DILUTE CHEMICAL DECONTAMINATION RESINS AND THE MIXED WASTE ISSUE

R. P. Denault, J. T. Hallman
LN Technologies Corporation
Columbia, South Carolina 29201

ABSTRACT

The decontamination of reactor primary systems, sub-systems and components is an important method used to reduce the occupational radiation exposure of nuclear plant personnel. The waste produced by the application of this technology is mainly solid in the form of ion exchange resins. As a result of a recent agreement between the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC), all radioactive waste must meet EPA burial criteria. The chemicals used in a decontamination and certain metals dissolved during the process, primarily chromium, could render the waste hazardous as well as radioactive or more commonly called a mixed waste.

This paper will define mixed waste as described in the EPA directive 9432.00-2, andexamine the criteria by which waste is categorized as hazardous. The decontamination waste resin generated by two processes, the CAN-DEREM and the LOMI process, will be described in detail.

Waste data obtained from decontaminations performed by LN Technologies Corporation including chemical, metal and radionuclide loadings on resins from both PWR and BWR applications will be presented. Also described will be the solidification process used by LN Technologies Corporation to stabilize the waste prior to burial.

A case will be made, supported by laboratory test data using the EP toxicity procedure, and the EPA definition of hazardous waste, to show that both processes generate non-hazardous waste.

INTRODUCTION

New criteria dealing with low level radioactive waste (LLW) have recently been introduced by Government agencies. The regulations now address the hazardous nature of the waste as defined by 40 CFR Part 260 as well as the radioactive nature as defined in 10CFR Part 61. Mixed waste generation, transportation, storage, treatment and disposal are now jointly regulated by the United States Nuclear Regulatory Commission, USNRC, and the Environmental Protection Agency, EPA.

Wastes from chemical decontaminations are radioactive and potentially hazardous because of chemicals used during the process and heavy metals dissolved from primary surfaces. Although the generator is responsible for identification of any potentially hazardous material, in this case the nuclear station, vendors of chemical decontamination technology, such as LN Technologies, must help their customers identify the properties of the waste generated. LN has demonstrated conclusively that its decontamination waste is not hazardous. This paper defines waste produced from two dilute chemical decontamination processes and describes the test program undertaken to define its nature.

WHAT IS MIXED WASTE

Mixed low-level radioactive and hazardous waste (mixed LLW) is defined as waste that satisfies the definition of low-level radioactive waste (LLW) in the Low-Level Radioactive Waste Policy Amendments Act (LLRWPAA) of 1985 and contains hazardous waste that either (1)is listed as a hazardous waste in Subpart D of 40CFR Part 261 or (2) causes the LLW to exhibit any of the hazardous waste characteristics identified in Subpart C of 40 CFR Part 261 (1).

Subpart D of 40CFR Part 261 lists sources of hazardous wastes which include discarded chemical products, waste from specific and non-specific process sources,off-specification species, container residues and spill residues. Most of the chemicals listed are organic liquids such as cleaning and decreasing solvents, halogenated hydrocarbons, liquid scintillation fluids and oils. Also included are heavy metals and metal based solutions such as lead and chromates used extensively in the nuclear industry.

Subpart C of 40CFR Part 261 describes the characteristics of a hazardous waste which is not specifically listed in Subpart D. The four characteristics which will cause a waste to be hazardous are reactivity, corrosivity, ignitability and toxicity. Definitions of each are given below.

Reactivity: A waste exhibits the characteristic of reactivity if it is normally unstable, reacts violently with water, forms potentially explosive mixtures with water or generates toxic gases, vapors or fumes when mixed with water.

Ignitability: A waste exhibits the characteristics of ignitability if it is a non-aqueous liquid with a flash point below 60°C, if it is not a liquid and is capable, under standard temperature and pressure of causing

fire through friction, absorption of moisture or spontaneous chemical charges, if it is an ignitable compressed gas or it is an oxider.

Corrosivity: A waste exhibits the characteristic of corrosivity if it is an aqueous solution with a pH less than or equal to 2 or greater than or equal to 12.5 or if it is a liquid and corrodes steel at a rate greater than 0.250 in. per year at 55°C.

Toxicity: A waste exhibits the characteristic of toxicity if, using the Extraction Procedure Test Method described as the EP Toxicity Procedure, the extract contains any of the contaminates listed in the EP Toxicity list in concentrations greater than or equal to the value given in the list. The list is reproduced in Table I below.

METHODOLOGY TO DETERMINE NATURE OF WASTE

The EPA has developed a methodology which may be used by generators of commercial LLW to identify mixed LLW. This quidance is based on NRC and EPA regulations currently in effect. It is important that generators use applicable regulations that are in effect at the time of implementation of the methodology.

Step 1. Identify LLW

The generator determines whether the waste is LLW as defined in the LLRWPAA.

Step 2. Identify Listed Hazardous Waste

TABLE I

Maximum Concentration of Contaminants in EP Toxicity Leachant

Contaminant	Maximum Permissable Concentration (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5
2,4-D	10.0
2,4,5-TP	1.0

The generator determines whether the LLW contains any hazardous waste listed in Subpart D of 40 CFR Part 261.

Step 3. Identify Hazardous Characteristics

The generator determines whether the waste exhibits any of the hazardous waste characteristics identified in Subpart C of 40 CFR Part 261.

If the waste is LLW and also is a listed hazardous waste and/or exhibits one or more of the hazardous waste characteristics. The waste is Mixed LLW and must, therefore, be managed and disposed of in compliance with EPA's RCRA Regulations in 40 CFR Parts 124, and 260 through 270, and NRC's Regulations in 10 CFR Parts 20, 30, 40, 61 and 70. Fig. 1 shows graphically this methodology.

DECONTAMINATION PROCESSES

Description of the LOMI Process

The LOMI process was developed by scientists of the Central Electricity Generating Board (UK) with funding from the Electrical Power Research Institute (EPRI). The process uses vanadous picolinate, a strong reducing agent, to rapidly dissolve iron rich oxide films. The reaction involves an electron transfer between the vanadous ion and the ferric ion in the film (Eq. 1).

$$V{:}Pic_3^- + Fe^{+3} \dashrightarrow Fe^{+2} + V{:}Pic_3 \qquad (1)$$

The iron ion is destabilized in the oxide by this process and is released into solution. The ferrous ion is then stabilized in solution by complexing with picolinate. Other ions, such as zinc and nickel, can also be released into solution when associated with ferric ion in the deposit according to Eq. (2).

$$18\ Pic{:}H + ZnFe_2O_4 + NiFe_2O_4 + 4V{:}Pic_3^- \dashrightarrow \qquad (2)$$

$$Zn{:}Pic_3^- + Ni{:}Pic_3^- + 4\ Fe{:}Pic_3^- + 4V{:}Pic^3$$

$$+ 8\ H_2O + 2H^+$$

The LOMI reagent and the dissolved metals and radionuclides can be removed from the system by ion exchange resins. A cation bed is used to break the picolinate complex of vanadous and other metal ions (Eq. 3).

$$V{:}Pic_3 + 3H{:}R \dashrightarrow V{:}R_3 + 3\ Pic{:}H \qquad (3)$$

An anion bed is then used to remove picolinate and formate (Eq. 4).

$$H{:}Pic + HFOR + 2R{:}OH \text{ -- } R{:}Pic + R{:}FOR + 2\ H_2O \qquad (4)$$

Description of the CAN-DEREM Process

CAN-DEREM is a modification of the original CAN-DECON process. CAN-DEREM is a dilute regenerative

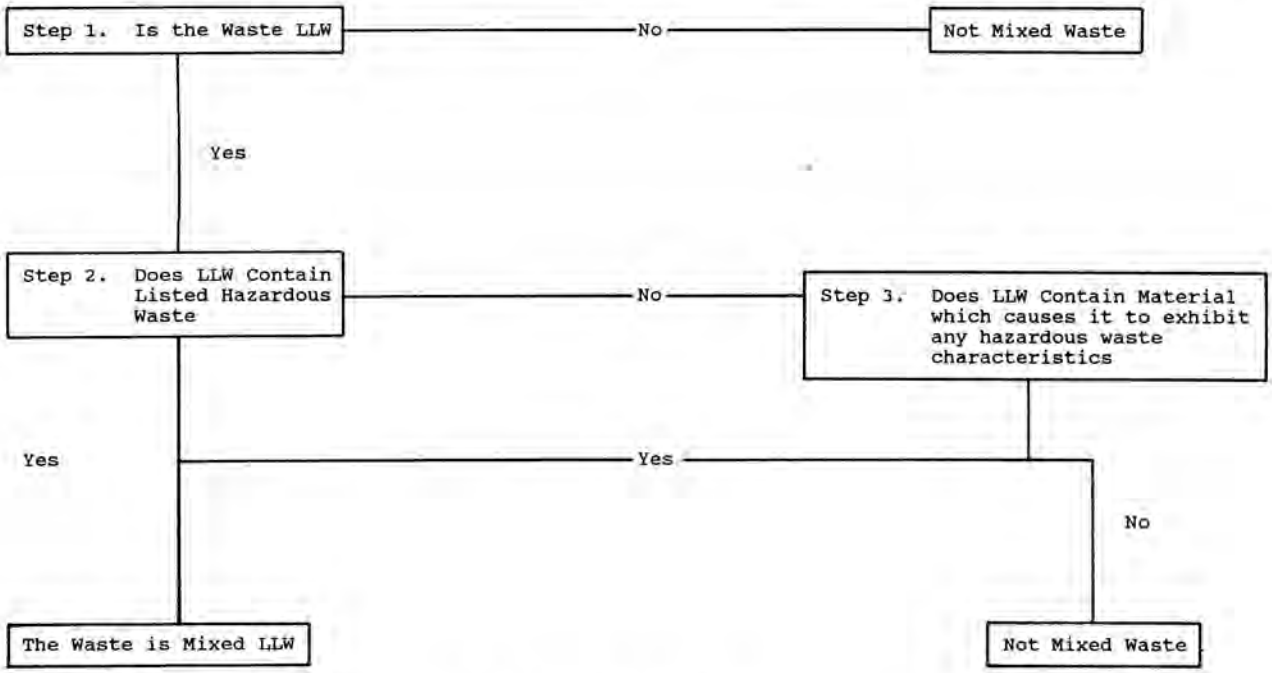

Fig. 1. Identification of Mixed LLW.

chemical decontamination process. The proprietary chemicals, a mixture of organic acids, reducing agents and complexing agents dissolve the oxide film by acidic and reductive dissolution (Eq. 5 and 6).

$$Fe_2O_3 + 6H^+ \rightarrow 2\,Fe^{+3} + 3H_2O \quad (5)$$

$$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2\,Fe^{+2} + 3\,H_2O \quad (6)$$

Once the contaminants are in solution, they are stabilized with organic acid complexing agents (Eq. 7).

$$Fe^{+2} + y^{-m} \rightarrow Fe{:}\,y^{2-m} \quad (7)$$

By valving in a cation ion exchange bed, the dissolved metals are removed from solution (Eq. 8).

$$Fe{:}y^{2-m} + 2H{:}R \rightarrow Fe{:}R_2 + 2H^+ + y^{-m} \quad (8)$$

As well as removing dissolved metals, the cation resin performs another important function. It converts the spent contaminated solution into a clean reusable form. This is termed "regeneration". The regenerated stream is recirculated to the contaminated system to be used over and over again.

The decontamination is terminated by valving out the cation resin and valving in a mixed cationic plus anionic resin bed. The anionic resin removes the chemical reagents and the cationic resin removes any remaining dissolved metals.

Oxidation Process

The oxide films that form in PWRs and occasionally in BWRs consist of a mixture of iron, nickel and chromium oxides. Above a certain concentration, typically 10-15%, the chromium stabilizes these films and renders them insoluble to reductive dissolution. The chromium exists in the +3 valence state, a very insoluble species. To dissolve these films, it is first necessary to remove the chromium. This is achieved by oxidizing the Cr^{+3} to Cr^{+6} which is very soluble. LN performs the oxidation with permanganate according to Eq. (9).

$$Cr^3 + MnO_4^- + 2\,H_2O \rightarrow HCrO_4^- + MnO_2 + 3H^+ \quad (9)$$

Once the chromium has been removed the reducing step is applied to dissolve the remaining iron rich oxide film.

AMOUNT AND TYPE OF DECONTAMINATION WASTES

Dilute chemical decontamination processes such as CAN-DEREM and LOMI produce only solid waste in the form of ion exchange resin. The CAN-DEREM process uses strong base OH form anion and strong acid H form cation. The LOMI process uses weak base OH form anion and strong acid H form resins. The cation resins remove the metals and radio- nuclides dissolved from the radioactive oxide deposit. The anion resins remove the reagent chemicals.

A range of waste volumes generated from actual CAN-DEREM and LOMI applications by LN for several PWR and BWR system and component decontaminations are

TABLE II

Volume of Resin Produced During Typical Decontaminations

System or Component	Resin Volume (cuft) CAN-DEREM	LOMI
BWR Recirculation System	40-50	80-120
BWR RWCU	5-15	15-25
BWR Recirculation Pump	10-15	20-25
PWR S/G Channel Heads	35-50	45-65
PWR Recirculation Pump	10-15	20-40

TABLE III

Typical Decontamination Resin Loadings

Chemical Species	PWR		BWR	
	CAN-DEREM	LOMI	CAN-DEREM	LOMI
Chelants (wt%)	2-5	4-6	3-5	4-7
Iron (ppt)	3-7	1-2	3-28	2-6
Chromium (ppm)	200-3000	1000-2000	400-500	30-120
Nickel (ppm)	200-4000	200-2000	200-900	90-300
Manganese (ppm)	200-300	100-200	40-50	8-50
Zinc (ppm)	N/A	N/A	10-30	10-20
Copper (ppm)	N/A	N/A	10-50	2-6
Radionuclides (mCi/l)	7-30	1-30	40-100	10-30

shown in Table II. Table III lists the chemical constituents on the resins.

TREATMENT OF DECON WASTE

Resins generated during a chemical decontamination are typically Class A and are stabilized before burial. Stabilization is normally done with concrete. This treatment is necessary due to the chelant loading and to the activity concentration on the resin. Both Barnwell and Hanford radioactive burial sites require stabilization of waste if the chelant loading is above 0.1 wt%. In addition, if the radionuclide concentration is above 1 uCi/cc stabilization is also required.(2,3) Generally, both criteria are met for stabilization.

LN Technologies stabilizes decontamination waste with cement based formulae. Typically, a solidified liner contains 35 to 40% resin by volume. Our formulae meet the NRC criteria for waste form stabilization as described in 10 CFR Part 61 and the NRC Branch Technical Position on Waste Form.

HAZARDOUS NATURE OF WASTE

Both the CAN-DEREM and LOMI processes have in their formulas organic acids and chelants. The CAN-DEREM chemicals are considered proprietary. None, however, are listed in Part 261 Subpart D. The LOMI process chemicals include vanadous formate and sodium-picolinate. Again, none of these chemicals are listed in Subpart D. We can conclude,therefore, that the spent chemical solutions are not hazardous waste.

One chemical common to both processes used to deoxygenate the water prior to performing the decontamination is hydrazine. Hydrazine is listed in Subpart D. This chemical is added at a low concentration of 10 ppm. Any hydrazine which does not react with oxygen is converted to the ammonium ion (NH_4^+), a non-hazardous species. This is removed by ion exchange during cleanup.

Of the four characteristics which define hazardous waste, only toxicity is of concern once the waste resins are stabilized in cement. Cement does not exhibit ignitability, corrosivity nor reactivity.

The waste may be hazardous because of heavy metals removed from the radioactive primary surface oxides. Of the eight heavy metals listed in Subpart C only chromium is found in any appreciable quantities. This is of particular concern in PWRs(see Section on Oxidation Process). Up to 3000 ppm chromium can be found on the waste resins. To determine if decontamination resin waste with high chromium levels are toxic, LN prepared simulated waste forms for both CAN-DEREM and LOMI. Both were stabilized in cement using LN's PCP formulae (4) and subjected to an EP Toxicity Test after a 28-day cure.

EP TOXICITY TESTS

All tests were performed on simulated waste samples to avoid unnecessary exposure to workers as per ALARA Guidelines.

Simulated LOMI ion exchange resin waste was prepared and doped with high levels of chromium. Four samples were prepared. Two consisted only of anion resin, one with 1000ppm, the other with 2000 ppm chromium on the unstabilized resin. The other two samples consisted of an equal mixture of cation and anion resin, one with an overall chromium concentration of 1000 ppm, the other with 2000 ppm. The chromium was added in the hexavalent form. Each was stabilized with LN's LOMI cement PCP formulation.

Under normal site conditions, resins slurried to the burial liner are mixtures of cation and anion resins. The test

program included straight anion resin to represent a worst case.

The chromium concentration in the test samples is representative of that in the waste resin resulting from a PWR decontamination, and is much higher than that in BWR decontamination resin waste. The mixed resin samples also contained 1200 ppm Fe and 630ppm Ni to more accurately reflect decontamination waste.

Two CAN-DEREM samples were prepared in a similar manner. One, a strong base anion resin, was loaded with 6000 ppm chromium in the hexavalent state. The other, a 50/50 mix (by volume) of strong acid cation and strong base anion was loaded with 3000 ppm chromium. The mixed resin samples also contained 2740 ppm Fe and 2360 ppm Ni. Each was stabilized with LN's CAN-DEREM cement PCP formulation.

Each of the LOMI and CAN-DEREM samples were cured for two days at 60°C followed by 26 days of curing at ambient temperature. Each was then sent to an independent laboratory for EP Toxicity testing. The test procedure can be briefly described as a leach test with agitation at a pH of 5.0 adjusted with acetic acid over a 24-hour period. A more detailed explanation of the test procedure can be found in Appendix II of 40 CFR Part 261. The leachate is then analyzed for the eight heavy metals listed in Table I of part 261.24 and given in Table I of this report with their maximum allowable concentrations. Results obtained for LOMI and CAN-DEREM resins are given in Tables IV and V.

TABLE IV

EP Toxicity Test Results for Stabilized LOMI Resin.

Sample	Contaminant Concentration (mg/L)							
	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver
Mixed, 1000ppmCr	0.01	0.88	<0.01	0.03	<0.05	<0.0002	0.01	<0.01
Mixed, 2000ppmCr	<0.01	3.97	<0.01	1.39	0.21	<0.0002	<0.01	0.01
Anion, 1000ppmCr	<0.01	5.39	<0.01	0.35	0.18	<0.0002	0.02	<0.01
Anion, 1000ppmCr	<0.01	6.62	<0.01	2.14	0.39	<0.00048	<0.01	0.02
Maximum Permissible Concentration	5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0

TABLE V

EP Toxicity Test Results for Stabilized CAN-DEREM Resin.

Sample	Contaminant Concentration (mg/L)							
	Arsenic	Barium	Cadmium	Chromium	Lead	Mercury	Selenium	Silver
Anion, 6000ppmCr	0.01	1.43	<0.01	0.19	0.08	<0.0002	0.01	<0.01
Mixed, 3000ppmCr	<0.01	1.15	<0.01	0.14	0.10	<0.0002	<0.01	<0.01
Maximum Permissible Concentration	5.0	100.0	1.0	5.0	5.0	0.2	1.0	5.0

CONCLUSION

Waste generated from a LOMI or CAN-DEREM decontamination application and subsequently stabilized with an LN cement formula are not considered hazardous. None of the chemicals in the waste are listed in Subpart D of 40 CFR Part 261. The stabilized waste does not exhibit any of the characteristics of hazardous waste listed in Subpart C of 40 CFR Part 261. Waste from LOMI applications at three sites since the new criteria have come into effect has been buried after careful scrutiny by the plant and waste personnel and the burial site operators.

REFERENCES

1. Guidance on the Definition and Identification of Commercial Mixed Low-Level Radioactive and Hazardous Waste, Oswer Policy Directive No. 9432.00-2, (1987)

2. Barnwell Waste Management Facility Site Disposal Criteria, Chem-Nuclear Systems, Inc., Barnwell Office, Document No. S20-AD-010

3. Hanford Radioactive Solid Waste Packaging Storage and Disposal Requirements, Rockwell Hanford Operations Manual RHO-MA-222

4. LN Technologies Corporation Topical Report on 10CFR61 Radioactive Waste Forms, TR 002.