A COMPARATIVE STUDY OF TAILINGS ANALYSIS USING ACID/BASE ACCOUNTING, CELLS, COLUMNS AND SOXHLETS[1]

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Abstract. The overburden analytical techniques involving acid/base accounting, weathering cells, columns and soxhlet reactors were tested and compared using several tailings samples having a variety of NP/S ratios. Tailings were used to normalize the effect that particle size has on leachate quality and were characterized by acid/base accounting data. The results showed that samples with high NP's and high S percentage gave similar results in all testing procedures. For the weathering cells and soxhlet tests it was shown that the leaching technique, in addition to producing a unique quality leachate, modified the sample chemistry that caused shifts in acid/alkaline production. The fine-grained nature of the tailings afforded high specific retention of fluid, creating airlocks within the columns that skewed the results. When the leachate quality predicted and obtained by the various tests was compared to the actual drainage quality emanating from the sites from which the samples were collected, the least accurate were the column tests, next were the acid/base accounting projections, then the soxhlets, with the weathering cell tests being most accurate.

Additional Key Words: Acid mine drainage, overburden analyses, mine drainage quality prediction.

Introduction

The acid production potential of a sample is generally assessed through mine waste/overburden analyses, that can be grouped into two broad categories, static or dynamic techniques. In the static tests, whole rock analyses are used to predict mine drainage quality, the assumption being made that specific minerals comprising the mine waste/overburden will react with water to produce varying degrees of alkalinity and acidity. Alternatively, dynamic tests empirically determine leachate quality by subjecting the samples to simulated weathering conditions while monitoring the quality of the effluent produced. Within these two categories a variety of mine waste/overburden analytical techniques are available, each having advantages and disadvantages relative to the others.

Through a computer literature search (through 1986), examining 679 titles and 36 abstracts dealing with various aspects of mine drainage quality and predictive methods, we identified several mine waste/overburden analytical techniques that are used in the United States and Canada, both in the coal fields and sulfide mines. The methods include

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simulated weathering chamber tests (column and humidity cells), soxhlet reactors (infrequently used), biological confirmation tests (commonly referred to as B.C. Bacterial test), whole rock analyses (acid/base accounting, extensively used in coal fields), and B.C. Research Initial test (extensively used for base metal and gold mines in Canada and western United States). A test involving the peroxide oxidation of the sample has been recently published but lacks widespread usage. The tests that are most commonly used are described in Table 1.

Many questions exist as to the accuracy of the testing procedures and the ability of the tests to adequately project the long-term (decades) chemical weathering attributes of mine waste/overburden material based on laboratory results obtained in relatively short time periods (days to weeks). For example, fine grained particles may afford the sample with a large water holding capacity (specific retention) and create an "air lock" that will effectively inhibit the transfer of oxygen required for pyrite oxidation. In addition, the variety of environmental conditions relative to climate, mining operation, enrichment or processing methods and manner of disposal affect the oxidation of the sulfide and the manner by which the weathering products are mobilized from the site (Erickson and Hedin, 1988, Perry, 1985, Sullivan and Sobek, 1988).

In previous investigations, Caruccio and Geidel (1986) found the column tests to approximate the quality of the leachate derived from field tests using tubs. The same study showed the humidity cell tests to overestimate the acidity, while the soxhlet tests greatly overestimate the acidity. The observed variations in acid production were explained by differences in grain size mandated by a specific test. Accordingly, particle size plays a major role in acid production, with acid loads varying inversely with particle size.

To eliminate the sample size bias, the Mine Environmental Neutral Drainage (MEND of Canada Energy, Mines and Resources) tailings samples were chosen for a comparative study testing several tailings having a variety of chemical compositions. The MEND samples' relatively common particle size reduced the factors in acid production to three: percentage sulfur, neutralization potential, and leaching method.

Materials and Methods

The samples showed much variation in chemistry (Table 2). Of interest is the ratio of acid potential (sulfur % X 31.25) to neutralization potential.

Three leaching methods were employed in the experiment: weathering cells (Caruccio 1968), columns (Hood and Oerter 1984), and soxhlet extractors (Renton et al. 1988). Ten samples were utilized and each sample was subjected in duplicate to each leaching method, for a total of 60 tests. The samples were leached on a weekly basis for approximately eight months.

The leachate samples were analyzed for pH, specific conductance, and net acidity throughout the course of the experiment. In addition, sulfate concentrations were measured for the first twelve weeks and correlated to specific conductance, in order to use conductance as a measure of sulfate load. Leachate samples for three of the samples (WEM, CUR, and BLD) were analyzed for calcium, and porosity determinations were made at the completion of the investigation.

Results and Discussion

For each leaching method, the MEND samples produced a leachate quality reflecting the differences in controlling factors: %S, NP, and leaching method.

Weathering Cells

Samples BLD, EQS, and NOB produced alkaline leachate through the course of the experiment, whereas samples CIN, INC, WAA, WEM, CUR, HES were acidic in nature. The HBM sample was initially acidic and became alkaline.

The first group, the alkaline producing samples, exhibited some degree of pyrite oxidation, as evidenced by moderate sulfate loads. However, the dissolution of the carbonates predominated, neutralized the acidity, and resulted in a net alkaline leachate.

The second group, the acid producing samples, exhibited the opposite behavior. These samples have low NP's and the expression of pyrite oxidation completely overwhelmed any impact the neutralization potential may have had on the leachate. Consequently, the leachate is acidic.

The HBM sample, which represents a transition between the high sulfur-low NP group and the low sulfur-high NP group, produced an interesting trend. Initially acidic despite the highest NP of any sample studied, the HBM weathering cells, after the first two weeks of leaching, gradually became a net alkaline producer. Accordingly, the HBM sample represents the transition between alkaline leachate producers and acidic leachate producers.

Columns

The column leachings can also be grouped into distinct categories. The BLD, EQS, NOB, WEM and CUR columns were alkaline producers. The HBM, CIN, INC, WAA, and HES columns were acid producers, although the HES column did not produce as much acid as would be predicted by sample chemistry.

TABLE 1. SUMMARY OF COMMONLY USED MINE WASTE/OVERBURDEN ANALYTICAL TECHNIQUES

	Method	Advantages	Disadvantages
Static Tests (Whole Rock Analyses)			
• Acid/Base Accounting (Sobek et al. 1978)	Whole rock analyses completed on a pulverized sample. Acid potential related to sulfur content, neutralization potential determined by hot acid digestion with HCl.	Easy to perform, quick turn-around time, useful in areas that are acid or alkaline prone. Relatively inexpensive.	Does not relate to kinetic data. Assumes parallel release of acidity and alkalinity.
Dynamic Tests			
• Soxhlet Reactor (Renton et al. 1988)	Leachate generated on pulverized sample which is cycled in a soxhlet reactor. During interim, sample is stored at 105° C.	Easy to perform quick turn-around time, purported kinetic data.	Expensive apparatus, extremely aggressive oxidation of sample.
• Humidity Cells (Caruccio 1968)	Crushed rock is placed in humidified atmosphere and leached periodically. Volume and character of leachate related to rock weight to produce alkaline/acid production potential.	Produces kinetic data, rates of acidity per unit weight of sample obtained, approximates field conditions.	Long time required, large data base generated. Relatively expensive.
• Column Weathering Test (Hood and Oerter 1984)	Field sample placed in large columns and leached periodically. Leachate is analyzed and related to rock weight.	Best approximator of field conditions.	Same as above, in addition, large volume of samples required, channelization problem encountered.

TABLE 2. MEND SAMPLE CHARACTERISTICS

Sample	% Sulfur	Neutralization Potential (p/1000)	Acid, ppt / NP, ppt	CaO wt %	MgO wt %	Column Porosity (ave.)
HBM	13.36	50.2	8.3	2.92	16.00	0.60
EQS	4.48	30.0	4.7	1.96	1.78	0.31
NOB	3.97	44.0	2.8	2.76	1.74	0.36
WAA	16.03	17.0	29	2.22	7.90	0.64
INC	1.14	-5.7	-NP	0.52	4.69	0.63
WEM	24.58	7.5	102	1.20	2.98	0.38
HES	73.75	-6.3	-NP	0.36	3.89	0.37
CUR	30.46	38.8	24.5	0.49	2.06	0.32
BLD	0.13	8.8	0.46	0.15	0.19	0.50
CIN	1.40	-0.7	-NP	0.08	0.15	0.37

As in the weathering cells, the BLD, EQS, and NOB columns exhibited the predominance of NP over pyrite oxidation. Similarly, the HBM, CIN, INC, WAA, and HES column leachate indicates that dissolution of carbonates was not adequate to overcome the effects of pyrite oxidation.

Measurements of column porosity provide an explanation for the apparent contradictory behavior of the WEM and CUR columns as well as the suppression of acid production of the HES columns. The data in Table 2 reveal that the EQS, NOB, CUR, WEM, and HES columns had much lower porosities than the other columns and thus constitute a category of their own. When these columns were leached during the experiment, we noted water to pond on top of the samples and typically required seven days to drain down through the column. In addition, when the columns were dismantled at the completion of the experiment, the samples exhibited mottling and cracking, and in the case of the CUR sample, a hard rind of oxidized sample was found against the column wall, encasing the rest of the sample.

These data suggest the existence of "airlocks" within leaching column samples marked by such low porosities and permeabilities, that they effectively isolated the samples from oxygen infiltration, and thus inhibit pyrite oxidation. In samples of high neutralization potential, the dissolution of carbonates is favored by water retention, and the resulting leachate is alkaline. For samples with high sulfur and low neutralization potential, as in the case of the HES sample, the result is reduced acid loads.

Soxhlets

The soxhlet samples were stored in a drying oven at 105° C, and leached on a weekly basis in a soxhlet extractor for two hours. Following leaching, the samples were returned to the oven for storage.

The NOB and EQS samples produced alkaline leachate throughout the testing period. WAA, INC, WEM, HES, CUR, BLD, and CIN samples were acidic. Once again, the transition sample HBM, exhibited an unusual behavior by remaining alkaline for roughly twenty weeks, at which time the character of the leachate reversed itself and became acidic.

Sulfate data showed that pyrite oxidation occurred in all soxhlet leachings. Leachate quality therefore became a function of the ratio of alkaline water to acidic water produced by the leaching process. The high NP-low sulfur samples, NOB and EQS, thus exhibited alkaline leachate. Samples with high sulfur to NP ratios correspondingly produced acidic leachate.

The HBM soxhlet samples behaved in an odd manner. Initially, the leachate was alkaline to neutral. Sulfate on the order of 20,000 mg/kg, however, gave evidence that considerable pyrite oxidation was occurring. After approximately twenty weeks the leachate became acidic. There was, however, no corresponding increase in sulfate loads. In fact, sulfate loads continued along the same general decline begun after the initial leachings.

As in the other MEND samples, leachate quality is governed by the mixing of acidic water and alkaline water. Examination of the HBM soxhlet data suggests that the soxhlet extraction process actually encompasses two environments. The first, the actual extraction process, uses continuous flushings with hot water. The second environment is present in the drying oven during the period in which the sample is wet but drying.

Dissolution of calcium carbonate is enhanced during the hot extraction process. A comparison of the calcium contents of the leachates of the WEM samples for the weathering cells, columns and soxhlet tests illustrates this point (Figure 1). On the other hand, pyrite oxidation occurs minimally during extraction and is accelerated while the sample is stored in the oven. The kinetics favor the dissolution of calcium carbonate by hot condensed water while pyrite oxidation is enhanced during the time the sample is stored in the oven.

The first twenty weeks of the HBM testing data exhibit alkalinity production equalling or exceeding acid production, resulting in a net neutral or alkaline leachate. The sharp rise in acidity occurred when sufficient calcium carbonate had been leached from the system to allow the expression of the acidity reactions in the leachate. The lack of a sharp rise in sulfate corresponding to the rise in acidity indicates that the rate of acid production remains the same. What has changed, therefore, is the ratio of alkaline material to acid material.

Interestingly, after a sharp rise in acidity, the HBM sample returned to a condition in which acid production was once again balanced by alkalinity production. This suggests the possibility that the ratio of alkaline to acidic producing material has returned to one that favors neutral or alkaline leachate.

Comparison to Field Data

Contained within the MEND report is a summary of the drainage qualities associated with each location from which the tailings samples used in this study were obtained. BLD and HBM data were solicited by telephone and the CIN data represent test pad results. The drainage quality for each of the sites is presented

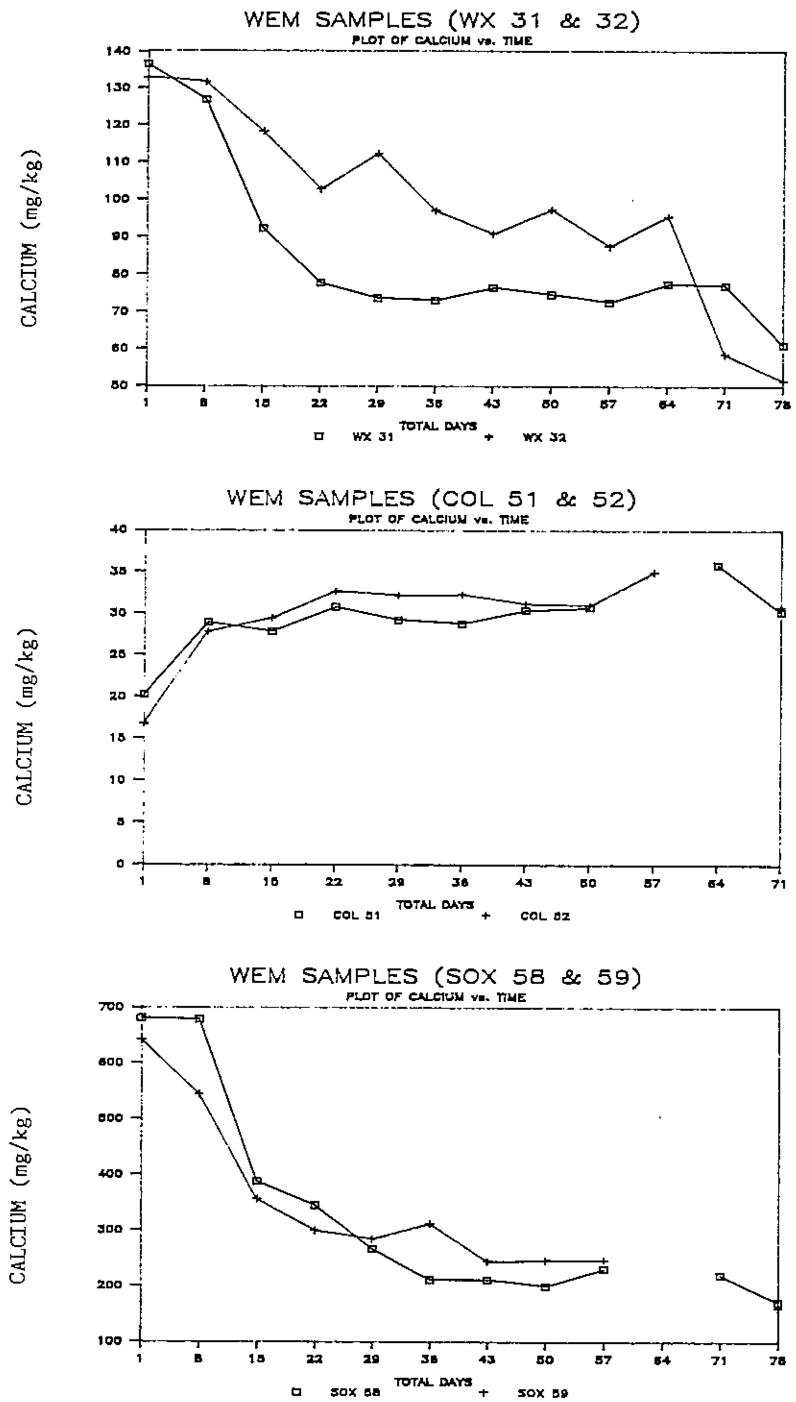

Figure 1. Relative rates of $CaCO_3$ dissolution in weathering cells (Wx), Columns (Col) and Soxhlets (Sox) for WEM sample.

in Table 3 as well as the leachate quality predicted or obtained by the various tests.

A comparison of the results shows that the acid/base accounting method correctly predicted eight out of ten, the weathering cell tests ten out of ten, the soxhlets nine out of ten and the columns seven out of ten.

Conclusions

As evidenced by sulfate loads present even in neutral or alkaline leachates, it is apparent that leachate quality for the MEND samples varies as a function of the amount of acidic leachate produced and the amount of alkaline leachate present to neutralize. As both reactions occur in all samples, with the exception of the

Table 3. Leachate Quality Predicted/Obtained by Various Tests Compared to Field Data.

Ac = Acid Al = Alkalinity

Sample	Acid/ Base	Cell	Column	Soxhlet	Acid/ Alk.ratio	Field Data
NOB	Ac	Al	Al	Al	2.8	Al
EOS	Ac	Al	Al	Al	4.7	Al
BLD	Al	Al	Al	Ac	0.46	Al
CIN	Ac	Ac	Ac	Ac	-NP	Ac*
INC	Ac	Ac	Ac	Ac	-NP	Ac
HBM	Ac	Ac/Al	Ac	Al/Ac	8.3	Ac
WAA	Ac	Ac	Ac	Ac	29	Ac
CUR	Ac	Ac	Al	Ac	24.5	Ac
WEM	Ac	Ac	Al	Ac	102	Ac
HES	Ac	Ac	Ac	Ac	-NP	Ac

* Test Pad Results

"air locked" columns, the leachate quality depends on the balance between the amount of alkaline and acidic material present in the sample, and the rates at which both reactions occur. In turn, the leaching methods control the reaction rates.

Column tests utilizing well-sorted, coarse-grained samples (i.e., greater then 0.5 cm) most accurately resemble field test conditions. The samples are kept somewhat moist and, again excluding the "air locked" columns that develop when fine grained samples (i.e., less than 1 mm) are used, allow oxygen to permeate through most of the sample. The presence of "air locks", however, limits the transfer of oxygen required for pyrite oxidation and restricts acid production to the exterior surface of the sample.

Weathering cells, on the other hand, by providing more moisture and oxygen, as well as having a greater reactive surface area, accelerate the rate of pyrite oxidation relative to the rate of the dissolution of calcium carbonate. The result of this change in rates is a greater proportion of acidic to alkaline leachate. Further, the rate of pyrite oxidation is increased relative to the dissolution of calcium carbonate and these rate differences change sample chemistry through time. In the so called "transition" samples, such as the HBM sample, this property is manifested by the sample's migration from the field of acid producing samples to that of the alkaline producing samples.

The soxhlet extractors accelerate the dissolution of calcium carbonate relative to pyrite oxidation. The HBM soxhlet sample, therefore, migrates from the alkaline producing field to the acid producing field.

In summary, the leachate quality of the MEND sample leachings depends on the balance of the production of acid leachate to alkaline leachate. This, in turn, is a function of the amount of acid and alkaline producing materials, and of the rates of both reactions.

When compared to observed field drainage quality emanating from areas from whence the tailings samples were collected, the predictions made by the columns were least accurate (70% success), acid-base accounting next, followed by the soxhlet tests, and the weathering cell tests were most accurate (100% success).

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