RECLAIMING HEAVY METALS FROM WASTEWATER WITH MAGNESIUM OXIDE

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ABSTRACT

The unusual electrokinetic properties of the magnesium oxide aqueous interface has been utilized to make superior filters for suspended solids and precipitants for heavy metals in wastewater streams. While the electrocapillary maxima or points of zero charge for most oxides and hydroxides are at a pH of about 6 (range 2.5 to 10.5), that of MgO is around pH 12.4. Lippmann's theory of electrocapillarity and the thermodynamics of surfaces would predict MgO to be positively charged at pH values below 12.4, while most other solids surfaces are negatively charged at pH values above 6. An electrokinetic attractive force between unlike charges has been found to aid in removing asbestos fibers and other solid particulates from water. Likewise, the basicity at the MgO surface is strong enough to precipitate many of the heavy and hazardous metals encountered in wastewater streams. Because the embryonic metal precipitates are negatively charged, many of them cement to the MgO surface thus forming more compact sludges and much denser residues than obtained with lime... the traditional precipitant. Regeneration of the MgO filter/precipitant by backwashing and chemical stripping with EDTA would allow for the recovery of heavy metals in a concentrated form. Since many of these heavy metals are critical and strategic, the technique can be adapted not only to recycle process water from mineral and milling waste streams, but also to reclaim their metal values.

INTRODUCTION

Conventional practice for treating mine drainage and other water sources contaminated with heavy metals is lime precipitation and settling of the hydrous oxides. This produces a voluminous toxic sludge which results in another type of disposal problem. In addition, settling of the precipitated hydrous oxides often does not produce sufficiently pure water to meet statutory limits for discharge so the decant has to be polished by filtration through sand or other granular media. Metal hydroxides are difficult to filter because of their small size and their low resistance to the hydraulic shear forces encountered in conventional granular filters. Flocculation with organic polyelectrolytes is often necessary to achieve efficient filtration.

Magnesium oxide, MgO, is similar to lime, CaO, and can be used analogously to precipitate heavy metals. Although MgO is less soluble than lime at high pH, in acidic to slightly alkaline water, MgO provides more neutralization capacity per unit weight than lime, owing to its lower molecular weight. When a stoichiometric excess of MgO is used to precipitate heavy metals from wastewater, the resulting sludge is up to 4 times more compact than that produced by liming (1). This was attributed to the unique positive electrokinetic charge of the MgO surface at neutral and slightly basic pH, in contrast to the negative surface charge of most metal hydroxides. The resulting electrostatic attractive force causes the fresh heavy metal precipitate to cement, or adhere to, on the MgO surface and expel water molecules from the spaces between the precipitated particles giving a denser solid.

Forms of Magnesia

MgO is often obtained from sea water or other brines which are rich in $MgCl_2$. Lime is added to the brine to produce $Mg(OH)_2$ precipitate and $CaCl_2$ brine. The precipitate is dehydrated by calcining to produce MgO. Depending on the temperature and duration of the calcination a multitude of MgO products can be obtained with different properties and reactivities. By calcining at lower temperatures (<700 °C), much of the original porosity associated with the crystal structure of $Mg(OH)_2$ is retained and a very active magnesia is produced. By calcining at higher temperatures ("dead burning") the MgO is fused, the porosity is lost, and a tough, relatively inert, crystalline material is produced (2).

Periclase is a natural magnesium oxide mineral sometimes found in marble. It easily alters to brucite of hydrous magnesia, MgO H_2O, which is one of the many sources of dead-burned magnesite. Granular, dead burned, MgO has been demonstrated to be an efficient deep bed filter medium for removing particulates flocculated with aluminum salts (1). In previous research (1), pure MgO powder was used as a precipitant to remove heavy metals. One objective of this research was to find whether granular periclase can also precipitate heavy metals, thereby acheiving both precipitation and filtration steps in the same bed. It was found that the granular filter material has sufficient activity to raise the pH of unbuffered water several units. At typical flow rates in deep-bed filters the effluent can have a pH 10 or greater when the influent pH is about 7. This increase in pH is enough to cause heavy metals to precipitate as oxides or hydroxides as they pass through the filter. These precipitates were observed to be quite strongly attached to the MgO granules.

As part of the investigation of suspended particle removal with MgO filter media, a study was undertaken to determine whether or not the presence of dissolved heavy metals in the influent would impair the filter ability of the MgO with respect to suspended particles. Results of this study indicated that it may be feasible to remove trace amounts of dissolved heavy metals while filtering suspended solids in the same bed of MgO. In addition, it appeared feasible that the heavy metals could be recovered by eluting them off the MgO granules with complexing agents or acids.

Electrical Phenomena at Interfaces

The presence of a net electric charge on a surface lowers the surface tension because repulsion between like charges decreases the work done in extending the surface area. A quantitative measure of this effect is shown by the ideal electrocapillary curve in figure 1, which depicts the variation of surface tension, γ, with the interfacial potential, E. For metal hydroxides or hydroxides, the electric potential E_H with respect to the standard hydrogen electrode is given by:

$$E_H = \frac{RT}{F} \ln a_{H^+} = 0.06 \log {}^{a}{}_{H^+} = -0.06 \text{ pH} \qquad (1)$$

where R is the molar gas constant (1.987 cal mole^{-1} deg^{-1}), T is the temperature (^{o}K), F is the Faraday constant (23,060 cal volt^{-1}), and $^{a}H+$ is the hydrogen ion activity. At 25 ^{o}C, the quotient RT/F = 0.06 volts.

Thermodynamic equilibrium of the surface at constant temperature, pressure and chemical composition requires the Gibbs free Energy function, G to be at a minimum, i.e.

$$\delta G = A\,\delta\gamma + Q\,\delta E = 0 \qquad (2)$$

where A is the surface area and Q is the surface charge. This equation indicates that the variation in Gibbs free energy due to the change in γ just balances that due to the change in the electric potential of the charge Q at the surface. Lippmann's equation involves a rearrangement of equation 2 to give

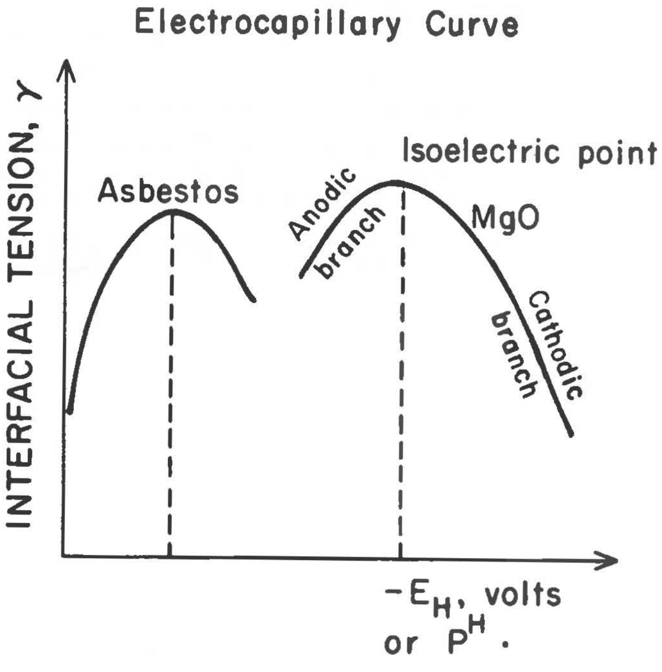
$$\frac{\partial\gamma}{\partial E} = -\frac{Q}{A} = -\sigma \qquad \text{or}$$

$$\sigma = -\frac{\partial\gamma}{\partial E} = 17\frac{\partial\gamma}{\partial \text{pH}} \qquad (3)$$

where σ is the surface charge density, i.e. charge per unit surface area.

Applying equation 3 to the curves of figure 1 shows that the maximum of the electrocapillary curve corresponds to a surface charge density of zero. The pH that results in zero electric charge is called the zero point of charge (ZPC) or isoelectric point (IEP). Also, the surface charge density would be positive in the ascending branch of the electrocapillary curve and negative in the descending branch. The surface charge of a solid metal oxide is, therefore dependent on the pH of the surrounding water and varies from positive to negative with increasing pH, becoming zero at some intermediate pH. The ZPC values vary from oxide to oxide and correspond to the pH of minimum solubility of the metal oxide.

The curves of figure 1 depict the electrocapillary curvesof a silicate mineral such as most asbestos fibers and that of MgO. It is obvious from the proceeding analysis that at neutral or near neutral pH values, a typical asbestos fiber, except for chrysotile which is rich in MgO, will carry a net negative charge while the MgO surface is positively charged. A method to remove asbestos fibers from mineral waters was developed (3) based on the electrokinetic attractive forces between the unlike charges on asbestos and the MgO surface. The method was found to work equally well with other suspended particulates such as fine quartzite, iron ore particulates and kaolin.



$$\text{Surface charge density, } \sigma = -\frac{\partial \gamma}{\partial E} = 17\,\frac{\partial \gamma}{\partial p^{H}}$$

∴ σ is positive in anodic or ascending branch and negative in cathodic or descending branch

Figure 1 - Lippmann's Electrocapillarity

In general, oxides with cations in higher oxidation states are more acidic and will have a lower ZPC. The ZPC is mainly dependent on the ratio of charge (Z) to radius (R) of the cation in the pure solid (4). In a simple electrostatic model the ZPC decreases with increasing ionic potential, Z/R, and corrections for crystal field effects (coordination number) are made to refine the model (4). The ZPC of various metal oxides were compiled by Parks (4) and are shown in Table 1. Depending on the measurement method employed and the exact sample preparation, the reported value of ZPC for some of the metal oxides vary over a wide range.

The Stern model of electrical double layer (Figure 2) presents a fairly simple and useful picture of the electric potential around a solid in water. It predicts electrical potential based on the ionic double layer theory. The electrical potential difference that develops between the solid surface and the bulk solution is the balance between electrostatic attraction of the solution counterions to the solid surface and their tendency to diffuse away from the surface. In absence of specific adsorption, the equilibrium concentration gradient of the potential determining ions creates the electrical potential shown in figure 2. The double layer thickness, $1/\kappa$, is

TABLE I. pH of Zero Point Charge and Solubility Product Data for Selected Metal Hydroxides

Metal Ion	ph of Zero Point Charge (ZPC) Value	Range	Log Ksp	Reference Ksp
Al(III)	7.5	(6.2 to 7.7)	-31.2, -33.5	(6,7)
Cd(II)	11.7	(11.4 to 12.3	-14.2, -14.35	(6,7)
Cr(III)	8.4	(8.2 to 9.3)	-29.8	(5)
Co(II)	10.8	(8.9 to 11.8)	-14.2	(7)*
Cu(II)	9.4	(9.4 to 10.1)	-20.35, -20.35	(6,7)
Fe(II)	12.4	(11.3 to 12.4)	-15.1	(6)
Fe(III)	8.0	(7.4 to 8.4)	-37.4, -40.4, -38.45	(6,7,7)
Pb(II)	10.8	(10.6 to 11.1)	-15.6, -19.8	(6,7)*
Mn(II)	11.8	----	-12.7, -12.8	(6,7)
Ni(II)	9.4	(7.9 to 10.3)	-14.5	(5)
Zn(II)	10.0	(8.7 to 10.6)	-16.9, -15.55	(7)
Mg(II)	12.4	----	-11.16	(7)

* Calculated from Gibb's Free Energy of Formation Given in Stumm and Morgan (7)

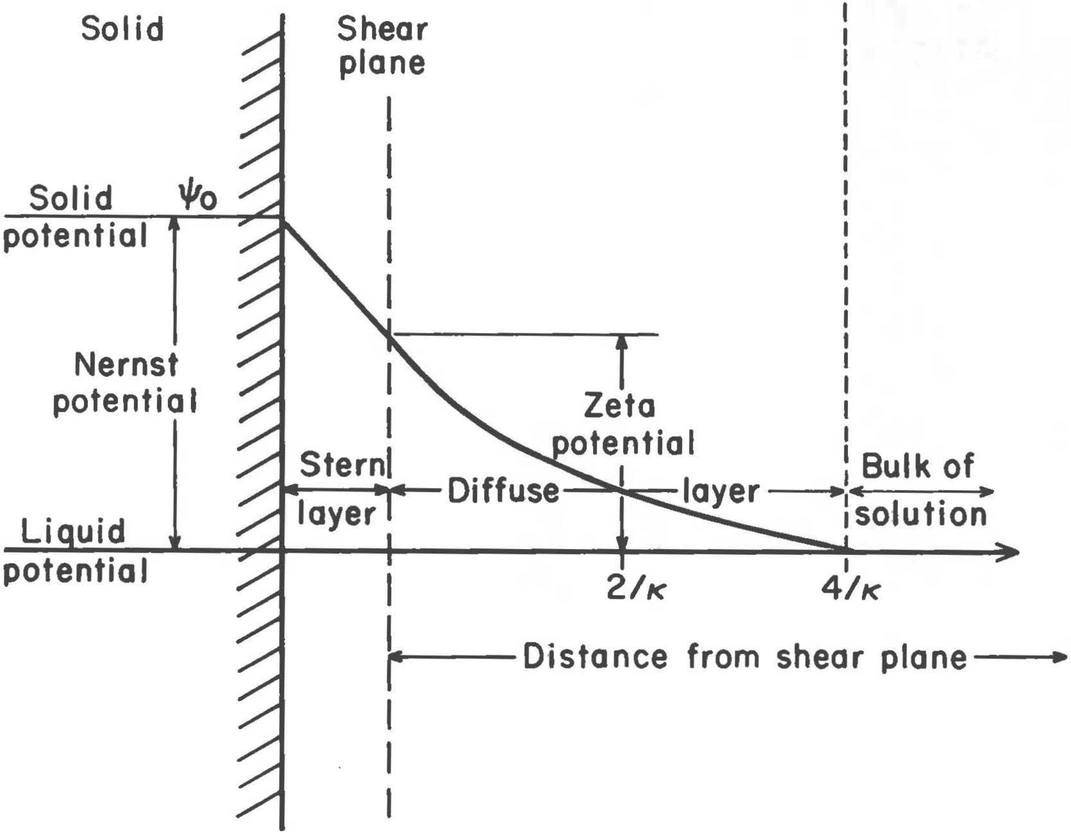


Figure 2 - Stern model of electrical potential at MgO surface.

a function of ionic strength and temperature. At room temperature, for example, in a 10^{-5} M NaCl solution, $1/\kappa$ is about 0.1 m or 1,000Å. Since OH^- and H^+ are potential determining ions, the pH at the solid surface can be quite different from that measured in the bulk solution. For an electrical potential of less than 25 mv this difference can be approximated (8) (with some qualifications) by:

$$pH_{Surface} - pH_{Bulk} = \frac{1}{2.3}\frac{F}{RT}E = 17E \qquad (4)$$

Colloid stability theory considers the net effect of the London-van der Waals force of attraction and the interaction of ionic double layers which can produce attractive or repulsive forces (9). The total potential energy of the particles is a function of their separation distance (figure 3). For strong electrostatic attractions, a primary minimum in the potential energy curve exists very close to the solid surface (the global minimum). A secondary minimum is observed at about four times the equivalent thickness of the double layer, $1/\kappa$. The exact positions of these two minima depend on the electrokinetic properties of the embryonic metal precipitates (and hence on the nature of the heavy metal) as well as the available MgO surface. Depending upon whether there is a) strongly favorable (unlike charges), b) weakly favorable, or c) unfavorable (like charges) ionic double layer interactions, a nascent precipitate will be respectively a) cemented, b) adheredt or c) dispersed away from the solid surface. Under the right conditions, favorable surface interactions are important for capturing suspended solids in granular filters (10).

Dual Role of MgO as a Filter and Precipitant

Flow in conventional water filters is usually laminar (or transitional) and the granules of filter medium are surrounded by a boundary layer of relatively stagnant fluid. In a water filter the chemical conditions near the surface of the MgO granules may vary considerably from that of the bulk solution. Not only does the pH of the bulk solution increase as a result of passing through the filter but ions and particles that cross streamlines to be captured by the MgO encounter an increase in the Mg^{2+} and OH^- concentrations. Dissolved heavy metals will precipitate in this region before the pH in the bulk solution would be raised sufficiently to cause insolubility and precipitation. The charge on the newly precipitated metal hydroxide particles will depend on the local pH level and will tend to become more negative as they approach the MgO surface due to the increasing pH. The more soluble or mobile metals will form hydroxides near the MgO surface where the ionic double layer interactions are the strongest and will be more strongly bound than ordinary filter deposits because the MgO surface is positively charged (ZPC of MgO is 12.4, table 1). Strong bonding should be related to the solubility product and the ZPC of the individual metal hydroxides.

Removal of heavy metals in the MgO filter can be thought of as an ion exchange process where one mole of Mg^{2+} is exchanged for each mole of M^{2+}. Any CaO impurity in the MgO material will also contribute. Metals either pass through the filter or are bound as metal oxides or hydroxides. Depending upon how tightly they are bound, the metals retained in the filter will be removed by conventional backwashing or else they will accumulate on the filter over successive cycles of filtration and backwashing.

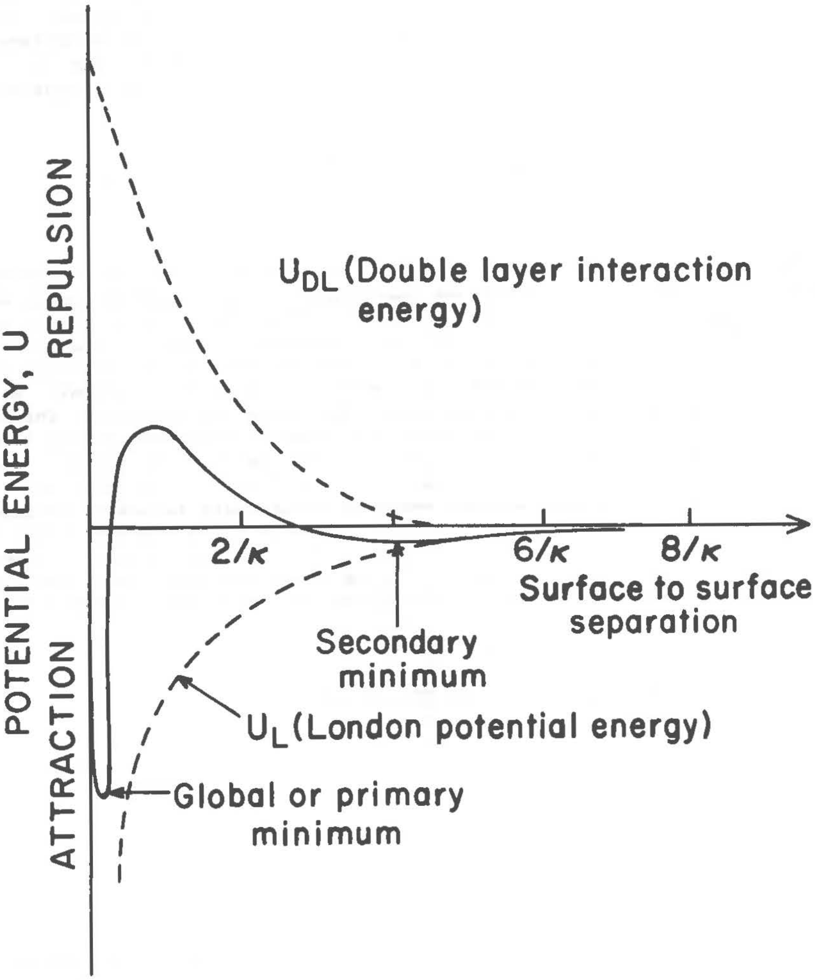


Figure 3 - Total potential energy curve at MgO surface displaying primary and secondary minima.

Dilute mineral acid or chelating agents such as EDTA (disodium salt of ethylene-diammine-tetra-acetic acid) are necessary to strip the tightly bound metals away from the MgO. Weakly bound metal hydroxides will be removed in normal backwashing, while strongly cemented hydroxides will need chemical stripping by acid or EDTA or other selective leachants. Preliminary experiments showed that 1% EDTA solution recovered metals as efficiently as 1% HCl, however the dissolution of MgO was much less with the former reagent. EDTA was, therefore, chosen as the stripping reagent in this work. Acidifying the EDTA sloution containing the stripped metal precipitated its hydrogen form which was filtered out and then reacted with NaOH to regenerate its sodium form. The objectives of this research are, therefore, not only to use granular MgO for the combined precipitation and filtration of heavy metals, but also to investigate the recovery of the precipitated metal values from simulated mining and mineral processing waste streams.

EXPERIMENTAL PROCEDURE

Filter beds were comprised of granular periclase (MgO) from Basic Chemical*. This is a dead burned product obtained from high temperature calcining of $Mg(OH)_2$ derived from a sea water brine. This filter material assayed 95.7, 2.8, 0.8, 0.3, and 0.3 pct MgO, CaO, SiO_2, Al_2O_3 and Fe_2O_3, respectively. Two experimental filter systems were used. The first system was comprised of 3 acrylic columns in series, 2.5 cm x 25 cm, each filled to a depth of 15.2 cm with MgO. The second filter was a 5.0 cm I.D. column of acrylic plastic about 1 m in height with a 46 cm bed of 0.5 mm MgO. Support for the medium was 50 mesh stainless steel screen. Filtration velocity through both beds was 0.34 cm/s.

Stock solutions of each of the heavy metals employed were prepared with distilled water and contained 5.0 g/L of each heavy metal. Reagent grade hydrated nitrate or sulfate solids of the various heavy metals were used to make these solutions. The appropiate volume of stock solution was diluted to 100 L in a large plastic reservoir with tap water filtered through PALL MCY1001NAE* cartridge filters. Manganese was available as a reagent grade 50 pct $Mn(NO_3)_2$ solution; the appropiate volume of this solution was pipetted directly into the reservoir. Influent was pumped by one channel of a dual channel Masterflex* pump . Dilute HCl or HNO_3 solution was added via the second channel as needed to maintain the influent at a pH of 7.0 as it entered the filter. The dilution due to the second channel was about 4 pct and was approximately compensated when adding the stock solutions to the reservoir. Influent concentrations of the metals were below the solubility limit at pH 7.0 calculated from solubility products.

Filtrate turbidity was measured at 15 minute intervals with a Hach* 2100A turbidimeter. Influent turbidities were measured at the beginning and end of the tests, which lasted 6 hours. Filtrate pH measurements were made concurrently with turbidity measurements. pH was measured with an Orion 901* Ionanalyzer or Orion 601* pH meter using 91-02 double junction research grade glass electrode. Filtrate samples were taken at 30 minute intervals and analyzed chemically by atomic absorption spectroscopy (A.A.S.) together with the influent samples. Aliquots were preserved with 0.5 ml HNO_3 per 25 ml sample to prevent post-precipitation of the heavy metals. The lower level detection limit for the direct atomic absorption analysis was 0.1 mg/L (0.1 ppm).

Two methods of backwashing were used. For the 3 column unit the contents of each column were agitated by roller tumbling for 10 min in a 500cc jar containing about 200ml of:1) distilled water, or 2) 1 pct EDTA. Each column went through 4-6 cycles of cleaning and samples of each backwash

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* Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

were acidified and analyzed by A.A.S. The larger filter column was backwashed by a method similar to conventional water treatment practice; 30 minutes of air-assisted backwash followed by 30 minutes high rate fluidization at 50 pct bed expansion. Residual metal values were stripped with an upward flow of 1 pct EDTA solution at a rate of 500ml/min (0.43 cm/s), which was less than the minimum fluidization velocity. Backwash samples were withdrawn at 20 min. intervals for chemical analysis.

RESULTS AND DISCUSSION

Heavy Metal Retention on MgO Filter Beds

The three column filtration unit was packed with 1.09 mm granular periclase as the filter media. An influent solution containing 0.8 ppm Cu, 3.2 ppm Cd and 3.6 ppm Zn at a pH of 6.9 gave an effluent containing <0.1 ppm of each of the three metals for the first 15 minutes. During the five hour duration of this experiment, Cu and Zn in the effluent remained <0.1 ppm, but the Cd concentration rose gradually from 1.0 ppm after 100 minutes to 1.8 ppm at the end of the test. The filtrate pH dropped from 9.29 at the beginning of the test to 8.94 at the end of the test. Pressure drop across each of the three columns rose only 0.18, 0.07, and 0.07 m H_2O, respectively during the test. It appears that the pH was not kept high enough throughout the the MgO beds to precipitate all of the Cd, which has the highest solubility product of the three metals (table 1).

A duplicate test employing 0.50 mm periclase grains instead of the 1.09 mm grains enabled the bed pH to be kept at a higher level for a longer time. The result was a filtrate containing less than 0.10 ppm of the three metals with the Cd concentration remaining at that level for the first 90 minutes, instead of 15 minutes for the coarser MgO. Also, after five hours the filtrate contained only 0.39 ppm Cd compared to 1.8 ppm with the 1.09 mm MgO grains.

In order to maintain enough precipitation ability for MgO without sacrificing its filtration capacity, all subsequent tests were performed with 0.50 mm MgO grains. A synthetic waste stream containing approximately 1 mg/L Cu, 4 mg/L Cd and 4 mg/L Zn was passed through the three column unit. The influent pH was kept between 6.9 and 7.2. Filtrate pH decreased steadily with successive runs when only water backwashing was used. Data for this series of tests are shown in figure 4. After 1 cycle very little Cd was retained on the column, while the Zn broke through after 2 cycles. Cu was retained until the fifth cycle. About 150 bed volumes were passed through the filter in each cycle except the third, which was cut short because the columns were blinded with air bubbles. The data indicate that the filter bed was saturated with metals after 5 cycles and that of Cd, the most mobile of the three heavy metal cations, broke through first, followed by the second most mobile cation, Zn, as would be expected. EDTA backwashing restored the performance of the filter to its original level or better as indicated by the higher filtrate pH and better metals retention in the sixth cycle (figure 4).

Two synthetic waste solutions, one containing only 25 ppm suspended kaolin and the other containing 4.5 ppm Zn, 3.7 ppm Cd, 5 ppm Ni, and 6.3 ppm Mn in addition to the 25 ppm suspended kaolin were alternately flowed through a 2 inch diameter plexiglas column containing 45.7 cm of 0.50 mm periclase grains at a rate of 400 ml/min for 6-hour intervals. Starting with the plain kaolin solution, a total of 30 hours of filtration (three 6-hour runs

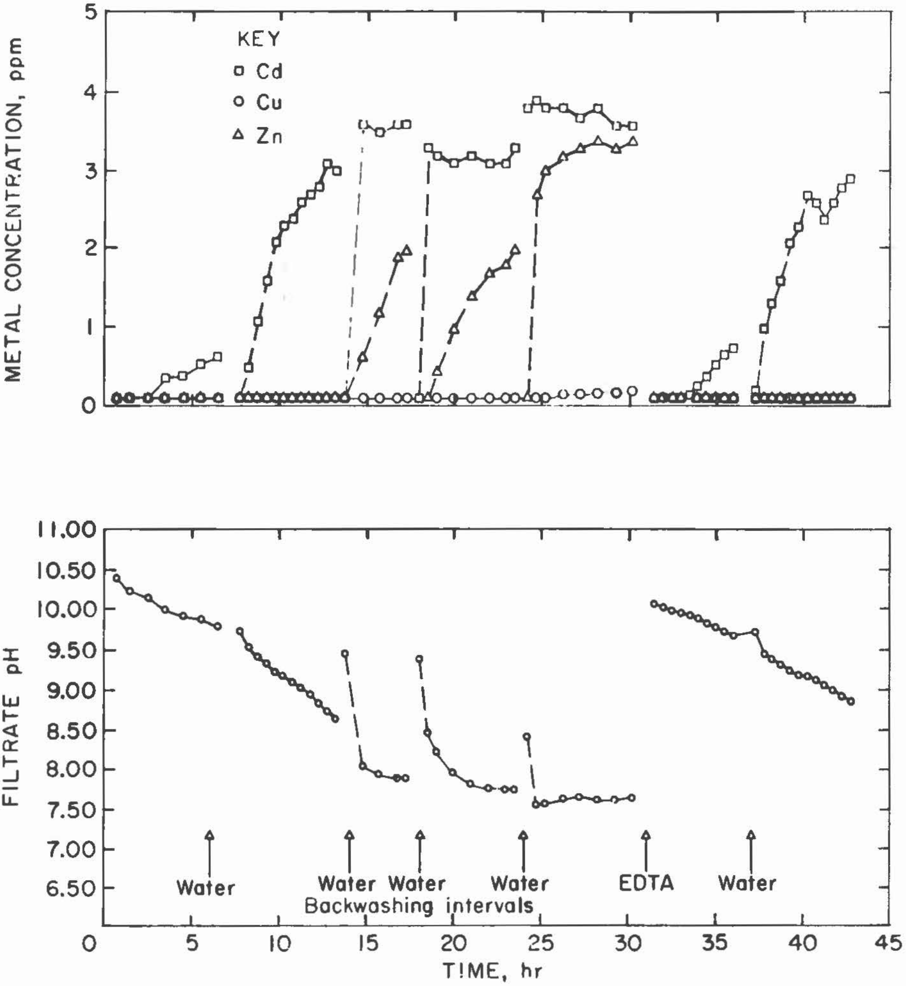

Figure 4 - Heavy metal retention in 3-stage MgO filter.
(upper) - Breakthrough curves.
(lower) - Filtrate pH.

with plain kaolin solution and two 6-hour runs with kaolin and heavy metals) were accomplished. After each 6-hour interval the column was water backwashed with air scouring. Filtration of kaolin solution resulted in pH drops of 0.25, 0.15, and 0.24 pH units, and increases in bed pressure of 0.20, 0.14, and 0.07 m H_2O. Influent turbidities in these tests were 16 NTU while final turbidities were 0.77, 0.84 and 0.34 NTU.

Filtration of kaolin with heavy metals resulted in pH drops of 1.62 and 1.64 pH units and increases of bed pressure of 5.17 and 4.65 m H_2O. Influent turbidities in these tests were 17 NTU while final turbidities were 0.08 and 0.26 NTU. In both of these tests the Zn was almost completely removed (<0.1 ppm) throughout the 6-hour tests. Ni concentration was initially less than 0.1 ppm in both tests but Cd concentration was initially less than 0.1 ppm only in the first test. The large drops in filtrate pH indicate that the pH was not always high enough to completely precipitate metals with higher Ksp values, i.e. Mn, Ni, and Cd. Heavy metal removal and recovery can, therefore, be done simultaneously with suspended particle removal. The precipitation of the heavy metals resulted in lower filtrate turbidity throughout the 6-hour tests, however this also resulted in an increase in bed pressure. The quantity of moderately insoluble metal such as Mn, Ni, and Cd in the waste stream solution dictates either deeper filtration beds or a bed comprised of finer sized MgO grains to maintain the high level of pH necessary to precipitate these metal values.

Stripping of Heavy Metals from MgO Filters

A new synthetic solution was passed through the three column unit containing 0.5 mm MgO at a rate of 100 ml/min for 6 hours. This solution contained 2.5 mg/L Al, 2.2 mg/L Cd, 2.1 mg/L Co, 1.0 mg/L Cr, 1.8 mg/L Cu, 1.9 mg/L Fe, 1.4 mg/L Mn, 1.8 mg/L Ni, 1.4 mg/L Pb, and 1.8 mg/L Zn and had an influent pH of about 6.9. All the metal values were almost totally removed (<0.1 mg/L) throughout the 6-hour test. The filtrate pH dropped from 10.51 at the beginning of the test to 9.68 at the end of the test. Each of the three columns were backwashed once with water and five times with 1 pct EDTA solution. The results of these tests are in table II. Recoveries of the 10 elements from the MgO column ranged from 93.6 to 97.7 pct (water followed by EDTA backwashing). For Pb, Al, Co, Cd, Mn, Cu, Zn, and Ni the majority of each metal was recovered in the EDTA backwash. For Fe and Cr the majority of each metal was recovered in the water backwash. Except for Mn, Cd, Al and Co, a substantial amount of the metal was collected in the first column. For Co and Al only about half of the metal value is collected in the first column. Cd was equally collected on the first and second columns while more Mn was collected on the second column compared to either the first column or third column.

The quantity of each metal value retained on the columns was calculated by numerically integratng the area under the concentration versus time curves for the filtration tests, multiplying by the volumetric flow rate (which was maintained at 100ml/min) to get the total amount of each metal passing through the filter, but not being captured. This was subtracted from the product of the influent concentration times the flow rate times the total run length to obtain the net amount retained on the columns. Many of the reported concentration values for the effluent were below the detection limit of the chemical analysis. In these cases a value of 0.1 mg/L was used for these points in the integration process. The quantity of each metal stripped from the column was calculated by summing the products of backwash volumes and reported concentrations from each column.

TABLE II. Heavy Metal Recovery and Distribution in 3 Column MgO Filter

Column	Backwashing Reagent	Recovery, Percent									
		Al	Co	Cd	Cu	Fe	Zn	Mn	Cr	Ni	Pb
I	Water	19.82	19.53	19.43	41.13	38.96	37.96	5.69	48.42	23.73	25.22
I	EDTA	29.36	29.14	22.23	25.84	13.95	50.08	18.79	19.27	31.33	33.59
II	Water	5.81	13.55	12.18	.86	13.52	2.22	8.37	.25	12.41	5.18
II	EDTA	23.43	28.53	27.94	17.70	15.98	4.95	33.51	7.50	24.20	23.33
III	Water	1.21	1.11	2.27	1.74	5.62	.37	3.22	9.52	.81	.71
III	EDTA	17.86	3.78	13.18	7.75	7.98	2.07	26.35	8.62	3.04	7.84
I	Water + EDTA	49.18	48.67	41.66	66.97	52.91	88.04	24.48	67.69	55.06	58.81
II	Water + EDTA	29.24	42.09	40.12	18.56	29.50	7.17	41.88	7.75	36.61	28.51
III	Water + EDTA	19.07	4.89	15.45	9.49	13.60	2.44	29.57	18.14	3.85	8.55
I + II + III	Water	26.84	34.19	33.88	43.73	58.10	40.55	17.28	58.19	36.95	31.11
I + II + III	EDTA	70.65	61.46	63.35	51.29	37.91	57.10	78.65	35.39	58.57	64.79
I + II + III	Total Recovery	97.49	95.65	97.23	95.02	96.01	97.65	95.93	93.58	95.52	95.87
Ratio of EDTA-, to Total-, Recovery		0.72	0.64	0.65	0.54	0.39	0.58	0.82	0.38	0.61	0.68

For each metal, the fraction recovered during the EDTA backwash relative to the total recovered by water plus EDTA backwash is plotted versus ZPC's for these metals in Figure 5. Aside from Al(III), the percentage recovery of metals increases with increasing ZPC, as would be expected since the higher the pH for the zero point of charge, the higher the pH of minimum solubility of the metal and the more mobile the metal ion. Thus, precipitation of the more mobile ions occurs closer to the MgO surface, probably at the distance corresponding to the global potential energy minimum of figure 3. Here the pH is higher and bonding of the metal hydroxide or oxide to the MgO is highly probable so that chemical stripping of the metal oxide or hydroxide is required. The brackets span the range of ZPC values selected by Parks from the literature (4) and given in table 1. A straight line is drawn through as many of the bracketed values of ZPC as possible; no theoretical importance at this time has been attributed to the slope, intercept or linearity of the plot. Only Cd(II) fails to contact the line and only a single value was reported for Mn(II) so no bracketing values are available. The recovery of Cd(II) appears to be lower than it should be in these tests as results decribed later indicate.

A third synthetic waste solution containing about 1 mg/L Cu, 4 mg/L Cd, 6 mg/L Mn and 4 mg/L Zn was passed through the single MgO filter column at a rate of 400 ml/min for 6 hours. The column was not allowed to saturate as was done with the three column unit. After each cycle of loading the filter was backwashed with air and water, then stripped with 1 pct EDTA solution. The metals eluted off the column quickly as shown in Figure 6. The area under each curve was determined by numerical integration and multiplied by the volumetric flow rate to obtain the total recovery of each metal. Two duplicate tests were run and the results are given in table III. Most of the

TABLE III. - Loading and Stripping of Single MgO Column

Metal	Quantity, mg				Ratio of Chemically-Recovered to Loaded Metal	
	Loaded on Filter*		Stripped with EDTA After Water Backwash			
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Cu	113.0	118.0	44.0	30.1	0.39	0.26
Zn	635.0	648.0	357.0	328.0	0.56	0.51
Cd	538.0	510.0	502.0	548.0	0.93	(1.08)**
Mn	837.0	795.0	773.0	894.0	0.92	(1.12)**

* calculated from influent and effluent chemical analyses.

** ratio exceeding 1.00 is due to experimental and computational uncertainti Probable source of error is taking an analysis of <0.1 ppm as 0.1 ppm for integration purposes. If zero ppm was used, the loaded metal in the denominator would be slightly higher.

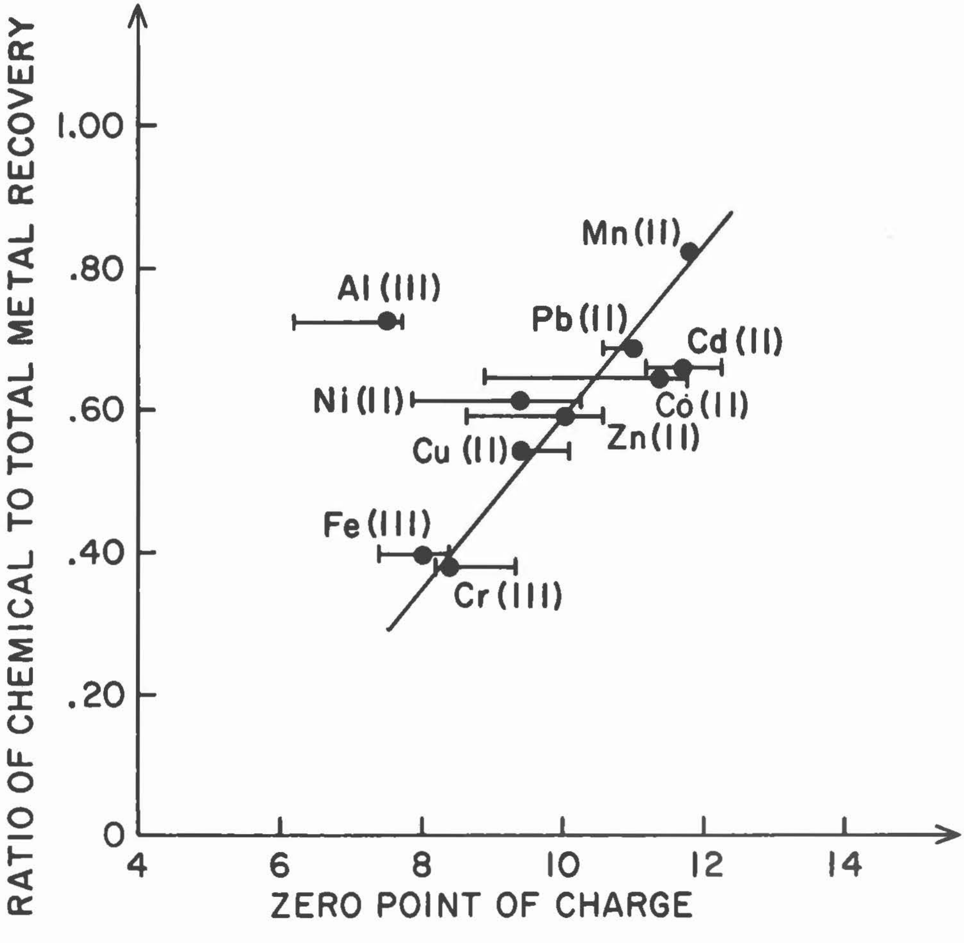

Figure 5 - Correlation of fractional metal recovery by EDTA stripping with the metal oxide ZPC.

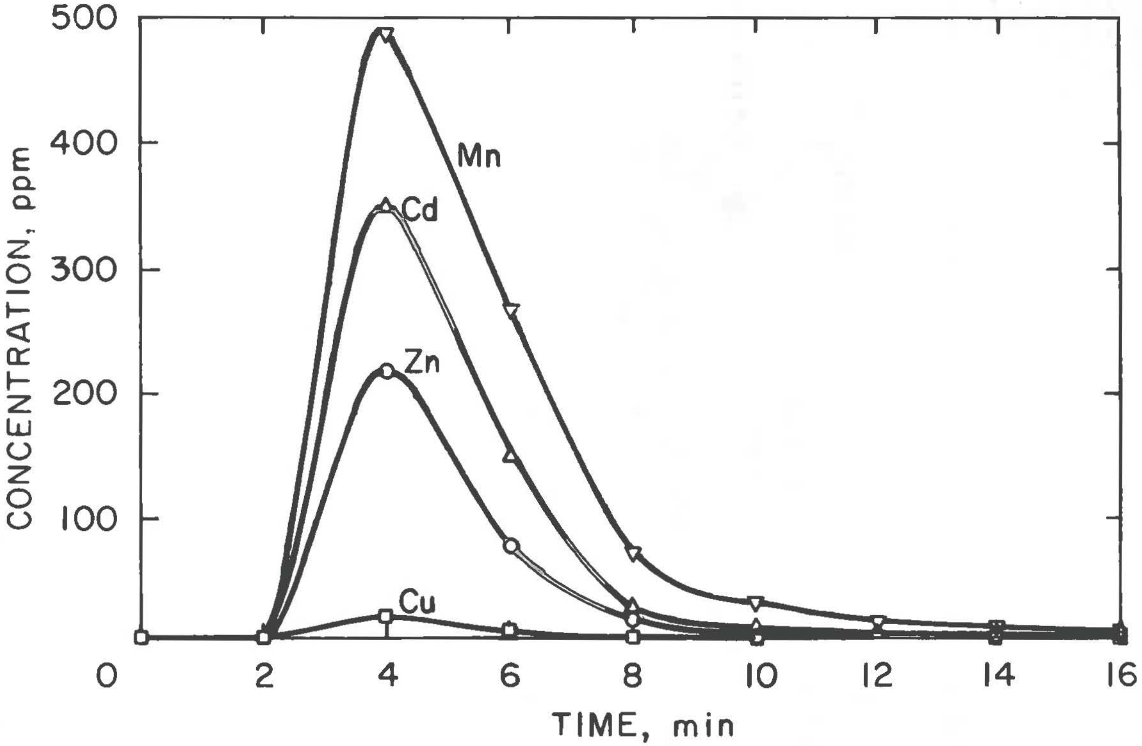

Figure 6 - Metal elution curves with 1% EDTA from single column MgO filter.

Cu was removed by water and air backwashing which accounts for the low Cu recovery by EDTA stripping. Recovery efficiency is much better for the Zn, Cd and Mn by this method than by tumbling. The coating of metal hydroxides is dissolved and the heavy metals elute off together in a concentrated solution (as evidenced by the peak in the concentration versus time plot). This quick elution of the heavy metals means that the EDTA solution has limited contact time with the MgO and therefore MgO dissolution is kept at a minimum.

The total amount of Mg and Ca leached out of the column by the EDTA solution was determined by the same methods used for the heavy metals. A total of 1.34 and 1.62 grams of Mg and 0.54 and 0.25 grams of Ca were dissolved by the EDTA in the two tests. About 1.67 and 1.80 total grams of heavy metals were stripped from the column. On a molar basis this amounts to 72 m mol Ca plus Mg to 26 m mol total heavy metals stripped.

The efficiency of the process is fair; 160 bed volumes of some of the most mobile metal cations were successfully treated in each cycle before breakthrough. During filtration about 2 m mol Ca plus Mg (about 50 pct each on a molar basis) is exchanged per total m mol of heavy metals. The metals can be recovered in less than 8 liters of EDTA brine and the metals are concentrated as much as 20 fold, with the exception of Cu which is removed by normal backwashing. It is obvious from figure 6 that the bulk of the metals are stripped within a 6-8 minute period and thus a volume equal to about half that actually used would be sufficient for removal.

Metals recovery is apparently a strong function of ZPC as shown in figure 5 for the metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, and in figure 7 for the metals Cd, Cu, Zn, and Mn. The EDTA backwash data plotted in figure 7 are the average of both tests reported in table IIIThe vertical brackets span the range of experimental values. The data fit very well to a straight line suggesting a strong correlation between adherence to the MgO surface and the ZPC of the precipitate.

Several factors probably influence the ZPC and bonding of the heavy metals to the MgO. In the test with a stock solution of 10 heavy metals the initial turbidity was higher than that for the 4 metals which indicates that more precipitate was formed in the 10 metal filter influent compared to that with the 4 metals. These precipitates, once formed would tend to be captured by the mechanism operating in conventional filtration. Normal backwashing with water is sufficient to remove these hydroxide precipitates so the quantity of metals requiring removal by EDTA is lowered. Secondly, the ZPC is affected by defect structures and impurities (water, anions and cations) occluded in the precipitate. Various metals could be coprecipitating which would explain why Al(III) recovery is unexpectedly high in the test results of figure 5. Interactions between 4 metals are diminished with respect to those possible for 10 metals so the differences in stripping behavior are more pronounced. Thirdly, it should be pointed out that the precipitates are nascent precipitates, i.e. they are formed and captured within a matter of minutes or even seconds. There is most likely not enough time to form equilibrium structures, a process which may require days. The precipitates are likely to be disordered, to contain H_2O at the expense of OH^- or $O^=$, and other impurities. The more ordered, high purity structures with OH^- and $O^=$ replacing H_2O, tend to have lower ZPC, so the nascent precipitates may be bonded more strongly than expected based on ZPC values determined for aged precipitates.

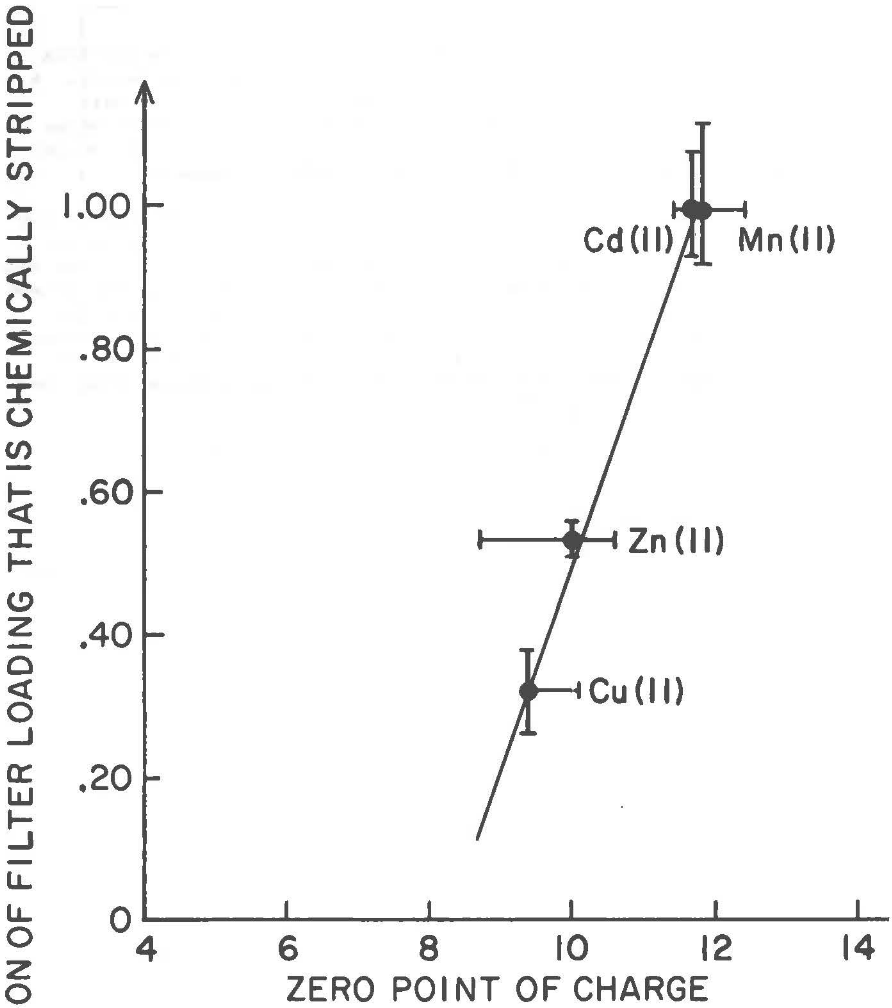

Figure 7 - Fractional metal recovery by EDTA stripping from single column filter as a function of ZPC of metal oxide.

SUMMARY AND CONCLUSION

The granular MgO precipitation/filter process appears to have merit for removing and recovering heavy metals from waste streams that have at least been partially neutralized by liming. Metal concentrations have been reduced to less than 0.1 mg/L by passage through a bed of granular dead burned MgO. Recoveries of heavy metals from the MgO bed in excess of 95 percent were obtained by combined water backwashing and stripping with EDTA solutions. The metal concentration of the waste stream to be treated cannot be too high, nor can the pH of the waste stream be too low, otherwise the reactivity of the dead burned MgO will not be sufficient to treat the wastewater or excessive dissolution of the MgO will occur. In acid mine drainage it is fairly standard practice to neutralize to pH 7.0 and aerate to remove the iron. This is not sufficient to remove the more soluble heavy metals. With the granular MgO filter heavy metal removal could be accomplished without further addition of lime or flocculant. The MgO filter is easily cleaned and the metals recovery is relatively unaffected by the presence of suspended solids as is the case with ion exchange columns. Fine tuning of the procedure and reducing the dead volume in the column could improve the heavy metal removal and recovery. By employing more columns of MgO and varying the reactivity of the MgO, the particle size of the MgO granules and the depth of the MgO bed it may be possible to improve the removal of the most mobile heavy metal ions and at the same time segregate the metals on different columns for easier recovery. It may also be possible to selectively strip and separate the metals from one column by using a series of metal-specific eluants. Metal values removed from the column by normal backwashing can be collected in a small volume of solution and then acidified to give a concentrated solution. Taking into account the OH^- gradient around the MgO granules and the ZPC of the metals explains at least in part the need for chemical stripping of the more mobile metal cations from the beds of MgO.

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RECYCLE AND SECONDARY RECOVERY OF METALS

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