Eurasian ChemTech Journal 11 (2009) 13-23

Performance Improvements Through Structural Design and Comparisons with Polystyrene Resins of Silica Polyamine Composites

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Abstract

Over the past ten years research at the University of Montana in collaboration with Purity Systems Inc, both located in Missoula, Montana, has resulted in a novel class of chelator materials composed of amorphous, nanoporous silica gels and modified polyamines. These materials offer some distinct advantages over conventional polystyrene based resins especially for applications in the mining industry. This paper will report on some recent advances in the technology, some direct comparisons with polystyrene resins and proof of concept studies on the development of anion capturing materials made by immobilizing highly charged metal ions on various silica-polyamine supports.

Introduction

A research collaboration between the Department of Chemistry at the University of Montana and Purity Systems Inc both located in Missoula, Montana has resulted in a novel class of chelator materials composed of nanoporous amorphous silica gels and hydrophilic polymers [1-6].

These composite materials utilize silica gels with average pore diameters of 25 nanometers, surface areas of ~300-400 m^2/g and pore volumes >1.0 mL/g. It has been found that the distribution of pore sizes is critical to obtaining composite materials with the desired characteristics. Silica gels with a relatively small number of pores that are less than 10 nm in diameter are optimal. We have found that the best trade off between back pressure and good mass transfer kinetics is obtained with silica gels having particle sizes in the 150-250 micron range for use in fixed bed or rotating column reactors. The hydrophilic polymers employed are either branched or linear polyamines with molecular weights ranging from 1200-25,000. The techniques used for silanizing the silica gel, grafting the polyamine to the silanized surface and covalently binding ligands which make the composite selective for a given metal or group of metals have been previously reported [5-8]. In our IWC 2 presentation in 2005 we reported cation and anion separations on real mining leaches and waste streams [7]. In this paper we report some recent advances in the technology, sample comparisons with conventional polystyrene resins and proof of concept studies on the use of immobilized metals to extend the technology to the capture of environmentally important anions using mock solutions to demonstrate these performance improvements.

Results and Discussion

Recent Advances in the Technology

The use of mixed silanes in the synthesis of the composites. In our previous studies the silica polyamine composites were prepared by silanizing the silica gel using chloropropyl trichlorosilane (CPTCS) [5,6]. The chloropropyl group subsequently reacts with the polyamine and the carbon nitrogen bond that forms by displacement of chloride grafts the polymer to the surface. Analysis of the composites resulting from using only CPTCS revealed that only about 45-55% of the surface of the silica was covered with silane propyl groups and that about 40% of the polymer amine groups are bound to the propyl silane in the case of the linear polymer poly(allylamine) (PAA, MW = 15,000) [5].

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Printed in Kazakhstan

Recently we discovered that by mixing the smaller and more reactive methyl trichlorosilane (MTCS) with CPTCS we could obtain surface coverage of 85% at MTCS:CPTCS ratios of 7.5:1 for PAA [8]. Diluting the CPTCS with MTCS has the effect of reducing the number of anchor points of the polymer to the silanized surface. This in turn results in increasing the flexibility of the grafted polymer and in increasing the number amines not bound to the surface. Based on the subsequent analysis of the mixed silane composites we found that this resulted in a marked increase in metal ion capacity due to the increased polymer flexibility (which increases the access to amine sites) and the increased number amines not bound to the surface. This effect was even more dramatic for composites that are subsequently modified with metal selective ligands. For the higher molecular weight branched polymer poly(ethyleneimine) (PEI, MW = 23,000) the optimal ratio of MTCS: CPTCS for improving composite performance was found to be 12.5:1. Table 1 shows the impact of using these mixed silane ratios on metal ion capacity.

Table 1.
Comparison of metal ion capacities between propyl silane and mixed silane (MS) composites

L	%, L/N[a] (MS)	Polymer (MW)	Metal cation	MTCS: CPTCS	Metal Cap., g/kg (MS)
Aminoacetate	60 (71)	PEI 23k	Cu^{2+} pH = 2	12.5:1	22 (40)
EDTA	29 (57)	PAA 11k	Ni^{2+} pH = 2	7.5:1	34 (51)
Picolylamine	44 (47)	PAA 11k	Cu^{2+} pH = 1	7.5:1	25 (40)
Oxine	77 (94)	PAA 11k	Fe^{3+} pH = 1.25	7.5:1	29 (35)

[a] L/N is the approximate % of amine sites that are modified by L

The modifying ligand L which is bound to the polyamine by a nitrogen carbon bond lends selectivity to the resulting composite for a particular metal. The amino acetate ligand allows capture of divalent transition metal ions at lower pH than the unmodified amine polymer. The EDTA ligand allows the clean separation of nickel from cobalt at low pH (<2), the picolyl amine allows the separation of copper from all other divalent metals and ferric at pH = 1 and the oxine ligand allows the extraction of ferric ion from divalent transition metals at low pH. It can be seen from Table 1 that using the mixed silane at the ratios specified results in a significant increase in the number of amine sites modified by L and in the capacity of the composite for the target metal. Most interestingly, the % increase in metal capacity is consistently larger than the percent increase in ligand loading. This implies that the decrease in the number of anchor points results in an increase in the kinetic accessibility of the active sites on the composite, probably as a result of a less crowded polymer environment and increased flexibility in the polymer chain. it should be noted that repeated use of the composite (250 load-strip-regenerate cycles; previous tests with the original composites showed no loss of capacity for up to 7000 cycles) resulted in no loss of capacity and the selectivity of the composite remains unchanged on going to the mixed silane platform. At the MTCS/CPTCS ratios specified in Table 1 our analysis of the composite composition reveals that for the PAA there are 122 anchor points per molecule on average instead of 488 for composites prepared with only CPTCS. Thus it is not surprising that polymer stability is unaffected. More extensive longevity studies are currently underway in our laboratories.

Comperisons with Polystrene Chelator Resins

In general, the silica polyamines shown in Table 1 have lower batch capacities than conventional polystyrene resins with similar functionality. However, the silica polyamine chelator materials have better mass transfer kinetics. This means that that there are fewer bed volumes between the initial breakthrough of an ion and the point where the flow through reaches the feed concentration. This will result in sharper separations for multi-component solutions and overall better system economics under fast flow conditions. This is in part due to the smaller particle sizes available for the polyamine composites (150-250 micron) compared with most commercially available polystyrene resins (300-500 microns) and to the requirement for leaving a void volume in the bed to allow for the shrink-swell associated with polystyrene resins. We have previously measured capture kinetics on silica polyamine composites with particle sizes of 500 microns and found that capture kinetics, as defined above, were still superior to related polystyrene resins [5,9].

The comparisons made herein are not intended to discredit the polystyrene resins studied but rather to better define where the polyamine composites might be a better choice, *i.e.* in metal separations encountered in the mining and metal processing industries. Finally, it should be noted that silane functionalized silica gels represent another technology that has been in development in recent years. These materials usually use trimethoxy aminopropyl silane to silanize amorphous silica gel and then react the amino group with a modifying ligand. These materials have much lower capacities than the silica polyamine composites discussed here and suffer from unwanted interactions of the functional group with the silica surface [10]. In addition, the longevity demonstrated for the silica polyamine composites has not been demonstrated for the these materials [10].

Comparison of CuWRAM with Dowex M-4195

The silica polyamine composite CuWRAM is based on a mixed silane-PAA platform modified by reaction with 2-picolyl chloride. It has been shown to be effective for the separation of copper from ferric ion at low pH [3,4,11]. Dowex M-4195 is obtained from chloromethylated polystyrene by reaction with bis-picolylamine. This resin has been shown to be effective for the separation of nickel from cobalt (*vide infra*) [12]. It also has a high affinity for the copper over ferric ion but the copper has proven difficult to strip. More recently, Dow has developed a polystyrene resin Dowex 43084, containing a 2-hydroxypropyl picolyl 4 ligand more similar to CuWRAM which has better stripping characteristics than Dowex M-4195.13. We were unable to obtain a sample of the Dowex 43084 resin as it is currently not available. However, we previously reported a preliminary comparison of CuWRAM with this resin [11].

We report here a comparison between Dowex M-4195 and CuWRAM for copper-ferric separation and for nickelcobalt separation. The tests were performed under identical conditions and following the recommended procedures for the polystyrene resin including leaving an appropriate void space in the column (20%) for both resins but only required for M-4195.

Equilibrium batch studies revealed that the Dowex M-4195 had a pH independent capacity of 0.85 mmol/g while the CuWRAM had an equilibrium batch capacity which varied from 0.35 to 0.55 mmol/g between pH values of 0.0 to 2.0 The densities of the two materials are 0.67 and 0.57 g/mL respectively. Breakthrough curves for the separation of copper from ferric with CuWRAM and Dowex M-4195 using feed solutions containing 1.0 g/L copper and 4 g/L ferric as sulfate salts are shown in Fig. 1.

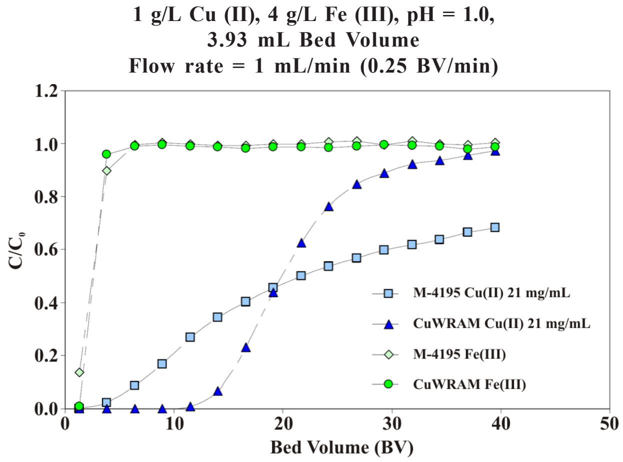


Fig. 1. Break through curves for copperferric separations using Dowex M-4195 and CuWRAM.

It can be seen from Figure 1 that both materials show very good iron rejection. However, CuWRAM begins to break at 12 bed volumes while Dowex M-4195 begins to break after only 4 bed volumes. The copper absorbed over the 40 bed volumes of the experiment is 21 mg/mL for both materials but the CuWRAM breaks to full feed concentration more quickly and the steeper slope of the graph testifies to a cleaner separation. Strip profiles for both materials using 4.5M sulfuric acid are shown in Figures 2 and 3. It can be seen that Dowex M-4195 did not strip cleanly with this strip reagent and required a second strip with 4M ammonia to recover all the copper. The CuWRAM on the other hand stripped cleanly and efficiently with the 4.5M acid.

The purity of the strip for CuWRAM was 99.3% while for the acid stripped fraction for M-4195 was 90.1%. The copper capacities for the two materials up to the 40 bed volumes run were the same at 21

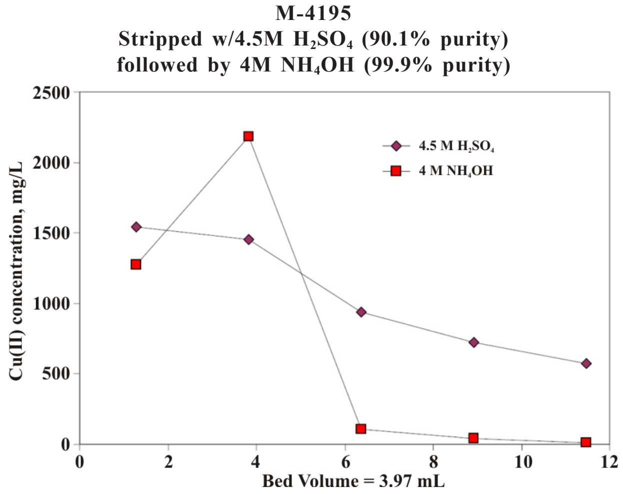


Fig. 2. Strip profile for Dowex M-4195 with 4.5M sulfuric acid and 4M ammonia.

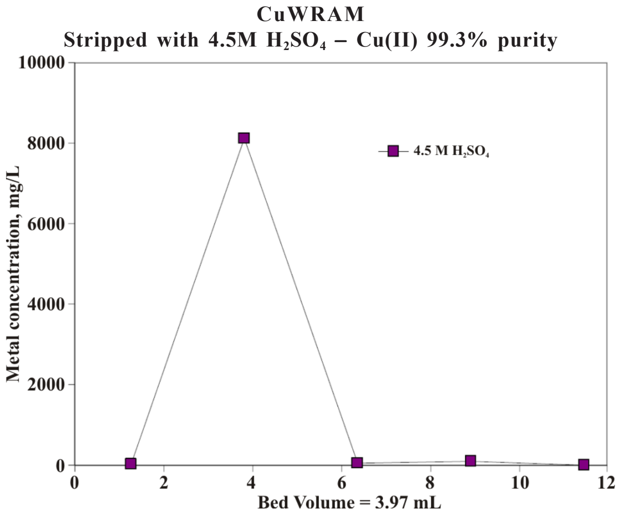


Fig. 3. Strip profile for CuWRAM with 4.5M sulfuric acid.

mg/mL. Dowex M-4195 has been shown tobe an effective resin for separating nickel from cobalt and it is therefore worthwhile to examine the performance of CuWRAM for this purpose. The break through curves for both materials using a solution containing 1.5 g/L nickel and 1.5g/L cobalt at pH = 2 are shown in Figure 4. Strip profiles are shown in Figs. 5 and 6.

It can be seen from the Figure 4 that at these relatively high metal ion concentration both materials breakthrough fairly soon, M- 4195 almost immediately and CuWRAM at about 4 bed volumes. Figures 5 and 6 show the consequences of this small difference as the strip from the M-4195 is only 92.3% pure nickel while the strip from CuWRAM is 99.9% pure nickel. On the other hand, the M-4195 absorbed 2.5 times as much nickel over the course of the 40 bed volume run. This is due, in part, to the intrinsically higher number of active sites present in M-4195 (*vide supra*). Note that this difference was not seen in the case of copper absorption. This is because copper requires a coordination number of 4 (square planar) whereas nickel usually requires a coordination number of 6 (octahedral) with amine ligands. M-4195 is a tridentate ligand while CuWRAM is a bidentate ligand and therefore it makes sense that the metal requiring higher coordination number is more favored with M-4195. It is also important to note the high concentration of cobalt in the early flow through for CuWRAM (Figure 4). This means that cobalt binds initially and is then pushed off by nickel. This bodes well for separations with high cobalt and low nickel but not the other way around. The same effect is seen with M-4195 later in the run but is less pronounced owing to the overall poorer kinetics. If the M-4195 were run to full break through nickel purity would be better.

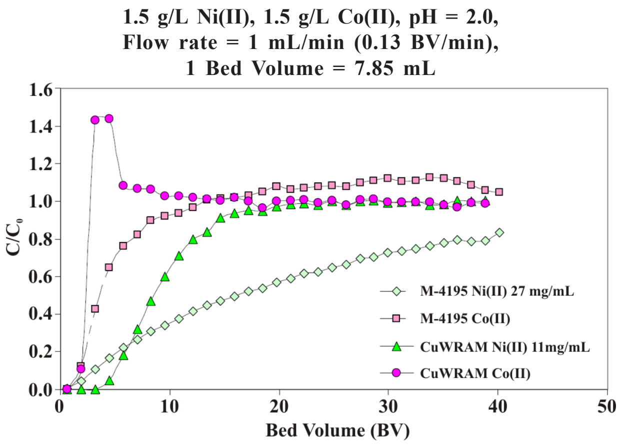


Fig. 4. Breakthrough data for nickelcobalt separation with Dowex M-4195 and CuWRAM.

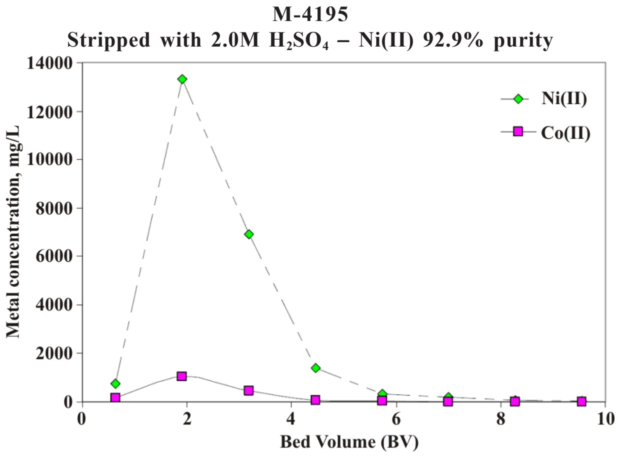


Fig. 5. Strip profile for nickel cobalt separation with Dowex M-4195.

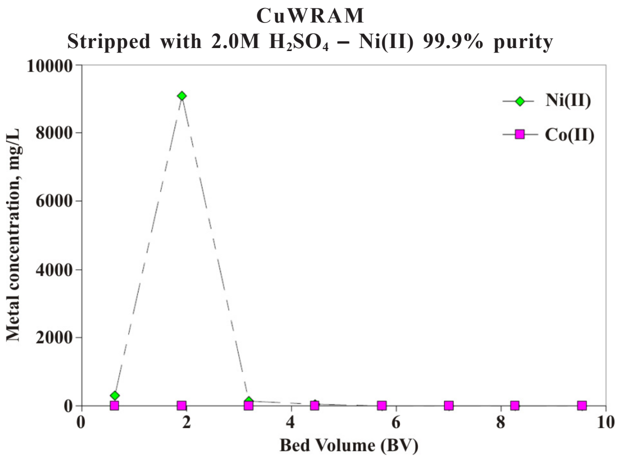


Fig. 6. Strip profile for nickel cobalt separation with CuWRAM.

Comparison between WP-2 and IRC-748

The separation of copper from nickel at low pH is of interest to the mining and metal processing industries and represents an ideal application for ion exchange. We have conducted a series of experiments with solutions containing high concentrations of both of these metals using the polystyrene based resin IRC-748 which has an amino diacetic acid functional group and compared its performance with a related silica polyamine composite that has an amino acetic acid functional group. The results of these tests are illustrated in Figures 7-10. It can be seen that both materials are effective for this separation at pH =1.

Unlike the previous tests with M-4195 the IRC-748 shows a reasonably sharp break through but the WP-2 is even sharper. The copper purity is slightly better for the IRC 748 at 99.9% compared with 98.4% for WP-2. However the loading of copper is somewhat higher for WP-2 at 10 mg/mL compared with 6.5 mg/mL for IRC-748. This difference is somewhat reflected in their equilibrium batch capacities which are 0.55 and 0.48 mmol/g for WP-2 and IRC 748 respectively. The higher copper loading results in a more concentrated strip for WP-2, the reverse of the situation for CuWRAM versus M-4195 in the cobalt – nickel separation. It should be noted that the WP-2 break through shows nickel coming out at higher than the feed concentration indicating that nickel co-loads and is then pushed off by copper. This is not the case for IRC 748 where nickel breaks through immediately. This difference is also reflected in their equilibrium batch capacities for nickel which are 0.20 and 0.05 mmol/g for WP-2 and IRC-748 respectively. Indeed WP-2 has been used to capture

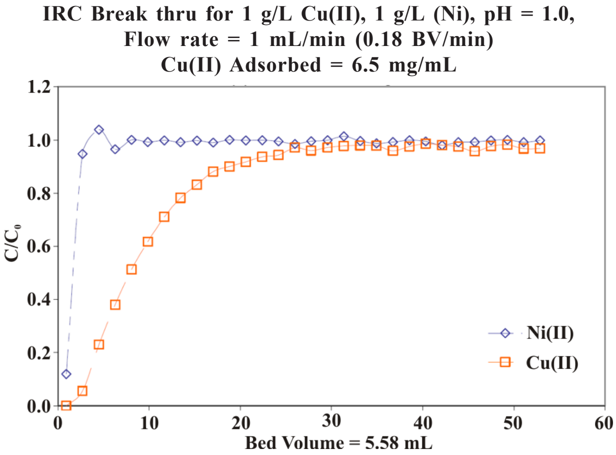


Fig. 7. Break through curve for coppernickel separation at pH = 1 for IRC 748.

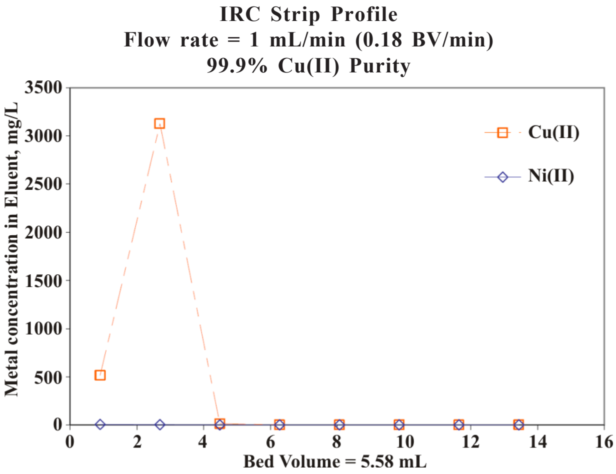


Fig. 8. Strip profile for copper-nickel separation for IRC 748 using 2M sulfuric acid.

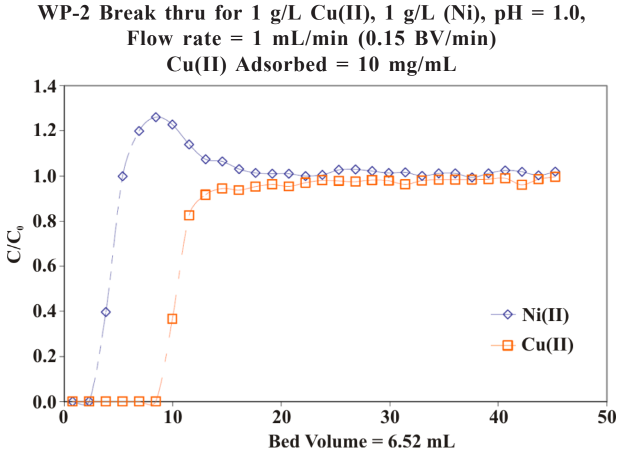


Fig. 9. Break through curve for coppernickel separation at pH = 1 using WP-2.

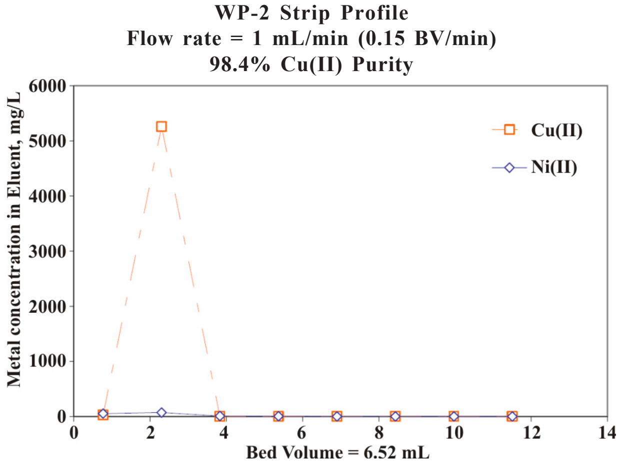


Fig. 10. Strip profile for copper nickel separation with WP-2 using 2M sulfuric acid.

nickel in the absence of copper in previous applications of this composite. The comparisons presented here for the separation of first row transition metals would be relevant to processing laterite ore leaches, raffinates from solvent extractions and other metal processing streams. The concentrations chosen for these tests were chosen to demonstrate statistically significant breakthrough profiles using the column volumes convenient for laboratory testing. Previous reports have shown that these results can be carried over to actual mine leaches [1-7].

Immobilized metal polyamine composites (IMPACS)

The Concept

Anion capture with conventional ion exchange resins generally relies on the use of quartenized ammonium functionality, so-called strong base resins. This approach is also accessible using the silica polyamine platform and we have employed this approach as well (*vide infra*). However, based on our prior work we decided to take a different approach to anion capture which relies on the fact that highly charged metals (+3 or +4) can be immobilized on a variety of these composites and will have a net positive charge. The idea is that by varying the metal and the functional group that binds it to the composite one could tune the anion selectivity and the operational pH range based on the factors governing the anionimmobilized metal interaction (Equation 1):

$$L_nM^{m+} + E(O)_x{}^{y-}{}_{(aq)} \rightleftharpoons L_nM[E(O)_x]^{(m-y)} \quad (1)$$

L = ligand bound to polymer composite.

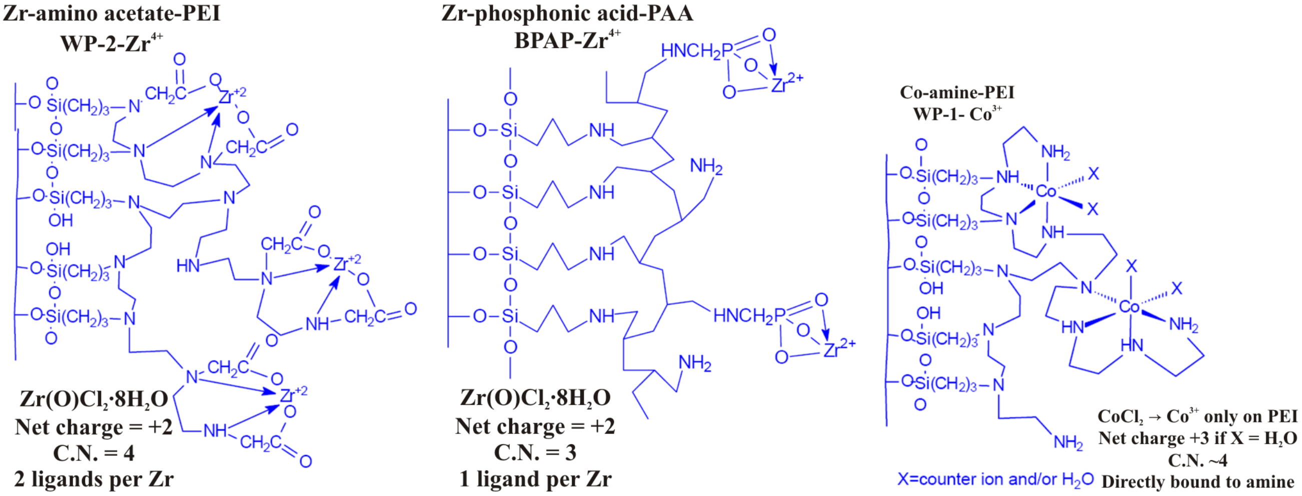
The stability of the complex will depend on:

1. Effective charge on L_nM^{m+}
2. Polarizability of the anion andits charge.
3. The hydration energy of the anion.
4. The net charge on the complex (0, +1).

In our initial investigations we focused on a system that immobilized Zr^{4+} on the polyamine composite having an amino acetate functionality on PEI (WP-2-Zr^{4+}, Fig. 11). We found that this combination was very effective for the capture of arsenate, selenate and selenite from actual mining waste streams, but only at pH = 4 [6,7]. This system compared quite favorably with a previously reported system using Zr^{4+} immobilized on polystyrene. This work was reported in last year's contribution to the IWC conference [7].

In the past year we have extended these studies to two additional systems, one using Zr^{4+} immobilized on a phosphonic acid modified PAA composite (BPAP-Zr^{4+}, Figure 11) and another using Co^{3+} immobilized on PEI (WP-1-Co^{3+}, Figure 11). We report here our initial studies on these two new IMPAC systems along with a system, BP-QA containing quartenized nitrogen (made by reacting the PAA composite with methyl iodide) and a commercially available strong base polystyrene resin. These initial studies have focused on arsenate and we are currently investigating arsenite and other anions.

The WP-1-Co^{3+} system is made by simply mixing a solution of a Co^{2+} with a suspension of WP-1 in water. The Co^{2+} is rapidly adsorbed by the WP-1 and then is slowly oxidized by oxygen dissolved in the water. The resulting composite is diamagnetic and



Zr-amino acetate-PEI
WP-2-Zr^{4+}
$Zr(O)Cl_2{\cdot}8H_2O$
Net charge = +2
C.N. = 4
2 ligands per Zr

Zr-phosphonic acid-PAA
BPAP-Zr^{4+}
$Zr(O)Cl_2{\cdot}8H_2O$
Net charge = +2
C.N. = 3
1 ligand per Zr

Co-amine-PEI
WP-1- Co^{3+}
$CoCl_2 \rightarrow Co^{3+}$ only on PEI
Net charge +3 if X = H_2O
C.N. ~4
X=counter ion and/or H_2O **Directly bound to amine**

Fig. 11. Schematic structures of trial immobilized metal polyamine composites (IMPACS) indicating the proposed structural properties of each system.

resists leaching of cobalt even with concentrated hydrochloric acid indicating there is no residual Co^{2+} on the composite. This type of chelation driven oxidation in water has considerable precedent in the solution chemistry of Co^{2+} with polydentate amine ligands [14]. In the absence of dissolved oxygen the process, which is driven by the stabilization energy associated with the Co^{2+} to Co^{3+} conversion in the presence of strongly binding chelator ligands, is quenched. The same conversion occurs in solution with dissolved PEI. Interestingly, this conversion does not take place with the PAA polyamine composite BP-1. This is because the branched polymer PEI provides more than two proximal amine groups for one metal ion while the linear PAA provides only two without involving a second polymer chain or significant chain bending (the latter is not accessible for the surface grafted polymer). Studies are underway in our laboratories to define the exact coordination modes of cobalt in these systems.

Equilibrium batch capacities for arsenate

Table 2 shows the equilibrium batch capacities for two of the three IMPAC systems synthesized so far. In order to understand the impact of metal charge on the BPAP systems we also include measurements of a ferric loaded BPAP. However, the BPAP-Fe system is not suitable for further development since under flow conditions the ferric leaches considerably when arsenate is eluted from the column. The commercially quartenized amine (strong base) polystyrene resin, ASM-10HP and the quartenized amine polyamine composite BP-QA are also included for comparison. The batch tests were performed on 200 mg samples of the material shaken for 24 h with 3 g/L sodium arsenate pH adjusted with sulfuric acid. All the materials have reasonably good batch capacities for arsenate except WP-2-Zr^{4+} composites are due to the large difference in densities between these materials (0.6 g/mL) and the polystyrene material (1.2 g/mL) The major species in solution at pH =4 is $H_2AsO_4^-$ and this species is sufficiently attracted to the net charge on WP-2-Zr^{4+} to bind to the immobilized metal. At higher pH $HAsO_4^{2-}$ becomes the major species and apparently the charge and covalent binding forces with zirconium are not sufficient to out weigh the energy of hydration of this larger and more highly charged anion for the WP-2-Zr^{4+} system. At lower pH the neutral H_3AsO_4 begins to appear. On going to the BPAP systems with iron or zirconium we observe good arsenic adsorption over the entire pH = 2-8 range. This is because the lower coordination number and more ionic bonding associated with the phosphonate ligand create a more open and more positively charged zirconium or ferric site that is able to bind all the arsenate species in solution. Energy dispersive X-ray measurements on the arsenate loaded BPAP-Zr^{4+} show that at pH = 4 the ratio of arsenate: Zr: phosphorous is approximately 1:1:1. At pH = 8 this ratio approaches 1:2:2. We interpret this to mean that at higher pH two zirconium sites are required to bind one $HAsO_4^{2-}$ ions (Fig. 12). This explains the significant decrease in arsenate capacity on going from pH = 6 to 8.

Significantly, the batch capacity of the polystyrene quartenized amine resin is fairly pH independent indicating that the nature of the interaction with the anion is strictly electrostatic and strong enough to overcome competing factors of hydration energy and charge on the anion. This is a distinct advantage for arsenate capture. Curiously, the BP-QA does show a decrease in arsenate capacity on going from pH 6 to 8 and this could be due to the presence of unquartenized amine sites which would create a repulsive interaction with the more highly charged arsenate species present at higher pH.

Break Through Testing of the IMPACS with Arsenate

Break through tests were conducted at pH = 6 for arsenate on solutions containing 3 g/mL sodium arsenate pH adjusted with sulfuric acid.

The break through and strip profile data for arsenate using BPAP-Zr^{4+} is illustrated in Figures 13 and 14. It is noteworthy that the flow capacity to

Table 2
Equilibrium batch capacities for IMPACS and quartenized amine materials

PH	2	4	6	8
	As(V), mg/mL	As(V), mg/mL	As(V), mg/mL	As(V), mg/mL
WP-2-Zr	C	46	--	--
BPAP-Zr	85	103	93	66
BPAP-Fe	81	61	76	55
ASM10HP	48	43	50	49
BP-QA	--	--	100	81

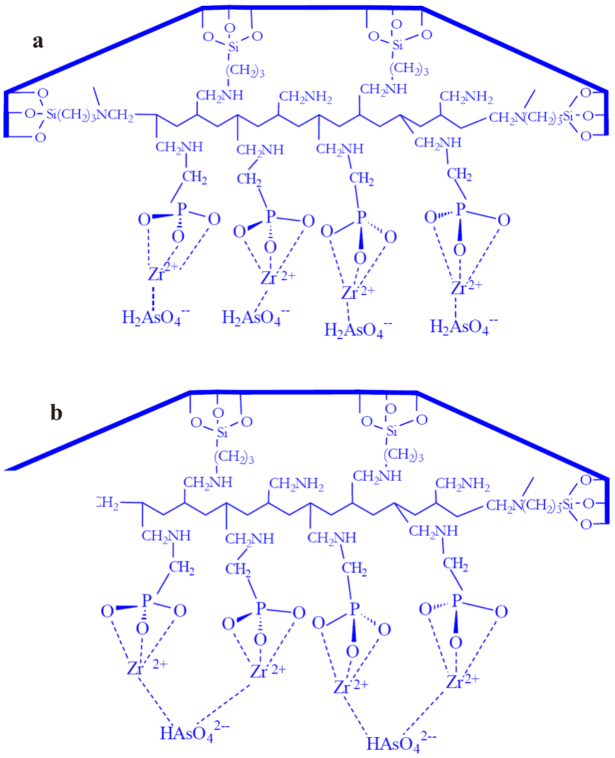


Fig. 12. a – proposed interaction of BPAPZr^{4+} with arsenate at pH = 4. b – at pH = 8.

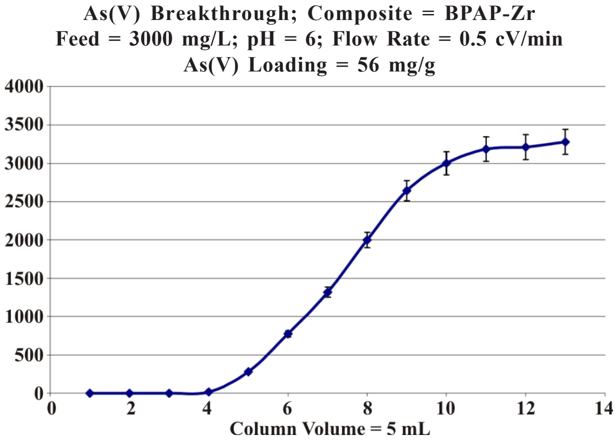


Fig. 13. Break through plot of BPAPZr^{4+} with Arsenate at pH = 6

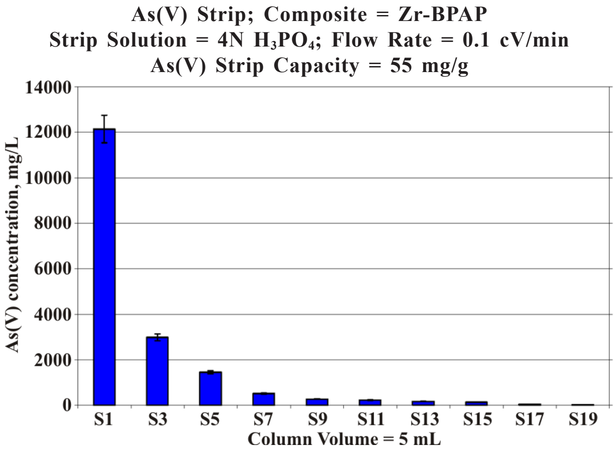


Fig. 14. Strip profile for arsenate on BPAP-Zr^{4+} 1.33M phosphoric acid.

100% break through is the same as the batch capacity at a relatively high flow rate of 0.5 bed volumes per minute (55 mg/g or 91 mg/mL, Table 2) . This is typical for the polyamine composites where mass transfer kinetics are rapid and the break through is relatively sharp. Stripping of arsenate from this IMPAC is however problematic. Even at a relatively slow strip rate of 0.1 bed volumes per minute striping in the first four bed volumes accounts for only 91% of the arsenate adsorbed. In addition sulfuric acid did not strip the arsenate and it was necessary to use phosphoric acid followed by a sulfuric acid regeneration step.

Zirconium leaching was negligible during the load-strip regenerate cycle. The use of the more expensive phosphoric acid does offer the advantage that addition of lime to the strip results in the precipitation of arsenohydroxyapatite which is an immobilized form of arsenic that can taken to a landfill.[7] However, the regeneration of this IMPAC with sulfuric acid is incomplete and the inefficient stripping of arsenate from this IMPAC represents a serious drawback for future arsenate applications.

Although we have not yet completed pH profile batch equilibrium studies on the WP-1-Co^{3+} system we did do a break through study on arsenate using this system at pH = 6 in a 5 mL column at a flow rate of 0.5 bed volumes per minute using a solution of 3 g/L sodium arsenate pH adjusted with sulfuric acid . The results of the break through and the strip profile are in Figs. 15 and 16.

Based on the break through curve the capture kinetics are similar to the BPAPZr^{4+} but the loading was significantly lower at 43 mg/g (or 71 mg/mL). Cobalt loading on this sample was 45 mg/g of composite. The strip profile however, is much better (98%) than BPAP-Zr^{4+} and the strip could done with the usual 2M sulfuric acid (Fig. 16).

Although this data is only preliminary the cobalt system shows promise for further development based on the cheaper price of cobalt relative to zirconium and the better stripping characteristics of this system relative to the other two zirconium based systems.

The break through curve and strip profile for the ASM-HP10 are shown in Figs. 17 and 18.

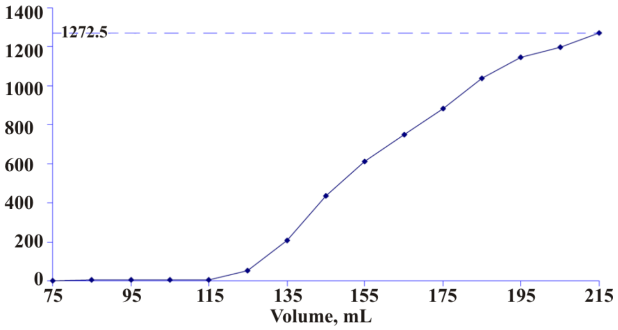


Fig. 15. Arsenate loading break through with WP-1-Co^{3+} at pH = 6 and 0.5 bed volumes per minute.

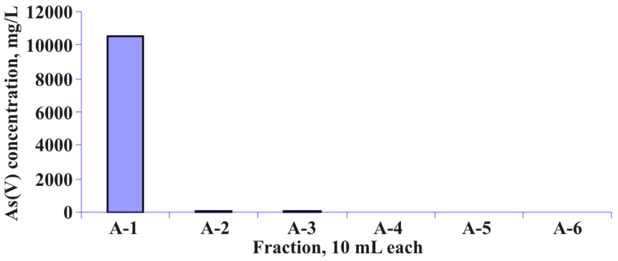


Fig. 16. Strip profile for arsenate on WP-1-Co^{3+} using 2M sulfuric acid at 0.5 bed volumes per minute.

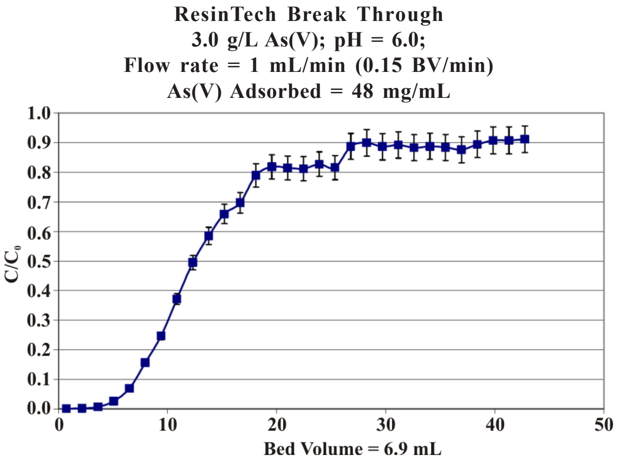


Fig. 17. Break through curve for arsenate loading on ASM-HP10 with 3 g/mL sodium arsenate at pH=6, 0.15 BV/min.

It can be seen from Figure 17 that the polystyrene resin ASM-HP10 loads arsenate with reasonably good capacity and kinetics. The flow through capacity is however, much lower than for the $BPAPZr^{+4}$ and WP-1-Co^{3+} IMPACS. In addition, using the manufacturer's recommended stripping agent, alkaline brine we observe only 56% recovery of the arsenic, thus making this material only partially regenerable.

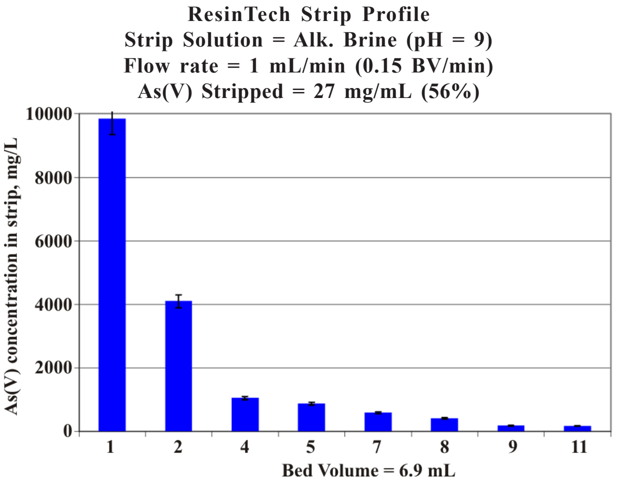


Fig. 18. Strip profile for ASM-HP10 with alkaline brine (pH = 9) at 0.15 BV/min.

The polyamine composite analog of ASM-HP10 is BP-QA where the poly(allylamine) composite has been reacted with methyl iodide. The break through curve and strip profile for this system are shown in Figs. 19 and 20.

The flow capacity for BP-QA is considerably higher than for ASM-HP10 at 56 mg/g (or 93 mg/mL) even though this test was done at a faster flow rate (0.5 BV/min). More importantly, the strip profile again done at a faster flow rate (0.5 BV/min) shown in Figure 20 reveals that 91% of the arsenate can be recovered with just 2 bed volumes of 2M sulfuric acid. Based on these initial results the best candidates for arsenate removal and recovery are the BP-QA and the WP-1 Co^{3+} sytems. Further studies using these materials for removal and recovery of other anions and more detailed comparisons of the systems shown in Table 2 for low-level arsenate removal are currently underway in our laboratories.

We are also currently investigating the capacities of these materials for arsenite under both flow and

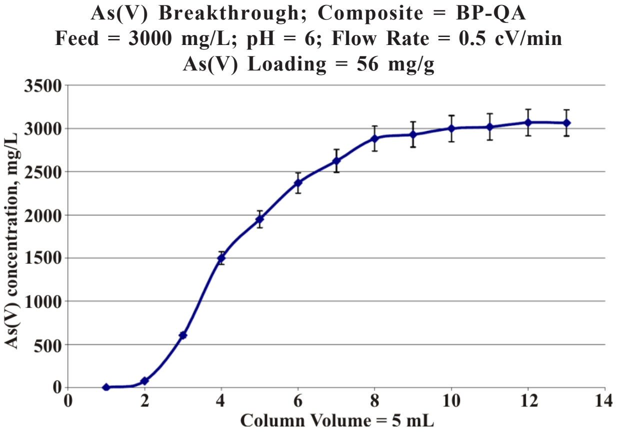


Fig 19. Break through curve for arsenate loading on BP-QA at pH = 6 at 0.5 BV/min.

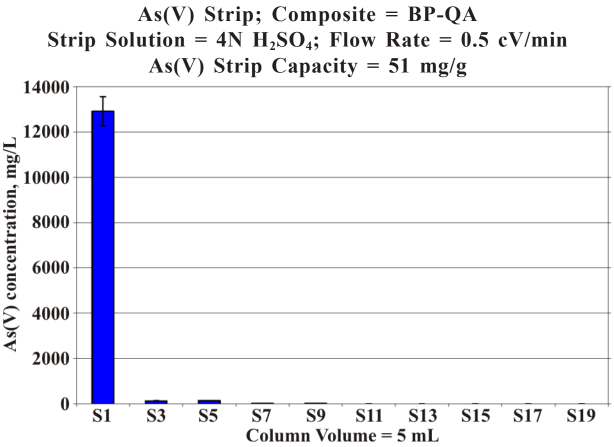


Fig. 20. Strip profile for arsenate on BPQA using 2M sulfuric acid at 0.5 BV/min.

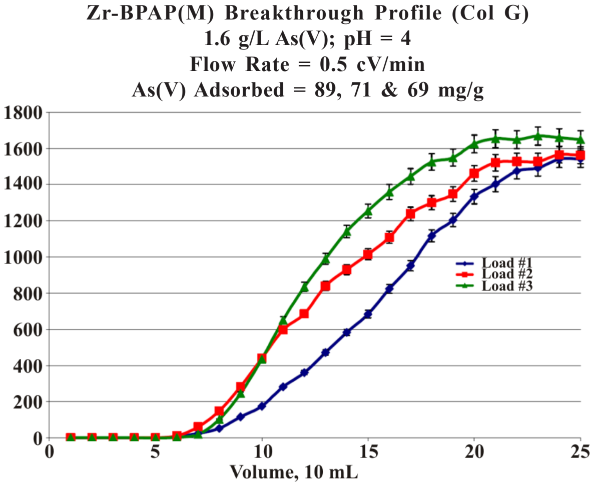


Fig. 21. Arsenate capture with mixed silane Zr^{4+}-BPAP.

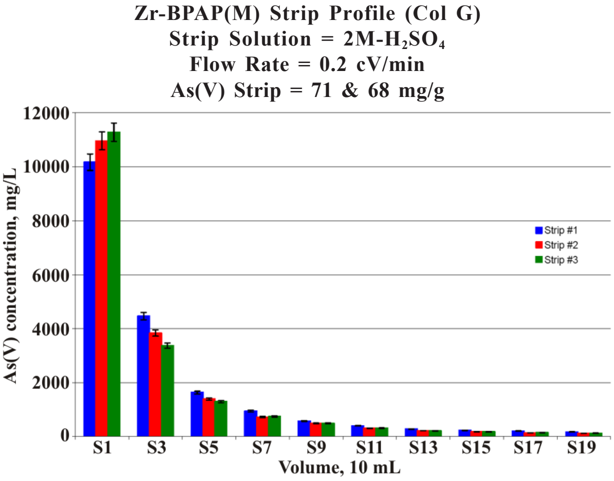


Fig. 22. Strip profile fro three successive strips with 2M sulfuric acid with the mixed silane Zr^{4+}-BPAP.

batch conditions at pH = 10. Below this pH arsenite exits as a neutral species, $As(OH)_3$ and would not be expected to bind to cationic sites. All the materials shown in Table 2 show good batch capacities for arsenite at pH = 10 and flow studies comparing them will be the subject of a future report.

The further development of the cobalt and zirconium IMPACS offers significant advantages over conventional techniques such as coagulation. First of all the IMPACS can be regenerated and used over and over again. Our testing so far has shown that cobalt and zirconium do not leach from the composite even with strong acids (20% sulfuric or hydrochloric acid). Furthermore, the concentrations of arsenic that can be achieved with these materials is much greater than those achievable with coagulation methods and the strip solution is uncontaminated with iron and chlorine. Finally, our most recent work using the mixed silane approach for Zr^{4+}-BPAP resulted in a 50% increase in arsenate capacity and the ability to effectively stripusing sulfuric acid instead of phosphoric acid (Figs. 21 and 22).

Conclusions

Based on the work reported here some fairly sound generalizations can be made:

1. Decreasing the number of anchor points by which the polyamine is bound to the silanized silica surface has a significant impact metal ion capacities without compromising selectivity and composite longevity.
2. The trial comparisons between silica polyamine composites and polystyrene chelator resins show that the polyamine composites give sharper separations and cleaner elutions of the target metals. In some cases overall resin loadings of the target metals are lower for the silica composites but metal purity is generally higher.
3. The concept represented by the proposed anion capturing IMPACS has been demonstrated. That is, changing either the nature of the immobilized metal and or the functional group to which it bound has a significant impact on anion selectivity and the operational pH range of the composite.

Future work will focus on further extensions of both the cation and anion sequestering composites by the use different surface bound lixavents and different immobilized metal-ligand combinations as well as the use of multibed separations aimed at efficient separation of multi-component metal streams.

We are also interested in extending the arsenic work to other environmentally and industrially important anions such as selenate(ite), chromate and molybdate, tungstate.

Finally, the development of economically viable amorphous silica gels with a more uniform pore size distribution would be of great value for the manufacture and use of these composite materials. The use of sol-gel chemistry is currently being explored in our laboratories towards this end.

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Received 15 September 2008.