THE UNIVERSAL SEPARATION PROCESS (USEP): DEVELOPMENT AND DEMONSTRATION OF AN INNOVATIVE PROCESS FOR REMOVAL OF TRITIUM AND OTHER RADIONUCLIDES FROM MIXED LIQUID WASTE

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Abstract

Historically, oily Mixed Liquid Waste (MLW) drums containing Tritium 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 (e.g. Tritium surcharge). Because of this, Kinectricshad developed a novel and flexible process for disposing ofoily as well as other (solvents, aqueous etc.) MLW within Canada.This avoids the need for cross-border shipments and significantly reduces the complexity as well as cost for waste disposal. An overview of the various approaches and activities undertaken by Kinectrics during the period 2009-2013 for successfully processing and disposing several MLW drums has been reported previously [1-3].

Kinectrics was recently contracted by a Canadian nuclear customer for the disposal of its legacy MLW inventory (referred to as ProjectsA and B henceforth). The objective of these projects was to treat the various MLW drums in order to reduce the radionuclide concentration to below unconditional clearance criteria followed by disposal of the waste at a conventional chemical waste facility. A small amount of radioactive secondary waste (the captured radionuclides)was returned to the customer. Waste treatment processes used previously by Kinectrics for unconditional clearance of oily MLW were ineffective for treatment of legacy waste drums that were part of ProjectsA and B. Waste drums from Project-A were particularly challenging to process since H-3 was chemically associated with the oil backbone. To address these challenges, Kinectrics recently developed the novel and flexible Universal SEParation(USEP) process as a Canadian solution for disposal of problematic mixed liquid waste. This paper presents an overview of the USEP process and results of the process development as well as large scale demonstration work undertaken to date to successfully process and disposeof several MLW drums.

1. Introduction

1.1. Historical perspective

Mixed liquid wastes (MLW) from Canadian nuclear facilities consist of radioactive solvents, Poly Chlorinated Biphenyls(PCB)and non-PCB contaminated oils and aqueous wastes. Historically, oily MLW drums containing H-3 and other radionuclides were shipped to a licensed US facility for destruction via incineration. This option is relatively complex considering the significant logistics associated with cross-border shipments and the destruction costs (including substantial Tritium surcharge). In addition, commercial waste destruction facilities in US cannot accept PCB wastes from non-US jurisdictions.

1.2. Kinectrics' overall approach

In order to address the above mentioned challenges, Kinectrics has developed a flexible process for disposing 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 waste disposal.Since 2010, this process has been successfully implemented on several projects. The various approaches developed for disposal of MLW were as follows:

1.2.1. Conditional clearance

Several MLW drums could potentially be conditionally cleared through the application of the Pathways Analysis (PA) methodology [4]. 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 [4-5]. Based on Pathways Analysis, qualifying waste drums can potentially be shipped for incineration and disposal at a conventional chemical/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
- Submit PA report to Canadian Nuclear Safety Commission (CNSC) for concurrence

1.2.2. Unconditional clearance

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

Table 1: Unconditional clearance levels for various radionuclides expected in the waste

Radionuclides	Unconditional clearance levels (Bq/kg)
Am-241, Cs-137, Co-60, Pu-238 …Pu-241	1E+02
C-14, Cm-244, Sr-90, U-235, U-238	1E+03
H-3, Ni-63	1E+05
Fe-55	1E+06

1.2.3. 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 (i.e. licensed nuclear facility) for storage and final disposal. Because of the increase in volume experienced due to solidification, this is generally the least preferred option.

1.3. Kinectrics' past experience

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

Initially, conditional clearance was the preferred approach for processing MLW. However, in the aftermath of the Fukushima incident in March 2011, significant challenges arose with regards to disposal of MLW via the conditional clearance approach [3]. 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.Complex PCB waste drums that could not be unconditionally cleared were treated via a modified version of Kinectrics' proprietary PCB destruction process [6] prior to solidification and disposal as radioactive waste.

1.4. Objective of current paper

Kinectrics was recently contracted by a Canadian nuclear industry customer for the disposal of its accumulated/legacy MLW inventory (referred to as ProjectsA and B henceforth). Project-A involved several drums of oily MLW that contained large concentrations of H-3 and other radionuclides. Project-Bwas comprised several drums of legacy MLWcontaining mainly oils and oily sludges. Key radionuclides were U-235, U-238, C-14 and H-3. The objective of both these projects was to treat the various MLW drums in order to reduce the radionuclide concentration to below unconditional clearance criteria followed by disposal of the processed waste at a conventional chemical/hazardous waste facility. A small amount of radioactive secondary waste (the captured radionuclides) were returned to the customer.

A range of process options such as phase separation, filtration, pH adjustment, sorption/treatment with solid sorbents (e.g. IX resins and clays)etc., were successfully employed for unconditional clearance of MLW in previous projects carried out by Kinectrics [1-3]. However, these methods were ineffective for treatment of the legacy wastes that were part of Projects A and B.Waste drums from Project-A were particularly challenging to process since H-3 was chemically associated with the oil backbone. To address these challenges, Kinectrics developed the new and flexible Universal SEParation(USEP) process as a Canadian solution for disposal of problematic mixed liquid waste. This paper presents an overview of the USEP process and results of the process development as well as large scale demonstration work undertaken to-date to successfully process and dispose MLW drums from ProjectsA and B.

2. Characteristics of project-A and project-B mixed liquid wastes

Representative samples from the MLW drums were obtained and characterized as follows:

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

2.1. Project-A wastes

Three (3) drums contained dual oil/water phases. The remaining waste drums contained a single oil phase. In addition, all of the waste drums contained some suspended solids and/or sediments. Table 2 summarizes their physico-chemical characteristics, and Table 3 their overall radiochemical characteristics.Composite phase gamma activity wasmeasured for the dualphased wastes, while tritium was measured for all individual phases. Results for Difficult-to-Measure (DTM) radionuclides, namely,C-14, Ni-63, Sr-90, Fe-55 and alpha activity were developed for consolidated (4 composites) samples only.

In general, wastes are characterized by elevated tritium levels, low beta/gamma and alpha activity and relatively modest levels of other (C-14, Fe-55, Ni-63 and Sr-90) radionuclides. The elemental composition data were developed for 4 consolidated composite samples. In general, they indicate the elevated presence of elementssuch as sulfur, calcium and phosphorous which are commonly associated with oil additives, and alsochlorine which may be due to the presence of a small content of chlorinated solvents in the oilwaste. In general, the wastes contain less than 1 wt. % of the listed elements.

Table 2: Typical physico-chemical characteristics of project-Awastes

Flash Point	96-150^{0}C
pH	4-5.5
PCBs	< 2 ppm
Elemental analysis	• < 1wt% of listed elements (based on 40 element scan) • High concentrations (100-2000 ppm) of Ca, Cl, Fe, Mg, P, Na, S and Zn

Table 3:Typical radiochemical characteristics of project-A wastes

Radionuclides	Concentration (Bq/Kg)		
	Minimum	Maximum	Geometric mean (LM)
Co-60	16	409	98.1
Cs-137	23.4	1930	185.1
Ag-108m	10.1	20	12.1
H-3	**9.0E+06**	**5.8E+10**	**1.3E+08**
C-14	1100	7000	2908
Ni-63	790	4000	1205
Fe-55	410	3300	1049
Sr-90	6.1	3600	93.7
Pu-238	1.3	7.5	2.6
Pu-239/40	3.3	11	6.5
Am-241	3.7	25	6.6
Cm-244	0.65	21	2.6

2.2. Project-Bwastes

Project-Bincludedlegacy MLW drums comprising of aqueous, oils, and oily sludges. The USEP process was applied to the drums that contained measurable amounts of oils/oily sludge. Tables 4 and 5 present a summary of the overall characteristics of the drums that were processed.

Table 4: Typical physico-chemical characteristics of project-Bwastes

Flash Point	>93.3^{0}C
pH	3.6-8.5
PCBs	< 2 ppm
Elemental analysis	• Up to 1860 ppm of toxic elements such as Pb, As, Cr, Cd, Hg • High concentrations (100-4500ppm) of P, Na, S and Zn
Halogen analysis	• Up to 7.4% Fluoride and Up to 1.5% Chloride

Table 5:Typical radiochemical characteristics of project-Bwastes#

Radionuclides	Concentration (Bq/Kg)		
	Minimum	Maximum	Geometric mean (LM)
Th-234	3520	787000	111259
U-235	199	54500	8511
U-238	3520	787000	111259
C-14	1030	190000	8355
H-3	3020	397000	27051

#Only data for MLW drums containing oils or oily sludges is presented

In general, the waste drums are characterized by the presence of varying levels of H-3, C-14, Th-234, U-235 and U-238. Other salient characteristics of the waste drums include presence of toxic metals such as arsenic, cadmium, chromium, lead, mercury and halogens.

3. Evaluation of processing options

A range of process options were evaluated previously for treatment of 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 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
- Dehydration
- Treatment with commercially available sorbents such as Florisil(US Silica) and Alumina (Dynamic Absorbents).

A series of bench scale tests were initially carried out on composite samples prepared from various drums associated with Project-A. The objective of these tests was to evaluate various process options that were successful in the past (and listed above) to reduce activity levels in the MLW samples to below unconditional clearance criteria. Highlights of these tests were as follows:

- A combination of treatments such as phase separation, vacuum dehydration, pH adjustment, treatment with commercial clays and filtration resulted in lowering of most radionuclides except H-3 to below unconditional clearance limits.
- The above process options result in maximum tritium removal in the range 88-93.5%. However, in order to achieve unconditional clearance limits, ≥99.9% of the tritium in the waste neededto be removed. This was a challenge in view of the fact that in these legacy waste drums some of the H-3 is associated chemically with the oil backbone (incorporated via isotopic exchange) and could not be removed by conventional treatment processes.

In order to address the above mentioned challenges, Kinectrics developed the proprietary Universal SEParation (USEP) process with the following objectives:

- Removal of all radionuclides including H-3 to below unconditional clearance levels
- Cost effective treatment of waste
- Minimal secondary waste that needs to be returned to client nuclear waste site

Further description of the USEP process is provided in section 3.1.

3.1. The universal separation (USEP) process

A schematic for the proprietary USEP process developed by Kinectrics is provided in Figure1.This is the only known process to remove all radionuclides in the mixed waste (including tritium associated with chemical backbone of the waste) to below unconditional clearance limits thereby permitting its disposal as conventional hazardous waste.Highlights of the innovative USEP process are as follows:

- The USEP process involves a combination of the following steps:
    - Removal and capture of bulk tritium from the waste via dehydration
    - Cyclic acid-base treatment of waste followed by filtration for removal and capture of residual tritium and other radionuclides
    - The captured radionuclides are solidified to meet the criteria for disposal at a radioactive waste facility
    - The clean processed waste is sent to a conventional hazardous waste site for final disposal

Figure1: Schematic of USEP process

Processing equipments used for drum scale treatment of MLW are shown in Figure 2. A visual representation of MLW as a function of its treatment using the USEP process is shown in Figure 3.

Vacuum Dehydrator	**Cyclic Acid-Base Treatment System**
Filtration and Phase Separation	**Filter Press**
Scrubber	**Waste Solidification System**

Figure 2: Key processing equipment

		
Mixed Liquid WasteContains H-3 and other radionuclides	Post-Dehydration ~90% H-3 removal	Waste that meet unconditional clearance limits after cyclic acid-base treatment

Figure 3: Visual representation of MLW treatment using USEP process

Table 6 summarizes the results of bench scale tests performed on composite samples from Project-A drums by using the USEP process. Dehydration resulted in 88-93.5% removal of tritium. The waste samples were then treated using the cyclic acid-base treatment step which resulted in removal of H-3 as well as all other radionuclides to below unconditional clearance limits. As shown in Table 7, scale-up of the USEP for drum scale treatment of Project-A waste drums were also successful. The processed waste was sent to a conventional chemical waste facility for incineration.

Bench scale tests were first performed on composite samples from Project-B drums by using the USEP process. Dehydration was not required for the waste samples from these drums. Only the cyclic-acid base treatment step of the USEP process was employed for these wastes and found to be successful in reducing all radionuclides in the waste to below unconditional clearance criteria. As shown in Table 8, scale-up of the USEP for drum scale treatment of Project-B waste drums were also successful. The processed waste was sent to a conventional chemical waste facility for incineration.

Table 6: Bench scale test results for project-A MLW

Stage description	**Tritium concentration (Bq/Kg)**	**Cumulative removal (%)**
Initial composite feed-1	1.53E+08	-
Stage-1: Dehydration	1.01E+07	93.40
Stage-2: Cyclic acid-base treatment	7.86E+04	99.95
Initial composite feed-2	8.54E+07	-
Stage-1: Dehydration	9.86E+06	88.45
Stage-2: Cyclic acid-base treatment	9.34E+04	99.9
Target H-3 Level (Unconditional clearance limit)	**<1E+05**	**≥99.9**

Note: 1. Other radionuclides present in the initial feed varied as follows: C-14: 1100-7000 Bq/Kg, Ni-63: 790-4000 Bq/Kg, Fe-55: 410-3300 Bq/Kg, Sr-90: 6.1-3600 Bq/Kg
2. After cyclic acid-base treatment all of the above radionuclides met unconditional release criteria. In all cases concentration of these radionuclides was close to or < MDLs.

Table 7: Typicalresults from treatment of project-Adrums employing the USEP process

Drum ID	Untreated waste		Post-treatment results via vacuum dehydration	Post-treatment results via cyclic acid-base treatment	
	H-3 (Bq/kg)	(β,γ) (Bq/Kg)	H-3 (Bq/kg)	H-3 (Bq/kg)	(β,γ) (Bq/Kg)
KIN-A 001	1.0E+08	196.5	7.32E+06	5.78E+04	<61
KIN-A002	7.9E+07	166.4	6.54E+06	6.37E+04	<55
KIN-A003	7.1E+07	187.7	6.95E+06	6.53E+04	<90
KIN-A004	7.5E+07	40.9	9.95E+06	7.3E+04	<29
KIN-A005	5.6E+07	650.6	2.60E+07	4.78E+04	<7.53

Note: 1. Other radionuclides present in the initial feed varied as follows: C-14: 1100-7000 Bq/Kg, Ni-63: 790-4000 Bq/Kg, Fe-55: 410-3300 Bq/Kg, Sr-90: 6.1-3600 Bq/Kg
2. After cyclic acid-base treatment all of the above radionuclides met unconditional release criteria. In all cases concentration of these radionuclides was close to or < MDLs.

Table 8: Selected processing results for project-Bdrums employing the USEP process

Drum ID	Untreated waste			Treated waste via cyclic acid-base treatment		
	U-235 (Bq/kg)	U-238 (Bq/kg)	C-14 (Bq/Kg)	U-235 (Bq/kg)	U-238 (Bq/kg)	C-14 (Bq/Kg)
KIN-B 001	1370	23500	<MDL	80	810	<MDL
KIN-B 002	199	4830	1030	7.5	130	460
KIN-B 003	360	6860	190,000	6.0	60	460
KIN-B 004	<MDL	3520	<MDL	<MDL	380	<MDL

4. Conclusion

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. Since 2010, over 200mixed waste drums from various Canadian nuclear facilities have been successfully disposed. Both conditional and unconditional clearance approaches are/were used depending on the preference of the client.

None of the treatment methods used previously for unconditional clearance of MLW were suitable for reducing H-3 in legacy MLW to below unconditional clearance limits. Kinectrics therefore developed the innovative UniversalSEParation (USEP)Process as a Canadian solution for disposal of problematic mixed liquid waste. Highlights of this process are as follows:

- Removes all radionuclides in the mixed waste to below unconditional clearance limits permitting its disposal as conventional hazardous waste

- Removes tritium that is not present in the water phase (e.g. incorporated into the backbone of the oil molecule)
- Avoids the need for cross-border shipments thus significantly reducing the complexity and cost for waste disposal
- Environmentally friendly- with no tritium release to the environment
- Successfully demonstrated on several drums of legacy oily MLW from a Canadian nuclear facility

5. References

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