Selenium Leaching from Coal Waste Rock in the Elk Valley, B.C.

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Abstract
Teck Coal operates five open pit coal mines in south-eastern British Columbia. As a result of increasing selenium concentrations in the Elk River, the mechanism of selenium release from waste rock material and coal processing wastes is being investigated using a series of field and laboratory kinetic experiments (columns and humidity cells in the laboratory (1 to 6 kg), field barrels (300 kg) and leach piles (300 tonnes)). The tests relate leaching under well characterized experimental conditions to *in-situ* leaching rates.

Results indicate that selenium appears to be mainly associated with pyrite at these sites. A significant portion of the sulphur occurs in carbonaceous form (coaly materials) but it contains minor selenium. Based on mineralogy and leachate correlations, the origin of selenium leaching from the waste rock is likely oxidative dissolution of pyrite. This is also consistent with the lowest selenium rates in this study being associated with submerged column tests.

Leaching rates for waste rock expressed on a per weight basis decrease as the scale of the experiment increases. These differences were attributed to the larger particle sizes of site materials, lower temperatures under site conditions and reduced water contact.

Key Words: Geochemical, scaling, oxidative, dissolution.

Introduction
Coal mining in the Elk Valley in south-eastern British Columbia, Canada, started in the late nineteenth century near the town of Fernie. Over the last century, mining in the Elk Valley has increased substantially and Teck Coal now produces coal from five open pit mines that is transported by train to a port near Vancouver B.C. for export to mainly Asian markets

Water quality management at the Elk Valley mines was historically focused on total suspended solids (TSS) and nitrogen forms (nitrate, nitrite and ammonia). Since the 1980's, selenium concentrations have been increasing in the Elk River and selenium is now a part of water quality management. Beginning in the late 1990's, Teck Coal began a concerted effort towards understanding the potential for environmental effects, mechanism of selenium leaching and potential attenuation pathways. More background information is provided in Day *et al.* (2012, these proceedings), which interprets flow and monitoring data from the five Teck Coal dumps in the Elk Valley.

This paper presents the results of specific studies at Teck Coal's Line Creek Operation (LCO) focused on understanding selenium occurrence and release at three different "geochemical scales", from laboratory to small-scale field experiments. "Geochemical scaling" refers to experiments performed at a variety of scales with an attempt to link the results obtained from the different experiments using "scaling factors". Scaling factors account for differences in ambient temperatures between laboratory (warm) and field (cool) conditions that affect reaction rates (for example, as defined by the Arrhenius equation), differences in particle size distribution that affect the surface area available for reactions, and differences in rock contacted by infiltrating water as the size of the facility increases. Typically, scaling calculations use one scale of experiment (a 1 kg humidity cell) to calculate leachate chemistry for the full scale. These

calculations often result in predicted concentrations that are much higher than expected from thermodynamic calculations and site experience. The reason is that the calculations do not take into account factors that can limit the reactions (e.g. oxygen availability), the various factors beyond temperature that affect reaction kinetics, the limited solubility of reaction products and attenuation effects.

The approach for this study was to perform experiments and monitoring at several scales to understand how selenium leaching changes as factors such as the water to rock contact ratio decreases and flow path length increases. Only small changes in scale can be observed in laboratory tests, and the requirement to obtain sufficient leachate for analysis often results in significant dilution effects preventing observation of solubility related effects. It was proposed therefore to do testing at four scales: two laboratory scale (1 kg humidity cell and 6 kg columns), two field scales with constructed tests (300 kg barrel and 300 tonne pile) and one full scale (existing waste rock dump containing hundreds of million tonnes of waste). This represents a scale range of roughly eleven orders-of-magnitude. The scaling experiments were designed so that leachate chemistry can be interpreted in the context of the mineralogy, bulk chemistry and solid speciation of selenium in rocks from the Mist Mountain formation. The basis for selenium leaching previously developed by SRK is described by Day *et al.* (2012, these proceedings).

Experimental Methods

Sample Collection

Six different waste material types were collected from Teck Coal's Line Creek Operations (LCO) for laboratory and field experiments in the fall of 2008. The aim was to test discrete lithologies; however, in practice discrete lithologies (other than coal) cannot be mined as they occur in layers thinner than can be practically extracted using the mining equipment. As a result, the material types represent mixtures of different lithologies as follows:

- Sample #1 – "Waste Rock". Contained mudstone, coal, and up to 15% sandstone.
- Sample #2 – "Coal Cleaning". Contained mudstones and traces of coal. Coal cleanings are the waste removed from the top of the seam using small equipment before coal is recovered.
- Sample #3 – "Waste Rock". Contained a mixture of siltstone, mudstone, coal and up to 30% Sandstone.
- Sample #4 – "Waste Rock". Contained shales, coal, and traces of sandstone.
- Sample #5 – "Coarse Coal Rejects" (CCR). Contained both non-recoverable coal and waste rock layers that report to the waste rock dumps. CCR is the coarse waste product of raw coal processing.
- Sample #6 – "Raw Coal".

Solids Characterization

Two sets of composited samples were tested to assess variability of bulk samples from the field for the six different sample types as listed above. The samples were prepared for characterization by particle gradation of dry samples to produce six fractions (+75mm; -75+6.4 mm; -6.4+2 mm; -2+0.149 mm); -0.149+0.053 mm; -0.053 mm).

The individual fractions (except +75 mm) were characterized by a number of methods. Mineralogical characterization was performed by optical petrography on polished thin sections and quantitative X-ray diffraction (XRD) using Rietveld refinement. Chemical analyses by total sulphur and total carbon were determined by Leco furnace; carbon as carbonate; sulphate sulphur by HCl leach and Na_2CO_3 leach; sulphide sulphur by a modified version of ASTM

D2492-02 (ASTM 2007), where the modification consisted of analyzing the extract for sulphate (rather than sulphur as per standard method) after leaching with nitric acid; four acid digestion (perchloric, nitric, hydrochloric, and hydrofluoric acids) followed by determination of 41 elements by ICP-MS; aqua regia digestion (1:3 ratio of nitric acid to hydrochloric acid) followed by determination of 36 elements by ICP-MS; and neutralization potential (NP) was determined by the method of Sobek et al. (1978).

Water Soluble Sulphur and Selenium

Shake flask extraction tests (MEND 2009) were performed on all samples, with the exception of coal cleaning material as there was insufficient material available. The procedure involved placing 250 g of material in a glass shake flask with 750 mL of deionized water and gently agitating for 24 hours. At the conclusion of the test, the leachate was analyzed for sulphate and selenium.

Laboratory kinetic tests – columns and humidity cells

Laboratory kinetic tests were conducted on all samples and included subaqueous column tests, partially-saturated column tests and humidity cell tests. Samples for testing were generated by recombining the six sieve fractions described above under 'Solids Characterization' in the as-received proportions. Analysis of weekly leachate from all laboratory tests included lab pH and conductivity, hardness, anions and nutrients (acidity, alkalinity, bromide, chloride, fluoride, sulphate, ammonia, nitrate, nitrite, dissolved phosphate), dissolved organic carbon (DOC), and dissolved elements (including major elements and selenium). Selenium speciation was also performed after approximately six months of leaching.

Two subaqueous column tests were performed on one 6-kg sample of sample 2 material, and one composite of three sample types (samples 1, 3 and 4). Columns were packed with sample material to a height ranging from 23.5 to 36 cm, then flooded with deionized water to establish a water cover of 30 cm above the saturated sample. The columns are operated by six days of saturation, followed by leaching on the seventh day. On the day of leaching, the water cover is replaced as soon as possible, typically on the order of hours. Deionized water was added on a weekly basis to maintain a constant water level in the column. Partially-saturated columns were operated the same way. One 6 kg composite (samples 1, 3 and 4) was tested. The construction, operation and analysis of the partially saturated columns are identical to the subaqueous columns described above, except that the water level is maintained at approximately half the sample height (leaving half the sample unsaturated).

Humidity cell tests are being carried out on 1 kg samples according to the procedure described in MEND (1991). The procedure involves six days of aeration followed by leaching using 500 mL of deionized water and analysis of the leachates. A total of 15 humidity cells were initiated in May 2009 which includes one test for each composite (two humidity cells for each sample), two laboratory duplicates and one method blank.

Field kinetic tests – barrels and leach piles

Barrel tests

Six material types were set-up in duplicate by placing approximately 300 kg of each material type into 200 L plastic barrels on metal stands (12 barrels in total). The mass of rock in each barrel was determined by calculating the volume of rock in each barrel (in m3) and multiplying this value by a loose cubic metre (LCM) density of 1.7 tonnes/m3. The barrels were open to the atmosphere and infiltrating

water exits through a drain pipe located at the base of the barrel which drains to a plastic pail. The stands were designed to allow the barrels to sag slightly thereby limiting pooling in the bottom of the barrel. Air vents in the side of the barrel ensure the test materials are not oxygen limited. When sufficient water was available, samples were collected monthly and shipped to ALS Environmental for analysis of the same parameters as for laboratory monitoring, described above.

Leach Piles

Leach piles were constructed on liners and contained between 200 and 800 tonnes of test material. The mass of each rock pile was determined by calculating the volume of rock in each pile (in m3) and then multiplying that value by an LCM density of 1.7 tonnes/m^3. The volume of each pile was calculated from ground survey dimensions provided by Teck Coal. Oversize material (+75 mm) was measured by Split Engineering using image analysis of pile material with scaling balls. Undersize material was measured as described above under 'Solids Characterization'. Leachate from the piles proceeds through a collection drain directed to instruments that enable measurement of water flows using tipping buckets and a pail for collection of water samples once a month following similar protocols to the barrel tests. The field cells are instrumented at three locations in each pile for monitoring of infiltration, temperature, pore gas composition, and moisture content. The targeted download frequency of the dataloggers attached to the field cells was monthly.

Quality Control

In addition to routine QA/QC procedures, the test program included duplication at all scales except the leach piles.

Results

Sample Characteristics

Mass and surface area

The mass and surface area of each test material is provided in Table 1. Surface areas were calculated from image analysis and particle size analyses. The difference in surface areas is a result of sample preparation. Humidity cells were sieved in the laboratory to contain only – ¼" material, while the barrels and leach pads were loaded with mine waste on site. The leach pads generally have a smaller surface area than the barrels as rocks with diameters as large as 10% of the pile height (i.e. 20 cm) were placed, while the majority of rock diameters in the barrels was less than 1cm. The one exception to this result was in sample 1, where the particle size analysis indicated that there were more fines in the leach pile sample than in the barrel.

Table 1: Mass and surface area calculations of test materials

		LEACH PILES		BARRELS		HUMIDITY CELLS	
Sample	**Material**	**Mass tonnes**	**Surface Area m^2/kg**	**Avg. mass kg**	**Surface Area m^2/kg**	**Mass kg**	**Surface Area m^2/kg**
1	Waste Rock	210	11	180	11	1	27
2	Coal Cleaning	290	1.6	190	13	1	29
3	Waste Rock	430	5.5	220	8.5	1	38
4	Waste Rock	370	2.3	200	8.2	1	31
5	CCR	750	11	190	16	1	28
6	Raw Coal	230	7.5	190	20	1	34

Mineralogy

All of the samples consist of various amounts of coal fragments and sedimentary rocks. The sedimentary rocks consist of sandstone, siltstone, carbonate, mudstone and possibly chert. The dominant minerals were quartz and clays (kaolinite, illite-muscovite). Siderite was the dominant carbonate ranging between one and five percent, followed by dolomite and then calcite. Pyrite was the most common sulphide observed in all samples, although typically below 1% and only in thin section. It occurred predominantly as framboids and less commonly as anhedral to subhedral grains.

Chemical composition

Complete chemical analysis of waste rock samples was performed; however, only the results used to determine the form of sulphur and selenium in the materials at LCO are presented below. Six tests performed in this study provided a basis for assigning the reactive form of sulphur and selenium. The basis for assigning form is as follows:

- SFE tests provide water soluble form;
- Hydrochloric acid extraction is for non-acidic sulphate minerals (predominantly gypsum);
- Nitric acid extraction provides water soluble, sulphate and a fraction of sulphide form;
- Aqua regia extraction provides water soluble, sulphate and sulphide;
- 4-acid extraction is assumed to capture all selenium forms, including the organic form; and
- Total sulphur is assumed to capture all forms by combustion (Leco is an order of magnitude more precise than 4-acid digestion).

Carbon was predominantly present as organic carbon in all of the samples, ranging from 9 to 60% of the total sample, whereas carbonate ranged from 1.1 to only 3.8%. Interestingly, samples one and two contained as much organic carbon as the coarse coal rejects (35 versus 33%, respectively). Sample three contained the least amount of organic carbon.

The average sulphur and selenium values for each material type composite are provided in Table 2 and Table 3. Sulphur concentrations increased with strength of lixiviant and approximately 50% was present as organic sulphur (calculated by dividing the difference between aqua regia and Leco sulphur by Leco sulphur). Selenium displayed the same trend as sulphur where concentrations increased with strength of lixiviant, although selenium association ranged from 50% to 99% sulphide (water soluble plus aqua regia divided by 4-acid). The ratio of selenium to sulphur was always highest in the sulphide form and ranged from 0.0026 to 0.0069 (Table 5).

Table 2: Sulphur form concentrations

Sample Information		**Sulphur Analysis**				
Sample	**Material**	**Water Soluble %S**	**HCl leach wt.%**	**HNO_3 leach wt%**	**Aqua Regia wt%**	**Leco wt.%**
1	Waste Rock	0.0022	0.01	0.02	0.06	0.14
2	Seam Cleaning	-	0.01	0.03	0.07	0.19
3	Waste Rock	0.0031	0.01	0.04	0.06	0.09
4	Waste Rock	0.0051	0.01	0.035	0.065	0.11
5	Coarse Rejects	0.016	0.01	0.02	0.06	0.08
6	Raw Coal	0.0013	0.01	0.03	0.05	0.065

Table 3: Selenium form concentrations

Sample Information		Selenium Analysis			
Sample	**Material**	**Water Soluble mg/kg**	**HNO_3 leach mg/kg**	**Aqua Regia mg/kg**	**4 acid digestion mg/kg**
1	Waste Rock	0.03	0.52	1.4	2.0
2	Seam Cleaning	-	0.45	2.0	2.9
3	Waste Rock	0.065	0.74	1.4	1.8
4	Waste Rock	0.11	1.1	3.7	4.8
5	Coarse Rejects	0.06	0.4	2.2	2.7
6	Raw Coal	0.02	0.34	1.7	1.6

Laboratory kinetic tests

Fully saturated (FS) and partially saturated (PS) column tests were run for 77 weeks. Leachate pHs for both fully- and partially-saturated columns were between pH 7.6 and 8.4 throughout the duration of testing, with a slight downward trend. Leachate sulphate release rates showed steady declines in both saturated and partially saturated column tests. Rates decreased roughly an order of magnitude over the 77 weeks of testing, with rates from the partially saturated columns approximately four to five times higher than the saturated columns. Selenium leaching rates were approximately two orders-of-magnitude lower in the fully saturated column (0.00001 mg/kg/week) compared to the partially saturated column (0.001 mg/kg/week) and approximately two to three orders-of-magnitude lower than the humidity cells. Sulphate and selenium leaching were well correlated (r values greater than 0.89). Seam cleaning samples had a lower correlation coefficient (r = 0.77) though the correlation remained significant with a probability level of better than 0.01. When measured, selenate was the only detectable form of selenium.

Based on 86 weeks of humidity cell testing, leachate pH stabilized between pH 7.5 and 8.2 after week 10 for all samples except raw coal, although there was still a slight upward trend. Raw coal fluctuated slightly above and below pH 7.5. Sulphate showed initial rapid declines in most samples through Week 5, and then generally continued to decline at a slower rate for the duration of testing to date. Most samples showed a rapid decline in selenium leaching rates through Week 5, then slowly declining leaching rates thereafter (Figure 1). Waste rock from sample 4 and CCR (sample 5) showed the highest initial selenium leaching rates. Leaching rates for the waste rock samples have declined from 0.03 mg/kg/week to around 0.004 mg/kg/week. CCR is now among the lowest leaching rates under test at 0.001 mg/kg/week. Raw coal and other waste rock samples showed similar leaching rates, with loadings declining from around 0.003 to 0.005 mg/kg/week in Week 5 to between 0.001 to 0.002 mg/kg/week. Sulphate and selenium loadings were significantly correlated at a probability level greater than 0.01. When measured, selenate was the only detectable form of selenium.

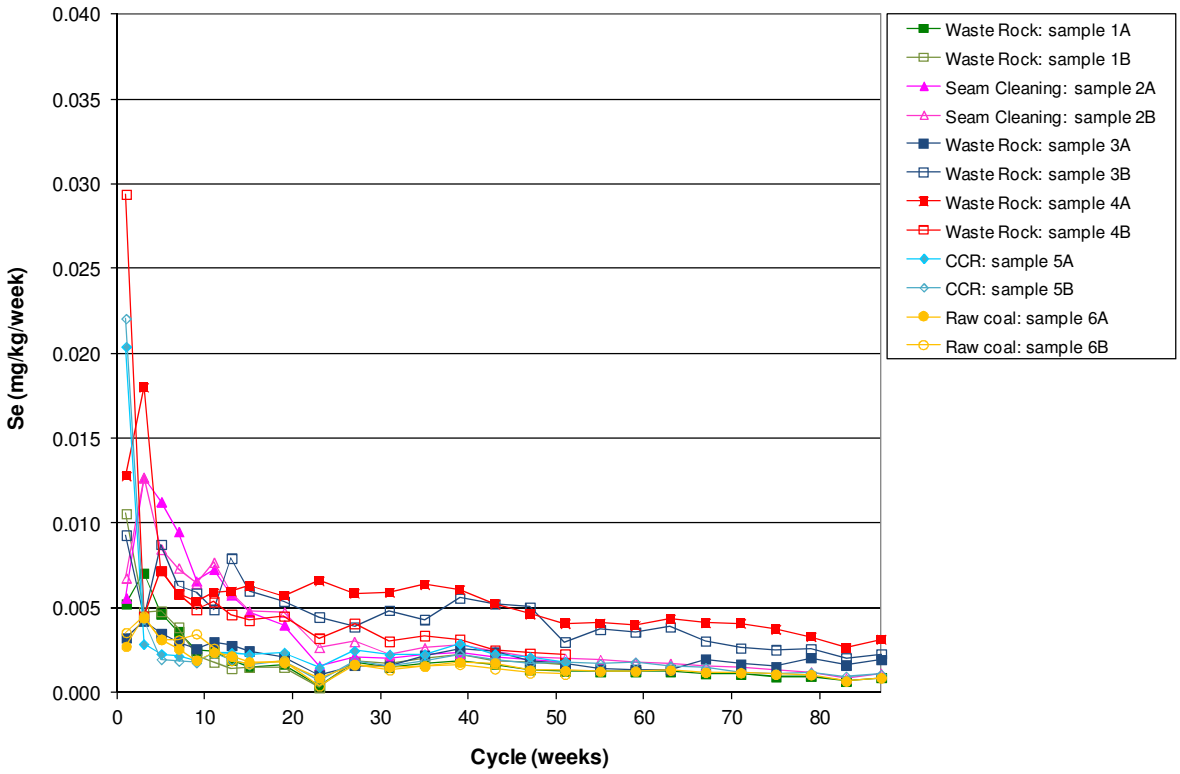

Figure 1: Selenium humidity cell data for waste rock, CCR and raw coal samples from LCO.

Barrel tests

Barrel leachate sampling began in May 2009 and data reported here includes up to December 2010. The barrel sampling frequency goal was once per month, however, the number of samples collected varied depending on the precipitation received. Sulphate and selenium loadings for field barrels were calculated as follows:

Loading in mg/kg/week = {SO_4 or Se mg/L} x {volume of water (L)}/{ mass of rock in the barrel (kg)}/{number of weeks to produce the given volume of water} (1)

Water volume was calculated from the depth of water in the collection pails at the time of sampling and assumed the pails were cylinders and the mass of rock in the barrel as explained above in the Methods section. Time was determined by the number of weeks required to produce a sample as water was discarded after each sampling round.

Barrel leachate pH ranged between 7.4 and 8.4, with an overall upwards trend that appeared to fluctuate seasonally, being highest during freshet and the fall and lowest during drier months. Sulphate leaching fluctuated seasonally, with maximum leaching occurring in late summer to early fall. This likely coincides with evaporate salts forming during dry periods, followed by flushing during heavier precipitation events. The range of loading was from 2 to nearly 7 mg/kg/week. Waste rock and seam cleaning material appear to be releasing the most sulphate. Selenium leaching exhibited the same behaviour as sulphate, with waste rock and seam cleaning releasing the most selenium (Figure 2). When measured, selenate was the only detectable form of selenium.

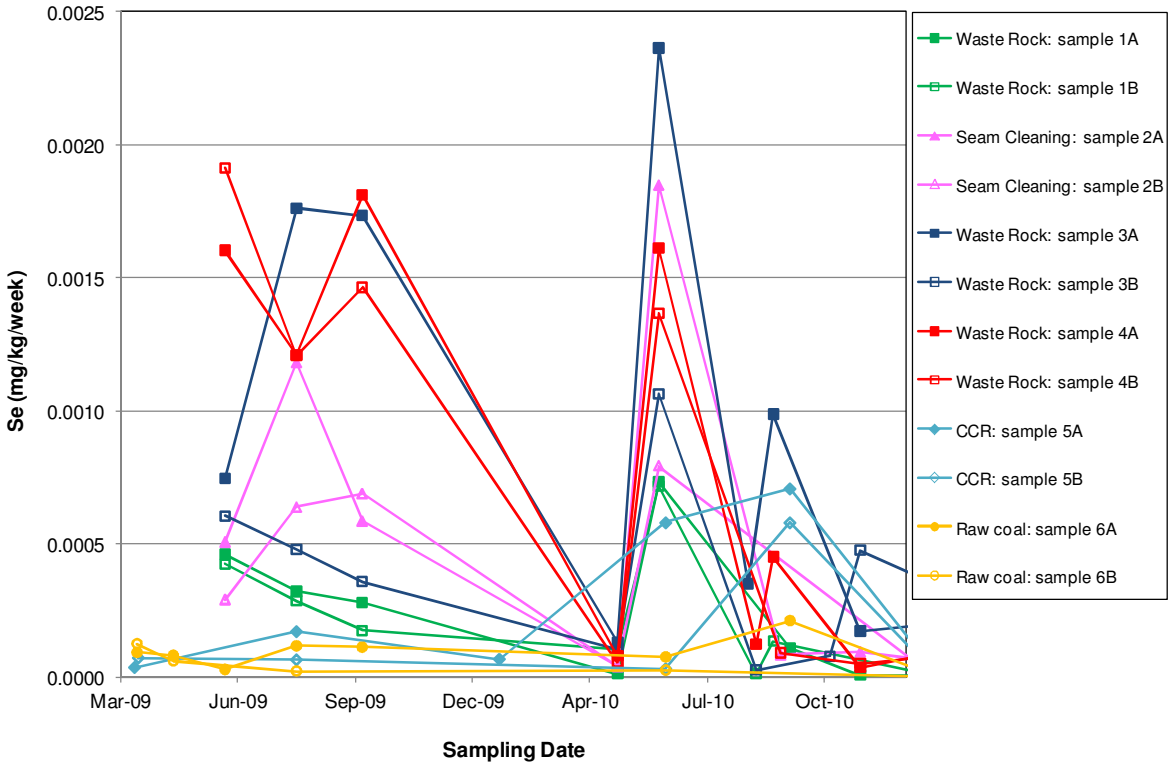

Figure 2: Selenium leaching from field barrel tests.

Leach pile tests

Leach pile sampling began in April 2009 and data presented here is up to December 2010. The sampling frequency goal was once per month, however, the number of samples collected varied depending on the precipitation received. Dataloggers have been recording water volumes, gas composition, moisture content and temperature. Sulphate and selenium loadings for leach piles was calculated as follows:

Loading in mg/kg/week = {SO_4 or Se mg/L} x {volume of water (L)}/{ mass of rock on the leach pile (kg)}/{number of weeks to produce the given volume of water} (2)

Water volume was calculated from the total volume of water recorded by the tipping buckets on the day of sampling plus the preceding six days. The mass of rock on the pile was calculated as explained in the Methods section. Time was set from recording the volume of water per week as noted above.

Leachate pH has remained fairly constant between pH 7 and 8.5 for all samples. Sulphate loading fluctuated strongly, likely from precipitation events. Selenium loadings followed a similar pattern to sulphate, and its leaching behaviour is shown in Figure 3. When measured, selenate was the only form of selenium detected.

Results from datalogger monitoring of the leach piles indicated that spring and fall are the wettest times of year based on average precipitation, with periods of dryness that facilitate accumulation of weathering products followed by high flow, or flushing events, that result in "spiked" loadings. Precipitation was calculated by taking the tipping bucket flow rate (in litres) and dividing by the surface area of each leach pile. Temperature variation throughout the season reflects the local climate in the Elk Valley, with an approximate 30°C range from summer to winter. There is also nearly a 15°C temperature difference in the vertical profile of the pile during the winter and summer extremes, with the most damped section at the

base of the pile. Moisture content of the piles showed that some the material is always wetted, with the base of the pile containing more moisture than the surface.

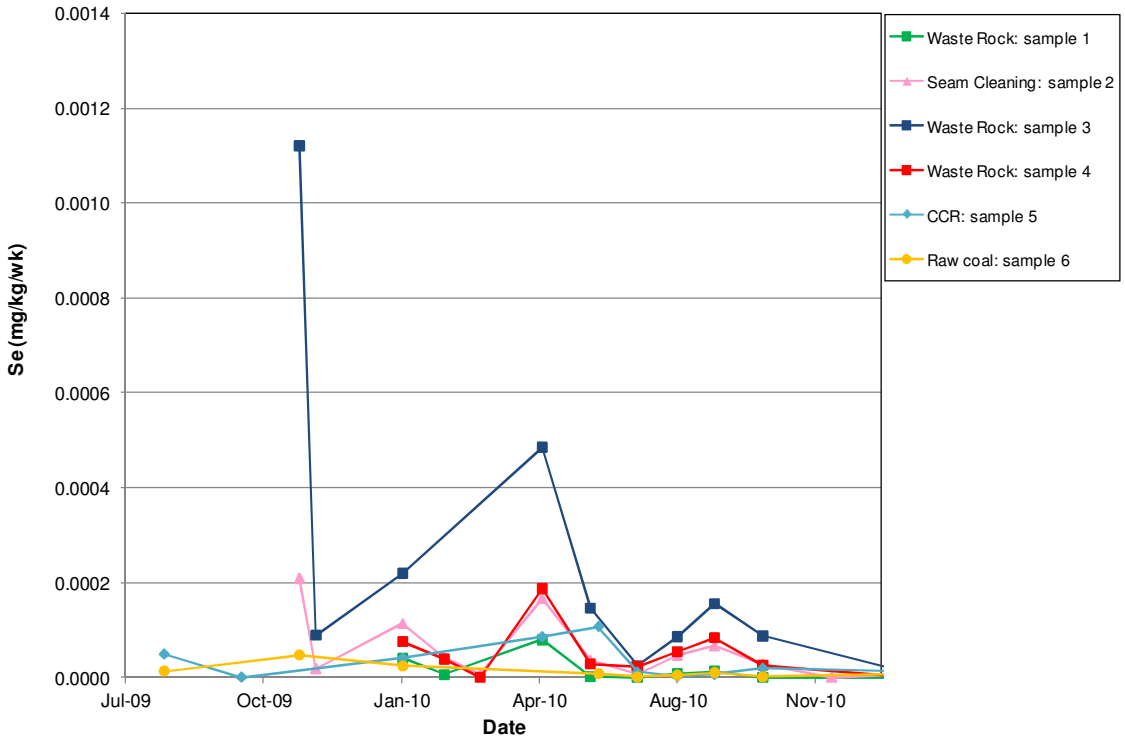

Figure 3: Leach pile selenium leaching.

Gas composition (O_2 and CO_2) for all of the piles was unchanged from atmospheric concentrations with the exception of samples 5 & 6 (CCR and raw coal, respectively). At approximately 1 m below the surface of these piles, a small depletion of O_2 (20.1%) was coincident with a small increase in CO_2 concentrations (0.3%).

Comparison of Selenium Leaching Rates – Laboratory and Field

Loadings from columns, humidity cells, on-site barrels and leach piles are compared in Table 4. Note that columns were 6 kg composites of material types. The mean for each sample was calculated by dividing the total load by the total monitoring period. Sulphate leaching rates decreased from one to two orders of magnitude between the humidity cells and leach piles. Only one order of magnitude decrease was observed in raw coal and the two waste rock samples with the least amount of coal (samples 3 & 4), while waste rock from sample 1 (containing up to 80% coal), coal cleaning material, and CCR decreased by two orders of magnitude. The fully saturated columns leached at approximately half the rate of the humidity cells, whereas the partially water saturated columns showed relatively minor difference. Selenium leaching rates followed a similar pattern to sulphate leaching, with the difference being raw coal. Two orders of magnitude were observed between humidity cells and the leach piles for the predominantly coal waste rock sample in addition to seam cleaning material, CCR and raw coal. The other two waste rock samples decreased by only one order of magnitude.

Table 4: Comparison of selenium leaching rates

Selenium Loading Statistics (mg/kg/week)				
Test Sample	**Statistic**	**Fully Saturated Sample 2**	**Fully Saturated Samples 1, 3, 4**	**Partially Saturated Samples 1, 3, 4**

Columns	P5	4.7E-06	5.2E-06	8.3E-04
	MEAN	3.8E-04	5.9E-04	1.6E-03
	P95	4.3E-04	3.2E-03	2.6E-03

Selenium Loading Statistics (mg/kg/week)							
Test Sample	**Statistic**	**Sample 1: Waste Rock**	**Sample 2: Coal Cleaning**	**Sample 3: Waste Rock**	**Sample 4: Waste Rock**	**Sample 5: CCR**	**Sample 6: Raw Coal**
Humidity Cells	P5	1.09E-03	1.45E-03	1.95E-03	2.85E-03	1.40E-03	9.35E-04
	MEAN	2.53E-03	4.40E-03	3.50E-03	5.75E-03	2.95E-03	1.95E-03
	P95	5.70E-03	1.02E-02	6.00E-03	1.20E-02	5.15E-03	3.40E-03
Barrels	P5	6.03E-05	2.50E-04	3.85E-04	2.35E-04	9.80E-05	5.80E-05
	MEAN	3.08E-04	6.70E-04	9.40E-04	9.65E-04	9.35E-04	1.90E-04
	P95	6.50E-04	1.24E-03	1.49E-03	1.75E-03	2.60E-03	4.70E-04
Leach Piles	P5	3.10E-07	1.10E-05	9.50E-05	2.20E-05	3.60E-06	4.00E-06
	MEAN	4.90E-05	1.60E-04	5.20E-04	1.30E-04	8.90E-05	4.60E-05
	P95	1.70E-04	4.70E-04	1.70E-03	3.30E-04	2.40E-04	1.30E-04

Discussion

Evaluation of the Selenium Release Model

The initial model developed by SRK (SRK 2004) to explain the release of selenium in the Elk Valley postulated that the main variables controlling selenium mobility were:

- The initial form of selenium released (i.e., selenate versus selenite);
- The oxidation conditions in the disposal area (oxidizing or reducing); and
- The pH conditions in the disposal area (acidic or basic).

Selenium is typically found in crustal rocks as a substitution element due to its relatively low abundance. The crystal lattice of many sulphur minerals (sulphides and sulphates) appears to easily incorporate selenium and so understanding the mineralogical occurrence of sulphur is critical to predicting the behaviour of selenium leaching.

Waste rock from LCO contains sulphur (i.e. > 0.1%) that is mainly a mixture of organic sulphur and sulphide sulphur prior to being mined. This is based on the test sample materials as they represent fresh waste rock and contained only minor sulphate and water soluble sulphur. The high percentage of organic sulphur is consistent with the paleoenvironent required for coal formation (i.e. high organics), with the highest concentration of organic sulphur in raw coal. The presence of high levels of organic sulphur values (Table 3) in the waste rock was unexpected as they were targeted to be mainly sandstone and siltstone. However, mineralogical characterization revealed that these materials contained up to 80% coal, which is consistent with the percentage of organic sulphur present.

Selenium appeared to be predominantly associated with sulphide sulphur in waste rock and CCR so that the distribution of selenium favours sulphide rather than a carbon association (Table 3). Very minor water soluble selenium was detected (less than 4% in all cases). This likely reflects the slow oxidation rate of pyrite and also the high solubility of selenate (the water soluble form), which would result in very little accumulation in the solid phase for detection by any extraction method for waste contacted by water.

Based on the results from this study, the most significant pathway for selenium release appears to be from oxidation of primary sulphide minerals in waste rock (i.e., pyrite) containing selenium. After oxidation, selenate (SeO_4^{2-}) is the primary selenium species due to the oxidizing and basic waters that result from water-rock interactions in samples from LCO.

Selenium and sulphate leaching has been shown to well correlated in the drainage from the field and laboratory samples. In addition, the ratios of selenium to sulphur in the sulphide fraction also indicate that sulphides contribute the most to selenium leaching (Table 5). Water soluble ratios are very similar to leachate ratios; however, the majority of selenium must first oxidize to a water soluble form before it can be leached, which would inherently produce similar ratios unless there is a primary sulphate such as gypsum. Primary gypsum content appears to be low based on the detection limit levels of sulphate in the samples.

Table 5: Comparison of selenium to sulphur ratios.

Selenium : Sulphur Ratio (mg Se/mg S)					
Sample	**Material Type**	**Solid: Water Soluble**	**Solid: Sulphide**	**Solid: Organic**	**Leachate: Humidity Cell**
1	Waste Rock	0.0013	0.0029	0.0008	0.0010
2	Seam Cleaning	-	0.0036	0.0007	0.0017
3	Waste Rock	0.0022	0.0027	0.0011	0.0022
4	Waste Rock	0.0030	0.0069	0.0026	0.0038
5	Coarse Rejects	0.0004	0.0043	0.00050	0.0013
6	Raw Coal	0.0014	0.0041	0.0013	0.0015

Selenium to sulphur ratios associated with organic matter are consistently lower than the humidity cell leachate sample ratios, which would indicate that selenium is leaching faster than sulphur from organic matter and it is difficult to propose a mechanism for this to occur (the humidity cell rate is used here as it is the fastest rate for the scales tested in this study). These observations are good evidence that the primary mechanism of selenium leaching at LCO is by oxidative dissolution from primary sulphides. The consistently lower Se/S ratios in leachate suggests that selenium is not being completely leached or that other forms (pre-existing water soluble or organic forms) are contributing to both sulphate and selenium release. Incomplete leaching could also occur if selenium is locally sorbed at the oxidation site onto iron hydroxide forms.

The contribution of selenium leaching from the oxidation of carbonaceous matter under test conditions seems an unlikely contributor, which leaves leaching of traces of gypsum. It is possible that sulphate and selenate ions could be released from the dissolution of oxidized sulphur minerals (i.e., gypsum), however, there is insufficient mass available to account for the observed loadings. For example, in one year, waste rock in the humidity cell for sample 4 will leach approximately 0.3 mg of selenium. Shake flask extraction tests indicated that the total available water soluble selenium from all forms is only 0.11 mg, indicating that this source will have depleted in approximately twenty weeks, despite the test data to date demonstrating 86 weeks of selenium leaching.

Predicting Selenium Leaching

The geochemical scaling experiments used in this study included 1 kg humidity cells, ~300 kg barrels, and ~ 300,000 kg leach pads, encompassing approximately five orders-of-magnitude. While mass and flow data were not available at the time of this study for one of the full scale dumps at LCO (the West Line Creek Dump), it likely contains hundreds of millions of tonnes of rock, which increases the range to at least 11 orders-of-magnitude. These ranges have provided the opportunity to initially interpret scaling effects (i.e., differences in field versus laboratory temperature, gas exchange, surface areas) on water quality predictions. Ongoing monitoring of field experiments will allow these interpretations to be refined.

The decreases in leaching rate observed for sulphate and selenium ranged from one to two orders of magnitude between the lab and field, and another order of magnitude when compared to the estimated valley wide rate (Day *et al.* 2012). In addition, changes in leach rates were observed to be the same for sulphate and selenium in similar test materials. Typical considerations for scaling differences are particle size surface area, temperature differences, oxygen limitations and water contact.

The surface area of the field test material is less than the humidity cells, although the decrease ranges by only half (samples 1 and 5, which are waste rock with 80% coal and CCR) to one order-of magnitude for all others. Sulphate and selenium leaching rates in samples 1, 2, and 5 all decreased by up to two orders of magnitude. Surface area will affect leaching rates, but it does not appear that a change in surface area alone can account for the up to two orders of magnitude difference observed for some of the samples.

Oxygen is not expected to be significantly limiting reactant in any of the lab or field experiments. Temperature differences between the laboratory (constant 22^{o}C) and the barrels (mean annual temperature of 6.7^{o}C as measured by leach pad dataloggers) indicate a possible order of magnitude difference in oxidation rates. The difference in leaching rates between the barrels and leach piles is attributed to gas exchange (some limitation in the bottom of the piles), decreased surface area for leach pile material and the possibility of decreased leachate contact in the leach piles. With regards to leachate contact, flow paths likely develop in the leach piles that would result in portions of the rock not coming into contact with precipitation, and these differences are likely exacerbated in full scale dumps. It should be noted that a comparison of the leaching rates between barrels and leach pads is slightly skewed as the barrels tend to completely freeze in the winter and do not provide leachate for analysis, while the core of the leach piles remains above freezing, which will actually enhance leaching rates during the winter in comparison to the barrels, or if the leach piles were smaller and also frozen in the winter.

Potential Attenuation Mechanisms

As the oxidation state of selenium decreases, it becomes less soluble due to reduction to selenite and will more readily adsorb onto other surfaces. While analyses did not detect reduced forms of selenium in any of the experiments, fully saturated and partially saturated columns provide a basis for comparing the effects of limiting oxygen availability. The reduction in selenium leaching with increased levels of submergence is attributed to limited oxygen availability for sulphide oxidation (and subsequent selenium release) under saturated conditions. The columns were flushed on a weekly basis, which likely inhibited establishing reducing conditions and the potential to observe any selenium reduction and attenuation. Saturated waste rock in full scale dumps likely presents an opportunity for *in-situ* attenuation, and work is ongoing to understand the biogeochemical nature of this process.

Conclusions

Based on the results of this study, selenium in the rock samples from the Mist Mountain Formation is mainly associated with sulphide, the dominant form of which is pyrite and the origin of selenium leaching is likely oxidative dissolution of pyrite. A significant portion of the sulphur occurs as organic sulphur in association with coaly materials, but the association of selenium with this fraction is limited. Comparison of results from one full year of monitoring field experiment with humidity cell results shows that sulphate and selenium release under field conditions is at least an order of magnitude lower than under laboratory conditions. The differences can be accounted for by the larger particle sizes of site materials, lower temperatures under site conditions and reduced water contact. Submerging samples in water reduces the rate of pyrite oxidation and associated selenium leaching.

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References

ASTM (2007). ASTM D2492-02: Standard Test Method for Forms of Sulfur in Coal.

Day, S., Kennedy, C., Pumphrey, J. (2012). Interpretation of Selenium Release from Coal Mine Waste Rock Dumps, Southeastern British Columbia, Canada. ICARD 2012.

MEND (Mine Environment Neutral Drainage Program) (1991). Acid Rock Drainage Prediction Manual, MEND Project 1.16.1 (b). Prepared by Coastech Research Inc., North Vancouver, B.C. March 1991.

MEND (2009). Prediction Manual for Drainage Chemistry from Sulphidic Geologic Material, MEND Report 1.20.1; Version 0 - Dec. 2009. Prepared by CANMET – Mining and Mineral Sciences Laboratories, Smithers, B.C.

Price, W.A. 1997. Draft Manual of Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. B.C. Ministry of Employment and Investment. 141 pages plus appendices. Note: Ministry of Employment and Investment was the former home of Ministry of Energy, Mines, and Petroleum Resources.

Sobek A A, Schuller W A, Freeman J R, and Smith R M., 1978. Field and laboratory methods applicable to overburden and minesoils. USEPA Report No. 600/2-78-054, 203 pp.

SRK Consulting (Canada) Inc. 2004. Evaluation of Selenium Geochemistry: Elkview Coal Mine. Report prepared for Elk Valley Coal Corporation, November 2004.