

# DEVELOPMENT OF A SIMPLE SCHEME TO DETERMINE THE CHEMICAL TOXICITY OF MINE WASTES<sup>1</sup>

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**Abstract.** A decision tree that uses simple physical and chemical tests has been developed to determine whether a mine waste poses a toxicity threat to the aquatic environment. For the chemical portion of the tree, leachate tests developed by the US Geological Survey (USGS), the Colorado Division of Minerals and Geology (CDMG), and modified 1311 TCLP test of the EPA have been extensively used. The multi-element power of modern inductively coupled plasma, atomic-emission spectroscopy (ICP-AES) is also a necessary component of the scheme. At two sites in Colorado, Virginia Canyon in the Idaho Springs/Central City Superfund Site and in the Upper Animas River Basin, 25 sediment samples and the water flowing over the sediments were collected. General analytical measurements were made in the field, and then, the water and extracts from the three leachate tests were analyzed for 31 elements by ICP-AES. Then, element concentration pattern graphs (ECPG) were produced that compared selected groups of the elements from the three leachates and the water. When the pHs of the water and the leachate were below 5.0, the element concentration patterns of all four solutions were quite similar and aquatic toxicity from metals such as Pb, Cu, Zn, Mn and Al was clearly indicated. When the pHs of the water and the leachate were above 5.0, the element concentration patterns from the four solutions were different and inferred aquatic toxicity depended on the leachate test. Usually when there was a difference, it was found that in the TCLP test, elements from carbonate minerals and oxides dissolved and these elements in the CDMG and USGS tests were not as readily released from solution. In a study done in 2002 in Russell Gulch near Central City, CO, that rated mine waste piles, it was necessary to rate the contamination possibility of the piles on separate physical and chemical scales for the most complete assessment.

Additional Key Words: aquatic toxicity, metal contaminants, aquatic chemistry

<sup>1</sup> Paper presented at the 2003 National Meeting of the American Society for Mining and Reclamation, and the 9<sup>th</sup> Billings Land Reclamation Symposium, Billings, Montana, June 3-6, 2003. Published by ASMR, 3134 Montavesta Rd. Lexington KY 40502.

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Proceedings American Society of Mining and Reclamation, 2003 pp 1501-1516

DOI: 10.21000/JASMR03011501

<https://doi.org/10.21000/JASMR03011501>

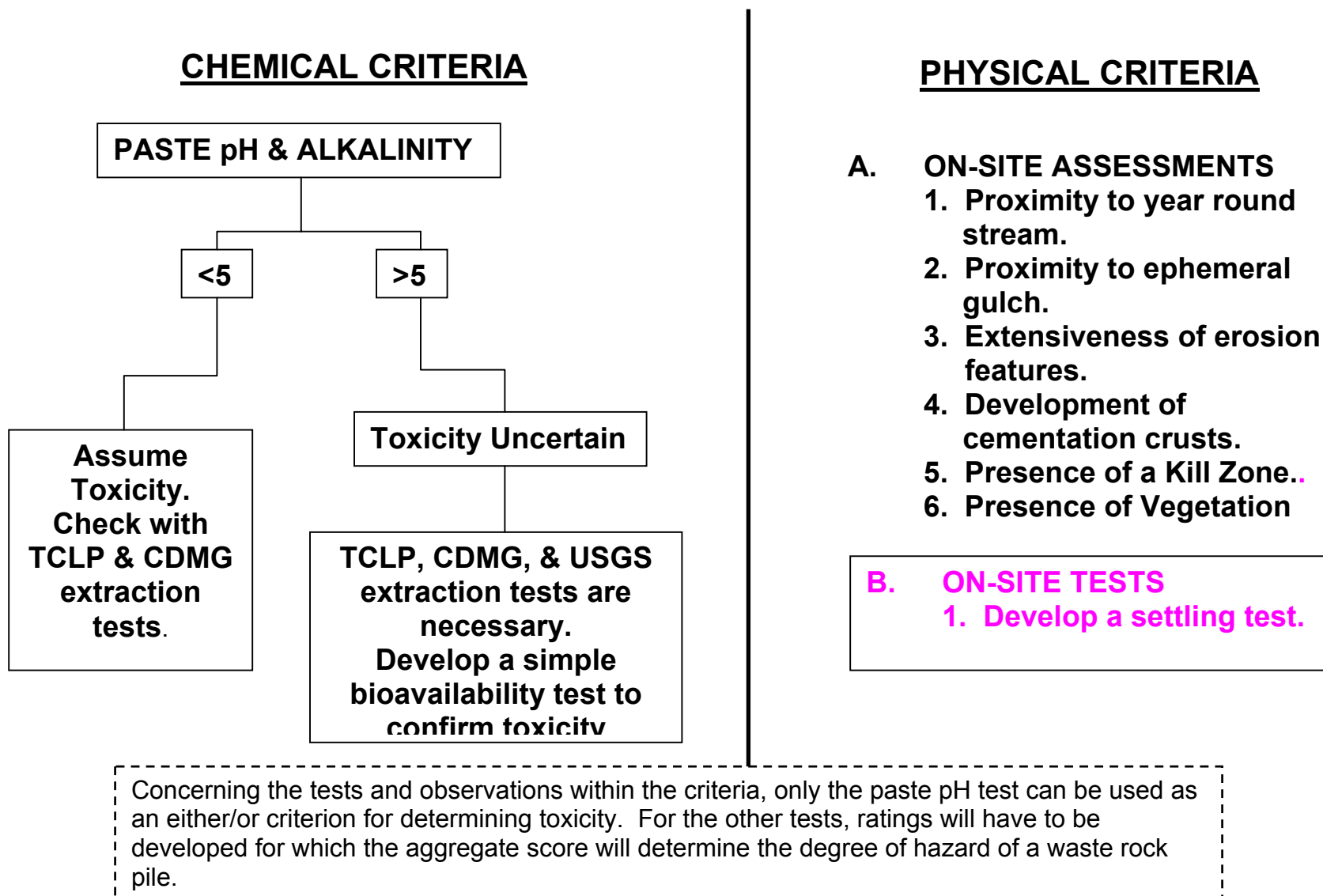
## **Introduction**

When one sees a waste pile at a mine site, the thought of whether this pile is contributing to the toxicity of the environment often comes to mind. If the site is abandoned, the question is more difficult to answer for two reasons: the site is often remote, so carrying back enough material to perform a regulatory test is difficult, and often funds are not available to perform the study. The purpose of this paper is to present a scheme for the assessment of mine wastes that requires a minor amount of material, uses simple physical observations, and requires simple chemical tests. This scheme has been developed over the last five years (Winkler et al., 2000) and owes much to the efforts of scientists from the U.S. Geological Survey (USGS) (Hageman and Briggs, 2000, Smith et al., 2000) and the Colorado Division of Minerals and Geology (CDMG) (Herron et al., 1999, Herron et al., 2001). The decision tree has been based on the study of about 100 mine waste piles that have been studied by the authors. Currently, it is our opinion is that this assessment requires additional development. For example, almost all of the 100 waste rock piles that have been sampled are the result of mining sulfidic ores. However, we want to make interested parties aware of this scheme because it is quite simple and other parties need to test its robustness.

The mine waste assessment is put in the form of the decision tree that you see in Figure 1. It has a physical and chemical component. Indeed, in a recent study performed in the Russell Gulch region of the Central City/ Idaho Springs Superfund site, waste rocks piles were highlighted for remedial action for physical as well as chemical problems. The USGS has made an excellent study of how to collect a representative sample from the surface of a waste rock pile (Smith et al., 2000). The solids sample from the pile that is required for the chemical studies uses this collection method. Perhaps the one portion of the assessment process that is most complex is the requirement of the multi-element analytical capability of inductively-coupled plasma atomic emission spectroscopy (ICP-AES).

This paper gives the analytical procedures used to accumulate the information needed to apply the assessment. Also, key results from previous studies that provided the basis for why the assessment is considered to be effective are also presented.

Figure 1. Assessment scheme for determining waste rock impact on aquatic organisms



### **Procedures for the Physical Assessment**

For mine waste piles, the approximate longitude and latitude of the site is recorded, and the volume of the pile is estimated by walking off the area using a tape measure and then estimating the depth of the pile. The approximate distance from a defined drainage channel is estimated. The channel does not have to have year-round drainage. The erosion caused by storm events is rated as follows: 0= none, 1= sheet wash, 2= rills less than 6”(15 cm) deep, 3= rills between 6-12” (15-30 cm) deep, 4= gullies over 12” (30 cm) deep. The presence of a vegetative kill zone around or below the pile is noted. In addition, the presence or absence of vegetation on the pile is recorded. The presence of cementation crust and the hardness of the crusts are also recorded (Herron, et al., 2001).

For obtaining solid samples of waste piles and sediments, the general guideline that is used is that material of small grain size will be more homogeneous as well as being more reactive. A representative sample of the top 15 cm surface of a pile is taken according to the guidelines published in Smith et al. 2000. This involves dividing the pile into 30 areas of roughly equal area and securing a sample of at least 100 g from each area,. These samples are combined and sieved so that a composite sample of at least one kilogram of minus 2 mm particles is obtained. If the sample is moist, it is dried before sieving. To eliminate contamination, plastic containers are used for obtaining the 100 g samples and for storing the composite. If sediment is being sampled, an effort is made to obtain a number of subsamples of material whose grain size is less than 5 mm. This material is then air dried before being sieved for the leachate tests. If possible, a water sample that is in close proximity to the sediment or waste pile is also obtained.

### **Procedures for the Chemical Assessment**

Three leachate tests are performed on the composite or sediment sample. In previous research conducted on acidic samples, these tests were found to give the best correlation with element concentrations in waters adjacent to the sediment or waste pile (Herron et al. 2001). If possible, a water sample related to the solid sample is collected and field tests for pH, Eh, ionic conductivity, and alkalinity or mineral acidity are made. For the CDMG or the USGS leachate test, a large enough volume of water is used so that pH, Eh, ionic conductivity, and alkalinity or

mineral acidity analyses are made on the excess water. The specific directions for each leachate test are given below.

The water samples and the leachate solutions are analyzed for elemental concentrations using ICP-AES. Approximately 10 ml of filtered sample, acidified with nitric acid, is required. The samples were then analyzed on a Perkin Elmer Optima 3000 ICP-AES for the following 31 elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, and Zn. All concentration results are given in mg/L. During the ICP-AES analysis, an internal standard of Sc is used to correct for adjustments in sample uptake and plasma conditions. Also, concentration check standards are analyzed in the beginning and after every 20 samples to monitor the stability of all analytical conditions. Results on collocated water samples show the relative standard deviation of a concentration value is about 5 % as long as the concentration is 10 times the limit of detection.

#### Colorado Division of Minerals and Geology (CDMG) Test

This 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 procedure is as follows: A volume of 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 this time, approximately 10 ml of leachate is filtered with a 0.45  $\mu\text{m}$  syringe filter, acidified with nitric acid, and analyzed using ICP-AES. Also, after 90 minutes, the pH, Eh, ionic conductivity, and alkalinity are also measured on the leachate.

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

This test was developed by the United States Geological Survey and also determines the potential for metals release from soils when exposed to natural waters (Hageman and Briggs, 2000). However, this test uses a mass basis. A mass of 50 g of <10 mesh sediment sample is massed into a 1 L Nalgene® bottle. Approximately 1 L deionized water is added slowly so that no dust would be lost. The bottle is capped and vigorously hand-shaken for 5 minutes. The contents are then allowed to settle for 10 minutes. The leachate is then filtered with a 0.45  $\mu\text{m}$

syringe filter, acidified with nitric acid, and analyzed using ICP-AES. The pH of the sample is also measured after 10 minutes.

#### Toxicity Characteristic Leaching Procedure (TCLP)

This test is a modified version of Method 1311 developed by the Environmental Protection Agency (US EPA, 2002). The test as originally conceived by the EPA was to evaluate metals mobility in landfills. Here, the test determines the mobility of metals in the presence of mildly acidic waters. It also 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 1 L using deionized water. The pH of this solution should be  $4.93 \pm 0.05$ . A volume of 40 ml of this extraction fluid is added to 2.00 g of < 80 mesh sediment sample in a 125 ml Nalgene® bottle. The bottles are then agitated end over end using a rotary tumbler for 24 hours. The leachate is then filtered with a 0.45 µm syringe filter, acidified with nitric acid, and analyzed using ICP-AES.

#### Virginia Canyon Results

In the spring and summer of 1999, Colorado School of Mines (CSM) students assisted James Herron of the CDMG in an assessment of waste rock piles in Virginia Canyon within the Central City/Idaho Springs Superfund Site (Herron, et al., 2001). This canyon contains a number of ephemeral gulches that drain into a main gulch that has a perennial flow of less than 40 liters per minute. The area has over 100 abandoned mine sites. In this study, Herron refined the methods that make up the physical assessment portion of the decision tree. The goals of the CSM portion of the study were to determine the chemical character of the water, especially during spring runoff and extreme storm events and to find how well various leachate tests correlate with the water that flows in the gulches.

Figure 2: Seasonal Water Data  
Base of Virginia Canyon (pH 3.00)

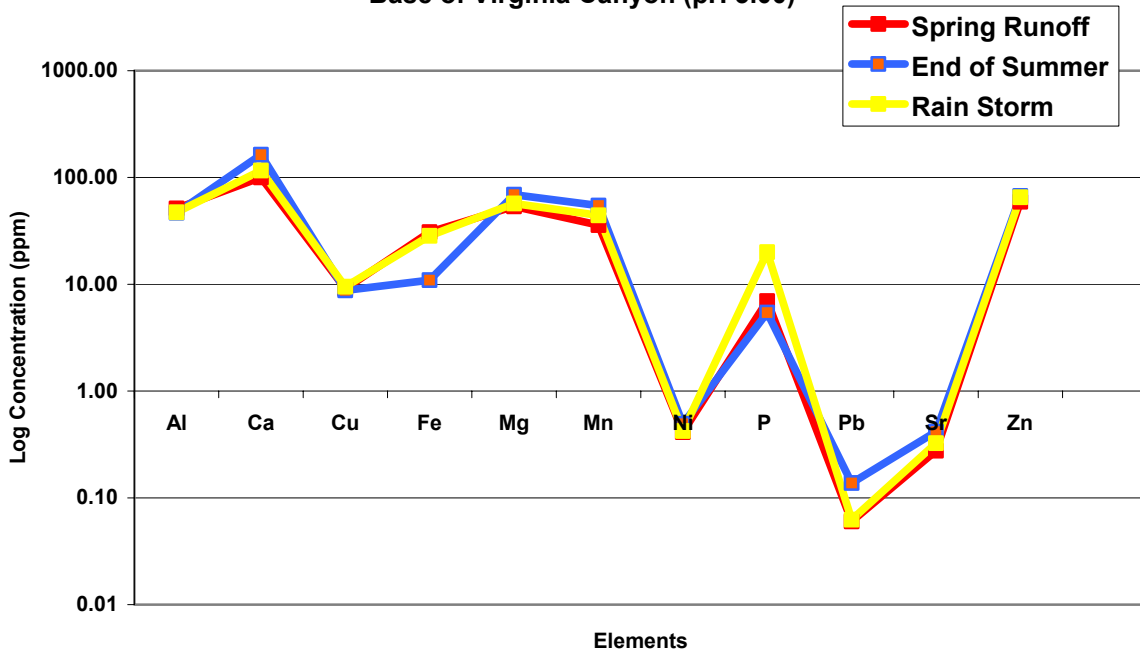
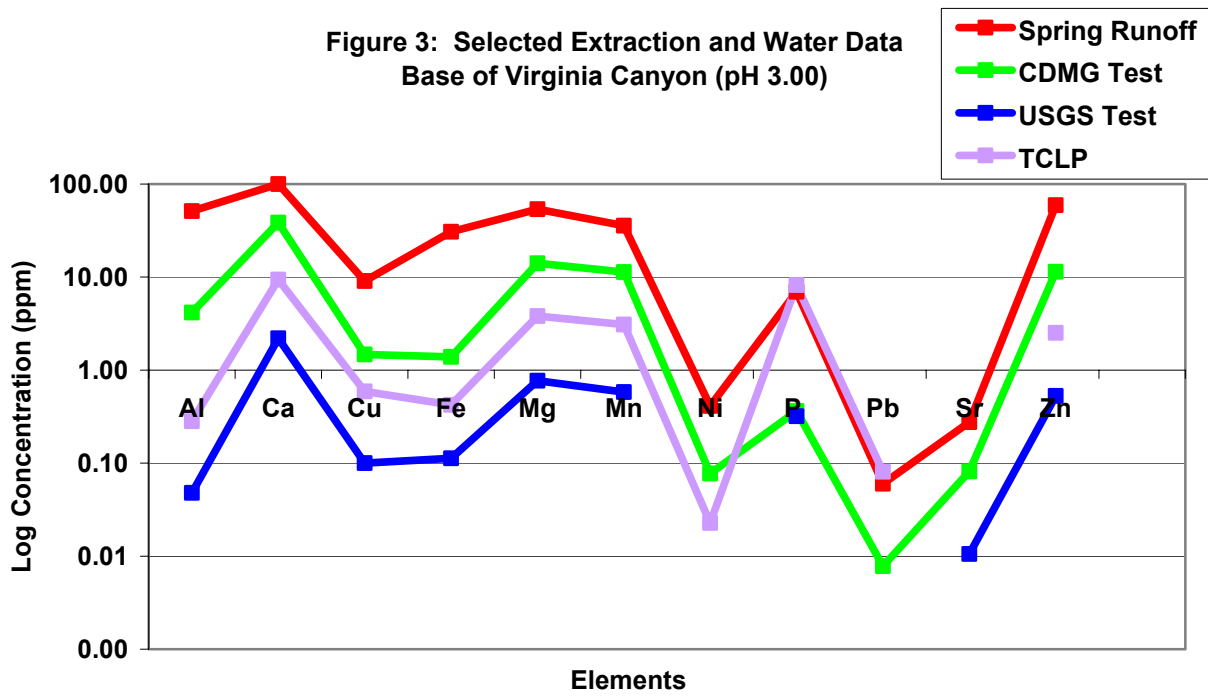


Figure 3: Selected Extraction and Water Data  
Base of Virginia Canyon (pH 3.00)



The results on the water in the gulches at different times of the year were surprising. As shown in Figure 2, the chemistry of the water was the same at spring runoff, during low flow in the summer, and during a summer storm event. Note in Figure 2, that the concentrations are presented on a log scale so that relative changes among concentrations for the three sampling times can be better evaluated. This result of very similar concentrations for all three sampling events was found at all sites in the canyon where water was sampled. It is important to note that all waters sampled were below a pH of 5.0. It must be the case that at these low pHs, there are some readily soluble phases in the sediment and in waste rock piles that control the chemistry of the waters in association with these solids. The conclusion that can be drawn from this result is that when the pH of a mine site water is below 5, such that it has mineral acidity from Fe and Al, then the chemistry of the water does not change significantly throughout the year and during storm events. Although in Figure 2 waters from only one site are shown, the same result was found in the waters from 13 other sites in Virginia Canyon (Herron et al, 2001). Consequently, it is not necessary to catch water during a storm event to estimate the chemistry of water issuing from an area that has been highly impacted by metals mining.

In the Virginia Canyon study, 29 gulch sediments in close proximity to the waters were collected, dried, and sieved for use in extraction and leachate tests. In Figure 3, the results for the USGS, CDMG, and modified TCLP test as well as the spring runoff waters are shown for the gulch site at the base of the canyon. Again, the concentrations are plotted on a logarithmic scale so that relative changes from sample to sample can be better assessed. The important thing to notice is the good correlation in the element concentration patterns among the three tests and the water. Because the USGS test uses the the highest ratio of water to solids and because the water and solids are mixed for only 15 minutes, the element concentrations from this test are usually the lowest. The low ratio of water to solids and longer mixing time usually results in the CDMG test showing the highest element concentrations. Note that, from examination of the three leachate tests, one can conclude that water flowing from this waste pile would have Al, Cu, Mn, Ni, Pb, and Zn above acute aquatic toxicity limits for Colorado cold waters that have a hardness of 100 mg CaCO<sub>3</sub> / L. Note also that if water from the gulch were not available, rough estimates on the concentrations of the elements in the water could be made from the leachate tests.

In the Virginia Canyon study, three other leachate tests were conducted to determine how well these extractions would match with the gulch water. In Figure 4, the results of these tests



show they do not match up as well as the tests shown in Figure 3. The SPLP test is one the EPA uses to simulate acid rain falling on a material (US EPA, 2002). Note that the element concentrations are far lower than the spring runoff water. The FeO test uses hydroxyl amine hydrochloride to dissolve iron and manganese oxides (Clayton and Wildeman, 1998). Note that this test causes release of more iron and aluminum than is contained in the spring runoff water. This implies that the metals dissolving from the sediments into the gulch water are not coming from iron or manganese oxides. The APP test uses hydrogen peroxide to dissolve sulfide phases that may be in the sediment. The element concentrations from this test are quite low, about the same as the SPLP test. Note that the test does not release any Fe, Cu, Zn, or Pb, the elements that one would expect to be released if pyrite or acid volatile sulfides were dissolved.

In Figure 5, the results from the three leachate tests as well as the water concentrations are shown for Robinson Gulch, a tributary gulch of Virginia Canyon. The water at this site has a pH of about 4.4 and so the element patterns at this site are indicative of what would be leached from sediments that have a more moderate paste pH. Note that the patterns do not show as good a correlation as that seen in Figure 3 where the pH of the water is 3.0. Still the patterns are good enough to predict that when elements are leached from this sediment that Al, Cu, Ni, and Zn would probably exceed acute aquatic toxicity limits for Colorado cold waters that have a hardness of 100 mg CaCO<sub>3</sub> / L. The results from this Virginia Canyon study as well as studies done by the USGS using their leachate test (Hageman and Briggs, 2000) lead us to the decision that, if a sulfidic mine waste gives a paste pH below 5, then it is probably toxic to aquatic organisms. That is the basis for an either/or decision on toxicity depending upon whether the paste pH of a mine waste is greater or less than 5.0.

### **The Element Concentration Pattern Graph (ECPG)**

The link between the leachate tests and the assessment of whether water issuing from a mine waste is toxic to aquatic organisms is based on the fact that not just one or two elements are considered. Instead, using the analytical power of the ICP-AES, 10 to 13 elements make up the pattern graph and this establishment of a pattern helps to corroborate the concentrations of important contaminants. Consequently, it was decided to standardize these graphs as much as

Figure 4: Selected Extraction and Water Data  
Base of Virginia Canyon (pH 3.00)

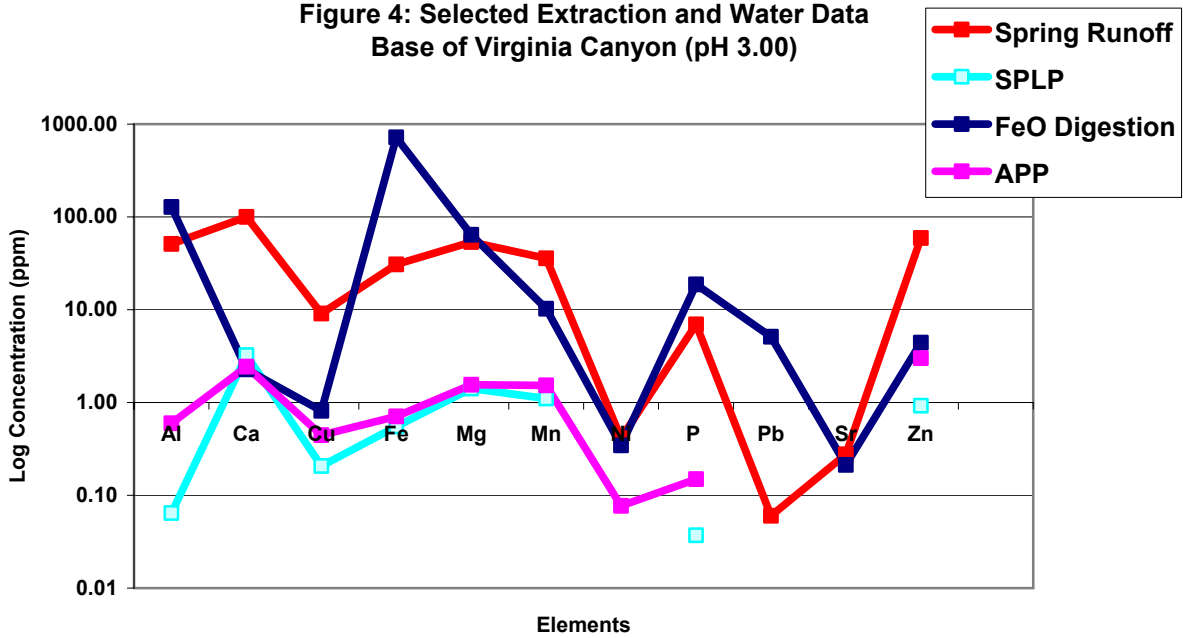
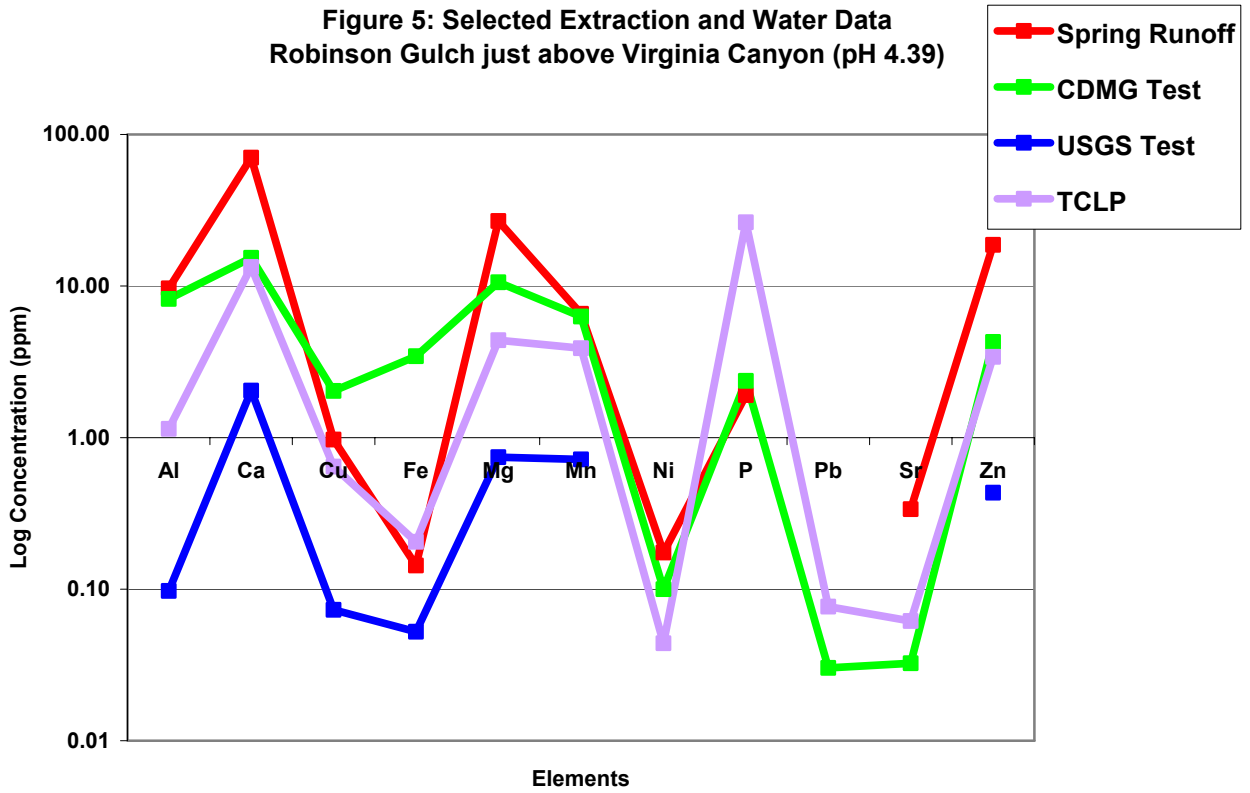


Figure 5: Selected Extraction and Water Data  
Robinson Gulch just above Virginia Canyon (pH 4.39)



possible and give them a title: Element Concentration Pattern Graph (ECPG). For the ECPG, the concentrations are plotted on a logarithmic scale so that relative differences among the leachate tests and water can be better determined. Then, the order of elements was standardized so that correlations can be better established. The x-axis order of elements is as follows:

1. Na, K, and S: These are readily soluble elements and should correlate best with the adjacent waters. Note this assumes that the sulfur species in the water is primarily sulfate.

2. Ca, Mg, and Sr: Carbonate minerals could control the concentrations of these elements if these were present in the mine waste/water system.

3. Pb, Cu, Zn and Ni: Either sulfide minerals or carbonate minerals could control the concentrations of these elements if these were present in the mine waste/water system.

4. Fe, Mn, and Al: Oxide minerals could control the concentrations of these elements if these sedimentary minerals were present in the mine waste/water system. Figures 6, 7, and 8 use this format and note the good correlation of the elements in the first two groups. Although none of these elements cause aquatic toxicity problems, the good correlation of these elements among the leachate tests helps to pin down the element concentration pattern.

### **Results From the Upper Animas River Basin**

The results from Virginia Canyon show that mine wastes that have a paste pH below 5 can be considered to be toxic to aquatic life. The next question is how would mine wastes that have a paste pH above 5 respond to the leachate tests and would they also show toxicity to aquatic organisms. To study this question, sediment samples and adjacent waters were collected from the Upper Animas River Basin, which is the location of the Silverton, CO Ore District. The ore deposits contain considerable carbonate gangue minerals and 11 places were found where water flows over mill tailings and waste rock piles that have paste pH's above 5.0. Figures 6 and 7 are ECPGs for two sediments taken from perennial streams from the Silverton area that contain considerable amounts of mill tailings. Note that, for elements in the first two groups, the correlation among element concentrations is quite good and this shows that if all of the elements were responding in the same manner in each of the leachate tests, then the elements in groups 3 and 4 should show good correlation. However, for groups 3 and 4, the element concentrations

Figure 6: Sediment Sample From Well 10 surface Tailings (pH = 5.2)

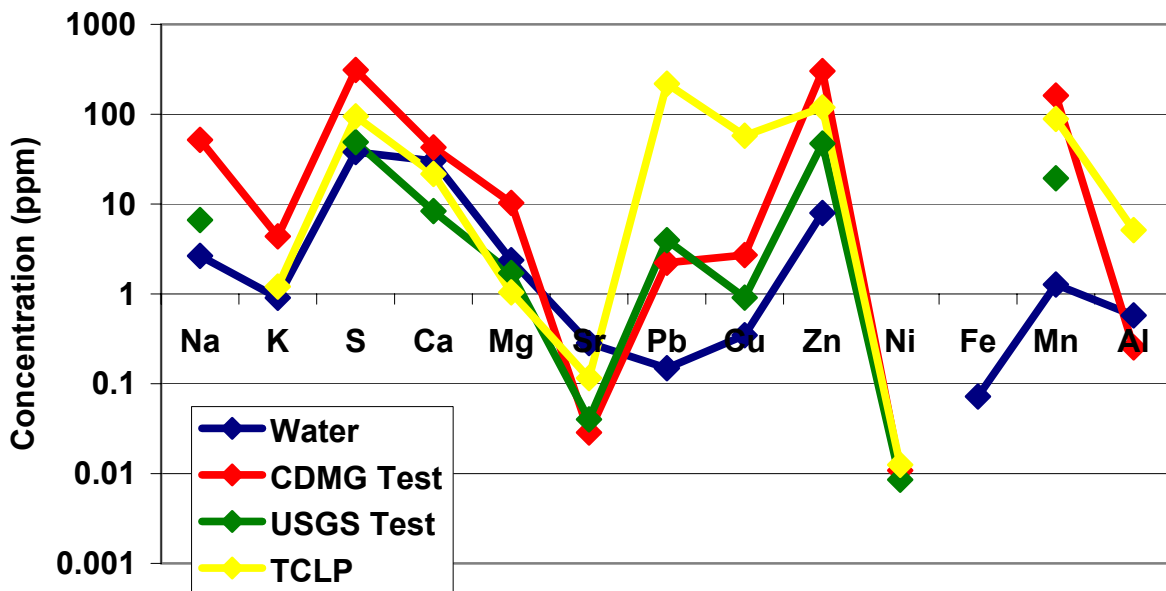
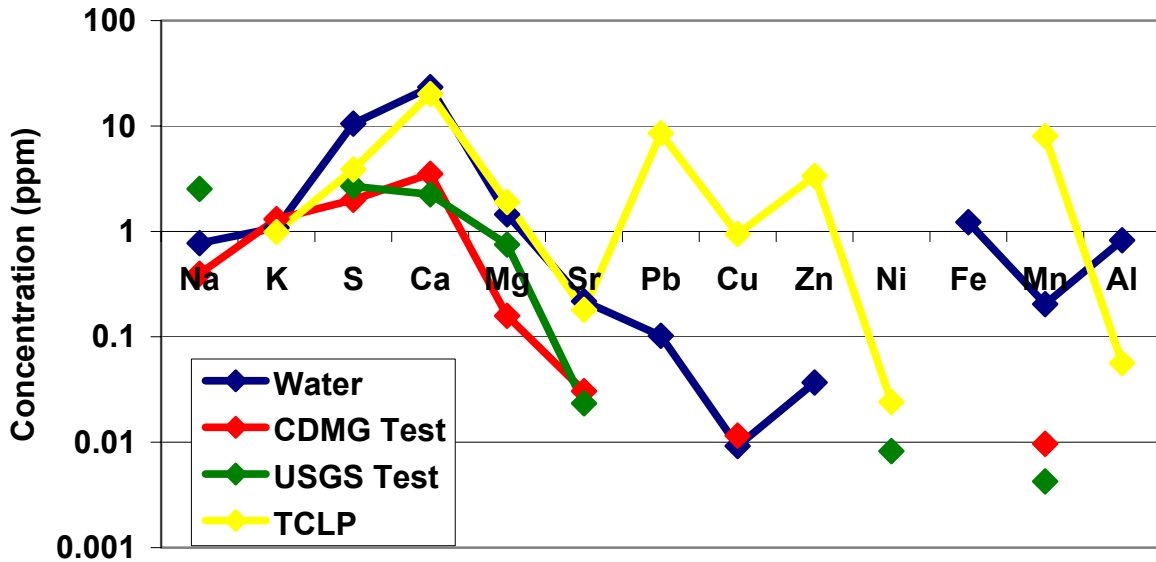


Figure 7: Highland Mary Tailings Pond Berm Sediment (pH = 6.5)



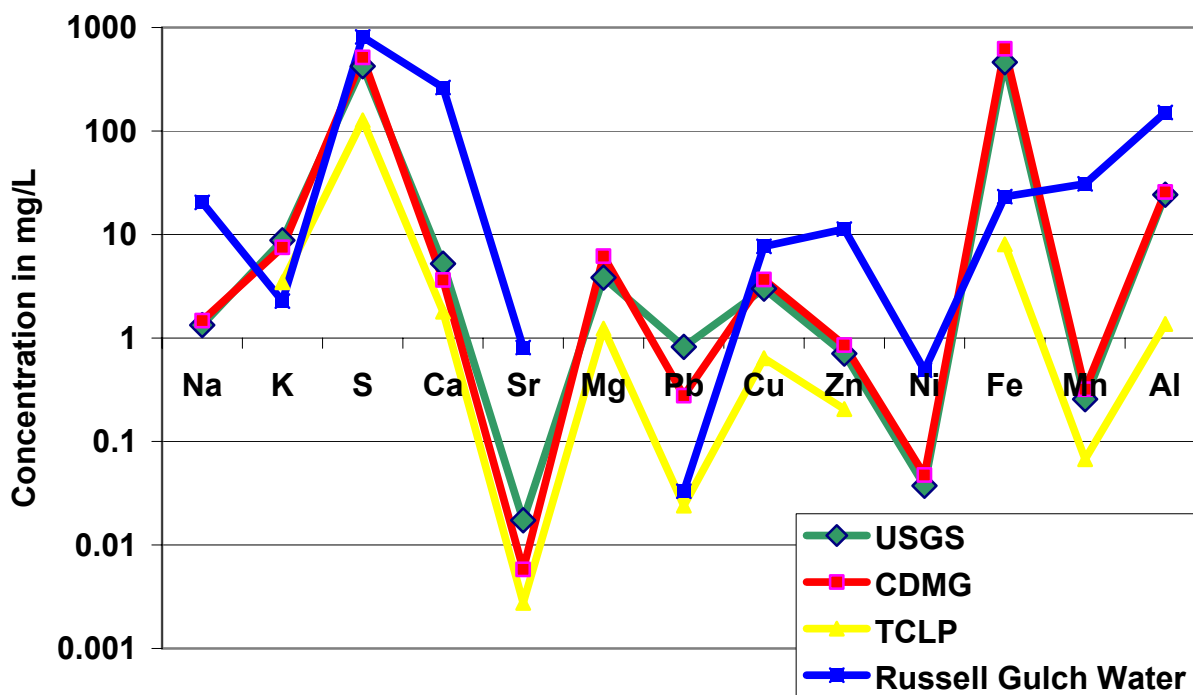
from the leachate tests deviate substantially from the concentrations in the adjacent water. In particular, note that the Pb, Cu and Zn concentrations in the solution developed from the TCLP test show much higher concentrations than what is in the adjacent water. The current thought is that the acetate solution used in the TCLP test complexes these metals and thus draws them into solution. Also, the figures show that the Fe, Al, and Mn can vary greatly among tests. Thus, it is the case that, for those waste materials that have a paste pH above 5, the leachate tests are needed to assess the possibility of aquatic toxicity.

### **Results From Russell Gulch**

In 2002, personnel from Region 8 of the EPA desired a study of Russell Gulch near Central City, CO that was comparable to the study that Herron et al. (2001) did in Virginia Canyon. In this gulch and its tributaries, there is only an ephemeral flow and, because 2002 was a drought year, very little water was found in the area. Thus, to assess the mine waste piles in the area, only the three leachate tests could be used. In addition, the decision tree shown in Figure 1 was devised before the study and was used as the basis for rating the toxicity of the mine wastes piles. In this project, 27 mine waste piles were sampled.

In general, all of the mine waste piles in this area showed a paste pH below 5. However, it was still necessary to determine which piles were the worst contributors. The preliminary results show that some piles pose serious risks on a physical basis but are not the worst on a chemical basis. Consequently, it was necessary to make separate physical and chemical ratings of the environmental risks the piles posed. In no cases was water found on the mine waste piles but in some cases water was found in the nearby gulches. So, the ECPGs used this water for comparison with the three leachate tests. Figure 8 is an ECPG for the leachate tests from a composite sample of a waste rock pile and the nearby gulch water. Note the close correlation for

Figure 8. Russell Gulch: Unknown Mine #2 (pH = 2.5)



the first two groups of elements for all three tests. The nearby water represents best the base flow from the area and roughly correlates with the three tests. For the elements in groups 3 and 4, the correlation is not as good. Nevertheless, acute aquatic toxicity limits for Colorado cold waters that have a hardness of 100 mg CaCO<sub>3</sub> / L to aquatic organisms are exceeded for Pb, Cu, Zn, Ni, and Al. Although the decision tree would say that the leachate tests did not have to be done to show toxicity, the results of the tests do confirm that aquatic organisms could not live in the waters leached from this mine waste pile.

### Discussion

It should be considered that use of the decision tree is still in the verification stage. The results from Russell Gulch show that toxicity ratings can be made using the decision tree. Its use in an area that has mine wastes with a paste pH greater than 5 and has minimal water for comparison would be a good next test. Two other tests would help to make a better assessment. On the chemical side, a leachate test for mine wastes that do not show severe toxicity and would

approximate the metabolic uptake of metals by aquatic organisms would help in the evaluation of aquatic toxicity. On the side of physical tests, a simple on-site test that would estimate how much suspended solids would wash from a mine waste pile in a severe storm event needs to be developed.

On another front, it would be useful to determine why, for those mine wastes that have low paste pHs, the elements correlate so well. This would involve determining the actual minerals in the mine waste samples and assessing which minerals would rapidly dissolve. Attempts at geochemical modeling to determine the minerals in equilibrium with the elements in the water have proved unsuccessful. The current hypothesis is that, at low pHs, jarosite minerals are formed as the primary minerals in the mine waste weather, and these secondary minerals are capable of rapidly dissolving.

Finally, the issue of whether the cementation crust that develops on some mine waste piles protects or dissolves during a storm event needs to be investigated. Based on the investigations that have already been done, it appears that those piles with have the most developed crusts also have the most severe toxicity as shown in the ECPG. Thus, it appears that the cementation crust is related to the formation of highly reactive secondary minerals. Nevertheless the tendency of mine wastes to form crusts needs to be investigated because the idea that these crusts can protect the pile from generating toxic waters during a storm event needs to be substantiated or disproved.

### **Conclusions**

A decision tree for the assessment of mine wastes is presented in Figure 1 and the background studies that serve as the basis for the tree have been discussed. Although the use of this tree for making waste pile assessments is still in the development stages, all the projects that have used this approach for assessment have found it to be robust and conclusive. Comments and suggestions from others that have used a similar approach or see the need for changes to the decision tree would be most welcome.

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