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CALCINATION/DISSOLUTION TESTING FOR HANFORD SITE WASTES

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ABSTRACT

Thermal treatment by calcination offers several benefits for the treatment of Hanford Site tank wastes, including the destruction of organics and ferrocyanides and an hydroxide fusion that permits the bulk of the mostly soluble nonradioactive constituents to be easily separated from the insoluble transuranic residue. Critical design parameters were tested, including: (1) calciner equipment design, (2) hydroxide fusion chemistry, and (3) equipment corrosion.

A 2 gal/minute pilot plant processed a simulated Tank 101-SY waste and produced a free flowing 700 °C molten calcine with an average calciner retention time of 20 minutes and >95% organic, nitrate, and nitrite destruction. Laboratory experiments using actual radioactive tank waste and the simulated waste pilot experiments indicate that 98 wt% of the calcine produced is soluble in water, leaving an insoluble transuranic fraction. All of the Hanford Site tank wastes can benefit from calcination/dissolution processing, contingent upon blending various tank waste types to ensure a target of 70 wt% sodium hydroxide/nitrate/nitrite fluxing agent. Finally, corrosion testing indicates that a jacketed nickel liner cooled to below 400 °C would corrode <2 mil/year (0.05 mm/year) from molten calcine attack.

BACKGROUND

Plans exist to partition defense wastes stored in underground tanks at the U.S. Department of Energy's Hanford Site into low-level and high-level wastes (LLW and HLW, respectively) fractions. The LLW and HLW distinction will be based on the concentrations of the radionuclides, especially the transuranic (TRU) isotopes (elements with an atomic number >92).

Ideally, the LLW fraction would contain most of the chemical inventory of the Hanford Site waste but little of the radioactivity; the HLW fraction, conversely, would contain most of the radioactivity but little of the bulk waste chemicals. Following processing, the LLW will be vitrified to a glass waste form and stored in a retrievable form on the Hanford Site. The HLW waste fraction will be vitrified, cast into high-integrity canisters, and disposed of in the national long-term underground storage repository.

Because storage in the HLW repository is anticipated to be more expensive on a volume basis than LLW storage, incentive exists to minimize the quantity of the Hanford chemical waste inventory relegated to the HLW fraction. Certain of the waste components (e.g., phosphate, aluminum, chromium) can substantially increase glass volumes and, thus, are economical to remove from the HLW fraction. Secondly, incentive also exists to ameliorate glass production problems caused by offgassing during the melt formation caused by nitrate and nitrite thermal decomposition.

Calcination pretreatment at about 700 °C is proposed as a method to achieve the thermal decomposition of nitrate, nitrite, and organic carbon. In addition, solubilization of waste solids containing phosphate, aluminum, and chromium, via the fusion in NaOH occasioned by calcination followed by partial dissolution in water, is offered as a way to solubilize bulk waste components, such as phosphate, aluminum, and chromium, while leaving many radionuclides with low solubilities (e.g., strontium and TRU) behind in the solids residue.

THE HANFORD WASTE INVENTORY

The Hanford Site wastes are contained in 177 underground mild steel-lined concrete tanks having capacities ranging from 50,000 to 1,000,000 gal (190 to 3,800 m³). The Hanford Site waste inventory is 61,000,000 gal (230,000 m³), representing 330,000 tonnes total wet material or 220,000 tonnes dry.

The Hanford Site wastes originated from the various plutonium separation, uranium recovery, and waste minimization and processing operations conducted in the 50 years of Hanford Site production. The separation and recovery processes were conducted in nitric acid. Neutralization of the process wastes with sodium hydroxide to pH > 10 was performed for corrosion control before disposal to the mild steel waste tanks. All wastes, therefore, are alkaline and contain sodium and nitrate salts.

The inventory of the waste is classified as salt cake, sludge, and solution materials. The crystallized water soluble salts (primarily sodium nitrate, nitrite, and carbonate) are known as salt cake. Compounds, such as, transition metal hydroxides, aluminum hydroxide (gibbsite and bayerite), aluminum oxyhydroxide (böhmite), sodium aluminosilicates (e.g., cancrinite), and bismuth phosphate, identified in the water-insoluble balance of the Hanford wastes are known as sludge. Solutions containing the sodium salts exist separately and also are within the salt cake and sludge wastes.

Because of the variety of processes, subsequent waste handling, and the natural segregation based on solubilities, the waste compositions are highly varied, not only from tank to tank but also within individual tanks. Despite the variability of the wastes, the overall composition is relatively well known based on records of essential process materials consumed during Hanford operations. The essential materials records show sodium as the principal cationic component while nitrate, hydroxide, and nitrite are the main anionic species in the Hanford waste. The principal fission product radionuclides are ⁹⁰Sr, ⁹⁹Tc, and ¹³⁷Cs. The principal transuranic radionuclides are ²³⁷Np, ^{239,240}Pu, and ²⁴¹Am.

CALCINATION EQUIPMENT TESTING

Two demonstration tests of the calcination/dissolution process using a simulated waste were carried out by Westinghouse Science and Technology Center in 1992 and 1993 using an existing pilot-scale plasma calcination facility located at the Westinghouse Plasma Center in Madison, Pennsylvania. Figure 1 presents a schematic of the plasma calcination facility, with Figure 2 illustrating details of the calciner internals and product collection crucible. The waste was injected at a feed rate of between 1 and 2 gal/minute into the 20-cm-diameter entrance duct (or tuyere), directly into the super heated plume of a 1,000-kW nontransferred plasma arc torch, having a plume temperature of roughly 5,000 °C. The working gas for the torch was air, but other gases may be used. Complete evaporation of the water occurred in the tuyere along with partial calcination, resulting in a computed mixing temperature of roughly 1,700 °C. This mixture then rapidly expanded into the much larger crucible (75-cm diameter); the associated cooling dropped the product temperature, resulting in a crucible operating temperature of about 700 °C.

The residence time in the crucible region was approximately 20 minutes, during which the nitrate and nitrite dissociation continued with final overall destruction efficiencies for these species of 91% and 86%, respectively. Destruction efficiencies of greater than 99% were observed for total organic carbon (TOC). After an initial stabilization period, steady state production and collection of fluid calcine product was maintained for a period of 3 hours with no plugging or fouling problems, processing a total of nearly 4 tonnes (700 gal) of simulated waste.

Figure 1. Schematic Diagram of Plasma Calcination Pilot Plant Facilities at Westinghouse Plasma Center.

Figure 2. Detailed Diagram of Reaction Zone of Plasma Calcination Test Facility.

The offgas mixture, consisting mainly of N_2 , O_2 , CO_2 , and steam, was processed in a conventional high-efficiency quench-scrub system. The venture scrubber trapped aerosols and vapors, which escaped from the calciner, including fugitive sodium and cesium, as well as NO_x , which was produced in the plasma discharge. Total calciner sodium loss, resulting from evaporation and aerosolization, amounted to only 15%, while nearly 50% of the cesium in the simulant was retained in the calcine product. Note that negligible NO_x production was observed as a result of nitrate/nitrite calcination, presumably because the extremely high heat-up rate experienced by the waste and the high reaction temperature permitted these species to achieve their equilibrium reaction products (i.e., N_2 and O_2).

The calciner design thus provides three critical features necessary for successful calcination: (1) the high temperatures needed for rapid destruction of nitrate, nitrite, and organics; (2) rapid and efficient disengagement of calcine product from the gas stream; and (3) collection of the molten calcine product at a much lower temperature where volatilization of NaOH is minimal, hydroxide fluxing is maintained, and the product remains a free-flowing liquid.

Although the demonstration tests were highly successful, the pilot plant is designed primarily as a melting facility and was not optimized for calcination of high-sodium wastes. Many features of the design affecting volatile retention and the residence time in the tuyere and crucible could be shortened in a dedicated calciner design. For example, if sufficient time-temperature exposure were provided for in the tuyere to accomplish the desired degree of calcination, the molten product could be directly quenched into water, eliminating the need for the collection crucible entirely.

THERMODYNAMIC SIMULATION

Equilibrium thermodynamic simulations were carried out to help determine operating parameters for the calcination equipment demonstration of waste slurries similar in composition to the Hanford complexant concentrate waste (Garfield 1992). These studies used the NASA CET89 code, coupled with the Westinghouse CHEMEQ thermochemical database of roughly 5,000 species (Svehla 1973). The CET89 code minimizes global free energy and computes the distribution of reaction products as a function of output temperature.

Figure 3 illustrates the predicted calcine product composition. Nitrates and nitrites are decomposed into N_2 and O_2 , with the sodium reporting as hydroxide. At all temperatures below 1,050 °C, the equilibrium mixture is dominated by NaOH and Na_2CO_3 , which form a binary liquid phase comprising roughly 80% of the total (Cook 1989). The balance is largely solid sodium aluminate, which is sparingly soluble in molten hydroxide (Craighead 1952).

As the temperature is increased above 1,050 °C the volatility of NaOH increases and hydroxide begins to evaporate from the product, leaving behind a mixture in which the only liquid species are sodium carbonate and a few minor components (Na_2CrO_4 , Na_2SO_4 , and NaCl). The solids fraction of the calcine rapidly increases in excess of 90%, resulting in a change from a free-flowing, low viscosity liquid to a viscous sticky paste. This behavior has been observed in previous unsuccessful attempts to calcine high-sodium tank wastes. Production of a free-flowing product is, thus, critically dependent on maintaining operating conditions that retain NaOH flux and discourage hydroxide evaporation (i.e., avoiding excessively high temperatures in the product collection region and minimizing any sparging action of the offgases through the molten product).

Another critical factor in maintaining fluid slag is providing adequate sodium content in the waste mixture. Some Hanford tank waste simulants contain far less sodium than does complexant concentrate waste and substantially higher levels of metals-producing solid products; Redox Process sludge, for example, contains roughly 12% sodium and 12% aluminum (Tank S-104 analysis), as compared to 16% sodium and 2% aluminum for complexant concentrate waste. Calcination of Redox Process sludge is predicted to yield an essentially "dry" product with no greater than 4% total liquid phase. Successful conversion of the total Hanford tank waste inventory to free-flowing slag would, therefore, require blending of low- and high-sodium feed materials to ensure adequate NaOH flux content in the product.

Figure 3. Predicted Product Composition from Calcination of Complexant Concentrate Waste.

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CHEMISTRY DEVELOPMENT

PREDOMINANCE OF SODIUM HYDROXIDE IN THE CALCINED WASTE

Figure 4 shows the distribution of the 15 leading chemical components (over 99.7 mole%) of the total Hanford waste. As shown in Figure 4, the calcined waste will be predominantly sodium and hydroxide with aluminum, carbonate, and phosphate comprising other significant fractions of the waste.

ANALOGY OF CALCINATION TO ALKALINE FUSION

Because of the high fraction of sodium hydroxide in the projected calcine, calcination processing can be compared with the well-known chemistry of analytical fusions in molten alkali. Molten sodium hydroxide is a highly aggressive and oxidizing solvent that has been used in classical chemical analyses to digest minerals and refractories before acid dissolution and measurement. The oxidizing properties are enhanced in chemical analyses by the addition of sodium nitrate and nitrite salts (as are present in the Hanford wastes) to the analytical melt.

The oxidizing conditions achieved in molten NaOH drive many transition metals (e.g., iron, chromium, manganese, nickel, as well as bismuth and cerium) to higher oxidation states. The actinides of neptunium, plutonium, and americium also oxidize in molten NaOH to (V) or greater oxidation states and form ternary oxides with sodium (Keller 1972).

Figure 4. Chemical Inventory of Hanford Site Waste.

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Application of the reactive molten NaOH medium to the reconstitution and digestion of Hanford sludge components during calcination is attractive because formerly insoluble materials (e.g., aluminum [oxy]hydroxides, chromium hydroxide, bismuth phosphate) can be transformed to water-soluble salts. The expected chemical transformations achieved by calcination of Hanford salt cake and sludge components in molten sodium hydroxide can be derived by study of the technical literature (D'Ans and Löffler 1930 and Bock 1979).

Examples of the various reactions relevant to the calcination of Hanford wastes are summarized in Table 1. Organic oxidation will occur readily at the 850 °C calcination temperature, and the product carbon dioxide will be efficiently scrubbed and retained in the melt by the abundant NaOH. The nitrate and nitrite thermal decompositions to form oxygen and nitrogen offgas are well known. The nitrate decomposition proceeds through the nitrite intermediate. Reactions of aluminum hydroxide and silica with NaOH are conjugate acid-base reactions in which the aluminum hydroxide and silica are acids accepting the base hydroxide. Oxidations of transition metal oxides and hydroxides readily occur in the oxygenated NaOH melt because of the stabilizing effect hydroxide has on the higher transition metal oxidation states. Finally, the powerful solvating effect of hydroxide is reflected in the decrystallization, metathesis, and dissolution reactions known to exist in molten NaOH.

Generally > 70 wt% NaOH flux is used in analytical chemistry fusions; the calcine composite shown in Table 1 is about 62 wt% NaOH. Blending of sludge waste types with salt cake wastes (high in NaNO₃) will be necessary to achieve efficient waste component dissolution in both the molten calcine and in the subsequent aqueous processing. Sodium carbonate, which represents about 4 mole% of the composite waste calcine, also can serve as a fluxing agent as shown by analytical chemistry experience, but at the < 850 °C calcination temperature will not decompose to form the Na₂O/NaOH required for fusion reactions.

Table 1. Calcination Reactions.

Reaction Type	Examples
Organic oxidations	$\text{NaC}_2\text{H}_3\text{O}_2 + 2 \text{O}_2 + 3 \text{NaOH} \rightarrow 2 \text{Na}_2\text{CO}_3 + 3 \text{H}_2\text{O}$ $\text{Na}_2\text{C}_2\text{O}_4 + \frac{1}{2} \text{O}_2 + 2 \text{NaOH} \rightarrow 2 \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
Nitrate and nitrite decompositions to form hydroxide	$\text{NaNO}_3 \rightarrow \text{NaNO}_2 + \frac{1}{2} \text{O}_2$ $2 \text{NaNO}_3 + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{N}_2 + 2\frac{1}{2} \text{O}_2$ $2 \text{NaNO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} + \text{N}_2 + 1\frac{1}{2} \text{O}_2$
Acid-base reactions	$\text{Al}(\text{OH})_3 + \text{NaOH} \rightarrow \text{NaAlO}_2 + 2 \text{H}_2\text{O}$ $\text{SiO}_2 + 2 \text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$
Inorganic oxidations	$4 \text{Cr}(\text{OH})_3 + 8 \text{NaOH} + 3 \text{O}_2 \rightarrow 4 \text{Na}_2\text{CrO}_4 + 10 \text{H}_2\text{O}$ $4 \text{Fe}(\text{OH})_3 + 8 \text{NaOH} + 3 \text{O}_2 \rightarrow 4 \text{Na}_2\text{FeO}_4 + 10 \text{H}_2\text{O} \text{ (part)}$ $4 \text{MnO}_2 + 4 \text{NaOH} + 3 \text{O}_2 \rightarrow 4 \text{NaMnO}_4 + 2 \text{H}_2\text{O}$
Decrystallization	$\text{Fe}_2\text{O}_3 \text{ (c)} + 3 \text{H}_2\text{O} \rightarrow 2 \text{Fe}(\text{OH})_3 \text{ (am)}$
Metathesis	$\text{BiPO}_4 + 3 \text{NaOH} \rightarrow \text{Bi}(\text{OH})_3 + \text{Na}_3\text{PO}_4$
Dissolution in molten NaOH	$\text{Na}_2\text{CO}_3 \text{ (c)} + \text{NaOH (liq.)} \rightarrow \text{Na}_2\text{CO}_3 \text{ (NaOH sol'n.)}$

DISSOLUTION OF THE CALCINED WASTE

The calcined waste inventory presented in Figure 4 is primarily water-soluble sodium (and potassium) salts. Such salts include hydroxide, aluminate, phosphate, carbonate, fluoride, sulfate, and silicate. Hence, contact with water is expected to dissolve the bulk of the calcine leaving insoluble residues of transition metals, lanthanides, and alkaline earths.

Sodium salts of phosphate, carbonate, and aluminate dissolved in NaOH solution will encompass 94 mole% of the calcined Hanford wastes. Sodium phosphate and sodium carbonate are soluble in NaOH solution, though the common ion (sodium) effect depresses the solubility of the carbonate and phosphate salts.

The special case of NaAlO_2 and $\text{Al}(\text{OH})_3$ (gibbsite) solubility in NaOH has been extensively studied and exploited by the aluminum industry via the Bayer process (Wefers 1967 and Wefers and Misra 1987). The formation of sodium aluminosilicate solids of low solubility from dissolution and reprecipitation of calcined silicon- and aluminum-bearing waste, however, also is predicted based on aluminum industry experience (Hudson 1987).

Dissolution of transition metals (e.g., manganese and iron) oxidized in the Hanford waste calcine will at least temporarily impose oxidizing conditions in the sodium hydroxide solution. Permanganate (MnO_4^-) and ferrate (FeO_4^{2-}) are thermodynamically able to oxidize hydroxide to form oxygen gas and, thus, will have limited stability in alkaline solution. Chromate (CrO_4^{2-}) is a less powerful oxidant, however, and will remain as soluble Na_2CrO_4 . In this oxidizing aqueous medium, the transuranics (neptunium, plutonium, and americium), if oxidized to the (V) or higher oxidation state, will report, at least initially, to the solution phase.

The residue remaining following dissolution is expected to contain sodium aluminosilicates, transition and lanthanide metal oxides, and hydroxides and alkaline earth sulfates, phosphates, or carbonates. Thorium is expected to remain in the solid residue, but uranium will dissolve to some extent.

EXPERIMENTS WITH SIMULATED AND GENUINE HANFORD SITE WASTES

Experiments with simulated Hanford wastes were conducted to confirm predictions of chemical component behavior to calcination/dissolution processing. The tests with simulants also allowed test apparatus and conditions to be proven before conducting experiments with genuine waste materials. Testing of genuine wastes was then performed and compared with simple water dissolution of the same waste materials.

EXPERIMENTS WITH SIMULATED WASTES

Tests using simplified waste compositions confirmed that sodium aluminate, carbonate, and phosphate formed no solids that were difficult to dissolve. Formation of slightly soluble sodium aluminosilicates (sodalite and Zeolite A) occurred by processing materials containing high concentrations of both silica and aluminum hydroxide.

The formation of slightly soluble calcium hydroxyphosphate [$\text{Ca}_3(\text{PO}_4)_2\text{OH}$, apatite] also was observed in processing materials containing calcium ion and phosphate. Some release of phosphate from precipitation by calcium, however, was observed if carbonate was included in simulated waste formulations having calcium ion and phosphate [the solid phase found, $\text{Ca}_{10}(\text{PO}_4)_3(\text{CO}_3)(\text{OH})_2$, has a $\text{Ca}^{2+}:\text{PO}_4^{3-}$ mole ratio twice as large as that of apatite]. Evidence of highly oxidizing conditions available in the NaOH melt was confirmed in the partial conversion of iron (III) oxide to form soluble iron (VI) species (the ferrate ion, FeO_4^{2-}).

Calcination kinetics tests were conducted using wastes simulating the contents of Hanford Tank 101-SY and a hypothetical composite waste based upon the entire Hanford waste tank inventory. As shown in Figure 5, the tests confirmed that nitrate decomposed thermally, through nitrite, and that nitrite, in turn, was rapidly decomposed to form hydroxide. About 20 minutes of calcination at 850 °C were required to effect 90% nitrate decomposition. Quantitative conversion of organic carbon to carbonate (Figure 6) and chromium (III) hydroxide oxidative dissolution to form chromate, CrO_4^{2-} (Figure 7), occurred within 1 to 3 minutes. Calcination beyond about 20 minutes' time had little effect on the behavior of other elements (Figures 7 and 8).

As shown in Table 2, calcination and dissolution of simulants destroyed 90% or greater of the contained organic carbon, nitrate, and nitrite. Aluminum, chlorine, chromium, potassium, sodium, lead, sulfur, and silicon dissolved entirely while the alkaline earths, bismuth, and the transition metals other than chromium (iron, zirconium, and manganese) remained in the insoluble residue.

EXPERIMENTS WITH GENUINE WASTES

Calcination/dissolution tests with genuine waste materials obtained from Tanks 107-BX, 104-S, 104-T, and 101-SY generally confirmed the behaviors of the principal chemical components observed in tests with simulants. On the basis of the kinetic tests with simulants, calcination tests with the genuine wastes were conducted for 20 minutes at 850 °C.

The compositions (dry basis) of the genuine wastes tested, presented in Figure 9, show the inherent variability of Hanford Site waste. For example, the waste from Tank 104-S is about 30 mole% aluminum (versus 5 to 10 mole% for the other three wastes) while wastes from Tanks 104-T and 107-BX have relatively high concentrations of bismuth, iron, fluoride, phosphate, and sulfate. The waste from Tank 101-SY contains more hydroxide and organic carbon than the other wastes and, except for chromium, is low in concentrations of nonalkali metals. All wastes contained roughly 20 to 30 mole% nitrate and nitrite (designated NO_x in Figure 9), which can decompose by calcination to form hydroxide.

Figure 5. Calcination/Dissolution
Simulated Composite Hanford Site Waste
(OH, NO₃, and NO₂).

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Figure 6. Calcination/Dissolution
Simulated Composite Hanford Site Waste
(TIC and TOC).

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Figure 7. Calcination/Dissolution
Simulated Composite Hanford Site Waste
(Al, Fe, Cr, Bi, Pb, Si).

39408074.8

Figure 8. Calcination/Dissolution
Simulated Composite Hanford Site Waste
(S, P, F, Zr, Ca, Sr).

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Table 2. Calcination/Dissolution Behavior of Chemical Components in Simulated Hanford Waste.

Component	Amount Destroyed (%)
Organic carbon	95
NO ₃ ⁻	90
NO ₂ ⁻	99.9
Component	Amount Dissolved (%)
Al, Cl, Cr, K, Na, Pb, S, Si	~ 100
F, P	10 to 100
Bi, Fe, Zr	1 to 10
Ca, Sr, Mn	Less than 1

Figure 9. Hanford Site Waste Compositions Used in Laboratory Testing.

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Because the wastes from Tanks 104-S, 104-T, and 107-BX contain materials difficult to dissolve, some calcination tests were conducted using fluxing agents blended with the relevant waste. For the Tank 104-S and 107-BX waste, the fluxing agent tested was waste from Tank 101-SY. For the waste from Tank 104-S, reagent sodium nitrate (NaNO_3) was used as a fluxing agent. The NaNO_3 was used as a surrogate for Hanford salt cake waste, which was not available for these tests. Hanford salt cakes have been shown to be predominantly NaNO_3 (Kupfer 1981).

Waste calcinations were conducted using both unblended and blended wastes. Tests with genuine waste were conducted in parallel with simple water dissolution of the same waste materials, and the results of the two waste treatments were compared. The test results are presented in Tables 3 and 4.

The tests also demonstrated that redistribution of chromium and aluminum from solid phases to the solution phase (i.e., from the HLW to the LLW stream) could be achieved. The amount of chromium dissolved from Tank 101-SY waste (a high chromium waste) increased from about 4% via simple water washing to 99.95% by calcination/dissolution processing. Speciation tests confirmed that the dissolved chromium was present in solution as chromate. The wastes from the other tanks tested showed comparable enhancements in chromium dissolution from calcination/dissolution processing.

Similarly, enhanced aluminum dissolution from Tank 104-S waste (a high aluminum waste containing aluminum (oxy)hydroxide phases) occurred. Simple water washing dissolved only about 4% of the aluminum, calcination/dissolution of the unblended waste raised the amount of aluminum dissolved to 53%, and calcination/dissolution of blended waste from Tanks 104-S and 101-SY resulted in over 99% aluminum dissolved. Comparable enhanced dissolutions of aluminum phases in wastes from Tanks 107-BX and 104-T also were observed.

A sodium fluoride-sodium phosphate double salt [$\text{NaF} \cdot 2(\text{Na}_3\text{PO}_4) \cdot 19\text{H}_2\text{O}$] was observed by X-ray diffraction analyses of the residue remaining from calcination/dissolution processing of waste from Tank 107-BX. Like trisodium phosphate, this salt has a moderate water solubility, which is decreased by the sodium common ion effect.

To improve phosphate dissolution, calcination followed by three water-wash dissolution contacts was tested to process waste from Tank 104-T, a waste similar in composition to that of Tank 107-BX. The Tank 104-T waste was calcined with NaNO_3 as a salt cake surrogate. Analyses of the individual wash solutions confirmed that dissolution of the $\text{NaF} \cdot 2(\text{Na}_3\text{PO}_4) \cdot 19\text{H}_2\text{O}$ occurred. Phosphate dissolution was about 19% for simple water-wash contacts of Tank 104-T waste. With calcination/dissolution and multiple water washes, phosphate dissolution exceeded 96%.

Iron and bismuth dissolution was increased marginally by calcination/dissolution processing as compared to simple water washing. Qualitative evidence of iron dissolution was observed in the intensely blue colored solution because of FeO_4^{2-} , which was obtained by calcination/dissolution processing. The fraction of iron and bismuth dissolved was insufficient to redistribute these elements substantially from the HLW fraction to the soluble LLW fraction.

Manganese, however, became appreciably more soluble with calcination/dissolution processing. As in the case for chromium, the distribution of manganese to the solution phase resulted from oxidative dissolution caused by conversion from an insoluble oxide or hydroxide to an oxidized soluble anion. Visible absorption spectra of solution produced from Tank 111-T (composition similar to those of wastes from Tanks 104-T and 107-BX) confirmed the presence of permanganate ion, MnO_4^- . The permanganate ion concentration decreased with time to form manganate ion, MnO_4^{2-} , thus indicating the instability of this oxidized species to chemical reduction by hydroxide.

**Table 3. Comparison of Water Wash and Calcination/Dissolution Processing
With and Without Waste Blending: Chemical Components.**

Waste Type	Waste Blend and Treatment	Amount Destroyed (%)			Amount Dissolved (%)					
		NO ₂ ⁻	NO ₃ ⁻	TOC	Al	Cr	PO ₄ ³⁻	Fe	Bi	Mn
101-SY	Water wash	0	0	0	94	4.1	94	3.2	—*	—
	Direct C/D	40**	32**	98	99.8	99.95	98.6	5.3	—	—
104-S	Water wash	0	0	—	4.2	53	10	0.03	—	0.001
	Direct C/D	99	99.6	—	53	97.8	44	0.1	—	18
	101-SY blend C/D	97.2	82	—	99.2	99.7	97	0.2	—	46
107-BX	Water wash	0	0	—	0.1	25	13	0.03	0.14	0.2
	Direct C/D	99.3	99.6	—	14	89	81	0.4	2.7	1.6
	101-SY blend C/D	90	92	—	80	96	17	0.07	0.06	70
104-T	Water washes	0	0	—	0.2	13	19	<0.1	<0.1	<0.2
	NaNO ₃ blend C/D, three washes	95	99.8	—	80	98	96.5	<0.1	<0.1	27

* Below detection limit

** Insufficient heating

**Table 4. Comparison of Water Wash and Calcination/Dissolution Processing
With and Without Waste Blending: Radioelements.**

Waste Type	Waste Blend and Treatment	Amount Dissolved (%)						
		⁹⁰ Sr	⁹⁹ Tc	¹³⁷ Cs	U	²³⁷ Np	^{239,240} Pu	²⁴¹ Am
101-SY	Water wash	23	64	95	0.20	—*	—	86
	Direct C/D	7.3	99.99	99.7	90	94	—	2.8
104-S	Water wash	0.037	50	92	0.003	—	0.16	0.035
	Direct C/D	0.00002	—	93	1.9	—	1.6	0.17
	101-SY blend C/D	1.9	99	99	10	—	44	2.1
107-BX	Water wash	0.035	87	15	20	—	1.7	3.1
	Direct C/D	13	58	89	1.3	—	0.92	5.5
	101-SY blend C/D	0.13	90	71	5.0	—	13	0.43
104-T	Water washes	0.12	—	27	1.4	—	3.0	—
	NaNO ₃ blend C/D, three washes	0.15	—	72	20	—	24	—

* Below detection level

CORROSION DEVELOPMENT

A major disadvantage of the calcining process is that oxygenated, molten NaOH provides an extremely corrosive environment. A recent paper (Paul et al. 1992) on the effects of NaOH on the corrosion of Type 304L stainless steel shows that corrosion rates are about 7 mm/year in 370 °C (molten) NaOH but decrease to zero at 324 °C, at which point the salt is frozen. The present scoping study was carried out to evaluate the corrosion performance of a variety of metals to begin the process of specifying the optimal material for construction of the calciner.

The study was carried out with carbon steel, types 304L and 904L stainless steels, Ni-200, and Inconel 625, as a function of temperature in a simulated calcine mixture (Inco Alloys 1988). Commercially built electrical resistance corrosion probes were inserted into a simulated calcine mixture that was predominantly NaOH. The corrosion of the materials was measured by the increase in electrical resistance of the probes as metal was consumed. The principal advantage of electrical resistance probes is that they can accurately measure uniform corrosion rates in fairly short periods of time, thereby permitting the efficient exploration of a wide range of test conditions. The more commonly used weight loss specimen technique would require an inordinate amount of manpower and time to cover the same range of conditions because a different set of coupons would have to be prepared before and sacrificed after each test condition.

TEST PROCEDURE

The mixture shown in Table 5 was placed in a graphite crucible and transferred to an electrically heated furnace. The calcine simulant was melted at approximately 300 °C, the corrosion probes and an Alloy 600 sheathed thermocouple were inserted into the melt, and the furnace temperature was immediately reduced to 230 °C to freeze the salt bath. Measurements of corrosion rates were made, starting at a temperature approximately 50 °C below the melting point. Corrosion rates were measured on a daily basis using manually operated instrumentation. When a steady state corrosion rate was achieved, the temperature was increased. Measurements were made at temperatures of approximately 230, 260, 292, 335, 410, 480, and 549 °C (Paul et al. 1992).

Table 5. Composition of Calcine Simulant.

Composition	Mol. Fraction	Reagent	Weight (g)
Al(OH) ₃	0.0553	Al(OH) ₃	517.7
Fe(OH) ₃	0.00487	²⁰⁰ Fe	46.7
KOH	0.0098	KOH	66.0
NaOH	0.817	NaOH	3915.4
SiO ₂	0.00597	SiO ₂	43.1
NaCl	0.00407	NaCl	27.1
Na ₂ CO ₃	0.037	Na ₂ CO ₃ ·H ₂ O	550.6
NaF	0.00193	NaF	9.7
Na ₃ PO ₄	0.0314	Na ₃ PO ₄ ·12H ₂ O	1432.4
Na ₂ SO ₄	0.00696	Na ₂ SO ₄	118.7

EXPERIMENTAL RESULTS

The corrosion probe output data and temperature as a function of time are shown in Figure 10. The corrosion data are expressed as the loss of metal resulting from a uniform corrosion process. The corrosion rate was calculated by taking a derivative of this data with respect to time. Corrosion rate data are shown in Table 6.

Figure 10. Temperature and Corrosometer Data.

Table 6. Average Corrosion Rate Data (mil/year).

Temperature °C	C-steel	304L	904L	²⁰⁰ Ni	A-625
230 frozen	0	0	not working	0	0
260 frozen	0	0	0, erratic	4	0
290 molten	46	32	0	1	30
340	2	35	36	1	16, erratic
418	2	85	10	2	9
480	0	78	22	1	26
549	10	failed	failed	erratic	18

The corrosion rate data support the hypothesis that a frozen condition greatly reduces the corrosion rate. At both 230 and 260 °C, when the bath is frozen, the corrosion rates are essentially zero for all materials except the 904L. When the bath is molten, corrosion rates rapidly increase. Nickel-200 has the lowest corrosion rates under all temperature conditions, with carbon steel a close second. The worst performer was 304L, and the 304L probe eventually had to be removed from the test because the sensing element was penetrated. From these results, ²⁰⁰Ni would be the construction material of choice.

VISUAL OBSERVATIONS

At the end of the test, all probes were cleaned and visually examined. The results are shown in Table 7. In all cases, the probe body has the same composition as the sensing element.

The visual examination of the sensing elements would indicate that the probes were functioning correctly. The surprise comes from the major corrosive attack observed on the ²⁰⁰Ni and to a much lesser extent on the carbon steel at the lower temperature condensation zone (located 230 mm above the tip and 76 mm or more above the melt, near the furnace lid). The temperature at which this attack took place is uncertain, but the attack probably reached its maximum rate during the 549 °C portion of the test. The crust on the probes was 76 mm or more long and was green colored, probably from the dissolved nickel. The crust composition was predominantly carbonate, formed from NaOH that reacted with CO₂ from the oxidation of the crucible by the surrounding air. The local environment in the condensation zone would vary greatly from that in the crucible. Curiously, the alloyed materials were immune to the condensation zone attack, implying that this local environment is not high in hydroxide. If this carbonate-rich environment existed in the calciner, ²⁰⁰Ni would be a poor choice of materials. It should be noted that the test chemistry did not contain the nitrate and nitrites that would be found in the actual waste. Clearly, a better understanding of the calciner chemistry must be achieved before the materials of construction can be finally specified.

Upon post-test handling of the ²⁰⁰Ni corrosion probe, the nickel-sensing tip and the internal nickel electrical wires failed in a brittle fashion in two locations. Nickel-200 is prone to embrittlement from prolonged exposure to elevated temperatures because carbides precipitate at the grain boundaries. Nickel-201, a metal containing less carbon, would be less susceptible to this problem and will be included in the next round of tests.

Table 7. Visual Observations.

Material	Sensing Element	Probe Body
C-steel	Thin, black film; uniform attack	1-mm-deep attack at condensation zone
304L	Thin black film; nonuniform attack	Almost no attack at condensation zone
904L	Thin, black film; nonuniform attack	No attack at condensation zone
²⁰⁰ Ni	Thin, black film; uniform attack	Complete penetration (3.3 mm) of probe body in condensation zone
A-625	Thin, black film; nonuniform attack	Almost no attack at condensation zone

CONCLUSIONS

EQUIPMENT DEVELOPMENT

1. The Westinghouse Plasma Torch Cupola System has successfully demonstrated key design parameters for continuous calcination/dissolution of Hanford nuclear waste sludge. Calcination efficiency of 95%, as determined by the weight percent of nitrates and nitrites thermally destroyed, has been achieved. Organic carbon components in the simulated waste chemistry were thermally destroyed during processing.
2. Offgas products from calcination of nitrates and nitrites consist primarily of nitrogen and oxygen with low concentrations of NO_x, CO, and CO₂.
3. The product for the process consists of a molten salt mixture of sodium hydroxide and sodium carbonate containing in excess of 15% by weight of aluminum oxide complex and trace amounts of heavy metal oxides and phosphates. Volume reduction of 80% and weight reduction of 50 to 60% for simulant waste sludge feedstock has been demonstrated.
4. The thermodynamic simulation successfully determined the operating conditions for the demonstration test.

CHEMISTRY DEVELOPMENT

1. Chemistry development tests showed calcination/dissolution processing to be a promising process alternative for treatment of Hanford Site wastes. The similarity of the calcination step to alkaline fusion digestion used in analytical chemistry allowed accurate predictions to be made of process variables and chemical reactions. In tests with both simulated and genuine Hanford wastes, thermal decompositions of nitrate, nitrite, and organic carbon occurred with nitrate- and nitrite-furnishing hydroxide and organic carbon-producing carbonate.
2. Comparisons of calcination/dissolution processing with simple water washing were performed for tests with genuine wastes. For a high aluminum sludge from Tank 104-S, aluminum dissolution improved from 5% (using simple water washing) to 99%. For the high chromium Tank 101-SY waste, chromium dissolution improved from 4% (water washing) to >99.9%. For high phosphate wastes, phosphate dissolution was also increased (to about 96%) provided sufficient water dissolution contacts were made.
3. Strongly oxidizing conditions were imposed by the alkaline fusions. In addition to the oxidations of organic carbon and chromium (III), oxidations of Fe(III) to form Fe(VI) (ferrate) and Mn(IV) to form Mn(VII) (permanganate) were observed. Oxidative dissolution of plutonium was inferred by the increased solubility of plutonium following calcination/dissolution processing when compared to water washing. Increased cesium, technetium, and uranium dissolutions occurred by calcination/dissolution processing. Except for waste containing significant organic carbon (from Tank 101-SY), strontium and americium solubilities were low for both water-washed and calcination/dissolution processed materials.

CORROSION DEVELOPMENT

1. Almost all the materials investigated in this study have acceptable corrosion performance under frozen salt conditions. The most conservative design approach would be to maintain a frozen wall of calcine over metal.

2. Relative to the frozen condition, corrosion rates increase when the salt is molten. Nickel-200 has the lowest corrosion rates, with carbon steel a close second. Nickel-201, with lower carbon content than ^{200}Ni , should be evaluated as the material of choice for lining the inner calciner wall.
3. There is a concern that the corrosion rates measured in the present study under static-melt conditions underestimate the rates that would be obtained under more prototypic calcining conditions. More realistic tests, including aerated calcine, should be conducted before a material selection is made.
4. The visual examination of the probes at the conclusion of the tests indicated massive corrosive attack on the ^{200}Ni at the salt condensation zone. The chemical composition at that location is presently unknown but is hypothesized to be very low in hydroxide. This observation indicates that there must be a better understanding of the calciner chemistry before the materials of construction can be specified.

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