where A_0 = initial activity of the solution, A_F = final activity of solution, V = volume of solution (in cm^3), and W = weight of compound (1)–(15) (in g).

Table 1. Compositions of the solutions (in mol dm^{-3}).

Solution	(1)	(2)	(3) ^a
Na_2CO_3	—	—	0.0028
NaNO_3	5	2.5	0.01
NaOH	—	—	0.005
HNO_3	0.15	0.08	—
Ru-NO^b	$3.63 \times 10^{-6} \text{ M}$ for each solution		

^a Solution (3) simulates storage pond water used to contain spent fuel elements. ^b Ru-NO signifies species which contain this group.

'breakthrough' plots for small columns of the dithiocarbamates prepared from primary amines on functionalised zeolite 13X and the silica are given in Figure 1. The breakthrough appears to be fairly sharp for the size of column used but clearly larger columns should be used.

The maximum ratio of $\text{Ru} : \text{CS}_2$ was 1 : 2.5 which suggests a co-ordinative mechanism. In nuclear waste waters ruthenium is commonly present as a ruthenium nitrosyl complex and therefore contains the Ru-NO group. It is probable that the dithiocarbamate co-ordinates to the metal. Support for the co-ordination mechanism comes from the fact that the loading capacity of the thiuams, which are obtained by oxidation of dithiocarbamates, is lower than that of dithiocarbamates. Dithiocarbamates are strongly co-ordinating ligands, whereas the thiuams are less so. Uptake of ruthenium by the thiuams

Table 2. Comparative K_D values ($\text{cm}^3 \text{g}^{-1}$).

Compound	Solution		
	(1)	(2)	(3)
(1) Zeolite 13X-dithiocarbamate	200	210	10 100
(2) Silica-dithiocarbamate	150	150	8 700
(3) Zeolite 13X-dithiocarbamate	310	440	7 300
(4) Lapis lazuli	70	60	5 400
(5) Silica-dithiocarbamate	120	130	4 900
(6) MoS_2	10	5	3 900
(7) Zeolite 13X-amine	1	1	3 400
(8) CdS	ND ^b	ND	3 300
(9) CaS	ND	ND	1 900
(10) Zeolite 13X-thiourea	80	50	900
(11) Silica-thiuram	35	90	400
(12) Zeolite 13X-N-NO (nitrosamine)	125	100	550
(13) Zeolite 13X-thiuram	90	100	200
(14) Zeolite-N-O (N-oxide)	80	90	110
(15) CuS	ND	40	40

^a Preparation of derivatives: (1), (2) primary amine with CS_2 and NaOH; (3), (5) secondary amine (NHMe) with CS_2 and NaOH; (7) primary amine from silylation; (10) ethyl isothiocyanate with (7); (11) H_2O_2 oxidation of (2); (12) secondary amine with HNO_2 ; (13) H_2O_2 oxidation of (1); (14) secondary amine with H_2O_2 . ^b ND = not determined.

is principally by adsorption. It is interesting to note that ruthenium is also extracted by amines (entry 7) which are covalently bound to the inorganic phases. Such reagents may be more suitable when loading capacity is not the principal factor since it may not be possible to have sulphur reagents present as sulphate or sulphide as these attack stainless steel. The lower K_D values for the nitrosamine and N-oxides arise because oxygen ligands have a low affinity for ruthenium(III). The reason for the low value for the thiourea sample is not clear at present.

The unfunctionalised inorganic sulphides were interesting as lapis lazuli appears to have a surprisingly high affinity for ruthenium. Lapis lazuli is an aluminosilicate mineral with the ultramarine type of framework structure. The formula approximates to $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\cdot\text{S}$. The ultramarines are anhydrous, unlike the zeolites. One major advantage of inorganic-based materials over organic materials for nuclear waste storage is their greater resistance to radiation. Preliminary results for γ irradiation (^{60}Co source) for two of the loaded materials are given in Table 3. These show that the amount of ruthenium released from the loaded material back into the liquid in contact with the material does increase with radiation dosage but the totals are quite low. The zeolite 13X-dithio-

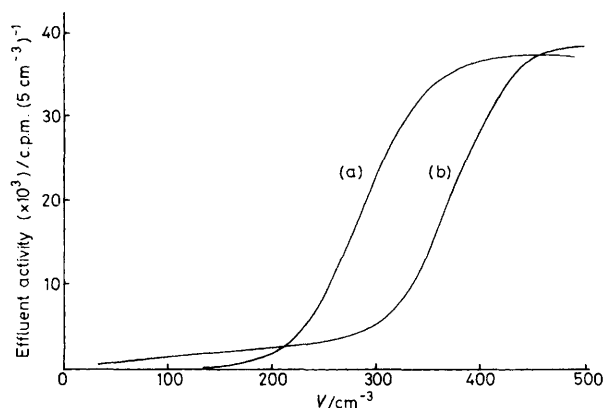


Figure 1. Preliminary breakthrough plots for (a) silica gel; (b) zeolite 13X with functional dithiocarbamate groups and simulated pond water [solution (3)]. The effective bed volume was ca. 1 cm^3 . Flow rates (a) $1 \text{ cm}^3 \text{ min}^{-1}$; (b) $3.3 \text{ cm}^3 \text{ min}^{-1}$. C.p.m. = counts per minute.

Table 3. Estimate of ^{106}Ru released by the loaded functionalised silica or zeolite on γ irradiation.^a

\log_{10} (dose in rad)	7	8	9
Compound			
(1)	3	9	7
(2)	5	6	11

^a Determined by measuring the increase in ^{106}Ru in the liquid in contact with the loaded material, expressed as a percentage of the original loading.

carbamate material is particularly effective, which is encouraging since zeolites are already being used for removing ^{137}Cs and ^{90}Sr , with subsequent incorporation into cement matrices for storage.

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