Geochemical Characteristics of Oil Sand Tailings and Bitumen Upgrading By-Products, Alberta, Canada

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ABSTRACT

Few studies have characterized the metal leaching and acid rock drainage (ML/ARD) potential of tailings from oil sand production, and associated by-products from bitumen upgrading. In order to address this gap, Suncor Energy Inc. undertook sampling to characterize their various tailings and by-products using ML/ARD characterization methodologies typically applied to coal and metal mine wastes. Tailings types characterized were mature fine tailings (MFT), dried mature fine tailings (DMFT), and froth treatment tailings (FTT). Bitumen upgrading by-products characterized were coke and coke ash. Methods used included conventional acid-base accounting, net acid generation testing, X-ray diffraction, and humidity-cell testing.

The characteristics of MFT, DMFT, and FTT reflected the mineralogy of the McMurray Formation, which includes pyrite, siderite, ankerite, and various clay minerals. In contrast, the characteristics of coke are carried over from the bitumen though pyrite is not destroyed because cokers operate under reducing conditions. Coke ash is mostly composed of amorphous aluminosilicate melts, and contains readily leachable concentrations of nickel and vanadium. The application of standard ML/ARD characterization methods to oil sands is complicated by the presence of residual bitumen, which makes tailings hydrophobic and rich in organic carbon.

Keywords: oil sands, metal leaching, acid rock drainage

INTRODUCTION

Tailings management remains one of the most difficult environmental challenges for the oil sands mining sector with over 77 square kilometers of oil sands tailings ponds in Alberta (Alberta Government, 2013). Government regulations introduced in 2009 (Directive 074) require operators to dewater the tailings ponds for reclamation purposes, and to reuse the water for production. In response, recent studies have focused on developing methods to reduce water within the ponds (COSIA, 2014a; Wang *et al.*, 2014). Few studies have characterized the metal leaching and acid rock drainage (ML/ARD) potential of tailings from oil sand production, and associated by-products from bitumen upgrading, or assessed the ML/ARD implications of dewatering the saturated tailings (Kuznetsov *et al*., 2015). Furthermore, guidance on addressing ML/ARD potential is not available within best practice guidelines for oil sands tailings management (COSIA, 2012 and 2014b). In order to address this gap, Suncor undertook sampling to characterize the ML/ARD potential of their various tailings and bitumen upgrading by-products using existing methodologies typically applied to coal and metal mine wastes.

Suncor extracts bitumen from oil sands in the Lower Cretaceous McMurray Formation of northern Alberta, Canada, which are mainly deposits of fine-grained quartzitic bituminous sands and sandstones (Flach, 1984). Bitumen is extracted from crushed oil sand ore through a process of gravity separation and flotation. The process yields bitumen, bitumen froth, fluid tailings, and coarse sand tailings. The bitumen froth contains some fine minerals and oleophilic heavy minerals (including pyrite), and is mixed with naphtha to allow further separation of bitumen from residual water and minerals in centrifuges and inclined plate settlers. The residual water and minerals in the froth stream constitute the bulk of *froth treatment tailings* (FTT). FTT is a small percentage of the tailings produced during bitumen extraction and is handled separately from the rest of the tailings stream. Fluid tailings from the primary flotation circuit are further processed in secondary flotation circuits to remove residual bitumen. Fine tailings from the flotation circuits are combined with coarse sand tailings, and transported to a sand placement area where the sand fraction deposits along shallow slopes, and the fines are transferred to a pond where they settle to form *mature fine tailings* (MFT). After a few years, MFT settles to a solids content of approximately 30 to 40 wt%. MFT are later removed from the pond, mixed with polymer and placed in thin lifts in a dedicated disposal area where they are dewatered and dried to become *dried MFT* (DMFT).

Extracted bitumen is upgraded to lighter hydrocarbon products through a process of reductive coking at approximately 450 °C. The resulting *coke* is disposed in coke pits, or utilized for heat generation and reclamation purposes. Combusted coke results in *coke ash,* which is transported to storage ponds as slurry. The ash is composed of approximately 20 % bottom and mid-ash and 80 % fly ash.

This paper details the geochemical characterization of the oil sand tailings (MFT, DMFT, and FTT) and bitumen upgrading by-products (coke and coke ash), discusses the application of standard ML/ARD characterization methodologies, and highlights some of the methodological limitations for practitioners to consider when interpreting the results.

METHODOLOGY

Sample Collection

Suncor collected 57 MFT, 12 DMFT, five FTT, eight coke, and three coke ash samples for geochemical and mineralogical analysis. MFT samples were collected from three depths at various pond locations using a suction dredge. DMFT samples were collected as grab samples directly from dedicated disposal areas. Two FTT samples were collected from the tailings line prior to discharge, and three were collected as deposited samples from 3, 5, and 20 m below the pond water line in order to capture any compositional differences as a result of tailings deposition. Coke was collected monthly as grab samples across an eight-month period. Coke ash sampling consisted of a bottom ash, fly ash, and a combined coke ash grab sample collected from an ash storage pond.

Sample Preparation and Analysis

Samples were prepared and analyzed by Maxxam Analytics in Calgary, Alberta, and Vancouver, British Columbia. Coke and coke ash samples were air-dried prior to analysis. Each tailings sample was split into two subsamples, with one fraction air-dried to remove the bulk of the water and volatile hydrocarbons, and the second fraction taken as-received for Dean Stark extraction to determine the bitumen, mineral, and water contents (Dean and Stark, 1920). The method uses hot toluene to extract hydrocarbons.

The air-dried coke and coke ash, and toluene-treated tailings were analyzed for major elements by X-ray fluorescence (XRF) spectroscopy, minor elements by four-acid digestion and inductively coupled plasma mass spectrometry (ICP-MS), and particle size by dry and wet sieving methods.

Acid-base accounting (ABA) was undertaken on coke, coke ash, and air-dried tailings. This included total sulfur (Leco), sulfur speciation (ASTM D2492-02), total carbon (Leco), total organic carbon (TOC) (Leco analysis on residue of hydrochloric acid leach), total inorganic carbon (TIC) (by difference), paste pH and electrical conductivity, and neutralization potential (Sobek *et al.*, 1978) with siderite correction (Skousen 1997).

Net acid generation (NAG) testing (EGi 2006) was undertaken on air-dried and toluene-treated tailings. The toluene-treated tailings were hydrophobic. Therefore, when the NAG reagents were first added to the samples, they were dispersed in an ultrasonic bath until streaming birefringence was observed signifying complete dispersion.

Humidity-cell tests (Price 2009) were undertaken on coke, coke ash, and air-dried tailings for a minimum duration of 20 weeks, with leachates analyzed for pH, conductivity, sulfate, acidity, alkalinity, hardness, and trace elements by ICP-MS.

Mineralogy by X-ray diffraction (XRD), with quantification by Rietveld Refinement was undertaken by the University of British Columbia on the toluene-treated tailings. Selected FTT, coke, and coke ash samples were analyzed by Laue X-ray diffraction (μ-XRD) by the Canadian Light Source Inc. at the University of Saskatchewan.

Quality Assurance

No quality issues were identified in the final data on the basis of satisfactory certified reference material recoveries, laboratory duplicates, and ion balances for leachate analyses. Analytical and data interpretation issues encountered as a result of sample hydrophobicity and organic matter content are discussed within the results.

RESULTS

Mineralogy

In MFT, DMFT, and FTT, major minerals (those greater than 10 wt%) were quartz, kaolinite, and mica. Minor minerals (1 to 10 wt%) were microcline, clinochlore, and albite. Trace minerals (those less than 1 wt%) were pyrite, siderite, calcite, ankerite, various titanium oxides, zircon, and tourmaline.

Coke was composed of refractory organic matter with no crystalline phases detected by μ-XRD. Coke ash was mostly composed of an amorphous aluminosilicate melt (69 % for bottom ash, 91 % for fly ash, 93% for combined coke ash) with crystalline phases consisting of silica (quartz and cristobalite), aluminosilicate (mullite), feldspars (microcline, and plagioclase), and titanium and aluminum oxides (pseudobrookite and hercynite, respectively). Gypsum and magnesite were also identified in the combined coke ash sample.

Acid Potential

The presence of pyrite in MFT, DMFT, and FTT indicated that it is likely to be the principal source of acidity. Total sulfur by Leco analysis was not a good measure of pyrite content due to significant sulfur concentrations being associated with the insoluble fraction (mostly organic) (Figure 1a). Sulfide determined by the ASTM D2492 method correlated well with mineralogical sulfide by XRD for DMFT and most MFT samples (Figure 1b), although the correlation was poor for FTT and three MFT samples that contained FTT. These samples were likely to have contained amorphous phases that resulted in an over-estimation of mineral sulfide by XRD due to normalization of reported mineral abundances to 100 %.

FTT had the highest sulfide content, ranging from 0.29 to 0.58 % as S. Elevated sulfide concentrations in MFT samples were associated with the presence of small amounts of FTT. Coke contained no detectable sulfide. Sulfur was inferred to be present as refractory carbonaceous matter. Coke ash contained the highest sulfate concentrations, which were present as gypsum on the basis of μ-XRD results. In fly ash, sulfate was likely to be present as iron and aluminum sulfates on the basis of contact water chemistry. Elemental sulfur was not detected but is expected based on the conditions under which the ash is formed.

Acid potential in the tailings is conventionally associated with oxidation of pyrite, whereas coke has negligible acid potential, and coke ash has acid potential associated with soluble acid sulfates and possibly elemental sulfur.

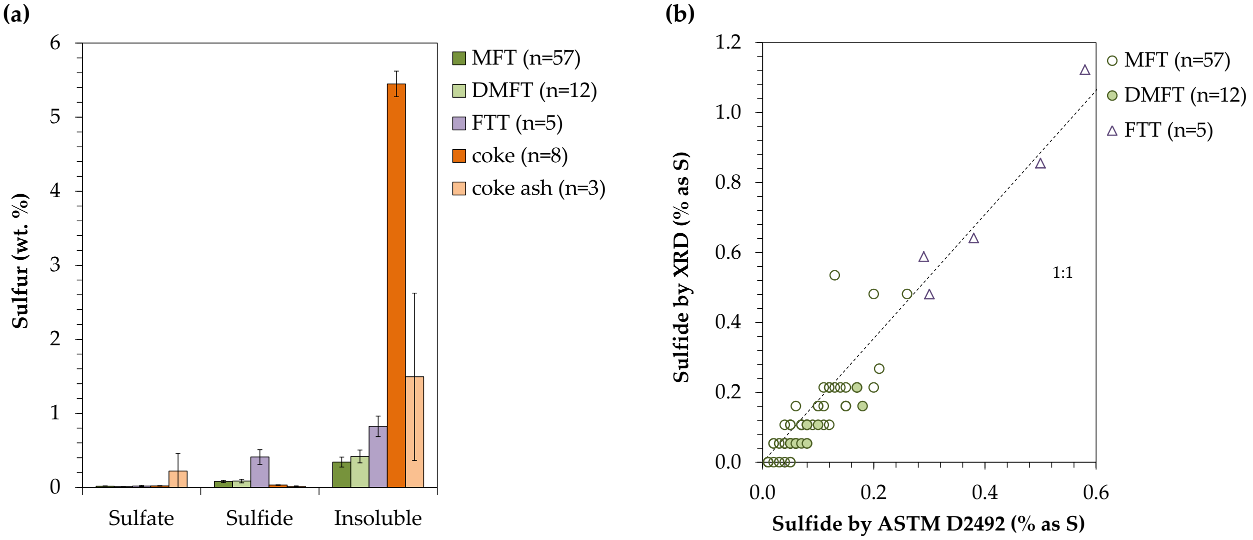

Figure 1 (a) Sulfur speciation (ASTM D2492) of oil sand tailings, coke, and coke ash presented as arithmetic average values with error bars indicating 95 % confidence intervals; and (b) comparison of sulfide concentrations in tailings as determined by ASTM D2492 and quantitative XRD

Acid Neutralization Potential

The form of neutralization potential in MFT, DMFT, and FTT was evaluated by comparing carbonate analyses, measured Sobek neutralization potentials (NPs), and carbonate neutralization potentials (CaNPs) calculated from quantitative XRD. Carbonate content was determined by difference between total carbon and residual carbon following hydrochloric acid leach. It was not correlated with carbonate content estimated from mineralogy (Figure 2a). This effect is likely attributable to the high organic carbon content and hydrophobic nature of the samples. The results of this procedure were not considered further.

XRD determinations of carbonate mineral content were used to calculate the neutralization potential associated with calcium and magnesium in calcite and ankerite (Day, 2009). Ankerite composition was assumed to be $CaFe(CO_3)_2$ for the purpose of the calculation. When compared to NP determined using the siderite-corrected method (Skousen, 1997), CaNP was correlated but generally lower (Figure 2b). Possible explanations are that the siderite-corrected NP included the influence of silicates, and that the peroxide treatment did not fully oxidize Fe^{2+} released by dissolution of siderite and ankerite. Carbonaceous matter in the samples may have competed for the hydrogen peroxide and also allowed redox to remain low. Due to these uncertainties, the mineralogical method was considered more reliable though it likely over-estimated bulk carbonate content as a result of amorphous phases in the samples.

Coke and coke ash samples had relatively low siderite-corrected NP (average 2.3 kg $CaCO_3$/t and -0.6 kg $CaCO_3$/t, respectively). Quantitative mineralogical data were not obtained. Due to the thermal process involved in converting coke to ash, carbonate minerals are not expected to be present except possibly as a result of carbonation by atmospheric CO_2 of calcium and magnesium oxides.

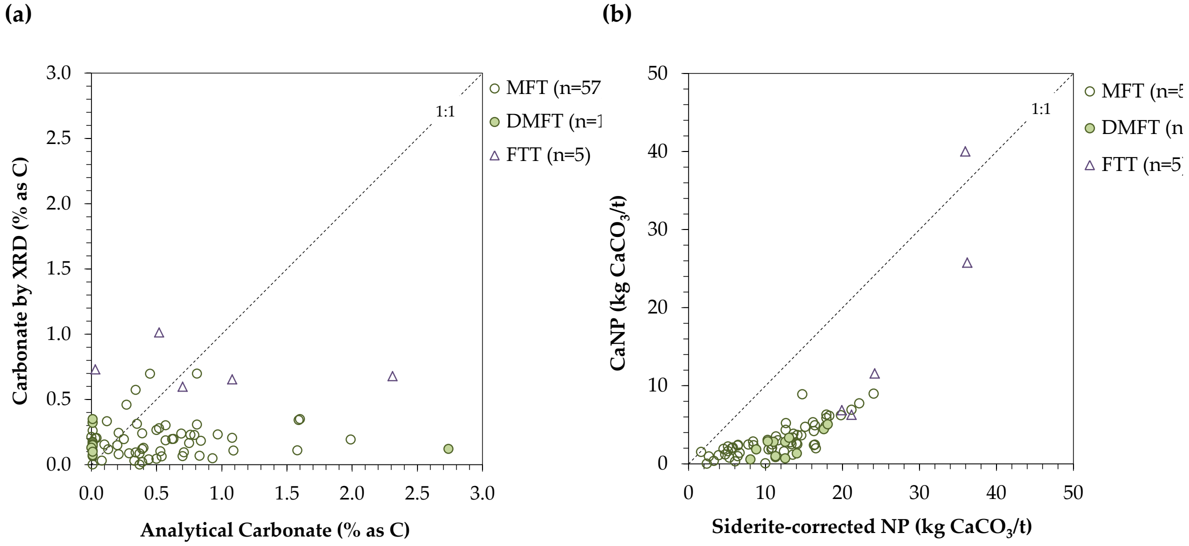

Figure 2 (a) Comparison of analytical carbonate determined as the difference between total carbon and total organic carbon, and carbonate by quantitative XRD; and (b) comparison of siderite-corrected NP and carbonate NP, whereby CaNP is calculated from calcium and magnesium-bearing carbonates

ARD Potential

ARD potential for tailings was assessed using CaNP/AP ratios. Potentially ARD-generating (PAG) tailings were defined by a CaNP/AP ratio of less than 1, whereas non-PAG tailings were defined by a CaNP/AP ratio greater than 2. CaNP/AP ratios between these limits were classified as uncertain. A value of 2 was considered to be appropriate because NP was based on Ca and Mg carbonate. Siderite-corrected NPs were not used due to their apparent tendency to over-estimate reactive carbonate NP as indicated by mineralogy. A second consideration for classification of ARD potential is that at very low sulfide content, the rate of acid generation is sufficiently slow that silicate minerals can play a role in consuming acid. For the purpose of this project, a sulfide concentration of 0.1% (acid potential 3.1 kg $CaCO_3$/t) was selected.

The majority of MFT and DMFT samples were classified as non-PAG on the basis of low sulfide content (Figure 3a). Three of the five FTT samples were classified as PAG, with variability in classification largely attributable to variable calcium and magnesium carbonate content.

In the absence of quantitative mineralogical data, ARD potential for coke and coke ash was assessed using siderite-corrected NP/AP ratios. A ratio of 3 was used to delineate uncertain and non-PAG classifications given the uncertainty in the source of NP. Coke was classified as non-PAG because it had low sulfide content (average 1.0 kg $CaCO_3$/t) and low NP (average 2.3 kg $CaCO_3$/t). Similarly, coke ash samples were low in sulfide content (average 0.4 kg $CaCO_3$/t) and NP (average -0.6 kg $CaCO_3$/t). The bottom ash and combined ash samples were non-PAG, whereas the fly ash sample was acidic (paste pH 2.8) due to the likely presence of elemental sulfur and acid sulfates.

NAG test results were compared to ARD potential classifications (Figure 3b). Samples classified as PAG by the NAG test (NAG pH < 4.5) were also classified as PAG by CaNP/AP. However, the majority of samples classified as PAG or uncertain by CaNP/AP had NAG pH greater than 4.5. The weak relationship between NAG pH and CaNP/AP may be a result of low sulfide content in the tailings, and the contribution of silicates to acid neutralization.

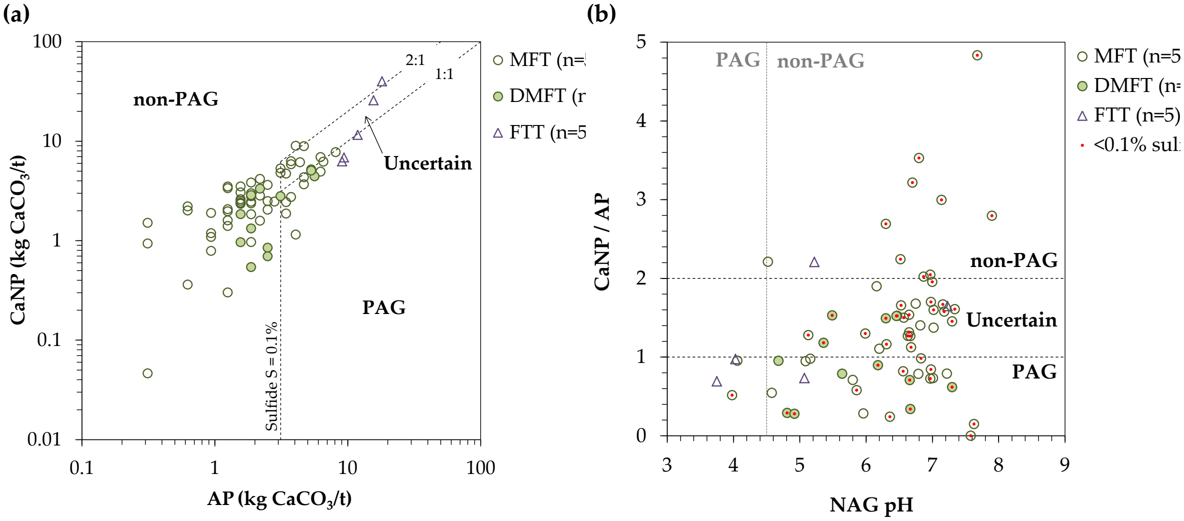

Figure 3 (a) ARD potential classifications for MFT, DMFT, and FTT; and (b) comparison of neutralization potential ratio (defined by CaNP and AP) and NAG pH

Pretreatment of the samples using the method of Dean and Stark (1920) removed bitumen prior to the NAG test. Samples pretreated to remove bitumen were characterized by greater NAG pH values than samples not subject to pretreatment (Figure 4). Sample pretreatment appears to have been effective in reducing bitumen contents and the subsequent formation of organic acids during the NAG test.

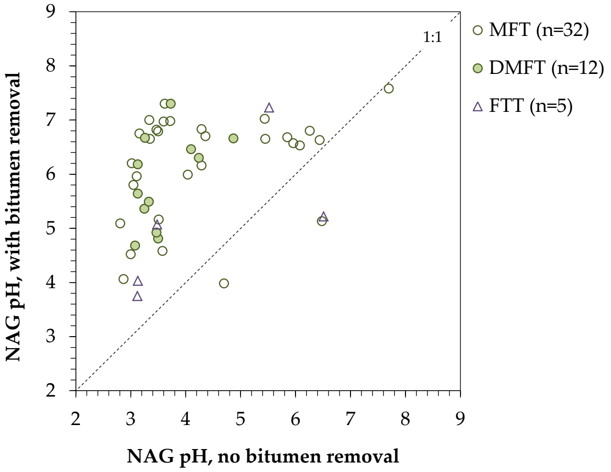

Figure 4 NAG pH before and after bitumen removal using the Dean and Stark (1920) method

Trace Element Leaching

Comparison with Global Average Values

Potential for trace element leaching was inferred by comparing concentrations in MFT, DMFT and FTT with global average values for sandstone and shale (Price 1997). The McMurray Formation is mainly sandstone but shale is locally present. As a result, tailings may have characteristics intermediate between that of sandstone and shale. Concentrations more than an order of magnitude higher than global average values were considered significant; however, potential for metal leaching needs to be considered in the context of the element-phase associations.

Relative to sandstones, cobalt, molybdenum, nickel, selenium, and uranium were enriched in MFT; cobalt and nickel were enriched in DMFT; and cobalt, molybdenum, nickel, selenium, and uranium were enriched in FTT (Table 1). These elements were not enriched relative to shale. Cobalt, molybdenum, and nickel in MFT and DMFT were correlated ($r \geq 0.78$) with insoluble sulfur and sulfide inferring an indistinguishable association with organic matter and pyrite, respectively. Cobalt ($r=0.84$) and nickel ($r=0.88$) in FTT were correlated with insoluble sulfur, whereas molybdenum ($r=0.91$) was correlated with sulfide. Uranium was correlated ($r \geq 0.96$) with titanium in all tailings implying an association with rutile, anatase, and ilmenite. These minerals are resistant to weathering and are not expected to leach uranium.

Comparison of trace concentrations in coke and coke ash with lithological average values did not yield meaningful indications of trace element leaching potential because the original minerals do not exist in these materials. The main feature of these products is the presence of percent level nickel and vanadium which occur in the organic structures of metalloporphyrins (Dechaine and Gray, 2010). Molybdenum concentrations were elevated due to the use of a Mo-based catalyst for coking.

Table 1 Element concentrations summarized as average ± 95% confidence interval

Material Type	**Element Concentration (mg/kg)**					
	Co	**Mo**	**Ni**	**Se**	**U**	**V**
MFT (n=57)	12±1.6	1.2±0.23	21±3.3	0.72±0.088	3.3±0.78	110±14
DMFT (n=12)	11±1.8	0.98±0.38	23±5.7	<0.5	3.3±1.2	99±27
FTT (n=5)	28±3.8	2.2±0.68	44±6.8	1.2±0.23	26±8	190±13
Coke (n=8)	7.2±0.49	47±2.5	370±15	n.d.	n.d.	930±41
Coke ash (n=3)	150±100	370±430	1900±600	0.63±0.26	18±13	>10000
Avg. sandstone (Price 1997)	0.3	0.2	2	0.05	0.45	20
Avg. shale (Price 1997)	19	2.6	68	0.6	3.7	130

Humidity Cells

Humidity cells are weathering tests, which provide some indication of how leaching potential correlates to concentrations in contact waters. None of the 12 tests on MFT, DMFT and FTT generated acid during the 20 weeks of testing. Tests on four PAG tailings were extended to 49 weeks, and did not generate acid. The lack of acidic conditions during the test reflects the neutralizing effects of carbonate minerals, thereby confirming their role in consuming sulfuric acid. The humidity cell tests, therefore, indicated leaching effects under neutral to slightly alkaline conditions (pH 6.3 to 8.6).

Initial humidity cell leachate chemistry was influenced by process water which is dominated by sodium, bicarbonate, and chloride. As the tests proceeded, leachate chemistry became increasingly influenced by weathering of the materials themselves including sulfate concentrations (correlated with sulfide content) and products of acid neutralization (calcium and magnesium). Increasing trends in manganese concentrations suggested that siderite was dissolving. Low leachable uranium concentrations were consistent with the expected association with chemically resistant oxides. Humidity cells on coke and coke ash generally showed leaching effects consistent with dissolution of soluble phases likely to occur in association with refractory organic matter in coke, and amorphous aluminosilicate melt in coke ash.

DISCUSSION

ML/ARD Potential of Oil Sands Processing Products

Test work performed for this study indicated that ARD potential of tailings (MFT, DMFT and FTT) is generally low because sulfide content is low relative to carbonate content. Calcite and ankerite contribute sufficient reactive neutralization potential as Ca and Mg carbonate to offset acid potential from sulfide. The exception to this general conclusion is that FTT, and DMFT and MFT containing mixed-in FTT may be classified as PAG due to the presence of pyrite. These conclusions are clearly linked to the host mineralogy of the McMurray Formation, and indicate that a site specific approach is needed to evaluate ARD potential.

Based on ABA characteristics and humidity cell test results, these oil sand tailings are expected to weather under basic conditions so that mobility of the trace constituents of pyrite (inferred to be cobalt, molybdenum, nickel, and selenium) will depend on how they speciate in waters. Cobalt and nickel are expected to have low mobility at neutral to alkaline pH, whereas the elements forming oxyanions may be more mobile. Dissolution of siderite during acid neutralization may release manganese into solution. Elements associated with carbonaceous matter (nickel and vanadium) and those associated with detrital oxides (uranium) are not expected to be mobile due to their relative stability of their hosts compared to pyrite.

Coke and coke ash contained relatively little sulfide. Coke is the most stable due to the occurrence of metals primarily hosted in refractory organic matter. Coke ash shows greater leachability due to the presence of soluble sulfate and oxide minerals.

Application of Standard ML/ARD Potential Characterization Methods

In addition to providing data on the ML/ARD potential of various oil sand tailings and bitumen upgrading by-products, this study also highlighted the challenges of applying standard methods developed for coal and metal mine wastes. One challenge was related to the hydrophobicity of the samples, which affected the application of water-based methods. For example, determining neutralization potential required the use of dispersants to break up the oil and sonification to allow the reagent to properly react with the sample. Hydrophobicity is due to the presence of bitumen in the samples, which is a source of organic carbon.

The high amounts of organic carbon relative to carbonate affected the determination of carbonate content. The use of hydrochloric acid to remove the carbonates was not effective on the basis of the poor correlation between the carbonate determinations and mineralogy. As a result, quantitative XRD may represent an alternative to the determination of carbonate mineralogy provided that measures are included to correct for the presence of amorphous matter, such as the addition of mineral standards in XRD samples.

Finally, humidity cells were used to evaluate weathering. The procedure appeared to be effective as results could be interpreted within the context of pore water leaching and mineralogical characteristics of the samples. Application of the results to site conditions requires careful consideration of sample hydrophobicity and scaling. The dominant presence of organic carbon and high moisture content of the tailings is likely to limit oxygen diffusion under field conditions.

CONCLUSIONS

The ML/ARD potential of the oil sand tailings sampled by this study and analyzed using standard ML/ARD characterization methods appears low and restricted to FTT. Metal leaching predominantly occurs under basic weathering conditions. Coke produced in the bitumen upgraders has low ARD potential but ash generated by burning coke contains soluble sulfates and oxides, some of which may be acidic. This study provides an important basis for the design of future oil sand ML/ARD characterization programs that should include careful consideration of analytical measures to address the presence of residual bitumen and associated hydrophobicity and organic carbon content.

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