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POTENTIAL USES OF SILICA-BONDED MACROCYCLIC LIGANDS

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November 1991

Presented at the
Annual Meeting of American
Institute of Chemical Engineers
November 17-22, 1991
Los Angeles, California

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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POTENTIAL USES OF SILICA-BONDED MACROCYCLIC LIGANDS FOR SEPARATION OF METAL IONS FROM NUCLEAR WASTE

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September 1991

Prepared for presentation at
American Institute of Chemical Engineers Annual Meeting

under U.S. Department of Energy contract
DE-AC06-76RLO 1830

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Potential Uses of Silica-Bonded Macrocyclic Ligands for Nuclear Waste Treatment

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Advanced or emergent chemical separation technologies are of definite interest for applications to nuclear waste treatment and environmental remediation problems. Enormous volumes of nuclear defense wastes must be treated and isolated from the environment for thousands of years to ensure that radioactivity will decay to levels not hazardous to living organisms. Current treatment plans call for partitioning the wastes into high- and low-level radioactive wastes and hazardous wastes; the high level wastes would be vitrified and sent to long term storage in a geologic repository, the low level wastes would be grouted and stored in above-ground repositories, and the hazardous wastes would destroyed by appropriate environmentally-acceptable methods [1]. The treatment costs will be enormous: tens of billion dollars at the Hanford site alone. Numerous chemical and physical separations are necessary to accomplish this feat. Significant reductions in cost and markedly improved environmental acceptability could accrue if advanced chemical separations of the wastes could be implemented without increasing the waste volume.

Stored waste and byproducts of nuclear production are largely solid and aqueous solutions of ionic compounds (i.e. salts) in which acutely hazardous and/or radioactive compounds/ions are present in low concentrations relative to nonradioactive ions of sodium, nitrate, aluminum, iron, etc. Also, where environmental contamination has occurred and remediation is required, hazardous or radioactive elements are present in low concentrations. Such conditions require that separation technologies be capable of achieving very high degrees of selectivity for specific ions of interest. Thus, separation technologies based on molecular recognition of ions [2, 3, 4] are attracting attention. Materials derived from macrocyclic ligands such as crown ethers, cryptands, cavitands, spherands, etc. are most promising and their use in separations based on solvent extraction [5, 6, 7, 8, 9, 10], membranes [11, 12], polymer resins [13], and solid supports [14, 15] are being actively investigated.

This paper explores the potential of a relatively new separation material that is obtained by covalently binding macrocyclic ligands to silica gel [14]. Fortunately, neutral macrocyclic ligands can be bound to silica gel such that metal binding constants do not differ significantly from the binding constants of the free ligands so that selectivities of free macrocyclic ligands [4] can be used in designing silica-bound materials with appropriate selectivities [16]. Accordingly, macrocyclic ligands known to have selectivities for Pd$^{2+}$, Ag$^+$, Ru$^{3+}$, Sr$^{2+}$, and Cs$^+$ were covalently bound to silica gel. These materials were then tested for their ability to separate these ions from a synthetic test solution representative of a nuclear process waste stream [1]. Cs$^+$ and Sr$^{2+}$ are of interest because their radioactive isotopes are major radioactive constituents of defense nuclear wastes accumulated at the Hanford site. Removal of precious metals such as Pd$^{2+}$, Ag$^+$ and Ru$^{3+}$ present in nuclear defense waste are of interest not just because of their obvious economic value, but also because these metals may hinder the waste vitrification process for confining radionuclides.

† Portions of the work described in this paper were supported by the Pacific Northwest Laboratory Office of Waste Minimization with funds provided by the U.S. Department of Energy (DOE). The Pacific Northwest Laboratory is operated for DOE by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.
EXPERIMENTAL SECTION

General. SuperLig™ materials, 35-60 mesh silica gel with covalently bound macrocyclic ligands selective for Pd$^{2+}$, Ru$^{3+}$, Ag$^+$, Cs$^+$, Rb$^+$, Sr$^{2+}$, and Ba$^{2+}$ ions were prepared by IBC Advanced Technologies, Inc (Provo, UT). Test solutions containing the above ions and other ions common to nuclear process waste streams were prepared. Composition of a representative solution is given in Table I. Typically, 10- or 20-g quantities of SuperLig™ materials were dry-packed in glass columns and wetted with 1 M nitric acid prior to loading with test solution. After loading, the column was washed with water or nitric acid solutions and then the sequestered elements were eluted with solutions of sequestering agents. Flow rates of solutions through the columns were not rigorously controlled, although flow rates were generally held to less than 30 ml or 2 bed volumes per minute. Feed, and elutions were analyzed for elements of interest by atomic absorption (AA), atomic emission (AE) or inductively coupled plasma (ICP) spectroscopy. Specific details for individual experiments are given below.

Separations of Barium and Strontium. 450 ml of synthetic test solution were fed into a column containing 20 g SuperLig™ 601. This volume contained ~1.1 mmol Ba$^{2+}$ and 0.8 mmol Sr$^{2+}$, representing ~33 percent of the 3 mmol column load capacity. The column was washed with 1 M HNO$_3$. 0.1 M Na$_3$Citrate was added to elute Sr$^{2+}$ followed by 0.03 M Na$_4$EDTA (pH-10.5) to elute Ba$^{2+}$.

Separations of Cesium and Rubidium. 30 ml of test solutions eluted through SuperLig™ 601 were fed into a column containing 20 g SuperLig™ 602. This volume contained ~0.12 mmol Cs$^+$ and 0.03 mmol Rb$^+$, ~2.5 percent of the 6 mmol load capacity. The column was washed with water, and 0.01 M HNO$_3$ was added to elute both Cs$^+$ and Rb$^+$. 

Separations of Palladium. In one set of experiments, 450 ml of test solutions were fed into a column containing 10 g SuperLig™ 27. This volume contained ~1 mmol Pd$^{2+}$, representing ~33 percent of the 3 mmol ligand load capacity. The column was washed with 1 M HNO$_3$, followed by elution of Pd$^{2+}$ with a solution of 1 M thiourea/1 M acetic acid. Alternatively, a 16 M HNO$_3$ wash was used to remove Zr from the blank gel sites followed by an acetic acid wash to displace the nitric acid and prevent oxidation of thiourea. Once 0.02 M TiCl$_3$ was added to the thiourea/acetic acid eluent to facilitate release of Ru(III) held in the column by reducing it to the larger Ru(II) ion. In another set of experiments, 2000 ml of test solutions were fed into the SuperLig™ 27 column. These experiments were performed to show that the column could be fully loaded and subsequently eluted to yield a purified and concentrated solution of Pd$^{2+}$. The column was washed with 5 M HNO$_3$ followed by water. 1 M thiourea/1 M acetic acid was added to elute Pd$^{2+}$.

Separations of Silver and Ruthenium. 450 ml of test solution eluted from SuperLig™ 27 were fed into a column containing 10 g SuperLig™ II. This volume contained ~2.1 mmol Ru and 0.1 mmol Ag$^+$, representing ~73% of the 3 mmol ligand load capacity. The column was washed with 1 M HNO$_3$ followed by addition of a hot (60°C) solution containing 1 M thiourea/1 M acetic acid/0.02 M TiCl$_3$ to elute Ru and Ag$^+$. In similar experiments, instead the column was washed with 100 ml aliquots of 16 M nitric acid and water followed by elution of the Ag$^+$ with 9 M HB$_3$.
RESULTS AND DISCUSSION

Experimental results for separations of Ba\(^{2+}\), Sr\(^{2+}\), Cs\(^{+}\) and Rb\(^{+}\) ions are presented graphically in Figures 1 and 2 and explained below. Descriptions of results for separation of Pd\(^{2+}\), Ag\(^{+}\) and Ru ions then follow.

Separations of Barium and Strontium. Analytical results for SuperLig\textsuperscript{TM} 601 used to separate Ba\(^{2+}\) and Sr\(^{2+}\) from synthetic solution are depicted graphically in Figure 1. Sr\(^{2+}\) and Ba\(^{2+}\) were efficiently removed (100\%) from the test solution and selectively eluted with Na\(_3\)Citrate and Na\(_4\)EDTA respectively; 90\% of the Sr\(^{2+}\) and 100\% of the Ba\(^{2+}\) were recovered in the elutions. All the other elements in the elution were present at levels below a detection limit of 1 ppm. SuperLig\textsuperscript{TM} 601 exhibited a weak affinity for Rb\(^{+}\), but it was displaced from the column by the HNO\(_3\) washes and did not contaminate the Ba\(^{2+}\) and Sr\(^{2+}\) elutions.

Separations of Cesium and Rubidium. Ba\(^{2+}\) has a strong affinity for SuperLig\textsuperscript{TM} 602, so it along with Sr\(^{2+}\) was removed by first passing the test solution through SuperLig\textsuperscript{TM} 601. The results for SuperLig\textsuperscript{TM} 602 used to separate Cs\(^{+}\) and Rb\(^{+}\) are depicted in Figure 2. Cs\(^{+}\) and Rb\(^{+}\) were quantitatively separated from the test solution by the 20 g column and readily eluted with dilute HNO\(_3\). These separations could only be accomplished from the synthetic matrix in 30 ml aliquots because of weak binding constants between the Cs\(^{+}\) and Rb\(^{+}\) and bound ligand. Accordingly, the separation was chromatographic rather than extractive, requiring small loadings (10\% of the equilibrium capacity of the column) and elution with dilute (0.01 M) HNO\(_3\). Under these conditions, good separation of Cs\(^{+}\) and Rb\(^{+}\) from the other elements in the test solution was observed, however Cs\(^{+}\) and Rb\(^{+}\) could not be separated from each other. Material balances on the two elements were essentially quantitative. However, the volume of elution containing Cs\(^{+}\) and Rb\(^{+}\) was approximately three times that of the volume of the original test solution feed to the column. Unlike the experiments with Sr\(^{2+}\) and Ba\(^{2+}\), a step gradient elution using sequestering agents to facilitate release of Cs\(^{+}\) and Rb\(^{+}\) from the column could not be used because few sequestering agents bind Cs\(^{+}\) or Rb\(^{+}\) better than the silica-bound macrocycle in the column. Future experiments should be able to take advantage of the macrocycles greater affinity for other metal ions. For example, we expect that using a Ba\(^{2+}\) solution as an eluent will concentrate Cs\(^{+}\) and Rb\(^{+}\).

Separation of Palladium. SuperLig\textsuperscript{TM} 27 strongly binds Pd\(^{2+}\) and therefore can be used to separate Pd\(^{2+}\) quantitatively from the test solution. Results for both partial (450 ml) and full (2000 ml) loadings of the column with synthetic test solution were obtained. Data for the 450 ml loading, indicate Pd\(^{2+}\) was efficiently separated (100\%) from the test solution and efficiently eluted (100\%) with a thiourea/acetic acid solution. Ru also was sequestered by the column and partially eluted by the eluent containing 0.02 M TiCl\(_3\). In one experiment, 5.8 mg were detected in the Pd\(^{2+}\) containing elution. This amount corresponds to about 3 \% of the Ru originally present in the test solution, which was nearly twice the original concentration of Pd\(^{2+}\). For the 2000 ml loading, 3.16 mmoles Pd\(^{2+}\) were separated from the test solution, which contained a total of 5.50 mmoles Pd\(^{2+}\). This accounted for 97\% of the possible column load capacity. When 16 M nitric acid washes were used prior to eluting the Pd\(^{2+}\), all other elements in the subsequent eluents were present below a detection limit of 1 ppm. Ru was displaced from the column by Pd\(^{2+}\) which binds more strongly than Ru such that the Pd\(^{2+}\) containing elutions were uncontaminated by Ru.

Separation of Silver and Ruthenium. Ag\(^{-}\) was readily eluted from SuperLig\textsuperscript{TM} II using either 9 M HBr or thiourea/acetic solution. In one experiment, essentially all of the Ag\(^{-}\) (≈45 mg) was recovered in a 50-ml elution of 9 M HBr. Also, about 10 ppm of Ru and 15 ppm of Sn were detected in the solution, but none of the other test elements were present above their detection.
Elution with thiourea/acetic acid eluents gives similar results. SuperLig™ II strongly binds Ru and releases it to other ligands slowly. Only 40-50% of the bound Ru could be eluted from the column, even when TiCl₃ was added to the thiourea/acetic acid eluent in an attempt to facilitate the release of Ru³⁺ by reducing it to the larger Ru²⁺ ion. Afterwards, the SuperLig™ II column retained a dark bluish green color, indicating that Ru was still held in the column. Energy dispersive x-ray (EDX) analysis of the dried SuperLig™ II material showed that Ru was still bound to the material.

CONCLUSIONS

The above results show the potential for this technology to selectively separate metal ions from a complex mixture. The performance of SuperLig™ 27 materials is good enough that it is being used commercially for recovering Pd²⁺. In the cases of SuperLig™ 601 and 602 materials, clean separations of Sr²⁺ and Cs⁺ from the test solutions were obtained. The 601 material is promising and should be further evaluated. However, higher binding efficiencies for Cs⁺ than observed for the 602 material are desired for nuclear waste applications. The low efficiency is directly attributable to the binding constant of the macrocyclic ligand in these material. Suitable separations of this ion should be possible if a macrocyclic ligand with larger binding constant is employed. The field of ion recognition research is large and vital. Discoveries and syntheses of suitable ligands for Cs⁺ as well as other metal ions of interest should accrue from vigorous research now in progress.

Many advantages and some disadvantages of this approach could be raised now. However, much of the discussion would be speculative and resulting conclusions premature. It is best to postpone such discussion until forthcoming separation materials with appropriate selectivities for radioactive elements are in hand and investigated more thoroughly.

REFERENCES


Table 1. Composition of Synthetic Test Solution

<table>
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<tr>
<th>Element/Specie(^a)</th>
<th>Target (\mu g/mL)</th>
<th>ICP (\mu g/mL)</th>
<th>AA/AE (\mu g/mL)</th>
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<td>450</td>
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<td>Ba</td>
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<tr>
<td>Na</td>
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<td>87115</td>
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\(^a\)In 5 M nitric acid. * No analysis performed
Figure 1. Separation of Sr and Ba from synthetic nuclear waste process solution. Feed: 5 M nitric acid solution containing 27 metal species (see Table I); Wash: 50 ml of 16 M nitric acid followed by 50 ml of 1 M nitric acid; Citrate: 0.1 M trisodiumcitrate; EDTA: 0.03 M tetrasodiummethylenediaminetetraacetic acid. See experimental section for details.

Figure 2. Separation of Cs and Rb from synthetic nuclear waste process solution. Feed: 5 M nitric acid solution containing 27 metal ions (see Table I); Wash: 30 ml of water. See experimental section for details.