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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius		mL	milliliter
g	gram		min	minute
h	hour		ppm	parts per million
L	liter		pct	percent

USE OF LIGNOCHEMICALS AND HUMIC ACIDS TO REMOVE HEAVY METALS FROM PROCESS WASTE STREAMS

By John E. Pahlman[1] and Sanaa E. Khalafalla[1]

ABSTRACT

The Bureau of Mines investigated the feasibility of removing heavy metals from mineral-process waste streams by precipitation with lignochemicals and humic acids. Lignochemicals are byproducts from the paper industry, while humic acids are obtained by caustic treatment of peat, subbituminous coal, and lignite. These high-molecular-weight organic materials have many functional groups, which can coordinate and form innercomplex salts with heavy metals that are crystalline precipitates.

Filtering of a humic-acid- or lignochemical-treated solution or waste stream containing these precipitates removes the heavy metal sequstrates. Tests were conducted with two lignochemical samples, three humic acid samples, lime (CaO), and sodium hydroxide (NaOH) in which increasing amounts of these additives were reacted with 50 mL of solution containing Fe^{3+}, Al^{3+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, and Hg^{1+}. At the appropriate pH, greater than 90- and 99-pct removal was achieved for these 11 heavy metal ions from the 10- and 100-ppm solutions, respectively, using lignochemicals and humic acids. Removal efficiency with these organic materials is better than that with CaO, especially for the more toxic ions, Hg^{1+}, Cd^{2+}, and Pb^{2+}. Unlike the precipitates formed with NaOH or CaO, those with lignochemicals and humic acids are compact and noncolloidal. The volume of their sludge is sharply lower than that of the finely dispersed lime or soda precipitates; thus, their removal in settling tanks or by simple filtration is enhanced.

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INTRODUCTION

Federal and State pollution-control standards for heavy-metal content of mineral-processing discharges have become more and more stringent. Where such metals have to be removed from a waste stream prior to discharge, precipitation is the most common method. This is usually done by precipitating the hydrous oxide by CaO addition. Although relatively simple and cheap, this method has a number of disadvantages: (1) it results in a great volume of sludge, which is both costly and hazardous to dispose; (2) the precipitation layer in settling ponds undergoes an inversion at temperatures around 4° C; (3) because of incomplete reaction, it often does not give an effluent of sufficiently low metal concentration; and (4) the metal values are not recovered and are thereby wasted.

To help meet present and possible future more stringent Environmental Protection Agency (EPA) and State requirements, the Bureau of Mines has investigated methods other than CaO precipitation for removing metals from solution. In one such method unsulfonated, Kraft-pine[2] lignin forms water-insoluble metal sequestrates that can be removed from the solution by simple filtration. In a second method, the sodium salt of humic acids forms water-insoluble sequestrates that also can be removed by filtration.

Kraft-pine lignin is an abundant byproduct of the paper industry. It is a complex, naturally occurring phenolic polyester, which in admixture with hemicelluloses forms the cementing material for the cellulose fibrils of all major plants. It is dissolved away from the cellulose fibrils by chemical attack in the sulfite and alkaline pulping process in paper production. Consisting of an aromatic core and a large number of hydrogen bonds and functional groups, these high-molecular weight, polymeric, organic molecules have many cation exchange sites owing to the geometry and distribution of the functional groups. These are the active sites for removing heavy metals from waste streams.

Humic acids are akin to lignin in that they are also high-molecular weight, polymeric, organic molecules with aromatic cores, and a large number of hydrogen bonds and functional groups. They also have cation exchange sites owing to the distribution of those functional groups, which are active for the removal of heavy metals. Humic acids can be obtained by caustic treatment of peat, lignite, and subbituminous coal. They naturally occur in soils, sediments, streams, lakes, and oceans. Their ability to bind cations in the environment has been studied in detail (1, 3-6).[3]

The objective of this Bureau investigation was to determine the feasibility of using commercially available lignin-derived products and humic acids to remove heavy metals from solutions and waste streams and to compare their removal efficiency with that of CaO addition and NaOH precipitation.

TEST MATERIALS AND SOLUTIONS

LIGNOCHEMICALS, HUMIC ACIDS, AND OTHER TEST REAGENTS

Two lignochemical samples were obtained from the chemical division of a paper company. One sample was a sodium salt of lignin (Na-L) which was water soluble above a pH of about 2. The pH of a 10-pct solution of this reagent was about 10.5. The other sample was a spray dried product that contained mostly the hydrogen form of lignin (H-L). As received, this lignochemical also contained some Na-L. A pure H-L form was prepared for testing by washing and filtering the sample and discarding the filtrate that contained the solubilized Na-L.

Preparation of three humic acid solutions involved caustic treatment of a North Dakota lignite (humic acid 1), a Montana subbituminous coal (humic acid 2), and a Minnesota peat (humic acid 3), with NaOH. For this purpose, 100 g of minus 200-mesh lignite, subbituminous coal, or peat were stirred in 2 L of 1-pct NaOH solution for 2 h. NaOH and CaO were reagent-grade chemicals.

100- AND 10-PPM SOLUTIONS

A solution, referred to as the 100-ppm solution, was prepared containing the 11 heavy metal constituents Fe^{3+}, Al^{3+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Mn^{2+}, and Hg^{1+} in either their nitrate or chloride form, each at the 100-ppm level of the metal ion. The 10-ppm solution, which contained 10 ppm of each ion, was prepared by a tenfold dilution of the 100-ppm solution.

MINE- AND PROCESS-WASTE STREAMS

A process-waste stream containing 35 ppm Zn was obtained from a commercial zinc plating operation. A sulfide, ore pile runoff sample, containing 2.8 ppm Ni, 0.3 ppm Cu, and 0.8 ppm Fe, was obtained from a northern Minnesota site. Two mine drainage streams, one containing 20 ppm Fe, 41 ppm Zn, and 41 ppm Mn, and the other containing 5.0 ppm Fe, 0.6 ppm Zn, 8 ppm Mn, and 6 ppm Mo, were obtained from two Colorado mining operations.

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[2]Reference to specific products does not imply endorsement by the Bureau of Mines.

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENTAL PROCEDURE

Various volumes or weights of humic acids, lignochemicals, NaOH, or CaO were stirred with 50 mL of heavy-metal containing solutions for 5 min. The solution pH was determined with a pH meter for each test. After 5 min of reaction the filtrate was removed and analyzed for residual ions. H-L and CaO were added as solids, while Na-L, NaOH, and the humic acids were added as liquids.

Tests with mixed lignite and subbituminous coal humic acid solutions involved pipetting out a desired volume of these solutions, while the residual lignite and coal particles of the stock solution were kept in suspension. Tests with unmixed lignite and subbituminous coal humic acid solutions involved pipetting out the desired volume of humic acid solution after the residual lignite and coal particles had settled to the bottom of the stock solution container. All humic acid solutions had a pH of around 11.5.

RESULTS AND DISCUSSION

100-PPM SOLUTION

Since in lignochemicals and humic acids there is one nonequilibrium exchangeable hydrogen per coordination site, the pH titration curves (figs. 1-2), demonstrate the presence of more than one coordination site in these materials. The variation of pH with the volume of Na-L added to the 100-ppm solution indicates the presence of at least three sites for metal coordination (fig. 1). Constant volume of Na-L (10 mL) is required between the successive inflection points in this stepwise titration. The molecule of Na-L appears, therefore, to be polydentate,
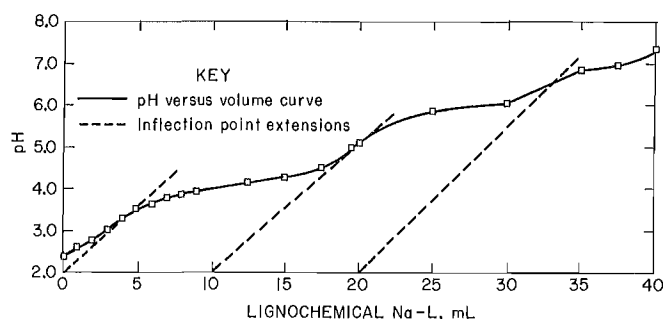

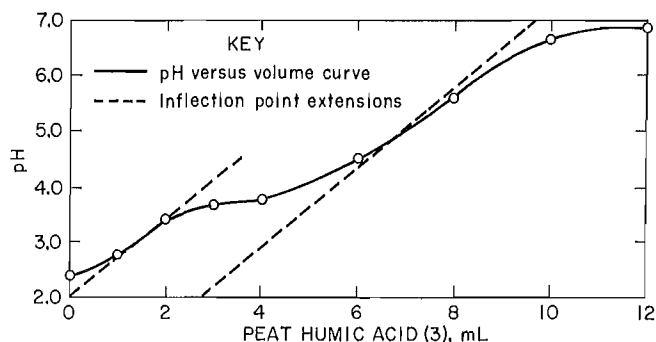Figure 1.—pH change as function of Na-L addition to 100-ppm solution.

Figure 2.—pH change as function of peat humic acid 3 addition to 100-ppm solution.

capable of chelation with heavy metal ions. Similar results are portrayed in titrations with a peat humic acid where two inflection points are discernible (fig. 2).

When the metal chelate is neutral, it belongs to the inner complex salt category (2) and may be extracted by various organic solvents, or it may merely precipitate from solution. The equilibrium involving the formation of such chelates indicates a competition between the metal and hydrogen ions (or sodium ions in case of the alkali solubilized chelating agent). Hence, the more stable the chelate, the lower the pH at which it is capable of existing, and being precipitated or extracted from aqueous solutions. This pH effect has been utilized to compare the relative stabilities of various metal chelates with a given ligand. Thus the pH's of incipient precipitation (50 pct precipitation), or 99 pct precipitation can be taken as a measure of metal removal efficiency with these polydentate chelating reagents.

Figures 3 and 4 show the efficiency of mixed lignite humic acid 1 and CaO, respectively, in removing the 11 heavy metals from the 100-ppm solution as a function of pH. Table 1 lists the pH values at which 99 pct of the respective heavy metals were removed (pH_{99}) for humic acids 1, 2, and 3, CaO, and lignochemical Na-L. The order of heavy metal ions with respect to ease of their removal by humic acid 1 is Hg^{1+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, and Mn^{2+} (fig. 3). This order is also followed by humic acids 2 and 3 as well as lignochemical Na-L, except that Hg^{1+} falls between Cu^{2+} and Zn^{2+} in the order of removal. The order of removal of heavy metals with lime (fig. 4) is Al^{3+}, Cr^{3+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+} Co^{2+}, Mn^{2+}, Cd^{2+}, and Hg^{1+}. The obvious differences between lime and humic acids are apparent for Fe^{3+}, Pb^{2+}, Hg^{1+}, and Cd^{2+}.

Mixed lignite humic acid 1 is superior to CaO in removal of all 11 heavy metals, as shown in figures 3 and 4, and by comparing pH_{99} values in table 1. Comparison of pH_{99} values for humic acids 2 and 3 to those for CaO shows that mixed subbituminous coal humic acid 2 is comparable or superior to CaO addition for removal of all metal ions except Cu^{2+}, while peat humic acid 3 is comparable or superior to CaO only for Hg^{1+}, Fe^{3+}, Pb^{2+},

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KEY

O Cr	▽ Zn
● Hg	▼ Ni
□ Al	◇ Cd
■ Fe	◆ Co
△ Cu	⬡ Mn
▲ Pb	
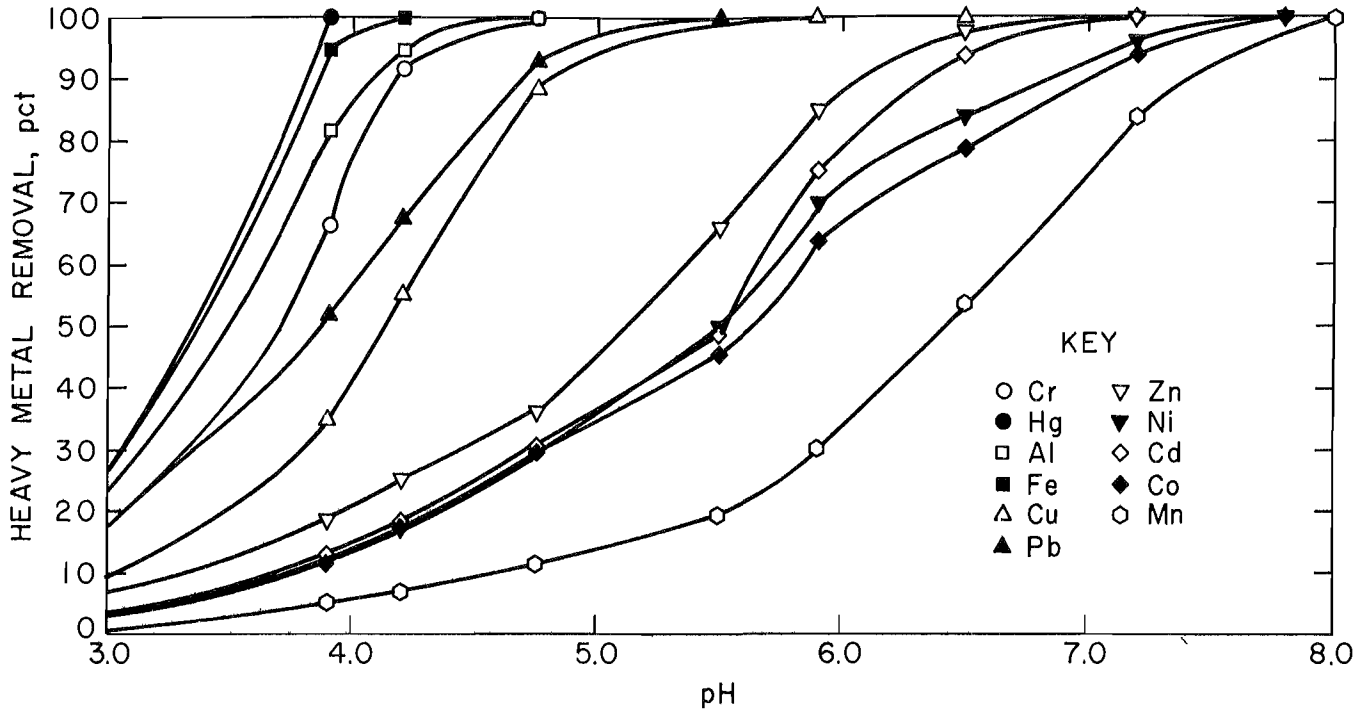
Figure 3.—Efficiency of heavy metals removal from 100-ppm solution by mixed humic acid 1.

KEY

O Cr	▽ Zn
● Hg	▼ Ni
□ Al	◇ Cd
■ Fe	◆ Co
△ Cu	⬡ Mn
▲ Pb	

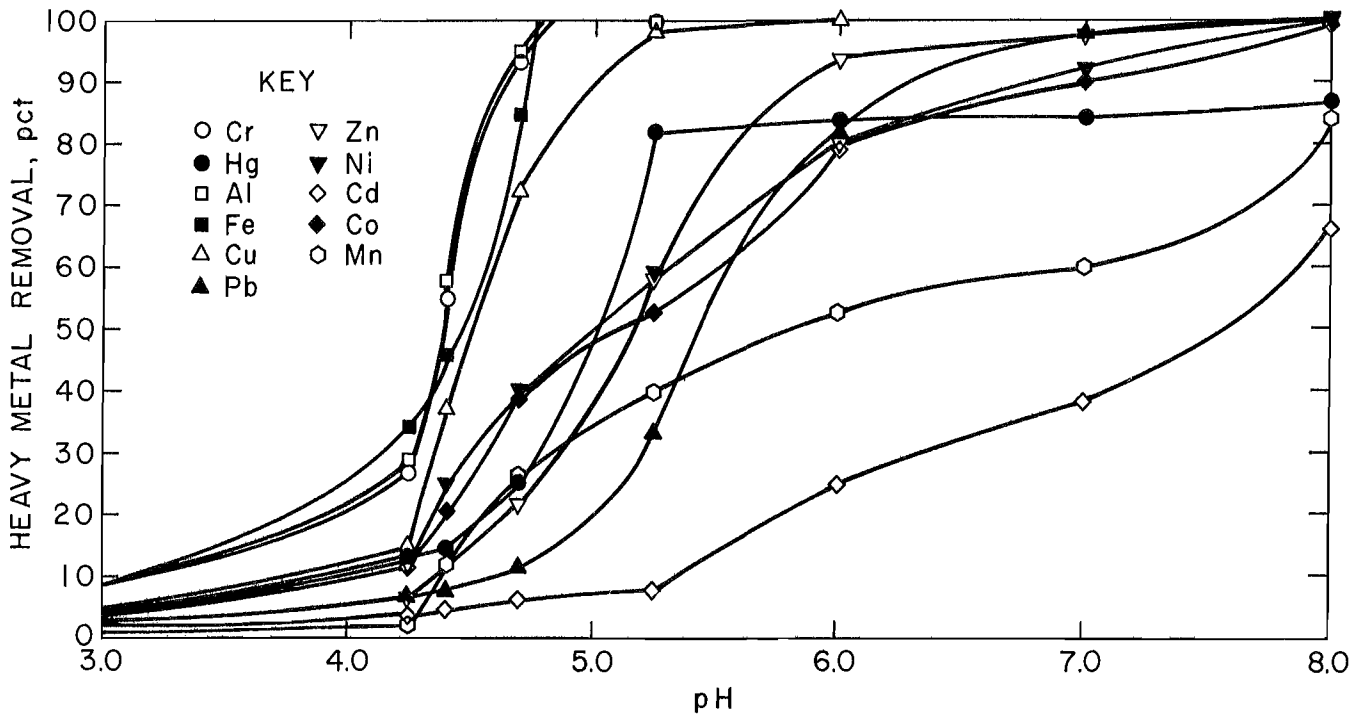Figure 4.—Efficiency of heavy metals removal from 100-ppm solution by CaO.

TABLE 1. - pH values at which 99 pct of heavy metals were removed from 100-ppm solution

(Values in parentheses are extrapolated values)

| Heavy metal ion | Humic acid | | | Lignochemical Na-L | CaO |
| | Mixed | | Unmixed | | |
	1	2	3		
Hg^{1+}	3.9	4.2	4.3	(7.5)	11.5
Fe^{3+}	4.1	4.5	4.5	4.9	4.8
Al^{3+}	4.4	4.6	4.9	5.4	4.7
Cr^{3+}	4.7	4.7	5.0	6.4	4.8
Pb^{2+}	5.2	5.9	5.3	5.5	7.3
Cu^{2+}	5.5	6.1	6.5	(7.5)	5.6
Zn^{2+}	6.9	6.9	7.3	(7.5)	7.3
Cd^{2+}	7.0	8.0	7.8	(8.1)	9.3
Ni^{2+}	7.5	8.0	(8.2)	(9.5)	8.0
Co^{2+}	7.6	8.0	(8.2)	(9.5)	8.0
Mn^{2+}	7.8	8.0	(8.5)	(10.5)	8.6

Zn^{2+}, Cd^{2+}, and Mn^{2+} removal. CaO is slightly better than humic acid 3 in the removal of Ni^{2+}, Co^{2+}, Cr^{3+}, Al^{3+}, and Cu^{2+}. Of the reagents tested mixed lignite humic acid 1 is the best for heavy metal removal, followed by mixed subbituminous coal humic acid 2 and then peat humic acid 3.

One advantage of using humic acids is that they greatly surpass CaO in the removal of Cd^{2+}, Hg^{1+}, and Pb^{2+}. This is of particular importance because these metals are among the most toxic heavy metals and their removal by CaO is incomplete, especially at near neutral pH (6-8). The three humic acids have an affinity for these toxic ions; therefore, their addition to waste streams containing them is a promising way for effecting almost total removal of these ions from the waste streams.

Lignochemical Na-L is also better than CaO in the removal of Cd^{2+}, Pb^{2+}, and Hg^{1+}. A disadvantage of this reagent, however, is the partial solubilization of Na-L and its sequestrates above pH 7. This makes filtering difficult and reduces the degree of metal ion removal. With Na-L treatment at a pH of 7.5, Hg^{1+}, Fe^{3+}, Al^{3+}, Cr^{3+}, and Pb^{2+} were essentially completely removed (<0.1 ppm), while Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} were 98, 97, 90, 73, 73, and 62 pct removed, respectively. The filtered solution was light brown owing to the partially solubilized Na-L and its sequestrates. Adding 2 g of carbon black adsorbed the organics, cleared the solution, and made the filtration easier. Also, the cleared filtrate contained <0.1 ppm Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+}. Carbon black addition is useful in enhancing the removal of heavy metals with respect to Na-L alone at pH >7.

Reagent H-L also removes heavy metals from solutions; however, because it remains as a solid powder in solution, only the surface functional groups of this reagent can react with the heavy metals. Its capacity for heavy metals per weight added is therefore limited. Adding 10 g of H-L to 50 mL of the 100-ppm solution removed 98, 96, 92, 90, 67, 57, 51, 44, 31, 29, and 18 pct of the Fe^{3+}, Pb^{2+}, Cu^{2+}, Hg^{1+}, Al^{3+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+}, Co^{2+}, and Mn^{2+} ions, respectively.

Although using NaOH for hydrous oxide precipitation was slightly better than CaO addition for Cd^{2+}, Pb^{2+}, and Hg^{1+} removal, it still was incomplete at near-neutral pH.

In general, removal of the other heavy metals by NaOH precipitation was not as good as by CaO precipitation at pH below 7.5. Above pH 7.5, NaOH precipitation was slightly better than CaO precipitation. Both the NaOH and CaO precipitates were gelatinous and voluminous, compared to the humic acid and lignochemical precipitates.

Results of tests with mixed and unmixed lignite humic acid 1 are shown in figure 5 for Pb^{2+}, Zn^{2+}, and Mn^{2+} to illustrate the part residual lignite particles (after humic acid solubilization) take in the removal of heavy metals. Comparison of these curves show that the residual lignite particles do help remove the heavy metals. For example, with 6- and 8-mL additions of the reagent, 47 and 19 pct more Pb is removed by the mixed solution; for 8- and 12-mL additions, 66 and 39 pct more Zn is removed; and for 12- and 14-mL additions, 61 and 52 pct more Mn is removed. Similar differences were obtained for the other eight ions with mixed and unmixed lignite humic acid 1 and for all 11 ions with mixed and unmixed subbituminous coal humic acid 2. Additions of either minus 200-mesh lignite, or subbituminous coal (1 g), without humic acid solubilization removed very little of the heavy metals. Another advantage of these mixed solutions is that
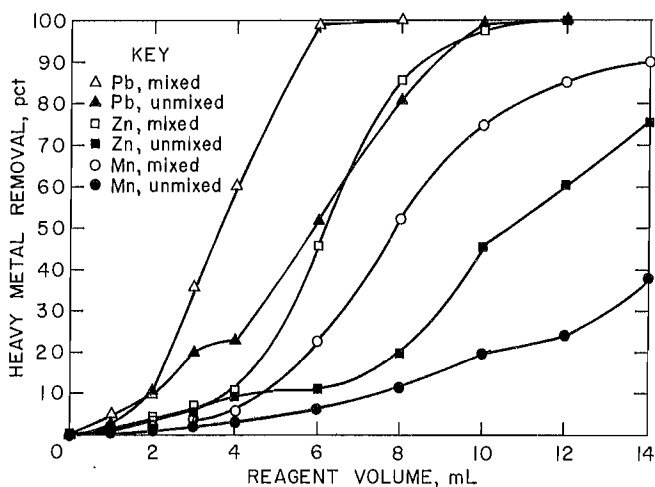

Figure 5.—Results of heavy metals removal with mixed and unmixed lignite humic acid 1 for Pb, Zn, and Mn.

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heavy metal ion removal could be carried out at a higher pH than that for the onset of solubilization of humic acid sequestrates, which, like solubilization of Na-L sequestrates, makes filtering difficult. This is possible because the residual carbon particles adsorb the solubilized sequestrates.

10-PPM SOLUTION

The superiority of humic acids, 1, 2, and 3 and lignochemical Na-L over CaO was also demonstrated by the results on the 10-ppm solution. Figures 6 and 7 show the efficiency of mixed lignite humic acid 1 and CaO,
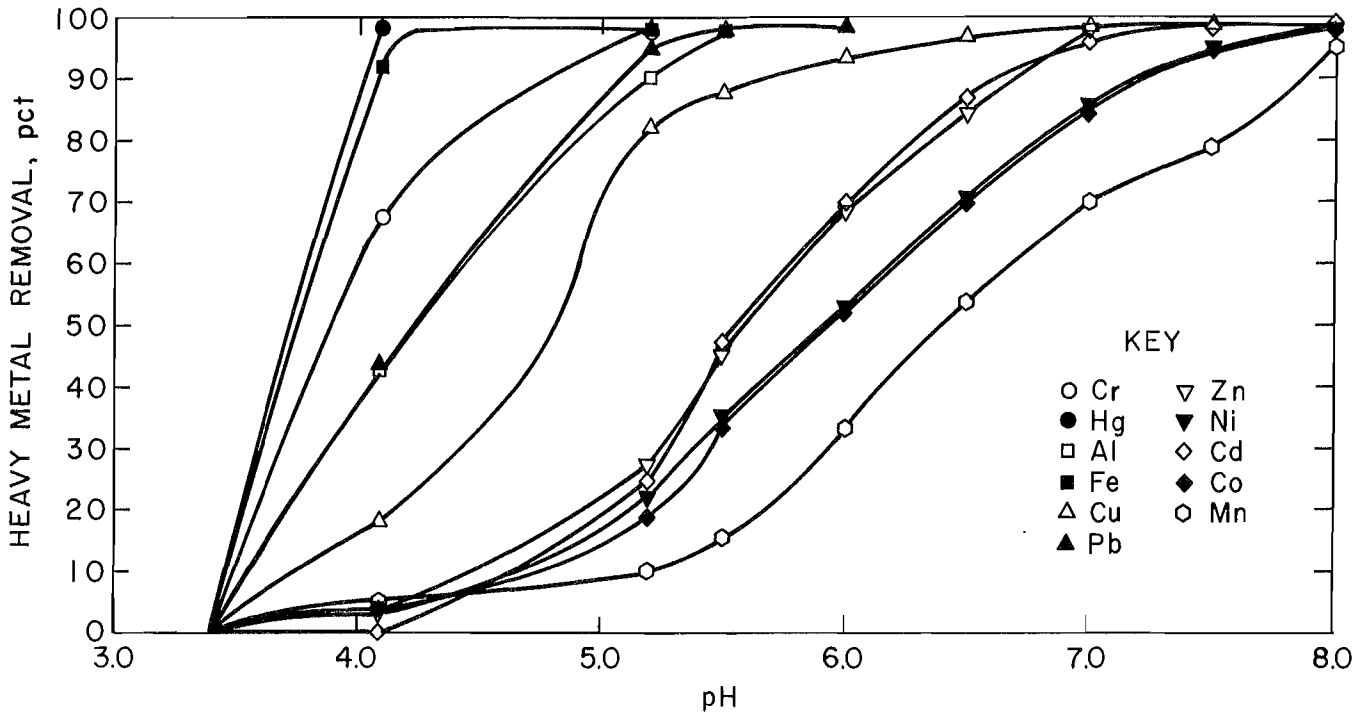

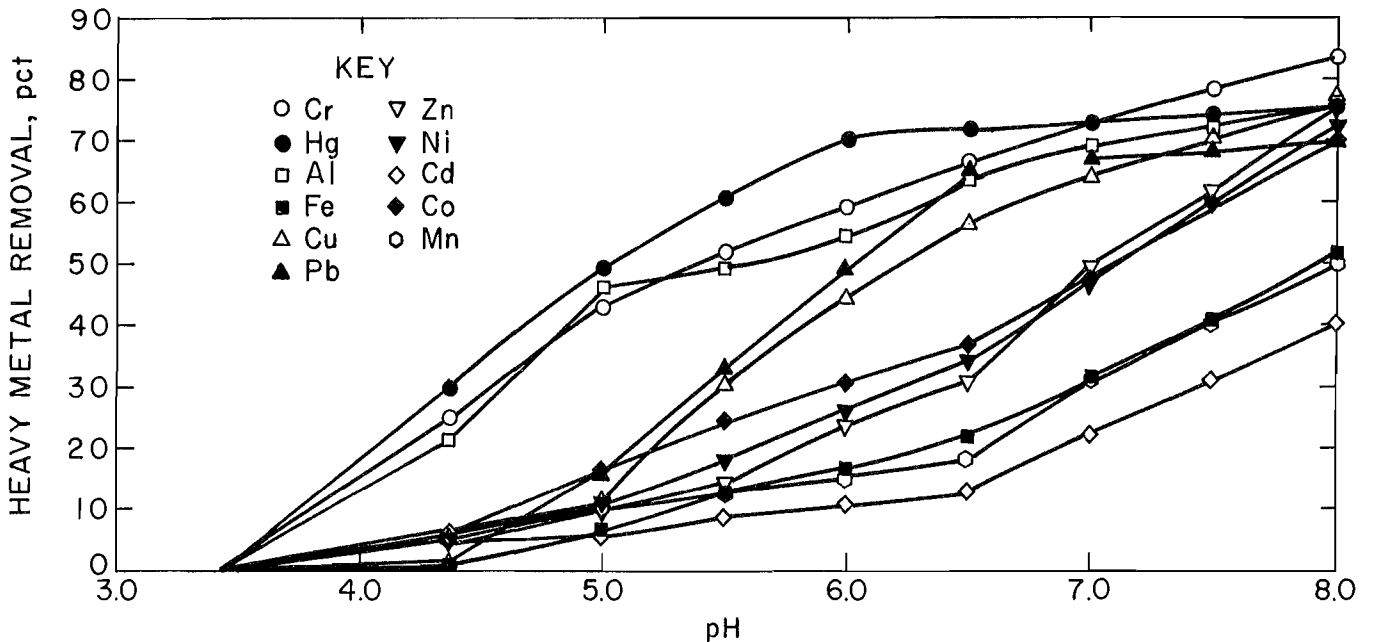Figure 6.—Efficiency of heavy metals removal from 10-ppm solution by mixed humic acid 1.

Figure 7.—Efficiency of heavy metals removal from 10-ppm solution by CaO.

respectively in removing the 11 heavy metals at the 10-ppm level as a function of pH. Table 2 lists the pH at which 90 pct of the respective heavy metals were removed (pH_{90}) for humic acids 1, 2, and 3, CaO, and Na-L. The order of removal with humic acid 1 from the 10-ppm solution is the same as that from the 100-ppm solution, except that Al^{3+} falls between Pb^{2+} and Cu^{2+} instead of between Fe^{3+} and Cr^{3+} and the curves for the diads Cd^{2+}/Zn^{2+} and Ni^{2+}/Co^{2+} are so similar that they are coranked. For humic acid 2 the diads Hg^{1+}/Fe^{3+}, Al^{3+}/Cr^{3+} are coranked in that order, followed by Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}/Co^{2+}, coranked, and Mn^{2+}. For humic acid 3 the ranking is Fe^{3+}, Hg^{1+}, Cr^{3+}, Al^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+}. For Na-L the ranking is Hg^{1+}, Fe^{3+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+}. For CaO at the 50-pct removal level the ranking is Hg^{1+}, Cr^{3+}, Al^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}/Co^{2+}, coranked, Fe^{3+}, Mn^{2+}, and Cd^{2+}.

Mixed lignite humic acid 2 is far superior to CaO in removal of all 11 heavy metals at the 10-ppm level (fig. 6-7, and table 2). Comparison of pH_{90} values for humic acids 2 and 3 to those for CaO shows that humic acids are also far superior to CaO in metal removal at the 10-ppm level. Humic acid 1 is the best reagent for Pb^{2+}, and Cu^{2+} removal and is coranked with humic acid 2 for removal of Hg^{1+}, Cr^{3+}, and Zn^{2+}. Humic acid 2 is best for Cd^{2+}, Ni^{2+}, Co^{2+}, Al^{3+}, and Mn^{2+} while humic acid 3 is the best for Fe^{3+}.

The superiority of the Na-L and all three humic acids over CaO addition in removal of Cd^{2+}, Pb^{2+}, and Hg^{1+} is again demonstrated by the results in table 2.

Lignochemical H-L addition did remove heavy metals, but its capacity was again limited. At the 2-g addition level >99, >98, >98, 96, 82, 80, 79, 76, 65, 55, and 45 pct of the Hg^{1+}, Pb^{2+}, Fe^{3+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}, and Mn^{2+} ions, respectively, were removed. Total ion removal was about 79 pct.

At pH 7 percent removal of Hg^{1+}, Fe^{3+}, Al^{3+}, Pb^{2+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+} was >99, >98, >98, >98, 94, 90, 67, 66, 61, 58, and 32 for Na-L while for CaO it was 73, 32, 69, 67, 73, 64, 50, 23, 48, 48, and 32 thereby indicating the superiority of Na-L over CaO.

WASTE STREAMS

Because the most success in removing heavy metals from the 100- and 10-ppm solutions was achieved with mixed lignite 1 and mixed subbituminous coal 2 humic acids, these reagents were tested on various waste-stream samples.

With both of these reagents the Zn content of the Zn-plating waste stream was reduced from 35 ppm at pH 3 to less than 0.5 ppm at pH 7.5

Mixed lignite humic acid 1 addition reduced the Ni, Cu, and Fe content of the sulfide ore pile runoff from 2.8 ppm, 0.3 ppm, and 0.8 ppm, respectively, at pH 4.0 to 4.5 to <0.1 ppm for all three heavy metals at pH 6.9. Adding mixed subbituminous coal humic acid 2 resulted in a similar decrease in metal content at pH 6.7.

Both humic acid 1 and 2 solutions reduced the Fe content of the mine drainage stream containing 20 ppm Fe, 41 ppm Zn, and 41 ppm Mn at pH 3.2 to less than 0.1 ppm at pH 5.5. Manganese and zinc contents were decreased to less than 0.4 ppm at pH 9.5.

Addition of humic acids 1 and 2 to the other mine-drainage stream, containing 8 ppm Mn, 6 ppm Mo, 6 ppm Fe, 0.6 ppm Zn, and 0.5 ppm Cu at pH 2.9, reduced the Fe, Zn, and Cu content to less than 0.1 ppm at pH 6.5, while Mo removal remained constant at 1.5 ppm (4.5 ppm left in solution) in the pH range 6.5 to 9.5. At pH 9.5, less than 0.1 ppm Mn remained in solution. At pH 4.8, Mo removal was 3.1 and 3.6 ppm (52 and 60 pct), respectively, for the mixed subbituminous coal 2 and mixed lignite 1 humic acids. Since the amount of Mo removed increased at a lower pH for these reagents, further investigation was made with peat humic acid 3 and the lignochemicals, Na-L and H-L.

With peat humic acid 3, 2.7 and 2.4 ppm Mo (45 and 40 pct) were removed at pH's of 3.5 and 4.3,

TABLE 2. - pH values at which 90 pct of heavy metals were removed from 10-ppm solution

(Values in parentheses are extrapolated values)

Heavy metal ion	Humic acid			Lignochemical Na-L	CaO
	Mixed		Unmixed		
	1	2	3		
Hg^{1+}	4.0	4.0	4.3	4.2	>10.0
Fe^{3+}	4.1	4.0	3.9	4.2	8.7
Al^{3+}	5.2	4.8	5.1	5.1	9.5
Cr^{3+}	4.8	4.8	4.7	5.5	8.5
Pb^{2+}	5.1	6.1	5.2	5.5	8.7
Cu^{2+}	5.7	6.2	6.4	7.0	8.7
Zn^{2+}	6.7	6.7	6.8	(7.8)	8.7
Cd^{2+}	6.6	6.2	7.1	(7.8)	9.5
Ni^{2+}	7.2	7.1	7.7	(8.0)	8.6
Co^{2+}	7.3	7.1	7.5	(7.8)	8.7
Mn^{2+}	7.9	7.4	8.0	(>10.0)	8.7

respectively. With lignochemical Na-L, 3.1 and 2.8 ppm Mo (52 and 47 pct) were removed at pH's of 3.4 and 4.7, respectively. With lignochemical H-L, 3.2, 4.5, >5.0, and 4.9 ppm Mo (53, 74, >83, and 82 pct) were removed at pH's of 3.1, 3.4, 3.9, and 4.2, respectively. Very little removal was observed for any other ions in these cases.

These results indicated that it is possible to remove certain heavy metals as anions at low pH levels (2.0 to 4.0).

ADVANTAGES OF HUMIC ACIDS AND LIGNOCHEMICALS OVER LIME

Humic acids and lignochemicals for the most part are superior to CaO for removing heavy metals in the pH range 4.0 to 8.0. They are especially excellent in the removal of the toxic metals, Cd, Hg, and Pb, for which CaO addition is poor to fair in removing.

The precipitates formed between heavy metals ions and either humic acids or lignochemicals are compact and noncolloidal. The volume of their sludge is sharply reduced in comparison to that of finely dispersed CaO precipitates, thereby enhancing their removal by either simple filtration or settling. Lignochemical H-L sequestrates are easier to filter because they are powders.

Although not in the scope of this investigation, it should be possible to recover the metal values sequestered in the humic acids and lignochemicals if desired, in a concentrated form. Since sequestering involves cation-exchange sites, it should be possible to elute them from the precipitates with an appropriate acid.

A typical reaction for precipitating heavy metals with humic acid or lignochemical is

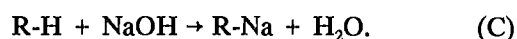$$2R\text{-}Na + Cd^{2+} \rightarrow R_2Cd \downarrow + 2Na^{1+} \qquad (A)$$
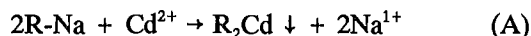
where R is a functional group of the humic acid or lignochemical and R-Na is the sodium salt of that functional group. Elution of the heavy metal should occur by a reaction such as

$$R_2Cd + 2H^{1+} \rightarrow 2R\text{-}H \downarrow + Cd^{2+}. \qquad (B)$$
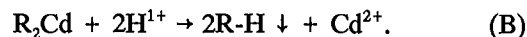
Regeneration of the sodium form of the lignochemical or humic acid is possible by addition of sodium hydroxide

$$R\text{-}H + NaOH \rightarrow R\text{-}Na + H_2O. \qquad (C)$$

Alternatively, if it is not possible or desirable to elute the heavy metals and regenerate the humic acid or lignochemical, the dried, metal sequestrates can be combusted for process heat, since the humic acids and lignochemicals are organic molecules. The heavy metals would be concentrated in the combustion ash for recovery or disposal.

The problems of voluminous amount of sludge, that are hazardous and costly to dispose, and the loss of the metals are solved with lignochemical or humic acid precipitation, followed by either elution and regeneration of the sodium form of the organic molecule, or by combustion of dried precipitates.

With humic acids and lignochemicals anionic forms of heavy metals can be successfully removed at pH 2 to 4. This is not possible with CaO addition.

SUMMARY AND CONCLUSIONS

Humic acids of lignite, subbituminous coal and peat, as well as the sodium or hydrogen forms of lignin can be employed to remove heavy metals from waste streams. Humic acids of lignite and subbituminous coal with suspended, residual coal particles are far superior to CaO addition as a means of heavy metal removal from waste streams, especially at the 10-ppm level. The sodium form of lignin and peat humic acids are comparable or superior to CaO for heavy-metal removal.

The sodium salt of lignin and the humic acids of peat, lignite, and subbituminous coal are excellent for removing the more toxic heavy metal ions, Cd^{2+}, Pb^{2+}, and Hg^{1+}, while CaO addition is poor to fair for their removal. The solubility of the heavy metal sequestrates of the lignin sodium salt at pH 7 makes removal less efficient and

causes difficulty in filtration. This can be circumvented by removing the metals with a combination of the lignochemical and carbon black. The hydrogen form of lignochemical can be employed to remove dilute solutions of heavy metals.

Addition of humic acids of lignite and subbituminous coal to process and mine waste streams resulted in almost complete removal of the heavy metal cations in the pH range 6.5 to 9.5. Efficient removal of molybdenum anions was accomplished with the hydrogen form of lignin at pH below 4.

Precipitates formed by lignochemical and humic acid addition are compact and noncolloidal. The volume of sludge is sharply reduced in comparison to that of the finely dispersed CaO precipitates.

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