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Development of a Copper Selective Silica-Polyamine Composite

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Development of a Copper Selective Silica-Polyamine Composite

Edward Rosenberg Committee Chair

Silica-polyamine composite materials have been developed that have the ability to extract metal ions from aqueous solutions. These materials are synthesized through a unique route that renders them chemically robust enough to withstand the rigors of extreme pH environments encountered in industrial processes. They also extract metal ions to a lower final concentration and at faster flow rates than the current standard polystyrene resin bead materials. Modifications of these materials can be made, usually through straightforward chemical reactions, to tune their selectivity, to enhance the extraction of a particular class of metal ions. Early modifications of the silica-polyamine materials were successful in increasing the affinity and adsorptive capacity for the soft metals, for instance. But the new materials were not exclusively selective for that target class. The focus of the work presented here is development of a material selective for copper(II) extraction, even in the presence of large concentrations of iron(III).

The important features of the parent silica-polyamine materials such as the chemical and physical integrity of the material,and the ability to extract metal ions efficiently from low concentration solutions at fast flow rates, are explored in some detail. The critical synthetic steps are also thoroughly investigated.

Finally the synthesis and performance characteristics of a new copper selective silica-polyamine composite material – CuWRAM – are presented. CuWRAM was tested under batch and flow conditions using synthetic and real world challenge solutions. Many of these tests were carried out using CuWRAM and the industry standard Dowex XFS 45084 for a direct comparison. It has been demonstrated that CuWRAM is more effective than the Dowex resin under flow conditions, low pH, and under conditions of low metal ion concentration.

I would like to thank:

My parents for instilling in me the belief that I
can accomplish those things that I set my mind to
do

My mentor Ed Rosenberg for taking a chance on
me and presenting me with the opportunity to
work on this project

And

Last but not least

Beth, Kiki and Hans for all of their support
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1.1 Introduction

Separations chemistry is quite possibly the oldest and most important field of chemistry and yet new separation technologies are continuously being developed. Every branch of chemistry depends on separating the desired products from unwanted by-products and reactants. This has been true since the infancy of chemistry as a science and still is true today. While separation techniques are utilized every day, even some of the most utilized seemingly mundane separation techniques are not completely understood. For instance reverse phase high performance liquid chromatography (reverse phase HPLC), a technique that is widely used by organic chemists, is still not completely understood. Of particular interest in these systems are the interactions at the interface of the solid support, the active surface of the support, the elution solution and the molecules being separated. Nonetheless, these systems are being applied in broader contexts than ever before. With advancements in environmental and green chemistries, separations using chromatography techniques are being used in environmental remediation projects as well as industrial pollution abatement programs. These techniques employ a solid phase extractant to separate the target substance from solution. The use of solid-liquid phase separations in these more industrial settings requires solid phase materials that possess characteristics much different from those used in the typical analytical and process separations. This class of separation materials needs to be more robust under pH and temperature extremes, possess the ability to separate relatively large quantities of a specific material from the bulk solution at relatively fast process rates, and be fairly inexpensive. Such a material was developed in 1994 by Professor Edward Rosenberg of The University of Montana and David Pang of Purity Systems Inc. (PSI). This material, dubbed WP-1, is a silica-polyamine composite material useful for the general removal of transition metal ions from aqueous bulk phases. Since that time a number of new materials have been developed based upon the physical-chemical properties of WP-1. These are materials that can be used to extract a broad range of transition metal ions, and even more exciting, materials designed to selectively extract a specific metal ion. The focus of this dissertation is the development of the first truly selective material derived from these silica-polyamine composite materials. This material, CuWRAM, is selective for copper(II) ions in the presence of a wide variety of metal ions, is chemically stable at pH extremes, extracts copper from aqueous solutions at extremely low pH, and has been subjected to 1,500 extraction cycles with no discernable physical degradation or loss in copper capacity.

1.2 Metal Extraction and Separations Applications for the New Technology

The occurrence of transition metals in industrial wastewaters is widespread; from the obvious i.e. mines, to initially surprising sources such as medical and dental facilities. Industries that generate wastewater containing transition metals include: metal plating, steel pickling, photograph developing, wood preservative manufacture, nuclear and coal-fired power generation, computer chip manufacturing, and aircraft maintenance procedures to name a few.[1]

The development of CuWRAM began as an attempt to address a specific application; that is the extraction of copper from copper mine leach liquors containing large concentrations of iron(III), and generation of solutions of pure highly concentrated copper(II) ions. Although there are many applications for copper selective materials and possible strategies for extracting copper from aqueous solutions the driving force for this research is copper mining and water purification; that bias will be reflected through out this document.

1.2.1 Plating facilities

Copper plating is used extensively in the manufacture of printed circuit boards and recently a method to copper plate computer chips has been developed. In these facilities copper waste is generated at the plating baths, rinse baths, and in etching baths.[2] The amount of waste copper generated from a printed circuit board facility producing 1,600 circuit boards per day is 1.225 Kg copper per hour, much of which is in low pH solutions.[2] While copper is the primary metal present in the wastewater it also may contain lead, tin, iron, manganese, silver, and aluminum.[2] In addition to these other metals in the waste water there are also reducing agents, chelating agents, and stabilizers.[3] The chelating agents which are added to the plating baths to control the plate-out rate also interfere with the ability of ion exchange resins to extract the copper from the waste water.

1.2.2 Mining legacy remediation

The problem of remediation of mining sites is of particular importance, but not unique, to Montana. Contaminated sites include non-operating mines, mine tailings, and watersheds contaminated by mining operations. The problem of acid mine drainage begins as abandoned mines containing metal sulfide minerals begin to fill with water. The metal sulfide ore, pyrite FeS_2 for instance, is oxidized to produce in this instance, ferrous ion, two sulfate ions, and two hydrogen ions (i). This step increases the acidity of the water which causes the dissolution of other metal ions.[4] The ferrous ion is then further oxidized to ferric ion (ii) which in turn promotes further oxidation of iron sulfide resulting in greater acidity (iii). The reactions represented by equations **ii** and **iii** are very slow until the acid mine water reaches the surface and oxygen is more available.[5] The process is highly accelerated by soil bacteria such as *Thiobacillus*, *Thiomicrospira*, and *Thiothrix* among others, that thrive in acidic conditions.[6] Acid mine waters typically contain high concentrations of low value iron and lesser concentrations of more valuable metals such as copper. The sites, which are currently an environmental liability, could conceivably be utilized as a source for selected metals if a technology could be developed to extract, separate and concentrate the metals they contain.

$$FeS_2 + 7/2O_2 + H_2O \rightleftharpoons Fe^{+2} + 2SO_4^{-2} + 2H^+ \qquad \text{(i)}$$

$$Fe^{+2} + 1/4O_2 + H^+ \rightleftharpoons Fe^{+3} + 1/2\,H_2O \qquad \text{(ii)}$$

$$FeS_2 + 14Fe^{+3} + 8H_2O \rightleftharpoons 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad \text{(iii)}$$

Mine tailings present a direct danger to surrounding surface waters. Tailings are made up of the ore that contained too low a concentration of the target metal to make extraction of the metal economically feasible. This low-grade ore was then deposited in heaps in close proximity to the mine site. While the metal in this ore is of low concentration and or in a form that was difficult to extract using technology available at the time of excavation, the tailings piles do contain available metals. In fact in some cases the copper content of tailings may as great or greater than that of the copper content in currently operating copper mine ore bodies.[7] Over time these metals begin to leach from the excavated ore which has been deposited on the surface. As the water primarily from precipitation percolates through the tailings piles the concentration of dissolved metals increases. This water is then available to flow directly into surface and subsurface waters bringing with it an increase in metal content, sulfate and acidity. Erosion of the tailings piles also directly contributes to metal loading of surface waters. This phenomenon can cause elevated metal concentrations to occur hundreds of miles from the source. Extraction techniques have improved to the point that it may be economically feasible to extract copper from the low-grade ore that constitutes many tailings piles. The major hurdle remaining is recovery of the copper from the relatively low copper concentrations present in the resulting leach liquors.

1.2.3 Copper mining

The current state of the art in copper extraction from ore is hydrometallurgy. Hydrometallurgical processes have supplanted pyrometallurgical methods due to environmental concerns as well as increased efficiency in extracting copper from low grade ores.[8] As of 1992 750,000 tons of copper were recovered from hydrometallurgical leaching processes worldwide.[9] These techniques involve acid extraction of copper (leaching) from copper ores into aqueous solutions. Sulfuric acid is used to leach copper from copper oxide and oxide/sulfide containing ores. Ferric (iron (III)) ions are also added to improve the efficiency of the leaching

$$CuFeS_2 + 4FeCl_3 \longrightarrow CuCl_2 + 5FeCl_2 + S_2 \qquad \textbf{(iv)}$$

$$Cu_2S + 4FeCl_3 \longrightarrow 2CuCl_2 + 4FeCl_2 + S \qquad \textbf{(v)}$$

process by oxidizing the copper (I) to its more soluble copper (II) form and sulfide to sulfur. These leach solutions contain low concentrations of a variety of metals including iron, manganese, aluminum, magnesium, and molybdenum at low pH. The copper concentrations in these solutions can range from <1 g/L to 50 g/L with typical concentrations falling between 1 g/L and 6 g/L. The pH of these solutions ranges between 1.2 and 2.2 pH units.[9] Another efficient leaching system is chloride leaching. Chloride leaching is particularly effective at leaching copper from sulfide containing copper ores such as chalcopyrite $CuFeS_2$. In this process, ferric chloride is often used as the source of chloride ions to complex the copper and to oxidize the copper (I) to copper (II) as shown in equations **iv** and **v**.[10]

The final step in recovering pure copper is electrowinning. Electrowinning is a process in which copper is plated onto an electrode from an aqueous solution containing a high concentration of copper ions. Typically the copper concentration in the electrowinning tank lies between 30 g/L and 35 g/L.

The technical challenge posed in the recovery of high grade copper from low grade ore is to devise an efficient, environmentally safe method of selectively extracting copper from low concentration low pH leach solutions and producing high concentration high purity aqueous solutions suitable for electrowinning (i.e. free of ferric and chloride ions).

1.3 Traditional Industrial Separation Technologies

1.3.1 Evaporation

Evaporation is a low-tech method of concentrating solutes from a dilute solution. The solution is heated and as it evaporates the materials dissolved in the water remain in the vessel. The evaporative process can be stopped when the concentration of the solute reaches the desired level or when a sludge is produced. Usually all of the solutes, including contaminants and by-products, are also concentrated in the resultant solution. This limits the number of times the solute of interest can be recovered in this way; therefore, evaporation is used primarily as a wastewater treatment method where a sludge is produced and discarded. Evaporative techniques are generally expensive due to the high energy input required to evaporate the solvent. If water is the solvent the energy requirements can be met using solar energy. Large evaporating ponds are dug and the wastewater is deposited in them when the ponds fill with sludge they are capped. This method requires large tracts of undeveloped land which can be expensive even when practical. A further drawback to this method is that it tends to be most effective in hot dry climates where water is expensive and it is desirable to recover it.

1.3.2 Precipitation

Precipitation is widely used to treat wastewater generated by the metal plating industry, in fact it is the primary conventional method of wastewater treatment in use industrially. This method is employed when there is no interest in recovering the precipitate.[11] Precipitation occurs when solute molecules form compounds in solution that are supersaturated in relation to the solvent. Precipitation of the solute from solution is initiated in a number of ways, pH adjustment, oxidation, reduction, and secondary coprecipitation.[11] The primary drawback of precipitation is the generation of mixed waste sludge generated during the process.

1.3.3 Solvent Extraction

The technology most widely used in extracting copper from the mixed metal acidic leach solutions (aqueous phase) produced during the hydrometallurgical extraction of copper from copper containing ores is solvent extraction. In the solvent extraction process water soluble heavy metal salts are complexed with organic ligands to produce low or non-polar complexes that have limited solubility in water but are highly soluble in an organic solvent (organic phase) which is immiscible with water. In some instances water soluble ligands such as hydroxyoximes are added to the aqueous phase. These ligands selectively bind to the copper ions in the mixed metal solution to create a non-polar copper complex. These complexes are, however, soluble in an organic solvent. In this way, copper is selectively transferred into the organic phase. Salts can also be added to the aqueous phase to force the metal complexes into the organic phase. Other variations incorporate ligands, which form micelles in the aqueous phase, or ligands, which stay in the organic phase, are polar on one end, and so are drawn to the aqueous-organic interface where they react with the metals to form non-polar organic soluble complexes soluble in the organic phase. When the organic phase becomes saturated with relatively high concentrations of complexed copper, the copper must be decomplexed and released into a clean aqueous phase for final electrowinning. Some of the problems associated with the solvent extraction process include the necessity to execute multiple wash steps of the organic phase when chloride leach solutions are being treated, the need to add equilibrium modifiers to facilitate the uptake into and release of copper from the organic phase and the formation of "crud" which forms at the aqueous-organic phase interface causing equipment fouling and organic solvent loss.[9] The primary drawback with this technology is the organic phase. The solvents used in the organic phase include benzene, toluene, chloroform, hexanes and octanes among others; kerosene is the solvent of choice for most large scale production mining opperations.[9] These solvents are typically toxic, flammable, and have adverse environmental impacts. Solvent loss during the extraction process exacts a negative economic toll on the process. Ligand and equilibrium modifier loss is also an environmental and economic problem associated with the solvent extraction process.

1.4 Developing Extraction Technologies

1.4.1 Bioextraction

The term bioextraction describes a broad range of extraction strategies utilizing living or recently living organisms. Phytoremediation utilizes living plants to extract metals from highly contaminated soils such as tailings piles. Plants that have a high tolerance to the contaminants are grown in the contaminated soil, the metals are accumulated by the plants are harvested, and the metals and the biomass are disposed of. This method can be somewhat effective at removing metals from contaminated soils at a particular site but the contaminated biomass still poses a disposal problem.

The extraction of metals from aqueous solution by shredded coniferous tree bark, living algae, non-living fungus, and treated shrimp shells have been investigated.[12-14] Although metal recovery from the biomass was demonstrated in all of the studies, with the exception of the tree bark studies, the effectiveness of the extractant decreased with each use. Furthermore, the total metal ion capacity for the materials was low. The benefits of these systems lie primarily in their cost. The extractants are produced from waste materials or by-products from other processes so their cost is low and they will decrease the overall generation of waste. These systems may find a niche in wastewater treatment operations that have low metal loading, have no desire to reclaim the metals, and require low capital input.

Another approach to immobilizing aqueous metals utilizing bacteria is metal sulfide precipitation. In this process sulfate reducing bacteria are employed to reduce sulfate to sulfide. This method is particularly suited to acid mine drainage remediation where the metal laden water is sulfate laden. The general equation for this reaction is:

$$SO_4^{-2} + M^{+2} + 2C \longrightarrow MS\downarrow + 2CO_2 \qquad \textbf{(vi)}$$

where M is a dissolved metal and C is organic carbon. Addition of an organic carbon source to the system not only provides a carbon source to the bacteria but

$$2\ \mathrm{FeS} + {}^{1}/_{2}\ \mathrm{O_2} + 2\ \mathrm{H^+} \longrightarrow \mathrm{FeS_2} + \mathrm{Fe^{+2}} + \mathrm{H_2O} \quad \textbf{(vii)}$$

also reduces oxygen in the system driving the reaction toward sulfide formation.[15] In wastewaters containing large iron loads the pH is also remediated as amorphous iron sulfide is gradually converted to pyrite (**vii**).[15] Under optimal conditions the metal concentration, and sulfate loads are reduced and the acidic conditions neutralized. The primary drawback though is that the recoverable valuable metals are precipitated out as sludge.

Conversely, bacteria can be used to extract copper from copper sulfide deposits in tailings heaps, contaminated soil, and from undisturbed copper sulfide deposits. The environmental sulfur cycle is outlined in Figure 1.1. Through aerobic respiration, the bacteria oxidize sulfide to sulfate to obtain energy. This biological process is the same one that paradoxically causes acid mine drainage conditions. In recent years the technology has been developed to harness these bacterial processes to extract the metals entrained in the low grade ore that make up the tailings piles. This process is known as bioleaching. Bioleaching has a double benefit; the metals are extracted from the tailings reducing their environmental impact, and the metals can be recovered reducing the need to open new mines. This technology may ultimately change the way copper mining is carried out. A process involving drilling injection wells inoculating them with aerobic bacteria then pumping out the copper containing water for recovery of the copper is being investigated. This method may, in the

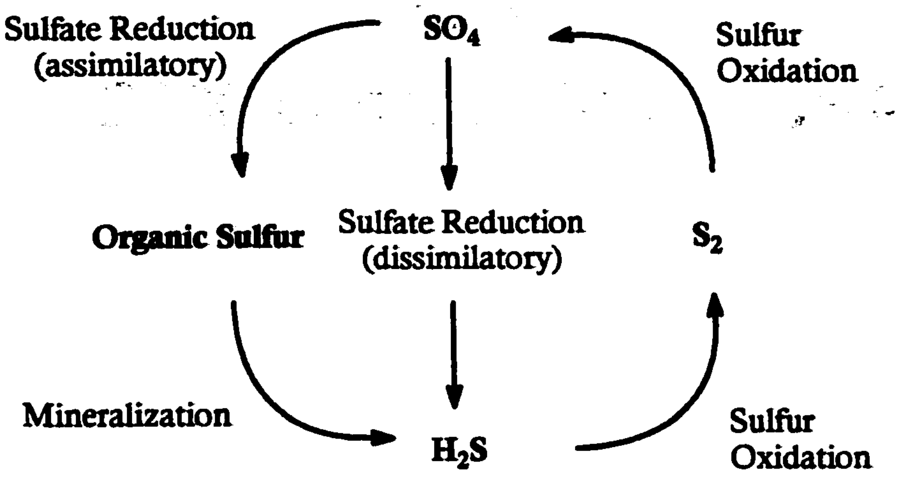


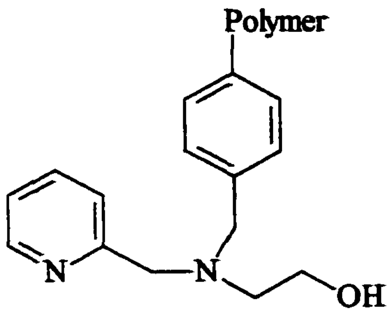
Figure 1.1 A simplified environmental sulfur cycle. In the dissimilatory sulfur reduction process, which represents an aerobic respiration, bacteria utilize sulfate as an oxidant and produce sulfides, which include metal sulfides when metals are present. Under aerobic conditions colorless sulfur bacteria oxidize sulfide and elemental sulfur to sulfate. *Thiobacillus ferrooxidans* can also use ferrous iron as an electron donor and produces ferric iron as well as sulfuric acid.[6]

future, supplant the need for the traditional open pit copper mines. One obstacle facing this process is the low concentration of copper in the leach solution. Until now, it has not been economically feasible to extract copper from such low concentration copper solutions for recovery.

1.4.2 Resin Based Extraction Materials

Swellable resin beads have a long history as the matrix on which ion exchange and metal ion chelation technologies are built. These swellable resin beads are generally lightly cross-linked polystyrene, which is then modified to accommodate the addition of pendant ion exchange or chelating ligands. Occasionally other groups are also added to the resin to decrease the hydrophobicity of the polymer. Polystyrene beads are the solid matrix of the ion exchange system found in most residential water softening systems. There is varied and prolific research in the field of resin modification with the express purpose of developing resins with greater specificity and capacity. Modifying ligands include: phosphonic acid, and bifunctional phosphonic acid-sulfate ligands, linear catechol, thiourea, crown ethers, bis-1,3-diketones, and chelating polymers to name a few.[16-21]

Copper selective ligands have been added to polystyrene beads for the processing of copper leaches.[22] The Dow Chemical XFS materials are a series of aminomethyl pyridine based poly styrene materials. XFS 4196 contains N-(2-hydroxyethyl)-picolylamine (HEPA) **1** and XFS 43084 contains the ligand N-(2-hydroxypropyl)-picolylamine **2**.[22] There are however problems associated with using swellable resin bead technology in high throughput operations. Lightly crosslinked polystyrene beads are highly porous and the extractant ligands are bound throughout the polymer matrix. Many, if not most, of the ligands are buried deep within the polymer bead. The feed solution must diffuse through the bead to reach these sites for extraction to take place. The problem is that process flow rates are much faster than the rate of



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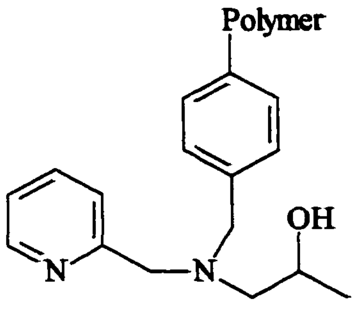

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diffusion through the resin bead. For this reason a material that may have a high capacity in a batch application where the extractant and the feed solution have long contact times has greatly reduced capacity in flow applications.[23] Because of the porous nature of the resin beads they also have a tendency to collapse when subjected to the pressures generated by the fast moving solution in a column application. The beads at the exit end of the column flatten and pack more tightly together which in turn causes an increase in the backpressure of the system. This causes a decrease in metal ion capacity and necessitates periodic backwashing of the column thereby limiting the useful lifetime of the material. In communications with our industrial contacts we have learned that a further problem they have encountered with the resin based material they are testing for copper extraction from leach liquors is that the chloride ion content of the strip solution is high.

1.5 Silica-Polyamine Composite Metal Extraction Materials WP-1, VP-1 and BP-1

WP-1, VP-1, and BP-1 are silica-polyamine composite materials designed to extract metal ions from aqueous solutions while withstanding the rigors of large-scale industrial extraction processes. An anchoring group is horizontally polymerized on porous silica gel in such a way that a monolayer of anchoring molecules is is covalently bound to the silica surface. The anchor containing silica is then reacted with a polyamine to create the silica-polyamine composite extraction material. The polyamines used to create the materials are of two distinct types. Poly (ethyl imine), PEI is a branched polymer with branching occurring at the nitrogen atoms forming a polymer containing primary, secondary and tertiary nitrogens. PEI is used to make WP-1. The other type of polyamine used to make these materials is linear. Linear polyamines consist of a hydrocarbon backbone with pendant amine nitrogen atoms. These polyamines contain only primary amines. Poly (vinyl amine), PVA is a linear polymer in which the nitrogen atom is immediately adjacent to the hydrocarbon backbone and is used to make VP-1. BP-1 is made with another linear polyamine, poly (allyl amine) (PAA). PAA differs from PVA in that there is a methylene carbon inserted between the hydrocarbon backbone of the polymer and the primary amine. The polymers will be discussed in greater detail in a later section.

The revolutionary nature of these materials lies not in the components of the materials but in the properties afforded the materials through the synthetic route. Silica gel materials have a long-standing history of use as separation materials. These materials are traditionally used in chromatographic applications under mild conditions. Silica gel based materials have been avoided for use in large scale industrial separations of metals due to their inability to withstand the harsh conditions associated with these separations. The synthetic process developed at The University of Montana in collaboration with Purity Systems Inc. has led to the development of a silica gel based material that has overcome these problems.[24] WP-1 has been tested through 3000 extraction cycles with less than 10% loss in capacity while BP-1 and VP-1 have been tested through 1500 cycles with negligible to no loss in capacity. Each cycle subjected the materials to loading with copper, elution of the copper with 4N sulfuric acid, and regeneration of the material with 4N ammonium hydroxide all at a flow rate of 10 column volumes per minute (cv/min). The capacity was checked periodically at a flow rate of 2 cv/min.

To complement the long material lifetimes WP-1, BP-1 and VP-1 hold the following characteristics as well, high capacities for many heavy metal ions, selectivity for heavy metal ions with no interference from alkali or alkaline earth metals, the ability to extract these metal ions at high flow rates to very low levels, and the ability to release these captured metals in highly concentrated solutions. WP-1 has copper (II) capacities of 0.93 mmol/g in batch tests and 0.84 mmol/g at flows of 2 cv/min. At flows of 2 cv/min VP-1 has a copper (II) capacity of ~1 mmol/g. WP-1 modified with an ethyl sulfide group has reduced lead concentrations from 150 ppb to less than 2 ppb at flow rates of 40 cv/min.[25] Strip solution fractions containing 32,000 ppm copper have been isolated from a 5 cm^3 column of WP-1. Large volumes (100 ml) of a highly concentrated iron (II) strip solution (40,000 ppm) were collected as well by reusing the same strip solution repeatedly to strip the column after successive loadings.

WP-1 and VP-1 have both been tested under a variety of real and simulated industrial and mine wastewater conditions extracting heavy metal ions from low pH solutions, solutions containing competing chelating ligands such as EDTA, and high temperature (96°-100° C) solutions. In all cases these materials have suffered no adverse effects in performance.[23,26]

1.5.1 Advantages of the Silica-Polyamine Composite Technology

Silica-polyamine composite materials offer many advantages as a scaffolding from which to build many selective metal ion removal materials. The structure of these materials is such that, if one were to look at a cross section of a single particle one would see the silica gel in the center surrounded by a polymer coating. The large surface pores on the silica gel surface, which increase the surface area of the silica gel particle, also act as pockets that fill with polymer crating regions of high polymer density. .

1.5.1.1 *Advantages of Silica-Polyamine Composites as a Foundation on Which to Build Selective Materials*

Much research has been carried out by the Rosenberg group on WP-1, VP-1 and BP-1 describing their physical and chemical characteristics under a variety of conditions. The factors which lead us to believe that the silica-polyamine material WP-1 and its sister materials VP-1 and BP-1 will be effective foundations on which to build a copper selective material are: Physical stability, chemical stability, flow rates and capacity for metal ions.

<u>Physical stability</u> In order to effectively engineer a system utilizing a particular material the physical characteristics of the material should remain constant. For instance resin beads may perform well in an open bed application but their use in a column system is limited due to their fluctuating volumes. Copper selective resin materials can lose up to 24% of their volume when converted from the protonated

acid form to the deprotonated base form.[8] Unlike resin beads polyamine - silica composites retain their physical structure over a broad pH range. Over the course of 3000 cycles described previously there was no discernable change in volume.[27] Ethyl sulfide modified WP-1 was used to extract lead at a flow rate of 40 cv/min producing a back pressure of 30 psi which fluctuated only +/- 2 psi over 750 gal.[25] WP-1 and VP-1 have also been tested at high temperatures with no change in volume or performance.

Chemical Stability Heavy metal extraction materials must be able to withstand the acidic conditions associated with most feed stocks containing dissolved metal ions. They must also withstand the conditions associated with stripping and regenerating the material. The polyamine - silica composites have been subjected to concentrated hydrochloric acid, concentrated sulfuric acid and are routinely subjected to 4 N ammonium hydroxide and 1M sodium hydroxide with no loss in capacity.

Flow rate This is particularly important for materials targeted at high throughput column applications. Materials in these applications must be able to maintain extraction efficiency as well as retain their capacity for the extractant with little contact time. The early work on silica-polyamine composite materials was based on 90 – 105 μm silica gel with an average pore diameter of 150Å The materials were routinely tested at flow rates of 2-3 cv/min. As previously pointed out polyamine - silica composites have been effective at removing heavy metals at flow rates of 40 cv/min. It has been determined however that materials based on larger particle sizes with a smaller average pore diameter require slower flow rates to effectively remove the metal ions to low levels.[26] Unlike resin beads the capacity of polyamine - silica composite materials is relatively unchanged whether tested in batch tests or at flows of 2-3 cv/min.

High capacity The capacity of a material to hold large amounts of extractant is important to process efficiency. A material that retains more metal per cycle will need to undergo fewer strip cycles to recover the same amount of metal as a material of lower capacity. A comparison of WP-1 to IRC-718, a swellable polystyrene based metal extractant containing aminodiacetic acid functional groups, reveals that while IRC-718 has a higher capacity for copper under batch conditions WP-1 retains almost twice as much copper than IRC-718 when the feed stock is flowing at 2 cv/min.

Knowing the parameters within which an extraction material will perform effectively is critical to targeting applications for which the material will be effective. From an industrial standpoint some of the critical factors to be addressed are: How long will the material last? What is the rate at which the processing can be carried out? Will the material change over the period of use? What is the capacity of the material for the extractant? How effective is the material? Under what conditions is it effective? Some of these factors should remain constant throughout a class of materials while others will change with each material.

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CHAPTER 2 The Synthesis of Silica-Polyamine Composite Materials with an Emphasis on Silica Gel and Silanization of the Surface

2.1 Silica Gel – Silanization of the Surface

The use of silica gel as the solid support and its modification is the foundation of the materials developed during the course of this research and therefore will be described in some detail. Silica gel has a long history as the support medium on which to carry out separations. Silica gel is a porous material that can be made in a wide range of sizes, with variable pore volumes, pore diameters and pore configurations. Silica gel is formed through the polymerization of sodium silicate under acidic conditions (**vii** and **ix**). Physical characteristics such as pore diameter and volume, particle size and shape, and surface area are controlled through careful control of acid addition, reaction temperature and reaction pressures. The physical and chemical properties of silica gel contribute to its effectiveness as a solid support over an extensive variety of conditions. Unlike resin beads, silica gel will not shrink or swell depending on the surrounding chemical environment. This is an important factor when considering what to use as a solid support for materials to be used in separations carried out in a column type configuration. Silica is unreactive towards Cl_2, H_2, most acids and most

$$SiO_{2(s)} + Na_2CO_{3(aq)} \longrightarrow Na_2SiO_{3(aq)} + CO_2 \uparrow \tag{\textbf{viii}}$$

$$2HCl_{(aq)} + Na_2SiO_{3(aq)} \longrightarrow SiO_{2(s)} + H_2O + 2NaCl_{(aq)} \tag{\textbf{ix}}$$

metals although it is attacked by F_2, aqueous HF, and alkali hydroxides.[1] It is this last point that is of particular importance to this project because the silica-polyamine composite materials being developed contain an amine polymer, which may require a base regeneration step during their use and or elevated pH during subsequent modification reactions. Overcoming the susceptibility of silica gel to basic pH conditions was the first step in developing a successful silica-polyamine composite material.

Silica gel is a type of silica (SiO_2) also known as amorphous silica. Crystalline silica compounds are arranged such that four shared oxygen atoms surround each silicon atom in a tetrahedral arrangement. In silica gel the crystalline structure is disrupted by hydroxyl groups to give regions of $Si(OSi\text{-})_3OH$, $Si(OSi\text{-})_2OH_2$ as well as the $Si(OSi\text{-})_4$ structure. The silanol groups terminate the Si-O polymer building where they occur, consequently creating the pores and therefore the surface of the silica gel is rich in silanol groups. The silanol groups on the surface of silica gel are responsible for the polar nature of silica gel and its ability to hydrogen bond, which is important when carrying out normal phase chromatography with silica gel. These sites are also the primary sites of base hydrolysis causing the breakdown of the gel when exposed to basic pH conditions. Another well known use of silica gel is as a desiccant, the surface silanol groups cause the silica gel to be very hygroscopic. It was through this property of silica gel that Mary Wirth and coworkers at the University of Delaware developed a strategy to create a protective ultrahigh density surface covering on the silica gel.[2] Professor Edward Rosenberg of The University of

Montana applied this technique to attaching an anchoring molecule to larger particle silica gel for subsequent attachment of the polyamine.[3]

Traditionally, chelating groups are bound to silica gel by first reacting the chelating group with a functionalized silane followed by bonding to the silica surface (Figure 2.1).[4-6] These organosilanes hydrolyze then bind to the silanol sites on the silica through the process of hydrogen bonding followed by covalent bond formation with concomitant loss of water.[7] When large molecules such as polymers are introduced, steric hindrance becomes a factor in preventing uniform coverage of the silica surface. Typical silica surface coverage with organochlorosilanes for reverse-phase chromatography coatings is less than 50% due to steric effects.[8] The presence of water in the hydrolysis step (either added, on the substrate surface, or from the atmosphere) will produce polymeric oligomers in solution, increasing steric effects and causing the polymer to deposit on the silica surface in clumps rather than in uniform sheets. As a consequence, many silanol sites on the silica surface remain unreacted and exposed. The regeneration of many chelating materials involves a step in which the material is rinsed in base. Attack of the unreacted silanol groups by hydroxide ions results in eventual disintegration of the silica, rendering the silica-chelate systems prepared in this manner inappropriate for use in remediation or industrial recovery projects.

Alternatively, the organosilane can be bound to the surface of the silica gel by a process known as horizontal polymerization.[9] In this process the silica gel is first washed in acid to remove any salts that may have been entrained in the silica gel during its synthesis and to ensure that the surface hydroxyl groups are fully protonated. The silica gel is then dried completely and then rehydrated to produce a

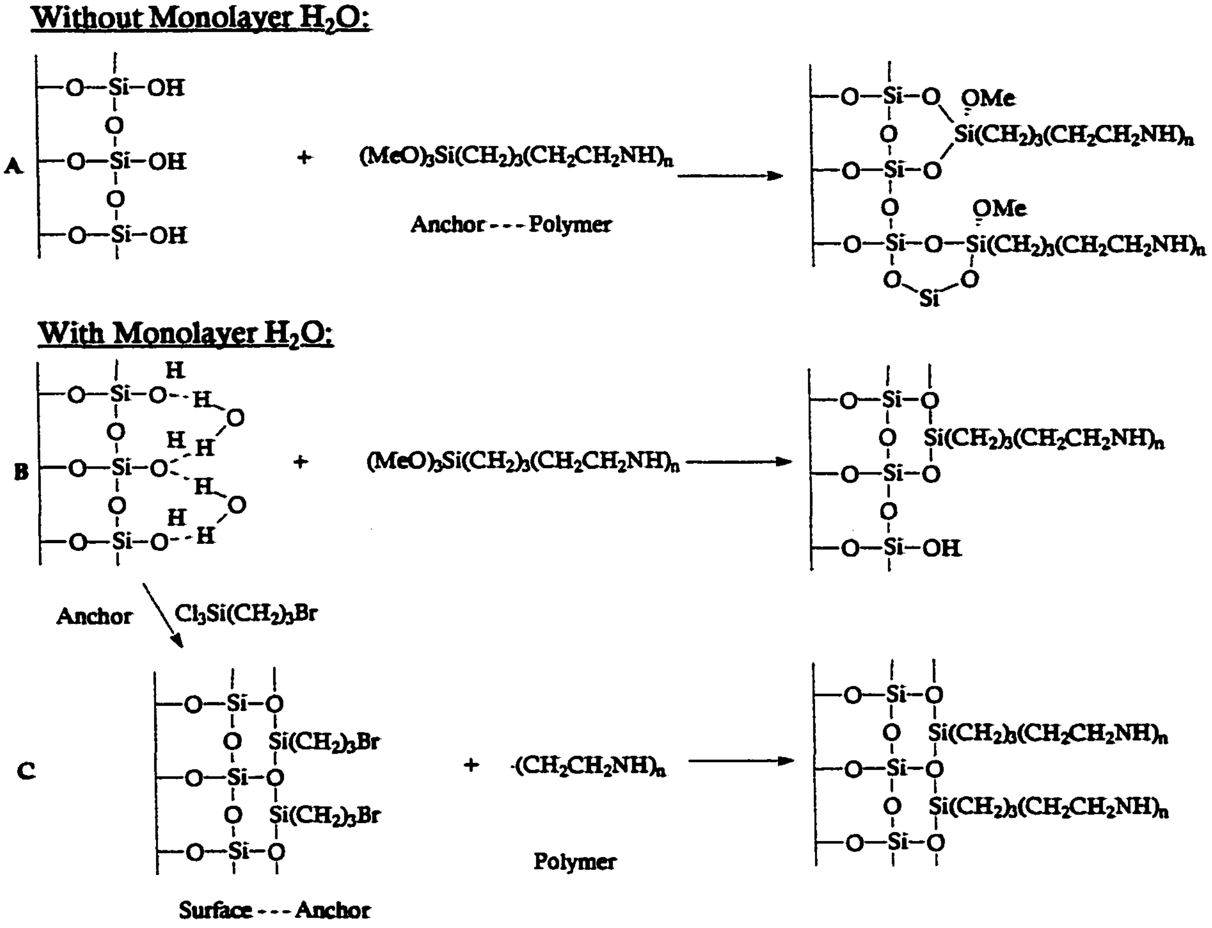

Figure 2.1 Organosilane anchor attachment schematic. Although a highly stylized schematic; it is useful to show the higher organizational structure of the stepwise hydration-anchor-polymer synthetic route. Route A represents the Ramsden synthesis, route B hydrated Ramsden synthesis and route C the horizontal polymerization used in the present discussion of silica-polyamine composite materials.

monolayer covering of water on the surface of the gel. The hydrated silica gel is then reacted with a trifunctional organosilane anchor in a nonpolar solvent to produce a silica surface that contains a horizontally polymerized monolayer of anchor. The critical factors in this portion of the synthesis of the silica-polyamine are the hydration of the silica gel surface with a monolayer of water and the use of a trifunctional organsilane reagent in this case a organotrichlorosilane ($RSiCl_3$). The water on the surface of the silica gel ensures that reaction of the silane reagent does not occur until the reagent reaches the surface of the gel where the silane reagent then reacts with neighboring silane groups as well as with the surface of the silica gel. Utilization of a nonpolar solvent helps to drive the reaction to completion as the resulting HCl is released from the reaction medium as a gas.

Characterization of the surface bonding is very difficult by infrared (IR), and far infrared (FIR) techniques. One method that can elucidate the surface bonding characteristics is cross-polarization magic angle spinning nuclear magnetic resonance spectroscopy (CP-MAS NMR). The cross-polarization technique is particularly useful in elucidating the surface of the silica gel in ^{29}Si NMR, as the efficiency of the cross-polarization is dependant on the Si-H distance the internal silicon atoms do not contribute to the CP-MAS spectrum.[10] It has been shown by CP/MAS ^{29}Si NMR that surface silanol groups decrease as the functional silanes increase from mono- to trifunctional.[11] It has also been inferred from CP/MAS ^{29}Si NMR studies that unreacted geminal silanol groups, $(\text{-O})_2Si(OH)_2$, remaining on the surface of the silica gel are distorted resulting in a decrease in the distance between the silicon atom and the hydrogen atom. This distortion may be caused by the resulting horizontally polymerized surface which covers them or a rearrangement of these atoms on the silica surface.[12] It was believed that by following this method of washing the silica gel, drying, hydrating the surface with a monolayer of water, and applying the organosilane anchor prior to attaching the polyamine a material could be produced which would be stable to the pH extremes the material would be subjected to during industrial use.

During the course of filing for a U.S. patent it was discovered that H. E. Ramsden had synthesized and patented a chromatographic packing material by reacting poly(ethylene-iminopropyl) trimethoxysilane (available from Unified Chemicals) directly with unmodified silica gel, followed by heat curing (Reaction path A, Figure 2.1).[13] This produces a material which at first glance appears to be identical with WP-1 (that is, silica gel-Si-Propyl-PEI). However, it was believed, for the reasons outlined above, that the different synthetic route to WP-1 - hydration of the silica surface, followed by the addition of a short-chained anchor before binding of the polymer (Reaction path C, Figure 2.1) - leads to an intrinsically different material. To investigate the capacity and durability differences between WP-1 and the Ramsden material, copper ion capacity and material lifetimes tests were performed.

A third silica composite material was also synthesized by first hydrating the silica gel, then continuing in the same fashion as the Ramsden material synthesis (Reaction path B, Figure 2.1). Examination of this "Hydrated Ramsden" composite allows a direct comparison between horizontal polymerization of a small-chain organosilane anchor to the silica surface prior to polymer addition and traditional vertical polymerization of the silane groups on the surface while attached to a large polymer, as demonstrated by material performance and mechanical durability.

To investigate the effectiveness of horizontal polymerization on the chemical stability of WP-1 a number of experiments were carried out. CP-MAS ^{13}C NMR experiments were carried out on two organosilane modified gels. One gel was synthesized using raw unmodified silica gel and the other was synthesized on acid washed, hydrated gel. Two sets of experiments were carried out to compare the performance characteristics of WP-1, the material developed by Ramsden (hereafter called Ramsden), and a material Hydrated Ramsden. The first experiment tested the dynamic (flow) capacity of each material using a constant metal ion concentration for five loading, strip, and regeneration cycles. Each cycle also exposes the material to 4N sulfuric acid and 4N ammonium hydroxide these are the pH extremes necessary to strip the loaded metal from the column and to regenerate the material respectively. The practical lifetime of the materials was determined by continuing the cycle tests and the checking the capacity at predetermined intervals up to 3000 cycles. Further, Scanning Electron Microscope (SEM) studies were performed on WP-1 and Ramsden before Cu(II) adsorption, and after Cu(II) loading.

2.2 Results and Discussion

2.2.1 Material Synthesis

The basic approach to the synthesis of silica-polyamine materials is shown in Figure 2.1 reaction path C. Commercially available silica gel is humidified to yield a surface possessing a monolayer of water.[9] To achieve a monolayer of water on the silica gel the silica gel is dried at 110°C and weighed until there is no further weight loss between successive measurements. The dried silica gel is then rehydrated by passing humidified (50% - 60% humidity) air over the silica gel and weighing until no further weight gain is recorded. This process is reported to achieve a monolayer of water molecules on the silica gel surface.[9] The humidified silica gel is then reacted with an organotrichlorosilane in a nonpolar solvent. The process provides a surface which is at least 80% coated with an organosilane silane anchor ($Si(CH_2)_nY$), to which chelating groups can be attached. According to ^{29}Si analysis by Wirth, a comparison of the mole ratio of covalently bonded ≡SiR groups to the total original surface silanols, showed that a coverage of a of 94% could be reached.[12] The surface silanol groups can be measured in a number of ways including infrared (IR) spectroscopy and solid state NMR spectroscopy. These methods usually involve addition of a monohalodimethylsilane to the silica gel under anhydrous conditions. IR analysis of the surface modified silica gel focuses on the peaks at 3743 and 975 cm^{-1}, the peaks associated with Si-O-H stretching frequencies, and peaks at 2962, 2148, and 912 cm^{-1}, peaks associated with C-H, Si-H and Si-CH3 stretching frequencies, respectively.[14] Comparison of the spectra of unmodified silica gel and modified silica gel show the disappearance of the peaks at 3743 and 975 cm^{-1} and the appearance of peaks at 2962, 2148 and 912 cm^{-1}.[14] Furthermore these peaks can be compared with an internal standard to quantify the resulting peaks based on peak area or peak height.[14]

The synthesis of the Ramsden materials (Reaction paths A and B Figure 2.1) suffers in two ways from the use of $(MeO)_3Si(CH_2)_3PEI$. First, the addition of such a large reagent sterically hinders complete, uniform coverage of the silica surface by the pendant silane groups. Secondly, although water promotes bonding of the reagent to the silica surface, addition of water to the reaction medium inhibits complete uniform deposition of silane groups by assisting the water-catalyzed self-polymerization of $(MeO)_3Si(CH_2)_3PEI$ in solution before bonding, which induces clumping of this material. Thus, although the outer surface may appear to be covered by $-Si(CH_2)_3PEI$ group, the silica surface has not been covered effectively, leaving it vulnerable to degradation by base.

By initially binding $Cl_3Si(CH_2)_3Br$ to the hydrated silica surface in the presence of only trace amounts of water (specifically, that present as the monolayer on the silica surface), the horizontal polymerization of these groups is maximized, resulting in more complete coverage of the silica surface. This can be seen in the comparison of solid state CP-MAS ^{13}C NMR spectra for the organosilane anchor $-Si(CH_2)_3Br$ bound to unmodified silica gel (Figure 2.2 top) and to hydrated silica gel (Figure 2.2 bottom). The spectrum of the non-hydrated gel shows a methoxide peak, due to the reaction of exposed chlorosilane with a methanol wash. The presence of the methoxide peak indicates incomplete surface coverage of the silica surface with polymer. The same peak is barely visible in the spectrum of the hydrated gel, and shows that not only is our surface coverage better using the hydrating process, but that ^{13}C NMR can be used to determine relative silica surface polymer coverage. A more complex ^{29}Si analysis, which led to the same conclusion, was previously reported.[12] Additionally, the use of a dry hydrophobic solvent (in this case,

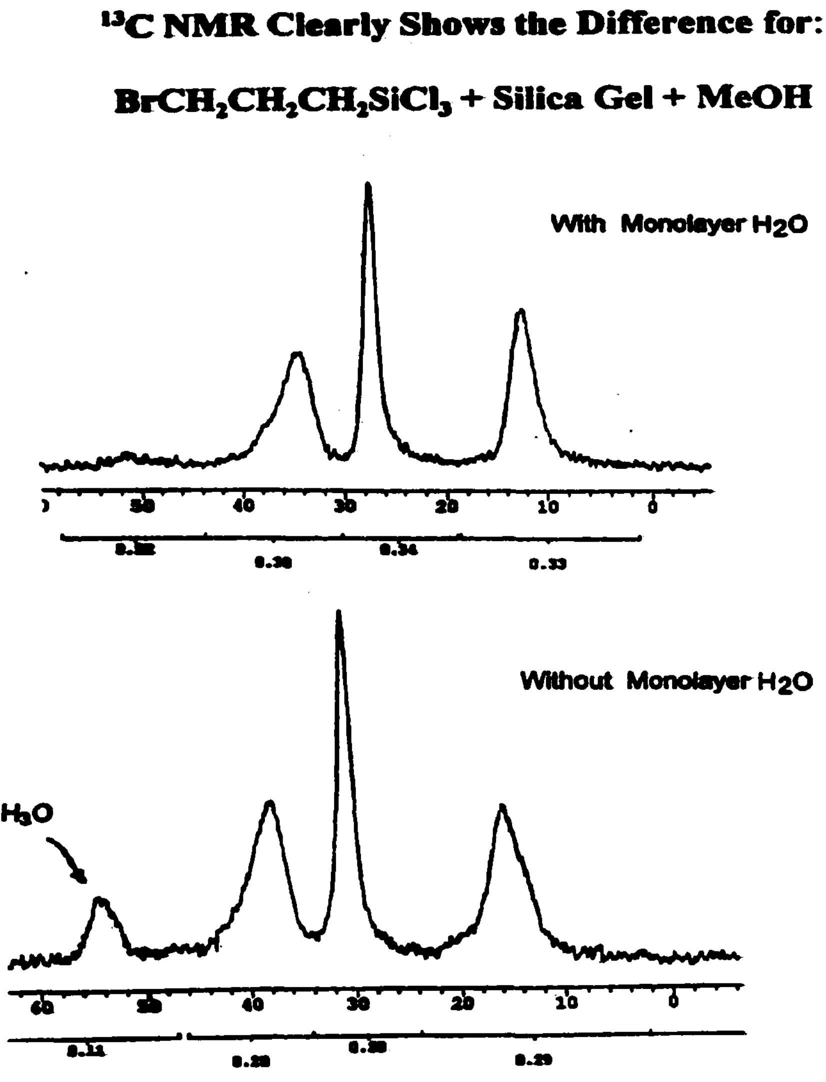

Figure 2.2CP-MAS ^{13}C NMR Spectra of the silane anchor, $Br(CH_3)_3SiCl_3$, attached to hydrated silica gel top, and untreated silica gel bottom. The other three peaks are due to the three carbons of the propyl group.

heptane) acts in two ways to improve surface coverage. First, it keeps the monolayer of water on the silica surface intact, preventing self-polymerization of the silane reagent in solution before reaching the silica surface, and secondly, the reaction by-product, HCl, is immiscible in the solvent which causes it to leave the reaction medium as a gas, pushing the reaction further to completion. Furthermore, there is no bulky polymer molecule bound to the organosilane molecule to further complicate the attachment of the silane to the silica gel surface.

The next step in the gel synthesis is the addition of the polyamine chelator PEI, a highly branched polymer with an approximate 35:35:30 distribution of primary:secondary:tertiary amine sites. The morphology and function of the polymer will be discussed in more detail in the next chapter.

2.2.2 Analysis of Performance Characteristics

The most prominent physical difference between our gels and the Ramsden and Hydrated Ramsden gels was their density; WP-1 is 41% more dense than Ramsden and Hydrated Ramsden (WP-1 has a working density of about 0.45 g/cm^3 vs. and about 0.32 g/cm^3 for the Ramsden gels). When wet, Ramsden and Hydrated Ramsden appear more translucent than WP-1. During the first five cycle tests of Ramsden material, a small void pocket began to form on the inlet side of the column. After 100 cycles a 2 mm void was present on the inlet side of the column, which increased to 5 mm by 500 cycles. Hydrated Ramsden also formed a small void pocket during the initial capacity test. During the lifetime cycle test a 1 mm void formed at 50 cycles which increased to 4 mm by 1000 cycles. In contrast the WP-1 column showed no change in occupied volume in either test.

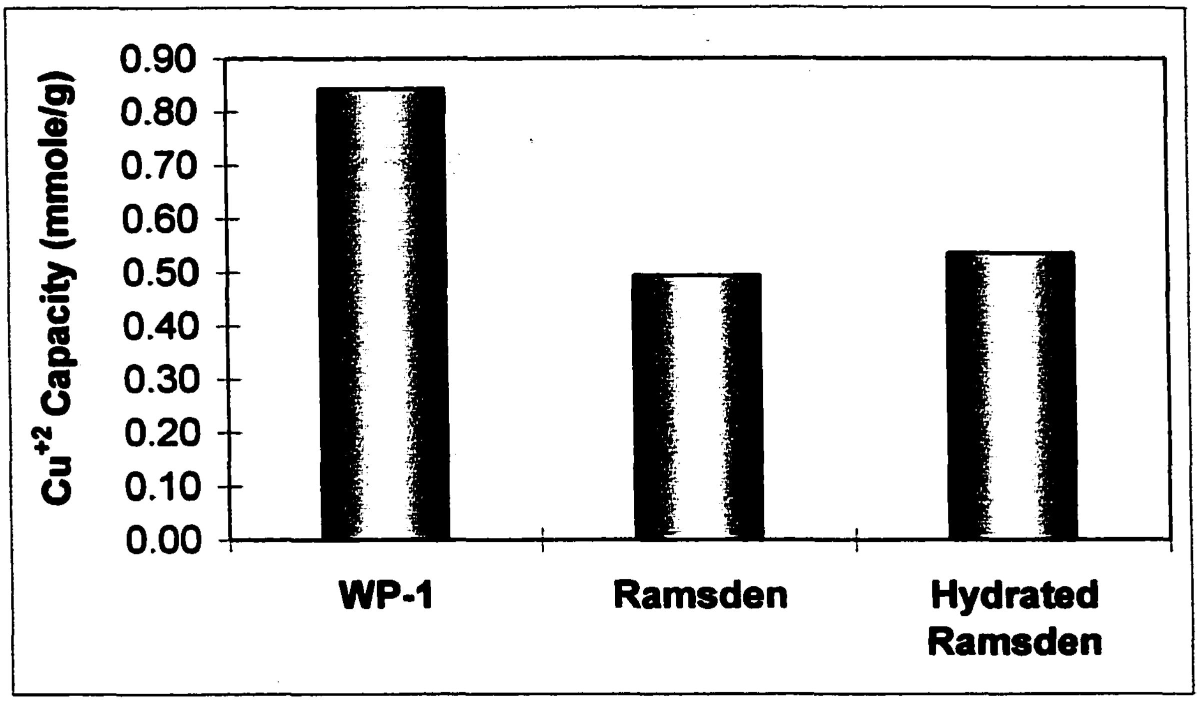

Figure 2.3 The copper(II) capacity of three silica-polyamine composite materials under flow conditions of 2 bed volumes per minute. The feed stock was 50 mM $CuSO_4$ at intrinsic pH.

As shown in Figure 2.3, the maximum Cu(II) ion capacity per gram of the Ramsden and Hydrated Ramsden materials were only 59% and 64% the highest capacity of WP-1 (0.50 mmole/g for Ramsden and 0.54 mmole/g for Hydrated Ramsden vs. 0.84 mmole/g for WP-1). In industrial and remediation applications capacity per volume of gel is also important. Based on 5.5 mm^3 of gel material per column, WP-1 has an average copper capacity approximately 145% of the maximum capacity for both Ramsden and Hydrated Ramsden materials.

Of utmost importance in industrial and remediation applications is how long a material will maintain its original performance characteristics. The cycle test was designed to determine how repeated use affects the capacity of gels. Figure 2.4

shows the comparison of lifetime cycle tests of WP-1, Ramsden and Hydrated Ramsden materials. After 3000 cycles there was no visible change in the volume of WP-1 and the capacity was 94% of the highest capacity recorded. On the other hand, the testing of the Ramsden gel was stopped after 500 cycles due to an increase in back pressure that compromised the structural integrity of the column. Similarly, Hydrated Ramsden testing had to be stopped prematurely due to increased back pressure. While there are not enough data points to comment conclusively on the capacity behavior of the Ramsden materials, the data do indicate a steep and steady decline in the capacities of Ramsden and Hydrated Ramsden even if the gels remained useable. The compression of Ramsden and Hydrated Ramsden suggests a

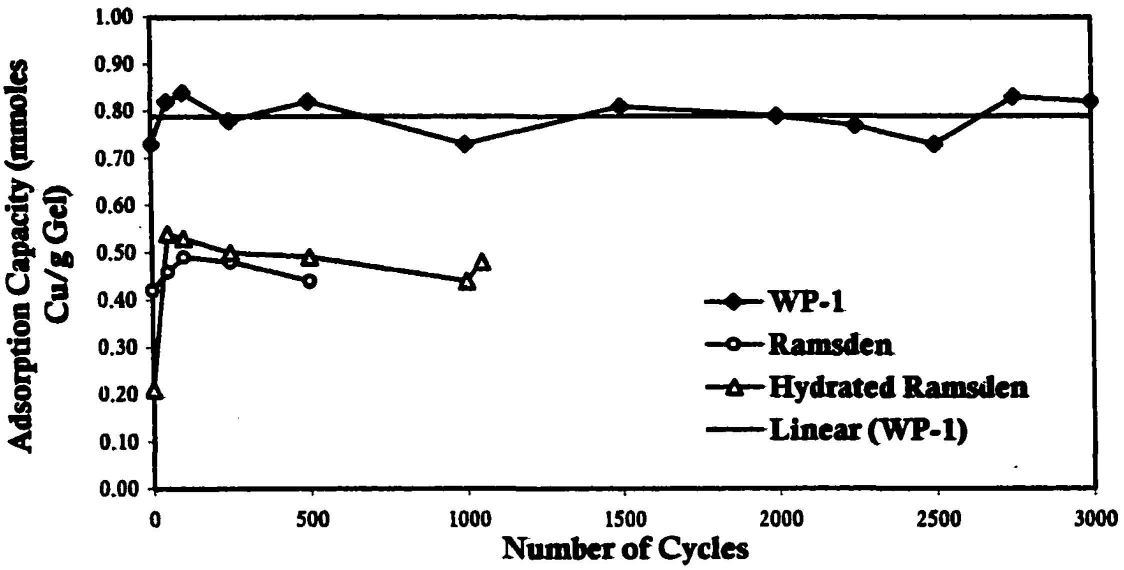

Figure 2.4 The lifetime of three different silica-polyamine materials as measured by the copper capacity of the material. Each cycle comprises loading, acid strip and base regeneration. The Ramsden and Hydrated Ramsden materials failed prior to 1500 cycles. WP-1 did not fail over the course of testing.

deterioration of the materials due to instability of unprotected silica surface when exposed to base.

A more physical view of our materials can be gained from SEM (Scanning Electron Microscopy), which enables us to visualize differences in the gross topography of the surfaces of metal-free and metal-containing gels. Micrographs of the surfaces of metal-free WP-1 and the Ramdsen materials are indistinguishable from that of bare silica gel. Micrographs of the copper-loaded composite materials reveal a surface that appears to be more densely packed and uniform for WP-1 than the Ramsden material (Figure 2.5a and b). This difference is consistent with an improved surface coverage of the silica surface using our two-step synthetic method.

2.3 Conclusions

Solid state CP-MAS NMR has been shown to be an effective tool to determine the type and extent of silane bonding at the surface of the silica gel. While this method may be the only way to get a clear picture of the surface chemistry it is not a tool available to this project due to the vast NMR time demand required to carry out the experiments.

Empirical evidence however strongly suggests the superiority of the horizontal polymerization over conventional methods for attaching a silane anchor to the surface of silica gel. The decreased copper(II) capacity of the material made following the Ramsden preparation, the much shorter useful lifetime of the material, and the more clumped appearance of the polymer on the surface of the silica gel, coupled to the synthetic procedure for making the material all lead one to the

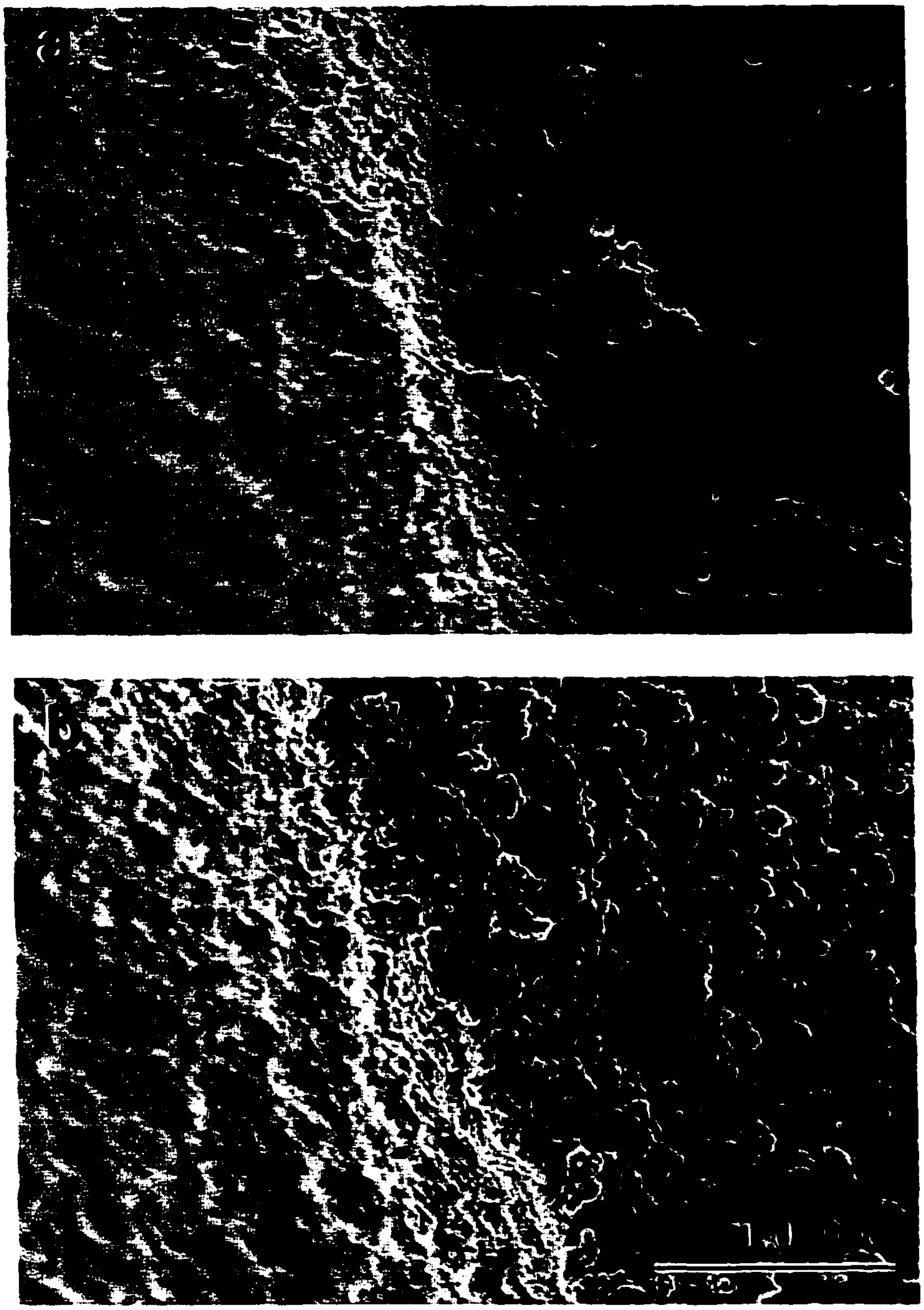

Figure 2.5 Scanning electron micrographs of a) WP-1 b) Ramsden. It is clear from the micrographs that the WP-1 has a much smoother surface and appearance than does the Ramsden material. The Ramsden has a more clumped appearance which one would expect from the synthetic procedure used to make the material. The WP-1 has a much more uniform surface morphology which one would also expect due to the synthetic route used to produce the material

following scenario. In the Ramsden procedure the polymer is prebound to the silane containing anchor. To react the silane/polymer moiety with the silica gel surface the two reactants are combined in a non-polar solvent and water is added; this water promotes intramolecular reaction between the silane groups as well as between the silane groups and the silica gel surface. Some, if not most, of the silane groups react with each other before coming in contact with the silica gel surface, thus causing the large bulky polymer molecule to bunch-up. The silane anchor, which is the point of attachment between the polymer and the silica gel, has diminished reactivity due to the intramolecular reactions and the remaining reactive silanes may be buried within the polymer. Also the steric hindrance of the large bulky polymer may cause vast areas of unreacted surface on the silica. The surface binding can be envisioned as analogous to a deciduous forest. From the air the canopy appears to be a solid covering of the earth, while in reality the points of attachment, the trunks, are few and far between with vast expanses of bare ground. The unreacted surface of the silica gel is prone to attack by the hydroxide ions in basic solutions, which leads to degradation of the silica gel on repeated exposure to the highly alkaline solutions that are required to regenerate the materials. On the other hand the WP-1 showed no such degradation suggesting that bonding a surface monolayer of organosilane anchor to the surface of the silica gel allows a smoother, denser layer of polymer to be applied to the silica gel surface resulting in higher copper capacities. The lack of material degradation points to greater surface coverage of the silica surface which may be coupled to a self repair mechanism in which the polymer acts to hold the hydrolyzed anchor in place relative to the silica surface allowing it to rebond under the right conditions.

2.4 Experimental

2.4.1 Synthesis

WP-1 and Ramsden were synthesized as outlined in United States Patents # 5,695,882 and 4,540,486, respectively. Hydrated Ramsden was synthesized in an identical fashion to the Ramsden material, except hydrated silica gel was used.

2.4.2 Analysis

2.4.2.1 Reagents

Deionized water was used to prepare all solutions and for all rinses unless otherwise noted. Metal solutions were prepared from reagent grade metal salts ($CuSO_4 \cdot 5H_2O$, $FeSO_4 \cdot 4H_2O$ or $NiCl_2 \cdot 6H_2O$) and the pH of the solutions was adjusted as required using reagent grade H_2SO_4 (JT Baker Chemical), and NH_4OH (EM Science). 4N sulfuric acid and 4N ammonium hydroxide solutions were prepared from the same reagent grade sulfuric acid and ammonium hydroxide, respectively.

2.4.2.2 Apparatus

Dynamic flow experiments were carried out using a column fashioned from a 5 mL disposable syringe fitted with frits at both ends and filled with the material being tested. The column was attached to a variable flow FMI Lab Pump Model QG150 (Fluid Metering Inc., Syosset, NY), set to a flow rate of 10 mL/min. Solution intakes were controlled by computer activated solenoid valves (Cole-Parmer) using a PC with software developed for this application by Gamble and Associates Ltd., LLC (Pasadena, CA).

2.4.2.3 Equipment

UV-Vis data were measured on a Perkin-Elmer Lambda-II Spectrometer. Flame Atomic Absorption data were measured on Unicam 969 Flame Atomic Absorption (FAA) Spectrometer. ^{13}C NMR data were obtained on a Varian Unity Plus 400 MHz NMR with CP-MAS solid state attachments. Batch samples were shaken on a Mistral Multi-mixer at speed setting 4. Samples were mounted for scanning electron microscopy (SEM) with carbon adhesive tape to aluminum studs, coated with 100Å chromium in an IBS/TM200S ion beam sputterer (VCR Group, Inc., South San Francisco, CA) and viewed on a S-4500 cold field emission scanning electron microscope (Hitachi Ltd., Japan).

2.4.2.4 Experimental Methods

2.4.2.4.1 Batch Tests

WP-1 (0.2000 ± 0.0001 g) was weighed into a glass vial with a screw top. 20 mL of a metal ion solution at pH 3.4 and 25°C was added to the vial via volumetric pipette and the vial capped. For concentration studies, the initial solution concentrations were 0.003125, 0.00625, 0.0125, 0.0250, 0.0500, 0.100 and 0.200 M. For all other studies, the solution concentrations were 1.0 mM. After 24 hours of shaking, each solution was filtered, preserved with 1 drop of trace metal quality HNO_3 (Fisher Scientific), and tested for metal ion concentration.

2.4.2.4.2 Dynamic Flow Capacity Tests

For each test, a column containing ~5.5 cm^3 of material (2.50 g of WP-1, 1.75 g of Patent 4,540,486 (Ramsden), or 1.75 g of Hydrated Ramsden was assembled. The column was attached to the pump, and 50 mL of H_2O was run through the column to wet the gel surface. Depending on the material being tested, 40, 60, or 80 mL of 50 mM copper ion solution was pumped through column, followed by a 40 mL H_2O rinse. Copper ion solution volumes were chosen to ensure full loading of the column with a minimum volume of metal solution. The total flowthrough volume was collected for analysis by UV-Vis. The Cu(II) on the column was eluted with 5 mL of 4N H_2SO_4, followed by 15 mL of H_2O to create an elution volume of 20 mL which was also collected for UV-Vis analysis. The column was rinsed with an additional 85 mL of H_2O. Regeneration with 10 mL of 4N ammonia was followed by a final H_2O rinse (100 mL). This cycle, excluding the first (wetting) step, was repeated 5 times for each column.

2.4.2.4.3 Material Lifetime Test

The initial capacity of the materials for copper was determined as for the dynamic capacity tests, and the capacity of each material determined after 50, 100, 250, 500, 1000, 1500, 2000, 2250, 2500, 2750 and 3000 cycles (as permitted by the material). Between capacity measurements the cycle was modified to the following protocol: the pump flow rate was increased to 50 mL/min; none of the flowthrough was collected, and the volumes of solutions were changed to: 5 mL of copper sulfate, 2.5 mL water rinse, 5 mL of 4N H_2SO_4, 12.5 mL water rinse, 8.3 mL regeneration with 4N NH_4OH and a final 7.13 mL water rinse.

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CHAPTER 3 The Polyamines

3.1 Introduction

The polymers investigated over the course of the investigation of the metal extraction materials were limited almost exclusively to a class of polymers known as polyamines. There were three polyamines that were investigated. These were poly(ethylene imine) (PEI), poly(vinyl amine) (PVA), and poly(allyl amine) (PAA). The chemical composition of these three polymers is quite similar while the structure is different enough to give the materials that are made from them unique properties. They do however, all share some common characteristics that make them a particularly exciting class of polymers for creating materials designed to extract metal ions from aqueous media.

3.1.1 Advantages of Using Polyamines

The polymer itself offers many advantages in these types of applications: 1) The polyamines are water soluble, which makes the particle surface more hydrophilic than the surface of resin based materials. 2) The polymers contain the metal binding agents (chelating agents) as an integral part of their structure. 3) These chelating agents also offer sites for facile addition of ligands, molecules which can fine tune the metal selectivity of the material.

3.1.1.1 Water Solubility

The water solubility of the polymer is important in two respects. From an environmental standpoint it negates the use of highly toxic organic solvents in reactions involving the polymer. Addition of the polymer to the treated silica gel and many of the ligand addition reactions carried out to date have been done in water, methyl alcohol or a mixture of the two. Another critical environmental factor is that these materials can be used to extract the metal atoms, ions and complexes directly from aqueous media without first extracting them out into a highly toxic often flammable organic phase first.

The performance of the material is also enhanced due to water soluble nature of the polymer. When the material is in an aqueous environment the polymer is able to flow through the polymer coating and into the silica gel pores, which are also coated with polymer. This allows more contact between the dissolved metal ions and the chelating elements of the polymer and hence more efficient extraction at high flow rates.

3.1.1.2 Integrated Chelating Agents

The polyamines PEI and PVA contain approximately 35% by weight amine nitrogen atoms. Nitrogen atoms have five valence electrons, three of which participate in covalent bonding the other two, the lone pair, do not. It is the lone pair of electrons that are important for metal chelation. The lone pair of electrons on nitrogen is however available for participation in coordinate covalent bonding with metal atoms, ions and complexes. The strength of these bonds depends on the nature of the nitrogen atom and the nature of the metal being bound. The lone pair of electrons is also able to coordinate with hydrogen ions, which is responsible for nitrogen's basisity. The ability of the polyamine to complex a given metal depends on the stability constant of the metal complex relative to dissociation of

$$R_xNH_{4-x}{}^{+} + M^{+}n \rightleftharpoons R_xH_{3-x}M^{+n} + H^{+} \qquad \textbf{(x)}$$

the protonated amine. This relationship is shown in equation **x**. These nitrogen atoms are incorporated into the polymer through chemically robust carbon - nitrogen bonds that have the ability to withstand the conditions likely encountered during metal extraction processes. The sheer density of the nitrogen atoms coupled with the conformational freedom afforded through their incorporation into a water soluble polymer makes this arrangement particularly effective at removing contaminant metals from aqueous solutions.

3.1.1.3 Ease of ligand addition

The unshared pair of electrons on the nitrogen offers another advantage besides its ability to form coordinate covalent bonds with metal atoms and ions. These electrons also allow facile nucleophilic substitution reactions to occur at 1° and 2° amine sites. These amines react readily with aliphatic halogen containing molecules, as well as other electrophilic molecular substituents, to form chemically robust carbon - nitrogen bonds. This is important for three reasons 1) the physical stability of the material is entirely dependent on the nature of the chemical bonds holding the material together, 2) many molecules which could be of interest as modifying ligands are already available commercially containing electrophilic aliphatic substituents, and 3) the relative ease with which most of these reactions takes place means that addition of the ligands to the polymer can usually be accomplished in one step and under mild reaction conditions.

3.1.2 The polymers

3.1.2.1 Poly(ethylene imine) PEI

Poly (ethylene imine) is a highly branched water soluble polymer containing carbon, hydrogen and nitrogen atoms (Figure 3.1). The ratio of nitrogen to carbon atoms is 2:1 with the nitrogen atoms in a 35:35:30 ratio of RNH_2 : R_2NH : R_3N ($R \neq H$). PEI is synthesized via acid catalyzed polymerization of ethyleneimine (3), which is formed from monoethanolamine (xi). The

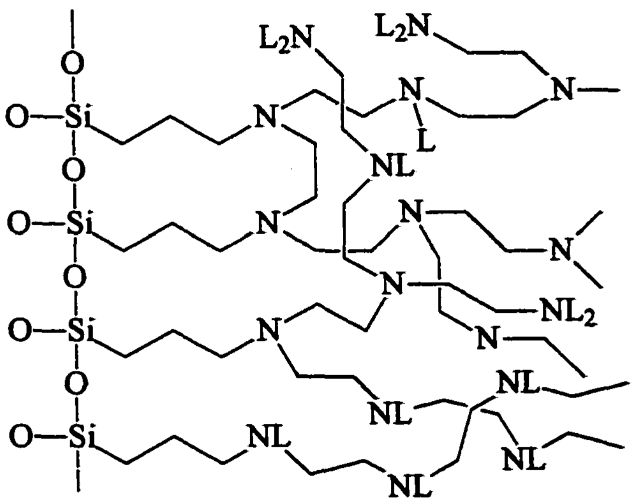
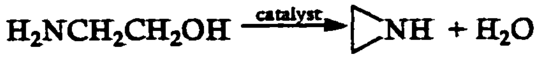
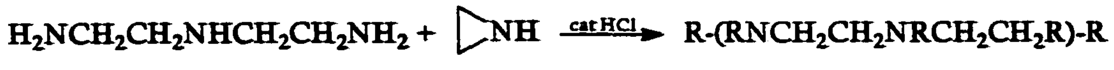


Figure 3.1 The generalized structure of PEI bound to the surface of silica gel. On WP-1 L=H on PEI modified gels WP-2 and WP-3 L=H or the added ligand.



$$H_2NCH_2CH_2OH \xrightarrow{catalyst} \text{(CH}_2\text{)}_2NH + H_2O \qquad \text{(xi)}$$

3



$$H_2NCH_2CH_2NHCH_2CH_2NH_2 + \text{(CH}_2\text{)}_2NH \xrightarrow{cat\,HCl} R\text{-}(RNCH_2CH_2NRCH_2CH_2R)\text{-}R \qquad \text{(xii)}$$

polymerization is started on seed N-(2-aminoethyl)-1,2-ethylenediamine (xii). WP-1 is the silica - polyamine composite material synthesized by covalently bonding poly (ethylene imine) to porous silica gel via a halopropyl anchor. Many versions of WP-1 have been made utilizing two different molecular weights of the polymer. WP-1 1,200 and WP-1 23,000 utilize 1,200 M.W. poly (ethylene imine) and 23,000 M.W. poly (ethylene imine) respectively and PEI as large as 750,000 M.W. has been used to make WP-1. PEI was the first polymer to be used in creating the silica-polyamines in the Rosenberg lab. Because of its sheet-like highly branched structure it was dubbed the "fishnet" polymer. Modification of PEI is limited to the 1° and 2° amines contained in the polymer. Because the modifying ligand cannot react at the 3° sites and may be hindered from reaction with the 2° amines inside the polymer network the modifying ligand may be present in such low abundance that the resulting material will not possess the desired characteristics. Furthermore, the 3° amines detract from the uniformity of a ligand modified system and may interfere with the overall selectivity of the material, especially at high pH. It has however been modified to produce WP-2, which contains aminoacetic acid functional groups and WP-3, which contains either an aminoethylene sulfide functionality on the early materials or a dithiocarbamate functional group on more recent WP-3. Both of these materials posses characteristics distinctly different than the parent WP-1, and will be discussed more fully in a later section.

3.1.2.2 Poly(vinyl amine) PVA

Poly (vinyl amine) is a linear water soluble polyamine also containing carbon, hydrogen, and nitrogen atoms. The ratio of nitrogen to carbon atoms is again 2:1 but the nitrogen atoms in the polymer are exclusively primary amines. The silica -

polyamine composite material synthesized by covalently bonding poly (vinyl amine) to halopropyl coated porous silica gel is known as VP-1. Versions of VP-1 have been synthesized utilizing different molecular weight poly (vinyl amine) they are PVA 2000, PVA 5000, PVA 23,000, and PVA 40,000. The number signifies the molecular weight of the polymer. PVA was the second polymer extensively tested for use in the silica-polyamine composites. The primary attraction of this material is that it contains exclusively primary amines. Addition of modifying ligands to materials based on PVA should react with equal ease throughout the polymer network, with the possible exception of the amine groups that bind the polymer to the surface anchor which will have become 2° or 3°. Additionally the 1° amine sites open the possibility of reacting two modifying ligands at each nitrogen yielding tridentate ligands or even bifunctional modifications.[1] There are some drawbacks to the use of PVA however, primary among them is cost and availability. PVA is not yet produced on a commercial scale, therefore the cost was high when considering large industrial scale

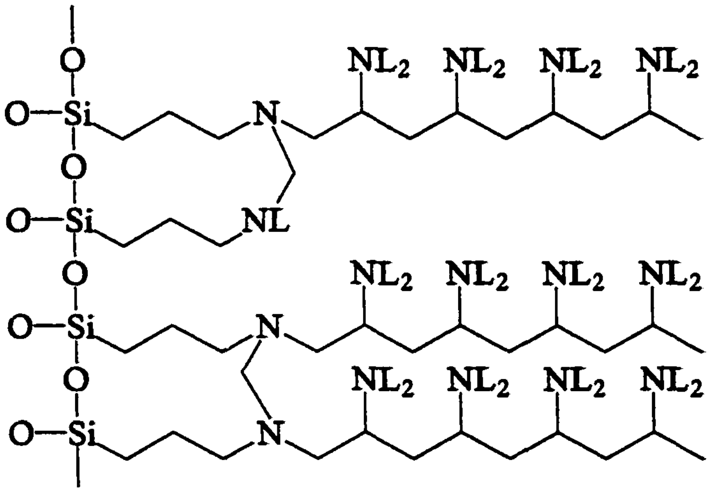
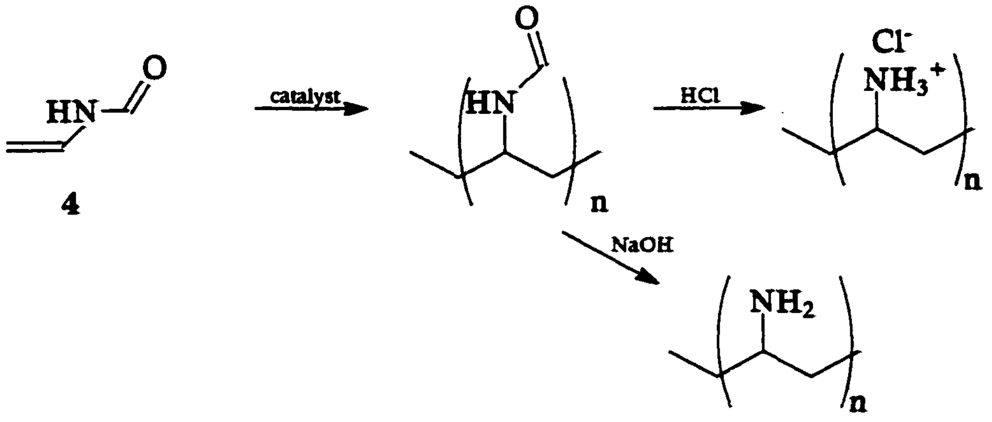


Figure 3.2 The generalized structure of PVA bound to the surface of silica gel. On PVA L=H on modified PVA L=H or the added ligand.

production even if the availability could be assured, which it wasn't. A further consequence of limited production is that the research quantities of PVA polymer that were obtained were quite variable from batch to batch. VP-1 has also been modified to create an array of materials that possess different characteristics. Baa-WRAM is analogous to WP-2 and contains an aminoacetic acid functionality while WRAM-ets the aminoethylene sulfide moiety.

Despite it's name, poly(vinyl amine) is not synthesized from the vinylamine



(xiii)

monomer. The amine must be protected to decrease its reactivity. One such monomer is N-vinyl-formamide (4). The monomer is polymerized via a free radical polymerization and then hydrolyzed via acid or base hydrolysis to yield poly(vinyl amine) or the ammonium salt of the polymer (xiii).[2] The problem though is that complete hydrolysis is not obtained. Laboratory bench scale synthesis using concentrated HCl to hydrolyze the protecting group yielded only 70% hydrolysis.[3] Modification of the polymer is therefore limited to 70% of the polymer at most and this figure may be worse depending on the efficiency of the hydrolysis for a particular batch of PVA.

3.1.2.3 Poly(allyl amine) PAA

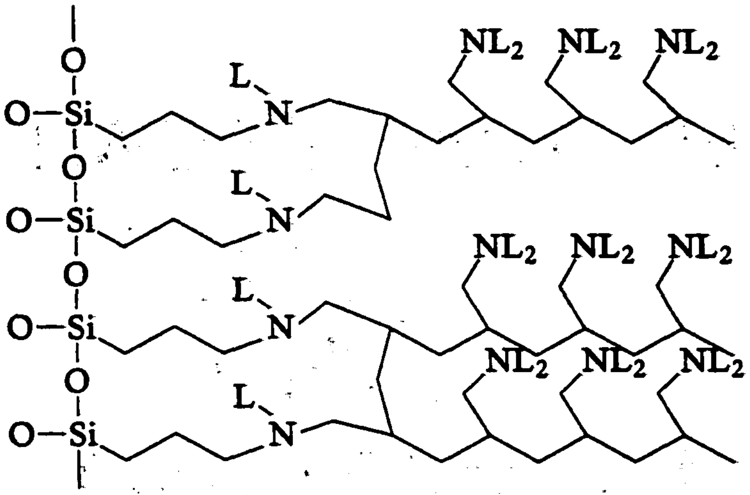
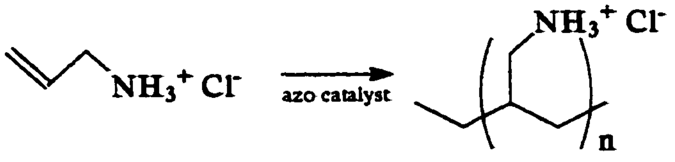


Figure 3.3 Poly (allyl amine) PAA is a linear polyamine with a methyl carbon inserted between the hydrocarbon backbone and the amine nitrogen. This figure represents a stylized depiction of the attachment to the silane anchor.



(xiv)

Poly(allyl amine) PAA is another linear polyamine containing exclusively primary amine atoms. The feature that distinguishes PAA from poly(vinyl amine) is a methylene group between the primary amine and the hydrocarbon backbone, thus the carbon to nitrogen ratio is 3:1 rather than the 2:1 carbon:nitrogen ratio of the other two polymers. Poly (allyl amine) is synthesized (**xiv**) through radical polymerization of the ammonium salt of the monomer in a polar solvent such as water. The reaction is propagated through the addition of a radical generator such as 2,2'-Diamidinyl-2,2'-azopropane hydrochloride.[4] The materials based on PAA are the BP- series; thus BP-1 is the material containing the unmodified PAA, BP-2 contains the amino acetic acid functionality and BP-3 is the dithiocarbamate containing material. PAA is produced on a commercial scale and is available in large quantities and while it is more expensive than PEI it is still an economically viable alternative. It is conceivable that the addition of the methylene group between the polar amine functionality and the non-polar hydrocarbon backbone will affect the behavior of the molecule in aqueous solutions. The unmodified polymer is very water soluble and 60,000 dalton PAA is sold in an aqueous solution. Addition of large non-polar groups to the polymer may be of concern though; this could create a situation where the non-polar areas of the polymer agglomerate producing a hydrophobic surface to the solution and the ligands become inaccessible to the metal ions.

3.2 Results and Discussion

3.2.1 Polymer Binding to the Silica Surface

The discussion of polymer to surface anchor binding will focus on the difference and similarities of the two types of polyamine, branched "fishnet" and linear. While these polymers are similar in their chemical composition the structural morphologies of the molecules are distinct and affect the way in which they bind to the surface of the silica gel and in the ways they can be modified.

Attachment of the linear polymers to the surface anchor could occur in a number of well defined modes. The linear polymers could bind "tail-on" to the surface in which the region of bonding would occur at one end of the polymer molecule and the other end would be free to extend out into solution. The polymer molecule could also attach by "looping" in which nonadjacent amines dispersed along the chain attach to the surface in close proximity to each other. Finally the polymer molecule could lay flat on the surface and all of the amines could participate in the surface bonding.

The branched PEI could bind in a similar yet structurally distinct fashion. The fishnet configuration of this polymer would make the following configurations possible, the polymer sheet could attach "end on" in which the amines on the periphery of one side of the molecule would comprise the primary point of attachment to the surface, the polymer could attach by "polymer bunching" in which amines throughout the molecule could attach to the surface in close proximity to each other causing areas of "bunching" throughout the molecule analogous to "looping" of the linear polymer, the polymer molecule could attach through the bonding of the amines on the total periphery to cause a "ballooning" effect a condition similar to large loops in the linear polymer, or the polymer could blanket the surface and create a surface that would approach a monolayer type coverage. The degree of surface bonding should determine the metal loading capacity of the resulting material. Less surface bonding should allow more polymer molecules to bind to the silica gel surface producing higher metal capacities because the material will contain more metal binding sites. There will also be less conformational constraint on the polymeric amines the farther they are from the surface. This would allow the polymer to conform more readily to the preferred binding configurations of different metals.

The affect of the molecular weight of the polymer on the capacity of the resulting silica-polyamine has been previously studied by Dana Hagars.[5] She found that the molecular weight of the polymer had very little effect on the capacity of the material.[5] Initially, one might suspect that as the average molecular weight of the polymer increases that more of the polymeric structure might extend from the surface out into solution. And from this one would also conclude that if more of the polymer were extended out into solution that there could be more reactive amine sites available for metal capture and thus the metal loading of the material would increase. This would occur as a result of steric hindrance with the larger molecules competing for positions on the gel surface causing the polymer molecules to attach with relatively fewer bonds, leaving more of the molecule to extend into solution. The fact that this is not observed can be explained by the way the polymer solutions are used. The polymer solutions are used as a weight percentage solution. Therefore the concentration of repeating units remains constant regardless of the average molecular weight of the polymer. If the lower molecular weight polymers are blanketing the surface in a relative monolayer then it is reasonable to believe that the higher molecular weight polymers would behave similarly.

Mass %	**Carbon**	**Chlorine**	**Nitrogen**
Chloropropyl gel	7.21	6.07	NA
BP-1	11.64	1.71	2.73
Moles / 100g			
Chloropropyl gel	0.60	0.17	NA
BP-1	0.97	0.048	0.19

Table 3.1 This table show the results of carbon, chlorine and nitrogen analysis carried out on chloropropyl gel and BP-1 as % mass. The % mass figures were converted to moles/100g by dividing the % mass by the atomic mass of the element.

Elemental analysis of the silica-polyamine composites at each stage of the synthesis helps elucidate the way in which the polymers bind to the silica gel surface through the chloropropyl anchor. Table 3.1 shows the results of carbon, chlorine and nitrogen analysis for chloropropyl (CP) gel and BP-1. To determine the moles/ 100g the mass percentage was divided by the atomic mass of the element. The polymer attaches to the silica anchor by forming a C – N bond and displacing a chloride. To determine the number of C-N bonds formed it was assumed that one nitrogen would displace one chloride. Therefore the number of C-N bonds formed would equal the number of chlorides displaced. One must also take into account the 14% mass gain incurred upon addition of the polymer. Due to this mass gain 0.88g of CP gel becomes 1.0g of BP-1. Returning to Table 3.1 0.17 moles/100g of chloride on the CP gel is multiplied by 0.88 to determine the number of moles of chloride available for displacement in 100g of BP-1. Thus 0.15 moles of chloride were available for displacement. The 0.048 moles of chloride remaining on BP-1 is subtracted from 0.15 moles of starting chloride to yield 0.10 of chloride was displaced during the polymer addition reaction. The BP-1 contains 0.19 moles of nitrogen/100g of which 0.10 are bound to the silane anchor. Therefore about half (54%) of the amines making up BP-1 are bound to the silica surface through the silylpropyl anchor. Similar calculations reveal that about two thirds (64%) of the reactive amines (1° and 2°) contained in WP-1 are bound to the Silica gel through the silylpropyl anchor.

The high percentage of reactive amines involved in attachment of PEI to the surface indicates that the polymer must be attaching to the surface in a "blanketing" fashion or with small bunches. This is consistent with Figure 3.4, the scanning electron micrograph (SEM), which shows that the appearance of the copper loaded surface of WP-1 is very similar in appearance to bare silica gel. The linear polyamines on the other hand present a different picture. The loaded PVA demonstrates a crystalline structure while the loaded PAA is similar in appearance to the surface of the loaded PEI. This seems to indicate that the PVA attaches to the surface in a "tail-on" arrangement while the surface attachment of the PAA is more of a "looped" configuration. These results were surprising, as it was expected that both linear polymers would exhibit similar surface morphologies resulting in the crystalline configuration of the loaded material. The lowest energy configuration of a polymer molecule is rarely the linearly extended form. Polymer molecules in solution usually exhibit some degree of intramolecular interaction causing the molecule to ball-up. PAA has more conformational freedom than PVA; stemming from the methylene carbon inserted between the hydrocarbon backbone of the polymer and the primary amine. The greater conformational freedom of the PAA could favor more intramolecular interactions and increase the extent of "balling-up" of the polymer molecule. The more rigid structure of the PVA would favor intermolecular interactions over intramolecular attractions. The rigid linear configuration of the PVA would favor attachment of the polymer molecule in a "tail-on" arrangement or laying flat on the surface. In fact it may be a combination of the two modes of attachment that accounts for the crystalline morphology. Initially the molecules may lay flat on the surface but as the surface

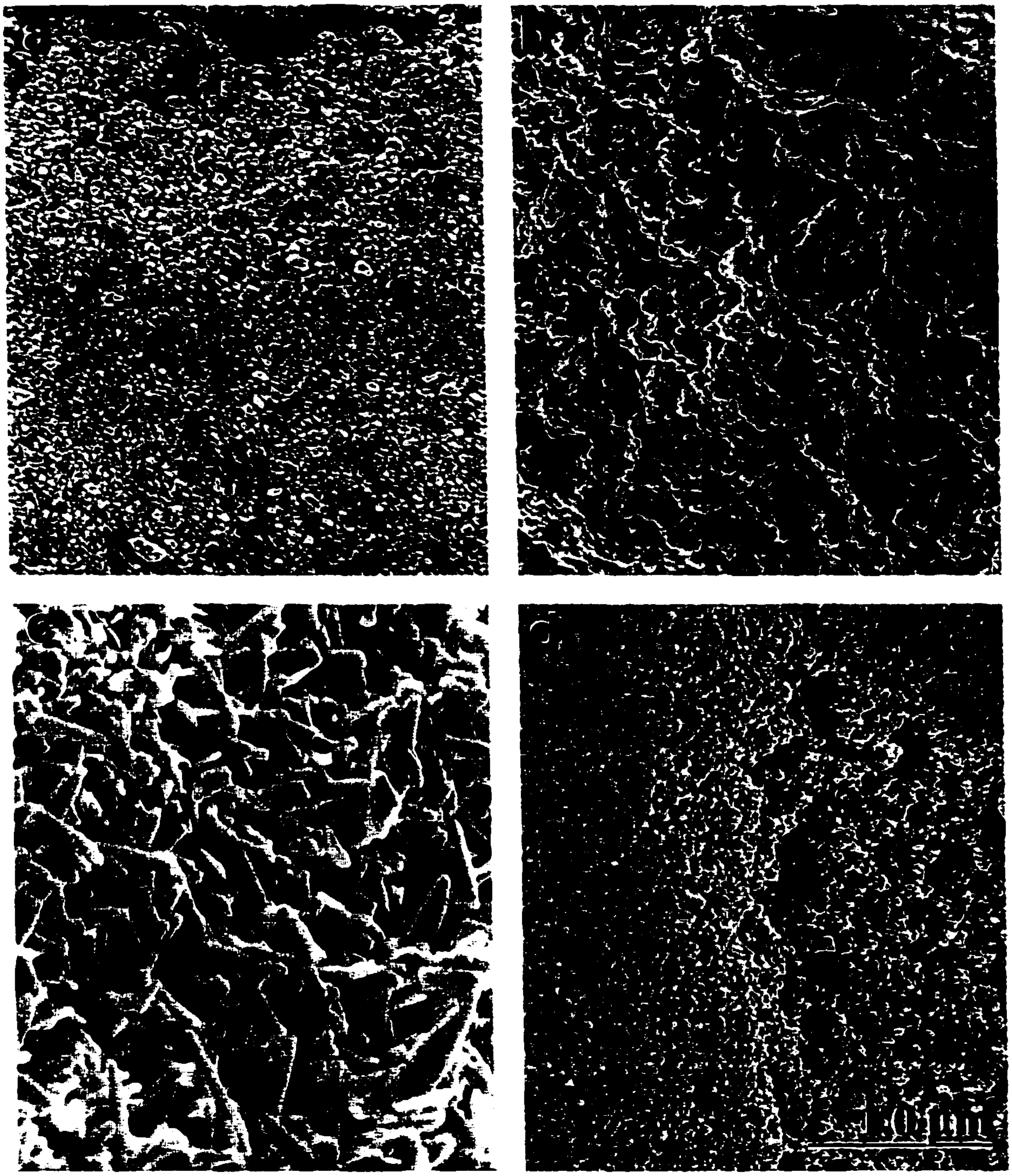


Figure 3.4 Scanning electron micrographs of a) bare silica gel b) WP-1 loaded with copper c) VP-1 loaded with copper and d) BP-1 loaded with copper. All three materials were made on the same silica gel and are represented at the same magnification. The crystalline structure of the VP-1 is readily evident while the WP-1 and BP-1 have a similar bunched appearance.

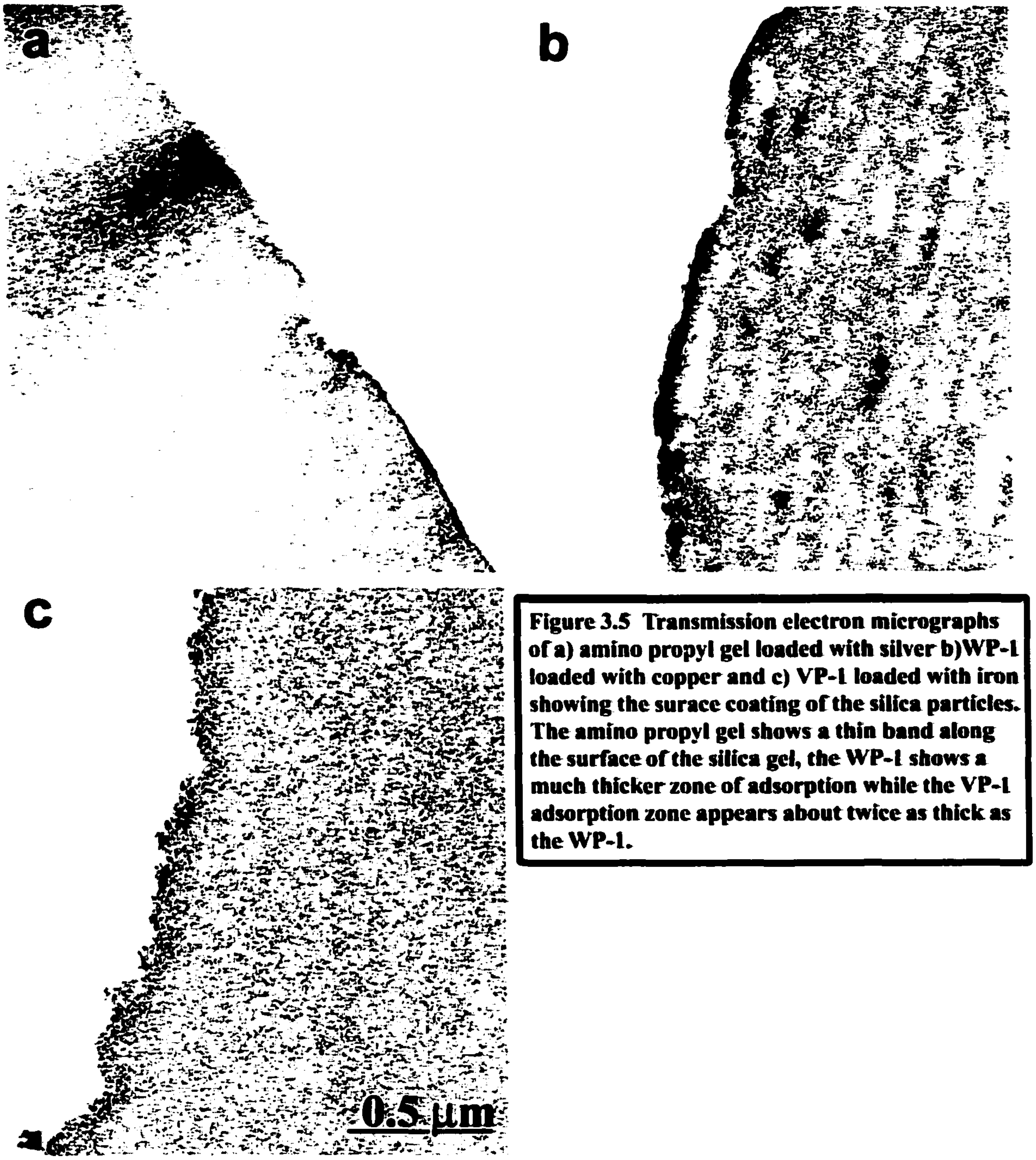


Figure 3.5 Transmission electron micrographs of a) amino propyl gel loaded with silver b)WP-1 loaded with copper and c) VP-1 loaded with iron showing the surace coating of the silica particles. The amino propyl gel shows a thin band along the surface of the silica gel, the WP-1 shows a much thicker zone of adsorption while the VP-1 adsorption zone appears about twice as thick as the WP-1.

becomes more crowded tail-on binding may predominate the extent of the tail-on binding may be enough to create the observed surface morphology. The transition electron micrographs shown in Figure 3.5 also support these observations. It is clearly evident that the polymer coating on the silica gel surface becomes thicker in the order of aminopropyl, PEI, PVA coatings. Aminopropyl gel is analogous to chloropropyl gel with a nitrogen atom at the distal end of the propyl chain instead of a chlorine atom.

3.2.2 Affect of polymer addition on silica gel surface

What Hagars did find to be the critical element in the metal loading capacity of the silica-polyamine materials was the pore size of the silica gel component of the material; more specifically the pore diameter of the pores. Over 99% of the silica gel surface is contained within the pores.[5] The accessibility of these pores is therefore critical to material performance. The metal containing solution must easily enter the pores to allow contact between the metal ions and the chelating polymer. Under flow conditions accessibility to the pore spaces increases as the pore diameter approaches the diameter of the void spaces between the particles. Decreasing the void diameter via closer packing increases the pressure drop through the system, which needs to be decreased in high throughput applications. This means that the pore diameter needs to be increased to optimize pore accessibility. If the pore diameter and pore volume are to great however, the silica gel particle becomes brittle and prone to physical breakage. Additionally, as the polymer is added to the silica surface the pore volume and pore diameters decrease as a function of addition of the halopropyl anchor, the polyamine and any additional modifying ligands. The manner in which the polymer binds to the silica surface will influence the degree to which the pore diameter is diminished. If the polymer adds in a flat or "blanketing" manner the reduction in pore diameter will be less than if the polymer adds in a "tail-on" or "looped" manner. However, the effects of adding water soluble polymers such as the polyamines may exert little effect on the accessibility of the pore interiors as water can flow through them relatively unhindered and the pore interiors may be regions of high polymer density where the metals may be easily chelated.

3.2.3 Material modification via ligand addition

The original goal of the silica-polyamine research was to remove lead from drinking water. While WP-1 had the ability to remove lead from the water it was felt that the lead capacity of the material could be improved and the amount of lead breaking through a column of the material could be decreased. To accomplish this, two ligands were investigated with which to tune the selectivity of WP-1. The two moieties successfully added to WP-1 were acetic acid and ethylene sulfide.

The acetic acid moiety was added to WP-1 by reacting WP-1 with bromoacetic acid under controlled pH conditions at room temperature. This creates a material containing aminoacetic acid functional groups. This material is the silica-polyamine analog of the Rohm and Haas IRC-718 and IRC-748, which are the industry standard ion exchange resins. These are polystyrene resins containing aminodiacetic acid functional groups. The creation of aminoacetic acid groups on the polyamine resulted in a material that reduced the lead breakthrough to less than 2 ppb for 250 gallons under typical household tap water conditions using the National Sanitary foundation recommended challenge level of 150 ppb. There are other differences between this material, WP-2, and WP-1. Principal among these are the elimination of the base regeneration step and the ability to effectively operate under more acidic conditions. Because WP-2 contains an acetic acid functional group it acts as a chelating ion exchange resin. The pK_a of the H_2 of aminoacetic acid is 2.36, loss of this proton results in formation of a zwitter ion. The pK_a of H_1 is 9.54 loss of this proton results in anion formation. At pH's above 2.5 the majority of the acetic acid moieties will be in the anionic acetate form. The anionic polymeric functional group then interacts with the cationic metal ion. This interaction then will retain the metal ion long enough for a further exchange in which a polymeric amine, which will undoubtedly be in the protonated ammonium form, can lose the associated proton and form a coordinate bond with the metal. For this reason it is unnecessary to strip the protons from the amines with base and furthermore the material WP-2 is effective at lower pH than WP-1. WP-2 is not particularly selective although it was discovered during testing on waters of the Berkeley Pit that aluminum was not being extracted by WP-2 while WP-1 extracted aluminum and copper concurrently.[6] This is attributed to the form of the aluminum; under the local basic pH of base regenerated WP-2 conditions the aluminum will be in an oxoanion state which would be repelled by the acetate anion.[6] During those tests the WP-2 was being regenerated. Under present conditions, no base regeneration, the aqueous aluminum at pH ~2 will be in the plus three hexaquo state. This form is acidic enough to protonate the acetate anion through the following equation:

$$[Al(H_2O)_6]^{+3} + MeCO_2^- \xrightarrow{K_{eq}} [Al(H_2O)_5OH]^{+2} + MeCO_2H \qquad \textbf{(xv)}$$

$$K_{eq} = \frac{K_a Al(H_2O)_5(OH)^{+2}}{K_a Acetate} \qquad \textbf{(xvi)}$$

$$K_a\, Al(H_2O)_5(OH)^{+2} = \frac{[Al(H_2O)_5(OH)^{+2}][H^+]}{[Al(H_2O)_6{}^{+3}]} = 1.2\times10^{-5} \qquad \textbf{(xvii)}$$

$$K_a\, acetate = \frac{[H^+][Ac^-]}{[HAc]} = 1.8\times10^{-5} \qquad \textbf{(xviii)}$$

$$K_{eq} = \frac{[Al(H_2O)_5(OH)^{+2}][HAc]}{[Ac^-][Al(H_2O)_6{}^{+3}]} = .67 \qquad \textbf{(xix)}$$

The equilibrium constant K_{eq} of the acetate – aluminum hydroxide system of 0.67 indicates that protonation of the acetate ion by the aluminum hydroxide would be substantial and could prevent the aluminum from being extracted from the solution by WP-2.[7] However, the functional group on WP-2 is actually aminoacetic acid which has a H_1 pK_a of 2.36. The K_{eq} for this system is 4.3 X 10^{-3} indicating that this reaction will not appreciably affect the capacity of WP-2 for aluminum.

To extract lead, a soft metal, a soft ligand is more efficient. Oxygen and nitrogen are hard and intermediate ligands respectively; therefore WP-1 was modified with a soft ligand. The modifying ligand was ethylene sulfide, which contains a soft sulfur atom. WP-1 was reacted with ethylene sulfide to produce WP-3 a material that was subsequently shown to be effective at removing lead and cadmium from water under household drinking water conditions.[6] Over 500 gallons of water were treated to reduce lead from 150 ppb to less than 2 ppb at a flow rate of 42 bed volumes per minute. The free ligand though is toxic and difficult to work with; self-polymerization is readily evident on the walls of the reaction flask. A second Soft metal extraction material was synthesized that utilized carbon disulfide reacted with the linear polyamine of BP-1 to produce a polymeric dithiocarbamate. This material was relatively easy to synthesize and when tested on mercury showed high capacities and the ability to reduce mercury to below 2 ppb from aqueous mercury(II) concentrations of 50,000 ppb.[8] Furthermore the mercury(II) could not be stripped from the material even with concentrated mineral acid, making the material a good choice for applications where mercury immobilization is required. While these materials have a high affinity for soft metals they are not selective for them, WP-3 will also extract copper and iron from solution.

3.3 Conclusions

Anchoring a polyamine to silica gel can produce effective metal ion extraction materials. The performance characteristics seem to be dictated more by the physical characteristics of the silica gel than by the amine polymer. Pore diameter and volume are important characteristics of the silica gel, increased pore volume increases the total surface area of the silica gel while an increase in pore diameter increases the accessibility of the interior surfaces to the surrounding solution.

The molecular weight of the polymer has little effect on the overall capacity of the resulting material. This phenomenon almost certainly arises from the method of calculating the amount of reagent to be used in the reaction attaching the polymer to the silica gel. The concentration of polymer in solution is measured as a percent by weight figure. Therefore when the polymer is added to the silica gel the polymer concentration and more importantly the polymeric amine:halopropyl anchor ratio is constant regardless of the molecular weight of the polymer. This has not been the focus of a detailed investigation and the above hypothesis is based on empirical observation.

The polymer type does have an effect on the resulting material. The linear polymers have a higher metal capacity than the branched polymer. Scanning electron micrographs (SEM) indicate that the branched polymer blankets the surface of the silica gel. This yields a thin polymer coating of the silica gel particle. The linear polymer PVA seems to favor an "end-on" attachment to the silica gel as shown by SEM. Micrographs of the linear PAA show that it attaches in a loop arrangement so that the morphology of the copper loaded material BP-1 is similar to that of WP-1.

The materials, WP-1, BP-1 and VP-1 made from PEI, PAA, and PVA respectively, have all been modified to tune their selectively. Addition of an acetic acid moiety to the parent material yields a material that works at lower pH and needs no base regeneration. Addition of an ethylene sulfide moiety yields a material with an increased affinity for soft metal ions. While these modifications increase the affinity for a selected group of molecules or extend the working range of the materials they are not truly selective. All of these materials will still extract a broad range of aqueous metal ions.

3.4 Experimental

3.4.1 Synthesis

WP-2 In a 500 mL 3-neck round bottom flask dissolve 90.00g of bromoacetic acid. Add 8N NaOH in water dropwise until the pH reaches 7. Add 100g of WP-1 to the bromoacetic acid solution and degass the gel under vacuum. Stir the resulting slurry with a paddle stirrer while adjusting the pH to 10 with additional 8N NaOH. Monitor and adjust the pH to 10 as needed for 1 hr. Allow the reaction to proceed for 16 hr at room temperature. At the end of 16 hr check the pH and adjust to 13 with additional 8N NaOH. Allow the reaction to proceed for an additional hour before separating the slurry from the reaction mixture. Using a fritted funnel and vacuum aspiration rinse the resulting material 3 times with 400 mL of DI H_2O and 2 times with 400 mL of methanol. Air dry.

Expected weight gain 15% - 20%

WP-3 (ethylene sulfide) In a 1L 1-neck round bottom flask 100g of WP-1 is placed on a rotary evaporator in a 100°C bath for 2 hours. The WP-1 is then transferred to a 1L 3-neck round bottom flask. To the WP-1 is added 400 mL of methanol and the resulting slurry degassed under vacuum for five minutes. After degassing the flask is placed into a heating well and fitted with a Teflon and glass paddle stirrer.

The contents of the flask are heated to reflux with stirring. Using an addition funnel 10.8 mL of ethylene sulfide are added over 10 minutes. The reaction is allowed to proceed at reflux for 16 hours. The reaction mixture is cooled and emptied into a fritted filter funnel. Vacuum is applied and the reaction mixture separated from the resulting material. While continuing the vacuum the material is rinsed 3 times with 400 mL of methanol, 3 times with 400 mL of DI water, 1 time with 400 mL of !N ammonium hydroxide, 3 times with 400 mL of DI water, and 3 times with 400 mL of methanol. The material is then air dried.

Expected weight gain 7% - 10%

WP-3 (dithiocarbamate) In a 1L 1-neck round bottom flask dissolve 40.8g of NaOH in 360 mL of DI water. Add 100.0g of WP-1 then 43.3mL of carbon disulfide degas the slurry under vacuum aspiration. Stir with a rotary stirred at room temperature for four hours. Empty the contents into a fritted funnel and vacuum filter the reaction solution. In the same manner rinse the resulting material 3 times with 400 mL of methanol, 3 times with 400 mL of DI water and 2 times with 400 mL of methanol. Air dry.

Expected weight gain 2% - 6%

3.4.2 Analysis

3.4.2.1 Equipment

Samples for scanning electron microscopy (SEM) were mounted with carbon adhesive tape to aluminum studs, coated with 100Å chromium in an IBS/TM200S ion beam sputterer (VCR Group, Inc., South San Francisco, CA) and viewed on a S-4500 cold field emission scanning electron microscope (Hitachi Ltd., Japan). Transmission electron microscopy samples were imbedded in Spurr's resin. 80 nm thick sections were cut with an RMC MT-7000 ultramicrotome (Boeckeler Instrument Tucson, AZ), and viewed on a Philips CM-10 transmission electron microscope (FEI Hillsboro, OR) at 60 Kv. Images were processed using Adobe photoshop V 7.0 (Adobe Systems Inc. San Jose, CA).

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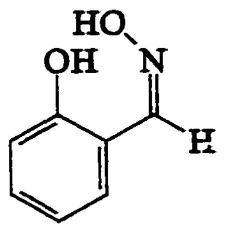
CHAPTER 4 The Search for a Copper Selective Material

4.1 Introduction

It has been demonstrated that WP-1 used in conjunction with WP-2 can selectively extract copper, zinc, aluminum and manganese from a mixed solution.[1] This selectivity is based on engineering the extraction system to singularly extract metal ions with the greatest affinity for the chelating polymer in multiple passes. This type of system may work very well for large scale remediation projects such as the Berkeley Pit where metal ion concentrations remain relatively stable, but in smaller scale industrial applications where ion concentrations and ion types can vary "designer gels" may be a more feasible waste water treatment option. "Designer gels" refers to silica gel based composite extraction materials designed to extract only one type of metal ion in a mixed media waste stream. WP-2, WP-3, BP-2 and BP-3 are a first step in this direction since these materials incorporate different ligands into the polymer which may help fine tune the base polymer towards oxophilic metal species and softer metals, but are not specific to extracting a single type of metal ion even in the presence of closely related metal ions.

In the quest for heavy metal pollution abatement procedures applicable to 'real world' waste streams it was discovered that there was a need in the industrial sector for a material that could capture Cu(II) ions in the presence of Fe(III) ions.[2] This presents a huge challenge, work on a previous project had shown that Fe(III) has a very high affinity for the amine based polymers, even higher than that of copper(II).

It was suggested by Dr. Peterson of the Idaho National Engineering and Environmental Laboratories (INEEL) that salicylaldoxime **5** could be a good ligand to begin development of a polymer - ligand system to extract Cu(II) from a mixed metal ion waste stream. Salicylaldoxime has been used as far back as the 1930's in a quantitative analytical technique for the determination of copper.[3,4] 5-methyl-salicylaldoxime was found to selectively precipitate out copper(II) in the presence of an overwhelming concentration of iron(III).[5]



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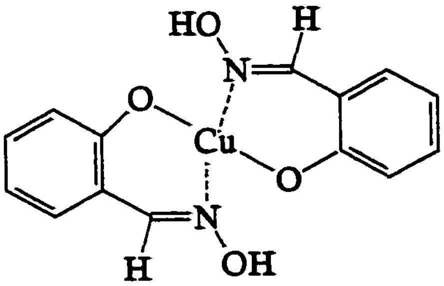

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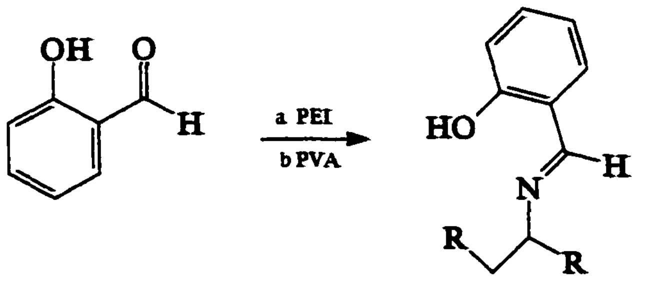
This suggested a salicylaldehyde derivative as a likely candidate to begin with in synthesizing a "designer gel" which will selectively bind copper in the presence of other ions.

The salicylaldehyde - copper(II) complexes formed at pH, 3 - 10 are insoluble in aqueous solution, while those formed at pH ≥ 11 are soluble.[6] The structure of the copper - salicylaldoxime complex **6** is reported to be square planer and incorporating two salicylaldoxime molecules $Cu(SAO)_2$ (SAO = salicylaldoxime molecule).

Initial work focused on modifying poly (ethylene imine) based WP-1 and poly (vinyl amine) based VP-1 to contain the salicylaldoxime ligand or a ligand with similar structural characteristics. Polymeric amines which remain unreacted with the salicylaldoxime ligand, specifically the 2° and 3° amines of PEI and any unreacted 1° amines of PVA, may interfere with the selectivity of the ligand by preferentially binding with Fe(III) in the waste stream.

4.2 Results and Discussion

Four categories of chemical reaction were utilized in attempting to attach the salicylaldoxime to the silica gel surface. These were alkylation via nucleophilic attack on an alkylhalide by amine groups attached to the gel surface or to the ligand, carbodiimide coupling, Friedal-Crafts alkylation of the benzene ring, and nucleophilic attack on an alkylhalide by the anion of the oxalate salt of the ligand.



a $R=(C_2H_4N)_n$ N is 1°,2°,3°

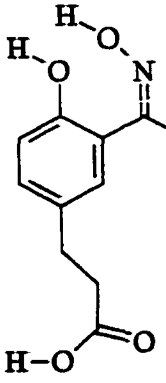
b $R=(C_2H_3N)_n$ N is 1°

(xx)

7 **8**

Throughout the remainder of this chapter the silica-polyamine composite materials being modified will be referred to by the acronym of the polyamine therefore WP-1 will be called PEI, BP-1 will be called PAA, and VP-1 will be called PVA.

The initial goal was to bind a salicylaldoxime derivative to the silica bound polymer substrate; and for comparison to the silica anchor. First 2-hydroxy-benzaldehyde **7** was reacted directly with the polyamine gels (xx). In this reaction the carbonyl group will react with any primary amines to produce an imine; PEI-SALI **8a** or PVA-SALI **8b**.



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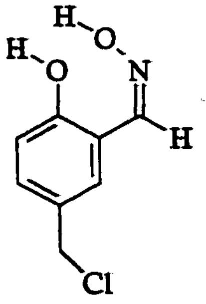

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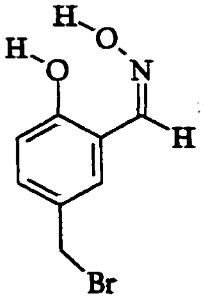

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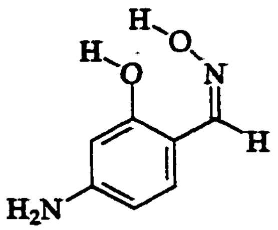

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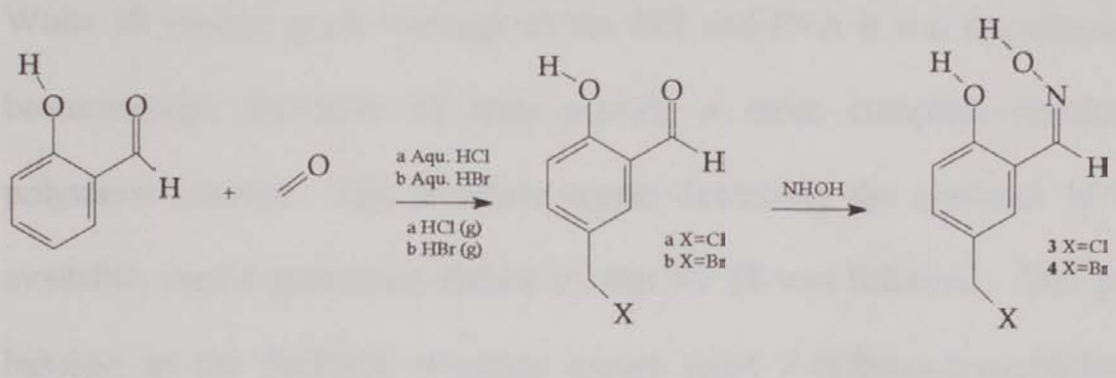
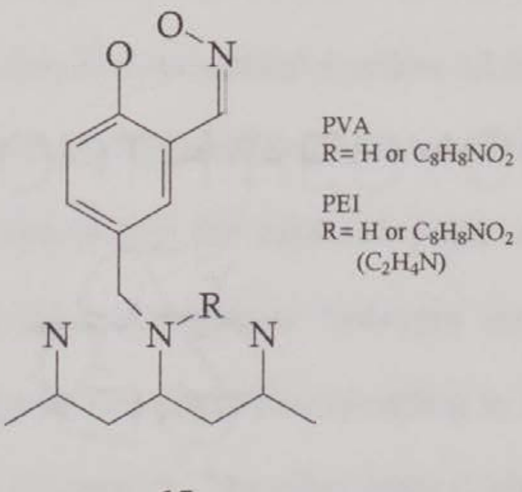
An extensive structure search yielded four other candidate molecules for attachment to the polymers while keeping the phenol and aldoxime moieties: β-(3-formyl-4-hydroxyphenyl)-propionic acid **9**, 5-chloromethyl-2-hydroxy-benzaldehyde-oxime (5-chloromethyl salicylaldoxime) **10**, 5-bromomethyl-2-hydroxy-benzaldehyde-oxime (5-bromomethyl salicylaldoxime) **11**, and 4-amino-2-hydroxy-benzaldehyde-oxime (4-amino salicylaldoxime) **12**. Upon consulting the literature **9** was ruled out because the aldehyde was reportedly produced with a 13% yield[7] and there was no report on the synthesis of the oxime.

Synthesis of **10** was carried out in two parts. The 5-chloromethyl-2-hydroxybenzaldehyde **14a** was prepared according to the preparation of Angyal et al (**xxi**).[8] Salicylaldehyde **13** was reacted with formaldehyde in hydrochloric acid while bubbling through anhydrous hydrogen chloride to produce **14a**. During the recrystalization step almost no material was dissolved in the petroleum ether as was outlined in the paper; ether was then used as the solvent with limited success. The ether was allowed to evaporate overnight which yielded large colorless needles. Both the crystals and the undissolved solids were analyzed by NMR revealing that both fractions were the same compound **14a**. This was reacted with one molar equivalent of hydroxyl amine to produce a yellow oil which was never successfully crystallized. NMR



(**xxi**)

13 **14** **10** or **11**



15

revealed the salicylaldoxime product **10** with very little impurity. This was reacted with both the PEI and PVA gels to yield PEI-SALO and PVA-SALO **15**. The resulting gel was a bright yellow color. Gel performance will be discussed in the next section.

While **10** yielded good coverage of the PEI and PVA it was hypothesized that the bromomethyl derivative **11** may provide a more complete reaction with the polymeric amines. The literature report describing the synthesis of **11** was not available, thus a procedure similar to that for **10** was followed. This plan was not baseless as the Beilstein structure report listed 2-hydroxy-benzaldehyde **13**, and formaldehyde as the reactants and HBr as the reagent for the preparation of 5-bromomethyl-2-hydroxy-benzaldehyde **14b**. The NMR of the compound produced from this step of the synthesis produced a spectrum consistent with the expected spectrum of **14b**. Reaction of **14b** with hydroxylamine yielded a yellow oil similar to the oil **10**. NMR analysis of the oil however produced a spectra which was not consistent with the predicted spectra. Specifically the expected peaks at about δ10.03 and δ10.67, which correspond to the hydroxylimine hydrogen and to the phenol hydrogen respectively, are missing and two peaks corresponding to an ethyl group by both multiplicity and integration are present. The ethyl peaks could be due to solvation, coordination of the solvent between molecules of **11** or due to displacement of the bromine with an ethoxy constituent. The oximation of the aldehyde **14b** was carried out in ethanol and the oil recovered and washed in an ether extraction. Either of these two steps could lead to the ethyl peaks found in the

NMR; but because of the way these peaks integrate with the rest of the molecule it is believed that the source of the peaks is the ethanol used in the oximation step. To test this theory a small scale reaction of **14b** and hydroxylamine was carried out in 1,2,-dimethoxy ethane (glyme) to see if the peaks would vanish. Two fractions of this reaction were analyzed by NMR and neither show the desired product **11**.

It was evident from the mass gain and color change of the material, that the 5-chloromethyl salcylaldoxime was incorporated into the polymer, thus the lack of copper selectivity was troubling. It was felt that the lack of selectivity could be due to interference from unbound amines incorporated in the amine polymer. It was known that the unmodified polyamines had a greater affinity for iron(III) than copper(II) and it was hypothesized that unreacted amines may still have the ability to extract iron(III) from the solutions. A number of strategies were employed to combat this problem. One approach to the problem was to "cap" the unreacted amines by reacting PVA-salicylaldoxime and PEI-salicylaldoxime with acetic anhydride to convert all the primary amines into less reactive tertiary and or quarternary amines, a technique which has been used successfully in the pharmaceutical industry.[9] A second approach was to reduce the chelating ability of the amines by reacting the PEI-salicylaldoxime with methyl iodide to form quarternized amines. The quarternized material showed copper capacity and even some selectivity, in the limited testing performed in our lab. The "capped" materials were sent out directly for testing due to the limited quantity synthesized. Both of these materials were prone to ligand loss in the metal ion capture process apparently at the quarternized amine which becomes a good leaving group. A third approach to reducing the interference from unreacted amines was to achieve more complete coverage of the polyamine with the salicylaldehyde ligand. To achieve this the chlorine on 5-chloromethylsalicylaldoxime was exchanged for the more reactive iodide ion through a halogen exchange reaction to create 5-iodomethylsalicylaldoxime and the ligand was reacted with PEI and PVA. More complete coverage of the gel was obtained as exhibited by a 17% and 18% weight gain on PEI and PVA respectively as compared to a 5% and 8% weight gain produced by the reaction of 5-chloromethylsalicylaldoxime with PEI and PVA respectively.

Another approach to solving the problem of interference on selectivity from the polymeric amines was to dispense with the polyamines altogether. To do this a different functional anchor needed to be bound to the salicylaldoxime ligand. The ligand created for this was 5-aminosalicylaldoxime. This ligand was then reacted directly with bromopropyl gel to achieve a four member chain to anchor to the silica gel at the 5 position of the salicylaldoxime. This reaction did not seem to proceed as planned possibly due to rapid oxidation of the 5-aminosalicylaldoxime ligand. This was evident in the deviation from the expected final weight of the material, the ever deepening red color of the ligand resulting in a salmon pink colored gel, and the lack of copper capacity for this material.

Simultaneously with the creation of 5-aminosalicylaldoxime work was being carried out to create an aminopropyl anchor on the silica gel. This could be useful in a number of different scenarios. The 5-chloromethylsalicylaldoxime could be reacted with it to produce a five member chain to anchor to the silica gel at the 5 position of the salicylaldoxime, an alternate pathway to the material described earlier. To increase the capacity of the material to levels similar to that of PEI or PVA a poly (vinyl halide) could be reacted with the propylamine anchor and then further reacted with 5-aminosalicylaldoxime to create a material with high capacities and high selectivity due to the absence of primary amines. It was initially thought that the bromo propyl gel could be converted to amino propyl gel relatively simply by reacting the bromyl propyl gel with ammonia. This was an exciting proposition because the amino propyl gel would be a metal ion extraction material in its own right and this would allow us to evaluate the physical stability of the bromo propyl gel as compared to PEI. This is useful information in assessing the importance of the density of the bromopropyl trichlorosilane on the silica gel surface versus the importance of the polymer network integral to PEI. None of the attempts at ammination of the bromo propyl gel were successful; but amino propyl gel was synthesized by reacting aminopropyl trimethoxy silane with hydrated silica gel. This produced a material with an initial copper capacity of .545 mM/g of gel but each successive cycle reduced the copper capacity by about 1/3. This was a visual phenomenon and one could see, first the bottom 1/3 remain devoid of copper, then the bottom 2/3, and finally the whole column remained white as copper passed through it.

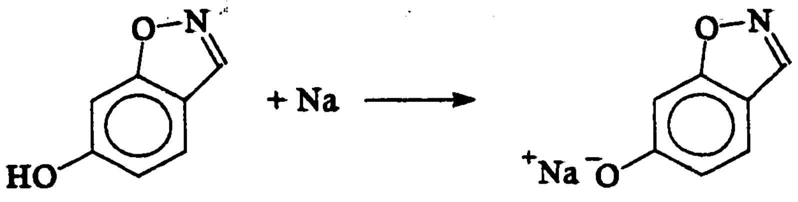
Poly (vinyl chloride) was reacted with amino propyl gel and this was further reacted with 5-aminosalicylaldoxime. This material initially held .44 mM of copper/g of gel but this diminished over subsequent cycles.

The flaw seemingly inherent in all of these materials was lack of stability; the ligands seemed to dissociate themselves from the rest of the materials during the process of capturing and eluting metal ions from aqueous solution. The newly created 5-aminosalicylaldoxime coupled with the polyamines suggested a carbodiimide coupling reaction could be attempted. Carbodiimide coupling is a class of reactions used in biochemistry to synthesize peptide bonds. It was hoped that the amide bond formed in this reaction would produce a less reactive nitrogen creating a more robust material with greater selectivity. Reactions utilizing both water soluble and organic soluble coupling reagents were carried out in a variety of solvents but the viscous solutions created in these reactions did not seem to interact with the solid surface of the coated silica gel. The copper capacities of these materials were typically high for the first cycle then dramatically dropping to near zero by the second cycle and remaining there for subsequent cycles.

In an attempt to increase the physical integrity of the materials incorporating the salicylaldoxime ligand, connecting bonds other than carbon-nitrogen bonds were investigated. A zinc coupling reaction in which zinc catalyzes a reaction between two alkylhalides was attempted. The resulting gel had no copper capacity. It seems reasonable to believe that the catalytic amount of zinc dissolved in the reaction solution could be chelated by the ligand we were attempting to react.

The same may be said for this next set of attempted reactions as well, the Friedal-Crafts reactions, where a reactive anhydrous metal halide is used to mediate a reaction between an alkyl halide and an aromatic ring structure. These reactions produced a weight loss or deterioration of the silica gel and no copper capacity.

At this point the emphasis changed slightly again to attaching the ligand to the silica gel via a carbon-oxygen bond. The ligand of interest became 5-hydroxybenzisoxizole



16 17

16. The advantage of this molecule is that the isoxizole ring is less reactive under many conditions than the oxime is. The anchor to the silica gel was also changed from a bromopropyl group to a bromooctyl group; this gives the ligand a longer tether allowing more conformational freedom. The strategy for attaching the ligand to the silica gel was to create the sodium salt of the 5-hydroxybenzisoxizole **17** to facilitate the nucleophilic attack on the bromooctyl anchor. The problem we encountered here was solubility of the salt. Once we synthesized the salt and it precipitated out it would not go back into solution. This greatly hindered any reaction at the silica gel surface.

4.3 Analysis of Gel Performance

Extensive testing on gel performance was not carried out in this lab for two reasons: 1) synthesis was the main focus of this lab, analysis of gel performance was carried out at Idaho National Engineering Laboratories in Idaho Falls, Idaho, and 2) not enough concrete information was known about the potential operating conditions in which the gel was expected to perform. That said, some cursory tests were conducted to determine if the synthesized gels were exhibiting any of the desired traits. The tests were all carried out in a similar manner; the gel was loaded into an ~5 cm^3 column, fitted to a pump set at a flow rate of ~10 mL/min, the column loading and elution were controlled manually, while the regeneration step was regulated using a computer and software designed for this purpose. Only one column of each material was loaded and all the tests conducted on each material were conducted on that one column. Periodically the columns were cleaned with conc. HCl; these cleanings were carried out when visual inspection revealed a build-up of iron (III) on the column. The visual indicator used was when the color of the material in the column remained a rust brown color after the acid elution step or the regeneration step. These washings always restored the original bright yellow color of the gel.

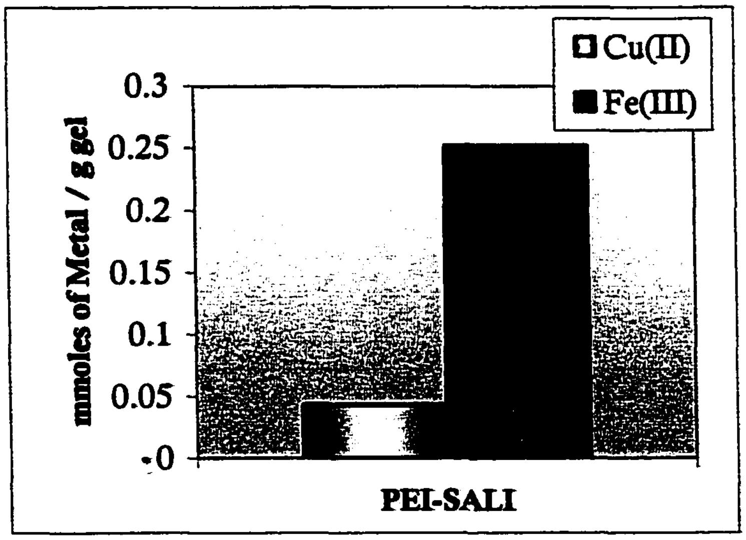


Figure 4.1. This graph depicts the reverse selectivity of PEI – SALI. The iron(III) is extracted and recovered in a 5:1 ratio with the copper

PEI-SALI has a definite preference for Fe(III) as is shown in Figure 4.1. This may be due to the unreacted 2° and 3° integrated into the polymer. While the structure of the chelating ligand 3 should not hinder the formation of a ligand copper complex similar to III iron chelated to proximal amines may compromise the ability of a second ligand aligning itself with the square planer dimensions of the copper ion.

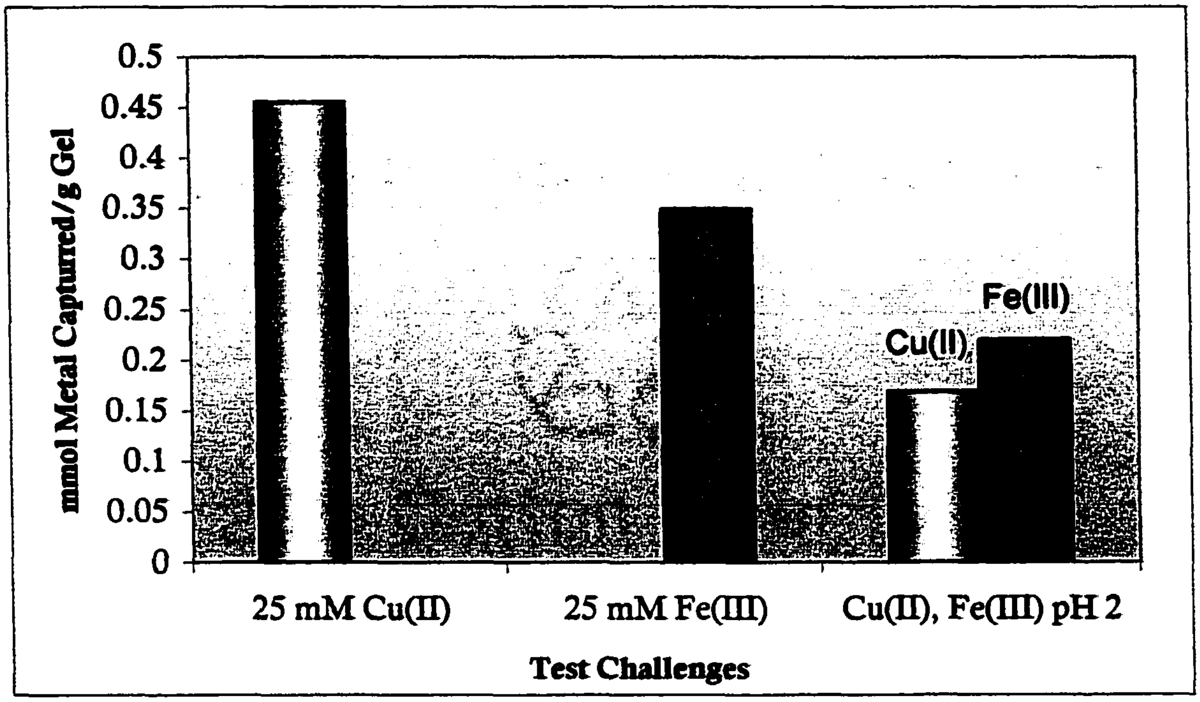


Figure 4.2. A short battery of PEI - SALO gel performance tests. All tests were conducted on the same column which were periodically cleaned with conc. HCl. Relative standard deviations were all within 10% below the graphed value except 25 mM Fe(III) which varied up to 96% below the displayed value.

Figures 4.2 and 4.3 both show the capacities of the gels for Fe(III) and Cu(II) in an isotonic solution as well as from mixed challenges. The Cu(II) capacity of the PEI from which the PEI-SALO was synthesized is .56 mmol/g gel at pH 2.11 and that of PEI - SALO is .46 mmol /g gel a 19% capacity loss. Looking at both graphs the first thing that stands out is the fact that at this point the best selectivity obtained is about a 1:1 ratio Fe(III) to Cu(II). The test labeled pH 1 sv on the graph in Figure 4.3 is a test in which a small volume of challenge solution was passed through the column. The flow of challenge solution was stopped as soon as the column appeared fully loaded as determined by visual inspection. It is interesting to note that in Figure 4.2 the capacity for Cu(II) from an isotonic solution is approximately 25% greater than that for Fe(III). The interesting aspect of Figure 4.3 is that at pH 2 the gel captured the full amount of iron as compared to the Fe(III) capacity test while at the same time an additional 0.15 mmol of Cu(II) per g of gel was captured. This may be an indication that there are sites on the gel which are specific to the binding of Cu(II), but that the coverage of the gel with these sites is poor.

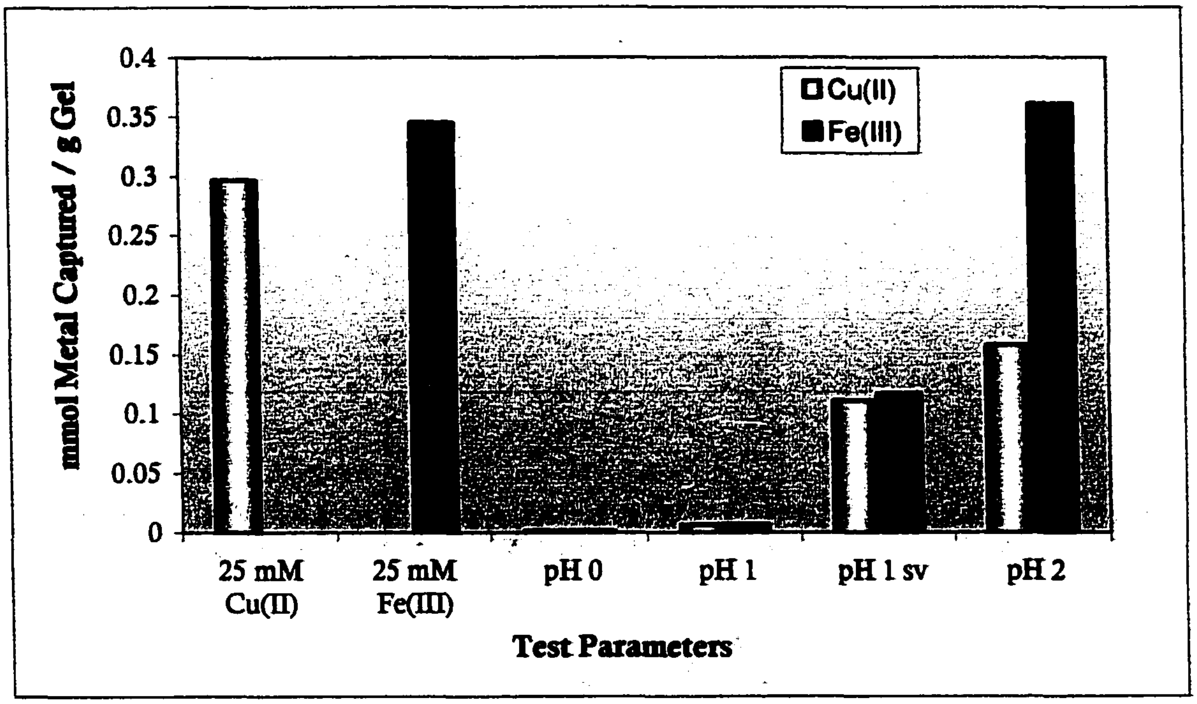


Figure 4.3 A short battery of PVA-SALO gel performance tests. All tests were conducted on the same column, which was periodically cleaned with conc. HCl. Test solutions were a mixed metal solution containing 25 mM each of Fe(III) and Cu(II). The two tests depicted at the left of the graph represent the gel capacity from isotonic solutions at intrinsic pH. PH 1 sv is a test in which the challenge flow was stopped as soon as it appeared that the column was fully loaded. sv stands for small volume.

4.4 Conclusions

It is clear that new materials were synthesized, based on weight gains and color changes observed. All the salicylaldehyde and salicylaldoxime containing materials are some shade of yellow. This demonstrates that the polymeric amines of bound PEI and PVA will react with aldehydes to produce imenes, and with the chloride of an aromatic attached chloromethyl group, neither of which had been demonstrated previously on the silica-polyamine composite materials. Initial indications based on the reported preliminary tests seem positive. It can be concluded that there are sites on the gels which are specific for copper (II) in the presence of iron (III) and that at this point more research needs to conducted on ways to optimize those sites on the gels.

The non-selective nature of the materials may be attributable to a variety of factors. It has been shown that oximes can rearrange in the presence of solutions containing 25% H_2SO_4.[10] The Beckman rearrangement typically yields an amide from the oxime.[11] In the example of salicylaldoxime it is conceivable that instead of rearrangement to the amide there is a rearrangement of the molecule resulting in formation of a second five member ring to form benzisoxizole. Alternatively the reaction could proceed to form a nitrile from the oxime. Any of these scenarios could result in reduced selectivity of the material.

Additionally the mechanism of extraction in the solvent system may not be directly transferable to the solid phase system. In the solvent extraction system the salicylaldoxime moiety works as a chelating ion exchange ligand. When complexed to a copper(II) ion the result is a neutral square planar complex **6** that readily transfers into the organic phase. Iron(III) on the other hand would require three salicylaldoxime ligands to neutralize the charge and to form the octahedral configuration preferred by iron(III). Steric hindrance from the bulky, fairly rigid salicylaldoxime ligand may severely limit the formation of this complex. Addition of one or two salicylaldoxime ligands to iron(III) may occur in the aqueous phase; but the complex would still carry an overall charge of +2 or +1 respectively. The remaining charge on the complex would severely inhibit transfer into the organic phase thus creating the selectivity of the extraction system. In the solid phase – liquid phase separations systems the new materials are employed in the extraction mechanism is different. If the iron(III) ion is complexed by one or two salicylaldoxime ligands it will be bound to the surface of the solid phase. The additional coordination sites may be occupied by counter ions in the feed solution and or water molecules. The resulting complex may be stable enough to remain bound to the solid phase and the fact that it is charged has no bearing on the selectivity of the extraction system.

4.5 Experimental

The small molecules reported here are know with the exception of the 5-halomethyl-benzaldehyde oximes. There were no literature references discovered for those molecules. NMR (nuclear magnetic resonance spectroscopy) data are recorded for the synthesized ligand molecules and their precursors. TLC (thin layer chromatography) and IR (infrared spectroscopy) data are also given for the compounds that were isolated. Successful ligand addition was evaluated by mass gain, color change of the silica-polyamine, and performance of the material. Silica-polyamine composites with the desired performance characteristics were sent out for elemental analysis (Schwartzkopf Analytical Laboratories, Woodside, NY). No further testing was carried out on materials with poor performance characteristics.

4.5.1 Synthesis

Preparation of PEI-SALI (3a). A slurry of 20g PEI in 84.5 mL of toluene was vacuum aspirated and the vacuum released under nitrogen. The reaction vessel was connected to a Dean - Stark apparatus with a reflux condenser and the slurry heated to 101°C and held for 30 min with stirring. 5.5 mL of salicylaldehyde was added and the reaction allowed to reflux for 2 h. 2 mL of water was collected in the Dean - Stark apparatus. The resulting slurry was vacuum filtered over a fritted glass funnel; rinsed 3 times with 80 mL of toluene, rinsed 3 times with 80 mL of MeOH, rinsed 1 time with water, soaked overnight in MeOH and rotary evaporated until dry. Final wt. 27.78 g. No further analysis was carried out on the resulting compound.

Preparation of PVA-SALI (3b). A slurry of 20g PVA in 83.5 mL of toluene was vacuum aspirated and the vacuum released under nitrogen. The reaction vessel was connected to a Dean - Stark apparatus with a reflux condenser and the slurry heated to 101°C and held overnight with stirring. 6.5 mL of salicylaldehyde was added and the reaction allowed to reflux for 3 h. Only trace amounts of water were collected in the Dean - Stark apparatus. The resulting slurry was vacuum filtered over a fritted glass funnel; rinsed 5 times with 80 mL of MeOH, rinsed 3 times with 80 mL of toluene, rinsed 3 times with 80 mL of MeOH, and turned out overnight to dry. Final wt. 21.61 g. No further analysis was carried out on the resulting compound.

Preparation of 5-chloromethyl-2-hydroxy-benzaldehyde (9a). 30.00 g of salicylaldehyde was added to a 500 mL three-neck round bottom flask fitted so that one neck contained a fritted glass bubbler attached to a lecture bottle of HCl(g), the middle neck contained a glass stirring rod, and the third neck led to a 2 L bubbler containing 1 L of 1M NaOH. The reaction vessel was immersed in a cold water bath cooled to 18.5°C .At no time was the reaction, or product subjected to temperatures above room temp. To the reaction vessel was added 18.5 mL formaldehyde 38% and 255 mL conc. HCl. The reaction proceeded for 3 h. with HCl (g) bubbling through the reaction mixture the entire time. The resulting precipitate was collected by vacuum filtration over a fritted glass funnel. The reaction vessel and glassware was rinsed with ether to collect all the product adhering to it. This solution was emptied into the funnel with the previously collected precipitate, further ether was added to fully dissolve the collected solid. A total of about 450 mL of ether was used to fully dissolve the precipitate. The ether solution was introduced into a separatory funnel and the water layer extracted. The organic layer was dried over $NaSO_4$ and allowed to evaporate overnight. The result was a white, with tinges of pink, residue on the sides of the beaker with long clear to white needle shape crystals on the bottom of the beaker.

Both fractions were analyzed by NMR and determined to be the same material.

IR (KBr pellet) 27 peaks 3222.6, 2876.5, 1718.9, 1656.8, 1623.6, 1578.8, 1484.8, 1437.8, 1381.7, 1309.7, 1283.3, 1261.2, 1242.9, 1192.2, 1149.8, 1117.5, 949.5, 915.3, 904.0, 849.6, 800.1, 769.9, 726.0, 690.5, 673.4, 576.1, 500.4 cm^{-1}; ^{1}H NMR (400 MHz, acetone) δ 4.745 (s, 2H), 7.065 (d, 1H), 7.68 (d of d, 1H), 7.853 (s, 1H), 10.045 (s, 1H), 11.018 (s, 1H).

Preparation of 5-chloromethyl-2-hydroxy-benzaldehyde-oxime (5). 5 g of 5-chloromethyl-2-hydroxy-benzaldehyde was dissolved in 200 mL of EtOH. In a separate vessel 2.40 g of sodium acetate was dissolved in 200 mL EtOH and 2.04 g of hydroxylamine hydrochloride was added. This second solution was decanted into the first solution with stirring; this formed a small amount of vapor. This solution was stirred for 2 h. at room temperature. The resulting solution was decanted and rotary evaporated to the oil. The oil was redissolved in 100 mL ether and washed 3 times with 100 mL water; to the third wash was added 5 mL sat. $NaHCO_3$, a fourth water wash was then carried out. The organic layer was once again rotary evaporated to the oil and the oil placed on a high vacuum line for 1h. This yielded 4.18 g (76.8%) of a yellow oil. TLC (3% MeOH in $CHCl_3$) rrf light @ .79, heavy @ .38; IR (neat) 24 peaks 3276.0, 2976.0, 2870.2, 2359.4, 2341.3, 1901.9, 1655.0, 1624.4, 1588.0, 1495.1, 1374.4, 1351.8, 1304.9, 1267.9, 1225.2, 1157.2, 1073.0, 1011.1, 953.9, 880.2, 830.2, 798.5, 786.6, 673.7 cm^{-1}; ^{1}H NMR (400 MHz, acetone) δ 4.389 (s, 2H), 6.871 (d, 1H), 7.225 (d of d, 1H), 7.245 (d of d, 1H), 7.31 (s, 1H), 8.351 (s, 1H), 10.034 (s, 1H), 10.667 (s, 1H).

Attachment of 5-chloromethyl-2-hydroxy-benzealdehyde-oxime (5) to PEI gel. 5.84 g of 5-chloromethyl-2-hydroxy-benzealdehyde-oxime (5) was dissolved in 30 mL MeOH (pH 4.5). 1 N NaOH in MeOH was added drop wise to bring the pH up to 7 (actual pH rose to 8.0). MeOH was added to bring the total solution volume up to 40 mL (in this case the solution volume after the NaOH addition was 45 mL). To this was added 10.02 g of PEI which was vacuum degassed and rotary stirred overnight (22 h.). At this point 1 N methanolic NaOH was added, with magnetic stirring, until the pH of the slurry reached 10. The slurry was then vacuum filtered over a fritted glass funnel, rinsed 3 times with 40 mL of MeOH, rinsed 3 times with 40 mL of DI H_2O, rinsed 3 times with 40 mL of MeOH, and allowed to air dry overnight. 10.51 g of a bright yellow powder were produced (5% weight gain); IR (nujol mull) a comparison with PEI reveals an increased peak intensity of 27% at 1633 cm^{-1}; Reflectance IR shows a peak in the =N region.

Attachment of 5-chloromethyl-2-hydroxy-benzealdehyde-oxime (5) to PVA gel. 7.54 g of 5-chloromethyl-2-hydroxy-benzealdehyde-oxime (5) was dissolved in 10 mL MeOH (pH 4.5). 1 N NaOH in MeOH was added drop wise to bring the pH up to 8. MeOH was added to bring the total solution volume up to 20 mL. To this was added 3.14 g of PEI which was vacuum degassed and rotary stirred overnight (24 h.). At this point 1 N methanolic NaOH was added, with magnetic stirring, until the pH of the slurry reached 10. The slurry was then vacuum filtered over a fritted glass funnel, rinsed 3 times with 20 mL of MeOH, rinsed 3 times with 20 mL of DI H_2O, rinsed 3 times with 20 mL of MeOH, and allowed to air dry overnight. 3.38 g of a bright yellow powder were produced (8% weight gain).

Preparation of 5-bromomethyl-2-hydroxy-benzaldehyde (9b). 5.00 g of salicylaldehyde was added to a 500 mL three-neck round bottom flask fitted so that one neck contained a fritted glass bubbler attached to a lecture bottle of HBr(g), the middle neck was stoppered, and the third neck led to a 2 L bubbler containing 1 L of 1M NaOH. The reaction was stirred with a magnetic stirrer and run in an ice bath kept between 15° and 20 °C .At no time was the reaction, or product subjected to temperatures above room temp. To the reaction vessel was added 2.8 mL formaldehyde 38% and 42.5 mL conc. HCl. The reaction proceeded for 3 h. with HBr (g) bubbling through the reaction mixture the entire time. The resulting precipitate was collected by vacuum filtration over a fritted glass funnel. The reaction vessel and glassware was rinsed with ether to collect all the product adhering to it. This solution was emptied into the funnel with the previously collected precipitate, further ether was added to fully dissolve the collected solid. A total of about 100 mL of ether was used to fully dissolve the precipitate. The ether solution was introduced into a separatory funnel and washed with water 1 time. The organic layer was dried over $NaSO_4$ and rotary evaporated to dryness in a room temp. water bath. The resulting white powder was redissolved in 100 mL benzene and washed 3 times with 150 mL of water. The organic layer was dried over $NaSO_4$ and then rotary evaporated to dryness. The resulting powder was redissolved in ether which was allowed to evaporate in air overnight.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.483 (s, 2H), 4.564 (s, 1/2H), 6.965 (d, 1H), 7.54 (d of d, 1H), 7.574 (ss, 1H), 9.867 (s, 1H), 11.061 (s, 1/2H).

Preparation of 5-bromomethyl-2-hydroxy-benzaldehyde-oxime (6). 5 g of 5-bromomethyl-2-hydroxy-benzaldehyde was dissolved in 200 mL of EtOH. In a separate vessel 1.91 g of sodium acetate was dissolved in 200 mL EtOH and 1.62 g of hydroxylamine hydrochloride was added. This second solution was poured into the first solution with stirring; this formed a small amount of vapor. This solution was stirred for 3 h. at room temperature. The resulting solution was decanted and rotary evaporated to the oil. The oil was redissolved in 100 mL ether and washed 4 times with 100 mL water; to the fourth wash was added 10 mL sat. $NaHCO_3$, two more water washes were then carried out. The organic layer was once again rotary evaporated to the oil and placed overnight on a high vacuum line. This yielded 3.42 g (64%) of a yellow oil. TLC (3% MeOH in $CHCl_3$) rrf med. light @ .91, heavy @ .36; ^{1}H NMR (400 MHz, acetone) δ 1.145 (t, 3H), 3.463 (q, 2H), 4.378 (s, 2H), 6.876 (d, 1H), 7.230 (d of d, 1H), 7.302 (s, 1H), 8.342 (s, 1H).

Preparation of 5-bromomethyl-2-hydroxy-benzaldehyde-oxime (6) using 1,2-dimethoxy ethane (glyme) as the solvent. In a beaker 0.12 g of sodium acetate and 0.11 g of hydroxylamine hydrochloride were stirred overnight in 14 mL of 1,2-dimethoxy ethane. In a separate beaker 0.35 g 5-bromomethyl-2-hydroxy-benzaldehyde were dissolved in another 14 mL of 1,2-dimethoxy ethane. The two solutions were combined and allowed to react for three hours. The resulting solution was rotary evaporated until an oily solid was formed. This was redissolved in MeOH, which was once again rotary evaporated to the oily solid. Ether (24 mL) was introduced into the flask to dissolve the portion hoped to be the desired product. This fraction was rotary evaporated to the oil. An NMR was taken of both fractions;

neither spectra was clean. The results will not be reported but the spectra are included in this report.

Quarternization of PEI-Salicylaldoxime. In a 50 mL two neck round bottom flask 2 g of PEI-Salicylaldoxime were immersed in 12 mL of methyl iodide and the resulting slurry was degassed under vacuum. A glass rod stirrer was inserted into one neck of the flask and a reflux condenser into the remaining neck. The slurry was then refluxed with stirring for 2 hr. At the end of the reflux period the slurry was vacuum filtered over a fritted funnel and rinsed three times with 10 mL of MeOH, three times with 10 mL of H2O, and finally three times with 10 mL of MeOH. This was air dried overnight. The final weight was 2.32 g a weight gain of 16%.

Capping the unreacted free amines in PVA-salicylaldoxime.[9] In a 25 mL round bottom flask 0.25 mL of acetic anhydride and 0.05 mL of pyridine were dissolved in 5.4 mL of methylene chloride. 1.35 g of PVA-salicylaldoxime were added and the slurry was degassed. The flask was placed on the rotary stirrer and stirred for 30 min. Then the resulting slurry was emptied into a fritted funnel and vacuum filtered, rinsed 3 times with 5 mL of methanol, rinsed 3 times with 5 mL of DI water, and rinsed 3 times with 5 mL of methanol. The resulting gel material was then dried overnight. Final weight 1.21 g. Weight loss 0.14 g.

Capping the unreacted free amines in PEI-salicylaldoxime. In a 25 mL round bottom flask 0.28 mL of acetic anhydride and .06 mL of pyridine were dissolved in 4.8 mL of methylene chloride. 1.2040 g of PVA-salicylaldoxime were added and the slurry was degassed. The flask was placed on the rotary stirrer and stirred for 30 min. Then the resulting slurry was emptied into a fritted funnel and vacuum filtered, rinsed 3 times with 5 mL of methanol, rinsed 3 times with 5 mL of DI water, rinsed 1 time with 20 mL of DI water, and rinsed 3 times with 5 mL of methanol. The resulting gel material was then dried overnight. Final weight 1.20 g. No weight change

Addition of 5-methylsalicylaldoxime to PVA via iodination of 5-chloromethylsalicylaldoxime. In a 100 mL round bottom flask 6.71 g of 5-chloromethylsalicylaldoxime were dissolved in 50 mL of regent grade acetone. 5.40 g of sodium iodide were added and the solution was refluxed for 2 hr. The solvent was rotary evaporated to yield the oil. The resulting oil was redissolved in 40 mL of methanol, 5.00 g of PVA were added and the slurry was degassed under vacuum. The slurry was rotary stirred for 2 days then the contents were emptied into a fritted funnel over a vacuum flask, rinsed 3 times with 40 mL of methanol, 3 times with 40 mL of DI water, 3 times with 40 mL of methanol, and air dried overnight. Total weight 5.90 g Weight gain 0.90 g Percent weight gain 18%

Addition of 5-methylsalicylaldoxime to PEI via iodination of 5-chloromethylsalicylaldoxime In a 100 mL round bottom flask 6.68 g of 5-chloromethylsalicylaldoxime were dissolved in 20 mL of methanol. 0.54 g of sodium iodide were added and the solution swirled until the sodium iodide dissolved, 5.00 g of PVA were added and the slurry was degassed under vacuum. The slurry was rotary stirred for 3 days then the contents were emptied into a fritted funnel over a vacuum flask, rinsed 3 times with 40 mL of methanol, 3 times with 40 mL of DI water, 3 times with 40 mL of methanol, and air dried overnight. Total weight 5.85 g Weight gain 0.85 g Percent weight gain 17%

Synthesis of *p*-amino salicylaldoxime from *p*-nitro salicylaldehyde: the Thiosemicarbazide route.[12] In 1L of boiling DI H_2O 16.7g of *p*-nitro salicylaldehyde are dissolved with constant stirring with a stir bar. 10.00g of thiosemicarbazide are added immediately forming a yellow precipitate. The precipitate, the *p*-nitro salicylaldehyde thiosemicarbazone, was collected by vacuum filtering through a Buchner funnel.

20.00g of the *p*-nitro salicylaldehyde thiosemicarbazone were suspended in a 50°-60° solution of 2.00g of thiosemicarbazide dissolved in 400 mL of DI water with the addition of 13.5 mL of ammonium hydroxide. After 0.5 hr 200 mL of 20% ammonium hydroxide was slowly added followed by 10-15 min of heating over a boiling water bath. The pH was then adjusted to 7.5 with acetic acid, forming a yellow-orange precipitate which was filtered off and recrystalized from water. Yield 6.17 g of p-amino-salicylaldehyde thiosemicarbazone.

A suspension of 10 g of p-amino-salicylaldehyde thiosemicarbazone was boiled in a solution 80 mL of concentrated hydrochloric acid and 360 mL of DI water until completely dissolved. As the solution cooled a red precipitate formed; this was filtered off and immediately resuspended in a hot solution of 2 g of hydroxylamine hydrochloride in 220 mL of DI water. The solution was neutralized with sodium acetate and heated until the product went into solution. The reaction flask containing the solution was placed in the refrigerator overnight yielding yellow-brown crystals which were filtered and collected. Yield 0.87 g

Addition of 5-amino salicylaldoxime to bromopropyl gel. In a 25 mL round bottom flask containing a magnetic stirrer 0.43 g of 5-aminosalicylaldoxime was dissolved in 10 mL of methanol 1.75 g of gel were added and degassed. The flask was fitted with a reflux condenser and the contents were refluxed overnight. The slurry was vacuum filtered in a fritted funnel and rinsed three times with 10 mL of methanol, three times with 10 mL of DI water, and three times with 10 mL of methanol, the gel was then air dried overnight. The recovered powder revealed disintegration of the gel.

The second half of the 5-aminosalicylaldehyde produced in the previous procedure was combined with 1.75 g of bromo propyl gel in 10 mL of methanol and placed on the rotary stirrer overnight at room temperature. The resulting slurry was vacuum filtered in a fritted funnel and rinsed three times with 10 mL of methanol, three times with 10 mL of DI water, and three times with 10 mL of methanol, the gel was then air dried overnight. Final weight 1.72 g.

Synthesis of 5- nitro salicylaldoxime from 5- nitro salicylaldehyde.[13] In a 1 L beaker 8.27 g of 5-nitro salicylaldehyde was dissolved in 500 mL of boiling DI H2O while stirring. 4 g of hydroxylamine hydrochloride were added and the solution immediately neutralized with sodium acetate. The pH of the solution was raised to 6.4 with the addition of just over 4.72 g of sodium acetate. This solution was allowed to stir with continued heating for 15 min. The precipitate that formed was filtered out with a Buchner funnel and the mother liquor that was collected was passed over carbon, rotary evaporated to about 1/3 its original volume and cooled in the refrigerator to crystallize the remaining product. Total yield 8.68 g Theoretical yield 9.01 g % yield 94%.

Catalytic Hydrogenation of 5-nitro salicylaldoxime to yield 5-amino salicylaldoxime. In a 50 mL round bottom flask a couple of drops of DI H2O were added to 0.10 g of 5% palladium on carbon prior to the addition of 10 mL of ethanol (95%). To this was added 0.50 g of 5-nitro salicylaldoxime and the pH was adjusted to 7.5 with 10% sodium hydroxide in ethanol. The flask with the solution was attached to a low pressure hydrogenator, the air evacuated and replaced with a measured volume of hydrogen gas. The reaction was allowed to proceed for 2 hr.

Conversion of 5-nitro salicylaldoxime to 5-amino salicylaldoxime via sodium dithionite reduction.[14] In a 250 mL beaker 10.00 g of 5-nitro salicylaldehyde was dissolved in 150 mL of a 20% aqueous ammonium hydroxide solution. This was slowly added to a solution of 44.83 g of sodium dithionite in 180 mL of DI H2O in a 500 mL erlenmeyer flask. The 5-amino salicylaldoxime was extracted with 150 mL of ether, the ether was dried with magnesium sulfate, and filtered over charcoal. The ether was rotary evaporated off and the residue collected. Yield 4.49 g Theoretical yield 8.53 g Percent yield 54%

Addition of 5-amino salicylaldoxime to bromopropyl gel. In a 100 mL round bottom flask 5.00 g of bromopropyl gel were combined with 40 mL of ethanol (95%). The slurry was degassed under vacuum and the vacuum released under nitrogen, this was done three times. 3.80 g of 5-amino salicylaldoxime was then added and the above degassing procedure was carried out three more times. The resulting slurry was put on the rotary stirrer and stirred for 72 hr. The slurry was vacuum filtered in a fritted funnel and rinsed three times with 40 mL of ethanol, three times with 40 mL of DI water, and three times with 40 mL of methanol, the gel was then air dried overnight. The initial color of the slurry was brown which turned reddish-brown by the end and resulted in a salmon colored gel. Final gel weight 4.89 g Theoretical gel weight 4.92 g

Ammination of Bromo Propyl gel to yield Amino Propyl gel. In a 300 mL round bottom flask 20 mL of 2.0 M ammonia in methanol was combined with 60 mL of methanol. 19.99 g of bromopropyl gel was added and the slurry was degassed. This was allowed to react for 30 min on the rotary stirrer then vacuum filtered in a fritted funnel, rinsed 3 times with 80 mL of methanol, rinsed 3 times with 80 mL of DI water, rinsed 3 times with 80 mL of methanol, and allowed to air dry overnight. Final weight 19.69 g Theoretical weight 17.35 g The resulting gel showed no capacity for copper.

In a 100 mL round bottom flask 20 mL of 2 N ammonia in methanol was mixed with 20 mL of distilled methanol. To this was added 10.00 g of bromo propyl gel, the resulting slurry degassed and rotary stirred for 1 hr. After this time the contents were vacuum filtered in a fritted funnel, rinsed 3 times with 40 mL of methanol, rinsed 3 times with 40 mL of DI water, rinsed 3 times with 40 mL of methanol, and air dried overnight. Final weight 9.81 g

In a 100 mL round bottom flask 40 mL of 2 N ammonia in methanol was combined with 10.00 g of bromo propyl gel, the resulting slurry degassed and rotary stirred for 96 hr. After this time the contents were vacuum filtered in a fritted funnel, rinsed 3 times with 40 mL of methanol, rinsed 3 times with 40 mL of DI water, rinsed 3 times with 40 mL of methanol, and air dried overnight. Final weight 9.61 g

In a 100 mL 3-neck round bottom flask fitted with a paddle stirrer and a fritted glass bubbler attached to a supply of ammonia gas, 40 mL of 2 N ammonia in methanol was combined with 10.00 g of bromo propyl gel, the resulting slurry degassed and immersed in a 50° C bath. The slurry was stirred while ammonia was bubbled through for 2 hr. After this time the contents were vacuum filtered in a fritted funnel, rinsed 3 times with 40 mL of methanol, rinsed 3 times with 40 mL of DI water, rinsed 3 times with 40 mL of methanol, and air dried overnight. Final weight 9.65 g

Synthesis of Amino Propyl Gel from Aminopropyl trimethoxysilane. In a 300 mL round bottom flask 10.76 g of aminopropyl trimethoxysilane was combined with 80 mL of heptane, 20.00 g of hydrated silica gel was added and the slurry was degassed under vacuum. The flask was then attached to a rotary stirrer and allowed to react for 3 days. The heptane was then rotary evaporated off and the gel was rinsed in a fritted funnel over vacuum 3 times with 80 mL of methanol, 3 times with 80 mL of DI water, 3 times with 80 mL of methanol, and allowed to air dry overnight. Final weight 22.79 g Weight gain 2.79 g Percent weight gain 14%

Addition of 5-chloromethylsalicylaldoxime to Amino propyl Gel. In a 50 mL round bottom flask 5-chloromethylsalicylaldoxime was dissolved in 20 mL of methanol, 5.00 g of aminopropyl gel was added and the resulting slurry degassed under vacuum. The contents were rotary stirred for 48 hr emptied into a fritted funnel over a vacuum flask, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 3 times with 20 mL of methanol, and allowed to air dry overnight. Final weight 5.73 g Weight gain 0.73 g Percent weight gain 14.6%

Attachment of PVC (Poly(vinyl Chloride)) to Aminopropyl Gel. In a 500 mL beaker 25 g of PVC was dissolved in 75 g of 1,2-dichlorobenzene. 25 g of the resulting slurry was added to a 100 mL round bottom flask with an additional 40 mL of 1,2-dichlorobenzene and 5.00 g of aminopropyl gel. The resulting slurry was degassed under vacuum and rotary stirred for 5 days. The contents of the flask were emptied into a fritted glass funnel over vacuum, rinsed 3 times with 40 mL 1,2-dichlorobenzene, 3 times with 40 mL methanol, 3 times with 40 mL DI water, 3 times with 40 mL methanol, and air dried overnight. Final weight 7.67 g Weight gain 2.67 g Percent weight gain 53%

Attachment of 5-aminopropylsalicylaldoxime to PVC Gel. In a 100 mL round bottom flask 1.73 g of 5-aminosalicylaldoxime was dissolved in 40 mL of 1,2-dichlorobenzene, 5.00 g of PVC gel was added and degassed under vacuum. The flask was attached to a rotary stirrer and immersed in a 95° C bath for 3 hr. The contents were emptied into a fritted glass funnel over vacuum, rinsed 3 times with 40 mL 1,2-dichlorobezene, 3 times with 40 mL methanol, 3 times with 40 mL DI water, 3 times with 40 mL methanol, and air dried overnight. Final weight 5.32 g Weight gain 0.32 g Percent weight gain 6%

Addition of 5-aminosalicylaldoxime to PVA Gel via Carbodiimide Coupling I. In a 300 mL round bottom flask 4.56 g of 5-aminosalicylaldoxime was dissolved in a mixture of 65 mL of *i*-propanol and 20 mL of DI water. 3.00 g of ground succinic anhydride was and added and allowed to react for 30 min. The solution turned deep red and the pH remained approximately neutral. The resulting product was recovered by rotary evaporation of the solvent yielding a pale brown caked substance. This was redissolved in a solution of 50 mL of DI water and 10 mL *i*-propanol with heating and stirring until all the material was dissolved. Next 5.57 g of EDC was added and stirred causing a red mud-like glob to form on the bottom of the flask. 5.00 g of PVA was added and the mixture was degassed under vacuum; the vacuum was released with nitrogen. The flask was then put on the rotary stirrer for 36 hr. The contents of the flask were then put into a fritted funnel over vacuum and rinsed 2 times with 40 mL of DI water, then 1 time with 40 mL of saturated sodium bicarbonate solution. At this time the filtration process almost stopped so some *i*-propanol was added to increase the solubility of the byproducts and aid the filtration process. It didn't speed the process. The product was finally isolated and air dried overnight, the product contained too much fine brown powder indicating that the gel had not been sufficiently rinsed. Additional rinsing and filtering was carried out, 3 times with 40 mL of 2N sulfuric acid, 3 times with 40 mL of saturated sodium bicarbonate, 3 times with 40 mL of DI water, 3 times with 40 mL of methanol, and air dried overnight, Final weight 4.38 g

Addition of 5-aminosalicylaldoxime to PVA Gel via Carbodiimide Coupling II. In a 100 mL round bottom flask 3.08 g of 5-aminosalicylaldoxime was dissolved in 15 mL of distilled THF (tetrahydrofuran) on the rotary stirrer for 15 min. 2.03 g of ground succinic anhydride was added to the flask and the stirring continued until the reaction cooled to room temperature. 3.88 g of EDC were added, this didn't adequately dissolve so an additional 10 mL of THF were added as well as 3 drops of triethyl amine. The EDC still remained undissolved after 45 min of stirring. 3.25 g of PVA were added and the mixture was rotary stirred for 24 hr. The contents were emptied into a fritted funnel over a vacuum flask and the large gummy lumps removed and placed in a beaker of water overnight to dissolve them and recover any gel they may contain. (They remained insoluble.) The gel was rinsed 2 times with 40 mL of THF, 2 times with 40 mL of dilute sulfuric acid, 5 times with 40 mL of saturated sodium bicarbonate, 2 times with 40 mL of DI water, 3 times with 40 mL of methanol, and air dried overnight. Final weight 2.55 g

Addition of 5-aminosalicylaldoxime to PVA Gel via Carbodiimide Coupling III. In a 100 mL 3-neck round bottom flask fitted with a paddle stirrer 4.56 mL of 5-aminosalicylaldoxime was dissolved in 20 mL of THF. 3.00 g of ground succinic anhydride was added and stirred until dissolved. 5.00 g of PVA was added and the resulting slurry degassed. In a separate beaker 6.19 g of DCC was dissolved in 20 mL of THF, placed in an addition funnel and added to the reaction flask over 30 min. The reaction proceeded overnight. The contents of the flask were emptied into a fritted funnel over a vacuum flask and rinsed 3 times with 20 mL of THF, 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 3 times with 20 mL of methanol, and air dried overnight. Final weight 4.28 g.

Attachment of 5-chloromethylsalicylaldoxime to Bromooctyl Gel via Zinc Coupling.[15] In a 50 mL 3-neck round bottom flask fitted with an addition funnel and a nitrogen inlet 2.68 g of zinc dust was mixed in 3.0 mL of dry THF. In a 50 mL beaker 2.96 g of 5-chloromethylsalicylaldoxime was dissolved in 11 mL of dry THF and 3 mL of dimethylsulfoxide (DMSO)then transferred to the addition funnel. The solution in the addition funnel was added to the zinc dust in an atmosphere of nitrogen and stirred with a magnetic stirred for 24 hr. The zinc dust was removed from the solution by filtering the solution through a Buchner funnel into a 50 mL round bottom flask and rinsing with ~2 mL of THF. 3.00 g of bromooctyl gel was added to the flask along with an additional 2 mL of THF to ensure total wetting of the gel. This was stirred for 3 days on the rotary stirrer then the contents were emptied into a fritted glass funnel over vacuum and rinsed 2 times with 10 mL of THF, 2 times with 80 mL of methanol, 2 times with 80 mL of DI water, 1 time with 80 mL of 0.5N hydrochloric acid, 2 times with 80 mL of DI water, 3 times with 80 mL of methanol, and allowed to air dry overnight. Final weight 2.82 g

Attaching Salicylaldoxime to Bromopropyl gel via a Friedal-Crafts alkalation.[16] In a 500 mL round bottom flask 6.86 g of salicylaldoxime was dissolved in 150 mL of $CHCl_3$. To this 10.00 g of bromopropyl gel was added and degassed under vacuum. 6.0 mL of anhydrous $SnCl_4$ was added with stirring from a magnetic stir bar. A reflux condenser was fitted to the flask and the slurry was refluxed with stirring for

20 hr. At the end of the reflux period the slurry was vacuum filtered over a fritted funnel and rinsed three times with 40 mL of $CHCl_3$, three times with 40 mL of MeOH, three times with 40 mL of DI H_2O, one time with 40 mL of conc. HCl, three times with 40 mL of DI H_2O, three times with 40 mL of MeOH, three times with 40 mL of $CHCl_3$, three times with 40 mL of .5 M $N(Et)_3$, three times with 40 mL of $CHCl_3$. This was air dried overnight. The final weight was 9.6 g.

The above experiment was also conducted using 150 mL of Diglyme (2-methoxyethyl ether) as the solvent and reducing the reflux time to 1 hr.

Attaching Salicylaldoxime to Bromopropyl gel via a Friedal-Crafts alkalation II. In a 100 mL round bottom flask 5.00 g of bromo octyl gel was mixed with 15 mL of carbon disulfide to make a slurry which was degassed under vacuum. 2.5 mL of carbon disulfide was added to 2.5 mL of benzisoxizole in a 50 mL round bottom flask then 5 g of anhydrous aluminum tribromide was added. The benzisoxizole/aluminum tribromide solution was pipetted to the flask containing the gel slurry. The flask containing the reaction mixture was then rotary stirred while immersed in an ice bath for 2 hr. The slurry was then vacuum filtered over a fritted funnel and rinsed three times with 40 mL of $CHCl_3$, three times with 20 mL of MeOH, three times with 20 mL of DI H_2O, 3 times with 20 mL of 4 N sulfuric acid, three times with 20 mL of DI H_2O, three times with 20 mL of MeOH, and air dried overnight. The final weight was 4.80 g.

Synthesis of 5-hydroxybenzisoxizole.[17] In a 50 mL beaker 9.52 g of hydroxylamine-O-sulfonic acid was dissolved in 31 mL of DI water, 0.76 g of sodium sulfate was added and stirred with a magnetic stirrer until dissolved. This solution was added to 10.00 g of 5-hydroxybenzaldehyde in a 500 mL erlenmeyer flask and stirred for 15 min. The flask was then placed in an ice bath, 8 mL of DI water and 6.43 g of sodium bicarbonate were slowly added with the flask periodically being removed from the ice bath and swirled to dissipate some of the foam and 12 mL of DI water were also added periodically added to break up some of the foam. Upon the complete addition of the sodium bicarbonate, the flask was removed from the ice bath, the sides of the flask were washed down with a minimal amount of DI water and the reaction was allowed to proceed at room temperature for 1 hr. After 30 min at room temp 100 mL of diethylether was added to the flask. At the completion of 1 hr the solution was emptied into a separatory funnel and the aqueous layer was returned to the flask with an additional 0.57 g of sodium bicarbonate and 20 mL of diethylether and reacted for an additional hour. The organic layer was separated off and combined with the first organic fraction and the aqueous layer was extracted once more with 20 mL of diethylether and the organic layer combined with the first two fractions. The combined organic phases were then dried over magnesium sulfate, filtered and the diethylether allowed to evaporate off overnight. The resulting crystals were washed with boiling DI water and cooled in the refrigerator to recrystallize any dissolved product. The crystals were filtered out and dried under high vacuum for 1 hr. Yield 8.50 g Theoretical yield 9.72 g Percent yield 87%

<u>Synthesis of *n*-8-bromooctyl trichlorosilane</u> 5.00 g of 8-bromo-1-octene and .001 g of chloroplatanic acid were placed in a 25 mL 2-neck round bottom flask fitted with a condensing coil and an addition funnel. The exit from the condenser lead to a cold

finger immersed in acetone and dry ice. 3.00 mL of trichlorosilane was added without stirring over 6 hr using the addition funnel. The flask was then placed in a 65° C water bath and swirled periodically over three days. At this point NMR showed almost total conversion.

Synthesis of Bromo Octyl (BO) Gel from n-8-bromooctyl trichlorosilane. In a 100 mL beaker 8.05 g of *n*-8-bromooctyl trichlorosilane was mixed with 27 mL of heptane. This was added to 8.25 g of hydrated gel in a 100 mL round bottom flask immediately releasing copious amounts of hydrogen chloride. The flask was fixed to a rotary stirrer using a vented stopper and stirred for 16 hr. The heptane was then rotary evaporated off and the dry gel placed in a fritted funnel over vacuum, rinsed 3 times with 40 mL of methanol, 3 times with 40 mL of DI water, 3 times with 40 mL of methanol, and air dried overnight. Final weight 11.21 g Weight gain 2.96 g Percent weight gain 26.4% Bromine analysis carried out by Schwartzkopf Microanalytical Laboratory, Inc. revealed 10.44%-10.53% bromine

Attachment of 5-hydroxybenzisoxizole onto Bromo Octyl Gel I. Potassium Carbonate Reaction. In a 50 mL round bottom flask 2.70 g of 5-hydroxybenzisoxizole was dissolved in 16 mL of dry reagent grade acetone. 4.00 g of bromo octyl gel was added and degassed under vacuum. 2.76 g of potassium carbonate was added to the mixture and the flask was stirred on a rotary stirrer for 4 days. The contents of the flask were emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of acetone, , rinsed 3 times with 20 mL of methanol, , rinsed 3 times with 20 mL of DI water, , rinsed 3 times with 20 mL of methanol, and air dried overnight. Final weight 3.81 g

Conversion of 5-hydroxybenzisoxizole to the Sodium 5-hydroxybenzisoxizolate Salt. Under anhydrous conditions 20 mL of distilled dioxane was introduced into a 50 mL nitrogen filled schlank tube containing a magnetic stir bar. 1 g of freshly cut sodium was added followed by 5.27 g of 5-hydroxybenzisoxizole which quickly produced a light beige precipitate. More dioxane was added in an unsuccessful attempt to dissolve the precipitate.

Addition of 5-hydroxybenzisoxizole to Bromo Octyl Gel II. Sodium 5-hydroxybenzisoxizolate in Dioxane. In a 50 mL Schlank tube 4 g of bromo octyl gel was degassed in 10 mL of distilled dioxane and the vessel refilled with nitrogen. 25 mL of the solution prepared in the preceding procedure were syringed into the bromo octyl gel slurry produced in the preceding step. This was stirred for 4 days with a magnetic “football” stirrer with no noticeable diminution of the light brown Sodium 5-hydroxybenzisoxizolate precipitate. The contents of the reaction were emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 3 times with 20 mL of methanol, and air dried overnight. The resulting product was a very fine powder indicating disintegration of the silica gel.

Addition of 5-hydroxybenzisoxizole to Bromo Octyl Gel III. Sodium 5-hydroxybenzisoxizolate Refluxed in Dioxane. In a 100 mL 3-neck round bottom flask fitted with a glass rod stirrer, reflux condenser, and a nitrogen inlet 4 g of bromo octyl gel was degassed in 10 mL of distilled dioxane and a nitrogen atmosphere introduced. 25 mL of the sodium 5-hydroxybenzisoxizolate solution prepared previously was syringed in and the solution allowed to reflux with stirring overnight. The resulting material was emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 3 times with 20 mL of methanol, and air dried overnight.

Conversion of 5-hydroxybenzisoxizole to the Sodium 5-hydroxybenzisoxizolate Salt

In a 50 mL nitrogen filled Schlank tube containing a magnetic stir bar, 4.29 g of 5-hydroxybenzisoxizole was dissolved in 50 mL of distilled dioxane. 1.3851 g of sodium hydride was added and the solution went milky white, this reaction was allowed to proceed for 2 hr.

Addition of 5-hydroxybenzisoxizole to Bromo Octyl Gel IV. Sodium 5-hydroxybenzisoxizolate in Dioxane. In a 50 mL Schlank tube 4 g of bromo octyl gel was degassed in 10 mL of distilled dioxane and the vessel refilled with nitrogen. 25 mL of the solution prepared in the preceding procedure were syringed into the bromo octyl gel slurry produced in the preceding step. This was stirred for 20 hr with a magnetic "football" stirrer with no noticable diminution of the light brown Sodium 5-hydroxybenzisoxizolate precipitate. The contents of the reaction were emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, followed by a steady water wash until all the gummy residue was gone, 3 times with 20 mL of methanol, and air dried overnight. The resulting product was a very fine powder indicating disintegration of the silica gel. Final weight 3.53 g

Conversion of 5-hydroxybenzisoxizole to the Sodium 5-hydroxybenzisoxizolate Salt. In a 250 mL Schlank tube 5.41 g of 5-hydroxybenzisoxizole was dissolved in 100 mL of THF in a nitrogen atmosphere. 0.92 g of freshly cut sodium were added which reacted readily and produced a beige precipitate the reaction was allowed to proceed for approximately 4 hr. An additional 100 mL of THF was added in an unsuccessful attempt to dissolve the precipitate.

Addition of 5-hydroxybenzisoxizole to Bromo Octyl Gel V. Sodium 5-hydroxybenzisoxizolate in THF. In a 100 mL round bottom flask with a stop cock side arm 4 g of bromo octyl gel was degassed in 10 mL of distilled THF and the vessel refilled with nitrogen. 25 mL of the solution prepared in the preceding procedure were syringed into the bromo octyl gel slurry produced in the preceding step. This was stirred for 4 days with a paddle stirrer with no noticeable diminution of the light brown Sodium 5-hydroxybenzisoxizolate precipitate. The contents of the reaction were emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 3 times with 20 mL of methanol, and air dried overnight. The resulting product was a very fine powder indicating disintegration of the silica gel. Final weight 3.55 g

Addition of 5-hydroxybenzisoxizole to Bromo Octyl Gel VI. Sodium 5-hydroxybenzisoxizolate Refluxed in THF. In a 100 mL 3-neck round bottom flask fitted with a glass rod stirrer, reflux condenser, and a nitrogen inlet 4 g of bromo octyl gel was degassed in 10 mL of distilled dioxane and a nitrogen atmosphere introduced. 25 mL of the sodium 5-hydroxybenzisoxizolate solution prepared previously was syringed in and the solution allowed to reflux with stirring overnight. The resulting material was emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 3 times with 20 mL of methanol, and air dried overnight. Final Weight 3.52 g

Conversion of 5-hydroxybenzisoxizole to the Sodium 5-hydroxybenzisoxizolate Salt. In a 50 mL beaker 0.79 g of pulverized sodium hydroxide was dissolved in 20 mL of absolute ethanol and transferred to an addition funnel. In a 100 mL 3-neck round bottom flask fitted with a paddle stirrer, an addition funnel and a nitrogen inlet 2.70 g of 5-hydroxybenzisoxizole were dissolved in 30 mL of absolute ethanol. The sodium hydroxide solution was added to the reaction flask over the course of 1 hr and the reaction proceeded for 1 additional hour forming a light brown precipitate. An additional 20 mL of absolute ethanol was added in an unsuccessful attempt to dissolve the precipitate that formed.

Addition of 5-hydroxybenzisoxizole to Bromo Octyl Gel VII. Sodium 5-hydroxybenzisoxizolate in Ethanol. 4.00 g of bromopropyl gel was added to the flask degassed under vacuum and the mixture was stirred for three days. The precipitate remained at this time so 20 mL of dry reagent grade methanol was added. This dissolved the precipitate creating a green-black solution. This mixture was allowed to stir for 3 more days, after which it was emptied into a fritted glass funnel over vacuum, rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 1 time with 20 mL of 0.5 N sulfuric acid, 2 times with 20 mL of DI water, 1 time with 20 mL of 0.5 N sulfuric acid, 2 times with 20 mL of DI water, 3 times with 20 mL of methanol, and air dried overnight. Final Weight 3.90 g

Synthesis of (N,N,N-trimethylammonium chloride) propyl (TMAP) Gel. In a 300 mL round bottom flask 65 mL of dry hexane were mixed with 14.34 mL of trimethoxysilylpropyl N,N,N-trimethylammonium chloride. 20.00 g of hydrated silica gel were added and degassed under vacuum. The contents of the flask were allowed to react for 20 hr on a rotary stirrer. The contents of the flask were then rotary evaporated to dryness. Final weight 25.01 g Percent weight gain 25%.

4.5.2 Analysis

General test procedures. The capacity tests for the gels were all run in the same fashion, the only variable besides the gel and challenge solution composition, was the challenge solution volume. All tests were conducted at a flow rate of about 10 mL/min.

A volume of challenge solution was pumped through the column, followed by an equal volume of deionized water. This was all collected and analyzed as the flowthrough. Next 5 mL of 4N H_2SO_4 was pumped through the column followed by 15 mL of deionized water, this was collected and analyzed as the elution. The above steps were done using the PC controlled valve switcher in the manual mode. The regeneration was carried out in the automatic mode controlled by software designed for the purpose by Gamble and Associates. First, 85 mL of deionized water was pumped through the column followed by 10 mL of 4N NH_4OH, with a final 100 mL deionized water rinse.

Challenge solutions:

1) 25 mM Fe(III) - 7.40 g $Fe(NO_3)_3$ in 1 L deionized water pH = 2.14

2) 25 mM Cu(II) - 6.24 g $CuSO_4$ in 1 L deionized water pH = 1.98

3) 25 mM Cu(II) and 25 mM Fe(III) - 7.40 g $Fe(NO_3)_3$ and 6.24 g $CuSO_4$ in 1 L deionized water pH = 2.02

4) 25 mM Cu(II) and 25 mM Fe(III) - 7.40 g $Fe(NO_3)_3$ and 6.24 g $CuSO_4$ in 1 L deionized water adjusted with conc. HCl to pH = 1.05

5) 25 mM Cu(II) and 25 mM Fe(III) - 7.40 g $Fe(NO_3)_3$ and 6.24 g $CuSO_4$ in 1 L 1N HCl pH ≈ 0

PEI-SALI. Weight of gel in column - 3.25 g. Volume of challenge solution passed through the column - Solution 1 - 50 mL

PEI-SALO. Weight of gel in column - 2.50 g. Volume of challenge solution passed through the column - Solution 1 - 30 mL; Solution 2 - 50 mL; Solution 3 - 20 mL

PVA-SALO. Weight of gel in column - 2.00 g. Volume of challenge solution passed through the column - Solution 1 - 30 mL; Solution 2 - 50 mL; Solution 3 - 20 mL; Solution 5 - 40 mL; Solution 4 - 40 mL; In the test labeled pH 1 sv solution 4 was pumped through until it looked as though the column was loaded to its maximum capacity (sv = small volume) - 14 mL.

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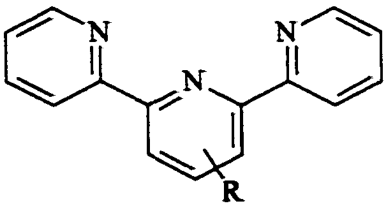
CHAPTER 5 Copper Selective CuWRAM

5.1 CuWRAM A copper selective material

While addition of the salicylaldoxime ligand appeared not to have the desired effect of extracting copper(II) and rejecting iron(III) from solution the goal to create such a material still remained. At the onset of the project, while researching the salicylaldoxime ligand one ligand that seemed a good candidate for creating a copper selective material was terpyridine **18**. This ligand contains three joined pyridine rings



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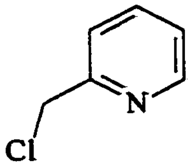

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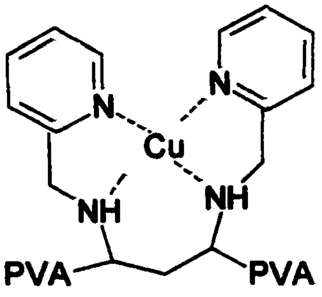
which would be able to form a planer tridentate chelate. The pyridine rings may be bulky enough to hinder the octahedral coordination favored by iron(III) resulting in a selective material. Terpyridine however is too expensive to be practical for use in a large scale extraction material. It was during this time, while developing a different strategy for creating a copper selective material, that 2-chloromethylpyridine (picolyl chloride) **19** came to light. Addition of picolyl chloride to a linear polyamine containing only primary amines, PVA the linear polymer being used exclusively at the time, or PAA would produce a bi- or tridentate ligand **20,21** depending on the efficiency of the reaction . A search of the literature revealed that a similar ligand system was being used on a resin support.[1,2]



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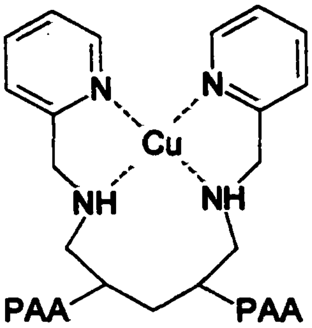

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5.2 Results and Discussion

5.2.1 Synthesis

Addition of the picolyl chloride to the primary amine of the polyamine should be a straightforward reaction. Nucleophilic attack by the amine nitrogen of the

	mmol M^{+n}/g CuWRAM	mg M^{+n}/g CuWRAM
Copper(II)	0.21	13.5
Iron(III)	0.02	1.0

Table 5.1 The copper(II) and iron(III) capacities for an early version of CuWRAM. The feed solution contained 17mM copper(II) and 57 mM iron(III).

polyamine, on the methylene carbon of the picolyl chloride produces a picolylolamine moiety on the polymer and hydrogen chloride as a by-product. The initial reactions were successful based on copper(II)/iron(III) separations but the copper capacities were low. An example of the metal loading on an early material is shown in Table 5.1.

When comparing the numbers in the table it is easy to see that the copper (II) loading was 10 times that of the iron(III) on a mole basis. This is even more impressive when the concentration of metals in the feed solution is taken into consideration. The feed solution metal concentrations were 17 mM Cu(II) and 57 mM Fe(III). This indicated that a material selective for copper(II) in the presence of iron(III) had been synthesized but as was stated above, the overall copper capacity was marginal for any practical use.

The hypothesis, that guided the original work plan, was that the addition of excess base caused oxidation of the pyridine ring of the ligand and possible ring opening which hindered the addition of the ligand to the silica-polyamine material. This hypothesis was formed on the basis that the free-base picolyl chloride in a pH 7 solution was yellow but that addition of base to the solution turned the solution a deep crimson red. To combat the possibility of ring oxidation from solvated oxygen in the solvents the reaction was carried out in solvents that had been oxygen purged by alternately placing the solvent under vacuum and then introducing nitrogen to displace the oxygen. The reaction was carried out using these deoxygenated solvents both under a normal air atmosphere and under an inert nitrogen atmosphere. In both cases there was no increase in the addition of the ligand to the polymer as evidenced by no increase in copper capacity.

The next parameter to be investigated was the addition of base to the reaction. The pyridine ligand was transformed to its free base form using one equivalent of KOH and added to the polymer at 0°C. The solution remained yellow but the material lost weight upon completion of the reaction and had a low capacity for copper(II). Further experiments were carried out adjusting the reaction conditions to control the color of the reaction solution. The reaction was carried out at reflux temperatures, slowly adding a second equivalent of base throughout the reaction. A reaction in which the base and the ligand were alternately added to the silica-polyamine material refluxing in ethanol was also carried out. These reaction conditions also controlled the color change but also resulted in an overall weight loss from the reaction and poorer capacities for copper(II). At this point an experiment was conducted to try and determine the chemical nature of the difference between the yellow solution and the red solution obtained upon addition of base to the picolyl chloride solution the resulting ^{1}H NMR's show no difference in the chemical shifts of the protons in the yellow or red solutions. At this point it was decided that the addition of base resulting in the red color was not the major impediment to better loading and that the problem may be too little base in the reaction to remove the free protons in solution causing the reactivity of the polymeric amines to be diminished.

These findings led into the next phase of investigation, which was to add more base in a calculated manner. In one experiment two equivalents of base were added to the silica-polyamine / free base ligand reaction mixture at reflux temperatures. This produced a material that underwent weight loss and material degradation to a point that during testing the backpressures created were too high to complete the testing. Carrying out the reaction using one equivalent of KOH in the reaction of the free base ligand with the silica-polyamine yielded a material that underwent a weight loss and severly reduced capacities for copper (II).

Another approach to the synthesis was to carry out the reaction between the polymer and the ligand in the solution phase prior to adding the polymer to the silica gel. In these experiments both temperature effects and the effects of the reactant concentrations were investigated. In all cases the resulting material had a poorer capacity for copper than that of the standard (original) method. The practicality and economics of using protecting groups and then deprotecting led us to abandon any investigations along those lines.

Another aspect of the synthesis, which was investigated, was the effect of solvents on the reaction. In the original synthesis the solvent system was a 50:50 v:v mix of methanol and tetrahydrofuran. The object was to remove the tetrahydrofuran component from the synthesis due primarily to ill environmental effects associated with its disposal. Solvent systems of 100% water, 100% methanol, 100% tetrahydrofuran, and 50% water with 50% methanol were investigated.

The method that finally produced the best results was simple although it pushed the envelope of conditions that the material could withstand. It seemed reasonable to believe that the polymer would be most reactive if it was at its intrinsic pH. The pH of the free-base polymer solutions is ~12. This pH can prove to be very detrimental to silica gel, which readily degrades under basic conditions. Coupled to that is the fact that in all of the previous reactions carried out on the silica-polyamine composites in which a chloride ion was being displaced heat was required to increase the effectiveness of the reaction. The silica-polyamine was able to withstand the conditions however, and the general conditions for the reaction are: refluxing the reagents for six hours in methanol with careful monitoring and adjustment of the pH to 12. CuWRAM made under these conditions have demonstrated copper capacities of .72 mmol Cu(II)/g CuWRAM from an actual mining raffinate solution containing a copper(II) concentration of 14.2 mM.

Discussions with insiders in the metal separations and recovery industry revealed that to compete with the resin bead technology as a direct replacement for the beads, without major tooling of the industrial systems, a material based on a larger particle size would need to be produced. Conversations with our contact at Calgon Carbon Inc., Gordon Rositer, led us to synthesize CuWRAM on a larger silica particle size for testing in the more industrially relevant larger-scale tests. To this end CuWRAM was synthesized on 250 - 500 μm silica gel following the procedure used to synthesize CuWRAM on the smaller particle size. It was tested in batch tests along with the 90 - 105 μm CuWRAM and 250 - 500 μm XFS (Dow) copper selective polystyrene bead material.

5.2.2 Flow Tests

Flow tests were carried out to determine the performance of a material under flow processing conditions. CuWRAM is designed to excel in flow type applications. These tests confirmed that at flow rates of 2 bed volumes / min 90-105 µm CuWRAM has a copper capacity of over twice that of 250-500 µm XFS resin.

5.2.2.1 Flow Capacity

These tests may be the best indicator of how a material will perform in a process setting. Although the small column size is not optimal for obtaining all the data needed to scale-up to pilot scale or industrial scale some tests can be performed to obtain useful information, namely capacity tests. The results of flow capacity tests for four materials are presented below in Table 5.2.

Material	**Cu^{++} Capacity (mmol/g)**	**Fe^{+++} Capacity (mmol/g)**	**Separation Factor**
90-105 µm CuWRAM	0.369	0.006	1046.8
250-500 µm CuWRAM	0.132	.007	81.4
250-500 µm XFS	0.187	0.021	60.0
90-105 µm WP-4	0.182	0.008	130

Table 5.2 The copper(II), iron(III) capacities and separation factors for four copper selective materials. WP-4 is WP-1 modified with 2-picolyl chloride. Flowthrough data is compared to the strip values to validate the metal capacity. The standard deviation of multiple cycles is less than 10% to be considered valid.

Here the separation factor is defined as Separation Factor = q_e^{Cu}/c_e^{Cu} / q_e^{Fe}/c_e^{Fe} where q_e^{Cu} q_e^{Fe} are the amount of copper and iron adsorbed onto the extractant at equilibrium respectively and c_e^{Cu} c_e^{Fe} are the amount of copper and iron in solution at equilibrium respectively.

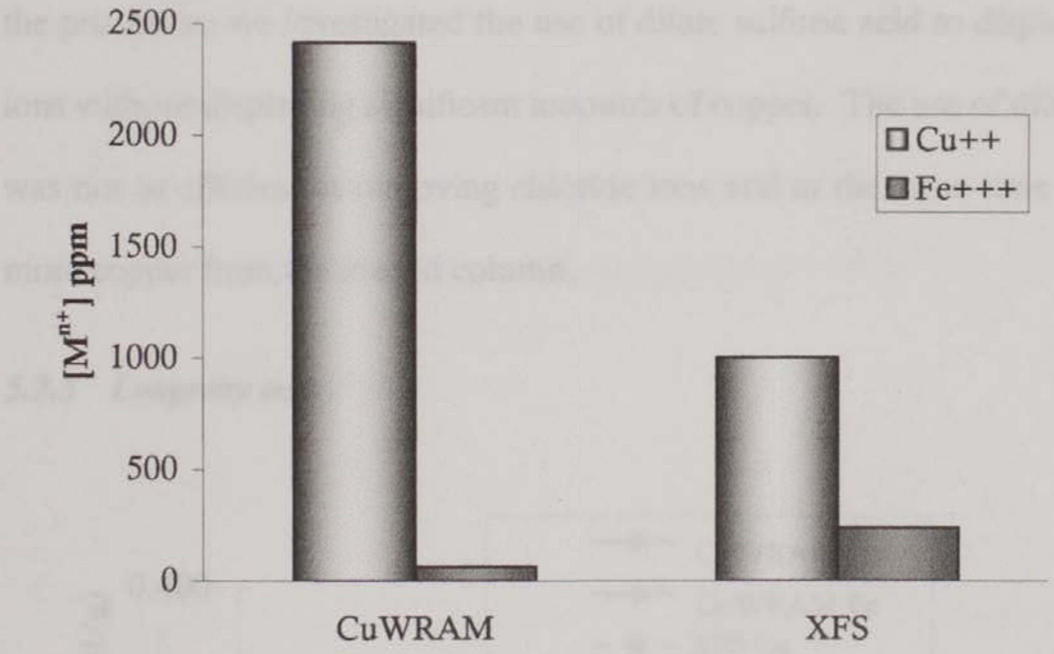

Figure 5.1 This graph shows the concentration of metal in the strip solutions of CuWRAM and XFS. The concentrations are not intended to represent the maximum concentration achievable but to illustrate the difference in copper(II) iron(III) separation.

Figure 5.1 clearly illustrates the much greater separation of copper(II) and iron(III) by CuWRAM when compared to XFS at flows of two column volumes per minute. This graph attempts to show only the separation ability of CuWRAM the strip solution is highly diluted with a water rinse.

A second factor investigated during the flow testing was the feasability of stripping chloride ions from the copper while the copper was still bound to the CuWRAM.

This was accomplished by pumping 1 bed volume of saturated sodium sulfate through the column immediately after loading the column with copper._ The chloride ion content in the strip solution was below detection using ion chromatography. The sodium sulfate solution was analyzed for copper and was found to contain only low concentrations of the metal. Sodium sulfate (salt cake) represents an added cost to the process so we investigated the use of dilute sulfuric acid to displace the chloride ions without displacing significant amounts of copper. The use of dilute sulfuric acid was not as efficient at removing chloride ions and at the same time it also stripped more copper from the loaded column.

5.2.3 Longevity tests

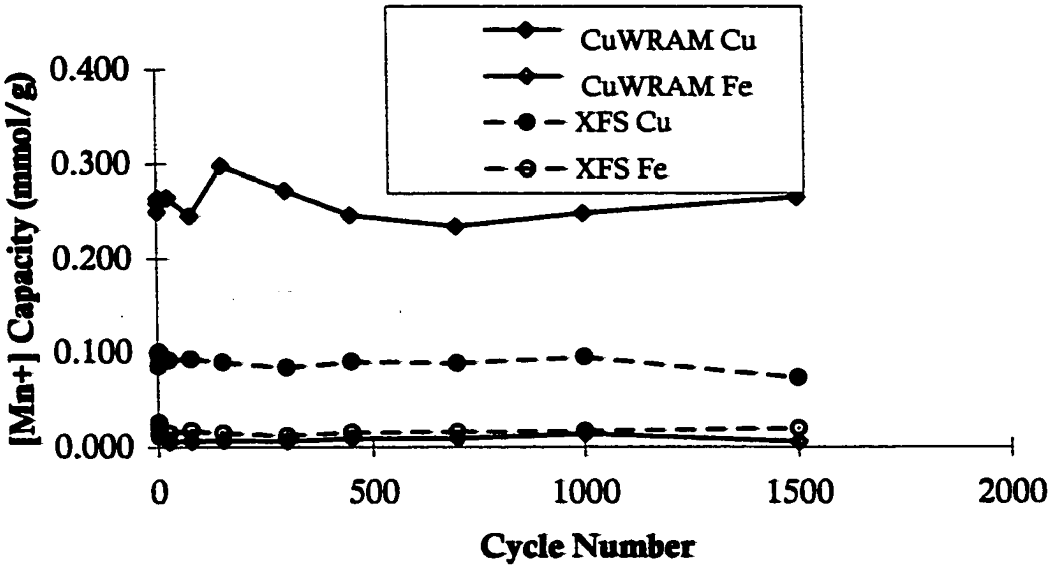

Figure 5.2 In this graph the copper(II) and iron(III) capacity (mmol/g) of 90-105 μm CuWRAM, and 250-500 μm XFS are traced over an extended period of use in a column type system., The capacities were tested at a flow rate of 2 bed volumes/min.

The absorbence data from the FAA was converted to mmoles of metal ion per gram of extractive material and plotted on the following graph. At 1500 cycles both materials seem to have retained their capacity for copper(II) and rejection for iron(III). It is also very clear from Figure 5.2 that at a flow rate of 2 column volumes / min CuWRAM has a higher copper(II) capacity than XFS. The greater separation power of the CuWRAM is also clearly demonstrated as the distance between the copper(II) and iron(III) lines of each material. A key difference between the two materials is that throughout the duration of testing CuWRAM retained its volume while the XFS occupied less than 75% of its original volume.

5.2.4 Pressure Drop Tests

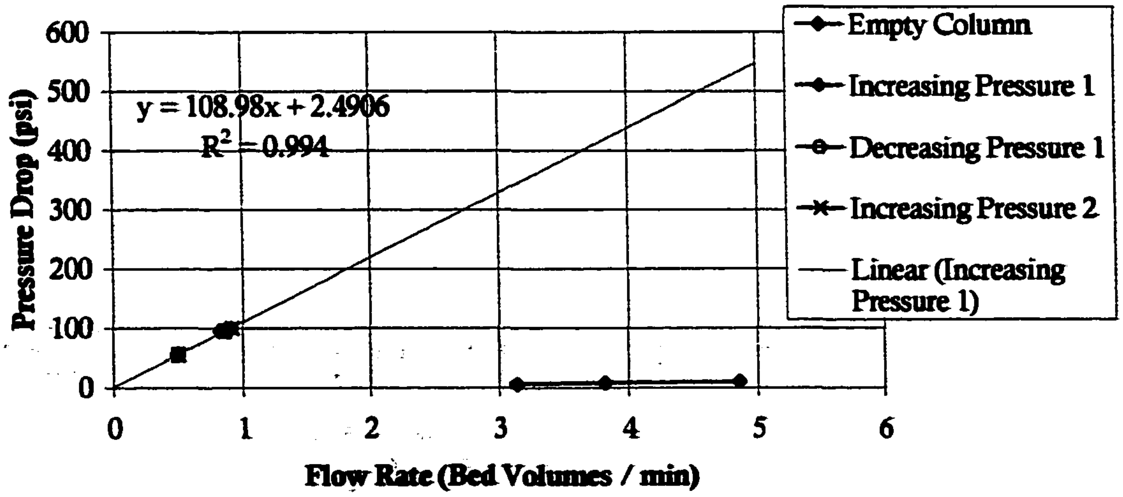

Figure 5.3 The pressure drop profile of 90-105 μm CuWRAM with varying flow rates. From this figure it is clear that the pressure drop is directly related to flow rate in a linear fashion

Pressure drop tests were carried out on a scale that would readily translate to pilot and process scales. To achieve this we used a 25 mm X 600 mm column attached to pump with the ability to produce flow rates of 1.2 L/min and operate at pressures of up to 300 psi. These columns were packed with 90-105 µm CuWRAM and experiments were conducted to evaluate the pressure drop produced by a column of material. The line near the baseline between 3 and 5 bed volumes in Figure 5.3 shows the pressure drop produced by an empty column. The best fit line produced by a column loaded with 90 – 105 micron CuWRAM was generated using Microsoft Excel. A pressure drop of approximately 110 psi per bed volume of flow is realized in this system.

5.2.5 Breakthrough Curve

The breakthrough curve was established to determine the point at which the concentration of copper exiting the column in the flowthrough reaches a concentration considered too large for a particular application. The breakthrough curve depicted in Figure 5.4 was generated by pumping mine raffinate containing 836 ppm Cu+2 and 3,224 ppm Fe+3 through 125g of CuWRAM at a flow rate of 220mL/min. Samples were collected for analysis every 110 mL. The copper concentration in the flowthrough was less than 1 ppm through 11 bed volumes and less than 5 ppm through 12 bed volumes. The copper capacity of CuWRAM in this test was 21 g Cu/Kg CuWRAM. The column was stripped with 16N sulfuric acid and a 30mL sample was collected for analysis when the most concentrated copper solution was seen exiting the column. This produced a solution of 99% copper

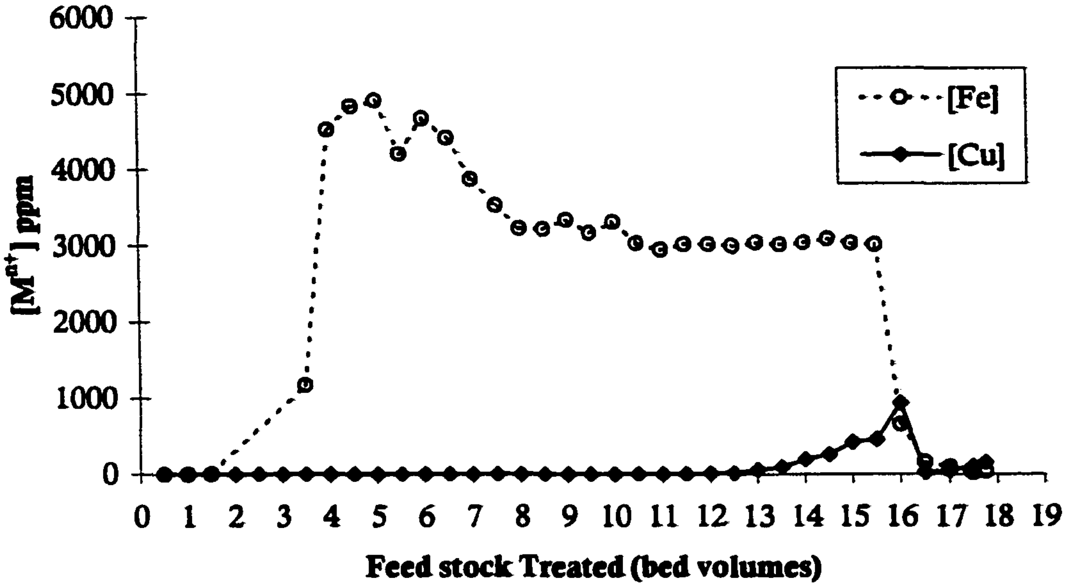

Figure 5.4 Breakthrough curve on a 220 cm^3 column with a 1 bed volume / min flow rate. The copper doesn't begin to breakthrough until 13 bed volumes of raffinate solution have been treated while the iron begins to break through almost immediately.

purity at a copper concentration of 79 g Cu/L. The strip solution concentration is not included in Figure 5.4 because at 79,000 ppm it flattens out the other data.

5.2.6 Batch Tests

Batch tests were carried out to ascertain the performance with regard to the following parameters: equilibrium, kinetics and pH. In each of the figures the y axis is the distribution coefficient (K_D) where K_D=concentration of metal adsorbed to the extratant / concentration of metal in the original solution. The error bars are calculated from the relative standard deviation of the concentration of metal in the final solution and applied to the K_D. These error bars in some instances are too small to be seen through the series icon.

5.2.6.1 Equilibrium Tests

The equilibrium tests demonstrate how the material will perform when exposed to various metal concentrations in solution. The materials were exposed to various concentrations of copper(II), iron(III) and a 3:1 iron(III):copper(II) mix. These data were used to graphically represent the effectiveness at various metal concentrations by plotting distribution coefficients over original metal ion solution concentration. The distribution coefficient is taken to be $K_d = q_e / c_o$. Where q_e is the metal ion concentration in the solid phase (adsorbed onto the material) which can be determined from $q_e = c_o - c_e$ where c_o is the metal ion concentration in the original solution and c_e is the metal ion concentration in solution at equilibrium. The data were also used to construct Langmuir plots that are used to predict how much metal will be absorbed by a material at various metal concentrations. The Langmuir plots are constructed by plotting c_e/q_e vs. c_e.[3] To determine the maximum number of binding sites the material has for a given metal the slope of the plot can be fitted to the rearranged Langmuir equation such that $c_e/q_e = 1/Q{*}c_e + 1/K_L{*}Q$ where Q is the maximum number of metal binding sites in the material, also referred to as R_{max}, and K_L is the Langmuir absorption equilibrium constant.[3] Each test was carried out in triplicate and the average of the three tests was plotted graphically. The results of these tests demonstrate that CuWRAM is much more effective at extracting copper from very dilute solutions than the XFS resin. This indicates that in applications such as treating copper plating rinse baths and recovering copper from low-grade ore leachate CuWRAM will exhibit superior performance characteristics.

Figure 5.5 shows the results of the tests conducted on the mixed metal solutions. From this data it is clear that while the XFS is more efficient at higher copper concentrations

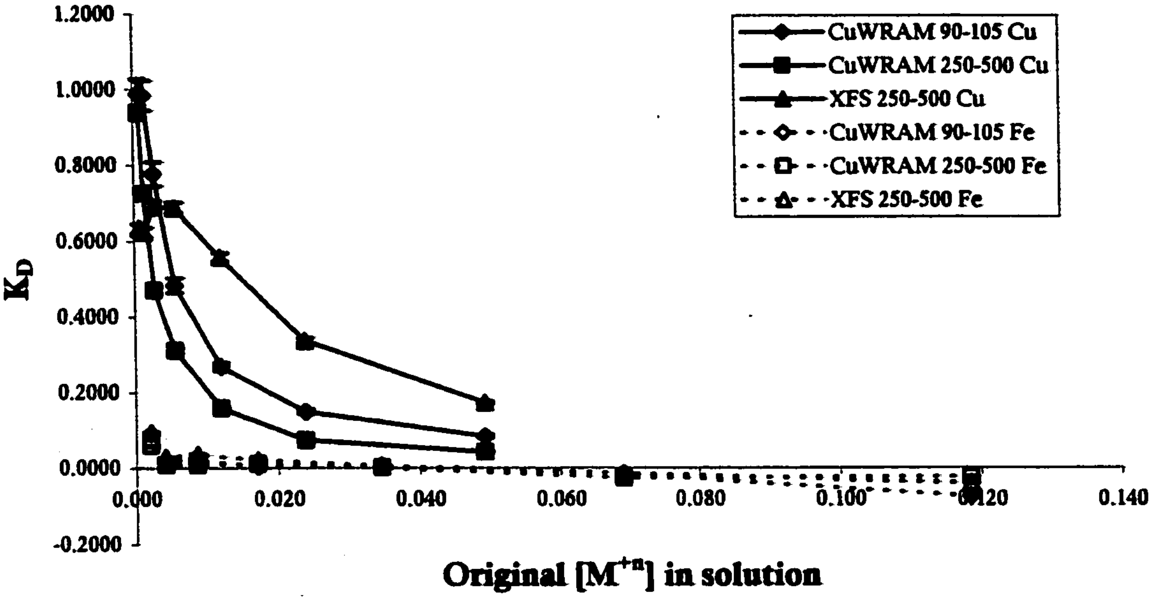

Figure 5.5 This graph plots the molar fraction of metal ion adsorbed from solution against the the original metal ion concentration of that solution. The negative values for iron result because more iron precipitated from the control than from the samples.

due to its higher copper capacity but its effectiveness drops off as the copper concentration goes down. After standing 24 hours at an elevated pH (2.0) the high iron(III) concentrations began to form iron(III) precipitates. The negative values are due to the fact that at the higher iron(III) concentrations more iron(III) precipitated out from the control solutions than from the samples containing the extraction material.

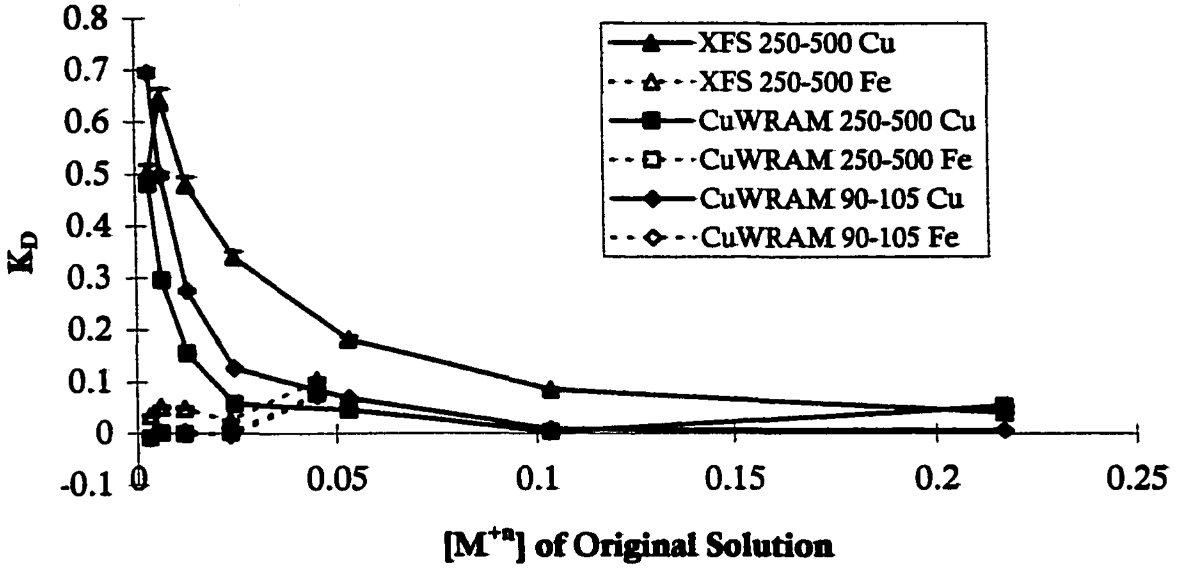

Figure 5.6 This graph plots the molar fraction of metal adsorbed onto the extractant from a monotonic solution.

Figure 5.6 depicts the results of the above experiment carried out on monotonic metal ion solutions. The *x* scale is changed, as the metal ion concentration in the monotonic solutions is much higher for each individual metal while the total metal ion concentration at the highest concentration is constant at 0.2 M. In this set of experiments the solutions containing the two highest concentrations of iron(III) were discounted due to the extensive precipitation of iron(III) in all the samples. The control solutions however contained no visible precipitate. The data for iron(III) presented in the graph should also be considered suspect for the same reason.

The most important information conveyed by these graphs is the effectiveness of the two CuWRAM materials at low concentrations. It is easily seen that as the copper(II) concentrations diminish the percentage of copper that is removed by XFS actually decreases but that the percentage of copper(II) removed by CuWRAM increases until it reaches approximately 99%. This information indicates that in addition to mining operations the CuWRAM will be superior to resin materials in remediation and wastewater treatment applications where low metal ion concentrations in the outflow are important.

The data collected from execution of the equilibrium studies was also used to construct Langmuir plots and from these plots calculate the maximum number of adsorption sites per gram of extraction material and also the Langmuir adsorption equilibrium constant. The Langmuir theory of adsorption was developed to describe the adsorption of gasses onto a solid surface. According to the Langmuir theory the surface contains only one type of elementary space and each space can contain only one molecule adsorbed to it.[4] The Langmuir model has been successfully applied to the adsorption of metal ions from aqueous solutions by activated carbon.[5]

	R_{max} Cu^{++}	K_L Cu^{++}
CuWRAM	$4.11X10^{-4}$	6353.7
XFS	$9.36X10^{-4}$	4057.6

Table 5.3 The maximum number of adsorption sites in moles or R_{max}, and the Langmuir equilibrium constant as M^{-1} or K_L as calculated from the Langmuir plots for 90-105 μm CuWRAM, and , 250-500 μm XFS. No data is included in the table for iron(III) because the adsorption data when fitted to the Langmuir equation did not conform to a straight line.

Figure 5.7 is an illustrative Langmuir plot for all three materials, including the R^2 value of the nearest fit straight line. It can be seen from the R^2 value for the best-fit iron(III) line that it is not a good fit to the data; which indicates that the adsorption

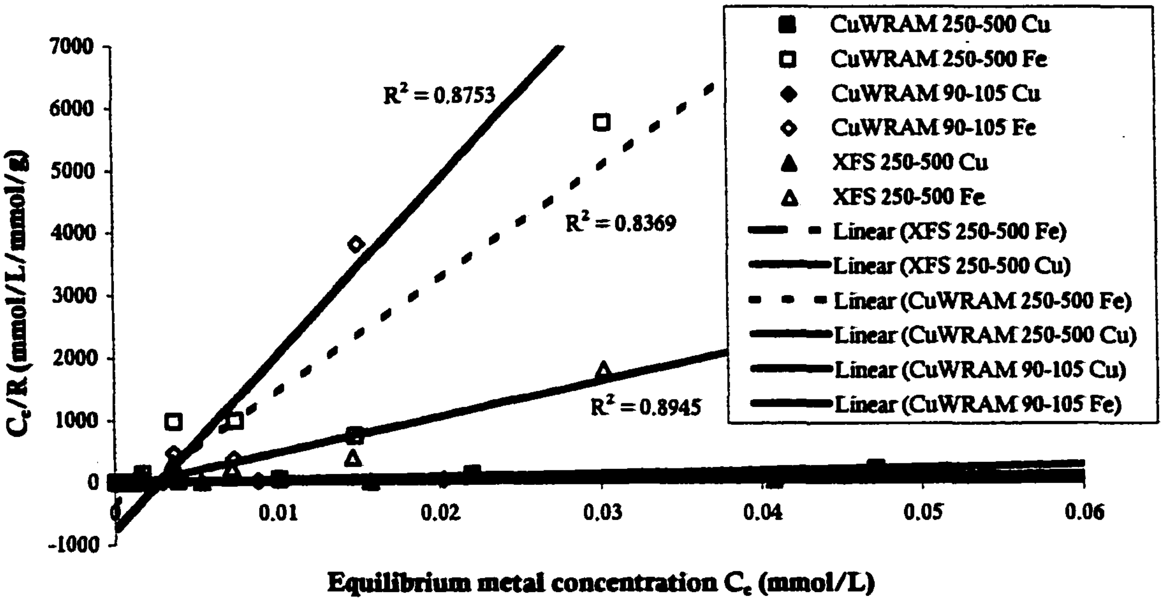

Figure 5.7 The Langmuir isotherms for copper(II) and iron(III) loading onto CuWRAM. The copper loading conforms to the Langmuir equation but as seen in this plot the iron loading does not. The R^2 values are shown for iron to illustrate that point. This indicates that the iron does not load as a surface monolayer.

of iron(III) to the adsorbent does not occur in a Langmuir fashion; therefore, the Langmuir plots cannot be used to calculate the R_{max} or K_L of iron adsorption to the materials tested. Copper on the other hand does appear to bind to the adsorbent in a Langmuir fashion. The axis terms have been described earlier and will not be restated here.

Only copper data is presented in Table 5.3 because the iron(III) data does not conform to Langmuir type adsorption. The Langmuir equilibrium constant or K_L is defined as $K_L=[M^{n+}]k_M/[Aq]k_S$ where $[M^{n+}]$ is the concentration of metal ions adsorbed to the extractant, [Aq] is the concentration of solution molecules adsorbed to the extractant and k_M and k_S are the activity coefficients of the metal ion and the solution respectively.[6] A higher K_L value indicates that the material will perform more efficiently at lower metal ion concentrations.

5.2.6.2 Kinetics Tests

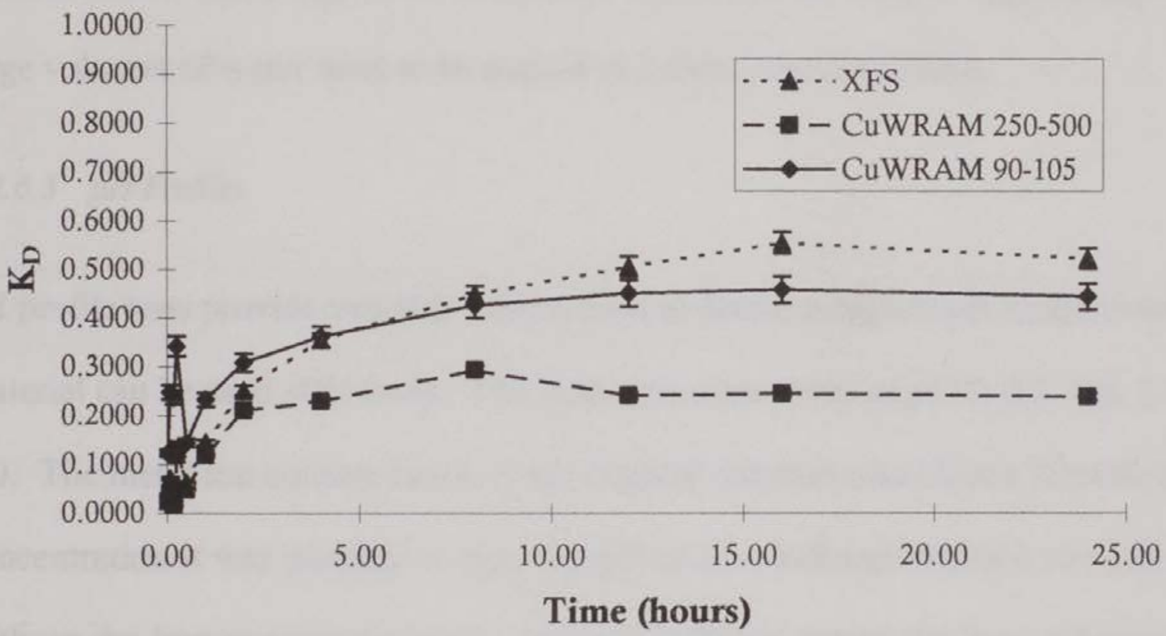

Figure 5.8 This plot demonstrates the faster uptake of copper(II) from solution by 90-105μm CuWRAM than by XFS resin. Although the XFS resin has a higher capacity overall, the faster kinetic uptake of copper by CuWRAM make it perform better in flow applications.

The kinetics tests are used to calculate the rates that the metals load onto the material. This information can be used to determine the best type of application a particular material may be suited for i.e. batch or flow processing. These tests are conducted by exposing the material to a metal solution for predetermined amounts of time. The results are then plotted as the distribution coefficient over time. These tests were also carried out in triplicate. The results of these tests, presented in Figure 5.8, clearly demonstrate the more rapid binding kinetics of CuWRAM when compared to XFS resin. This is a clear indication of the potential superiority of the CuWRAM in a column system at accelerated treatment flow rates. It is due to the much faster capture kinetics of this material that enables the same amount of copper(II) solution to be processed with a smaller amount of extraction material. These results predict that CuWRAM will exhibit superior performance characteristics under high flow conditions and could be used in applications where large volumes of water need to be treated in a short amount of time.

5.2.6.3 pH Profiles

pH profile tests provide valuable information in determining the pH range in which a material can be used effectively. The materials were tested at pH 0, 0.5, 1.0, 1.5, and 2.0. The metal ion concentration in the original solution was chosen because at that concentration it was possible to raise the pH of the challenge solution to a pH of 2.5 without the iron precipitating out. Upon standing however the iron did precipitate from solution at pH 2.5 and those samples were discounted. The results of these tests plotted in Figure 5.9 demonstrate that CuWRAM can be used to extract copper from low pH solutions effectively.

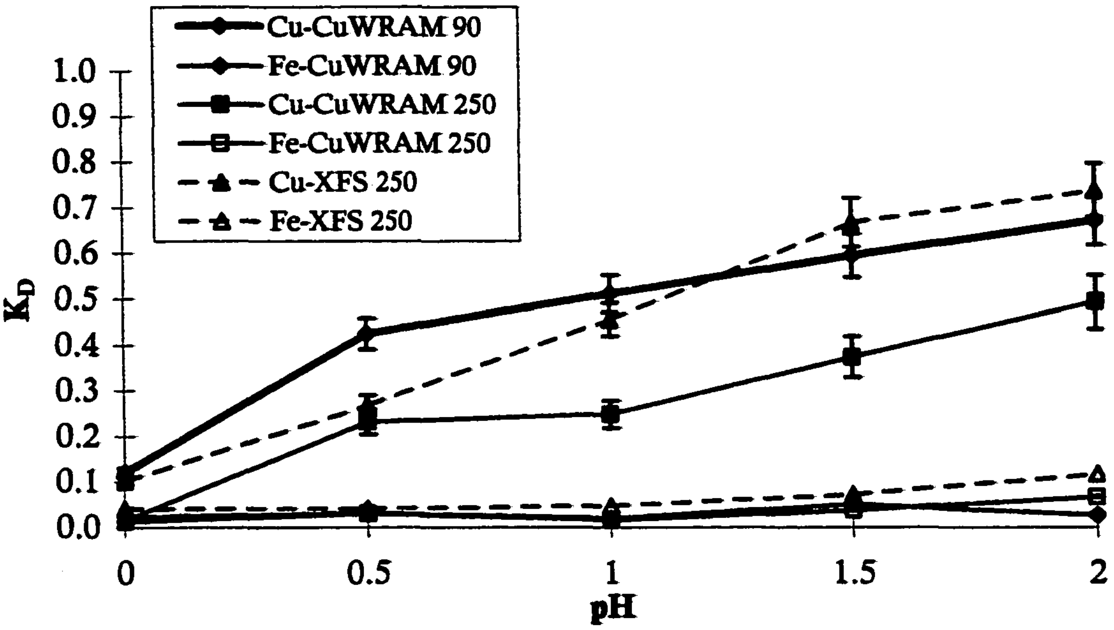

Figure 5.9 The adsorption profiles of the copper selective extraction materials over a range of pH's. This experiment was carried out on solutions with a pH up to 2.5 although extensive iron(III) precipitation at the highest pH made these data unusable.

At pH's between 0.5 and 1 CuWRAM 90 is more effective at extracting copper(II). This is important not only in mining process but also in industry where waste streams can be very acidic. If valuable metals such as copper can be extracted before the pH is adjusted they will not have to be recovered from the heavy metal sludge, which can form on pH adjustment making recovery easier.

5.2.7 Physical morphology of CuWRAM

In an attempt to determine the reason for the low copper capacity of 177 – 250 µm CuWRAM when compared to 90 – 105 µm CuWRAM, the surface morphology of the two materials was investigated by SEM. The 177-250 µm size range BP-1 represents a particle size that is large enough to alleviate pressure drop concerns while retaining high metal capacities. Batch tests for BP-1 currently being made in the 177-250 μm size range can have copper capacities at pH 3 of 92 g Cu/Kg BP-1. CuWRAM however, made from this BP-1 have a batch capacity for copper of 10 g CU/Kg of CuWRAM. Batch tests on CuWRAM 90-105μm material have achieved copper capacities of over 40 g Cu/Kg CuWRAM A collection of four micrographs of 90 – 105 μm CuWRAM is presented in Figure 5.10 while four micrographs of 177 – 250 μm CuWRAM are presented in figure 5.11 for comparison. The most striking difference is the shape of the material particles. The larger diameter material is spherical while the smaller particle material is granular. The spherical shape allows the fluid flowing through it to pass more easily thus creating less pressure drop in the system. On the other hand the irregular shape of the smaller particle material (Figure 5.10 a) will create more eddies and turbulence as fluid passes through it. This turbulence creates a greater pressure drop in the system but also will create more opportunities for the metal ions to contact the chelating polymer on the surface of the particles. Secondly the large particle CuWRAM has a much smoother surface appearance. This is especially evident when comparing the two micrographs Figures 5.10c and 5.11c. The smooth surface may be a manifestation of a more hydrophobic surface coating. Lastly is the long rod-like structures that are evident on the small particle material but are absent on the larger particle material. It is not clear what they are. While some of them appear somewhat crystalline many are actually tubes; evidenced by close inspection of the center of Figure 5.10b. Over all there appears to

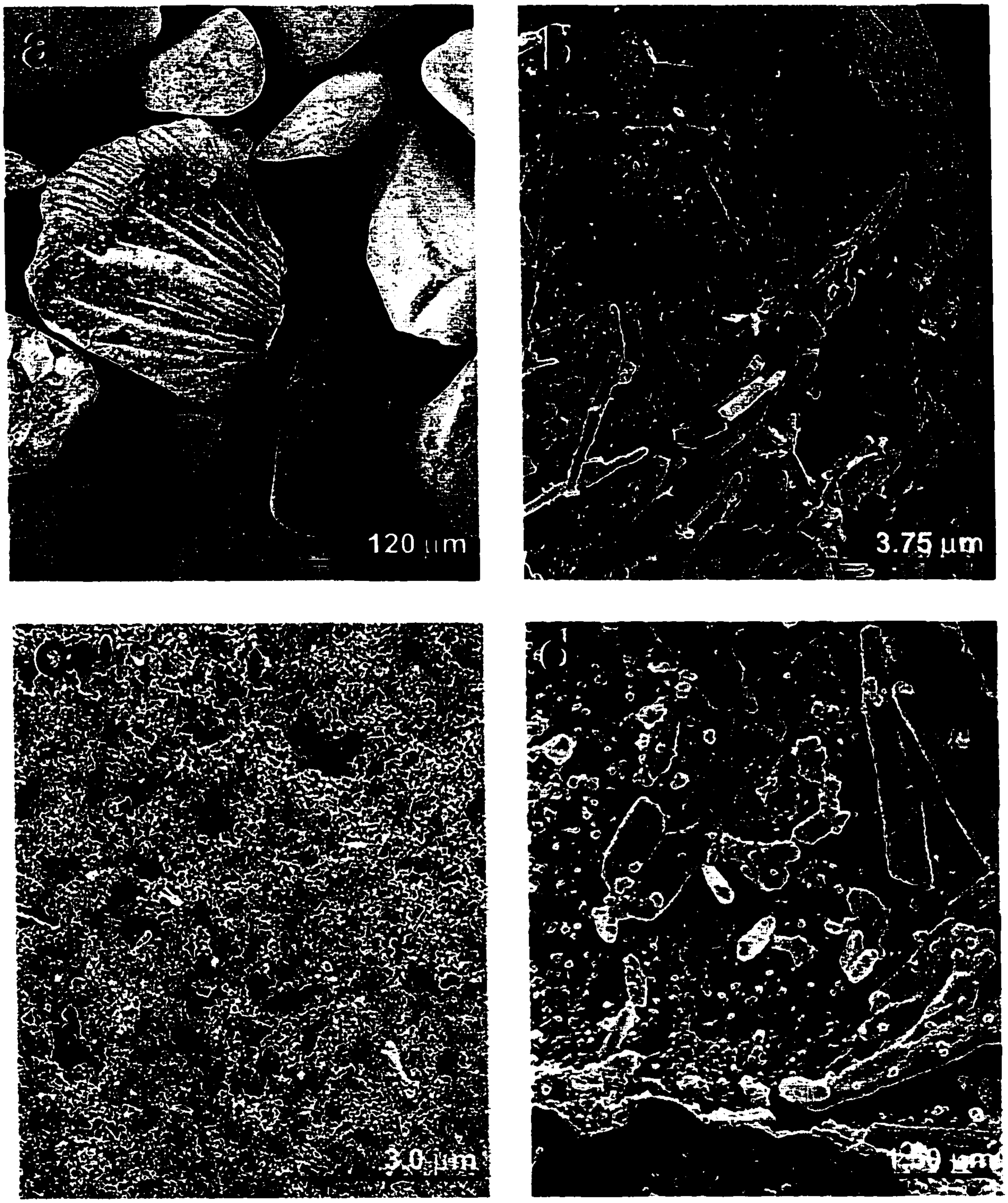

Figure 5.10 Four SEM micrographs showing the surface morphology of 90-105 µm CuWRAM. Photo (a) shows the shape of the particle while (b-d) show more surface detail with increasing magnification. It is unclear what the rod-shaped structures are: some appear crystalline while others are tubular.

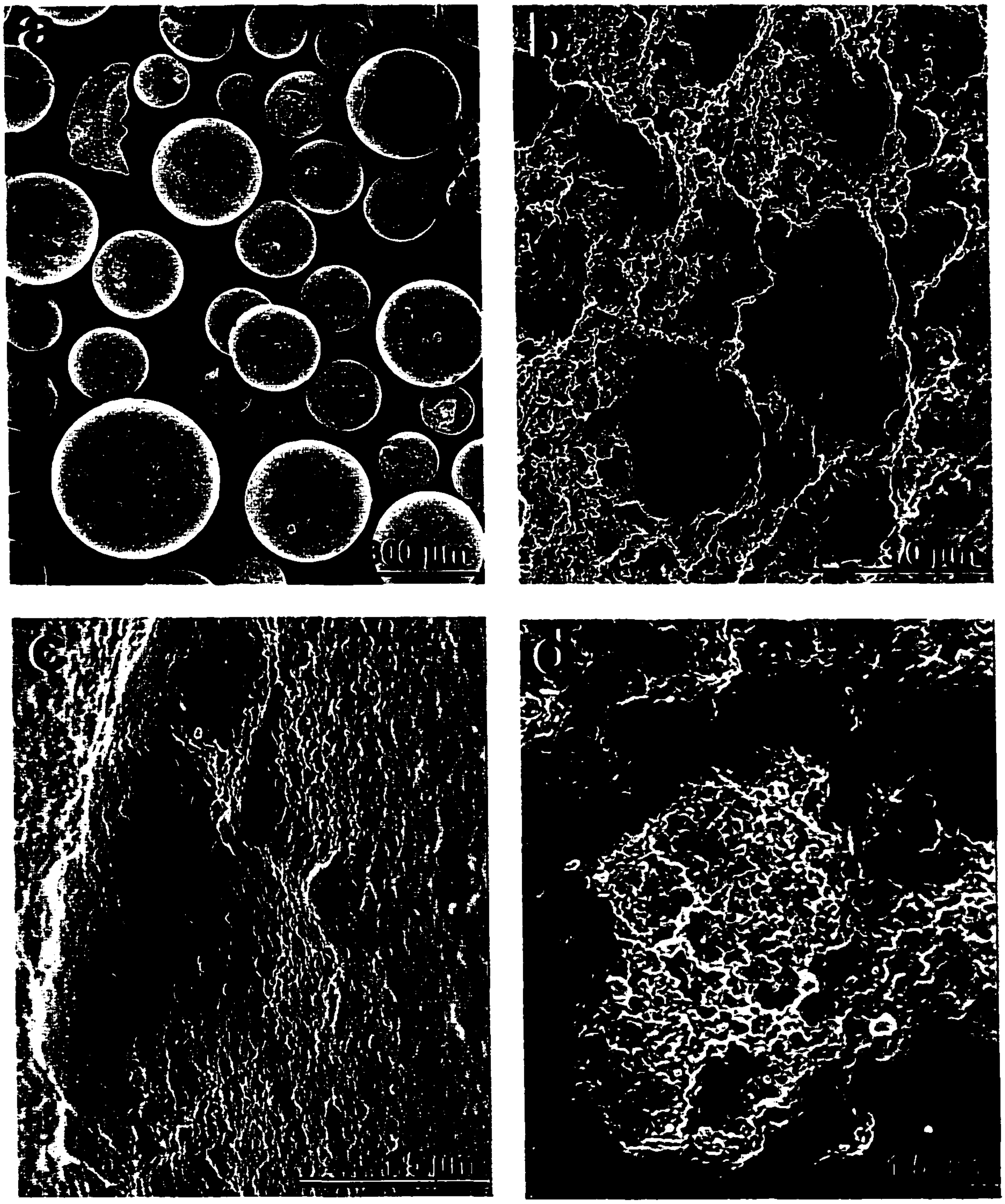

Figure 5.11 Four SEM micrographs of 177 - 250 CuWRAM showing surface morphology. Clearly evident in panel (a) is the spherical nature of the material. Panels (b-d) which progressively increase in magnification, show a smoother surface texture and absence of rod-like structures as compared with Figure 5.10.

be a greater number of pores available on the 90 – 105 μm CuWRAM while the 177 – 250 CuWRAM presents a much smoother surface. Since much of the chelating polymer is contained in the pores access of the metal ion containing solution to these pores is of paramount importance. The surface morphology of the 90 – 105 CuWRAM would seem to favor greater polymer metal ion interaction than the 177 – 250 CuWRAM under flow conditions.

5.2.8 Tests carried out on actual mining solutions

The true test of these materials is their ability to perform under real life conditions. These are the pilot tests carried out at a site on a scale smaller than the actual intended scale of use but still much larger than bench scale. The pilot scale tests can cost into the millions of dollars to set up and carry out. For this reason it is important to carry out tests that simulate as closely as possible the conditions anticipated for the pilot tests. One of these conditions is the solution from which the metals will be extracted. Different ore bodies, extraction protocols, and solution source will each produce their own challenges. Tests using CuWRAM were carried out on two different mining solutions. The first was a raffinate solution from a solvent extraction system and the second was the leach solution from a ferric chloride leaching process. The raffinate solution is the copper containing leach solution that cannot be effectively processed by solvent extraction. The ore leach solution passes through the solvent extraction cycle and then is fed back into the leach solution. As the solution is recycled it builds up impurities, which decrease the effectiveness of the solvent extraction process. The rafinate solution is what is bled

Column Volume	53 mL
Column Dimentions	15 mm X 300 mm
Material	90 – 105 micron CuWRAM
Material Mass	42.4 g
Flow Rate	30 bed volumes/hour
Pressure Drop	63 psi
Feed Concentrations	
Cu^{+2}	555 ppm
Fe^{+3}	4036 ppm
Strip Solution	4N H_2SO_4
Strip Solution Volume	3 bed volumes

Table 5.4 The parameters of the tests carried out on copper mine solvent extraction raffinate.

off from the extraction circuit and becomes wastewater. These tests were also conducted on a scale that mining engineers could use to anticipate performance in pilot scale tests. The columns used were 53 mL, 15mm X 300mm columns with a pressure gauge and the tests were carried out at a process relevant flow rate of 30 bed volumes per hour.

5.2.8.1 Copper mine raffinate

In the solvent extraction process the raffinate is the aqueous phase solution that has had the copper extracted from it. This solution is typically recycled but with each recycling step the concentration of ferric ion, chloride ion, organic solvent, and other interferences also builds up. At some point the solution needs to be changed and the old one discarded. The problem is that among other things the raffinate solution still contains up to one gram of copper(II) per liter of solution. This represents a significant amount of copper in a concentration too low to effectively extract but too high to meet discharge levels for copper. The extraction of copper(II) from the raffinate solution represents possibly the ultimate challenge for a material such as CuWRAM.

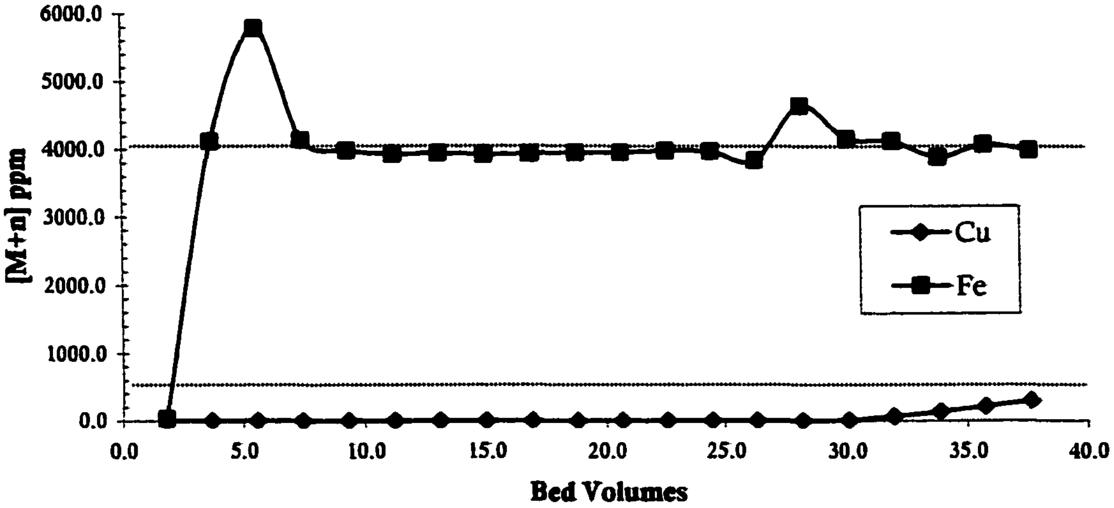

Figure 5.12 Breakthrough curve of solvent extraction raffinate treated with 90 – 105 micron CuWRAM. The upper bold solid horizontal line represents the original iron concentration in the raffinate and the lower solid horizontal line represents the original copper concentration in the raffinate.

Copper containing solvent extraction raffinate was obtained from a copper mining operation in Arizona, USA. The raffinate was used a received with no pretreatment. The concentration of copper and iron in the raffinate solution were determined by

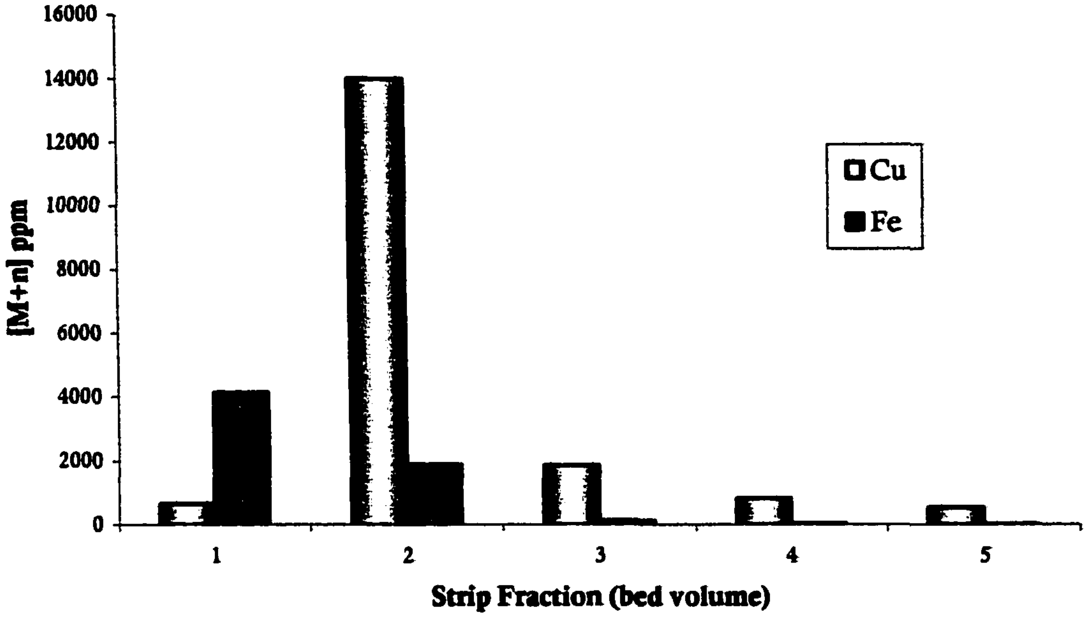

Figure 5.13 This graph shows the concentration of copper and iron in 5 successive strip fractions. The column was not rinsed between loading and stripping to mimic the desired industrial procedure. Skipping this step appears to decrease the selectivity of the material by leaving too much iron in the system prior to stripping. The strip was carried out with three bed volumes of 4N H_2SO_4.

flame atomic absorption spectroscopy (FAA) each time it was used. Under the test conditions represented by Table 5.4 raffinate solution was pumped through the column at a rate of 30 bed volumes per hour. 10 mL fractions were collected for analysis every 1.8 bed volumes. The collected samples were diluted 1:100 for copper analysis and 1:1000 for iron analysis. One can see by following the line representing iron in the flowthrough that iron is initially somewhat retained by CuWRAM but then a large plug of iron is released from the column and the iron concentration settles to the level in the original raffinate solution. The copper on the other hand remains at below 1 ppm for 28 bed volumes and finally breaks through to over 10% of the concentration of the original raffinate at 32 bed volumes. The 10% is not a critical point in this particular application but it does give an indication of the effectiveness of the material at low concentrations. A material that breaks through early will leave a higher concentration of copper in the treated solution that may require further treatment.

Figure 5.13 shows the concentration of copper and iron in the strip solution generated from the loading depicted in Figure 5.12. Each strip fraction is one bed volume. The strip solution was 4N sulfuric acid and 3 bed volumes were used to strip the column followed by 2 bed volumes of water. In this test the strip was started immediately following the rinse this was done to mimic a proposed industrial procedure. The poor separation of copper apparent in the first and second fractions is due to the iron in the entrained feed solution. The percentage of copper as a function of the entire metal load (copper and iron), the copper purity is 74% for the entire strip. If the first fraction is disregarded the copper purity increases to 89%. The copper capacity of CuWRAM in this test was 22 g Cu/Kg CuWRAM.

5.2.8.2 Ferric chloride process ore leach solution

A second solution used to test the copper selectivity of CuWRAM was a ore leach solution from Western Australia. This solution contained a mix of ten transition metals and metalloids. A breakthrough test was conducted on this solution. The test

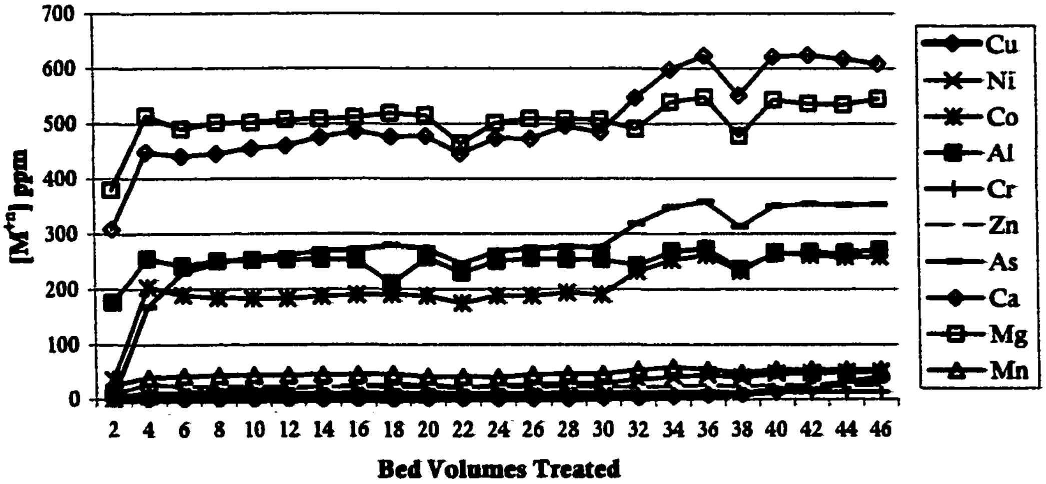

Figure 5.14 This plot shows the almost immediate breakthrough of all the metals in the leach solution except copper. The second rise in metal concentration at around 36 bed volumes is thought to be displacement of the small amount of other metals from adsorption sites by copper as available sites diminish in number.

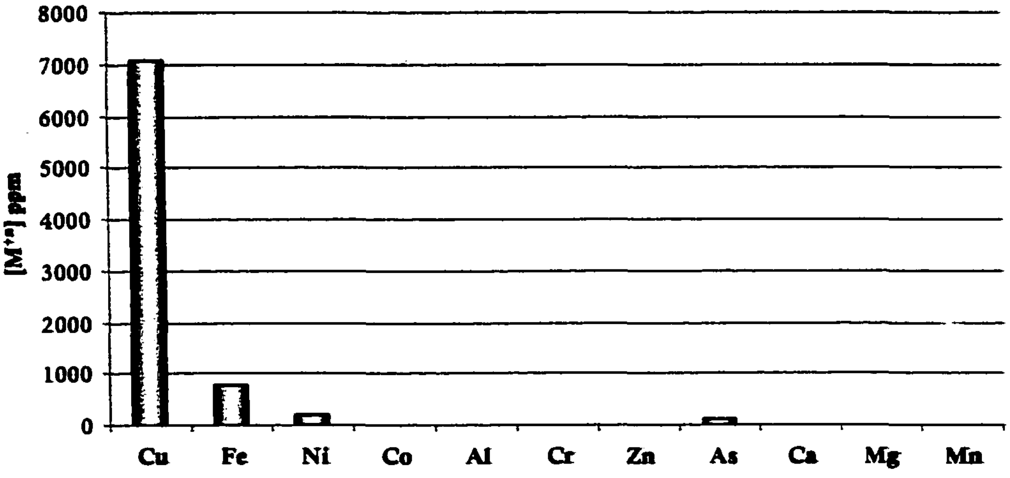

Figure 5.15 Metal concentrations in the strip solution produced from the Figure 5.14 loading. There is a small amount of coloading of nickel and iron. The arsenic is believed to be present because of coloading with the ferric iron.

was conducted using a 5 mL column packed with 4.75g of CuWRAM. 10mL fractions were collected continuously and analyzed by ICPES (Inductively Coupled Plasma Emission Spectroscopy). The material was stripped with one column volume of 4N sulfuric acid and the strip was analyzed by ICPES as well. The copper load adsorbed to the material and recovered in the strip was 22 g Cu^{+2}/Kg CuWRAM. The total strip volume was 4column volumes and the copper concentration was 7.9 g/L. This test revealed the selectivity of the material for copper over a broad range of metals and metalloids. The copper contained in the strip was 90% pure with 10% ferric iron. The copper selectivity can easily be seen in Figure 5.14, from the graph it is clear that all of the evaluated metals begin to break through immediately. The curves all roughly follow the same shape as the iron curve in Figure 5.12. The metal concentrations rise almost immediately then level off for a time. At 30bed volumes there is a second rise in the metal concentrations, after which the metal concentrations level off again. This second rise coincides with the point at which copper begins to break through. One possible explanation for this is that at 30 bed volumes all of the available chelation sites are occupied and then the copper begins to occupy the sites occupied by other metals displacing them into solution. The graph of the metal content and concentration of the strip solution also shows the selectivity of CuWRAM over all of the other metals. There is still some nickel in the strip solution as well as iron and arsenic. The arsenic is thought to be in the strip in a form associated with iron. This trend has been seen in other tests that have been conducted using silica-polyamine composite materials and in which iron and arsenic have been analyzed.

5.3 Conclusions

It is clear that a material has been developed that will selectively extract copper from solutions containing a mix of transition metals including iron(III) under extremely acidic conditions. The material retains the capacity for copper and the ability to separate the copper from iron(III) over an extended period of use.

The Langmuir isotherms plotted from the absorption data indicates that copper(II) and iron(III) are adsorbed to CuWRAM through different means. The copper conforms to the Langmuir equation indicating that it adsorbs in a controlled one copper ion to one adsorption site on the CuWRAM. The iron on the other hand does not conform to the Langmuir plot indicating that it is not adsorbed in the same manner. Investigation into the extraction of iron(II) from mine waste water using WP-1 provide evidence that the same is true in this situation. SEM micrographs of WP-1, and WRAM-Ex show that the iron is adsorbed to the material in amorphous surface clusters and not as a uniform adsorption onto the surface of the material. It is possible therefore that iron adsorption onto the silica-polyamine materials is primarily a precipitation event triggered by a high local pH associated with the polyamine. The local pH associated with CuWRAM is low as it is washed/stripped with acid then rinsed with water before reloading with copper.

It is clear from all of the experiments carried out on the CuWRAM materials that there is a large capacity difference between the 90-105 μm CuWRAM and the 177-250 μm CuWRAM. The difference in performance stems from a charicteristic of the silica gel alluded to in Chapter 3, namely the pore size. The 90-105 μm silica gel contains pores with an average diameter of 150Å while the 177-250 μm silica gel contains pores with an average diameter of 80Å.[7] The effect of the pore diameter on material performance is negligible when considering the materials that only contain the polymer i.e. WP-1 and BP-1. In the case of CuWRAM however the situation is more complicated. As explained in Chapter 3 the polyamine, PAA, has the most hydrophobic character of the polyamines investigated thus far. To compound this the ligand that is add to the polymer is also adds hydrophobic character to the material. The free base picolyl chloride is immiscible with water. These hydrophobic areas surrounding the pores are thought to greatly reduce diffusion into the pores. Couple this with the larger particle size and spherical nature of the silica gel particles which act to increase the hydrodynamic efficiency of the flow around the particles and the result is a material almost useless for flow applications. The dramatically slower capture kinetics are readily observed in the batch tests. When the smaller particle CuWRAM is introduced to a copper containing solution the amber colored gel immediately begins turning a deep blue-black color while the larger particle material turns color very slowly, over a matter of hours. The theory that the poor performance of the 177-250 μm CuWRAM is directly related to pore size was corroborated in a recent set of experiments in which CuWRAM was made on silica gel that had a particle size of 250-500 μm and possessed pores with an average diameter of 200Å. Even with the large particle size, this material, under flow conditions, had a copper capacity close to that of the 90-105μm CuWRAM. The problem with the material based on the larger particle size though, is the fragility of the silica gel. Only about 25% of the starting material ended up as usable

CuWRAM. Presently a method of stirring utilizing air bubbling through the material is being investigated to provide good mixing with less stress on the material.

5.3.1 Future Work

The most immediate problem that needs to be addressed is the issue of pore diameter. Industrial applications require large particle diameters to decrease pumping costs while a large pore diameter is necessary to achieve a viable material. This problem will be addressed by locating a supplier that produces a silica gel that can meet the needs of this project. The larger pore diameter will mean a more fragile material if pore volume remains constant this will mean developing mixing and handling procedures that are more delicate, however the material will still have to withstand the rigors of large scale industrial processes.

The long-term development of silica-polyamine composite materials will include developing more selective materials and exploring the applications for these materials. Currently the Rosenberg group is working to develop a silica-polyamine material that has a high affinity for manganese and one with a high affinity for gallium. Future projects include silica-polyamine composites that will extract arsenic, rare earth metals, platinum group metals and the other coinage metals. CuWRAM represents the dawn of a new direction of metal separations, a route that will lead to economical and environmentally responsible metal extraction, separation and recovery.

5.4 Experimental

5.4.1 Synthesis

Original CuWRAM Synthesis

In a 250 mL beaker 24.61 g of 2-picolylchloride hydrochloride was dissolved in 60 mL of methanol. 8.42 g of ground potassium hydroxide was added to render the 2-picolylchloride in the free base form. The resulting potassium chloride precipitate was filtered off and the collected filtrate added to a 500 mL, 3-neck round bottom flask. Also added to the flask were 60 mL of THF and 30.00 g of PVA 5000. The resulting slurry was degassed under vacuum. The flask was then fitted with a paddle stirrer and a reflux condenser and the third neck was stoppered. The pH of the solution was checked using indicator paper and the pH was brought up to 9-10 with 2N KOH in water. The color of the solution turned deep blood red upon the addition of base. The slurry was refluxed with stirring for 9 hours. The pH was checked hourly and adjusted as needed to keep the pH at about 10. The resulting material was emptied into a fritted funnel and the reaction solution filtered off. The Material was then rinsed 3 times with 120 mL of methanol, 3 times with 120 mL of water, 1 time with 120 mL of concentrated sulfuric acid, 3 times with 120 mL of water, and 3 times with 120 mL of methanol. The material was then air dried overnight and weighed.

Final weight 38.64 g Weight gain 8.64 g % Weight gain 29%

CuWRAM alternate drip method In a 100 mL 3-neck round bottom flask 5.00 g of PVA 5000 was added to 15 mL of absolute ethanol stored over molecular sieves and the resulting slurry was degassed with vacuum aspiration. 4.62 g of 2-picolylchloride

(0.03 mol) was dissolved in 20 mL of absolute ethanol and 3.37 g of KOH (0.06 mol) was dissolved in an additional 20 mL of absolute ethanol. Using an addition funnel 5 mL of the picolyl solution was added to the gel slurry over 3 min. the pH was checked with indicator paper after 15 min. and found to be 7. Then 5 mL of the KOH solution was added over 15 min, allowed to react for 5 min. and the pH checked. The pH was 10. 5 mL of the picolyl solution was added and allowed to react for 15 min. the pH was 7. 5 mL of KOH solution was added over 10 min. and allowed to react for 5 min. more. The resulting pH was 10-11. This was repeated until all of the reagents had been used. The reaction proceeded for an additional 30 min. The slurry was placed into a filter funnel and the reaction solution filtered off. The resulting material was rinsed 3 times with 20 mL of ethanol, 3 times with 20 mL of DI water and 3 times with 20 mL of methanol. The material was then air dried.

Final weight 4.82 g Weight loss 0.18 g % Weight loss 3.6%

<u>CuWRAM synthesis using 2 equivalents of base during the reaction</u> In a 100 mL beaker 7.38 g (0.045 mol) of 2-picolylchloride hydrochloride were dissolved in 10 mL of methanol stored over molecular sieves. In a separate beaker 2.52 g (0.045 mol) of KOH were dissolved in an additional 10 mL of methanol. The KOH solution was slowly added to the picolyl solution and the resulting precipitate was filtered off. The filtrate was added to 5.00 g of PVA 40,000 in a 100 mL 3-neck flask. The resulting slurry was degassed with vacuum aspiration and paddle stirred while refluxing. An additional 5.04 g (0.090 mol) of KOH were dissolved in 10 mL of methanol and slowly added to the reaction over the course of an hour using an addition funnel. The reaction was allowed to proceed at reflux for an additional hour. The resulting

material was separated from the reaction solution via vacuum filtration and rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 1 time with 20 mL of concentratrd sulfuric acid, 6 times with 20 mL of DI water and 3 times with 20 mL of methanol then air dried.

Final weight 4.27 g Weight loss 0.73 g % Weight loss 15%

Solution phase ligand addition This was tried under a variety of conditions. All produced weight gains in the final material ranging from 12% to 38%. Given is a representative procedure. In a 1-neck 100 mL round bottom flask the pH of 20 mL of an 18% by weight solution of PVA 12,000 in water was adjusted to 11.8 with 108 mL of 8N NaOH. To this solution 6.70 g of 2-picolylchloride hydrochloride was added and the reaction mixture refluxed for one hour. The reaction was cooled and the pH checked and found to be 4.2 the pH was then elevated to 12.6 with 5.6 mL of 8N NaOH. To the solution 5.00 g of bromopropyl gel was added and the resulting slurry degassed. The slurry was then rotary stirred for 60 hours at room temperature. The resulting material was separated from the reaction solution via vacuum filtration and rinsed 3 times with 20 mL of methanol, 3 times with 20 mL of DI water, 1 time with 20 mL of concentrated sulfuric acid, 3 times with DI water, and 3 times with methanol then air dried.

Final weight 6.92 g Weight gain 1.92 g % Weight gain 38%

Exploration of Solvent Systems The reactions were carried out in a manner consistent with the conditions described in the section Original CuWRAM Synthesis described above. As always the solution volume is four volume equivalents of the gel mass. Solvent systems investigated were 100% water, 100% THF, 100% methanol, and 50% water with 50% methanol.

Present Synthesis In a 200 mL beaker 53.16 g of 2-picolylchloride hydrochloride are dissolved in 60 mL of DI water. In a separate beaker 19.98 g of KOH are dissolved in an additional 60 mL of DI water. The KOH solution is slowly added to the picolyl solution in an ice bath while stirring. The solution is stirred for 10 min and then introduced into a separatory funnel. The layers are allowed to separate and the lower free-base 2-picolylchloride is delivered into a graduated cylinder and the total solution volume brought up to 120 mL with methanol. The methanol/picolyl solution is then added to 30.00 g of BP-1 gel in a 300 mL 3-neck round bottom flask. The flask is fitted with a paddle stirrer in the center neck, a reflux condenser, and a pH electrode is fitted to the third neck. The resulting slurry is degassed and the flask heated to reflux. The pH is constantly monitored and kept at pH 12. 8N KOH in methanol is added dropwise if the pH falls below 11. The reaction is carried out at reflux for 6 hours. The resulting material is then cooled, and the CuWRAM is separated from the reaction solution by vacuum filtration. The CuWRAM is then rinsed 3 times with 120 mL of methanol, 3 times with 120 mL of DI water, 1 time with 120 mL of 4N sulfuric acid, 3 times with 120 mL of DI water and 2 times with 120 mL of methanol. And air dried.

Typical weight gain is 30% to 50%

Elemental Analysis: Carbon 23.5% Nitrogen 4.98% Hydrogen 3.4%

5.4.2 Analysis

5.4.2.1 Reagents

Deionized water was used to prepare all solutions and for all rinses unless otherwise noted. Metal solutions were prepared from reagent grade metal salts ($CuSO_4 \cdot 5H_2O$, and or $FeCl_3 \cdot 6H_2O$) and the pH of the solutions was adjusted as required using reagent grade H_2SO_4 (JT Baker Chemical), and NH_4OH (EM Science). Sulfuric acid solutions were prepared from the same reagent grade sulfuric acid. Mining solutions were obtained from two sources; the raffinate was obtained from Phelps-Dodge Mining Company (Phoenix, AZ) and the bioleach solution was obtained from the Mt. Gordon project (Electrometals Technologies, Western Australia, Australia).

5.4.2.2 Apparatus

Dynamic flow experiments were carried out using a column fashioned from a 5 mL disposable syringe fitted with frits at both ends and filled with the material being tested. The column was attached to a variable flow FMI Lab Pump Model QG150 (Fluid Metering Inc., Syosset, NY), set to a flow rate of 0.5 bed volumes/min. During longevity testing the solution intakes were controlled by computer activated solenoid valves (Cole-Parmer) using a PC with software developed for this application by Gamble and Associates Ltd., LLC (Pasadena, CA). The pressure drop tests and the tests carried out on actual mine solutions were carried out using 25mm X 600mm, 25mm X 400mm, or 15 mm X 300 mm glass column (Ace Glass Inc. Vineland, NJ) and the solutions pumped with a FMI Lab Pump Model QD-2 (Fluid Metering Inc., Syosset, NY).

5.4.2.3 Equipment

UV-Vis data were measured on a Perkin-Elmer Lambda-II Spectrometer. Flame Atomic Absorption data were measured on Unicam 969 Flame Atomic Absorption (FAA) Spectrometer. ICPES data were obtained by measuring the metal ion content of the samples with a Jerrel-Ash ICAPES IRIS. Samples were mounted for scanning electron microscopy (SEM) with carbon adhesive tape to aluminum studs, coated with 100Å chromium in an IBS/TM200S ion beam sputterer (VCR Group, Inc., South San Francisco, CA) and viewed on a S-4500 cold field emission scanning electron microscope (Hitachi Ltd., Japan).

5.4.2.4 Experimental Methods

5.4.2.4.1 Batch Tests

The batch tests were carried out on the following materials. XFS 45084 is a Dowex resin expressly for the selective extraction of copper(II). XFS comes in a large range of particle sizes with the bulk being above 500 µm. To achieve a size uniformity and diameter closer to CuWRAM for these tests we mechanically sieved the bulk resin and extracted the fraction of particles between 250 µm and 500 µm.. The XFS was weighed out for these experiments in the moist dry state in which it was received. The CuWRAM materials were weighed in the air-dry state. In the execution of these batch tests the concentration of the original solution was calculated from a solution that was treated in a manner similar to the test samples and diluted for analysis at the same time as the sample solutions. This was done because we anticipated that at elevated concentrations and pH iron(III) would begin to precipitate from solution.

Because we could not prevent this without adjusting the pH we took the metal ion concentration value of the control to be the original metal ion solution.

In each of the figures the y axis is the distribution coefficient (K_D) where K_D=concentration of metal adsorbed to the extratant / concentration of metal in the original solution.

5.4.2.4.2 Adsorption isotherms

Cu in Cu:Fe Mix	Fe in Cu:Fe Mix	Cu Only	Fe Only
0.05 M	0.15 M	0.2 M	0.2 M
0.025 M	0.075 M	0.1 M	0.1 M
0.013 M	0.038 M	0.05 M	0.05 M
0.0063 M	0.019 M	0.025 M	0.025 M
0.0032 M	0.0094 M	0.013 M	0.013 M
0.0016 M	0.0047 M	0.0063 M	0.0063 M
0.00078 M	0.0023 M	0.0031 M	0.0031 M

Table 5.5. The metal ion concentration in each of the twenty-one solutions used in the batch testing.

XFS, 90-105 µm and 250-500 µm CuWRAM (0.2000 g (± 0.0002 g)) were weighed out into glass screw top vials. 20 mL of a solution containing various concentrations of iron(III) only, copper(II) only, and of iron(III) copper(II) mix pH adjusted to 2.0 were added using a volumetric pipette. Table 5.5 contains the metal ion concentrations in the solutions used in this set of tests.

The vials were placed on a shaker for 24 hours to ensure constant agitation. At that time an aliquot of the metal ion solution was removed for analysis and preserved with trace metal grade nitric acid. This test was carried out in triplicate to ensure reliability of the data. The collected samples were then diluted to bring the metal concentrations into a range which could be analyzed by FAA spectroscopy.

5.4.2.4.3 Capture kinetics

The material (0.2000 g (± 0.0002 g)) was placed in a glass screw top vial. 20 mL of a 0.00625 M Cu^{++} and 0.01875 M Fe^{+++} solution was added using a volumetric pipette. The vials were placed on a shaker to ensure constant agitation. An aliquot of the metal ion solution was removed for analysis and preserved with trace metal grade nitric acid at the following times: 1 min, 5 min, 10 min, 15 min, 30 min, 1 hr, 2 hr, 4 hr, 8 hr, 12 hr, 16 hr, and 24 hr. This test was carried out in triplicate to ensure reliability of the data. The collected samples were then diluted to bring the metal concentrations into a range which could be analyzed by FAA spectroscopy. The results of the kinetics experiments are shown below. This graph clearly show the much faster capture kinetics of 90-105 µm CuWRAM, this is a clear indication of the potential superiority in a column system at accelerated treatment flow rates. It is due to the much faster capture kinetics of this material that enables the same amount of copper(II) solution to be processed with a smaller amount of extraction material.

5.4.2.4.4 pH Profile

In these experiments 0.2000 g (± 0.0002 g) of extraction material was placed in a glass screw top vial. 20 mL of a 0.003125 M Cu^{++} and 0.009375 M Fe^{+++} solution was added using a volumetric pipette. The solutions were pH adjusted to pH 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 using conc. sulfuric acid or 8N sodium hydroxide prior to being placed into the vials. The vials were placed on a shaker to ensure constant agitation. An aliquot of the metal ion solution was removed for analysis and preserved with trace metal grade nitric acid after 24 hrs. This test was carried out in triplicate to ensure reliability of the data. The collected samples were then diluted to bring the metal concentrations into a range which could be analyzed by FAA spectroscopy.

5.4.2.4.5 Longevity Tests

To determine how long the materials will last a series of longevity tests were carried out. Although this test was not described in the proposal it is a very important test. If the material can't repeatedly withstand the extremes of the chemical and physical environment to which it will be exposed then there would be no sense in developing the material further. Longevity tests were carried out in the following manner. A 5cc column was loaded with the material being tested and the copper capacity checked following these procedures:

1. 100 mL of DI water is pumped through the column to wet the material

2. 70 mL of a 1000 ppm Cu^{++} : 3000 ppm Fe^{+++}, from copper sulfate and ferric chloride, solution is pumped through the column at a flow rate of 2 column volumes / min. and the flowthrough is collected
3. 30 mL of DI water is pumped through the column to rinse the column; this water is collected along the flowthrough from step 2
4. The collected solution from above is preserved with trace metal grade nitric acid and diluted to enable FAA spectroscopic analysis for Cu^{++} and Fe^{+++}
5. The column is then stripped of metal by pumping through 4 ml of sulfuric acid; XFS is stripped with 8N H_2SO_4, CuWRAM is stripped with conc. acid
6. The strip solution as well as 16 mL of DI water is collected and later diluted for analysis for Fe^{+++} and Cu^{++} by FAA spectroscopy
7. The column is then rinsed with 100 mL of DI water which is discarded

The above procedure was used each time the metal ion capacity of the column was checked. Between capacity checks the following procedure was used:

1. The column was attached to a six way manifold equipped with solenoid valves wired to a computer containing software to carry out the procedure
2. The pump was adjusted to produce a flow rate of 10 column volumes / min
3. The challenge solution was pumped through for 6 sec.
4. DI water followed for 10 sec
5. Conc. sulfuric acid for 5 sec
6. DI water for 36 sec
7. Repeat steps 3 – 6

The metal ion capacity was checked after 25, 75, 150, 300, 450, 700, 1000, and 1500 cycles. The absorbence data from the FAA was converted to mmoles of metal ion per gram of extractive material and plotted

5.4.2.4.6 Flow Capacity Tests

The flow capacity tests were described in the above section Steps 1 – 7. These tests may be the best indicator of how a material will perform in a process setting.

5.4.2.4.7 Breakthrough curves on actual mining solutions

These breakthrough curves were carried out in the following manner. The mine solution was pumped through the column and 20 mL of flowthrough solution was collected every 2 bed volumes minus 10 mL. The tests were conducted until the column was visibly saturated and then an additional two to ten column volumes of solution were pumped through. Depending on the test the column was then rinsed with two to five column volumes of water or the rinse step was skipped. The column was then stripped with sulfuric acid and the strip collected in fractions or as a single fraction. The flowthrough samples were preserved with trace metal grade nitric acid and diluted as necessary. Typically samples were diluted 1:1000 and 1:100 and analyzed by flame atomic absorption spectroscopy, or diluted to the propper concentration and analized by ICPES.

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