CATION EXCHANGE AND HIGH ALKALINE MINE WATER A CASE STUDY

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ABSTRACT

Two abandoned underground mining areas and seepage from a coal refuse impoundment are currently producing high alkaline drainage. The highly alkaline water is unexpected at the locations, and could not have been predicted by acid base accounting or leach column testing.

Laboratory testing has indicated that the Meigs thickener underflow has significant cation exchange capacity. Laboratory testing was conducted to measure the release of sodium, potassium, and magnesium from Meigs thickener underflow in a calcium chloride solution vs time. Laboratory testing was also conducted to measure the cation exchange of Meigs thickener underflow at different solution pH levels.

Cation exchange is believed to be very significant in the prediction of acidic drainage at the sites studied. The data suggests that the weathering of the shale and claystone results in fine particle size that has significant cation exchange capacity. The cation exchange capacity of the clay in the coal refuse results in the removal of calcium from solution and increases the alkalinity of water that is in the presence of calcium carbonate.

The presence of anoxic or low dissolved oxygen conditions is also believed to be important in the formation of the high alkalinity.

The occurrence of high alkaline drainage in areas that are predicted to be highly acidic indicates that more is involved in acidic generation than can be explained by column leach tests and acid baseaccounting.

The prediction and control of the high alkaline process could result in significant **advantages** in treatment options for refuse areas and abandoned portions of active and abandoned underground mines.

Introduction

Abandoned sections of two underground coal mines, located in Southeastern Ohio and West, Virginia, have recently produced alkaline drainage. Both mines have ,areas of limestone that are in contact with acidic drainage.

Two drains in the Meigs Slurry Impoundment, located in Southeastern Ohio are producing net alkaline drainage.

The mine drainage and the seepage have zero or low concentrations of dissolved oxygen.

A complete water analysis was conducted from the alkaline drainage. A complete analysis of the water can be helpful to describe what has occurred in the generation of the water.

			Water Samples				
			1	2	3	4	5
Alkalinity	$CaCO_3$	mg/L	186	541	781	1,000	722
Aluminum	Al^{+3}	mg/L			0.74	0.09	
Calcium	Ca^{+2}	mg/L	191	535	399	400	205
Ferrous Iron	Fe^{+2}	mg/L	0	265	125	200	2.6
Ferric Iron	Fe^{+3}	mg/L	0.1	0.0	11.0	0.0	28.3
Magnesium	Mg^{+2}	mg/L		104	91.8	180	39.7
Manganese	Mn^{+2}	mg/L	0.83	3.30	4.15	1.50	1.99
Potassium	K^{+1}	mg/L	15.3		34.7	32.0	13.0
Sodium	Na^{+1}	mg/	1,210	2,330	1,720	1,700	771
Bicarbonate	HCO_3-1	mg/L	113	330	476	610	440
Chloride	Cl_{-1}	mg/L	406	760	1'83	710	121
Sulfate	$S04^{-2}$	mg/L	2,470	5,500	5,410	5,445	1,280
Silicon	$Si03^{-2}$	mg/L			4.1	6.9	8.2
TDS		mg/L	4,420	9,822	12,000	9,696	2,812
% Accounte d			99.7	100	87.1	95.7	103
Ratio meq Na^{+1} / meq Cl^{-1}			4.60	4.73	31.35	3.69	9.83

Sample #1 Meigs Mine #31 Impoundment Discharge 3/18/98
Sample #2 Meigs Mine #31 Impoundment Upstream Drain 5/5/95
Sample #3 Meigs Mine #31 Impoundment #3 Lateral Drain 5/18/98
Sample #4 Pittsburgh #8 abandoned mine section 6/29/94
Sample #5 Meigs Mine #31, 4 South Seals (A Block) 5/17/96
Meigs Coal Refuse Impoundment (Samples 1, 2, and 3)

High alkaline seepage is present at the Meigs Coal Refuse Impoundment. The impoundment #3 lateral drain is highly alkaline and the upstream french drain is net alkaline, The source of the majority of the seepage is from the water in the impoundment.

The increase in the sodium and alkalinity from the water in the impoundment to the water from the drains, in the dam, suggests that cation exchange has influenced the alkalinity generation.

The surface drainage at the refuse dam is not alkaline like the seepage but is highly acidic in nature.

The Meigs Preparation Plant receives raw coal from Mine #31 and from Mine #2. Both mines are in the Clarion 4A seam, which was formed in a near marine environment. Limestone is immediately above the coal at Mine #31 but is not immediately above the coal at Mine #2.

Acid base accounting of the coal refuse indicates that the refuse would be expected to generate acidic drainage. A sample of the coal refuse was analyzed for pyritic sulfur in January 1984. The results of the analysis is as follows:

	Fine Refuse	Coarse Refuse
Potential Acidity	75.3	208.8
Neu lization Potential	36.98	45.57
% Pyritic Sulfur	2.41	6.68

Potential acidity and neutralization potential are in tons CaC03 equivalent per 1,000 tons of refuse.

Abandoned Section of Pittsburgh Number Eight Coal Mine (Sample #4)

The room and pillar mining was conducted in the Pittsburgh Number Eight Coal Seam. During mining the water pumped from active sections was highly acidic. Mine water collected from various sources since closure has also indicated highly acidic water in portions of the mine. The quality of mine water emanating from mines in the same coal seam were acidic in nature after closure.

Large portions of the old works have limestone in the mine roof. Shale roof falls to the limestone strata which results in mixing the acidic drainage with the limestone. The roof falls result in restricted air flow to various portions of the abandoned mine. Water flow in the mine is over and through the fallen weathered shale. The weathered shale is believed to have an influence on the cation exchange.

Concentrations of hydrogen sulfide are present in the. raw mine water. The hydrogen sulfide provides evidence of anaerobic conditions in the mine,

The high concentration of sodium (1,700 mg/L as Na+,) in the water suggests that ion exchange has occurred. Cation exchange would be expected to have resulted in reductions in the soluble calcium concentrations and increases in alkalinity.

The high concentration of sulfate (5,445 mg/L as SO, $_{-1)}$ in the water suggests the occurrence of acid generation. The iron concentration is however much lower than what would be expected from the high sulfate levels. The iron level has been reduced from the original pyritic oxidation levels.

Meigs Mine # 31 A Block (Sample #5)

The second underground mine producing high alkaline water is Meigs Mine #3 1. The A Block mining was completed in approximately September 1994. The area seals were completed in March 1995 and water from a previously abandoned portion of the mine was allowed to flow into the now sealed A Block. The water from the abandoned mine was acidic during mining.

The A Block has a limestone roof, and substantial quantities of carbon dioxide were observed while the area was active. The limestone roof subsided and fractured following longwall mining. Ile natural slope of A Block results in a significant portion of the limestone roof being under water. Water from the abandoned portion of the mine flows into the sealed section and flows through the fractured limestone before it is released from the sealed area. Short circuiting of this mine drainage is eliminated because of the routing of the water into A Block.

The Meigs Impoundment receives thickener underflow from the preparation plant, sludge from the Mine #2 water treatment facility, and large flows of caustic neutralized water from water treatment facilities at Mine # 31 and Mine # 2. The solids settle in the impoundment and the water is either discharged or recycled to the mine and preparation plant. The water that is discharged from the impoundment complies with or surpasses all environmental or regulatory permit standards.

The A Block mine drainage has an alkalinity of 722 mg/L (CaC03), an iron of 30.9 mg/L (Fe) and a manganese of 1.99 mg/L (Mn). The alkalinity of the impoundment water increased during the sealing of the A Block from approximately 70 mg/L to approximately 200 mg/L (CaC03) . The sodium concentration indicates that cation exchange has taken place.

The pH set point at the water treatment facility has been reduced since the increase in alkalinity was realized. Substantial reduction in reagent use has,resulted since the increase in alkalinity from A Block. The manganese concentrations remained low following the reduction of pH set point.

High Alkaline Water Chemistry

The water chemistry in an anoxic, reducing mine drainage is significantly different from the water chemistry that is present in water that contains significant dissolved oxygen concentrations and is exposed to the atmosphere.

The elevated partial pressure of CO, in the mines and seepage creates carbonic acid, which drives the dissolution of limestone and raises the alkalinity of the mine water. The neutralization of acidic drainage with calcium carbonate will result in the increase of the partial pressure of CO, if the water is isolated from the atmosphere. Lab tests however indicate that the measured concentrations of alkalinity are however higher than what would result from simply the neutralization of low pH water flowing into A Block.

Computer simulations with MINTEQA2 indicate that the highly alkaline water results in iron and manganese removal in mineral phases that are normally not possible with conventional surface water neutralization.

Siderite FeCO,(s) frequently controls the solubility of Fe*2 in anoxic alkaline water. (Stumm and Morgan 1996)

Once the partial pressure of C02 is established for a given water, then the alkalinity of that water is also determined as "follows:

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2CO_3$$

$$[H_2CO_3]\ Kh * PCO_2$$

$$[H_2CO_3] = K1\ [H_2CO_3^*]\ /\ [H^+]$$

$$[CO_3^{-2}] = K2 * [HCO_3^{-1}]\ [H^+]$$

$$\text{Alkalinity} = 50{,}000 * (\ [HCO_3^{-1}] + 2 * [CO_3^{-2}] + [OH-] - [H^+])$$

The above equations define the chemical equilibrium of a simple solution of calcium carbonate solids, and water in a CO_2 atmosphere.

Equilibrium concentrations of pH and alkalinity ($CaCO_3$) can be calculated for a given water from the above equations for any partial pressure of CO_2. (Frear and Johnston 1929) The calculations clearly indicate that even small increases in the partial pressure Of CO_2 can result in significant increases in alkalinity.

The elevated CO_2 partial pressure in the underground mine water and the impoundment seepage gives the water the ability to dissolve more calcium carbonate (limestone) and thereby raise the alkalinity of the water.

High sulfate concentrations will complex with some of the free calcium and magnesium in solution. The calcium complex reduces the free calcium in solution and results in an increase in the alkalinity of the solution.

Several references indicate that naturally occurring high alkaline water can be generated by neutralization of acidic drainage by insitu limestone and cation exchange. Foster demonstrates that naturally occurring high bicarbonate groundwater is the result of the action of limestone dissolution and cation exchange in elevated partial pressures of CO 2. Chemical Evolution of Natural Groundwater" describes the existence of groundwater with naturally occurring elevated concentrations of sodium and bicarbonate being the result of combined effects of cation exchange and calcite or dolomite dissolution.

Theodore Weaver, Robert Hedin, and Rosemary Capo document the existence of numerous large flow alkaline discharges from abandoned coal mines. The alkaline discharges are accompanied by large concentrations of sodium. The sodium concentrations suggest that cation exchange reactions, involving associated overburden, were involved.

Cation exchange of clays and silt result in the removal of calcium (and other ions) from solution and the addition of sodium (or other ions). It replaces the sodium that is associated at the surface of the clay particle with calcium and other cations that are in solution. The decrease in the calcium allows additional calcium carbonate to be dissolved and therefore an increase in the solution alkalinity.

The Clarion 4A coal was formed in a near marine environment. The clay particles that formed the claystone bottom and the shale that later formed the top would be expected to have been saturated with sodium. The weathering of the claystone and shale results in a generation of the original sodium saturated clay.

The existence of cation exchange is indicated by the presence of sodium concentrations in excess of the levels of sodium that can be explained by the chloride that is in solution.

Dissolved metals normally represent the major source of acidity in acidic mine drainage. A reduction in the dissolved metals will therefore result in a reduction in the mine drainage acidity. Dissolved metals can be reduced by cation exchange, formation of carbonate precipitates, and the formation of sulfide precipitates.

Laboratory Tests

A. High Partial Pressures of CO,

Laboratory tests were conducted to show the importance of high partial pressures of C02. An alkalinity of 800 mg/L as CaCO, was generated in the tab from a sample of deionized water and lab grade calcium carbonate that was mixed for 72 hours in a high CO, atmosphere. An alkalinity of 30 mg/L as CaCO, was generated in the lab from a sample of deionized water and lab grade calcium carbonate that was mixed for 72 hours in a beaker open to the atmosphere.

B. Cation Exchange

All of the fine refuse from the raw coal of Mine #31 and Mine #2 in The Meigs Coal Preparation Plant reports to the thickener. The cation exchange capacity of the Meigs Preparation Plant thickener underflow at a pH of 7.0 was measured at 11.8 meq/100 gram (271 mg sodium/100 gram). The data indicates that the cation exchange capacity is significant.

The pyritic sulfur of the Meigs thickener underflow was measured at 2.49%. The pH of the thickener underflow was measured at 8.22 S. U.

The Meigs thickener underflow typically contains refuse particles less than 28 mesh or 592 micron. The particle size distribution of the thickener underflow was measured using a Microtrac particle analyzer. The results indicate that 2 1 % of the particles are 96 to 704 micron in size, 46% of the particles are 6 to 96 micron in size and 33% of the particles are 0.2 to 6 micron in size.

Major Constituents of Meigs Thickener Underflow 6/11/98

Parameters	dry weight **basis**
Silicon Dioxide, SiO_2	30.4
Aluminum Oxide, Al_2O_3	15.6
Iron Oxide, Fe_2O	4.1
Titanium Dioxide, TiO_2	1.0
Calcium Oxide, CaO	2.2
Magnesium Oxide, MgO	0.5
Sodium Oxide, NaO	0.3
Potassium Oxide, K_2O	1.4

Sulfur Trioxide, SO_3	8.6
Organic Carbon, C	29.3
Carbonate Carbon, CO_2	2.7
Net Ignition Loss/Gain	5.1
Total	101.2

The release of cations from the thickener underflow was measured at various time intervals. An initial dried sample was leached with water to remove any dissolved cations. The sample was then put in contact with 0. 1 N calcium chloride (CaCl,). The results are reported below:

	Na	K	Mg
2 Hour	730	99.1	12.9
24 Hour	746	140.4	14.8
48 Hour	784	184.2	16.1
96 Hour	795	208.5	17.3

All results mg/L per 100 grams of sample

The variation of cation exchange with respect to changes in pH was also measured.

pH	meq / 100 grams sample
4	9.9
5	12.0
6	12.7
7	11.8
8	12.2
9	11.2

We had expected to see a larger drop in the cation exchange capacity as the pH was lowered.

What Does This Suggest ?

The data suggests that cation exchange is a major factor in determining if acidic drainage will occur at the locations mentioned. We simply do not know if cation exchange is a major factor at other sites.

Cation exchange is generally only significant in fine particle sizes. It is believed that the small particle size is generated during the extraction of the coal and the weathering of the shale and claystone. The cation exchange capacity of the fine refuse results in the removal of calcium from solution. The removal of iron and manganese (acidity) from solution would also be expected.

Cation exchange is independent of alkaline generation, and therefore would be expected to be present if limestone is present or not. The cation exchange would be expected to reduce the acidity of the seepage below that of what would otherwise be generated. The cation exchange would be expected to increase with increases in seepage pH levels.

The surface drainage is acidic, while the subsurface seepage is alkaline. The differences are believed to be due, at least in part, to the reduced acidic generation and differing water chemistry in the low or anoxic dissolved oxygen seepage.

Why isn't the cation exchange measured in the leach tests?

Column leach tests must deal with coarse refuse, and not fine refuse, because of the favorable permeability of the coarse reftise. The addition of water in the column forces air and water into the column, forcing pyritic oxidation. The column tests assume that there is no difference in the coarse and fine refuse.

Acid base accounting also assumes that the acid generation is not a function of the particle size of the refuse.

In the real world the coal refuse contains significant quantities of fine refuse. (sometimes there is more fine refuse than there is coarse refuse) The fine refuse limits the water and oxygen to the refuse and reduces the rate of (or stops) pyritic oxidation. Cation exchange is also more significant in the fine refuse. In highly oxidizing conditions I would expect pyritic oxidation to be much more easily observed than cation exchange.

Fine refuse is in fact very significant in coal refuse disposal. Fine refuse is typically -28 mesh in size and can represent from 20 to 50% of the total refuse generated on a dry weight basis. The fine refuse in a refuse impoundment obtains a final dry weight density of only 55 to 60 lb/cf while coarse refuse dry weight compacted density is typically 110 lb/cf.

Shale top in abandoned underground mines (such as the Pittsburgh #8 seam) can fall and weather, resulting in the generation of fines. These fines can then influence the mine water chemistry.

The total volume of fine refuse placed in a slurry impoundment will represent a larger percentage of the total refuse volume than is indicated on dry weight basis because of the low fine refuse dry weight density. The Meigs Impoundment fine refuse represents 28% of the dry weight of the refuse but represents 41.6% of the total disposal volume.

Refuse distribution at Meigs

Refuse	Dry Wt	Dry Wt	Dry Wt	Volume	Volume
		Percent	Density	cf	Percent
Fines	28 lb	28 %	60 lb/cf	0.467 cf	41.62 %
Coarse	72 lb	72 %	110 lb/cf	0.655 cf	58.38 %
Total	100 lb	100 %	lb/cf	1.122 cf	100.00 %

Conclusions

1. The occurrence of high alkaline drainage in areas that are predicted to be highly acidic indicates that more is involved in acidic generation than can be explained by column leach tests and acid base accounting.
2. Cation exchange is believed to be very significant in the prediction of acidic drainage at the sites studied. The data suggests that the weathering of the shale and claystone results in fine particle size that has significant cation exchange capacity.
3. The cation exchange capacity of the clay in the coal refuse results in the removal of calcium from solution and increases the alkalinity of water that is in the presence of calcium carbonate. The removal of iron and manganese (acidity) from solution would also be expected.
4. The data indicates that high alkaline water can be generated by the neutralization of acidic mine drainage with limestone, and in the presence of fines that have a significant cation exchange capacity, and in low or zero dissolved oxygen conditions.
5. The improved prediction and control of high alkaline drainage can result in significant advantages in treatment options.

A research of cation exchange in other related fields indicates that one should not be surprised that cation exchange is significant in the formatio0n of acid mine drainage.

<u>Sometimes God opens our eyes to the obvious</u>

References

Final Draft - Handbook of Acid Mine Drainage Avoidance and Remediation Technologies - prepared by Avoidance and Remediation Working Group of the Acid Drainage Technology Initiative (ADTI) 1998

Foster, M. D. 1950. The Origin of High Sodium Bicarbonate Waters in the Atlantic and Gulf Coastal Plains. U. S. Geological Survey, Washington, D. C.

Frear, G. L. and Johnston, J. 1929. The Solubility of Calcium Carbonate (calcite) in Certain Aqueous Solutions at 25 degrees C. American Chemical Society Journal, v. 5 1, p. 2082-2093

Hem, J. D. 1985, Study and Interpretation of the Chemical Characteristics of Natural Water. Third Printing U. S. Geological Survey

Freeze R. A. and Cherry J. A. 1979. Groundwater. Prentice Hall

Lambe, T. W. and Whitman, R. V. 1969. Soil Mechanics John Wiley & Sons, Inc.

Sawyer, C. N. McCarty, P. L. and Parkin G. F. 1994, Chemistry for Environmental Engineering. Fourth Edition McGraw Hill, Inc.

Stumm, W and Morgan J. J. 1996. Aquatic Chemistry: chemical equilibria and rates in natural waters. Third Edition p. 390 John Wiley & Sons, Inc.

Weaver, T. J. Hedin, R. S. and Capo, R. C. 1999. Geochemical Evolution of Alkaline Discharges from Abandoned Coal Mines, Draft Report