

MANAGEMENT OF MIXED WASTE RESIDUALS FROM DECONTAMINATION OF METALS

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ABSTRACT

Manufacturing Sciences Corporation (MSC), located in Oak Ridge, Tennessee, operates a commercial facility specializing in the recycling of radioactively contaminated metals. The metal components originate from maintenance and D&D activities within DOE and the nuclear power industry. They can be cleaned using a combination of physical and chemical techniques then free released into the scrap metal market or melted and formed into plate or billets for recycle.

One of the unit operations at this facility is a chemical decontamination line that utilizes a series of immersion tanks to remove fixed radionuclides from the surface of metal components. The mixed acids, contained in these immersion tanks, dissolve scale, corrosion products and some base metal to effect removal of surface contamination. Over time, as the various metal species and radionuclides accumulate in the tanks, the performance deteriorates and the decontamination reagent must be changed. This paper describes the performance of the chemical decontamination line and of the multi-step batch treatment, residuals management system.

INTRODUCTION

The Manufacturing Sciences Corporation (MSC), Radioactive Scrap Metal Recycling facility (RSMR) was designed and built incorporating modern best practice from the manufacturing industry as a vehicle to deploy emerging decontamination and waste treatment technologies for the recycle of RSM. Decontamination and Decommissioning activities in the US DOE and Utility sectors have and will continue to generate a significant volume of radioactive scrap metal (RSM), ranging from PWR inconel components contaminated with activation and fission products to aluminum components contaminated with transuranics.

The variety of RSM in the market place provides the radioactive metals recycling business with a very wide feedstock both in terms of radionuclide contamination and metallic substrates. In developing a process which could offer a cost saving to customers over direct disposal, a number of technologies and manufacturing principles were integrated to realize the concept of the automated, high throughput recycling process. One of the key components of this process was the flexible, robust decontamination and waste treatment technology, developed specifically for the MSC high throughput, minimal cost operating regime.

Decontamination and waste treatment operations at the MSC are comprised of the following unit operations: (See Fig 1)

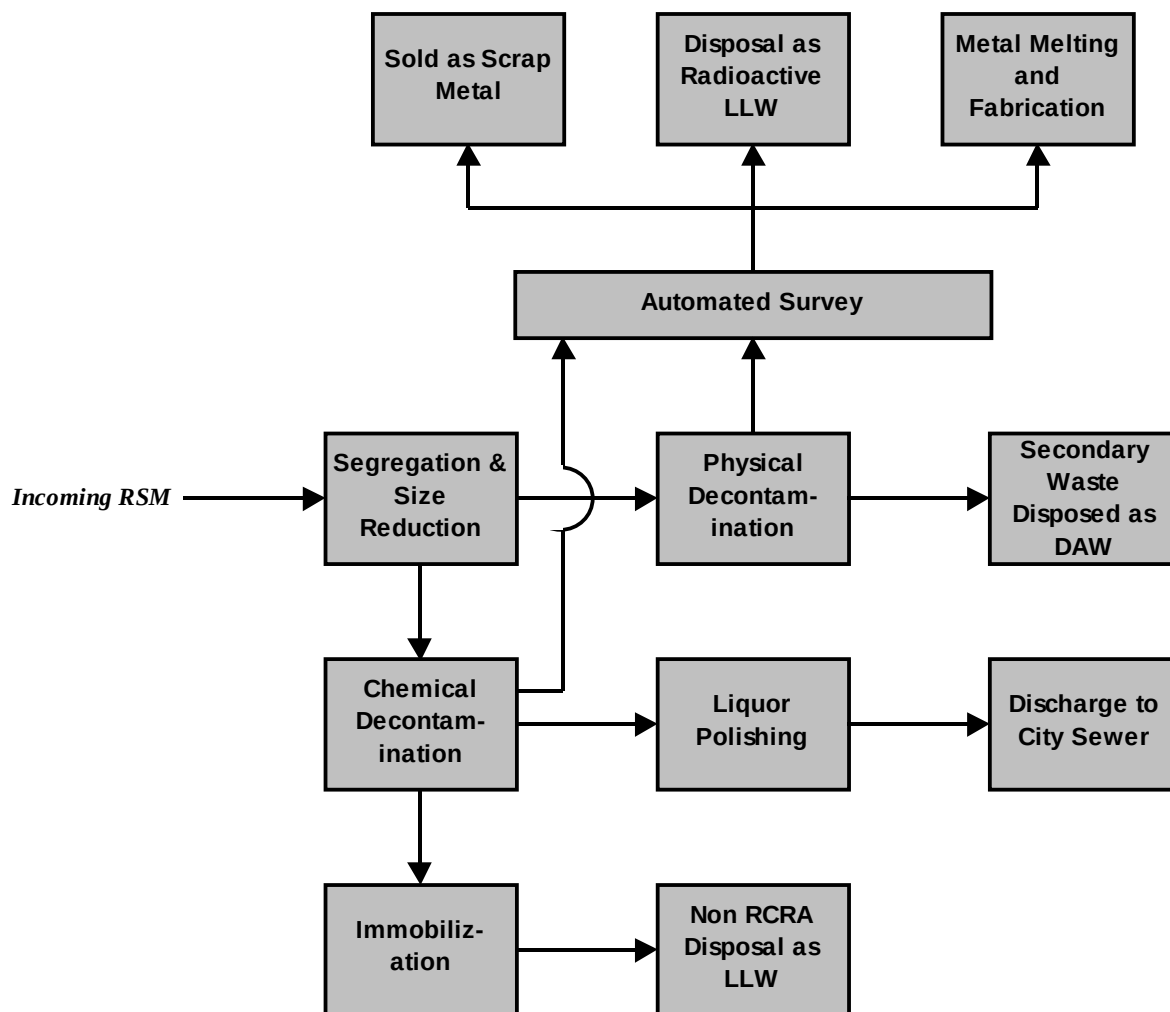


Figure 1
Flow Diagram of Decontamination Process

- Receipt, segregation and size reduction of components
- Sentencing for physical or chemical decontamination
- Processing through decontamination line
- Radionuclide contamination survey of processed metals
- Dispatch of decontaminated metals for recycle, disposal as LLW or sale into scrap metal market
- Treatment of spent decontamination liquor

- Solid / liquid separation
- Treatment of process liquors to meet local sewer discharge limits
- Immobilization of process sludges for disposal as non-RCRA dry active waste

Of the process steps described above the chemical decontamination, treatment of spent liquors and the final waste water polishing to meet discharge limits required the greatest process development, to meet the challenging requirements of the commercial MSC radioactive scrap metal recycling facility.

CHEMICAL DECONTAMINATION

A development program was initiated to address the technology requirements of the MSC chemical decontamination line, objectives of the program were to deliver:

- A safe and cost effective process for the decontamination of RSM
- Capable of accepting a wide variation in feedstock
- Offer a cost saving over direct disposal of RSM
- Produce a minimal volume of non RCRA secondary waste
- Process liquors suitable for discharge to the Oak Ridge sewer

A literature review was conducted of decontamination practice worldwide and this was compared with BNFL's considerable practical experience in the field of decontamination and residuals waste treatment. Findings of the review concluded that a decontamination liquor composed of nitric and hydrofluoric acids would prove suitably generic and robust for the decontamination of the varied feedstock at high throughput levels.

The aggressive nature of the nitric / hydrofluoric acid decontamination process would require careful control of the process parameters to achieve the optimum surface corrosion rate for a given substrate. Optimizing surface corrosion for a given substrate has the following advantages:

- Minimization of base metal corrosion
- Prolongs decontamination tank lifetime
- Ensures uniform surface corrosion without pitting of base metal
- Minimizes volumes of secondary waste by avoiding dissolution of uncontaminated base metal

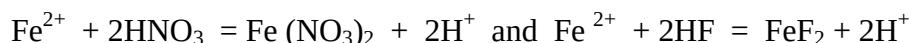
- Avoids uncontrolled dissolution reactions giving rise to off gases as the acids break down

Achieving the optimal surface corrosion rate for a varied feedstock using a single chemical decontamination reagent required careful control of:

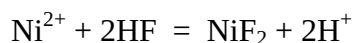
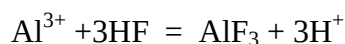
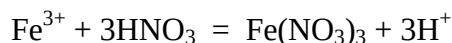
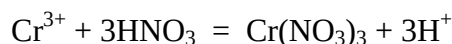
- Temperature of the decontamination tank
- Concentrations of the mixed acids
- Agitation and oxidation potential of the decontamination reagent
- Concentration of dissolved metals and radionuclides in the decontamination tanks
- Sequencing and immersion time in the decontamination tanks

This control philosophy was used to define a number of contaminant and substrate decontamination “recipes”, which were programmed into an automated monorail tasked with immersing the components in the decontamination tanks in a prescribed sequence. By defining initial parameters for the system and then refining these as operational experience was gained and captured, the optimum efficiency of the acid immersion tanks and the chemical decontamination line as a whole was realized.

As the fresh acid solution is placed in contact with a contaminated metal surface dissolution occurs and the metal is dissolved in the acid solution. This results in metal loading of the acid bath. Although the reaction of the acids upon surfaces is complex and involves a number of equilibrium reactions we can in the first instance for the dissolution of iron by nitric acid, simplify the reaction to the following:



And similarly for other metals:



Theoretically for the case of iron dissolution by nitric acid for every one mole of iron dissolved two moles of nitric acid are needed. However due to passivation of the metal surface, plate-out, oxidation of iron and the extremely slow dissolution rate as the acid is consumed in the dissolution reactions, such metal loading is impractical.

As a first order approximation the metal dissolution rate of the acids is directly proportional to the concentration of the acids. Thus for a high throughput of metal in the decontamination line two factors have a significant impact on decontamination performance:

- Concentration of dissolved metals in the acids, overburdening the acids with dissolved metals results in insufficient free acid to achieve significant dissolution of the metal substrate
- Minimization of free acid present in the spent acid sentenced for waste treatment. Unreacted acid is neutralized during waste treatment and this generates a significant volume of secondary waste.

Hence in operating the decontamination process a balance has been struck between metal loading of the acids and dissolution rates, with due regard for surface pitting and off gas production. Minimization of off gasses that require scrubbing, resulting in the generation of a secondary waste form and depletion of the acid capacity, is an important issue when decontaminating the more reactive metals such as carbon steel and aluminum.

Considerable testing of the decontamination recipes and evaluation of results was performed in order to optimize the chemical decontamination process to a point where it could be operated on a high throughput, minimal secondary waste basis. It became necessary to introduce an additional process parameter during the optimization program and that was to operate the decontamination tanks on a lag basis. This involved designating the tanks as low, medium and high dissolved metal content, each fulfilling a particular duty within the overall decontamination process:

- The low tank was used for final polishing of the decontaminated metal as this had the least radionuclide inventory and highest dissolution kinetics.
- The high tank was used for initial decontamination where the highest levels of radionuclides associated with the outer most surface were removed.
- The medium tank was a transitional one, which was additionally used for “special” materials, which were substantially different from the majority of the campaign feedstock.

The tanks were rotated from low through to high based on a predetermined dissolved metal and radionuclide inventory, with the high tank being taken off line and designated spent once decontamination had become ineffective. This process required a daily sampling and analysis procedure to measure and record trends in tank performance. In order to simplify and reduce the cost of analysis the operational experience gained was used to devise a “finger print” which could be used to determine when a tank was required to be reclassified.

The economic case for decontamination to free release or re-categorization to LLW for disposal was based on the degree of surface contamination, which drives processing costs and value of the recovered metal plus the cost of treating any secondary waste. Examples are:

- PWR primary loop components which have been exposed to a high temperature, high pressure liquid environment generally require the removal of 20 to 30 μ m of corrosion film and base metal to achieve re-categorization to LLW. Achieving free release levels can require the removal of an additional 150 to 200 μ m of metal.
- Components from fuel cooling pools such as stainless fuel racks can be decontaminated to LLW by removing 5 to 8 μ m of surface and free release can be achieved by removing 15 μ m of surface metal. The less demanding metal removal could favor free release.

The operational flexibility designed into the chemical decontamination line allows both decontamination for re-categorization to LLW and also to free release. This has been performed simultaneously utilizing the tank lag system, where decontamination to free release would be performed in the low activity tank and decontamination for re-categorization to LLW would be performed initially in the high and subsequently in the medium activity tank.

An additional advantage of the lag system was the degree of uniformity, in terms of dissolved metal and radionuclide content, that it introduced to the spent tank waste treatment process.

SPENT ACID WASTE TREATMENT

This spent acid was treated in the MSC facility wastewater treatment system (WTS). This system consists of a number of batch treatment tanks, a small UV system and an ion exchange skid. A final ultrafiltration unit completes the treatment system.

The WTS is operated under an industrial wastewater discharge permit from the City of Oak Ridge, TN and discharges to the Oak Ridge publicly owned treatment works (POTW). The primary duty of the WTS is treatment of water from the facility laundry water system, but the spent acids are processed on an intermittent basis, in separate batch treatment tanks as they are generated. All treated water is stored in one of two final effluent tanks and held for analysis prior to discharge. The treated spent acid and the laundry water is combined in these effluent tanks for discharge. Treatment of the spent acids in the WTS produces two waste streams:

1. An alkaline wastewater, sentenced to the water treatment tank for final polishing by chelant oxidation followed by ion exchange and discharge to the City sewer in accordance with the Oak Ridge wastewater treatment permit.
2. A sludge containing the major metal species, (iron, chromium, nickel) and radionuclides (cobalt, cesium) for direct solidification by grouting with Portland cement to meet the Envirocare waste acceptance criteria.

The spent acid from the chemical decontamination process contained a high concentration of dissolved metals and radionuclides, as shown in the following table:

Table I.
Spent acid dissolved metal and radionuclide content.

Contaminant	Cr	Ni	Fe	Cu	⁶⁰ Co	^{134/137} Cs	²⁴¹ Am ⁵⁴ Mn	Anions (nitrate fluoride chloride)
Concentration	1600 mg/ L	2000 mg/L	12,500 mg/L	2000 mg/L	80,000 pCi/L	3000 pCi/L	1000 pCi/L	>10%

Again a robust high throughput waste treatment system was required with the objective of producing a minimal volume of non-RCRA solid waste. Since the types of alloys processed in the chemical decontamination system effects the ratios of metals in the spent acid, a highly flexible batch treatment approach was required. BNFL has considerable practical experience of co-precipitation, solid / liquid separation, ion exchange and immobilization using grouts, at the large industrial scale. This experience and an extensive development program, conducted on samples of spent acids from the MSC facility, resulted in the MSC waste treatment process, which comprises the following process steps: (See Fig 2)

- Partial neutralization and conditioning of spent acids using calcium hydroxide
- Adjustment of pH to a range of 9 to 10 using sodium hydroxide.
- Flocculation, seeding with inorganic adsorbents and co-precipitation of metals and radionuclides.
- Addition of polymers to aid gravity settling of solids.
- Solid / liquid separation.
- Grouting of solids.
- Oxidation of chelates in wastewater by UV / sodium hypochlorite addition.
- Wastewater polishing by ion exchange using clinoptilolite.

The above process steps are performed sequentially over a 24 hour period and the acid tank, when empty, is replenished with fresh acid and returned to service. The waste treatment process was developed to be robust and simple to operate using readily available, low cost chemicals and process equipment.

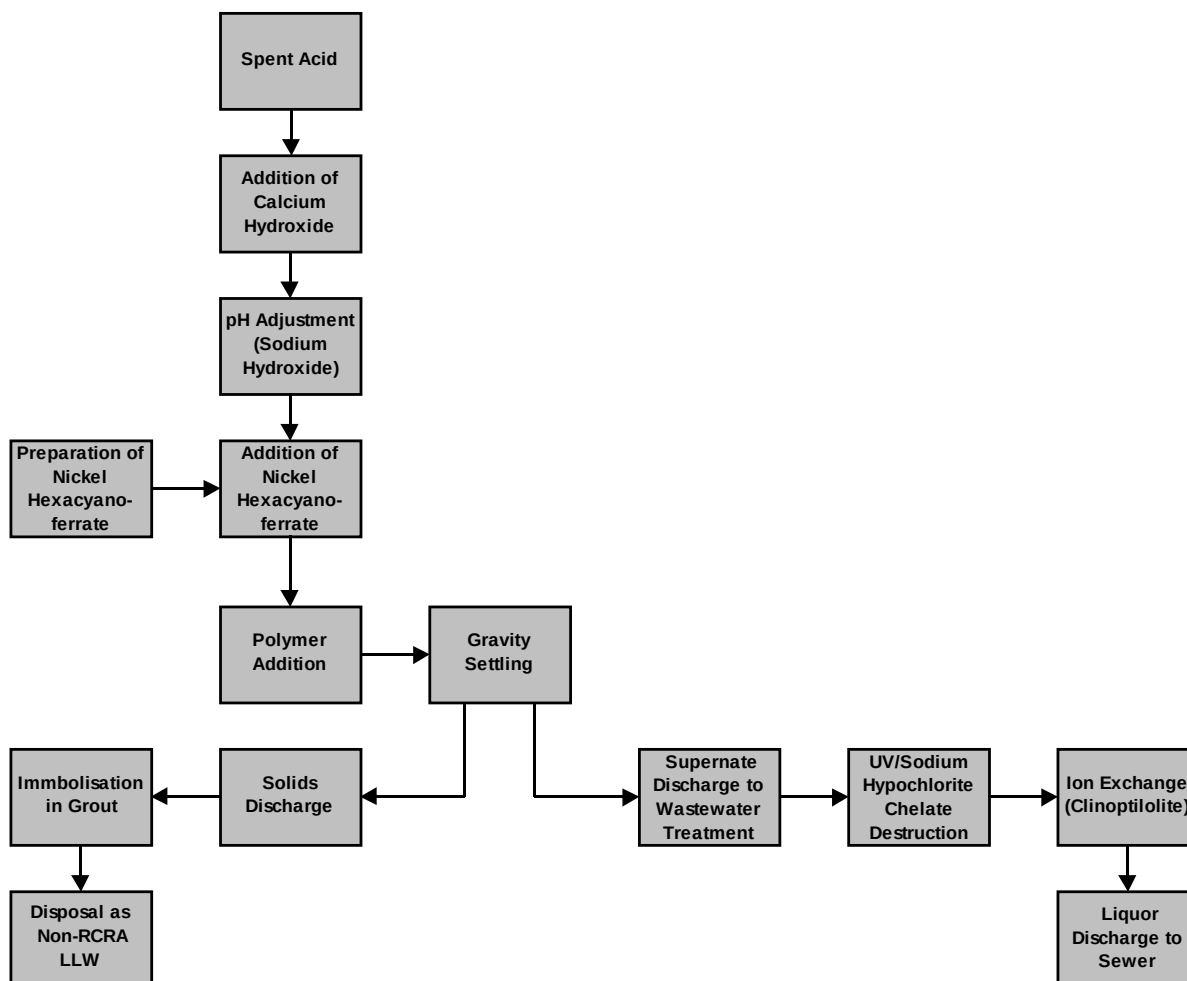


Figure 2
Flow Diagram of Waste Treatment Process

Calcium hydroxide is used principally to condition the resultant metal hydroxide floc by assisting in the binding of leachable metals, principally chromium. The calcium fluoride formed in the partial neutralization forms the body of the floc and improves sludge settling characteristics. The calcium hydroxide is not used for pH control as this would result in the formation of an excessive amount of calcium sludge requiring disposal as a secondary waste product. Therefore final pH adjustment is accomplished using sodium hydroxide, which is highly soluble and results in a sharp inflection point in pH allowing greater process control.

The presence of dissolved iron assists in chromium removal due to the $\text{Fe (II)} \leftrightarrow \text{Fe (III)}$ couple ensuring the chromium is present as the reduced Cr (III) State. In some cases, if the Fe (II) / Cr. ratio in the spent acid is less than 4: 1 wt/wt, additional ferrous iron may be required to reduce chromium to the less soluble form. This can also be controlled by management of the processing

of nickel / chromium alloys and stainless or carbon steels, which supply the iron ratio needed for chromium reduction.

The two-stage neutralization forms a floc that contains virtually all the radionuclide and metal contaminants, with the exception of cesium, which is highly soluble. Typically cesium is removed from wastewater processing through an ion exchange column. Testing indicated that, for the spent acid liquor, this approach has a number of disadvantages i.e.

- Slow processing rate due to slow kinetics
- Proprietary, highly selective ion exchange media for column use in high salt streams is expensive
- Less selective ion exchange media were rapidly exhausted by other metals and radionuclides, which produced excessive secondary waste
- Pretreatment to remove particulate which has the potential to blind the columns is required and this produces an additional waste stream

Because of the above disadvantages an alternative method was developed for cesium removal using nickel hexacyanoferrate. This involved producing the solid nickel hexacyanoferrate (HCF) ion exchanger, on-site from laboratory grade chemicals and adding 300 ppm as a dilute slurry directly into the batch treatment tank once the pH has been adjusted. Cesium removal was aided by isotopic dilution by addition of 10 ppm of non-radioactive cesium chloride. The HCF was more effective immediately after it was formulated and resulted in lower cesium removal and higher residual nickel if aged. The kinetics of the cesium complexation with HCF is very rapid and the complex formed is removed from solution by adsorption and agglomeration with the metal hydroxide floc. A decontamination factor of 600 was achieved for cesium and the supernatant liquor was free of all metals except a few ppm of nickel and chromium and trace levels of cesium. Final cesium removal was accomplished by adsorption on clinoptilolite, a natural zeolite.

Separation of the floc from the supernate can be achieved by a number of mechanical separation devices, though all of them are either costly, generate a secondary waste in the form a filter media or require frequent manual intervention. For these reasons gravity settling and decanting the supernate was chosen, as this was a low cost simple solution. It does however have the disadvantage of being a time consuming process. Increasing the rate of settling and clarity of the supernate was achieved by adding several hundred ppm of an anionic polymer and slowly rotating the tank contents using the in tank stirrer.

After a period of 4 to 8 hours the supernate from the HCF step was decanted and processed through the wastewater treatment, polishing step. This was performed by:

- Dosing with 0.25 to 0.5 % sodium hypochlorite and treatment with UV light to oxidize the soluble heavy metal complexes (nickel and ^{60}Co) and yield insoluble compounds. Treatment times were 6 to 18 hours.
- Removal of particulate by mechanical filtration by passing through a bed of sand and charcoal followed by cartridge filters.

This step resulted in a reduction of the heavy metals, primarily nickel, from 10 - 20 mg/L to the required discharge limit of not greater than 1.5 mg/L. The ^{60}Co was similarly reduced from 20 - 50 pCi/L to the required discharge limit of less than 1 pCi/L.

Following this last chemical treatment, the cesium level slightly exceeded the discharge criteria. Further cesium removal was achieved by mixing the decant liquor with laundry water from the final effluent tank. This dilution lowered the concentration of nitrate and fluoride salts in the wastewater and improved the efficiency of the cesium removal by ion exchange using two columns packed with clinoptilolite. The clinoptilolite column had a residence time of 60 to 80 minutes and the resulting wastewater met the discharge criteria for disposal to the Oak Ridge City sewer. The capacity of the ion exchange column was found to be between 80,000 to 90,000 bed volumes and the sand bed filter did not require to be changed out.

The second waste stream from the WTS consisted of the radionuclide and metal contaminated sludge from the settling and decanting step. This sludge or metal floc passed the TCLP criteria for leachable metals and were directly solidified in a cementitious grout. The settled solids were pumped from the batch treatment tank into 55-gallon drums. A helical drum mixer was used to incorporate 0.75 to 1.0 pounds of Portland cement per pound of sludge. This was accomplished with very little heat rise and 20 to 30 minutes mixing. The grout was then dumped from the drums into molds that were designed to produce a final waste form that met the Envirocare of Utah waste acceptance criteria for size requirements for debris. The resulting grouted waste incurred a minimal volume increase of 20 %, cured overnight with no bleed, strength of over 50 psi and passed the TCLP test for disposal as non RCRA LLW.

CONCLUSION

The Manufacturing Sciences Corporation (MSC) radioactive scrap metal recycling facility operates a high throughput, safe, cost effective decontamination and waste treatment process. Chemical decontamination has been shown to be capable of simultaneously decontaminating a wide range of feedstock from both DOE and Utility nuclear facilities.

Chemical decontamination can be used to re-categorize RSM for disposal as LLW or can be pursued to the point where the RSM is suitable for free release. The criteria for determining the degree of decontamination are complex and heavily influenced by waste disposal costs. The performance and experience data base at MSC has allowed the use of chemical decontamination to be optimized ensuring that processing cost and secondary waste generation are minimized.

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Resultant spent acid decontamination liquors are processed in a continuous, generic residuals waste management system. All wastes generated are suitable for discharge to the City sewer or disposal as non-RCRA solid LLW.