

Leachability of cokes from Syncrude stockpiles

Five samples of coke taken from Syncrude stockpiles were evaluated according to the Toxicity Characteristics Leaching Procedure to determine content of regulated elements, such as arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver as well as volatile organics. One sample of drainage water from the stockpile was also evaluated. For all samples, contents of the elements and volatile organics were lower than detection limits of the analyzer confirming that the cokes are virtually non-leachable. The increased severity, i.e., leaching at pH=2 and pH=4 had little effect on leachability of regulated species and volatile organics.

Syncrude Canada Ltd. in Fort McMurray, Alberta operates the largest synthetic crude oil plant in the world, converting the Athabasca bitumen to Syncrude Sweet Blend crude (1). As part of this operation, about 2,000 tonne/day of the coke are being stockpiled in proximity to the plant. After many years of the operation, the stockpiled coke represents a significant amount of a high heating value solid fuel (2).

At present, the utilization of the coke to produce hydrogen, electricity and steam for plant and local consumption cannot compete with the natural gas which is available at much lower cost, or a high heating value gas produced as a by-product in the plant. However, once economics are attractive, combustion and gasification appear to be the technologies of choice for coke utilization. In the meantime, it is the primary objective of Syncrude Canada Ltd. to ensure that the stockpiles of coke do not pose any environmental hazards.

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In this regard, it is essential to ensure that the leachability of the Environmental Protection Agency (EPA) designated priority inorganic contaminants, as well as that of the volatile polynuclear aromatics and other organics, is within the acceptable limits. Thus, the long term effects of the stockpiles on surface and groundwaters should be clearly understood. This requires a sufficient database established according to the methods and procedures accepted by the environmental authorities. Such methods were used for evaluation of leachability of the coke samples from Syncrude stockpiles. For one sample, the leachability was performed at different pH levels which were adjusted by sulphuric acid. The aim was to simulate potential leaching from the stockpile under extremely severe leaching conditions.

The EPA's Toxicity Characteristics Leaching Procedure (TCLP) was used for the coke evaluations. This method determines the leachability of solid residues and the mobility of both organic and inorganic contaminants present in liquid, solid and multiphase systems. The method is consid-



ered representative of the situation in a solid waste landfill. It is generally accepted that TCLP method is adequate for indicating the potential of landfill wastes to pose hazards if disposed improperly. The method has been adapted by some other countries.

Environmental Regulations

Extensive efforts have been made in all industrialized countries to develop and maintain regulations and laws to control handling, transportation, storage and disposal of the wastes generated by various industrial processes. For example, the Electric Power Research Institute (3) in the USA, the Cana-

dian Electrical Association (4) in Canada and the International Energy Agency (5) published numerous studies on environmental aspects of solid and liquid wastes from power plants. The National Petroleum Refiner Association (6) in the USA has focused attention on hazardous wastes generated by the refining industry. The Canadian refining industry is carefully monitoring all related developments as well. The information on this subject is extensive and beyond the scope of this study.

In Canada, regulations exist related to the generation, storage and transportation of solid wastes (7). These solid wastes have to be assessed for their content of inorganic and organic pollutants. For example, utilities have to satisfy these regulations for bottom and fly ashes from coal combustion. In the US, hazardous wastes are regulated by the "Toxicity Characteristic" rule and administered by the EPA. It states that a solid waste exhibits the characteristic of toxicity if, when using the approved methods, the extract from a representative sample of the waste contains any of the regulated contaminants at the concentration equal to or greater than the respective regulatory level. The list of the EPA regulatory contaminants can be found in the EPA Federal Register (March 29, 1990). The EPA sets all regulatory levels for hazardous chemicals on a health-based concentration threshold and a dilution attenuation factor. For inorganic priority elements, these levels are shown in Table 1.

The concentration threshold identified as the Chronic Toxicity Reference

Level (CTRL) indicates how much of the chemical adversely affects human health while the dilution/attenuation factor indicates how easily the chemical could leach into ground water. However, it is established that by the time the chemical reaches the ground water, it will be diluted by at least a factor of 100. Thus, the levels set by the "Toxicity Characteristic" rule were determined by multiplying the health-based number by a dilution/attenuation factor of 100.

Syncrude Coke

During fluid coking operation in Syncrude plant, schematics of which are

Table 1: Toxicity characteristic constituents and regulatory levels.

Constituent	Chronic toxicity reference level (ppm)	Regulatory level (ppm)
Arsenic	0.05	5.0
Barium	1.0	100.0
Cadmium	0.01	1.0
Chromium	0.05	5.0
Lead	0.05	5.0
Mercury	0.002	0.2
Selenium	0.01	1.0
Silver	0.05	5.0

shown in Fig. 1, bitumen previously separated from oil sands using the hot water separation process, is sprayed into the fluidized bed of the hot coke in the coker reactor. Part of the coke is being steam stripped and continuously withdrawn from the coker reactor and transferred to the burner for partial combustion.

As a result of combustion, the temperature of the coke is increased. The hot coke is then transferred back to the coker reactor as the source of heat for coking reactions. About 2000 tonne/day of the coke is being continuously withdrawn from the burner and transferred to the stockpiles. It can be estimated from the flow rates of the coke streams that most of coke particles will travel many times between the coker and the burner. The prolonged exposure of coke particles at these temperatures will result in the formation of graphite like structures. Such structures are known to have a low reactivity. Thus, it was observed that ignition of the coke particles occurred above 400 °C compared with about 250 °C for medium reactive coals (8). This suggests that self-ignition of Syncrude coke in the stockpiles can be ruled out completely.

It is also believed that metal-containing compounds in the coke are buried in the carbon matrix in such a way that they cannot be accessible by water. This ensures low leachability of the metals during stockpiling. Syncrude operates five coke cells of which #1 to 4 are filled and #5 is being currently filled. It is anticipated that elemental sulphur, which is another by-product of the Syncrude operation, could be stockpiled on top of coke cells in the future.

EXPERIMENTAL

Coke samples

The coke samples were taken from five stockpiles, numbered 1 to 5, in proximity to the Syncrude plant. Proximate, ultimate and ash analyses of the samples are shown in Table 2, where numbers in brackets indicate years of the coke stockpiling. One sample of drainage water, taken from the coke cell #4, was also submitted for the evaluations.

Description of TCLP

All details of the method are given in the Federal Register Part II; EPA 40 CFR 261 et al. "Hazardous Waste Management System; Identification and Listing of Hazardous Waste; Toxicity Characteristics Revisions;

Final Rule. In the present work, representative samples were taken from bulk samples in accordance with RCRA guidelines using "Test Method for Evaluating Solid Waste" (SW-846). The Method 1311 TCLP of the Federal Register was used for the sample

apparatus. The resulting slurry was filtered using a Millipore 142 mm Hazardous Waste holder, containing a glass fibre filter (Nucleopore GFF, nominal pore size 0.7 µm). The TCLP extracts were treated according to the RCRA SW-846 guidelines.

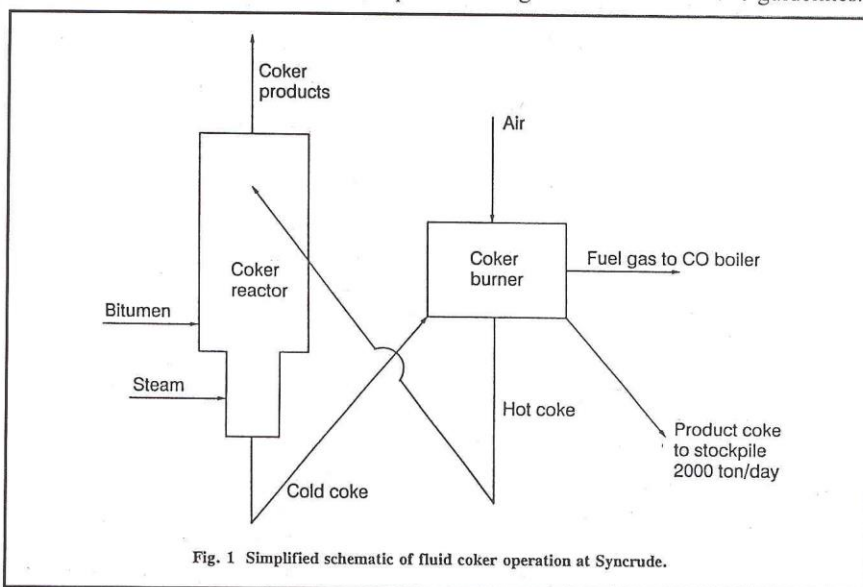


Fig. 1 Simplified schematic of fluid coker operation at Syncrude.

preparation. A preliminary evaluation, carried out on a 5 g sub-sample of each coke confirmed that sodium acetate is the most suitable extraction liquid. To simulate severe leaching conditions, two diluted H₂SO₄ extraction solutions having pH=2 and pH=4, were used. Subsequently, 100 g of each coke was extracted for 18 h in a rotary agitation

ANALYSIS OF EXTRACTS

Inorganic contaminants

SW-846 method 3020 was used for acid digestion of the extracts for metal analysis by ICP-AES (Jarred Ash model 9000 simultaneous spectrometer). In addition to the "Toxicity Characteristic" rule regulated metals such as Ag, As, Hg, Se, Ba, Cd, Cr and

Table 2 Analysis of Syncrude cokes from stockpiles.

Coke #	1	2	3	4	5
Years	(79/80)	(80/82)	(82/83)	(83/85)	(85-present)
Proximate, wt. %					
Moisture	0.44	0.60	0.50	0.69	0.25
Ash	5.40	7.21	5.18	7.52	4.81
Volatiles	4.85	5.11	6.23	6.10	4.99
Fixed carbon	89.31	87.08	88.09	85.69	89.95
Ultimate, wt. %					
Carbon	82.73	80.73	81.80	80.94	83.74
Hydrogen	1.72	1.63	1.66	1.56	1.77
Nitrogen	1.75	1.70	1.98	1.73	2.03
Sulphur	6.78	6.63	6.84	6.15	6.52
Oxygen	1.18	1.50	2.04	1.41	0.88
Ash composition					
SiO ₂	38.80	50.06	41.60	41.26	37.64
Al ₂ O ₃	24.35	20.94	24.22	24.94	24.23
Fe ₂ O ₃	9.72	8.18	9.26	12.14	11.42
TiO ₂	3.64	2.86	3.25	4.84	4.63
P ₂ O ₅	0.25	0.21	0.23	0.35	0.40
CaO	4.26	2.58	4.20	1.63	2.94
MgO	1.62	1.29	1.44	1.40	1.46
SO ₃	3.59	2.73	2.65	1.87	2.88
Na ₂ O	1.51	1.17	1.57	1.16	1.67
K ₂ O	1.83	1.78	1.83	1.93	1.72
BaO	0.20	0.15	0.07	0.14	0.09
SrO	0.11	0.06	0.09	0.06	0.11
V ₂ O ₅	4.46	3.20	4.86	3.21	4.94
NiO	1.08	0.80	1.16	0.82	1.24
MnO	0.26	0.21	0.25	0.29	0.27
Cr ₂ O ₃	0.08	0.05	0.08	0.08	0.09
LOF	2.90	2.30	1.82	2.50	2.62
SUM	98.66	98.58	98.57	98.63	98.35

Coke leachate, cont'd.

Table 3 Content of elements in cokes (ppm).

COKE #	1	2	3	4	5
Elements					
Arsenic	18	10	10	14	14
Barium	61	48	38	73	46
Cadmium	0.05	0.06	0.05	0.08	0.05
Chromium	19	20	18	25	18
Lead	11	11	11	15	12
Mercury	(0.006)	(0.006)	(0.006)	(0.006)	(0.006)
Selenium	1.5	1.3	1.7	1.9	1.3
Silver	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
Beryllium	0.5	0.5	0.4	0.7	0.5
Boron	12	12	10	18	11
Calcium	1892	1486	1657	941	1092
Cobalt	14	13	13	17	12
Copper	10	9	8	19	12
Iron	4138	4396	3538	6721	4095
Magnesium	603	619	497	698	456
Manganese	131	132	111	194	111
Molybdenum	73	66	66	102	88
Nickel	517	475	496	520	498
Phosphorus	93	86	75	136	94
Potassium	1011	1204	894	1358	768
Sodium	703	698	568	699	625
Strontium	65	47	50	51	57
Tin	(28)	(24)	(26)	(26)	(26)
Titanium	1400	1372	1150	2367	1458
Vanadium	1766	1599	1713	1662	1639
Zinc	14	14	13	25	20
Halogens					
Chlorine	19	45	13	32	74
Fluorine	11	10	17	12	10

Pb, 20 other elements were also determined. SW-846 method 7470 was used to prepare samples for determining of Hg by cold vapour atomic absorption (AA). Methods 7061 and 7741 were used for sample preparation for determination of As and Se, respectively, by hydride generation AA. A Perkin-Elmer 500 AA spectrometer, equipped with a MHS-20 Mercury/Hydride system was used for determining the three regulated constituents.

Volatile organics

The leachates from the TCLP extraction were analyzed for a series of polynuclear aromatics. The procedure used was the adaptation of the EPA Method 525.1. This procedure was modified to use a fused silica capillary column with a flame ionization detector as developed by Supelco Corporation in conjunction with EPA. The ENVI-18 solid phase extraction cartridges are a specially cleaned organic phase, an improvement to the original phases used in EPA 525.1 development. Sensitivity of the method was confirmed by the analysis of known amounts of several polynuclear compounds. The average level of detection was estimated to be 2.1 ppm.

RESULTS AND DISCUSSION

All results shown in brackets in Tables 3, 4 and 5 indicate the element is lower than the value listed. For example, the concentrations of lead and cadmium for all leachates listed in Table 4 are lower than 0.003 and 0.001 ppm, respectively.

Characterization of cokes

Proximate and ultimate analyses (Table 2) indicate that the composition of the samples exhibited little change over the years. Interestingly enough, rather low oxygen content, in spite of a prolonged weathering, indicates a resistance of the coke to oxidation. In similar situations, the uptake of oxygen by coal can be significant. This observation confirms a low prob-

ability of self-ignition of the coke samples (8).

The content of elements including the regulated elements (Table 1) and halogens in the coke samples is shown in Table 3. Compared with other carbonaceous solids, e.g., some coals, these values are low. For example, there is no detectable mercury content. The content of halogens is low as well. Relatively high contents of vanadium, nickel and titanium are typical for cokes derived from bitumen. It is expected that at least vanadium and nickel could be added to the list of the regulated metals in the future.

Leachability of Inorganic Elements

Results on leachability of the cokes are shown in Table 4. Mercury is not shown in Table 4. This analysis was not performed because no mercury was detected in the cokes. Also, it can be calculated from the results in Table 3 and volume of the leaching solutions used for TCLP that even if all cadmium and selenium present in cokes were leached out, their amounts in leachates would be significantly lower than their regulatory levels. It is quite obvious that a total leaching of these metals from coke is impossible to achieve. Thus, based on the regulatory levels of the regulated elements (Table 1), all five samples of the coke can be classified as virtually non-leachable. Concentrations of the elements which may be regulated in the future, i.e., vanadium, nickel, zinc, beryllium, copper, strontium, cobalt and other are also low.

The results on leachability performed for pH=2 and pH=4 as well as for deionized water are shown in Table 5. The leachate which was spiked by some priority elements is also included to indicate the reliability of the method. All currently regulated elements were unaffected by increasing the severity of leaching, i.e., changing pH from about 7 to 2. It is emphasized that the pH=2 represents a very severe environment. It is unlikely that such an environment can be encountered in stockpiles. The concentrations of iron, nickel, vanadium and manganese in the leachate obtained at pH=2 were significantly higher than those at pH=4, but still very low to be of any concern.

Leachability of Volatile Organics

No organic substances could be detected in the leachates in spite of a high sensitivity of the instrument employed. Thus, little difference was observed between the trace of the extract from the extraction of the deionized water (blank) and that of the leachates. The only peaks observed were the same as those of trace amounts of

Table 4 Analysis of leachates (ppm).

COKE #	1	2	3	4	4 SPIKE	5
Regulatory Level						
Arsenic	5	(0.23)	(0.23)	(0.23)	(0.23)	1.97
Barium	100	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)
Cadmium	1	(0.001)	(0.001)	(0.001)	(0.001)	1.55
Chromium	5	(0.016)	(0.016)	(0.016)	(0.016)	1.79
Lead	5	(0.003)	(0.003)	(0.003)	(0.003)	1.81
Mercury	0.2	ND	ND	ND	ND	ND
Selenium	1	(0.005)	(0.005)	(0.005)	(0.005)	(0.005)
Silver	5	(1.0)	(1.0)	(1.0)	(1.0)	(1.0)
Beryllium		(0.004)	(0.004)	(0.004)	(0.004)	(0.004)
Boron		(0.09)	(0.09)	(0.09)	(0.09)	(0.09)
Calcium	12		3	17	7	1
Cobalt		(0.04)	(0.04)	(0.04)	(0.04)	(0.04)
Copper		(0.03)	(0.03)	(0.03)	(0.03)	(0.03)
Iron		(0.07)	(0.07)	0.09	(0.07)	(0.07)
Magnesium	2.3	0.4	3.8	1	1	0.1
Manganese	0.11	0.02	0.17	0.06	0.06	0.06
Molybdenum	(0.017)	(0.017)	(0.017)	(0.017)	(0.017)	(0.017)
Nickel	0.028	0.042	0.018	0.043	0.033	0.068
Phosphorus	(0.29)	(0.29)	(0.29)	(0.29)	(0.29)	(0.29)
Potassium	0.24	(0.18)	0.31	(0.18)	0.25	(0.18)
Strontium	(0.15)	(0.15)	(0.15)	(0.15)	(0.15)	(0.15)
Tin	(1.06)	(1.06)	(1.06)	(1.06)	(1.06)	(1.06)
Titanium	(0.05)	(0.05)	(0.05)	(0.05)	(0.45)	(0.45)
Vanadium	0.11	0.34	0.07	0.47	0.47	0.08
Zinc	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)	(0.05)
ND - Not determined.						
4SPIKE - Leachate 4 was spiked with 2 ppm of As, Pb, Cr and Cd.						

Table 5 Effect of pH on leachability (ppm).

PH	Regulatory Level	Water	PH 4	PH 2	Drainage
Elements					
Arsenic	5	(0.23)	(0.23)	(0.23)	(0.23)
Barium	100	(0.05)	(0.05)	(0.05)	(0.05)
Cadmium	1	(0.001)	(0.001)	(0.001)	(0.001)
Chromium	5	(0.016)	(0.016)	(0.016)	(0.016)
Lead	5	(0.003)	(0.003)	(0.003)	(0.003)
Mercury	0.2	ND	ND	ND	ND
Selenium	1	(0.005)	(0.005)	(0.005)	(0.005)
Silver	5	(1.0)	(1.0)	(1.0)	(1.0)
Beryllium		(0.004)	(0.004)	(0.004)	(0.004)
Boron		(0.09)	(0.09)	0.28	1.5
Calcium		(0.11)	0.7	1.3	35
Cobalt		(0.04)	(0.04)	(0.04)	(0.04)
Copper		(0.03)	(0.03)	(0.03)	(0.03)
Iron		(0.07)	(0.07)	0.09	1.6
Magnesium		(0.05)	0.1	0.3	16
Manganese		(0.01)	0.03	0.16	(0.07)
Molybdenum		(0.017)	(0.017)	(0.017)	0.7
Nickel		(0.018)	0.029	0.16	(0.018)
Phosphorus		(0.29)	(0.29)	(0.29)	(0.29)
Potassium		(0.18)	(0.18)	(0.18)	4.2
Strontium		(0.15)	(0.15)	(0.15)	0.3
Tin		(1.06)	(1.06)	(1.06)	(1.06)
Titanium		(0.05)	(0.05)	(0.05)	(0.05)
Vanadium		0.04	0.03	0.55	(0.03)

ND - Not determined.

contaminants detected in the extraction agent (methylene chloride). It is emphasized that the change of pH (from about 7 to 2) had no effect on the leachability of the organic constituents. Thus, it may be concluded with certainty that, with respect to the leachability of organic constituents, all tested samples of coke are virtually non-leachable under

all conditions employed during the analysis. The submitted sample of the drainage water was also analyzed. In this case, a single peak representing an unknown substance in quantities smaller than 1 ppm was found. No effort was made to identify this peak. This single peak was not found in any leachate. Nevertheless, the content of this compound is very low and may be well below regulatory limits.

Conclusions

The present results confirm that the coke produced during the fluid coking operation in Syncrude is virtually non-leachable residue, therefore its disposal in landfills poses no hazard to the environment and underground waters. In view of the stringent environmental regulations, processes which can convert heavy feedstocks to liquid fuels without generating solid hazardous wastes are considered to be the processes of the future (9). The fluid coking process in Syncrude is one of such processes.

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