Application of Column Leaching Tests to Predict Seepage Water Quality from Waste Rock in the Southeast Idaho Phosphate District

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Abstract Evaluation of waste rock seepage chemistry is a key component of baseline characterization work for phosphate mine permitting in southeast Idaho. Column leaching studies provide insight into chemical processes in waste rock dumps and pit backfills and can be used to predict metal mobility. This information can be used to improve the design and environmental performance of waste rock disposal facilities. This paper presents recommendations for development of a standard column testing method that will help ensure that leaching tests provide comparable data consistent with observed seepage chemistry from full-scale mine facilities in the Southeast Idaho Phosphate District.

Keywords seepage chemistry, column leaching tests, Southeast Idaho Phosphate District

Introduction

The Southeast Idaho Phosphate District is an active mining area with currently operating and historic mines. Mining has typically been from the surface, with overlying lithologies and inter-burden deposited as external piles, pit backfill, or valley fill. Mining-related impacts have included increased concentrations of constituents of potential concern (COPCs) including selenium, cadmium, manganese, nickel, sulfate, and zinc in groundwater and surface water. Selenium has been the primary COPC due to high concentrations in waste rock seepage and notable environmental impacts to fish and mammals. Cadmium, manganese, nickel, sulfate and zinc also have significant mobility in waste rock seepage.

Column leaching studies have been used to provide information about the potential for metals mobility of waste rock for five mining projects in the district. The testing methodology has varied from site to site and has evolved with increased understanding of the chemistry and issues associated with phosphate mine rock seepage. Variables in the testing methodologies have included sample composition (mixed versus monolithologic), water:rock ratio, degree of saturation, solution application rate, and introduction of air or biota. Data from column leaching tests have been used to develop selective handling and placement strategies for waste rock, to evaluate the need for engineered covers and seepage collection systems for disposal facilities, and as source term inputs for predictive models of contaminate fate and transport.

Development of a standard column testing method will provide consistency in data that are used to predict seepage chemistry and will provide guidelines for the how data are generated to support mine planning and permitting. This paper reviews column testing programs that have been completed in the Southeast Idaho Phosphate District and compares the results to observed seepage chemistry from mining-impacted sites. Recommendations are also provided for a standardized column testing procedure to ensure that comparable data are available to evaluate the environmental performance of planned waste rock disposal facilities.

Constituents of Concern in the Southeast Idaho Phosphate District

Mines in southeast Idaho produce phosphate ore from the Meade Peak Member of the Phosphoria Formation. Waste rock associated with the ore includes marine shales and siltstone that have the potential to leach selenium, cadmium, sulfate, manganese, nickel, zinc, and other constituents at levels of regulatory concern (Maxim 2002a and 2005, Herring 2004, Whetstone 2010a). Selenium has been of primary concern in the district and has been implicated in livestock deaths and deformities in wildlife (Presser *et al.* 2004). Seepage from mining has also resulted in wide-spread contamination of surface water and groundwater in the Blackfoot River watershed (Hamilton *et al.* 2004).

Processes that Affect Selenium Mobility in Waste Rock Seepage

Selenium mobility in seepage from waste rock dumps and pit backfills is affected by redox conditions, pH, microbial activity, and sorption. Reduced forms, including selenide (Se^{2-}) and elemental selenium (Se^{0}), are relatively insoluble and have low environmental mobility (Seed *et al.* 2000). Exposure of waste rock to atmospheric conditions can oxidize selenide and elemental selenium into the more mobile forms, selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}), which are easily transported in groundwater and surface water. Redox reaction rates for selenium can be rapid and are strongly affected by microbial processes (Pickering *et al.* 1995, Beauwens *et al.* 2005). Sorption to clay, carbonate minerals, organic compounds, and oxyhydroxides of iron, manganese, and aluminum may also affect the mobility of selenium in water (Hayes *et al.* 1987, Balistrieri and Chao 1990, Rajan 1979). The mobility of other COPCsin water is affected by the same processes to differing degrees.

Regional Waste Rock Seepage Chemistry

Seepage water quality data for 12 phosphate mining sites in southeast Idaho have been compiled to provide a baseline for comparison of leaching data from column tests. The data span 12 years (1997 through 2008) and include analyses for selenium, cadmium, nickel, manganese, and zinc. Observed COPC concentrations in waste rock seepage are summarized in table 1.

Regional data indicate that selenium concentrations in waste rock seepage vary by more than five orders of magnitude (<0.0001 to 13.3 mg/L). This wide range is attributable to compositional and chemical variability of waste rock and other factors including facility construction (*e.g.* backfills *vs.* eternal dumps, plug dumping *vs.* end dumping), meteoric water infiltration rates, oxygen availability, and degree of saturation. Individual seeps also exhibit seasonality with selenium concentrations that vary by more than two orders of magnitude (Whetstone 2010b). The highest selenium concentrations are typically observed in the spring. Other COPCs exhibit similar variability in concentration over a narrower range.

Given the observed range of concentrations in waste rock seepage, selection of a single value or narrow range of values that represent the average concentration of COPCs is problematic. The mean selenium concentration for the seepage data (n = 278) is 0.70 mg/L. The median value is 0.12 mg/L and the geometric mean is 0.10 mg/L. Because the highest selenium concentrations in seepage typically occur during high infiltration conditions (spring snow melt) and represent a disproportionally large percentage of the seepage volume, it is likely that a relatively broad range centered on the mean(0.7 mg/L)provides the best estimate of regional selenium concentration in seepage. Concentrations for other COPCs have similar seasonal patterns.

	Sulfate (mg/L)	Cadmium (mg/L)	Manganese (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Zinc (mg/L)
Ballard[1]					0.44 - 0.44	
Champ[1]					0.0149 - 0.041	
Conda[1]	30 - 540	0.00006 - 0.01	0.005 - 0.04	0.003 - 0.31	0.0041 – 4.0	0.001 - 0.59
Dry Valley[1]	220 – 3,170	0.0001 - 0.08	0.002 - 4.8	0.0005 – 4.0	0.0023 - 0.18	0.007 – 17
Enoch Valley[1]					0.002 - 0.3	
Henry[1]					0.001 - 0.001	
Mountain Fuel[1]					0.0005 - 0.34	
North Maybe[1]					0.0336 - 0.49	
S. Rasmussen Ridge[1]	270 - 1,200	0.0008 - 0.014	---	0.02 – 1.0	0.048 - 0.75	0.04 – 3.0
Smoky Canyon[1]	24.7 - 1,120	0.0001 - 0.02	0.005 - 2.4	0.005 - 0.17	0.0003 - 13.3	0.001 - 0.43
WooleyValley[1]					0.0028 - 1.4	
Conda[2]	260 – 353	0.00002 - 0.006	0.05 - 0.07	0.01 - 0.05	0.0098 - 0.35	0.009 - 0.23
Henry[2]	66- 76	0.0004 - 0.003	0.027 - 1.5	0.005 - 0.04	0.00028 - 0.00065	0.002 - 0.01
Maybe Canyon[2]					0.64 - 1.5	
Smoky Canyon[2]					0.07 - 2.35	
Ballard[3]	27 – 905	0.0001 - 0.0003	0.006 - 1.98	0.02 - 0.02	0.03 - 1.94	0.01 - 0.01
Dry Valley[3]	526 - 957	0.003 - 0.62	0.34 - 2.4	0.07 - 2.2	0.0001 - 0.0567	0.16 - 20
Maybe Canyon[3]					0.0019 - 9.85	
Smoky Canyon[3]	1,484 - 1,666	0.0836 - 0.172	0.0058 - 0.0108	0.449 - 0.916	0.299 - 1.06	3.85 - 4.54

Notes: 1 = Seeps, 2 = Under Drains, 3 = Saturated Backfill
Source: Whetstone 2010b

Table 1 *Observed Concentrations of Selected Elements in Seepage from Phosphate Mine Rock.*

Previous Column Leaching Tests for Phosphate Mine Rock in Southeast Idaho

Column leaching studies have been completed for five mines in the district over the past decade. Common aspects of most column testing programs include water:rock ratios of less than 0.5:1 and solution contact periods of a week or more. Variables in column construction have included sample size and composition, particle size, column size, degree of saturation, inoculation with bacteria, water:rock ratio, air cycling, and solution application rates. Columns have been prepared to test both single and mixed rock material. Monolithologic columns have provided information about COPC mobility from specific units that are amenable to selective handling. They also provide data that can be used to evaluate changes to the mining plan. Mixed rock columns provide a closer analog to the complex chemical reactions that occur in waste rock piles. They have typically been constructed to reflect the average composition of specific facilities. Columns have been operated under saturated, unsaturated, and variably saturated conditions. Operational parameters for columns are summarized in table 2.

As indicated earlier, particle size has varied in previous phosphate mine rock columns. Leached rock has included hand-broken or jaw-crushed core screened to 100 % passing ¾-inch and finer cuttings from air-reverse and sonic drilling. A study of the available reactive surface area for different particle sizes was completed by Whetstone (2010a). The study involved adsorption of a monolayer of nitrogen gas to the solid material using Brunauer, Emmett, and Teller (BET) testing. The mass of sorbed nitrogen was used to calculate the surface area of the solid based on the interatomic spacing of the gas monolayer. The results of the analysis indicate that reactive surface area is a function of the grain size of the sedimentary rocks rather than the size of the clasts. This suggests that leachates should not be particularly sensitive to the gross particle size of the packed material provided that the sizing is small enough to prevent preferential flow within the columns. As a general rule, the column diameter should be at least four times greater than the largest particle (Potter

	SC, Panels B & C	SC, Panels F & G	NRRM	DVM, South Ext.	BFBM
# of Columns	9	25	11	2	13
Column Diameter	6"	4" - 6"	6"	6"	6"
Sample Mass	5 kg	5 - 22 kg	5 kg	25 - 45 kg	20 kg
Monolithologic Columns	8 unsat.	13 unsat. 8 variable	11 unsat.	---	---
Mixed Comp. Columns	1 unsat.	2 unsat. 2 partial	---	1 sat. 1 unsat.	9 unsat. 4 sat.
# of Cycles	10	5-20	10	10 - 13	11 - 19
Cycle Length	4 - 8 days		4 - 6 days	3 - 4 weeks	19 days
Innoculation	yes	23 of 25	no	no	no
Aeration Cycle	1 - 2 days	2 - 3 days	1 - 2 days	no	3 days
Application Rate (mL/hr)	30 – 100	15 - 22	30	15	15

Notes: SC = Smoky Canyon, DVM = Dry Valley Mine, NRRM = North Rasmussen Ridge Mine, BFBM = Blackfoot Bridge Mine

***Table 2** Summary of Operational Parameters for Column Leachate Tests.*

1981,Cathles and Breen 1983). Previous testing in the district has used column diameters greater than eight times the largest particle.

Columns have been operated under unsaturated, variably saturated, and saturated conditions. Time series plots for leachates from unsaturated columns show pronounced washout curves for selenium and other COPCs that decrease to low asymptotic levels during latecycles. Saturated columns have lower initial release rates for selenium for the same rocks, while other elements such as manganese show increased mobility (Whetstone 2010a). The column study prepared for the Blackfoot Bridge Mine paired unsaturated and saturated columns of identical mixed-rock composition. The range of concentrations for selected COPCs for the unsaturated and saturated columns are presented in table 3. Saturated leachates also have higher dissolved carbon dioxide concentrations which are interpreted to indicate increased microbial activity (Whetstone 2010a). Work by Lisa Kirk of Enviromin Inc. suggests that naturally occurring bacteria of the genus Dechloromonas are responsible for selenium reduction and reduced selenium mobility in saturated column leachates (Kirk *et al.* 2009, Kirk *et al.* 2010). Columns that were inoculated with cultured bacteria had similar release characteristics for other COPCs as non-inoculated columns.

Despite the variability associated with previous column testing methods, effluents from the first 1 or 2 cycles have generally provided reasonable models of COPC concentrations in seepage from field-scale facilities (Whetstone 2010b). Selenium releases in first-cycle leachates from unsaturated columns have ranged from 0.11 to 9.32 mg/L and have mean and median values of 1.36 and 0.89 mg/L, respectively. This range is compared to a mean selenium concentration of 0.70 for field observed seepage. Other COPCs are similarly comparable. The range ofCOPC concentrations in first cycle column leachates for the Blackfoot Bridge Mine (table 3) can be compared with ranges for seepage from field-scale facilities presented in table 1.

Conclusions

Standardization of column testing methods for phosphate waste rock in southeast Idaho

	Sulfate mg/l	Cadmium mg/l	Manganese mg/l	Nickel mg/l	Selenium mg/l	Zinc mg/l
Unsaturated Mixed Rock	629 - 1340	0.0014 - 0.0064	0.54 - 0.72	0.06 - 0.16	0.74 - 2.5	0.02 - 0.29
Saturated Mixed Rock	234 - 609	0.0015 - 0.0042	1.07 - 2.18	0.05 - 0.29	0.001 - 0.008	0.01 - 0.45

***Table 3** Observed First Cycle Leachate Concentrations of Selected Elements inthe Blackfoot Bridge Column Test.*

will facilitate comparison between mining sites and improve confidence in predictions of COPC mobility in seepage. It is recommended that both monolithologic and mixed rock columns be prepared to characterize new waste rock disposal facilities. Monolithologic columns provide information that can be used to evaluate selective handling strategies and changes to mining plans and should be prepared for each rock type that comprises 5 % or more of the material balance. Mixed rock columns are a better analog of the complex reactions that occur in heterogeneous dumps and backfills and can be used to calibrate equilibrium-based mixing models of monolithologic leachates. Mixing models may be prepared to evaluate the inevitable differences between planned and constructed facilities.

The operating condition of the columns (saturated *vs.* unsaturated) should be selected to model the site-specific environment. Unsaturated columns should be prepared for materials that will be stored above the water table in external piles, pit backfills, and valley fills. If any portion of a facility extends below the water table, a saturated column should be prepared. Other factors, such as plans to infiltrate dewatering water through pit backfill, should be considered when planning saturated *vs.* unsaturated columns. Continuation of the variably saturated column testing method is not recommended because of difficulty in interpreting the results. However, the method may be applicable to evaluate attenuation of COPC concentrations under specific circumstances.

The authors have a preference for larger columns over smaller columns and recommend that leaching tests be performed in six-inch diameter columns packed with 20 kg of material. This size is large enough to accommodate samples that represent the run-of-mine composition of modeled facilities, but small enough that sufficient material is usually available from exploration boreholes that were used to define the ore body. The packed material should be sized to 100 % passing ¾-inch mesh, but should not be overly disaggregated if possible.

Although bacteria mediate redox reactions involving selenium and other COPCs, inoculation of the columns is not recommended. Bacteria are known to be naturally present in phosphate mine waste rock and flourish in the columns under favorable (saturated) conditions. Regulatory agencies have expressed concerns regarding the feasibility of collecting, identifying, and culturing representative populations of bacteria in inoculants. Monitoring of constructed facilities to determine if biologic communities reflect those in the columns is also problematic.

Standardization of the solution application rate, length of leaching cycle, water:rock ratio, and air cycle is also recommended. Infiltration rates in field-scale facilities are often more than an order of magnitude less than in columns. The head solution application rate should therefore be as low as practical. Experience indicates that accurate application of 15 mL/h is achievable with readily available metering pumps. This application rate provides for a 19-day leaching cycle to generate approximately 5 L of effluent. For unsaturated columns, each cycle includes 14 days of solution application, a two day drain-down period, and a three dayaeration period. Saturated columns include a 14-day solution application period and a five day reaction period.

Finally, it is recommended that columns be operated for a minimum of five cycles. Observed wash-out curves for COPCs from previous tests typically become asymptotic by the fifth cycle as processes within the columns approach quasi-equilibrium. However, additional cycles may be required to provide documentation of steady-state release rates.

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