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Waste Classification of Slag Generated in a Pilot-Scale Entrained-Flow Gasifier

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ABSTRACT

Series of gasification tests have been completed in the pilot-scale entrained-flow slagging gasifier at CanmetENERGY using Canadian coals, oil-sand coke, and blends of these fuels to determine if the produced slags are nonhazardous in nature. Solid wastes generated during these tests were analyzed for their trace metals, crystallinity, and toxic constituent leaching tendency in an attempt to provide more insight into the possibility of disposal or by-product use of gasifier-produced solid waste. The gasification tests were performed at conditions representative of commercial gasifiers using a dry-fuel-feed configuration. The lower-volatility elements were found to partition between the slag and process-water solids (PWS) collected after gasification of the oil-sand coke. The less volatile group 1 elements tended to be enriched in both solid streams, whereas the slightly more volatile group 2 elements tended to exhibit higher enrichment in the PWS. Slag samples were found to be inert with regard to their leaching potential, and so these materials can be considered nonhazardous.

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1. Introduction

The expected increase in bitumen upgrading in Alberta, Canada, will result in increased production of solid wastes both from upgraders employing coking technology and to a lesser extent upgraders employing gasification technology. As of 2008, there were 57 Mt of petroleum coke “stored” in Alberta (Du Plessis, 2009). The production of coke at this time was 6 to 6.5 Mt/yr, with a minor fraction of production being sold to third parties for subsequent use. Forecasted production has been estimated to be between 7 and 16 Mt/yr, with a possibility of the stockpile approaching 500 Mt by 2040.

Interest in entrained-flow gasification technology use is expanding in Western Canada at this time and could lead to a reduction in annual petroleum coke production as the heaviest

portion of the bitumen is gasified rather than transformed into coke. In 2008, Opti-Nexen began commissioning the Long Lake project, which uses gasification to generate hydrogen for oil upgrading, power production for the facility, and steam generation for steam-assisted gravity drainage (SAGD) operations. The use of gasification technology has nearly eliminated the requirement for natural gas—the leading operating expense at the previously established upgraders. At the time of commissioning, the gasifiers for this project were the largest Shell gasifiers in the world, each with a design throughput of 1033 t/day (Rettger et al., 2006). NorthWest Upgrading has proposed gasification of hydrocracker residue to produce the hydrogen required for upgrading the bitumen to a high-quality product (NorthWest Upgrading, 2005). Other proposed projects have included gasification of liquid residues or coke (Colt Engineering, 2007), including the BA Heartland Upgrader, the Fort Hills Upgrader, and the North American Oil Sands Upgrader, though many of these projects are now on hold or have been canceled due to current market conditions.

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Currently, there is a limited market for gasification by-products such as slag, given the small number of integrated gasification combined cycle (IGCC) plants currently in operation (Adams, 2004). For slag formed after oil-sand coke gasification, the remoteness of the plants may also be a roadblock to its commercial use due to transportation costs. As a result, landfilling may be the most economic option for these materials. If this is the case, then care needs to be taken to ensure that these by-products will not adversely affect the environment through leaching of the trace elements they contain.

Oil-sand petroleum coke and soot contain metals including vanadium (V), nickel (Ni), iron (Fe), and titanium (Ti), which are susceptible to leaching given appropriate acidic conditions (Jack et al., 1979). Leaching of these metals is also increased in the presence of certain salts and redox agents (Jack et al., 1979). Greater than 50% recovery of the V, Fe, and Ni can be achieved by acid leaches, while ~30% of Ni is leached out under weakly acidic conditions (Jack et al., 1979). Hypothesizing that metals associated with petroleum coke may leach into the surrounding environment, Puttaswamy et al. (2010) characterized the toxicity and chemistry of coke leachates. The toxicity of key metals found in coke leachate recovered from field lysimeters were evaluated, including Al, Mn, Ni, and V. These toxicity tests revealed that whole-coke leachates were acutely toxic to *Ceriodaphnia dubia*, with 7 day LC₅₀ (lethal concentration that results in the death of 50% of the test population) values less than 25% vol/vol (i.e., diluted leachate). V concentrations were higher than the other metals for all test sites and showed a concentration-response relationship with *C. dubia* survival. Their analysis suggests that V was the likely cause of toxicity in the deep lysimeter leachates, whereas both V and Ni were likely responsible for the observed toxicity in shallow lysimeters (Puttaswamy et al., 2010).

Trace metals from the gasifier feed fuel partition to the various output streams as a result of the gasification conditions and the activity of the elements (Clarke, 1993; Bunt and Waanders, 2008, 2009, 2010; Ilyushechkin et al., 2011). The elements are often grouped based on their volatility and presence in these output streams after combustion/gasification (Clarke, 1993; Meij, 1994; Querol et al., 1995). Volatile elements (e.g., Hg, Br, Cl, F), labeled group 3 elements, predominantly pass into the gas streams leaving the reaction chamber. Moderately volatile elements (e.g., As, Cd, Ga, Ge, Pb, Sb, Sn, Zn) are labeled group 2 elements. These elements may volatilize in the reaction chamber and condense in cooler downstream locations. The least volatile elements (e.g., Eu, Hf, La, Mn, Rb, Sc, Sm, Th, Zr), labeled group 1 elements, tend to be found in the slag/bottom ash. Other elements exhibit behaviors between these three groups. While some elements, such as Hg, are predominantly found in the fuel gas, studies on trace-element partitioning during entrained-flow gasification have shown that most trace elements end up in the slag (Beishon et al., 1989; Cooke and Taylor, 1993; Reed et al., 2001; Holt and Raivio, 2006; Font et al., 2010). Ilyushechkin et al. (2011) looked at the partitioning of trace metals between slag and fly ash samples after the gasification of four different Australian coals in a pilot-scale entrained-flow slagging gasifier. They concluded that thermodynamic modeling of trace-element behavior during gasification was only suitable for some elements. Thus, tests completed under realistic conditions are required to determine the fate of these elements after gasification, particularly when using opportunity fuels such as oil-sand coke.

Many studies have been completed on the leachability of residues from combustion processes; however, less information is

available regarding the leachable potential of trace elements in gasification residues (Font et al., 2005; Kim, 2009). Even less information is available on the stability of gasifier slags produced using opportunity fuels such as oil-sand coke. Schellberg and Ullrich (1989) provided information relating to leaching tests conducted on the solid streams (slag, fly ash, and filter cake) taken from the Fürstenhausen Prenflo pilot-scale gasifier. The solid residues were leached using the Resource Conservation and Recovery Act (RCRA) extraction procedure. All trace elements tested were well below toxicity limits (less than 1% of the extraction procedure [EP] toxicity limit for As, Ba, Cd, Cr, Pb, Hg, and Se). They noted that the slag had a coarse-grained, vitreous structure that could not be leached by either water or other solvents. Slag from a British Gas Lurgi (BGL) pilot plant gasifier was similarly found to be relatively inert under leaching conditions (Beishon et al., 1989), with only Fe being measured above acceptable values (taken to be 100 times the RCRA water-quality standard; Cooke and Taylor, 1993). Petroleum coke was used as the feed for the IGCC at the Wabash River repowering demonstration plant, Indiana (Keeler, 1999). Slurries of petroleum coke (66 wt%) were fired in an E-gas gasifier (40.2% higher heating value). Solid, liquid, and gas samples were taken at various points around the plant to monitor trace-element partitioning. About 80% of the Ni and 99% of the V were captured in the slag. This was found to be an inert, nonleaching solid as outlined by the toxicity characteristic leaching procedure (Dowd, 2000). The partitioning of trace elements and their leaching potential from waste products produced from the gasification of opportunity fuels such as oil-sand coke under dry-firing conditions are, however, unknown.

A series of tests was completed on the pilot-scale entrained-flow gasifier at CanmetENERGY. Pure and blended feeds of sub-bituminous and lignite coals with an oil-sand coke were gasified. An overview of the gasification runs and performance of the gasifier during the tests used to generate the slag samples is outlined in Cousins et al. (2008). Slag samples were collected from the gasifier quench vessel at the end of a run. Trace-metal composition, crystalline fraction, and leachability were determined for the collected samples. These results are reported in this paper.

2. Experimental Materials and Methods

2.1. Fuel characteristics

The fuels used in this study include a sub-bituminous coal (designated GN from the Genesee mine, Alberta), a lignite (designated BD from the Boundary Dam mine, Saskatchewan), and an oil-sand coke (designated SC, Alberta). Fuel blends are identified as follows: SC:GN is a 1-to-1 ratio of oil-sand coke to sub-bituminous coal on an as received basis, 3SC:BD is a 3-to-1 ratio of oil-sand coke to lignite. The proximate and ultimate analyses of these fuels and blends are provided in Table 1.

Coal samples were pulverized to an average particle size in the range 40–65 µm and dried to <5 wt% moisture. This preparation has been found to reduce difficulties in conveying the coal into the gasifier through the current 4-mm (inner diameter) conveying system. The coal and oil-sand coke were pulverized in-house using a roller mill. Fuels were blended after preparation, prior to running. Details of the blending method can be found elsewhere (Cousins et al., 2008).

Table 1
Proximate and ultimate analysis of fuels (wt%, as received)¹

	GN	BD	SC	SC:GN	SC:BD	3SC:BD
Moisture	6.8	4.2	0.1	3.5	2.2	1.2
Ash	22.0	14.3	4.0	14.3	9.8	6.9
Volatiles	28.4	39.3	12.2	19.0	23.6	17.9
Fixed C	42.8	42.2	83.7	63.2	64.5	74.0
C	54.2	59.9	83.9	67.7	71.6	77.9
H	3.2	3.8	3.6	3.3	3.7	3.6
N	0.8	1.0	1.6	1.2	1.3	1.5
S	0.3	0.9	6.4	3.3	3.6	4.9
O	12.7	15.9	0.4	6.7	7.8	4.2
HHV (MJ/kg)	20.9	23.2	33.7	27.0	28.5	31.0

¹ GN = sub-bituminous coal; BD = lignite; SC = oil-sand coke; HHV = higher heating value.

Inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) were used to determine the trace metals present in the fuel samples. Samples were analyzed according to ASTM D6357. These results are provided in Table 2.

2.2. Pilot plant

A schematic of the gasification system at CanmetENERGY is given in Figure 1. This is a down-fired pilot-scale entrained-flow gasifier typically operated at 0.3 MW_{th} fuel rate with a castable protective lining made from a high-alumina refractory. The reactor was fired at ~20 kg/h of pulverized fuel with 8–13 kg/h of entraining gas. For all tests, the same nominal carbon (C) flow rate into the gasifier was maintained. In addition, O₂ flow rates were controlled to ensure that oxygen-to-carbon (O/C) molar ratios in the range 1–1.4 were maintained for all tests. Steam was used to regulate gasifier temperatures during the tests and was injected at 1–2 kg/h. Reactor pressure was maintained at 750 kPa. The operating temperature of the gasifier was dependent on the particular fuel being fed and the selected O/C ratio for a given run. However, mid-gasifier thermocouple readings (typically the highest temperature measurement) were in the range 1200–1450°C. During the gasification tests, C conversion efficiencies in the range 65–85% were obtained, depending on the O/C ratio. As a result, some C (in the form of char) was able to enter the gasifier quench vessel. This char was then carried by the water leaving the quench vessel into the bag filters. Char/fly ash leaving the gasifier in the fuel gas was collected in the wet scrubber (~65°C) and also passed through bag filters in which the water pH was approximately 6.05. Solid samples collected from the bag filter are referred to as process-water solids (PWS) and were a mixture of char and fly ash. Additional information regarding this test campaign can be found in Cousins et al. (2008), including reactant and product characteristics. Slag and PWS samples were collected from the quench vessel and bag filters, respectively. They were stored in sealed containers under ambient conditions to ensure no loss of volatile components from the sample.

2.3. Analytical techniques

2.3.1. Toxicity characteristic leaching procedure (TCLP)

The TCLP is an analytical method designed to simulate leaching through a landfill. It determines the mobility of both inorganic and organic analytes present in liquid, solid, and multiphase wastes. This method was developed by the U.S. Environmental Protection Agency (U.S. EPA) to identify wastes likely to leach dangerous

Table 2
Fuel samples trace-metals analysis (ICP-MS/AES with ashing and acid digestion, ppm)¹

	GN	BD	SC	SC:GN	SC:BD	3SC:BD
Barium	2940	4444	214	1594	2331	1376
Boron	46.7	134	7.4	23.4	72.6	38.5
Cadmium	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Chromium	3.4	<0.1	<0.1	<0.1	<0.1	<0.1
Copper	4.8	7.8	5.8	4.2	7.7	7.9
Lead	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Manganese	87	21.4	32.6	58.8	30	31.6
Molybdenum	14.7	<0.1	32.6	25.1	23.8	24
Nickel	5.6	2.3	88.3	60.8	30.2	50.8
Phosphorus	<0.1	191	<0.1	<0.1	117	67.6
Strontium	165	467	18.1	92.9	259	139
Tin	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Titanium	117	236	133	56.2	124	105
Vanadium	<0.1	<0.1	427	333	365	422
Zinc	13.4	3.9	<0.1	4.8	<0.1	<0.1

¹ ICP-MS/AES = inductively coupled plasma mass spectrometry/atomic emission spectrometry; GN = sub-bituminous coal; BD = lignite; SC = oil-sand coke.

concentrations of certain known toxic chemicals into groundwater. For wastes containing solid phases, the particle size is reduced if necessary (until surface area > 3.1 cm²/g), followed by extraction with an extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the waste (refer to U.S. EPA, 1992, method 1311). A special extractor vessel is used when testing volatile species. The solid/liquid extract is then agitated for 18 hours at ambient temperature. The liquid extract is then separated from the solid phase by filtration and analyzed for the presence of trace metals.

Many of the trace metals present in the coal and petroleum coke feed tend to concentrate in the solid waste (slag) streams from the gasifier. As a result, slag samples collected from the quench after tests were analyzed to determine the leachability of the toxic components (U.S. EPA, 1992). One PWS sample was collected from the bag filters after operation of the gasifier using the oil-sand coke as feed. The PWS sample was tested for trace-metal leachability using the TCLP.

2.3.2. Scanning electron microscopy (SEM)

A Hitachi S-3400N SEM was used to observe cross sections of a slag-refractory core drilled from the inside of the gasifier after operation. Core samples were mounted in an epoxy resin. The samples were then ground using diamond grinding discs and polished using diamond sprays to a fineness of 1 µm. Polished cross sections were then coated with a layer of Au/Pd (typically 24-nm thickness) to enhance conductivity. Backscattered images of the samples were collected using an accelerating voltage of 20 kV and a working distance of 10 mm. Energy dispersive X-ray (EDX) analysis was performed to determine the species present in the samples (limit of detection, ~1%).

2.3.3. X-ray diffraction (XRD)

XRD was used to determine the proportion of amorphous and crystalline phases in the slag samples. The composition of the crystalline phases in the slag samples was also determined. XRD data of the samples were collected on a Bruker D5000TT diffractometer over the angular range 5° to 75° (2 theta) in 0.05° steps. The Bruker D5000TT XRD system operates in the theta:theta geometry, uses Cu(K α) radiation, 1.5405981 Å, and is equipped with a diffracted-beam graphite monochromator, a scintillation detector, and solid-

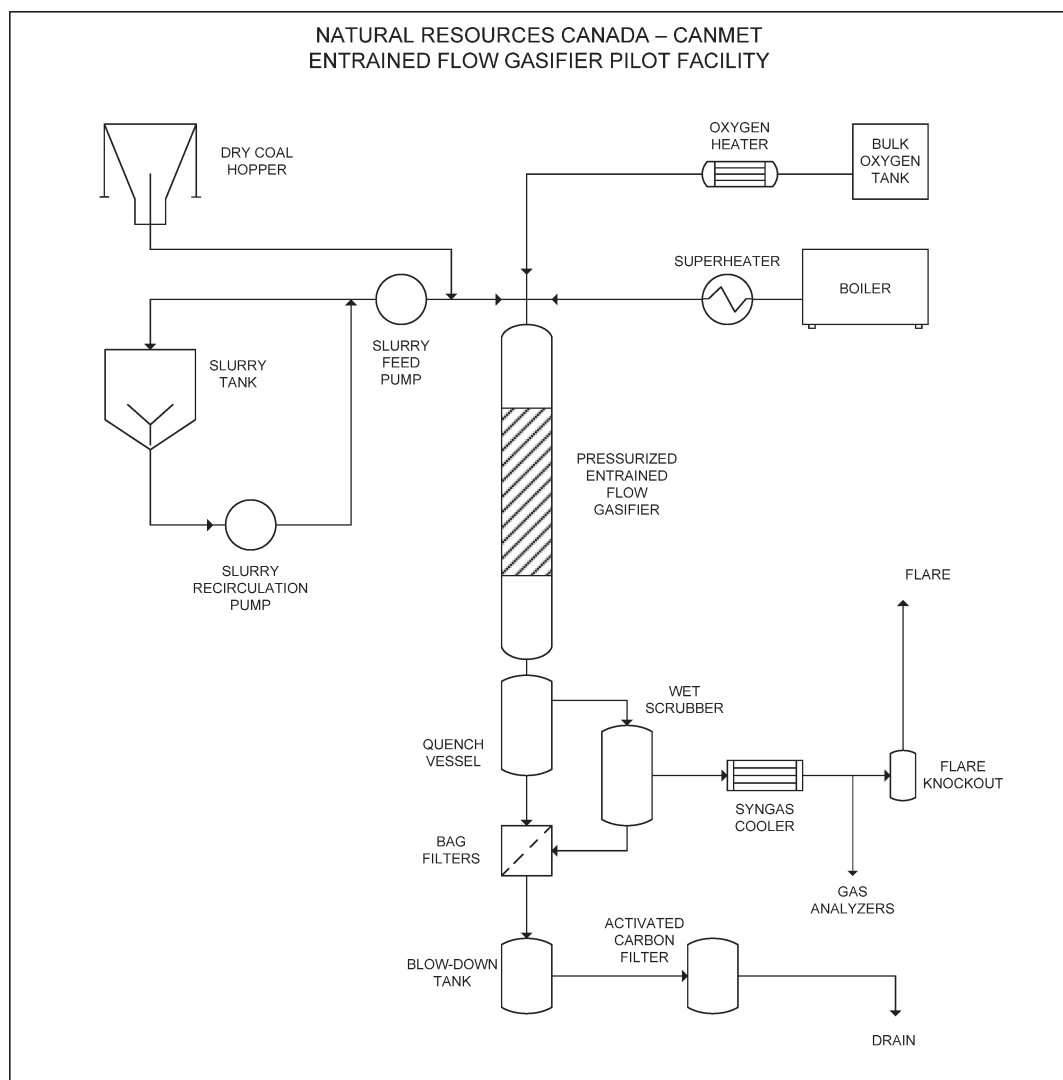


Fig. 1. Schematic diagram of gasification system.

state counting electronics. The generator voltage and current settings were 40 kV and 30 mA, respectively. The diffraction spectra were processed using the JADE version 6.5 XRD processing software. Identification of the chemical or mineral compounds was performed using the search/match option in JADE. Accurate integrated intensities of diffraction peaks were derived through “peak deconvolution” or, more commonly, “line profile fitting,” another software tool in JADE. These data were used for quantitative analysis. Quantitative analysis of the samples was originally done using alpha-alumina (Al_2O_3) as an internal spiking standard. This technique is known as the reference intensity ratio (RIR) method and was developed by Chung (1974, 1975). All the “ I/I_c ” values used in this work are from the powder diffraction file. For quantitative XRD, 0.8 g of each sample was mixed with ~ 0.008 g of Al_2O_3 . The resulting mixture was thoroughly ground for ~ 5 minutes using a mortar and pestle. Each resulting powdered mixture was loaded into a holder. The holder was transferred to the XRD instrument, and data were collected. Integrated intensities for strong diffracting peaks of each phase were obtained using JADE. Concentrations of the chemicals identified in each sample were calculated using the method mentioned previously.

3. Results and Discussion

3.1. Slag microstructure

The main crystals contained in the slag samples are given in Table 3. These were corundum (Al_2O_3), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), anhydrite (CaSO_4), and maghemite (Fe_2O_3). Except for the Boundary Dam sample, the majority of the crystalline content appears to be from Al_2O_3 . The primary phase fields expected in gasifier slags can be determined based on the ash composition of the original fuel. It is likely that the phases seen in the collected samples will differ from this for a number of reasons, including the kinetics of the reactions being such that phase equilibrium is not achieved within the gasifier residence time, and reaction with wall slag could shift the bulk composition of the liquid slag to another primary phase field. Further work is required in this area.

It has been noted that the presence of crystal structures in some slags has been shown to be influential in preventing the leaching of heavy metals (Nishida et al., 2001). However, the presence of crystalline phases does not necessarily represent the leachable potential of all trace metals present in solid samples. The leachable

Table 3
XRD analysis of slag samples (% chemical compound)¹

	GN	BD	SC	SC:GN	SC:BD
Corundum, syn (Al ₂ O ₃)	9.6	26.3	30.8	74.7	44.2
Ferrihydrite, syn (FeO[OH])	0	0	0.8	2.1	2.3
Anorthite, ordered (CaAl ₂ Si ₂ O ₈)	4.5	62.1	7.6	0	0
Spinel, ferrian (Mg[Al,Fe] ₂ O ₄)	0	8	4.3	0	0
Anhydrite, syn (CaSO ₄)	0	0	5.7	8.5	6.7
Maghemite-C, syn (Fe ₂ O ₃)	0	0	4.3	7.2	3.1
Quartz, syn (SiO ₂)	0.2	0	0.7	0	0.3
Crystallinity (%)	14.2	96.3	54.1	92.6	56.6
Amorphous content (%)	85.8	3.7	45.9	7.4	43.4

¹ XRD = X-ray diffraction; GN = sub-bituminous coal; BD = lignite; SC = oil-sand coke.

potential of the elements is more likely dependent on slag origin and its phase composition.

3.2. Slag-refractory interactions

Frozen slag coating the inside of the gasifier was noted to have a reddish color on the surface. Subsequent slag layers and slag collected from the quench, however, were gray in color. In addition, it was noted on inspection that some of the slag samples contained 2–5-mm rectangular white inclusions that were similar in appearance to the refractory material used in the gasifier. The castable protective lining used in the gasifier is a high-alumina refractory. Most molten gasifier slags are undersaturated with respect to Al₂O₃ at the operating temperature. As a result, high-alumina refractories are susceptible to attack (Dogan et al., 2003).

To determine whether the white inclusions noted in the slag samples were from the refractory, a 25.4-mm-diameter refractory and slag core sample was drilled out of the gasifier wall. The sample was collected following runs completed with Genesee coal, Boundary Dam lignite, coke, and blends. As a result, it is likely that the slag sample collected is a mixture of one or more of the feedstocks. Figure 2 provides backscattered images of the frozen slag and refractory core. These images show a cross section from the surface of the frozen slag layer up to a depth of approximately 4 mm into the core sample. There appear to be at least three distinct assemblies present in the cross section, labeled (1), (2), and (3) in Figure 3 and Table 4. EDX analysis of these assemblies is outlined in Table 4.

The light-gray area, labeled (1) in Figure 2, consists predominantly of Al and O, and is most likely alumina from the gasifier refractory. The dark-gray area, labeled (2), consists predominantly of Si, O, and Al, and is most likely frozen slag. The black area, labeled (3), consists mostly of Al and O but also contains a significant proportion of Fe. The Fe-rich black area is only observed to a depth of ~2 mm, while Si-rich slag penetration is present at all depths considered here. As can be seen in Figure 3b, (3), there is a concentration of the darker Fe-rich area in a layer at the slag surface. Segregation of Fe from the Si-Al melt may occur due to the immiscibility of the Fe-rich liquid and the Si-rich liquid. The Fe-rich layer at the slag surface is likely the cause of the red appearance of the frozen slag surface inside the gasifier. Behind this surface layer, there is an Si-rich frozen slag coating the surface of the gasifier refractory, labeled (2). As can be seen in Figure 3a and labeled (1), near the surface of the frozen slag an Fe-rich black area has formed tendrils. This is likely a frozen liquid, most likely spinel, forming in the Al-saturated slag layer.

Slag penetration into gasifier refractories tends to be by interconnected porosity and along matrix grain boundaries (Dogan et al., 2003). This appears to be the case for the sample under

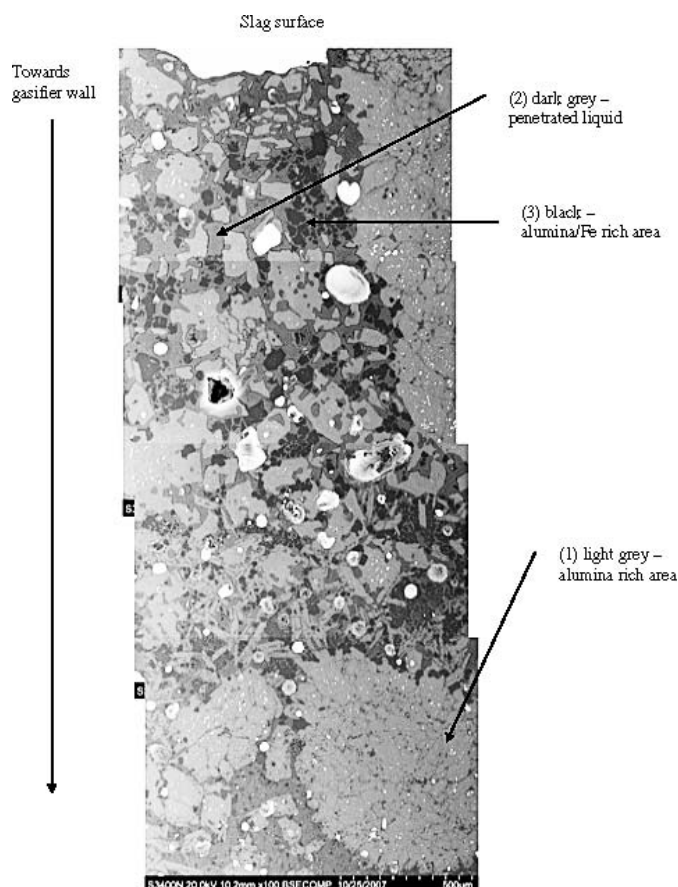


Fig. 2. Backscattered scanning electron microscopy image of cross section of refractory-slag core sample bored from gasifier.

consideration here outlined in Figure 2. From Figure 3a, an Fe-rich darker area is noted to form along the sides of the light-gray alumina particles. This highlights the likely reaction of the Fe with the alumina particles. Wells et al. (2003) looked at slag bonding to the surface of refractory samples taken from the inside of a commercial combustor. Fe from the slag was noted to have penetrated into the refractory to a depth of 2–3 mm. Under gasification conditions, Fe also penetrates into the refractory to a similar depth. The reaction of the Fe with the refractory alumina particles could facilitate the erosion of the gasifier refractory.

Slag-refractory reaction rates are dependent on slag composition, wettability and solubility of the slag, and the gasification temperature (Bennett and Kwong, 2004). Given that some refractory loss will occur during operation of the gasifier, consideration needs to be given to the properties of the refractory when considering the further use or disposal of gasification solid waste streams. Some gasifier refractories contain high Cr contents, as this has been found to reduce slag attack of the refractory (Rawers et al., 1999). Chromium is listed as one of the elements of concern regarding leaching, and is tested for by the TCLP analysis (limit, 5 mg/L). If high-Cr refractories are to be used, slag samples collected from these gasifiers should be analyzed for their leaching potential.

3.3. Distribution of trace metals after gasification of oil-sand coke

3.3.1. Trace element enrichment

As can be seen in Table 2, the trace-metal concentrations vary between the different fuel types. The coal samples have the highest

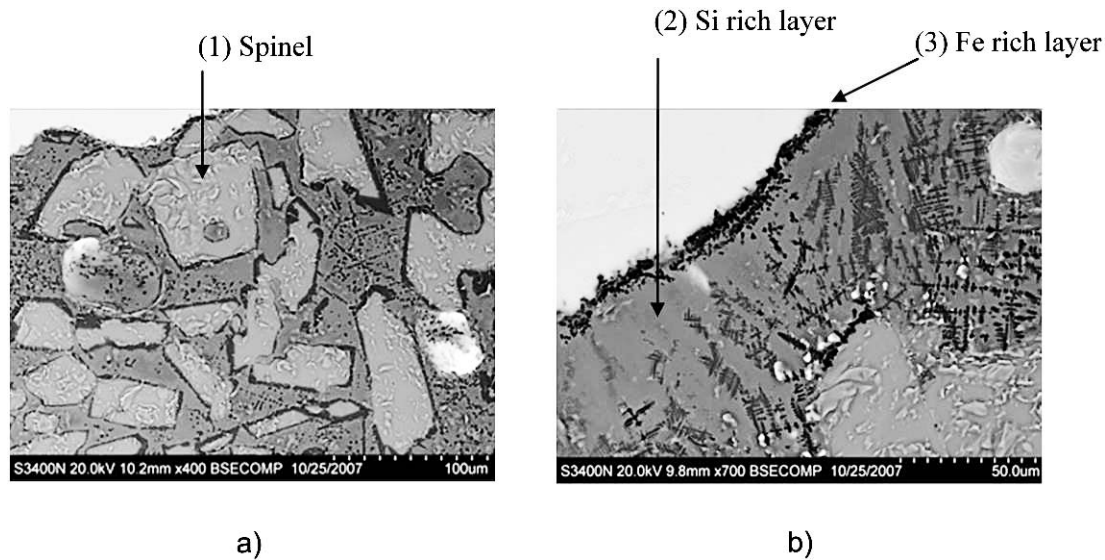


Fig. 3. Backscattered scanning electron microscopy image of slag-refractory cross section taken at slag surface at (a) $\times 400$ magnification and (b) $\times 700$ magnification.

concentrations of most trace metals considered here. The sub-bituminous Genesee coal has the highest ash content and the highest concentrations of Al, Fe, Cr, Zn, Si, and Mg. The Boundary Dam lignite has the highest concentrations of Cu, Ti, P, Ca, Ba, Mn, B, Sr, and Na. The oil-sand coke has the highest concentration of Ni, Mo, and V.

As mentioned previously, trace metals from the gasifier feed fuel partition to the various output streams as a result of the gasification conditions and the activity of the elements. As trace metals in the PWS and slag samples are the ones under consideration here, volatile group 3 elements are not considered. Some elements are present at concentrations below the level of quantification (in either original fuel or slag/PWS analysis). These elements are also not considered here (Sn, Cr, Pb, Cd, Zn, P, Ag, As, Se).

The concentrations of the trace metals in the coke, PWS, and slag collected after operation of the gasifier using the oil-sand coke as feed are given in Table 5, along with the enrichment factors (EF) of these elements in the PWS and slag. Enrichment of a particular element in the solid waste stream can be calculated by a number of methods. The methods proposed by Meij (1994, EF_{Meij}) and Querol et al. (1995, EF_{Querol}) are considered here.

$$EF_{Meij} = \left(\frac{[E]_{ash}}{[E]_{coal}} \right) \times \left(\frac{A}{100} \right) \quad (1)$$

where $[E]_{ash}$ is the element concentration in the PWS/slag, $[E]_{coal}$ is the element concentration in the coal, and A is the % ash content in the coal.

$$EF_{Querol} = \frac{([E]_{ash}/[I]_{ash})}{([E]_{coal}/[I]_{coal})} \quad (2)$$

where $[E]_{ash}$ is the element concentration in the PWS/slag, $[E]_{coal}$ is the element concentration in the coal/coke, $[I]_{ash}$ is the concentration of one of the nonvolatile group 1 elements in the PWS/slag, and $[I]_{coal}$ is the concentration of one of the nonvolatile group 1 elements in the coal/coke. In their work, Querol et al. (1995) use [Al] for [I]. However, as mentioned in section 3.2, as dissolution of Al from the gasifier refractory may be occurring, this calculation was also completed using [Ca] for [I]. These results are also presented in Table 5. While the EFs calculated by the different methods vary, the trends shown in the results are similar. In the following sections, we discuss the observed enrichment factors with the elements grouped according to Meij (1994), as is often done as a reference for partitioning studies (Font et al., 2010).

3.3.2. Group 1 elements

The group 1 elements considered here include Al, Fe, Ca, Ti, Mg, and Sr. Most exhibit EFs greater than 1 in the slag and/or PWS. An EF of 1 would be expected for a nonvolatile element that passes into the gasifier slag/PWS. Higher/lower numbers than this could be a result of contamination with slag from previous runs. In the case of Al, however, this could also be a result of dissolution of the gasifier refractory. Al, Ca, and Mg show similar EFs in both the slag and PWS samples. Ti and Sr show higher EFs in the PWS than in the slag. This could be a result of the partial volatilization of these elements under gasification conditions, and re-condensation on the smaller PWS particles in the cooler downstream parts of the gasifier (some of the highest measured gasifier temperatures occurred when running with coke as feed). Only Fe shows an EF less than 1 for all methods in both the char and slag samples. One possible explanation could be the result of the reaction occurring

Table 4
Quantitative energy dispersive X-ray analysis of assemblies observed in slag-refractory cross section (composition given in atomic %)

Element	Assembly color		
	Light gray (1)	Dark gray (2)	Black (3)
C	2.36		3.04
Al	36.71	8.99	26.38
Fe	0.57	1.38	8.98
O	60.36	62.68	58.06
Na		1.29	
Mg		0.26	3.24
Si		21.61	
K		0.77	
Ca		2.72	
Ti		0.28	

Table 5

Concentration of selected major, minor, and trace metals in coke and element concentration and EF in slag/PWS collected after operation with coke¹

Element	Concentration (ppm)			EF _{Meij}		EF _{Quero1-Al}		EF _{Quero1-Ca}	
	Coke	PWS	Slag	Slag	PWS	Slag	PWS	Slag	PWS
Group 1									
Al	1835	119,250	99,299	2.2	2.6	1.0	1.0	1.4	1.4
Fe	2170	42,812	27,843	0.5	0.8	0.2	0.3	0.3	0.4
Ca	613	28,231	23,404	1.5	1.8	0.7	0.7	1.0	1.0
Ti	133	9862	2092	0.6	3.0	0.3	1.1	0.4	1.6
Mg	131	8476	7281	2.2	2.6	1.0	1.0	1.5	1.4
Sr	18	581	232	0.5	1.3	0.2	0.5	0.3	0.7
Group 2c									
Na	181	14,109	6855	1.5	3.1	0.7	1.2	1.0	1.7
Ba	214	1354	647	0.1	0.3	0.1	0.1	0.1	0.1
Mn	59	606	242	0.3	0.7	0.1	0.3	0.2	0.4
Group 2b									
V	427	5703	632	0.1	0.5	0.0	0.2	0.0	0.3
Ni	88	2466	340	0.2	1.1	0.1	0.4	0.1	0.6
Cu	6	188	80	0.6	1.3	0.3	0.5	0.4	0.7
Group 2a									
Mo	33	285	10	0.0	0.3	0.0	0.1	0.0	0.2

¹ EF = enrichment factor; PWS = process-water solids.

between Fe and gasifier refractory (as suggested previously in section 3.2). This could also be explained by contamination with slag from previous runs. However, as both coal samples contained higher levels of Fe than the coke, if contamination were the cause, an EF greater than 1 would be expected. Further work is required here to determine the explanation for these discrepancies.

3.3.3. Group 2 elements

The group 2 elements considered here include Na, Ba, Mn, V, Ni, Cu, and Mo. Most tend to exhibit EFs less than 1 in both the slag and PWS samples, except for Na. For all methods used, the EF for the trace metals in the PWS is higher than that in the slag. This is in agreement with the description of group 2 elements being volatilized in the gasifier chamber but re-condensing in cooler downstream parts of the gasifier on the smaller PWS particles. Font et al. (2010) similarly found higher EFs for Na, V, Ni, Cu, and Mo in fly ash compared with slag collected from a commercial entrained-flow slagging gasifier. Ilyushechkin et al. (2011) found higher concentrations of Mo, Cu, Ni, and Ba in PWS compared with slag collected from operation with a pilot-scale entrained-flow slagging gasifier. Mo and Cu showed higher concentrations in the PWS than in the original coal fuel (i.e., EF > 1). Ilyushechkin et al. (2011) also reported higher concentrations for V in the slag compared with the PWS. V concentrations in the slag were lower than in the original fuel (i.e., EF < 1).

Some enrichment of elements seen in the slag and PWS samples considered here may be a result of different processes, including contamination/reaction with wall slag left over from previous gasification runs, migration of elements into the frozen wall slag inside the gasifier, interaction/reaction between the slag and the gasifier refractory lining, and dissolution of the gasifier refractory lining.

3.4. Slag leachability

Slag samples collected directly from the gasifier quench after operation with the different fuels were analyzed for their leaching potential via the TCLP analysis. One PWS sample collected after

Table 6

Slag TCLP results with Alberta Environment's associated limits¹

Element	Unit	GN	SC	BD	SC PWS	Limit
Ag	ppb	<0.2	<0.2	<0.2	<0.2	
Al	ppm	1	3.1	3.7	2.8	
As	ppb	<2	<2	<2	<2	5000
B	ppm	<0.05	<0.05	1.05	0.36	500
Ba	ppm	0.04	0.04	1.38	0.68	100
Be	ppb	<0.1	0.14	0.54	1.3	
Ca	ppm	<0.2	0.89	13.2	32.7	
Cd	ppb	<0.4	<0.4	<0.4	3.8	1000
Ce	ppb	2.4	2.6	21.6	42.8	
Co	ppb	1	1	1	31	100,000
Cr	ppm	<0.01	<0.01	<0.01	<0.01	5
Cs	ppb	<0.2	<0.2	0.3	<0.2	
Cu	ppb	30	23	37	38	100,000
Fe	ppm	0.57	0.81	3.6	0.06	
K	ppm	<0.5	0.61	0.7	0.52	
La	ppb	1.3	1.3	13.7	26.5	
Lu	ppb	<0.1	<0.1	0.1	0.23	
Mg	ppm	<0.05	0.2	1.84	2.31	
Mn	ppm	0.01	0.02	0.09	0.71	
Mo	ppb	3	1	16	54	
Ni	ppb	528	107	192	2097	5000
P	ppm	<0.5	<0.5	<0.5	<0.5	
Pb	ppb	15.7	2.1	<0.2	20.2	5000
Rb	ppb	<1	1	1	2	
Sb	ppb	0.55	<0.2	<0.2	1.7	500
Se	ppb	<20	<20	<20	<20	1000
Sm	ppb	0.19	0.22	1.5	3.9	
Sr	ppm	0.02	0.01	0.94	0.55	
Tb	ppb	<0.1	<0.1	0.24	0.5	
Th	ppb	0.25	0.22	0.76	<0.2	5000
Ti	ppm	<0.01	<0.01	<0.01	<0.01	
Tl	ppb	<0.1	<0.1	<0.1	0.81	
U	ppb	0.2	0.26	5.4	0.44	2000
V	ppm	<0.02	<0.02	0.02	<0.02	100,000
Yb	ppb	0.1	0.11	0.77	1.4	
Zn	ppb	18	4	<2	539	500,000

¹ TCLP = toxicity characteristic leaching procedure; GN = sub-bituminous coal; SC = oil-sand coke; BD = lignite; PWS = process-water solids.

operation using the oil-sand coke as the gasifier feed was collected from the gasifier bag filters and also analyzed. The TCLP results for these samples are given in Table 6. Other information provided in the table includes the chemical constituents and leachate limits in Alberta (Alberta User Guide for Waste Managers, 1995). If the extract from the TCLP analysis contains an amount, for one or more of the toxic constituents, equal to or in excess of the thresholds given, then the sample is considered toxic and must be treated as a hazardous waste during disposal. From Table 6, it can be seen that the concentrations of the controlled elements are well within the limits listed for the leachates in Alberta.

Despite having the highest concentrations of Al, Fe, Cr, and Mn in the original coal, slag collected after operation with Genesee material did not have the highest levels of these elements in the leachate. Of the slag samples collected, only Zn, Pb, Sb, and Ni showed the highest concentration in the leachate for the Genesee slag. Similarly, despite having the highest levels of Mo, Ni, and V of the fuel samples considered here, the leachate produced from slag collected after operation with the oil-sand coke did not show the highest concentrations of these elements.

Slag collected after operation with the Boundary Dam lignite, and PWS collected after operation with the oil-sand coke tended to have the highest levels of leaching elements. This is despite slag

collected after operation with the Boundary Dam coal having one of the highest crystalline contents measured. For the PWS sample, this could be a result of some elements re-condensing on the PWS ash particles after gasification. These elements may be more prone to removal during the leaching process. Elements in highest concentration in the PWS leachate tended to be from the more volatile group 2 and 3 elements, suggesting this may be the cause.

Despite the retention of some of the trace metals in the gasification solid waste samples after operation with the oil-sand coke, the levels of elements leached from the samples were below regulations. Leachates from slag samples collected after operation of the gasifier with the coal fuel feeds were also within regulation limits. In addition, despite the possible dissolution of refractory into the collected slag samples, the Al measured in the slag leachates was still low, at around 1–4 ppm.

4. Summary

A series of gasification runs using Canadian fuels was successfully completed on the pilot-scale entrained-flow reactor at CanmetENERGY. Runs were completed using delayed oil-sand coke, Genesee sub-bituminous coal, Boundary Dam lignite, and blends. Samples of slag collected after the runs were analyzed for their leaching potential using the TCLP procedure. Leaching analysis showed that slag samples collected from the gasifier after operation with Canadian feedstocks appropriate to oil-sand development are inert and should not cause any problems regarding disposal.

XRD analysis of the samples showed that the crystalline content of the slag samples varied greatly. The most common crystalline phase found in the samples was Al_2O_3 . From SEM-EDX analysis of the frozen wall slag, it appears that dissolution of the alumina refractory into the slag is occurring. When considering the disposal or secondary use of the solid waste streams from slagging gasifiers, thought should be given to the properties of the gasifier refractory lining.

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