

A NOVEL CANADIAN SOLUTION FOR MANAGEMENT OF PCB MIXED WASTE

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Abstract

Historically, options for management of Mixed Wastes (both solid and liquid) contaminated with Poly Chlorinated Biphenyls (PCB) have been limited in Canada. In addition, licensed waste destruction facilities in US cannot accept PCB mixed wastes from non-US jurisdictions. Because of this, Kinectrics developed an innovative turnkey solution for processing and disposal of PCB mixed waste within Canada. In the past, over 100 drums of PCB solid and liquid mixed wastes were successfully processed and disposed using a suite of proprietary processes developed by Kinectrics.

More recently, Kinectrics was contracted by a Canadian nuclear customer for disposal of its remaining PCB mixed waste inventory. The complexities associated with these drums presented significant processability challenges. This paper presents an overview of the various approaches developed by Kinectrics for successful processing and disposal of these challenging solid and liquid PCB mixed wastes within Canada. A summary of the results, challenges faced and how they were overcome will be presented.

1. Introduction and Background

1.1. Historical perspective

Mixed wastes (contain both radioactive as well as hazardous constituents) from Canadian nuclear facilities consist of solvents, Poly Chlorinated Biphenyls (PCB) and non-PCB contaminated oils, aqueous wastes and PCB contaminated solids. Historically, Mixed Liquid Waste (MLW) drums containing tritium (H-3) and other radionuclides were shipped to a licensed US facility for destruction via incineration. This option is relatively complex considering the logistics associated with cross-border shipments and the destruction costs (including H-3 surcharge). In addition, commercial waste destruction facilities in the US cannot accept PCB wastes or PCB contaminated mixed wastes from non-US jurisdictions.

1.2. Kinectrics' overall approach

Because of the limited disposal options available in Canada, Kinectrics had developed a flexible process for disposal of both PCB and non-PCB contaminated MLW within Canada [1-3]. This approach avoids the need for cross-border shipments, thus significantly reducing the complexity and cost for PCB and non-PCB contaminated MLW disposal. Since 2010, this process has been successfully implemented on several projects. The various approaches developed for disposal of mixed waste have been described in detail previously [1-3] and can be summarized as follows:

- **Conditional clearance:**Wastes can potentially be conditionally cleared through the application of the Pathways Analysis (PA) methodology (dose impact assessment) [4]. Based on PA, qualifying waste drums can potentially be shipped for incineration and disposal at a conventional chemical/hazardous waste facility.
- **Unconditional clearance:**In this approach, the MLW is processed to reduce radionuclide activity levels to below the unconditional clearance criteria outlined in the Canadian Nuclear Substances and Radiation Devices Regulation (NSRDR) [5]. The processed waste is then destroyed at a conventional hazardous waste facility.
- **Solidification:**This approach was developed as a back-up option for radioactive wastes which cannot be conditionally or unconditionally disposed. To exercise this option for PCB mixed waste, the wastes would first undergo a PCB destruction process to lower the PCB concentration in the waste to below provincial regulatory contamination criteria of <50 parts per million (ppm) [6]. Solidified wastes are returned to the waste generator (i.e. licensed nuclear facility) for storage and final disposal.
- **Clean-up of solid PCB mixed waste:**
Following removal of the heels (small amounts of liquid that cannot be easily pumped out), the drums can be cleaned to achieve the regulatory PCB surface contamination criterion of less than 10 micrograms (μg) per 100 square centimeter (cm^2) [6]. Cleaning of these drums was achieved by a triple rinse procedure that involved application of various commercially available chemicals/cleaning agents. In some cases, these cleaning processes also resulted in the drums meeting the unconditional clearance criteria and hence were disposed via conventional metal recycling. The drums that did not meet this criterion were then returned to the generator as radioactive waste for further volume reduction/recycling at a licensed facility.

1.3. Kinectrics' past experience

Since 2009, the work carried out at Kinectrics has set the stage for the future management of mixed wastes (aqueous, PCB contaminated oils and solids, non-PCB oils, solvents etc) originating from various Canadian nuclear sites with disposal pathways exclusively within Canada [1-3]. An overview of the various approaches and activities undertaken by Kinectrics during the period 2009-2012 for successfully processing and disposing several mixed waste drums has been reported previously [1-3]. Over 200 drums of mixed waste (including approximately 100 drums of PCB solid waste and MLW) were successfully processed at Kinectrics up to end of 2014.

Initially, conditional clearance was the preferred approach for processing MLW. Subsequently, in view of the client's preference to change MLW processing approach, Kinectrics developed innovative treatment methods to render the waste suitable for final disposal via the unconditional clearance approach [3,7]. Another alternative used for non-PCB MLW was solidification followed by disposal at a licensed nuclear facility.

1.4. Objective of current paper

More recently, Kinectrics was contracted by a Canadian nuclear customer for the disposal of the following PCB mixed waste inventory:

- Two drums of MLW containing complex mixtures of laboratory chemicals.
- Several drums containing heels that had been solidified using a commonly available universal sorbent (kitty litter/vermiculite).
- Several drums containing assorted metallic and non-metallic solid waste (includes gloves, plastic tubing, absorbent sheets, cardboard, small metallic pieces, glass etc.).

Processing these waste drums proved to be challenging due to the following:

- A range of process options successfully employed for unconditional clearance of PCB MLW in previous projects could not be employed for processing these waste streams due to the complexities associated with the liquid waste.
- Kinectrics' patented PCB destruction method (based on addition of sodium dispersion [8]) was ineffective due to the presence of chemical inhibitors in the liquid waste and could not be used on solid wastes.
- Conventional treatment chemicals (degreasers and other cleaning chemicals) used successfully in the past for cleaning up assorted solid waste were ineffective.

This paper presents an overview of the following:

- Processes developed and employed by Kinectrics to address the challenges outlined above.
- Results of large scale demonstration work undertaken to-date to successfully process and dispose liquid as well as solid PCB mixed waste.

2. Characteristics of PCB mixed waste

Characteristics of the MLW drums containing complex mixtures of laboratory chemicals, the drums with the heels, and the drums of other assorted solid waste are listed in Tables 1-3. Photos of assorted solid waste and one of the sorbent heels are shown in Figure 1.

Both of the MLW drums contained some suspended solids as well as sediments. Radiochemical characterization of both top and bottom phases of each drum were carried out. This included gamma spectrometry, H-3 analysis and measurement of Difficult-to-Measure (DTM) radionuclides namely, C-14, Ni-63, Sr-90, Fe-55 and alpha activity. In general, MLW wastes were found to be characterized by elevated levels of Am-241, Cs-137 and DTM radionuclides. PCB concentrations in the waste drums ranged from 1930 to 20200 ppm. Preliminary physico-chemical characteristics of both drums (e.g. solubility in oil and water, viscosity and density) combined with historic information, provided by the customer, indicated the presence of a complex mixture of various laboratory chemicals. Further characterization of the samples was then carried out by employing Gas Chromatography-Mass Spectrometry (GC-MS) analysis in order to identify individual compounds present in the various phases. The following major chemical components were identified in the waste samples based on mass spectral (MS) fit: trimethyl benzene, toluene, ethylbenzene, xylene, triethylphosphate, tributyl phosphate, substituted/derivatized naphthalenes, diethyl benzene, octanol and its isomers.

The sorbent wastes showed elevated levels of uranium isotopes (upto 1.3E6 Bq/Kg of U-238), while the PCB concentration in these drums ranged from 800 to 4040 ppm. Typical radionuclides

present in the solid waste were Co-60, Cs-137, U-235, U-238 and Nb-94. The PCB concentration of select solid waste samples varied up to a maximum of 328ppm (bulk contamination) and 120 µg/100cm² (surface contamination).

Table 1: Characteristics of MLW drums

	Drum-1		Drum-2	
	Top phase	Bottom phase	Top phase	Bottom phase
PCB (ppm)	10600	4300	20200	1930
Am-241 (Bq/Kg)	5120	11700	802	35900
Co-60 (Bq/Kg)	3.4	7.9	21	860
Cs-137 (Bq/Kg)	5700	13000	42	3400000
Eu-154 (Bq/Kg)	7.1	27	12	<100
Nb-94 (Bq/Kg)	2.2	<2	75	<500
Nb-95 (Bq/Kg)	27	<70	1.3	<1000
U-235 (Bq/kg)	120	395	150	3.04
U-238 (Bq/kg)	7500	29200	230	5.69
H-3 (Bq/kg)	3290	8500	296	183000
C-14 (Bq/kg)	1370	1100	19000	<100
Pu-238 (Bq/kg)	1010	3440	137	2870
Pu-239+240 (Bq/kg)	6410	15300	452	6830
Pu-241 (Bq/kg)	82300	113000	12500	196000
Ni-63 (Bq/kg)	125000	21600	9540	193000
Sr-90 (Bq/kg)	3210	15500	1300	253000
Fe-55 (Bq/kg)	77800	219000	18900	527000

Table 2: Typical characteristics of sorbent wastes

	PCB (ppm)	Co-60 (Bq/Kg)	Cs-137 (Bq/Kg)	U-235 (Bq/Kg)	U-238 (Bq/Kg)	C-14 (Bq/Kg)	H-3 (Bq/Kg)
Minimum	800	8	21.4	2670	133000	60.3	3910
Maximum	4040	386	155	92300	1320000	490	434000
Geometric Mean (LM)	2151	23	68	20681	509784	227	12323

Table 3: Typical characteristics of solid wastes

	PCB (ppm)	Co-60 (Bq/Kg)	Cs-137 (Bq/Kg)	U-235 (Bq/Kg)	U-238 (Bq/Kg)	Nb-94 (Bq/Kg)
Minimum	0.4	1.87	2.23	16.8	99.5	1.07
Maximum	328	28.9	257	8720	174000	8.21
Geometric Mean (LM)	24.4	4.8	10.9	327.7	2236.9	3.6

a. Metallic and plastic waste	b. Gloves	c. Cardboard
d. Chemical suits	e. Absorbent sheets	f. Sorbent (Kitty litter/vermiculite)

Figure 1: Examples of solid PCB mixed waste

Options available for processing mixed waste drums typically involve their conversion to non-mixed waste followed by final disposal. This can be achieved by either of the following two methods:

- Removal of radioactivity in the waste to unconditional clearance limits followed by disposal (via incineration) as hazardous waste.
- Destruction of PCB in the waste followed by solidification and disposal at a licensed nuclear facility.

An assessment of the analytical results described above and past experience, indicated the following with regards to the treatability of the PCB mixed waste via both of the above methods:

- Removal of radioactivity from the two MLW drums to unconditional clearance limits in an efficient manner would be challenging in view of the presence of large number of laboratory chemicals (including organic extractants) in the waste. Added to this complexity is the presence of a large variety of radionuclides (including those with low ionic potential such as Cs-137) in the wastes that are challenging to separate using conventional separation processes.
- The sorbent waste comprises of kitty litter/vermiculite. These universal sorbents typically comprise of natural clay that act as strong ion exchangers (for radionuclides). Also they are known to sorb PCBs as well as oil. Hence conversion of this mixed waste into non-mixed could be a challenge.
- Extraction of PCBs from the solid waste samples (especially cellulosic materials such as cardboard, plastics and absorbent sheets that would have bulk contamination) would be challenging. In case of metallic waste, the contamination would typically be isolated to the surface and hence easier to remove.

Overall, the analytical results indicated the need for evaluation of a range of process options prior to large scale processing of the PCB mixed wastes.

3. Evaluation of processing options

3.1. Processing of PCB contaminated MLW and sorbent waste

3.1.1. Evaluation of options for removal of radioactivity to unconditional clearance limits

A range of process options were evaluated previously for treatment of PCB contaminated MLW [1-3]. Some of these investigations were of a scoping nature while others were more detailed. In several cases, activity levels could be reduced to unconditional clearance criteria using a combination of one or more of the following options:

- Treatment with commercial clays (natural ion exchangers)
- Polymeric mixed bed ion exchange resins
- pH adjustment
- Centrifugation
- Filtration
- Phase separation

A series of bench scale tests were initially carried out on samples collected from the PCB contaminated MLW and sorbent waste drums. The objective of these tests was to evaluate various process options that were successful in the past (and listed above) as well as other commonly known treatment methods such as acid leaching/extraction to reduce activity levels in the MLW and sorbent waste samples to below unconditional clearance criteria. None of the above mentioned treatment methods were successful in removal of radioactivity in these waste streams to unconditional clearance limits. Processing these waste samples proved to be challenging due to the physico-chemical complexities associated with the waste.

3.1.2. Evaluation of options for PCB destruction followed by disposal as radioactive waste

Destruction of PCB in the MLW to below regulatory criteria followed by solidification and disposal as radioactive waste was then evaluated. Kinectrics had previously developed a patented PCB destruction process based on the addition of metallic sodium dispersion for destruction of PCB [8], a process which was originally developed for destruction of PCBs in relatively clean transformer oils. An assessment of the physico-chemical characteristics of both the PCB contaminated MLW as well as the sorbent waste indicated that Kinectrics' process for destruction of PCBs would need to be modified/enhanced in order to be effective. A generalized schematic representation of Kinectrics' process for management of PCB contaminated mixed waste is presented in Figure 2 below. Key process steps are as follows:

1. Dehydration of the MLW/sorbent-oil slurry to remove moisture and volatile constituents (required to avoid undesirable reactions with sodium).
2. Destruction of PCBs in the oily mixed waste using metallic sodium dispersion to destroy PCBs followed by quenching of unreacted sodium.
3. Solidification of resulting radioactive waste using various immobilization agents.

Figure 2: Kinectrics' process for treatment of PCB contaminated mixed liquid waste

A series of bench scale PCB destruction tests were first carried out on the MLW as well as the sorbent slurry. The top phases of MLW drums were processed as is. The bottom phases of both MLW drums were mixed (1:1 mixture) with other PCB MLW oil waste prior to PCB destruction. Typically, a 1:1 mixture of sorbent:non-PCB transformer oil was used for PCB destruction of sorbent mixed waste. Preparation of this sorbent-oil slurry mixture was required to facilitate PCB destruction. As expected, Kinectrics' original PCB destruction method was only partially effective due to the presence of recalcitrant contaminants in the waste that inhibit the interaction of metallic sodium with PCBs. Therefore, in order to improve the PCB destruction efficiency, an enhanced version of the destruction process was developed. Key features of this enhanced process

included application of small quantities of two chemicals (an organic peroxide and a radical initiator/reaction accelerator) for effective destruction of PCBs in the waste. The role of these chemicals is that they help destroy some of the reaction inhibiting recalcitrant contaminants in the waste and help accelerate the PCB destruction process. A small amount of de-foaming agent was also added in order to minimize foaming during the PCB destruction process. Excess sodium present after PCB destruction was quenched using water or isopropanol.

Following success of bench scale tests, the process was implemented on a drum scale. Select results from processing of MLW as well as sorbent waste drums are outlined in Table 4. Kinectrics' enhanced destruction process was successful in reducing the PCBs in both MLW as well as sorbent waste to well below regulatory criteria. The resultant radioactive waste was solidified using commercial clay type agents (Petroset and Petroset-II from FluidTech) prior to disposal. The process equipment used for PCB destruction, scrubbing of volatile organic emissions, and waste solidification are outlined in Figure 3.

Table 4: Selected processing results for MLW and sorbent waste drums employing Kinectrics' enhanced PCB destruction process

Waste type	Drum ID	Untreated waste	Processed Waste
		PCB (ppm)	PCB (ppm)
Mixed Liquid Waste (MLW)	Drum #1 top	10600	3.7
	Drum #2 bottom	1930	<2
Sorbent Waste	Sorbent #1	800	<2
	Sorbent #2	1540	<2

3.1.3. Processing and disposal of solid PCB mixed waste

In the past, solid PCB mixed waste such as empty drums and other metallic waste such as spill trays were subjected to a triple rinse process using a combination of agents such as transformer oil, commercial degreaser/cleaning solutions and organic solvents (for example xylene) [3]. Both the internal and the external surfaces of the drums that were contaminated were cleaned. To determine residual PCB contamination levels, the cleaned surfaces were swiped (swipe area 100 cm²) using a hexane soaked gauze which was then analyzed. In cases where the PCB surface contamination exceeded 10 µg/100cm², additional cleaning was carried out. The cleaned drums were returned to the generator as solid radioactive waste for further volume reduction and recycling.

In order to improve process efficiency and reduce amount of secondary waste generated as well as cost, Kinectrics developed an improved process for processing solid PCB mixed waste. At the heart of this process is the application of a commercial dry-cleaning solvent for clean-up of the waste. A schematic representation of Kinectrics' enhanced process for removal of PCB contamination in solid PCB mixed waste is presented in Figure 4. Key process steps are as follows:

PCB destruction reactor		Drum roller
Solvent recycler	Scrubber	Waste Solidification System

Figure 3: Key processing equipment

1. Sorting and size reduction of the waste to make it amenable to effective solvent rinsing.
2. Solvent rinsing to separate PCB from the solid waste.
3. Spent solvent from the above step is recovered to obtain PCB rich oily waste residue; clean solvent is recycled for additional rinsing steps as required.
4. Destruction of PCBs in the PCB rich oily residue from above step using Kinectrics' proprietary process.
5. Solidification of resulting radioactive waste using solidification agents in order to meet the nuclear waste site's Waste Acceptance Criteria (WAC).
6. The cleaned solid waste is dried prior to packaging.
7. The solidified waste from above step and cleaned solid waste (i.e. solid waste from original mixed waste drum that has undergone solvent cleaning process described above) is sent back to the licensed nuclear waste site.
8. Final wastes below free release criteria are disposed of conventionally instead of being returned to customer.

Figure 4: Kinectrics' process for treatment of PCB contaminated solid mixed waste

A series of bench scale PCB removal tests were carried out on segregated/size reduced solid mixed waste samples. Conventional cutting tools were employed for size reduction of the waste. Typically, 2-4 rinsing steps were required in order to remove PCB in the solid waste to below regulatory criteria for bulk or surface contaminated objects. Following the success of bench scale tests, drum scale processing was carried out. A drum roller (as shown in Figure 3) was employed for mixing of the size reduced solid waste with the dry cleaning solvent. The spent solvent was recycled using a commercial solvent recycler (shown in Figure 3) and reused. Select results from processing of solid mixed waste drums are outlined in Table 5. Kinectrics' enhanced PCB removal process was successful in reduction of PCBs in all of the solid wastes to below regulatory criteria.

Table 5: Select results for PCB contaminated solid mixed waste that were processed employing Kinectrics' enhanced PCB removal process

Waste Type	PCB concentration	
	Untreated waste	Processed Waste
Absorbent sheets	328 ppm	2.85 ppm
Cardboard and paper	210 ppm	0.07 ppm
Gloves	16.8 ppm	1.05 ppm
Surface contaminated objects (metals and glass)	Upto 120 µg/100cm ²	<0.17 µg/100cm ²

4. Concluding remarks

Since 2010, approximately 100 drums of PCB solid and liquid mixed wastes have been successfully processed and disposed of using a suite of proprietary processes developed by Kinectrics. More recently, Kinectrics was contracted by a Canadian nuclear customer for disposal of its remaining PCB mixed waste drum inventory. This specifically included two drums of MLW containing complex laboratory chemicals, several drums of sorbent and assorted solid (metallic as well as non-metallic) waste. The complexities associated with these drums presented significant processability challenges. A range of Kinectrics' process options successfully employed in previous projects for unconditional clearance of PCB mixed liquid waste [1-3] could not be employed for these waste streams. Likewise, Kinectrics' patented PCB destruction method based on addition of sodium dispersion [8] was ineffective due to the presence of chemical inhibitors in the liquid waste. Also, conventional treatment chemicals (degreasers and other cleaning chemicals) used successfully in the past for cleaning up assorted solid waste were found to be ineffective. In order to address these challenges, Kinectrics developed and successfully applied two enhanced treatment processes that specifically involved:

- PCB destruction process based on application of an organic peroxide and radical initiator.
- PCB removal process employing a commercial dry cleaning solvent followed by solvent recycling to minimize amount of secondary waste generated.

These enhanced processes were successfully used to process drum quantities of complex PCB mixed waste. The proven processes developed by Kinectrics for treatment of challenging PCB mixed waste described in this paper sets the stage for successful management of future PCB mixed waste arisings (for example from decommissioning activities) from the Canadian nuclear industry.

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