REMOVAL OF SELECTED TRACE ELEMENTS FROM ACID MINE DRAINAGE USING EXISTING TECHNOLOGY

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INTRODUCTION

The presence of trace elements in acid mine drainage (AMD) has received little attention in the past; however, recent cognizance has prompted the research community to address the situation. AMD offers a favorable medium for existence of trace elements because many are acid-soluble and are leached from strata associated with the mining process. Some trace elements are on the U.S. Environmental Protection Agency list of Priority Pollutants.

The purpose of this study was to determine the effectiveness of lime neutralization, reverse osmosis, and ion exchange treatment processes in removing several of the trace elements. The study was conducted at the EPA Crown Field Site, which is located near Morgantown, West Virginia. At Crown, appropriate concentrations of trace elements could be injected into a moderately acid AMD stream to simulate the field situation.

The selection of the parameters to be studied and their respective concentrations was made on the basis of levels found in mine discharges. Table I illustrates the matrix of data used in the selection. These choices are summarized in Table II. Eight of the 10 are listed by EPA as toxic substances. For this study the 10 compounds were combined in one concentrated bulk solution and were continuously injected into the AMD feed streams to the neutralization, reverse osmosis, and ion exchange processes to form the desired concentrations. Some precipitation problems were encountered during lab-scale concentrate preparation, necessitating substituting different compound forms of two elements and eliminating lead from the original study list. Table II contains the final choice of compounds.

TREATMENT STUDIES

Background Information

Lime neutralization, reverse osmosis, and ion exchange were studied to determine their effectiveness in removing the 10 trace elements of interest. EPA awarded a contract to Hydroscience, Inc., a subsidiary of Dow Chemical, to provide analytical services for the trace element analyses and to provide technical assistance. Most of the work summarized in this paper was excerpted from an upcoming final report by Wilmoth, Scott, Hall, and Stuewe, which will be published early in 1979. EPA Methods were

Table I. Selected Mine Drainage Analyses

	Pollutant Source														
	Iron Ore[a]	Copper	Lead/ Zinc	Lead/ Zinc	Gold	Silver	Bauxite	U/Ra/V	Platinum	Coal Mining Maximum[d]	Coal Mining Mean[d]	AMD[b]	AMD[c]	Crown AMD	Chosen Levels
pH	5	3.5	8.1	3.0	6	8	2.8				2.4	2.8	2.6	5.0	5.0
Ag															
Al							88	0.5		530	43	62	240	15	15
As					0.08			0.03				22	0.9		2.0
B		2.0			0.2	0.1			0.01						1.0
Be								0.01							
Ca	260				87	45		120	95					370	370
Cd		1.3	0.02	0.06	0.03							1.0	0.9		1.0
Chl	120		57	220	1.8	1.2			0.160						10
Co		2.0													1.0
Cr	0.01		0.4												0.4
Cu	1.0	90		0.04	0.05							128	18		5.0
Cyn	0.02														0.5
Fe	180	2000		2.5	25	2.0	64	15	0.3	9300	350	800	640	300	300
Fluoride			1.2	0.8	2.1	0.3	0.6		3.2						2.0
Hg	2.0	0.07				0.002									0.5
K					44	15			13						10
Mg	120				80	32		45	26					110	110
Mn	18	100		57	12	6.3	7.7	0.3		92	7.3	19	9.0	6	6.0
Na	15				80	12			140					480	480
Ni	0.1	0.2			0.1	0.09	0.3			5.6	0.7	0.5	0.5		0.5
P		0.15		0.08											1.0
Pb	0.1		4.9	0.3	0.8	0.2			0.01			0.5	0.9		1.0
Sb															
Se		0.04				0.13			0.8						0.8
SO_4			63	780	1200	340	890		270	9700	2400	3800	3310	3000	3000
Sr		120			0.8										1.0
Te		0.6			0.1										0.5
Ti								1.1							1.0
Zn	8.0		0.7	38	7.3		0.8	0.03	0.03	13	1.5	250	23		5.0

[a] Development Document for Interim Final and Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Ore Mining and Dressing Industry.

[b] Ross, Laurence W., Removal of Heavy Metals from Mine Drainage by Precipitation, EPA Report 670/2-73-080, September 1973, Washington, D.C.

[c] Miller, Ian D., Removal of Dissolved Contaminants from Mine Drainage.

[d] Development Document for Interim Final Effluent Limitations Guidelines and New Source Performance Standards for the Coal Mining Point Source Category.

Table II. Selected Pollutants and Desired Concentration for Treatability Study

Pollutant	Concentration (mg/l)	Compound Used
Arsenic	2.0	Arsenic pentoxide
Boron	1.0	Boric acid
Cadmium	1.0	Cadmium sulfate
Chromium	0.4	Chromium chloride
Copper	5.0	Chromium chloride
Mercury	0.5	Mercuric chloride
Nickel	0.5	Nickelous sulfate
Phosphorus	1.0	Sodium phosphate
Selenium	0.8	Selenious acid
Zinc	5.0	Zinc chloride

Table III. Crown AMD Water Quality Data, 9/19/77 Through 10/12/77

Parameter	Unit	Mean	Maximum	Minimum	Standard Deviation
pH	pH	5.2	5.6	4.7	0.21
Specific Conductance	µmhos/cm	2610	2950	2300	153
Acidity as $CaCO_3$	mg/l	440	660	300	82
Calcium	mg/l	350	390	310	18
Magnesium	mg/l	100	110	90	5.3
Total Iron	mg/l	160	200	130	14
Ferrous Iron	mg/l	150	200	130	15
Sodium	mg/l	350	410	300	20
Aluminum	mg/l	6.6	14	2.5	2.5
Manganese	mg/l	5.0	6.2	3.7	0.46
Sulfate	mg/l	2380	2660	2180	104
Alkalinity	mg/l	26	55	0	13
Total Dissolved Solids	mg/l	3350	3640	3110	124

used for all the metal determinations. The EPA Methods manual requires samples preservation with nitric acid; however, it was later discovered that nitrates interfere with the determination of boron and much of the boron data was lost in this manner. Typical characteristics for the Crown AMD are presented in Table III.

The desired level of the spiked trace elements in the AMD is compared in Table IV with those actually achieved. The desired levels conformed very well to the achieved level for all parameters except phosphorus. Extremely high variations in phosphorus content were observed in the raw AMD and remain largely unexplained. The phosphorus variation was prominent only during the neutralization phase of the study when influent values above 40 mg/l were observed.

Lime Neutralization

Lime neutralization represents the Best Practical Technology (BPT) for acid mine drainage treatment. A schematic of the lime neutralization process utilized at the Crown facility is shown in Figure 1. The neutralization system consists of two identical treatment processes that operated at 0.9 liter/sec AMD flow each. Twin chemical metering pumps injected 100 ml/min each of bulk trace element solution into the separate treatment lines to achieve the desired final concentrations shown in Table II. The lime neutralization process investigated trace element removal effectiveness as a function of pH. Two pH levels were studied at one time. Approximately seven days were required to characterize a particular pH level (*i.e.*, two days to achieve equilibrium and five days data collection). The study spanned pH levels in single pH increments between pH 7 and pH 12.

A coagulant (Dowell M-144 anionic type) was injected into each flow stream just prior to the clarifier at approximately a 5 mg/l rate to achieve optimal clarifier performance. Samples included raw AMD, spiked AMD A, spiked AMD B, product A, and

Table IV. Trace Element Levels in Spiked Acid Mine Drainage (mg/l)

Element	Desired Level	Actual Level Achieved (Means) Lime Neutralization	Reverse Osmosis	Ion Exchange
Arsenic	2.0	1.96	2.29	2.47
Boron	1.0	2.36	2.01	2.38
Cadmium	1.0	0.90	0.83	0.94
Chromium	0.4	0.54	0.54	0.62
Copper	5.0	5.30	6.18	7.27
Mercury	0.5	0.50	0.28	0.72
Nickel	0.5	0.66	0.74	0.86
Phosphorus	1.0	9.83	1.50	1.47
Selenium	0.8	0.94	1.17	1.34
Zinc	5.0	5.65	6.25	7.44

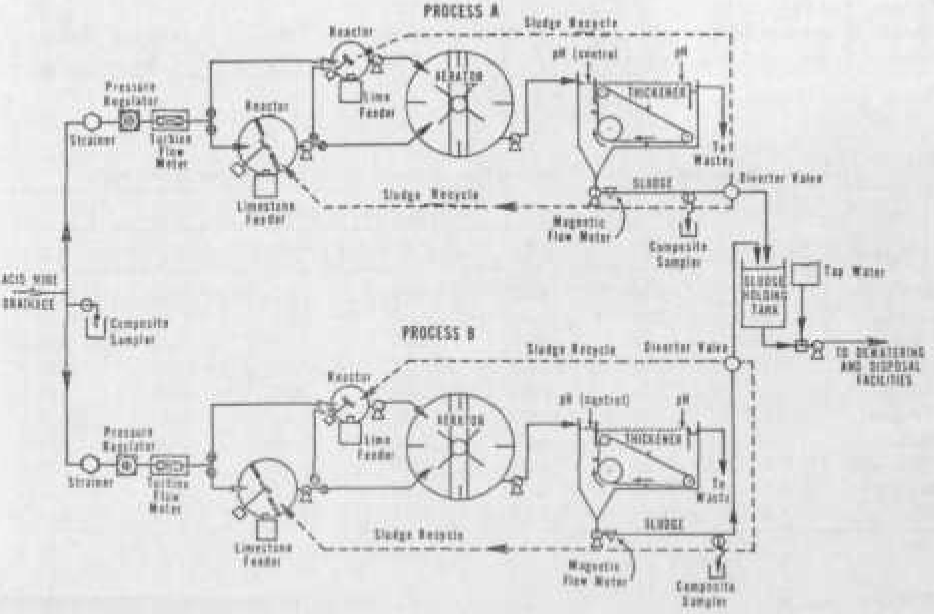

Figure 1. Schematic flow diagram for the EPA neutralization facility.

product B, sludge A, and sludge B. These samples were collected automatically by composite samplers. Samples were sent for analysis twice per day for a daily total of 14 separate samples from both processes, and 168 samples from the entire neutralization study.

The operational data are summarized in Table V as a function of pH and indicate normal trends except for slightly high lime usage at pH 9. These sorts of anomalies are not unusual for neutralization processes applied to AMD treatment.

Analyses for the trace elements are summarized as a function of pH in Table VI. Significant removals were observed for all elements except boron and phosphorus. The inability to remove phosphorus below the levels observed was very unexpected. Phosphorus removal by lime addition is state-of-the-art technology in tertiary sewage treatment systems.

Table V. Neutralization Data Summaries for Trace Element Study

Item	Mean Value					
Effluent, pH	7.0	8.0	9.1	10.1	11.0	12.1
Neutralizer Usage, kg/cu m	0.28	0.43	0.82	0.85	0.91	2.63
Neutralizer Usage, lb/1000 gal	2.3	3.6	6.8	7.1	7.6	22
Neutralizer Usage, g/cu m/ppm Influent Acidity	0.6	1.2	2.1	1.8	2.0	5.4
Cost, cents/1000 gal[a]	4.1	6.3	12	12	13	39
Cost, cents/cu m	1.1	1.7	3.1	3.3	3.5	10
Cost, cents/10^3 cu m/ppm Influent Acidity	2.4	4.4	8.0	7.0	7.7	21
Utilization Efficiency, %	132	71	39	45	44	51
Stoichiometric Factor Influent Acidity	0.8	1.5	2.8	2.5	2.7	7.3
Sludge to Waste, % of Influent AMD	10	8.7	10	9.7	10	14
Dry Solids to Waste, lb/1000 gal	9.9	4.6	18	8.7	13	17
Dry Solids to Waste, kg/cu m	1.2	0.5	2.1	1.0	1.6	2.0
Underflow Solids, %	1.2	0.6	2.1	1.1	1.5	1.5
Effluent Turbidity, JTU	24	11	10	7	7	3
Reactor Suspended Solids, mg/l	380	530	1130	1310	1440	2500
Effluent Suspended Solids, mg/l	25	12	24	12	15	15

[a] Lime cost $38.58/tonne ($35.00/ton).

Table VI. Summary of Lime Neutralization Effluent Trace Element Analyses (mg/l)

		Nominal pH of Effluent					
Element	Influent	7	8	9	10	11	12
Arsenic	1.96	0.10	0.05	0.04	0.02	0.03	0.02
Boron	2.36	2.25	–	–	1.68	1.90	1.45
Cadmium	0.90	0.18	0.06	0.02	0.01	0.01	0.003
Chromium	0.54	0.04	0.07	0.07	0.06	0.05	0.04
Copper	5.30	0.30	0.16	0.11	0.05	0.06	0.08
Mercury	0.50	0.02	0.01	0.01	0.01	0.02	0.01
Nickel	0.66	0.34	0.18	0.06	0.06	0.06	0.06
Phosphorus	9.8	3.81	2.67	2.30	2.88	3.56	1.09
Selenium	0.94	0.05	0.06	0.16	0.28	0.39	0.15
Zinc	5.65	1.01	0.23	0.11	0.08	0.13	0.06

Reverse Osmosis

A Universal Oil Products spiral-wound type reverse osmosis unit (Figure 2) with a capacity of 15 cu m/day (4000 gpd) of product flow was studied in a one-day test. The unit operated at 35.15 kg/sq cm (500 psi) to achieve optimal rejection characteristics, at a moderate recovery rate (40%) to prevent fouling interferences with rejection ability, at a minimum 10:1 brine:product flow ratio to prevent boundary layer problems, and with sulfuric acid injection to control iron precipitation.

Operational parameters for the study are presented in Table VII. Although the system was on-stream for several days, all of the water samples were collected on a grab-sample basis throughout one day's operation. Four grab-samples were taken per data set (*i.e.*, raw AMD, spiked AMD, product, and brine). Ten sets of samples (40 samples total) were collected.

A summary of chemical data is presented in Table VIII. Since reverse osmosis product quality is not directly related to ion solubility, rejection rate or precent removal calculations are appropriate. As seen in Table VIII, the rejections were below

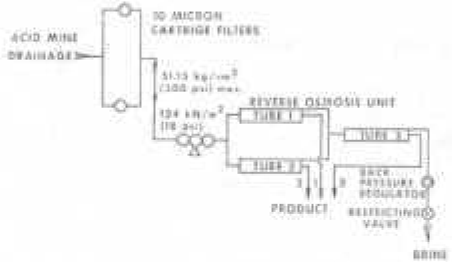

Figure 2. Flow diagram for 4K spiral-wound reverse osmosis unit.

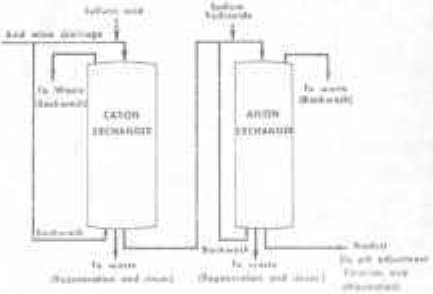

Figure 3. Schematic flow diagram of EPA 2-resin ion exchange unit.

Table VII. Mean Operating Parameters for Crown Spiral-Wound Reverse Osmosis Study

Parameter	Value
AMD Feed Flow, liter/sec	0.65
Product Flow, liter/sec	0.25
Brine Flow, liter/sec	0.40
Water Recovery, %	38
Feed Pressure, kg/cm^2	35.50
Feed Temperature, $^\circ$C	15.5
Tube One Flux, liters/m^2/day @ 35.15 kg/cm^2 and 25°C	616
Tube Two Flux, liters/m^2/day @ 35.15 kg/cm^2 and 25°C	600
Tube Three Flux, liters/m^2/day @ 35.15 kg/cm^2 and 25°C	587

Table VIII. Summary of Reverse Osmosis Trace Element Analyses

	Concentration (mg/l)			Rejection
Element	Spiked Feed	Product	Brine	(%)[a]
Arsenic	2.29	0.01	3.58	99.6
Boron	2.01	0.88	3.08	56.2
Cadmium	0.83	0.003	1.22	99.6
Chromium	0.54	0.01	0.82	98.1
Copper	6.18	0.01	9.12	99.8
Mercury	0.28	0.06	0.17	78.6
Nickel	0.74	0.01	1.10	98.6
Phosphorus	1.50	0.32	1.93	78.7
Selenium	1.17	0.11	1.83	90.6
Zinc	6.25	0.06	9.63	99.1

[a] Rejection equals feed concentration-product concentration/feed concentration x 100.

80% for boron, mercury and phosphorus and were above 90% for the remainder of the elements. Material balances of the system were satisfactory (within 15% indicated gain or loss) for all elements except mercury where 56% of the indicated influent failed to exit the system. It was postulated by Stuewe and Hall that the mercury was precipitated upon contact with the sulfuric acid pretreatment injection and was collected on the filters in front of the reverse osmosis unit and/or on the membranes. Tests to investigate this confirmed the presence of mercury on the filters. No analyses were made of the membrane.

Ion Exchange

A two-resin ion exchange unit (Figure 3) was studied for effectiveness of trace element removal in a one-day test. The ion exchange system, which operates at 40-liter/min (10.5 gpm) product flow rate was being regenerated at high dosage rates to achieve minimum leakage cation rates. The intended regeneration dosage for the cation column was 144 grams of sulfuric acid per liter of resin; for the anion column, the intended dosage was 64 grams of sodium hydroxide per liter of resin. Six grab samples (raw AMD, spiked AMD, cation effluent, anion effluent, cation regenerant, and anion regenerant) were taken per data set. Eight sets of samples were taken during the one-day study period for a total of 48 separate samples from the test. Detailed design specifications for the two-resin unit are given in Table IX. The two-resin system operates with a strong-acid cation resin that exchanges H^+ ions for the cations (arsenic, cadmium, chromium, and etc.) in the AMD. The effluent from the cation column becomes mostly sulfuric acid since the predominant anion in the AMD is sulfate. This solution of H_2SO_4 then enters the weak-base resin column where the acid is adsorbed by the weak-base resin.

The actual operating parameters for the unit during the test study are presented in Table X. Cost of regenerant chemicals alone for this study were $9.70 per 1000 gallons, illustrating that the unit was operated in the mode optimum for effluent quality and not optimum for cost/effectiveness. Regenerant utilization efficiencies for the sulfuric acid and sodium hydroxide were 22 and 42% respectively.

The ion exchange product quality data have been summarized along with those from the neutralization and reverse osmosis processes in Table XI for ease of process comparison. Interestingly, phosphorus was not removed by the ion exchange process.

In summary, as seen in Table XI, the neutralization process appeared to be the logical process choice, because of cost, for trace material removal for all the elements studied except boron and phosphorus. None of the three processes were effective on boron and phosphorus. Although ion exchange and reverse osmosis were slightly more effective overall than lime neutralization, the cost of the processes and need for subsequent waste treatment offset their slight advantage in removal effectiveness.

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Table IX. General Design Specifications for EPA Ion Exchange Treatment Unit (Two-Resin System)

	Cation Exchanger	Anion Exchanger
Type	Strong acid	Weak base
Resin	Duolite C-20	Dowex WGR
Volume of resin, cu m	0.93	0.54
Approximate tank size, cm	91 x 213	76 x 213
Approximate tank area, sq m	0.65	0.45
Service flow rate, liter/min	40	40
Service flow rate, liter/min/cu m	43	74
Service flow direction	Downflow	Downflow
Backwash flow rate, liter/min	115	100
Backwash flow rate, liter/min/sq m	180	190
Backwash flow direction	Upflow	Upflow
Bed expansion during backwash, %	50	75
Regenerant flow rate, liter/min	100	40
Regenerant flow rate, liter/min/sq m	150	90
Regenerant flow rate, liter/min/cu m	110	74
Regenerant flow direction	Downflow	Downflow
First rinse flow rate, liter/min	100	40
First rinse flow rate, liter/min/cu m	110	90
First rinse flow direction	Downflow	Downflow
Second rinse flow rate, liter/min	115	100
Second rinse flow rate, liter/min/cu m	120	190
Second flow direction	Downflow	Downflow
Regenerant	Sulfuric acid	Sodium hydroxide
Regenerant concentration, % by weight	2	3 to 5

Table X. Ion Exchange Operating Parameters

	Cation	Anion
Regenerant	H_2SO_4	NaOH
Bulk regenerant cost, cents/kg	7.72	11.0[a]
Bulk solution concentration, weight %	93	20
Desired regenerant concentration, weight %	2.0	4.0
Desired dosage, grams of regenerant/liter of resin	144	64
Desired dosage, lb of regenerant/cu ft of resin	9	4
Influent load, milligrams/liter as $CaCO_3$	2450	2650
Effluent load (leakage), milligrams/liter as $CaCO_3$	200	0
Effective removal, milligrams/liter as $CaCO_3$	2250	2650
Number of regeneration cycles during this test	5	5
Average actual dosage, grams of regenerant/liter of resin	140	61
Average actual regenerant concentration, % by weight	2.0	3.8
Exchanger capacity, grams/liter of resin as $CaCO_3$	30.8	36.1
Exchanger capacity, kilograms/cu ft of resin as $CaCO_3$	13.4	15.8
Regenerant utilization efficiency, %	22	42
Regenerant cost, cents/cu m	93	110
Regenerant cost, cents/1000 gal	350	420
Total volume to waste, liter/regeneration	10650	3200

[a] Price of 50% concentration and diluting on-site to 20%.

Table XI. Summary of Optimum Removal of Trace Element Pollutants

Pollutant	Typical Influent Concentration (mg/l)	Optimum Effluent Concentration (mg/l)			
		Lime Neutralization		Reverse Osmosis	Ion Exchange
		pH 7-9 Range	pH 10-12 Range		
Arsenic	2.3	0.04 @ pH 9	0.02 @ pH 12	0.01	0.52
Boron	2.2	2.25 @ pH 7	1.45 @ pH 12	0.88	0.6
Cadmium	0.9	0.02 @ pH 9	0.003 @ pH 12	0.003	0.001
Chromium	0.06	0.04 @ pH 7	0.04 @ pH 12	0.01	0.01
Copper	6.2	0.11 @ pH 9	0.05 @ pH 10	0.01	0.03
Mercury	0.5	0.009 @ pH 9	0.009 @ pH 10	0.06	0.001
Nickel	0.7	0.06 @ pH 9	0.06 @ pH 10	0.01	0.02
Phosphorus	1.5 to 10	2.3 @ pH 9	1.09 @ pH 12	0.32	no removal
Selenium	1.2	0.05 @ pH 7	0.15 @ pH 12	0.11	0.09
Zinc	6.3	0.11 @ pH 9	0.06 @ pH 12	0.06	0.03