Thermal Treatment of EDTA Solutions

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ABSTRACT

Chemical cleaning of commercial nuclear power facility secondary systems, using EDTA, results in large volumes of chelated liquids requiring some form of treatment prior to disposal. The Nuclear Regulatory Commission regulates the presence of chelates in disposal cells and this paper will look at several methods used to ensure compliance with disposal site criteria. The emphasis of this paper will be on results achieved through thermal treatment of chemical cleaning wastes at the Pacific EcoSolutions' (PEcoS) low level and mixed radioactive waste processing facility in Richland, Washington. We will discuss challenges in transportation, receipt, storage, processing, and disposal associated with EDTA solutions and how those challenges are overcome.

INTRODUCTION

Pacific EcoSolutions, Inc. (PEcoS) is a small business low level waste and mixed low level waste processor located in Richland, Washington. PEcoS is a wholly owned subsidiary of Nuvotec $_{USA}$, Inc. PEcoS was formed when local businessmen purchased the assets of ATG, Inc.'s Richland, Washington facility out of bankruptcy in September of 2003. The management of Nuvotec $_{USA}$, Inc. is committed to continue to grow the PEcoS facility to ensure it is able to meet the needs of generators of radioactive and mixed radioactive wastes throughout the United States and eventually world-wide.

PEcoS occupies 45 acres of land adjacent to the Department of Energy's (DOE) Hanford Site in Southeastern Washington State. The mixed waste and low level waste facilities of PEcoS share a common fence but are issued separate radioactive materials licenses by the State of Washington in agreement with the NRC. The mixed waste facility also has an active RCRA Part B permit.

PEcoS utilizes a mixture of thermal and non-thermal treatment technologies to ensure low level radioactive and mixed wastes are compliant for near-surface disposal or return to the generator. This paper focuses on the treatment of EDTA solutions as generated from system cleanouts at commercial nuclear power facilities. In addition to being radioactive, EDTA solutions are considered chelating agents and as such, are highly regulated by the NRC in near surface disposal. It is important to note PEcoS' ability to receive both low level and mixed wastes since EDTA solutions, as generated, may be considered a mixed waste either by state or Federal regulations. Those that are state hazardous only will be received at the fully permitted PEcoS mixed waste facility and transferred to the low level waste facility for treatment. Those solutions that are EPA hazardous will remain at the mixed waste facility for treatment.

Systems capable of thermally treating EDTA solutions as mixed wastes are currently being tested. PEcoS anticipates it will have the ability to begin accepting these solutions as mixed wastes in late summer of 2006. EDTA solutions would typically only be mixed wastes due to the presence regulated quantities of RCRA metals. PEcoS will volume reduce the EDTA solutions, via thermal treatment, and then stabilize the RCRA metals, as necessary, to meet Land Disposal Restrictions (LDR).

SUMMARY OF TOPICS DISCUSSED

The primary focus of this paper is the thermal treatment of low level radioactive waste solutions of EDTA; specifically, those generated from the chemical cleaning of secondary side steam generators at commercial nuclear power facilities. The following items will be addressed:

- methods of packaging and transport of EDTA solutions;
- types, volumes, and concentrations of EDTA solutions treated;
- methods of treatment available and resultant disposal volumes; and,
- chemical analysis of thermally treated EDTA solution residues.

Packaging Methods

PEcoS has received EDTA solutions and chelated materials in a variety of packages. The goal is to try and accommodate the requests of the generators. The following packagings have been received at PEcoS:

- 55 gallon drums;
- 300 gallon totes;
- portable Dana tankers (designed for truck or rail tie-down); and,
- heated and un-heated tankers (~4,400 gallon capacity).

The preferred method of receipt is in large tanker trailers either heated or unheated (see Figure 1). PEcoS has not seen any appreciable settling of solids from the use of unheated tankers until ambient temperatures drop below about 30 degrees F. In fact, most EDTA solutions received have a tendency to be slightly exothermic. Heated tankers usually maintain solutions at about 140 degrees F and PEcoS has the ability to maintain this temperature in storage if needed.

Fig. 1. Tanker receipt bay with four, 10,000 gallon nominal capacity storage tanks.

One generator utilized approximately 300 gallon, carbon steel, double-walled totes for shipment of EDTA solutions to PEcoS over two shipment campaigns. One campaign was in the fall and one in the spring. Those shipped in colder months had a tendency to release solids from solution making tote cleanout more difficult. It is important to note solutions shipped in totes were concentrated to nearly 50 weight percent EDTA. A discussion of EDTA concentrations will follow.

Shipment of EDTA solutions in 55 gallon drums is typically reserved for very small quantities and is usually not applicable to commercial reactor campaigns.

PEcoS is completing the logistics associated with receiving EDTA solutions, as well as other liquids, by rail. PEcoS will be fully ready to receive rail shipments of EDTA by early 2006. This will make shipment of large quantities of EDTA solutions more economical when shipping from longer distances. PEcoS is already receiving rail shipments of solid materials.

Types, Volumes, and Concentrations of EDTA Solutions Received

PEcoS' Richland Facility has received many types of EDTA solutions over the years and not all solutions handle, store, and treat equally. Each type of solution, as well as the concentrations of each, presented new challenges for plant personnel the first few times it was received. Dealing with these solutions over time has allowed for significant improvements in process efficiency. Two primary contractors provide chemical cleaning services to the commercial nuclear industry and each has its own recipes based on customer needs. Two types of solutions were typically encountered: iron-based and copper-based solutions. The predominant solutions received were iron based. PEcoS has only received one campaign of copper-based solutions. There have not been any appreciable differences between treatment of iron and copper based solutions.

Volumes received depend on several factors including whether or not the solutions were radioactive and whether or not the solutions were concentrated prior to leaving the plant. Copper solutions are typically not radioactive. Experience has shown the following (see Table I).

Table I. Volumes of EDTA Received vs. Expected EDTA Concentration

Volume Received per Campaign	Concentration (weight % EDTA)
20,000 to 30,000 gallons	40-50%
60,000 to 80,000 gallons	25-35%
120,000 to 180,000 gallons	1-3%

Solutions also varied greatly in odor from odorless to a strong ammonia odor. The ammonia odor varied depending on the chemical cleaning vendor's choice of solution and whether or not the solutions were kept heated. Solutions that did contain ammonia and were kept heated, did present more of an ammonia odor to the workers.

Solutions when received are stored in 10,000 gallon capacity poly tanks and/or 20,000 gallon capacity, stainless steel FRAC tanks. PEcoS has four such poly tanks and two FRAC tanks with the ability to bring in more tanks if necessary. Experience has shown the need to limit storage times in FRAC or similar type tanks due to the aggressive nature of EDTA on the tank welds. Because of shipping schedules and process times, PEcoS has never needed storage capacity beyond that currently available on site.

Chemical cleaning projects typically generate some amount of chelated resins and wet process filter media. Receipt of these materials typically occurs in standard boxes or drums as these items also have minimal dose rates.

Methods of Treatment and Resultant Volumes

Two prime methods of treatment exist for EDTA solutions: non-thermal through absorption and thermal destruction. Non-thermal treatment is acceptable when volume reduction is of no concern and when concentrations of chelates in disposal cells allow. The NRC indicates the presence of chelates in licensed disposal cells may not exceed 0.1 percent by weight (w/o). Above those levels, sites must be evaluated for the presence of chelates with limits and conditions applied. Wastes disposed of at Barnwell are limited to 8 w/o or less chelates and those wastes must be placed in high integrity containers. Envirocare disposal is limited to 23 w/o and those wastes must be disposed of in the mixed waste trench. At this time, requests for information from Tennessee state regulators remain unanswered with regards to the limitations of chelates for bulk survey for release to Tennessee regulated landfills. Bulk survey for release to a regulated landfill of these EDTA materials would be limited to those with very low concentrations of radioactive materials. Typically those below 1E-6 uCi/cc may be a candidate for this method of treatment and disposal. Regardless of the disposal facility, non-thermal treatment through absorption would not result in any volume reduction.

Thermal treatment is the method of choice for many generators for two primary reasons:

- full destruction of the chelate rendering the resultant waste acceptable for disposal at any of the NRC licensed or agreement state facilities; and,
- significant volume reduction resulting in significantly less liability in the disposal trench.

At PEcoS, EDTA is pumped from the storage tanks at a rate that ensures no pooling of liquids in the thermal treatment Bulk Processing Unit (BPU). This rate is highly dependent upon the concentration of EDTA in the liquid stream and the BTU's available from other feed materials. EDTA may be processed separately or with other available wastes. Typical feed rates range from 0.5 to 2 gallons permit (gpm).

The EDTA solutions are run through an atomizing nozzle inside the burn chamber that is directed at the natural gas flame to ensure complete volatization of any liquids present (see Figure 2). The BPU operates at approximately 1,800 degrees F. This temperature fluctuates up or down depending up feed stock but can be somewhat controlled with the introduction of oxygen or other feed materials. Regardless of actual temperature, the chamber is maintained well above the temperature necessary to ensure complete destruction of chelates.

Fig. 2. Inside of a BPU burn chamber this picture depicts EDTA mixing with natural gas flame and residual inorganic material collection.

Inside the burn chamber, a stainless steel bin collects inorganic residues separated from the liquid stream through rapid evaporation. The amount of residue is highly dependent on the aggressiveness of the chemical cleaning at the plants and the amount of solids entrapped by the cleaning agents or undissolved in the liquid. Table II below represents various treatment campaigns with volume of EDTA treated, in gallons, and amount of residue disposed of in ft^3:

Table II. PEcoS Historical Pre-Treatment Receipt Volumes and Post-Treatment Disposal volumes

Campaign	Gallons Treated	Ft^3 Disposed
Plant A 1999	43,000	411
Plant B 2000	20,870	119
Plant C 2001	100,455	310
Plant D 2002	15,260	214
Plant D 2003	18,789	526
Plant E 2004	168,583	441
Plant E 2005	133,839	346
Total	**500,796**	**2,367**

Disposal volumes varied depending upon total solids in solution as well as available additional materials for use of residue as void space filler. Resultant residue resembles crumbled charcoal, much like what would be seen after dousing campfire embers with water (see Figure 3). Residues are non-dispersible with typical moisture content in the range of 10-20%. Since the residue is the result of thermal treatment of waste materials, some amount of water is used to cool the embers prior to removal from the burn chamber, giving it a granular, crumbly consistency. The thermal treatment residues make excellent void filler for other materials destined for disposal, thus adding to overall volume reduction.

In addition to treatment of liquids, destruction of chelated filters and resins from cleanup projects was successfully achieved through thermal treatment. Thermal treatment of 360 ft3 of spent resin and 50 ft3 of filters has been completed. Due to the aggressive nature of resins on thermal unit secondary systems, it is best if resin volumes treated are kept below 100 ft3 per campaign. Since the resins and filters are mostly organic, residues for disposal after thermal treatment are negligible.

Fig. 3. Residue from thermal treatment of EDTA liquids

Chemical and Radiochemical Analysis of Thermally Treated Residue

From time to time, thermal treatment residues are analyzed to ensure the materials are acceptable for disposal as low level wastes. Parameters such as moisture content, TCLP for RCRA metals, and pH are tested. As previously mentioned, moisture content ranges from about 10 to 20% with higher amounts possible dependent upon the amount of water used for cooling the embers. pH is slightly basic at about a pH of 9 for the samples.

Of particular concern is the production of hexavalent chrome. While total chrome may be high in incoming liquids and outgoing residue, hexavalent chrome has been reported as either non-detectable or well below the toxicity limit of 5 ppm. The concern that the thermal treatment process may somehow create hexavalent chrome through oxidation/reduction has been unfounded to date. No other RCRA listed metals are reported near RCRA reporting limits.

Waste processing facilities have a variety of methods at their disposal to account for the presence of radioactivity. While actual sample analysis for hard to detect radionuclides is available, it is costly. If a generator is agreeable to disposal through bulk survey and release, residues could be analyzed to determine if release criteria is met. To avoid the cost of sampling, processors typically use the NRC Branch Technical Position allowed method of accountability to determine radionuclide content. A combination of accountability and direct measurement could also be used to determine acceptability at various facilities. Utilizing all the methods at PEcoS' disposal provides the generator with the ability to make sound economic and environmental decisions concerning ultimate disposal of their wastes.

CONCLUSIONS

Thermal treatment of EDTA chemical cleaning solutions, spent resins and cartridge filters has been demonstrated. The residue from this treatment has also been successfully buried in a LLW burial site. If a company is considering long term liability reduction, thermal treatment of EDTA chemical cleaning solutions may well be the best long term and economically sound solution. Thermal treatment destroys the NRC regulated chelate group rendering the resultant residue acceptable to disposal at NRC regulated facilities. It is known that the presence of chelating agents increases mobility of radionuclides in disposal trenches and that is why they are regulated by the NRC.

History has shown the possibility that wastes once thought to be safely disposed of were in fact not. Federal law dictates responsibility for generated and disposed of wastes always remains with the original generator and therefore, the cost to cleanup abandoned sites, or sites found to be out of compliance with regulations due to improperly disposed of wastes, remains with the original generator. When making waste treatment decisions it pays to consider the long term effects of disposing large volumes of both treated and untreated materials. In many instances, the volume reduction through thermal destruction of generated wastes is the best long term solution.