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# Crown Ether-Doped Sol–Gel Materials for Strontium(II) Separation

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**Hybrid organic/inorganic sol–gel materials containing an encapsulated crown ether ligand were found to selectively remove  $91.4 \pm 1.3\%$  of  $\text{Sr}^{2+}$  from a solution containing excess of competing ions such as  $\text{Ca}^{2+}$ . The crown ether ligand, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-bis(malonate) ligand ( $\text{Na}_4\text{oddm}$ ), with known high affinity for  $\text{Sr}^{2+}$  was encapsulated in hydrophilic  $\text{SiO}_2$  through a simple sol–gel process. Washing the  $\text{Sr}^{2+}$ -loaded gel with acid or ethylenediaminetetraacetic acid disodium salt recovered the  $\text{Sr}^{2+}$  from the sol–gel sorbent and regenerated the doped gel for subsequent  $\text{Sr}^{2+}$  intake. The approach reported here is a new alternative to the use of crown ethers in metal ion separation through, for example, solvent extraction or the use of sorbents containing chemically grafted crown ether ligands.**

Crown ethers, a class of macrocyclic ligands with high affinity and selectivity for alkali and alkaline earth metal ions, have proven to be effective in solvent extraction processes.<sup>1,2</sup> Although these methods are effective at extracting metal ions, they also usually generate secondary organic waste. Ligands grafted onto organic and inorganic supports for toxic metal separation have been developed as an alternative in part to reduce organic waste.<sup>1,3–7</sup> Grafting ligands onto solid supports usually requires multistep syntheses, and sometimes additional functional groups are required to achieve selectivity or fast metal intake kinetics.<sup>3</sup>

Recently, doping of functional molecules in sol–gels has been studied, and these doped molecules were often found to retain

their chemical activities.<sup>8,9</sup> Small reagents in solution can diffuse into the porous sol–gel matrixes and chemically interact with dopant molecules. Crown ether ligands have been entrapped in sol–gel matrixes and their ion transport properties studied to develop new ion-sensing materials and electrode membranes.<sup>10</sup>

We reasoned that crown ethers, encapsulated in porous sol–gels, could bind target metal ions and remove them from aqueous solution. Because  $\text{SiO}_2$  sol–gel sorbents are hydrophilic, fast aqueous metal ion diffusion in the gels and thus fast metal ion intake by the ligand-doped gels can be achieved. We chose  $\text{Sr}^{2+}$  as the target metal ion in the current studies to investigate this new approach of doping crown ether ligands in sol–gel materials.

- (4) See, e.g.: (a) Bradshaw, J. S.; Izatt, R. M. *Acc. Chem. Res.* **1997**, *30*, 338. (b) Sessler, J. L.; Kral, V.; Genge, J. W.; Thomas, R. E.; Iverson, B. L. *Anal. Chem.* **1998**, *70*, 2516. (c) Hankins, M. G.; Hayashita, T.; Kasprzyk, S. P.; Bartsch, R. A. *Anal. Chem.* **1996**, *68*, 2811. (d) Espinola, J. G. P.; Defreitas, J. M. P.; Deoliveira, S. F.; Aioldi, C. *Colloids Surf.* **1992**, *68*, 261. (e) Dudler, V.; Lindoy, L. F.; Sallin, D.; Schlaepfer, C. W. *Aust. J. Chem.* **1987**, *40*, 1557. (f) Leyden, D. E.; Luttrell, G. H. *Anal. Chem.* **1975**, *47*, 1612. (g) Fischer, R. J.; Pang, D.; Beatty, S. T.; Rosenberg, E. *Sep. Sci. Technol.* **1999**, *34*, 3125. (h) Dai, S.; Burleigh, M. C.; Shin, Y.; Morrow, C. C.; Barnes, C. E.; Xue, Z. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1235. (i) Dai, S.; Shin, Y.; Ju, Y.; Burleigh, M. C.; Lin, J. S.; Barnes, C. E.; Xue, Z. *Adv. Mater.* **1999**, *11*, 1226. (j) Dai, S.; Burleigh, M. C.; Ju, Y. H.; Gao, H. J.; Lin, J. S.; Pennycook, S. J.; Barnes, C. E.; Xue, Z. *J. Am. Chem. Soc.* **2000**, *122*, 992. (k) Im, H.-J.; Yang, Y.; Allain, L. R.; Barnes, C. E.; Dai, S.; Xue, Z. *Environ. Sci. Technol.* **2000**, *34*, 2209.
- (5) (a) Sharma, C. V. K.; Clearfield, A. *J. Am. Chem. Soc.* **2000**, *122*, 1558. (b) Zhang, B.; Clearfield, A. *J. Am. Chem. Soc.* **1997**, *119*, 2751.
- (6) Bartsch, R. A.; Hayashita, T. *ACS Symp. Ser.* **1999**, No. 716, 183 (Metal Ion Separation and Preconcentration).
- (7) (a) Feng, X.; Fryxell, G. E.; Wang, L. Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science*, **1997**, *276*, 923. (b) Chen, X.; Feng X.; Liu, J.; Fryxell, G. E.; Gong, M. *Sep. Sci. Technol.* **1999**, *34*, 1121.
- (8) (a) Lev, O. *Analysis* **1992**, *20*, 543. (b) Avnir, D. *Acc. Chem. Res.* **1995**, *28*, 328. (c) Lan, E. H.; Dave, B. C.; Fukuto, J. M.; Dunn, B.; Zink, J. I.; Valentine, J. S. *J. Mater. Chem.* **1999**, *9*, 45. (d) Collinson, M. M. *Crit. Rev. Anal. Chem.* **1999**, *29*, 289. (e) Collinson, M. M. *Mikrochim. Acta* **1998**, *129*, 149. (f) Wolfbeis, O. S.; Reisfeld, R.; Oehme, I. *Struct. Bonding (Berlin)* **1996**, *85*, 51. (g) Lin, J.; Brown, C. W. *Trends Anal. Chem.* **1997**, *16*, 200. (h) Allain, L. R.; Sorasane, K.; Xue, Z. *Anal. Chem.* **1997**, *69*, 3076. (i) Allain, L. R.; Xue, Z.; Roberts, M. J. *AT-PROCESS*. **1998**, *3*, 98. (j) Allain, L. R.; Xue, Z. *Anal. Chem.* **2000**, *72*, 1078.
- (9) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic Press: Boston, 1990.
- (10) (a) Jimenez-Morales, A.; Galvan, J. C.; Aranda, P.; Ruiz-Hitzky, E. *Mater. Res. Soc. Symp. Proc.* **1998**, *519*, 211. (b) Kimura, K.; Sunagawa, T.; Yokoyama, M. *Anal. Chem.* **1997**, *69*, 2379.

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<sup>‡</sup> Oak Ridge National Laboratory.

- (1) Watson, J. S. *Separation Methods for Waste and Environmental Applications*; Marcel Dekker: New York, 1999.
- (2) (a) *Principles and Practices of Solvent Extraction*; Rydberg, J., Musikas, C., Choppin G. R., Eds.; Dekker: New York, 1992. (b) Bradshaw, J. S.; Izatt, R. M.; Bordunov, A. V.; Zhu, C. Y.; Hathaway, J. K. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., Macnicol, D. D., Vogtle, F., Lehn, J. M., Gokel, G. W., Eds.; Elsevier: New York, 1996; Vol. 1, Chapter 2. (c) Moyer, B. A. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., Macnicol, D. D., Vogtle, F., Lehn, J. M., Gokel, G. W., Eds.; Elsevier: New York, 1996; Vol. 1, Chapter 10. (d) Gokel, G. W. *Crown Ethers and Cryptands*; Royal Society of Chemistry: Cambridge, U.K., 1991. (e) Yordanov, A. T.; Roundhill, D. M. *Coord. Chem. Rev.* **1998**, *170*, 93.
- (3) Alexandratos, S. D.; Crick, D. W. *Ind. Eng. Chem. Res.* **1996**, *35*, 635.

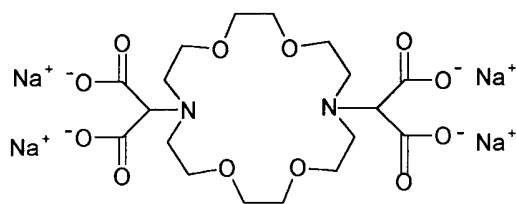


Figure 1. Structure of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-bis(malonate) ( $\text{Na}_4\text{oddm}$ ).

$^{90}\text{Sr}$ , a fission product,<sup>11a</sup> has been generated in large quantities from the production of nuclear power and weapons.<sup>11b</sup> It is a relatively long-lived radionuclide with a half-life of 29.1 years.<sup>11c</sup> Because of its chemical similarities to Ca,  $^{90}\text{Sr}$  is known to incorporate into biological systems and be stored in the bones of vertebrates.<sup>12a</sup>  $^{90}\text{Sr}$  exposure has thus been linked to various forms of cancer including leukemia.<sup>12b</sup> Leaching of  $^{90}\text{Sr}$  into neighboring groundwater from the current storage facilities for high-level radioactive waste has been reported.<sup>11b</sup> It is of intense current interest to develop new and efficient ways to separate  $^{90}\text{Sr}^{2+}$  from contaminated groundwater.<sup>11b</sup>

In the current work, a simple, one-step approach has been developed to encapsulate crown ether molecules with known high affinity for  $\text{Sr}^{2+}$  into sol-gel. The resulting materials were found to remove  $91.4 \pm 1.3\%$  of the target  $\text{Sr}^{2+}$  ions from aqueous solution in the presence of excess  $\text{Ca}^{2+}$ . The doped sol-gel was easily regenerated and used in the subsequent removal of  $\text{Sr}^{2+}$  in multiple cycles. These readily prepared crown ether-doped sol-gel materials are a good alternative to solvent extraction and sorbents containing grafted crown ether ligands for metal ion separation.

## EXPERIMENTAL SECTION

The chemicals used in this study,  $\text{Si}(\text{OMe})_4$  (Aldrich, 99%),  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  (Fisher, Certified ACS),  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Fisher, Certified ACS), HCl (Mallinckrodt, 37% in  $\text{H}_2\text{O}$ , Analytical Reagent), and ethylenediaminetetraacetic acid (EDTA) disodium salt (Mallinckrodt, 99.3%), were used as received. Deionized water was used in the reactions and the preparation of aqueous solutions. Distilled water was used in gel washing. 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane-7,16-bis(malonate) ligand ( $\text{Na}_4\text{oddm}$ ) (Figure 1) was prepared according to the literature procedure.<sup>13</sup>  $\text{Sr}^{2+}$  concentrations were determined by atomic emission (AE) spectroscopy. Emission measurements were conducted at the 460.7-nm line on an upgraded Perkin-Elmer 5100 atomic absorption spectrophotometer. Leaching of  $\text{Na}_4\text{oddm}$  was quantified by  $^1\text{H}$  NMR spectroscopy using a Bruker AC-250 spectrometer and sodium acetate as internal standard. Brunauer-Emmett-Teller (BET) surface area and pore size distribution measurements were conducted on a Quantachrome Corp. Nova-1000 gas sorption

analyzer. Scanning electron microscopy (SEM) images were obtained at 5.0 kV on a Hitachi S-4100 field emission scanning electron microscope. Sol-gel samples were placed on a carbon tape for SEM.

**Preparation of the  $\text{Na}_4\text{oddm}$ -Doped Sol-Gel Sorbents.** To  $\text{Na}_4\text{oddm}$  (75 mg) dissolved in deionized  $\text{H}_2\text{O}$  (200  $\mu\text{L}$ ) was added  $\text{CH}_3\text{OH}$  (400  $\mu\text{L}$ ), HCl (0.5 M, 100  $\mu\text{L}$ ), and  $\text{Si}(\text{OMe})_4$  (400  $\mu\text{L}$ ). The resulting solution was stirred vigorously in a capped vial until gelation occurred ( $\sim 60$  min). The sol-gel was then cured in the capped vial for 3 days. Following this curing period, the sol-gel sorbents were dried in a 45  $^\circ\text{C}$  oven for 2 days. During drying, shrinkage of the gel occurred, and the gel cracked into pieces that were 100–1000  $\mu\text{m}$  in diameter. Pieces of gel in this size range were used in all experiments. No physical degradation of the sol-gel sorbents was observed during the experiments.

**Preparation of Control Sol-Gels.** The control (blank) sol-gels that did not contain the  $\text{Na}_4\text{oddm}$  ligand were prepared for comparison.  $\text{Si}(\text{OMe})_4$  (400  $\mu\text{L}$ ),  $\text{CH}_3\text{OH}$  (400  $\mu\text{L}$ ), HCl (0.5 M, 100  $\mu\text{L}$ ), and  $\text{H}_2\text{O}$  (200  $\mu\text{L}$ ) were mixed and stirred in a capped vial until gelation occurred ( $\sim 1$  day). The sol-gel was then cured in the capped vial at room temperature for 3 days and dried at 45  $^\circ\text{C}$  for 2 days.

**Conditioning of the Ligand-Doped Gels.** Upon drying, the sol-gels were soaked in  $\text{H}_2\text{O}$  (10.0 mL, three aliquots) for 72 h to condition the materials. In this process, some of the doped ligand leached out of the sol-gel. The extent of ligand leaching was quantified using  $^1\text{H}$  NMR as an analytical tool. After 72 h, no further leaching of the ligand was observed. Leaching experiments were performed on 13 samples, and  $13 \pm 3\%$  of the doped ligand was found to have leached from the sol-gel. After the leaching process, the sol-gels were oven dried at 45  $^\circ\text{C}$  for 18 h.

**$\text{Sr}^{2+}$  Extraction Studies.** Freshly conditioned sol-gel (30–35 mg) was placed in glass vials along with 5.0 mL of a  $\text{SrCl}_2$  solution at 23  $^\circ\text{C}$ . Samples were then placed on a mechanical shaker for up to 24 h at 23  $^\circ\text{C}$ . Samples were then prepared by removing 1.0 mL of the supernatant solution and diluting as necessary for atomic emission measurements.

**Regeneration of the Sol-Gel Sorbents.** Once  $\text{Sr}^{2+}$  loading was complete, the metal ions were removed from the sorbents by washing with 5.0 mL of either HCl (6.0 or 1.0 M) or EDTA (0.1 or 0.01 M). The sorbents stripped with HCl were rinsed several times with deionized water and then neutralized in 5.0 mL of a  $\text{NaHCO}_3$  solution (pH 8.2) for up to 3 days to ensure complete  $\text{H}^+$  neutralization.<sup>14</sup> The sol-gel materials were then washed again with deionized water and placed in a 45  $^\circ\text{C}$  oven to dry before another extraction cycle. Sol-gel sorbents stripped with EDTA were simply rinsed with  $\text{H}_2\text{O}$  to remove the stripping reagent and then dried at 45  $^\circ\text{C}$  before another extraction cycle. The cycle of  $\text{Sr}^{2+}$  extraction/gel regeneration is shown in Figure 2.

## RESULTS AND DISCUSSION

Tests with 12 freshly conditioned,  $\text{Na}_4\text{oddm}$ -doped sol-gel samples (33–37 mg) showed that they effectively removed up to  $90 \pm 6\%$  of  $\text{Sr}^{2+}$  in 5.0 mL of 25.0 ppm  $\text{Sr}^{2+}$  solutions. In comparison, the control blank sol-gel without any ligand was

(11) (a) Ehmman, W. D.; Vance, D. E. *Radiochemistry and Nuclear Methods of Analysis*; Wiley: New York, 1991. (b) U.S. Department of Energy Office of Environmental Management, *Linking Legacies*, DOE/EM-0319, January 1997; p 32. (c) *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R., Editor-in-Chief; CRC Press: Boca Raton, FL, 1994; pp 11–54.

(12) (a) Thomasset, M. In *Radionuclide: Metab. Toxic. Proc. Symp.* Galle, P.; Masse, R. Eds. **1982**, 98. (b) Spiers, F. W.; Vaughan, J. *Leuk. Res.* **1989**, 13, 347.

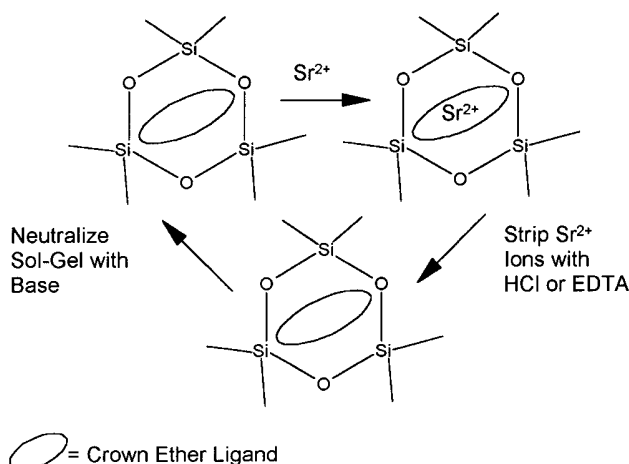
(13) Brucher, E.; Gyori, B.; Emri, J.; Jakab, S.; Kovacs, Z.; Solymosi, P.; Toth, I. *J. Chem. Soc., Dalton Trans.* **1995**, 3353.

(14) One wash with 5.0 mL of  $\text{NaHCO}_3$  was conducted here. Washing with additional  $\text{NaHCO}_3$  may reduce the time required for  $\text{H}^+$  neutralization.

Table 1.  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  Extraction Results

gel used	initial concn <sup>a</sup>	final concn	% removed	capacity <sup>b</sup>	$K_d$ <sup>c</sup>
control gel <sup>d</sup> (33 mg)	27.6 ppm $\text{Sr}^{2+}$	$24.3 \pm 1.8$ ppm $\text{Sr}^{2+}$	$12 \pm 7$	$5.7 \times 10^{-3}$	21
doped gel (34 mg)	25.0 ppm $\text{Sr}^{2+}$	$2.4 \pm 1.5$ ppm $\text{Sr}^{2+}$	$90 \pm 6$	$3.8 \times 10^{-2}$	$1.4 \times 10^3$
doped gel (34 mg)	44.7 ppm $\text{Ca}^{2+}$	$22 \pm 2$ ppm $\text{Ca}^{2+}$	$51 \pm 5$	$8.3 \times 10^{-2}$	$1.5 \times 10^2$
doped gel (32 mg)	31.3 ppm $\text{Sr}^{2+}$ 137.0 ppm $\text{Ca}^{2+}$	$2.7 \pm 0.4$ ppm $\text{Sr}^{2+}$ $67 \pm 7$ ppm $\text{Ca}^{2+}$	$91.4 \pm 1.3$ $51 \pm 5$	$5.1 \times 10^{-2}$ $2.7 \times 10^{-1}$	$1.7 \times 10^3$ $1.6 \times 10^2$

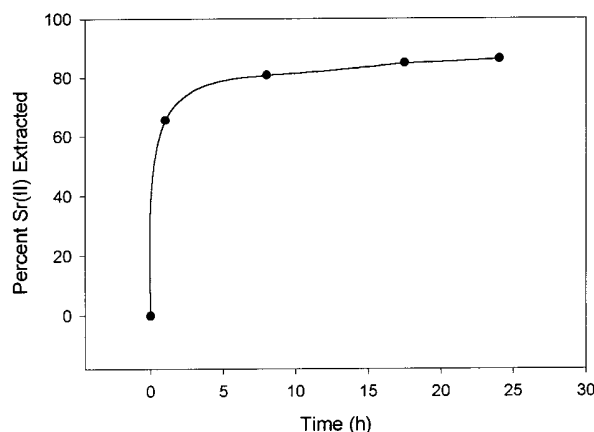
<sup>a</sup> The solutions were prepared with  $\text{SrCl}_2$  or  $\text{CaCl}_2$ . Extraction was conducted at 23 °C. <sup>b</sup> Capacity in mmol of  $\text{Sr}^{2+}$ /g of gel or in mmol of  $\text{Ca}^{2+}$ /g of gel. <sup>c</sup>  $K_d$  in  $[\mu\text{g of Sr}^{2+}/\text{g of gel}]/[\text{ppm of Sr}^{2+} \text{ remaining}]$  or in  $[\mu\text{g of Ca}^{2+}/\text{g of gel}]/[\text{ppm of Ca}^{2+} \text{ remaining}]$ . <sup>d</sup> The control sol-gel sample was prepared by a process similar to that in the preparation of  $\text{Na}_4\text{oddm}$ -doped sorbents. Only  $\text{Si}(\text{OMe})_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{HCl}$ , and water were used.

Figure 2.  $\text{Sr}^{2+}$  extraction/gel regeneration cycle.

ineffective in  $\text{Sr}^{2+}$  removal. In a solution containing 31.25 ppm  $\text{Sr}^{2+}$  (0.357 mM) and 137.0 ppm  $\text{Ca}^{2+}$  (3.42 mM), the sol-gel materials removed  $91.4 \pm 1.3\%$  of the  $\text{Sr}^{2+}$  in the presence of a 9-fold excess of competing  $\text{Ca}^{2+}$  ions. In these tests,  $51 \pm 5\%$  of the  $\text{Ca}^{2+}$  ions were removed from solution. In a series of four experiments to test the performance of the sorbents in a solution containing only  $\text{Ca}^{2+}$ , the crown ether-doped sol-gels removed  $51 \pm 5\%$  of the  $\text{Ca}^{2+}$  ions from a 44.7 ppm solution. Thus, the extractions of  $\text{Ca}^{2+}$  alone by the sorbents and in the presence of  $\text{Sr}^{2+}$  are similar.

In a separate test of the doped-gel sorbent capacity, the gel was soaked in 251 ppm  $\text{Sr}^{2+}$ . After 24 h, 74% of the  $\text{Sr}^{2+}$  was removed, and up to 52% of the ligand remaining in the sol-gel sorbents was used for binding  $\text{Sr}^{2+}$ . The results of these  $\text{Sr}^{2+}$  extraction studies are summarized in Table 1. The  $\text{Na}_4\text{oddm}$ -doped sol-gel sorbents offer reasonable  $\text{Sr}^{2+}$  kinetics. Experiments show that up to 65% of the  $\text{Sr}^{2+}$  in solution was absorbed into the sorbent in the first hour of the extraction (Figure 3).

In a test of sorbent recyclability, the sol-gel was used to extract  $\text{Sr}^{2+}$  through four extraction/stripping cycles. The stripping agent used in this experiment was  $\text{HCl}$  (6.0 M, 5.0 mL). No physical degradation of the crown ether-doped gels was observed after the four cycles of  $\text{Sr}^{2+}$  extraction/stripping. The results of the recyclability studies are shown in Table 2. Through four extraction cycles, the same sample of sol-gel was found to remove  $92 \pm 7\%$  of the  $\text{Sr}^{2+}$  from solution. The capacity of the gels in these four cycles is similar to  $90 \pm 6\%$  observed for 12 freshly conditioned gels (Table 1). The sol-gel sorbents are thus

Figure 3.  $\text{Sr}^{2+}$  uptake kinetics.Table 2. Extraction Recyclability through Four Extraction/Stripping Cycles with 33 mg of Sol-Gel in 5.0 mL of  $\text{SrCl}_2$  Solutions<sup>a</sup>

extractn cycle	$[\text{Sr}^{2+}]$ (ppm)		capacity	$K_d$	% $\text{Sr}^{2+}$ removed
	initial	final			
1	25.0	$2.50 \pm 0.18$	$3.9 \times 10^{-2}$	$1.4 \times 10^3$	$90.0 \pm 0.2$
2	32.25	$5.2 \pm 0.4$	$4.7 \times 10^{-2}$	$7.8 \times 10^2$	$83.8 \pm 0.4$
3	24.7	$0.29 \pm 0.02$	$2.8 \times 10^{-2}$	$1.3 \times 10^4$	$98.8 \pm 0.2$
4	27.6	$1.44 \pm 0.11$	$4.2 \times 10^{-2}$	$2.8 \times 10^3$	$94.8 \pm 0.1$

<sup>a</sup> The solutions were prepared with  $\text{SrCl}_2$ . Extraction was conducted at 23 °C.

regenerable without degradation of their capacity.

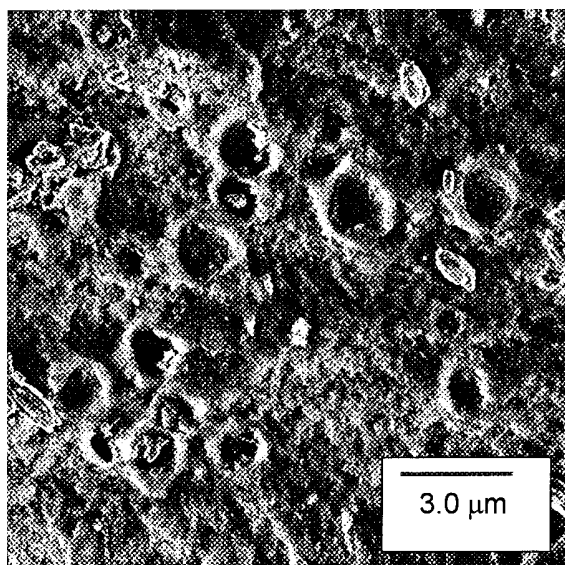
The capacity of the sol-gel sorbents (Tables 1 and 2) is defined as millimoles of  $\text{Sr}^{2+}$  absorbed per gram of sol-gel. The value of the capacity was found to depend to a large degree on the initial concentration of metal ions in solution. The  $K_d$  term (Tables 1 and 2) is defined as

$$K_d (\text{mL/g}) = \frac{\mu\text{g of Sr}^{2+} \text{ absorbed/g of gel}}{\mu\text{g/mL of Sr}^{2+} \text{ remaining}}$$

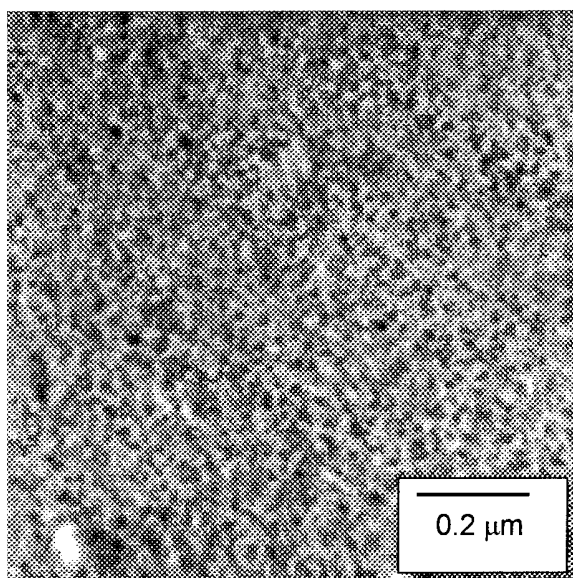
and is often used to describe the efficiency of an extraction system.<sup>7</sup> The value of  $K_d$  was found to depend on the final concentration of the target metal ions in solution and may vary extensively with only small differences in the final metal ion concentrations.

The ligand  $\text{Na}_4\text{oddm}$  was chosen for its ability to bind  $\text{Sr}^{2+}$  ions selectively over  $\text{Ca}^{2+}$  ions.<sup>13</sup> In addition, the lariat arms





(a)



(b)

Figure 4. SEM image (5.0 kV) of  $\text{Na}_4\text{oddm}$ -doped sol-gel materials: (a) 4000 $\times$ ; (b) 60000 $\times$  magnification.

containing charged functional groups on  $\text{Na}_4\text{oddm}$  (Figure 1) may help prevent excessive leaching of the doped ligand through increased size and hydrogen-bonding interactions with the sol-gel framework. Leaching studies show that only  $13 \pm 3\%$  of the doped ligand leached from within the sol-gel after the newly formed gel was placed in water for 72 h as monitored by  $^1\text{H}$  NMR. After this initial conditioning period, no additional leaching of the doped ligand was detected.

BET gas adsorption experiments showed that the  $\text{Na}_4\text{oddm}$ -doped sol-gel materials had a narrow pore size distribution and an average pore diameter of 8.5 nm. This is in agreement with

Table 3. Effects of Stripping Agents on  $\text{Sr}^{2+}$  Recovery<sup>a</sup>

stripping agent	% $\text{Sr}^{2+}$ recovery
6.0 M HCl	$100 \pm 3$
1.0 M HCl	$80.7 \pm 1.4$
0.1 M EDTA	$90.6 \pm 1.1$
0.01 M EDTA	$72.3 \pm 1.5$

<sup>a</sup> 5.0 mL of the stripping agent; 30 mg of the sol-gels; 24 h.

the pore size determinations calculated from images generated by SEM (Figure 4). SEM reveals large craters (up to 1.5  $\mu\text{m}$  in diameter) on the surface of the sol-gel (Figure 4a) as well as cavities throughout the surface (Figure 4b). The surface cavities with diameters of 8–10 nm are perhaps from pores in the sol-gel material.

Several stripping agents other than 6.0 M HCl were evaluated, and the results are summarized in Table 3. It was found that 1.0 M HCl was fairly effective at removing metal ions from the sol-gel matrix. With a single wash of 1.0 M HCl (5.0 mL),  $80.7 \pm 1.4\%$  of the  $\text{Sr}^{2+}$  ions were recovered. Even more effective was 0.1 M EDTA in removing  $\text{Sr}^{2+}$  ions from the gels. It was found that  $90.6 \pm 1.1\%$  of the metal ions were recovered by a single wash with the chelating agent EDTA. Sol-gels are amorphous materials and do not have uniform pore size. We assume the remaining 10% of  $\text{Sr}^{2+}$  ions are complexed strongly to ligands that are in smaller pores. The remaining  $\text{Sr}^{2+}$  ions, other than reducing the  $\text{Sr}^{2+}$  uptake capacity by  $\sim 10\%$ , were not found to affect the gel performance in the subsequent cycles. After washing with  $\text{H}_2\text{O}$  to remove EDTA, the gels were ready for subsequent  $\text{Sr}^{2+}$  extraction cycles. By using EDTA as the stripping agent, the amount of hazardous waste produced in the extraction process is minimal. In addition, no acid neutralization was required when EDTA was used as stripping agent.

$\text{Na}_4\text{oddm}$ -doped sol-gel sorbents offer several advantages to traditional metal ion extraction techniques. Once the sorbents have been prepared, the extraction with the sol-gel sorbents does not require organic solvents. In addition, this process does not require chemical modification of the crown ether ligands. This significantly simplifies the process, and a variety of macrocyclic ligands may be encapsulated in sol-gels to potentially give a new class of sorbents as an alternative to the other better developed metal ion extraction techniques such as solvent extraction and ligand-grafted sorbents.

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