MIXED WASTE PROCESSING -- A CRITICAL ASSESSMENT OF AVAILABLE TECHNOLOGIES

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ABSTRACT

The use of treatment processes to convert mixed waste to radioactive waste is explored. The regulations regarding treatment of mixed waste are reviewed, followed by a description of mixed waste types at DOE facilities and nuclear power plants. Eight treatment processes are discussed, and the applicability of each process for various physical waste forms is given. Three case studies of treatment processes with which the authors are familiar are discussed.

INTRODUCTION

Management of mixed hazardous and low-level radioactive wastes (LLW), or mixed waste, is currently of concern because the lack of regulatory guidelines and disposal facilities has required mixed waste generators to store their mixed waste until a disposal facility becomes available. However, this solution has its own problem; the generator may be required to obtain a RCRA permit for storage of the mixed waste since the hazardous component is regulated under RCRA.

A potential solution to this problem is to treat the mixed waste to eliminate the hazardous portion and convert it to LLW. The form of the mixed waste determines the treatment process; therefore, typical mixed waste streams are described, and suitable treatment technologies are identified for each waste stream.

REVIEW OF REGULATIONS REGARDING MIXED WASTE

Mixed waste is defined as a waste that is both LLW, as defined in 10 CFR 61, and a hazardous waste, as defined in 40 CFR 261.

A waste is considered hazardous if it exhibits one of the characteristics defined in Subpart C of 40 CFR 261 or is listed in Subpart D. The four characteristics in Subpart C are ignitibility, corrosivity, reactivity, and Extraction Procedure Toxicity (EP Toxic). Subpart D listed wastes include wastes from processes and specific chemicals. A waste can be listed in Subpart D because it exhibits one of six characteristics: it can be ignitable, corrosive, reactive, EP Toxic, acutely hazardous, or toxic. The first four characteristics are the same as those defined in Subpart C. If a waste is listed because it has one of these four characteristics, it can be called a Subpart C characteristic listed waste.

It is possible to treat a mixed waste to convert it to LLW, but the regulations governing the conversion are complicated.

If the waste is hazardous because it exhibits the characteristics of Subpart C and the residue left after treatment does not exhibit these characteristics, then the waste is no longer considered hazardous. Subpart D listed wastes are of two types: those that are listed because they exhibit Subpart C characteristics, and those that are listed because they are either toxic (as opposed to EP Toxic) or acutely hazardous waste. If the waste is of the first type, i.e., it is listed for Subpart C characteristics, then the regulations allow treatment of the waste so it is nonhazardous. However, if the waste is of the second type, i.e., listed because it is either toxic or acutely hazardous waste, then its regulatory status is not changed by treatment. The only Subpart B listed wastes that are listed solely because of Subpart C characteristics are nonhalogenated solvents and wastes associated with explosives manufacture. It is possible to request the EPA to delist a treated waste; however, delisting is a lengthy and cumbersome procedure.

As can be seen from the above discussion, for certain types of mixed waste, the most important goal of treatment, i.e., converting mixed waste to LLW, cannot be achieved. However, it may still be beneficial to treat these types of mixed waste for other purposes such as volume reduction. The product of the treatment will still be a mixed waste.

EFFECT OF RADIOACTIVE COMPONENT ON SELECTION OF TREATMENT TECHNOLOGY

Obviously, it is impossible to destroy the radioactive component of a mixed waste. Generally, therefore, the goal of treating mixed waste is to convert the hazardous component to a nonhazardous condition. The process must not cause the radioactive component to escape to the environment.

The form of the radioactive component can have an effect on the selection of the treatment technology. Certain radioactive isotopes, such as tritium (H-3) or carbon-14 (C-14), can be easily volatilized by thermal treatment and escape from the system as tritiated water or carbon dioxide. Tritiated water (HTO) and water have a boiling point difference of 1.6°C. Tritiated water (which forms from tritium) cannot be effectively separated from the discharge water by conventional separation techniques. A very tall distillation column with a very large number of separation trays is required to separate HTO from water. Separation of radioactive carbon dioxide will require expensive and elaborate gas cleanup technologies. Mixed wastes containing large amounts of potentially volatile isotopes such as tritium or

C-14 are not good candidates for separation by thermal treatment.

Iodine (I-125, I-131) is an example of a common radioactive isotope that is easily volatilized. Iodine is a fission product and may occur as a component of mixed waste at nuclear power plants, particularly in spent ion exchange resins and depleted carbon.In reprocessing plants, iodine is commonly found as I-129. Iodine also combines with alkyl groups to form compounds such as methyl iodide that are easily volatilized and not adsorbed by activated carbon. Radioiodine-bearing mixed wastes are not recommended for thermal treatment.

Most radioactive isotopes are not volatile. The principal radioactive isotopes at DOE facilities and nuclear power plants are the actinides, fission products, and activated metals. A few fission products can become volatile, but for the most part, radioactive isotopes will not be affected by thermal treatment and will remain in the residue.

The difficulty of processing mixed wastes containing halogenated compounds and transuranics (TRU waste) is illustrated by the following example. Some soils and sediments around DOE's production facilities are contaminated with halogenated/nitrated transuranics. Application of conventional thermal treatment processes to soils and sediments will not separate the hazardous constituents from the transuranics. Chemical hydrodehalogenation will convert the halogens to water-soluble acids that will require scrubbing. The nitrates could potentially form gases that will require separation. Depending upon the temperature of hydrodehalogenation and entrainment control in the reactor, the off-gas stream could be contaminated with transuranic dust, and the off-gas scrubber effluent could also be considered a mixed waste stream. Further processing to convert this mixed waste stream to a TRU waste stream can be achieved but will require additional unit operations and costs.

TYPICAL MIXED WASTE

Most of the mixed waste inventory in the United States is at DOE facilities. The wastes are produced by operations such as isotope production, fuel reprocessing, laboratory research, metal fabrication and plating, and maintenance and cleaning. Table I presents types of hazardous components of mixed wastes generated at DOE facilities, grouped by physical form (1).

Commercial nuclear power plants can produce mixed waste during maintenance, decontamination, laboratory activities, and waste processing. Some specific types of hazardous components of mixed waste from nuclear power plants are listed in Table II (2). To these wastes types may be added soil, sludges, and sediments that have been contaminated by both hazardous and radioactive materials.

TREATMENT PROCESSES

This section presents a review of treatment technologies that could potentially be used on mixed waste. As stated previously, only those technologies that accomplish the goal of converting the hazardous component of a mixed waste to nonhazardous while retaining the radioactive component in the treatment residue here are considered. The technologies considered are listed and described in Table III. The applicability of each treatment technology for the various waste types is listed in Table IV.

TABLE I
Hazardous Components
of Mixed Wastes At DOE Facilities

LIQUID ORGANIC WASTES
Chlorinated solvents
Nonchlorinated solvents
Waste oils
Scintillation fluids
PCBs-contaminated transformer oils
Polynuclear aromatic hydrocarbons
SOLID COMBUSTIBLE WASTES
Painting wastes/pigments
Degreasing wastes
Miscellaneous contaminated clothing, rags, etc.
INORGANIC WASTES
Inorganic acids/bases
Plating wastes
Metal cleaning wastes
Reactive metals/heavy metals
Cyanide wastes
Extraction Procedure Toxic metals
Photographic wastes
Ash
MISCELLANEOUS WASTES
Laboratory chemicals
Oxidizers
Explosives
Asbestos
Pesticides/herbicides

TABLE II
Hazardous Components Of Mixed Wastes At Nuclear Power Plants

LIQUID WASTES
Cleaning solvents
Scintillation liquids
Laboratory organic wastes
Pump oils/machine oils
Dry cleaning still bottoms
SOLID COMBUSTIBLE WASTES
System decontamination resin changeout
INORGANIC WASTES
Welding rods
Blast grit
Lead

APPLICABILITY OF TREATMENT PROCESSES

The mixed wastes identified previously are grouped by physical form. The suitability of each treatment process is indicated in Table IV. The judgement of suitability is based upon the effectiveness of the treatment process and the cost.

CASE STUDIES

Three cases with which the authors are familiar are discussed to further illustrate mixed waste processing technologies. The cases have been selected to illustrate three different treatment methods. In each case the mixed waste is described and the reason for the selection of the treatment process is explained. Additional details are given about the process itself.

Thorium-Containing Waste From a Chemical Plant

An example of solidification as a treatment technique for mixed waste occurred when thorium nitrate had to be disposed of at a chemical plant. Thorium, like uranium, is considered a source material for nuclear fuel and is radioactive. This material was not mill tailings or waste products from processing thorium-containing ore; therefore, it did not qualify for the exclusion contained in 10 CFR 61.2 that allows these materials to not be considered LLW. Nitrates are hazardous because they are considered oxidizers and hence exhibit the characteristic of ignitibility as defined in 40 CFR 261 Subpart C. Therefore, thorium nitrate is a mixed waste.

Fortunately, disposal was fairly straightforward. The Beatty, Nevada, LLW disposal facility was contacted, and they said they would accept thorium nitrate if it was solidified with concrete. No testing of the solidified product was required. Solidification in concrete was sufficient to remove the ignitable characteristic of the waste and, therefore, make it nonhazardous. It then became a LLW waste and was accepted by Beatty.

Radioactive Wastewater Containing Organic Solvents from a Defunct Fuel Reprocessing Plant

At West Valley, New York, decontamination and decommissioning operations are going on to clean up the nation's only commercial nuclear fuel reprocessing plant ever operated. A typical waste stream from the cleanup operation was a decontamination wastewater containing radioisotopes like Cs-137 and Sr-90 and reprocessing solvents like tributyl phosphate (TBP) and white kerosene. The wastewater was a mixed waste stream that required separation of the TBP and white kerosene from the radioactive wastewater.

To accomplish the separation of the solvents, the wastewater was evaporated/steam distilled, and the overhead was condensed to collect the TBP and white kerosene as a separate liquid phase. The cesium and strontium isotopes, being nonvolatile at the temperature of distillation, essentially remained in the bottom phase. The bottom phase thus became low-level radioactive wastewater.

The overhead, which was a mixture of the solvents and distilled water, was treated and disposed of as hazardous waste. The bottom product, which was radioactive waste, was ion exchanged to remove the Cs-137 and Sr-90 isotopes, and the treated water was suitable for uncontrolled discharge after meeting the 10 CFR 20, Appendix B requirements. The isotope-loaded ion exchange resin was solidified with cement and disposed of as low-level radwaste.

Mixed Waste From a Defunct Uranium Processing Plant

A feasibility study was performed for remediation of a former uranium processing facility at Weldon Spring, Missouri. The plant operated during World War II and up to the late 1950s, supplying uranium to the U.S. government. Remediation/cleanup of the site will generate various types of mixed waste, one of which is shown in Table V with applicable treatment technologies.

CONCLUSION

The assessment of available technologies indicates that certain mixed wastes can be converted to radioactive wastes by separation/treatment of the hazardous constituents. The selection of appropriate technologies is critical for effective conversion of mixed wastes to radioactive wastes. The treatment technology selection should be based upon actual testing on a representative scale. The assessment also concludes that for certain types of waste, it is not possible to convert the mixed waste to radioactive waste.

REFERENCES

1. L.J. Mezga and B.M. Eisenhower, "Overview of Mixed Waste Issues at the Defence Installations of the United States Department of Energy," Int. Symposium on Management of Low- and Intermediate-Level Radioactive Wastes, Stockholm, May 16-20, 1988, Vol. 1, p. 379, Int. Atomic Energy Agency.

2. R. Baird, E. Jennrich, E. Murphy, G. Merrell, and R. Shuman, "The Management of Mixed Low-Level Radioactive Waste in the Nuclear Power Industry," RAE-8807-1, Rogers & Associates Engineering Corp. (1989).

TABLE III

Treatment Technologies

Physical/Chemical Treatment Technologies

ACID DIGESTION	
Waste Type:	Best on nonvolatile organic liquids; not as effective for volatiles such as light paraffinic compounds, carbon tetrachloride, or benzene.
Description:	The organic waste is dehydrogenated with concentrated sulfuric acid at elevated temperature ($>250^{\circ}C$) followed by oxidation of the resulting carbon to carbon monoxide and carbon dioxide with nitric acid or hydrogen peroxide. The residue can be distilled to produce a solid. If necessary the solid residue can be put in a solidification matrix.
Advantages:	Can handle a wide range of waste types; operates at low temperature.
Disadvantages:	Some organics will vaporize before reacting. Uses corrosive reagents that require special materials of construction. The residue is liquid and will require further processing. The radioisotopes may react.
Cost:	Low.
By-Products	Process may produce insoluble sulfates, nitrates, or oxide residues. Off-gas must go through liquid scrubber.
Status:	Developed at DOE Hanford Engineering Development Laboratory, where work continues at this time.
NEUTRALIZATION	
Waste Type:	Acid and caustic liquid wastes.
Description:	Liquid waste is treated in an agitated tank or basin. Alkaline waste is treated with sulfuric or hydrochloric acid, and acid waste is treated with sodium hydroxide, lime, or ammonium hydroxide. Addition of neutralization agent is generally automatically controlled by pH monitoring unit.
Advantages:	Simple process that is widely used; inexpensive.
Disadvantages:	Use of corrosive materials may require special materials of construction. Toxic gases may be emitted during reaction. Liquid residue requires solidification. The radioisotopes may neutralize and end up in the off-gas.
Cost:	Low.
By-Products:	There is the potential for formation of toxic gases.
Status:	Widely used and commercially available.
SOLIDIFICATION	
Waste Type:	Most liquid or solid wastes can be solidified. Generally, the proper mix must be determined on a case-by-case basis. Solidification by itself will not change the mixed waste status of a listed waste.
Description:	Liquid or solid wastes are mixed with a solidification agent such as cement, asphalt, thermosetting polymers, or glass.

Advantages:	May allow a waste that was considered hazardous because of its characteristics to be considered nonhazardous; widely used technique.
Disadvantages:	Some wastes do not solidify easily (e.g., ion exchange resins). Increases volume; may require waste form development work for each specific waste. Will not separate hazardous constituents from radioisotopes.
Cost:	Low.
By-Products:	None.
Status:	Already in wide use at nuclear power plants and DOE facilities.

WET-AIR OXIDATION

Waste Type:	Organic liquid wastes that are soluble in water. Not effective on halogenated aromatics. Good for aliphatic, chlorinated aliphatic, and aromatic hydrocarbons and phenols.
Description:	Waste heated with water and air at 250°C. Oxygen in air reacts with organic matter to produce carbon dioxide and water.
Advantages:	Low cost; well suited for aqueous waste not economical to incinerate (5 percent organics). Highly effective on most aliphatic hydrocarbons.
Disadvantages:	Not as effective as incineration for high organic concentrations. Not effective for organics that are insoluble in water. Temperature too low for oxidation of highly chlorinated chemicals (e.g., hexachlorobenzene, PCBs). Volatile isotopes (I-125, 131, and 129) may end up in the off-gas. Liquid residue requires solidification.
Cost:	Low; for aqueous wastes that have a concentration of oxidizable materials between 2 and 20 percent.
By-Products:	Off-gas may include volatile organics such as acetaldehyde, acetone, acetic acid, or methanol. The liquid phase usually contains carboxylic acids and other carbonyl group compounds.
Status:	Used commercially for municipal sludge and some industrial waste. Generally used in conjunction with post treatment by biological process to eliminate volatile components. Has been used to treat industrial solvent waste. Recommend pilot test before processing.

EVAPORATION/ION EXCHANGE

Waste Type:	Liquid waste with organics and soluble radioisotopes.
Description:	Waste is evaporated/steam distilled to separate the organics, followed by ion exchange of the evaporator bottom.
Advantages:	Effective for low to medium volatile organics and soluble isotopes.
Disadvantages:	Volatile organics and evaporator bottom will require further processing.
Cost:	Moderate.
By-Products:	Hazardous organic stream.
Status:	Used at DOE facilities.

THERMAL TREATMENT TECHNOLOGIES:

INCINERATION

Waste Type:	Combustible solid and liquid wastes where the radioactive component is a noncombustible material.
Description:	Wastes are incinerated at high temperature, mainly forming water, carbon dioxide, and a solid ash. Air pollution control devices are necessary to remove by-products such as sulfur oxides, nitrogen oxides, hydrogen chloride, and metal aerosols.

Advantages:	Generally complete destruction of waste. The residue is ash.
Disadvantages:	Ash may still be hazardous waste if it contains metals. Incineration has a relatively high cost. Produces particulates and airborne emissions that must be controlled by air pollution control devices (e.g., baghouses, high-temperature ceramic filters, scrubbers, electrostatic precipitators, etc.). Often, corrosion problems occur because of temperature and corrosive by-products. Some radioactivity may end up in the off-gas by entrainment.
Cost:	High.
By-Products:	Off-gas will contain sulfur oxides, nitrogen oxides, hydrogen chloride, metal compounds, and particulates.
Status:	Widely used to treat hazardous waste, and used at DOE facilities to process radioactive waste.

LOW-TEMPERATURE VOLATILIZATION (LTV)

Waste Type:	Soils and sludges with low-boiling organic contaminants at generally low contaminant concentrations.
Description:	Soil is heated in an agitated unit to 300 to 800°F (depending on model) to volatilize the organic contaminants. The gaseous organics are either condensed and collected, or ignited in an afterburner.
Advantages:	Lower operating temperature reduces formation of metal fumes and nitrogen oxides. Process is less expensive then incineration.
Disadvantages:	Not as effective as an incinerator in destroying low-boiling organics. May not destroy all organics in soils or sludges. Some radioisotopes may volatilize.
Cost:	Relatively high, but less than an incinerator.
By-Products:	The treated soil may retain high-boiling organic compounds. The off-gases includes organics and will require further treatment.
Status:	Commercially used to treat hazardous waste.

MOLTEN-GLASS ENCAPSULATION

Waste Type:	Any solid or liquid. Inappropriate for soils because of high volume. Good for highly toxic waste, waste containing heavy metals. One operator has limited moisture content to $<20\%$.
Description:	Waste is added to pool of liquid glass. High temperature (1,200°C) destroys organics and nitrates, and residue is immobilized in glass. The glass is an effective solidification agent. Volatile materials and elements are off-gassed and must be treated.
Advantages:	Effective in destroying organics and nitrates.
Disadvantages:	May not effectively destroy highly volatile materials. High cost. Contaminated waste, such as sodium sulfate, may affect integrity of glass binder. Significant amount of radioactivity will end up in the off-gas stream.
Cost:	High.
By-Products:	Products of combustion such as nitrogen oxides, sulfur oxides, hydrogen chloride, and some volatile organics need to be treated by an off-gas processing system.
Status:	Method has been used in pilot studies for radioactive waste.

TABLE IV
Suitability of Treatment Processes for Waste Forms

	Acid Digestion	Neutralization	Solidification	Wet-Air Oxidation	Evaporation/ Ion exchange	Incineration	LTV	Molten Glass
Liquid Organics	X	NA	NA	X	X	X	NA	NA
Aqueous Wastes	NA	NA	NA	X	X	NA	NA	NA
Solid Combustibles	NA	NA	NA	NA	NA	X	NA	X
Acid and Caustic Wastes	NA	X	NA	NA	NA	NA	NA	NA
Soils, Sludges	NA	NA	X	NA	NA	X	X	X
Toxic Wastes	NA	NA	X	NA	X	NA	NA	X

X - Suitable
NA - Not Appropriate

TABLE V
Remediation of Mixed Waste at Weldon Spring Facility

Waste Stream	Principle Contaminants	Remedial Technology
Soil	Various solvents, acids, uranium (U-238 and U-235), and americium (Am-241).	For Hazardous Constituents: Neutralization followed by detoxification using low-temperature volatilization followed by catalytic oxidation. For Radioactive Constituents: After removal/destruction of the hazardous constituents, solvent extraction followed by ion exchange to remove U-235, U-238, and Am-241.