Silica Polyamine Composites: New Supramolecular Materials for Cation and Anion Recovery and Remediation

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Summary: The surface coverage of amorphous silica gels used in the synthesis of silica polyamine composites has been investigated by ^{29}Si NMR. By diluting the polyamine anchor silane, chloropropyl trichlorosilane, with methyl trichlorosilane it was found that surface coverage could be markedly improved for a range of amine polymers after grafting to the silica surface. The commensurate decrease in the number of anchor points and increase in the number of free amines results in an increase in metal capacity and/or an improvement in capture kinetics. Solid state CPMAS-^{13}C NMR has been employed to investigate the structure and metal ion binding of a series of these composite materials. It is reported that the highly branched polymer, poly(ethyleneimine) (PEI) exhibits much broader ^{13}C NMR resonances than the linear polymers poly(allylamine) (PAA) and poly(vinylamine) (PVA). These results are understood in terms of the low energy conformations calculated from molecular modeling studies. Three new applications of the technology are also presented: 1) separation of lanthanides as a group from ferric ion and all other divalent ions; 2) a multi step process for recovering and concentrating the valuable metals in acid mine drainage; 3) a process for removing low level arsenic and selenium in the presence of sulfate using immobilized cations on the composite materials.

Keywords: composites; metal polymer complexes; polyamines; solid state NMR; supramolecular structures

Introduction

The use of solid phase adsorbents for the removal and recovery of metal cations and oxyanions from industrial and mining waste streams has been gaining in popularity due to the greater efficiency and environmental friendliness of this method relative to bulk hydrometallurgy or solvent extraction.[1] In general the solid phases of choice have been lightly cross linked polystyrene or methyl methacrylate polymers.[2] In cases where dilution of a waste stream is not practical, or in the case of waste streams containing valuable metals, ion exchange offers a viable method for offsetting the price of environmental remediation using relatively simple and safe process designs. Moreover, the increased use of oxidative pressure leaching and bioleaching for metal ore extraction of sulfide ores in the mining industry is even more compatible with ion exchange than with solvent extraction because it avoids the use of flammable solvents and takes metal concentrations to lower effluent values.[3,4] The polymer based matrices, however, are not particularly well suited to these large scale applications because they often involve

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the use of hot solutions and wide swings in pH where the shrink-swell properties of the polymers lead to shorter life times or requires the use of dead volumes in plant design. In order to overcome these disadvantages we have turned to amorphous silica gel-polyamine composites. These materials do not shrink or swell, can be used at higher temperatures and have much longer usable lifetimes than their polystyrene counterparts.[5–13] Furthermore, the polar nature of the silica polyamine surface also makes for better mass transfer kinetics in the case of aqueous solutions and the polyamine can be easily modified with metal selective functional groups, without the use of swelling solvents, to form robust carbon-nitrogen single bonds. The platform materials consist of linear or branched water soluble chelating polyamines covalently bound to a silica gel support. For example, the material designated as WP-1 consists of poly(ethyleneimine), (M.W. 1,200) covalently bound to porous silica gel. Poly(ethyleneimine) is a highly branched, water soluble amine polymer containing 1°, 2°, and 3° amino groups in a ratio of 0.35:0.35:0.30, respectively. The synthetic route (Figure 1) yields ~50% coverage of the silica gel surface with an organic coating and uses a polymer where the chelating agent is an integral part of the matrix coating and where the chelator is bound at multiple points to the anchor silane. These are key factors in creating a material that has remarkable durability.[7,9]

These resins have been tested through 7000 cycles with no visible loss of physical stability and less than 10% loss in capacity. The copper capacity of the basic polyamine composites is in the range of 0.7–1.1 mmol/g, and depends on the polymer being used. To date we have tried three polyamines: poly(ethyleneimine) (PEI), poly(vinylamine) (PVA), and poly(allylamine) (PAA) (Figure 2). These polyamine composites can be readily modified to make them selective for a given metal or group of metals over a particular pH range, in similar ways to those used for polystyrene resins.[14] These materials, however, offer distinct advantages over polystyrene resins (Table 1). These advantages have been demonstrated through studies that directly compare the properties of the polyamine

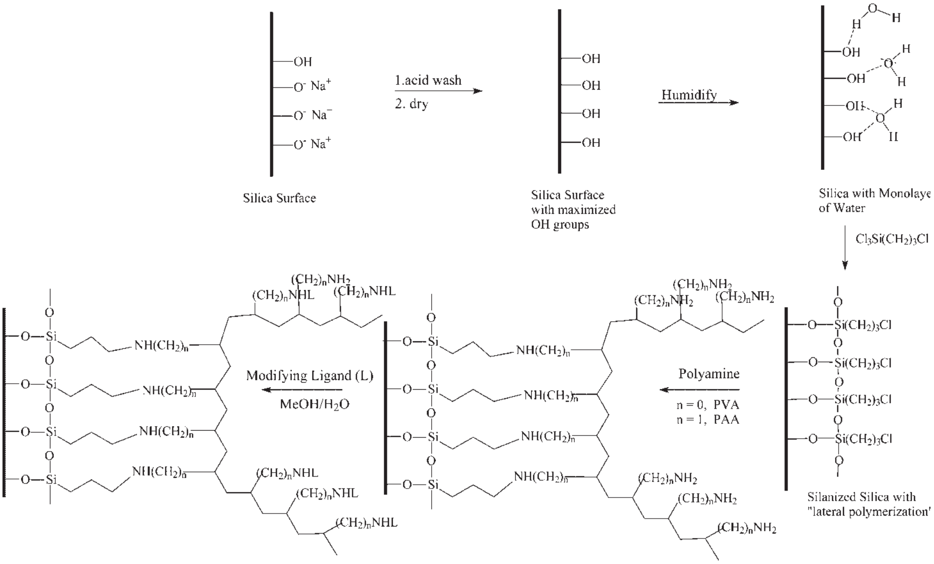

Figure 1.
Synthetic scheme for making silica polyamine composites, illustrating the key features of humidification to promote "lateral polymerization" for maximization of surface coverage and the addition of the modifying ligand.

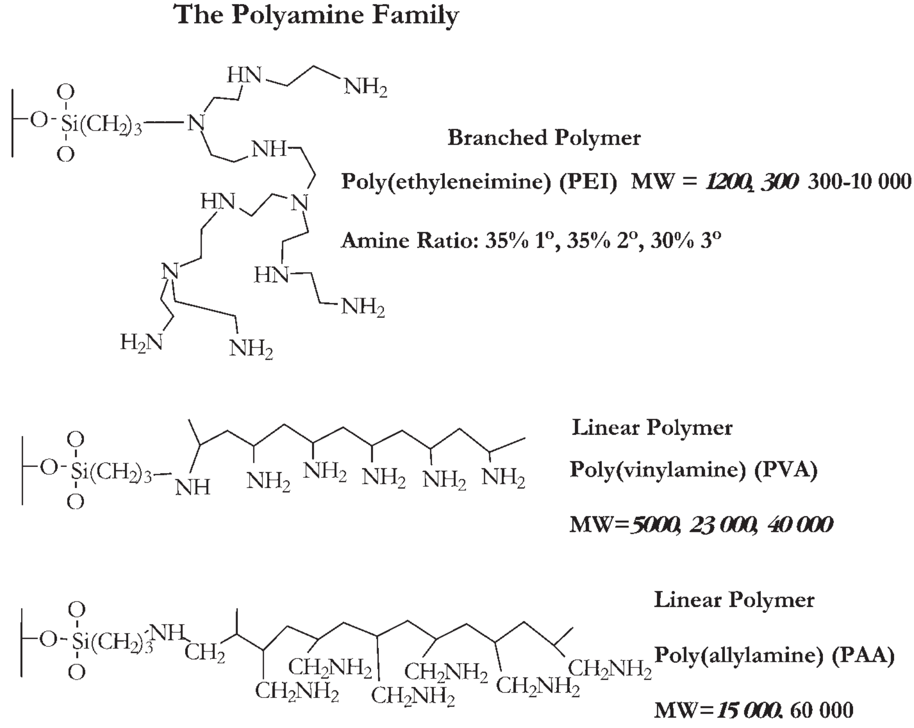

Figure 2.
The polyamines used to synthesize the silica-polyamine composites, showing the schematic structure.

composites with commercially available polystyrene resins.[7,9]

We report here the results of our initial studies of the structural features of these materials using solid state NMR techniques. Three new application of the technology are also presented: 1) separation of lanthanides as a group from ferric ion and all other divalent ions; 2) a multi step process for recovering and concentrating the valuable metals in acid mine drainage; 3) a process for removing low level arsenic and selenium in the presence of sulfate using immobilized cations on the composite materials.

Table 1.
Advantages of Purity Systems Inc Composites over Polystyrene Resins

1. No shrink-swell in load-strip-regenerate cycles. Ideal for up or down flow fixed beds.
2. Faster capture kinetics allows use of shallower beds.
3. Much longer usable lifetimes due to more rigid structure.
4. Higher maximum operating temperature (110 °C compared with 70 °C for polystyrene).
5. More stable to radiolytic decomposition.

Results and Discussion

Structural Investigations

^{29}Si NMR and Metal Capacity Studies of Surface Coverage as A Function of Anchor Dilution

The ^{29}Si cross polarization magic angle spinning (CPMAS) spectrum of amorphous silica gel (100 μm particle size, 225 Å average pore diameter, INEOS) after treatment with chloropropyl trichlorosilane is shown in Figure 3.[11] The assignments shown are based on the prior work of M. J. Wirth *et. al.*[15] All the species expected on the surface of the silanized gel are resolved: 1) the bulk siloxane; 2) the unreacted surface silanols; 3) the reagent geminal silanols ($(\text{-O-})\text{Si(OH)}_2\text{R}$); 4) the reagent silanols ($(\text{-O-})_2\text{Si(OH)R}$; 5) the reagent siloxane ($(\text{-O-})_3\text{SiR}$). The relative intensities of these resonances are not however reflective

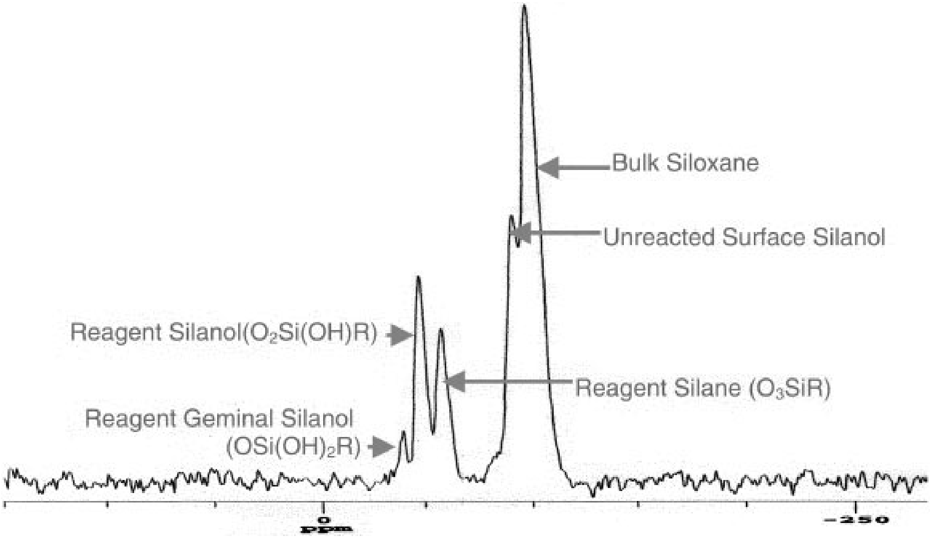

Figure 3.
CPMAS ^{29}Si NMR spectrum of amorphous silica gel after reaction with CPTCS at 99.5MHz. Assignments made according to reference 15.

of their concentration in the material owing to their different degrees of polarization. We therefore ran the spectra without cross polarization with relaxation delays of 150 seconds in order to get truer relative intensities especially for the reagent (CPTCS) resonances. The spectra obtained were not as sharp as the cross polarized spectra but with the aid of standard spectral deconvolution techniques, using elemental analysis data and the fact that amorphous silica gels have approximately 8 μmole/m^2 of surface silanol, we are able to estimate the percent of each species present and the percent of surface coverage (Table 2). In an attempt to understand how the size of the alkyl group influences the percent coverage and the percent of each reagent silane species, we treated the amorphous silica with a 1:1 mixture of CPTCS and methyl trichlorosilane (MTS) and with pure MTS.

We then measured the MAS ^{29}Si NMR under the same conditions as for the CPTCS treated gel. As can be seen in Table 2 the degree of surface coverage dramatically increases as does the percent of reagent siloxane while the percent geminal reagent silanol significantly decreases. The 1:1 mixture is only slightly different from the pure CPTCS sample. Increasing the surface coverage and decreasing the percent of reagent silanol would undoubtedly improve the overall durability of the silica and therefore the resulting composite materials. In order to accomplish this however, the ratio of MTS:CPTCS will have to be quite high. We previously reported, based on stepwise elemental analysis of the composite material made with PAA, that approximately 40% of the amines were bound to the surface silanols.[5] In the case of PAA with a molecular weight of 15,000 and a monomer molecular mass of 58 there are about 100 anchor points per polymer molecule on average. This figure must be considered to have a wide distribution range since the distribution of surface silanols on silica gel is not uniform and therefore the number of silane anchors will not be distributed evenly. Nonetheless it seems reasonable that one could find an optimum ratio of MTS:CPTCS where the surface coverage is maximized and where the number of anchor points is sufficient to maintain composite stability. This approach should be particularly amenable to the higher molecular weight polymers we have used

Table 2.
Percent of Reagent Species and Surface Coverage for Silanized Silica Gels

Reagent	%(O_3SiR)	%($O_2Si(OH)R$)	%($OSi(OH)_2R$)	% Coverage
$Cl(CH_2)_3SiCl_3$	28	59	13	50
$Cl(CH_2)_3SiCl_3/CH_3SiCl_3$	30	56	14	56
CH_3SiCl_3	48	44	7	88

(i.e. PAA (MW = 15,000) and PVA(MW = 50,000) but not PEI (MW1200)). Diluting the number of anchor points in this manner would have the additional benefit of increasing the number of free amines which could increase the metal capacity and the number of sites for binding metal selective modifying ligands.[5]

We therefore undertook a study of the impact of silanizing amorphous silica gel with ratios of MTS:CPTCS of 2.5:1 to 12:1 for both 50,000 MW PVA and 15,000 MW PAA. These studies were done with a larger silica gel (150–250 μm, 250 Å average pore diameter, INEOS) as it more closely resembles the gel used in commercial applications of these materials.[7] The presence of the mixture on the surface of the silica gel is clear from the ^{13}C NMR where a methyl resonance of increasing intensity is observed at −5.6 ppm in addition to the n-propyl resonances at 45.7, 26.9 and 10.50 ppm as the ratio of MTS:CPTCS is increased. The results of these studies are summarized in Figures 4–7.

Figure 4 shows the actual ratio of MTS to CPTCS based on elemental analysis (total moles C – moles halide ×3 = moles C due to MTS) compared with measured ratio prior to reaction. That the percent difference is larger (the ratio being higher than expected) for the lower ratios suggests that the less bulky MTS reacts more rapidly than CPTCS when they are present in more comparable concentrations. At higher ratios this difference is minimized and the greater percent difference at 12:1 may be due to errors in the measurement of small amounts of CPTCS. The surface coverage at all the tested ratios is much higher than for the pure CPTCS and does not vary very much over the range investigated (2.5–2.8 versus 1.5 mmole/g for the pure CPTCS).[15]

A measure of the impact of decreasing the number of anchor points is the measurement of the metal ion capacity. In the past we have used copper capacity as a base line for determining the general coordination properties of a given composite.[5] The results of these measurements are shown in Figure 5 which plots copper versus the ratio of MTS:CPTCS on the 50,000 molecular weight PVA.

There are several important conclusions that can be drawn from these data. First, as the number of anchor points decreases and the number of free amines increases the capacity increases in a corresponding way (a separate plot of copper capacity versus the calculated free amines gives a linear correlation coefficient of 0.82). Second, there is an optimum value for the ratio of MTS:CPTCS which comes at the measured ratio 7.5:1 and corresponds to a 17% increase in copper capacity relative to pure CPTCS. After this point higher ratios of MTS:CPTCS apparently result in lower polymer loading. We also observe a significant increase in the coordination number of copper from 2.25 to 2.70 on going from pure CPTCS to the 12:1 ratio. Finally, it should be noted that the total amine concentration is greatest for pure CPTCS while the copper capacity is the lowest in the range of 0 to 7.5 (Figure 5). This means that for this particular polymer not all the amines are accessible for metal coordination. This is not the case for example for PEI as we previously reported.[12]

For the lower molecular weight polymer PAA (MW = 11,000–15,000) the ratio studies give quite different results that are illustrated in Figure 6. It can be seen that copper capacity is greatest for pure CPTCS and decreases by about 15% at the lower MTS:CPTCS ratios. Interestingly

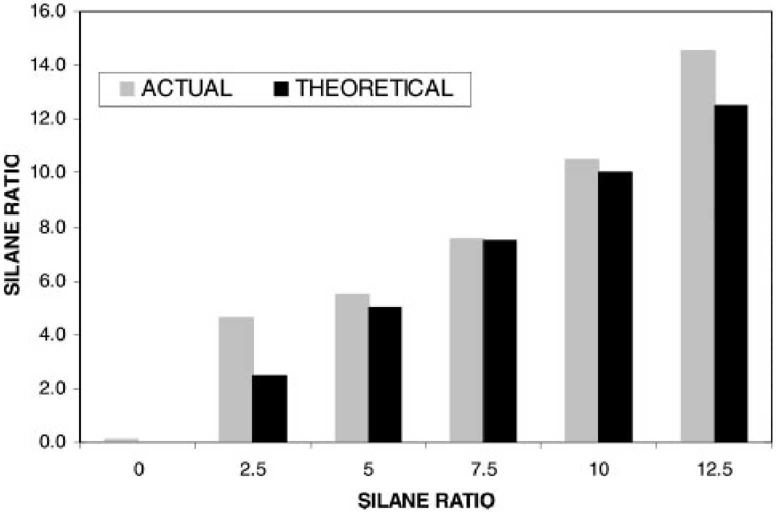

Figure 4.
Bar graph illustrating the actual ratio of MTS: CPTCS as determined by elemental analysis compared with the measured ratio used in the silanization reaction.

the copper capacity gradually increases until it is within 5% of the value for pure CPTCS at a ratio of 7.5:1 and then gradually decreases again at higher ratios. These data indicate that for this polymer all the amines are available for metal coordination and that polymer loading is highest for the pure CPTCS. However, increasing the MTS:CPTCS ratio and therefore the number of free amines still has a positive impact

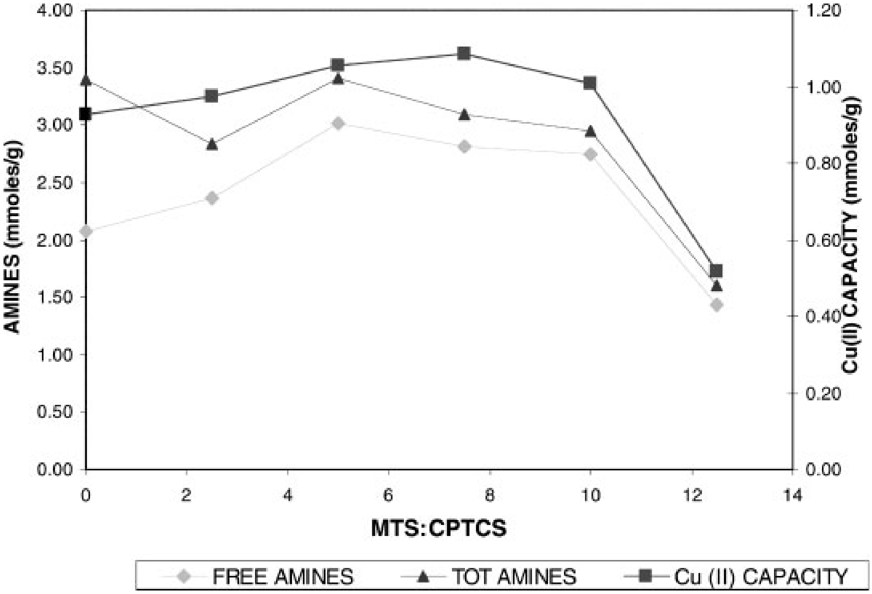

Figure 5.
Plots of copper capacity, total amines and free amines versus MTS:CPTCS ratios.

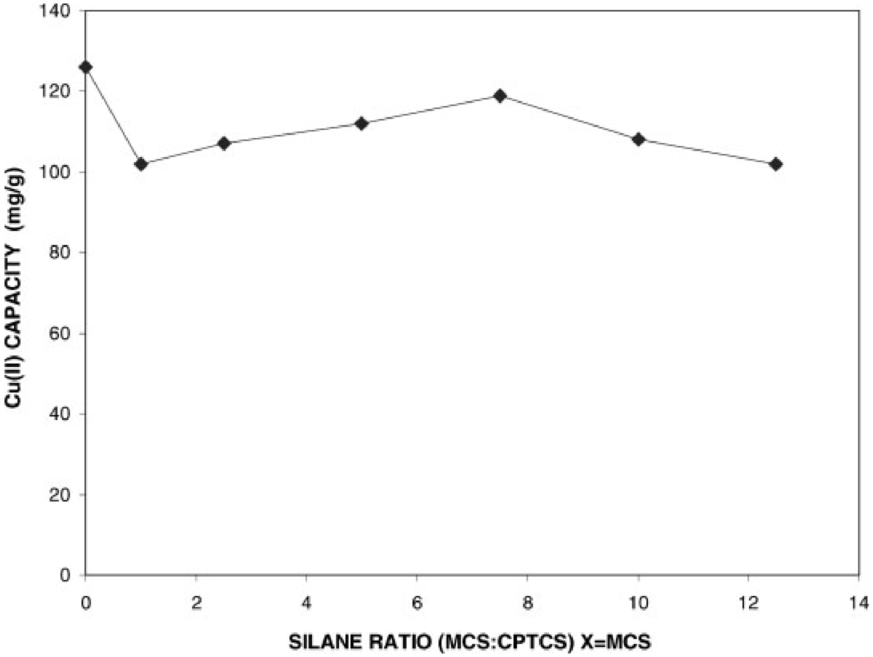

Figure 6.
Plot of copper capacity versus MTS:CPTCS for the polymer PAA.

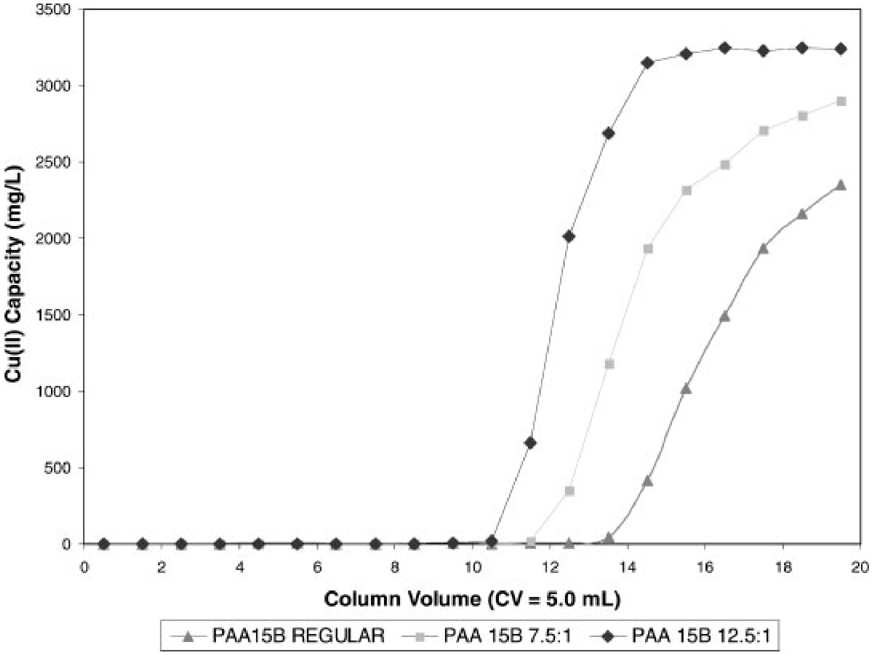

Figure 7.
Break through curves for copper binding to pure CPTCS, 7.5:1 and 12:1 MTS:CPTCS.

on the copper capacity and is optimum relative to polymer loading at the same ratio (7.5:1) as for the higher molecular weight linear polymer. Although the percent change over the whole range is less than for the higher molecular weight PVA the apparent increase in free amines could still have a significant impact on the degree to which the grafted polymer can be modified with metal selective organic groups.[13]

Perhaps even more importantly, the dilution for the number of anchor points has a significant and positive impact on the mass transfer kinetics of metal ion capture. This can be seen from the slope of the break through curves for the undiluted CPTCS sample compared with the 7.5:1 and 12:1 samples (Figure 7). The steepness of this curve is an indication of the rate of mass transfer from solution to the surface metal binding sites. This effect is also observed for the higher molecular weight polymer as might be expected.

Overall these studies have demonstrated that increasing the number of free amines can have a significant impact on metal ion capacity but that this impact is mitigated by the molecular weight of the polymer. The data also indicate that for the higher molecular weight polyamines not all the amine sites are kinetically accessible. In the particular case of PVA other factors may play a role as well (*vide infra*). Finally the overall kinetics of metal binding are improved by anchor point dilution.

^{13}C NMR and Molecular Modeling Studies of Grafted Polymer Conformations

It would be expected that the lower molecular weight branched polymer PEI (MW = 1200) would have a more rigid structure when bound to the surface of the CPTCS silanized silica gel since there would be more anchor points per polymer molecule. Stepwise elemental analysis reveals that five out of six of the primary and secondary amine groups are bound to the silane anchors if one assumes that the tertiary amines are not quarternized under the reaction conditions for grafting the polymer to the surface.[11] This is supported by metal binding studies that indicate that all of the amine groups are involved in metal coordination.[12] Taken together with the fact that the nitrogen atoms of this polymer are located on the backbone one would expect a very rigid microenvironment for composites made with this polymer. On the other hand, the polymer PAA (MW = 11,000–15,000) where the amine groups are located on a side chain would be expected to have a more flexible microenvironment and elemental analysis indicates that two of every five amine groups are bound to the surface. This difference is clearly demonstrated in the appearance of the CPMAS ^{13}C NMR in the aliphatic region, where the relatively sharp propyl methylene groups observed for the CPTCS (45.7, 26.9 and 10.50 ppm) remain sharp and unshifted except for slight downfield shift for C(3) to 47 ppm (as expected on substituting N for Cl) after grafting PAA to the surface (Figure 8a left and middle). The polymer methylene groups appear as a broad but smooth envelope of resonances which partially overlap with the propyl methylene groups centered at 34.0 ppm. The spectrum of the PEI composite in the same region is very different (Figure 8a right). The resonance that appears at 10.5 ppm in CPTCS and in the PAA composite which can be assigned to the silicon bound methylene group is shifted to higher field (5.2 ppm) and broadened. The resonance at 26.9 ppm in both CPTCS and in the PAA composite is no longer observed and a broader resonance of lower intensity appears at 19.0 ppm. The PEI methylene resonances appear as a broad asymmetric envelope centered at 49 ppm. The appearance of the spectrum is consistent with a more rigid microenvironment and this interpretation is supported by molecular modeling calculations. We used the molecular mechanics program, Sybyl 6.7, and the calculations were done on an Octane R12000 computer operating in a Silicon Graphics environment.[16] A tenmer of each polymer was constrained on a simulated silica surface which was based on

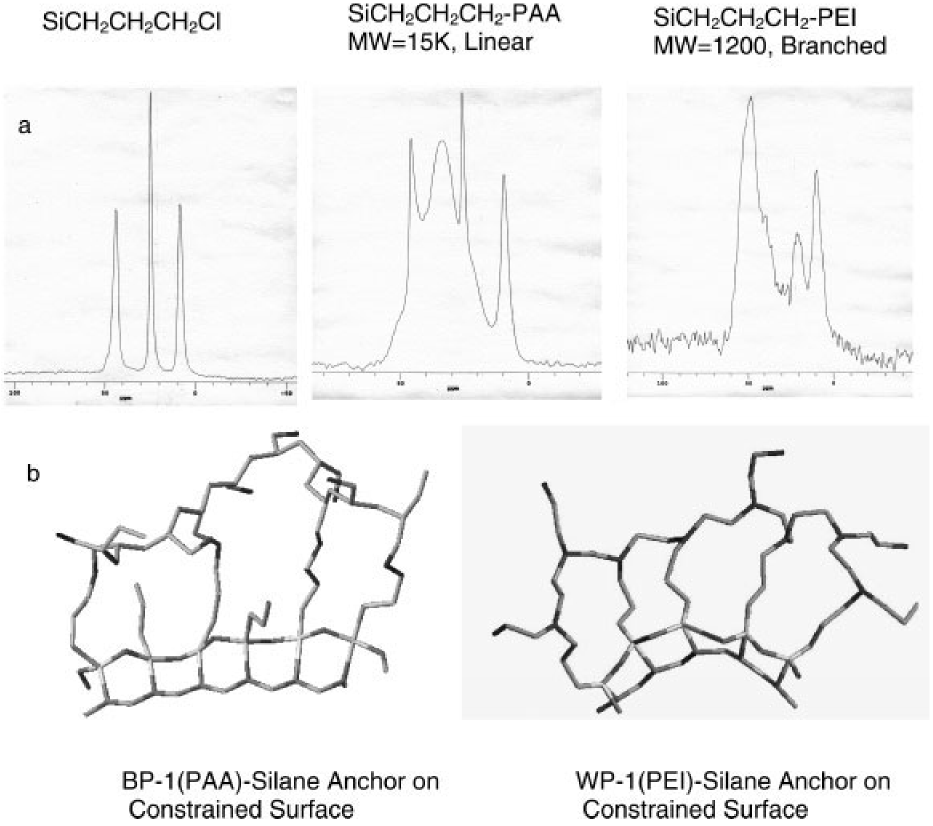

Figure 8.

a) CPMAS ^{13}C NMR at 125 MHz of the aliphatic region of CPTCS on silica gel (left), PAA grafted to CPTCS on silica gel (middle) and PEI grafted to CPTCS on silica gel (right). b) Calculated low energy conformations of a ten mer of PAA (left) and PEI (right) anchored onto a simulated silica surface.

the 100 surface of the mineral β-crystobalite which has been shown to be a reasonable surface model for amorphous silica gel.[17] The calculations searched for low energy conformations and two such conformations are shown in Figure 8b.

It can be seen that the simulated silica surface is significantly bent in the PEI model (Figure 8b, right) indicating significant strain at the polymer-silica interface. In the case of the more flexible polymer, PAA, this is not observed and the simulated silica surface maintains its original geometry. Of course, in reality the silica gel surface would not distort but rather the polymer would be in a highly rigid and perhaps strained conformation. This information is very useful for directing the further modification applications of these composite systems.

New Applications

Separation of Lanthanides from Ferric ion and Divalent ions

Lanthanide ores (rare earth elements, REE), like many valuable metal ores, are often found in the presence of large amounts of iron, other transition metals and large amounts of alkali and alkaline earth metals. We have developed a polyamine composite based on poly(allylamine) modified with an oxine ligand which is selective for ferric ion over all divalent metals and aluminum at low pH. This material called WP-4 (L = 8-hydroxy qui-

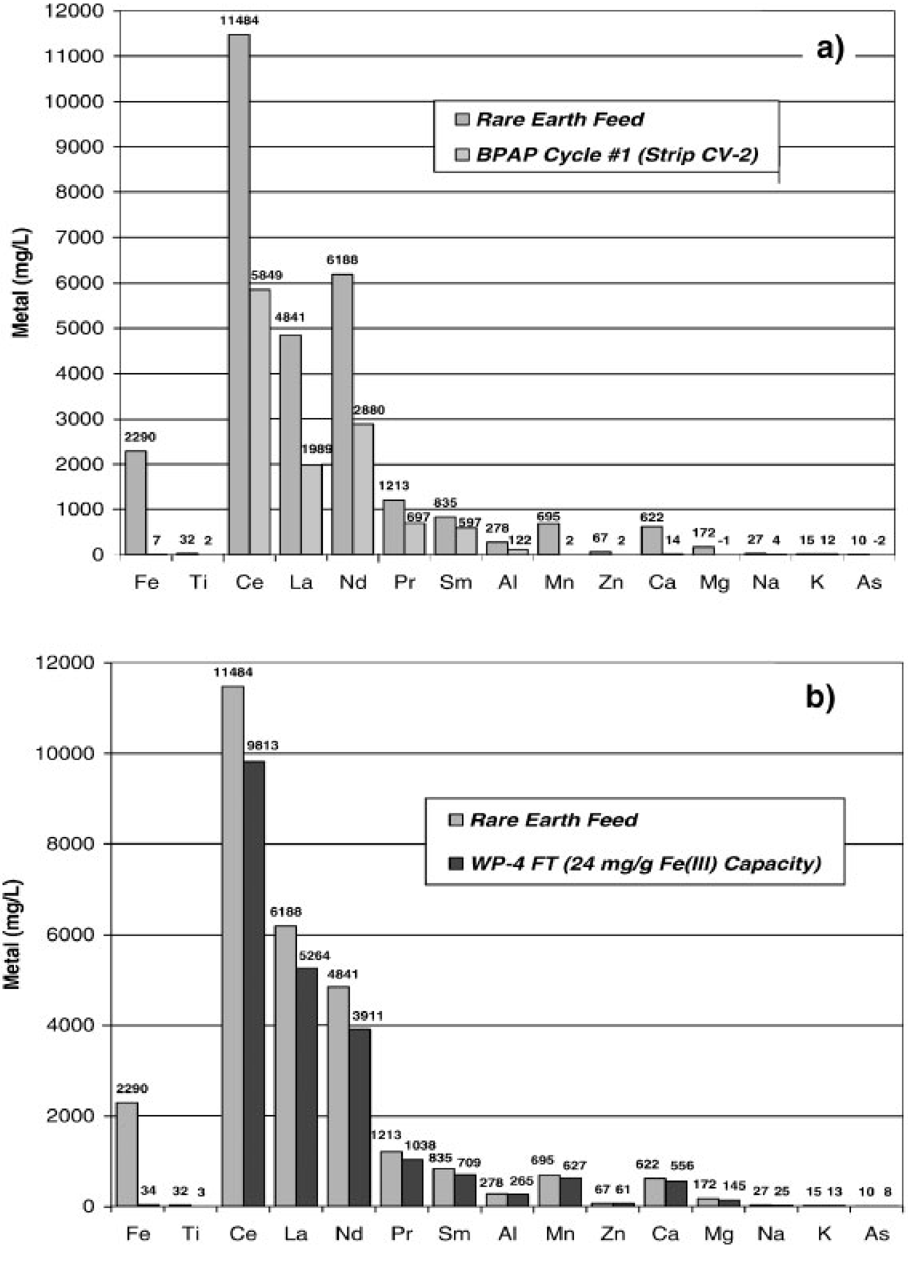

Figure 9.

a) Bar graph showing the feed concentrations of all metal ion components in a lanthanide acid ore leach at pH = 1 before and after passing through a column of WP-4. **b)** bar graph showing the feed concentrations of all metal ion components in a lanthanide acid ore leach at pH = 1 before and after passing through a column of BPAP.

noline, Figure 1), also separates gallium from aluminum and from large excesses of ferrous and zinc at pH~2.[18] We have also modified the same polyamine composite with a phosphonic acid group and found that the entire family of lanthanides is selectively removed from mixtures of transition metal, alkali and alkaline earth

Table 3.
Metal concentrations (mg/L) of Berkeley Pit water (at various depths)[i, ii]

BP Water depth	SO_4	Fe	Zn	Mg	Ca	Al	Mn	Cu	Cd	As
ft	mg/1									
0	6345	270	378	430	512	195	179	86.8	1.84	<0.22
50	8994	892	578	538	494	281	212	145	2.39	0.34
500	9105	986	580	536	494	281	209	177	2.43	0.78

[i] Moore, J.N.; Study conducted Nov. 6th, 2001, HSB analyses courtesy of Montana Bureau of Mines and Geology (sampled May 3rd, 2001).[ii] www.epa.gov

metals at low pH. This material called BPAP, also captures ferric ion and so it was decided to use a two step ion exchange process to separate the lanthanide group from ferric ion, transition metals and alkali-alkaline earth metals. We obtained an ore leach from an Australian mine which contained all of the above components at pH = 1. A 30 cc syringe was packed with 19.3 g of WP-4. WP-4 was then rinsed with 4 column volumes (CV) of pH 2.0 (H_2SO_4) de-ionized (DI) water, striped with 4 CV 9 N [14%(m/m)] H_2SO_4, regenerated with 4 CV pH 2.0 (H_2SO_4) in DI water. WP-4 was then loaded first with the REE solution. 15 CV (450 mL) of the REE solution was treated at 0.20 CV/min. The first 6 CV of flow through were collected in 0.5 CV (15 mL) fractions and analyzed by flame AAS using minimal volume of flow through (0.5 mL). The ''minus'' Fe(III) flow through (CV 0.0–5.0) was combined to yield 136 mL of solution. WP-4 also showed an affinity towards Ti(IV) and was removed with the Fe(III). WP-4 was striped using 9 N [14% (m/m)] H_2SO_4 DI water. WP-4 exhibited a 24.4 mg/g strip capacity.

A 10 cc syringe was packed with 5.48 g of BPAP. The column of BPAP was rinsed with 4 CV pH 2.0 (HNO_3) DI water, striped with 4 N [18% (m/m)] HNO_3 DI water, and regenerated with 4 CV pH 2.0 (HNO_3) DI water. The filtered minus Fe(III) solution (136 mL) was then passed through BPAP. The flow through was collected in one fraction and a sample was taken for ICP analysis. BPAP was immediately rinsed with 4 CV pH 2.0 (HNO_3), and striped with 6 CV 18% (m/m) HNO_3 (fractioned each strip CV (10 mL). BPAP was regenerated with 4 CV pH 2.0 (HNO_3). The collected flow through was passed through the 10 mL column of BPAP five more times following the above rinsing, striping and regeneration protocol for each cycle. The flow rate was held constant at 0.50 CV/min. for BPAP rinsing, loading, striping, and regeneration. The strip was analyzed by ICP and was shown to contain only REE with only trace amounts of aluminum and zinc (Figure 9b).

This study shows the feasibility to separate the REE metals from the metal matrix. BPAP does not efficiently elute the REE metals. Cycle #1 was the original loading of raw BPAP but did strip 70–100% of each REE. In cycle #2 BPAP striped 90–100% of the loaded metals using 5 CV of strip solution [4 N HNO_3 (18% by weight)]. Cycle #3 - #6 were not capable of loading BPAP fully due to the decreasing feed concentrations. A 9 N [14% (m/m)] H_2SO_4 solution could also be used but does show slightly slower striping kinetics.

Separation and Concentration of Valuable Metal from Acid Mine Drainage

The creation of acid mine drainage by the exposure of sulfide pyrite minerals during mining operations is a worldwide problem.[16] In many cases the contaminated flows are too large for containment or for a

Table 4.
Berkeley Pit Lake Metal Ion Recovery Data.

	Cu(II)	Zn(II)	Mn(II)
Berkeley Pit (% purity)	5.0	18	6.0
Recovery (% purity)	97	99.98	83
Berkeley Pit (g/l)	0.17	0.58	0.21
Recovery (g/l)	10	6.5	9.0

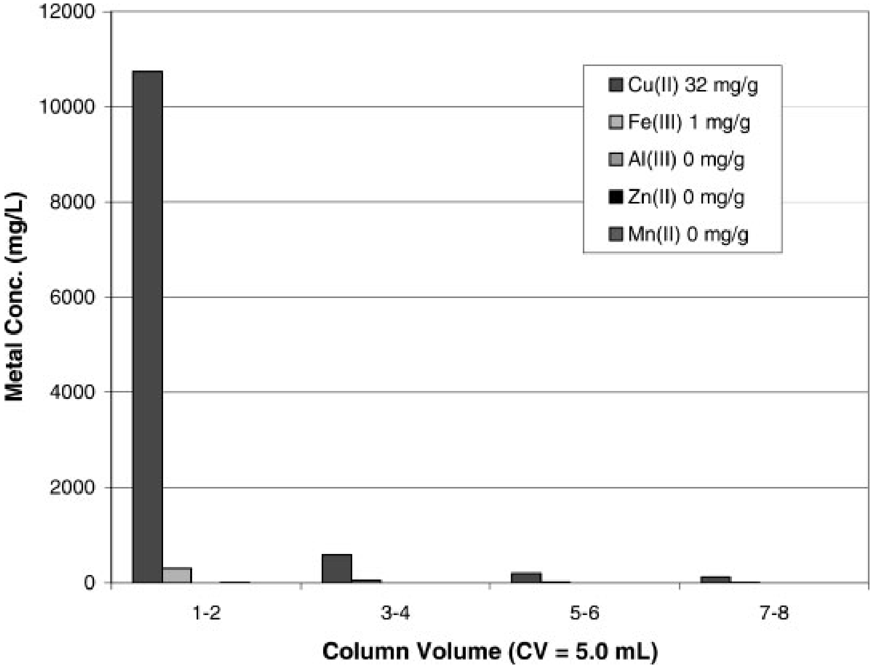

Figure 10.
CuWRAM strip fractions, 0.50 CV/min, 97% Cu(II) purity.

one time liming procedure. Continuous liming is cheap but creates problems for sludge disposal. Remediation of the metal contamination and acidity of such waste streams using ion exchange could be feasible in cases where the streams contain valuable metals if these metals could be separated and concentrated to offset the cost of remediation. The metal selective silica polyamine composites that are the subject of this report present such an opportunity. A case in point is the Berkeley Pit in Butte, MT which is one of the largest superfund sites in the USA.[19] The site was created by drainage from abandoned shaft mines into a large abandoned open pit mine. Currently, the pit is being continuously limed to keep contamination at a constant though not exactly acceptable level. The lake that now occupies the Berkeley Pit at Butte, MT, is a well-known example of a highly acidic pit lake with high levels of metals and sulfate. It has a pH value near 2.6 and is high in iron, zinc, magnesium, calcium, aluminum, manganese, and copper as revealed in Table 3.

Given the commercial value of copper manganese and zinc we undertook a study to evaluate the feasibility of separating and concentrating these metals from the calcium, magnesium, iron and aluminum which are the other major components in the pit water.

Although the iron in the pit is a mixture of ferrous and ferric the iron was completely in the ferric form under the conditions of our study owing to aeration. In the approach described here this turned out to be efficacious. Bench-scale separation of Cu(II), Zn(II), and Mn(II) was achieved producing high purity, highly concentrated recovery solutions of each target metal ion (Table 4).

The Treatment Pathway Investigated to Produce the Results in Table 4

Berkeley Pit water pumped from a depth 150 ft (to obtain higher metal concentrations) is collected in a holding tank. Oxidation of Fe(II) can be accelerated by spraying the water up into the air upon collection, and/or by bubbling compressed

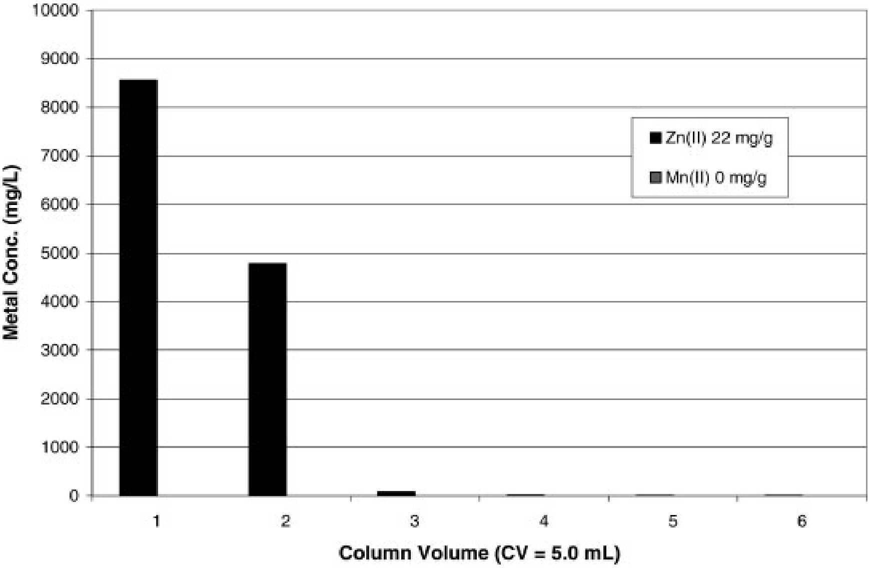

Figure 11.
WP-2 strip fractions, 0.50 CV/min., 99.98% Zn(II) purity.

air throughout the collection reservoir. The solution is then pumped to an array of columns containing CuWRAM. CuWRAM exhibits a remarkable ability to extract copper in the presence of high levels of ferric iron and other metals. After loading a CuWRAM column with copper to capacity the column is rinsed with pH 2 DI water to flush out the entrained metals not captured. The column is then stripped with 4N H2SO$_4$ to give a solution with the concentration and purity shown in Figure 10. After

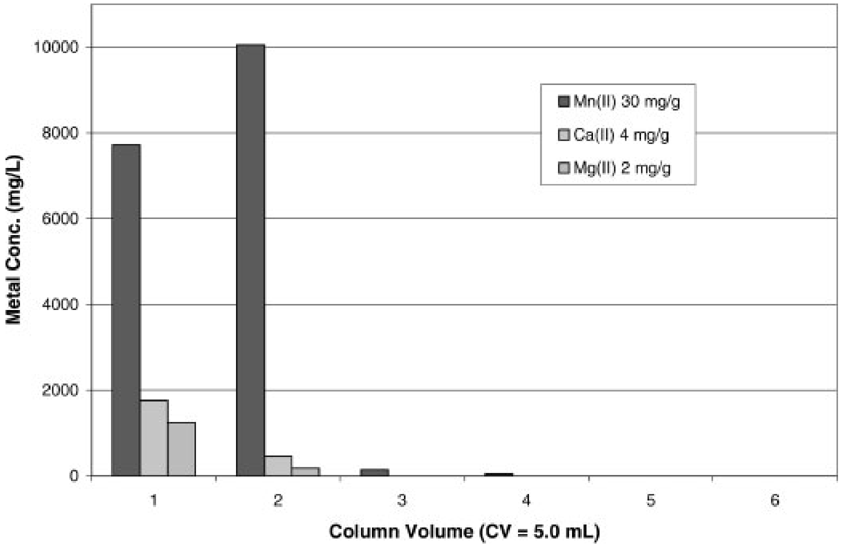

Figure 12.
BP-2 strip fractions, 0.50 CV/min., 83% Mn(II) purity.

stripping the column it is regenerated by passing DI water through the column.

The effluent from CuWRAM is then adjusted to pH 5.2 with NaOH (or other base), precipitating the iron (which co-precipitates the arsenic present), and aluminum, as the metal hydroxides. A flocculent can be added to assist settling of the precipitate which is then filter pressed (recycling the filtrate) and disposed of at an appropriate repository.

Zinc(II) is then separated from manganese(II) utilizing the acetate functionalized composite WP-2. WP-2 was regenerated using 4 CV 0.01 N NaOH (followed by 4 CV DI H_2O) to increase the capacity towards Zn(II), but not compromising the selectivity over Mn(II). Figure 11 illustrates WP-2′s affinity towards Zn(II), while Mn(II) quickly breaks through the column. WP-2 was rinsed with 4 CV pH 2 DI H_2O before striping with 9 N H_2SO_4.

Manganese (II) was separated from calcium(II) and magnesium(II) using a composite with amine functionality, BP-2. BP-2 was base regenerated using 13 CV of 0.10 N NaOH, followed by 4 CV of DI H_2O. Mn(II) loaded onto BP-2, while Ca(II) and Mg(II) quickly exit the column. After loading Mn(II) to capacity, BP-2 was rinsed with 4 CV DI H_2O before striping with 9 N acid (Figure 12).

These results suggest that a combination of ion exchange and precipitation techniques can be effectively applied to the remediation of acid mine drainage with recovery of the valuable metals at concentrations that would be amenable to electrowhinning for recovery of the metal or isolated as salts after evaporation of water. The economic feasibility of such a process for offsetting the cost of remediation would need to be examined on a case by case basis and would depend on waste stream flow volume, metal content and general process parameters.

Removal of Low Level Arsenic and Selenium from Mine Waste Solutions

The contamination of surface waters and aquifers with toxic anions such as arsenate, arsenite, selenate, selenite and borate as a result of mining activities, industrial processes and geothermal mobilization (of arsenic in particular) is a global problem.[20–23] Numerous technologies have been developed to provide a solution. These include: adsorption on activated alumina,[24] the use of nanofiltration membranes,[25] the use of liquid membranes,[26] microbial reduction to elemental selenium,[27] ion exchange with strong base anion exchangers[28] and precipitation with ferric oxy hydroxides (the so-called ferrihydrite process). The latter is by far the most economical and effective and has been widely employed on a large scale but has the significant disadvantage of creating a large amount of sludge for ultimate disposal.[29,30] The other methods suffer from a lack of specificity, selectivity over sulfate (ion exchange) low mass to volume concentrations (bio-reduction) and high cost (membrane technologies).

Recently, tailored chelating polymers containing immobilized metal cations have been employed in anion capture.[31,32] These materials exhibit much higher selectivity over sulfate than the other techniques and offer the advantage of providing highly concentrated solutions for further recovery or high mass to volume precipitation. This higher selectivity is attributable to the formation of Lewis acid-base complexes rather than strictly electrostatic interactions.[31,32] On the other hand, one material that used immobilized Cu^{2+} was only effective for As(V) and Se (IV)[31] The other polymer system used immobilized Zr^{4+} and was effective for As(III) from pH 1–12, As (V) from pH 2–8 Se (IV) from pH 2–8 and Se (VI) from pH 2–4.[32] These results point to the fact that the formation of the complex between the oxyanion and the metal cation is dependent on the nature of the metal and the degree of protonation of the oxyanion and suggests that one might be able to tune the selectivity of the immobilized metal by varying its oxidation state, size and affinity for oxyanions. What is needed is a family of materials that can be made to operate over the full range of pH for all the oxyanions found in contaminated streams. Furthermore, the materials must be durable over many load – removal cycles with little or no leaching of the immobilized metal. Removal of the adsorbed oxyanion must be accomplished in an effective economical fashion. This was not the case for the material containing immobilized Zr^{4+} on polystyrene which required washing with a pH 4 buffer solution followed by stripping with caustic soda.[13] Finally, the polymer systems employed so far suffer from the intrinsic disadvantages of plastic resins. They undergo shrink and swell with significant changes in pH and require rather elaborate synthetic procedures to create the appropriate environment for metal cation immobilization.[31,32]

The initial work of Suzuki *et. al.* immobilized zirconium on a specially prepared polystyrene resin containing the ethylenediamine tetraacetic acid (EDTA) ligand using $ZrOCl_2 \cdot 8H_2O$.[29] This provided the impetus for us to try to immobilize the same metal using our previously reported WP-2, a silica polyamine resin functionalized with amino acetic acid groups. Zirconium loading onto the resin averaged about 40mg/g resin (0.46 mmol/g). Based on elemental analysis of the starting resin and the zirconium loading we estimate that approximately two amino acetic acid residues are bound to each zirconium. The zirconium loading is lower than that reported by Suzuki *et. al* (0.8 mmol/g) and the properties of the materials are different in interesting ways. The Suzuki material captures arsenite but Zr-WP-2 does not. On the other hand, Zr-WP-2 captures selenate as well as selenite while

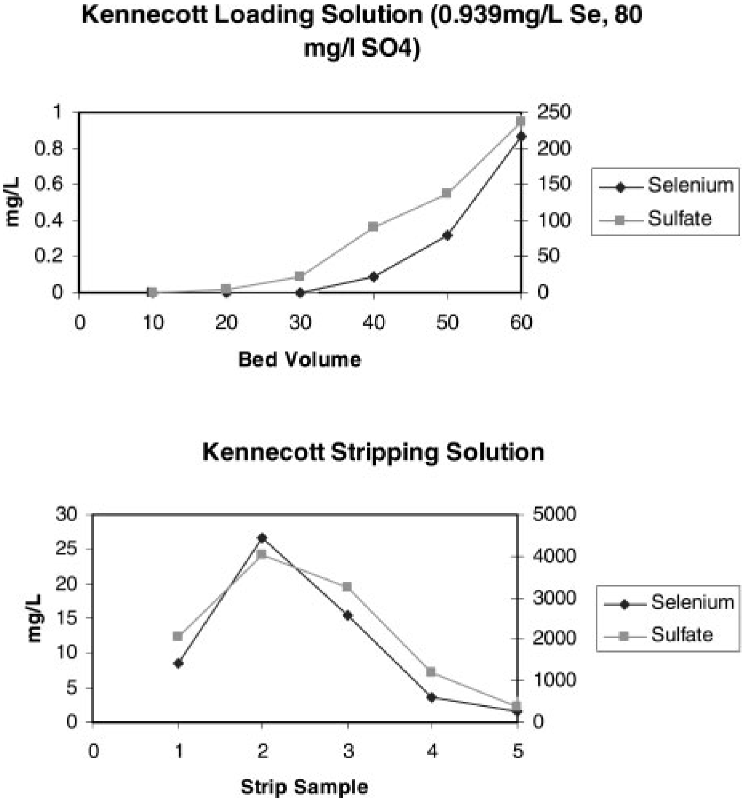

Figure 13.

Selenium removal (upper graph) and recovery (lower graph) from the Kennecott Mine process solution using Zr-WP-2.

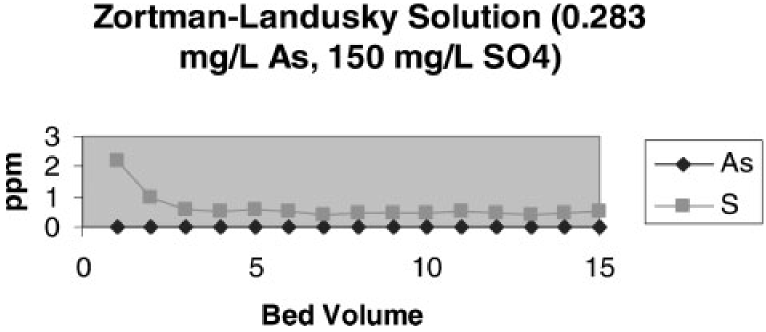

Figure 14.
Arsenate removal from a mine waste solution containing only As (V) and sulfate.

the Suzuki resin only captures selenite. Both capture arsenate up to pH= 8. These results are difficult to rationalize but a working hypothesis is that that Zr-WP-2 has an overall higher average charge on the zirconium making it capable of capturing $SeO_4{}^{2-}$ which is a weaker Lewis base than SeO_3^{2-} and exists as $HSeO_3^{1-}$ at the reported pH of 4.[32] That the Suzuki resin captures arsenite is more difficult to understand in that it exists as a neutral compound up to pH = 10 It may be that the Zr center is essentially neutral or only +1 and therefore captures only neutral or +1 ions as is reported (As(V) exists as $H_2AsO_4^{1-}$ at pH = 4).[33] At pH>8 the performance of both systems falls off presumably because of increasing ionization and competition with hydroxide. From this initial data, it would appear that whether a given oxyanion is captured or not depends on a combination of the net charge on the immobilized metal anion complex and the matching of the covalent binding characteristics of the pair. If the complex has a net negative charge binding will be weak while neutral or net positive complexes can be stable if there is sufficient donor acceptor bonding to outweigh hydration energy (Equation 1).

$$L_xM^{n+} + M'O_y^{m-} \rightleftharpoons L_xM^{n+}(M'O_y^{m-}) \qquad (1)$$

complex is stable if $n^+ + m^- =$ or > 0

From the above discussion it would appear that the Zr-WP-2 and polystyrene EDTA analog each have different advantages. However, PSI has tested Zr-WP-2 on actual contaminated mine waste streams from three mine sites in Montana and on a process waste stream from a gallium arsenide plant. All of these tests were run on a 30 mL column containing 18 g of Zr-WP-2.

We evaluated selenium containing process solutions from the Kennecott Mining Company which contained 0.93 mg/L selenium as both selenite and selenate and 80 mg/L sulfate (Figure 13). The Zr-WP-2 removed all the selenium to below detection limit (<1ppb) at the operational pH of 4. There was sulfate co-loading but the calculated selectivity factor over sulfate was 67/1 for selenate and 103/1 for selenite based on the strip concentrations. The selenate was stripped using 1M phosphoric acid at pH = 4. This represents distinct advantages over the caustic soda strip used with the polystyrene resin. First the silica polyamines are much more resistant to acid than to base. More importantly, the phosphate strip solution can be limed to produce arsenohydroxyapatite ($Ca_{10}(PO_4)_3(AsO_4)_6(OH)_2$) a very stable matrix for immobilizing arsenic.[34]

The use of caustic soda as a strip leaves oxyanion solution as soluble species to which lime and phosphate would have to be added. The concentration factors achieved were ~1500.

No concentration factors or working flow capacities were reported for the related polystyrene gel.[29] Mass balances of >95% were obtained with the PSI resins.

We then tested a solution from a mine waste site that contained only arsenate at 0.283 mg/L and 150 mg/L sulfate obtained from the Zortman-Landusky mine site in Montana (supplied by John Koerth of the Montana Department of Environmental Quality). As can be seen in Figure 14 the arsenic was removed to below detection limit for the duration of the test. Again there was some sulfate co-loading but strip composition gave a selectivity factor of 92/1 over sulfate.

In addition to the above tests we also entered the Zr-WP-2 in a gallium and arsenic recovery challenge conducted in Albuquerque, NM in 2003. The challenge was sponsored by Bechtel Corporation and pits teams of undergraduate engineering students against remediation problems encountered by industrial companies. In this case a solution containing 11 μg/L of gallium and an equivalent amount of arsenic was provided to a team of engineering students from Montana Tech. PSI provided samples of Zr-WP-2 and WP-4 a resin that was developed specifically for gallium recovery in neutral to acidic medium. The students were able to remove 99% of the gallium and arsenic and won first prize in the challenge. It should be pointed out here that no leaching of zirconium from the WP-2 was observed during ten runs on the same Zr-WP-2 sample. Similar results were reported for the EDTA-polystyrene system.[32] The PSI anion removal technology shows great promise for commercialization in the environmental remediation and metal processing industries. However, the materials are not very effective for arsenite and to date are efficient in a limited pH range (4–6). In addition the fundamental chemistry that governs performance is not well understood and the effectiveness of the general approach of immobilizing metals on solid matrices for recovering oxyanions other than those of arsenic and selenium has not been evaluated. Using the approach of varying the metal and the functional group on the composite we hope to broaden the range of the technology developed so far and provide a path to its commercialization. The technology could be further extended to include recovery of radionuclide oxyanions such as pertechnetate (TcO_4^{1-}). The PSI resins are much more resistant to radiolytic decomposition than polystyrene resins owing to their lower carbon content and the absence of C=C bonds in the case of WP-2 and the other resin proposed for use as as a potential anion removal material.

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