

## Minimizing the Environmental Impacts of Coal Waste Disposal

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### ABSTRACT

To assess strategies aimed at minimizing the impact of disposal of coal waste materials on the environment, two long-term leaching experiments of up to five months duration were performed using waste materials from two plants cleaning high and low sulfur bituminous coal. The tests evaluated the mobility of major trace elements under different disposal scenarios: (i) a static leaching test designed to simulate the quiescent conditions encountered by coal waste material stored under water in a stable impoundment, and (ii) a dynamic test to simulate waste materials exposed to the atmosphere, either in variable wet/dry storage conditions, or in unusual circumstances like those resulting from breaching of an impoundment containment wall. The results indicate that the mobility of most elements is enhanced under highly alkaline or acidic conditions with a few being mobilized under both conditions, suggesting that the minimization of element mobility requires the pH value of the medium to be maintained around neutral. In this paper, the effects of a strategy of co-disposing coarse and fine refuse to control pH are presented as a method to maintain near neutral pH values and thus minimize trace element mobility. The co-disposal strategy was found to reduce the mobility of trace elements in the static leaching tests whereas the opposite was found from dynamic experiments. The results indicate that such controlled storage under water could retard acid generation and the mobility of trace elements.

### INTRODUCTION

Trace elements generally refer to elements present in a natural material at concentrations below 1,000 ppm. Most of the trace elements of environmental concern in coal (e.g., As, Cr, Se, etc.) are mineral-associated and therefore tend to be enriched in refuse from coal cleaning operation. As a result, the behavior of trace elements in coal cleaning waste streams must be well understood in disposal situations, particularly with the aim of protecting ground water quality. Illite and pyrite are generally the two major coal minerals that contain most of the trace elements in eastern U.S. bituminous coals. The clay mineral, illite, typically contains most of the lithophilic trace elements such as vanadium and chromium, whereas the sulfide mineral, pyrite, typically controls the behavior of chalcophilic elements such as arsenic, selenium, mercury and lead. A number of other elements, such as manganese, nickel and zinc, may have a mixed association with both of these minerals (Huggins et al., 2009). Therefore, these two minerals typically host most of the trace elements that are subject to federal and state regulations and statutes, such as the Clean Air Act Amendments (U.S. Congress 1990), and may be of concern as a result of possible mobilization from coal waste impoundments. The behavior of illite and pyrite in coal cleaning processes determines to a large extent how much and with what tailing fraction trace elements are distributed in coal wastes.

The oxidative weathering of pyrite has the potential to degrade water quality, yielding high acidity and mobilization of metals in concentrations that exceed water quality standards (Moses 1990). The weathering of pyrite can yield highly acidic waters even when initiated in waters of near-neutral pH. "On the other hand, pyrite weathering does not always produce very high levels of acidity or metals because of pH buffering by natural chemical or biological processes, such as carbonate mineral dissolution" (Toran, 1987; Nicholson et al. 1988) or bacterial reduction (Herlihy et al., 1988; Moses, 1990). Also Huggins et al. (2011) in their study of leaching of rejects of Illinois based coal concluded that the dissolution of first Na and then Ca, which give rise to the formation of insoluble sulfate minerals, and other alkaline earth elements is an effective buffer that maintains the pH of the leachates close to neutral and minimizes mobilization of iron and trace elements associated with pyrite (Evangelou and Zhang, 1995; Moses and Herman, 1991, Huggins et al., 2011).

Such observations suggest that leaching of trace elements can be repressed by enhancing the buffering capacities of the waste streams. Clearly, one strategy to enhance such capability would be to add alkali or alkaline-earth buffering capability like lime or fly ash to the impoundment, (Jastrow et al., 1981, Stewart et al., 1997, Hassett et al., 2005), but it is likely to add significantly to the cost of the disposal and storage of the cleaning rejects and related combustion wastes as well as increase the mass of material in the impoundment. A better cost strategy, which is explored in this study, would be to modify coal cleaning processes and/or storage practices to maximize the buffering capability of the waste materials and thereby repress the leachability of trace elements from coal waste streams.

### EXPERIMENTAL

#### Coal Samples

Samples of raw coal, clean coal, and different coal waste streams (coarse refuse, thickener underflow, spiral refuse, high frequency screen over) from two different processing plants treating two

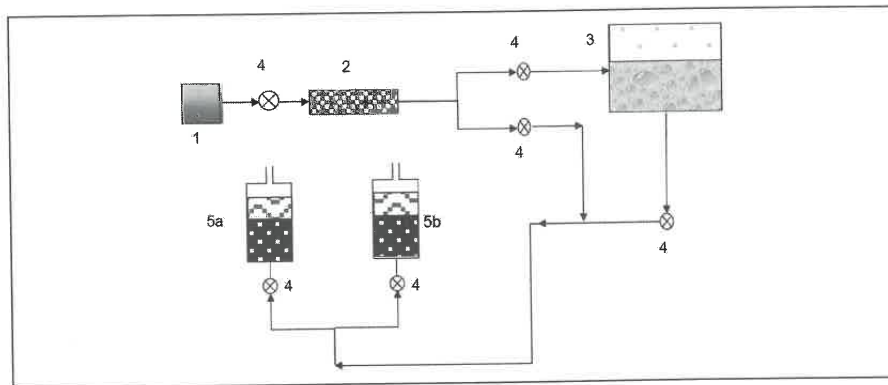
different coal seams (Coalburg seam, WV and 5-B central seam, IN) were collected. 5-B Central seam is characterized as high-sulfur bituminous while the Coalburg seam is an oxidized bituminous coal seam of low sulfur content. The following analyses were carried out on each major coal fraction:

- Ultimate, proximate, forms of sulfur, heating value, size analysis;
- X-ray fluorescence (XRF) of major elements in 500°C ash from each fraction;
- Trace element analyses by inductively coupled plasma mass spectrometry (ICP-MS);
- Mineral matter by X-ray diffraction (XRD) using Rietveld method.
- Fe speciation and oxidation state determinations by Mössbauer spectroscopy;
- Speciation of sulfur and key trace elements by X-ray absorption fine structure (XAFS) spectroscopy.

#### Leaching Tests

The standard ASTM method D 5744 was designed specifically to meet regulatory requirements for mining wastes and ores. As shown in Figure 1, the experimental setup involved holding the waste streams samples in humidity cells made of PVC. The samples rested on 22- $\mu$ m polypropylene felt filter media to allow air and water to flow through while retaining the 150  $\mu$ m (100 mesh) samples. The dynamic tests were carried out on two parallel sets of representative coal seam samples with each weighing 200 g. The humidity cells were setup to receive an upward flow of air through the bottom valve. Dry air was obtained from the laboratory compressed air line routed through a desiccant, while the humid air was generated by passing air through water held at 30°C in the humidifier. The water temperature of the humidifier was kept constant by immersing it in a water bath with a thermostat controlled temperature setting.

The samples in the humidity cells were subjected to a weekly cycle involving alternating periods of dry air (3 days), humid air (3 days), followed by leaching with 200 ml of de-ionized water on the seventh day. Each flooded cell was



**Figure 1.** Experimental setup for the dynamic leaching test based on ASTM method D 5744–96. Numbered items indicate: (1) compressed air source, (2) desiccant chamber, (3) humidifier, (4) air-flow control valves, and (5) humidity series cells containing 200 g of (a) high sulfur content waste samples, and (b) low sulfur content waste samples (Huggins et al., 2012).

then allowed to sit for a period of 2 hour before draining the leachant into plastic bottles. The two-hour leach time commenced after all of the leachant had been placed in the cell, thus ensuring that the samples were saturated and completely immersed by the leachant water. The valve at the bottom of the humidity cell was opened and the leachant allowed to drain into the plastic bottles. The volume, pH, and conductivity of the collected leachant solutions were then recorded. At the conclusion of the 7th day, the cycle was repeated. After a number of weekly cycles, the collected leachant waters were combined, based on the pH change, and submitted for Eh, sulfate concentration, and major and trace elements composition analysis using ICP-MS. The 0th cycle corresponds to the initial aqueous leaching of the rejects conducted prior to the first cycle of exposure to dry and humid air.

In the dynamic column leaching test weekly leaching with deionized water, or low ionic strength water, promote the removal of leachable mineral dissolution product generated from the previous week's weathering cycle. The purpose of the three-day dry air part of the weekly cycle is to evaporate some of the water that remains in the pores of the sample after the weakly leach without totally drying out the sample. Therefore,

the sample saturation is reduced and air contact is enhanced. During the three-day dry-air period of the weekly cycle, the oxygen diffusion rate through the sample may be enhanced several orders of magnitude as compared to its diffusion rate under more saturated conditions of the leach, which helps promote the oxidation of such constituents as iron sulfide. This evaporation also increased pore water cation/anion concentrations and may cause increased acidity (e.g., by increasing the hydrogen ion concentration generated from previously oxidized iron sulfide). Increased acid generation will increase the dissolution of additional sample constituents. As evaporation continues, the remaining water might become over-saturated in regard to some mineral phases, and therefore causing them to precipitate. Some precipitated mineral are potential sources of acidity when re-dissolved (like melanterite,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; and jarosite,  $\text{K}_2\text{Fe}_6(\text{OH})_{12}(\text{SO}_4)_4$ ). Three-day wet (saturated)-air portion of the cycle helps maintain a relatively constant mass of pore water in the sample, and promote some diffusion of weathering products (e.g. re-dissolved precipitation products) in the residual pore water without totally saturating the sample and adversely affecting oxygen diffusion (ASTM D5744, Huggins et al., 2012).

**Table 1.** Ultimate, forms of sulfur analysis of coal samples

Samples	Ultimate Analysis of Coal Samples						Forms of Sulfur			
	%Ash	%Moisture	%C	%H	%N	%O	%Total S	%Sulfate	%Organic	%Pyritic
High Sulfur Feed	19.4	8.3	53.6	4.9	0.6	14.1	7.4	0.3	3.5	3.6
High Sulfur Coarse Refuse	54.5	1.6	17.9	1.6	0.4	<0.01	29.3	1.1	7.6	20.7
High Sulfur Spiral Refuse	66.8	1.2	16.4	1.6	0.4	<0.01	20.1	0.6	4.1	15.3
High Sulfur Thickener Underflow	41.7	1.8	45.2	3.1	0.6	<0.01	9.6	0.6	2.1	6.9
High Sulfur Clean coal	10.4	8.5	64.8	5.7	0.8	14.7	3.6	0.4	1.2	2.0
Coalburg Coarse Refuse	62.3	1.1	29.3	2.6	0.5	4.9	0.3	<0.01	0.2	0.2
Coalburg Thickener Underflow	55.5	1.4	35.2	2.7	0.5	5.6	0.5	0.0	<0.01	0.5
Coalburg High Freq. Screen Over	72.5	0.9	19.5	2.0	0.5	5.0	0.5	0.0	0.4	0.1

**Table 2.** Semi-quantitative mineralogy of coal fractions (5-B Central seam, IN)

Coal Fractions	%Mineral (as wt% of mineral matter)				
	Pyrite	Quartz	Illite	Kaolinite	Calcite
Spiral Refuse	28	17	15	21	17
Thickener underflow	23	18	36	23	<5
Coarse Reject	43	20	19	18	<5
Feed Coal	25	16	16	43	<5
Clean Coal	27	23	27	22	<5

## RESULTS AND DISCUSSION

### Coal Analyses

Ultimate and forms of sulfur analyses of coal samples from the two different sources are summarized in Table 1.

Table 1 indicates that the Coalburg, WV, samples have relatively low sulfur content, while 5-B Central seam, IN, samples have high sulfur content. Among the reject fractions of 5-B Central seam, coarse refuse has the highest total sulfur and pyritic sulfur, and thickener underflow has the lowest total and pyritic sulfur, indicating coarse refuse generates lower pH in contact with water and since has higher pyritic sulfur, more trace elements associated with pyrite would be released.

The mineralogical information of high sulfur coal samples obtained from XRD is shown in Table 2.

Table 2 indicates that there is significant variation in the mineralogy of the three coal refuse fractions. This variation arises because of the different size distributions and ways in which the individual minerals occur physically in the coal, resulting in different behavior they exhibit in the coal cleaning processes. The spiral refuse is the only fraction to contain significant calcite

( $\text{CaCO}_3$ ); this result is consistent with the ash chemistry analyses (Table 3), which show that the spiral refuse sample has by far the highest CaO percentage. Conversely, the coarse reject fraction is much enriched in pyrite compared to the other refuse fractions and the corresponding ash chemistry also shows the highest iron oxide content.

Weight percentages (ash basis) of major elements obtained from ash chemistry analysis of coal samples are shown in Table 3. Higher amount of Al, iron and silicon than other elements can be recognized in this table. It is also the same for calcium in spiral refuse.

More advanced characterization methods were also performed on these materials, including speciation analyses by  $^{57}\text{Fe}$  Mossbauer and X-ray absorption fine structure (XAFS) spectroscopies. Based on the Mossbauer data, almost all of the iron in the coal and refuse fractions was present in the form of pyrite ( $\text{FeS}_2$ ). Preliminary XAFS results have shown that arsenic is quite significant and largely associated with pyrite, whereas selenium is barely detectable in the coal. Both iron Mossbauer and arsenic XAFS spectra indicate that slight oxidation of the pyrite has already commenced, particularly in the finer refuse fractions.

**Table 3. Major element analyses (ash basis) of 500°C ash prepared from the coal samples**

Oxide*	Clean Coal	Feed	Course Refuse	Spiral Refuse	Thickener Underflow
Al <sub>2</sub> O <sub>3</sub>	18.27	15.76	10.41	13.02	16.76
BaO	0.04	0.03	0.02	0.03	0.07
CaO	0.62	1.66	0.45	14.71	5.41
Fe <sub>2</sub> O <sub>3</sub>	35.23	40.99	61.48	35.68	26.99
MgO	0.83	0.75	0.58	0.72	1.09
P <sub>2</sub> O <sub>5</sub>	0.21	0.19	0.15	0.2	0.24
K <sub>2</sub> O	2.37	2.05	1.38	1.56	2.28
SiO <sub>2</sub>	40.7	36.25	24.41	28.99	44.13
Na <sub>2</sub> O	0.43	0.36	0.24	0.23	0.35
SrO	0.05	0.04	0.02	0.03	0.03
SO <sub>3</sub>	0.32	1.17	0.45	4.41	1.91
TiO <sub>2</sub>	0.93	0.75	0.43	0.45	0.73

\*by X-ray fluorescence (XRF)

### Leaching Characteristics of Waste Samples

In this study, static and kinetic leaching tests were initiated on the individual samples of the different coal refuse streams. Frequent measurements of pH, Eh, and conductivity have been made on the supernatant liquids in the static test and similar measurements are also being conducted on the leach water collected weekly from the kinetic tests. Variation of pH with time for dynamic and static leaching tests is shown in Figures 2 and 3. The values of pH and Eh of the supernatant liquids in both tests showed a wide range for the different fractions, varying from neutral to relatively acidic (pH ~3 for the coarse high sulfur coal refuse), and each remained fairly constant for the entire leaching period (19 weeks). The variation of pH in both static and dynamic tests for refuse samples of the two different coal seams also is shown in Figures 4 and 5 separately. The difference in the pH values is due to the difference in mineralogy of the different fractions. Among high pyritic coal refuse samples, the coarse refuse has the highest content of pyritic sulfur, and in contact with water generates a lower pH than the other fractions. The spiral refuse and thickener underflow fractions have higher amounts of alkali and alkaline earth elements which buffer the pH of the solution, especially in static leaching test where the ions stay in the solution of the entire period of leaching test.

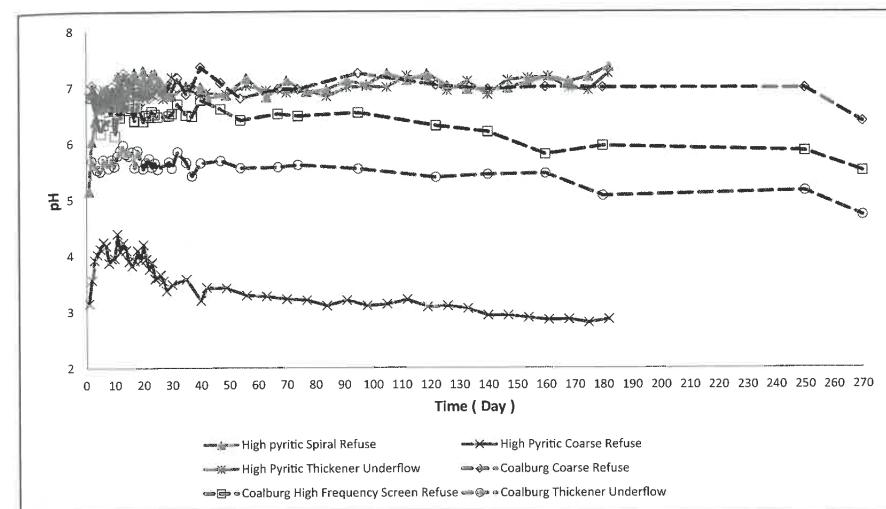
The pH of the supernatant liquids in contact with various coal refuse fractions of oxidized Coalburg seam in the leaching tests is close to neutral. The pH of the supernatant liquids in the static leaching test is slightly lower than those of the dynamic leaching test. Our hypothesis is that since these samples are oxidized coal, in contact with water they release humic acid and therefore slightly decrease the pH of the solution (Pawlik et al., 1977).

The electrical conductivity of a solution provides an indirect measure of the amount of dissolved ions in that solution (Rhoades, 1982; Stewart et al., 2001). The variation of conductivity with time for the dynamic leaching test is shown in Figure 6.

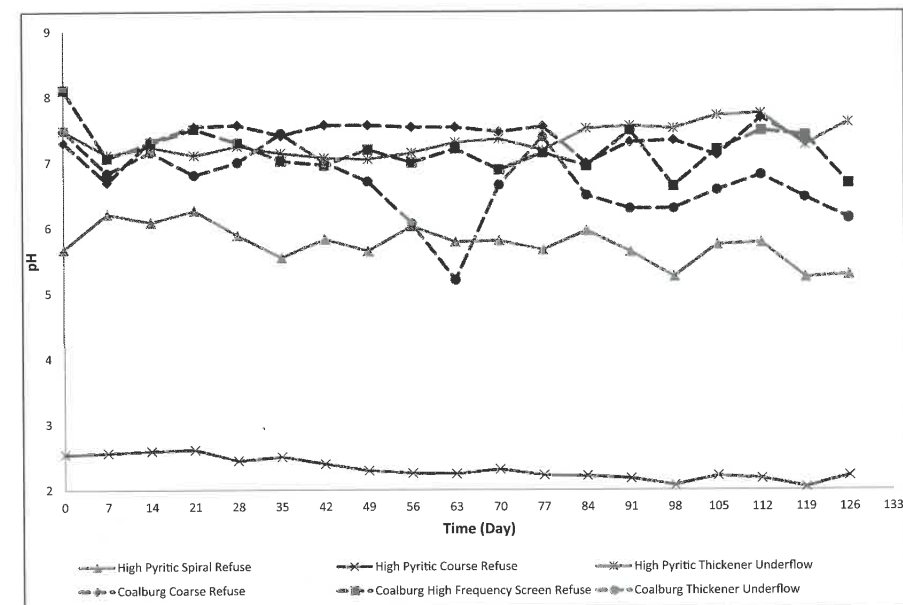
Figure 6 shows that the conductivity of supernatant liquids in contact with different refuse fractions of the Coalburg seam is much lower than those of the high pyritic coal seam. The reason is likely due to the higher pyritic content of the 5-B central coal seam, IN, and therefore more sulfate and trace elements associated with pyrite are released, resulting in increasing the conductivity of the leachate solution.

In Figure 7, the conductivity of the combined leachate of the dynamic leaching tests versus static tests, for the different coal waste stream is depicted.

The correlation of conductivity and released ions in the dynamic column leaching test for the



**Figure 2. Plots of the variation over time of the pH of supernatant liquids in contact with various coal refuse fractions in the static leaching test. Note the wide range of pH exhibited by the different fractions.**



**Figure 3. Plots of the variation over time of the pH of supernatant liquids in contact with various coal refuse fractions in the dynamic leaching test. Note the wide range of pH exhibited by the different fractions.**



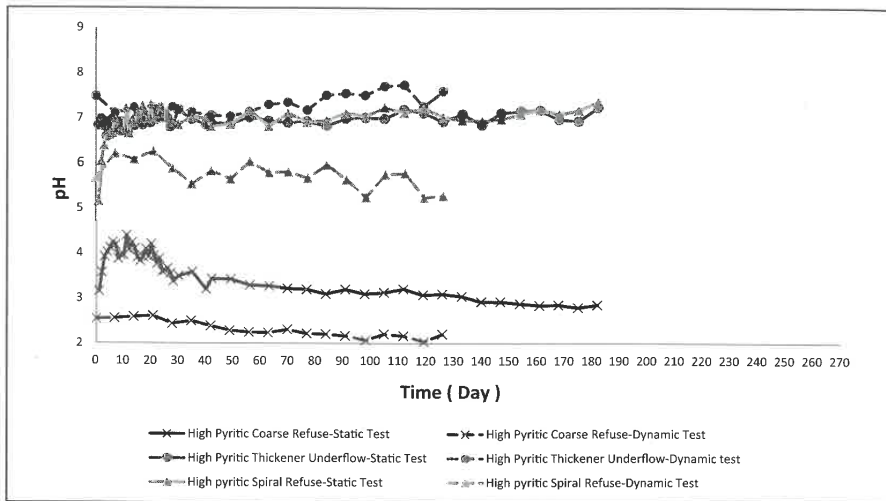


Figure 4. Plots of the variation over time of the pH of supernatant liquids in contact with various coal refuse fractions of high pyritic coal seam, IN, in the both static and dynamic leaching test. Note the wide range of pH exhibited by the different fractions.

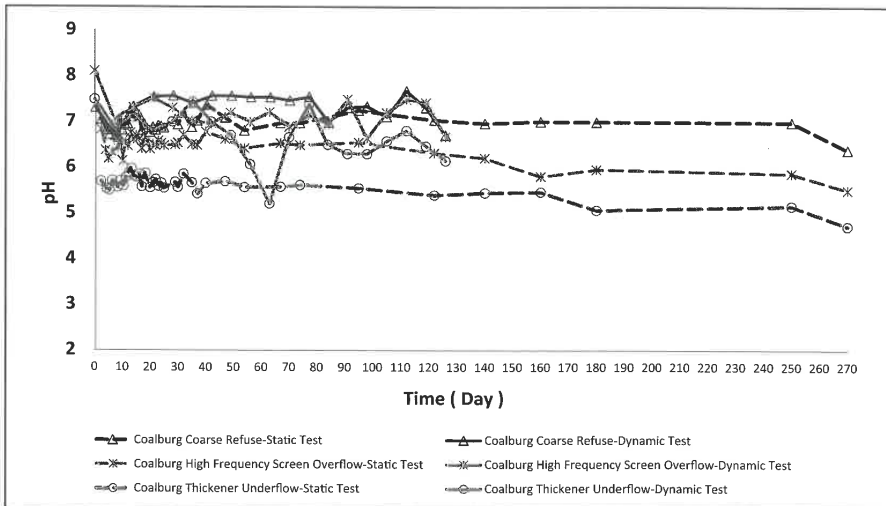


Figure 5. Plots of the variation over time of the pH of supernatant liquids in contact with various coal refuse fractions of Coalburg seam, WV, in the both static and dynamic leaching test

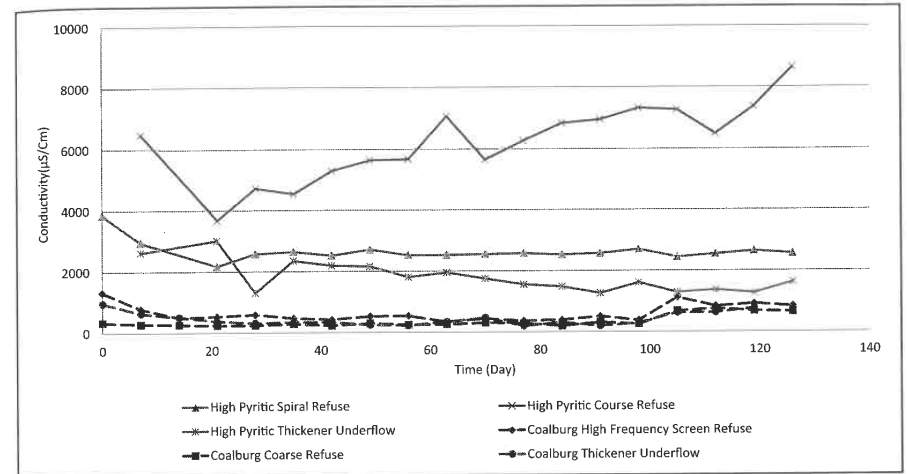


Figure 6. Plots of the variation over time of the conductivity of supernatant liquids in contact with various coal refuse fractions in the dynamic leaching test

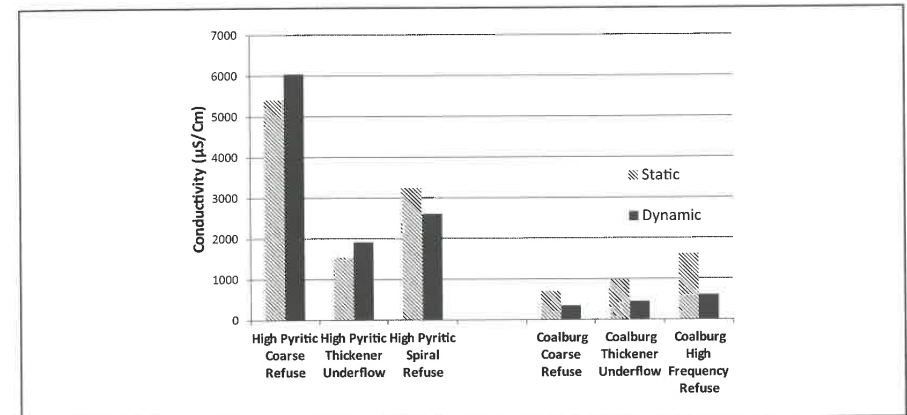


Figure 7. Plots of the conductivity of supernatant liquids in contact with various coal refuse fractions in the static and dynamic leaching tests

high pyritic thickener underflow, spiral refuse and coarse refuse has been determined to be 0.95, 0.85, and 0.33, respectively. The high correlation between conductivity and sulfate for thickener underflow and spiral refuse implies that sulfate anions are the predominant soluble anions being extracted in the dynamic leaching test for these samples (Huggins et al., 2012; Gray, 1996). The

lower correlation value for the coarse refuse sample would appear to indicate a more complicated situation at lower pH values.

The concentration of thirty elements in leachates was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). In Table 4, the ICP data of 19 weeks cyclic dynamic leaching test are listed, even for those

Table 4. Element concentration (mg/L) data from ICP measurements on leachates from the kinetic leaching test on high pyritic waste material

Elements/Cycle(s)	Coarse Refuse					Thickener Underflow					Spiral Refuse								
	1_2	3_4	5_7	8_11	12_15	16_19	1_2	3_4	5_7	8_11	12_15	16_19	1	2	3_4	5_7	8_11	12_15	16_19
Aluminum	56.5	18	24	32.5	44.1	55.4	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.16
Antimony	0.1	0.05	0.06	0.07	0.07	0.08	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Arsenic	1.55	0.32	1.12	3.21	5.17	6.3	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Barium	0.02	0.02	0.02	0.02	0.02	0.02	0.04	0.03	0.02	0.025	0.03	0.04	0.025	0.02	0.02	0.02	0.02	0.02	0.02
Beryllium	0.07	0.02	0.01	0.009	0.006	0.006	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.001
Boron	4.77	1.99	2.55	2.51	3.97	5.81	1.35	1.85	1.08	0.67	0.71	0.78	0.91	0.62	0.33	0.33	0.21	0.39	0.27
Cadmium	0.08	0.02	0.04	0.03	0.07	0.08	0.001	<MDL	<MDL	<MDL	<MDL	<MDL	0.02	0.01	0.005	0.008	0.004	0.005	0.005
Calcium	257	135	88.7	70.9	57.5	50.1	400	686	642	508	357	337	540	605	514	673	679	666	662
Chromium	0.81	0.32	0.42	0.45	0.4	0.41	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Cobalt	2	0.39	0.18	0.11	0.09	0.09	1.46	0.28	0.15	0.04	0.03	0.03	3.79	1.21	0.41	0.35	0.13	0.09	0.07
Copper	0.79	0.26	0.27	0.27	0.37	1.14	0.02	0.02	0.01	0.006	0.02	0.02	0.03	<MDL	0.009	0.04	0.05	0.07	0.07
Gold	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Iron	2570	1070	1550	1900	1960	2130	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.06	204	16.3	34.2	32.5	39.8	46.5
Lead	0.09	<MDL	<MDL	0.02	0.06	0.09	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.02	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Lithium	0.3	0.08	0.06	0.09	0.14	0.17	0.11	0.06	0.02	0.01	0.02	0.02	0.25	0.08	0.03	0.03	0.02	0.03	0.04
Magnesium	108	40.7	26.7	24.2	36.8	41.5	105	80	22.7	7.75	6.87	7.58	106	82.1	24.9	17.7	10.2	11.1	13.9
Manganese	31.4	14.5	10.4	6.89	4.09	3.57	7.29	6.73	4.04	1.47	1.5	1.73	22.6	18.8	9.39	12.2	8.71	9.9	12
Nickel	6.77	1.29	0.79	0.62	0.64	0.58	2.31	0.44	0.24	0.08	0.09	0.09	7.12	2.45	0.81	0.93	0.54	0.45	0.42
Phosphorus	2.15	0.44	1.54	5.33	8.8	9.38	0.1	<MDL	0.03	0.02	0.02	0.03	0.04	0.02	<MDL	<MDL	<MDL	0.01	0.02
Potassium	7.9	3.66	4.6	5.17	33.7	12.1	16.3	14.3	7.33	4.06	7.69	5.84	13.4	6.3	3.36	3.66	3.57	10.3	6.93
Selenium	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.16	0.12	0.05	0.025	0.015	<MDL	0.09	0.19	0.07	0.06	0.04	0.03	0.04
Silicon	4.56	3.18	3.02	5.04	24.1	19.7	1.62	2.28	1.89	1.9	9.14	9.44	2.65	2.83	2.09	2.91	3.06	11.7	8.37
Silver	<MDL	<MDL	<MDL	<MDL	0.004	0.007	<MDL	<MDL	<MDL	<MDL	0.005	0.005	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.004
Sodium	149	10.7	5.97	7.28	23.1	29.3	111	34	7.99	3.51	3.92	5.25	230	80.8	11.1	5.67	4.08	4.57	4.81
Strontium	1.56	0.37	0.21	0.23	0.29	0.32	1.52	1.57	1.07	0.73	0.52	0.48	1.72	0.97	0.59	0.74	0.84	0.86	0.96
Sulfur	2240	891	1190	1400	1480	1670	576	898	600	397	286	253	927	747	526	712	736	669	612
Thallium	0.08	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Tin	0.02	<MDL	<MDL	<MDL	<MDL	0.013	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
Vanadium	0.09	0.03	0.05	0.05	0.04	0.03	0.07	0.07	0.03	0.02	0.02	0.01	0.55	0.32	0.07	0.13	0.17	0.35	0.5
Zinc	1.52	0.71	0.59	0.57	0.74	1.3	0.07	0.07	0.03	0.02	0.02	0.01	2500	1820	1240	1560	1460	1670	1900
Sulfate	6600	2560	3730	1590	4730	5250	1440	1670	1470	1100	868	818	120	130	288	397	511	540	472
Leachate volume (ml)	265	299	412	552	536	504	139	192	315	407	354	337							

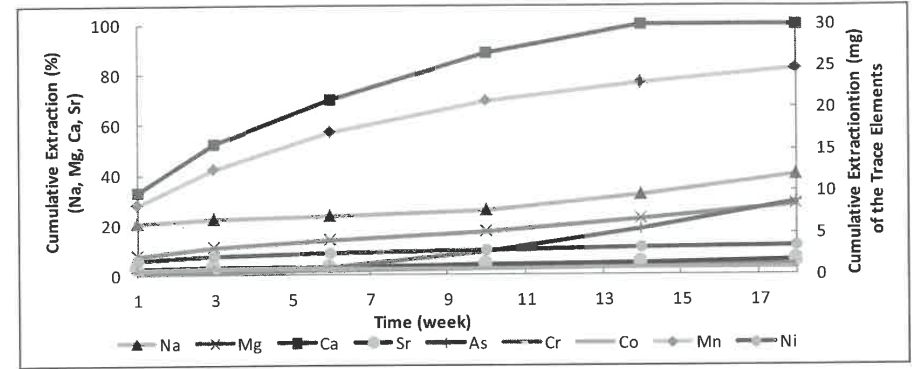


Figure 8. ICP-MS results for the coarse refuse of high sulfur content coal

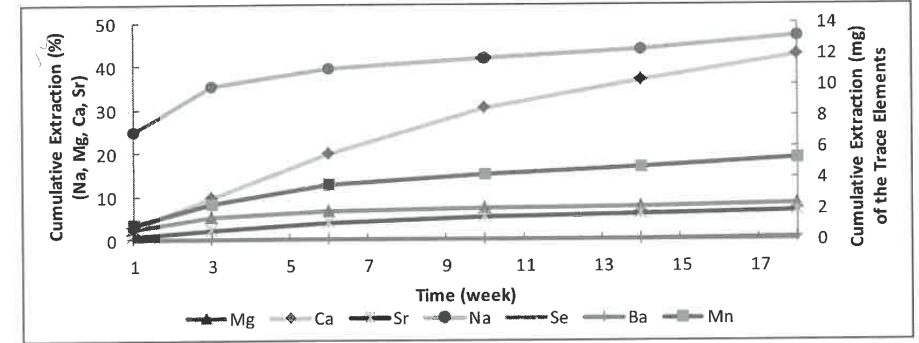


Figure 9. ICP-MS results for the thickener underflow of high sulfur content coal

having concentrations below minimum detection limit (MDL) in all samplings. The elemental mass leached can be easily derived by multiplying the concentration by the volume of leachant collected for each cycle. The coarse refuse also shows by far the highest leaching of iron and arsenic (q.v. Table 4) and this is due to the high content of pyrite in the fraction, the strong association of arsenic with pyrite, and the highly acidic solution that is generated when water is in contact with the coarse refuse. In contrast, the spiral refuse shows minimal or negligible releases of arsenic and iron, but significant release of calcium. For this fraction, dissolution of calcium is retarding acid generation and related leaching of elements

from pyrite. These observations help explain the different pH response and leaching behavior that we have seen with the different refuse fractions and emphasize the importance of the role of the mineralogy in determining the leachability of elements from different coal refuse streams. The extraction amount (mg) of the trace elements of concern in the CAAA over the period of time of the dynamic leaching test for different high pyritic waste samples are depicted in Figures 8 to 10. In Figures 8 to 10, Na, Mg, Ca, Sr release (%) are shown separately since these metal ions are relatively readily soluble in water and can buffer the pH of solution, while the larger metal ions in these groups, K<sup>+</sup> and Ba<sup>2+</sup> were more resistant

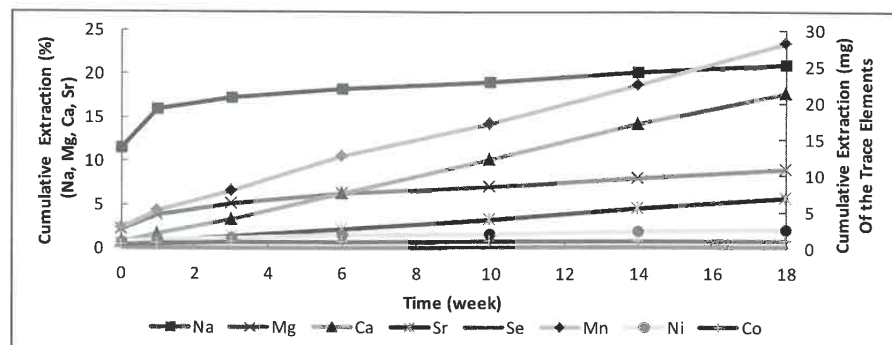


Figure 10. ICP-MS results for the spiral refuse of high sulfur content coal

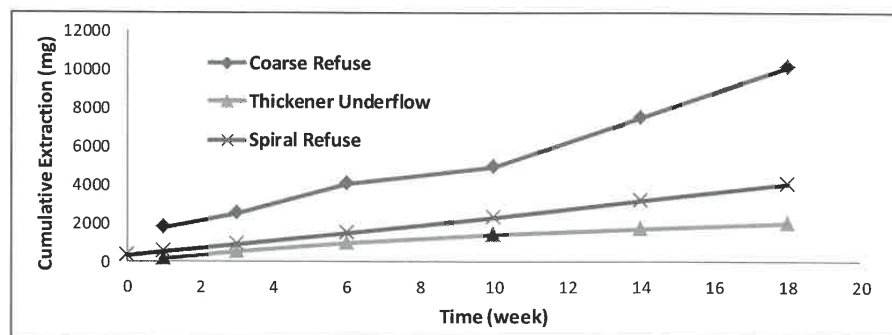


Figure 11. Cumulative extraction of sulfate during cyclic dynamic leaching test

to leaching. The trace elements that were not released or their amount of release was negligible are not plotted.

In Figure 11, the cumulative extraction (mg) of sulfate for the different waste samples during the dynamic leaching test has been depicted. The sulfate concentration and iron concentration are indicators of pyrite oxidation in each sample and the highest amount and rate for both ions and therefore for the pyrite oxidation is related to the coarse refuse.

The total extractions of trace elements from the high pyritic waste samples after 19 weeks of the dynamic leaching tests and 6 months of the static leaching tests are summarized in Table 5.

These data confirm that the dynamic leaching test is more aggressive than the static

leaching test with respect to leaching of most elements from the waste samples. The maximum release of the trace elements is related to coarse refuse sample where it is subjected to the dynamic leaching test, where the high amount of pyrite is oxidized and most of the trace elements are released under the acidic conditions. In contrast, lower amount of release of the trace elements under neutral pH condition in spiral refuse and thickener underflow leaching tests. Hence, to minimize mobility of elements, a good strategy would be to keep the pH as close to neutral as possible.

The total extractions (mg) of trace elements from the waste samples of low pyritic Coalburg coal seam after 19 weeks of the dynamic leaching tests also are summarized in Table 6.

Table 5. Cumulative amounts (in mg) based on ICP measurements of elements in leachates over the 19 week long dynamic and 6 month long static leaching tests on 200 g of each waste sample

Elements	Coarse Refuse		Spiral Refuse		Thickener Underflow	
	Dynamic	Static	Dynamic	Static	Dynamic	Static
Aluminum	99.74	2.79	0.11	0.00	0.00	0.00
Antimony	0.18	0.00	0.00	0.00	0.00	0.00
Arsenic	8.69	0.01	0.00	0.00	0.00	0.00
Barium	0.05	0.00	0.05	0.00	0.05	0.00
Beryllium	0.04	0.01	0.00	0.00	0.00	0.00
Boron	9.35	0.43	0.86	0.07	1.67	0.13
Cadmium	0.14	0.00	0.02	0.00	0.00	0.00
Calcium	240.22	70.88	1577.74	62.94	836.25	40.26
Chromium	1.15	0.02	0.00	0.00	0.00	0.00
Cobalt	0.88	0.02	1.02	0.00	0.34	0.00
Copper	1.32	0.06	0.12	0.00	0.03	0.00
Gold	0.00	0.00	0.00	0.00	0.00	0.00
Iron	4812.46	95.17	104.01	0.00	0.02	0.00
Lead	0.11	0.01	0.00	0.00	0.00	0.00
Lithium	0.34	0.05	0.11	0.02	0.05	0.01
Magnesium	105.79	27.98	55.36	8.71	45.25	5.10
Manganese	24.74	9.12	28.16	0.30	5.29	0.10
Nickel	3.48	0.23	2.49	0.00	0.58	0.01
Phosphorus	13.72	0.00	0.03	0.00	0.05	0.00
Potassium	32.10	1.14	15.50	2.08	13.66	1.03
Selenium	0.00	0.00	0.14	0.00	0.08	0.00
Silicon	29.03	6.42	14.28	0.13	8.45	0.18
Silver	0.01	0.00	0.00	0.00	0.00	0.00
Sodium	76.31	36.96	50.37	28.00	29.06	7.26
Strontium	1.05	0.19	2.14	0.23	1.49	0.13
Sulfur	3758.05	187.44	1668.72	79.07	789.56	38.67
Thalium	0.02	0.01	0.00	0.00	0.00	0.00
Tin	0.01	0.00	0.00	0.00	0.00	0.00
Vanadium	0.12	0.00	0.00	0.00	0.00	0.00
Zinc	2.22	0.21	0.69	0.00	0.05	0.00
Sulfate	10110.16	578.16	4057.70	238.56	2014.49	122.65
TM	5463.27	251.71	1853.20	102.48	942.37	54.21

TM = total metals leached ( $\Sigma$  of all elements except sulfur).

The comparison between the cumulative amount (mg) of release of the trace elements of the dynamic leaching tests for the refuse samples of high pyritic 5-B central seam, IN, and low pyritic Coalburg seam, WV, shows that for trace elements especially those elements expected to be associated with pyrite or other sulfide minerals in the coal refuse (viz. chalcophilic elements such as Sb, As, Cd, Co, Fe, Pb, Mn, Ni, Cu, Se and Th) there are huge differences in their apparent mobility in the waste streams of processing

of the two coal seams, and release of alkali and alkaline earth elements have enough buffer capability to keep the medium neutral and prevent the release of the trace elements. Therefore, adding the processing units to the plants to separate pyrite from refuse streams, and then storing pyrite separately after applying some other strategies like solidification to keep pyrite from oxidation, may decrease not only the conductivity (Figure 7) but also the release of the trace elements.

**Table 6. Cumulative amounts (in mg) based on ICP measurements of elements in leachates over the 19 week long dynamic on 200 g of refuse samples of the Coalburg seam**

Element	Coarse Refuse	High Freq. Over	Thickener Underflow
Aluminum	0	0	0
Antimony	0	0	0
Arsenic	0	0	0
Barium	0.41	0.07	0.14
Beryllium	0	0	0
Boron	0.14	0.04	0.07
Cadmium	0	0	0
Calcium	152.3	100.22	35.48
Chromium	0	0	0
Cobalt	0.01	0.07	0.02
Copper	0.14	0.43	0.07
Gold	0	0	0
Iron	0	0.02	0.04
Lead	0.07	0	0.02
Lithium	0.2	0.11	0.03
Magnesium	57.33	44.39	17.91
Manganese	0.54	5.52	0.71
Nickel	0.05	0.07	0.02
Phosphorus	0.54	0.07	0.16
Potassium	58.15	27.35	17.56
Selenium	0.2	0.09	0.03
Silicon	40.28	7.91	11.77
Silver	0	0	0
Sodium	123.87	55.83	61.73
Strontium	0.81	0.81	0.59
Sulfur	141.47	140.13	77.39
Thalium	0	0	0
Tin	0	0	0
Vanadium	0	0	0
Zinc	0.47	0.43	0.1
Sulfate	494.14	425.98	233.03
TM	435.51	243.43	146.45

TM = total metals leached ( $\Sigma$  of all elements except sulfur).

### Intermediate Leaching Experiment

Based on the stated strategy, in order to preliminary feasibility study of neutralizing the pH of coarse refuse stream and minimizing the release of trace elements of this stream by using buffer capability of the other waste streams, a set of static leaching tests were conducted over a range of thickener underflow-to-coarse refuse ratios. Test results shown in Figure 12 indicate that all

ratios  $\geq 2$  provide the buffering action needed to maintain the pH near neutral.

### Leaching Characteristics of Co-Disposed Coarse Refuse and Thickener Underflow

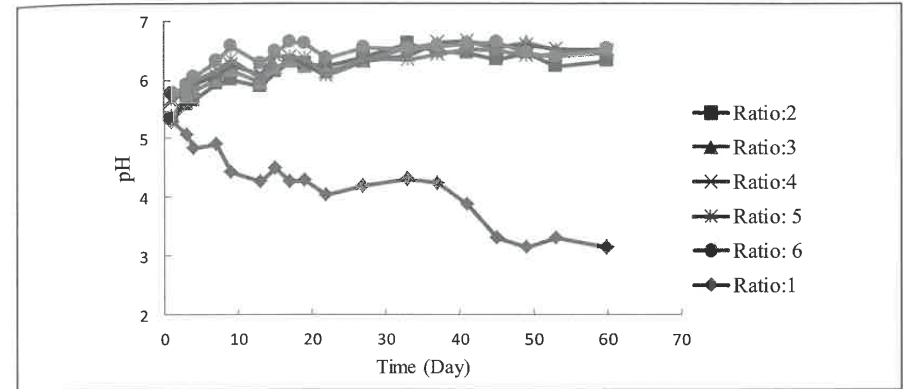
To evaluate the long term effect of co-disposal coarse refuse and thickener underflow strategy, longer static leaching (9 months) and dynamic leaching (5 months) tests were conducted on the co-disposed samples with the ratio of 1 and 2 thickener underflow to coarse refuse.

Variation of pH with time for dynamic and static leaching tests is shown in Figures 13. The pH variation of supernatant liquids in static leaching tests is consistent with the results of intermediate test, and the ratio of thickener underflow to coarse refuse should be at least equal to 2 in order to have enough buffering capability to neutralize the pH of the medium. However, in dynamic leaching tests, even with mixing ratio of 2, pH decreased to acidic conditions and trace elements were released. This is because in dynamic test condition pyrite is oxidized much faster than static test and also alkali and alkaline earth elements are leached out from the sample.

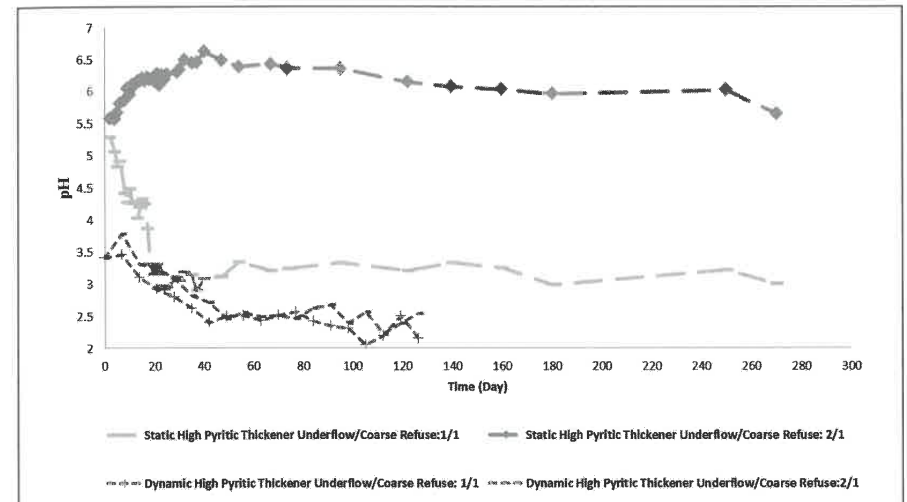
The comparison of the conductivity of combined leachant water from the samples over the entire period of dynamic leaching tests and the related values of static leaching tests are demonstrated in Figure 14, indicating the more effectiveness of static condition than dynamic condition to decrease the conductivity of high pyritic sulfur coarse refuse stream.

The total extractions (mg) of trace elements from the co-disposed samples after 19 weeks of the dynamic leaching tests and 9 months of the static leaching tests are summarized in Table 7.

The data indicates that the effectiveness of the test conditions, exist of enough buffering ions in the solution and the pH of the solution in mobility of the trace elements: Dynamic thickener underflow-to-coarse refuse: 1:1 >> Dynamic thickener underflow-to-coarse refuse: 2:1 >> Static thickener underflow-to-coarse refuse: 1:1 >> Static thickener underflow-to-coarse refuse: 2:1. Comparing the data of table 5 and 6 indicates that storage of co-disposed coarse refuse and



**Figure 12. Variation of leachate pH over a range of thickener underflow-to-coarse coal refuse ratios for the high sulfur content coal**



**Figure 13. Plots of the variation over time of the pH of supernatant liquids in contact with co-disposed coarse refuse and thickener underflow of high pyritic coal samples, in the both static and dynamic leaching test**

thickener underflow under water retards pyrite oxidation, acid generation and release of trace elements by neutralizing the pH using buffer capability of alkali and alkaline earth elements.

The other advantages of co-disposal have been well discussed by Williams (1995). Some of the advantages are: it eliminates the need for a coarse reject truck hauling system, the disposal

operating costs can be reduced by up to 85%, it can provide up to 40% more water recovery from the waste than that of the separate disposal of coarse reject and wet tailings, it provides 40% a denser packing results due to the wide size distribution and therefore can save 40% storage volume compared with separate disposal.



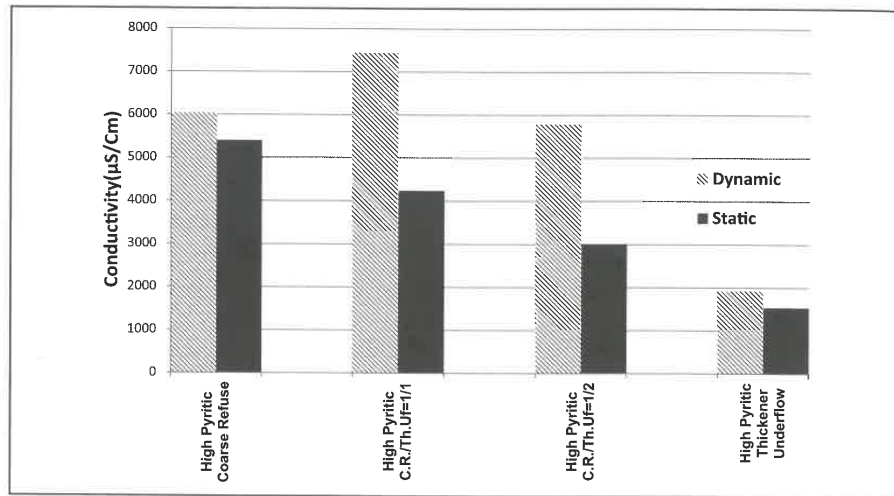


Figure 14. Plots of the conductivity of supernatant liquids in contact with various coal refuse and co-disposed coarse refuse and thickener underflow, in the static and dynamic leaching tests

## CONCLUSIONS

To develop strategies to minimize the release of the trace elements in coal waste impoundments, coal waste samples (coarse refuse, thickener underflow, spiral refuse and high frequency screen overflow) from plants treating high and low sulfur coal content were subjected to two types of long term leaching experiments. These two leaching tests, static and dynamic, simulate coal waste disposal under different disposal scenarios, and provide the data regarding the amount, the rate and oxidation form of the elements released during the tests.

In contact with water, the different waste samples generated a wide range of the pH conditions in both types of leaching tests due to differences in their mineralogy differences. The elements data analysis by ICP-OES, suggested that most of the trace elements are released from coal waste material under either acidic or alkaline pH conditions, and just a few of them can be released in both conditions. So a good strategy to minimize the release of trace elements is keep the pH of medium as close as neutral and the best cost effective method for that is modifying coal cleaning processes and/or storage practices

to maximize the buffering capability of the waste materials and thereby repress the leachability of heavy metals from coal reject streams.

Among the samples, the high pyritic coarse refuse sample had the highest amount of pyrite and in contact with water generated highly acidic condition and released much more trace elements in compare to the other streams. In contrast, high pyritic spiral refuse and thickener underflow samples had higher alkali and alkaline earth elements which neutralize the pH and repress acid generation and release of trace elements. On the other hand, low pyritic coal refuse samples showed much lower conductivity and very low mobility of trace elements especially those associated with pyrite.

The co-disposal coarse refuse and thickener underflow scenario was examined to evaluate the self-neutralizing potential of the waste streams, by using static and dynamic leaching tests. The results showed that storage of the co-disposed waste material with the ratio of thickener underflow to coarse refuse  $\geq 2$  under water retards the pyrite oxidation, acid generation and the release of the trace elements.

Table 7. Cumulative amounts (in mg) based on ICP measurements of elements in leachates over the 19 week long dynamic and 9 month long static leaching tests on 200 g of each codisposed sample

Elements	Th.U/F/C.R.=1/1		Th.U/F/C.R.=1/2	
	Dynamic	Static	Dynamic	Static
Aluminum	160.03	1.75	113.97	0.21
Antimony	0.16	<MDL	0.11	<MDL
Arsenic	2.84	0	0.58	<MDL
Barium	0.04	0	0.04	0
Beryllium	0.04	0	0.04	<MDL
Boron	8.18	0.31	5.92	0.19
Cadmium	0.09	0	0.09	<MDL
Calcium	1175.61	58.61	1164.2	68.79
Chromium	0.98	0	0.73	<MDL
Cobalt	1.65	0.01	1.76	0
Copper	3.31	0.03	2.34	0.01
Gold	<MDL	<MDL	<MDL	<MDL
Iron	4385.07	2.42	3000.65	1.46
Lead	0.11	0.01	0.09	<MDL
Lithium	0.45	0.04	0.33	0.02
Magnesium	129.85	32.3	103.51	16.82
Manganese	37.55	9.36	35.84	1.59
Nickel	6.01	0.03	5.61	0
Phosphorus	23.47	0	11.11	0.01
Potassium	17.28	1.76	10.37	1.15
Selenium	<MDL	0.01	<MDL	0
Silicon	38.22	4.3	38.73	0.42
Silver	0.01	0	0.01	0
Sodium	86.94	19.09	48.97	9.54
Strontium	1.27	0.35	1.47	0.27
Sulfur	4347.08	111.22	3323.42	82.13
Thalium	0.11	0.01	0.09	<MDL
Tin	0.04	<MDL	0.04	<MDL
Vanadium	0.25	<MDL	0.16	<MDL
Zinc	6.28	0.09	5.94	0.01
Sulfate	12739.5	348.54	9660.84	279.56
TM	6085.84	130.48	4552.7	100.49

In overall, based on the results of this study separation high density fraction especially pyrite from refuse streams and storing that separately after applying solidification, encapsulation or other methods to prevent pyrite from oxidation, and then applying codisposal scenario for lower density fraction is suggested to be an ideal solution regarding minimizing conductivity and release of trace elements from waste streams.

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