A Canadian Solution for Management of Mixed Liquid Waste – 13384

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ABSTRACT

Mixed liquid wastes (MLW) from Canadian nuclear facilities consist of solvents, PCB (Poly Chlorinated Biphenyls) and non-PCB contaminated oils and aqueous wastes. Historically, MLW drums were shipped to a licensed US facility for destruction via incineration. This option is relatively expensive considering the significant logistics and destruction costs involved. In addition, commercial waste destruction facilities in US cannot accept PCB wastes from non-US jurisdictions. Because of this, Kinectrics has recently developed a novel and flexible process for disposing both PCB as well as non-PCB contaminated MLW within Canada. This avoids the need for cross-border shipments which significantly reduces the complexity and cost for waste disposal. This paper presents an overview of the various approaches and activities undertaken to date by Kinectrics for successfully processing and disposing the MLW drums. A summary of the results, challenges and how they were overcome are also presented.

INTRODUCTION AND BACKGROUND

Historically, Mixed Liquid Waste (MLW) drums originating from Canadian nuclear facilities were shipped to a licensed US facility for destruction via incineration. This option is relatively expensive considering the significant logistics and destruction costs involved. In addition, restrictions on export of PCB containing wastes to the US also apply. Hence, some wastes simply could not be treated via this pathway. There was, therefore, a need to develop a wholly Canadian solution for disposing MLW.

Kinectrics has recently developed a flexible process for disposing of both PCB and non-PCB contaminated MLW within Canada. The approach avoids the need for cross-border shipments, thus significantly reducing the complexity and cost for waste disposal. The process has been successfully implemented on two projects.

Project-1 involved approximately 50 aqueous, oil and solvent MLW drums originating from a Canadian nuclear utility. The solvents consisted of petroleum based distillates, aliphatic hydrocarbons and aromatic hydrocarbons. The oils consisted of lubes and oily water emulsions, five of which were also contaminated with PCBs. The radioactivity in the wastes was principally due to cobalt-60, cesium-137 and tritium.

Project-2 involved 43 legacy radioactive, PCB contaminated oil/solvent waste drums that had accumulated over several years at a non-utility nuclear site. As a result of drum integrity concerns, the wastes were transferred into new drums before shipment to Kinectrics. The transfer, however, generated an additional 43 empty drums containing heels.

The initial work carried out on Project-1 has been presented previously [1]. This paper presents an overview of the work undertaken to date to successfully process and dispose MLW drums. A summary of the results and the challenges overcome are presented.

OVERALL APPROACHES FOR DISPOSAL OF MIXED LIQUID WASTES

The various approaches developed for disposal of MLW were as follows:

1. Conditional Clearance

Several MLW drums could potentially be conditionally cleared through the application of the Pathways Analysis (PA) methodology [2]. The Canadian Nuclear Safety Commission (CNSC) requires that an application for conditional release of radioactive waste to unlicensed facilities be based on an assessment of the associated dose impacts to workers and members of the general public; exposure to the critical individual must be limited to 10 μSv per annum [2, 3]. Based on Pathways Analysis, qualifying waste drums can potentially be shipped for incineration and disposal at a conventional hazardous waste facility. The Pathways Analysis performed involved the following steps:

- Establish waste processing and final disposal path for each type of waste,
- Gather input information for dose calculations,
- Estimate the dose associated with transportation and for incineration/disposal of waste.

Pathways Analysis reports were prepared for both projects. However, only the Project-1report was submitted to CNSC (Canadian Nuclear Safety Commission) for concurrence. Part way through the implementation of the Project-1 PA report, the approach was abandoned because of heightened concerns with radioactivity arising from the events at Fukushima - hazardous waste destruction sites who hitherto had accepted the wastes, declined to do so anymore. For this reason and because of lack of support from the licensing group in the client's organization, the PA report for Project-2 was not submitted to the CNSC for their concurrence.

During implementation of the PA report for Project-1, Kinectrics, for good measure and consistent with ALARA principles, undertook simple processing to reduce the easily removed radioactivity present in the wastes before shipping the wastes to conventional hazardous waste destruction facilities.

2. Unconditional Clearance

In this approach the MLW is processed using various unit operations such as filtration, phase separation, centrifugation, treatment with sorbents as well as other novel and proprietary treatment methods developed at Kinectrics to reduce radionuclide activity levels below their unconditional clearance criteria (see Table 1). The processed waste is then destroyed at a conventional hazardous waste facility.

Table 1: Unconditional Clearance Criteria

Radionuclide	Criterion (Bq/kg)
(β, γ) activity	1E+02
H-3	1E+05
U-235	1E+03
U-238	1E+03

3. Waste Solidification

Solidification was developed as a back-up option for cases where wastes cannot be conditionally or unconditionally disposed. Solidified wastes are returned to the waste generator for storage and final disposal. Because of the increase in volume experienced due to solidification, this was the least preferred option.

Initially, in Project-1, only selected drums with activity exceeding self-imposed threshold levels of radioactivity were solidified even though Pathways Analysis showed that the drums met conditional release criteria; this was done for ALARA reasons. Subsequently, because of vendor non-acceptance issues and schedule pressures, solidification was implemented for all the remaining waste drums. In Project-2, only separated non-PCB contaminated liquid waste phases with radionuclide concentrations above free release criteria were solidified.

4. Cleaning of Empty PCB Contaminated Drums

Following removal of the heels, the drums were cleaned to achieve the regulatory PCB surface contamination criterion of 10 μg/100 cm^2 [4]. They were then returned to the generator as radioactive waste for further volume reduction and recycling. Initially, a triple rinse procedure [4] was followed; this was subsequently replaced by a simpler solvent rinse procedure to reduce secondary waste generation.

KINECTRICS' FACILITY FOR PROCESSING MLW

MLW processing is carried out within Kinectrics Radioactive Laboratory which has been granted a Waste License by the CNSC. Kinectrics' also has been granted the following approvals from the Ontario Ministry of the Environment (MOE):

- Certificate of Approval (Air & Noise) [5]
- Provisional Certificate of Approval (C of A) for a Waste Disposal Site [6-8],

The Approval for a Waste Disposal Site permits Kinectrics to receive, process and transfer liquid industrial wastes and solids or liquid hazardous wastes. Up to 20 drums of wastes encompassing over 25 different MOE waste classes can be received and processed at any time subject to a maximum of 200 drums per year. The wastes may contain up to 15,000 ppm PCBs. All air emissions are required to be appropriately scrubbed prior to release. At present, the wastes may originate only from licensed facilities in Ontario.

Shipment of contaminated wastes, to and from Kinectrics, is carried out by qualified shippers/brokers as per requirements of Transport of Dangerous Goods and Canadian nuclear regulations. In addition, transportation of PCB contaminated wastes is carried out as per MOE Director's Instructions (Regulation 362).

Key equipment utilized for processing the wastes are shown in Figure 1.

CHARACTERISTICS OF PROJECT-1 and PROJECT-2 MIXED LIQUID WASTES

Representative samples from the MLW drums were obtained using Coliwasa samplers and then characterized as follows:

- Inventory and visual examination
- Physico-chemical characterization (pH, flash point, viscosity, PCB, elemental etc.)
- Radiochemical characterization (gamma, H-3, C-14 and other Difficult-to-Measure radionuclides, gross alpha and beta)

Project-1 Wastes

The wastes typically had multiple phases as well as suspended solids and/or sediments. Table 2 summarizes their physico-chemical characteristics and Table 3, their overall radiochemical characteristics. Key radiochemical contaminants were typically Co-60, Cs-137 and H-3. Following radiochemical characterization, 17 out of the 69 drums (see Table 3) were found to be free releasable and hence shipped directly by the client for disposal at a hazardous waste facility.

Table 2: Physico-Chemical Characteristics of Project-1 Wastes

Flash Point	> 60^0C
pH	3.5-11.3
PCBs*	99-9300 ppm
Toxic Elements	Up to 12,000 ppm Pb, As, Cr, Cd, Hg

* PCBs present only in 5 oil drums

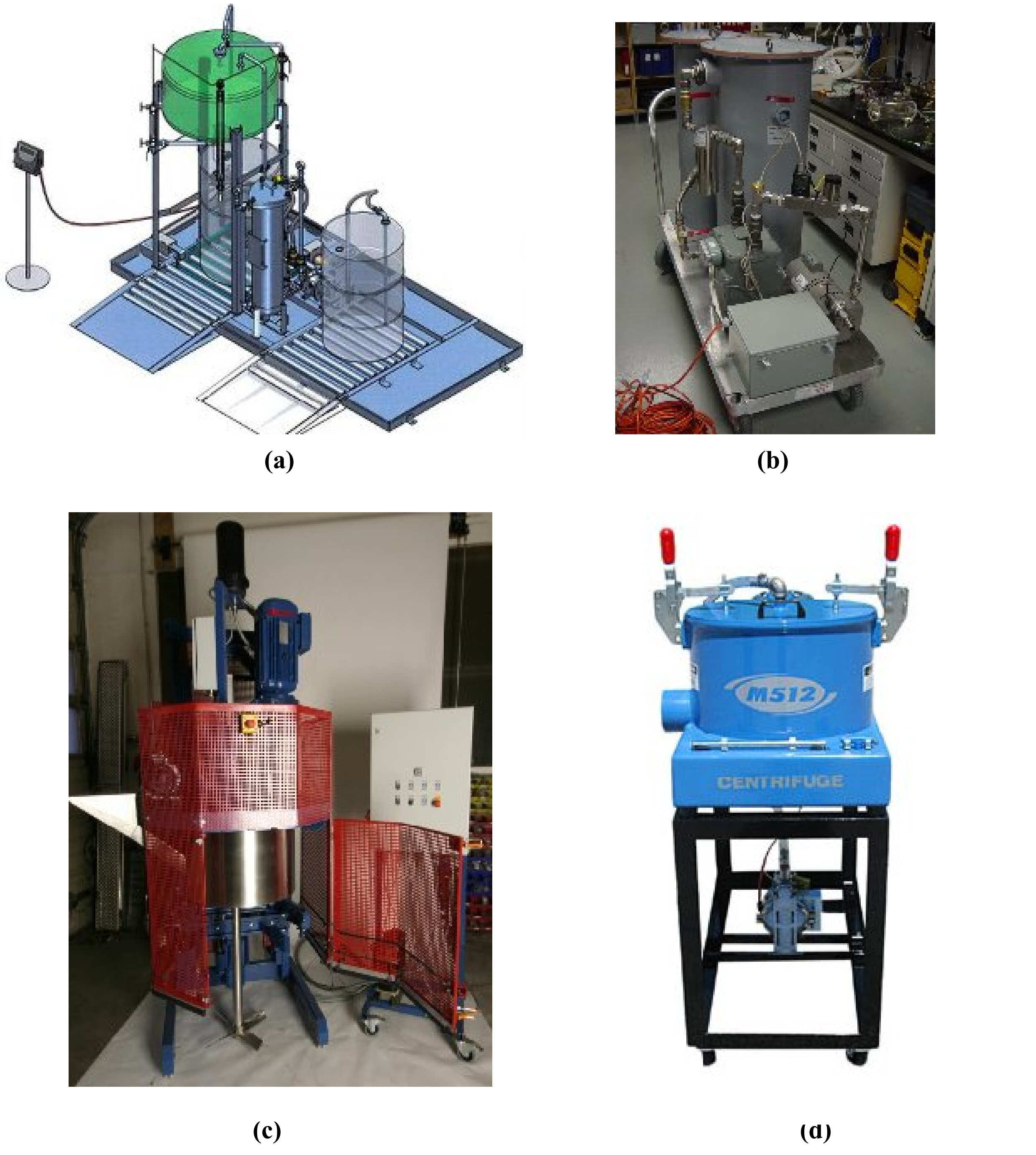

Figure 1: Key Processing Equipment (a) Skid for Filtration and Phase Separation of MLW, (b) Skid for Scrubbing Emmisions, (c) Liquid Waste Solidification System, and (d) Centrifugation System

Table 3: Overall Radiochemical Characteristics of Project-1 Wastes

Type of MLW	No. of drums	H-3 activity (nCi/Kg)			(β, γ) Activity (nCi/Kg)		
		Min.	Max.	LM*	Min.	Max.	LM*
PCB oil	5	127	1.7E+04	1470	0.09	4.2	0.42
Non-PCB oil	5	20	1.5E+06	7365	0.52	139.2	4.6
Aqueous	8	2270	3.4E+05	1.6E+05	0.09	24.2	1.3
Solvent	51	<0.2	3.3E+08	425	0.04	3110	1.0

* LM indicates Log or Geometric Mean.

Project-2 Wastes

Table 4 presents a summary of the overall characteristics of the PCB contaminated Project-2 MLW. These also represent the characteristics of the heels contained in the 43 empty drums also received. Note the following:

- The bottom aqueous phase contained PCBs substantially below the Ontario Ministry of Environment (MOE) 50 ppm limit for PCB wastes;

- Tritium and gamma activity preferentially partitioned into the bottom aqueous phase. For most drums, the overall tritium and gamma activity levels were below their respective clearance levels.

- While levels of U-235 appeared to be generally less than 1000 Bq/kg, those of U-238 exceeded this level in most instances (clearance levels for both U-235 and U-238 are 1000 Bq/kg).

Table 4: Overall Characteristics of PCB Contaminated Project-2 Wastes

Number of Drums	43
Waste Contents	Top Phase: Oil/Solvent; Bottom Phase: Aqueous 11 drums contained 100% oil; 32 drums contained 15-87% aqueous phase Most drums had visible suspended solids and/or sediments.
Volume of Waste	Top Phase: 4.3 m^3 , Bottom Phase: 2.8 m^3
Flash point	90-236^{0}C
pH	4-8
PCB Content	Top Phase: 36 (55)-8360 ppm; Bottom Phase: < 2 ppm generally
Tritium Content	Top Phase: <300-5300 Bq/kg (most drums); maximum 2.1E+07 Bq/kg Bottom Phase: <300-1.3E+04 Bq/kg (most drums); maximum 3.9E+10 Bq/kg
Gamma Activity	Top Phase: Co-60 up to 10 Bq/kg; Cs-137 up to 480 Bq/kg; Bottom Phase: Co-60 up to 305 Bq/kg; Cs-137 up to 1.4E+05 Bq/kg;
U-235	Top Phase: 5.4E+05 Bq; Bottom Phase: 4.0E+06 Bq; Total: 4.5E+06 Bq (56.3 g)
U-238	Top Phase: 1.4E+07 Bq; Bottom Phase: 5.8E+07 Bq; Total: 7.2E+07 Bq (5700 g)

EVALUATION OF PROCESSING OPTIONS

Bench scale studies were carried out to assess the feasibility of selected processing options, such as phase separation, filtration, sorption/treatment with solid sorbents (e.g. IX resins and clays) and waste solidification. Some of these investigations were of a scoping nature while others were more detailed. Key outcomes of these investigations are outlined below:

- Filtration (5 µm) generally was found to significantly reduce (β, γ) activity and levels of uranium isotopes. In specific cases, it also reduced H-3 and C-14 content.
- Because of preferential partitioning of tritium into the bottom aqueous phases, phase separation simplified further processing of the top phase; the bottom aqueous phase containing most of the tritium could be solidified and disposed as radioactive waste.
- In general, all wastes could be solidified using a combination of Petroset and Petroset-II solidification agents from Fluidtech. A loading ratio of 4-6 lbs binder per gallon waste was sufficient in most cases. A homogenous waste form with no free liquid that passed the slump test was obtained. This option was employed only for non-PCB wastes.
- In several cases, activity levels could be reduced to unconditional clearance criteria using one or more of the following options:
  - ❖ Treatment with commercial clays (natural ion exchangers),
  - ❖ Polymeric mixed bed ion exchange resins
  - ❖ pH adjustment
- Following treatment, the added media along with sorbed activity was removed by centrifuging and filtration.
- In limited tests, removal of both H-3 and PCB contamination from oils was achieved using commercially available sorbents such as Florisil (US Silica) and Alumina (Dynamic Absorbents).

Based on the results of various bench scale tests, an assessment of the waste characteristics and the overall approach for processing and disposal of MLW described above, the key unit operations needed to process drum quantities of MLW were determined to be filtration, phase separation, centrifugation and solidification.

RESULTS

Table 5 summarizes the results achieved to date. For conditional clearance, minimal processing such as filtration and phase separation were carried to eliminate easily removable activity prior to shipment of the wastes for disposal. For unconditional clearance, additional processing was carried out using a suite of well-known and proprietary methods so that the wastes could be sent to a conventional hazardous waste facility for destruction. Note the following:

Table 5: Summary of Activities

Project	Type of MLW	Number of Drums to Date		
		Conditionally Cleared	Unconditionally Cleared	Disposed as Radioactive Waste
1	PCB oil	5	-	-
	Non-PCB oil	1	-	2*
	Aqueous	-	-	8*
	Solvent	19	-	17*
2	PCB oil and solvents	-	41	-
	PCB contaminated empty drums	-	-	29

*solidified.

- As shown in Table 5, 25 Project-1 drums in total were processed for Conditional Clearance and 27 drums were solidified. Phase separation was performed only when H-3 in the bottom aqueous phase was over 10 times its free release criteria of 1E+05 Bq/Kg. Results for selected solvent drums, shown in Table 6, indicate the effectiveness of H-3 and (β, γ) activity removal by filtration.

Table 6: Selected Results from Filtration of Project-1 Solvents

Drum ID	Untreated Waste		Treated Waste		% Reduction in Activity	
	H-3 (Bq/kg)	(β, γ) (Bq/kg)	H-3 (Bq/kg)	(β, γ) (Bq/kg)	H-3	(β, γ)
KIN-001	1.1E+04	1.5E+02	3.2E+03	1.5E+01	70.4	90.4
KIN-002	7.6E+04	7.1E+01	4.7E+04	6.3E+00	38.1	91.0

- 41 Project-2 drums were processed using one or more of the following unit operations: centrifugation, filtration, phase separation, treatment with sorbents and pH adjustment. Table 7 presents results for select drums: while only results for uranium isotopes are given, the methods employed also lowered the concentrations of other radionuclides such as H-3 and C-14.

Table 7: Selected Processing Results for Project-2 Drums

Drum ID	Untreated Waste		Treated Waste	
	U-235 (Bq/kg)	U-238 (Bq/kg)	U-235 (Bq/kg)	U-238 (Bq/kg)
PCB-1	170	3100	0.43	7.76
PCB-2	86	1200	1.05	18.2
PCB-3	170	3100	0.43	7.76

- PCB contaminated Project-2 empty drums were prepared for cleaning by first cutting open their tops. After suctioning the heels, the drums were subjected to a triple rinse using a combination of agents such as transformer oil, degreaser solutions and organic solvents (e.g. xylene). Both the internal and the external surfaces of the drums were contaminated and hence cleaned. To determine residual PCB contamination levels, the cleaned surfaces were swiped (swipe area 100 cm^2) using a hexane soaked gauze which was then analyzed. In cases where the PCB surface contamination exceeded 10 μg/100 cm^2, additional cleaning was carried out. The cleaned drums were returned to the generator as solid radioactive waste for further volume reduction and recycling. Selected results are presented in Table 8.

Table 8: Selected Results for Cleaned PCB Contaminated Project-2 Drums

Drum ID	PCB Concentration in Heel (ppm)	Surface Contamination after Cleaning (μg/100cm^2)
PCB-4	2320	0.7
PCB-5	1280	0.8
PCB-6	89	4.2
PCB-7	820	7.0
PCB-8	61	0.4

CHALLENGES AND LESSONS LEARNT

The initial approach for disposal of the MLW was to conditionally clear waste drums after undertaking (for ALARA reasons) minimal processing such as filtration and phase separation. Such wastes were sent for incineration at a conventional hazardous waste facility. Waste drums with relatively elevated radionuclide concentrations were solidified, even though they met the criteria for conditional clearance. Midway through Project-1, as a result of the Fukushima nuclear accident and the resulting heightened concerns with radioactivity, the hazardous waste vendor who hitherto had accepted the low activity wastes for destruction, declined to do so any more. In the absence of a binding long term waste services agreement with the vendor, unanticipated project delays occurred and eventually led to the exercising of the solidification option (with the client's agreement) for the remaining Project-1 drums.

To avoid similar difficulties in the future, Kinectrics initiated the development of processing methods to permit unconditional clearance of the wastes. Additional processing equipment such as the centrifuge was acquired. Kinectrics also entered into a binding long term waste services agreement with an alternate vendor with greater familiarity and understanding of low level radioactivity.

Limited tests to lower the radioactivity in the waste below unconditional clearance criteria were carried out on selected Project-2 drum samples using commercial sorbents such as ion exchange resins and clays. While the tests were successful on the bench scale, mixed results were obtained in drum scale processing. This was attributed to inhomogeneity of the waste, inadequate mixing and the inability to effectively sample the bottom 0.5-1 inch layer in a drum using a Coliwasa sampler. Typically, this bottom layer contained a disproportionately large fraction of the radioactivity in the drum. In order to address this issue, every drum was re-sampled upon receipt at Kinectrics and bench scale tests were repeated and modified as necessary to ensure successful drum scale processing.

The empty Project-2 drums were expected to be PCB contaminated only on their internal surfaces. However, a routine check showed that the external surfaces of several drums were also contaminated. Therefore, both the internal as well as the external surfaces of each drum were cleaned. Cleaning the drum surfaces presented some handling challenges because the drums were severely corroded. Initially, a triple rinse (oil/detergent/water) procedure was followed which proved ineffective and generated excessive secondary waste; this was subsequently replaced by a more effective solvent rinse procedure which also reduced secondary wastes.

CONCLUDING REMARKS

The work to date has set the stage for the future management of mixed liquid wastes originating from various Canadian nuclear sites exclusively based on disposal within Canada. All key technical, regulatory and logistical issues pertaining to the receipt, handling, processing and shipment of the wastes have been addressed. Kinectrics has the required MOE approvals for processing wastes within its Radioactive Facility. Equipment has been installed for processing of incoming wastes. Since late 2010, over 120 drums from various Canadian nuclear facilities have been successfully disposed.

In the aftermath of the Fukushima incident in March 2011, significant challenges arose with regards to disposal of MLW via the conditional clearance approach. Kinectrics overcame these challenges by developing innovative treatment methods to render the MLW suitable for final disposal via the unconditional clearance approach. Another alternative used for non-PCB waste was solidification followed by disposal as radioactive waste.

REFERENCES

1. Suryanarayan, S., Husain, A., Grey, M., Husain, S., Disposal of Bruce Power's Mixed Liquid Wastes, WM 2011 Conference, March 7-11, 2011, Phoenix, AZ.

2. Canadian Standards Association, "Guidelines for the exemption or clearance from regulatory control of materials that contain, or potentially contain, nuclear substances", N292.5-11 Standard (July, 2011).

3. Canadian Nuclear Safety Commission, "Radiation protection requisites for the exemption of certain radioactive materials from further licensing upon transferral for disposal", Regulatory Document R-85, August (1989).

4. Protocol for Sampling and Testing at PCB Storage Sites in Ontario, Prepared by: Technology Standards Section, Standards Development Branch, Ontario Ministry of the Environment, ISBN 0-7794-0020-8PIBS, January 2000.

5. Certificate of Approval-Air, Number 3216-842LAZ issued by Ontario Ministry of Environment, April 19 (2010).

6. Provisional Certificate of Approval-Waste Disposal Site, Number 4059-84YJY4 issued by Ontario Ministry of Environment, August 13 (2010).

7. Amendment to Provisional Certificate of Approval-Waste Disposal Site, Number 4059-84YJY4 issued by Ontario Ministry of Environment, July 12 (2011).

8. Amendment to Environmental Compliance Approval, Number 4059-84YJY4 Notice No.2, issued by Ontario Ministry of Environment, July 24 (2012).