

# Stabilization Using Phosphate Bonded Ceramics

Salt Containing Mixed Waste Treatment

Mixed Waste Focus Area



*Prepared for*  
**U.S. Department of Energy**  
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**Salt Containing Mixed Waste Treatment**

OST Reference #117

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*Demonstrated at*  
Argonne National Laboratories-East  
Chicago, Illinois



## ***Purpose of this document***

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine if a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at <http://OST.em.doe.gov> under "Publications."

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## SECTION 1

# SUMMARY

### Technology Summary

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Throughout the Department of Energy (DOE) complex there are large inventories of homogeneous mixed waste solids, such as wastewater treatment residues, fly ashes, and sludges that contain relatively high concentrations (greater than 15% by weight) of salts. The inherent solubility of salts (e.g., nitrates, chlorides, and sulfates) makes traditional treatment of these waste streams difficult, expensive, and challenging. Many of these materials are in a dry granular form and are the by-product of solidifying spent acidic and metal solutions used to recover and reformulate nuclear weapons materials over the past 50 years. At the Idaho National Engineering and Environmental Laboratory (INEEL) alone there is approximately 8,000 cubic meters of nitrate salts (potassium and sodium nitrate) stored aboveground with an earthen cover. Current estimates indicate that over 200 million kg of contaminated salt wastes currently exist at DOE sites. Continued operations involving wastewater treatment facilities and mixed waste incinerators could generate an additional 5 million kg a year.

One of the obvious treatment solutions is to immobilize the hazardous components to meet Environmental Protection Agency/Resource Conservation and Recovery Act (EPA/RCRA) Land Disposal Restrictions (LDR), thus rendering the salt-containing mixed waste to a radioactive waste classification only. One proposed solution is to use thermal treatment via vitrification to immobilize the hazardous component and thereby substantially reduce the volume, as well as provide exceptional durability. However, these melter systems involve expensive capital apparatus with complicated offgas systems and generate secondary mixed wastes. In addition, the vitrification of high salt wastes may cause foaming and usually requires extensive development to specify glass formulation recipes. As an alternative to thermal treatments, stabilization of these materials in cementitious grouts has also been widely employed. However, salts interfere with the basic hydration reactions of cement, leading to an inadequate set or deterioration of the waste form over time.

Sufficient and compliant stabilization in cement can be achieved by lowering waste loadings, but this involves a large and costly increase in the volume of material requiring handling, transporting, and disposal. As a consequence of these stabilization deficiencies associated with salt containing mixed wastes, the Mixed Waste Focus Area (MWFA), a DOE Environmental Management (EM)-50 program, sponsored the development of five low-temperature stabilization methods as an alternative to cement grouting.

One alternative is low-temperature stabilization by chemically bonded phosphate ceramics (CBPCs). The process involves reacting magnesium oxide with monopotassium phosphate with the salt waste to produce a dense monolith as shown in Figure 1. The ceramic makes a strong environmental barrier and the metals are converted to insoluble, low leaching phosphate salts. The process has been tested on a variety of surrogates and actual mixed waste streams, including soils, wastewater, flyashes, and crushed debris. It has also been demonstrated at scales ranging from 5 to 55 gallons. In some applications, the CBPC technology provides higher waste loadings and a more durable salt waste form than the baseline method of cementitious grouting. Application of a polymer coating to the CBPC may decrease the leaching of salt anions, but continued waste form evaluations are needed to fully assess the deteriorating effects of this leaching, if any, over time.



## Demonstration Summary

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Under MWFA sponsorship, investigators at DOE's Argonne National Laboratory- East (ANL-E), performed a series of development tests to validate the stabilization of salt-containing mixed wastes with their patented CBPC process. The low-temperature process uses binders of magnesium oxide and monopotassium phosphate to form a low porosity, dense waste form consisting mainly of a ceramic magnesium potassium phosphate (MKP) barrier. The technology is also referred to as *Ceramicrete*.

Various testing done with surrogates of mixed wastes containing salts were completed, including tests with saturated salt solutions and two MWFA recommended dry salt waste surrogates representative of actual wastes in the DOE complex. The tests consisted of preparing various CBPC waste forms with waste loadings of up to 70 wt%, corresponding to salt loadings of up to over 40%. This salt waste loading is ~2.8 times that achievable with the baseline Portland cement stabilization method.

Waste form test specimens were subjected to a variety of performance tests, including compressive strength, RCRA (Resource Conservation and Recovery Act) metal leachability per the (Environmental Protection Agency's) EPA's toxicity characterization leaching procedure (TCLP) method, and salt anion leachability per American National Standards Institute (ANSI) 16.1. Results of waste form performance testing concluded that CBPC forms made with salt wastes meet or exceed both RCRA and recommended Nuclear Regulatory Commission (NRC) low-level waste (LLW) disposal criteria. Flammability tests validated that CBPC waste forms containing oxidizing salts (e.g., nitrates) are also stable and safe. A modification to the process, including that of coating the waste form in a commercial polymer, increases its salt anion retention and therefore, its perceived long-term durability.

**Figure 1. Cut-a-way view of an operational scale CBPC waste form.**



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## SECTION 2

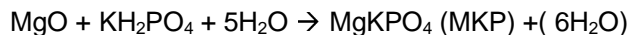
### TECHNOLOGY DESCRIPTION

#### Overall Process Definition

The ANL-E- developed, CBPC process is one of several phosphate based, low-temperature waste stabilization processes available. Like basic Portland cement, CBPC is a stabilization /solidification (S/S) method, as opposed to just a microencapsulation technique. Its classification as an S/S process is justified since the hazardous and radiological components of the mixed waste loaded in the form are not only entrapped, but also immobilized through a lowering of their solubility or an elimination of their toxicity.

CBPC is unique in that it is formed at room temperatures like a Portland cement, but has the properties of a thermally fused ceramic. The ceramic strength of CBPC is derived from its acid – base chemistry, which produces strong covalent bonds, as compared to the weaker hydration bonds of simple cements. Acid-base cements have been in existence for over 50 years, but their application as a mixed waste stabilization method has been only recently evaluated.

As given by the equation below, low-temperature stabilization of mixed waste with CBPC is based on the acid-base exothermic reaction between magnesium oxide (MgO) and monopotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>) binders. The binders are ground to a powder and blended. The MgO is also completely calcined to reduce its reactivity. The reaction produces MKP that is hydrated by six moles of water. Class C or F fly ash is routinely added to the binders and waste to increase waste form strength and integrity. Under most conditions, heat from the reaction causes a temperature increase up to less than 80 degrees C, until the waste form starts cooling upon curing.



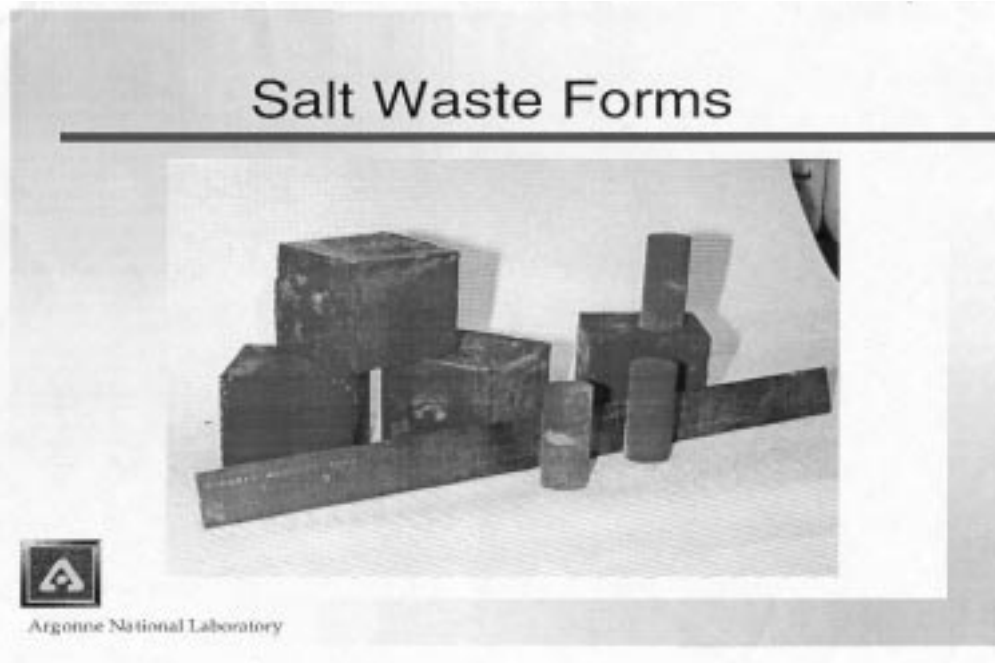
The hard, insoluble, stable, and dense ceramic of MKP hydrate acts as a crystalline host matrix for the mixed waste. The RCRA hazardous heavy metals and radioactive contaminants in the waste also react with the KH<sub>2</sub>PO<sub>4</sub> to form highly insoluble phosphates. In addition, the formation of phosphate minerals such as monazite are natural hosts to radioactive elements and are highly insoluble. The final waste forms routinely have compressive strengths greater than 2,000 psi and porosities ~50% less than those fabricated of cement. The density of the ceramic waste form (~1.8 g/ml) is also routinely less than that of a cement form (~2.4 g/ml).

A 50 wt. % concentrated phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) solution can be substituted for the KH<sub>2</sub>PO<sub>4</sub> binder to form the insoluble newberyite, MgHPO<sub>4</sub>(3H<sub>2</sub>O), ceramic. However, the MKP system is usually preferred over the acid system, since it generates less heat and improves leachability performance.

The porosity of the CBPC waste form can be further decreased by adding fly ash to the mix before curing or coating the waste form by dipping it into a polymer. These methods are most applicable to CBPC forms stabilizing high levels of salt-containing mixed wastes (as shown in Figure 2). The method can decrease the notable leaching of the salt anions over time, which may eventually deteriorate the waste form.







**Figure 2. Stabilized surrogate salt waste forms made from CBPC**

## System Operation

A simple flowsheet for performing the CBPC stabilization technology on a testing, development, or operational scale is provided in Figure 3. A dry mix consisting of a 50/50 blend of the magnesium oxide and monopotassium phosphate powders is added to the mixing vessel (or disposal drum), along with any needed water and additional additives (e.g., class C fly ash for strength;  $K_2S$  for mercury). Stoichiometric water levels are used, unless the waste is a wet sludge or is aqueous. Water is added first to the mixing vessel before the addition of the binder and, if required, any special additives. Low-level radioactive or hazardous wastewater is recommended to optimize waste loading.

The appropriate amount of salt-containing mixed waste is then added to achieve the desired waste loading and the blend is mixed for an average of 30 minutes. Depending on the characteristics of the waste, smaller portions of the binder and waste quantities may have to be alternatively batched to the system to control mixing and heat generation. After mixing is terminated, the waste form fully sets in about 2 hours. Complete curing of the CBPC waste usually requires an additional 15 days.

Deployment of the CBPC process at an operational 55-gallon scale has been successfully carried out using a planetary type mixer as shown in figure 4. The hydraulic mixer contains one or several impeller blades that spin as they rotate in an orbit ~ equal to that of the circumference of a standard 55-gallon drum. Hydraulics allow lifting of the mixing assembly to facilitate easy drum insertion and removal.

Operation of the mixer is simple and consists of using the potential disposal drum as the mixing vessel. The empty drum is placed in the mixer and binder, waste, additives, and water are charged to the drum using hoppers, feeding chutes, and piping integrated into the system. Mixing



is initiated and then terminated when the amperage rate on the mixing blades increases sufficiently to indicate the on-set of setting.

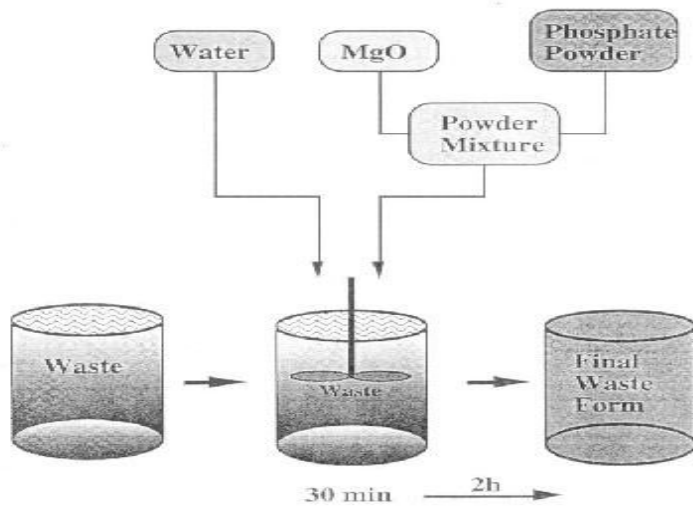


Figure 3. Simple flowsheet for the CBPC mixed waste stabilization process.

Figure 4. Planetary drum mixer for the deployment of mixed waste stabilization using CBPC.



## SECTION 3

# PERFORMANCE

### Demonstration Plan

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Development of the CBPC process for salt-containing mixed waste consisted of numerous tests with surrogate waste streams. Before conducting tests with the two types of salt waste surrogates recommended by the MWFA, (and also tested by investigators of other low-temperature salt waste stabilization processes), the CBPC method was evaluated under various scenarios. The various CBPC test scenarios were required to determine the response of specific CBPC waste form properties when applied to salt wastes and for predicting the optimum conditions and parameters for the MWFA recommended salt surrogates. These test scenarios were as follows:

- Testing of CBPC waste forms fabricated with simple saturated solutions of  $\text{NaNO}_3$  and  $\text{NaCl}$  was completed. Saturation levels for these two salts were 50 and 10-wt%, respectively. RCRA metals of cadmium (Cd), chromium (Cr), lead (Pb), and mercury (Hg) were added as nitrate and chloride salts to these waste streams at concentrations of 5,000 ppm. To enhance the strength of the CBPC binders, 50-wt% of Class-F fly ash was added to the  $\text{MgO}$  and  $\text{KH}_2\text{PO}_4$  binding mix. Less than 1 wt%  $\text{K}_2\text{S}$  was also added to tie up the Hg and potentially decrease its solubility, and thus its leachability. The same saturated salt solutions were also stabilized in Portland cement for comparison. Setting times, as well as waste form appearance, were recorded and all waste forms were tested for compression strength and leachability of RCRA hazardous metals via the TCLP method. Waste form densities were calculated. ANSI 16.1 leach testing of the saturated nitrate and chloride solution CBPC waste forms was then completed. This leach test is not required by RCRA for land disposal, but is recommended by the NRC. The test determines a leach index for any chemical or radiochemical anion or cation in the waste form, and is an excellent indication of the waste form's ability to stay intact over time. Technically, the determined index is the negative base 10 log of the particular leaching species' diffusion coefficient; thus the higher value the better. Values of 6 or more are desired.
- Since nitrates are strong oxidizers, the CBPC waste forms containing the saturated sodium nitrate solution were subjected to a flammability test as specified in 40CFR CH.1 (Appendix F to Part 173). The test involved mixing powdered amounts of the waste form with sawdust, igniting the mix, and noting its burn time relative to a standard and pure sodium nitrate. A lesser burn time than the standard indicates a stable and safe waste form for oxidizing nitrate salts.
- Testing of the CBPC technology on a DOE surrogate waste stream containing activated carbon, ion exchange resins,  $\text{Na}_2\text{CO}_3$ , and nitrate, sulfate, and chloride salts (at a mix of ~30%) was completed.  $\text{CsCl}$  was added to the surrogate to simulate a radioactive component. CBPC waste forms were fabricated at 60 and 70 wt% waste loading and the forms were subjected to both compression strength and TCLP-type (RCRA hazard metals) leaching tests. Waste form density was also determined.

Based on the performance of waste forms generated from the above three test scenarios, CBPC waste forms of the two MWFA salt surrogates were prepared at waste loadings of 58 and 70 wt%. The two surrogate waste formulations are detailed in Table 1. One of the surrogate waste streams contained a high quantity of nitrate salts and represented a waste stream that had previously been unsuccessfully stabilized with simple Portland cement. Such waste streams are



not that uncommon in the DOE complex. The other surrogate waste stream contained salts of chloride and sulfate at levels representative of a dried, but not concentrated, spent incinerator off-gas scrub solution (i.e., blowdown). Both of the surrogates were free of moisture, contained oxide forms of RCRA heavy metals in the 1,000-ppm range, and contained trichloroethylene as a trace organic contaminant. To obtain comparable waste form performance data, the same surrogate formulations were provided to other investigators involved in parallel efforts to also develop salt waste stabilization alternatives. Conditions for fabrication of the two MWFA surrogate salt waste forms via the CBPC method were as follows:

Mix time: 20-30 minutes  
Cure Time: 14 days

The waste forms were then tested for compression strength and RCRA hazardous metal leachability via the TCLP method. Waste form density was also calculated, as well as the retention of compressive strength on immersion. ANSI 16.1 leach testing, specifically for the NO<sub>3</sub> and Cl anions, were then completed. Based on the marginally successful results of the ANSI 16.1 tests for the CBPC salt waste forms, additional waste fabrication metals were added to the base CBPC process. These method modifications consisted of adding fly ash to the binder or dipping the waste form in a commercial polymer. ANSI 16.1 tests were then repeated on waste forms fabricated with the additional methods to quantify the enhancement of the particular modification.

**Table 1. Composition of MWFA surrogate salt waste streams**

Constituent	High chloride	High nitrate
<b>Bulk components (wt%)</b>		
Fe <sub>2</sub> O <sub>3</sub>	12.75	6.0
Al(OH) <sub>3</sub>	8.5	4.0
Mg(OH) <sub>2</sub>	8.5	4.0
Na <sub>3</sub> PO <sub>4</sub>	4.25	2.0
MicroCel E (calcium silicate)	17.0	8.0
Portland Cement (type II)	4.25	2.0
H <sub>2</sub> O	29.75	14.0
<b>Salts (wt%)</b>		
NaCl	10.0	0.0
CaSO <sub>4</sub>	5.0	0.0
NaNO <sub>3</sub>	0.0	60.0
TOTAL	100	100
<b>Contaminants (mg/kg)<sup>1</sup></b>		
PbO	1,000	1,000
CrO <sub>3</sub>	1,000	1,000
HgO	1,000	1,000
CdO	1,000	1,000
NiO	1,000	1,000
trichloroethylene	1,000	1,000

1. Contaminants make up less than 1% of the surrogate composition and are not included in the total.



## Results

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CBPC waste forms prepared with the two surrogate salt waste solutions had densities (1.8 g/cm<sup>3</sup>, 1.72 g/cm<sup>3</sup>) and compressive strengths (1,800 psi, 3,500 psi) less than that of the simple cement based waste forms (2.5 g/cm<sup>3</sup>, 4,000 psi). However, the compression strength is well above the 500 psi recommended by the NRC for disposal. The cure time of the forms was slightly slower than that obtained with a simple CBPC application (i.e., no fly ash and a nonsalt waste stabilization). The K<sub>2</sub>S was successful in lowering the solubility of Hg so that it passed the TCLP leach tests at the more stringent Universal Treatment Standard (UTS) level. RCRA hazardous metals of chromium (Cr) and lead (Pb) also passed at this level, but cadmium (Cd) failed. Cadmium's poor leachability results may be attributed to its presence as a salt as opposed to an oxide. As a salt it may not as readily react with the phosphate as is needed to lower its solubility. Cadmium's reaction with phosphate is rather slow at the less acidic conditions (i.e., pH = 4) present in these tests. A remedy for this condition was found in later testing with a mixed waste fly ash. During this test it was found that the addition of a small amount of phosphoric acid lowered the pH sufficiently to fully stabilize the cadmium.

ANSI 16.1 leach tests, completed specifically for the nitrate and chloride ions, marginally passed the criteria level of 6. The 6.86 and 6.7 indexes, for chloride and nitrate respectively, indicated some slow salt leaching. Salt leaching may in time deteriorate the waste. This result caused the investigators to consider additional binder or coating techniques for future surrogate waste tests.

All flammability testing with the nitrate surrogate waste forms clearly indicate a stable and safe condition for stabilizing the oxidizing salt. The burn time of the forms was in excess, by a factor of 6 to 40, of that obtained for either the standard, pure NaNO<sub>3</sub>, or the unstabilized surrogate NO<sub>3</sub> waste solution.

CBPC waste forms prepared with the salt surrogate containing activated carbon and ion exchange resins had densities of 1.24 g/ml and 1.32 g/ml, and compressive strengths of 2,224 and 5,809 psi for the two waste loadings tested (i.e., 60 and 70 wt%). TCLP leach testing conducted on the waste forms gave leach levels for Cd, Cr, Ni, and Pb at a magnitude below the UTS limits. Unlike the previous surrogate tests, these CBPC waste forms were prepared with a H<sub>3</sub>PO<sub>4</sub> solution as a substitute for the KH<sub>2</sub>PO<sub>4</sub> binder. This resulted in an acidic solution, which led to decomposing Na<sub>2</sub>CO<sub>3</sub> in the waste and generating undesirable CO<sub>2</sub>. As a consequence, the investigators exclusively used only the KH<sub>2</sub>PO<sub>4</sub> binder for any subsequent studies involving the salt waste surrogates recommended by the MWFA.

CBPC waste forms fabricated with the two MWFA-recommended salt surrogates had densities ranging from 1.7-2.00 g/cm<sup>3</sup> and compressive strengths (above the 500 psi criteria) in the range of 1,400 to 1,900 psi.

As indicated in Table 2, concentrations of the RCRA hazardous metals in the leachate were well below the EPA UTS limits. This was validated by a scanning electron microscopy (SEM) of the waste forms, which indicated a very homogeneous distribution of the heavy metals.

As with the earlier surrogate salt waste forms, ANSI 16.1 leach testing indicated that the CBPC process is only marginally successful in retaining the NO<sub>3</sub> and Cl anions. As a consequence, modifications to the basic CBPC waste formulation process were made. These modifications consisted of adding fly ash to the binder and coating a basic CBPC waste form by dipping it in a commercial polymer. The goal of the modifications was to plug the surface pores that were providing pathways for the highly soluble NO<sub>3</sub> and Cl anions. As evident by Table 3, the modifications were successful as noted by the increases in the ANS 16.1 determined leach indices for the various salt anions.



**Table 2. -RCRA metal TCLP results for surrogate nitrate salt waste forms.**

Waste forms	Cr	Cd	Hg	Ni	Pb
Concentrations in ppm in waste form with nitrate waste loading of					
58 -wt%	300	510	540	460	540
70- wt%	360	610	650	550	650
TCLP results (mg/L) for waste form with nitrate waste loading of					
58 wt%	0.04	<0.01	<0.00004	<0.05	<0.20
70 wt%	0.02	<0.01	<0.00005	<0.05	<0.02
EPA regulatory limit	0.86	0.19	0.025	5.0	0.37

**Table 3. - ANS 16.1 leach test results for various surrogate salt waste forms.**

Waste forms	Total amount of NO <sub>3</sub> and Cl anions in waste form (ppm)	Fraction of NO <sub>3</sub> and Cl anions leached out	Combined NO <sub>3</sub> and Cl anion Effective diffusivity (cm <sup>2</sup> /sec)	Combined NO <sub>3</sub> and Cl anion Leachability index
Uncoated NO <sub>3</sub> samples, waste loading of 58 wt%	218,700	0.33	6.31 x 10 <sup>-8</sup>	7.2
MKP+ fly-ash-coated NO <sub>3</sub> samples, waste loading of 58 wt%	218,700	0.1997	2.88 x 10 <sup>-10</sup>	9.54
Polymer-coated NO <sub>3</sub> samples, waste loading of 58 wt%	218,700	0.0169	6.87 x 10 <sup>-13</sup>	12.6
Uncoated Cl samples, waste loading of 60 wt%	46,535	0.0669	1.26 x 10 <sup>9</sup>	8.9



## SECTION 4

# TECHNOLOGY APPLICABILITY AND ALTERNATIVES

### Competing Technologies

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Over the last 50 years of DOE operations, large quantities of mixed low-level wastes (MLLW) were generated from past nuclear weapons based industries and more recently from waste treatment processes. Stabilization has been and still is an effective, inexpensive, and simple treatment alternative for many types of these mixed wastes. This alternative is also accepted as safe and environmentally sound by both the regulators and the concerned public. A review of the technical literature and of past DOE operating experience shows that low-temperature hydraulic cement and bitumen grout based stabilization methods produce waste forms that meet or exceed final disposal requirements. The success level of the waste form is dependent on the original waste medium and the type and amount of hazardous and/or troublesome components in the untreated waste. Unfortunately, these current stabilization techniques have had limited success in accommodating homogeneous solid and sludge wastes containing relatively high concentrations of salts in addition to RCRA hazardous heavy metals.

Salts (defined as the reaction product generated when a metal ion replaces the hydrogen ion of an acid) are highly soluble, easily hydrated, and reactive. As a consequence of these characteristics, low-temperature stabilized forms of MLLW containing salts do not adequately cure or are susceptible to deterioration over time due to the salt mineral expansions in the micropores of the cement microstructure. The deterioration may lower the durability and strength of the stabilized waste form and create pathways for the hazardous and radiological constituents to be released from the immobilized waste. Salts also interfere with the basic hydration reactions of cements and can create a separate surface phase on the cement waste form.

In some cases, leach resistant salt waste forms of sufficient durability are possible with the current stabilization techniques. However, these techniques usually result in forms with excessive increases in waste volume due to low waste loadings. Basic Portland cement formulations can only accommodate ~15 wt% of salts. These process inefficiencies and subsequent high disposal costs offset any benefits. The limitations of these current methods are of immediate concern since future volumes of salt wastes are anticipated as other MLLW treatment processes are implemented. Future effluents from MLLW wastewater treatment systems and scrubber blowdown from future and present MLLW thermal systems (i.e., incinerators and melters) will significantly add to the MLLW salt inventory.

There are many mixed waste stabilization/solidification technologies at various stages of development that could be considered as competing with the CBPC process. Numerous tests with low-temperature microencapsulation techniques involving sol-gels (e.g., polycerams) and polymers indicate that greater waste loadings (than those achievable with conventional Portland cement) are possible with even the troublesome salt-containing wastes. In addition, alternatives involving thermal-sintering techniques also may lead to acceptable waste forms with considerably more volume reduction compared to that achievable with grouts, polymers or low-temperature ceramics. Mixed waste stabilization methods currently in the later stages of development include enhanced concretes using proprietary additives and several methods provided by commercial vendors. Microencapsulation techniques involving polyesters, polyethylene, and polysiloxane have also been demonstrated on surrogate and/or actual wastes.



Sintering differs from vitrification in that only melting at grain phase boundaries occur without the complete amorphous restructuring that takes place in glass formation. Like vitrification, sintering occurs at temperatures over 1,000°C and can emit volatile hazardous metals. Even though densification is possible for some additional volume reduction, slight volume increases usually occur. However, waste loadings as high as 80% are possible. The equipment for sintering is less complex than vitrification, but more complex than grouting or microencapsulation. For a typical sintering process, grinding, mixing, and extruding equipment are required, as well as ovens, calciners, and offgas treatment systems. For most waste streams, sintering methods will require an extensive process development effort involving statistically designed experiments.

Recently developed thermosetting and thermoplastic polymeric methods using batch mixers or extruder systems are currently available. These low-temperature microencapsulation techniques do not chemically incorporate the waste, but create an impermeable barrier between the hazardous components in the waste and the environment. Waste loadings in these organic media are usually on the order of 50% for many troublesome wastes, such as incinerator fly ash or those containing appreciable salts. This value is nearly twice that achievable with conventional cement grout methods.

Table 4 and Figure 5 give ‘head –to –head’ comparisons of the waste form performance between that of CBPC and some of the other more recently developed salt-containing mixed waste stabilization methods as described above. Table 4 provides waste loading, strength, and leachability results for five low-temperature technologies stabilizing the same two types of salt surrogates. The pass criteria for TCLP leachability in Table 4 are the less stringent non-UTS values. Figure 5 graphically represents the waste loading benefit achieved over simple Portland cement grouting when using CBPC or any of the other recently tested methods. The values provided graphically in Figure 5 have been normalized to the approximate salt-waste loading limit (i.e., 15-wt%) of basic Portland cement. Therefore the ~ value of 2.8 for CBPC represents an ~ 42-wt% (i.e. 2.8 x 15-wt%) salt loading (e.g., a 70-wt% loading of a surrogate waste containing 60-wt% nitrate salts).

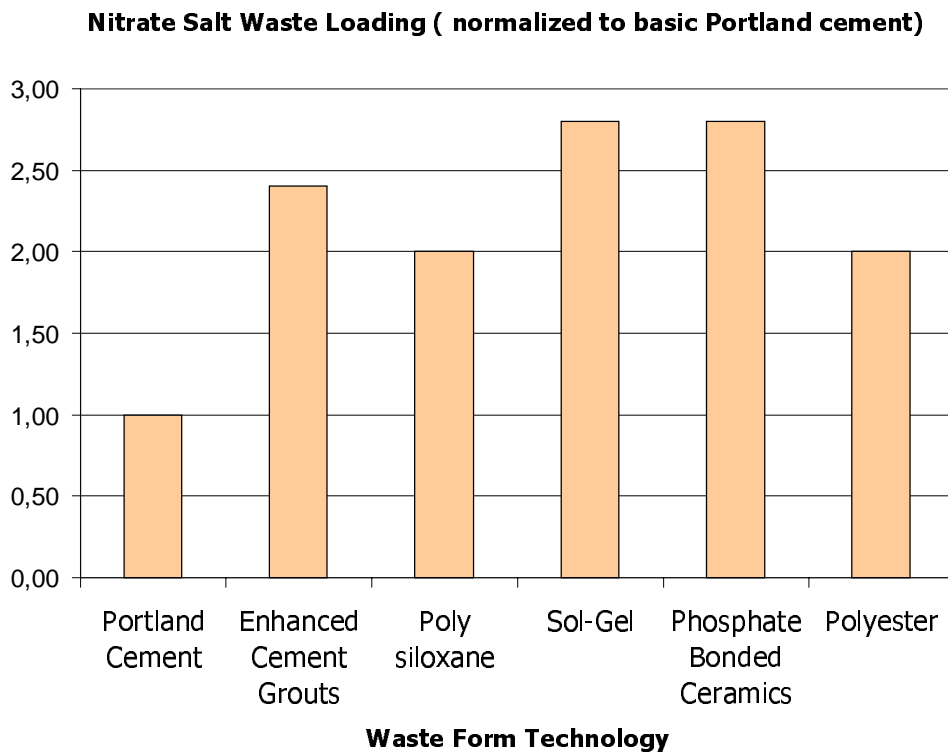
**Table 4. - Selected salt waste stabilization results and waste performance data with the MWFA surrogates**

Waste form performance measure	Waste loading wt%	Salt loading wt%	Compressive strength psi	Leachability TCLP	Leachability ANSI 16.1 index
Surrogate type	NO <sub>3</sub> /Cl	NO <sub>3</sub> /Cl	NO <sub>3</sub> /Cl	NO <sub>3</sub> /Cl	NO <sub>3</sub> /Cl
<b>Technology</b>					
Enhanced concrete	69/55	36.3/8.2	1,032/535	Passed for Cd, Cr, Ni, and Pb	NA
Polyester ( vinyl ester resin only)	50/50	30/7.5	6,200/5,100	Passed for Cr, Pb, Hg	7.7/7.6 for Na ions
Polysiloxane	50/50	30/7.5	420/>637	Passed for Cd, Cr, Hg	NA
<b>Phosphate bonded ceramics</b>	<b>70/58</b>	<b>42/9.0</b>	<b>3,500/1,800</b>	<b>Passed for Cd, Cr, Pb, Hg, Ni</b>	<b>7.1 for Cl 9.0 for NO<sub>3</sub></b>
Sol-gel	70/60	43.5/11.5	1,513/1,050	Passed for Cd, Cr and Hg	7.6/7.5 for Na ions





**Figure 5. Salt waste loading comparisons for five low temperature stabilization methods and Portland cement.**



As indicated by the comparison data in Table 4 and Figure 5, no cement alternative, low-temperature stabilization technology for salt waste clearly outperforms the others. Potential end users may need to consider other factors outside of waste form performance in choosing an alternative. These factors include, but are not limited to, the issue of ‘stabilization versus encapsulation’ technology, the availability of equipment, previous operating experience, the applicability of the technology to other types of waste media, and issues involving both safety and stakeholder concerns.

## Technology Applicability

The CBPC technology is applicable to a wide range of waste forms typically treated with conventional grouting techniques, including evaporator residues, contaminated soils, various salt wastes, small homogenous debris wastes, wastewater residues, sludges from uranium ore processing operations, incinerator ash, and spent incinerator scrub solution. The CBPC technology has also encapsulated lead and mercury-contaminated crushed debris, as well as stabilized TRU contaminated residues for safe shipping to and storage at the Waste Isolation Pilot Plant (WIPP). The process is usually not suitable for large debris, organic wastes, reactive, or explosive wastes.

The technology can be used in a small batch mode, or scaled up to treat large volumes of waste (e.g., 55-gallon drums) on a continuous basis after specific treatment characteristics of the waste form have been evaluated, and operating parameters have been determined.



## Patents/Commercialization/Sponsor

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The investigators and inventors of the CBPC technology at ANL-E have exclusive rights to the process as a mixed waste stabilization method. In particular, patent # 5,645,518 (entitled "A Method for Stabilization of Low-level Mixed Waste at Room Temperature) covers its application to high salt-containing mixed waste as detailed in this ITSR. The patent was issued July 8, 1997. Envirocare of Utah is in the process of obtaining a CBPC technology license from ANL-E, and has installed mixer systems for its deployment on mixed and hazardous waste. Currently, testing is being done on selected waste streams to verify its application toward specific DOE mixed wastes currently stored at Envirocare.

Wangtec of Woodridge, IL has also licensed the CBPC technology from ANL-E and is marketing it for high chloride mixed waste incinerator ashes and for low-level wastes from Taiwan power plants. In addition Bindan Corporation of Oakbrook, IL has licensed this technology for road and highway repairs during cold winters in several states that include Minnesota, Wisconsin, Indiana, and Illinois. Similar nonceramic phosphate based stabilization processes are commercially available from the private sector. Most notably are Rocky Mountain Remediation Systems L.L.C./RRMS and American Minerals.



## SECTION 5

### COST

#### Methodology

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Cost estimates for deploying an operational scale system for the CBPC stabilization of salt-containing mixed wastes are based on previously established systems for cementitious or other low temperature, solid mixed waste, stabilization methods. Particularly, if these existing operational scale systems include planetary type mixers. Capital, labor, and material cost estimates assumed a batch 55-gallon drum capacity system with a waste form production rate of three barrels per shift, --- or nine barrels a day for an 'around the clock' operation. This rate corresponds to a waste throughput of ~1.4 cubic meters per day, assuming an average waste – to- waste form volume expansion of only ~35%. The mixed waste throughput is based on waste form performance data collected during the development of the polyester process as reported in this ITSR. These data indicate that the polyester waste forms can consistently and reliably maintain a 50 wt-% loading of dry mixed waste containing a 60 wt% salt component (i.e., the final waste form contains ~ 30wt% of the salt). This loading is twice that achievable with the cement process.

Labor costs assume four Full-Time Equivalents (FTEs) at the fully loaded rate of \$70.00 per hour. Labor accounted for by the four FTEs include two full-time operational technicians, as well as part-time management, engineering, safety, maintenance, health physics, manifesting, and transportation. CBPC binder costs (a blend of MgO and KHPO<sub>4</sub>) are assumed at the supplier bulk rate of \$0.85/lb as quoted by the ANL-E investigators. New standard DOT 7A barrels are estimated at \$100.00 each and the assumed operation consists of using the same drum for the mixing, curing, and final disposal of each 55-gallon batch.

Disposal costs vary depending on which available low-level waste (LLW), Subtitle D disposal site is used. At the INEEL's Radioactive Waste Management Complex (RWMC), a relatively low cost of \$20 per cubic feet of waste form is available, whereas at the Barnwell Site in South Carolina costs can run as high as \$1,500 per cubic foot of waste form. Commercial sites, such as Envirocare of Utah, charge ~ \$35 per cubic feet following a one time waste fee of \$20,000. For this particular analysis, a value of \$60 per cubic foot of waste form was chosen, since it represents an average, as well as a number frequently used in cost and system engineering studies on mixed waste management throughout the DOE complex. Therefore, assuming that the densities of a CBPC and cementitious waste form are 1800 kg/M<sup>3</sup> and 2650 kg/M<sup>3</sup>, the cost of disposing an equal mass of waste in a CBPC matrix is 71% that of cement.

#### Cost Analysis

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Available cost documentation for existing or planned stabilization systems at ANL-E and INEEL indicate capital costs, including equipment design and development, of ~\$2,000K. Because standard and similar equipment is deployed, this cost is valid for either stabilization (i.e., CBPC) or nonextruder microencapsulation (i.e., polymeric) systems. The capital cost estimate assumes a 55-gallon batch system and also assumes available infrastructure and facility housing to support the system. Operating costs, which include labor and material costs, are estimated at ~ \$6510 per cubic meter of waste form based on the data provided in the above methodology. A corresponding cost for the baseline cement process is lower at ~\$4,300 per cubic meters of waste form because of its inexpensive materials costs. However, the disposal cost of the CBPC



waste form (~\$ 2836 cubic meter of waste) is less than that for cement (~\$3700) as a result of its higher densification and its accommodation of higher waste loadings. All estimates are based on immobilizing a sodium nitrate sludge waste with a specific gravity (Sp. Gr.) of 2.0 and a bulk density of 700kg/M<sup>3</sup>.

## Cost Conclusions

The cost-effectiveness of the CBPC mixed waste stabilization process is best determined through its comparison to its baseline process, basic Portland cement stabilization. A summary of the costs and associated data calculated for the two waste forms are provided in Table 5. The assumption that labor and capital costs for the two processes are the same is a valid one, considering that for a given waste throughput, the processing times, batch capacities, and types and sizes of equipment are similar, if not identical. Therefore the cost benefit of CBPC over that of the baseline is based exclusively on material and disposal costs. Cost estimates for treating waste volumes over 100 cubic meters indicate that with the higher waste loadings achievable with the CBPC method, the process more than recovers the higher initial development and material costs. However, for small waste volumes, higher waste loading becomes less of a factor and cement stabilization may be just as cost- effective.

Table 5. Calculated cost, material, and performance data for comparing CBPC and cement waste forms

	CBPC Waste Form	Cement Waste Form
<b>Waste Form Production Rate</b> bbls/day	9	9
gals/day	495	495
cubic meters/day	1.874	1.874
kgs/day	3478	4994
<b>Waste-to-waste form volume expansion</b>	35%	75%
<b>Waste Throughput</b> cubic meters / day	1.39	1.07
kgs/day	1043	749
<b>Waste Loading</b>	30-wt%	15-wt%
<b>CBPC (MKP binders) Use</b> kgs/day	2435	0
cubic meters/ day	0.81	0
<b>CBPC (MKP binders) : waste weight ratio</b>	2.33	0
<b>Cement : waste weight ratio</b>	0	5.66
<b>CBPC (MKP binders): waste form weight ratio</b>	0.7	0
<b>Cement :waste form weight ratio</b>	0	0.85
<b>Labor</b> \$/day	6720	6720
\$/ kg of waste	5.86	8.97
<b>Barrels</b> \$/day	900	900
\$/kg of waste	0.86	1.20
<b>Materials-CBPC (MKP binders) \$/day</b>	4553	0
\$/kg of waste	4.37	0
\$/kg of waste form	1.31	0
<b>Materials-Cement \$/day</b>	0	425
\$/kg of waste	0	0.57
\$/kg of waste form	0	.09
<b>Disposal</b> \$/M <sup>3</sup> of waste form	2118	2118
\$/kg of waste	3.78	5.29
\$/kg of waste form	1.14	0.80
<b>Total (Labor+Material+Disposal)</b>		
\$/day	16,115	12,261
\$/kg of waste	15.45	16.37



## SECTION 6

# REGULATORY AND POLICY ISSUES

### Regulatory Considerations

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The regulatory goal of any end user deploying the CBPC process is to produce ceramic waste forms that meet Land Disposal Restrictions (LDRs) for land burial. In most applications, this means that the RCRA 40 CFR 268.40 treatment standards must be met at the lower limits proposed by the UTS, if the waste form is to be placed in a Subtitle D landfill. As a result, any full-scale, CBPC treatment facility will require a Part B RCRA permit or a modification to an existing permit.

In addition, Nuclear Regulatory Commission (NRC) 10 CFR 61 waste form testing will be necessary if disposal is to be in an NRC licensed facility. Additional requirements for applying the CBPC process at a federal facility include a National Environmental Policy Act (NEPA) review (a categorical exclusion is most likely to be applied), and any air emission considerations and/or permits as required under the National Environmental Standards for Hazardous Air Pollutants (NESHAPS). Any commercial facility treating radiological waste must secure an NRC permit.

If future development of the CBPC process requires testing with actual waste streams, a NEPA approval through categorical treatability study exclusion must be obtained. The state cognizant environmental agency in which the treatability study is to be performed must be notified 45 days before receiving archived samples for testing. In addition, the regional EPA must be notified.

### Safety, Risks, Benefits, and Community Reaction

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CBPC stabilization is a relatively simple and safe process. Excessively high temperatures are not achieved (e.g., less than 100 degrees C), pressures are ambient, and with the exception of the mixing impeller, there are few complex or moving parts.

The process generates no potentially hazardous off gases or secondary wastes, and therefore should bring little or no resistance from community stakeholder groups. These groups may even favor the technology, since it will generate less disposal volume when compared to the baseline Portland cement method.

However, there maybe concern in regard to the limited CBPC leaching of salt anions over time, even though the ions are not RCRA related hazardous species. Leaching of any component can deteriorate the integrity of the waste form over time, resulting in the potential release of undesired hazardous and radioactive species. However macroencapsulation of the final waste form will mitigate this concern. Stakeholders may also take issue with the presence of the needed phosphates and waste nitrates present in the CBPC waste form. These compounds can be vegetation fertilizers and biological food sources. To date, no data is available on the effects of potential vegetation in growth or biological degradation of a CBPC waste form over time.



## SECTION 7

# LESSONS LEARNED

### Implementation Considerations

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Given its operational similarity to that of basic Portland cement stabilization, CBPC's implementation into full-scale deployment for mixed waste should be fairly straightforward. CBPC system designers will need to choose among the numerous mixer and system options. Planetary mixer systems have been deployed in the DOE complex, but commercial entities are deploying alternative systems involving tumblers and subsequent pouring into disposal drums before setting. Potential end users will also need to provide analytical and development support in order to qualify wastes for disposal and verify the operating parameters for new waste streams.

### Technology Limitations and Needs for Future Development

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Based on the results of the CBPC salt waste form testing reported in this ITSR, the following development on CBPC waste forms needs to be continued:

1. tests to determine additives or treatment steps necessary to stabilize the RCRA hazardous metals when they are excessive and in the salt form. ( The ANL-E investigators were able to develop pretreatment steps to address these concerns as they related specifically to stabilization applications at INEEL and Fernald)
2. tests to qualify and quantify any biological degradation,
3. tests to assess the effects on CBPC waste form durability as a result of salt anion leaching over time.

### Technology Selection Considerations

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Obviously, DOE complex wide end users with the responsibility of mixed waste management need to consider multiple factors when selecting a low-temperature stabilization technology, like the CBPC method. The most important factors are usually total waste volume, waste characteristics and constituents, technology simplicity, and stakeholder concerns.

#### Waste Volume

The greater the volume of a relatively homogeneous waste inventory, the greater the benefits of a cement grout alternative, like the CBPC method. The more waste treated, the greater the savings in handling, transportation, and disposal costs as a result of the greater waste loadings CBPC waste forms can provide. If there is sufficient waste volume, these greater savings can more than recover the higher up-front development and material costs.

#### Waste Characteristics and Constituents

Past development with CBPC waste forms has shown that RCRA hazardous metals in the salt form are more difficult to stabilize than when they are in an oxide form. Overall thermodynamics of the CBPC binder and waste mix appears to control how the phosphates will react with the RCRA metals to form the desired insoluble compounds. In addition, the presence of nuisance metals such as zinc may have a higher affinity for the phosphate over that of the RCRA metal.



Such conditions and results may require extensive development to identify special additives and pretreatment steps above and beyond the basic CBPC process. Such actions may not be worth the effort and other alternative, low temperature, stabilization processes should be considered.

#### Technology Simplicity

Very limited engineering development would be required to build a prototype CBPC facility, which could eventually be expanded into a full production operation capable of handling a variety of waste streams. No major investments would be required to perform engineering design studies; rather, the pilot plant could be designed using system integration of off-the shelf systems. In some instances, CBPC stabilization systems could be retrofitted from basic Portland cement systems.

#### Stakeholder Concerns

In general, stakeholders desire, low –temperature, nonoffgas producing stabilization technologies that generate no secondary wastes, minimize disposal volumes, and ensure long term durability. CBPC stabilization meets the first four criteria, but very little data exist to support its long-term effectiveness in maintaining durability over its indefinite disposal life. Critics of the technology question CBPC's ability to remain durable over time, especially after stabilizing wastes containing high levels of salts and RCRA hazardous metals.



## APPENDIX A

### Bibliography

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4. A.S. Wagh, D. Singh, K. Patel, S.Y. Jeong, and J.Y. Park *Salt Waste Stabilization in Chemically Bonded Phosphate Ceramics*, Argonne National Laboratories–East Final Report on TTPCH24MW45 for the Mixed Waste Focus Area, November 1998





## APPENDIX B

### TMS DATA ELEMENTS

#### Funding Source

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This section provides cross-reference information in regards to the EM-50 Mixed Waste Focus Area contract established for development of the CBPC salt-containing, mixed waste stabilization process. The Department of Energy- Headquarters (DOE-HQ) Technology Management System (TMS) title and tracking number is provided, as well as that of the specific Technical Task Plan (TTP).

TMS # 117-Stabilize Waste Using Phosphate Ceramics

TTP # CH24MW45- Salt Stabilization in Low-Temperature Ceramic Waste Forms



## APPENDIX C

### ACRONYMS

ANL-E	Argonne National Laboratory-East
ANSI	American National Standards Institute
CBPC	Chemically bonded phosphate ceramic
DOE	Department of Energy
DOE-HQ	Department of Energy Headquarters
EM	Environmental Management
EPA	Environmental Protection Agency
FR	Federal Register
FTE	Full-Time Equivalent
INEEL	Idaho National Engineering and Environmental Laboratory
ITSR	Innovative Technology Summary Report
LDR	Land Disposal Restriction
LLW	Low-Level Waste
MKP	magnesium potassium phosphate
MLLW	Mixed Low-Level Waste
MWFA	Mixed Waste Focus Area
NEPA	National Environmental Policy Act
NESHAPS	National Environmental Standards for Hazardous Air Pollutants
NRC	Nuclear Regulatory Commission
OST	Office of Science and Technology
RCRA	Resource Conservation and Recovery Act
RWMC	Radioactive Waste Management Complex
SEM	Scanning electron microscopy
Sp. Gr.	Specific gravity
S/S	Stabilization/Solidification
TCE	Trichloroethylene
TCLP	toxicity characterization leaching procedure
TMS	Technology Management System
TRU	transuranic
TTP	Technical Task Plan
UTS	Universal Treatment Standard
WIPP	Waste Isolation Pilot Plant

