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Prepared by:

R. G. Seymour

**Westinghouse Hanford Company
May 1995**

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**EVALUATION OF ALTERNATIVE CHEMICAL
ADDITIVES FOR HIGH-LEVEL WASTE VITRIFICATION
FEED PREPARATION PROCESSING**

R. G. Seymour

ABSTRACT

During the development of the feed processing flowsheet for the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS), research had shown that use of formic acid (HCOOH) could accomplish several processing objectives with one chemical addition. These objectives included the decomposition of tetraphenylborate, chemical reduction of mercury, production of acceptable rheological properties in the feed slurry, and controlling the oxidation state of the glass melt pool. However, the DWPF research had not shown that some vitrification slurry feeds had a tendency to evolve hydrogen (H_2) and ammonia (NH_3) as the result of catalytic decomposition of HCOOH with noble metals (rhodium, ruthenium, palladium) in the feed.

Testing conducted at Pacific Northwest Laboratory and later at the Savannah River Technical Center showed that the H_2 and NH_3 could evolve at appreciable rates and quantities. The explosive nature of H_2 and NH_3 (as ammonium nitrate) warranted significant mitigation control and redesign of both facilities. At the time the explosive gas evolution was discovered, the DWPF was already under construction and an immediate hardware fix in tandem with flowsheet changes was necessary. However, the Hanford Waste Vitrification Plant (HWVP) was in the design phase and could afford to take time to investigate flowsheet manipulations that could solve the problem,

rather than a hardware fix. Thus, the HWVP began to investigate alternatives to using HCOOH in the vitrification process.

This document describes the selection, evaluation criteria, and strategy used to evaluate the performance of the alternative chemical additives to HCOOH. The status of the evaluation is also discussed.

To date, several phases of the evaluation have been completed. During the initial phases of the evaluation, several organic acids (carboxylic acids) similar to HCOOH were selected for evaluation in a series of lab-scale tests. Alternative chemical additives were then eliminated as testing proceeded based on established criteria. The most promising candidate was then recommended for larger-scale testing in an integrated melter system.

Currently, lab-scale testing has reduced the field of candidates to glycolic acid. This acid was then tested in a small-scale high-temperature melter system. Additional testing with this acid is likely to be conducted with other types of melter systems and feed compositions in support of the Hanford Site high-level waste melter evaluation.

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EVALUATION OF ALTERNATIVE CHEMICAL ADDITIVES FOR HIGH-LEVEL WASTE VITRIFICATION FEED PREPARATION PROCESSING

1.0 INTRODUCTION

During the course of development of the Defense Waste Processing Facility (DWPF) vitrification flowsheet at the Savannah River Site (SRS), research had shown that by using formic acid (HCOOH) in the process, several processing objectives were met with one chemical addition (Ritter et al. 1990):

- Decomposition of tetraphenylborate (TPB) for subsequent steam stripping of aromatics
- Reduction of mercury in the feed slurry to its metallic state during feed preparation for subsequent removal by steam stripping
- Decrease in the feed slurry pH to yield acceptable rheological characteristics for efficient pumping and agitation at reasonably high oxide concentrations
- Control of the glass melt pool oxidation state to prevent excessive volatilization of certain components (e.g., ruthenium oxide [RuO₄], technetium oxide [Tc₂O₇]) and/or foaming of the melt pool.

However, the initial DWPF research had not shown that some vitrification slurry feeds had a tendency to evolve hydrogen (H₂) and ammonia (NH₃) via catalytic decomposition of HCOOH with noble metals (rhodium [Rh], ruthenium [Ru], palladium [Pd]) in the feed. Unfortunately, the noble metals had been excluded from the DWPF simulants because of their exorbitant cost in large-scale testing and minimal concentration in the feed.^a

In parallel to the development and construction of the DWPF, the U.S. Department of Energy (DOE) had initiated the Hanford Waste Vitrification Plant (HWVP) Project, which was envisioned as a "carbon copy" of the DWPF. Confirmatory lab-scale testing of the HWVP feed preparation flowsheet conducted at Pacific Northwest Laboratory (PNL) showed that although the noble metals are present in very small concentrations in the feed, they play a significant role in the evolution of H₂ and NH₃ (Wiemers 1988, 1990). This phenomenon was later replicated in larger-scale tests at DWPF with both Hanford Site- and SRS-type melter feeds (Hutson 1993 and Ritter et al. 1992).

^aIt should be noted that cost, minimal concentration, and toxicity were the bases for omitting many of the other minor feed constituents. Interest in including noble metals in the simulant initially developed out of concern that testing programs should include as many of the minor constituents to simulate the actual waste as closely as possible. Coincidentally, concern was also growing with regards to precipitation and accumulation of the noble metals in the melter, as had been experienced in European melters (Elliott et al. 1994).

The potentially explosive nature of H_2 containing atmosphere set into motion a considerable amount of safety analysis and offgas system redesign (estimated at nearly \$10 million for the HWVP alone).^a No immediate concern was formally voiced regarding the presence of NH_3 in the HWVP. However, it was soon recognized by those conducting a preliminary safety analysis of the HWVP that the current design of the HWVP (and DWPF) could lead to the formation of ammonium nitrate (NH_4NO_3) in the offgas system (Englehardt 1992). Because of the presence of organics in the feed slurry, an NH_4NO_3 sensitizing agent was available and a detonation could be postulated. At that point, it was believed there was sufficient time in the HWVP design schedule to mitigate the NH_3 evolution by manipulation of the feed preparation process flowsheet. However, the DWPF was nearing completion of construction, and a hardware fix (combined with flowsheet modifications) was necessary (at an estimated cost exceeding \$10 million [Stegen 1992]) to mitigate the NH_3/NH_4NO_3 source term (Palowitch 1993).

With these cost incentives in mind, the HWVP Project began to research manipulations of the reference flowsheet to minimize NH_3 (and H_2 if possible) generation during feed preparation. Two approaches were initiated simultaneously. The first approach was to manipulate the $HCOOH$ acid flowsheet by controlling the slurry pH, slurry temperature, and chemical addition timing. Although this approach reduced the level of H_2 and NH_3 evolution by 25% of that nominally observed (Smith et al. 1994), this variation of the flowsheet yielded a melter feed that had the potential for considerable gas evolution should the melter feed be inadvertently and uncontrollably heated. A considerable amount of the carbon dioxide (CO_2)- and NO_x -producing species were still present in the melter feed, which could evolve at a rate that could over-pressurize the feed preparation system and/or cause the melter feed to foam and carry over a large amount of solids into the offgas train. The risk from this kind of an event is minimal and could be easily mitigated. Thus, this flowsheet is generally regarded as a backup should the alternate flowsheets perform inadequately.

The other approach was to begin investigating other chemical additions that could possibly be substituted for $HCOOH$. To this end, this document recounts the process by which PNL and Westinghouse Hanford Company (WHC) cognizant staff proceeded to select and eliminate possible alternative chemical additives to $HCOOH$. The intent of this document is not to report all of the data obtained during the testing described herein. However, enough data are presented to allow one to follow the decision path regarding the selection of the alternative chemical additives for testing. Some data reported in this document are preliminary, and should be treated as such.

^aThe concern over hydrogen buildup in the feed preparation process was not so much for the amount of hydrogen that was evolved but the rate at which it evolved. Thus, the offgas system had to be designed to handle the amount of dilution air required to keep the maximum hydrogen generation rate below the lower flammability limit (4% in air).

2.0 BASIS FOR CHEMICAL ADDITION REQUIREMENTS

The following sections discuss the bases for chemical additions such as HCOOH in the preparation of nuclear waste feed slurries for vitrification. As stated in Section 1, the four primary reasons for adding HCOOH in the DWPF vitrification process flowsheet were to facilitate TPB decomposition, obtain mercury reduction, adjust the rheological properties of the feed, and control the oxidation state of the glass melt pool.

2.1 TPB DECOMPOSITION

During pretreatment of the radioactive tank waste at the SRS, TPB is added to the low-level waste salt stream to precipitate cesium (Cs) (and potassium [K]).^a The salt stream is filtered, and the contaminated precipitate containing the TPB is sent to the salt processing cell in the DWPF. Upon entering the salt cell in the DWPF, the salt stream is treated with HCOOH and copper (as copper formate).^b Tetraphenylborate will decompose via acid hydrolysis in the presence of the HCOOH and copper to a mixture of boric acid, formate salts, and organics (benzene, phenol, biphenyl, diphenylamine, phenylboric acid, and traces of other organic compounds). The organics are subsequently steam stripped and the remaining solution is fed to the slurry receipt and adjustment tank as the precipitate hydrolysis aqueous solution (WSRC 1993).^c

A different approach to removing radionuclides from decanted wash supernates was used at the Hanford Site. Cesium and strontium were removed by solvent extraction and ion exchange during the tank scavaging and encapsulation operations (DOE 1987). Tetraphenylborate was not used in these processes.

Current baseline removal of cesium and strontium from the supernates from the decanted washes during pretreatment of Hanford Site wastes calls for ion exchange methods (Orme 1994). Thus, it is unlikely that the chemical additive selected for Hanford Site high-level waste (HLW) immobilization will be needed for a TPB decomposition process.

2.2 MERCURY REDUCTION

One of the original bases for using HCOOH in the DWPF feed preparation process was the acid's ability to effectively reduce the mercury in waste

^aThe salt stream is derived from concentration of supernate solutions from low- and high-level wash and decant operations (WSRC 1993).

^bHydroxylaminenitrate (HAN) is also added to the salt stream to destroy the nitrite, which interferes with the acid hydrolysis of the TPB.

^cParts of the acid hydrolysis process are being revised. Effort is being given to removing the HAN addition to mitigate ammonia source terms and replacing copper formate with copper nitrate.

sludges from mercuric oxide (HgO) to mercury's metallic state (Hg^0) (WSRC 1993).^a The majority of the metallic mercury is steam stripped to the offgas where it is condensed, cleaned, and returned to the uranium reprocessing plant. The remaining mercury in the sludge is sent to the melter where some may be incorporated in the glass, while the majority of the mercury will volatilize to the offgas. Mercury vapor in the melter offgas is condensed and combined with that which was steam stripped from the feed preparation process (WSRC 1993).

At the time the search for an alternative chemical additive was initiated under the HWVP Project, the HLW vitrification plant was only concerned with waste from the double-shell tanks (DST) in which no mercury had been reported. Thus, the ability of the chemical additive to reduce mercury to its metallic state was not included in the selection criteria. However, with recent mission changes at the Hanford Site (Ecology et al. 1994), sludges from the single-shell tanks (SST) have now been included in the feed inventory for the HLW vitrification plant. It has been reported that as much as 1,000 kg of mercury may be present in the SST sludges (Orme 1994). It is expected that carboxylic acids similar to HCOOH will reduce the mercury, but the degree to which this will occur relative to HCOOH is unknown and will have to be empirically assessed.

2.3 ADJUSTMENT OF RHEOLOGICAL PROPERTIES

One of the principal benefits of using an acid as a chemical additive is the significant improvement in the rheological properties of the alkaline waste slurries when the pH is decreased from waste tank levels (typically $\text{pH} > 12$) (Fowler 1981; Larson 1989). The improvement in rheological properties is thought to be the combined result of solubilization of some components of the waste slurries and adjustment of the electrostatic forces between waste slurry particles (Smith 1994a). These slurry modifications allow higher total oxide concentrations to be obtained, resulting in higher melter throughput.

The effect of acid on the rheological properties of alkaline waste and melter feed slurries is well documented (Fowler 1981; Lanning et al. 1993; Larson 1989; Smith 1994a) and is not discussed in this document.

Of particular importance has been the aging of the melter feeds. Feed preparation studies conducted with a frit (commonly referred to as the fiscal year (FY) 1991 frit) highlighted the susceptibility of HLW melter feeds to continual changes in rheological properties (Grünwald et al. 1993; Hutson 1993; Gaskill et al. 1995). Changes in frit composition have mitigated the aging effect to some degree, but it still persists in recent melter feed slurries (Smith et al. 1995a). Development of methods to adequately characterize this phenomenon are being developed.

^aThe mercury in DWPF wastes is a by-product of a mercury-catalyzed nitric acid dissolution of aluminum-uranium metal core fuel rods (Kraft 1970).

2.4 OXIDATION CONTROL

The use of a chemical additive to achieve oxidation control in the melter is not unique to nuclear waste glass processing. The commercial glass industry routinely adds reductants such as sugar or starch to its batch feeds to minimize the corrosive oxidation of metal electrodes and/or produce a glass with a prescribed oxidation state, particularly with colored glasses. Oxidants are also added in commercial glass making to counter the effect of a reducing atmosphere resulting from gas-fired melters (Tooley 1974).

The commercial glass oxidation control philosophy was subsequently adopted by nuclear waste vitrification. Studies at the Savannah River Technical Center (SRTC) indicated that oxidation control in the melter is necessary to prevent volatilization of certain components (primarily technetium and ruthenium oxides), to prevent a phenomenon commonly called "foaming" or "reboil," and to prevent precipitation of elemental metals and metal sulfides that adversely affect refractory life (Bickford and Diemer 1986; Bickford et al. 1986; and Bickford et al. 1990).

The DWPF and the HWVP^a have used HCOOH as the reductant because of the other benefits specific to their slurry feeds, while the West Valley Demonstration Project (WVDP) has opted for sugar as its reductant source due to a different operating philosophy (Bonner 1992).

2.4.1 Technetium/Ruthenium Volatility

While there are many semivolatile metal species in the Hanford Site waste inventory (e.g., cadmium [Cd], lead [Pb], arsenic [As], Cs), the volatility of technetium and ruthenium are of particular interest because the volatility of these multivalent elements can be effectively controlled by reduction-oxidation (redox) conditions in the glass melt. Technetium and ruthenium, in their oxidized form (Tc_2O_7 and RuO_4), will readily volatilize at temperatures typically found in the melter cold-cap region (Bickford et al. 1986; Lammertz et al. 1985; Rimshaw et al. 1980; Larson 1989). Thus, to prevent this from occurring, a reductant is introduced to the feed to provide a reducing environment in the cold-cap to maintain technetium and ruthenium in their less oxidized and less volatile forms (TcO_2 and RuO_2) (Larson 1989).

2.4.2 Melter Foaming

Of primary concern in the vitrification of alkaline HLW has been the foaming or reboil phenomenon, in which a foam blanket forms an insulating layer between the cold-cap and melt pool that prevents the heat transfer from the glass pool to the cold-cap and incoming feed thereby decreasing the slurry feed processing rate. Excessive foam can increase the melt and/or cold-cap volume to the point that the melter offgas system is plugged. The foam can also affect the density of the melt pool which can interfere with the electrical distribution of the melter (Herborn and Smith 1993).

^aThe HWVP flowsheet used HCOOH because the Hanford Site design was going to capitalize on flowsheet development already conducted for the DWPF.

Because this phenomenon is central to the need for adding a reductant, this issue is discussed at length. Moreover, there are several noteworthy advancements in understanding this phenomenon that have recently come to light.

The exact mechanism by which melt foaming is produced in nuclear waste glass processing is not understood. One of the primary considerations appears to be the origin of the gases that produce a foam in a melter situation. A recent literature review by J. L. Ryan (1994) suggests that foaming in nuclear waste glasses may be a function of feed alkalinity, viscosity and surface tension of molten layers at the cold-cap/glass pool interface, and redox reactions in the cold-cap and glass melt pool.

2.4.2.1 Viscosity and Surface Tension. One of the most important aspects in producing foam in any liquid medium is the viscosity and the surface tension of the surrounding fluid. It is stated in *Perry's Chemical Engineers' Handbook* (Perry and Green 1984) that foam stability is enhanced by increases in viscosity and a reduction in surface tension of the liquid medium.

Of most importance to glass production in a slurry-fed melter is the viscosity and surface tension of the glass-forming region at the base of the cold-cap sometimes referred to as the "fusion zone." This region is often quite viscous from the initial melting of silica (aided by alkali fluxing agents) at relatively low temperatures (700 to 900 °C). Gases produced from decomposition reactions and/or redox reactions in or below the fusion zone must penetrate this layer before exiting through the porous cold-cap. Thus, it is this layer that is the suspected origin of many glass-foaming incidents observed both in waste and commercial glass production (Woolley 1994).

The viscosity of the glass and/or the fusion zone can likely be controlled by composition. Goldman et al. (1986) suggest that the surface tension of the glass can be modified to avoid foaming by enhancing the amount of dissolved water in the glass. How this could be accomplished is not clear. Presumably, the treated alkaline feeds may already provide the necessary water because the alkalinity will have a tendency to maintain moisture content throughout the cold-cap.

2.4.2.2 Feed Alkalinity. The effect of alkalinity on nuclear waste glass processing may be considered by comparison of the pilot-scale ceramic melter (PSCM)-11 and PSCM-17 melter runs. The PSCM-11 run processed a simulated alkaline waste (e.g., neutralized current acid waste [NCAW]) and the PSCM-17 run processed a simulated acid waste (e.g., CAW). Both simulants were processed without adding a reductant to the feed and under similar conditions. The PSCM-11 run foamed severely, while the PSCM-17 did not produce foam (Ryan 1994).

As postulated by Ryan (1994), the presence of free strong bases (hydroxide [OH⁻] and aluminate [AlO₂⁻]) in alkaline feed favors the stability of higher oxidation state multivalent species (e.g., cerium [Ce], chromium [Cr], iron [Fe], manganese [Mn], uranium [U], etc.). However, the oxidized species will decompose as the temperature is increased, liberating oxygen. If the oxygen is released in the temperature range where initial melting occurs and where the melt is viscous, a stable foam may form from trapped oxygen in the melt.

Ryan (1994) also suggests that because alkaline wastes contain alkali carbonates, hydroxide, and nitrites that could react with silica at a lower temperature than sodium nitrate (NaNO_3), the viscosity of the fusion layer could be increased and the surrounding pore structure may be closed off at a low temperature where melt viscosity is high. Thus, decomposition gases which are subsequently generated from the NaNO_3 , alkali carbonates, hydroxides, or nitrites, could be trapped and form a stable foam.

2.4.2.3 Redox Reactions. In adopting commercial oxidation control philosophy, it is implicitly assumed that the foam production is caused by the release of oxygen in the glass melt via reduction-oxidation reactions. Evidence of foaming in the commercial glass industry caused by the decomposition of higher-valent oxides has been well documented (Woolley 1992 and 1994; Ryan 1994; Lucktong and Hrma 1988; Blair and Luckacs 1980). Extensive studies conducted by waste glass researchers have therefore concentrated on the factors that affect the redox equilibrium in the glass melt (Schreiber et al. 1986; Lucktong and Hrma 1988; Blair and Luckacs 1980; Goldman et al. 1986; Bickford and Diemier 1986; Bickford et al. 1986).

As seen in equation 2, there are three primary factors that will shift the redox state of the glass melt, including the melt pool temperature, the oxygen potential above the melt pool, and the valence state of the feed constituents. The following chemical equation represents the reduction of a metal species in the melt pool.

Writing the equilibrium constant for this reaction and rearranging yields the following equation, indicating the oxidation potential of the melt. Derivation of Equation 2 is shown in Appendix A.

$$-\log f_{O_{2,gas}} = \frac{4}{n} \log \left(\frac{[M_{(melt)}^{(m-n)+}]}{[M_{(melt)}^{m+}]} \right) - \frac{\Delta G^\circ}{2.3026 nRT} + 2 \log [O_{(melt)}^{2-}] \quad (2)$$

where:

- $fO_{2,gas}$ = oxygen fugacity in the melt
- n = number of electrons transferred during the reduction
- $[M]$ = concentration of any metal species
- m = valence state of the metal before reduction
- ΔG° = Gibbs free energy of reaction at standard state
- R = gas constant
- T = temperature
- $[O_{(melt)}^{2-}]$ = concentration of oxygen in the melt.

The effect of temperature on nuclear waste glass melter performance has been investigated by several researchers (Elliott et al. 1994). However, the temperature increases in these tests were relatively slow (resulting from powering up to higher temperature), and any oxygen liberated by shifts in redox reactions is dissipated at a slow enough rate to avoid foaming at the

melt surface. There is some indication that relatively fast changes in melt pool temperature have resulted in some incidences of foaming (Cooper et al. 1994; Burkholder and Jarrett 1986). It is clear from equation 1 that a sufficiently sharp increase in temperature^a would have a significant effect on the oxidation state of the glass.

An estimate of the oxygen release from the melt pool was calculated assuming 5% of each element of significance was reduced and is shown in Table 2-1. Values were calculated using the reference HWVP melter size and temperature. Both the NCAW and DST/SST blend glass compositions as cited in WHC-SP-1143, *Tank Waste Remediation System High-Level Waste Feed Processability Assessment Report* (Lambert and Kim 1994) were considered. Additional discussion of the basis for the values in Table 2-1 can be found in Appendix B.

Rapid thermal increases in the melt pool can have another effect directly related to the redox reactions. Sometimes referred to as electrochemical reboil, an electrochemical cell is created at the electrodes in which melt species could be reduced, producing oxygen (Wooley 1992). This effect is not really a thermal effect, but rather an electrochemical effect related to increasing the temperature of the glass melt pool. This effect is unique to electric melters in that it is related to power fluctuations to the melter electrodes.

The pressure over the melt can have a profound effect on the redox reactions in the melt pool, as seen in equation 2. A decrease in the oxygen partial pressure (f_{O_2}) can cause the redox reactions to shift, releasing oxygen. Depending on the properties of the melt and the rate of oxygen release, a foam may form at the melt surface. This is a version of the phenomenon called "reboil." This effect was studied extensively by Goldman et al. (1986). Goldman measured the tendency of a glass melt to foam by decreasing the pressure at constant temperature over the melt until it boils. The lower the "reboil pressure," the less likely the feed was to foam.

Another factor that affects the redox equilibria in the melt pool (and cold-cap) is the assimilation of metal oxides into the glass whose valence state is much higher than thermodynamically favored in the melt pool. As discussed in Section 2.2.2.2, alkaline feeds could maintain oxides in their higher valence state throughout the cold-cap until they begin to be assimilated into the glass. Oxides that are not thermodynamically or chemically stable under these conditions will decompose to a more reduced state, liberating oxygen. Because of the abundance of multivalent species such as Ce, Cr, Fe, Mn, and U in the waste feeds, the potential level of gas evolution is significant.

^aA preliminary estimate of how much of a temperature increase would cause a foaming episode was obtained from Cooper et al. (1994) and Burkholder and Jarrett (1986) at 10 to 20 °C/h. However, the graphs from which this estimate was obtained are highly compressed. More analysis of this data is required before such an estimate can be sufficiently quantified.

Table 2-1. Estimated Oxygen Release from the Melt Pool Based on 5% Reduction of Each Element of Significance.

Reduction	NCAW	DST/SST blend
	Volume of oxygen evolved based on 5% reduction (L of O ₂ /L of glass) ^a	Volume of oxygen evolved based on 5% reduction (L of O ₂ /L of glass) ^a
Fe(III) to Fe(II)	9.40	3.66
U(VI) to U(V)	0.45	1.36
U(V) to U(IV)	0.45	1.36
Total	10.30	6.38

^aBased on 1,695.0 L of glass in the melt pool.

DST = Double-shell tank

NCAW = Neutralized current acid waste

SST = Single-shell tank

An example of oxygen release for the reduction of several multivalent species at the melt/cold-cap interface has been calculated and is shown in Table 2-2. The estimate is based on the assumption that the equivalent of a 1-cm-thick portion of the cold-cap material is involved in the reduction in an HWVP reference melter. Both the NCAW and DST/SST blend glass compositions as cited in WHC-SP-1143 (Lambert and Kim 1994) were considered. Additional discussion of the basis for the values in Table 2-2 are provided in Appendix C.

It has been speculated that the foaming phenomenon in nuclear waste glasses is primarily attributed to excessive Mn reduction in the melt pool (Plodnic 1985; Bickford et al. 1990). Studies commissioned by the SRTC seem to indicate that if more than two-thirds of the Mn in the slurry feed is reduced to the Mn⁺² state during feed preparation, the glass will not foam during melter processing. Manganese reduction in an aqueous environment proceeds at a slow rate, even at boiling temperatures. Thus, a lengthy "digestion" period was added to the DWPF feed preparation flowsheet to accomplish the reduction of Mn (Larson 1989). The evidence linking melter feed composition to foaming in the melter is quite elusive as noted by Ryan (1994).

2.4.2.4 Effect of Reductant. Assuming temperature excursions in the melt pool can be effectively controlled, researchers have developed methods to control the oxidation state of the melt pool. As mentioned earlier, the oxidation state of commercial melters has been controlled using sugar, starch, powdered metals, etc. (Tooley 1974). Because HCOOH can act as a reductant in the cold-cap and was already being added for other purposes, studies have focussed on controlling the melt pool oxidation state by adjusting the HCOOH requirements during feed preparation (Bickford and Diemier 1986; Ramsey et al. 1991; Wiemers 1990).

Table 2-2. Estimated Oxygen Release at the Cold-Cap/Melt Interface Based on 100% Reduction of High Valence State Elements of Significance.

Reduction	NCAW	DST/SST blend
	Volume of oxygen evolved (L/m ² melt surface) ^a	Volume of oxygen evolved (L/m ² melt surface) ^a
Ce(IV) to Ce(III)	18.96	76.34
Cr(VI) to Cr(III)	49.41	85.50
Fe(III) to Fe(II)	1,700.55	663.10
Mn(III) to Mn(II)	118.48	100.76
U(VI) to U(V)	81.28	245.21
Total	1,968.68	1,170.92

^aBased on 2.26 m² of melt surface area.

DST = Double-shell tank
NCAW = Neutralized current acid waste
SST = Single-shell tank

The rationale for adding HCOOH as a reductant is discussed by Larson (1989). He states that the order in which reduction reactions occur in the cold-cap is based on the temperature at which the oxidation/reduction reactions become thermodynamically favorable. According to Larson, reduction in Hanford Site feeds is initiated by the reduction of high valence oxides (e.g., Cr₂O₇ and MnO₂) to lower valence oxides (Cr₂O₃ and MnO), and in the absence of a reductant would proceed at high temperatures after the oxides had fused into the glass. The oxygen release from the reduction of these oxides would then cause foaming. However, based on an Ellingham plot (Swalin 1972) the reduction would take place at a much lower temperature in the presence of a reductant (e.g., carbon oxidizing to CO₂). For high valence components, the temperature at which reduction starts in the presence of a reductant is much lower than the glass fusion temperature. Thus, the oxygen released will not cause foaming of the melt. The extent to which the reduction takes place is determined by the amount of reductant added. If too much reductant is added, the feed constituents could be reduced to their metallic state and precipitate to the melter floor, inhibiting the performance of the melter (see Section 2.4.3). If too little reductant is added, some of the high valence oxides reduce after fusing into the glass, causing foaming.

The exact mechanism by which the HCOOH affects the oxidation state of the melt pool is unknown. However, correlations between the amount of HCOOH added and the oxidation state of the glass have been well documented (Wiemers 1990; Goles and Nakaoka 1988). Ryan (1994) suggests that HCOOH may act as a reductant either by decomposing (through various routes) to form pyrolytic carbon or by forming reducing gases such as H₂ and carbon monoxide (CO) or (more likely) a combination thereof. Ryan further suggests that the reducing efficiency of HCOOH by these routes is probably poor. Studies recently conducted at PNL (Smith 1994b) indicate that there is evidence to support

Ryan's suppositions about the behavior of HCOOH in the cold-cap. However, considerably more work is required to understand the mechanisms in the cold-cap that may or may not drive the redox of the melt pool.

2.4.3 Precipitation of Metals and Metal Sulfides

The precipitation of elemental or alloyed metals and metal sulfides from the melt pool has been of considerable focus in HLW melter tests. Sufficient deposition of the metals on the melter floor can create a conductive layer through which the bottom electrodes (relative to the HWVP reference melter) can short circuit across the melt pool. The loss in current through the glass will ultimately impact the performance of the melter (Cooper et al. 1994).

Metals deposited on the melter floor also have been attributed to premature degradation of the melter floor refractories (often referred to as refractory drilling). The exact mechanism by which this phenomenon operates is unknown. Refractory drilling has been noted in commercial and nuclear glass processing. In a few commercial cases, holes several inches deep have been drilled causing the melter to drain its contents (Cooper et al. 1994).

Metal species most often attributed to the phenomenon mentioned above are the platinum group metals (noble metals) such as silver (Ag), Pd, Rh, and Ru in various forms; alloys of the noble metals with tellurium (Te), (nickel [Ni], Mn) (Fe, Cr) spinels; Rh-nucleated Cr/Ni/Fe spinels; and metal sulfides such as nickel sulfide (NiS) and ruthenium sulfide (RuS₂) (Cooper et al. 1994). Of the metal species on the melter floor, the noble metals and metal sulfides are known to be related to the redox conditions of the melt pool.

Schreiber et al. (1991) found that solubility of noble metals in glass is redox controlled. However, Schreiber et al. also stated that in a system with other redox components, especially Fe, the redox equilibria are shifted so that noble metals are virtually insoluble. Noble metals' solubility in silicate glasses is typically quite low, e.g., 0.05 wt% for Rh, 0.03 wt% for Pd, 0.01 wt% for Ru with sodium oxide (Na₂O) <25 mol% and 0.25 wt% with Na₂O >25 mol% (Elliott et al. 1994).

Precipitation of NiS and RuS₂ metal species are often found on the melter floor when reducing conditions exist in the melt pool. Studies at SRTC have established that precipitation of metal sulfide species is enhanced above an Fe²⁺/Fe³⁺=0.5, particularly NiS (Bickford et al. 1986). A redox control limit was subsequently instituted based on these findings.^a The same control limit was adopted by the HWVP.

^aThe upper redox limit was also established to prevent carburization and sulfidation attack of the Inconel melter components (Bickford et al. 1986). (Inconel is a trademark of Inco Alloys International, Incorporated.)

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3.0 IDENTIFICATION OF ALTERNATIVE CHEMICAL ADDITIVES

Alternative chemical additives to HCOOH were identified in discussions between WHC and PNL HLW feed preparation cognizant staff, including Dr. Bruce King^a of the University of Georgia (UGa) (Smith 1993; Powell 1994). An initial list of candidates was developed with an emphasis on replacing the reducing and acidic properties of HCOOH. Although nearly any organic can be used as a reducing agent in the melter, the list was limited to confine the search to a reasonable number of alternatives.

Formic acid is generally considered to be a part of a family of acids commonly referred to as carboxylic acids. Thus, other acids in this family were natural substitutions for HCOOH. The following is a list of the carboxylic acids considered:

acetic acid	butyric acid
glycolic acid	levulinic acid
glyoxylic acid	oxalic acid
glycine	malonic acid
lactic acid-d	tartaric acid-d
pyruvic acid	citric acid.

Other types of chemical additives were considered as well, such as sugar, corn starch, and aluminum powder.^b These three chemical additives were initially included on the list of candidates because they have been previously used in commercial or waste glass processing. However, these chemical additives will require an additional acid source to obtain acceptable rheological properties of the feed. While combinations of reducing and acid chemical additives can accomplish the same processing objectives as HCOOH, emphasis was placed on the need to minimize the number of additions during feed preparation to reduce the complexity of the flowsheet.

To facilitate subsequent down-selection of the alternative chemical additives, basic property information was obtained from *Lange's Handbook of Chemistry* (Dean 1992) for each of the candidates as shown in Table 3-1.

^aNOTE: Dr. King, a Professor of Chemistry at the UGa, has conducted research regarding the evolution of H₂ and NH₃ from process feed simulants for both the DWPF and HWVP Projects.

^bNitric acid (HNO₃) has also been seriously considered as a replacement for HCOOH. However, HNO₃ was evaluated in the feed preparation process at a much later date, under different circumstances, and for different reasons. The specifics regarding use of HNO₃ in the feed preparation flowsheet have been addressed in another document (Seymour 1995).

Table 3-1. Properties of Chemical Additives. (sheet 1 of 2)

Chemical additive	Chemical structure	Physical state at room temperature	Molecular weight (g/mole)	pKa at 25 °C	Melting point (°C)	Boiling point (°C)
Formic acid	$\text{H} - \text{COOH}$	Liquid	46.0	3.751	8.5	100.8
Acetic acid	$\text{CH}_3 - \text{COOH}$	Liquid	60.0	4.756	16.6	117.9
Glycolic acid (Hydroxyacetic acid)	$\text{HO} - \text{CH}_2 - \text{COOH}$	Solid	76.0	3.831	80.0	Decomposes
Glyoxylic acid	$\text{O} = \text{CH} - \text{COOH}$	Liquid	74.0	3.30	98.0	Not available
Glycine	$\text{H}_3\text{N} - \text{CH}_2 - \text{COOH}$	Solid	75.0	$\text{pK}_1 = 2.351$ $\text{pK}_2 = 9.70$	233.0	Not available
Lactic acid - D	$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{COOH}$	Liquid	90.0	3.858	53.0	119.0
Pyruvic acid (2-oxopropionic acid)	$\text{CH}_3 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{COOH}$	Liquid	88.0	2.49	11.8	165.0
Butyric acid	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$	Liquid	88.0	4.817	-5.3	163.3
Levulinic acid (4-oxopentanoic)	$\text{CH}_3 - \overset{\text{O}}{\underset{\text{ }}{\text{C}}} - \text{CH}_2 - \text{CH}_2 - \text{COOH}$	Liquid	116.0	4.59	33-35.0	245.8

Single acid group

Table 3-1. Properties of Chemical Additives. (sheet 2 of 2)

	Chemical additive	Chemical structure	Physical state at room temperature	Molecular weight (g/mole)	pKa at 25 °C	Melting point (°C)	Boiling point (°C)
Double acid group	Oxalic acid	HOOC — COOH	Solid	126.0	pK ₁ = 1.271 pK ₂ = 4.272	189.0	Not available
	Malonic acid		Solid	104.0	pK ₁ = 2.826 pK ₂ = 5.696	135.0	Decomposes
	Tartaric acid-D		Solid	150.0	pK ₁ = 3.036 pK ₂ = 4.366	168-170.0	275.0
Triple acid group	Citric acid		Solid	192.0	pK ₁ = 3.128 pK ₂ = 4.761 pK ₃ = 6.396	154.0	Decomposes
Other organics	Sugar (α-D-glucose = dextrose)		Solid	180.0	Not applicable	146.0	Not available
	Starch (amylum)		Solid	162.0	Not applicable	Decomposes	Not available
Metal powders	Aluminum powder	Al	Solid	27.0	Not applicable	660.0	2,467.0

pKa = acid dissociation constant

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4.0 EVALUATION CRITERIA

Evaluation criteria were identified through discussions with the cognizant WHC and PNL feed preparation staff (Powell 1994). The resulting evaluation criteria can be generally categorized into five groups:

- A. Gas generation
- B. Redox = oxidation control ($\text{Fe}^{+2}/\Sigma\text{Fe}$)
- C. Rheology
- D. Undesirable by-products/reactions
- E. Other considerations.

The categories are listed in their respective order of importance. Categories A through C were regarded as being particularly important to the performance and choice of the optimum alternative chemical additive. Gas generation was considered a major issue because the evolution of H_2/NH_3 is expected to have a significant effect on the design and performance of the HLW vitrification plant.

Another consideration is the melter-related performance of the candidates as measured by the foaming tendencies of the alternative chemical additives. Adjustment of the rheological properties of the feed is also an important consideration, but was not required because that can be accomplished using an acid such as HNO_3 . The remaining categories were used as an aid in this down-selection process. A description of each criterion is provided in Section 4.1. Table 4-1 presents a breakdown of the specific properties and attributes of each candidate chemical additive. The available experimental data as of December 1993 are included in the table. The table has not been updated to show the amount of data available at the time the initial decisions regarding down-selection of the candidates were made.

4.1 DISCUSSION OF THE EVALUATION CRITERIA

The following section describes evaluation criteria established by the cognizant staff.

4.1.1 Gas Generation

4.1.1.1 Exhibits Hydrogen Generation. As alluded to earlier, the production of H_2 during HLW feed preparation is the principal criterion by which a candidate's performance will be judged. Although complete elimination of the H_2 evolution during feed preparation is not required, it is highly desirable that the candidate show a significant reduction in the H_2 generation rate typically found in similar HCOOH experiments (Wiemers et al. 1993; Smith et al. 1995b). The HWVP maximum design limit for H_2 evolution is 6 lb/h (Kalia 1992).

NOTE: A candidate is not considered to have produced H_2 evolution when the hydrogen evolution is below the detection limits of the analytical equipment (≈ 1 ppm at PNL, ≈ 100 ppm at UGa).

Table 4-1. Chemical Additive Evaluation Criteria. (sheet 1 of 5)

Chemical additive	Gas generation		Redox		Rheology		Unacceptable by-products/reactions				
	Exhibits ¹ hydrogen generation	Exhibits ¹ ammonia generation	Reducing ³ power (free electrons: acid groups)	Exhibits melt foaming	Produces acceptable rheology	Additional acid needed	Offgas species (feed prep.)	Offgas species (melter)	Polymeric reactions	Precipitation reactions	Exhibits low ^{1,7} temperature decarboxylation
Formic acid ¹⁰	Yes	Yes	2	No	Yes	No	No	No	No	No	
Acetic acid			8								
Glycolic acid (Hydroxyacetic acid)	No	No	6								
Glyoxylic acid	No		4								
Glycine	No	Yes	14								
Lactic acid - D	No	No	12								
Pyruvic acid (2-oxopropionic acid)	No		10								
Butyric acid			20								
Levulinic acid (4-oxopentanoic)	No	No	22						May polymerize ⁶ because used in making nylon rubber and plastics		
Single acid group											

Table 4-1. Chemical Additive Evaluation Criteria. (sheet 2 of 5)

Chemical additive	Gas generation		Redox		Rheology		Unacceptable by-products/reactions				
	Exhibits ¹ hydrogen generation	Exhibits ¹ ammonia generation	Reducing ³ power (free electrons: acid groups)	Exhibits melt foaming	Produces acceptable rheology	Additional acid needed	Offgas species (feed prep.)	Offgas species (melter)	Polymeric reactions	Precipitation reactions	Exhibits low ^{1,7} temperature decarboxylation
Double acid group	Oxalic acid	No	No	1							
	Malonic acid	No	Yes	4							
	Tartaric acid - D	No	Yes	5							
Triple acid group	Citric acid	No	Yes	6							No
	Sugar ¹¹ (α -D-glucose = dextrose)	No	No	24 (No acid groups)		No	Yes	None observed	None observed	None observed	
Other organics	Starch (corn starch)			24 (No acid groups)		Yes					
	Aluminum powder						Reacts with HCl, H ₂ SO ₄ , KOH, and NaOH to form H ₂				
Metal powders											

Table 4-1. Chemical Additive Evaluation Criteria. (sheet 3 of 5)

Chemical additive	Other considerations							Comments
	Incompatibility with other feed constituents ³	Flammability ⁴ (flash point) (°C)	Corrosiveness ⁸ to metals (SS, Hastelloy, ^a Inconel ^b)	Health ³ hazard	Solubility ⁴ in water	Special ³ handling requirements	Cost ⁵ (\$ per lb per free electron)	
Formic acid ¹⁰	Strong acids and bases: HNO ₃ , H ₂ SO ₄ , strong oxidizers, PO ₅	68.0	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = No ¹² Inconel = Yes ¹²	Health = SEV Contact = SEV	Miscible with water		0.204 (85% solution)	Rapid delayed gas emission when mixed with HNO ₃ .
Acetic acid	See comments	39.0	SS304 = Yes ¹² SS316 = No ¹² Hast. C = No ¹² Inconel = Yes ¹²	Health = MOD Contact = SEV	Miscible with water	Special storage required because of flammability	0.041 (technical grade)	Strong oxidizing agents, most common metals except aluminum, chromic acid, HNO ₃ , H ₂ SO ₄ , H ₂ O ₂ , alkalies, carbonates, strong bases, amines, PCl ₃ , PCl ₅ .
Glycolic acid (Hydroxyacetic acid)	Strong oxidizers	Not available	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = Yes ¹² Inconel = Yes ¹²	Health = MOD Contact = MOD	Soluble ⁶		0.087 (70% solution)	
Glyoxylic acid	Most common metals	Not available		Health = MOD Contact = MOD	Very soluble		0.413 (See comments)	Based on a quote of \$1.65/lb in drums or bulk tanks, industrial grade, Hoechst Celanese Co., New Jersey.
Glycine	None identified	Not available		Health = SLGT Contact = NONE	25 g in 100 g H ₂ O at 25 °C		0.156 (See comments)	Based on a quote of \$2.19/lb in 200-lb fiber drums, industrial grade, W. R. Grace Company, Massachusetts.
Lactic acid - D	Strong oxidizing agents, strong bases, HNO ₃ , HF	> 110.0	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = Yes ¹² Inconel = Yes ¹²	Health = SLGT Contact = SEV	Very soluble		0.086 (88% technical grade)	
Pyruvic acid (2-oxopropionic acid)	Strong oxidizing agents, strong bases	82.0	SS304 = SS316 = Yes ¹² Hast. C = No ¹² Inconel =	Health = SLGT Contact = SEV	Miscible with water	Refrigeration required	1.45 (See comments)	Based on a quote of \$32/kg. for order of 10-20 tons, reagent grade sodium salt, Gallard-Schlesinger Industries, Carl Place, New York. Pure acid is not stable.

Single acid group

Table 4-1. Chemical Additive Evaluation Criteria. (sheet 4 of 5)

	Chemical additive	Other considerations							Comments
		Incompatibility with other feed constituents ³	Flammability ⁴ (flash point) (°C)	Corrosiveness ⁸ to metals (SS, Hastelloy, ^a Inconel ^b)	Health ³ hazard	Solubility ⁴ in water	Special ³ handling requirements	Cost ⁵ (\$ per lb per free electron)	
Single acid group (cont'd)	Butyric acid	Strong oxidizing agents, most common metals, aluminum, alkalis	71.0	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = No ¹² Inconel = Yes ¹²	Health = SLGT Contact = SEV	Miscible with water	Special storage required because of flammability	0.025	Obnoxious odor
	Levulinic acid (4-oxopentanoic)	Bases, oxidizing agents, reducing agents	137.0		Health = SEV Contact = SEV	Very soluble		See comments	Unable to find bulk quantities above 100 kg
Double acid group	Oxalic acid	Strong oxidizing agents, strong bases, silver and silver compounds, most common metals	Not readily flammable ³	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = Yes ¹² Inconel = Yes ¹²	Health = MOD Contact = MOD	8.3 g in 100 g H ₂ O at 20 °C		0.195	
	Malonic acid	None identified	157.0 (See note 3)		Health = SLGT Contact = MOD	154 g in 100 g H ₂ O at 25 °C		See comments	Unable to find bulk quantities
	Tartaric acid - D	Strong oxidizers, silver	210.0 (See note 3)	SS304 = No ¹² SS316 = No ¹² Hast. C = Yes ¹² Inconel = Yes ¹²	Health = SLGT Contact = NONE	135 g in 100 g H ₂ O at 25 °C (See note 6)		0.295	
Triple acid group	Citric acid	Strong bases	Not available	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = No ¹² Inconel = Yes ¹²	Health = NONE Contact = SLGT	59 g in 100 g H ₂ O at 25 °C		0.046 (Anhydrous granular)	
Other organics	Sugar ¹¹ (α-D-glucose = dextrose)	None identified	Not available	SS304 = Yes ¹² SS316 = Yes ¹² Hast. C = Inconel =	Health = NONE Contact = NONE	90.9 g in 100 g H ₂ O at 25 °C (See note 6)		0.01 (See comments)	Addition of this reductant retards melter processing rate. Price based on quote of \$0.24/lb in 100-lb bags, granulated, Great Western Chemicals, Washington.
	Starch (corn starch)	Strong oxidizing agents	Not available		Health = NONE Contact = SLGT	Insoluble in H ₂ O ⁶ at 25 °C Soluble in H ₂ O at 100 °C		0.0063 (See comments)	Price based on quote of \$15 per 100-lb bags, granulated, Great Western Chemicals, Washington.

Table 4-1. Chemical Additive Evaluation Criteria. (sheet 5 of 5)

	Chemical additive	Other considerations						Comments
		Incompatibility with other feed constituents ³	Flammability ⁴ (flash point) (°C)	Corrosiveness ⁸ to metals (SS, Hastelloy, ^a Inconel ^b)	Health ³ hazard	Solubility ⁴ in water	Special ³ handling requirements	
Metal powders	Aluminum powder	Strong acids, caustics, strong oxidizing agents, strong bases, combustible materials, water	Aluminum dust ⁶ is easily ignited		Health = SLGT Contact = SLGT			

NOTES:

1. Data obtained from the University of Georgia (UGa) monthly technical report entitled, Hanford Waste Vitrification Plant Hydrogen Generation Study: Preliminary Evaluation of Alternatives to Formic Acid, Prepared for Pacific Northwest Laboratory under contract #125770-A-A2, R. B. King, N. K. Bhattacharyya, and V. Kumar, University of Georgia, Augusta, Georgia, 1993a.
2. Calculated assuming +4 electrons for C, +1 for H, +5 for N, and -2 for O. Calculation assumes slurry pH adjustment proceeds downward to a minimum of pH = 7.
3. Data taken from material safety data sheets (MSDS) located on sitewide Hanford computer network (unless otherwise noted).
4. Data taken from Lange's Handbook of Chemistry, J. A. Dean, McGraw-Hill, Inc., New York, New York, 1992.
5. Data from Chemical Marketing Reporter, September 20, 1993.
6. Data taken from The Merck Index, fourth edition, Merck and Company, Inc., Rahway, New Jersey, 1976.
7. Exhibits substantial CO₂ release when titrated into a UGa Al(OH)₃ suspension at <90 °C.
8. Data taken from Perry's Chemical Engineers' Handbook, sixth edition, R. H. Perry and D. W. Green, McGraw-Hill Book Company, New York, New York, 1984. Positive response indicates corrosion rate is >0.002 in./yr at 100 °C for pure substance. No data available for corrosion rates at 0.005 in./yr. Perry's states that in general for acid ranging in strength from weak organic acids to nitric acid, Hastelloy C and SS have good to excellent, and Inconel-600 fair to good, corrosion properties.
9. Taken from the National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards, DHHS-90-117, U.S. Department of Health and Human Services, Washington, D.C., 1990.
10. Data obtained from the following documents unless otherwise noted: Hanford Waste Vitrification Program Pilot Scale Ceramic Melter Experiment Run Summary: HWVP-12/PSCM-22, HWVP-86-V1124A, R. K. Nakaoka, Pacific Northwest Laboratory, Richland, Washington, 1985; Hanford Waste Vitrification Program Pilot Scale Ceramic Melter Test Number 23 Summary Report, HWVP-88-V11024C/HWVP-88V110306A, R. W. Goles and R. K. Nakaoka, Pacific Northwest Laboratory, 1988; Integrated DWPF Melter System (IDMS) Campaign Report: Hanford Waste Vitrification Plant (HWVP) Process Demonstration (U), WSRC-TR-92-0403, Rev. 1, N. D. Hutson, Westinghouse Savannah River Company, Aiken, South Carolina, 1993; Vitrification of Noble Metals Containing NCAW-Simulant with an Engineering Scale Melter (ESM), Draft Report, W. Grünwald, G. Roth, W. Tobie, S. Weisenburger, K. Weiss, M. Elliott, and L. Eyler, Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, Federal Republic of Germany, 1993.
11. Data taken from Hanford Waste Vitrification Program Pilot Scale Ceramic Melter Experiment Run Summary: HWVP-12/PSCM-22, HWVP-86-V1124A, R. K. Nakaoka, Pacific Northwest Laboratory, Richland, Washington, 1985; and Hanford Waste Vitrification Program Pilot Scale Ceramic Melter Test Number 23 Summary Report, HWVP-88-V11024C/HWVP-88V110306A, R. W. Goles and R. K. Nakaoka, Pacific Northwest Laboratory, Richland, Washington, 1988.
12. Data taken from Corrosion Resistance Tables, third edition, P. A. Schweitzer, Marcel Dekker, Inc., New York, New York, 1991. Inconel in this data is 600 grade. Data only indicate corrosion rates <0.002 in./yr and 0.02 in./yr. Positive response indicates corrosion rate is >0.002 in./yr. Data taken from most concentrated form listed at 100 °C, i.e., acetic (glacial), butyric (pure), citric (conc.), formic (85%), glycolic (pure), glucose (pure), lactic (conc.), oxalic (sat.), pyruvic as propionic (pure), and tartaric(pure).

^aHastelloy is a trademark of Stoodly Deloro Stellite, Incorporated.^bInconel is a trademark of Inco Alloys International, Incorporated.

Hast. C = Hastelloy
 MOD = Moderate
 REDOX = Reduction-oxidation
 SEV = Severe
 SLGT = Slight
 SS = Stainless Steel
 UGa = University of Georgia

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4.1.1.2 Exhibits NH₃ Generation. The production of NH₃ during HLW feed preparation is another principal criterion on which a candidate's performance is judged. Again, complete elimination of the NH₃ production during feed preparation is not required, but it is highly desired that the candidate show a significant reduction in the NH₃ levels typically found in similar HCOOH experiments (Wiemers et al. 1993; Smith et al. 1995b). No HWVP maximum design limit for NH₃ production has been established.

NOTE: A candidate is not considered to exhibit NH₃ production when the NH₃ production is below the detection limits of the analytical equipment (≤ 0.0001 mol/L at PNL and UGa).

4.1.2 Oxidation Control

4.1.2.1 Reducing Power. This criterion highlights candidates that have excessive reducing power (long carbon chains) relative to their acidic capabilities based on the ratio of theoretical reducing power to acidic strength.

An estimate of the theoretical reducing power of a candidate was obtained based on the number of free electrons available. The free electron calculation was performed assuming the following values for the electronic state of each specie: +1 for H, +4 for C, +5 for N, and -2 for O.

The acidic power of a candidate was assessed based on the number of acid groups that would participate in reducing the pH of an aqueous solution at least to a pH of seven. The acid dissociation constant's (pKa) of each acid group were used to assess whether the acid group would participate in the buffering of the solution.

For Example: Citric Acid

Free Electron Calculation

Structure: C₆H₈O₇

Number of free electrons = (6X +4) + (8X +1) + (7X -2) = 18.0

Number of Acid Groups

pKa's: pKa₁ = 3.128
 pKa₂ = 4.761
 pKa₃ = 6.396

Number of acid groups which have a pKa ≤ 7.0 = 3.0

Reducing Power Calculation

$$\frac{(\text{Number of Free Electrons})}{(\text{Number of Acid Groups})} = \frac{18}{3} = 6$$

Ultimately, the reducing power of a candidate will have to be empirically assessed based on its affect on the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio in the glass.

4.1.2.2 Exhibits Melt Foaming. As discussed earlier, one of the principal reasons for adding a reducing chemical additive is to prevent foaming of the melt pool. Considerable discussion was evoked on how to proceed in determining if a candidate could prevent this phenomenon. This property is especially difficult to measure in the laboratory because foaming has only occurred during large-scale melter tests. A slightly modified method of that used by Goldman, Brite, and Richey (1986) was agreed upon.

In the modified method, dried melter feed simulant with the candidate reductant is heated in a quartz tube at a rate of 10 °C/min to a maximum temperature of 1000 to 1200 °C under ≈ 0.5 atm of pressure. During the heating cycle, the behavior of the simulant is continuously monitored with a video camera placed at a port in the side of the furnace.

The principle of this method was that melter feeds that formed viscous fusion zones may have an increased tendency to foam and should expand significantly when heated due to the entrapment of gas bubbles. The level of expansion would then be indicative of a melter feed's tendency to foam relative to other melter feeds treated with different chemical additives (Smith 1994b).

4.1.3 Rheology

4.1.3.1 Produces Acceptable Rheology. Although not required, it was generally preferred that the same candidate chemical additive could be used to modify the reducing and rheological properties of the melter feed. Chemical additive candidates requiring an additional acid would not necessarily be eliminated from consideration, but would be considered less desirable than additives that could perform both functions because the addition of another chemical increases the complexity of the feed preparation flowsheet.

The chemical additive should be one that can be used to adjust the pH of the slurry to around 5 without over-reducing the melter feed.^a Intuitively, this suggests that candidates with a reasonable balance between their reducing power and acid strength may be the optimum candidates for this application. Melter feeds adjusted to a pH of approximately 5 with HCOOH have typically rebounded to $\text{pH} \approx 6$ to 8 because of buffering reactions and reactions that are kinetically limited. Formic acid-doped melter feeds have a viscosity and yield stress that meet the *Hanford Waste Vitrification Plant Project Technical Data Package (TDP)*, WHC-SD-HWV-DP-001 (Kalia 1992) standards shown in Table 4-2. These same HWVP TDP standards were used to evaluate a candidate's performance during this evaluation.

^aAn over-reduced melter feed is considered to be one that would produce a glass with an iron redox ratio ($\text{Fe}^{2+}/\Sigma\text{Fe}$) > 0.3 . Reduction-oxidation (redox) control limits based on the iron(II)/iron(III) couple were used in this evaluation and are described in the HWVP TDP (Kalia 1992).

Table 4-2. Hanford Waste Vitrification Plant Project Technical Data Package (Kalia 1992)^a Specifications for Selected Processing Parameters.

Parameter	Formated slurry		Melter feed	
	Nominal	Design range	Nominal	Design range
Solids loading				
Total solids (wt%)	15	12-19	40	30-49
Total oxides (g/L)	125	100-150	500	400-600
Rheological				
Apparent viscosity ^b (cp at 25 °C) at 183 s ⁻¹	25	3-50	70	5-170
Yield stress ^b (dyne/cm ²)	25	4-100	100	5-260
Electrochemical				
pH	6	3.5-8	6	3.5-8

^aKalia, J., 1992, *Hanford Waste Vitrification Plant Project Technical Data Package*, WHC-SD-HWV-DP-001, Rev. 6, Westinghouse Hanford Company, Richland, Washington.

^bSubsequent analysis performed by J. R. Baker, 1992, *Design Basis Slurry Rheological Properties* (internal memo 7F133-92-036 to L. D. Swenson, May 14), Westinghouse Hanford Company, Richland, Washington, indicates that these parameters for melter feeds should have maximum values of 150 dynes/cm² and 15 cp (at maximum shear) for yield stress and apparent viscosity, respectively.

4.1.3.2 Supplemental Acid Required. As discussed in Section 4.1.3.1, candidates not possessing the ability to perform both reduction and acidification functions were also considered. A supplemental acid will be necessary for additives such as sugar, starch, and aluminum so that the slurry feed can be processed at reasonably high solids loadings (>400 gTO/L). Candidates requiring a supplemental acid are considered less desirable because the secondary addition will increase the complexity of the feed preparation flowsheet.

4.1.4 Undesirable By-Products/Reactions

The following section describes the criteria applied to the candidates that produce undesirable by-products and/or reactions during feed preparation and melter processing. Specifically, the concern is that the candidates will produce hazardous offgas species (e.g., cyanides, light hydrocarbon gases, azides, etc.) (either gaseous or particulate) and/or initiate a polymerization or precipitation reactions in the vitrification system. Obviously, such candidates will be removed from consideration in this down-selection process.

4.1.4.1 Offgas Species (Feed Prep). This criterion was included to remove from consideration candidates that produce undesirable offgas species in the feed preparation process such as hydrogen cyanide (HCN), methane (CH_4), methanol (CH_3OH), ethane (C_2H_6), ethanol ($\text{C}_2\text{H}_5\text{OH}$), azides (e.g., N_3Na), etc. Undesirable species in the offgas can be detected by anomalous peaks in a gas chromatograph (GC) or Fourier transform infrared spectrometer (FTIR) analysis during laboratory feed preparation tests.

4.1.4.2 Offgas Species (Melter). This criterion was included to remove from consideration candidates that create undesirable offgas species (either gaseous or particulate) during the cold-cap reactions in the melter such as those mentioned in Section 4.1.4.1.

The quartz crucible tests discussed in Section 4.1.2.2 may provide some indication of undesirable species in the offgas by detection of anomalous peaks in a GC or mass spectrometry analysis. However, the offgas profile from this "static" method may not correlate particularly well with offgas profiles in dynamic large-scale melter tests: small- or large-scale melter tests may be necessary to distinguish whether undesirable offgas components are produced with candidate reductants.

4.1.4.3 Polymerization Reactions. This criterion was included to remove from consideration candidates that either promote polymerization of a species in solution or will auto-polymerize during feed preparation. Polymerization of species in solution will adversely affect the rheological properties of the feed. This effect may be detected by visual observation of the treated slurry feed and/or rheological measurements.

4.1.4.4 Precipitation Reactions. This criterion was included to remove from consideration candidates that promote the precipitation of species from solution during feed preparation. Precipitation of certain species may adversely affect the rheological properties of the slurry feed.

Precipitation of slurry constituents can be detected from rheological property changes and visual observations of the slurry and equipment (i.e., plating out). Periodic solubility measurements can be performed where the supernate is analyzed for target metal species at various points during feed preparation processing.

4.1.4.5 Exhibits Low Temperature Decarboxylation. This criterion is primarily aimed at carboxylic acid candidates. The presumption is that if the candidate undergoes decarboxylation at low temperatures (20 to 100 °C), it is likely that the carbon will not be present at the appropriate points in the cold-cap to perform the necessary reductions, i.e., it will already have volatilized as CO_2 either in feed preparation or melter processing. The thermal stability of each candidate was assessed by heating the carboxylic acid in an aqueous solution of aluminum hydroxide $\text{Al}(\text{OH})_3$ and monitoring the CO_2 evolution (King et al. 1993b).

4.1.5 Other Considerations

The remaining criteria were included in this investigation to provide additional points on which to judge a candidate's value as a substitute for

HCOOH. The purpose of this category is to identify candidates that may require modification of existing facility designs. These criterion would be taken into consideration when deciding between candidates that performed similarly in the other categories discussed earlier.

4.1.5.1 Incompatibility with Other Feed Constituents. As is prudent in any chemical process, the candidates were investigated for any incompatibilities with other chemicals that could pose a considerable safety threat to the vitrification facility. Principal data for this criterion can be obtained from material safety data sheets (MSDS).

However, the incompatibilities identified by the MSDS need to be judged in relation to conditions under which the chemicals are to be used. For example, from Table 4, HCOOH is shown to be incompatible with HNO₃. This incompatibility is due to the energetic reactions between formic and nitric acid (Kelm et al. 1980), as follows:

However, these reactions only proceed at an appreciable rate in aqueous solutions containing acid (H⁺) concentrations >1M (Kelm et al. 1980).

4.1.5.2 Flammability. The flashpoint of a chemical is an important safety consideration. A low flashpoint may require that certain fire protection systems be installed as a regulatory requirement. At the time this investigation was initiated, candidates with flash points lower than HCOOH were removed from consideration because of the potential impact on facility design and cost. Moreover, excessively volatile chemical additives will evaporate from the slurry feed during feed preparation processing.

4.1.5.3 Corrosiveness to Metals. Certain organics may be quite corrosive when used with the primary materials of construction for the HWVP Project, such as 304/316 stainless steel, Hastelloy C,^b and Inconel. Limited data for this criterion can be found in *Perry's Chemical Engineers' Handbook* (Perry and Green 1984) and in *Corrosion Resistance Tables* (Schweitzer 1991). While the choice of an acceptable corrosion rate may be dictated by plant design considerations, a guideline of 0.005 in./yr at 100 °C was considered reasonably conservative (Elmore and Jensen 1991).

4.1.5.4 Health Hazard. Health effects to humans resulting from exposure to the candidate chemical additives was important because of handling considerations outside the processing cells. Pertinent data regarding this criterion can be readily found in an MSDS. In particular, the health hazard level listed under the *Baker Saf-T-Data*^c System was used to assess the hazard level on a consistent basis. The health hazard of the candidate was

^aCalculated from standard heats of formation obtained from the *CRC Handbook of Chemistry and Physics* (Weast 1990).

^bHastelloy is a trademark of Stoodly Deloro Stellite, Incorporated.

^c*Baker Saf-T-Data* is a trademark of J. T. Baker, Inc.

classified as either *severe*, *moderate*, or *slight* health or contact hazard to humans. The term "health" in the *Baker Saf-T-Data* System refers to health effects such as damage to the lungs or mucous membranes, renal failure, heart failure, etc. The term "contact" in the *Baker Saf-T-Data* System refers to the implications of exposure of the chemical to direct contact with the skin, eyes, and orifices of the body.

4.1.5.5 Solubility in Water. At the time this investigation was initiated, the solubility of the candidate chemical additive was of particular interest because the HLW vitrification plant was designed to handle only liquid chemical feeds. Water added to the feed from dilute chemical additions will have to be boiled off in the feed preparation system and/or in the melter thereby reducing processing rates. However, the feed system could be redesigned to handle solid feeds. Solubility data for the candidates are readily available in *Lange's Handbook of Chemistry* (Dean 1992).

4.1.5.6 Special Handling Requirements. This criterion was established to identify any special handling or storage requirements for the candidates. Such requirements could increase the complexity of the shipping and receiving process or require additional safety features in addition to those already in place for HCOOH.

4.1.5.7 Cost/Availability. Compared to other operating costs for the vitrification plant, the cost of the chemical additive was not viewed as a significant driver because of the small amount of material needed. However, it would be prudent to determine whether bulk quantities are available at reasonable prices. Cost of the chemical additives is easily obtained from various distributors throughout the United States or from the *Chemical Marketing Reporter*, September 20, 1993.

5.0 EVALUATION STRATEGY

The evaluation of the chemical additive candidates will be conducted in six phases with simulated HLW feed compositions:

- Phase I - Screening tests of the candidates at the UGa
- Phase II - Laboratory flowsheet tests of several candidates by PNL under bounding conditions
- Phase III - Limited laboratory testing of two candidates by PNL under nominal flowsheet operating conditions
- Phase IV - Small-scale melter system testing
- Phase V - Large-scale melter system testing
- Phase VI - Radioactive testing.

To date, testing in Phases I through IV has been conducted. More testing is required at the laboratory and larger scales to complete the evaluation. The results of the initial testing are discussed in Section 6.

5.1 PHASE I TESTING

In this phase of the evaluation, a majority of the candidates were tested with a limited-component NCAW simulant in a closed system at the UGa. These scoping studies processed the candidates through the feed preparation flowsheet until just after the acid addition. These tests were conducted under the same conditions that previously produced H_2 and NH_3 with $HCOOH$. Results of this testing will be used to screen the candidates and recommend several candidates for Phase II testing.

5.2 PHASE II TESTING

Phase II testing^a will evaluate 3 to 5 candidates in the laboratory feed preparation apparatus with a full NCAW composition simulant and under bounding conditions known to produce substantial amounts of H_2 and NH_3 with $HCOOH$.

Unlike the UGa closed system in which the feed preparation offgases build up with the progression of the experiment, the PNL lab-scale system is an "open" flow system in which argon is used to sweep the offgases to the gas analysis system. Because of the analytical capabilities of the PNL facility, condensates and slurry samples can be analyzed for ammonium ion (NH_4^+) and other possible detrimental reaction by-products. To limit cost, this testing was restricted to running the candidates through the HWVP feed preparation flowsheet until just after the acid addition phase (including concentrating the treated feed for 2 to 3 hours). Testing consisted of substituting the

^aSee Wiemers and Smith 1994a, 1994b for more details about this testing.

candidates for HCOOH in the HWVP flowsheet with minor modifications to the delivery rate to account for acid strength. More detailed testing of successful candidates was conducted in Phase III testing.

5.3 PHASE III TESTING

In Phase III testing,^a the field is narrowed to the two most promising candidates that were tested under nominal operating conditions for the HWVP feed preparation flowsheet. Testing of the reductant proceeded through the entire feed preparation flowsheet. In addition, rheological measurements will be obtained throughout the processing and subsequent aging period. Moreover, the melter feed slurry will be melted in the quartz crucible to check for melt foaming and "melter" offgas analysis. The most promising of the two candidates will then be used in small-scale melter testing in Phase IV.

5.4 PHASE IV TESTING

In Phase IV testing, the most promising candidate from Phase III testing is used to make 1,136 to 1,893 L (300 to 500 gal) of melter feed to be processed through a small-scale high-temperature melter (SSHTM) (melter size is relative to the reference HWVP melter). Additional testing in the SSHTM and other melter technologies (low-temperature crucible melter and cold-crucible melter) is being evaluated (Calmus 1995). This testing will be used to verify lab-scale testing observations and observe the behavior of the feeds in a melter (i.e., foaming, volatilization, melting rate, cold-cap behavior, glass redox, etc.).

5.5 PHASE V TESTING

Provided the candidate performed adequately in Phase IV testing, the candidate would be used to make 22,712 to 30,283 L (6,000 to 8,000 gal) of melter feed to be processed through a large-scale melter (melter size is relative to the reference HWVP melter). This testing will be used to verify lab-scale and small-scale testing observations on a large-scale basis. Testing of the candidate would be integrated with melter technology tests in support of the HLW melter selection (Calmus 1995).

5.6 PHASE VI TESTING

Radioactive testing may be conducted in parallel with other phases of testing. However, because of the exorbitant cost of radioactive testing, this testing will be limited to final flowsheet options. Testing may first proceed with depleted uranium added to a nonradioactive simulant because this testing can be conducted outside a hot cell. The final flowsheet will then be tested with a tank farm sample. It is likely that radioactive testing will first be done on the lab-scale and later followed by larger-scale radioactive melter testing.

^aSee Wiemers and Smith 1994a, 1994b for more details about this testing.

6.0 EVALUATION STATUS

During the meetings in which the criteria and strategy were developed (Powell 1994), the list of candidates shown in Section 3.0 was also generated. Subsequent to these meetings, the decision was made to initially proceed with only the carboxylic acids. The reduction in scope was necessary to limit cost expenditure to those candidates perceived as having the highest probability of succeeding. Sugar, starch, and aluminum were temporarily eliminated from consideration because they would require a supplemental acid to process the feeds through the feed preparation flowsheet. Nearly all of the carboxylic acids listed in Section 3.0 were carried into Phase I testing except acetic and butyric acids. Acetic acid was eliminated from consideration because of its tendency to initiate strong energetic reactions with nitrated feeds. Butyric acid was eliminated because of a combination of undesirable properties, including high reducing to acid ratio, low flashpoint, and its extremely noxious odor.

Phase I testing was essentially completed in September 1993 for most of the candidates and reported by Dr. King in a monthly report (King et al. 1993a). A more comprehensive report on this phase of testing can be found in another UGA report released in December 1993 (King et al. 1993b). The primary results of Phase I testing are summarized in Table 6-1.

From the Phase I testing results, four candidates were recommended for Phase II testing at PNL, including glycolic acid, oxalic acid, citric acid, and lactic acid-D. Although citric acid did evolve some NH_3 during processing, discussions with Dr. King revealed that too much citric acid was added compared with the other candidates. Thus, because citric acid was appealing in view of many of the criteria, it was recommended for testing at PNL. Phase II testing was completed in February 1994 for the four candidates. The results are summarized in Table 6-2. These results are preliminary and have not been documented.

Because lactic acid and citric acid produced some NH_3 during Phase II testing, they were eliminated from consideration and glycolic and oxalic acids were carried into Phase III testing. However, of particular concern (prior to cancellation of the HWVP) was the low solubility of oxalic acid at room temperature. The solubility of oxalic acid increases with an increase in temperature (see Appendix D, Figure D-1). Consultation with HWVP Systems Engineering revealed that a heating capability could easily be added to the current HWVP design to maintain the solubility of the oxalic acid. Thus, the oxalic acid was maintained as a viable candidate to be tested during Phase III.

Phase III testing of the candidates was conducted in conjunction with feed preparation flowsheet development for the high-temperature melter. The feed preparation flowsheet development effort was conducted in parallel to the alternative chemical additive evaluation and is described in another WHC FY94 milestone (Seymour 1995).

Table 6-1. Offgas Results from Phase I Testing (King et al. 1993).^a

Chemical additive	Amount of chemical added (mmoles)	H ₂ evolved (mmoles)	NH ₃ evolved (mmoles)	CO ₂ evolved (mmoles)	N ₂ evolved (mmoles)	N ₂ O evolved (mmoles)	NO evolved (mmoles)	Final pH	Disposition after Phase I testing ^b
Formic acid	~85.0	0.8	0.5	19.2	0.0	6.2	3.4	4.0	Not applicable; test performed as a baseline.
Glycolic acid	~85.0	0.0	0.0	9.4	0.0	2.4	8.7	--	No H ₂ or NH ₃ observed; acceptable in other criterion categories for data known to date. Recommended for Phase II testing.
Glyoxylic acid	~85.0	0.0	0.2	33.5	0.0	9.2	4.4	3.7	Some NH ₃ observed, excessive CO ₂ evolved, and exhibits low-temperature decarboxylation. NOT recommended for Phase II testing.
Glycine	~85.0	0.0	0.3	2.8	1.3	0.0	0.0	8.9	Some NH ₃ observed and a very weak acid.
Lactic acid	~85.0	0.0	0.0	10.9	--	4.5	8.9	--	No H ₂ or NH ₃ observed; acceptable in other criterion categories for data known to date. Recommended for Phase II testing.
Pyruvic acid	~85.0	0.0	--	45.9	--	3.5	0.0 ^c	--	Some NH ₃ observed, excessive CO ₂ evolved, and exhibits low-temperature decarboxylation. NOT recommended for Phase II testing.
Levulinic	~85.0	0.0	0.3	12.1	0.0	3.6	4.6	4.6	Some NH ₃ observed and has high reducing to acid ratio. NOT recommended for Phase II testing.
Oxalic acid	~85.0	0.0	0.0	9.5	0.0	0.0	11.1	1.7	No H ₂ or NH ₃ observed; acceptable in other criterion categories for data known to date, provided it can be delivered and stored at a reasonable solubility. Recommended for Phase II testing.
Malonic acid	~85.0	0.0	1.4	14.1	0.0	2.8	0.0	3.5	Some NH ₃ observed and exhibits low-temperature decarboxylation. NOT recommended for Phase II testing.
L-tartaric acid	~85.0	0.0	--	7.5	0.0	1.5	9.0	2.6	Test conducted very late in campaign (after Phase II testing was initiated). NH ₃ not measured but suspected from smell.
Citric acid	~85.0	0.0	0.0	25.3	--	1.8	2.0	--	No H ₂ or NH ₃ observed; acceptable in other criterion categories for data known to date. Recommended for Phase II testing.

^aKing, R. B., N. K. Bhattacharyya, and V. Kumar, 1993, Hanford Waste Vitrification Plant Hydrogen Generation Study: Preliminary Evaluation of Alternatives to Formic Acid, December Monthly Technical Report prepared for PNL under contract #125770-A-A2, University of Georgia, August, Georgia.

^bAcetic acid not tested because of objections raised relative to its strong reaction with HNO₃, low flashpoint, and special handling requirements. Butyric acid not tested because of special handling requirements, its obnoxious odor, it is a weak acid, and it has high reducing to acid power ratio. Sugar not tested because studies have already been conducted by West Valley Demonstration Project and at Pacific Northwest Laboratory, and sugar requires a secondary acid addition. Starch not tested because it is not expected to react to any significant extent in this type of testing (most significant events expected to occur in the melter), and starch requires a secondary acid addition. Aluminum powder not tested because it is not expected to react to any significant extent in this type of testing (most significant events expected to occur in the melter), and aluminum powder requires a secondary acid addition. Sugar, starch, and aluminum powder viewed as requiring long-term development to answer too many unknowns.

^cA maximum of 4.1 mmoles of NO was produced in this experiment but was consumed before the end of the experiment.

Table 6-2. Preliminary Offgas Results from Phase I-I Testing.

Chemical additive	Amount of chemical added (mmoles) ^a	H ₂ evolved (mmoles) ^a	NH ₃ evolved (mmoles) ^a	CO ₂ evolved (mmoles) ^a	N ₂ evolved (mmoles) ^a	N ₂ O evolved (mmoles) ^a	NO _x evolved (mmoles) ^a	Final pH ^b	Disposition after Phase II testing
Formic acid	1,209.6	44.0	5.8	314.8	None observed	14.0	59.2	5.4	Not applicable; test performed as a baseline.
Glycolic acid	1,202.4	0	<0.01	157.5	None observed	2.85	71.2	3.8	No H ₂ or NH ₃ observed; acceptable in other criterion categories for data known to date. Recommended for Phase III testing.
Lactic acid	1,205.2	0	3.0	155.7	None observed	12.4	56.7	4.0	Some NH ₃ observed. However, acceptable in other criterion categories for data known to date. NOT recommended for Phase III testing.
Oxalic acid	671.2	0	0.16	155.6	None observed	2.03	141.4	3.6	No H ₂ or NH ₃ observed; ^c acceptable in other criterion categories for data known to date. Recommended for Phase III testing.
Citric acid	601.2	0	4.8	290.7	None observed	4.36	62.4	3.0	Some NH ₃ observed. However, acceptable in other criterion categories for data known to date. NOT recommended for Phase III testing.

^aValues indicated have been normalized to 100 gWO and are for the first 300 minutes of the experiment (most reactions were complete by this point).

^bpH values are at 25 °C and taken at the end of each experiment.

^cThe amount of ammonia detected at this level is close to the detection limit, and is often considered "noise."

Briefly, flowsheet development was initiated in FY94 to investigate process alternatives that could improve the processing capacity of HLW vitrification in support of the new HLW vitrification mission (Ecology et al. 1994). The flowsheet development consisted of modifying the HWVP feed preparation flowsheet to accommodate new processing ideas and support scheduled high-temperature melter runs. Principal changes to the flowsheet were to the glass former additions, concentration cycles, and the type of chemical additive.

Three tests were conducted in Phase III testing (see Seymour 1995 for more detail on these tests): two with glycolic acid and one with oxalic acid. The first test with glycolic acid exhibited a small amount of hydrogen which temporarily removed glycolic acid from consideration. Oxalic acid was then tested and no H_2 or NH_3 was observed. However, the melter feed produced by oxalic acid had extremely poor rheological characteristics, i.e., viscous at low oxide concentrations. Because of the abundance of iron in the slurry feed, this was attributed to the precipitation of ferric oxalate, which is not very soluble even at elevated temperatures (Weast 1990).

Glycolic acid was then retested with some flowsheet modifications. All parameters were within reasonable bounds, but a minimal amount of hydrogen was observed. Because the scheduled Phase IV testing was approaching quickly and the volume of hydrogen produced was $\approx 1/100$ th the amount observed in similar $HCOOH$ tests, the decision was made to recommend this candidate for Phase IV testing. The results of the Phase III testing are shown in Table 6-3.

Currently, limited Phase IV testing with NCAW simulant has been conducted in the SSHTM (Smith and Wiemers 1994a, 1994b) with glycolic acid. Data from this testing are shown in Table 6-4. Based on observations during the test and the preliminary data in Table 6-4, it appears that the glycolic acid is acceptable for treating HLW feeds in the feed preparation flowsheet. Thus, glycolic acid is recommended for additional testing.

Additional Phase IV testing is anticipated with different types of melters in support of the HLW melter evaluation (Calmus 1995). Phase V large-scale testing may occur as an integrated melter test in support of the HLW reference melter selection.

In the meantime, low radioactive lab-scale testing using depleted uranium could be conducted in the near term. A fundamental shift in the testing simulant composition has tripled the uranium content, possibly making it impractical to substitute neodymium as was done in the NCAW composition. Current uranium simulant levels are expected to have a much more significant redox effect on processing nuclear waste feeds (Schreiber and Balazs 1982; Schreiber et al. 1982, 1984, 1985a, and 1985b).

Table 6-3. Preliminary Results from Phase III Testing
(Smith and Wiemers 1994).^a

Offgas and slurry data		Chemical additive	
		Glycolic acid ^b	Oxalic acid
Amount of chemical added	(mmoles)	1,185.0	957.8
H ₂ evolved	(mmoles)	1.25	0
NH ₃ evolved	(mmoles)	Below detection limit	Below detection limit
CO ₂ evolved	(mmoles)	315.0	724.0 ^d
N ₂ evolved	(mmoles)	None observed	None observed
N ₂ O evolved	(mmoles)	<0.50	2.5
NO evolved	(mmoles)	116.3	57.7
Final pH (at 95 °C) ^c		6.0	6.4
Melter feed data			
Oxide concentration	(gTO/L)	464.0	225.7 ^f
Solids concentration	(wt% solids)	45.0	Not available
Slurry density	(g/mL)	1.41	Not available
Bingham yield stress ^e	(Pa)	6.4	25.4
Bingham viscosity ^e	(Pa · s)	27.3	52.0
Disposition after Phase III testing		Minor amount of H ₂ and possibly NH ₃ observed; deemed acceptable for Phase IV testing after melter feeds prepared with oxalic acid exhibited abysmal rheological properties. Acceptable in other criterion categories for data known to date. Recommended for Phase IV testing.	No H ₂ or NH ₃ observed; but unacceptable rheological properties at relative low oxide concentrations was observed. NOT recommended for Phase IV testing.

^aSmith, G. L. and K. D. Wiemers, 1994, Small-Scale High Temperature Melter-1 (SSHTM-1) Test Plan, Milestone PHTD-C94-03.02J, Addendum, Pacific Northwest Laboratory, Richland, Washington. More definitive results from Phase II testing (with respect to glycolic acid) have recently become available (Smith, G. L., H. D. Smith, E. M. Tracey, R. L. Myers, J. A. Sills, D. L. Fisher, and K. D. Wiemers, 1995, Small-Scale High-Temperature Melter-1 (SSHTM-1) Data Package, Milestone PVTDC95-03.02Y, Rev. 0, Pacific Northwest Laboratory, Richland, Washington). However, the results in Table 8 were not updated to illustrate the data that was available at the time the decisions were made. Recent data include H₂ at a maximum rate of 0.0014 mmole/125 gWO/min and total of 0.219 mmole/125 gWO; NH₃ total is 0.03 mmole/125 gWO; CO₂ total is 153.0 mmole/125 gWO; N₂O total is 3.82 mmole/125 gWO; and NO_x total is 82.98 mmole/125 gWO; Fe²⁺/ΣFe=0.06.

^bThe offgas data presented in Smith et al. (1994b) represents the first Phase III test conducted with glycolic acid. The second Phase III test was conducted without offgas analysis because of the lockout on the 325 building. The second test was conducted under nominal flowsheet conditions to reassess rheological and redox properties of the melter feed (presented above). The offgas data is estimated from the Figure A.2 in Appendix A. The offgas data only includes the first two titrations of glycolic acid since this is approximately the amount of acid that would be used in normal operation of the feed preparation flowsheet.

^cpH after acid addition but before the addition of glass formers.

^dThis CO₂ level is excessive relative to normal operation of the flowsheet because NaHCO₃ was added at the beginning of this experiment to account for a deficiency in Na in the simulant.

^eRheological properties obtained at 25 °C.

^fEstimate based on values given by investigators. In the experiment, 84.6 g SiO₂ and 21.1 g NaHCO₃ (based on 40.6 g NaHCO₃ per 125 gWO) were added to 644 g of treated slurry, which was known to have a solids loading of 176 gTO/L before glass former additions. A 1.4 g/ml density of the slurry, 2.65 g/ml for the SiO₂, and 2.159 g/ml for the NaHCO₃ to find the final volume of the simulant after the glass former additions.

Table 6-4. Preliminary Results from Phase IV Testing
(Smith et al. 1995).^a

Offgas and slurry data		Chemical additive
		Glycolic acid
Amount of chemical added	(moles)	1,545.6
H ₂ evolved total	(mmoles/125 gWO)	0.483
Maximum rate	(mmoles/125 gWO/min)	0.0018
NH ₃ evolved	(mmoles/125 gWO)	0.07
CO ₂ evolved	(mmoles/125 gWO)	180.0
N ₂ evolved	(mmoles/125 gWO)	None observed
N ₂ O evolved	(mmoles/125 gWO)	Below detection limit
NO _x evolved	(mmoles/125 gWO)	76.75
Final pH (at 95 °C) ^b		7.5
Melter feed data		
Oxide concentration	(gTO/L)	422.0
Solids concentration	(wt% solids)	43.2
Slurry density	(g/ml)	1.3
Bingham yield stress ^c	(Pa)	16.0
Bingham viscosity ^c	(Pa·s)	19.0
Glass data		
Average redox (Fe ²⁺ /ΣFe)		0.94
Disposition after Phase IV testing	Minor amount of H ₂ and NH ₃ observed; preliminary results suggest rheological and redox properties resulting from glycolic addition are acceptable. Recommended for further testing.	

^aSmith, G. L., H. D. Smith, E. M. Tracey, R. L. Myers, J. A. Sills, D. L. Fisher, and K. D. Wiemers, 1995, Small-Scale High-Temperature Melter-1 (SSHTM-1) Data Package, Milestone PVTD-C95-03.02Y, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

^bpH after acid addition but before the addition of glass formers.

^cRheological properties obtained at 50 °C.

Redox = Reduction-oxidation

7.0 EVALUATION COMPLETION

The evaluation of a chemical additive's performance will continue through the HLW vitrification plant design phase and likely throughout its use in the operating plant. Ideally, funding for further evaluation of the selected chemical additive will be at a reduced level after the commencement of detailed design. This is based on the assumption, of course, that the chemical additive's performance has been adequately characterized prior to initiating detailed design of the HLW vitrification plant.

Based on experience with the design and construction of the DWPF and design of the HWVP, it is CRITICAL to assemble sufficient data regarding the performance of the chemical additives to the feed preparation system prior to initiation of detailed design of the HLW vitrification plant. As evident from HWVP, a "thrifty" approach to HLW vitrification system development will only result in cost overruns far exceeding the required development funding. Moreover, lack of development data will force the Architect-Engineer (A-E) of the HLW vitrification plant to assume considerable risk in the design of the plant. The A-E will respond to the level of risk by incorporating over-conservatism in the design, which ultimately severely impacts the capital cost of the plant.

This section discusses the general parameters that still need to be explored to ensure that performance of the selected chemical additive is consistent with the processing needs of the HLW vitrification system. This section makes no attempt to identify the logical order in which the data should be pursued. The preliminary data needs presented herein are consistent with data needed to initiate conceptual design of the HLW vitrification system. A detailed discussion of the data needs for the HLW feed preparation system relative to conceptual design will be presented in an FY 1996 WHC key milestone.^a

Several assumptions were made in developing the subsequent preliminary list of data needs.

- A reductant-based feed preparation flowsheet continues to be part of the baseline HLW vitrification flowsheet.
- Redox control of the melter will be required regardless of whether a feed drying system is incorporated into the feed preparation system.
- Evaporative concentration of the feed will be required to some degree to maximize feed processing capacity regardless of whether a feed drying system is incorporated into the feed preparation system.

Based on these assumptions, the following preliminary list of data needs were assembled to further evaluate the selected chemical additive. Assuming glycolic acid continues to be a viable alternative to HCOOH, detailed information about HCOOH (gathered under the HWVP and DWPF Projects) could

^aHigh-level waste feed preparation data needs will also be reflected in an FY 1995 PNL feed chemistry strategy document.

possibly be used to support glycolic data needs in some areas. Spot checking with glycolic acid may then only be necessary.

Rheological

At a minimum, rheological properties (e.g., viscosity yield stress) will be needed as a function of pH, temperature, with and without glass formers, and time (aging studies) to initiate conceptual design of an HLW feed preparation system.

Reduction-Oxidation

Although much more work needs to be conducted to begin to understand the complex chemistry of the cold-cap and melt pool and their interrelationship, traditional melter redox control methods should probably be pursued until further research can fine tune them. To this end, empirical lab and melter redox correlations need to be developed as a function of the amount of chemical additives fed. The redox control region defined for the HWVP and DWPF reference melters should be revisited for higher temperature melter types, but could be used as a basis for defining the control region for these types of melters.

Feed Chemistry

To date, much more is known regarding the feed chemistry (offgas, by-products, etc.) of the HLW feed types expected in the vitrification plant. However, some testing is still required to assess the importance of new and higher concentrations of feed constituents introduced by the SST sludges. Moreover, bounding assessments of combustible and regulated gases (NO_x , SO_x) are needed for conceptual, and eventually, for detailed design.

General Equipment Parameters

If similar rheologic properties to HCOOH are exhibited by the preferred alternative chemical additive, then only minimal pumping, homogeneity, and agitation assessments are probably needed (if at all) before conceptual design is initiated. Some investigation in this area will likely be needed prior to detailed design. Pumping characteristics such as pressure drop, critical velocity, and settling have proven to be of great importance during DWPF startup operations.

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9.0 GLOSSARY

ABBREVIATIONS AND ACRONYMS

A-E	Architect-Engineer
CAW	current acid waste
DOE	U. S. Department of Energy
DST	double-shell tank
DWPF	Defense Waste Processing Facility
FTIR	Fourier transform infrared spectrometer
FY	fiscal year
GC	gas chromatograph
HAN	hydroxylaminenitrate
HLW	high-level waste
HWVP	Hanford Waste Vitrification Plant
MSDS	material safety data sheet
NCAW	neutralized current acid waste
pKa	acid dissociation constant
PNL	Pacific Northwest Laboratory
PSCM	pilot-scale ceramic melter
redox	reduction-oxidation
SRS	Savannah River Site
SRTC	Savannah River Technical Center
SS	stainless steel
SSHTM	small-scale high-temperature melter
SST	single-shell tank
TDP	Technical Data Package
TPB	tetraphenylborate
UGa	University of Georgia
WHC	Westinghouse Hanford Company
WVDP	West Valley Demonstration Project

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APPENDIX A

DERIVATION OF EQUATION 2

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APPENDIX A

DERIVATION OF EQUATION 2

The following section discusses the derivation of equation 2 in Section 2.2.2.3.

For the following reduction reaction

where:

M = Any multivalent metal species (e.g., cerium, chromium, iron, manganese, uranium)

m = Valence state of the metal before reduction

n = Number of electrons transferred during the reduction.

The equilibrium constant can be written as

$$K = \frac{a_{M_{(melt)}^{(m-n)+}}^4 a_{O_{2,gas}}^n}{a_{M_{(melt)}^{m+}}^4 a_{O_{(melt)}^{2-}}^{2n}} \quad (A2)$$

where:

K = Equilibrium constant

a_i = Activity of species i .

Rearranging and taking the log of both sides of the equation,

$$\text{Log } a_{O_{2,gas}}^n = \text{Log} \left[\frac{K a_{M_{(melt)}^{(m-n)+}}^4 a_{O_{(melt)}^{2-}}^{2n}}{a_{M_{(melt)}^{m+}}^4} \right] \quad (A3)$$

Using rules for log-based functions,

$$n \text{Log } a_{O_{2,gas}} = \text{Log } K + 4 \text{Log } a_{M_{(melt)}^{(m-n)+}} + 2n \text{Log } a_{O_{(melt)}^{2-}} - 4 \text{Log } a_{M_{(melt)}^{m+}} \quad (A4)$$

Multiplying through by -1 and collecting like terms,

$$-n \text{Log } a_{O_{2,gas}} = 4 [\text{Log } a_{M_{(melt)}^{(m-n)+}} - \text{Log } a_{M_{(melt)}^{m+}}] - [\text{Log } K + 2n \text{Log } a_{O_{(melt)}^{2-}}] \quad (A5)$$

Dividing through by n and rearranging using the rules of logs,

$$- \text{Log } a_{\text{O}_2, \text{gas}} = \frac{4}{n} \text{Log} \left[\frac{a_{M^{(m-n)}(\text{melt})}}{a_{M^{n+}(\text{melt})}} \right] - \frac{\text{Log } K}{n} - 2 \text{Log } a_{\text{O}^{2-}(\text{melt})}. \quad (\text{A6})$$

It is known by definition that the following equations are true,

$$K = e^{\frac{-\Delta G^\circ}{R T}} \quad \text{OR} \quad -\ln K = \frac{\Delta G^\circ}{R T} \quad (\text{A7})$$

where:

ΔG° = Gibbs free energy of reaction at standard state

R = Gas constant

T = Temperature

and

$$a_i = \frac{f_i}{f_i^\circ} \quad \text{OR} \quad a_i = [i] \gamma_i \quad (\text{A8})$$

where:

f_i = Fugacity of species i

f_i° = Fugacity of species i at standard state

$[i]$ = Concentration of species i

γ_i = Activity coefficient of species i.

If it is assumed that f_i° and all γ_i are one, then substituting Equations A7 and A8 into A6 produces the following

$$- \text{Log } f_{\text{O}_2, \text{gas}} = \frac{4}{n} \text{Log} \left(\frac{[M^{(m-n)}(\text{melt})]}{[M^{n+}(\text{melt})]} \right) + \frac{\Delta G^\circ}{2.3026 n R T} - 2 \text{Log} [O^{2-}(\text{melt})]. \quad (\text{A9})$$

APPENDIX B

BASIS FOR VALUES IN TABLE 2-1

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APPENDIX B

BASIS FOR VALUES IN TABLE 2-1

This section describes the basis for the estimated oxygen release values cited in Table 2-1 of the text. In order to calculate the values, the following parameters were assumed.

B1.0 ASSUMPTIONS

Parameters

- The glass is being melted in the reference Hanford Waste Vitrification Plant (HWVP) liquid-fed ceramic melter at 1150 °C and operated such that the iron reduction-oxidation (redox) ratio ($\text{Fe}^{2+}/\text{Fe}^{3+}$) remains between 0.005 and 0.5, and the oxygen partial pressure above the melt is between 10^{-9} and 10^{-1} atm.
- The melt line in the melter is 0.75 m from the floor, and the melt surface area is 2.26 m² (Herborn and Smith 1993).
- The average temperature of the glass at the melt line is 900 °C and the pressure is 1 atm.
- Oxygen behaves as an ideal gas at melt temperatures.
- The glass is a borosilicate type glass with an average density for both the neutralized current acid waste (NCAW) and double-shell tank (DST)/single-shell tank (SST) blend glass compositions of 2.16 g/cm³ at 1150 °C (Cooper et al. 1994).
- The NCAW and DST/SST blend glass compositions were obtained from Lambert and Kim (1994) and are assumed to be accurate. Waste loading in NCAW is 33 wt% and 50 wt% in the DST/SST blend, and is formulated for 1150 °C.
- At least 5% of each constituent is present in the melt in an oxidized state, e.g., Fe^{3+} , U^{6+} , U^{5+} , etc.
- The relative position of the redox couples in Figure B-1 (see Appendix B) is applicable to NCAW and DST/SST blend glasses at concentrations exceeding 1.0 wt%.
- The following reduction-oxidation reactions are representative (Schreiber et al. 1983):

Based on these assumptions, the following could be formulated:

Melt volume = 1.695 m³

Mass of glass in melter = 4.24 X 10⁶ g

1 gmol O₂ = 96.27 L O₂ at 900 °C.

Because the melter is operating under the conditions assumed above, the number of redox pairs of concern in the melt can be reduced to three based on Figure B-1 (see Appendix B), which has been adapted from Schreiber et al. (1984). The shaded rectangle represents the operating region for the melter for the assumed conditions. In other words, oxygen released from the redox pairs outside this region are not likely to contribute much (if any) to the total volume released.

Thus, the major contributors to oxygen release in the event of a significant step increase in temperature are likely to be Cu²⁺, Fe³⁺, U⁶⁺, U⁵⁺, and V⁵⁺. Copper and vanadium are not considered in the calculations due to their minor contribution to the glass composition (<0.1 wt% oxide).

Oxygen partial pressure limits are based on bounds imposed by normal operating melter pressure of ≈0.95 atm and the minimum oxygen partial pressure required to prevent sulfide precipitation (Jantzen and Plodnic 1986).

Volume of Oxygen Released

Example for iron (NCAW):

$$\begin{aligned} \text{Vol. O}_2 \text{ Released (L)} &= \frac{\text{Mass of Glass} \times \text{Fraction of Species in Glass}}{\text{mol weight of species}} \times \left(\frac{\text{Mol Ratio of Species to O}_2}{\text{based on redox Eqn.}} \right) \times \frac{\text{Vol. gas @ 900 °C}}{\text{mol of species}} \\ &= \frac{(4.24 \times 10^6 \text{ g}) \times (0.2821)}{159.694 \text{ g Fe}_2\text{O}_3} \times \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} \times (0.05 \text{ Fe Used in Reaction}) \times \left(\frac{1 \text{ mol O}_2 \text{ Produced}}{4 \text{ mol Fe Reacted}} \right) \times \frac{96.27 \text{ L O}_2}{\text{mol O}_2} \\ &= 15926.03. \end{aligned}$$

B2.0 REFERENCES

Cooper, M. F., M. L. Elliott, L. L. Eyler, C. J. Freeman, J. J. Higginson, L. A. Mahoney, and M. R. Powell, 1994, *Research-Scale Melter Test Report*, PNL-9428, Pacific Northwest Laboratory, Richland, Washington.

Herborn, D. I., and D. A. Smith, 1993, *Hanford Waste Vittrification Plant Preliminary Safety Analysis Report*, WHC-SD-HWV-PSAR-001, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

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B3.0 GLOSSARY

ABBREVIATIONS AND ACRONYMS

DST	double-shell tank
NCAW	neutralized current acid waste
redox	reduction-oxidation
SST	single-shell tank

Figure B-1. Oxygen Partial Pressure Versus Analyzed Redox Ratio of Multivalent Elements Doped (1 wt%) into SRL-131 Borosilicate Melt at 1150 °C (Adapted from Schreiber et al. 1984, 1991).

Table B-1. Summary of Calculations for Estimated Oxygen Release from a Melt Pool.

NCAW													
Species	wt% in glass (%)	Mass in melter (g)	Moles in melter (mol)	% of element reduced =	Amount of liberated oxygen								
					50	50	25	25	10	10	5	5	
				Reduction equation	(mol)	(L)	(mol)	(L)	(mol)	(L)	(mol)	(L)	
Fe ₂ O ₃	28.21	1,056,732.50	6,617.23	4Fe ³⁺ + 2O ²⁻ <--> 4Fe ²⁺ + O ₂	1,654.31	159,253.63	827.15	79,626.82	330.86	31,850.73	165.43	15,925.36	33.09
U ₃ O ₈	4.74	177,558.03	210.86	4U ⁴⁺ + 2O ²⁻ <--> 4U ³⁺ + O ₂	79.07	7,611.80	39.54	3,805.90	15.81	1,522.36	7.91	761.18	1.58
U ₂ O ₅	4.74	177,558.03	210.86	4U ⁴⁺ + 2O ²⁻ <--> 4U ³⁺ + O ₂	79.07	7,611.80	39.54	3,805.90	15.81	1,522.36	7.91	761.18	1.58
-	-	-	-	Total	1,812.45	174,477.24	906.22	87,238.62	362.49	34,895.45	181.24	17,447.72	36.25
DST/SST BLEND													
Fe ₂ O ₃	11	412,054.50	2,580.28	4Fe ³⁺ + 2O ²⁻ <--> 4Fe ²⁺ + O ₂	645.07	62,098.19	322.53	31,049.10	129.01	12,419.64	64.51	6,209.82	12.90
U ₃ O ₈	14.3	535,670.85	636.12	4U ⁴⁺ + 2O ²⁻ <--> 4U ³⁺ + O ₂	238.55	22,963.88	119.27	11,481.94	47.71	4,592.78	23.85	2,296.39	4.77
U ₂ O ₅	14.3	535,670.85	636.12	4U ⁴⁺ + 2O ²⁻ <--> 4U ³⁺ + O ₂	238.55	22,963.88	119.27	11,481.94	47.71	4,592.78	23.85	2,296.39	4.77
-	-	-	-	Total	1,122.16	108,025.94	561.08	54,012.97	224.43	21,605.19	112.22	10,802.59	22.44

DST = Double-shell tank
NCAW = Neutralized current acid waste
SST = Single-shell tank

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APPENDIX C

BASIS FOR VALUES IN TABLE 2-2

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C2.0	REFERENCES	C-4
C3.0	GLOSSARY	C-5

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APPENDIX C

BASIS FOR VALUES IN TABLE 2-2

This section describes the basis for the estimated oxygen release values cited in Table 2-2 of the text. In order to calculate the values, the following parameters were assumed.

C1.0 ASSUMPTIONS

Parameters

- The glass is being melted in the reference Hanford Waste Vittrification Plant liquid-fed ceramic melter (LFCM) at 1150 °C.
- The melt surface area is 2.26 m² (Herborn and Smith 1993).
- The amount of material involved in the reduction reactions at any point in time is equivalent to a 1-cm layer of feed material. Typical cold-cap thickness has been 5 to 10 cm in LFCM melter tests.
- The elemental composition of the material involved in the reduction reactions is the same as the glass formulation.
- The neutralized current acid waste (NCAW) and double-shell tank (DST)/single-shell tank (SST) blend glass compositions were obtained from Lambert and Kim (1994) and are assumed to be accurate. Waste loading in NCAW is 33 wt% and 50 wt% in the DST/SST blend, and is formulated for 1150 °C.
- The average temperature of the glass at the melt/cold-cap interface is 900 °C and the pressure is 1 atm.
- Oxygen behaves as an ideal gas at melt temperatures.
- The material involved in the reduction reactions has an average density for both the NCAW and DST/SST blend glass compositions of 2.00 g/cm³ at 900 °C (Cooper et al. 1994).
- All of the material for each constituent of significant concentration (cerium [Ce], chromium [Cr], iron [Fe], manganese [Mn], and uranium [U]) is present in the cold-cap at its +4, +6, +3, +3, and +6 states, respectively, before the reduction.
- All of the material for each constituent (Ce, Cr, Fe, Mn, and U) reduces completely to its +3, +3, +2, +2, and +5 states, respectively.

- The following reduction-oxidation reactions are representative (Schreiber et al. 1983):

Based on these assumptions, the following could be calculated:

Material volume = 0.0452 m³

Mass of material = 9.04 X 10⁴ g

1 gmol O₂ = 96.27 L O₂ at 900 °C.

Volume of Oxygen Released

Example for chromium (NCAW):

$$\begin{aligned} \text{Vol. O}_2 \text{ Released (L)} &= \frac{\text{Mass of Material} \times \text{Fraction of Species in Material}}{\text{mol weight of species}} \times \left(\frac{\text{Mol Ratio of Species to O}_2}{\text{based on redox Eqn.}} \right) \times \frac{\text{Vol. gas @ 900 C}}{\text{mol of species}} \\ &= \frac{(9.04 \times 10^4 \text{ g} \times 0.0026)}{\frac{151.992 \text{ g Cr}_2\text{O}_3}{\text{mol Cr}_2\text{O}_3}} \times \frac{2 \text{ mol Cr}}{1 \text{ mol Cr}_2\text{O}_3} \times \left(\frac{3 \text{ mol O}_2 \text{ Produced}}{4 \text{ mol Cr Reacted}} \right) \times \frac{96.27 \text{ L O}_2}{\text{mol O}_2} \\ &= 223.31. \end{aligned}$$

C2.0 REFERENCES

- Cooper, M. F., M. L. Elliott, L. L. Eyler, C. J. Freeman, J. J. Higginson, L. A. Mahoney, and M. R. Powell, 1994, *Research-Scale Melter Test Report*, PNL-9428, Pacific Northwest Laboratory, Richland, Washington.
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C3.0 GLOSSARY

ABBREVIATIONS AND ACRONYMS

DST	double-shell tank
LFCM	liquid-fed ceramic melter
NCAW	neutralized current acid waste
SST	single-shell tank

Table C-1. Summary of Calculations for Estimated Oxygen Release from Reduction of Higher Valence Elements of Significance.

NCAW								
Species	wt% in glass (%)	Mass involved (g)	Moles involved (mol)	% of element reduced =	Amount of oxygen liberated			
					100	100	50	50
				Reduction equation	(mol)	(L)	(mol)	(L)
CeO ₂	0.60	271.20	1.58	$4\text{Ce}^{4+} + 2\text{O}^{2-} \leftrightarrow 4\text{Ce}^{3+} + \text{O}_2$	0.40	37.92	0.20	18.96
Cr ₂ O ₃	0.26	117.52	0.78	$4\text{Cr}^{6+} + 6\text{O}^{2-} \leftrightarrow 4\text{Cr}^{3+} + 3\text{O}_2$	1.16	111.65	0.58	55.83
Fe ₂ O ₃	28.21	12,750.92	79.85	$4\text{Fe}^{3+} + 2\text{O}^{2-} \leftrightarrow 4\text{Fe}^{2+} + \text{O}_2$	39.93	3,843.23	19.96	1,921.60
MnO ₂	2.14	967.28	11.13	$4\text{Mn}^{3+} + 2\text{O}^{2-} \leftrightarrow 4\text{Mn}^{2+} + \text{O}_2$	2.78	267.77	1.39	133.90
U ₃ O ₈	4.74	2,142.48	2.55	$4\text{U}^{6+} + 2\text{O}^{2-} \leftrightarrow 4\text{U}^{5+} + \text{O}_2$	1.91	183.7	0.96	91.85
--	--	--	--	Total	46.17	4,444.26	23.10	2,222.13
DST/SST BLEND								
CeO ₂	2.73	1,233.96	7.17	$4\text{Ce}^{4+} + 2\text{O}^{2-} \leftrightarrow 4\text{Ce}^{3+} + \text{O}_2$	1.79	172.54	0.90	86.27
Cr ₂ O ₃	0.45	203.4	1.34	$4\text{Cr}^{6+} + 6\text{O}^{2-} \leftrightarrow 4\text{Cr}^{3+} + 3\text{O}_2$	2.01	193.24	1.01	96.62
Fe ₂ O ₃	11.00	4,972.0	31.13	$4\text{Fe}^{3+} + 2\text{O}^{2-} \leftrightarrow 4\text{Fe}^{2+} + \text{O}_2$	15.57	1,498.60	7.79	749.3
MnO ₂	1.82	82.26	9.47	$4\text{Mn}^{3+} + 2\text{O}^{2-} \leftrightarrow 4\text{Mn}^{2+} + \text{O}_2$	2.37	227.73	1.19	113.87
U ₃ O ₈	14.30	6,463.60	7.68	$4\text{U}^{6+} + 2\text{O}^{2-} \leftrightarrow 4\text{U}^{5+} + \text{O}_2$	5.76	554.18	2.88	277.1
--	--	--	--	Total	27.49	2,646.28	13.75	1,323.14

DST = Double-shell tank

NCAW = Neutralized current acid waste

SST = Single-shell tank

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APPENDIX D

MISCELLANEOUS FIGURES

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Figure D-1. The Solubility Dependence of Oxalic Acid
in Water on Temperature (Stephen 1963).

Figure D-2. Process Profile for the First Phase III Glycolic Acid Test from the Start of the Glycolic Addition (Smith and Wiemers 1994).

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Stephen, H. T., 1963, *Solubilities of Inorganic and Organic Compounds*, vol. 1, p. 377, The Macmillan Company, New York, New York.

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