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The use of the chelating resin Dowex M-4195 in the adsorption ofselected heavy metal ions from manganese solutions

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Abstract

The increasing demand for batteries of higher performance characteristics has led to the development of several types of manganese dioxides with optimal battery characteristics. One of these types is produced by a partial leach of a manganese ore, to remove the non-manganese metals to a level acceptable for direct use in batteries. The resulting leach solution must, however, undergo treatment to remove the impurity metals. This paper reports the uptake of copper, nickel, cobalt, lead, iron and manganese from manganese chloride leach solution onto the chelating resin Dowex M-4195 in column experiments. The results demonstrate the ability to remove contaminants to an extent satisfying the quality criteria required for the utilization of the manganese chloride solution for preparing manganese chemicals. Column elution tests demonstrated that a two-stage elution scheme whereby sulfuric acid is first used to elute iron, nickel and cobalt from the resin, then a subsequent ammonium hydroxide elution recovers almost all of the copper is superior to a scheme in which ammonium hydroxide is used before sulfuric acid. However, neither of these elution schemes fully eluted all the metals tested in the study.

***Keywords**:* Chelating ion exchange resin; Elution; Heavy metal removal; Manganese solutions

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Introduction

There is a growing need for an environmentallysustainable method to separate heavy metals, some- times present in only trace concentrations, from man- ganese and iron in acidic leach solutions. This growth in demand reflects both an increasing amount of manganese ores undergoing hydrometallurgical treat- ment, along with growing problems associated with managing the waste materials generated in the more traditional hydrometallurgical processes.

Carbon–zinc batteries, the most common primary batteries worldwide, use a manganese dioxide cath-ode, with a carbon current feeder. Although the tradi- tional Leclanche´ cell contains natural manganese di-oxide, the so-called zinc chloride, heavy-duty carbon–zinc battery achieves a much higher capacity using synthetic manganese dioxide. Alkaline cells also use synthetic manganese dioxide (Kirk-Othmer, 1999). g- Manganese dioxide is the electrochemically active phase used in many batteries. This is a moderately crystalline, non-stoichiometric, hydrated phase; the electrochemical activity is due to cationic vacancies. Although g-manganese dioxide occurs naturally as the mineral nsutite, synthetic materials generally havesuperior properties. Various processes are used tosynthesize chemical manganese dioxide. Most involvean acid leach of manganese ores, followed by oxida- tive precipitation of MnO_2. Activated native ore is produced by converting ground ore to Mn_2O_3, then treating with sulfuric acid to disproportionate the Mn_2O_3 to soluble $MnSO_4$ and g-MnO_2, which pre- cipitates with a high specific surface area (Kirk-Oth- mer, 1999). Electrolytic manganese dioxide has also been used in batteries since 1918. This is formed at the anode by electrolysis of acidified manganese sul- fate solutions, and principally comprises q-MnO_2, another non-stoichiometric, hydrated phase.

Before precipitation or electrolysis, acidic manga- nese solutions must be purified to remove contami- nants that would interfere with the precipitation processes, or the battery performance. The principal contaminants are iron, aluminum, potassium, and heavy metals such as copper, cobalt, nickel and zinc. Similar purification is needed when manganese ores are used as a feedstock for the chemical industry, or to produce electrolytic manganese for use in non- ferrous alloys. Traditionally, purification proceeds by

(a) precipitating jarosite or alunite to remove potassi- um; (b) increasing the pH to precipitate iron and aluminum; or (c) precipitating heavy metals as sul- fides (Paixão et al., 1995). This approach generates solids that are difficult to dispose of, because of the heavy metals contained therein. There is also a sig- nificant cost associated with the necessary pH control. Accordingly, it would be highly desirable to remove (De Siegel and Valencia, 1982; Ravikumar and Fuerstenau, 1997), and deep-sea manganese nodules, which are a good source of copper, nickel and cobalt (Agarwal et al., 1976; Kanungo and Das, 1988; Kohga et al., 1995). Different hydrometallurgical processing routes, including acidic routes, have also been examined for treating these materials. As for the production of battery-grade manganese dioxide, it would be highly desirable to separate heavy metals values such as Cu(II), Ni(II), and Co(II) from manganese and iron (III), present at relatively high concentrations.

We have screened several commercial resins for their suitability for this separation, in a very acidic manganese chloride solution; the chelating resin Dowex M-4195 appears to be very promising (Diniz et al., 2000). Dowex M-4195, formerly marketed as Dow XFS 4195, is a macroporous resin, with a poly- styrene-divinylbenzene matrix, and a weakly basic chelating bispicolyl amine (bis(2-pyridylmethyl) amine) functional group (Grinstead and Nasutavicus, 1977, 1978). Bispicolyl amine is a heterocyclic poly- amine with three nitrogen donor atoms, as shown in Fig. 1.

Dowex M-4195 was developed in the early 1970s and has found some commercial applications, notably for adsorption of heavy metals. The resin is used at INCO's Port Colborne refinery in Canada (Melling and West, 1984), and at the Zambia Chambishi Cobalt Plant (Rao et al., 1993), for purifying cobalt electrolytes. Batch equilibration tests have shown that even at high total chloride and very low pH, Dowex M-4195 can adsorb many heavy metal ions from single-metal chloride solutions, but has a low affinity for manga-nese (Diniz et al., 2002). However, single-metal tests cannot fully predict the behavior that would be expected when using the resin on a real process solution, where the individual metal-bearing species would be competing for functional groups on the resin. Nor can equilibrium batch tests easily predict the behavior that might be expected in a packed the contaminants by a route that would enable the contaminants to be recovered as by-products.

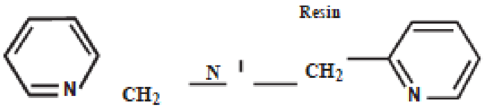


Fig. 1. Bis(2-pyridylmethyl) amine functional group on Dowex M-4195.

Certain manganese minerals are often associated with non-manganese values. These include the cop-per and silver rich wad deposits of South America column, where a solution element does not necessarily equilibrate with a given element of resin as it flows through the resin bed. Finally, the strong affinity of Dowex M-4195 for many heavy metals, even in acidic solutions with high chloride concentrations, suggests that elution may not be straightforward. Yet effective elution would be crucial in a commercial application of this resin.

To address these issues, the adsorption behavior of Dowex M-4195 was studied using a packed column of resin, and a concentrated, multi-component solu- tion obtained by leaching a manganese ore with hydrochloric acid. These studies confirmed that M- 4195 is capable of removing a range of heavy metal impurities from an acidic manganese chloride solu- tion. Elution studies were also done, and confirmed that elution would be the most challenging step in developing a commercial process for separating heavy metals from acidic manganese chloride solutions.

2. Experimental procedure

Materials and solutions

Dowex M-4195 resin was purchased from Supelco–Sigma Aldrich Division. The as-received resin was rinsed with water several times to remove any leached materials. It then underwent a wetting procedure (Supelco–Sigma-Aldrich, 1997) to ensure that it was wet, without introducing extraneous water into the test solutions.

Feed solution for the loading tests was obtained by leaching manganese ore from the Azul mine in Para

State (Brazil) at 908C for 40 min with a 2.91 mol/L

HCl solution, using a pulp density of 250 g of ore/ liter of lixiviant (Paixão et al., 1996). The resulting solution had a typical composition of 85 mg/L Cu, 100 mg/L Ni, 47.5 mg/L Co, 40 mg/L Pb, 6.0 g/L Fe, and 47.5 g/L Mn, along with minor amounts of Mg and Ca (which were not studied in the present work). The pH was then adjusted using NaOH (certified, Fisher Chemicals) to a typical free acid concentration of about 1.0 mol/L. The total chloride concentration was 3.6 mol/L.

Elution was done at 25 8C using 1 mol/L sulfuric

acid (certified, Fisher Chemicals) and 4 mol/L ammo- nium hydroxide (certified, Fisher Chemicals).

Loading and elution

Resin was placed in a Plexiglas column, 750 mm long, 25 mm in diameter, with a bed height of 500 mm. These dimensions comply with the minimum recommended by Slater (1991) for a fixed bed. Dis- tilled water was then introduced from the base of the column to eliminate air bubbles in the resin bed and associated channeling (Slater, 1991).

A peristaltic pump was used to add feed solutions and eluant (ambient temperature) to the top of the column at a rate of 2 mL/min or 1.78 BV (bed volumes) per hour. 46 BV were run for the loading tests. The elution tests were run in two different sequences, each using both eluants. In the first se- quence, 10 BV of sulfuric acid were initially passed through the column, followed by 10 BV of the am- monium hydroxide solution. The second sequence reversed the order in which these eluants were ap- plied. To avoid contamination of each solution, 10 BV of distilled water were passed through the column before starting the elution tests, then another 10 BV were passed after using the first eluant. During both loading and elution tests, samples of the column effluent or eluate were taken from the base of the column every hour, for 26 h.

Analysis

Metal concentrations were analyzed using a Per- kin Elmer model 3100 atomic absorption spectropho-

tometer, using flame absorption. All analyses were run at 25 8C in duplicate, except the samples from

elution, where the low sample volume dictated a single analysis. The pH of solutions and samples was measured using an Orion pH/ISE meter with an Orion Ross combination pH electrode, calibrated using pH 1.0, 3.0 and 7.0 buffers (certified, Fisher Chemicals).

3. Results and discussion

Loading tests

Fig. 2 shows normalized breakthrough curves for the different metals present in the acidic manga- nese chloride leach solution during resin loading.

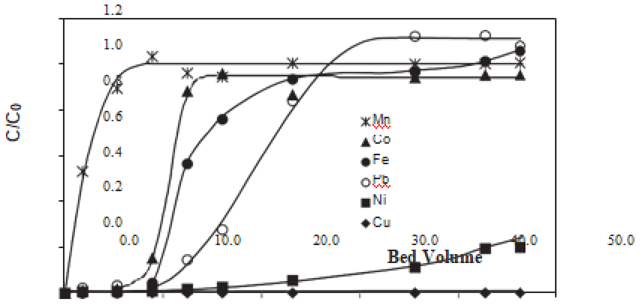
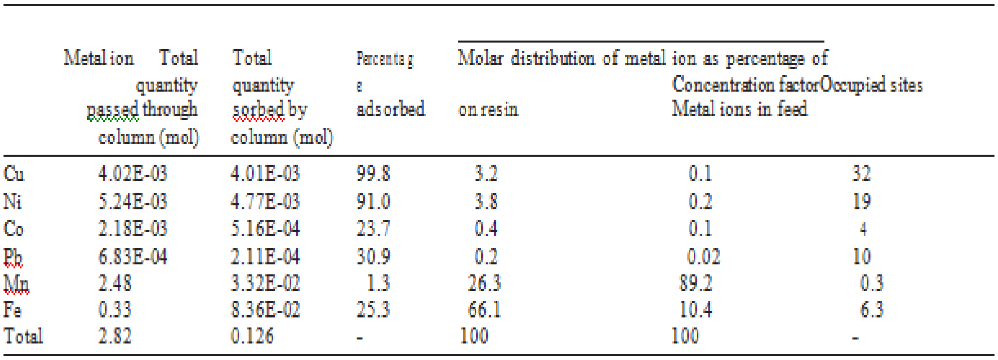


Fig. 2. Breakthrough curves of Cu^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+} and Mn^{2+} from a flow-through column test with manganese chloride leach solution. Solution composition: 85 mg/L Cu, 100 mg/L Ni, 47.5 mg/L Co, 40 mg/L Pb, 6.0 g/L Fe, 47.5 g/L Mn, 1.0 mol/L free acid, 3.6 mol/L total chloride (bed volume= 67.6 mL; flowrate= 2 mL/min, temperature= 25 8C). *C* denotes the concentration of each metal in the final effluent, C_0
the concentration in the feed.

The apparent sequence of affinity of metals is Cu NNi NPb NFe NCo NMn. This differs slightly from the sequence of affinity reported by Diniz et al.(2002) for uptake onto Dowex M-4195 from synthetic single-metal solutions in batch experiments (Cu NNi NCo NPb NFe NMn), demonstrating the im- portance of concentration effects and interactions. The curves clearly demonstrate the strong selectiv- ity of the resin for copper over the other metals present in the leach solution; after 46 BV, copper had still not broken through the column. Lead, cobalt and iron broke through at around 9 BV, whereas nickel broke through at around 15 BV. C/C_0 reached unity at approximately 16 BV for cobalt, at 30 BV for lead, and at 40 BV for iron, marking net saturation of the resin with these ions. For lead and iron, C/C_0 then increased above unity, due to displacement from the resin by ions with a stronger affinity for the resin, especially copper.

Manganese broke through the column shortly after feed was supplied, due to its low affinity for the resin, and its high concentration in the feed. The concentration of manganese in the effluent reached that in the feed ($C/C_0 = 1$) at approximately 9 BV, then remained constant, suggesting that man- ganese was subsequently neither taken up nor re- leased in significant quantities. In reality, it is probable that after saturation of the resin, manga- nese would have been displaced from the resin by other metal ions, as seen for lead and iron. How- ever, the concentration of manganese was so much higher than that of the other metals present that the resulting change in manganese concentration would have been imperceptible.

Table 1 Mass balance for Dowex M-4195 treating manganese chloride leach solution after 46 bed volumes



Metal ion	Total quantity passed through column (mol)	Total quantity sorbed by column (mol)	Percentage adsorbed	Molar distribution of metal ion as percentage of		
				on resin	Concentration factorOccupied sites Metal ions in feed	
Cu	4.02E-03	4.01E-03	99.8	3.2	0.1	32
Ni	5.24E-03	4.77E-03	91.0	3.8	0.2	19
Co	2.18E-03	5.16E-04	23.7	0.4	0.1	4
Pb	6.83E-04	2.11E-04	30.9	0.2	0.02	10
Mn	2.48	3.32E-02	1.3	26.3	89.2	0.3
Fe	0.33	8.36E-02	25.3	66.1	10.4	6.3
Total	2.82	0.126	-	100	100	-

Table 1 shows the mass balance of each metal for the column loading experiments, along with the per- centage of each metal that was adsorbed by the resin, relative to the total amount in the feed, after 46 bed volumes of solution had passed through the column (itis clear from Fig. 2 that the mass balances are depen- dent upon the bed volume passed). It is evident that the adsorption of copper and nickel was almost com- plete. Cobalt, lead and iron were only partially re- moved from the solution (having passed their breakthrough point). The adsorption of manganese was negligible.

Table 1 also shows the molar distribution of the individual metal ions as a percentage of the occupied resin sites, and as a percentage of the metals present in the feed. Most of the resin sites are occupied by iron, followed by manganese. Despite their strong affinity for the resin, copper, nickel, cobalt and lead occupy only a relatively small fraction of the resin sites, due to their extremely low concentration in the feed. The concentration factors (the ratio of the molar percen- tages of a given metal on the resin and in the feed) demonstrate the strong affinity of the resin for the copper and nickel ions, and the more modest affinity for lead, iron and cobalt. This order of affinity is consistent with the breakthrough profiles shown in Fig. 2.

The loading behavior tests suggest that it would be possible to use the M-4195 resin to purify a concen- trated manganese chloride solution containing moder-ate levels of iron and trace levels of Co, Pb, Ni and Cu, by stopping the feed before 9 BV. At this point, the effluent solution would satisfy the quality criteria required for the production of manganese carbonate, namely that heavy metals V 50 mg/L (as Pb) and Fe V 200 mg/L (Acros, 1998).

Fig. 3 shows the pH of the effluent from the column-loading test. After initial backwashing of the resin with distilled water, the column effluent had a pH of about 2.8. This increased slightly with the introduction of feed, possibly due to the high ionic strength of the feed decreasing the activity coefficient of the hydrogen ion. The pH of the effluent then decreased steadily to about 0.5 (at 15 bed volumes), somewhat lower than the pH of the feed (0.75), due to displacement of hydrogen ions from the protonated bispicolyl amine functional groups by metal ions. The effluent pH then increased to 0.75, the same as the feed pH.

Elution tests

Sulfuric acid (0.5–1 mol/L), hydrochloric acid (6 mol/L), nitric acid (1 mol/L) and ammonium hy- droxide (2–5 mol/L) have been reported to be useful eluants for Dowex M-4195 loaded with tran- sition metals (Jones and Grinstead, 1977; Rosato et al., 1984; Kennedy et al., 1987; Zhu et al., 1990; Mijangos Anton et al., 1991; Sengupta and Zhu, 1992; Nagib et al., 1999). Ammonium hydroxide has proved very effective for eluting copper. Sulfu- ric acid has proved effective for nickel, iron and

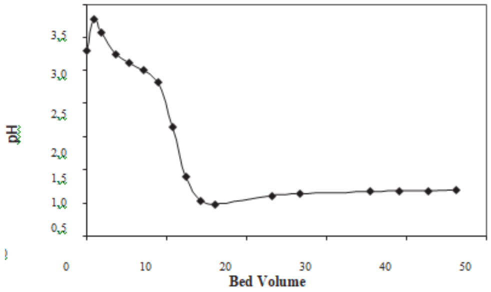


Fig. 3. pH of effluent from column loading test.

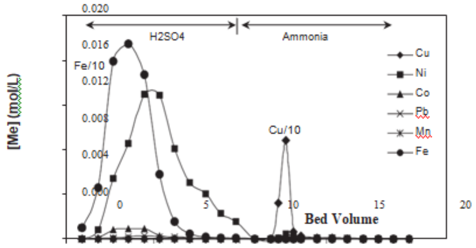


Fig. 4. Elution of Cu^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+} and Mn^{2+} from a column of Dowex M-4195, eluting first with 1 mol/L H_2SO_4, then with 4 mol/L NH_4OH (bed volume= 67.6 mL; flowrate= 2 mL/min, temperature= 25 8C).

Table 2 Mass balance for Dowex M-4195 elution process with 1 mol/L H_2SO_4 followed by 4 mol/L NH_4OH

Metal	Quantity sorbed by column (mol)	Quantity recovered in eluate (mol)		%Recovery NH_4OH		Total
		H_2SO_4	NH_4OH	H_2SO_4	NH_4OH	
Cu	4.01E-03	-	3.97E-03	-	99.0	99.0
Ni	4.77E-03	3.41E-03	4.1E-05	71.5	0.9	72.4
Co	5.16E-04	1.98E-04	2.79E-05	38.3	5.4	43.7
Pb	2.11E-04	6.31E-05	1.97E-05	29.8	9.3	39.1
Mn	3.32E-02	7.37E-06	-	0.02	-	0.02
Fe	8.36E-02	3.66E-02	-	43.1	-	43.1

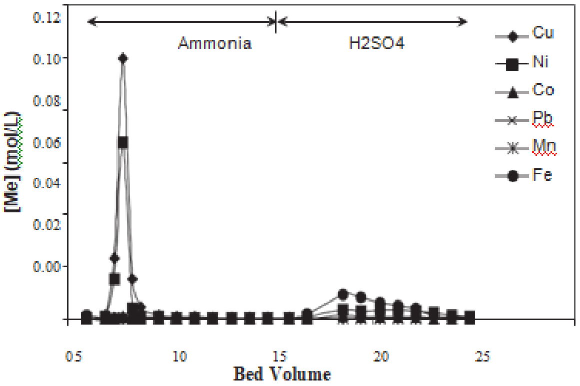


Fig. 5. Elution of Cu^{2+}, Ni^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+} and Mn^{2+} from a column of Dowex M-4195, eluting first with 4 mol/L NH_4OH, then with 1 mol/L H_2SO_4 (bed volume= 67.6 mL; flowrate= 2 mL/min, temperature= 25 8C).

while copper was being eluted by ammonium hydroxide solution.

Table 2 provides mass balances for the recoveries of individual metal ions from the resin when eluting with sulfuric acid, followed by ammonium hydroxide. It is apparent that the recovery of copper was near quantitative, and that of nickel was high. However, the recoveries of cobalt, lead and iron from the resin were modest. It is possible that higher concentrations of sulfuric acid would have improved the recoveries of these metal ions.

Fig. 5 shows the behavior for eluting first with 4 mol/L ammonium hydroxide solution, rinsing with distilled water (which did not remove measurable amounts of metals from the resin), then eluting with 1 mol/L sulfuric acid, while Table 3 provides mass balances for the recoveries of individual ions. Macroscopic flow was hindered during the initial stages of elution with sulfuric acid, presumably because of mobilization without complete dissolution of the hydrolyzed iron (III) phases that had formed in the presence of ammonium hydroxide, and blockage of flow channels by these phases. Although the ammonium hydroxide solution eluted some of the copper, the recovery was significantly lower than when the resin had first been eluted with sulfuric acid, presumably because mass transfer was limited by iron (III) precipitates. In contrast, the overall recovery of nickel was higher when eluting first with ammonium hydroxide, with most of the nickel appearing in the ammoniacal eluate rather than the acidic eluate, which would preclude this elution order as a means of separating copper and nickel. The recovery of lead was significantly lower when eluting first with ammonium hydroxide, presumably because the ammonia washed from the resin chloride ions that are needed to solubilize lead in sulfuric acid. The recovery of iron was somewhat lower, undoubtedly because of incomplete redissolution of iron (III) precipitates.

Table 3 Mass balance for Dowex M-4195 elution process with 4 mol/L NH_4OH followed by 1 mol/L H_2SO_4

Metal	Quantity sorbed by column (mol)	Quantity recovered in eluate (mol)		%Recovery		Total
		NH_4OH	H_2SO_4	NH_4OH	H_2SO_4	
Cu	4.01E-03	3.00E-03	–	74.7	–	74.7
Ni	4.77E-03	3.10E-03	9.75E-04	64.1	20.4	84.5
Co	5.16E-04	1.59E-06	2.27E-04	0.31	43.9	44.2
Pb	2.11E-04	–	1.51E-05	–	7.2	7.2
Mn	3.32E-02	–	3.73E-06	–	0.01	0.01
Fe	8.36E-02	–	2.81E-02	–	33.6	33.6

Overall, the first elution scheme, using sulfuric acid first, followed by ammonium hydroxide, would be preferable to the reverse. This gives better separation of individual ions, generally superior recoveries, and does not cause the flow problems induced when am- monium hydroxide was used as the first eluant. How-ever, the use of two separate eluants would be cumbersome in a practical plant, and the incomplete recoveries from the resin would be problematic. Work now underway in the laboratory of one of the authors is investigating the use of aqueous solutions of chelating agents such as EDTA as eluants for Dowex M-4195. Results to date, which will be reported separately, are more promising than more conventional approaches to elution. Since it would be possible to recover individ- ual metals from the eluate by electrolysis, this ap- proach may permit commercial adoption of Dowex M-4195 for treatment of manganese leach solutions.

4. Conclusions

Heavy metals, such as copper, nickel, cobalt and lead, can be effectively and selectively removed from a highly acidic manganese chloride solution using the chelating resin Dowex M-4195. Column experi- ments with a acidic leach solution containing 85 mg/ L Cu, 100 mg/L Ni, 47.5 mg/L Co, 40 mg/L Pb, 6.0 g/L Fe, and 47.5 g/L Mn indicated that at approxi- mately 9 BV, the heavy metals are removed to an extent that satisfies the quality criteria required for the production of manganese carbonate. The results confirm the high affinity of the resin for copper, which did not break through the column in tests lasting up to 46 BV. Even after saturation of the resin, copper continued to be adsorbed by the dis- placement of other sorbed metals. Based on the breakthrough curves, the overall affinity followed the sequence: Cu NNi NPb NFe(III) NCo HMn. Col- umn elution tests demonstrated that the resin can be eluted using a two-stage scheme whereby sulfuric acid is first used to elute iron, nickel and cobalt from the resin, then a subsequent ammonium hy- droxide elution recovers almost all of the copper. However, these eluants were unable to fully elute all the metals tested in the study. Work is now underway on the use of aqueous solutions of com- plexing agents as eluants, in an endeavor to improve elution.

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