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Recovery of Uranium from Seawater: Preparation and Development of Polymer-Supported Extractants

Fuel Cycle R&D

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FINAL REPORT

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Abstract

The primary amine $–CH_2NH_2$ ligand bound to cross-linked polystyrene has been discovered to have a high affinity for the uranyl ion from a matrix of artificial seawater. The uranyl capacity is 14.8 mg U / $g_{polymer}$ compared to 2.34 mg U / $g_{polymer}$ for a diamidoxime ligand on a polystyrene support. Secondary and tertiary amines have much lower affinities. The results with polystyrene-bound $–CH_2NH_2$ suggest at least a 3-fold increase in uranyl capacity (calculated on a per mole ligand basis (not per gram of polymer in order to make the results independent of the weight of the polymer support)) and a 4-fold increase when ligands with two primary amines per ligand are utilized. An additional advantage of the primary amine over amidoxime is that it is a simpler ligand to prepare.

Results

Figure 1 shows the structures of the amines whose uranyl capacities were studied. Table 1 gives their nitrogen and acid capacities, and % dry mass content. The theoretical nitrogen capacities are calculated on the basis of the structures shown in Fig. 1. Comparing the acid to the nitrogen capacity gives the number of amine sites that are in the HCl form and shows that amines with more than two nitrogens do not exceed two HCl per ligand.

Comparing the experimental to the theoretical nitrogen capacities shows that pA and pDMA consist only of the expected ligand; pMA crosslinks to the tertiary amine and the remaining amines have various levels of secondary crosslinking since the nitrogen capacities are lower than theoretical. FTIR spectra do not show the CH_2Cl band at 1265 cm^{-1} hence the lower nitrogen capacities are not due to incomplete reaction. The % yield indicates the extent to which the non-crosslinked ligand is produced. pA has the lowest dry mass content and so has the highest hydrophilicity which is consistent with it having the fewest carbons at the amine.

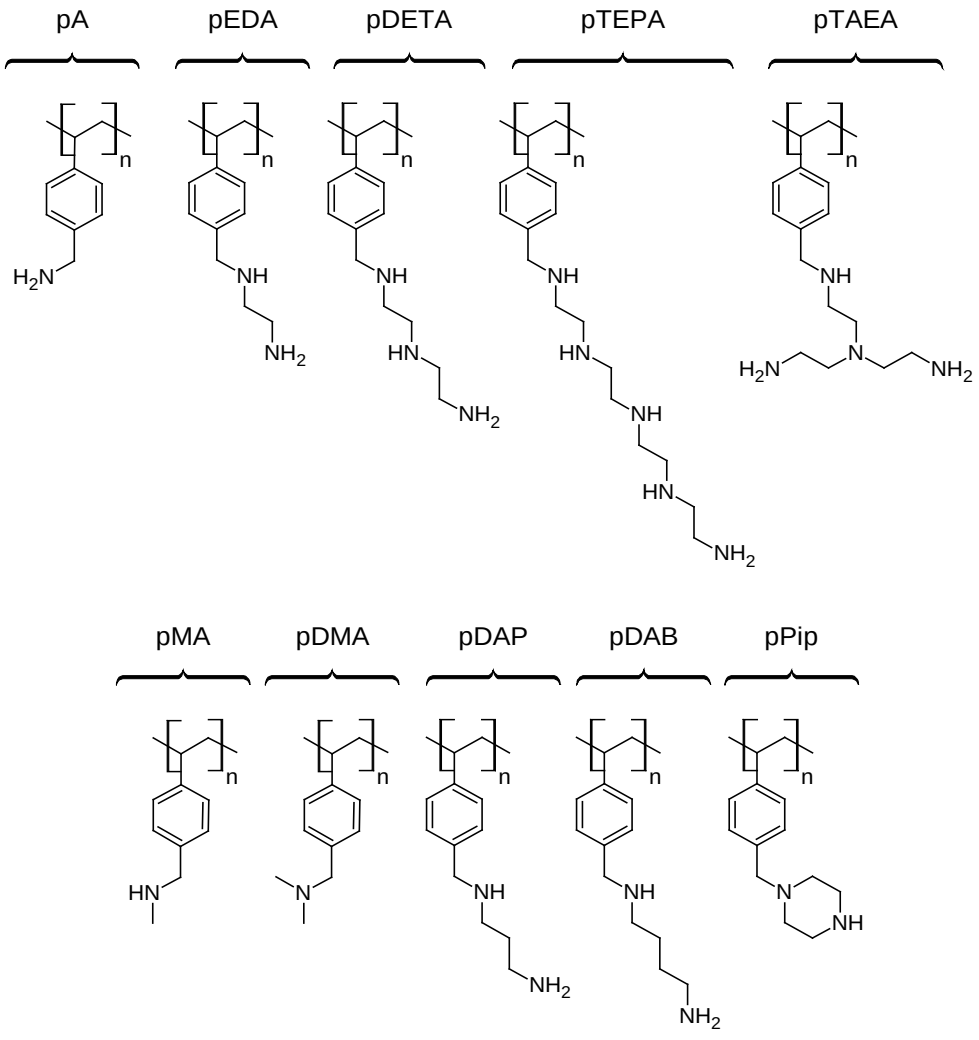

Figure 1. Structures of polymers synthesized.

Table 1. Physico-chemical properties of the polymers (nitrogen and acid capacities are to ±0.2 and the dried mass contents are to ±5%).

	N cap.		Yield	Acid cap.	D.M.C.
	mmol N / g		%	mmol H / g	%
polymer	Exp.	Theor.		Exp.	
pVBC	-	0	-	-	100
pA	5.46	5.71	95.6	5.00	18.6
pMA	3.60	5.24	68.7	4.88	49.3
pDMA	4.48	4.87	92.0	4.54	33.0
pDAP	5.56	7.32	76.0	5.50	33.5
pDAB	5.81	6.96	83.5	5.37	34.4
pEDA	6.61	7.74	85.4	6.13	30.0
pDETA	8.43	9.90	85.2	5.96	33.6
pTEPA	8.51	11.6	73.3	5.77	39.6
pPip	5.30	8.06	65.8	3.58	47.2
pTAEA	7.10	11.5	61.7	5.17	41.6

Table 2 compares the uranyl capacities of the polymers. A much higher capacity is evident for pA (14.8 mg U / $g_{polymer}$) than pMA and pDMA (0.14 and 0.09 mg U / $g_{polymer}$, respectively).

Table 2. Uranyl capacities as mg U / $g_{polymer}$ and mmolU / mol_{ligand} (all runs in duplicate and capacities (mg U / g) reproducible to ±5%).

Resin	U capacity	N capacity	U capacity
	mg U /$g_{polymer}$	mmol N /$g_{polymer}$	mmol U /mol_{ligand}
pVBC	0	-	0
pDMA	0.09	4.48	0.084
pMA	0.14	3.60	0.165
pPip	0.97	5.30	1.54
pDAP	6.05	5.56	9.14
pDAB	6.62	5.81	9.57
pA	14.8	5.46	11.4
pEDA	10.4	6.61	13.2
pDETA	8.89	8.43	13.3
pTEPA	7.17	8.51	17.7
pTAEA	6.78	7.10	16.0

The primary amine thus has a high affinity for the uranyl ion from seawater and complexation is sensitive to substituents at the amine nitrogen. All polymers with primary amine groups have a significant capacity for uranyl from seawater. (Note these are loadings from an initial solution of 50 mg / L and are not to be considered saturation capacities.)

Discussion

Comparison of capacities. The uranyl capacities for pDAP and pDAB seem lower than for pA, and there seems to be a decrease in capacity along the series pA, pEDA, pDETA, and pTEPA. However, a direct comparison of all polymers on a per gram basis is problematic since the molecular weight of the monomer unit changes as the ligand structure changes. A comparison on the basis of the nitrogen capacity is more useful. Converting mg U / $g_{polymer}$ to mmol U / mol_{ligand} allows for a more meaningful comparison of the ligands' inherent affinities on a molar basis. Table 2 reports the affinities on a per gram and per mole basis in order to indicate that high affinities are achieved with relatively low-mass ligands (a high-affinity ligand coupled to a high mass is not useful since the final polymer to be deployed must be of low total weight). The results in Table 2 underscore the significance of the primary amine to the removal of uranium from seawater. The pA value is still high (11.4 mmol U / mol_{ligand}) while pDAP and pDAB have comparable and only somewhat lower values (9.14 and 9.57 mmol U / mol_{ligand}, respectively). pEDA and pDETA are now seen to have the same capacities (13.2 and 13.3 mmol U / mol_{ligand}, respectively). pTEPA has a still higher value (17.7 mmol U / mol_{ligand}) that is almost equivalent to pTAEA (16.0 mmol U / mol_{ligand}). The results are consistent with the primary amine having a high affinity for the uranyl ion from seawater: TEPA immobilization occurs to some extent through one of the interior nitrogens giving two primary amines per ligand while TAEA inevitably gives two primary amines per ligand.

Comparison with amidoxime. It is relevant to compare the results reported in Table 2 with the amidoxime ligand in order to gauge the relative affinities of the primary amine and amidoxime ligands. The highest capacity attained for the amidoxime from seawater is 4 mg U / $g_{polymer}$ with the ligand on polyethylene fibers.[1] A comparison with pA (14.8 mg U / $g_{polymer}$) is problematic, however, because of the higher monomer molecular weight for the latter and the difference in initial solution uranyl levels (actual seawater in the former, spiked artificial seawater in the latter for analytical purposes). A more valid comparison would be between the values in Table 2 with amidoxime bound to the same polymer support and the same initial solution conditions. While the monoamidoxime is difficult to prepare on polystyrene, the diamidoxime has been

prepared (Fig. 2). It has a uranyl capacity of 2.34 mg U / $g_{polymer}$. With a nitrogen capacity of 10.4 mmol / g, this recalculates to 3.79 mmol U / mol_{ligand}. Since the diamidoxime has a higher uranyl affinity than the monoamidoxIme,[2] the results reported here with pA suggest at least a 3-fold increase in uranyl capacity by the primary amine ligand (calculated on a mole basis) and a 4-fold increase when ligands with two primary amines per ligand are utilized.

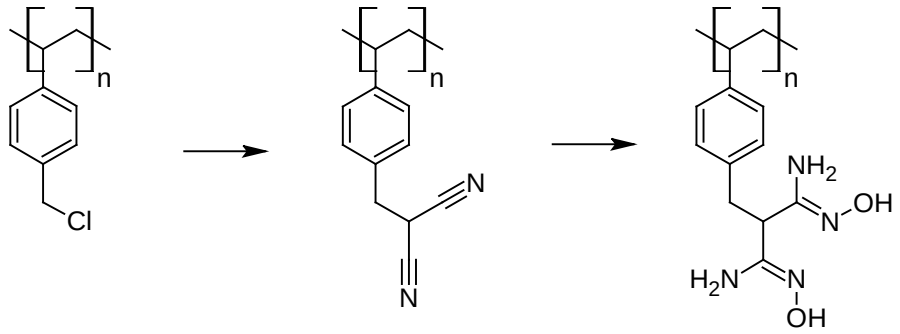

Figure 2. Polystyrene-bound diamidoxime prepared from immobilized malononitrile.

Binding Mechanism. The binding mechanism must account for the significantly higher affinity of the primary amine relative to secondary and tertiary amines. The conditions in seawater are such that the uranyl species[3] are primarily $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ and that they exist mostly as the calcium salt.[4] The amines are protonated at seawater pH with chloride as the counterions.[5] Given these conditions, it is proposed that the sorption mechanism is one of cation exchange at the uranyl species (Fig. 3).

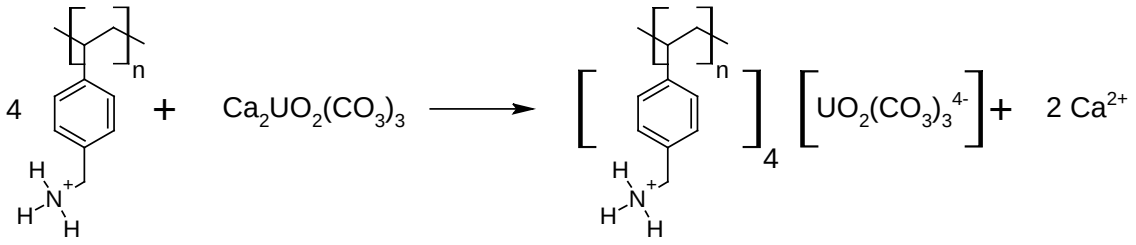

Figure 3. Sorption of uranyl from seawater by the primary amine via cation exchange.

An analogous reaction is the formation as a precipitate of ammonium uranyl carbonate from the combination of ammonium and uranyl carbonate ions (eq. 1).

$$4NH_4^+ + \left[UO_2(CO_3)_3\right]^{4-}_{sol} \rightarrow \left[NH_4^+\right]_4\left[UO_2(CO_3)_3\right]_s \quad (1)$$

In the present case, the binding site is the carbonate ion as the ammonium ion exchanges with the calcium. Carbonate is a hard anion[6] and the exchange requires ammonium (-NH_3^+) to be harder than calcium. This is supported by the observation that the NH_4^+ ion exchanges onto aluminosilicates in preference to Ca^{2+}, Mg^{2+} and K^+.[7] Consideration of the hard-soft aspect of the exchange is also consistent with the absence of significant activity by the secondary and tertiary amines: increasing the organophilicity at the nitrogen increases the softness of the ammonium ligand[8] and thus decreases their affinity for the hard carbonate complex.

Conclusions

The primary amine is found to have a dominant effect on the sorption of uranyl from seawater. This could become important in the preparation of sorbents with high uranyl capacities under seawater conditions. The extent of complex formation is limited by the decreasing probability of formation as molecularity increases. Such a limitation could be overcome by immobilizing ligands with a high density of primary amine sites. Mobility of the primary amine sites also appears crucial to allow the formation of the corresponding complexes around the equatorial plane of the uranyl cation or carbonate complex.

Current research is focused on increasing the uranyl capacity by increasing the primary amine density on new ligand structures involving pentaerythritol as a scaffold as well as immobilizing amines on polypropylene fiber.

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The original proposal had a three-year timetable for Milestones and Deliverables but the work was funded for the two-year period of which this report is the result. As required by the conditions of the award, a comparison is made between the Milestones and Deliverables and the accomplishments of this work.

NOTE: The proposal was written with the expectation that the ligand of choice for uranyl recovery would be the phosphonate ligand. This work, however, uncovered the fact that the amine ligand has a very high affinity for the uranyl ion from seawater and it became the focus of this two-year period.

I. Identify a phosphonate whose affinity for UO_2^{2+} from synthetic seawater is 50% greater than that of amidoxime.

ACCOMPLISHED: an *amine* ligand was identified whose affinity for UO_2^{2+} is *300%* greater than that of amidoxime (under synthetic seawater conditions)

II. Prepare a phosphonate (in the form of beads) whose sorption rate for UO_2^{2+} is 50% greater than amidoxime.

ACCOMPLISHED: An amine was prepared in the form of beads whose sorption rate for UO_2^{2+} is at least 50% greater than amidoxime (also in the form of beads)

III. Compare the performances of the best phosphonates with amidoxime; identify a phosphonate whose sorption characteristics, including rate of sorption, are 50% better than the amidoxime.

ACCOMPLISHED: The primary amine –CH2NH2 has been identified as performing significantly better that the amidoxime under all conditions tested

IV. Identify a phosphonate whose stability in repeated loading / regeneration cycles outperforms that of amidoxime.

ACCOMPLISHED: The primary amine ligand readily regenerates and is reusable.

V. Prepare a polypropylene fiber where grafting with polyVBC via $scCO_2$ technology is superior in terms of support degradation and homopolymer formation relative to irradiation technology.

ACCOMPLISHED: Conditions have been identified where polyVBC grafts onto polypropylene fiber with no support degradation whatsoever.

VI. Deliver a polypropylene fiber functionalized with the optimum phosphonate ligand that outperforms the best available amidoxime-bearing fiber in uranyl loading under actual seawater conditions.

NOT ACCOMPLISHED: While there is every expectation that the polyVBC can be converted to amine and that it will have at least the same performance characteristics of the beads, the award period ended before this could be studied.

DELIVERABLES: A sample of the beads functionalized with the primary amine ligand was delivered to PNNL for testing under authentic seawater conditions; their results are pending.

PUBLICATION

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PRESENTATION

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Polymer-Supported Primary Amines for the Recovery of Uranium from Seawater

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