

CHEMICALLY BONDED PHOSPHATE CERAMICS FOR STABILIZATION AND SOLIDIFICATION OF MIXED WASTE

Arun S. Wagh, Dileep Singh, and Seung-Young Jeong

Energy Technology Division

Argonne National Laboratory

9700 S. Cass Avenue, Argonne, IL 60439

Summary

This chapter reviews a novel chemically bonded phosphate ceramic technology developed at Argonne National Laboratory to stabilize low-level radioactive and transuranic mixed waste streams within the U.S. Department of Energy (DOE) complex. This cement-like technology, which can be used to treat solids, liquids, and sludges by micro- and/or macro-encapsulation and chemical immobilization, is based on chemical reaction between phosphate anions and metal cations to form a strong, dense, and durable matrix that stores the hazardous and radioactive contaminants as insoluble phosphates and microencapsulates insoluble radioactive components. In this chapter, we discuss the thermodynamic basis of phosphate stabilization and present several case studies to demonstrate the effectiveness of the process in a wide variety of actual waste streams that include low-level mixed ash, transuranics, fission products, radon-emanating wastes, salt solutions, and heterogeneous mercury-containing debris. These case studies demonstrate that the waste forms are not only stable in groundwater environments, but also are nonignitable and hence safe for storage and transportation. The process has been made very versatile and thus can be used to treat wide-ranging chemical species such as those in higher oxidation states, as well as very highly soluble salt solutions. To attain this versatility, we have developed reduction methods and coupled chemical immobilization with macroencapsulation. An independent study has found that this room-temperature phosphate stabilization process is one of the most economical processes available to treat low-level mixed waste within the DOE system.

1. Introduction

Approximately 250,000 m³ of mixed low-level waste resides within the U.S. Department of Energy (DOE) complex [Berry, 1994]. It exists in various forms in the following proportions: 39% aqueous liquids, 17% inorganic sludges and particulates, 25% heterogeneous debris, 3% soils, and 5% organic liquids. The volume will increase to 1,200,000 m³ in the next few years. In addition, DOE's treatment plans currently show a significant number of waste streams that require solidification and stabilization [Berry, 1994]. Because of the diverse nature of the physical and chemical composition of these waste streams, no single solidification and stabilization technology can be used to successfully treat and dispose of these wastes.

The low-level mixed wastes contain both hazardous chemical and low-level radioactive species. Stabilization of such wastes requires that contaminants of both kinds be immobilized effectively. Often, the contaminants are volatile compounds and hence cannot be treated effectively by high-temperature processes [Mayberry et al., 1992]. These volatiles are usually in the form of chlorides or fluorides of heavy metals and actinides. Fluorine and chlorine are introduced in the wastes from plastics such as polyvinyl chloride. In a conventional vitrification or plasma hearth process, such contaminants may be captured in secondary waste streams such as scrubber residues, or off-gas particulates that need further low-temperature treatment for stabilization. It may not be viable to continuously recycle these secondary waste streams in the feed stream of the high-temperature process because of the buildup of contaminant levels. These secondary waste streams will therefore require low-temperature treatment to meet existing Land Disposal Restrictions (LDRs). Also, some of these waste streams may contain pyrophorics that will ignite spontaneously during thermal treatment and thus cause hot spots that may require expensive control systems and equipment with demanding structural integrity on [Mayberry et al., 1992]. Therefore, there is a critical need for a low-temperature treatment-and-stabilization technology that will effectively treat the secondary wastes generated by high-temperature treatment processes and wastes that are not amenable to thermal treatment; this was the main objective in the development of chemically

bonded phosphate ceramics (CBPCs). Once developed, CBPCs have found their niche applications in treating most difficult wastes such as salts, ashes, liquids, and sludges.

Transuranic (TRU) wastes that contain incinerated residues such as ash, ash heels, i.e., ash calcined to get rid of loss-on-ignition fraction for safe transportation), and Pu-contaminated crucibles are stored at several DOE sites [Behrens et al., 1995]. Some of these wastes contain as much as 17 wt.% Pu and require stabilization for their safe transportation, safeguarding, and storage at facilities such as the Waste Isolation Pilot Plant (WIPP). Earlier attempts to stabilize such waste streams [Donald et al., 1997, Rask and Phillips 1993] employed thermal treatments that were based on encapsulating wastes in a dense, hard ceramic or glass matrix. Such heat treatment of TRU wastes is generally expensive. Formation of a good monolithic glass may also be difficult because hot spots develop in the matrix due to pyrophoric components in the waste streams. In addition, if the TRU wastes also contain hazardous components, the release of off-gases containing volatile species of the hazardous metals during heat treatment is always a concern. CBPC technology was successfully demonstrated for these wastes.

2. Chemically Bonded Phosphate Ceramics

CBPCs are fabricated by acid-base reactions between an inorganic oxide and either phosphoric acid solution or an acid-phosphate solution. Kingery [6] conducted preliminary studies of phosphate bonding in refractories at low-temperatures and identified several phosphate systems that form hard ceramics. The acid-base process has the advantage that it can be used to treat both acidic and alkaline wastes. In addition, because the process employs solid powder and phosphate solution for the reactions, both solid and liquid wastes can be treated. Solid wastes can be crushed and mixed with a starter powder and then reacted with liquid; liquid waste may be mixed with the phosphoric acid or acid-phosphate solution and then reacted with the inorganic-oxide powder. After the acid solution and base powder are mixed, the slurry can be transferred into molds for setting. Because of the acid-base reaction, this technology is applicable to systems within a wide pH range. These advantages broaden the applicability of this technology. Their low-temperature-

setting characteristics, good strength, and low porosity make these phosphates suitable for the stabilization of mixed wastes that cannot be treated by current technologies.

Previous work at Argonne National Laboratory (ANL) [7-10] and that of others [Sugama and Kukacka, 1983, and Sliva and Scheetz, 1984] on the development of the CBPCs demonstrates the inherent favorable properties of these materials for containment of mixed wastes. Some of these properties are summarized below.

- Natural analogs of radioactive and rare earth elements. Monazites ($[\text{Ce, La, Y, Th}]\text{PO}_4$) and apatites ($\text{Ca}_5[\text{PO}_4]_3$) are ores of U and Th and are natural host minerals of rare earths and radionuclides. These natural analogs suggest the suitability of phosphate systems for incorporating actinides [13].

- Extreme insolubility . Phosphates are extremely insoluble [14] in ground water and this will ensure that the phosphate-based final waste forms will protect ground water from contamination by the contained waste. A study by Sliva and Scheetz [12] shows good performance of the waste forms that simulated wastes from the Idaho Chemical Plant; retainment of Cs and Sr was excellent. Several long-term leaching tests conducted at ANL on Mg-phosphate systems showed that these phosphates are insoluble in water and brine [7-10]. These examples indicate that phosphate complexes are most suitable for containment of mixed waste.

- Phosphates can be processed in solid form at room temperature. As solidifying agents, phosphates can set at low [6]. We have exploited room-temperature-setting MgKPO_4 extensively in solidification of low-level mixed waste.

- Compounds. Phosphate-bonded ceramics are nonflammable inorganic materials and hence the phosphate waste forms are safe during transportation and storage.

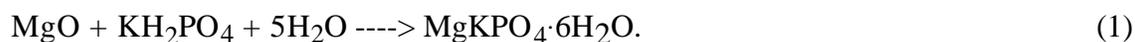
- Minimal secondary waste streams and heat. Because the final waste form is synthesized at a low temperature, volatilization is not a risk. Furthermore, because there is no thermal treatment of

the waste streams, the fabrication steps and processing equipment needs are simple. In addition, the entire stabilization reaction occurs within hours. The short setting time is particularly advantageous because it minimizes worker exposure when radioactive waste is treated.

- Low overall processing costs. The raw materials required for fabricating the waste forms are readily available at comparatively low cost. In addition, the fabrication technology is simple, very similar to cement stabilization, and uses the same equipment that is used to stabilize cement.
- Other favorable properties. The radiation stability of magnesium ammonium phosphate is excellent [Wagh et al., 1994]. Changes in the mechanical integrity of the material were not detected after gamma irradiation to a cumulative dosage of 10^8 rads. Also, aluminum phosphate is known to be a molecular sieve, and zirconium phosphate has a large ion-exchange capacity [Kanazawa, 1989]. Such properties make phosphates excellent host materials for radioactive isotopes.

3. Synthesis of CBPC

CBPCs are formed by reaction between magnesium oxide (MgO) and monopotassium phosphate (KH_2PO_4) in solution. The reaction is governed by the reaction



This reaction yields the hard, dense ceramic of magnesium potassium phosphate hydrate, $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ (MKP), which acts as a crystalline host matrix for the waste. During the reaction, the hazardous and radioactive contaminants also react with KH_2PO_4 to form highly insoluble phosphates. The bulk ceramic then microencapsulates the reacted contaminants in the dense crystalline matrix of MKP. The crystallinity of the CBPC and overall phase formation may be seen in the scanning electron microscopy (SEM) microphotograph and X-ray diffraction output in Figs. 1 and 2, respectively.

CBPC waste forms are fabricated by slowly stirring a mixture of the waste, MgO, and KH_2PO_4 , in water. Because of the dissolution of the KH_2PO_4 , the solution contains ions of potassium phosphates and protons (H^+) and is therefore acidic. The acidity of the solution increases the solubilities of MgO, oxides of hazardous metals, and to some extent, radioactive contaminants, and leads to the dissolution of the MgO and the contaminants. This, in turn, leads to the release of Mg^{2+} and metal ions of the contaminants. These cations subsequently react with the aqueous phosphate ions to produce phosphates.

To form a ceramic of MKP, it is necessary that Mg^{2+} react slowly with the phosphate ions. On the other hand, it is necessary that the hazardous metals and radioactive components react rapidly so they can be encapsulated in the MKP matrix. If the metals and radioactive components react at a rate that is slower than the formation of the MKP matrix, sufficient phosphate anions will not be available for them to react and they will not be fixed by the matrix as phosphates. Thus, for superior stabilization, it is necessary that contaminants be converted to phosphates spontaneously.

The setting reaction given by Eq. 1 may be quantitatively formulated by studying the thermodynamics of dissolution and overall reactions of the oxides in the KH_2PO_4 solution. The KH_2PO_4 has high solubility and its dissolution is represented by



where the superscripts represent the ionic charge. This reaction is endothermic and occurs before other components dissolve. When an alkaline oxide such as MgO is stirred into the acidic phosphate solution, the pH of the solution slowly rises because the acid is neutralized. Initially, the pH of the KH_2PO_4 is 4, but dissolution of the oxide neutralizes the acid solution and subsequently leads to the formation of ceramics at a pH of 8.

In the presence of the 2H^+ released by the KH_2PO_4 , MgO dissolves by the reaction



where (aq) means the ion is aquated. Equations 1-3 form the basis for binder development in the CBPC process. The ions from Eqs. 2 and 3, along with five additional moles of water, react to form the matrix material $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ as given in Eq. 1.

The reaction between the ions in Eqs. 2 and 3 is exothermic; the heat is partially offset by the cooling provided by the dissolution of KH_2PO_4 . This may be seen in Fig. 3, where we have plotted the temperature of the slurry vs. time. As the dissolution of KH_2PO_4 occurs, the slurry becomes acidic and cools. Within 10 min., due to this cooling, some condensation was observed on the sides of the 55-gal drum in which the stabilization was carried out for soils [Wescot et al., 1998]. In this acidic solution, MgO starts to dissolve according to Eq. 3 and then reacts with the phosphate ions to produce the matrix material and heat; thus, the temperature of the slurry starts to rise. At 55°C , the slurry thickens rapidly and solidifies almost instantaneously. The temperature of the newly formed monolithic solid continues to rise, which indicates that the reaction is not complete and continues. The maximum temperature observed in a full drum was 82°C . This temperature profile indicates that the slurry will not boil during formation of the ceramic and hence the process is safe for treating waste streams at full scale.

4. Contaminant Stabilization

The solubility of hazardous, radioactive, and fission product contaminants in the CBPC pH range of 4-8 plays a key role in the stabilization of these contaminants. Therefore, it is necessary to study the solubility of the contaminants in detail.

The solubility product constant K , which is the ionic concentration of solubilized products suitably normalized to the initial concentration of the reactants, is related to the net change in Gibb's free energy ΔG [Oxtoby et al., 1990] for a dissolution reaction, is given by

$$K = \exp(-\Delta G), \quad (4)$$

where $\beta = 1/k_B T$, and k_B and T are, respectively, the Boltzmann constant and the absolute temperature of the system. It is customary to report K as

$$pK_{sp} = -\log K = -\Delta G^\circ / (2.301 RT) \quad (5)$$

Using the values of ΔG° for each of the solubilization reactions of the hazardous metal oxides, Pourbaix [18] calculated pK_{sp} values of various hazardous contaminants and plotted them as a function of pH. His plots are reproduced in Fig. 4. These plots provide some insight into the solubilization behavior of the oxides of hazardous contaminants and their stabilization characteristics, which are given below.

- The solubility increases at low pH. Thus, in the acidic solution of KH_2PO_4 , the contaminant oxides are easily dissolved. With KH_2PO_4 , the minimum solubility is beyond the pH range of stabilization (4 -8) which ensures better solubilization of these contaminants and this reaction with the phosphate.
- Except for As_2O_3 and HgO , all of the other oxides generally show minimum solubility at alkaline pH. Only Cr_2O_3 shows a minimum at slightly acidic pH. These findings imply that the CBPC process, in which pH ranges from 4 to 8, the solubility is initially high and the contaminants readily solubilize and react with the phosphate and are stabilized. Even Cr_2O_3 will initially have a significant solubility and will readily react before the pH reaches that of minimum solubility.
- The solubilities of As_2O_3 and HgO are constant in a wide range of pH centered on neutral, and increase only at very low and very high pH.
- Among the divalent oxides, overall, HgO exhibits the lowest solubility in the entire acidic range when compared with other oxides.

These observations imply that stabilization of As_2O_3 , Cr_2O_3 , and HgO may be difficult in the CBPC or any other chemical process such as cement stabilization. These three oxides may require

additional stabilizers, such as a source of sulfides, to enhance their solubility. This will be demonstrated in relation to specific waste streams in later sections.

The value of ΔG determines the spontaneity of a chemical reaction. If $\Delta G < 0$, the dissolution will be spontaneous. If $\Delta G > 0$, the dissolution will be nonspontaneous.

A spontaneous dissolution will produce a precipitate and will not support the formation of ceramics; this implies that the solubilization reaction of MgO should be nonspontaneous. On the other hand, because, for purposes of chemical immobilization, we want contaminants to react with phosphates and form insoluble phosphates, it is necessary that they solubilize spontaneously. These observations lead to the following required stabilization conditions.

$$pK_{sp} < 0 \text{ for MgO,} \quad (6)$$

and

$$pK_{sp} > 0 \text{ for contaminants.} \quad (7)$$

Commercially available MgO does not satisfy the first condition, and hence development of CBPCs was elusive for a long time. We have been able to calcine MgO sufficiently to reduce its solubility so that the condition in Eq. 6 is satisfied near neutral pH and a ceramic is formed. When MgO is first stirred in, the solubilization reaction remains spontaneous and MgO dissolves in the acidic solution. This raises the pH of the solution. As the pH approaches the neutral range, MgO dissolves nonspontaneously and supports the formation of a ceramic.

As Fig. 4 shows, the solubility of the contaminants changes within the pH range of 4-8 (shown by shaded area), where the CBPC matrix is formed. The contaminants that will react spontaneously have positive solubility in this range. All of the contaminants that do have a positive total solubility satisfy Eq. 7 and will react spontaneously at that pH. Those contaminants that have only negative solubility will not satisfy the condition in Eq. 7 and will not react spontaneously at pH = 4. These contaminants will require additional stabilization. Oxides of Ag, Cd, Ni, Pb and Zn lie on the right-hand side of the line at pH = 4, and will spontaneously dissolve in the phosphate

solution, whereas oxides of As, Cr, Hg will not dissolve spontaneously and hence may not react readily.

As we shall see in the case studies presented in later sections, stabilization of contaminants, except for As, Cr, and Hg, has been easy. In the tests that were performed in our laboratory, As and Cr in small concentrations (ppm) were not a problem, partially because the Toxicity Characteristic Leaching Test (TCLP) passing limits for these substances [U.S. EPA, 1994] are high enough, i.e., 5 and 0.19 mg/L, respectively, and partial chemical stabilization and microencapsulation of these contaminants by the phosphate matrix could arrest their leaching. However, stabilization of Hg is very difficult, because the TCLP limit is very stringent (.0025 mg/L); hence, this contaminant requires an additional stabilization step. Certain mining wastes of As and Cr contain high levels of these contaminants, usually in a few percent. When As and Cr are in such high concentration in the waste, e.g., or when they occur in higher leachable oxidation states as arsenates and chromates, their stabilization is also difficult and they require additional stabilizers in the binder.

In the CBPC process, the problematic oxide components of Hg, As, and Cr are treated by a small addition (<1%) of a sulfide such as K_2S , which is added to the binder. Sulfidation of the oxides converts them into insoluble sulfides, which are then microencapsulated in the CBPC matrix. The oxides that are in higher oxidation states, e.g., Cr^{6+} or As^{5+} , may be reduced to lower oxidation states by addition of reductants to the binder; they are then stabilized.

Often, contaminants are present in excessive concentrations and the phosphate ion concentration is not adequate for stabilization. A good example of this case is that of the Waste Experimental Research Facility (WERF) ash from Idaho National Engineering and Environmental Laboratory (INEEL). The Zn concentration in this ash was very high. Thus, the Zn was competing with other contaminants to form phosphate, and the other contaminants were deprived of the phosphate ions they required for stabilization. The problem was remedied by adding a small amount of phosphoric acid to stabilize these contaminants.

Despite these exceptional cases, the CBPC process is simple to operate, but requires a detailed understanding of the waste stream composition and the stabilization mechanism. Sulfidation, reduction mechanisms, or pH adjustments make the process highly successful in treating a very wide range of waste streams.

Oxides of four-valent-state actinides, such as ThO_2 , UO_2 , PuO_2 and AmO_2 , are inherently insoluble in ground water. The values of pK_{sp} for some of these oxides, taken from Refs. 20-23, are provided in Table 1. One may notice that they are lower by several orders of magnitude than the pK_{sp} values of Mg or the hazardous contaminant oxides discussed in the previous section. Thus, because of their extremely low solubility, actinide oxides, for immobilization purposes, may be simply micro- or macroencapsulated in a dense matrix of phosphates. If actinides exist at a lower oxidation state and exhibit a higher solubility, they are fully oxidized to the four-valent state in the oxidation environment of the phosphate solution and insolubilized before encapsulation.

During encapsulation of these oxides in the CBPC matrix, these insoluble oxides are not expected to react with the matrix components, even in an acidic solution [Wagh et al., 1997]. This may be seen in the solubility diagram shown in Fig. 5, which was taken from Ref. 24 and plots the solubility of PbHPO_4 , $\text{Pu}(\text{OH})_4$, and $\text{Mg}(\text{OH})_2$. In the pH range of the reaction slurry (4-8), the solubility of $\text{Pu}(\text{OH})_2$ is the lowest, with a value of 8.5; hence, it is the most insoluble. On the other hand, $\text{Mg}(\text{OH})_2$ will solubilize readily in this pH range and form the matrix to encapsulate $\text{Pu}(\text{OH})_2$. Such a microencapsulation has been demonstrated for PuO_2 by SEM and is discussed in Section 5.3.

The four fission products Cs, Sr, Ba, and Tc have different solubility characteristics in the acidic phosphate systems than those of other contaminants and hence must be considered separately. Cs occurs as readily soluble compounds, e.g., CsCl , which are regarded as salt wastes that need not only chemical immobilization but also must be supplemented by enhanced physical macroencapsulation. We will discuss this in the context of salt waste stabilization. Sr and Ba

behave more like the other hazardous metals discussed above. Each of them will dissolve easily, react to form insoluble phosphates, and then become microencapsulated in the phosphate matrix.

Tc is more complex [Singh et al., 1998]; it normally exists in a four-valent state, but tends to oxidize when disposed of as pertechnetate (Tc^{7+}), which is easily leachable. To retain it in the four-valent state in the phosphate-bonded ceramic waste form, the CBPC process has been modified. Its performance will be discussed in Section 5.2.

5. Demonstration of the Process with Actual Wastes: Case Studies

Several case studies were conducted to demonstrate the superior performance of the CBPC waste forms as treatment of DOE waste streams. Below we present some of the major case studies that show various advantages of the process, including leach resistance of the waste forms, their long-term durability, removal of pyrophorocity from the waste streams, minimal gas generation, nonflammability of the final waste forms, and most importantly, the ability of the process to treat a very wide variety of waste streams that cannot be handled by other methods.

5.1 Stabilization of Low-Level Debris Waste

The CBPC technology was deployed to treat and dispose of low-level mixed waste at ANL's facility in Idaho (ANL-West) [Singh et al., 1998b]. Two debris wastes that contained hazardous metals and low-level fission product contaminants were treated.

Hg-contaminated crushed light bulbs. Visual inspection of this waste revealed that 90 vol.% was <60 mm in size; thus, it could not be classified as a debris waste [Singh et al., 1998b]. Typical sizes of the crushed glass ranged from 2-3 cm long by 1-2 cm wide down to fine particulates. Chemical analysis indicated an Hg concentration of 2.5 ppm. In addition, emissions from isotopes of ^{60}Co , ^{137}Cs , and ^{154}Eu were 1.1×10^{-5} , 4×10^{-4} , and 4×10^{-6} $\mu\text{Ci/g}$, respectively.

Radioactive contaminated lead-lined gloves. This waste was essentially Pb-lined gloves used in various hot-cell operations. Radioactive contamination in the gloves was ^{137}Cs (5×10^{-7} $\mu\text{Ci/g}$). To stabilize this waste, the gloves were first cryofractured in liquid N with a high-speed blender. Typical debris size from this operation ranged from powder to pieces as large as a few millimeters; thus, this waste also did not fall under the debris waste category [Singh et al., 1998b]. Chemical analysis indicated that 11.3 wt.% Pb is present in the waste.

CBPC waste forms were fabricated in 5-gal. drums. Typical waste loading ranged from 35 to 40 wt.%. For glass waste, small amounts of potassium sulfide was added to the binder mixture to stabilize Hg by converting it into least-soluble cinnabar (Hg_2S) form. After mixing for 30-35 min, the resulting slurry (see Fig. 6) was allowed to set in the drum. This procedure produced dense, hard ceramic waste forms.

TCLP test results (Table 2) showed excellent stabilization of both Hg and Pb in the waste forms. Hg levels of 0.05 ppb in the leachate are well below the Environmental Protection Agency's (EPA's) Universal Treatment Standard (UTS) of 25 ppb, whereas the level for Pb was <0.1 ppm, compared with the UTS limit of 0.37 ppm. The principal advantage of this technology is that immobilization of contaminants is the result of both chemical stabilization, and subsequent microencapsulation of the reaction products. Overall, 22 kg of the waste was treated, removed from the inventory, and sent to the Radioactive Waste Management Complex at INEEL for storage.

5.2 Stabilization of Fission Products

^{99}Tc , present in DOE high-level waste as a by-product of fission reactions, poses a serious environmental threat because it has a long half life and is highly mobile in its soluble Tc^{+7} form. Because of the volatility of ^{99}Tc , wastes that contain this material must be treated at low temperatures. CBPC process fulfills this need [Singh et al., 1998a].

The actual waste was ^{99}Tc that was partitioned and eluted from simulated high-level tank waste, such as Hanford supernatant, by using a complexation-elution process developed by Los Alamos National Laboratory (LANL) [Schroeder, 1995]. A typical composition of the waste solution generated in the complexation-elution process is 1 M NaOH, 1 methylene-diamine, and 0.005 M Sn (II). Tc concentration in the waste was as high as 150 ppm.

Waste forms were fabricated by first precipitating ^{99}Tc from the waste stream by using a reduction process [Briscoe et al., 1931] and subsequently solidifying the precipitated Tc-oxide in the CBPC. Tc loadings in the waste forms were as high as 900 ppm. The performance of the waste forms was established with various strength, leaching, and durability tests. Long-term leaching studies, as per the ANS 16.1 procedure, showed that leachability indices for ^{99}Tc under ambient conditions ranged between 13 and 14.6 (see Table 3). The normalized leach rate for ^{99}Tc determined by the Product Consistency Test [Mayberry et al., 1992] was as low as 1.1×10^{-3} g/cm²-d (see Table 4) under ambient conditions. The compressive strength of the waste forms was 30 MPa and the waste forms were durable in an aqueous environment. Superior containment of ^{99}Tc in the CBPC matrix is believed to be due to a combination of appropriate reducing environment (determined from Eh-pH measurements) and micro-encapsulation in a dense matrix.

5.3 Pu-Containing Combustion Residue Waste

A feasibility study was conducted on the use of CBPCs for stabilization of the combustion residue of TRU wastes [Wagh et. al., 1999]. Using the CBPC matrix, we made waste forms that contained 5 wt.% Pu to satisfy the safeguard termination limits of the WIPP.

To test the feasibility of incorporating Pu in the CBPC waste forms, we first conducted a detailed leaching study with Ce as a surrogate for Pu and then made bench-scale samples. The samples were tested for compressive strength and short- and long-term leaching by TCLP and 90-day immersion, respectively. Satisfied with the performance of these surrogate waste forms, we selected three actual waste streams, which are described in Table 5. The U-Pu oxide mixture was a

result of corrosion of a U-Pu alloy. The TRU combustion residue, which was obtained originally from Rocky Flats, was fully calcined for safe transport to ANL. Therefore, all organics and combustibles were completely incinerated and the Pu concentration was enhanced. Thus, to produce samples that were suitable for the study of the radiolysis effects of the organic components of the wastes in the waste form, it was necessary to add a polymer to the waste. We accomplished this by adding Bakelite mounting compound to the waste and thus produced the third waste.

The surrogate waste forms displayed high leaching resistance for both hazardous metals, and Ce. By using Ce_2O_3 as a surrogate for pyrophoric Pu_2O_3 and U_2O_3 , we also demonstrated that such components oxidize within the matrix and produce nonpyrophoric components such as Ce_2O_3 [Wagh et al., 1997]. Here, we will concentrate on the detailed study conducted on radiolytic gas generation from the actual waste forms. Hydrogen generation due to α -radiation of Pu at its high concentration (5 wt.%) was a major concern, because $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ is the CBPC matrix material and contains six moles of water for every mole of magnesium potassium phosphate. Radiolytic decomposition of this water and any organic compounds in the waste form may pressurize the containers during storage of the waste forms. The actual study of the waste form that contained 10 wt.% organics indicated that such a radiolytic generation of gases was not a significant issue.

Figure 7 shows the SEM back-scattered image of PuO_2 that is physically microencapsulated. It is physically immobilized in the dense, strong matrix. In addition, the fact that it is present in its fully oxidized state as PuO_2 implies that pyrophoricity is removed and, because the oxide of Pu is a most insoluble compound, leaching resistance is enhanced. Thus, the high leaching resistance is due to the very low solubility of PuO_2 and superior microencapsulation. These superior results, even at a concentration of 5 wt.% Pu, indicate that the waste forms satisfy the current Safeguard Termination Limit for storage of TRU combustion residues.

Table 6 gives the H₂ yield of samples subjected to gas generation studies. The H₂ yield is represented in terms of a G(H₂) value, which is defined as the ratio of the radiation chemical yield to the energy absorbed, expressed in terms of the number of molecules generated per 100 eV. The observed G(H₂) values for the various CBPC samples compare well with the G(H₂) values reported in the literature for alpha and gamma radiolysis in similar waste forms. They are comparable to a G(H₂) value of 0.6 molecule of H₂/100 eV investigated for solidification of tritiated water, 0.095 ± 0.005 total molecule/100 eV for the total gas production in FUETAP concrete, and 0-0.43 total molecule/100 eV (combined alpha and gamma radiolysis) for simulated Hanford current acid waste and double-shell slurry wastes immobilized in a cement-based grout [Dole and Friedman, 1986]. Siskind [30] summarized the G(H₂) values reported in the literature for cement-solidified low-level waste exposed to gamma radiation; these G(H₂) values range from 0.03 to 0.35 molecule of H₂/100 eV. Draganic and Draganic [31] reported G(H₂) values for the radiolysis of pure liquid water as a function of the linear energy transfer. For Pu-239, G(H₂) is 1.6 molecular H₂/100 eV. The values given in Table 6 for waste streams without organics compare well with these reported G(H₂) values. These observations indicate that the gas yield is minimal and will not lead to pressurizing the waste containers unless the waste contained very high levels of organics. Such a situation is unlikely since most of the Pu wastes are calcined to oxidize Pu to its fullest extent to make it stable in the waste stream.

5.4. Stabilization of Salt-Containing Waste

One of the key features of the CBPC process is that, unlike conventional cements, the phosphate binder sets even in the presence of salts such as nitrates and chlorides. This was demonstrated by producing monolithic solids of the binder through the use of sodium nitrate and sodium chloride solutions in place of water [Wagh et al., 1999b, Singh et al., 1998c]. The solids represented waste streams at DOE sites such as Hanford.

This demonstration was conducted with surrogate salt waste. The surrogate waste in this work represented the salt waste inventory within the DOE complex. Both chloride and nitrate waste contained Fe_2O_3 , $\text{Al}(\text{OH})_3$, Na_3PO_4 , synthetic calcium silicate, and water as the major components; NaCl , CaSO_4 , and NaNO_3 as the salts; and Pb , Cr , Hg , Cd , and Ni (up to 800-900 ppm) as the heavy metals in each of the contaminant oxides. Trichloroethylene was added to investigate whether setting of the ceramic was in any way affected by residual organics in the waste. Waste forms were fabricated with two waste loadings (58 and 70 wt.%) for each of the waste streams.

The hazardous contaminants were chemically immobilized and physically encapsulated in the matrix of the CBPC; thus, the TCLP leaching results were excellent. The density of the final waste forms ranged from 1.7 to 2.00 g/cm^3 and compression strengths ranged from 1400 to 1900 psi for both the chloride and nitrate waste forms. These values are significantly higher than Nuclear Regulatory Commission LDR of 500 psi for cement-based waste forms [Mayberry et al., 1992]. Thus, CBPC salt waste forms at extremely high loadings are relatively dense, hard materials and are suitable for salt waste stabilization. The TCLP performance was also excellent. The results showed that the leaching levels were well below the EPA's UTS limits for all of the contaminants.

To arrest leaching of NaNO_3 and NaCl , a macroencapsulation technique (in which a coating is applied to the waste forms) was investigated and appropriate coating materials were identified for successful retention of the anions [U.S. EPA, 1995]. Using this macroencapsulation technique, we fabricated specimens and tested them for nitrate and chloride leaching by using the ANS 16.1 standard test. Table 7 provides the leachability index of the various specimens and shows that the leaching levels of the anions are significantly reduced by the coating. The leaching index of 12.6, obtained with the coating, is one of the highest for the nitrate waste forms.

The efficient retention of the anions in the macroencapsulated waste forms may be attributed to the sealing of the pores on the surface of the waste forms by the coating material. To verify this,

we investigated the microstructure of the cross section of one of the macroencapsulated waste forms by SEM. Figure 7 provides the photomicrographs we obtained at low and high magnification.

As one may see in Fig. 7, the polymer seeps into the connected porosity of the phosphate waste forms very efficiently. As we move from the top to the bottom of the photomicrographs, the polymer fraction is reduced. At the top, the coating is continuous where the surface porosity of the samples was greater. As the coating penetrates into the sample, it plugs all of the pores and forms an impermeable coating that arrests leaching of the anions. In addition, this penetration helps to develop a durable physical bond between the sample and the coating.

To test the durability of the waste forms after 90-day-immersion leachability testing, we conducted compression strength measurements on the nitrate waste forms. Three nitrate waste form specimens were immersed in deionized water for 90 days. Compression strengths of the three specimens were determined at the end of the test period. The average compressive strength of the three waste forms was 770 psi for 58% waste loading and 640 psi for 70% waste loading. Once again, these values are higher than the minimal LDR of 500 psi.

Because nitrate waste is ignitable, it is necessary that the waste form be nonflammable for safe transportation and storage. To demonstrate that CBPC waste forms comply with this requirement, oxidation test was conducted on the nitrate waste forms. Using the procedure recommended by EPA [34], we prepared a mixture of the waste form powder and soft-wood dust (sawdust) in a wt. ratio of 1:1 and ignited it by passing using an electrical pulse through a Kanthal loop with a radius of 2 cms that was embedded in the pile of the mixture. The time taken for the flame to consume each of several mixtures was recorded and is presented in Table 8. The table shows that the time required to burn mixtures of sawdust and known flammable salts, e.g., potassium bromate and ammonium persulfate, was extremely short (19-197 sec), whereas the time required to burn the waste form-and-sawdust mixtures was >480 sec (>8 min.), which is much longer than the combustion time of ammonium persulfate, the minimum time for passing the test. This result

implies that salt waste solidified in CBPCs will not require any special packaging, because the CBPCs are inorganic ceramic-type materials that assist in inhibiting the spread of flames and can be excellent solidification media for flammable salt waste.

5.5. Packaging of Radium-Rich Fernald Silo Waste

Fernald Silo I and II wastes are radium-rich. Radium (Ra) disintegrates into radon (Rn) which is a gas. Therefore, the wastes need to be suitably packaged for disposal and transportation. For this reason, a demonstration of their packaging in the CBPC matrix was conducted at bench scale [Wagh et al., 1999c]. The waste received from the Fernald Environmental Management Project (FEMP) contained As^{5+} , Ba, Cr^{6+} , Ni, Pb, Se^{4+} , and Zn as the hazardous contaminants. The total specific activity of all the isotopes in the waste was $3.85 \mu\text{Ci/g}$; radium alone accounted for $0.477 \mu\text{Ci/g}$ of this activity. This indicated that Rn, as a daughter product of the Ra in the waste, could pose a serious handling problem during this study. We made waste-form samples in a glovebox with an actual Fernald waste loading of 66.05 wt.% and subjected them to the TCLP test. The results given in Table 9 show excellent stabilization of all contaminants. Actual levels detected in the leachate were well below the EPA's most stringent UTS limits and in almost all cases were one order of magnitude below this limit.

Table 10 gives the specific a, b, and total activities of the TCLP leachate. Although Ra activity in the waste was 0.477 mCi/g and the total specific activity of all the isotopes was 3.85 mCi/g , activity in the leachate is very low. In particular, because Ra is water soluble, the leachate could provide it with a pathway. The fact that the activity in the leachate is at the pCi/mL level implies that Ra and most of the other isotopes are stabilized in the waste forms. This is possible because Ra would form a phosphate that is insoluble in the leachate. Thus, the CBPC process is a good way to arrest leaching of radioactive contaminants.

5.6. Solidification of Radioactive Incinerator Waste

The incinerator at the DOE Savannah River Site (SRS) burns low-level mixed waste. Ash and scrubber residues are generated during the incineration process. Tests were being conducted to verify whether the ash and scrubber waste streams can be stabilized by the CBPC method. Acceptance criteria for the solid waste forms include leachability, bleed water, compression strength testing, and permeability. Other tests on the waste forms include X-ray diffraction and SEM.

The composition of the incinerator blowdown is presented in Table 11. The quench system is operated to produce blowdown that contains 10% total solids. The blowdown samples that were used in this study contained 1.5% suspended solids, mostly SiO_2 and $\text{Zn}(\text{OH})_2$. Dissolved-solids content, usually NaCl and Na_2SO_4 , was 8.2%. The pH of the blowdown was 8.77 and the water content, 90.3%.

Based on X-ray diffraction, the blowdown contained cristobalite as SiO_2 , other forms of silica, anorthoclase ($\text{NaK}(\text{AlSi}_3\text{O}_8)$), magnetite (Fe_3O_4); and hematite (Fe_2O_3). The ash, which was wet-quenched, contained $45 \pm 15\%$ quench water; pH of the water in contact with the ash was 10.55. Ash and blowdown used for sample preparation were generated at SRS by incineration of diatomaceous earth filter rolls.

CBPC waste forms with various proportions of ash, blowdown, and combinations of ash and blowdown were fabricated [Walker et al., 1999]. The test matrix of the waste form composition is given in Table 12. The blowdown solution was evaporated to achieve higher salt waste loadings in the waste form while maintaining the same amount of water. The samples were cured in sealed containers for 28 days before testing.

Compressive strength estimates with a concrete penetrometer gave reading >700 psi, which exceed our specification criterion of 500 psi. Permeability testing of the nonradioactive blank sample with a Permeameter (Model # K-670A, ELE Int., Lake Bluff, IL) gave a reading of

$1 \times 10^{-4} \text{ cm}^2/\text{s}$. A sample of ash that was not solidified passed the TCLP leachability limits so no further TCLP tests were needed on stabilized waste forms.

Initially, the blowdown solution contained < 0.01 ppm Hg, <0.025 ppm Ag, 2.56 ppm As, 0.12 ppm Ba, 0.211 ppm Cd, 2.11 ppm Cr, 0.325 ppm Pb, and .65 ppm Se. Results for Hg, Ag, Ba, Cd, and Pb were below the detection limit and only As, Cr, and Se levels were measurable; these are given in the Table 15. The detection limits for the various elements were as follows: Cr, 0.0056; As, 0.045; Se, 0.0045; Ba, 0.0051; Cd, 0.0044; Ag, 0.0073; Pb, 0.0159; and Hg, 0.00035 mg/L. Overall, all of the contaminants passed the TCLP limits assigned by the SRS [Walker et al., 1999]. Waste forms of Samples 2 and 3, made with blowdown, show a decrease in all chemical species. The Se level in the blowdown, which initially exceeded limits, is within compliance after solidification. The waste forms of Samples 4, 5, and 6, made with SRS ash, show a decrease in leaching of chemical species, except for As. The waste forms of Samples 7 and 8, made with both blowdown and SRS ash, show a leaching decrease in all blowdown chemical species.

In summary, the CBPC waste forms showed excellent performance. The only test that failed was the test for permeability of a blank that was made from phosphate ceramic that was above the minimum SRS acceptability criterion. Since this case study, excellent nonpermeable CBPCs have been developed; they must now be tested with actual waste streams.

6. Conclusions

CBPC is a novel stabilization and solidification technology, developed at Argonne, that can treat a very wide variety of mixed waste that contains low-level radioactivity, fission products, TRUs, and salt waste. The case studies used to demonstrate this technology address several issues faced at DOE sites. These issues include high TRU concentrations and gas generated by them; most leachable salts, for which CBPC is a unique technology; occurrence of most leachable contaminants, such as Tc^{7+} , that require reduction during stabilization; and Ra-containing Silo

waste that cannot be easily handled and treated. CBPC technology is a solution for each of these cases.

Schwinkendorf and Cooley [1999] conducted an economic evaluation of various technologies that are available for the treatment of mixed wastes in the DOE complex. They concluded that CBPC technology is one of the most economical methods to treat these wastes. Since this technology has been demonstrated in 55-gal trials, its superior performance and cost effectiveness puts it in the forefront for treatment of DOE and commercial wastes in the millennium.

References

1. Berry, J. B., 1994. Mixed Waste Integrated Program - Demonstration Technologies to Meet the Requirements of the Federal Facility Compliance Act, in Spectrum '94, Vol. 1, Nuclear and Hazardous Waste Management International Topical Meeting, American Nuclear Society, Atlanta, 249-254.
2. Mayberry, J., Dewitt, L., Darnell, R. Konyneburg, R., Singh, D., Schumacher, R., Ericksen, P., Davis, J., and Nakaoka, R., 1992. Technical Area Status for Low-Level Mixed Waste Final Waste Forms, Vol. I, DOE/MWIP-3.
3. Behrens, R., Buck, E., Dietz, N., Bates, J., Van Deventer, E., and Chaiko, D., 1995. Characterization of Plutonium-Bearing Wastes by Chemical Analysis and Analytical Electron Microscopy, Argonne National Laboratory Report ANL-95/35.
4. Donald, I., Metcalfe, B., and Taylor, R., 1997. Review of the Immobilization of High-Level Radioactive Wastes Using Ceramics and Glasses, J. Mater. Sci. 32: 5851-5887.
5. Rask, W. and Phillips, A., 1995. Ceramification: A Plutonium Immobilization Process, in Proc. U.S. DOE Pu Stabilization and Immobilization Workshop: 153-157.

6. Kingery, W., 1950. Fundamental Studies of Phosphate Bonding in Refractories, II. Cold-setting Properties, *J. Am. Ceram. Soc.*, 33: 242–247.
7. Wagh, A., Strain, R., Jeong, S., Reed, D., Krouse T., and Singh, D., 1999 (a). Stabilization of Rocky Flats Pu-Contaminated Ash within Chemically Bonded Phosphate Ceramics, *J. Nucl. Mater.*, 265: 295-307.
8. Singh, D., Wagh, A., Cunnane, J., and Mayberry, J., 1997. Chemically Bonded Phosphate Ceramics for Low-Level Mixed-Waste Stabilization, *J. Environ. Sci. Health*, A32(2): 527-541.
9. Wagh, A., Singh, D., Jeong, S., and Strain, R., 1997. Ceramicrete Stabilization of Low-Level Mixed Wastes - A Complete Story, in *Proc. 18th DOE Low-Level Radioactive Waste Management Conf.*, Salt Lake City, USDOE, May 20-22.
10. Wescot, J., Nelson, R., Wagh, A., and Singh, D., Jan. 1998. Low-Level and Mixed Radioactive Waste In-Drum Solidification, *Practice Periodical of Hazardous and Radioactive Waste Management*: 4-7.
11. Sugama T., and Kukacka, L., 1983. Magnesium Ammonium Monophosphate Cements Derived from Diammonium Phosphate Solutions, *Cem. Concr. Res.*, 13:407-416.
12. Sliva, P., and Scheetz, B., 1984. An ICPP Aluminum Phosphate Ceramic Waste Form: Synthesis and Room-Temperature Aqueous Stability, in *Nuclear Waste Management, Advances in Ceramics Vol. 8*, Amer. Ceram. Soc.: Westerville, OH, 263-272.
13. McCarthy, G., White, W., Smith, D., Lasaga, A., Ewing, R., Nicol, A., and Roy, R., 1982. Mineral Models for Crystalline Hosts for Radionuclides in Radioactive Waste Disposal, in *The Waste Package, Vol. 1*, ed. R. Roy. Pergamon Press, New York: 184-232.

14. Nriagu, J., and Moore, P., (eds.), 1984. *Phosphate Minerals*, Springer-Verlag, New York: 171-198.
15. Wagh, A., Singh, D., Sutaria, M., Kurokawa, S., and Mayberry, J., 1994. Low-Temperature-Setting Phosphate Ceramics for Stabilizing DOE Problem Low-Level Mixed Waste: II. Performance Studies of Final Waste Forms, in Proc. Waste Management 94 Conf., Tucson, AZ.
16. Kanazawa, T., ed., 1989. *Inorganic Phosphate Materials*, Elsevier, New York: 121 .
17. Oxtoby, D., Nachtrieb, N., and Freeman, W., 1990. *Chemistry, Science of Change*, Saunders College Pub., Philadelphia: 372-375.
18. Pourbaix, M., 1967. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, New York.
19. U.S. EPA, 1994. 40 CFR Part 268.45 for Treated Wastes.
20. Dean, J. A., 1992. Lange's Handbook of Chemistry, 14th Ed., McGraw-Hill, New York, 8.11.
21. Linke, W. F., 1958. Solubilities, Vol. II, 4th Ed. Am. Chem. Soc., Washington, DC.
22. Taylor, A. W., Frazier, A. W., and Gurney, E. L. 1963. Solubility Products of magnesium Ammonium and Magnesium Potassium Phosphate, Trans. Faraday Soc. 59, 1580.
23. Taylor, A. W., Frazier, A. W., Gurney, E. L., and Smith, J. P. 1963. Solubility Products of Di- and Trimagnesium Phosphate and Dissociation of Magnesium Phosphate Solutions, Trans. Faraday Soc. Vol. 59, 1585.
24. Puigdomenech, I., and Bruno, J., 1991. *Plutonium Solubilities*, Tech. Report 91-04. Swedish Nuclear Fuel and Waste Management Co., Stockholm.

25. Singh, D., Mandalika, V., Strain, R., Parulekar, S., and Wagh, A., 1998 (a). Magnesium Potassium Phosphate Ceramic for ^{99}Tc Immobilization, Communicated to J. Am. Ceram. Soc.
26. Singh, D., Barber, D., Wagh, A., Strain, R., and Tlustochowicz, M., 1998 (b). Proc. Waste Management 98 Conf., Tucson, AZ.
27. Schroeder, N., 1995. Technetium Partitioning for the Hanford Tank Waste Remediation System: Anion Exchange Studies for Partitioning Technetium from Synthetic DSSF and DSS Simulants and Actual Hanford Wastes (101-SY and 103-SY) Using ReillexTM-HPQ Resin, Annual Report, LA-UR-95-4440, Los Alamos National Laboratory.
28. Briscoe, H., Robinson, P., and Stoddort, E., 1931. The Reduction of Potassium Perhenate, J. Chem. Soc., Vol. I: 666-669.
29. Dole, L., Friedman, H., 1986. Radiolytic Gas Generation from Cement-Based Waste Hosts for DOE Low-Level Radioactive Wastes, Report No. CONF-860605-14, Oak Ridge National Laboratory.
30. Siskind, B., 1992. Gas Generation from Low-Level Waste: Concerns for Disposal, Report No. BNL-NUREG-47144, Brookhaven National Laboratory.
31. Draganic, G., and Draganic, Z., 1971. *The Radiation Chemistry of Water*, Academic Press, New York.
32. Wagh, A., Singh, D., Patel, K., Jeong S., and Park, J., 1999 (b). Salt Waste Stabilization In Chemically Bonded Phosphate Ceramics, Final Report to Mixed Waste Focus Area of U.S. Dept. of Energy.
33. Singh, D., Patel, K., Wagh, A., and Jeong, S., 1998 (c). Proc. Spectrum '98 Conf., Denver, Sept. 13-18: 553-560.

34. U.S. EPA, Guidelines for Classification and Packing Group Assignment of Division 5.1, Materials, 1995, CFR CH1 (10 - 1 -95 Ed.), Appendix F to Part 173.
35. Wagh, A., Singh, D., Jeong, S., Graczyk, D., and Tenkate, L., 1999 (c). Demonstration of Packaging of Fernald Silo I Waste in Chemically Bonded Phosphate Ceramic, in Proc. Waste Management 99 Conf., Tucson, AZ.
36. Walker, B., Langton, C., and Singh, D., 1999. Proc. 101st Annual Meeting of Am. Ceram. Soc., Indianapolis.
37. E. Schwinkendorf, E., and C. Cooley, C., 1999. Costs of Mixed Low-Level Waste Stabilization Options, in Proc. Waste Management Conf., Tucson, AZ .

Table 1. Solubility product constants of phosphates of radioactive and related materials

Phosphate	pK _{sp}	Reference
Radioactive Contaminants		
(UO ₂) ₃ (PO ₄) ₂	46.7	20
UO ₂ HPO ₄	10.69	20
UO ₂ KPO ₄	23.11	21
Pu(HPO ₄) ₂ ·xH ₂ O	27.7	20
Th ₃ (PO ₄) ₄	78.6	20
Th(HPO ₄) ₂	20	20
Matrix Phases		
MgKPO ₄ ·6H ₂ O	10.6	22
Newberyite	5.8	23
Surrogate Waste Form		
Monazite as CePO ₄	23	20

Table 2. TCLP results on CBPC waste forms

Contaminant	Source	Loading (wt.%)	Contaminant Conc. in Waste Form	TCLP Results on Source	TCLP Results on Waste Form
Hg	Hg waste	40	1000 ppb	24.4 ppb	0.05 ppb
Pb	Cryofractured Pb-lined gloves	35	4 wt.%	328 ppm	<0.1 ppm

Table 3. ANS 16.1 TCLP results for CBPC specimens fabricated by precipitating ^{99}Tc by reduction process and then solidifying precipitated Tc oxide in CBPC

Method of Preparation	^{99}Tc Conc. (ppm)	Effective Diffusivity (cm^2/s)	Leachability Index
MKP + SnCl_2 + precipitated ^{99}Tc	41	2.2×10^{-14}	14.6
MKP + SnCl_2 + precipitated ^{99}Tc	164	2.3×10^{-13}	13.3
MKP + SnCl_2 + precipitated ^{99}Tc	903	7.2×10^{-15}	14.6

Table 4. Product consistency test results for CBPC specimens fabricated from reduction-treated, precipitated ^{99}Tc

Method of Preparation	Test Temperature ($^{\circ}\text{C}$)	Tc Conc. (ppm)	Normalized Leach Rate ($\text{g}/\text{m}^2 \cdot \text{d}$)
MKP + SnCl_2 + precipitated ^{99}Tc	25	40	3.9×10^{-3}
		164	8.5×10^{-3}
		903	1.1×10^{-3}
MKP + SnCl_2 + precipitated ^{99}Tc	90	40	7.2×10^{-2}
		164	1.1×10^{-1}
		903	3.6×10^{-2}

Table 5. Origin, characteristics, and Pu content of test waste streams

Waste Stream	Origin and Characteristics	Content of Pu and Other Actinides (wt.%)
Mixture of U and Pu	U-Pu alloy, an ANL inventory item, fully oxidized and formed into fine powder.	U = 75, and Pu = 25
TRU combustion residue	Originally from Rocky Flats; subsequent operations led to high Pu concentration. Fine powder residue.	Pu = 31.8 as PuO ₂ , with minor reduced phase of Pu. ²⁴¹ Am = 0.1, ³⁹ Pu = 90, ²⁴⁰ Pu = 8.4, ²⁴¹ Pu = 1.
TRU combustion residue with addition of Bakelite mounting compound	63.7 wt.% mounting compound added to combustion residue. Waste form contained 10 wt.% organics.	Pu = 19.4 as PuO ₂ in combustion residue, with minor reduced phase of Pu. ²⁴¹ Am = 0.06 ²³⁹ Pu = 90, ²⁴⁰ Pu = 8.4, ²⁴¹ Pu = 1.3

Table 6. Yield of H₂ from samples investigated in gas generation studies

Sample	wt.% Pu	G(H ₂)Value (Molecular H ₂ • g Sample)	
		(Molecular H ₂ /100 eV)	(100 eV.gH ₂ O)
CBPC with U-Pu oxide mixture	5.245	0.13	0.65
CBPC with TRU combustible residue	7.87	0.10	0.48
CBPC with TRU combustible residue	5.00	0.23 ¹	1.1 ^a
CBPC with TRU combustible residue and Bakelite compound	31.8	31.8	NA

^aG(H₂) observed for >0.83 x 10²² eV of total released decay energy. An average of 0.57 molecular H₂/100 eV was observed for 0 to 0.83 x 10²² eV of total released decay energy. All G values were calculated assuming that 100% of decay energy is deposited into entire mass of sample.

Table 7. Results of ANS 16.1 test for various waste forms

Waste Forms	NO ₃ /Cl in Waste Form (ppm)	Fraction of NO ₃ /Cl Leached	Effective Diffusivity (cm ² /sec)	Leachability Index
Uncoated NO ₃ samples, waste loading 58 wt.%	218700	0.33	6.31 x 10 ⁻⁸	7.2
Coated NO ₃ samples, waste loading 58 wt.%	218700	0.0169	6.87 x 10 ⁻¹³	12.6
Uncoated Cl samples, waste loading 60 wt.%	46535	0.0669	1.26 x 10 ⁻⁹	8.9
Polymer coated Cl samples, waste loading 60 wt.%	46535		Readings mostly below detection limit	Readings mostly below detection limit

Table 8. Combustion time for various mixtures of waste form powder and sawdust subjected to oxidation test

Mixture	Combustion Time (sec)
1:1 Potassium bromate and sawdust	19
1:1 Ammonium persulfate and sawdust	49
1:1 Surrogate waste and sawdust	87
4:1 Surrogate waste and sawdust	197
1:1 Waste form and sawdust	>480

Table 9. TCLP results (mg/L) on stabilized samples of Fernald waste and UTS limits (mg/L) for various contaminants

Level/Limit	Contaminant									
	As	Cd	Ce	Cr	Co	Cu	Ni	Pb	Se	Sr
Level in leachate	0.22	<0.1	<.05	0.05	0.55	0.01	2.31	<0.1	0.82	0.13
UTS limit	5.0	0.2	-	0.85	-	-	13.6	0.75	5.7	-

Table 10. Specific activities (mCi/g) in various stabilized samples of Fernald waste

Sample Code	Alpha	Beta	Total
As-received waste			
Total specific activity	---	---	3.85
Specific activity of Ra ²²⁶	---	---	0.477
Waste form calculated activities			
Total specific activity	---	---	2.06
Specific activity of Ra ²²⁶	---	---	0.255
Specific activity in TCLP leachate (pCi/L)	25 ± 2	98 ± 10	221 ± 22 ^a

^aWe have assumed gamma activity beta activity.

Table 11. Composition of blowdown salts (mg/L)

Component	Concentration	Component	Concentration
Al	541.5	Cl	19,618
Ca	600.3	Nitrite	230
Fe	545.3	Nitrate	274
Mg	178.0	Sulfate	40,274
Na	32126.8	Oxalate	<10
F	639	Phosphates	646
Formate	<10	Phosphates	646

Table 12. Test matrix for SRS waste treatment

Sample No.	SRS ash (g)	<u>Blowdown (g)</u>		Binder (g)	Coal Ash (g)	Blowdown (wt.%)	SRS Ash (wt.%)
		10%	20%				
1	0	0	0	41.4	50	0	0
2	0	10	0	71.2	0	12	0
3	0	0	36.1	93.8	0	28	0
4	40	0	0	49.0	0	0	33
5	50	0	0	43.5	0	0	42
6	60	0	0	38.4	0	0	51
7	16.5	25	0	66.4	0	23	15
8	48	0	16	55.6	0	13	40

Table 13. TCLP results for SRS incinerator waste forms (mg/L)

Element	Sample No.						
	1	2	3	4	5	6	7
As	0.406	0.082	0.099	0.067	0.068	0.069	0.089
Cr	0.014	0.115	0.016	0.016	0.008	0.005	0.011
Se	0.084	-	0.028	Below detection limit			0.048

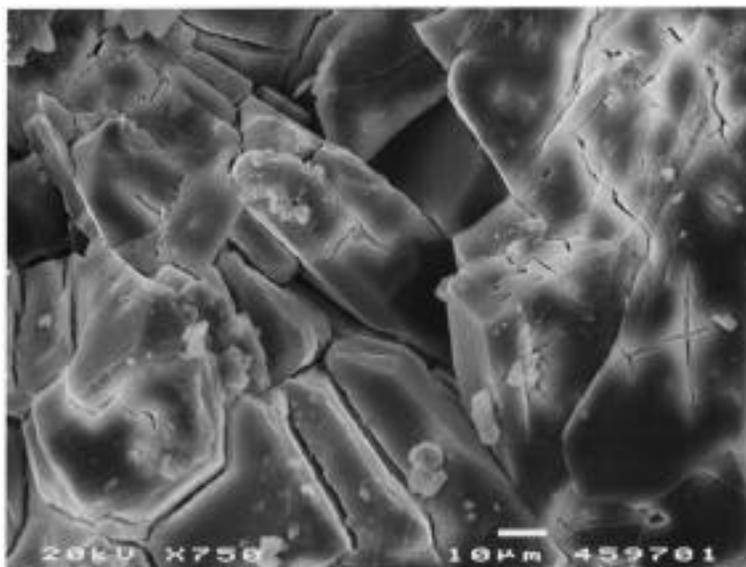


Fig. 1. SEM photomicrograph of CBPC matrix.

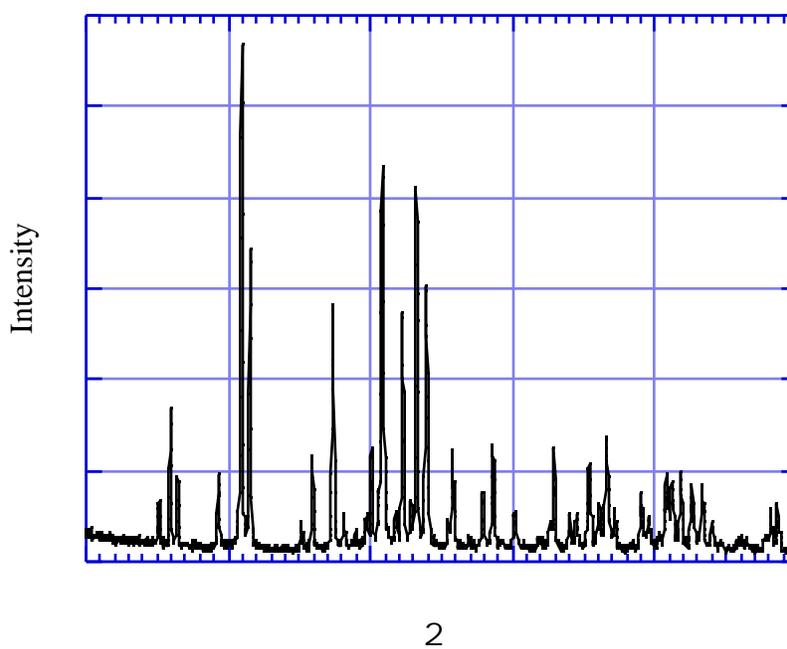


Fig. 2. X-ray diffraction output of CBPC matrix. All peaks have been identified as those of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$.

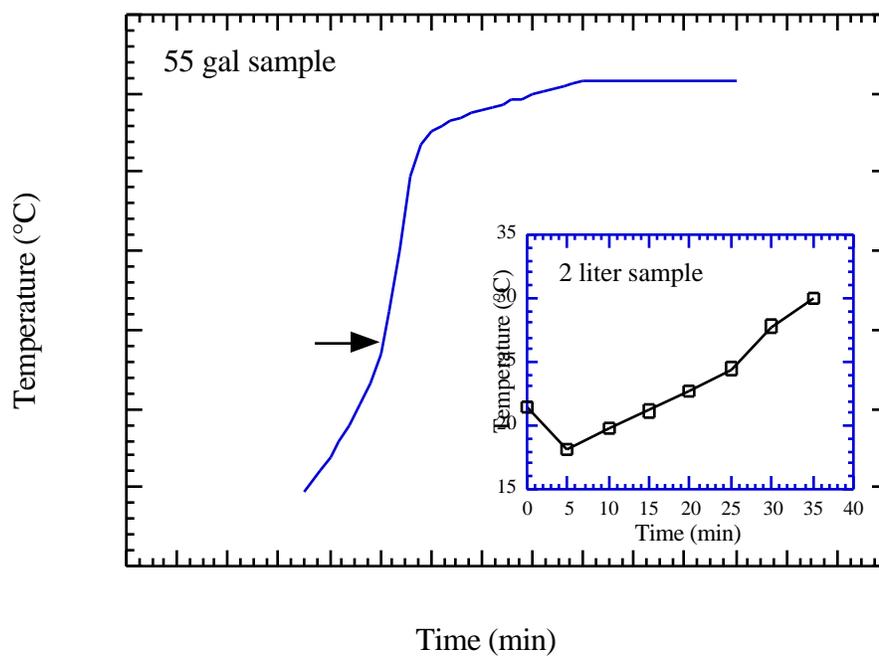


Fig. 3. Variation in temperature with time, which reflects pH (see text), during setting of soil in CBPC process at 55-gal and 2-L scales.

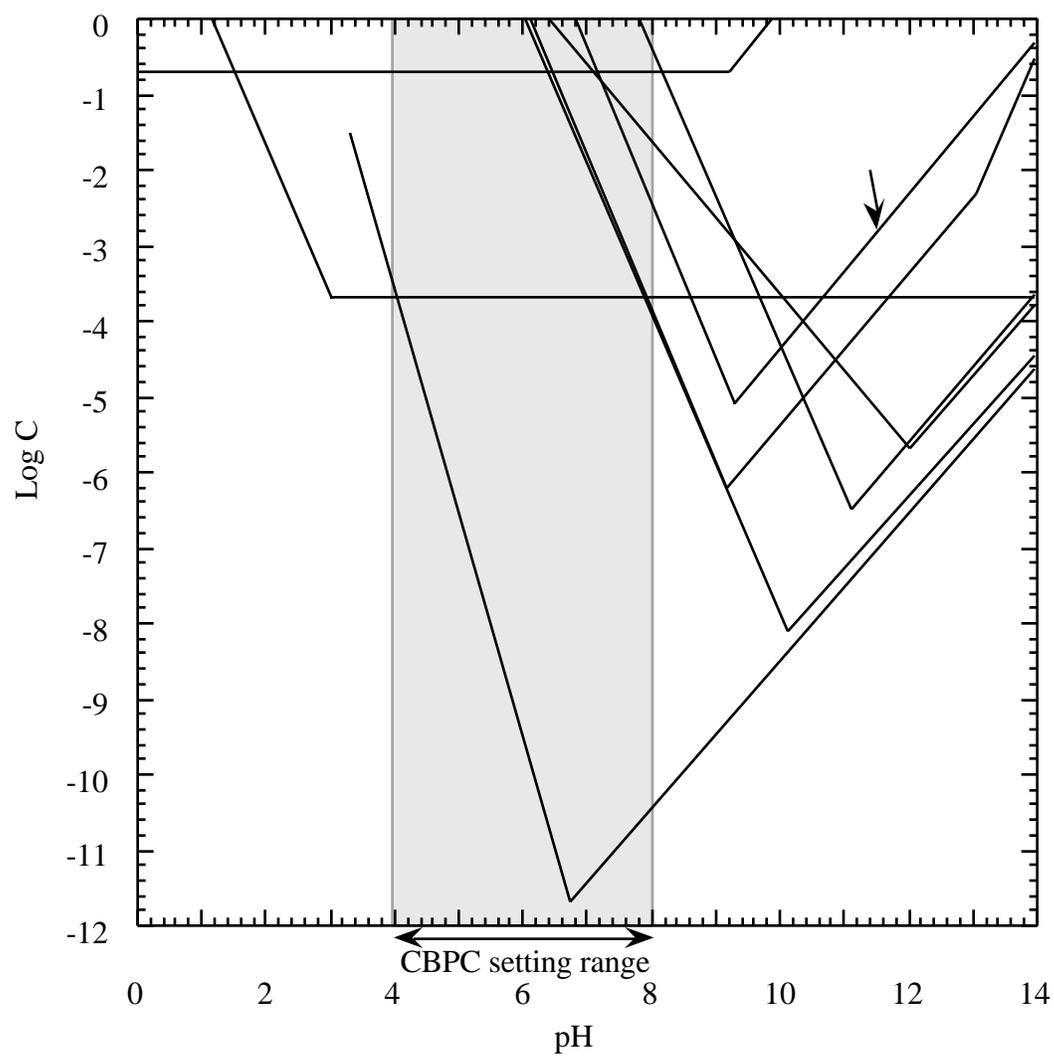


Fig. 4. Solubility pK_{sp} (shown as $\log C$) of hazardous contaminants as a function of pH. Adapted from Pourbaix [18].

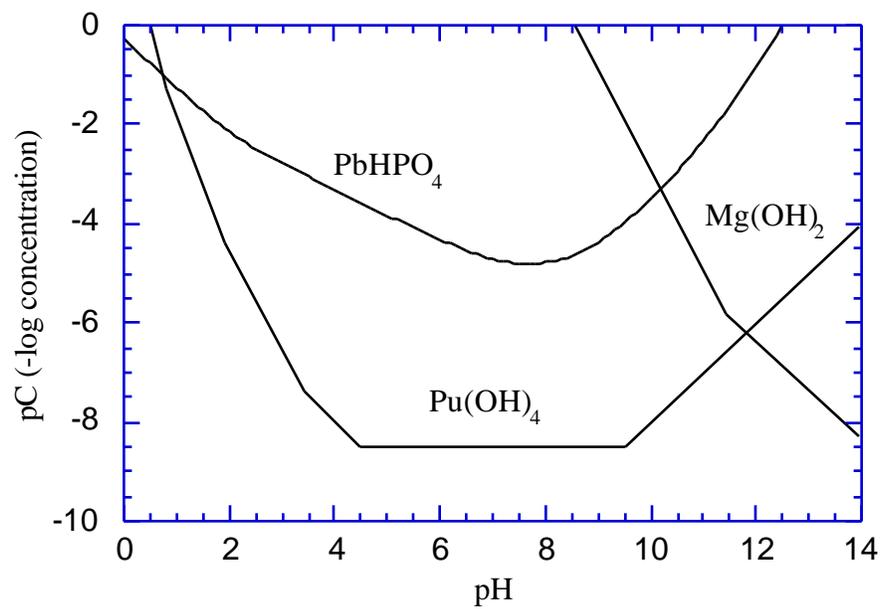


Fig. 5. Dissolution characteristics of $\text{Pu}(\text{OH})_4$, PbHPO_4 , and $\text{Mg}(\text{OH})_2$ in acid-base reaction of CBPC process [24].

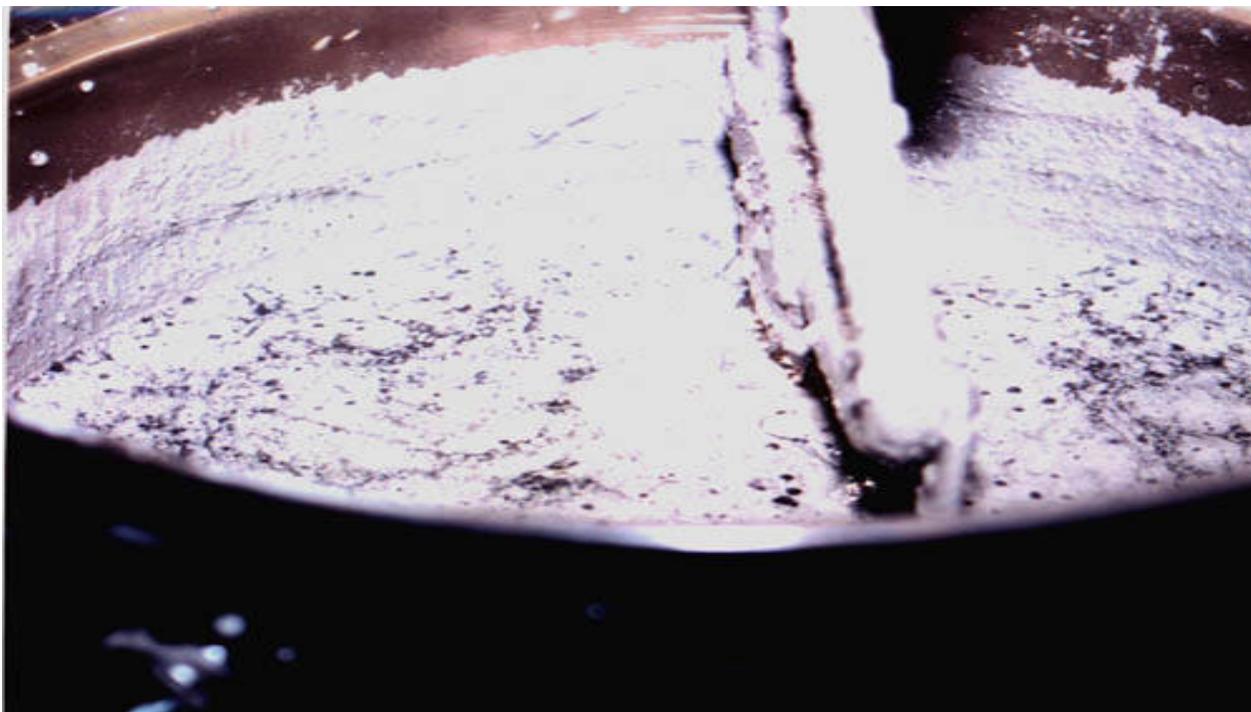


Fig. 6. CBPC-cryofractured low-level debris waste being mixed in 5-gal container.

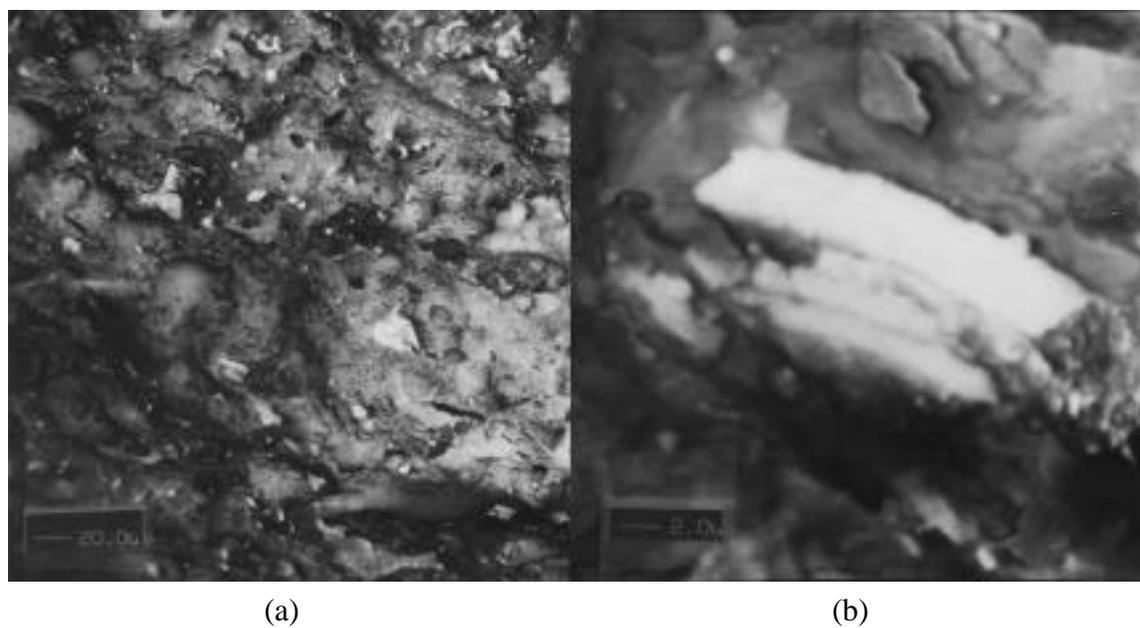


Fig. 7. Backscattered images of stabilized Pu waste form: (a) low magnification, (b) high magnification.

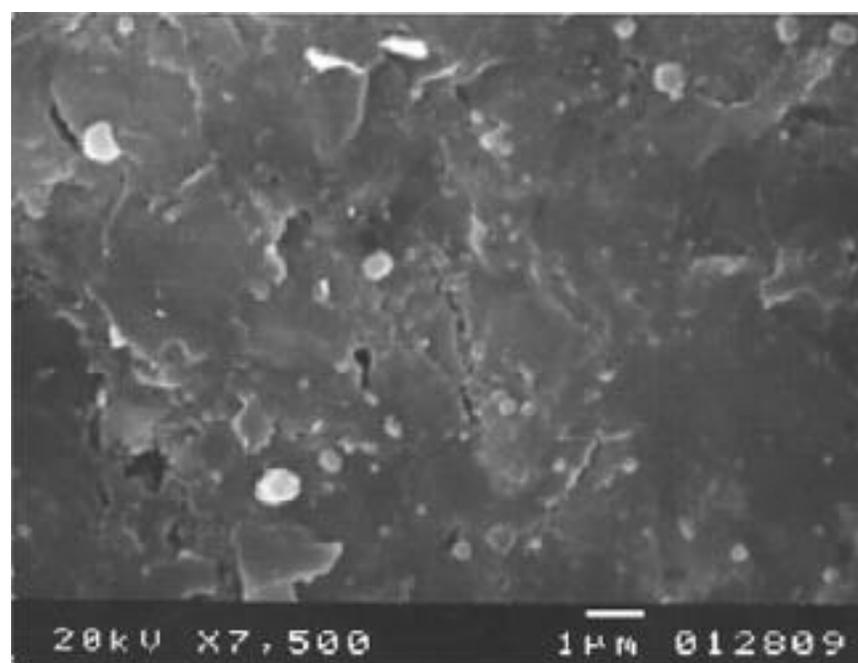


Fig. 8. SEM photomicrograph of the cross section of coated nitrate waste form.