COMPARISON OF MINE WASTE ASSESSMENT METHODS AT THE RATTLER MINE SITE, VIRGINIA CANYON, COLORADO[1]

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Abstract. In a joint project, the mine waste-piles at the Rattler Mine near Idaho Springs, Colorado, were sampled and analyzed by scientists from the U.S. Geological Survey (USGS) and the Colorado School of Mines (CSM). Separate sample collection, sample leaching, and leachate analyses were performed by both groups and the results were compared. For the study, both groups used the USGS sampling procedure and the USGS Field Leach Test (FLT). The leachates generated from these tests were analyzed for a suite of elements using ICP-AES (CSM) and ICP-MS (USGS). Leachate geochemical fingerprints produced by the two groups for composites collected from the same mine waste showed good agreement. In another set of tests, CSM collected another set of Rattler mine waste composite samples using the USGS sampling procedure. This set of composite samples was leached using the Colorado Division of Minerals and Geology (CDMG) leach test, and a modified Toxicity Characteristic Leaching Procedure (TCLP) leach test. Leachate geochemical fingerprints produced using these tests showed a variation of more than a factor of two from the geochemical fingerprints produced using the USGS FLT leach test. We have concluded that the variation in the results is due to the different parameters of the leaching tests and not due to the sampling or analytical methods.

Additional Key Words: mine wastes, contaminated soils and sediments, toxicity testing, leachate tests

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Introduction

Recently, simple methods for the assessment of metal mine waste-piles have been developed. (Wildeman et al., 2003; Hageman and Briggs, 2000). These procedures have been used to assess and characterize mine-waste produced from a wide variety of hard rock mines. Assessments have ranged from studies of moderately impacted sites (Bazin et al., 2003), to studies of severely impacted mining districts where numerous mine waste-piles have been compared in order to determine prioritization of the sites for possible cleanup (Hageman, 2004; Heflin et al., 2004). In 2004, scientists from the U.S. Geological Survey (USGS) and the Colorado School of Mines (CSM) had the opportunity to separately sample the Rattler Mine, a complex abandoned historical mine site, near Idaho Springs, Colorado, in order to compare sampling, preparation, and analytical methods. Also, because the site had four different waste-piles, the question of whether the piles would show different geochemical fingerprints was posed. This paper presents the results of this comparative study**.**

The Rattler Mine site (Fig. 1) is in the Virginia Canyon area of the Central City/Idaho Springs Ore District. The site contributes perennial drainage to Boomerang Gulch, which is a main tributary to Virginia Canyon, a two-mile gulch that is severely impacted by abandoned metal mines and flows into Clear Creek at Idaho Springs (Herron et al., 2001). Besides the main waste-pile of pyritic ore shown in Fig. 1, there is a smaller pyritic waste-pile above, and a large pyritic waste-pile below, the county road that cuts through the site. In addition, a very small waste-pile from an abandoned muscovite mine is situated on the upper area of the site. Water draining from a collapsed adit flows onto the upper pile, penetrates the waste rock, and reappears as a series of seeps issuing from the

Figure 1. Ore takeout at the Rattler Site in May 2004.

bottom of the pile below the county road. Of the abandoned sites in Virginia Canyon, Herron et al. (2001) gave the Rattler Mine the highest ranking for remediation. With the variety of waste rock piles and complex hydrology, the Rattler site is an excellent choice for a study comparing sampling and analytical techniques that are used for the assessment of mine wastes (Wildeman et al., 2003; Hageman and Briggs, 2000).

Because of this complexity, a number of techniques and situations can be compared. This study focused on the following:

- How does water chemistry from the adit compare with the chemistry of water issuing from seeps at the toe of the site and how does the water from the toe seeps change over the seasons?
- How does the leachate chemistry of a mine waste composite sample taken by USGS personnel compare with leachate chemistry of a different mine waste composite sample collected by CSM personnel? Included in this comparison is the use of different analytical techniques.
- Can sampling, analytical, and leaching techniques detect differences among the four piles on the site?
- Finally, a large rain event washed away a considerable amount of the Rattler main waste-pile. Will sampling and leaching tests performed on a composite sample collected after the wash-out show a different leachate geochemical fingerprint from the sample taken prior to the event?

Sampling and Analytical Methods

Sampling Methods

The site was first visited by personnel from the USGS and CSM in May of 2004. At that time, surface composite samples of all four piles were collected by CSM and a surface composite of the main pile was collected by the USGS.

The method for collecting a grid composite sample from a mine dump was developed by Smith et al. (2000). For this study, both groups used a modification of this procedure and collected a non-grid composite using the method described in Hageman and Briggs (2000). To collect a sample using the modified sampling method, an individual walks over all accessible parts of the mine waste-pile collecting a minimum of 30 increments of mine waste material in a completely random manner. Coarse material (larger than the top knuckle of the thumb) is discarded during collection. All increments are put into a 5-gallon plastic bucket and mixed. The mine waste composite is then sieved to pass a 2 mm stainless steel screen. The < 2 mm fraction is saved for leaching and further analysis and all material >2 mm is discarded. After preparation both groups split and exchanged a portion of each composite so that each group could leach and analyze the collocated composites. This was done to help define any differences in leachate chemistry introduced by collection of separate composites by different individuals and quantifying whether in-field modifications in sample collection affect the integrity of the composite sample. In addition, the CSM personnel collected a sample of the water from the seep at the toe of the lower pile. Because of the dry winter, the adit was not draining in May, 2004.

In June of 2004 there was significant rainfall in the area and in early July the CSM personnel revisited the site and took a sample of water from the adit, which was now draining. In August of 2004, a downpour washed out a considerable portion of the main pile (Fig. 2). In November of 2004, the site was revisited and CSM personnel took another surface composite sample from the main pile and also another water sample from the seep at the toe of the site.

Figure 2. Ore takeout at the Rattler site in November 2004 after the large rain event (Notice the barriers that were installed after the event to push back and retain washed out materials from blocking the road).

Analytical Methods

The composite waste-pile samples were split and portions were used by both parties to perform leaching tests that are integral to the Assessment Decision Tree that has been devised for mine waste-piles (Wildeman et al., 2003). The three leaching tests are described below. Table 1 lists the leaching parameters and differences between the techniques.

United States Geological Survey (USGS) Field Leach Test (FLT)

This leach test was developed by the USGS and determines the potential for metals and acid release from materials when exposed to natural waters (Hageman and Briggs, 2000). This test uses a mass basis and a 20:1 (20 parts extractant to 1 part solid) leaching ratio. For the procedure, 50.0 g of <10 mesh (<2mm) mine waste composite sample is weighed into a one-liter plastic bottle. Approximately 1.0 L deionized water is added slowly so that no dust is lost. The bottle is capped and vigorously hand shaken for 5 minutes. The contents are then allowed to settle for approximately 10 minutes. After settling, sub-samples of the leachate are measured for pH, specific conductance, and other tests as desired. A portion of leachate is filtered through a 0.45 μm pore-size nitrocellulose syringe filter. If filtration is difficult, a 0.70 μm glass fiber pre-filter can be used in conjunction with the 45 μm filter in a serial manner. Sub-samples of the filtrate are collected and preserved with nitric acid for analysis.

Modified Toxicity Characteristic Leaching Procedure (TCLP)

This test is a modified version of U.S. EPA Method 1311 TCLP (U.S. Environmental Protection Agency, 2002). The test as originally conceived by the EPA was designed to test metals mobility in landfills. For our purposes, the test determines the mobility of metals in the presence of mildly acidic waters. It closely approximates the carbonate mobility step that is performed in sequential leaching studies (Tessier, et al., 1979). An extraction fluid is prepared by adding 5.7 ml of concentrated glacial acetic acid to 500 ml of water. 64.3 ml of 1 N NaOH is added to the solution and then the solution is brought to a volume of one liter using deionized water. The pH of this solution should be 4.93 ± 0.05. 40 ml of this extraction fluid is added to 2.00 g of < 80 (<180µm) mesh sediment sample (20 parts extractant to one part solid) in a 125 ml plastic bottle. The bottles are agitated end over end using a rotary tumbler for 24 hours. The leachate is filtered with a 0.45 µm syringe filter and acidified with nitric acid.

Colorado Division of Minerals and Geology (CDMG) Leach Test

This leach test was developed by Herron et al. (2001) of the Colorado Division of Minerals and Geology. It uses a volume basis to determine the potential for metals release from soils when exposed to natural waters. The leaching ratio is 2:1 (2 parts extractant to 1 part solid). In this procedure, 150 ml of whole sediment sample is placed into an 800 ml plastic beaker and 300 ml of deionized water is added. The sample is stirred vigorously for 15 seconds and then the beaker is covered with Parafilm. The contents are allowed to settle for 90 minutes. After approximately 90 minutes, the pH, Eh, specific conductance, and alkalinity are measured on the leachate, and 10 ml of leachate is filtered with a 0.45 µm syringe filter and preserved with nitric acid.

Elemental Analyses

At CSM, the water and leachates were analyzed using inductively coupled plasma–atomic emission spectroscopy (ICP-AES). Approximately 10 ml of filtered sample, acidified with nitric acid, is required. The samples were analyzed on a Perkin Elmer Optima 3000 ICP-AES for 30 elements (Table 2).

At the USGS, leachates were analyzed using inductively coupled plasma–mass spectroscopy (ICP-MS) by the method described in Lamothe, et al., (2002). Data is presented for 30 elements (Table 3). Preservation of leachate samples for metals analysis requires that the sample be filtered and acidified to pH ≤ 1.5 with ultrapure nitric acid.

Other Analytical Procedures

For the water samples, pH, Eh, and specific conductance were measured in the field. If applicable, alkalinity was measured in the field using a Hach kit.

Table 1 Comparison of the USGS FLT, Modified TCLP, and CDMG leaching tests used in this study.

Parameter	**USGS FLT**	**Modified TCLP**	**CDMG**
Test Type	batch	batch	batch
Extract / Solid Ratio	20 : 1	20 : 1	2 : 1
Leaching Fluid	DI H_2O	CH_3CH_2OOH / NaOH	DI H_2O
pH of Leaching Fluid	~5.7	4.93 ± 0.05	~5.7
Particle Size of Solid	<10 mesh (< 2mm)	<80 mesh (< 180 µm)	whole sediment
Sample Mass	50.0 g	2.0 g	150 ml
Agitation Method	hand shaken	end-over-end	stirred
Agitation Time	(5 minutes)	(24 hours)	(15 seconds)
Total Leaching Time	15 minutes	24 hours	90 minutes
Filtration	syringe	syringe	syringe
Filter Type	nitro-cellulose	nitro-cellulose	nitro-cellulose
Filter Pore Size	0.45 micrometer	0.45 micrometer	0.45 micrometer

Results

The concentrations of the elements in the seep and adit waters are given in Table 2. The two samples collected in May were collocated and processed separately through all the sampling and analytical steps in order to quantify the amount of variation in the complete procedure. Comparison of the collocated samples shows that results were generally good to within 5%. Table 3 gives the leachate concentrations from the USGS Field Leach Test from samples collected from the Rattler Main Waste sub-pile. Two separate composite samples (USGS and CSM) were collected in May 2004, and an additional composite sample was collected by CSM personnel in November 2004.

Fig. 3-7 use Element Concentration Pattern Graphs (ECPG) to compare the concentrations of elements in the leachates and various waters. The USGS refers to the ECPG as the “leachate geochemical signature” or the “leachate geochemical fingerprint”. For this study the ECPG concentrations are plotted on a logarithmic scale so that relative differences in concentrations among samples can be better determined even if the values are relatively low. Element concentrations can be plotted in groups (i.e. major elements plotted together in one plot, and trace elements plotted in another). Plotting data in this manner allows the investigator to effectively evaluate both high and low values (Hageman, 2004). When compiling and plotting the data, the order of elements is standardized so that correlations can be better established. The x-axis order of elements is as follows:

1. Na, K, and S: Generally, these are readily soluble elements and should correlate best among the samples. Note that this assumes that the sulfur species in the water is primarily sulfate.

2. Ca, Sr, and Mg: Carbonate minerals are a possible source of these elements. Ca and Mg are also common elements in rock-forming minerals.

3. Pb, Cu, Zn, and Ni: Either sulfide minerals or carbonate minerals are possible sources of these elements.

4. Fe, Mn, and Al: Oxide minerals or mineral salts are probable sources of these elements.

Fig. 3 gives the ECPG's of the water collected from the adit and toe seep at the Rattler site.

Fig. 4 is an ECPG of the USGS FLT solutions. Note that in Table 3 and Figure 4 and in subsequent figures, where there are double parties listed, the first party collected the sample and the second party did the leach test and analyses.

Fig. 5, 6, and 7 are ECPG's of other solutions from leachate tests conducted on the waste rock samples taken from the Rattler Site. Fig. 5 gives the CDMG results from all of the composite samples taken at the Rattler Site. Figures 6 and 7 give the results from all of the leachate tests conducted on the lower waste rock pile and the muscovite pile, respectively. The water in Fig. 6 was collected in May 2004 from the seeps at the bottom of the lower waste rock sub-pile.

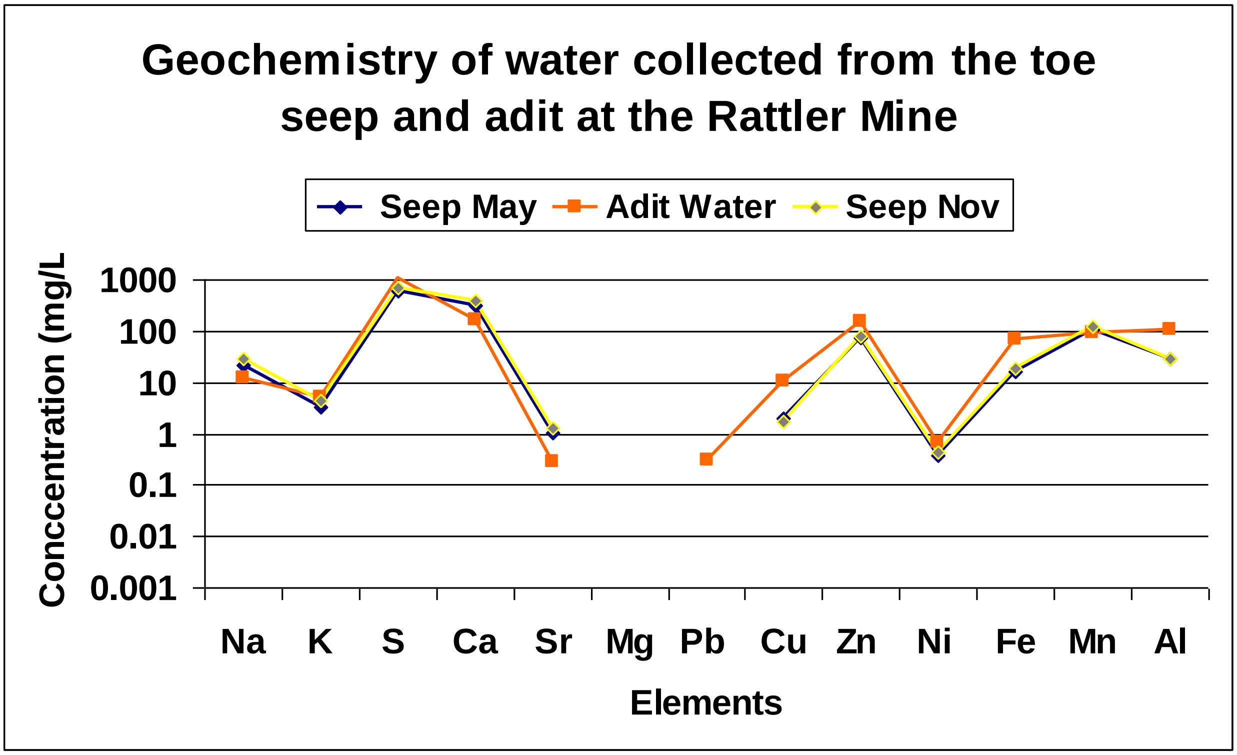

Figure 3. ICP-AES Element Concentration Pattern Graph (Geochemical Fingerprints) for the toe seeps and adit water at the Rattler mine site.

Table 2. Element concentrations (ICP-AES) from water samples collected from the toe seep, adit, and stream at the Rattler Mine Site. (All concentrations in mg/L; BDL = Below Detection Limit; NA = Element Not Analyzed)

Element	**Detection Limit**	**5/11/2004 Rattler Seep 1**	**5/11/2004 Rattler Seep 2**	**7/1/2004 Rattler Adit Water**	**11/6/2004 Rattler Seep in Nov.**
Ag	0.005	0.005	0.005	BDL	0.014
Al	0.031	28	28	110	28
As	0.036	BDL	BDL	BDL	BDL
B	0.008	0.10	0.080	0.38	0.31
Ba	0.003	BDL	BDL	0.044	BDL
Be	0.000	0.011	0.010	0.026	0.010
Ca	0.007	310	310	160	380
Cd	0.002	0.32	0.31	1.5	0.21
Co	0.005	0.31	0.31	0.40	0.33
Cr	0.003	0.025	0.023	0.054	0.031
Cu	0.003	2.0	2.0	10.4	1.80
Fe	0.003	16.5	16.2	67	18.3
K	0.077	3.29	3.27	5.17	4.5
Li	0.005	0.14	0.09	0.13	0.054
Mg	0.000	NA	NA	NA	NA
Mn	0.000	110	110	93.6	120
Mo	0.006	0.031	0.012	BDL	BDL
Na	0.014	22.1	22.2	11.9	29.7
Ni	0.003	0.38	0.38	0.65	0.43
P	0.113	BDL	BDL	0.31	BDL
Pb	0.023	BDL	BDL	0.29	BDL
S	0.055	620	620	1100	690
Sb	0.016	BDL	BDL	BDL	BDL
Se	0.039	0.085	0.090	0.041	BDL
Si	0.015	35.1	34.7	51.3	37.2
Sn	0.022	0.078	0.079	0.077	0.061
Sr	0.000	1.0	1.0	0.29	1.30
Ti	0.001	BDL	BDL	0.003	BDL
V	0.002	BDL	BDL	0.017	BDL
Zn	0.002	76.3	76.5	150	77

Table 3. Leachate geochemical results from the USGS FLT on Rattler main waste sub - pile composite samples collected by CSM (ICP-AES) and the USGS (ICP-MS) in May and an additional composite collected by CSM in November, 2004. (All concentrations in mg/L; BDL = Below Detection Limit). Note: In the columns with two-party headings, the first party collected the sample and the second party leached and analyzed the sample. First four columns of data are for samples collected in May of 2004.

Element	**Detection Limit**	**CSM**	**CSM/USGS**	**USGS**	**USGS/CSM**	**NOV. CSM**
Ag	0.005	BDL	BDL	BDL	BDL	BDL
Al	0.031	5.74	4.95	0.63	0.60	7.67
As	0.036	BDL	BDL	BDL	BDL	BDL
B	0.008	0.27			0.34	0.08
Ba	0.003	0.02	0.05	0.11	0.07	0.014
Be	0	BDL	0.001	0.001	0.002	BDL
Ca	0.007	27.4	26.7	8.9	10.5	14.4
Cd	0.002	0.06	0.06	0.02	0.02	0.08
Co	0.005	0.02	0.02	0.01	0.02	0.2
Cr	0.003	0.01	0.01	0.002	0.003	0.01
Cu	0.003	0.61	0.57	0.24	0.29	0.63
Fe	0.003	5.05	3.68	0.09	0.60	2.18
K	0.077	0.25	0.46	0.77	0.90	0.065
Li	0.005	0.01	0.005	0.002	BDL	0.013
Mg	0	5.48	4.94	2.16	2.89	5.06
Mn	0	3.44	3.29	1.59	1.95	4.07
Mo	0.006	BDL	BDL	BDL	BDL	0.04
Na	0.014	0.09	2.02	1.65	0.43	0.059
Ni	0.003	0.04	0.037	0.017	0.021	0.028
P	0.113	BDL	BDL	BDL	0.39	0.044
Pb	0.023	2.44	2.5	0.34	0.46	1.72
S	0.055	65	53.3	16.7	41.6	54.0
Sb	0.016	BDL	0.001	0.001	BDL	BDL
Se	0.039	BDL	BDL	BDL	BDL	BDL
Si	0.015	0.1	BDL	BDL	0.14	0.29
Sn	0.022	BDL	BDL	BDL	BDL	BDL
Sr	0	0.02	0.02	0.014	0.016	0.012
Ti	0.001	0	0.007	0.002	0.001	0
V	0.002	BDL	BDL	0	BDL	BDL
Zn	0.002	10.3	11	4	3.68	12.12

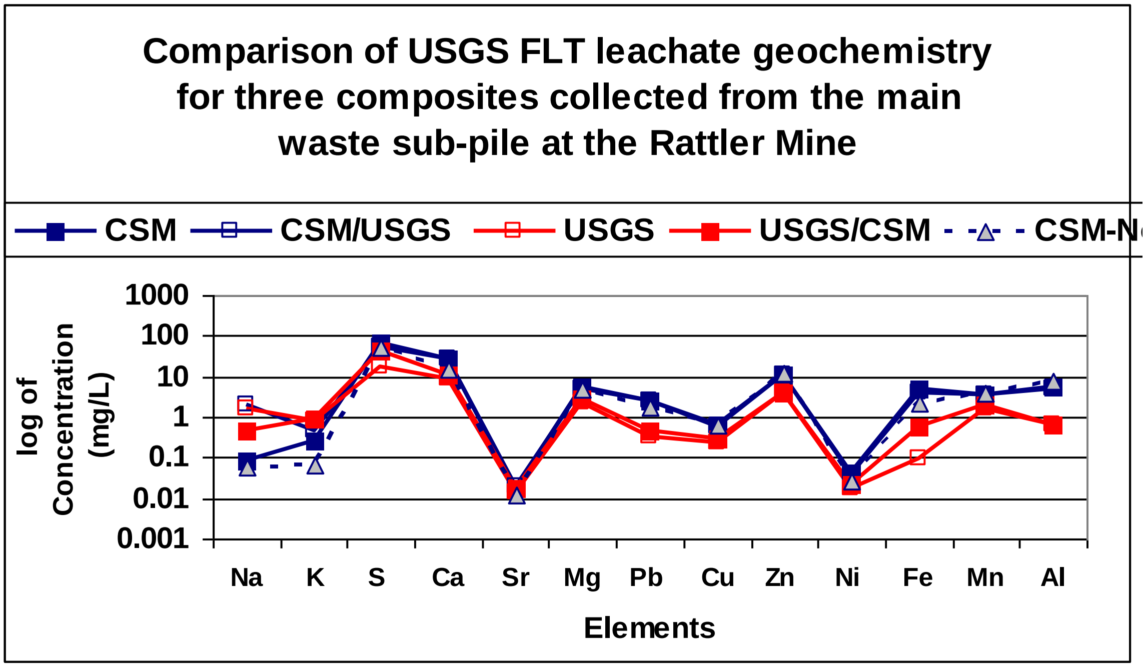

Figure 4. Element Concentration Pattern Graph (Geochemical Fingerprints) for Rattler main sub-pile composites leached using the USGS FLT. For legends with two-party headings, the first party collected the composite sample and the second party leached the sample using the USGS Field Leach Test, and analyzed the sample. CSM analysis by ICP-AES, USGS analysis by ICP-MS.

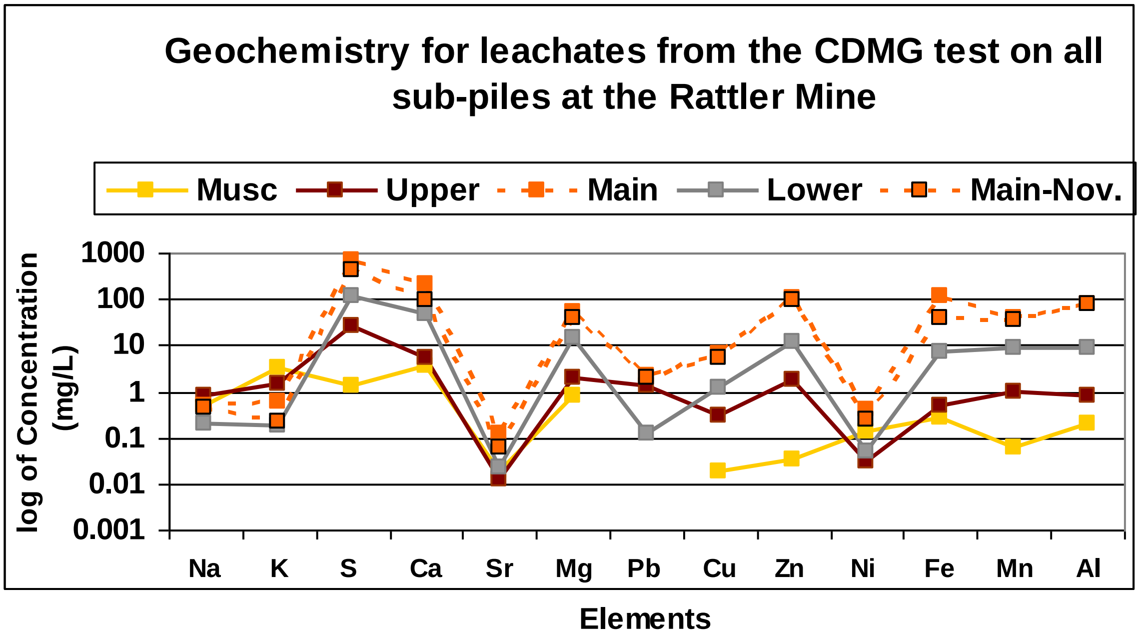

Figure 5. Element Concentration Pattern Graph (Geochemical Fingerprints) for the CDMG leachates from the sub-pile composites collected at the Rattler mine site. All analyses were performed by CSM using ICP-AES.

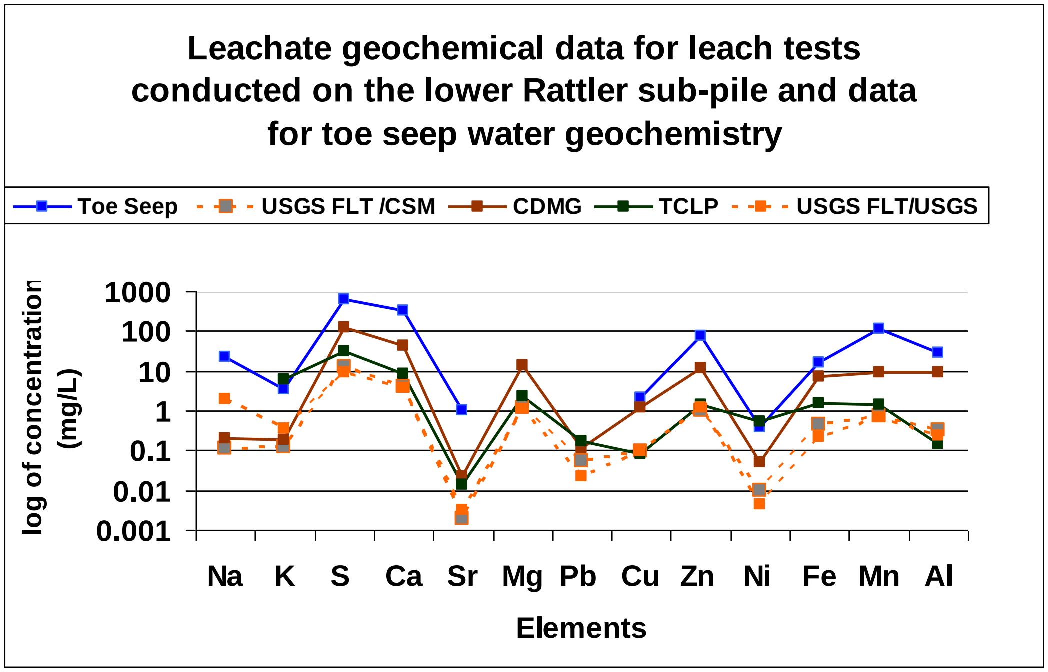

Figure 6. Element Concentration Pattern Graph (Geochemical Fingerprints) for leachates from four leach tests conducted on the composite sample from the lower sub-pile at the Rattler mine site. Also plotted are geochemical data for the toe seep water sample collected in May, 2004. For two-party headings, the first heading is the leach test performed and the second is the party that leached and analyzed the sample. USGS FLT/USGS analysis was done using ICP-MS, all others done by CSM using ICP-AES.

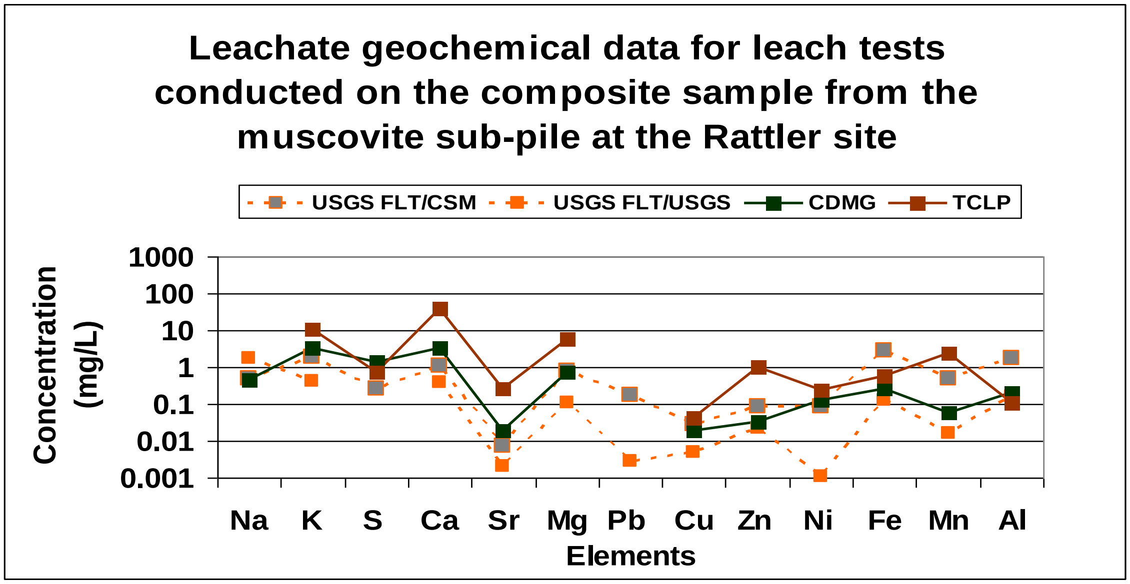

Figure 7. Element Concentration Pattern Graph (Geochemical Fingerprints) for leachates from the three leach tests conducted on the composite sample collected from the muscovite sub-pile at the Rattler mine site. For two-party headings, the first heading shows the leach test performed and the second is the party that leached and analyzed the sample. The USGS FLT/USGS analysis used ICP-MS; all others were done by CSM using ICP-AES.

Discussion

Rattler Site Waters

At least three observations can be made when analyzing Table 2 and Fig. 3. First, the excellent correlation of the results between the two collocated samples of water taken in May from the toe seep below the lower sub-pile implies that the sampling and analytical procedures are reliable. Except for Li and B, if the concentration of the element is above three times the detection limit, the range in concentration is about 3% of the average. Because both analyses were performed at CSM, this should be considered the precision of the results.

Secondly, the correlation in the water chemistry of the May and November seep samples is noteworthy. Except for boron, the concentrations of the elements in the May and November samples are within 10 to 20 % of each other. This is especially remarkable considering the large downpour that occurred in August. Such consistency in water chemistry has been noted before in mine waters when the source of the water is from deep aquifers that are little disturbed by storm events. This appears to be the case for this seep water. If this is so, then the source of the water may not be the waste rock piles but instead an adit buried by the piles.

Third, the concentrations in the adit water are a bit higher than those in the seep. However, analysis of Fig. 3 shows that except for iron and aluminum, the concentration pattern is the same as for the seep. The relatively higher concentrations of iron and aluminum suggest that if the adit water is related to the seep water, then perhaps these elements have been removed in secondary mineral precipitates as the water moves through the pile. This hypothesis is attractive because only water is used in the CDMG and USGS leach tests and, as seen in Table 3, iron and aluminum are two of the important elements in the leachate. However, this hypothesis is counter to the idea that the seep water comes from another adit buried by the waste-pile, although the water could come from a buried adit and then change as it moves through and has extended contact with the weathered mine waste. Clearly, further investigation is needed to determine the source of the water issuing from the seep at the bottom of the lower waste-pile.

USGS Field Leach Tests on the Main Waste Rock Pile

Several observations can be made when interpreting the leachate geochemical data presented in Table 3 and Fig. 4. First, the leachate geochemical fingerprints produced by the USGS Field Leach Test for the two collocated composites and the composite collected in November correlate very well. This is important because it indicates that the USGS sampling procedure is robust and produces a similar geochemical signature regardless of who collects the sample. These results also serve to re-emphasize the effectiveness of the USGS Field Leach Test as a rapid, inexpensive, reliable leach test that can be used to quickly produce a quantitative geochemical fingerprint of a mine waste. The fact that these samples were collected, processed, leached and analyzed independently and still provide very similar geochemical fingerprints for the Rattler Mine main sub-pile only serves to enhance the value of this procedure.

Secondly, because each group leached both its own composite and the other group's composite sample using the USGS Field Leach Test, and, each group analyzed the samples using its own ICP instruments, ICP-AES (CSM) and ICP-MS (USGS) can be compared. Leachate data from this study show little difference in the geochemical fingerprint produced by either instrument. Analytical data produced by both groups on splits of the same composite show very good correlation and emphasize that using either ICP-MS or ICP-AES is effective and acceptable.

CDMG Test on All Sub-piles at the Rattler Site

As Fig. 5 shows, for all sub-piles except the muscovite sub-pile, the leachate geochemical fingerprints produced by the CDMG leach test correlate fairly well. Although leachate element concentrations vary from sub-pile to sub-pile, the overall geochemical trends are consistent. Leachates derived from the two main sub-pile composites and the leachates from the lower sub-pile have similar geochemical fingerprints. This was expected because the main sub-pile and the lower sub-pile are one and the same, only a road divides the large pile into the sub-piles. Leachate concentrations are a little higher for the Rattler main sub-pile, perhaps because it is much flatter than the Lower sub-pile thus allowing more pronounced formation of soluble salts. It should be noted that the same individual collected all the sub-pile composites for the CDMG test and thus we would expect to see good sampling consistency. Using the same design, collection technique, and equipment minimizes the chances for bias.

The muscovite sub-pile CDMG leachate geochemistry did not correlate as well when compared with the other sub-piles. This is due to the fact that contrary to the other sub-pile composites which were heterogeneous, the muscovite-rich composite sample was relatively homogeneous and consisted mostly of muscovite in various stages of weathering. Importantly, the muscovite sub-pile did not have the secondary mineral salts or sulfides that were readily apparent on the other piles. The geochemical fingerprint for the CDMG leachate shows that for the muscovite sub-pile, sodium, potassium, calcium, strontium, magnesium, nickel, iron, and aluminum track reasonably well with the other sub-piles. Concentrations of sulfur, lead, copper, zinc, and manganese did not correlate as well.

Leachate data from the composite sample collected from the main sub-pile in November 2004 (after the large washout event in August) correlate well with leachate geochemical data from the main sub-pile composite sample collected prior to the washout. This finding indicates that the waste material at the Rattler Mine site is probably well-weathered and that even after the top material is washed away there is a reservoir of sulfides in the pile that readily re-form the same soluble, readily leachable secondary salts.

Comparison of Leach Tests and Seep Water for the Lower Rattler Sub-pile

For this comparison both groups leached splits of the same composite sample. Both the USGS and CSM used the USGS FLT and CSM also used the CDMG and modified TCLP leach tests. As shown in Figure 6, the USGS FLT performed by CSM, the USGS FLT performed by the USGS and the CDMG leach test all produce similar element trends in their geochemical fingerprints. The CDMG leach test produces higher concentrations of most elements because it uses a much lower leaching ratio (2:1) than the USGS FLT (20:1). The modified TCLP test produced a leachate geochemical signature somewhat different from the other leach tests. This is not unusual and has been seen in other studies. The modified TCLP requires an acidified leachate solution (4.93 ± 0.05), an extended agitation time (24 hours), and a smaller particle size. These factors lead to pronounced, selective extraction of certain constituents from mine waste, which may produce misleading results. In this case, the TCLP test produced elevated concentrations of potassium and nickel relative to the other tests.

Interestingly, the seep water chemistry profile correlated with the leachate the FLT and CDMG geochemical fingerprints. This indication suggests that the seep may be running through the mine waste and leaching the mine waste material as it percolates through the waste-pile. The data show that the concentration of most elements was slightly higher in the seep water. This could occur if the water from the seep is having extended contact time with the mine waste materials, enhancing the concentrations of these constituents.

Comparison of Leach Tests and Seep Water for the Muscovite Sub-pile

Fig. 7 shows the geochemical data for three separate leach tests. The leach tests were done on splits of the same composite sample collected from the small muscovite sub-pile. The USGS used its FLT, while CSM used all three leach tests. The sample splits were analyzed using ICP-AES at CSM and ICP-MS at the USGS.

The leachate geochemical fingerprints presented here correlate reasonably well with each other except for a couple of elements. As mentioned before, we expected to see some differences in the leachate signatures because of the relative lack of sulfides in this waste material. Because there is not as much soluble material available to be leached from the muscovite sub-pile, the overall leachate metal concentrations are lower than in the other sub-piles.

Muscovite sub-pile leachate geochemical fingerprints from the USGS FLT carried out by both CSM and the USGS are similar for most elements. The major exceptions are lead, zinc, and manganese, which occurred in somewhat higher concentrations in the leachate produced and analyzed by CSM. It is difficult to surmise whether the higher concentrations of these elements in the CSM leachate are due to instrument differences or interferences, or to the unusual nature or the mineralogy of the Muscovite sub-pile. Nickel was found in relatively low concentration in the USGS-analyzed leachate. Again, this is most likely due to the nature of this muscovite-rich, sulfide-poor sample. Geochemical data for the CDMG leach test generally correlate with the USGS tests; however, lead was not detected in the CDMG leachate whereas it was found in the CSM and USGS FLT leachates. The TCLP leachate contained higher concentrations of most elements but failed to show any concentration of sodium or lead. These spurious results may be due to the use of the acidified extractant, the longer agitation period, and the smaller particle size of the sample used in the TCLP test.

Conclusions

Producing a realistic quantification of the potential release of contaminants into an ecosystem due to natural leaching of historical mine waste piles remains important to geoscientists and others. This importance lies in the fact that the water-leachable fraction of a mine waste is often mobilized into the environment as the waste-pile is exposed to water by meteorological or anthropogenic events. When released, these constituents form plumes of potentially toxic leachate that may migrate through an ecosystem, often having negative impacts on the biota.

This and other studies show that leach tests like the USGS Field Leach Test or the CDMG leach test are effective tools that can be utilized to produce realistic leachate geochemical fingerprints that show which constituents can be expected to be released in run-off from a mine waste when it is leached in the natural environment. However, the modified TCLP procedure produces leachate geochemical results that do not correlate well with the USGS FLT or CDMG procedures.

The three leach tests compared in this study are quite different (see Table 1), and this study showed some of the advantages and disadvantages of each. The USGS Field Leach Test is much faster than the other two procedures, and produces more leachate by using a 20:1 leaching ratio. This ratio also ensures that most soluble components of the sample can be taken into solution without exceeding saturation. The 20:1 leaching ratio used in this procedure was based on the EPA 1312 SPLP procedure (U.S. Environmental Protection Agency, 2002), and results produced using the USGS Field Leach Test may be compared with other leaching studies that have used this EPA procedure. The USGS Field Leach Test is easy to do on-site, allows the geoscientist to leach samples at several sites in a day, and requires only that the preserved sub-samples be returned to the laboratory for analysis.

The CDMG leach test produces reliable geochemical fingerprints and yields leachate geochemical trends that correlate well with the USGS Field Leach Test. However, the concentrations are generally higher for most elements in the CDMG leachate due to the more concentrated leaching ratio of 2:1 used in this procedure. Because of this concentrated leaching ratio, it is possible that a portion of the soluble fraction of the sample may not be dissolved due to super-saturation of the extract solution. The CDMG leach test takes 90 minutes per sample versus 15 minutes for the USGS test, which makes the CDMG procedure less practical to do on-site.

The modified TCLP procedure produced leachate geochemical fingerprints that did not correlate as well as those produced by the USGS or CDMG leach tests. The primary reasons for the differences are the use of acidified (acetic acid) extractant in the TCLP test which may lead to selective leaching of certain elements when compared with the other leach tests used in this study that use deionized water as the extractant, and the longer, end-over-end agitation time used in the modified TCLP procedure pulverizes the sample for twenty four hours which does not mimic what happens to these materials in-situ. A further disadvantage of this test is that it must be performed in the laboratory due to its requirement of specialized equipment.

This study showed that regardless of who collected the composite sample, the leachate geochemical fingerprints produced for the collocated composites correlated well. Although the concentration varies for some elements, the geochemical fingerprints were relative for all the collocated composites collected from the same sub-pile. These findings indicate that the USGS sampling procedure is robust.

The leachate geochemical fingerprints produced by CSM using ICP-AES compared very well to the geochemical fingerprints produced by the USGS using ICP-MS. Either analytical procedure produces qualitative, accurate leachate geochemical fingerprints for the mine dump studied. The use of either of these procedures is acceptable.

The most important factors in producing reliable leachate geochemical fingerprints for mine waste are that:

- The objectives of the study must be clear to the investigator so that he/she can sample appropriately.
- Once identified, the samples must be collected in a consistent, unbiased manner at all sites studied.
- The investigator must use the same leach test for all samples. This allows the comparison of results from site to site.

Finally, the findings of this report show that the leachate geochemical fingerprints produced by the USGS Field Leach Test and the CDMG leach test correlate well with the geochemical signature of the "natural" water draining from the adit and toe seep at this site. This correlation indicates that the leachate fingerprints are accurate, reliable assessment tools that produce a qualitative picture of what can be expected to run off of a metal mine waste-pile should it be leached by a meteorological event.

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