

Investigations of Calcite Deposits in Streams Downstream of Coal Waste Rock Dumps, British Columbia and Alberta, Canada

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Abstract

Teck Resources Ltd. operates six large open pit coal mines in southeastern British Columbia and Alberta. The coal seams were deposited mainly in freshwater environments and are hosted by sandstones, siltstones and mudstones containing carbonate minerals and low concentrations of pyrite. Streams receiving basic pH drainage from the waste rock dumps at these mines are commonly observed to have calcite deposits, which in some cases have significantly altered stream bed and channel morphology.

Ongoing investigations, begun in 2009, have evaluated the origin, deposition and management options for the calcite deposits. Internal monitoring of waste dumps has shown elevated CO₂ concentrations which are probably the result of carbonate mineral dissolution by sulphuric acid produced by pyrite oxidation. Off-gassing of CO₂ from drainage waters causes pH to increase and calcite to deposit. The extent of calcite deposits appears to be limited by dilution and kinetic factors. The deposits will form on any natural or artificial substrate. Management options are largely focusing on measures to accelerate precipitation (by adding energy or increasing pH) or remove alkalinity by pH depression.

Key Words: Calcite, precipitation, carbon dioxide, waste rock.

Introduction

Mining of bituminous-grade coals has occurred within the Elk River watershed of southeastern British Columbia and within the McLeod River watershed of west central Alberta, Canada since the late nineteenth century. Early extraction occurred via underground mines; during the 1960s, open pit mining of coal began and has continued to the present day.

Teck Resources Ltd. owns and operates six open pit mines in these regions (Figure 1; Table 1). Each of the mines has waste facilities that include coarse and fine process residues as well as waste rock disposal facilities. A feature common to all six mines is at least one waste rock dump that has been constructed as a valley fill and that incorporates a rock drain to allow drainage of water that falls on the upgradient catchment. Each mine also has waste dumps that have been constructed by backfilling mined-out pits, and some of these also have considerable waste volumes located above the original pit rim elevation.

Calcium carbonate (calcite) precipitates have been observed in all streams that originate as discharge from waste dump rock drains (Hlushak 2011), and in the case of a number of streams, calcite precipitation has resulted in cementation of stream beds and changes in channel morphology. These physical changes to morphology and to the nature of the stream channel substrate have raised concerns about effects on fish and fish habitat, and these concerns have led to a series of multi-year investigations into the nature and causes of the calcite deposits.

Conceptualization of Calcite Release and Leaching

Introduction

The following paragraphs describe the current conceptual model for the leaching of carbonate from waste rock and the deposition of carbonate in receiving environment streams developed from first principles of mine waste weathering and carbonate equilibria. This model has formed the basis for subsequent field

investigations.

Table 1. Nomenclature of Teck Resources' Coal Mines

Mine	Abbreviation	Start of Operations
Coal Mountain Operations	CMO	1985
Elkview Operations	EVO	1969
Line Creek Operations	LCO	1982
Greenhills Operations	GHO	1982
Fording River Operations	FRO	1972
Cardinal River Operations	CRO	1969

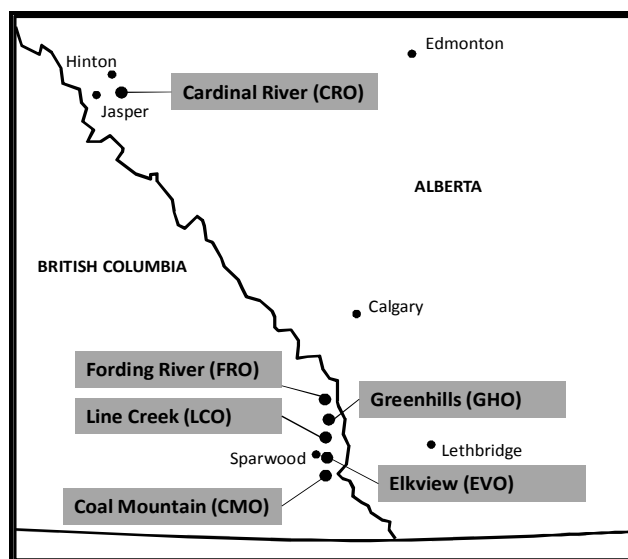
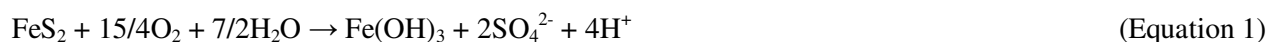


Figure 1. Location of Teck Resources' Coal Mines in BC and AB.

Sulfide oxidation and neutralization by carbonates

Carbonate minerals in waste rock are dissolved both through contact with pore water and through neutralization of acid produced by the oxidation of sulfide minerals within the waste rock. The following equations summarize this process, using the example case of pyrite (FeS_2) and dolomite ($\text{MgCa}(\text{CO}_3)_2$) to represent sulfide and carbonate minerals, respectively:



Within a carbonate-rich waste dump, the end result of sulfide oxidation is pore water in equilibrium with respect to both pore gas and carbonate minerals within the waste rock.

Waste rock pore gas

Pore gas composition in large waste rock dumps can be quite different from that of ambient air. If exchange between pore gas and ambient air is limited, pore gas oxygen can be depleted by sulfide oxidation (Equation 1) and CO_2 produced (Equation 4) when carbonate minerals react with sulfuric acid

can accumulate.

Transport

A portion of incident precipitation infiltrates into the waste rock and moves via unsaturated flow paths to the rock drain. In addition, surface water from upgradient catchment areas enters rock drains. Both precipitation and catchment runoff equilibrate with both carbonate minerals in the waste rock, and with the waste rock pore gas that contains elevated $p\text{CO}_2$ (as described by Henry's Law). The dissolved constituents are then transported out of the waste dump via gravity flow of water through the rock drain.

Gas exchange and disequilibrium

Water emerging from a rock drain is predicted to be oversaturated with CO_2 relative to the ambient atmosphere. CO_2 is transferred from the water to the ambient air via diffusion across the water-air interface (again, per Henry's Law). Diffusion is driven by the difference in $p\text{CO}_2$ on either side of the interface (i.e. the diffusive gradient) and is enhanced by both turbulent mixing within the stream (which maintains $p\text{CO}_2$ near the interface close to levels found in the bulk fluid) and by stream channel morphologies (such as riffles and cascades) that result in higher surface area of the water-air interface. Within a stream, $p\text{CO}_2$ decreases with distance downstream due to diffusive loss to the atmosphere. This causes the rate of gas exchange to decrease downstream, as the diffusive gradient decreases.

Downstream equilibration

As CO_2 is lost from stream waters, stream pH rises (equations 3 and 4). This increase in pH causes oversaturation of stream water with respect to calcite. Once a critical degree of oversaturation is reached, calcite precipitation is initiated. With increasing distance downstream, $p\text{CO}_2$ in stream water progresses towards equilibrium with the atmosphere, and calcium and alkalinity concentrations decrease due to precipitation of calcite. Stream water approaches an equilibrium condition with respect to calcite and the rate of calcite precipitation decreases. In cases where sufficient length of stream is available, gas equilibrium is achieved, pH conditions stabilize, and calcium and alkalinity concentrations decline to levels corresponding to a critical degree of oversaturation with respect to calcite (discussed further below).

Role of dilution

Streams draining undisturbed catchments are expected to be near saturation or oversaturated with respect to calcite if regional geological formations are calcareous. In many cases, streams originating from rock drains join larger regional streams prior to achieving a stable state with respect to $p\text{CO}_2$ and calcite saturation index (SI). In general, $p\text{CO}_2$ and SI of the combined flows will be lower than in rock drain effluent alone and the rate of gas exchange is reduced. As a result, calcite precipitates are expected to be limited or absent downstream of a confluence of rock drain discharge with a higher order stream.

Kinetic factors

An important factor that likely plays a role in extending the length of stream that experiences active precipitation is the kinetically slow transformation from bicarbonate to carbonic acid (Equations 3 and 4). This is reported to be a rate-limiting step in the calcite precipitation process (Zaihua and Dreybrodt 1997). For the case of flowing stream water, any factor that slows the transformations between inorganic carbon species will necessarily cause precipitation to occur

over a longer stream length. Another kinetic factor relates to the degree of oversaturation required to induce precipitation. In theory, calcite precipitation should occur when the SI exceeds zero. However, calcite oversaturation in natural streams is commonly reported in the literature (Zaihua *et al.*, 1995) and is not necessarily accompanied by calcite precipitates.

As previously noted, rates of water-air gas exchange also affect precipitation kinetics.

Alternative hypothesis: biological processes

Removal of dissolved CO₂ from stream water by aquatic plants and algae through photosynthesis has been identified as an alternative explanation for the observed calcite precipitation phenomenon (Hydroqual 2009), due to the accompanying increase in pH of stream water (Equations 3 and 4).

Background

Geological setting

Coals in the Elk River watershed are hosted by the Jurassic-Cretaceous Kootenay Group and primarily the Mist Mountain Formation, which is composed of inter-stratified dominantly non-marine siltstone, sandstone, mudstone, shale and thin to thick seams of low to high-volatile bituminous coal to semianthracite (Gibson 1985). This formation is underlain by the Morrissey Formation, which is composed mainly of massive sandstone which gets coarser upward. It contains rare interbeds of carbonaceous mudstone, siltstone and coal and is conglomeratic in places. Gibson (1985) described pyrite as occurring in low concentrations and carbonates at higher (percent) levels. The main carbonate mineral was noted to be dolomite, followed by calcite and siderite. The Mist Mountain Formation is overlain by the Elk Formation, which is a cliff-forming sequence of interbedded sandstone, siltstone, mudstone, shale conglomerate and thin coal seams. Sandstone is the main rock type. Like the Mist Mountain Formation, it is interpreted to have been deposited in a largely non-marine fluvial and deltaic environment. Due to the largely non-marine character of the coal-bearing strata, sulphur content of the rocks is generally low.

Coal in the CRO area is found in lower Cretaceous deposits. The Grande Cache Member contains the economic coal at its base and consists of sandstone, mudstones and other minor coal seams. This unit is non-marine in origin. Immediately below the Jewel Seam lies the Torrens Sandstone that consists of 30 m of bedded to massive sandstone of non-marine origin. Below the Torrens is the Moosebar Shale which is dominantly a marine shale up to 90 m thick and which becomes sandier in its upper portions.

Physical setting

All six mines are located in mountainous terrain. The mines in the Elk River (BC) watershed are drained by numerous moderate to high energy lower order streams that report either to major tributaries of the Elk River (Fording River and Michel Creek) or directly to the Elk River itself. In the McLeod River (AB) watershed, lower order streams draining the mining areas enter the McLeod River directly, with Luscar Creek being the largest mining-affected tributary.

Stream morphology typically ranges from cascade sections with coarse rock substrate to pool-and-riffle sections with finer gravel and sand substrate. In-stream moss, woody debris and organic detritus are common. Stream banks are typically vegetated with grasses, shrubs and trees.

Climate and hydrology

The climate at Sparwood, BC (elev. 1138 m above sea level, Figure 1) is characterized by average annual temperatures of 4.3° C with a monthly average daily range of -7.7°C (December) to 15.4°C (July) (Env. Canada 2011). Total precipitation averages 603 mm and about two-thirds of precipitation falls as rain. Stream flows in the Sparwood area are dominated by peak flows resulting from snowmelt in May.

The climate at Jasper, AB (elevation 1020 m above sea level, Figure 1) is characterized by average annual temperatures of 3.3° C with a monthly average daily range of -9.8°C (January) to 15°C (July)

(Env.Canada 2011). Total precipitation averages 399 mm and about three-quarters of precipitation falls as rain. Stream flows in the CRO area peak during May and June as a result of snowmelt.

Mining method

Mining occurs at all six mines by conventional drill-and-blast and truck-and-shovel methods. Raw coals are hauled and conveyed to processing plants located at lower elevations near each mining operation. Oversize process waste (referred to as coarse coal rejects, or CCR) is typically disposed in dedicated dumps located adjacent to the plants, and fine process wastes (tailings) are deposited in impoundments. Waste rock disposal occurs dominantly in external dumps with tipping faces varying from tens to hundreds of metres in height; these dumps are often placed as valley fills, with catchment drainage being maintained through the construction of basal drains made of coarse waste rock. Backfilling into exhausted sections of pits occurs at some locations. Historically, co-disposal of waste rock and CCR has taken place at some mines.

Methods

Field observations

Beginning in 2008, several rounds of regional scale field assessment were undertaken to determine the status of calcite deposition in both reference and mining-influenced streams in the Elk River watershed. Assessments were carried out in October 2008, July and October 2009, and July and October 2010. Field assessment methods consisted of establishing permanent monitoring stations that were representative of calcite deposition over a reach of stream bed; physical assessment of stream substrate at each monitoring station (including recording the degree of coverage of calcite precipitate, the dominant morphology of calcite precipitates, and the degree of cementation of the stream bed materials); and water quality monitoring. For each station and each monitoring round, the results of the physical assessment were aggregated in a Calcite Deposition Index (CDI) as described in Table 2 (Hlushak 2011). The regional scale field assessment has evolved to consist of monitoring at 57 stations within the Elk River watershed, 14 of which are reference stations (Hlushak 2011).

In addition to the regional scale field assessments, synoptic monitoring has been carried out at selected streams in an effort to understand what geochemical processes may be influencing the rate of calcite deposition and the related lateral extent of observed calcite precipitates downstream of discharge from emergence from mine wastes. Synoptic studies were carried out at Swift Creek (GHO- three rounds of monitoring) and Luscar Creek (CRO- one round of monitoring) and consisted of downstream traverses from the stream source to the confluence with a higher order stream. Monitoring stations along each traverse were situated to allow the effects of both stream length and physical features such as small inflows or significant cascades to be accounted for. Water quality monitoring was carried out at each station.

Field methods

Gas and thermal monitoring

In situ gas and temperature monitoring apparatus were installed in three boreholes at West Line Creek Dump at LCO in 2009 as part of a separate study to evaluate selenium release from waste rock (Kennedy *et al.*, 2012). The monitoring apparatuses were installed to depths up to approximately 100 m, or about half the total dump thickness. Quarterly monitoring was carried out using a hand-held gas analyzer with an integrated pump with manual recording of CO₂ and oxygen concentrations, and using an ohmmeter to measure resistance across thermistor beads.

Water quality

Water quality monitoring included field measurements of pH, temperature, conductivity, and oxidation-reduction potential, and collection of water samples for laboratory analysis of general parameters, anions, and dissolved elements by ICP methods.

Interpretation methods

Water quality monitoring results were modeled with PHREEQC (Parkhurst and Appelo, 1999) using field pH, field temperature, and selected analytical results (concentrations of alkalinity and dissolved major ion concentrations) to calculate the saturation index (SI) of calcite (Equation 5) for individual samples.

$$SI = \log (IAP/K_{sp}) \quad \text{(Equation 5)}$$

IAP is the calcite ion activity product for the solution and K_{sp} is the solubility product for calcite ($[Ca^{2+}][CO_3^{2-}] \approx 3.7 \times 10^{-9}$, at 25°C).

Table 2. Description of Calcite Deposition Index (modified from Hlushak 2011)

Calcite Deposition Index Value	Description
None	No deposition or accumulation of calcite observed within the stream channel or in, on, or below substrate at the site.
Trace	Evidence of calcite deposition within wetted width or channel margin. Calcite deposits generally only found on cobbles/boulders, and the majority of the substrate shows no evidence of calcite.
Low	Calcite deposition found within wetted width or channel margin with little effort. Hardened calcite deposits observed to be bonded to boulders, cobbles, or aquatic vegetation.
Moderate	Calcite deposition is evident across wetted portion of stream bed. Stream bed is generally partially concreted, meaning substrate is bonded together and very difficult to separate individual substrate particles.
High	An advanced state of calcite deposition present within the stream channel both within the wetted area and full bank channel width. Stream bed is often fully cemented with little to no potential for erosion or sediment transport. Rimstone dam formations and associated calcite laminate stream beds may have widened the natural full-bank channel width.

Results

Gas and thermal monitoring

Figure 2 displays results of 2008 through 2010 oxygen, CO₂ and temperature monitoring in borehole LC-3 (the deepest installation at LCO, located well away from the dump margins). In general, oxygen and CO₂ concentrations are inversely correlated, suggesting that when gas exchange with the atmosphere is limited, oxygen is depleted through oxidation reactions and CO₂ (which is produced through neutralization of acid by carbonates) accumulates. Variation in the gas profiles both with depth and over time indicate that there are likely both material controls (e.g. variations in air permeability due to grain size) and seasonal controls on gas exchange; the consistent temperature profile over time indicates that the seasonal controls on gas exchange occur at the dump scale and are not directly reflected in the thermal profile at borehole LC-3. CO₂ concentrations of up to 15% in the pore gas have been recorded. The other two instrumented boreholes also showed CO₂ concentrations of several percent at depth, similar thermal profiles to borehole LC-3, and broadly similar inverse correlation between oxygen and CO₂ concentration.

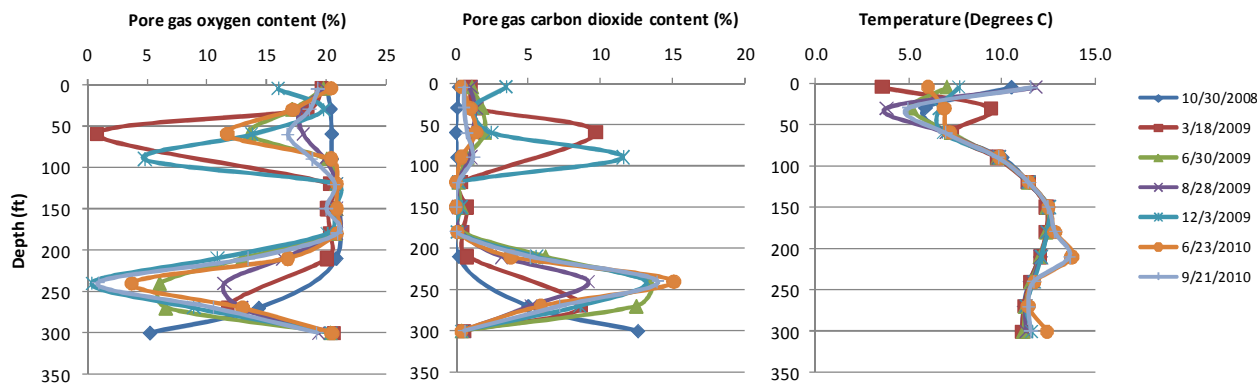


Figure 2. Thermal and gas monitoring results from borehole LC-3 (LCO). Note: depth in units of feet.

Regional Observations

Reference (background) streams

Monitoring of reference streams within the Elk River watershed has shown that calcite is either absent or occurs as rare nodules or coatings on individual cobbles and boulders (Hlushak 2011). Where present, all calcite precipitates observed at reference stations were associated with algae (periphyton). All reference monitoring stations had CDI values (Table 2) of either 'None' or 'Trace'. In the case of three individual reference stations, the CDI value changed from 'None' to 'Trace' over the 2008 through 2010 monitoring period; the remaining 11 reference stations had consistent CDI values across all monitoring rounds (Hlushak 2011).

Water quality analyses of reference stream waters has shown most reference streams are oversaturated with respect to calcite over the monitoring (open water) season. Typical calcite SI values at reference stations ranged from 0.3 to 0.7, whereas water in thermodynamic equilibrium with calcite would have an SI value of 0.0.

Mine-influenced streams

Calcite precipitates were observed in all streams draining waste dumps in both the Elk River (BC) and McLeod River (AB) watersheds, although individual stations in some streams were observed to have no calcite precipitates. Of note, calcite was rarely observed at stream origins at the discharge of rock drains. In a given stream, the first calcite precipitates were commonly observed to begin about 50 to 100 m downstream of discharge locations, and to occur downstream over stream lengths up to several kilometers (or apparently until a substantial volume of diluting water was added to stream flow).

Precipitate morphology, thickness and degree of bonding (cementation) varied both along individual streams and across the mine-influenced streams investigated. CDI values (Table 2) at mine-influenced ranged from 'None' to 'High', with 'High' values occurring (within a single exception) at stations located within 1 km of a rock drain. The seven stations located along the main stems of major regional drainages downstream of mine-influenced tributaries (Fording River, Elk River, and Michel Creek) had CDI values of 'None' and 'Trace'.

Case study #1: Swift Creek

Introduction

Swift Creek was selected for detailed synoptic study because it displayed a range of CDI values ('None' to 'High') over its length; it offered sufficient stream length to observed spatial variations along the stream; and the waste dump in the headwaters was inactive and safe access to the Swift Creek rock drain was possible. Eight monitoring stations were established over a channel length of approximately 1.5 km in June 2010, and were monitored again in August and November 2010. Groundwater seepage was identified at two locations during the initial survey and these locations were monitored in both June and November 2010. Figure 3 shows the layout of the Swift Creek study area.

Drain water chemistry

Swift Creek originates as discharge from a rock drain at station SWC1 (Figure 3); no calcite precipitates were observed at this location. Table 3 summarizes selected water chemistry data for the synoptic monitoring period.

Temperature of the rock drain discharge was nearly constant during the three monitoring rounds. Field pH was slightly lower in June. Concentrations of dissolved calcium and total alkalinity were lowest in June and highest in November, which is thought to reflect dilution due to higher infiltration rates during June and lower infiltration rates later in the year.

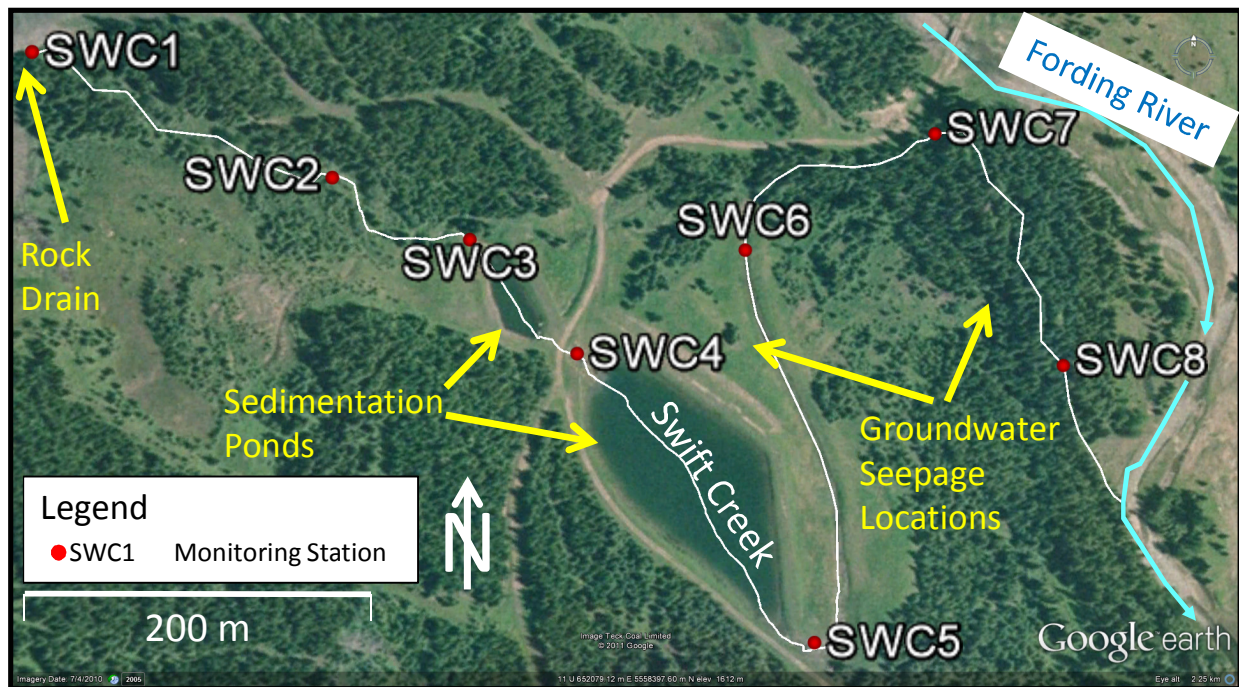


Figure 3. Layout of Swift Creek (GHO) study area

Synoptic observations

Selected June, August and November 2010 monitoring results are plotted against distance from the Swift Creek rock drain in Figure 4 and Figure 5. In all three monitoring rounds, field pH increased with distance over the first few hundred metres to approximately pH 8.3 (Figure 4), suggesting initial rapid gas exchange between CO₂-oversaturated rock drain discharge and the atmosphere. In June, field pH values continued to increase slowly with distance downstream, while field pH values stabilized downstream in August and November. Temperature increased with distance downstream during June and August monitoring, and showed minimal change from initial temperatures over the flow path in November. Calcium and alkalinity concentrations remained roughly constant with distance downstream during June (when concentrations were lowest), but decreased with distance downstream during both August and November (Figure 5). The most dramatic decreases occurred in August, when warm water temperatures and high initial concentrations of calcium and alkalinity would have been most favourable for calcite precipitation.

Table 3. Swift Creek rock drain (SWC1): selected water chemistry

Date	Field pH	Field Temp.	Calcium (dissolved)	Magnesium (dissolved)	Sodium (dissolved)	Alkalinity (Total)	Sulphate
		°C	mg/L	mg/L	mg/L	mg CaCO ₃ equiv./L	mg/L
June 4, 2010	7.9	2.2	218	129	<2	258	693
Aug. 11, 2010	8.1	2.5	332	195	<2	346	1140
Nov. 6, 2010	8.1	2.2	375	234	<2	368	1410

Saturation index

Equilibrium modelling using PHREEQC showed that all samples were oversaturated with respect to calcite ($SI > 0$); that SI values increase over the initial few hundred metres during all three monitoring rounds (most likely due to rapid exsolution of CO_2); and that there was a threshold SI value of around 1.2 to 1.3 that was not exceeded (Figure 6). The results suggest that a point is reached where precipitation rates are balanced with the tendency for CO_2 exchange to increase SI. It is likely that maximum precipitation rates corresponded to periods when the SI was near this threshold and when water temperatures were highest. Figure 6 also shows calculated partial pressure of CO_2 for each sample, and it is clear that rapid gas exchange takes place in the uppermost reaches of the stream immediately following emergence of water from the rock drain.

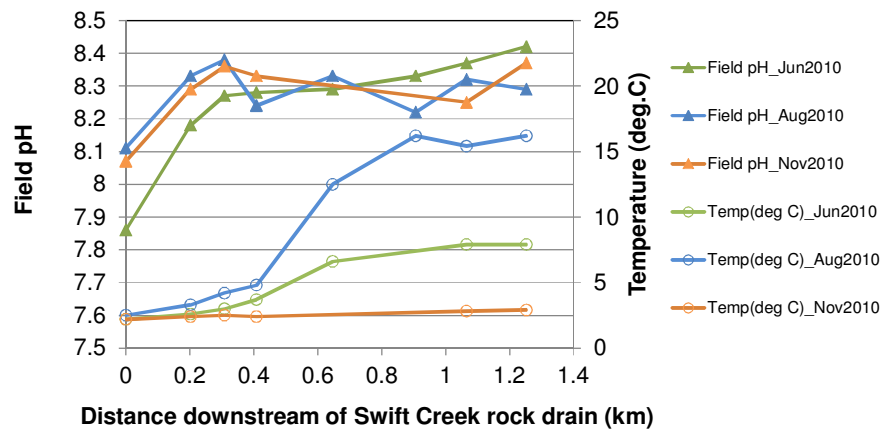


Figure 4. Swift Creek: synoptic results for temperature and field pH

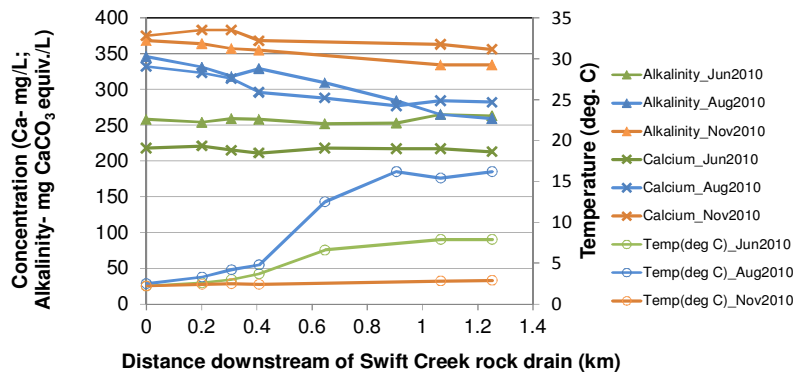


Figure 5. Swift Creek: synoptic results for temperature, calcium and alkalinity concentrations

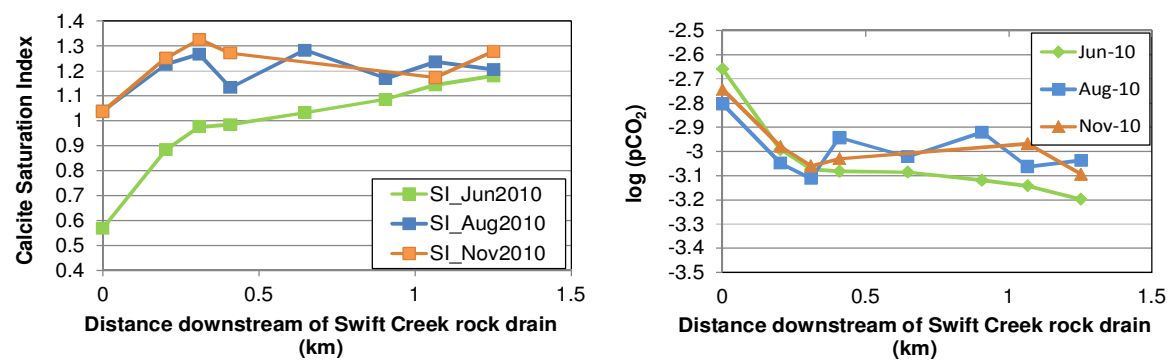


Figure 6. Calcite Saturation Index results and calculated pCO₂ for Swift Creek samples (2010)

Case study #2: Luscar Creek

Introduction

Luscar Creek (CRO- McLeod River watershed) was selected for study for comparison with studies in the Elk River watershed because significant calcite deposits were reported by site staff and also the creek discharges from the toe of a waste pile located partially in a backfilled open pit. Figure 7 shows the locations of the Luscar Creek monitoring stations and selected mine components that are relevant to the discussion.

Below the waste dump discharge point, Luscar Creek water flows through a short (<100 m) length of ditch into Luscar Pond (a sedimentation pond), then discharges from a culvert to the natural Luscar Creek streambed via a 1.5 m cascade. No calcite was observed upstream of Luscar Pond, however calcite was noted to be abundant below the Luscar Pond outfall. Below Luscar Pond, Luscar Creek flows over 6 km before joining the McLeod River; several tributary streams enter Luscar Creek, the largest of which is another mine-impacted creek (Jarvis Creek) which enters Luscar Creek below station LCr-03. A total of nine stations were sampled between Luscar Pond and McLeod River on August 19, 2010.

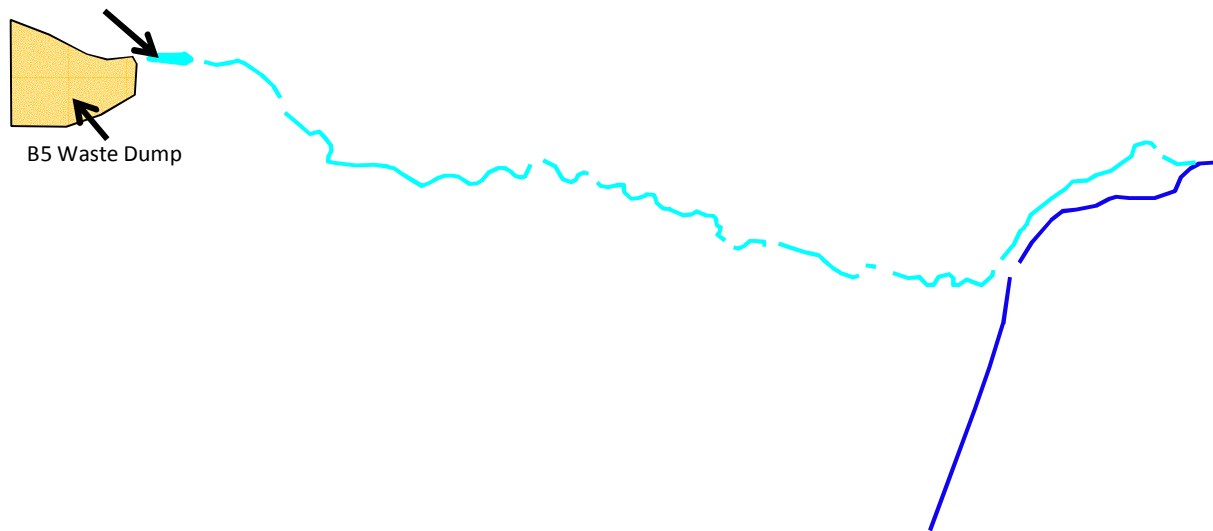


Figure 7. Layout of Luscar Creek (CRO) study area

Drain water chemistry

In contrast to the calcium-magnesium dominated waters downgradient of Teck's mines in southeast BC, the waters downgradient of mine wastes in Luscar Creek at CRO are typified by low calcium and magnesium concentrations, high sodium concentrations, and high alkalinity (Table 4).

Table 4. Luscar Creek rock drain (LCR1): selected water chemistry

Date	Field pH	Field Temp.	Calcium (dissolved)	Magnesium (dissolved)	Sodium (dissolved)	Alkalinity (Total)	Sulphate
		°C	mg/L	mg/L	mg/L	mg CaCO ₃	mg/L

						equiv./L	
Aug. 11, 2010	8.1	9.6	49	19	340	610	324

Synoptic observations

During the sampling and inspection activities, calcite was observed to have formed on a wide range of substrate types, including inorganic stream substrates (e.g. boulders, cobbles, gravel, sand), organic stream substrates (e.g. algal streamers and mats, aquatic plants, leaf litter, fallen branches and sticks), and debris that included dimension lumber, pieces of Styrofoam, and polyethylene (plastic film)). These observations are noteworthy, as the role of substrate in calcite deposition is debated.

Total alkalinity decreased with distance down Luscar Creek (Figure 8), with the greatest decrease occurring about 2.2 km below Luscar Pond, between stations LCr-03 and LCr-04. This dramatic decrease reflects the addition of water from Jarvis Creek, which had an alkalinity concentration of roughly half that measured at LCr-03 (Jarvis Creek data not shown). Sulphate and sodium concentrations showed a similar pattern of decreasing downstream.

Calcium concentrations do not show the same decreasing trend down the creek. Calcium concentrations increase slightly below the mouth of Jarvis Creek (due to the higher concentration in Jarvis Creek water), and then increase slightly again below station LCr-07 (km 4.2 in Figure 8). The cause of the slight increase below LCr-07 is not known, but may be related to other higher calcium sources entering Luscar Creek in the low-gradient broad marshy reach between LCr-07 and LCr-08.

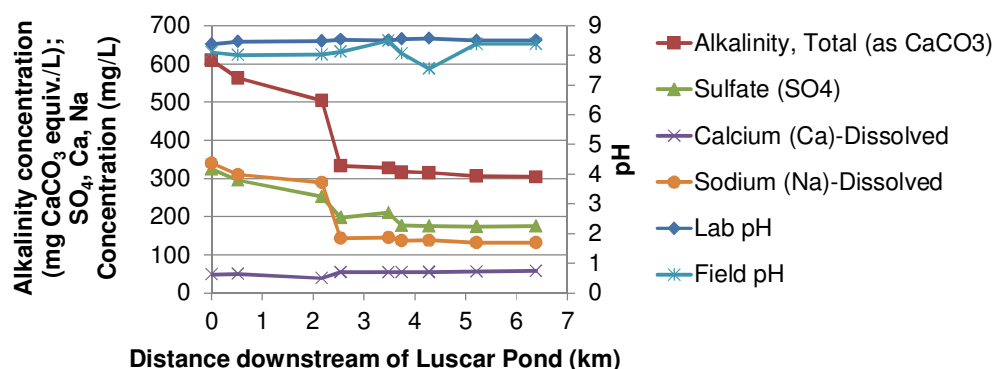


Figure 8. Selected results from synoptic monitoring, Luscar Creek, August 2010

Conclusions

Calcite precipitates are forming in the channels of streams draining waste dumps at Teck Resources' coal mines. Conditions that favour calcite deposition appear to result from the accumulation of CO₂ within the waste dump void space, the equilibration of pore water with the elevated CO₂ concentrations, followed by the discharge of waste dump porewater to streams. Under ambient atmospheric CO₂ conditions, the stream water is oversaturated with CO₂ and CO₂ exsolves from the stream water. CO₂ exsolution results in an increase in stream pH and a corresponding increase in the calcite saturation index. Calcite precipitation within the stream channel is initiated once an adequate degree of oversaturation is achieved. Exsolution of CO₂ (and increase in stream pH) continues until stream water CO₂ is equilibrated with the atmospheric CO₂ concentration.

Kinetic factors prevent calcite precipitation from proceeding to completion near discharge locations. The rate of CO₂ exsolution is diffusion limited, and is a function of surface area of the air-water interface. Transformation of inorganic carbon from bicarbonate to CO₂ is kinetically limiting as CO₂ exsolution proceeds towards an equilibrium condition. The occurrence of equi-molar concentrations of calcium and magnesium is also thought to increase the degree of oversaturation required to initiate calcite precipitation.

The combined result of all kinetic limitations to calcite precipitation and the downstream movement of water is that calcite precipitation commonly occurs over stream channel lengths extending over hundreds , even thousands of metres in the downstream direction.

Simple inorganic processes are sufficient to explain observed calcite precipitation. However, a biotic influence on formation of calcite precipitates has not been ruled out, and biotic processes may be important where the degree of calcite oversaturation is moderate.

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Acronyms

CO₂ carbon dioxide

pCO₂ partial pressure of carbon dioxide