

EVALUATION OF THE TCLP METHOD FOR TWO MILL TAILINGS¹

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Abstract.--Initial results are reported on determining the applicability of the toxicity characteristic leach procedure (TCLP) in predicting the potential for heavy metal contamination associated with mining wastes. TCLP tests, variations of the TCLP tests, and baseline tests were run on tailings samples from two mills to determine the sensitivity of laboratory protocol to slight procedural errors and to determine if any inherent factors produced a fatal flaw in using the test to evaluate mine tailings. Results from tailings A showed that metal ion concentration increased with higher liquid-to-solid ratios, with an increased volume of HOAc, and with longer mixing times. Results from tailings B showed the same general trends, but varied significantly in sensitivity to variations. The average yield of the standard TCLP tests as a percentage of the total digestion assay is 20% for tailings A and 10% for tailings B. This is a significant difference between the two types of tailings. Evaluation of these initial results indicates that the sensitivity of the three parameters to laboratory errors is probably acceptable if laboratory procedures are followed with normal attention to detail. These results are only the initial phase of a systematic evaluation of the TCLP method. Future research should emphasize how well the TCLP test actually simulates mine waste contamination phenomena. In particular, studies should focus on the applicability of the extraction fluid, chemical and mineralogical effects in and around the disposal area, time, pH effects, and oxidation effects.

INTRODUCTION

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Substantial public concern has been voiced regarding contamination of water resources caused by mining (non-coal) and resulting adverse effects on human health. This concern has prompted the Environmental Protection Agency (EPA) to initiate a regulatory development program for the mining industry, which in turn has created a need to predict contamination potential at mine sites (EPA-December 1985 Report to Congress). Members of the American Mining Congress, the mining industry's most prominent

collective organization, have stated that resolution of the mining waste problem is the mining industry's number one issue. Regulatory efforts under the Resource Conservation and Recovery Act (RCRA) initially utilized the EP toxicity test as a primary standard with which to evaluate contamination potential (EPA-Office of Solid Waste 1987). This test was selected for analyzing metal mine wastes since its use is standard practice in determining whether industrial wastes are categorized as hazardous and unacceptable waste for sanitary landfills. However, there have been many technical concerns about its applicability to mining wastes. These concerns have centered mainly around the assumptions inherent in the testing procedures; that is, certain assumptions cause the test to be a poor simulator of mine waste disposal conditions. For example, the preferential dissolution of lead by the acetic acid used in the test procedures skews tests for lead, a heavy metal of great importance in mining wastes (Lead Industries Association Report 1984).

As a result, the U.S. Bureau of Mines' Spokane Research Center (SRC) is performing research to determine more effective methods of evaluating the potential for contamination due to metal/nonmetal mining activity. As part of this effort, we are examining existing laboratory testing methods to determine what applicability they may have in assessing contamination potential. The first test now in the process of being reviewed is EPA's toxicity characteristics leach procedure (TCLP) (Federal Register, Volume 51, No. 9). This method was selected since it is currently being considered as a replacement for the EP toxicity test. Also, EPA is actively seeking evaluation methods for its Mine Waste Regulatory Development Program and it has been suggested that the TCLP method could be utilized.

This report examines the results of tests using the TCLP method for monitoring metal contamination from mill tailings from two different mills. Organics and volatiles were excluded from these experiments because they are of little concern in mine tailings. Eleven key elements were analyzed. Some modifications were made to the standard TCLP method in order to streamline laboratory procedures because there are no organics or volatiles to consider. For all tests, the organics testing portion was deleted and the leachant was filtered by gravity with a qualitative grade filter rather than by pressure or under a vacuum. Other experimental variations to the standard TCLP method were made as discussed below to evaluate the method.

MATERIALS AND METHODS

To determine what changes in metal concentrations would be seen in the TCLP

test, the liquid-to-solid ratio, acid strength, and mixing time were varied. The standard TCLP test procedures require a liquid-to-solid ratio of 20:1, a volume of 5.7 mL of glacial HOAc (acetic acid) made up to 1 L of extraction fluid with ASTM type 2 water to obtain a molarity of 0.10 and a rotation time of 18 hours. The liquid-to-solid ratio was varied by using a standard sample of 50 of solid and varying the total volume of slurry from 0.25 to 2.00 L. The molarity of HOAc was varied in our tests from 0.05 to 0.20, and the duration of rotation from 1 to 25 hours.

Total digestion analyses and modified TCLP tests using distilled water as an extraction fluid were also performed and the results compared to TCLP results to provide an indication of the stringency of the procedure. Tailings from two different mills were evaluated in these experiments. The first mill processed silver ore primarily while lead and zinc were secondary ores (tailings A). The second mill processed lead ore (tailings B).

The analyses were conducted on an AA spectrometer for aluminum (Al), silver (Ag), calcium (Ca), cadmium (Cd), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), nickel (Ni), lead (Pb), and zinc (Zn). The tailings were not tested for organics or volatiles because the project is concerned with metal contamination only. Results reported here include only Al, Cu, Fe, Ni, Pb, and Zn because concentrations of the other elements were very low or the variations were insignificant. TCLP test results are normally presented in milligrams per liter of slurry. However, results of most of these tests were converted to milligrams per gram of solid for comparing with digestion assays. This conversion is made by using the equation

$$A = (B \cdot C) / D \quad (1)$$

where A = mg of contaminant in each g of waste,
B = mg/L of contaminant in solution,
C = total volume of solution, L,
and D = total g of solid used.

This reporting unit (mg/g) also provides a more conceptually clear method of describing the contaminant release from a given amount of waste material.

RESULTS

In the first set of experiments, both the liquid-to-solid ratio and the acid strength were varied for tailings A as shown in table 1. Fifty grams of tailings were used in each test and the volume of leachant was varied to obtain variations in the liquid-to-solid ratio. The data for tailings A show a general increase in metal concentrations (1) as

Table 1.--Leaching of metal ions from tailings A with varying molarity of acetic acid and volume of leachant, mg ion/g of solid waste.

Volume, L	Al	Cu	Fe	Ni	Pb	Zn
0.05 Molar						
0.25.....	0.029	0.009	0.645	0.003	1.07	0.145
.50.....	.037	.024	1.08	.004	1.49	.149
.75.....	.040	.026	1.50	.005	1.84	.137
1.00.....	.044	.026	1.88	.005	2.13	.124
1.25.....	.044	.027	1.76	.005	2.15	.158
1.50.....	.047	.027	2.05	.005	2.21	.162
1.75.....	.051	.027	2.43	.005	2.01	.161
2.00.....	.053	.027	2.54	.005	1.92	.160
0.10 Molar						
0.25.....	0.041	0.024	0.90	0.003	1.26	0.164
.50.....	.050	.026	1.50	.003	1.73	.160
.75.....	.057	.028	1.94	.003	2.12	.176
1.00.....	.063 ¹	.029 ¹	2.31 ¹	.003 ¹	2.49 ¹	.180 ¹
1.25.....	.064	.028	2.63	.003	2.39	.340
1.50.....	.065	.028	2.89	.004	1.86	.174
1.75.....	.064	.029	3.07	.004	2.54	.182
2.00.....	.067	.029	3.81	.004	2.80	.172
0.20 Molar						
0.25.....	0.052	0.026	1.98	0.004	1.50	0.177
.50.....	.055	.028	2.83	.004	2.21	.171
.75.....	.058	.029	3.47	.004	2.25	.165
1.00.....	.062	.029	4.00	.004	2.69	.170
1.25.....	.064	.029	4.48	.004	2.79	.183
1.50.....	.067	.029	4.66	.003	2.75	.173
1.75.....	.066	.029	4.84	.003	2.94	.173
2.00.....	.070	.030	5.33	.003	3.04	.166

¹Results using standard TCLP test parameters (0.10 molar, 1.0 slurry).

Table 2.--Leaching of metal ions from tailings B with varying acetic acid molarity and volume of leachant, mg ion/g of solid waste.

Volume, L	Cu	Fe	Pb	Zn
0.05 Molar				
0.50.....	0.002	0.001	0.187	0.090
1.00.....	.008	.001	.528	.102
1.50.....	.010	.003	.480	.118
2.00.....	.013	.005	.612	.128
0.10 Molar				
0.50.....	0.009	0.001	0.338	0.125
1.00.....	.013 ¹	.010 ¹	.562 ¹	.129 ¹
1.50.....	.014	.211	.674	.138
2.00.....	.015	.638	.641	.135
0.20 Molar				
0.50.....	0.013	0.674	0.360	0.145
1.00.....	.011	.630	.720	.141
1.50.....	.016	1.58	.780	.154
2.00.....	.016	1.82	.896	.148

¹Result using standard TCLP parameters (0.10 molar, 1.0 L of slurry).

the volume of leachant was increased (increased liquid-to-solid ratio) and (2) as the molarity or acid strength was increased for all three molarity groups except for Ni, which remained constant throughout the test.

For tailings B (table 2), the parameters were varied, but fewer liquid-to-solid ratio data were collected since the results from the first set of experiments indicated the variations in concentrations were small and continually increasing with liquid amounts so that the measurement intervals could be made larger.

Aluminum and nickel are not reported here because concentrations were low and changes in values were insignificant. The same general trends in test results occurred in tailings B as in tailings A. Concentration of the metal ions increased with increasing volume (liquid-to-solid ratio) and with increasing molarity of acetic acid in the leachant.

In the third set of experiments, the mixing time parameter was varied for leachant in contact with tailings A (tables 3-6). The standard method calls for 18 hours of mixing by rotation at 30 rotations per minute. Four test containers were rotated and samples were taken from containers 1, 2, 3, and 4 at 1, 2, 3, and 5-hour intervals, respectively, for 25 hours. Multiple containers were used to determine if the removal of analytical samples during rotation influenced the results. Results showed that if the data are averaged for each element and container, there is good agreement among the four different interval times. This indicates that removal of analytical samples during rotation did not influence test results. It should be noted that leachate concentrations of Cu, and to a lesser extent Al and Ni, remained relatively constant for various durations of mixing, while those of the other ions (especially Fe) continued to increase as the duration of mixing increased.

The concentrations of the various metals obtained using the modified TCLP were compared with the total available

metal concentrations in the tailings. Assays were performed by the U.S. Bureau of Mines, Albany Research Center. The results of the analyses are reported in

table 7 for the six reported metals and represent the digestion assay concentration for each element in every gram of tailings.

Table 3.--Effect of mixing time on the amount of metal ions leached from tailings A, container 1, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
1.....	0.0406	0.0246	0.248	0.0028	1.86	0.132
2.....	.0584	.0256	.428	.0030	1.82	.138
3.....	.0490	.0264	.618	.0030	1.82	.146
4.....	.0478	.0264	.730	.0030	1.88	.146
5.....	.0484	.0266	.898	.0034	1.94	.150
6.....	.0490	.0266	1.11	.0034	2.08	.152
7.....	.0558	.0276	1.28	.0040	2.08	.154
8.....	.0568	.0274	1.46	.0036	2.22	.156
9.....	.0556	.0276	1.59	.0038	2.28	.160
10.....	.0508	.0270	1.73	.0040	2.18	.164
11.....	.0538	.0268	2.09	.0040	2.36	.164
12.....	.0546	.0274	2.24	.0040	2.40	.172
13.....	.0520	.0266	2.51	.0040	2.46	.174
14.....	.0514	.0272	3.10	.0042	2.54	.170
15.....	.0512	.0274	3.10	.0040	2.60	.172
16.....	.0500	.0270	3.10	.0036	2.56	.172
17.....	.0574	.0272	3.74	.0042	2.74	.178
18.....	.0556	.0272	3.89	.0040	2.60	.180
19.....	.0588	.0266	4.11	.0034	2.68	.182
20.....	.0602	.0266	4.51	.0034	2.72	.184
21.....	.0590	.0264	4.95	.0044	2.76	.182
22.....	.0684	.0258	5.53	.0042	2.80	.188
Ave....	.0538	.0267	2.41	.0037	2.34	.164

Table 4.--Effect of mixing time on the amount of metal ions leached from tailings A, container 2, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
2.....	0.0440	0.0256	0.400	0.0028	1.86	0.122
4.....	.0484	.0262	.736	.0032	1.88	.148
6.....	.0484	.0264	1.05	.0034	1.98	.146
8.....	.0574	.0272	1.59	.0038	2.16	.164
10.....	.0504	.0266	1.83	.0042	2.28	.158
12.....	.0536	.0274	2.11	.0044	2.32	.168
14.....	.0504	.0270	2.40	.0040	2.44	.168
16.....	.0500	.0270	2.74	.0056	2.46	.172
18.....	.0512	.0272	3.10	.0040	2.42	.176
20.....	.0530	.0268	3.38	.0034	2.60	.178
22.....	.0440	.0266	3.64	.0042	2.58	.176
24.....	.0530	.0266	3.84	.0040	2.56	.180
25.....	.0544	.0272	4.03	.0042	2.65	.182
Ave....	.0506	.0268	2.37	.0039	2.32	.164

Table 5.--Effect of mixing time on the amount of metal ions leached from tailings A, container 3, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
3.....	0.0488	0.0264	0.550	0.0026	1.82	0.150
6.....	.0490	.0268	1.03	.0034	2.00	.158
9.....	.0512	.0268	1.55	.0046	2.20	.164
12.....	.0532	.0272	2.13	.0040	2.44	.168
15.....	.0526	.0274	2.52	.0032	2.48	.170
18.....	.0496	.0274	2.97	.0040	2.48	.176
21.....	.0446	.0258	3.21	.0036	2.54	.180
24.....	.0518	.0270	3.64	.0038	2.54	.180
25.....	.0544	.0276	3.75	.0042	2.62	.182
Ave....	.0506	.0269	2.37	.0037	2.35	.170

Table 6.--Effect of mixing time on the amount of metal ions leached from tailings A, container 4, mg ions/g of solid waste.

Hours	Al	Cu	Fe	Ni	Pb	Zn
5.....	0.0492	0.0258	0.882	0.0034	1.88	0.148
10.....	.0504	.0258	1.74	.0032	2.26	.156
15.....	.0496	.0262	2.44	.0032	2.32	.160
18.....	.0488	.0258	2.89	.0034	2.36	.170
20.....	.0550	.0260	3.03	.0040	2.44	.170
25.....	.0514	.0260	3.45	.0040	2.38	.172
Ave....	.051	.026	2.41	.004	2.27	.163

Table 7.--Assay results for tailings A and B, mg/g, and standard TCLP results as a % of assay.

Tailings	Al	Cu	Fe	Ni	Pb	Zn	Ave.
A, mg/g (assay).....	0.199	0.141	68.1	0.015	5.41	1.60	
% TCLP is of assay..	32	20	4	20	36	10	20
B, mg/g (assay).....	.188	.318	27.7	.138	1.77	.934	
% TCLP is of assay..	6	4	0	4	30	14	10

Table 8.--Average of 10 standard TCLP tests for tailings A and B, mg/g and standard deviations (SD), and coefficient of variation (CV).

Tailings	Al	Cu	Fe	Ni	Pb	Zn
A.....	0.064	0.028	2.99	0.003	1.97	0.167
SD.....	.001	.0004	.284	.0004	.036	.016
CV.....	2	1	9	13	2	10
B.....	0.012	0.012	0.011	0.005	0.524	0.133
SD.....	.003	.0004	.003	.0004	.132	.005
CV.....	25	3	27	8	25	0

Table 9.--Metal concentrations using deionized water as leachant, ions/g of solid waste.

Tailings	Al	Cu	Fe	Ni	Pb	Zn
A.....	0.0002	nd	nd	nd	0.0014	0.0050
B.....	.0024	nd	0.0002	nd	.0018	.0004

nd - below detectable limits

Standard TCLP test results are compared to the baseline assay data in table 7. Note that tailings A had an average of 20% for the six metals while tailings B had an average of only 10%.

Ten individual analyses were made on both tailings samples to determine the statistical reliability of each metal concentration (table 8). The coefficient of variation was less than 15 for tailings A in most of the metal concentrations, while tailings B had three elements with a coefficient of variation of 25 or larger. However, concentrations of two of these three elements approached the detection limits of the spectrometer. There is good agreement between the 18-hour test (tables 3-6) and the data reported in table 8.

The leachability of these ions by rainwater may be considerably less than that inferred from TCLP results using 0.1M acetic acid as leachant. Results of a modified TCLP test in which 1 L of deionized water was mixed with 50-g

samples of tailings A and B are reported in table 9. Significantly less amounts of each element were leached by the water.

As previously stated, mill A was processing silver ore while mill B was processing lead. Because the ores from the two mills were different, the mill waste reacted quite differently to testing. The principal minerals present in mill A waste were silica, galena, and sphalerite; the principal mineral from mill B tailings was dolomite with trace amounts of sphalerite, pyrite, and galena.

A major difference observed during our investigation of these two mill tailings samples was the change in pH during the mixing period. The TCLP requires a starting pH of 2.88 but, unlike the EP toxicity method, does not specify the ending pH. For all our tests, the pH was measured before adding the mill waste and after the 18-hour mixing period. The pH increased to about 3.7 for mill tailings

A and to 5.0 for mill tailings B. Such an increase would be expected.

In another series of tests for tailings A, liquid samples (ready for AA analysis) were used to evaluate the time affect of sample storage. The samples were stored at room temperature and rerun after 2 weeks and again after 3 weeks to determine if delayed analysis affected the results. The average of all 52 runs was determined for Fe, Pb, and Zn and compared to the data in table 8. The results showed less than 6% difference between any of the delayed samples as compared to the 10 runs reported in table 8, indicating little change because of the 3-week delay before the filtered samples were analyzed.

CONCLUSIONS

The current project is the first phase of a detailed evaluation of the TCLP test to determine what, if any, applicability the test has in evaluating mine wastes. An evaluation of the results shows that there are many factors that may influence the TCLP laboratory test. The following points summarize the research to date.

- o The TCLP results are not highly sensitive to changes in the liquid-to-solid ratio, acid strength, and duration of mixing. Small laboratory measuring errors will not have a significant impact on TCLP test results unless gross errors are made.
- o Variations of the length of mixing time for the TCLP test show that equilibrium conditions for metal concentrations are attained for only some elements during the standard 18 hours. Other metal concentrations were increased at varying rates, indicating that the TCLP test results may be arbitrarily biased for certain elements as influenced by the length of mixing time.
- o The percentage of metals extracted using the TCLP method varied significantly between the two tailings tested (20% versus 10%). This may indicate a bias of the TCLP method to being influenced by the mineralogical properties of the waste, which are not leaching phenomena considered in the standard TCLP test.
- o Further research is needed to determine the applicability of the TCLP test to mining waste. The scope of this initial effort was limited to two tailings sources and assessment of only a few factors that could influence the applicability of the TCLP test to mining wastes.

Based on these results and other similar research at SRC, it appears that better laboratory assessment methods could be developed that more appropriately aid in the simulation or prediction of contamination from mine wastes. This preliminary assessment was made because of the great diversity in mineralogy, geology, hydrology, processing, and disposal methods of different mines, and because an accurate assessment of the hazards posed by any individual mining waste site is very difficult. Even in instances where the same material is mined, the disposal of waste may produce significantly different contamination effects from site to site. Significant factors, such as the effects of geologic formations and the hydrogeology between the source of the contaminant and the potential point of impact, should be considered. Such an evaluation may require assessment methods other than laboratory tests, such as field geophysical surveys. It is critical that these factors be taken into account when developing an effective assessment method for evaluating potential contamination from mine wastes.

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