The Innovative Universal Separation Process (USEP) for Disposal of Mixed Liquid Waste Via Unconditional Clearance Approach – 17570

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ABSTRACT

Historically, Mixed Liquid Waste (MLW) drums from Canadian nuclear facilities containing Tritium (H-3) and other radionuclides (alpha as well as beta/gamma emitting) 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. H-3 surcharge). Because of this, Kinectrics has developed a novel and flexible process for disposal of oily as well as other (solvents, aqueous etc.) MLW within Canada. This process 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 of several MLW drums (oils, solvents, aqueous and solids) was reported at the WM-2013 conference.

One of the key approaches for management of both oily Polychlorinated Biphenyls (PCB) as well as non-PCB MLW involves treatment of the mixed waste using various well-known unit operations such as filtration, treatment with commercial sorbents, and various proprietary treatment methods developed at Kinectrics.
These approaches result in reduction of radionuclide activity levels to below the unconditional clearance criteria and allows disposal of the waste via incineration at a conventional chemical waste facility. A small amount of radioactive secondary waste (the captured radionuclides) is returned to the customer. This approach was successfully employed for processing several drums of PCB and non-PCB MLW.

Kinectrics recently completed two projects involving processing for disposal of legacy oily and solvent MLW inventory for a Canadian nuclear customer. Waste treatment processes used previously for unconditional clearance of oily/solvent MLW were ineffective for treatment of these legacy waste drums. Some drums were particularly challenging to process since H-3 was chemically associated with the oil backbone. To address these challenges, Kinectrics developed the innovative Universal SEParation (USEP) process for disposal of problematic MLW. This paper presents an overview of the USEP process, the latest results of drum scale (205 L) process demonstration work, and the design concept of a Mobile Processing Unit (MPU) for large scale batch (1500 L) processing of MLW employing the USEP process.

INTRODUCTION

Historical perspective

Mixed liquid wastes (MLW) from Canadian nuclear facilities consist of radioactive solvents, Polychlorinated Biphenyls (PCB) and non-PCB contaminated oils and aqueous wastes. Historically, oil and solvent 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 H-3 surcharge). In addition, commercial waste destruction facilities in US cannot accept PCB wastes from non-US jurisdictions.

Kinectrics' overall approach

In order to address the above mentioned challenges, Kinectrics 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 waste disposal projects.

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

- ***Conditional clearance***
  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.

- **Unconditional clearance**
  In this approach, the MLW is processed using various unit operations such as filtration, phase separation, centrifugation, and treatment 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 [6]. The processed waste is then destroyed at a conventional hazardous waste facility.

- **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.

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 2009-2012 for 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 both PCB as well as non-PCB 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 both the non-PCB as well as PCB MLW suitable for final disposal via the unconditional clearance approach. The least-desirable alternative used for non-PCB MLW was solidification followed by disposal as radioactive waste. Complex PCB MLW drums that could not be unconditionally cleared were treated via a modified version of Kinectrics' proprietary PCB destruction process [7] prior to solidification and disposal as radioactive waste.

Kinectrics' recent experience

Kinectrics was recently contracted by a Canadian nuclear industry customer for the disposal of its accumulated/legacy non-PCB MLW inventory (referred to as Projects A and B henceforth) [8].

- Project-A involved several drums of oily MLW that contained large concentrations of tritium and other radionuclides.
- Project-B comprised several drums of legacy MLW containing 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. The small amount of radioactive secondary waste (the captured radionuclides) was to be solidified and 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 tritium was chemically associated with the oil backbone. To address these challenges, Kinectrics developed the new and flexible Universal SEParation (USEP) process for disposal of problematic mixed liquid waste. A detailed description of the initial activities undertaken by Kinectrics in support of development of the USEP process has been presented elsewhere [8]. This includes:

- Detailed characterization of the various waste drums from Projects A and B
- Results of bench scale process development results
- Process equipment for drum scale processing
- Initial results of drum scale process demonstration

Objective of current paper

The objective of this paper is to present the following:

- An overview of the USEP process
- A summary of waste characteristics and the latest results of drum scale (205 L) process demonstration work
- A design concept of a Mobile Processing Unit (MPU) for large batch scale (1500 L) processing of MLW including a discussion of:
  - The applicability of USEP to various challenging organic MLW
  - A process flow diagram
  - Kinectrics' past experience with design and building of MPUs for large scale PCB waste destruction
  - A design concept of a MPU for processing MLW employing the USEP process based on an adaptation of Kinectrics' MPU for PCB waste destruction

OVERVIEW OF THE UNIVERSAL SEPARATION (USEP) PROCESS

A schematic for the proprietary USEP process developed by Kinectrics is provided in Figure 1. This is the only known process to remove all radionuclides in the mixed waste (including H-3 associated with chemical backbone of the waste) to below unconditional clearance limits thereby permitting its disposal as conventional hazardous waste.

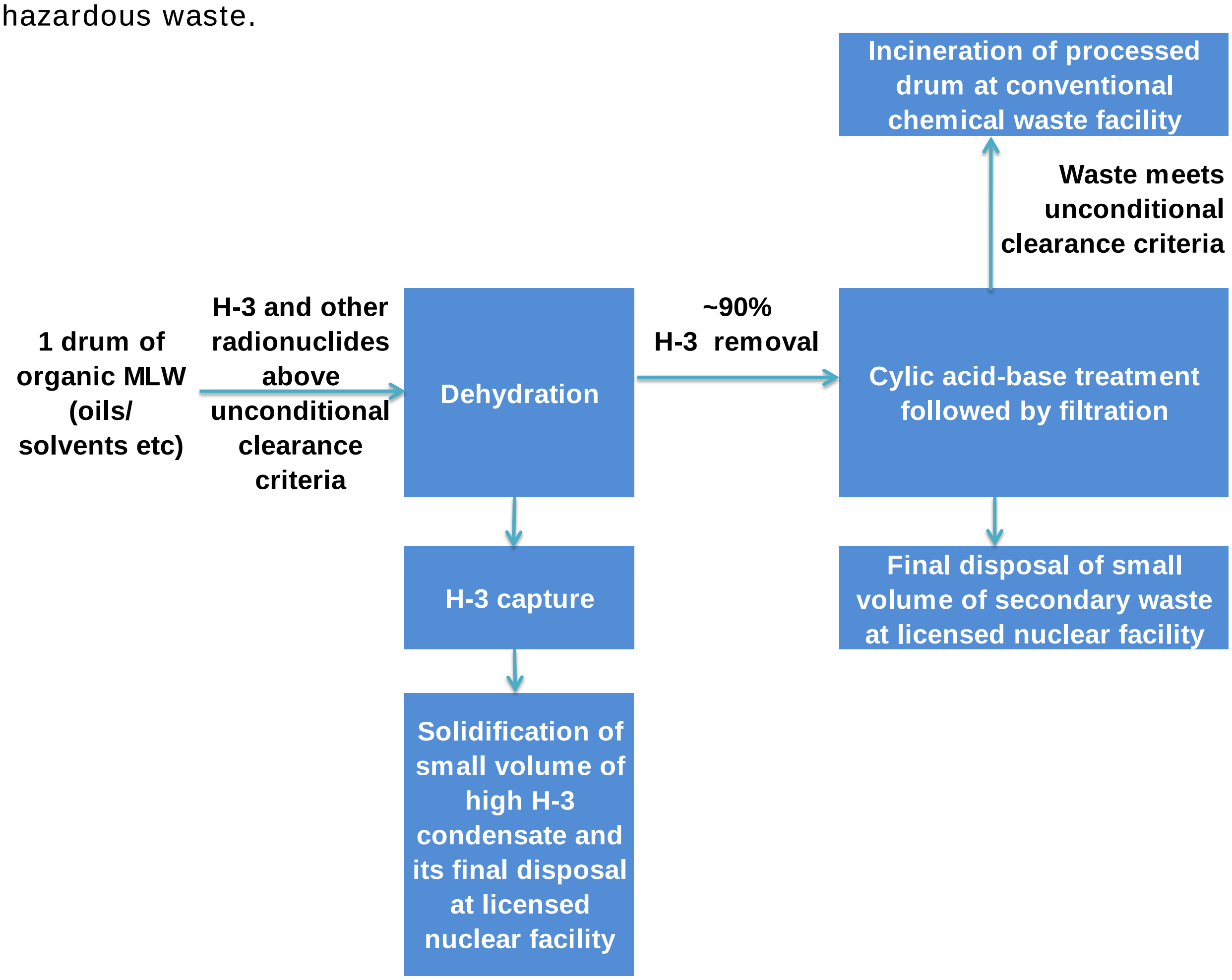


Figure 1: Schematic of USEP process

The USEP process involves a combination of the following steps:
- o Removal and capture of bulk H-3 from the waste via dehydration
- o Cyclic acid-base treatment of waste followed by filtration for removal and capture of the residual H-3 and other radionuclides
- o The captured radionuclides are solidified to meet the criteria for disposal at a radioactive waste facility
- o The clean processed waste is sent to a conventional hazardous waste site for final disposal

SUMMARY OF WASTE CHARACTERISTICS

Representative samples from Project A and B MLW drums were obtained using Coliwasa samplers and then characterized for physical, chemical, as well as radiochemical parameters such as pH, flash point, PCB, elemental, gamma spectroscopy, tritium, C-14 and other Difficult-to-Measure radionuclides. Detailed results were reported previously [8]. A summary of the characterization results are outlined in Table 1.

Table 1: Summary of Mixed Liquid Waste Characteristics

Chemical Analysis	**Project A**	**Project B**
Flash Point	96-150 °C	> 93.3 °C
pH	4-5.5	3.6-8.5
Elemental analysis	Upto 2000 ppm of Ca, Cl, Fe, Mg, P, Na, S and Zn	Upto 4500 ppm of Pb, As, Cr, Cd, Hg, P, Na, S and Zn Upto 7.5% Fluoride and 1.5% Chloride
Radiochemical Analysis		
Tritium (H-3)	Upto 5.8E+10 Bq/Kg	Upto 4.0E+05 Bq/Kg
Co-60	Upto 500 Bq/Kg	< F.R.
Cs-137	Upto 2000 Bq/Kg	< F.R.
C-14	Upto 7000 Bq/Kg	Upto 1.9E+05 Bq/Kg
Ni-63, Fe-55, Sr-90	Upto 4000 Bq/Kg	N.D.
U-235	< F.R.	Upto 5.5E+04 Bq/Kg
U-238	< F.R.	Upto 7.9E+05 Bq/Kg

Note: < F.R. indicates values that are significantly less than free release/unconditional clearance limits. N.D. indicates not detected.

In general, wastes from Project A are characterized by elevated H-3 levels and relatively modest levels of other radionuclides (Co-60, Cs-137, C-14, Fe-55, Ni-63, and Sr-90). The elemental composition data were developed only for 4 consolidated composite samples. In general, they indicate the elevated presence of elements such as sulfur, calcium and phosphorous which are likely associated with oil additives and also chlorine which may be due to the presence of a small amount of chlorinated solvents in the oil waste. In general, the wastes contain less than 1 wt.% of the listed elements.

In general, the waste drums from Project B were 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.

PROCESSING OF MIXED LIQUID WASTE: LATEST RESULTS

Results from initial application of USEP process for drum scale processing were reported previously [8]. More recently, additional drums from both Projects A and B were processed. Tables 2 and 3 summarize the latest results from recent drum scale process demonstration work on drums from Projects A and B respectively. In case of project A drums, dehydration resulted in 70-98.5% removal of H-3. The waste drums were then treated using the cyclic acid-base treatment step which resulted in removal of residual H-3 as well as all other radionuclides to below unconditional clearance limits. The processed waste was sent to a conventional chemical waste facility for incineration.

Dehydration was not required for the waste drums from Project B. Only the cyclic-acid base treatment step of the USEP process was employed for these waste drums. The USEP process was successful in reducing all radionuclides in from Project B waste drums to below unconditional clearance criteria. The processed waste was sent to a conventional chemical waste facility for incineration.

Table 2: Results of Drum Scale Processing (Project-A drums)

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 006	4.6E+07	187	8.44E+05	8.2E+04	<15
KIN-A 007	5.6E+07	1544	1.58E+07	7.3E+04	<20
KIN-A 008	1.3E+08	2164	9.41E+06	7.86E+04	<16
KIN-A 009	3.8E+08	712	6.31E+06	7.0E+04	<19

Note: In addition to typical β,γ emitting radionuclides (determined by gamma spectrometry), radionuclides such as C-14, Ni-63, Fe-55, and Sr-90 were also present in concentrations above unconditional clearance limits in various waste drums. 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 < Method Detection Limit (MDL).

Table 3: Results of Drum Scale Processing (Project-B drums)

Drum ID	Untreated Waste			Treated Waste via cyclic acid-base treatment		
	U-235 (Bq/kg)	U-238 (Bq/kg)	H-3 (Bq/kg)	U-235 (Bq/kg)	U-238 (Bq/kg)	H-3 (Bq/kg)
KIN-B 008	2.18E+04	4.16E+05	<F.R.	2.5	27	-
KIN-B 010	5.0E+04	6.82E+05	<F.R.	26	485	-
KIN-B 013	<MDL	<MDL	1.68E+05	<MDL	<MDL	5.25E+04
KIN-B 014	<MDL	<MDL	1.1E+05	<MDL	<MDL	5.8E+04

Note: <MDL indicates less than Method Detection Limit. < F.R. indicates values that are significantly less than free release/unconditional clearance limits. In addition to radionuclides such as H-3, U-235 and U-238, other radionuclides such as C-14 were also present in concentrations above unconditional clearance limits in various waste drums. After cyclic acid-base treatment all of the above radionuclides met unconditional release criteria.

APPLICABILTY OF USEP PROCESS

Figure 2 provides an outline of various organic MLW to which the USEP process has been successfully applied to-date. These include oils, solvents, PCB oils, and niche/legacy tritiated oils and uranium process waste originating in Canada. Based on results obtained to-date, the USEP process could potentially be applied to conventional MLW as well as niche/ legacy/orphaned mixed waste that are currently reported to be stored in various nuclear sites worldwide [9-12].

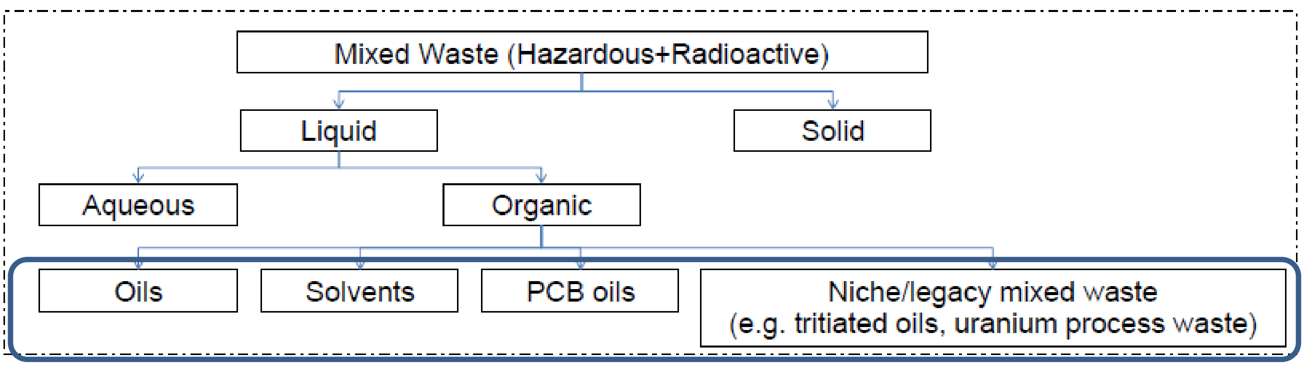


Figure 2: Applicability of USEP Process

USEP PROCESS SCALE-UP

The USEP process has to-date been successfully demonstrated on a variety of mixed liquid waste drums (205 L) employing small scale process equipment [8, Tables 2-3 of current paper]. In all cases, the waste could be processed to unconditional clearance limits followed by disposal via incineration at a conventional chemical/hazardous waste facility. In order to process larger quantities of MLW originating both from Canadian as well as international nuclear facilities, this process needs to scaled-up to achieve both higher throughput as well as to reduce the cost of processing the waste.

Options for scale-up include a Mobile Processing Unit (MPU) or a fixed facility. An initial step that could be taken in this direction is to design and build a prototype MPU to demonstrate that this process can be successfully scaled up. Based on Kinectrics' extensive experience in design and building MPUs for PCB destruction (1500 L batch), a decision was made to explore the option of modifying the existing MPU design to facilitate processing of MLW employing the USEP process. The process flow diagram for the USEP process, a description of Kinectrics' original MPU for PCB destruction and the design concept of a MPU for processing MLW employing the USEP process based on an adaptation of Kinectrics' MPU for PCB waste destruction are discussed in the following sections/subsections.

USEP Process Flow Diagram

The process flow diagrams for treatment of MLW to unconditional clearance limits employing the USEP process are outlined in Figures 3 and 4. Key unit operations/ treatment steps involved in processing MLW employing the USEP process can be summarized as follows:

- Dehydration
- Cyclic acid-base treatment
- Bleaching earth addition/treatment
- Solid-liquid separation
    - o Centrifugation
    - o Filtration
- Solidification

The overall process flow outlined in Figures 3 and 4 can be described as follows:

- **Dehydration step:** MLW is first dehydrated to remove moisture and hence H-3 associated with the moisture.
- **Base treatment step:** The waste then undergoes base treatment in the temperature range 35-120^{0}C. A suitable bleaching earth is then added to the waste followed by solid-liquid separation employing centrifugation and/or filtration.
- **Acid treatment step:** The waste then undergoes acid treatment in the temperature range 35-120^{0}C. A suitable bleaching earth is then added to the waste followed by solid-liquid separation employing centrifugation and/or filtration.
- **Waste characterization:** The processed waste is characterized to determine if it meets unconditional clearance criteria. If yes, it is shipped off-site for chemical waste incineration. If not, the waste is further processed via base and acid treatment steps in a cyclic manner until the unconditional clearance criteria are met.
- **Waste solidification:** Small amount of separated sludge comprising mainly of bleaching earth that contains high concentrations of radioactivity is further immobilized employing a suitable solidification agent and sent to nuclear waste site for disposal.

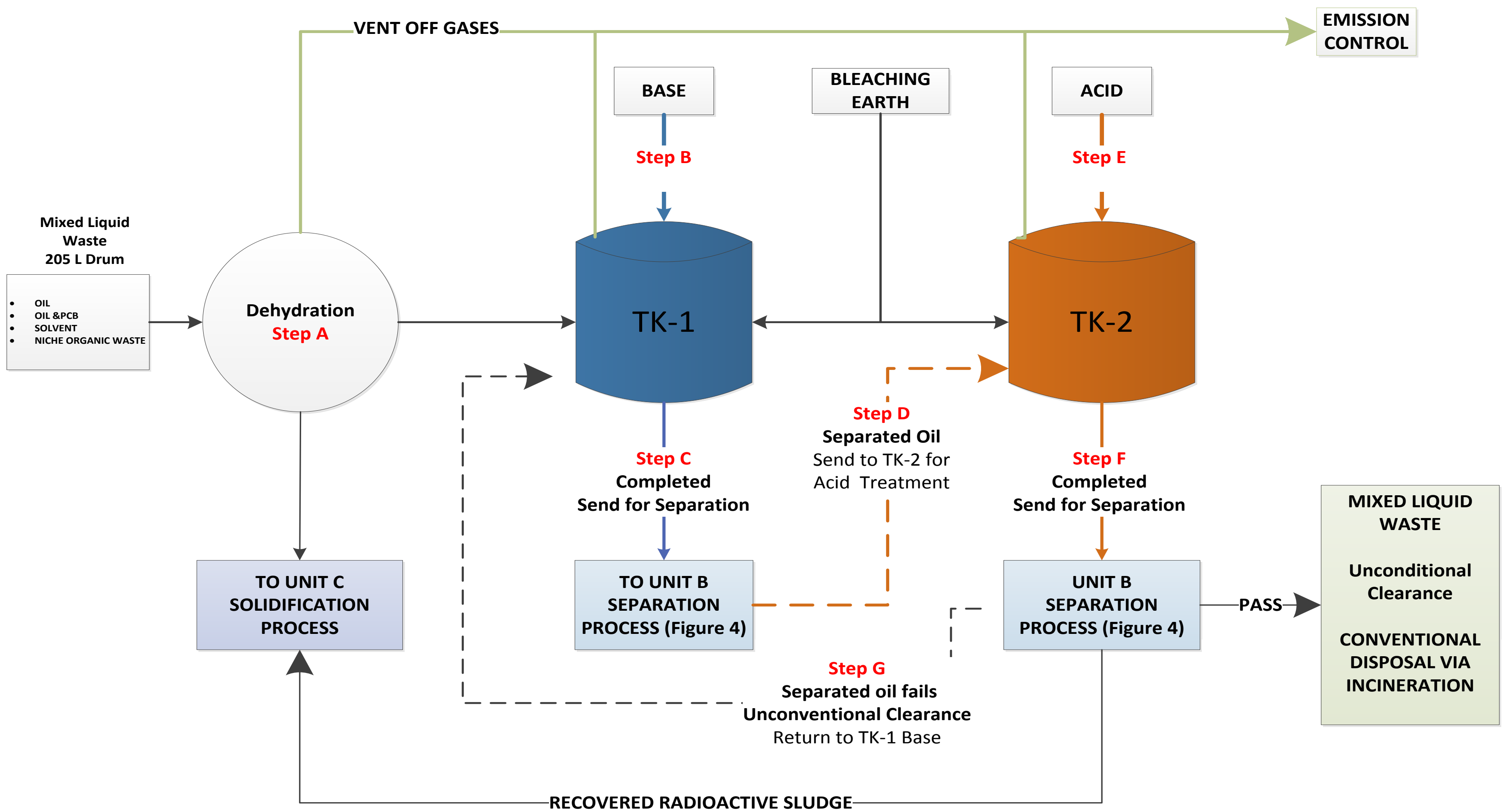


Figure 3: USEP Process Flow Diagram

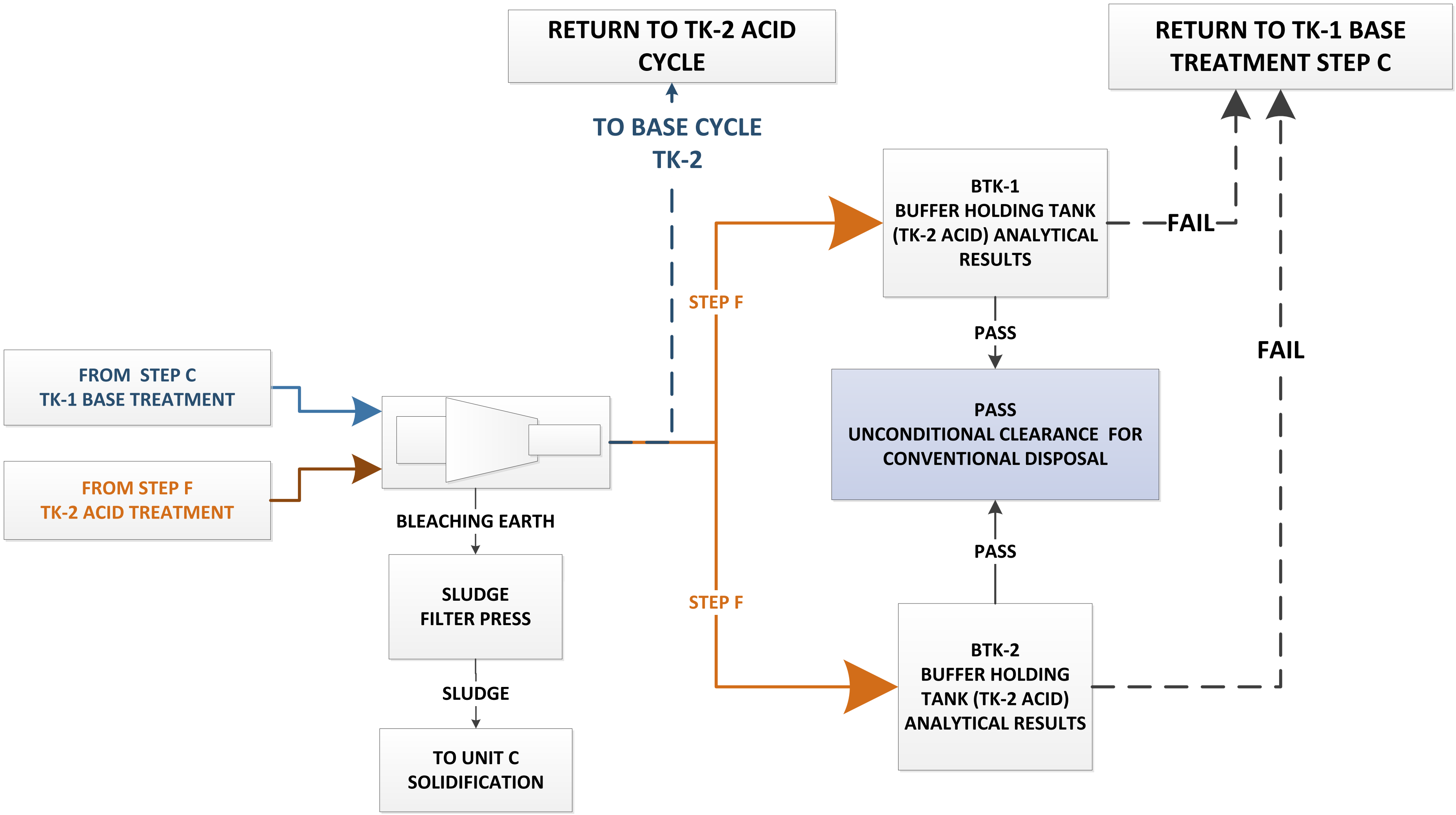


Figure 4: USEP Process: Unit B Separation Flow Diagram

KINECTRICS' PCB DESTRUCTION PROCESS AND MOBILE PROCESSING UNITS (MPUs)

PCB Destruction Process

Kinectrics' PCB destruction process is based on the low-temperature, atmospheric-pressure reaction between the chlorinated contaminant and finely dispersed active metallic sodium under carefully controlled conditions to form sodium chloride and hydrocarbon residues. The destruction efficiency meets or exceeds a value of 99.9999%, based on the destruction of pure aroclor 1242 PCBs. A detailed description of the process and its applications can be found in published literature [7, 13-16].

The principle reaction in the process is the direct removal of the chlorine atoms from the PCB molecules by sodium;

$$RCl_x + Na^+ \rightarrow NaCl + R^o_{x-1}$$

where RCl is a PCB molecule containing x number of chlorine atoms (x =1 to 10), Na^+ is a reactive sodium atom, and R^o_{x-1} is a PCB molecule with 1 chlorine atom removed. R^o_{x-1} is reactive free-radical from the biphenyl structure and combines with H^+, formed by the reaction of sodium with water or donated by the mineral oil, to form a neutral RH molecule. If RH contains additional chlorine, it is again attacked by sodium and the process is repeated until all chlorine atoms have been replaced by hydrogen atoms. At this point, the PCB molecule has been converted to a biphenyl molecule and all chlorine atoms have combined with sodium to form sodium chloride or table salt.

Important side reactions which can occur during the de-chlorination process include the reaction of sodium with trace water or with acidic organic oxidation products formed while the oils were in service. These side reactions render undesirable acidic oil components insoluble and therefore assist in their removal in subsequent settling to separate the by-product sludge from the usable oil.

While the principal organic product formed in the de-chlorination reaction is biphenyl, a small amount of an insoluble residue known as poly-phenyls is also produced as a result of biphenyl polymerization. The yield of poly-phenyls increases relative to that of biphenyl as the PCB concentration of the input oil increases and the amount of sodium dispersion used. As with neutralized oil acids, this material is removed from the oil in subsequent treatment stages. The complete de-chlorination reaction occurs in both highly concentrated PCB liquid waste (i.e., pure) or low concentration PCB contaminated mineral oil.

The PCB destruction process is operated as a batch process. The system is essentially a closed PCB destruction system. Although this mode of operation may reduce the throughput capacity of a similar size system when operated on a continuous mode, there are several practical advantages of the batch process, namely:

- Better emission control. In a batch process the reaction vessel remains close until batch analytical data confirms all PCBs in the reactor has been destroyed.

Once the PCB destruction has been confirmed, the reaction vessel is purged with nitrogen during the neutralization of the excess sodium used in the reaction. Obviously, the same level of control cannot be achieved on a continuous process.

- The batch operation mode avoids cross-contamination of already cleaned oil. Each batch of treated oil is analyzed prior to evacuation of the reaction vessel. In a continuous processing mode system samples are taken at different times and if there is fault in the operating conditions, this fault, translated as poor destruction reaction, could be detected only after it has already cross-contaminated the already cleaned oil.
- The sodium-based reaction, as with most PCB destruction reactions, is an exothermic process. The heat of reaction is significant and, depending on PCB concentration, could generate enough heat to increase the temperature of the reaction mixture well over the mineral oil flash point. This is even more important when destroying high level PCB liquid waste.

PCB Destruction Process Flow Diagram

The process flow diagram for a mobile processing unit (MPU) for destruction PCB in various PCB contaminated oils and other chlorinated solvents is outlined in Figure 5. Key unit operations/ treatment steps involved in the PCB destruction process can be summarized as follows:

- Dehydration
- Metallic sodium addition
- Quenching of excess sodium
- Solid-liquid separation by centrifugation

The overall process flow outlined in Figure 5 can be described as follows:

- **Dehydration / Degassing step:** Vacuum dehydration is employed in this step for removal of moisture and volatile organics whose presence would inhibit the PCB destruction reaction.
- **Metallic sodium addition:** The PCB contaminated waste is then heated up to 120˚C followed by the addition of metallic sodium dispersion for destruction of PCBs.
- **Waste characterization:** The processed waste is characterized to determine if it meets regulatory clearance criteria for PCBs (typically <2 ppm). If yes, then the excess sodium in the waste is quenched as described in the next step. If not, the waste is further processed by the addition of metallic sodium until PCB clearance criteria are met.
- **Quenching excess sodium:** The waste is then transferred to another tank for quenching of excess sodium by the addition of water.
- **Solid-Liquid separation:** The quenching reaction leads to formation of sodium chloride residues which are then separated from the bulk oil by centrifugation. The bulk oil can then be disposed by conventional chemical waste disposal or further processed (for example by replenishing the additive package) and reused.

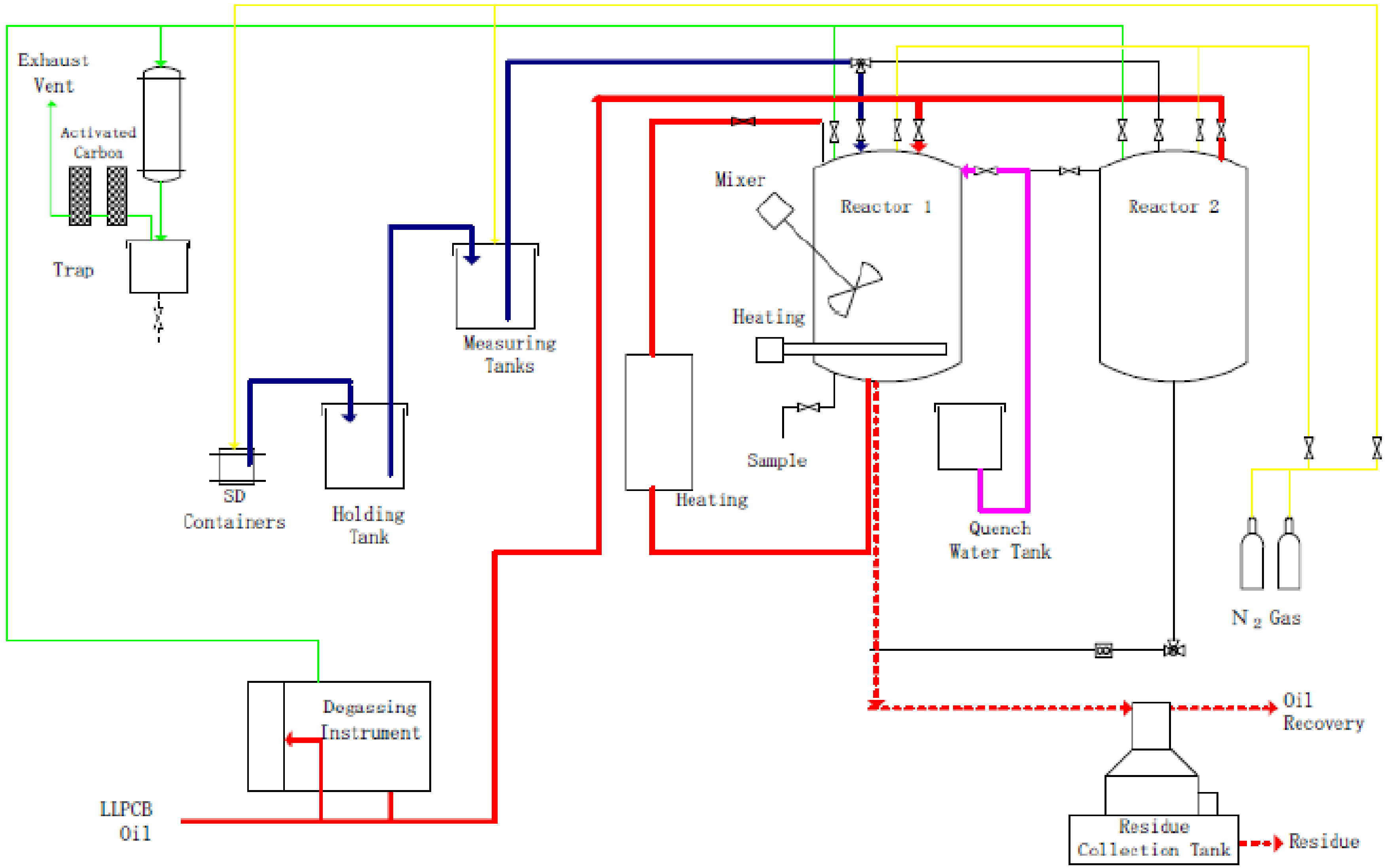


Figure 5: Process Flow Diagram for Mobile Processing Unit (MPU) for PCB Destruction

KINECTRICS' MOBILE PROCESSING UNIT FOR PCB DESTRUCTION

Kinectrics has extensive commercial and scientific experience in the design, construction and operation of mobile low temperature chemical processing units (MPUs) for the destruction of PCB from 2 to 1,000,000 ppm. To-date three generations/versions of MPUs (i.e., MPU-1, MPU-2, and MPU-3) have been designed and built. A summary of the commercial, engineering and operating history of MPUs based on Kinectrics' PCB Destruction Technology is outlined in Table 4.

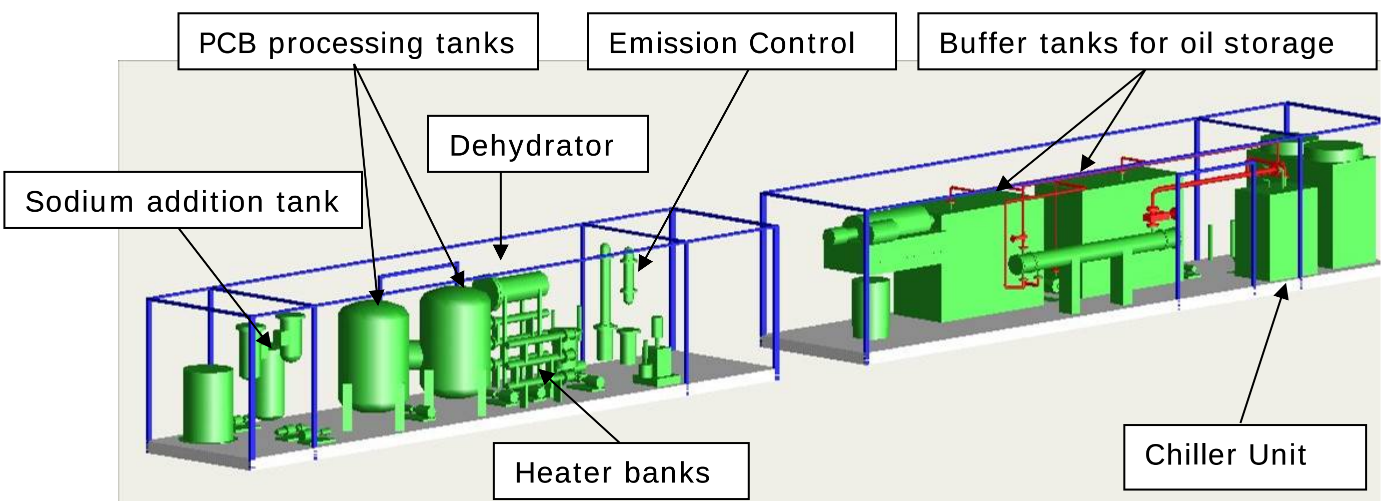
Table 4: Summary of Commercial, Engineering and Operating History of Kinectrics' PCB Destruction Technology

Client	Country	Year	Quantity Processed	Kinectrics Role
Ontario Hydro and successor companies.	Canada	1986 to 2000	~6,100,000 L of PCB contaminated mineral oil and 1950kg of pure PCB	Design, build, and MPU-2
Rondar Inc	Canada	1986 to 1997	~862,000 L of PCB contaminated transformer oil	Licence and sale of MPU-1
Quimica Wimer	Mexico	1999	20,000 L of PCB contaminated mineral oil and 200kg of pure PCBs	Demonstration MPU-2
Nuclear Fuels Industries Ltd	Japan	1999	MPU-3 - low level PCB (6000 L/day) and pure askarel chemical destruction 180 kg/day	MPU-3 Technology transfer - design
JESCO Toyota City PCB Destruction Plant (Licensee: Nuclear Fuel Industries Ltd.)	Japan	2005 to present	1,600,000 kg (estimated) of pure PCBs.	Full scale processing plant for pure PCB destruction- Technology transfer - design
Keuk Dong oil Refinery Co. Ltd.	South Korea	2006	50,000 L (estimated) of PCB contaminated mineral oil.	MPU-2 license and sale
Aveitas	Canada	2003 - Present	1,500,000 L (estimated) of PCB contaminated mineral oil	MPU-1 license and sale
Philippines PCB	Philippine s	2009	United Nations DIO contract - plant	Full scale PCB decontamination and PCB destruction plant -

Client	Country	Year	Quantity Processed	Kinectrics Role
Destruction Plant			commissioned and completed 2014	Technology transfer - design
India PCB Destruction Plant	India	2009	UNDIO contract - plant under construction	MPU technology transfer through licence arrangement with NPO Dekanter and the design and contruction of a full scale PCB decontamination and destruction plant

The mobile PCB processing system (MPUs) were initially developed to decontaminate in-house, Ontario Hydro low level PCB contaminated mineral oil from 2 to 7000 mg/kg. Since then, Kinectrics, the successor company of Ontario Hydro Research Division has been offering the transfer of the PCB destruction technology worldwide. A pictorial representation of the latest generation of PCB destruction processing unit i.e. MPU-3 and its various unit operations/components is provided in Figures 6 and 7 respectively.

a. ISO Containers Housing MPU-3



b. Pictorial Representation of MPU-3

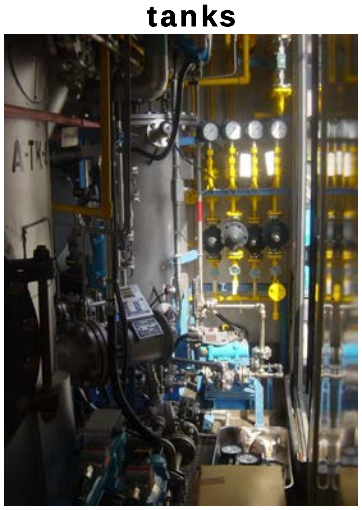
Figure 6: Pictorial Representation of MPU-3 for PCB Destruction

a. Dehydrator– remove moisture

b. Reactor Face

c. Sodium Dispersion Section – sodium dispersion holding and measuring tanks

d. Chemical Addition Tanks



e. Nitrogen Gas System- for actuated valve operation and heater element/reactor cover gas

f. Built in Secondary Oil Spill Containment System

Figure 7: Various Unit Operation/Components of MPU-3

MPU-3 Unit Specifications:

The specifications for the existing MPU-3 for PCB destruction include the following:

- Batch process system – ensures that the waste meets unconditional clearance criteria
- Two reactors 1500 L each
- Chemical addition tanks
- Process containment – closed system operation
- Internal secondary spill containment
- Programmable logic system control
- Emission control:
  - Condenser trap
  - Activated charcoal
- Explosion proof
- Nitrogen gas – to provide N_2 cover gas during sodium reaction and quenching
- Nitrogen gas is used to control pneumatic valves
- Fire suppression system –sodium bicarbonate
- Indirect electrical heating
- Decanter centrifuge
- Close circuit TV monitoring of the process section

MPU-3 Modes of Operation

The PCB destruction process has two modes of operation:

- **Low level PCB Destruction – (2 to <10,000 ppm):** The contaminated mineral oil is drawn into the unit through the dehydrator to remove moisture. The oil passes from the dehydrator to an empty reactor. The process logic fills the reactor to operating level and brings the oil to the reaction temperature. Once at the operating level and temperature a stoichiometric volume of sodium dispersion is added to the contaminated oil. The reaction runs for the predetermined reaction time and then a sample of the reactants is removed and the PCB concentration is measured employing the on-board Gas Chromatography-Electron Capture Detector (GC-ECD). When the PCB concentration is <2 ppm the sodium is quenched under nitrogen blanket and the reactants are discharged to the centrifuge to separate the sludge from the oil.
- **High level PCB Destruction – (>10,000 to 1,000,000 ppm):** The reactor is filled to 600 L of mineral oil and heated to the reaction temperature. Once the oil is at the reaction temperature a stoichiometric volume of sodium dispersion is added to the base oil. The high level PCB is transferred from the waste container into a tank in the MPU. The stored high level PCB is then transferred into a measuring tank. From the measuring tank the high level PCB oil is fed into the reactor with the base oil/sodium mix. The injection rate is controlled via a temperature feedback loop, cooling oil injection, and a cooling jacket on the reaction tank. The reaction temperature is controlled to <145°C. Once all of the high level PCB is delivered to the reactor the temperature is maintained at the reaction temperature until the reaction time is completed. At the end of the

reaction time a sample of the reactants is removed and the PCB concentration is measured employing the on-board GC-ECD. When the PCB concentration is <2 ppm the sodium is quenched under nitrogen blanket and the reactants are discharged to the centrifuge to separate the sludge from the oil.

DESIGN CONCEPT FOR A PROTOTYPE MPU TO TREAT MLW EMPLOYING THE USEP PROCESS BASED ON AN ADAPTATION OF THE MPU-3

The rigorous design of the Kinectrics' mobile PCB destruction technology (MPU-3) can be adapted to process mixed liquid waste (MLW) employing the USEP process to meet unconditional clearance criteria followed by disposal of the processed waste via incineration at a conventional chemical waste facility. The following sections outline the upgrade requirements to modify the process logic of MPU-3 and the mode of operation for processing MLW employing the USEP process.

Required Upgrades to MPU-3 Process Unit Specifications

The following upgrades to MPU-3 are required in order to adapt it for processing MLW employing the USEP process:

- Upgrades to the emission control system
  - Molecular sieve/Silica gel trap to capture H-3
  - Carbolime to capture C-14
  - HEPA filter
- Upgrades to the hazardous gas monitoring system
  - H-3 monitor
  - C-14 monitor
  - Hazardous gas monitor
- Bleaching earth addition system
- Filter press
- Upgrades to process monitoring equipment
  - Liquid Scintillation Counter (LSC)
  - Gamma spectrometer
- Process logic to reflect USEP operation
- Piping configuration between process units.

MPU-3 Modes of Operation- Mixed Liquid Waste Destruction

The MPU-3 would be upgraded to accommodate a third mode of operation i.e. MLW treatment using the USEP process as described below:

- **USEP Mode:** The new mode would draw mixed liquid waste into unit through the dehydrator to the reactor. The program logic would heat the waste to temperature and then add the required stoichiometric volume of base and bleaching earth. The mixture would be allowed to react for the desired reaction time. This would be followed by measurement of radionuclide concentration. The mixture is then discharged to the centrifuge/filter press and deposited into holding tank. When the reactor is emptied to the separation process the hold tank is transferred to the second reactor and the stoichiometric volume of acid and bleaching earth added to the mixture. The mixture would be allowed to react for the desired reaction time followed by measurement of radionuclide concentrations. The mixture is then discharged to the centrifuge/filter press and deposited into holding tank. The mixed waste is assessed to determine if it meets the unconditional clearance criteria. If yes, the processed waste is packaged and sent for conventional chemical waste disposal via incineration, otherwise it is processed again via cyclic acid-base treatment.

CONCLUDING REMARKS

Kinectrics has developed a novel and flexible process for disposing of oily as well as other (solvents, aqueous etc.) MLW within Canada. This process avoids the need for cross-border shipments and significantly reduces the complexity as well as cost for waste disposal. To-date around 300 mixed waste drums originating from various Canadian nuclear sites have been successfully processed and disposed within Canada. Both conditional and unconditional clearance approaches were used depending on the preference of the client.

Kinectrics recently completed two projects involving processing and disposal of legacy oily and solvent MLW inventory for a Canadian nuclear customer. Waste treatment processes used previously for unconditional clearance of organic (i.e. oils and solvents) MLW were ineffective for treatment of these legacy waste drums. To address this challenge, Kinectrics developed the innovative Universal SEParation (USEP) Process for disposal of problematic MLW. The USEP process has to-date been successfully demonstrated on a variety of mixed liquid waste drums (205 L batch) employing small scale process equipment. Results of these processing campaigns have shown that the USEP process can be used to remove all radionuclides from a variety of MLW including oils, solvents and other organic process waste to below unconditional clearance criteria.

In order to process larger quantities of MLW originating from Canadian as well as international nuclear facilities, this process needs to scaled up with the objective of achieving both higher throughput as well as to reduce cost of processing. Options for scale up include a Mobile Processing Unit (MPU) or a fixed facility. Initial step that could be taken in this direction is to design and build a prototype MPU to demonstrate that this process can be successfully scaled up. Kinectrics has extensive commercial and scientific experience in the design, construction and operation of mobile low temperature chemical processing units (MPUs) for the destruction of PCBs at a 1500 L batch scale. A design concept of a MPU for processing MLW employing the USEP process based on an adaptation of Kinectrics' MPU for PCB waste destruction has been discussed in this paper. Key upgrades required in order for the latest generation of Kinectrics' PCB destruction reactor i.e. MPU-3 to be able to treat MLW employing the USEP process can be summarized as follows as follows:

- Upgrades to emission control system
- Upgrades to the hazardous gas monitoring system
- Process equipment that includes filter aid addition system and filter press
- Upgrades to process monitoring equipment
- Process logic to reflect USEP operation

- Piping configuration between process units

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