IMPROVEMENTS IN WASTEWATER TREATMENT AT THE LEADVILLE MINE DRAINAGE TUNNEL

Department of Chemistry and Biochemistry
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This research demonstrates magnetic separation of contaminants from mine drainage at low temperature (15 °C) water. Two facets of this research were: (1) to achieve the appropriate water chemistry to form magnetite seeds to which the contaminants bind themselves, and (2) to develop a physical magnetic separation process using remnant fields. Ferromagnetic particles and non-ferromagnetic particles were removed the latter by introduction and/or creation of magnetite formed from chemical seeding. Advantages of this process are small footprints and minimal chemicals added or sludge produced.

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1 BRIEF BACKGROUND OF PROJECT

Heavy metal contamination of natural water sources continues to be a problem in the mining communities long after mining has ceased. Much effort and expense is necessary to remediate these problems, often with less than adequate results. Traditional methods (e.g., metal hydroxide precipitation) to remove heavy metals involve adding large quantities of chemicals to the waste stream which might contain quantities of contaminants at levels less than parts per thousand. Magnetic separation, a technology initially developed for other uses, is now being successfully applied to contaminated water streams. Its advantages are a smaller facilities footprint, less chemical additives and consequently, less sludge produced. Magnetic separation will even work on elements that are not intrinsically ferromagnetic or paramagnetic by the proper seeding of iron based compounds to the waste stream which act to scavenge the nonmagnetic contaminants. Methods have been developed that enable generation of magnetic particles (magnetite) in-situ at high temperatures (70 °C). Our recent work has developed in-situ magnetite formation at lower temperatures (15 °C). For this project, there were two distinct steps involved in developing our approach: One was to achieve the appropriate water chemistry to form the magnetite seeds to which the contaminants bind themselves. The other was to develop the physical magnetic separation process using remnant fields. This work will provide an avenue for treatment of a great many heavy metal contamination sites.

These two tasks were conducted at New Mexico State University (wet chemistry) and at Los Alamos National Laboratory (remnant magnetic field work). After a successful process has been established, it is anticipated that a small portable treatment pilot plant will be constructed and tested at the Leadville Mine Drainage Tunnel (LMDT), an adit historically used to dewater mining areas in Colorado.

2 RESTATEMENT OF PROJECT GOALS

The general project goal is to improve the removal of heavy metals from the LMDT flow stream in a manner that is practical and cost effective. We propose magnetic separation as a technique in a two-step process as follows: (1) binding/flocculation of the contaminants with in-situ formed magnetite and preformed magnetite and (2) removal of these magnetite particles by magnetic separation.

Specific Goals:

(1) Demonstration that the magnetite formation and remediation process will work at the 6 °C temperature of the LMDT facility. Although the literature states that magnetites cannot be formed below 40 °C, we have already established that formation at 15 °C is possible. Our work provides a method for formation of magnetites at even lower temperatures using LMDT waters. This work was carried out at New Mexico State University (NMSU).

(2) Determine the best initial design for a low field or remnant field magnetic separator. This work will *not* involve a high field magnet. This work was carried out at Los Alamos National Laboratory with Dr. Coyne Prenger and Dr. Laura Worl the investigators for magnetic separation work at LANL.

3 RESULTS AND DISCUSSION

This research is presented in the following order: (1) our findings on low-temperature synthesis of magnetites and their characterization; (2) remediation using magnetites (both in-situ formation and use of preformed magnetites) as well as the effects of organics, (3) the potential for magnetic separations and (4) conclusions with recommendations for further study. Four figures of significant parts of this research have been appended to this report.

3.1 Low Temperature Synthesis of Magnetites

We have investigated the formation of magnetites down to temperature as low as 6 °C and as high as 70 °C. Initial studies showed that our ability to form magnetites using our technique was dependent on the nature of the waters. That is to say, we can produce high quality magnetites from distilled water or LMDT waters at 70 °C. The procedure involved addition of a stoichiometric amount of iron (II) sulfate and iron(III) sulfate to a heated solution to be treated. Then the pH was adjusted to 9 using caustic soda and the solution was allowed to stir for one hour. Within the first few minutes the initially dark brown colored suspension turns dark black, indicating the formation of magnetites. The one hour stirring time results in large, better formed magnetite crystals. A brief description of the crystal size is presented in section 3 of this document.

In contrast, at low temperatures, 6 °C, the LMDT water impeded magnetite formation every time. Initially dissolved oxygen was believed to be an inhibitor due to oxidation of the iron (II) present in solution. Deoxygenation however with argon did not fully alleviate the problem. It was then concluded that the inhibition was apparently due to competition from other ions for hydroxide or from formation of another solid phase that competes with magnetite formation. Since calcium and magnesium are the two principle “other” ions in the LMDT water, we examined the formation efficacy in the presence of both of these at concentrations reported at the LMDT facility. It was observed that while magnesium produced a slightly more flocculent product, it did not interfere with magnetite formation whereas calcium completely inhibited the process.

It is generally believed that magnetite formation is a two stage process: initial formation of a "green rust" (Fe (II) hydroxides) followed by dehydration with Fe (III) to form magnetite. Using LMDT samples, the process appears to be interrupted in the dehydration step because the green rusts are observed to form as usual. As shown above, it appears that calcium is the principal interfering ion (83.5 ppm in LMDT waters) in the magnetite formation process.

Initially we attempted to remove calcium from water by alkaline precipitation (addition of sodium hydroxide to pH 11), followed by filtration to remove presumably calcium carbonate or calcium hydroxide. Once treated, the magnetites were successfully formed. Such an approach however, was deemed unacceptable since almost any contaminating metal would also precipitate thereby rendering further treatment unnecessary. This high pH would also result in enormous sludge volumes.

We also tried the addition of strong calcium complexing agents (NTA, EDTA) which worked, but again, the cost of these reagents was too high to form the basis of a treatment plan. These experiments confirmed our suspicions that calcium is the “bad” player in this process.

The next attempt to circumvent this obstacle was to seed samples with small amounts of pre-formed magnetite. This should provide a surface upon which nucleation and further magnetite formation should take place. Unlike the lack of success with the initial experiments using our standard magnetite synthesis, our work with this approach produced highly successful results toward low temperature synthesis of magnetites.

The first experiments were conducted by adding 50µm sized commercial magnetite particles to the water to be treated followed by stoichiometric additions of ferrous and ferric sulfates. Later, laboratory-synthesized magnetites of unknown size were examined. These solutions were deoxygenated using argon, chilled to 6 °C and caustic soda was added to adjust pH to 9. The reaction was monitored visually by watching the initially formed green floc change into black magnetite. Typical transformation times ranged between 30 seconds and 1 minute. The amounts of each substance and the results are shown in Table 1.

Table 1.—Low Temperature (6 °c) Seeding of Magnetites

Magnetite added	Ferrous sulfate added	Ferric sulfate added	Water source	Conversion to Magnetite?
100 ppm	31.2 ppm	68.8 ppm	SAMD	yes
0	31.2	68.8	SAMD	no
500	300	500	LMDT	yes
0	300	500	LMDT	no
216	83	133	distilled	yes
216	83	133	LMDT	yes
0	83	133	LMDT*	no

SAMD = simulated acid mind drain water
LMDT = actual Leadville facility water source
*15°

Interestingly enough, the preformed magnetites (magnetites made in the lab) showed distinct differences in catalysis dependent upon their origin. Commercially available magnetites showed less catalytic activity than preformed magnetites. We remain uncertain regarding the origin of this effect, although it most likely is due to differences in surface composition. Future studies should examine and contrast the crystal structure and surface characteristics of these two magnetite sources.

Regardless of the magnetite source, it is readily apparent in Table 1 that magnetites are formed at 6 °C using either distilled water, SAMD or LMDT water samples when seeded with magnetite. From work on the aforementioned experiments, we showed that the presence of calcium ions had a deleterious effect on the formation of magnetites. We believe that this was due to a competition between formation of calcium hydroxide and magnetite when the pH is adjusted to 9. We have conducted tests to determine whether calcium is removed by the preformed magnetite by surface adsorption. There is no indication that this occurs. The calcium levels before and after suspension of magnetite are exactly the same. We conclude therefore that the magnetite added actually catalyzes the growth of magnetite crystals.

We also performed XRD (x-ray diffraction) experiments on the magnetites formed both at high and low temperature as well as on commercial magnetite and magnetites synthesized from LMDT waters and synthesized magnetites with metal substitutes. The results of these studies showed diffraction lines identical to commercially available magnetites. This confirms that our process actually forms magnetites and not some other dark colored iron oxide. Literature XRD spectra (JCPDS)[1] of magnetite and hematite were also compared to our studies. Different spectra are reported for these forms of iron oxide, which confirmed that we synthesized magnetite and not these other iron oxides. Examples of XRD spectra are summarized in Table 2.

Table 2.—XRD Data on Magnetite Samples

Substrate	D-Spacing Values, in Å						
JCPDS	4.850	2.964	2.528	2.094	1.711	1.613	1.482
Commercial Magnetite	4.795	2.947	2.516	2.086	1.707	1.608	1.479
Synthetic magnetite, 70 °C	4.792	2.945	2.516	2.083	1.708	1.608	1.468
Synthetic magnetite, 5 °C	peak not resolved	2.953	2.523	2.085	1.703	1.607	1.482
Synthetic, Hg, 70 °C	peak not resolved	2.934	2.512	2.082	1.701	1.604	1.473
Synthetic, Cu, 70 °C	peak not resolved	2.938	2.514	2.083	1.705	1.611	1.480
Synthetic, Leadville, 5 °C	peak not resolved	2.953	2.523	2.085	1.703	1.607	1.482

3.1.1 Summary of the Low Temperature Studies

1. Magnetites may be formed at low temperatures using preformed magnetite seeding regardless of the preformed magnetite source of the water type tested.

2. The solids produced from this process have XRD spectra essentially equivalent to that of commercial magnetites.

3. Calcium has a deleterioius effect on the formation of magnetites. However, this effect can be overcome by seeding.

[1] From"Inorganic Phases," Powder Diffraction File, Joint Committee on Powder Difffraction Studies, 1982. Swarthmore, PN. File No. 19-629, p.403.

3.2 Remediation Studies

3.2.1 In-situ Magnetite Removal Studies

Remediation studies at 6 °C have been carried out using lead(II) and manganese(II) as test metals in nanopure water. Figure 1 shows the results of these studies. The magnetite *in situ* process effectively removes both lead and manganese down to the ppb range. It is important to note that at very low Fe:M ratios, incomplete ferrite formation occurs as evidenced by an unidentified brown compound precipitating from solution. It is interesting however that this is all removed when passed through a simple magnetic separation device in the NMSU lab (a magnet with a steel wool column) and does not appear to be a problem in separation.

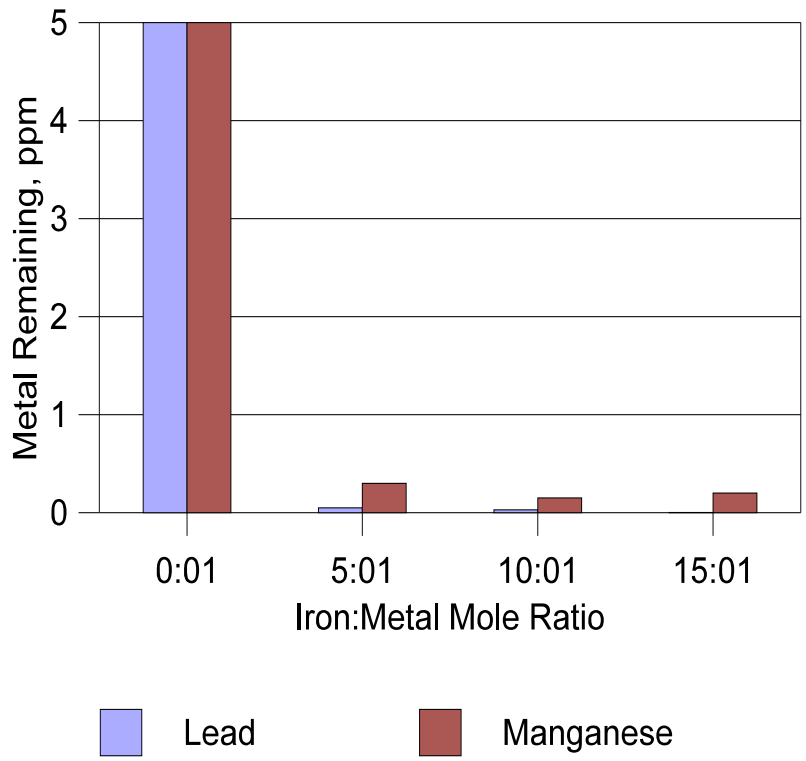


Figure 1.—Lead and Manganese Removal Using Magnetite. No Organics. Temperature = 6 °c.

We have also examined the removal of higher contaminating metal concentrations and these have yielded excellent results as well. These are shown in Tables 3 and 4.

Table 3.—Manganese Removal at Varying Mn Doses. T = 6.0 °C.

Iron dose:Metal Dose (mole ratios)(Fe_3O_4 dose)	Initial Mn dose (ppm)	Mn remaining (ppm)	Percent removal
20:1 (138 ppm)	5	below detection limits	>99
10:1 (69 ppm)	10	0.12	99
5:1 (35 ppm)	20	0.24	99
4:1 (28 ppm)	25	0.42	99
3.3:1 (23 ppm)	30	0.25	99

Table 4.—Lead Removal at Varying Pb Doses. T = 6.0 °C

Iron dose:Metal Dose (mole ratios)	Initial Pb dose (ppm)	Pb remaining (ppm)	percent removal
20:1 (138 ppm)	5	below detection limits	>99
10:1 (69 ppm)	10	below detection limits	>99
5:1 (28 ppm)	20	0.022	99
4.5:1 (31 ppm)	22	0.12	99

These studies showed that magnetite doses can remain fairly low with respect to contaminant levels and still provide good remediation.

In conjunction with magnetic separation studies carried out at Los Alamos National Laboratory, we examined the remediation of cadmium(II) from solution. In these studies magnetites were formed as described above and the magnetic separation was used to "filter" the water. In each instance, initial 50 ppb cadmium levels were remediated to below a 1 ppb detection limit. These experiments demonstrated the efficacy of the in-situ preparation method as well as magnetic separation.

3.2.2 Pre-formed Magnetite Removal Studies

Remediation studies at 6 °C and pH 9 have been carried out using cadmium(II), cobalt(II) and lead(II) as test metals. Initially cadmium(II) removal was studied using a both distilled and LMDT water sources with a variety of magnetites and with various cadmium contamination levels. The results are summarized in Tables 5a, 5b, and 5c.

Table 5a.—Removal of Cd from Aqueous Media

Initial Cd level	Magnetite dose	Final Cd level	Percent removal
Unactivated commercial magnetite distilled water source			
14 ppb	100 ppm	4.3 ppb	69
25 ppb	100 ppm	6 ppb	76
38 ppb	100 ppm	2 ppb	95
20 ppb	500 ppm	2 ppb	90
30 ppb	500 ppm	6 ppb	80
Unactivated commercial magnetite LMDT water source			
390 ppb	100 ppm	218 ppb	44
390 ppb	250 ppm	82 ppb	79
390 ppb	500 ppm	22 ppb	94
Activated commercial magnetite LMDT water source			
390 ppb	500 ppm	4 ppb	99
20 ppb	500 ppm	<4 ppb	>80
Synthesized magnetites LMDT water source			
20 ppb	100 ppm	below 1 ppb detection limit	>99

Table 5b.—Removal of Co from Aqueous Media

Initial Co level	Magnetite dose	Final Co level	Percent removal
Unactivated commercial magnetite LMDT water source			
200 ppb	100 ppm	41 ppb	80
200 ppb	250 ppm	2 ppb	99
200 ppb	500 ppm	<2 ppb	>99

Table 5c.—Removal of Pb from Aqueous Media

Initial Pb level	Magnetite dose	Final Pb level	Percent removal
Unactivated commercial magnetite LMDT water source			
5 ppm	25 ppm	53.4 ppb	99
5 ppm	50 ppm	63.3 ppb	99
5 ppm	75 ppm	2.6 ppb	>99
5 ppm	100 ppm	below det limit	>99
10 ppm	100 ppm	90.9 ppb	99
15 ppm	100 ppm	130 ppb	99
20 ppm	100 ppm	133.3 ppb	99

The magnetite process effectively removes cadmium from high and low concentrations to the ppb or sub-ppb range, depending on the initial cadmium concentration. There is a dependence upon the nature of the magnetite used. The best removal is observed for magnetites that are synthesized in the laboratory and used shortly thereafter. Using this source, excellent removal is observed at a magnetite dose of 100 ppm.

Although commercial magnetite is also effective in removing the target metal, higher doses, up to 500 ppm, are required. Activation of the commercial product is also important in cadmium(II) remediation. This process required "soaking" the commercial magnetite in 1.0M NaOH for 10-30 minutes followed by filtering off and washing the magnetites with distilled water to remove any remaining base. Activation using 0.5M $Ba(OH)_2$ shows equally effective activity.

Based on the above findings, the target cadmium concentration of 0.5 ppb, (LMDT effluent standard) should be achieved using this technique.

3.3 Binding Isotherms

In order to better understand the binding of metals to the magnetite surface, we have undertaken a brief study of the binding isotherms for cobalt and lead. This information provides a good basis for optimizing pH and dose levels for preformed magnetite treatment procedures. Although cadmium was initially examined, there was too much scatter in the results to produce good plots of the data.

The solution conditions started at pH 4-5 with a fixed amount of contaminant (200 ppb) and preformed magnetite. The solutions were bubbled with argon gas to prevent CO_2 dissolution and introduction of carbonates to the solution matrix. The solutions were stirred using a mechanical stirrer to keep the solids suspended in a quasi homogeneous fashion. Mixing was stopped and the solids were allowed to settle when samples were to be withdrawn. Typically, a 5 mL portion was filtered through a 0.45 micron filter paper and acidified to prevent metal adsorption. A background electrolyte was used in each experiment. The samples were then analyzed using atomic absorption-graphite furnace spectroscopy (AA-GF).

3.3.1 Binding in the Absence of Organics

Figures 2 and 3 show examples of the results for these experiments. At the initial low pH, very little removal of heavy metals was observed, typically around 5 percent. This is to be expected since this probably represents a competition between protons and heavy metals for the oxide surface sites. Once the pH is raised however, it is readily apparent in both plots that removal begins and increases as the pH continues to increase. By pH 9 or so, good removal is observed for all the metals studied. Plots such as these are similar to those found by other researchers using hydrated iron oxides such as akagonite, goethite, etc.

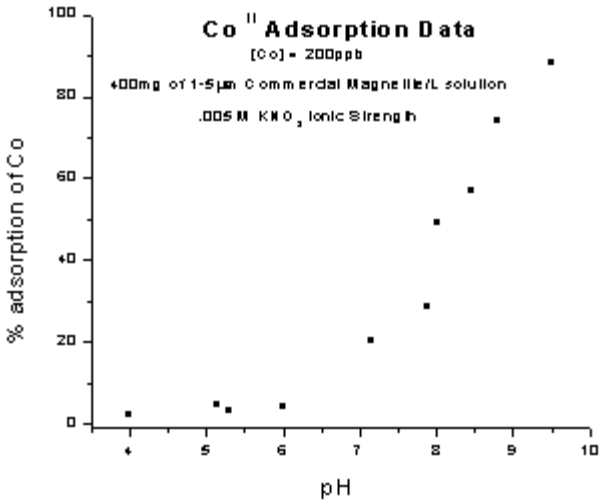


Figure 2.—Binding Isotherm for Co(II).

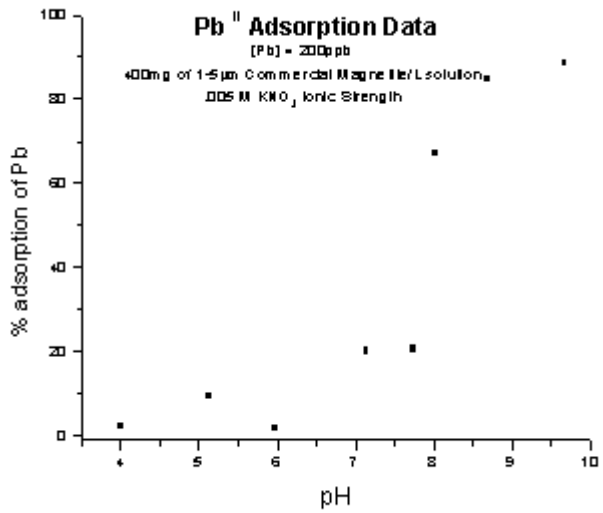


Figure 3.—Binding Isotherm for Pb(II).

3.3.2 Binding in the Presence of Organics

Since earlier studies in the NMSU laboratory had shown that added organics can influence the removal of heavy metals using magnetites, similar studies to those described above were carried out in the presence and absence of selected co-contaminants. Lead(II) was selected as the target metal since it has shown the best experimental reproducibility. The experiments were carried out as described above except that various concentrations of organic chelators were also added to the solution. The initial lead concentration is 10^{-5}M. Results of these studies are shown in figures 5 and 6.

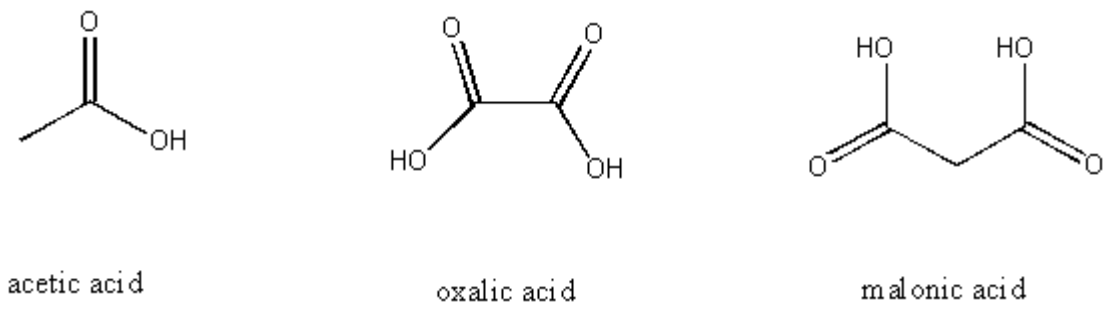


Figure 4.—Structure of Parent Acids.

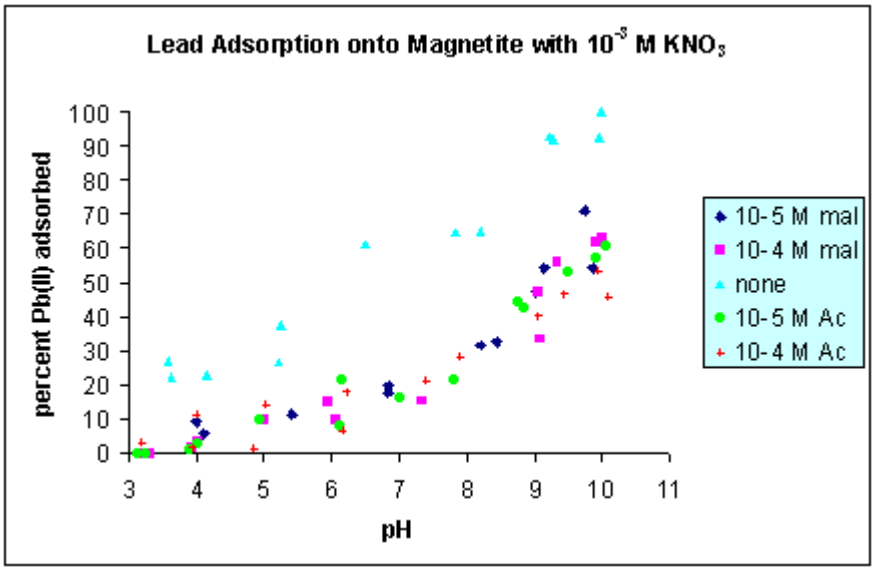


Figure 5.—Effect of Acetate and Malonate on Lead Removal.

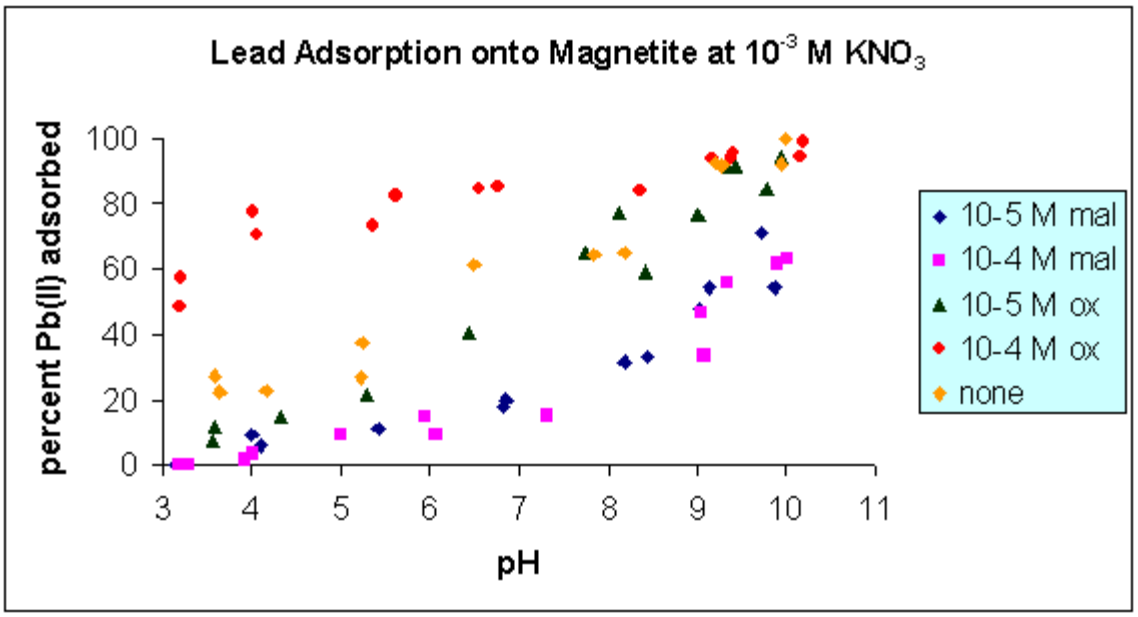


Figure 6.—Binding Isotherm for Pb(II)

Three structurally related chelating agents were studied to determine whether they can compete effectively with the magnetite surface for the Pb^{2+} ion. The chelators were acetate, oxalate and malonate as derived from the parent acids shown below. These three were used because of their structural similarities to each other as well as to functional groups found in humic acids and common man-made chelators such as EDTA.

As expected, there were significant differences between acetate or malonate being present versus no organics at all. At the highest pH used, greater than 90 percent removal of lead was observed for no organics present. This is in contrast to when acetic acid or malonic acid was present. Figure 5 shows that a marked decrease in removal efficiencies was observed, even at the 10^{-5}M level, which is approximately where the initial lead concentration was set. Even at the highest pH studied, no greater than about 65 percent removal of lead was observed. This must represent competition between the chelator with the magnetite for the lead ion. At the 10^{-4}M concentration, the lead is probably coordinated by two or three organic ligands to give the lead complex an overall negative charge since each ligand has a negative charge when fully deprotonated. The binding constants for lead with these ligands range between 10^2 to 10^6. As the pH of the solution is raised, the charge on the magnetite surface becomes more negative and unable to bind the acetato or malononatoplumbate(II) ion.

Based on the above observations, it is surprising that oxalic acid does not follow the same behavior even though the complexation constants for oxalate and malonate with lead are equal in magnitude. In this study, addition of oxalic acid to the solution enhances the removal of lead from solution. Although one could envision this to be due to precipitation of lead oxalate, the concentrations used in this study do not exceed the solubility of lead oxalate ($K_{sp} = 10^{-8}$) and at the highest oxalate concentration in this study $Q_{sp} = 10^{-9}$. Control experiments where the lead and oxalate ions are added in the absence of magnetite show no decrease in the lead concentrations before and after mixing, except at pH 10, where a decrease

that we tentatively attribute to precipitation of PbC_2O_4 is observed. At lower pH values however, no precipitation of lead(II) oxalate or lead(II) hydroxide was detected.

At present we are uncertain as to the origins of this effect, but we believe it to be real and may permit selective separations of ions from solution. We have observed similar behavior for other metals and chelators in our earlier studies on lead, thorium, uranium, copper and silver. This report shows the first set of binding isotherms which quantify the extent of this effect. Future studies will be carried out to understand and exploit this phenomenon.

3.4 Summary of Remediation Studies

1. In-situ formation of magnetite presents the most effective method for heavy metal removal in both pure water and LMDT water.

2. The use of preformed magnetites is also an effective method for the remediation of heavy metals from LMDT water sources.

3. Laboratory-synthesized magnetite required lower doses than commercially available magnetite for several metal remediation tests.

4. The use of organics can either inhibit or enhance the removal of heavy metals, depending upon which chelator is present. In this work, only oxalate and not malonate nor acetate, enhanced metal removal.

4 MAGNETIC SEPARATION STUDIES

4.1 Using Commercial Magnetite

A major focus of this project is to demonstrate low cost approaches to remove the ferromagnetic floc formed during magnetite pretreatment. Los Alamos has been involved in developing high gradient magnetic separation (HGMS) technology for use in environmental remediation and waste minimization of actinide contaminated materials. As a part of this work, numerical models of the process were developed, which subsequently led to proposing the use of a remnant magnetic field to achieve separation of the magnetite floc. If successful, this process would be considerably simpler and, therefore, less costly than current HGMS systems incorporating high field gradient, superconducting magnets.

We began with a series of experiments to demonstrate the feasibility of this approach. The proposed method is based on utilizing the magnetic hysteresis found in certain hard magnetic materials. Specifically, 430 series stainless steel wool possesses such characteristics and can be used as a suitable matrix material for magnetic capture of the magnetite floc. By applying a steady state magnetic field in excess of two tesla to this material, a saturation magnetization can be achieved. Upon removal of the applied field, a remnant magnetic field remains in the matrix material. Our calculations show that this remnant magnetic field should be sufficient for magnetite capture. It is also necessary to periodically remove the collected magnetite from the matrix. Because of the relatively low magnetic field gradients in the remnant field, it should be possible to accomplish matrix cleaning using a high superficial velocity backflush possibly accompanied by air sparging and/or mechanical vibration. The superficial velocity is defined as the volumetric flowrate divided by the inlet cross sectional flow area of the matrix canister.

A separator design based on a single-pass cylindrical matrix of uniform packing and containing a remnant magnetic field applied at two tesla is the preferred configuration. This design has the following attributes:

1. No magnet is required for normal operation of the separator; only for periodic recharge of the remnant magnetic field.

2. Backflushing is accomplished by flowrate control and gas injection, thus simplifying the configuration.

3. The matrix can be modularized, which enables convenient scaleup by plumbing several modules in parallel, allowing ease of replacement for maintenance.

4. Separator performance characteristics can be easily modified by changing the matrix material to accommodate a seasonal variation of the feed stream.

5. Matrix packing material is commercially available and inexpensive.

Results from the first set of experiments indicated the following:

1. Although the magnetite/water mixture used in the experiments was a surrogate for the actual material being developed at NMSU, the magnetite was effectively removed with a remnant magnetic field (induced by a 2-tesla field) at a very reasonable superficial velocity of 1.0 cm/s. Better results were obtained with larger diameter magnetite particles.

2. Backflushing of the remnant field matrix was successfully accomplished without any alterations in the magnetic field. This is desirable because it simplifies the configuration of the magnetic separator. However, as expected, sparging with nitrogen during the backflush was required to effect the magnetite removal.

3. Removal of magnetite from the matrix while any significant magnetic field is applied externally is not possible with traditional backflushing methods. This is a consequence of the ferromagnetic properties of magnetite.

Having demonstrated that the use of a remnant magnetic field for removal of the magnetite was feasible and that no configuration changes to the separator were required for backflushing, we focused on the simplest configuration for the separator. A tubular matrix containing the proper grade of 400 series stainless steel wool at the optimum packing density was selected as the primary candidate. After determining the optimum length, the cylindrical configuration is scalable by increasing its diameter to obtain the desired volume. As discussed above, backflushing of the matrix can be accomplished with an increased superficial velocity and air sparging. It was necessary to select the optimum matrix material for this application and we proceeded to quantify the performance of each of the matrix materials. Breakthrough tests, conducted under remnant field conditions, are used to define the matrix capacity under various operating conditions. The matrix capacity is a function of superficial velocity, magnetic field, magnetite particle size and carrier fluid viscosity. Because we are using water near 10 °C, viscosity is not a control variable. We have also measured the remnant field in the matrix and have determined that the maximum value is approximately 800 G. In addition, we anticipate that the magnetite particle size in the slurry will be similar to the seed material introduced to facilitate the in-situ formation of magnetite.

Therefore, the remaining variables affecting the breakthrough capacity are the superficial velocity, the bed length and the effective matrix fiber diameter.

We investigated a number of matrix samples because it is advantageous to use the coarsest grade of steel wool that provides adequate magnetite removal. The coarser grades are easier to backflush, which translates to shorter flush times and lower flush volumes.

The finer grades have higher capacity and increased capture efficiency. Results from the breakthrough tests were used in our computer model to provide design capability for subsequent prototype and full-scale systems. These results are summarized in figure 7. The data confirm that the finer matrix material has a higher capacity as evidenced by a larger breakthrough volume. Commercial steel wool is formed from shavings. We also included in the study a higher performance extruded material. Note that the extruded material, which at higher magnetic fields is superior to the commercial steel wool, does not perform as well as the extra-fine commercial grade at remnant field levels. Therefore, because of the higher cost of the extruded material, its use for this application is probably not worth further consideration.

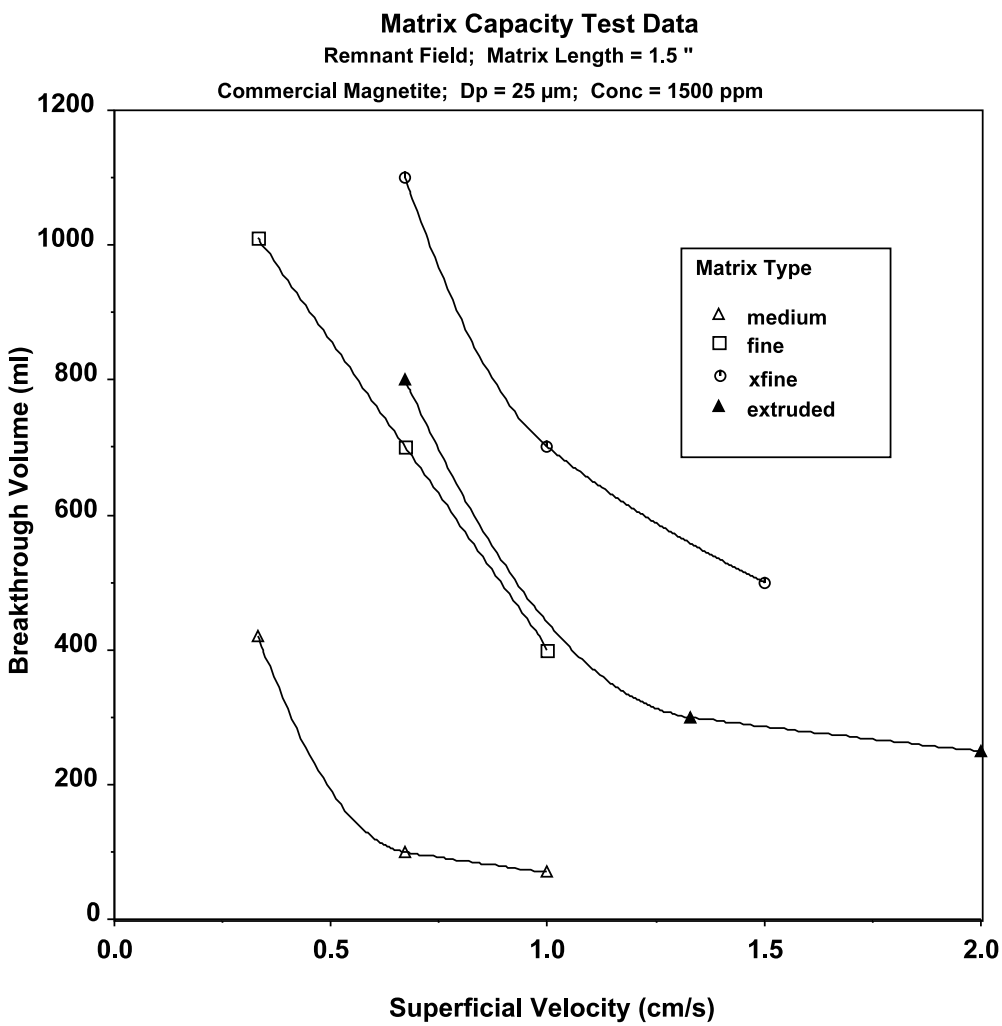


Figure 7.—Matrix Breakthrough Data for Three Commercial and One Specialty 400 Series Stainless Steel Wool.

A comparison of the test results with predictions from the LANL computer model is shown in figure 8. The term LF denotes Load Factor, a fraction of the total surface available for binding. Except for the under-performance of the extruded material as noted above, the model is in good agreement with the test data and only slightly under-predicts the matrix capacity.

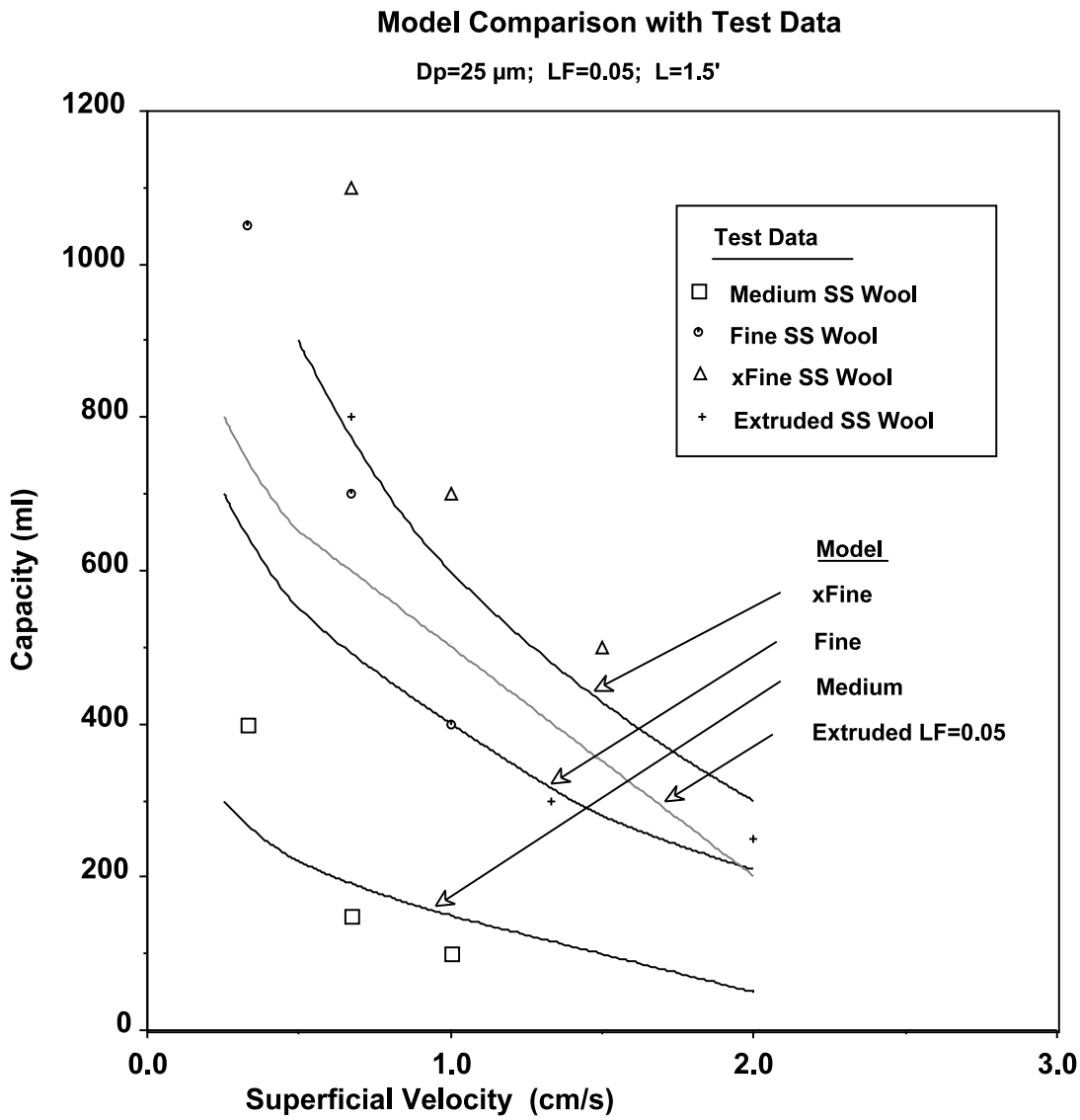


Figure 8.—Comparison of Test Data with LANL Computer Model for Commercial Grades of Stainless Steel wool.

These results are quite remarkable and are better than expected. Except for the significant under-performance of the extruded matrix at remnant field levels, the remaining samples performed as predicted by the model. However, these tests were performed on commercial magnetite and the results for in-situ formed magnetite were quite different. In addition, throughout these tests, we observed no significant degradation in the remnant magnetic field within the matrix. Figure 9 shows magnetization measurements for commercial magnetite, synthetic magnetite formed in nanopure water and synthetic

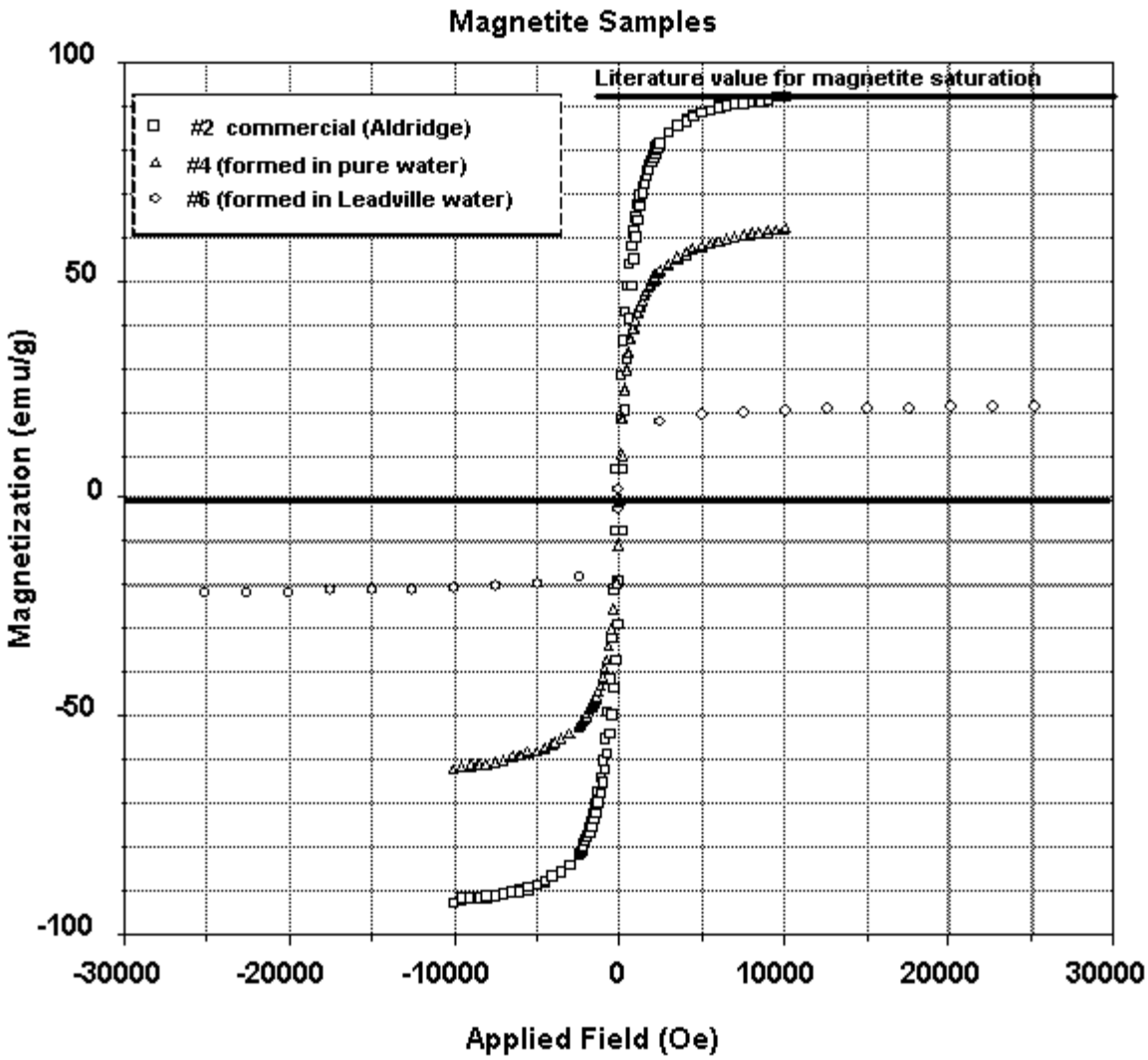


Figure 9.—Measured Magnetization of Commercial and Synthetic Magnetite.

magnetite formed in Leadville water. Results for the commercial magnetite are in good agreement with literature data for magnetite, whereas, the synthetic magnetites have lower values. It is uncertain why the synthetic magnetites have lower values of magnetization but the effect is also reported by others. Based on these results, it would appear that the presence of some commercial magnetite (from seed) in the precipitate would enhance the resulting magnetization.

The LANL computer model was used to generate a performance map for the proposed separator. Figure 10 shows the process volume ratio, defined as the volume of slurry processed before breakthrough divided by the matrix volume, as a function of feed concentration and magnetite particle size. The figure includes predictions for the extruded matrix, a material which, based on previous work, was expected to perform better than commercial SS wool. So far however, this material has fallen short of expectations. Examination of the results for the extra-fine SS wool and assuming a 5 μm particle size for the magnetite shows a process volume ratio of between 100 and 650 for a feed concentration range between 100 and 500 ppm.

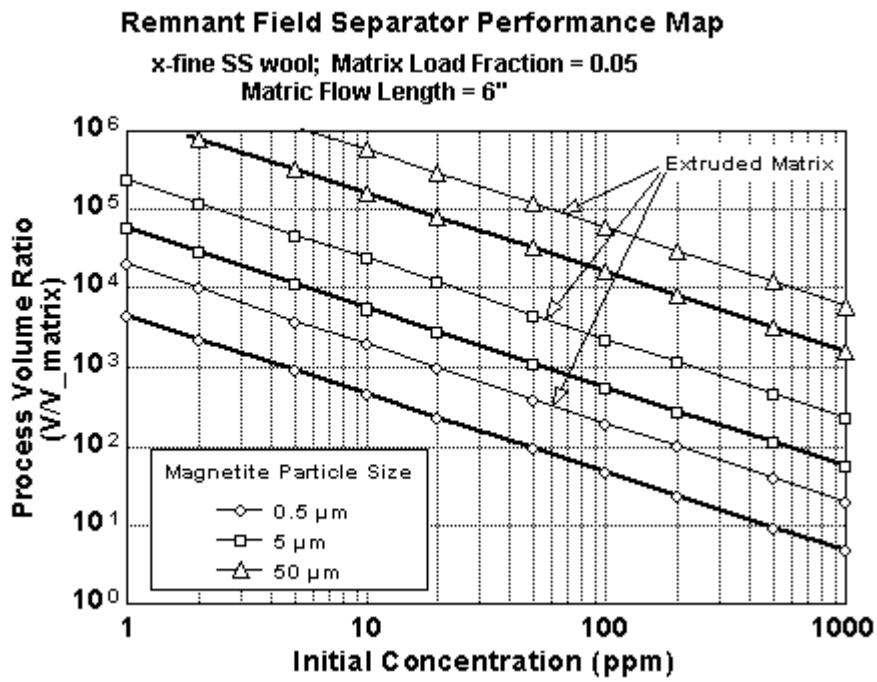


Figure 10.—Remnant Field Separator Performance Map Showing Dependence on Feed Concentration and Magnetite Particle Size.

Results for the Leadville Plant application are shown in figure 11. The required process flowrate for the plant is 1700 cfm (0.11 m^3/s). The maximum matrix superficial velocity is 10 mm/s and the minimum matrix length is 0.5 m (18 in). This fixes the minimum single bed diameter at 3.85 m (12.5 ft) and is shown as such in figure 11. A diameter smaller than this will result is a superficial velocity greater than 10 mm/s in the matrix; therefore a single bed cannot be smaller than this diameter (although multiple beds in parallel will reduce the bed diameter). Assuming a bed cycle time of one hour, figure 11 shows at what feed concentration the bed capacity is reached for several particle sizes. Small particles require a lower feed concentration to prevent bed saturation during a one-hour cycle. For a nominal magnetite particle size of 5 µm, the bed should accommodate feed concentrations up to 600 ppm.

4.2 Using In-situ Formed Magnetite

To determine if in-situ formed magnetite may better scavenge heavy metals than commercial magnetite, a series of experiments were performed on water samples identified in Table 6 to investigate what effect the in-situ formed material would have on the magnetic separation process. A magnetite seed was prepared using sulfate salts in an Fe^{+3}/Fe^{+2} ratio of 2:1 at 70 °C with no active oxygen removal. The magnetite seed was rinsed with distilled water and magnetically collected. The particle size distribution for this seed material is shown in figure 12. This material has a primary peak at 26 µm and a significant secondary peak at 1.7 µm. This seed was then introduced into the LMDT water samples along with additional sulfate salts in an Fe^{+3}/Fe^{+2} ratio of 2:1.2 at 9 °C with no active oxygen removal. The magnetite formation proceeded through the green rust phase and resulted in the formation of a magnetite floc. This floc was similar for all the LMDT water samples tested.

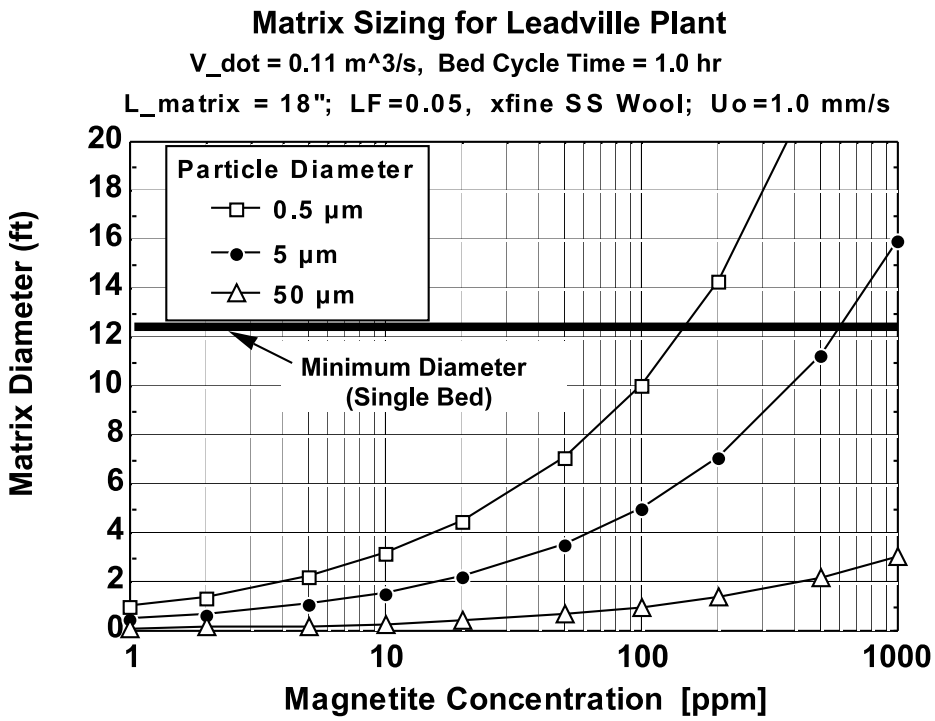


Figure 11.—Matrix Sizing for Leadville Plant. Minimum Single Bed Diameter Is Based on a Minimum Superficial Velocity of 10 Mm/s.

Table 6.—Leadville Water Samples

Sample Designation	Date Obtained
Leadville-I	8/97
Leadville-II	1/99
Leadville-III	4/99

MST-6 Characterization Laboratory
PARTICLE SIZE DISTRIBUTION DATA TABLE Standard 01/25/00
File Name: F008.TXT
Sample Name : F008 Magnetite Seed for PS
Sample ID#: 000125269 Dist. Mode: VOLUME
Shape: 1 Ref. Index: 1.82 - 0.01 Laser: 96.448 Red: 96.300 Blue: 88.970

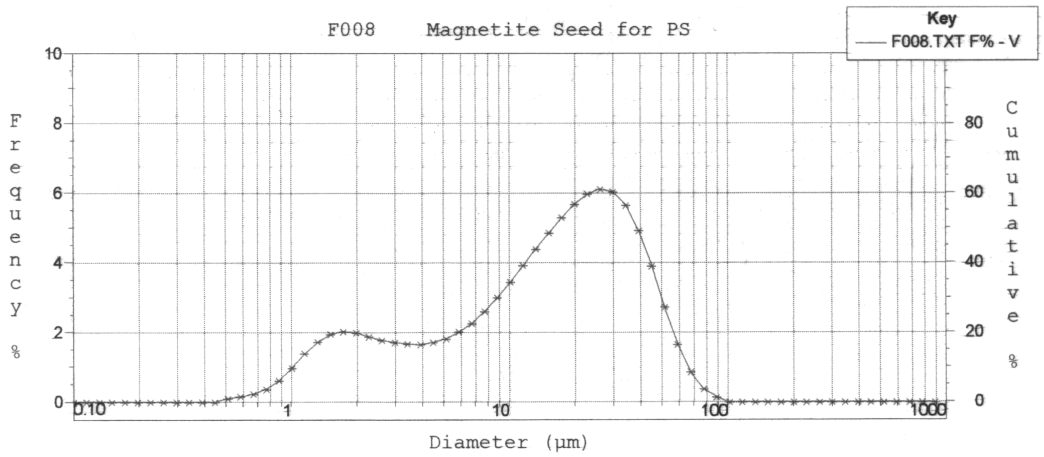


Figure 12.—Particle Size Distribution for Magnetite Seed Formed at 70 °C.

Figure 13 shows the particle size distribution representative for the Leadville III sample. Note the well-formed peak at approximately 18 µm and that less than 5 percent of the material is smaller than 4 µm. The particle size distribution was obtained 5 days after initial formation of the material and may not be representative of the size distribution actually processed in the magnetic separator.

MST-6 Characterization Laboratory
PARTICLE SIZE DISTRIBUTION DATA TABLE Standard 01/25/00
File Name: F009C.TXT
Sample Name : F009 1420 feed for PSA
Sample ID#: 000125273 Dist. Mode: VOLUME
Shape: 1 Ref. Index: 1.82 - 0.01 Laser: 93.917 Red: 91.644 Blue: 84.115

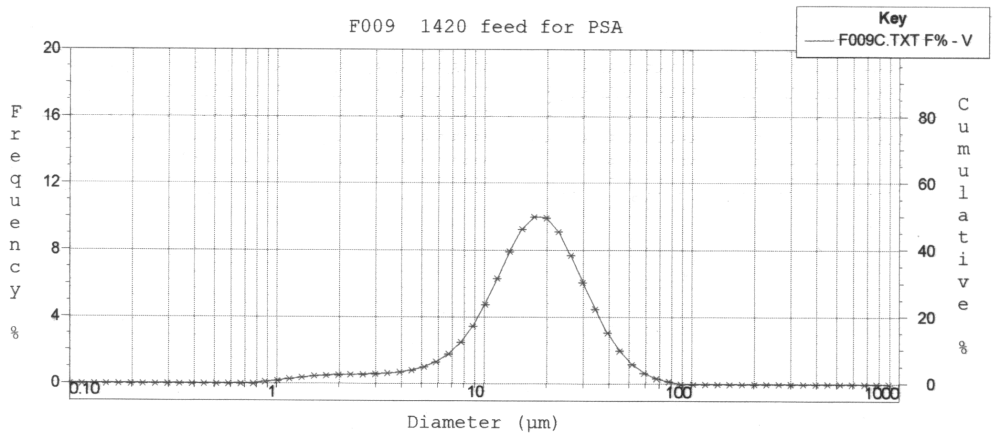


Figure 13.—Particle Size Distribution for Magnetite Formed In-situ, Leadville Iii Water Sample, at 9 °C.

The magnetic floc was then processed in the remnant field magnetic separator to evaluate the separation performance. The matrix consisted of extra-fine SS wool packed at a void fraction of 0.9 with a flow length of 150 mm. The matrix was magnetized on 8/9/99, almost three months prior to the experiment. The superficial velocity used for processing the magnetite was 5.0 mm/s. The results are shown in figure 14 where they are compared with model predictions. Model results for three matrix grades are shown; however, this test was performed with extra-fine SS wool matrix. We note from figure 13 that the particle size distribution for the in-situ formed magnetite is relatively broad ranging from 5 µm to 80 µm. The measured breakthrough is shown in the figure as a solid line at 375 ml extending over the particle size range. The experimental results fall short of the model predictions even at the low end of the particle size range. This may be evidence that the in-situ formed magnetite may have a lower magnetic susceptibility than the commercial form. A second run was performed using the Leadville-III sample to evaluate any degradation in the remnant field of the matrix. The matrix was remagnetized between runs and no significant change in performance was observed. This would indicate that the remnant field is stable over a period of several months. However, we have no data on the degradation effect, if any, from continuous matrix use.

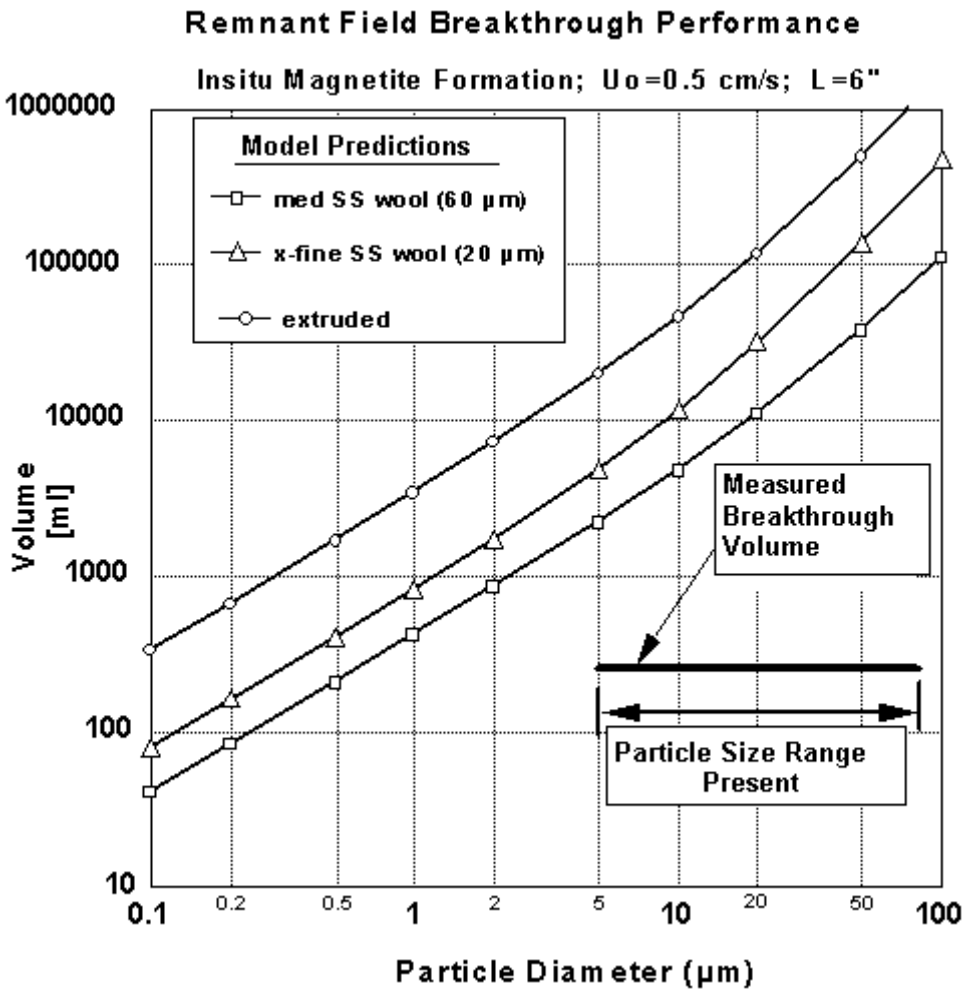


Figure 14.—Measured Breakthrough Volume for In-situ Formed Magnetite in Leadville-i Water Sample Compared with Model Predictions.

The presence of a significant fraction of magnetite particles below 1 to 2 µm which are difficult for the matrix to capture and hold may be addressed by including a finer grade matrix material such as ultra-fine SS wool at the downstream end of the matrix. This addition of finer material near the exit of the matrix serves as a polishing zone. The majority of the larger particles, which would tend to plug the finer material, would be removed upstream. The finer material with a smaller wire diameter would be more effective in capturing the smaller particles. Backflushing, which occurs with a flowrate reversal, would still liberate the particles effectively because the large particles would exit first followed by the finer particles. No plugging would be expected. We refer to this configuration as a graded matrix.

4.3 Summary of Magnetic Separation Studies

Our remnant field magnetic separation investigations have established the following:

1. Remnant field separator performance on commercial magnetite at particle sizes greater than 5µm appears more than adequate to support a low cost design.

2. Collection in and purging of the matrix can be controlled by superficial velocity and gas sparging. No magnetic field adjustment is required.

3. Compared with commercial magnetite, in-situ formation of magnetite in the Leadville samples results in the formation of a magnetite compound that is more difficult to remove magnetically.

4. Remnant field matrices appear to be magnetically stable and should require minimal maintenance.

5. High performance matrix materials such as extruded SS wool appear to offer no performance advantage over commercially available SS wool at remnant field levels.

6. Use of a graded matrix may effectively address a wider range of particle sizes should that be required.

Table 7 summarizes the remediation and magnetic separation results for in-situ and ex-situ magnetite formation. The remediation performance improves from top to bottom in the table, whereas, the magnetic separation becomes more difficult. Based on the results to date, a homogeneous remnant field magnetic separator should provide effective separation for all but the last configuration listed in Table` 7. For that configuration, a graded matrix may be required.

Table 7.—Performance Summary of the Magnetite-remnant Field Magnetic Separation Process

Magnetite Formation	Treatment Method	Remediation Effectiveness (Cd)	Magnetic Separation
Ex-Situ	Untreated Commercial	70 percent	Homogeneous Matrix
	Activated Commercial	80 percent	Homogeneous Matrix
	Synthetic Formed @ 70 ˚C	>99 percent	Homogeneous Matrix
In-Situ	Commercial Seed	Untried	Homogeneous Matrix
	Synthetic Seed	>99 percent	Graded Matrix

5 CONCLUSIONS

This research produced numerous conclusions on low temperature studies, remediation studies and on magnetic separation studies. These findings were described throughout this report and are not repeated here. Schematics of modes of magnetic treatment, a magnetic separator, and a proposed pilot treatment plant for the LMDT plus an electron micrograph of separator matrix material are found in appendix A. Major points of this study may be summarized as follows:

1. We have established that the use of magnetites to remove heavy metal contaminants is effective regardless of the mode of application. The relative order of efficiency is in-situ > preformed (laboratory prepared) > commercial (activated) > commercial (unactivated).

2. The binding of heavy metals to magnetites may be able to be enhanced with the selective use of organic chelators. The aspects requires further examination before its practicality can be established.

3. The use of remnant field magnets to perform magnetic separations has been firmly established. These fields appear stable over month-long time periods and the use of inexpensive stainless steel wool matrices is warranted.

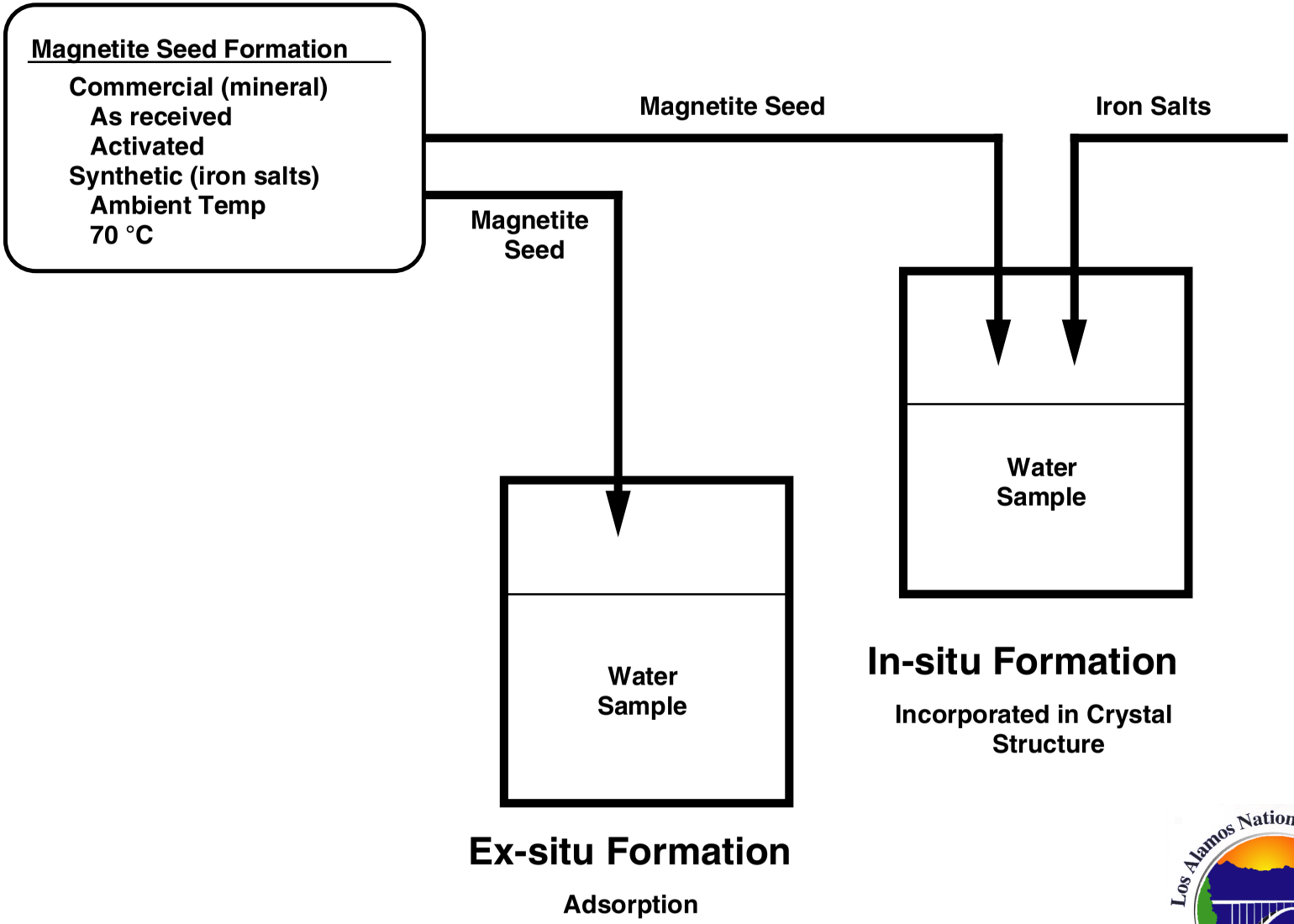
4. Separation of 5 micron sized particles is effective using these remnant field magnetic separators. Both loading and unloading of the magnetic separator can be controlled by flow velocity and gas sparging, respectively.

5.1 Recommendation for future study

We believe that this study has provided ample evidence for the use of a novel method for the remediation of heavy metals from a waste stream that requires inexpensive materials and equipment. Because the wastes generated from this approach are less, more compact and robust with respect to leaching (earlier studies), the disposal costs associated with this technique should be reduced as well. Based on these studies described in this report, we feel that taking this work to a small test facility is now both feasible and appropriate.

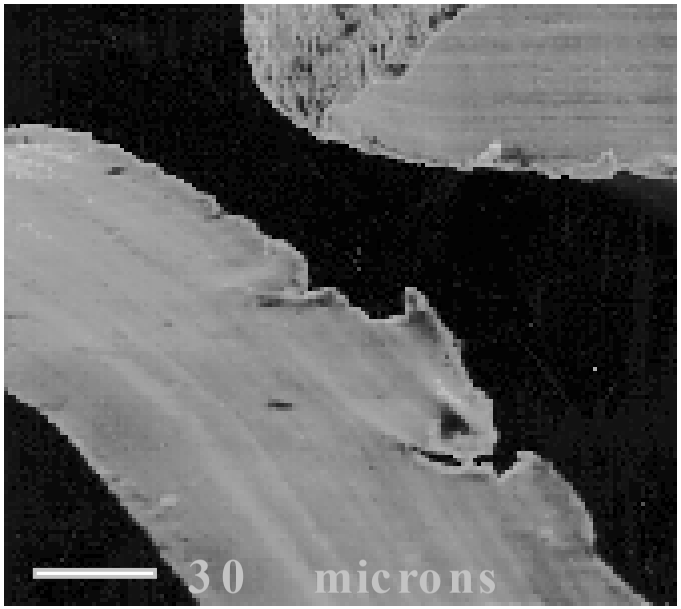
APPENDIX A

Several Modes of Magnetite Treatment are Possible

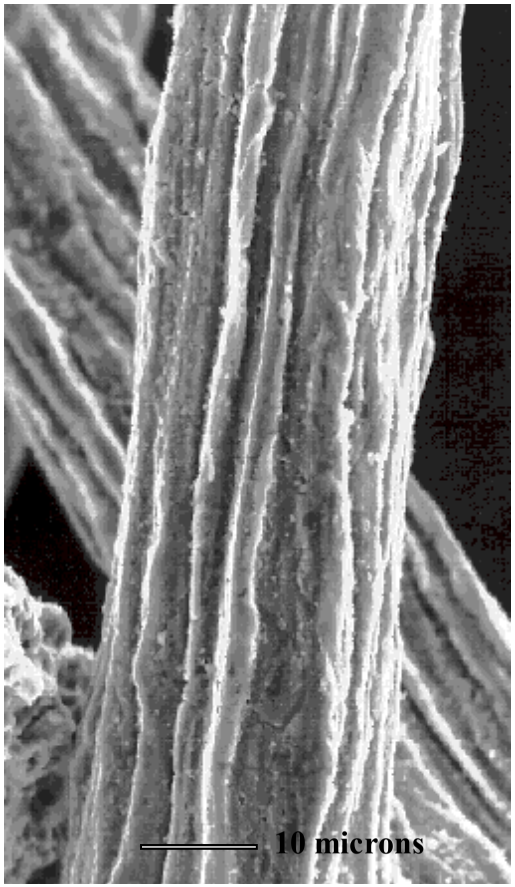


Matrix Materials Should Have a Small Effective Diameter and Large Surface Area

Candidate Matrix Materials



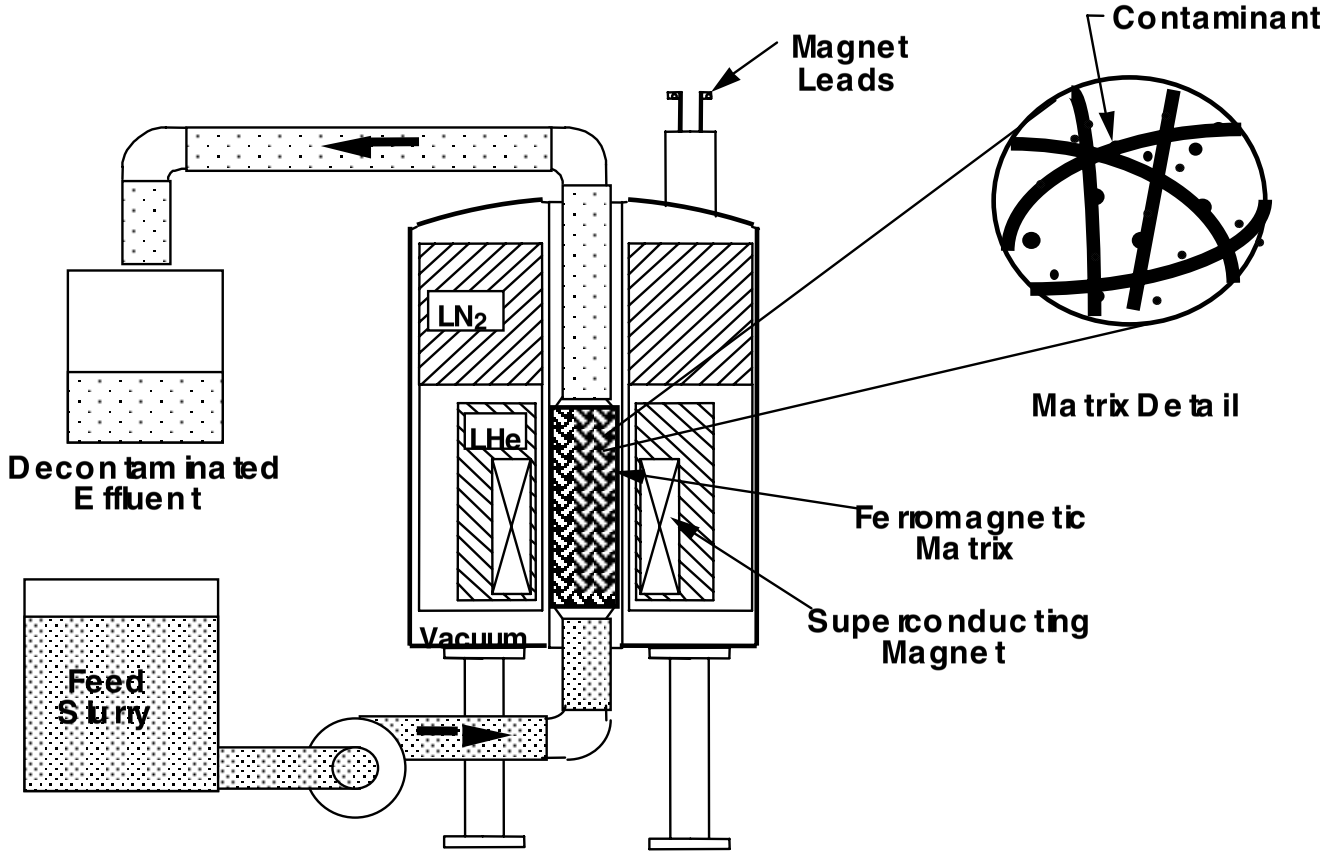
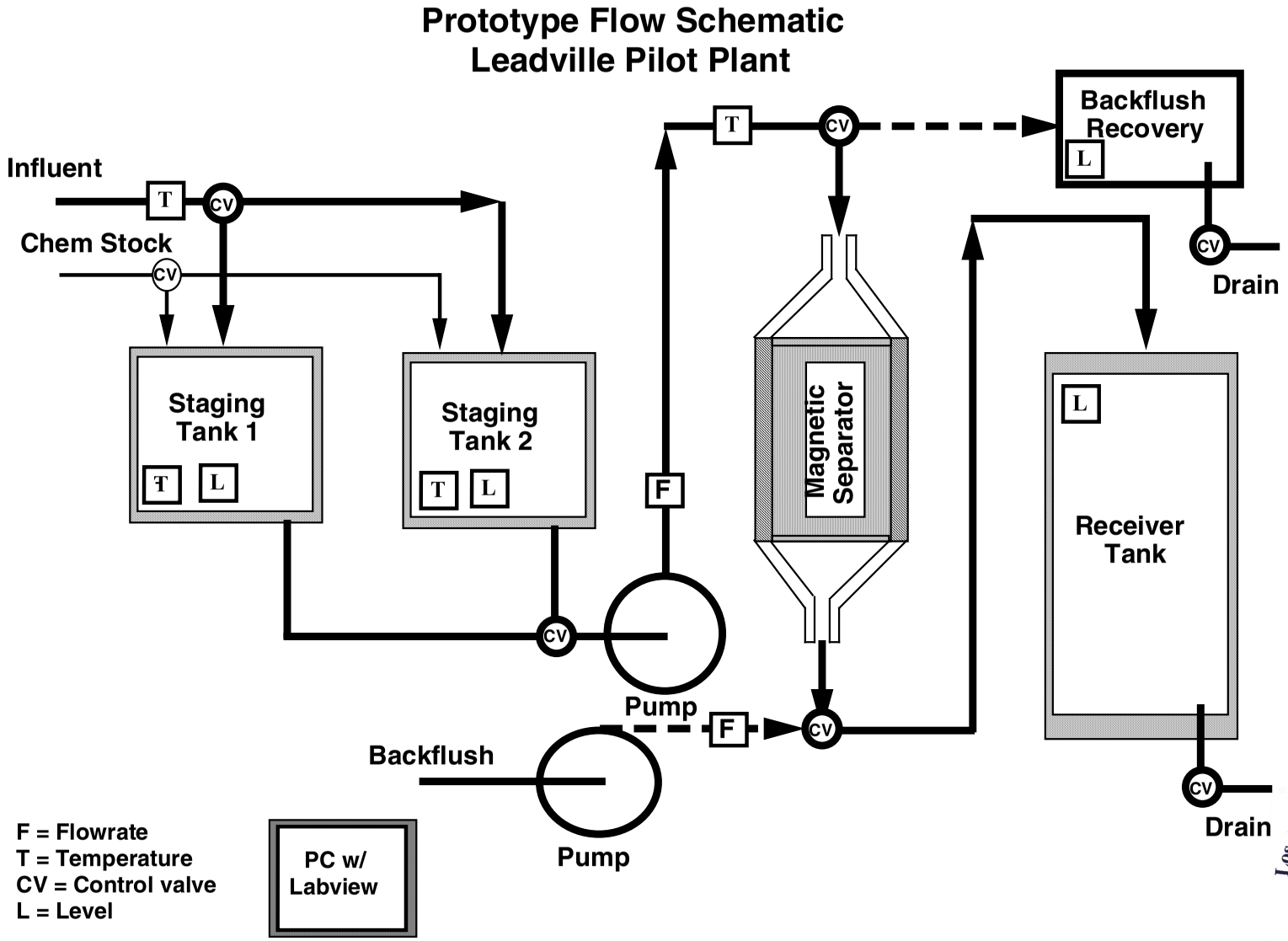
Stainless Steel Wool



Extruded Fibers

Feed Materials are Passed Through a Ferromagnetic Matrix Within a High Intensity Magnetic Field

High Gradient Magnetic Separation



The Proposed Leadville Prototype System Employs Continuous Flow with a Single Separator