CHEMICAL HAZARDS FROM DECONTAMINATION SOLUTIONS IN LOW LEVEL WASTE [a]

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ABSTRACT

Recent regulations are focussing more attention on the non-radioactive matrix materials associated with radioactive wastes. Decontamination of operating facilities is becoming a more significant source of low level waste. This study reviewed the chemical and biological hazards of over 50 decontamination processes. Seventeen of the most prominent hard and soft decontamination processes were examined in detail. The chemical and biological hazards of these seventeen are presented in this paper. These hazards influence the choice of radwaste processing and packaging operations and methods. Federal, state and local regulations further impact on operations and waste disposal. Hazards to personnel, in plant and off-site, resulting from the decontamination cycle are evaluated.

INTRODUCTION

Reagents employed in the decontamination of reactor coolant systems are potentially hazardous. Exposure to decontamination agents by operating personnel, or members of the general population, can occur during use, processing, transportation to, or disposal at a low-level waste site. Federal and state agencies have promulgated regulations relevant to the disposal of decontamination solution waste to prevent acute or chronic exposures. In particular, the Nuclear Regulatory Commission (NRC), U.S. Environmental Protection Agency (EPA), Department of Transportation (DOT), Department of Labor-Occupational Safety and Health Administration (OSHA), State of South Carolina, State of Nevada, and the State of Washington have such regulations. These regulations may impact the choice of decontamination solutions, operations procedures, processing methods and disposal methods.

REGULATORY IMPACT

Laws and regulations relate both to chemically hazardous and to radioactive hazards. Laws which regulate the exposure of workers and the general public to effluents and emissions during processing, disposal and transport have been abstracted. Table 1, Regulatory Impact on Decontamination Disposal, lists current legislation. As a result of these regulations, utilities monitor personnel and the on-site and off-site environment, provide proper protective clothing and ventilation, make certain the solutions are properly contained during use, storage and processing and destroy and/or properly immobilize the residues for disposal. Waste treatment processes such as neutralization, ion exchange, evaporation, incineration, etc., must not produce, nor result in hazardous emissions, effluents, residues, or hazards to workers. The laws also stipulate record keeping and documentation. Figure 1 illustrates the impact of these laws on waste processing. A number of these regulations impact on several operations.

DECONTAMINATION SOLUTION HAZARDS

A review of the literature revealed a wide variety of formulations used for chemical decontamination. Table II, lists the principal components of a decontaminating solution. These formulations may contain acids or alkalis, chelating or complexing agents, oxidizing or reducing agents, inhibitors, surfactants and criticality control agents. Rather than try to deal with processing and disposal methods for every possible formulation, it was decided to classify the solutions into different types to reduce the number of solutions to be examined. This classification then allowed some generalizations which both simplified our work and made the expansion of this work to new formulations easier. Table III, "Classification of Decontamination Solutions," lists the common applications of decontamination solutions. The least hazardous are the building and personnel solutions.

Virtually all of the chemicals employed in hard and soft decontamination solutions demonstrate some degree of biological toxicity. A number of these chemicals are classified as corrosive, explosive, combustible, or are a fire hazard. Toxic fumes may be emitted during drying or incineration. Some volume reduction and disposal options are therefore impacted by some of the above regulations. Table IV, "Summary of Hazards Associated with Chemicals in Selected Decontamination Processes," lists the chemical and physical hazards according to degree and type.

DECONTAMINATION WASTE PROCESSES

These hazards may influence the choice of radwaste processing and packaging operations and methods. During application, radioactive and non-radioactive metals and compounds are stripped from the surface. The reagents undergo physical and chemical change and are subjected to thermal and radiation degradation. The waste products of hard decontamination are radioactively contaminated chemicals, resins, filters and liquids. The radioactive waste products of soft decontamination are resins and filters.

Once the decontamination processes are completed and the liquid and/or resin wastes are collected in permanent or temporary tanks, the waste must be processed to a form which is suitable for disposal. The radwaste may be subjected to various pretreatment processes, depending on composition, prior to concentration and volume reduction. Table V, "Common Waste Treatment Methods," lists processing techniques. Pretreatment may involve neutralization of acids or alkalis, oxidation, or reduction, activated carbon absorption, or biodegradation. Concentration processes primarily involve removal of water. The more common methods are evaporation, ion exchange, chemical precipitation and settling and filtration. Some volume reduction techniques are drying, incineration, pyrolysis and calcination. Regulations now require liquid wastes to be solidified. Solidification of the waste for shipment is accomplished by incorporation in cement, asphalt, or proprietary agents. Each of these waste treatment operations could produce a personnel, or environmental hazard.

HAZARDS CONTROL

Hazards control of the non-radioactive waste components during waste treatment and packaging operations to minimize exposure of personnel and environmental degradation due to airborne and liquid effluents is mandatory. This includes removal of airborne aerosols and particulates by HEPA filters, centrifugation, scrubbing and electrostatic precipitation. Gases may be removed by chemical reactions, absorption, condensation, liquification and pressurization. Waste hazards, due to chemicals incorporated in waste disposal packages, are defined and controlled by 10CFR part 61. However, there are interactions which can occur between the chemicals, or by radiation, which can affect the integrity of the solidification agent and produce undesirable results. Radiolysis of water incorporated in cement and organic compounds in asphalt will produce hydrogen gas and may create stability and leachability problems with solidified resins at high activity levels. Asphalt is incompatible with oxidizing agents and is a fire hazard. Among the proprietary solidification agents, DOW media, a vinyl ester, may produce gases and is a fire hazard.

In plant, health physics rules are usually quite specific and due to the radiation hazard, apply to the waste operations. As a result, protective clothing, safety glasses, safety shoes, respirators (supplied air for vapors and volatile organics) are worn. These personnel safety measures take care of most non-radioactive operating requirements as well. In addition, the chemicals are maintained within closed systems during use and waste processing, which further protects workers.

Off-site, choice of waste treatment method and compliance with state and federal regulations will combine to limit the emissions and effluents to environmentally safe levels. The in-plant waste processing and packaging of decontamination wastes provides protection against chemical and biological hazards at the low level waste burial site.

TABLE I

Regulatory Impact On Decontamination Disposal

REGULATION	TITLE	DECONTAMINATION IMPACT
PL95-95	Clean Air Act of 1977	Requires permitting and monitoring for criteria and non-criteria pollutants.
40CFR Part 61	National Emissions Standards for Hazardous Air Pollutants: Standards for Radionuclides	Requires monitoring of emissions and calculations of pathway and dose equivalents whenever waste processing results in an off-site release.
40CFR Parts122-125	National Pollutants Discharge Elimination Systems (NPDES)	Requires permit to discharge and monitoring for required pollutants and for record keeping and reporting. This applies primarily to cleanup of residual decontaminants.
PL95-217	Clean Water Act of 1977	Prevents discharge of decontaminants regarded as pollutants. Limits concentration of residual decontamination chemicals in the effluent and requires monitoring.
PL93-533	Safe Drinking Water Act of 1974	Limits inorganics, organics and radioactive material discharged. Underground injections have to meet EPA and state requirements. Monitoring of effluent is required. Prevents entry of decontaminant solutions into the drinking water supply.
PL92-532	Marine Protection Research and Sanctuaries Act of 1982	No waste may be dumped at sea without a permit. Same as Section 402 of FWPCA and follow NPDES guidelines.
PL94-580	Resource Conservation and Recovery Act of 1976 (RCRA)	If classified as hazardous, the nonradioactive decontamination solutions must then have a permit to store, treat, or transport such waste.
PL96-469	Toxic Substance Control Act of 1976	May result in one or more of the decontamination chemicals being removed from manufacture, or its use restricted.
PL96-510	Comprehensive Environmental Response Compensation and Liability Act of 1980 (CERCLA)	Applies to hazardous, radioactive and mixed waste. Requires permit. Provides for EPA inspection of sites where such substances are stored, treated, disposed of, or transported.
PL91-190	National Environmental Policy Act of 1980 (NEPA)	May require an EIS for new volume reduction and concentration facilities if the process produces emissions, or effluents. May result in delayed installation, increased cost and possible adversary action.

TABLE I
(Continued)

Regulatory Impact On Decontamination Disposal

REGULATION	TITLE	DECONTAMINATION IMPACT
29CFR 1910	Occupational Health and Safety Act of 1970 (OSHA)	In most cases, radiation health and safety requirements will also result in OSHA compliance.
PL93-633	Hazardous Materials Transportation Act of 1974	Must follow proper safety procedures and complete manifest accurately. The transporter must register with the DOT.
49CFR Parts 171-178	Requirements for Transportation of Hazardous Substances	Relates to packaging, labeling and allowable external radiation levels.

TABLE II

Components Of A Decontaminating Solution

AGENT	APPLICATION
Oxidizer	Disrupt Corrosion Product Film
Reducer	Disrupt Corrosion Product Film
Acids	
Mineral	Dissolves Corrosion Product Film
Organic	Dissolves Corrosion Product Film
Chelating	Holds Metal Ions in Solution
Inhibitors	Reduces Corrosion of Base Metal
Surfactants	Wet Surfaces
Boric Acid	Criticality Control

TABLE III

Classification Of Decontamination Solutions

CATEGORY	DESCRIPTION OR USE
Hard	Concentrated >5%
Soft	Dilute <1%
System Decontamination	Piping System or Component in Place
Component Decontamination	Separated Components
Building Decontamination	Building Surface
Personnel Decontamination	Surfactants

TABLE IV

Summary Of Hazards Associated With Chemicals In Selected Decontamination Processes

RECIPE	HAZARD	
	BIOLOGICAL	CHEMICAL
Low Oxidation State Metallic Ion (LOMI)		
Vanadous Ion	Irritant or conjunctivae and respiratory tract	
Picolinic Acid	Unknown, isomer of nicotinic acid	Combustible, forms pyridine on heating
Formic Acid	High irr., ing., inh.	Moderate fire, corrosive
CAN-DECON (Proprietary)		
Chelating Agents	Food additive, slight irr., ing., inh.	Noncombustible
Organic Acids	Toxic on ingestion and inhalation	Decomposes on heating to complexing agents, noncombustible
Oxidizing Agent	Unknown	Fire hazard
NS-1 (DOW Proprietary)		
Chelating Agents	See CAN-DECON	Non-toxic, non-flammable
Inorganic Salts	Unknown	Decomposes to small molecules
Organic Acid	See CAN-DECON	
Kraftwerk Union(KWU)(Proprietary)		
Chelating Agents	See CAN-DECON	
Organic Acids	See CAN-DECON	
Oxidizing Agent	See CAN-DECON	
Reducing Agent	Unknown	
Westinghouse (Proprietary)		
Oxalic Acid	See OPG	

TABLE IV
(Continued)

Summary Of Hazards Associated With Chemicals In Selected Decontamination Processes

RECIPE	HAZARD	
	BIOLOGICAL	CHEMICAL
Westinghouse (Proprietary)		
Citric Acid	See Peroxide Plus Acid	
Chelant	See CAN-DECON	
Oxidizing Agent	See CAN-DECON	
Oxalic, Peroxide, Gluconic (OPG)		
Sodium Oxalate	Toxic, high irr., high ing.	Emits toxic fumes on heat decomposition
Oxalic Acid	Toxic, caustic, corrosive, high irr., ing., inh., 1.0 mg/cc TLV	Emits toxic fumes of NO_x on heat decomposition
Hydrogen Peroxide	High irr., ing., inh.	Dangerous, fire, severe explosion
Gluconic Acid	Protect from breathing dust	Not readily flammable
Sodium Gluconate	Sequestrant and food additive	
Oxidizing Decontamination Solutions (ODS)		
EDTA	Food additive for animals, skin and inh. irr.	Spill hazard (5,000 lbs.) Noncombustible
Hexamine	Skin rash, medication use mod. irr., ing.	Slight fire hazard, decom, in acid to HCHO
Acetanilide	Skin, medication use, slight all., mod. ing., slight inh.	Slight fire. Dangerous, emits toxic fumes on heat decomposition
H_2O_2	See OPG	
Sulfamic Acid	Mod. irr.	Dangerous, emits toxic fumes on decomposition, not readily flammable
Peroxide Plus Acid		
Hydrogen Peroxide	See OPG	
Sulfuric Acid	High irr., ing., inh.	Moderate fire, powerful oxidizer, dangerous when heated, emits highly toxic fumes.
Oxalic Acid	See OPG	
Citric Acid	Mild all., food additive	Slight fire hazard
Ammonium Oxalate	High irr., ing.	Emits toxic fumes on heat decomposition
Peroxide Bicarbonate		
Hydrogen Peroxide	See OPG	
Sodium Carbonate	Mild irr., ing., inh., food add.	No fire hazard
Sodium Bicarbonate	Realtively harmless, food add.	Used as extinguishing agent
8-Hydroxyquinoline	See OPG	
Alkaline Tartrate Peroxide (ATP)		
Sodium Hydroxide	High irr., high ing., mod. inh.	Dangerous, reacts with water or steam to produce caustic solution and heat.
Sodium Tartrate	Food	Not Combustible
Hydrogen Peroxide	See OPG	
Film Conditioning Agent (FCA)(Proprietary)		
Amine Salts	Somewhat toxic	Combustible and possibly highly flammable
Organic Acid Salts	Probably toxic on ing.	Probably combustible
Phenolic Bodies	Probably toxic	Flammable and explosion hazard
Potassium Hydroxide	See ATP, Sodium Hydroxide	

TABLE IV
(Continued)

Summary Of Hazards Associated With Chemicals In Selected Decontamination Processes

RECIPE	HAZARD	
	BIOLOGICAL	CHEMICAL
Mineral Acids		
Sulfuric Acid	See Peroxide Plus Acid	
Phosphoric Acid	Mod., irr., ing., inh., food add., TLV 1 mg/m³ air	Not flammable
Nitric Acid	See Cerium (IV)-Nitric Acid	
Sulfuric-Nitric Acid	See Cerium (IV)-Nitric Acid	
Cerium (IV)-Nitric Acid		
Cerium (IV)	Slight ing., inh.	Oxidizing agent
Nitric Acid	High irr., ing., inh.	Oxidizing agent, explosion hazard mod. fire hazard. Emits toxic fumes to NO_x and HNO_3 on heating to decomp. Corrosive
NS-3 (Dow Proprietary)		
Oxidizing Agent	Possible corrosive to skin	Possible fire hazard
Other components unknown		
Steam Generator Cleaning Solution		
Ethylenediaminetetra-acetic Acid	See ODS	
Hydrazine	High irr., ing., inh., TLV 1.3 mg/m³	Explosive, moderate fire when exposed to heat, flame or oxidizing agents
Ammonium Hydroxide	Mod. irr., ing., inh.	Slight fire hazard, dangerous fumes
CCI-80	Unknown	
Ethylenediamine	Mod. irr., ing., inh., TLV 30 mg/m³	Mod. fire when exposed to heat or flame
Hydrogen Peroxide	See OPG	
Alkaline Permaganate-Citrox (AP-Citrox)		
Sodium Hydroxide	See ATP	
Potassium Permaganate	High irr., ing., inh.	Strong oxidant, moderate fire, dangerous with combustible materials
Oxalic Acid	See OPG	
Dibasic Ammonium		
Citrate	Non-toxic	
Ferric Nitrate or,	Mod. irr., slight inh., ing.	Powerful oxidizing agent explosive, emits toxic fumes
Ferric Sulfate	Slight irr., ing., non-toxic	
Diethylthiourea	Possible carcinogen	
APACE		
Sodium Hydroxide	See ATP	
Potassium Permanganate	See AP-Citrox	
Dibasic Ammonium Citrate	See AP-Citrox	
Ethylenediaminetetra-acetic Acid	See CAN-DECON	
Phenylthiourea	Mildly toxic	Dangerous, emits toxic fumes of sulfur and NO_x when heated to decomposition.

irr. - Irritant
ing. - Ingestion hazard
inh. - Inhalation hazard
all. - Allergic reaction

TABLE V

Common Waste Treatment Methods

Neutralization - Acids or alkalis	Incineration, drying, pyrolysis, calcination
Reduction - oxidation	Immobilization in cement, asphalt, Dow media, HIC
Evaporation	Absorption
Reverse Osmosis	Biodegradation
Ion Exchange, settling and filtration, chem. prec.	UV Oxphytolysis
Wet-Air Oxidation	

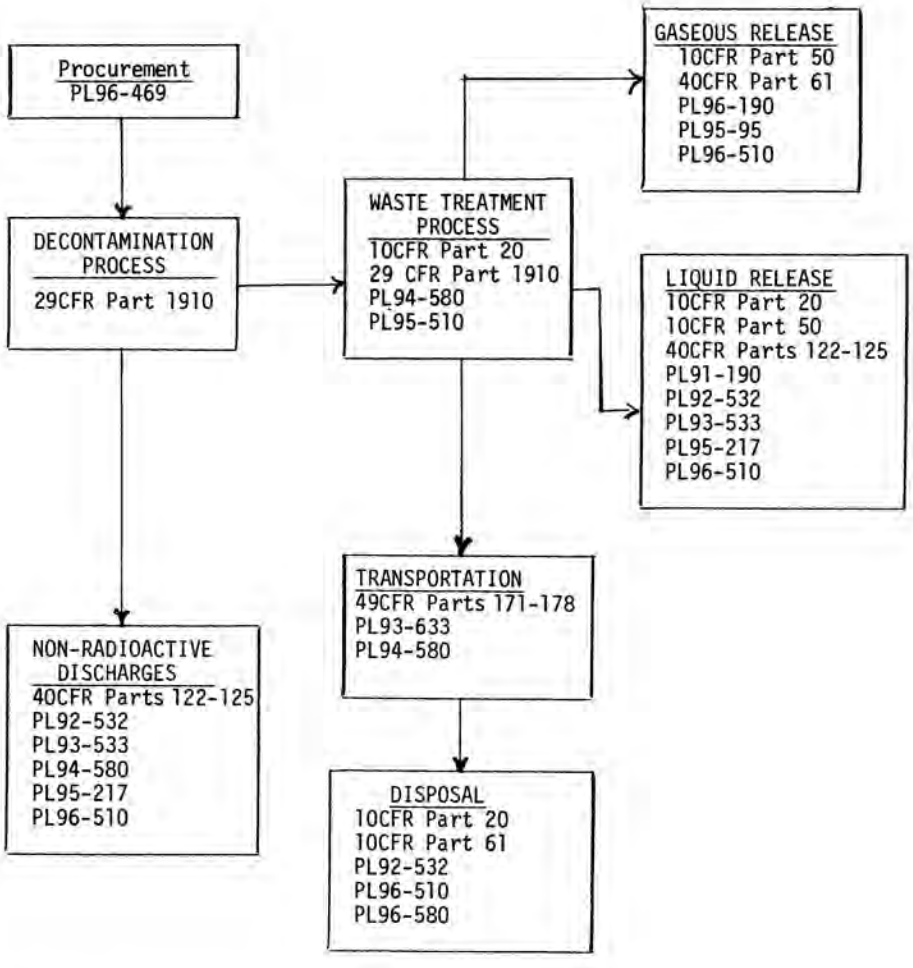

Fig. 1. Block Diagram Showing the Applicability of Regulations to Various Aspects of Decontamination and Decontamination Waste Disposal

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