

**INVESTIGATIONS IN
CERAMICRETE STABILIZATION OF HANFORD TANK WASTES ***

A. S. Wagh, M. D. Maloney,⁺ G. H. Thomson,⁺ and A. Antink
Energy Technology Division
Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

⁺Rocky Flats Environmental Technology Site
10808 Highway 93
Golden, CO 80403-8200

January, 2003

Paper submitted to Waste Management Conference 03, Tucson, AZ, February 2003.

*Work supported by CH2M Hill, Greenwood Village, CO.

INVESTIGATIONS IN CERAMICRETE STABILIZATION OF HANFORD TANK WASTES *

A. S. Wagh, M. D. Maloney,⁺ G. H. Thomson,⁺ and A. Antink
Argonne National Laboratory
9700 S. Cass Avenue, Argonne, IL 60439

⁺Rocky Flats Environmental Technology Site
10808 Highway 93
Golden, CO 80403-8200

ABSTRACT

This paper provides a summary of investigations done on feasibility of using Ceramicrete technology to stabilize high level salt waste streams typical of Hanford and other sites. We used two non-radioactive simulants that covered the range of properties from low activity to high level liquids and sludges. One represented tank supernate, containing Cr, Pb, and Ag as the major hazardous metals, and Cs as the fission products; the other, a waste sludge, contained Cd, Cr, Ag, Ni, and Ba as the major hazardous contaminants, and Cs, and Tc as the fission products. Both waste streams contained high levels of Na and NO₃⁻. They were stabilized in Ceramicrete at a waste loading of 39.8 wt.% and 32 wt.%. The high loading resulted from the water in the waste streams. This water was used for the stabilization reaction. Reducing this water the load factor can be increased. The solid monoliths of the waste forms were light weight ceramics. The toxicity characteristic leaching procedure (TCLP), 7-day Product Consistency Test (PCT) at 90 °F, and other tests to meet the disposal criteria were performed on the waste forms. Both the waste forms passed the TCLP test and the leaching levels of hazardous metals such as Cd, Cr, Ag, Pb, Zn, Ni and Ba were well below the Universal Testing Standards. The normalized leaching rates for the matrix components such as Mg, K, and P, as well as other significant components of the waste streams, viz., Na and NO₃, show that the NR are well below the 0.2 grams/m²day required of ceramic waste forms. The TCLP test results also showed that the leaching of the most soluble components such as Na and NO₃ was very low. The stabilization of both of these species is attributed to their chemical conversion to less soluble forms and subsequent micro encapsulation in the Ceramicrete matrix. These results demonstrate that Ceramicrete is an effective and simple alternative to thermal and grout-type stabilization technologies proposed for high level, transuranics, and low activity tank wastes, including high Na and nitrate salt wastes. Both the Ceramicrete process and the ceramified waste forms solve the problems with vitrification identified by the National Academy of Sciences in their call for alternative processes and waste forms. Since it employs a simple grout-type method, Ceramicrete also offers safety and economic advantages.

*Work supported by CH2M Hill, Greenwood Village, CO.

INTRODUCTION

Ceramicrete technology was developed at Argonne National Laboratory (ANL) with funding from U.S. Department of Energy (DOE) Environmental Management to treat streams of low-level mixed waste. Several DOE contractors are considering it for both micro- and macro-encapsulation of radioactive and hazardous waste streams. For example, CH2M Hill, a DOE contractor, is evaluating variations of Ceramicrete for stabilization of several types of waste streams now stored in underground tanks at Hanford and other sites. This paper summarizes the work between ANL and CH2M Hill done as part of a Cooperative Research and Development Agreement (CRADA).

High-temperature stabilization technologies such as vitrification have been proposed for treatment of many of these waste streams. The DOE has noted the high life cycle costs of producing a glass waste form. The National Academy of Sciences (NAS) (1) recently issued a report detailing these process and waste-stream concerns with vitrification and calling for new research including development of alternative immobilization technologies, in particular, glass-like and poly-phase ceramics.

Ceramicrete technology (2), invented by ANL and being modified under a joint project with CH2M Hill, has good potential to solve the technological and economic concerns. Unlike conventional ceramics, Ceramicrete is fabricated at room temperature using typical grout-plant equipment. It is a versatile, simple, reliable, and cost-competitive method of immobilization. In addition, ceramics offer many intrinsic advantages over glass waste forms for purposes of safe disposal. The CH2M Hill and ANL collaboration is motivated by these advantages.

Safety and cost are inherently linked, and both are significantly improved by going to a room temperature process. This reduces both the risks of occurrence and consequences of incidents that are driven by high temperature process operations. As a grout-type method, Ceramicrete offers the advantage that process control systems are simpler and hazardous off-gases are not an issue. As reported below, Ceramicrete can successfully immobilize the high level salt waste streams without any prior treatment. None of the waste constituents had to be separated prior to treatment due to concerns about volatilization or solubility. These factors eliminate the need to manage secondary wastes from separation and air and water pollution control processes. This further simplifies the operations and eliminates those safety and cost factors as well.

In essence, the results of this project indicate that Ceramicrete offers the performance of glass at the cost and safety of grout.

Besides the need to stabilize the large-volume high-level (HLW) liquid, sludge and solid wastes, there remain many needs for processing smaller volume problematic high-level wastes as well as side streams. These include certain unique wastes that are "outside-the-envelope" at each

site, secondary waste streams from the separation and off-gas processes associated with thermal treatment facilities, and contaminated soils at HLW tank farms and storage sites.

To address these needs, two surrogate waste stream simulants were tested in this project. They covered a wide range of needs at the DOE tank waste facilities at Hanford, Idaho, and Savannah River Sites and at similar non-U.S. facilities (as in Russia) for a storage medium that affords adequate solidification and stabilization.

The purpose of this project reported here was to determine whether and how a formulation of Ceramicrete could produce a waste form that complies with the waste acceptance criteria (WAC) at Yucca Mountain and Hanford. Work is continuing to modify the process to enhance the waste loading and further improve on the safety and cost advantages. The continuing work will also provide independent repetition and extension of the work to date.

WASTE STREAM COMPOSITION

Two surrogate mixed-waste streams of salt-containing liquid and sludge were synthesized and stabilized for bench-scale testing. One represented tank supernate, containing Cr, Pb, and Ag as the major hazardous metals, and Cs as the fission product; the other, a high-level waste sludge, contained Cd, Cr, Ag, Ni, and Ba as the major hazardous contaminants, and Cs, and Tc as the fission products. Both waste streams contained high levels of Na and NO_3^- . In the formulation of these waste streams, the radioactive isotopes were substituted by the corresponding non-radioactive, chemically equivalent components (surrogates) listed in Table I.

Table I. Radioactive surrogates used in the formulation of the waste streams

Radioactive isotope	Surrogate element
^{137}Cs $^{141}, ^{142}\text{Ba}$ ^{99}Tc	Nonradioactive Cs Nonradioactive Ba Re

In addition to these surrogate elements given in Table I, we also added surrogates of U, Pu, Am, and Sr in an appropriate form in the waste streams. Correspondingly their leaching was also studied with additional tests. Those results will be reported elsewhere. In this paper we concentrate on the soluble components and overall performance of the waste forms.

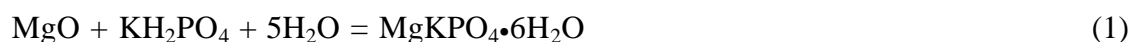
Table II describes the key properties of these two waste streams. As seen from this table, both waste streams are highly alkaline. The nitrate levels are also very high. This nitrate was mainly as NaNO_3 in the supernate and as nitrate combined with various elements in the sludge.

Table II. Properties of simulant waste streams

Property	Supernate	Sludge
Form	Liquid	Sludge
Solids content (wt.%)	53.38	25.2
Density (g/cm^3)	1.4	1.32
pH	13.68	12.83
Na content (wt.%)	17	3.26
NO_3 content (wt.%)	11.49	7.7

FABRICATION OF WASTE FORMS

The initial Ceramicrete formulation consisted of a blend of calcined magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4). Other formulations have proven to work, and some are being investigated to further improve cost, process simplicity, and performance. The blend is mixed with a stoichiometric amount of water to satisfy the following equation:



The reaction product on the right-hand side of Eq. 1 is Ceramicrete, a rapid-setting phosphate ceramic grout. Details of this material and mixing procedures for the components may be found in Reference (2).

Stabilization was done by adding the binder components to each of the waste streams and mixing the slurry for 10-15 min until it set into a hard ceramic monolith. Some variations in the procedure were made to ensure that the slurry mixed well and set sufficiently slowly to allow the needed mixing time. Since the two waste streams had sufficient water, we did not add any additional water, but used the water from these waste streams themselves to drive the stabilization reactions. This approach resulted in a waste loading of 39.8 wt.% for the supernate and 32 wt.% for the sludge. Since some of the water fraction can be easily and safely removed prior to stabilization, even higher waste loading is achievable and may prove to be economically feasible.

Table III provides the physical properties of the waste forms. The waste forms are lightweight because they contain a significant amount of bound water. We could not use mercury intrusion porosimetry to evaluate the open porosity, because the bound water started escaping

the samples when the samples were evacuated. So the porosity was estimated by the water intrusion method. The values given in the table may be an overestimation of actual porosity, because some of the water will remain on the surface of the small samples during weighing. The actual samples appeared much denser, and the data on porosity indicate that these waste forms are not porous.

Table III. Physical properties of the waste forms

Property	Supernate	Sludge
Loading (wt.%)	39.8	32
Density (g/cm ³)	1.88	1.72
Approximate open porosity (vol %)	7.9	4.5
Compressive strength (MPa)	12 - 24 [*]	

* These are typical values for salt wastes measured in earlier projects. For other waste streams they can be as high 56 – 84 MPa.

The samples were very hard. Their compressive strength was not measured because of hazardous debris that would be produced during crushing tests. Instead, Table III gives our earlier results on benign salt waste forms. The high strength exhibited by these earlier tests ensures that these materials have a compressive strength $\gg 3.5$ MPa required for the waste forms to meet the waste acceptance criteria (WAC) at the disposal site.

When both waste forms were heated to 150°C, most of the bound water escaped from the samples, but the integrity of the samples was unaffected. This result is important for two reasons. First heating of the samples will dehydrate the waste forms so that one can eliminate the bound water and hence avoid potential concerns about radiolysis. Second these waste forms will withstand internal radiation heating during storage, and their integrity will not be affected by the evaporation of bound water.

LEACHING TESTS

The supernate and sludge waste form samples (self-cured) were subjected to Toxicity Characteristic Leaching Procedure (TCLP) and Product Consistency Test (PCT) protocols. Details of these tests may be found in References (3) and (4). The TCLP tests were also conducted on

supernate waste form samples that were dehydrated at 150°C. Tables IV and V provide the results of the TCLP tests, as well as the concentrations of the hazardous constituents in the waste and in the waste forms. Also included are the Environmental Protection Agency's Universal Treatment Standard (UTS) limits for each contaminant so that the leaching levels for passing the TCLP test can be compared.

Table IV. Contaminant concentrations in supernate waste and its waste form, TCLP results, and UTS limits

Contaminant	Cd	Cr	Ag	Pb	Zn
In waste (ppm)	2.3	937.6	11.5	37	7.04
In waste form (ppm)	0.91	373	4.6	14.8	2.8
In heated waste form (ppm)	1.1	440.7	5.4	17.4	3.3
TCLP result on waste form (mg/L)	<0.01	0.01	<0.05	<0.05	<0.05
TCLP result on heated waste form (mg/L)	<0.01	<0.05	<0.05	<0.05	<0.10
UTS limits (mg/L)	0.11	0.6	0.14	0.75	4.3

In addition, we measured the leaching level of Na, Cs and Re from the sludge waste form, and the results are included in Table V. Although these elements are not subject to UTS standards, they are of interest in further understanding the leaching behavior of radioactive waste forms.

The TCLP results in Tables IV and V show that stabilization of hazardous contaminants is excellent and consistent with earlier results on Ceramicrete stabilization for various hazardous waste streams (2). In most cases, the leaching levels are at least one order of magnitude lower than the UTS limits. The TCLP results also show that dehydrating the waste forms by heat treatment does not affect their performance.

The leaching levels of Cs, Re, and Na in the sludge waste form (Table V) are very small when compared with their concentrations in the waste or waste forms. Stabilization of Cs, and Re in the simulant waste form ensures that Ceramicrete stabilization is ideal for ^{137}Cs and ^{99}Tc that they represent. The very low level of leaching of Na from the supernate waste form assures that this extremely mobile element is also immobilized during Ceramicrete stabilization. Because

the TCLP test is performed with crushed waste forms, there was sufficient surface area available for leaching of the contaminants. In spite of this condition, the leaching levels are very low. The Na immobilization is possibly due to its micro-encapsulation within the matrix, as well as formation of an additional stabilized ceramic compound (discussed below).

Table V. Contaminant concentrations in the sludge waste and its waste form, TCLP results, and UTS limits

Contaminant	Cd	Cr	Ni	Ag	Ba	Re	Cs	Na
In waste (ppm)	2568	126	1824	40	85	5.3	15	32625
In waste form (ppm)	852	42	605	13	28	1.7	5.0	10818
TCLP result on waste form (mg/L)	0.0043	0.0013	0.21	0.027	0.032	0.00004	0.16	634
UTS limits (mg/L)	0.11	0.6	11	0.14	21	NA	NA	NA

NA = not applicable

The Product Consistency Test was conducted by leaching samples over a period of 7 days at 90°C. The leachate was analyzed for the components of the ceramic structure, i.e. the "building blocks" or matrix components, namely, Mg, K, and P noted in Eq. (1). This test on Ceramicrete is analogous to testing for boron, silicon, and sodium in borosilicate glass. Although not required to meet the WAC, we also tested the leachate for Na and NO₃, since these are major components of the high-level tank wastes that are problematic during other treatment processes. The results are expressed in terms of the normalized leaching rate (NR) given by

$$NR = (i \times V) / (S \times f \times d), \quad (2)$$

where

i = concentration in the leachate in g/L,
 V = volume of the leachate water in L,
 S = surface area of the crushed sample in m²
 f = fraction of species in waste form, and
 d = days leached.

The test protocol for glass specifies that the crushed sample be subjected to repeated washings. The repeated washing takes away very fine debris from the surface of particles of a

definite size. As a result washing provides a very specific surface area. In the case of glass waste forms, this specific surface area has been determined to be $0.0199 \text{ m}^2/\text{g}$ (4), which is used for NR calculations in the standard procedure for glass. In our case, however, the solidified product is a ceramic, and the effect of crushing, sieving, and repeated washing is different than with glass. In fact, it has not been established as yet if the repeated washing take away any of the hazardous constituents in the waste form, whether it is ceramic or glass. Therefore, we included all particles without any prewashing in our test, so the leaching rate should be conservative (higher). Because all the particles were included, we measured the actual surface area of the crushed samples that were subjected to leaching without any further treatment and used that data in our calculations. The surface area was measured by a sedigraph method. For completeness, we also determined what effect the washing and sizing would have had on our results. To that end, we fabricated a "standard ceramic" using the supernate waste composition without hazardous constituents, subjected it to repeated washing by the prescribed method used for glass waste forms, and measured its surface area. The results are given in Table VI.

Table VI. Surface area of crushed waste forms

Waste forms	Process	Surface area (m^2/g)
Standard glass	Sized and washed	0.02
Supernate	Not sized or washed	15.65
Supernate (uncontaminated) standard ceramic	After sizing and washing	6.67

As shown in Table VI, the specific surface area of the supernate waste form after washing was much smaller than that of the unwashed sample, but larger than that of the standard glass waste form. Thus, since the powder was not washed, we used the measured specific surface area of $15.65 \text{ m}^2/\text{g}$ for the NR calculations given in Table VII. As can be seen, even if we had washed and sized the sample as prescribed for glass waste forms, the specific surface area of $6.67 \text{ m}^2/\text{g}$ would still have yielded excellent results.

The NR results include the major components of the matrix (Mg, K, and P) as well as other significant components of the waste streams (Na and NO_3). The NR values are well below the $0.2 \text{ g/m}^2 \cdot \text{day}$ required of ceramic waste forms. For borosilicate glass forms, the Yucca Mountain WAC requires 0.16 to $0.4 \text{ g/m}^2 \cdot \text{day}$, depending on the particular structural element (Si, Na, Li, and B). The WAC for the Hanford disposal facility for low-activity waste requires $0.28 \text{ g/m}^2 \cdot \text{day}$. For the recently cancelled Immobilization/Can-in-Canister project, the WAC for ceramic was established as $0.2 \text{ g/m}^2 \cdot \text{day}$ for the U mass loss.

Table VII. Normalized leaching rates ($\text{g/m}^2 \cdot \text{day}$) for the two waste forms tested.

Waste form (unwashed)	Mg	K	P	Na	NO ₃
Supernate	1.4×10^{-6}	0.009	0.006	0.008	0.077
Sludge	0.00011	0.00855	Not done	0.02	0.024

The NR for Mg in the supernate waste form is very low. Solubility of MgO in an alkaline medium is extremely low [5]. The supernate leachate had a pH of 10.83, which must have reduced the leachability of unreacted MgO considerably. Also, the unreacted MgO particles are covered by the phosphate matrix, and that must have provided additional protection to these particles. Thus, it is not surprising that the leaching level of MgO in the case of the supernate waste form is very low.

Also worth noting is that the normalized leaching rates for K and P in the case of the supernate waste form and K in the case of the sludge waste form are of the same order. This is to be expected because they are the component building blocks of the ceramic matrix for $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

As Table VII indicates, the leaching rates of Na and NO₃⁻ are low. X-ray diffraction studies and syntheses of sodium-based Ceramicrete samples indicate that the immobilization of Na is at least, in part, due to the formation of $\text{MgNaPO}_4 \cdot n\text{H}_2\text{O}$, and that of NO₃⁻ is due to formation of KNO₃ and its subsequent micro encapsulation by the insoluble matrix.

To summarize, Ceramicrete passes the PCT test by one to two orders of magnitude and performs better than borosilicate glass by a factor of three to six [6]. This is expected, since ceramic has generally been considered to outperform glass in many respects. The NAS [1] report recommends research in the direction of glass-like or poly-phase ceramic. The special advantage offered by Ceramicrete is that the stabilization and ceramification occur at room temperature in a grout type of process, using grout-plant equipment, yet yield the superior results expected of high-temperature ceramics.

CONCLUSIONS

The results of this study on two types of waste streams demonstrate that the Ceramicrete formulations and methods we employed offer an excellent alternative to vitrification and other stabilization technologies proposed for both high-level and low-activity-salt waste streams. The

technology is simple to operate, easily handles variations in waste consistency and characteristics, does not require any elements of the waste to be separated out, incorporates high waste loadings, is inexpensive, does not generate secondary waste streams, will not expose workers to any significant and unnecessary amount of radiation, and exhibits superior performance.

The Ceramicrete waste forms meet all the WAC requirements for safe disposal, including those for the current Yucca Mountain and the Hanford disposal facility WAC. Both the Ceramicrete process and waste forms solve the problems of immobilization identified by the National Academy of Sciences [1] in their recommendations for alternative processes and waste forms, in particular, for glass-like or poly-phase ceramics.

This project tested the ability of two formulations of Ceramicrete to stabilize two waste simulants – one a supernate with Cs, and one a sludge with Cs, Tc, and transuranic surrogates - that comprise the range of problematic constituents in the tank wastes at Hanford. The results of the leaching tests show that Ceramicrete-stabilized waste forms meet Hanford and Yucca WAC. In the case of the PCT, where a direct comparison with borosilicate glass could be made, Ceramicrete outperforms borosilicate glass waste forms by a factor of 3 to 6. This means the margin of security and the reliance on engineered barriers at Yucca Mountain would be 3 to 6 times better than the current baseline technology. The characteristics of the Idaho tank wastes, including sodium-bearing and calcine wastes, and of the salt wastes at Savannah River Site (SRS) appear to be well within the capabilities of Ceramicrete tested in this and previous studies. At SRS the DOE Inspector General [7] concluded that the salt waste separation process is not cost-effective, and recommended that the salt waste should instead be grouted directly, assuming that a grout formulation can be demonstrated to meet the WAC. The SRS is investigating various options for this, and Ceramicrete stabilization appears to provide just such an option.

Our studies were carried out using only one formulation and method for fabrication of each of the waste forms of the supernate and sludge simulants. Further work to optimize the formulation was not undertaken, although improvements have been identified and are being investigated. Other leaching tests such as ANS 16.1 and MCC-1 have been conducted, and they exhibit the same superior performance as TCLP and PCT. Taken together, these tests have shown that it is possible to treat even the most problematic tank wastes directly in a simple grout plant, without any pretreatment or separation processes, and without generating any secondary wastes that would themselves require additional treatment processes and disposal efforts.

The Ceramicrete process is fully developed. For nuclear shielding and civil structural applications, Ceramicrete is being used in the field at various commercial scales. For low level waste treatment applications, a drum scale unit has been operated at Argonne National Laboratory. This project opens the way for the first applications of Ceramicrete on high-level waste and low-activity tank wastes with high salt compositions and other constituents that have proven to be a problem for vitrification or other processes.

FUTURE PLANS

This project, funded by CH2M Hill, was planned to develop a precise method of stabilization using a simulated near-exact formulation of the high-level salt waste streams at the DOE sites. This is the first step towards a complete demonstration of this technology on actual waste streams. Using the formulations developed in this project and potential improvements identified during the course of this work, ANL and CH2M Hill intend to demonstrate the viability of this technology on radioactive waste stream simulants at the bench scale in the laboratory, and proceed with tests on actual waste streams at a pilot-scale plant. We look forward to expanding our current collaboration to include work with clean-up contractors and National Labs at the DOE sites. Such joint projects are intended to demonstrate, for each site, the benefits of this simple and effective technology to treat high-level liquid, sludge, and solid wastes at a much reduced risk, schedule, and cost.

REFERENCES

1. National Research Council, "Research Needs for High-Level Waste Stored in Tanks and Bins at U.S. Dept. of Energy Sites," National Academy Press, Washington, DC (2001).
2. A. S. WAGH, D. SINGH, and S. JEONG, "Chemically Bonded Phosphate Ceramics," in Handbook of Mixed Waste Management Technology, ed., C. Oh, CRC Press, Boca Raton, FL (2001) Chapter 6.3.
3. U.S. Environmental Protection Agency, 40CFR Part 268.45 (1994).
4. American Society for Testing of Materials, C 1285 – 97, Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (1997).
5. M. POURBAIX., Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, New York (1974).
6. G. L. SMITH et al, Vitrification and Product Testing of C-104 and AZ102 Pretreated Sludge Mixed with Flowsheet Quantities of Secondary Wastes, Report PNNL-13452, prepared for CH2MHill Hanford Group (2001).
7. DOE Inspector General, Audit Report on Salt Processing at the Savannah River Site, August 27, 2002.