

MAGNETIC ADSORPTION METHOD FOR THE TREATMENT OF METAL CONTAMINATED AQUEOUS WASTE

Gregory B. Cotten*

James D. Navratil

Idaho National Engineering & Environmental Laboratory

P.O. Box 1625 MS 3954

Idaho Falls, Idaho 83415-3954

H. Bradley Eldredge

University of Idaho

1776 Science Center Drive

Idaho Falls, Idaho 83405

ABSTRACT

There have been many recent developments in separation methods used for treating radioactive and non-radioactive metal bearing liquid wastes. These methods have included adsorption, ion exchange, solvent extraction and other chemical and physical techniques. To date very few, if any, of these processes can provide a low cost and environmentally benign solution. Recent research into the use of magnetite for wastewater treatment indicates the potential for magnetite meeting both cost and environmental drivers.

A brief review of recent work in using magnetite as a sorbent is presented as well as recent work performed in our laboratory using supported magnetite in the presence of an external magnetic field. The application to groundwater and other aqueous waste streams is discussed.

Recent research has focused on supporting magnetite in an economical (as compared to the magnetic polyamine-epichlorohydrine resin) and inert (non-reactive, chemically or otherwise) environment that promotes both adsorption and satisfactory flow characteristics.

INTRODUCTION

Magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$) has been used to separate a wide variety of substances, such as dissolved metal species, particulate matter, and organic and biological materials (1). In the absence of an external magnetic field, activated magnetite readily adsorbs numerous metal species including actinide elements (2). In the presence of an external magnetic field, a synergistic effect was observed in using supported magnetite in a fixed-bed for removal of plutonium and americium from wastewater (3,4). Using a magnetite-containing polyamine-epichlorohydrin (MPE) resin bead, Kochen and Navratil observed that in the presence of a relatively weak magnetic field (0.3 Tesla), the sorption capacity of the resin for both plutonium and americium increased by a factor of five compared to data that was obtained with unsupported magnetite particles in the absence of a magnetic field. These observations may be explained by a nanolevel high gradient magnetic

separation (HGMS) effect, as plutonium and americium are known to form colloidal particles with satisfactory magnetic properties at elevated pH (5). The surface irregularities of the MPE resin are large enough to permit the free displacement of the colloidal particles. When the field of the magnet is turned on, the magnetite particles are magnetically induced, creating a field, or locally induced magnetic moment, that contributes to the net field sensed by the colloidal particles. In the absence of convection and when the magnetic force is sufficiently greater than the force associated with Brownian (thermal) motion, the magnetic force created by the field can be attractive and large enough to allow the magnetite to adsorb the colloidal particles. When the field is turned off, the nanoparticles are released and dispersed in solution by thermal motion. This process could be referred to as magnetic swing adsorption (6).

Throughout the world, and in particular at the Idaho National Engineering and Environmental Laboratory (INEEL), there are urgent needs for improved, and primarily, less expensive processes for the treatment of toxic metal contaminated water (7-10). Metal contamination comes in many different forms. For example, industrial wastes such as those from the semiconductor, chrome plating, and mining industries result in large volumes of contaminated water either directly as effluent to a water supply or indirectly through leaching from storage lagoons to rivers, streams, or aquifers. Government programs for the production of military equipment and weapons have also contributed to metal contamination in various waters. In some cases these metals may be radioactive, as is the case at the INEEL where the aquifer beneath the Test Area North facility is contaminated with the fission products cesium-137 (^{137}Cs) and strontium-90 (^{90}Sr) above the United States drinking water standards (11). Municipal water systems can become contaminated with metals through the careless and/or intentional dumping of consumer and industrial products. Residential water systems can become contaminated in a similar manner to industrial supplies. In addition, where the residential source is a well, industrial activity upgradient of the well, as well as agricultural run-off and leaching, can also lead to metal contamination of water supplies.

World wide it is estimated that the annual cost of water purification exceeds \$100 Billion. With ever-stricter water quality standards and the need for improved methods, simple and inexpensive technologies for water treatment are significant business growth areas. The preliminary results reported here are for the development of such a process for water treatment using iron ferrite (magnetite) sorption enhanced with a magnetic field.

BACKGROUND

There is extensive coverage of magnetite and high gradient magnetic separation (HGMS) for water treatment in the scientific literature. A summary of the developments in the field from the past thirty years is presented below.

Magnetite, or iron ferrite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), is a naturally occurring mineral, but also can be easily prepared in the laboratory from solutions containing ferric and ferrous ions (12,13) with a Fe(III)/Fe(II) ratio of 2. Both chemical analysis and Mössbauer spectroscopy have measured the resulting magnetite to be within 10% of the stoichiometric composition (12). Magnetite has been shown to remove a variety of substances from water, such as dissolved metal species, particulate matter, and organic and biological materials (1). In the absence of an external magnetic field, activated magnetite or synthetically prepared iron ferrite readily adsorbs numerous metal species

including actinide elements and metals (2). In the presence of an external magnetic field, a synergistic effect has been observed in using supported magnetite in a fixed-bed for removal of plutonium-239 (^{239}Pu) and americium-241 (^{241}Am) from wastewater (3). This implies that the low adsorption properties of magnetite for metal ions can be overcome if the solution can be altered to place the metals in a solid form such as a colloid. Most mechanical filtration systems are only slightly effective at removing colloids, so this magnetic field-enhanced process offers a substantial improvement.

Kochen and Navratil (3,4) patented a process whereby a magnetic polymer resin provided for the efficient removal of actinides and other heavy metals from contaminated water. A polyamine-epichlorohydrine (PE) polymer was synthesized with magnetite to form the MPE resin. The patent further details the removal of ^{239}Pu and ^{241}Am from aqueous solutions at elevated pH. The patent goes on to describe how through the cycling of the electromagnetic field, elution of the contaminant was accomplished. This process clearly identifies a method where magnetically susceptible particles can be sorbed to other magnetically susceptible media (MPE resin) in the presence of an external magnetic field. The patent covers a variety of materials to support magnetite as well as claims for the removal of many hazardous metal species.

Magnetic separation and HGMS processes have been used extensively in the processing of minerals (14), and more recently for water treatment and environmental applications (15). This research differs significantly from common magnetic separation and HGMS processes. Conventional processes (16-18) use, for example, a fine steel wool to form a magnetic matrix within a flow field of a solution containing mineral particles to be separated. For this process, in order for effective separation to occur, precipitating or flocculation agents must first be added to effect formation of large particles (>1 micron in diameter). In contrast, the magnetic adsorption process of the Kochen and Navratil patent (3) is unique because the adsorbent material not only acts as a magnetic matrix, but it also contains an adsorptive component to the system. This adsorptive component allows for the removal of soluble metal species (hydroxide complexes) from solution, while the magnetic matrix allows for the removal of nanoparticles through a HGMS effect.

Other literature citations have reported varying degrees of contaminant removal with magnetite both in and out of an external magnetic field. Petković and Milonjić (19) reported the adsorption of cesium on magnetite through the presentation of Langmuir-type adsorption isotherms for various pH between 7.6 and 10.4 based on batch experiments. Adsorption of cesium was shown to increase with pH although the mechanism was not presented. Peak adsorption of 0.086 wt% ($6.5\text{E-}3 \text{ mMg}^{-1}$) was reported at pH of 10.40. Milonjić and Ruvarac (20) reported the adsorption of cesium (I), cobalt (II) and cerium (III) by magnetite at pH of 2.2 by batch experiments. Cobalt adsorption was reported as less than 5 [wt]% although actual data were not provided to verify the magnitude. Milonjić et al. (21) presented the adsorptive properties of magnetite with respect to alkali metal ions, also through batch experiments. They investigated the point of zero charge for magnetite through potentiometric titration studies. They presented a discussion on surface charge effects and double-layer theory for surface adsorption. Early work of Boyd et al. (22-25) reported the iron ferrite process was effective for plutonium removal in the pH range of nine to thirteen. Additionally the ferrite process was able to achieve similar contaminant reduction to flocculant processes with 80% less solid by-product formation. The ferrite process was evaluated on a three-stage process where two grams of ferrite per liter were added with

similar efficacy for containment removal and solids production. Kochen et al. (26) reported similar removal efficiencies for actinides when the magnetite was activated with sodium hydroxide and barium hydroxide solutions. Boyd et al. (27,28) reported the effect of dissolved chemical species on ferrite formation and plutonium removal as well as the evaluation of alternative methods for ferrite production including the use of commercially available magnetite. Dixon (29) reported the removal of “colour and turbidity” through the addition of 5-10 micron magnetite particles. Dixon identifies both the adsorption of colloidal impurities and soluble species at the magnetite surface.

EXPERIMENTAL

Figure 1 depicts the laboratory testing apparatus. The arrangement allowed for simultaneous testing of magnetite supported in a variety of ways in a column both in and out of magnetic field. Both columns received identical feed with the exception of any variances associated with the short (60 cm) section of tubing from the pump to the column.

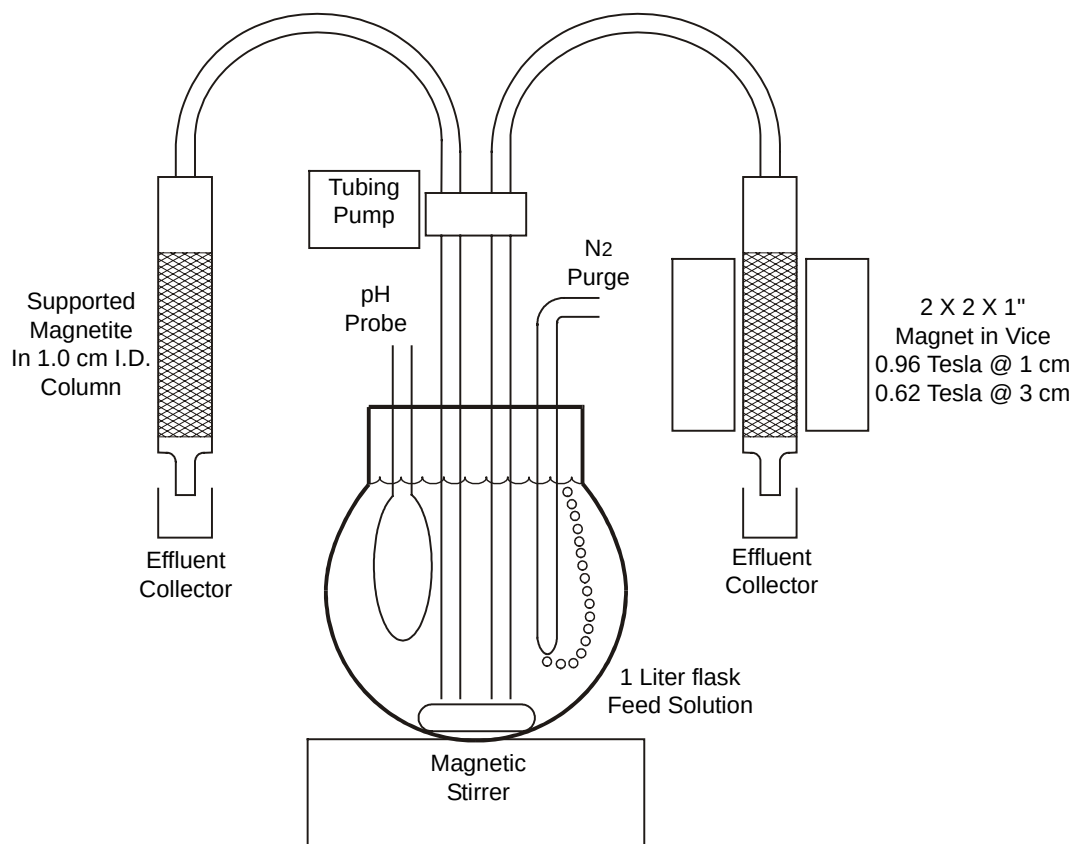


Figure 1 – Experimental Apparatus

The 1-liter flask containing the cobalt solution was continuously sparged with nitrogen and stirred with a Teflon coated magnetic stirring bar. A Corning pH probe (Deep Vessel Combo w/RJ, Model # 476306, Corning, NY, USA) connected to a Corning pH/Ion Analyzer (Model #

350) was used to record pH during the experiment. Values of pH were recorded at the completion of each sample activity. A single suction line was connected to a T-fitting just prior to the Masterflex[®] Console Drive (Model # 7521-50, Barrington, IL, USA) tubing pump fitted with two Masterflex[®] pump heads (Model # 7518-00) operating off of the same drive shaft. The individual feed lines went directly to the top of the test columns where they were fitted with a reducing union and a short (1cm) section of tubing to obtain a tight seal in the top of the column. The columns used are Fisherbrand[™] serological 10 mL pipets (Model # 13-678-315, Fisher Scientific, Pittsburgh, PA, USA) having an approximate outside diameter of 1 cm and an inside diameter of 0.8 cm for a column cross sectional area of 0.5 cm². The columns are preloaded with approximately 0.2 grams of glass wool as a support to hold the sorbent in place. The columns used in these experiments generally were loaded with 1-3 grams of the magnetite and support media mixture. The density of the test material varied from batch to batch so that we could evaluate loading and size for removal efficiency. The "rule of thumb" for the experiments was to use a mass of sorbent sufficient to obtain approximately 5 cm of column depth, which matches the vertical height of the magnet. The columns were supported in standard laboratory ring stands so that the orientation to the magnetic field could be maintained consistently throughout the experiments. The column located outside of the magnetic field was located approximately 30 cm away from the magnet apparatus where the magnetic flux density was measured to be less than 0.01 Tesla.

The magnet is a commercially available neodymium-iron-boron permanent magnet in a rectangular solid shape of approximately 5 by 5 by 2.5 centimeters in dimension. Two of these magnets are mounted on opposing base plates separated by two lead screws controlled by a chain driven hand crank. The magnets can be separated up to 20 centimeters down to zero by adjusting the hand crank. A maximum magnetic flux density of 1 Tesla can be achieved when the magnets are separated by less than 1 centimeter. Table I lists the various flux densities obtained as a function of distance between the magnets.

Table I – Magnetic Flux Density versus Magnet Separation Distance

Separation Distance (cm)	Magnetic Flux Density (Tesla)
1	0.98
3	0.62
5	0.28
7	0.14

Flow was downward (with gravity) for all of the experiments. The columns were flushed with water prior to introduction of the feed to stabilize the particles with regard to swelling due to moisture and Brownian and convective motion induced settling. The columns were initially filled with water to an equal mark representing approximately 6 to 8 mL of water above the top of the sorbent. This acted as a dispersion network and minimized the probability of initial channeling of the feed material. It should therefore be recognized that the first few sample points are artificially low as they represent some mixing of the feed with the initial volume of pure water. It is assumed

that after 50 mL of throughput the effluent should reasonably represent the feed with the exception of any material being sorbed by the sorbent.

SIMULATED WASTE STREAM PREPARATION

All column studies were carried out with a similar simulated feed preparation process. Laboratory grade water filtered to >17.4 megohm-cm was sparged with nitrogen for approximately ten minutes prior to the addition of the metal powder and the nitrogen sparge was continued throughout the experiment in an attempt to minimize oxidation variations. Cobalt (II) carbonate hydrate ($\text{CoCO}_3 \cdot x\text{H}_2\text{O}$), obtained from Aldrich (Milwaukee, WI), stock # 20,219-3, was added to obtain an approximate 10-25,000 $\mu\text{g/L}$ cobalt concentration.

Additional experiments were carried out using groundwater obtained from the Snake River Plain Aquifer in southeast Idaho. This groundwater was used to evaluate the natural pH, pH buffers, and ionic strength inherent to groundwater without having to formulate a laboratory surrogate. The groundwater was not sparged with nitrogen.

ANALYTICAL PROCEDURES

An Atomic Absorption Spectrophotometer (Perkin-Elmer, Model 5100, Norwalk, CT, USA), using an air-acetylene flame, was used for cobalt analysis of all samples. Feed samples were taken from the end of the tubing just prior to the test columns at the beginning and end of the experiment when practicable. Previous experiments showed cobalt sorption on the glassware and tubing internals tended to reduce the amount of cobalt actually running through the test column. Feed samples were collected in 15 mL centrifuge tubes diluted with 2 mL of 1-M nitric acid (HNO_3) yielding a 12 mL feed sample (1 mL void in sample tube). Column effluent samples were collected in 25 mL volumetric flasks diluted with 2 mL of 1-M HNO_3 yielding a 23 mL effluent sample. The effluent samples were mixed by hand shaking the flask and then approximately 14 mL was transferred to 15 mL tubes for analysis. Calibration standards were prepared with commercially available 1000 $\mu\text{g/mL}$ standard from VHG Labs, Inc. (Manchester, NH), Product No. PCON-100 for cobalt. Standards of 1000, 7000, 15,000 $\mu\text{g/L}$, and 25,000 $\mu\text{g/L}$ were used with a non-linear calibration protocol for cobalt. Sample blanks were run between every analysis and each individual result represents the average of two separate triplicate analyses performed by the spectrophotometer. Calibration checks were performed at the beginning and the end of the analysis run and periodically in between, roughly after every tenth sample.

Analytical results were manually entered into a Microsoft® Excel spreadsheet where dilution corrections and graphical plotting were performed. Plots of effluent concentration versus throughput require some clarification. The throughput data point represents an average value for the effluent concentration based on the throughput at the beginning of the sample and the end of the sample. For example, the first sample point is plotted at a throughput value of 11.5 mL which is the average of the throughput at 0 and 23 mL respectively although 23 mL have actually passed through the column. Plots of the ratio of the effluent concentration to the influent concentration (C/C_0) versus bed volumes (BV) of throughput are shown.

RESULTS

Various support media and mixture ratios were evaluated. Pure magnetite powder was obtained from commercial suppliers generally in the size range of 1-5 microns. A column of pure magnetite has very poor flow characteristics, namely virtual complete plugging except for under extreme pressure. It is therefore required to mix magnetite with a support media to allow reasonable flow characteristics to support reasonable treatment rates. Media such as glass wool, glass beads, silica gel, sand, natural fiber twine, etc., were evaluated in different magnetite/media proportions. We have selected a glass bead support media for further testing based on its superior flow characteristics compared to the other media evaluated.

Figure 2 depicts an experiment where column 1 contained 100% glass beads and column 2 contained a 50/50 mixture by weight of glass beads and magnetite. The glass bead column clearly achieves 100% breakthrough very quickly as expected while the magnetite mixture column achieves approximately 75% breakthrough and levels off.

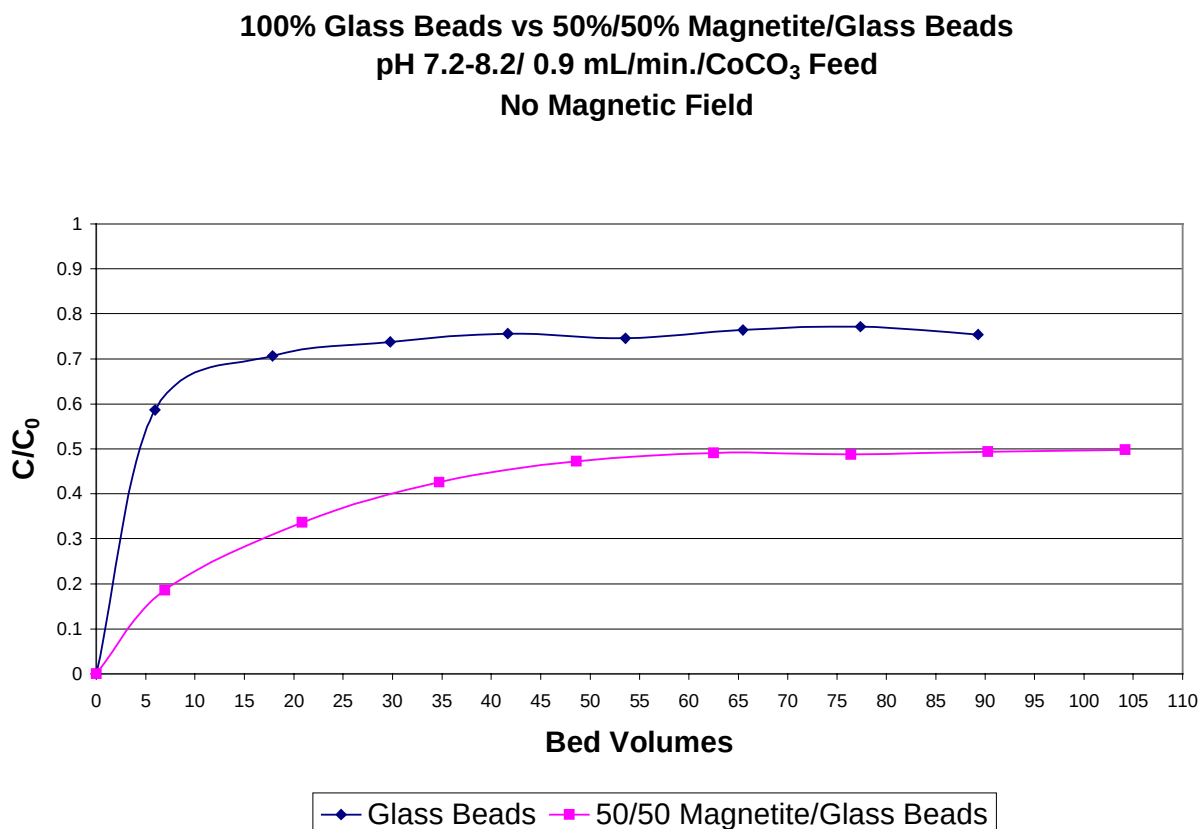


Figure 2 – Glass Bead versus Magnetite/Glass Bead Column

The initial rise in the effluent concentration of column 2 and subsequent leveling off at a steady state value can be explained as follows. The feed concentration consists of cobalt in three specific species, cobalt ion, cobalt hydroxylated complex ion, and cobalt hydroxide solid (as a

colloid or precipitate). Ionic sorption of cobalt and its complexes can take place either as an ion exchange with iron species within the spinel structure (most likely an insignificant amount) or surface sorption as a result of localized charged areas formed by the configuration of materials within the lattice as explained in layer theory (13). Contaminant removal may also be by mechanical filtration due to a more tortuous path developed by the glass bead and magnetite mixture. Another form of sorption is explained by HGMS theory whereby magnetically susceptible cobalt particles are attracted and sorbed to the surface of the magnetite particle in the presence of the magnetic field. HGMS is ruled out in Figure 2 due to the absence of a magnetic field. We believe the initial rise to steady state accounts for ionic sorption (as well as initial column dilution effects) and the steady state value represents particle capture. The steady state effluent value represents primarily the ionic cobalt species that are no longer capable of being sorbed by the magnetite due to exhaustion of the ionic sorption sites.

Figure 3 depicts an experiment where the column contains equivalent amounts of a 50/50 mixture of glass beads and magnetite. Column 1 is in the magnetic field and column 2 is out of the magnetic field. The enhanced sorption in the presence of the magnetic field is clearly shown.

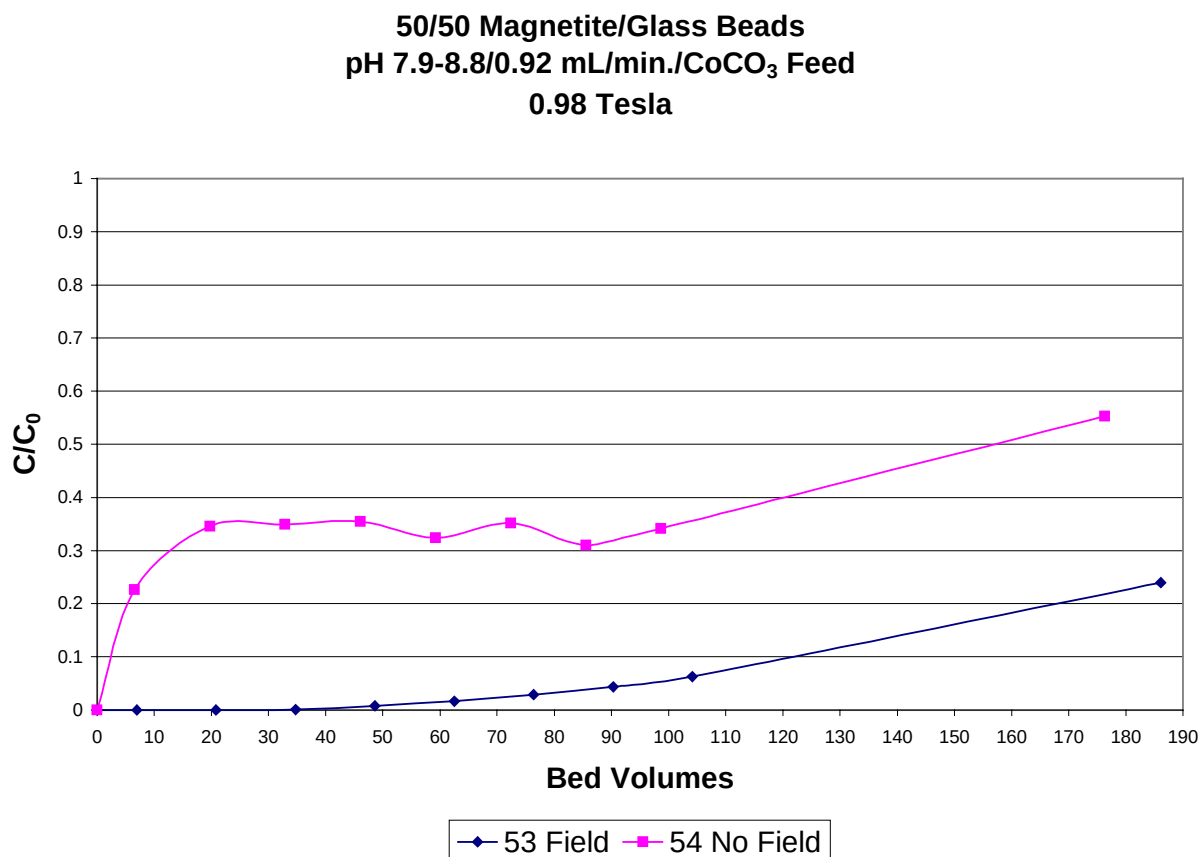


Figure 3 – Magnetic Field Enhanced Adsorption

The feed consisted of predominantly cobalt particles at this experimental pH. Similar explanations are applicable for these experiments. The ionic sorption fraction is small in

comparison to the particle sorption capacity. Therefore the rise to steady state for the column out of the magnetic field is primarily attributed to the small volume of pure water in the column providing initial dilution (as explained earlier) and the small ionic sorption capacity.

The three-step process shown between Figures 2 and 3 identifies successive improved contaminant removal capabilities as the sorbent goes from glass beads to glass beads and magnetite to glass beads and magnetite in a magnetic field.

CONCLUSION

We have identified suitable support media for mixing with natural magnetite that achieves satisfactory flow characteristics while retaining the magnetic field-enhanced sorption properties of magnetite. Additional experiments have been conducted to evaluate iron, calcium, magnesium, strontium, and cesium. Preliminary results indicate that natural components of groundwater such as calcium and magnesium have no deleterious effect on the process. Additional studies are underway to expand the list of test contaminants and to optimize the magnetite/support media ratio with regards to flow and sorption parameters.

REFERENCES

1. T.E. BOYD, M.J. CUSICK, and J.D. NAVRATIL, "Chapter 6: Ferrite Use in Separation Science and Technology, Recent Developments in Separation Science Volume VIII," N.N. Li, and J.D. Navratil, Editors, CRC Press, Inc., Boca Raton, FL (1986)
2. J.D. NAVRATIL, "Removal of Impurities Using Ferrites and Magnetite," Australian Patent Application PJ0198 (August 8, 1988)
3. R. L. KOCHEN, and J. D. NAVRATIL, "Removal of Radioactive Materials and Heavy Metals from Water Using Magnetic Resin," United States Patent 5,595,666 (January 21, 1997)
4. R. L. KOCHEN and J. D. NAVRATIL, "Method for Regenerating Magnetic Polyamine-Epichlorohydrine Resin," United States Patent 5,652,190 (July 29, 1997)
5. A.D. EBNER, J.A. RITTER, H.J. PLOEHN, R.L. KOCHEN, and J.D. NAVRATIL, "New Magnetic Field-Enhanced Process for the Treatment of Aqueous Waste," Separation Science and Technology, In Press (1998)
6. J.D. NAVRATIL, R.L. KOCHEN, and J.A. RITTER, "Magnetic Swing Adsorption Process," Proceedings for Waste Management Symposia 1995, Tucson, AZ (1995)
7. R.A. CORBITT, "Standard Handbook of Environmental Engineering," McGraw-Hill, New York (1990)
8. H.M. FREEMAN, "Standard Handbook of Hazardous Waste Treatment and Disposal," McGraw-Hill, New York (1998)

9. M.D. LAGREGA, P.L. BUCKINGHAM, J.C. EVANS and THE ENVIRONMENTAL RESOURCES MANAGEMENT GROUP, "Hazardous Waste Management," McGraw-Hill, New York (1994)
10. METCALF and EDDY, "Wastewater Engineering, Treatment, Disposal, and Reuse," Third Edition, McGraw-Hill, New York (1991)
11. UNITED STATES DEPARTMENT OF ENERGY, "Record of Decision Technical Support Facility (TSF) Injection Well (TSF-05) and Surrounding Groundwater Contamination (TSF-23), Operable Unit 1-07A, Waste Area Group 1, Idaho National Engineering Laboratory," September (1992)
12. U. SCHWERTMANN and R.M. CORNELL, "Iron Oxides in the Laboratory: Preparation and Characterization," VCH Publishers, Inc., New York (1991)
13. Z. SUN, F. SU, W. FORSLING, and P. SAMSKOG, "Surface Characteristics of Magnetite in Aqueous Suspension," Journal of Colloid and Interface Science, **197**, 151-159 (1998)
14. C.J. KING and J.D. NAVRATIL, "Chemical Separations," Litarvan, Denver CO (1986)
15. F. MACASEK and J.D. NAVRATIL, "Separation Chemistry," Horwood, New York (1992)
16. N. HARUSUKE, "Water Purifier Having a Magnetic Field Generation Device," United States Patent 5,628,900 (May 13, 1997)
17. A. STADMULLER, "Magnetic Separators," United States Patent 5,759,391 (June 2, 1998)
18. D. GUREVITZ, "Method and Apparatus for Processing Waste Water," United States Patent 5,759,407 (June 2, 1998)
19. D. M. PETKOVIĆ and S.K. MILONJIĆ, "Adsorption of Cesium From Basic Water Solutions on Natural Magnetite," Bulletin of the Boris Kidrič Institute of Nuclear Sciences, Vol. 20, Chemistry, No. 3 P/449 (May 1969)
20. S.K. MILONJIĆ and A. RUVARAC, "Adsorption of Cs^+ , Co^{2+} and Ce^{3+} From Acid Aqueous Solutions on Natural Magnetite," Bulletin of the Boris Kidrič Institute of Nuclear Sciences, Vol. 21, Chemistry, No. 3 P/462 (September 1970)
21. S.K. MILONJIĆ, M.M. KOPEČNI and Z.E.ILIĆ, "The Point of Zero Charge and Adsorption Properties of Natural Magnetite," Journal of Radiological Chemistry, Vol. 78, No. 1 (1983) 15-24

22. T.E. BOYD and R.L. KOCHEN, "Ferrite Treatment of Actinide Waste Solutions: A Preliminary Study," RFP-3299, CRD 81-064, Rockwell International, Golden, CO (July 30, 1982)
23. T.E. BOYD, R.L. KOCHEN, M.J. CHAMBERS and G. SHEKELL, "Ferrite Treatment of Actinide Waste Solutions: Continuous Processing of Rocky Flats Process Waste," RFP-3476, UC-10 Chemical Separations Processes for Plutonium and Uranium, DOE/TIC-4500 (Rev. 69) Rockwell International, Golden, CO (March 18, 1983)
24. T.E. BOYD, R.L. KOCHEN, G.A. RIORDAN and L.M. MORALES, "Ferrite Treatment of Actinide Waste Solutions: Multi-Stage Continuous Processing," RFP-3582, UC-4 Chemistry, DOE/TIC-4500 (Rev. 72), Rockwell International, Golden, CO (January 27, 1984)
25. T.E. BOYD, R.L. KOCHEN and M.Y. PRICE, "Removal of Radioactive Materials from Waste Solutions Via Magnetic Ferrites," Proceeding of American Nuclear Society Topical Meeting on Treatment and Handling of Radioactive Waste, Richland, WA, (April 19-22, 1982)
26. R.L. KOCHEN, R.L. THOMAS and L.M. MORALES, "Actinide Removal From Aqueous Solution with Activated Magnetite," RFP-4100, UC-4 Chemistry, DOE/TIC-4500 (Rev. 73), Rockwell International, Golden, CO (August 10, 1987)
27. T.E. BOYD, M.Y. PRICE, R.L. KOCHEN, C.A. DEITESFELD and J.C. DELANEY, "Ferrite Treatment of Actinide Waste Solutions: Chemical Interferences in Actinide Removal by Ferrite Treatment," RFP-3601, UC-10 Chemical Separations Processes for Plutonium and Uranium, DOE/TIC-4500 (Rev. 73), Rockwell International, Golden, CO (January 14, 1985)
28. T.E. BOYD, R.L. KOCHEN, M.Y. PRICE, C.A. DEITESFELD and L.M. MORALES, "Ferrite Treatment of Actinide Waste Solutions: Alternative Methods of Ferrite Productions For Use in Waste Treatment," RFP-3692, UC-10 Chemical Separations Processes for Plutonium and Uranium, DOE/TIC-4500 (Rev. 73), Rockwell International, Golden, CO (January 16, 1985)
29. D.R. DIXON, "Interaction of Alkaline-Earth-Metal Ions with Magnetite" Colloids and Surfaces, 13 (1985) 273-286