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ACID WASTE SLURRY DURING PROCESSING WITH FORMIC ACID**

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REACTION SEQUENCES IN SIMULATED NEUTRALIZED CURRENT ACID WASTE SLURRY DURING PROCESSING WITH FORMIC ACID

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ABSTRACT

The Hanford Waste Vitrification Plant (HWVP) is being designed for the Department of Energy to immobilize high-level and transuranic wastes as glass for permanent disposal. Pacific Northwest Laboratory is supporting the HWVP design activities by conducting laboratory-scale studies using a HWVP simulated waste slurry. Conditions which affect the slurry processing chemistry were evaluated in terms of offgas composition and peak generation rate and changes in slurry composition. A standard offgas profile defined in terms of three reaction phases, decomposition of H_2CO_3 , destruction of NO_2^- , and production of H_2 and NH_3 was used as a baseline against which changes were evaluated. The test variables include nitrite concentration, acid neutralization capacity, temperature, and formic acid addition rate. Results to date indicate that pH is an important parameter influencing the $\text{N}_2\text{O}/\text{NO}_x$ generation ratio; nitrite can both inhibit and activate rhodium as a catalyst for formic acid decomposition to CO_2 and H_2 ; and a separate reduced metal phase forms in the reducing environment. These data are being compiled to provide a basis for predicting the HWVP feed processing chemistry as a function of feed composition and operation variables, recommending criteria for chemical adjustments, and providing guidelines with respect to important control parameters to consider during routine and upset plant operation.

INTRODUCTION

High-level radioactive wastes on the Hanford (Washington) site presently reside in underground tank facilities that are recognized as temporary storage. It is planned to permanently dispose of the high-level and transuranic wastes by incorporating them into a durable borosilicate glass matrix which, with accompanying engineered barriers, makes a degradation resistant waste package suitable for burial in an appropriate geologic setting. Vitrification will be carried out in the Hanford Waste Vitrification Plant (HWVP).

The waste is incorporated into a glass melter feed slurry in a multi-step process. One of those steps consists of adjusting the pH and redox potential of the waste with the addition of an organic acid (HCOOH).

The generation of H_2 and NH_3 has been observed during the processing of simulated Hanford waste slurry with HCOOH (Wiemers 1988). Ritter et al. (1992) have observed similar gas generation phenomena at the Savannah River waste vitrification pilot-scale facility. The reaction sequences during slurry processing, focusing on H_2 and NH_3 generation, are under investigation with the objective of mitigating the hazards associated with these compounds. Hydrogen generation can lead to serious safety issues because of the possibility of producing flammable gas mixtures. Ammonia generation can also result in serious safety issues through the production of NH_4NO_3 , an unstable, strong oxidizer particularly in the presence of organic compounds. This paper, prepared by staff at Pacific Northwest Laboratory (PNL),^(a) discusses the results of

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treating simulated Neutralized Current Acid Waste (NCAW) slurry (represents wastes resulting from the reprocessing of spent reactor fuel) with HCOOH under several variations of the reference processing conditions.

METHOD

The target composition and source chemicals for the NCAW slurry simulant are given in Table I. The slurry simulant preparation procedure followed steps that would approximate the production of the actual waste (Peterson et al. 1989), i.e., an acid nitrate solution containing many of the elements was made basic with NaOH and then washed to the proper nitrate level; NaNO₂ and Na₂CO₃ were added to achieve target levels.

Simulated waste slurry was treated with HCOOH using a laboratory-scale system and test steps simulating the slurry processing that will occur in the Hanford Waste Vitrification Plant slurry receipt and adjustment tank (SRAT) and slurry mix evaporator (SME). About 1.5 L of slurry containing between 125 and 140 g of waste oxide per L^(b) was placed in a 2-L pyrex reaction vessel and boiled for at least 10 min to remove dissolved gases. Then a predetermined amount of HCOOH was added to the slurry at a specific rate (e.g., 13.5 mM/min) at the test temperature. After the HCOOH addition was completed, the treated slurry was "digested" by boiling for 4 h. The offgas was measured continuously from the beginning of HCOOH addition to the shutdown of the test. Conditions for nine tests described in this paper are summarized in Table II.

The offgas composition was determined by periodically analyzing an Ar sweep gas flowing through the headspace of the reaction vessel during the slurry processing. The offgas analytical system consisted of tuned infrared detectors for CO₂, CH₄, N₂O, and NO_x, and a gas chromatograph to measure H₂. Methane, injected downstream from the reaction vessel, was used as a tracer gas to calculate total gas volume. Chemical analyses of slurry and condensate samples, including a determination of the amounts of HCOO⁻, NO₂⁻, and NO₃⁻ using ion chromatography and NH₄⁺ using a selective ion electrode, complimented the offgas data.

RESULTS AND DISCUSSION

HWVP NCAW Slurry Processing Chemistry

The offgas profiles, such as those shown in Figure 1, reflect the progression of chemical reactions that are believed to occur as HCOOH is added to the alkaline NCAW slurry. Three reaction stages have been observed and are characterized by specific chemical reactions as follows:

(b) Grams of waste oxide per liter (gWO/L) is the weight of the oxide residue that would result from drying and then calcining 1 L of slurry simulant at 1050°C for 2 h.

Table I. NCAW Slurry Simulant Target Composition and Source Chemicals

Cations	(mole %)	Source Chemicals	
Na ⁺	43.24	Na salts which supply most of the anions.	
Fe ⁺³	22.10	Added as a group as part of a separately prepared hydroxide slurry originally made up from nitrates and permanganate.	
Al ⁺³	11.13		
Zr ⁺⁴	7.64		
Ni ⁺²	1.93		
Mn ⁺⁴	1.55		
Si ⁺⁴ , Ti ⁺⁴	4.20, 0.52	SiO ₂ , TiO ₂	
Cd ⁺²	1.47	Cd(OH) ₂	
K, Rb, Cs	Σ0.56	Nitrates and hydroxides	
Ca, Mg, Ba, Sr	Σ1.59		
Nd, La, Ce	Σ1.73		
Cr, Mo, Zn	Σ0.71	Cr, Zn nitrate, Mo oxide	
Ag, Cu, Pb, Se, Te	Σ0.48 (0.01 to 0.19)	Ag, Pb nitrate, Se, Te oxides Cu sulfate	
Pd, Rh, Ru	Σ0.30 (0.05 to 0.19)	Hydroxide slurry made up from nitrates	
Anions	Moles/L at 125 gWO/L	Anions	Moles/L at 125 gWO/L
NO ₃ ⁻	0.116	SO ₄ ⁻²	0.010
NO ₂ ⁻	0.435	Cl ⁻	0.011
CO ₃ ⁻²	0.125	F ⁻	0.006
PO ₄ ⁻³	0.016	OH ⁻	—

Table II. Conditions for Nine Laboratory-scale HWVP Feed Preparation Tests with an NCAW Simulant

Test Parameter	Base Case	Acid-Base Neutralization				Temperature			HCOOH Add Rate	NO ₂
Test	1	2	3	4	5	6	7	8	9	
HCOOH Add. Amount (M)	2.53	2.56	1.96	2.45	2.29	2.29	2.29	2.22	1.22	
HCOOH Add. Rate (mM/min)	*	*	*	*		*	*	5.3	10.9	
HCOOH Add. Temp. (°C)	*	*	*	*	85	85	75	*	*	
Digestion Temp. (°C)	*	*	*	*	*	85*	75*	*	*	
Duration (h)	*	*	*	*	*	2,4	2,4	*	*	
Slurry Composition										
Modification										
Add NaOH (M)	*	0.50	0.50	0.50	*	*	*	*	*	
Nitrite - % nominal	*	*	*	30	*	*	*	*	0	

***nominal test conditions:**

HCOOH Add. Rate (mM/min) - 13.5

HCOOH Add. Temp. (°C) - 95

Digestion Temp. - boiling conditions (101°C to 102°C)

Digestion Duration (h) - 4

Slurry Composition

Modification

Add NaOH (M) - 0

Nitrite - % nominal - 100% (0.435 moles/L at 125 gWO/L)

Test 1

Figure 1. Baseline HCOOH Addition Test. Formic acid was added constantly at 13.5 mM/min starting at time zero. Detector problem degraded NO_x data, but start and finish are accurately indicated. Length of labeled arrow near top of figure indicates the extent of each reaction stage. Stage III continued to the end of the test.

Reactions (1) and (2) progress as the slurry is acidified with HCOOH. Based on the dissociation constants, H₂CO₃ (Equation 1) would be expected to decompose before HNO₂ (Equation 2). Reactions (3) and (4) are redox reactions between NO₂⁻ and HCOOH. Initiation of NO generation marks the shift into Stage II. Reduction of NO₂⁻ to N₂O (Equation 3) predominates at pH > ~6 and reduction of NO₂⁻ to NO (Equation 4) is favored at pH < ~6. Transition from Stage II to Stage III is believed to be, in part, due to depletion of NO₂⁻ to a "critical level." At this critical NO₂⁻ level, significant generation of H₂ from noble metal catalyzed decomposition of HCOOH (Equation 5) and reduction of NO₃⁻ to NH₃ (Equation 6) begin. A characteristic of Stage III is that significant amounts of H₂ and NH₃ are generated.

Rhodium is the most active catalyst for the decomposition of HCOOH into CO₂ and H₂ in neutralized high-level waste, Reaction (5). King (1993) has shown that Rh can be inhibited or activated, depending on the concentration of NO₂⁻ in the slurry. The transition from inhibited to activated catalyst for Rh corresponds to the transition from Stage II to Stage III chemistry during slurry processing. This behavior was also reported by Ritter (1992) for the Defense Waste Processing Facility feed processing. Data from PNL confirm these observations for HWVP NCAW feed type. The data suggest that the H₂ generation rate peaks observed just after transition to Stage III as indicated in the previous paragraph may be examples of NO₂⁻ enhancing

Rh catalytic decomposition of HCOOH at a critical HCOOH/NO₂⁻ mole ratio.

Samples taken following Stage III processing contained NH₄⁺ consistent with Reaction (6). The total CO₂ measured could be accounted for by assuming it was a result of NH₃ and H₂ production.

A fine-particulate, gray-black to black residue was observed during Stage III, Reaction (7). Semiquantitative analyses indicate that this material is enriched in the more "noble" metals contained in the slurry, such as Pd, Rh, and Ru as well as Cu, Ag, Te, Se, and Pb. Pourbaix (1974) diagrams for the above elements indicate an elemental stability field under the test conditions observed during Stage III. However, the oxidation state of the residue elements has not been positively identified.

Effect of Processing Variables on H₂ and NH₃ Generation

Four processing variables: acid neutralization capacity, reduced NO₂⁻, HCOOH addition rate, and temperature were evaluated with respect to their effect on offgas and NH₃ generation using the slurry described in Table I. Test 1 was used as a base case for comparison. Peak gas generation rates and the total amounts of gases measured are given in Table III.

Table III. Peak Gas Generation Rates and Total Amounts of Gas Measured During Nine Laboratory-Scale HWVP Feed Preparation Tests with an NCAW Simulant

Test	1	2	3	4	5	6	7	8	9
<u>Total (mM)</u>									
CO ₂	907	989	696	631	784	830	665	730	454
NO	.(a)	56.5	40.3	122	492	441	466	369	0.7
N ₂ O	36.9	245	247	23.3	31.6	36.2	33.0	83.0	0.6
H ₂	106	48.0	2.70	98.0	77.0	74.0	69.0	69.0	53
NH ₃ ^{(b)1}	64	44	.(c)	52	64	71	41	32	54
NH ₃ ^(d)	47	43	5.9	18 ^(e)	50	46	27	21	43
<u>Peak Rate (mM/min)</u>									
CO ₂	12.6	9.1	8.7	7.1	7.0	7.8	5.8	2.9	7.1
NO	.(a)	0.7	0.6	4.7	5.9	5.0	3.4	2.6	0
N ₂ O	1.5	2.6	2.5	0.6	0.7	1.5	0.6	0.6	0
H ₂	0.8	0.5	0.03	1.34	0.9	0.4	1.0	0.7	0.30

(a) Detector problem - data unreliable

(b) Calculation based on quantity of CO₂ released in excess of that accounted for by other observed reaction products during Stage III. The stoichiometry is based on Equation 8.

(c) Calculation not made because CO₂ was being generated by the reaction of nitrite with HCOOH over the period of interest during this test.

(d) Ammonia was measured as NH₄⁺ in the slurry and condensate. Ammonia carried in the sweep gas downstream from the condensate trap was not measured.

(e) The reason for the discrepancy between the measured and calculated NH₄⁺ values is not known. The calculated value is consistent for other tests.

Acid Neutralization Capacity and Reduced Nitrite

To test increased acid neutralization capacity, 0.50 M of NaOH was added to about 1.5 L of the slurry for Tests 2, 3, and 4. Test 4 contained 30% nominal NO_2^- to illustrate the effects of reduced NO_2^- concentration. The changes in these two chemical parameters resulted in three observable changes in the offgas profiles as compared with the base line test and with each other. First, as illustrated by Figure 2, the increased basicity of Tests 3 and 4 delayed the drop in the system pH compared to Test 1 and consequently delayed the onset of carbonate decomposition by the amount of time needed to add 0.50 M of HCOOH ($0.50 \text{ M}_{\text{NaOH}}/0.0135 \text{ M}_{\text{HCOOH}}/\text{min} = 36.6 \text{ min}$). Second, as illustrated in Figure 3, for equivalent amounts of NO_2^- , reduction of NO_2^- to N_2O (Equation 3) is favored over NO generation (Equations 2 and 4) in the more alkaline systems (compare Tests 1 and 2). When the NO_2^- concentration is reduced as in Test 4, the reaction between HCOOH and NO_2^- again favors NO generation. {Note that reduction of NO_2^- to N_2O (Equation 3) consumes twice the HCOOH as the reaction producing NO (Equation 4). This appears to buffer the slurry during Test 2 and would account for the pH remaining higher during that test.} Third, as illustrated by Figure 4, at equivalent NO_2^- concentration (Tests 1 and 2), a reduced H_2 generation rate was observed in more alkaline systems. This may be related to the amount of undissociated HCOOH, perhaps the key reactant in H_2 production. The significantly higher peak H_2 generation observed in Test 4 is attributed to the high HCOOH/ NO_2^- ratio as discussed in the next section. Generation of NH_3 did not show a strong trend with respect to pH or NO_2^- concentration in these tests. It appears that pH is a controlling factor for reaction pathways and that some critical concentration of $\text{HNO}_2/\text{NO}_2^-$ and HCOOH must be present in the slurry before some reactions will proceed.

Reduced Nitrite Concentration

Lower NO_2^- concentrations were observed to yield higher H_2 generation rates with approximately equivalent amounts of HCOOH added (compare Test 4 and Test 1 in Table III). When NO_2^- is not added, as in Test 9, the H_2 generation is reduced, presumably because no NO_2^- was present to enhance the catalytic activity of Rh. The amount of NH_3 generated in the absence of added NO_2^- was approximately the same as the baseline case (refer to Table III). It was expected that the amount of H_2 generated would correlate better with the amount of NH_3 generated than observed. The almost complete lack of N_2O or NO during Test 9 indicated that the source of these oxides under the processing conditions is almost 100% due to NO_2^- rather than NO_3^- reduction.

Reduced HCOOH Addition Rate

The rate of HCOOH addition was reduced by a factor of 2.5 in Test 8 compared with the baseline case. The rate of HCOOH addition did not appear to have a significant effect on the rate of H_2 generation or the total amount of NH_3 generated (when compared with tests with equivalent amounts of HCOOH added). This is reasonable, because H_2 and NH_3 generation occurs primarily after HCOOH addition is completed. A generation rate that was proportional to the HCOOH addition rate was measured for gases that were generated during HCOOH addition (CO_2 , NO, and N_2O).

Correlation Between pH and CO₂ Generation Rate Profiles

Figure 2. Comparison of Test 1 (Baseline) and Tests 2 and 4 (0.50 M NaOH Added) Showing the Delay of CO₂ Generation Due to Added Base. Time is measured from the start of HCOOH addition for each test.

Nitric and Nitrous Oxide Profiles

Figure 3. Comparison of the NO_x and N₂O Offgas Profiles for Tests 1, 2, and 4. Time is measured from the start of HCOOH addition. The NO_x profile for Test 1 was not included because its shape has been distorted, and it would have been offscale on this diagram.

Hydrogen Generation Rate with Corresponding pH Profiles

Figure 4. Comparison of the H_2 Generation Peak Profiles for Tests 1, 2, and 4. Test 3 data were not included because the amounts of H_2 generated were very small and would not show up on the scale of the diagram. Time is measured from the beginning of $HCOOH$ addition.

Reduced Processing Temperature

The sensitivity of H_2 peak generation rate to process temperature control was demonstrated in Tests 5, 6, and 7. These tests varied in the temperature at which $HCOOH$ was added ($85^\circ C$, $85^\circ C$, and $75^\circ C$ respectively) and the time interval between the end of $HCOOH$ addition and of temperature ramp up to boiling (0 h, 2 h, 2 h, respectively). The baseline case (Test 1) was conducted at $95^\circ C$ with immediate ramp up to boiling after $HCOOH$ addition was complete. For Test 5 ($85^\circ C$, 0-h hold), the reaction sequence was transitioning into Stage III (i.e., significant H_2 generation was initiated) as the temperature ramp up was started. The H_2 generation rate was comparable with the baseline case. For Test 6 ($85^\circ C$, 2-h hold), Stage III was initiated 1.6 h before temperature ramp up was started. Two H_2 generation peaks were observed, before and after boiling. Both peaks were reduced by $\sim 50\%$ compared with the baseline case. For Test 7 ($75^\circ C$, 2-h hold), the reactions were significantly drawn out during Stage I and Stage II. For Test 7, the transition to Stage III occurred as the temperature ramp up was under way, resulting in a H_2 generation rate comparable to the baseline case. The amount of NH_3 generated was comparable to the baseline case for tests conducted at $85^\circ C$, and slightly lower for the test conducted at $75^\circ C$.

CONCLUSIONS

The peak generation rates of CO_2 , NO , and N_2O were found to be linearly proportional to the addition rate of $HCOOH$.

The acid neutralization capacity of a slurry establishes a relationship for that slurry between the amount of acid added and the amount of other reactive slurry components present at a given pH. This can lead to divergent reaction paths resulting in different NO_2^- reduction mechanisms, a considerable difference in pH at the completion of NO_2^- reduction, and a clear difference in H_2 generation rate in Stage III of the tests. The peak H_2 generation rate was reduced in alkaline

systems. At lower processing temperatures, the peak H_2 generation rate was reduced. These studies suggest that process control parameters for the mitigation of H_2 generation might include pH and temperature.

Hydrogen generation may also be reduced by maintaining the NO_2^- concentration in the processing slurry above the critical level required for catalyst inhibition. This value will need to be quantified.

It is not clear from these studies that in the presence of noble metals, NH_3 generation will be significantly reduced in the absence of H_2 production.

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