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EFFECTS OF Pd, Rh, AND Ru CONCENTRATION
ON HCOOH DECOMPOSITION DURING THE PROCESSING
OF NCAW WASTE SIMULANT

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**EFFECT OF Pd, Rh, AND Ru CONCENTRATION ON HCOOH DECOMPOSITION
DURING THE PROCESSING OF NCAW WASTE SIMULANT**

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ABSTRACT

The noble metals Pd, Rh, and Ru^{that} are present in the Hanford high-level waste ~~that~~ will be processed into a melter feed for vitrification and permanent disposal. The treatment of waste slurry with HCOOH, a step in producing a melter feed, results in the production of H₂ and NH₃ due to the catalytic activity of the noble metals. The presence of H₂ and NH₃ could lead to hazardous conditions in a treatment facility. This study determined the relationship between noble metals concentration and H₂ and NH₃ production for application in future pilot-scale studies and prediction of catalytic activity for a waste with known noble metals concentration. Hydrogen production increased as noble metals concentration increased until a saturation level was reached. Ammonia production increased with noble metal concentration. Due to the limited number of tests, these relationships require confirmation.

INTRODUCTION

The Hanford Waste Vitrification Plant (HWVP) is being designed for the U.S. Department of Energy (DOE) to immobilize high level and transuranic wastes as glass for permanent disposal. Pacific

Northwest Laboratory* is supporting the HWVP project by conducting laboratory-scale studies of the HWVP feed preparation chemistry. These studies were performed using a simulated (nonradioactive) pretreated neutralized current acid waste (NCAW). Neutralized current acid waste is a high-level waste originating from the plutonium/uranium extraction (PUREX) plant that has been partially denitrated with sugar, neutralized with NaOH, and presently stored in double-shell tanks (Peterson, Scheele, and Tingey 1989).

The objective of the current study is to determine the effect of noble metal concentration in the waste on H_2 and NH_3 production during the batch preparation of melter feed. The noble metals, Pd, Ru, and Rh, are present in the waste as uranium fission products and are catalytically active toward H_2 production (Wiemers 1988). The Savannah River waste vitrification pilot-scale facility observed similar gas generation phenomena (Ritter, Zamecnik, and Hsu 1992). 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 , which is an unstable, strong oxidizer, particularly in the presence of organic compounds.

PROCEDURES

A NCAW simulant was prepared for this study by a procedure that simulated the process history of the waste. The composition of the simulant (Table I) included the same components found in the waste with the exception of using surrogates for radioactive and toxic compounds. Noble metals were added to the simulant by means of a noble metals hydroxide slurry. The mole ratio of noble metals in the slurry was 1.21:1.00:3.70 for Pd:Rh:Ru. The nominal concentration of noble metals in the slurry is shown in Table I.

* Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

Table I. NCAW Simulant Composition

Oxide	Weight Percent	Moles Element/L Feed (125 gW0/L)	Oxide	Weight Percent	Moles Element/L Feed (125 gW0/L)
Ag ₂ O	1.22e-01	1.32e-03	Nd ₂ O ₃	3.56e+00	2.64e-02
Al ₂ O ₃	9.25e+00	2.27e-01	NiO	2.35e+00	3.93e-02
B ₂ O ₃	5.86e-03	2.10e-04	P ₂ O ₅	8.70e-02	5.60e-03
BaO	1.79e-01	1.46e-03	PbO ₂	7.15e-01	3.74e-03
CaO	8.06e-01	1.80e-02	PdO	1.23e-01	1.26e-03
CdO	3.08e+00	3.00e-02	Pr ₂ O ₃	1.56e-01	1.18e-03
CeO ₂	6.56e-01	4.77e-03	Rb ₂ O ₃	5.87e-02	6.70e-04
Cr ₂ O ₃	2.67e-01	4.39e-03	Rh ₂ O ₃	1.06e-01	1.04e-03
Cs ₂ O	6.12e-01	5.43e-03	Ru ₂ O ₃	3.87e-01	3.85e-03
CuO	2.50e-01	3.93e-03	SO ₃	6.69e-01	1.04e-02
F	9.90e-02	6.52e-03	Sb ₂ O ₃	5.95e-03	5.11e-05
Fe ₂ O ₃	2.88e+01	4.51e-01	SeO ₂	1.61e-02	1.82e-04
GeO ₂	1.56e-04	1.86e-06	SiO ₂	4.11e+00	8.56e-02
I	4.60e-06	4.53e-08	Sm ₂ O ₃	7.72e-02	5.54e-04
K ₂ O	2.00e-01	5.32e-03	SnO	1.08e-02	9.99e-05
La ₂ O ₃	6.67e-01	5.12e-03	SrO	1.21e-01	1.46e-03
Li ₂ O	7.23e-05	6.05e-06	Ta ₂ O ₅	3.39e-03	1.92e-05
MgO	3.72e-01	1.15e-02	TeO ₂	1.01e-01	7.94e-04
MnO ₂	2.19e+00	3.15e-02	TiO ₂	6.66e-01	1.04e-02
MoO ₃	5.70e-01	4.95e-03	Y ₂ O ₃	8.17e-02	9.04e-04
Na ₂ O	2.19e+01	8.82e-01	ZnO	3.41e-01	5.24e-03
Nb ₂ O ₃	1.03e-02	1.10e-04	ZrO ₂	1.54e+01	1.56e-01

Anions	moles anion/L
NO ₃	1.16e-01
NO ₂	4.35e-01
Cl ⁻	1.06e-02
SO ₄ ⁻	1.03e-02
CO ₃ ⁻	1.25e-01
F ⁻	6.42e-03
TOC	1.39e-02
I ⁻	4.46E-08

Four tests were conducted with different noble metals concentrations; one at nominal concentration (100%) and three with reduced noble metals concentration (10%, 25%, 50% of the nominal noble metals concentration).

The simulated waste slurry was treated with HCOOH using a laboratory-scale system and test steps simulating the slurry processing that will occur in the HWVP 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 liter (gWO/L)* was placed in a 2-L Pyrex reaction vessel (Figure 1) and boiled for at least 10 min to remove dissolved gases. Then, a predetermined amount of HCOOH (approximately 136 g) was added to the slurry at a specific rate (0.6 g/min) at test temperature 95°C. The addition of HCOOH is referred to as forming. After forming was completed, the treated slurry was "digested" by boiling for approximately 4 h. The off gas was measured continuously from the beginning of the HCOOH addition to the completion of the test. A schematic of the off gas system is shown in Figure 2.

The off gas composition was determined by periodically analyzing an Ar gas that swept through the head space of the reaction vessel during the slurry processing. The off gas analytical system consisted of a gas chromatograph (GC), which measured H₂, CO₂, and N₂O, and a NO_x analyzer, which measured NO and NO_x gases. Helium was used as a tracer to determine the gas flowrate in the system. Slurry and condensate samples were taken before forming, after forming but before digestion, and after digestion. The samples were analyzed for COOH⁻, NO₂⁻, and NO₃⁻ using ion chromatography, and for NH₃ using a selective ion electrode.

RESULTS AND DISCUSSION

The off gas profiles for the four tests with 10%, 25%, 50% and 100% nominal noble metals concentration are shown in Figure 3 and Figure 4. Three reaction stages can be identified in the

* Grams of waste oxide per liter is the weight of the oxide residue that would result from drying and calcining 1 L of slurry simulant at 1050°C for 2 hours.

profiles. These stages were defined by Smith, et al. (1993) in previous work. The reactions in each stage are shown below.

Stage I and II reactions occur during forming while stage III reactions occur during digestion. Hydrogen and NH_3 are produced during stage III; therefore, stage III is of primary interest for this study.

Figure 5 shows the H_2 off gas profiles for the four noble metals concentrations. It is evident from Figure 5 that noble metals concentration causes only a slight difference in the start times of H_2 generation relative to the start of HCOOH addition. Based on the four tests performed, it appears that the maximum H_2 generation rate increases with increasing noble metals concentration, and reaches a threshold between 10% and 25% nominal noble metals concentration (Figure 6). The data are normalized with respect to the slurry volume, which varied from 1.1 to 1.3 L. It should be noted that repeat tests were not performed, and therefore scatter in the data was not evaluated.

The slope of the initial H_2 generation rate peak increases with increasing noble metals concentration, with the exception of the 50% test (Figure 7). The slopes of the 50% and 25% tests are very similar, and the difference observed may be attributed to experimental error. It is difficult to distinguish between a linear trend or a trend leading to a threshold because of the limited data. The slope signifies the rate of increase in the H_2 generation rate; these data are important in designing a ventilation system for removing H_2 gas in a batch process.

The total H_2 measured in each test is shown in Figure 8. This value was calculated using the area under the generation rate curve over a time interval that started at 0 min and ended at 444 min. The ending time was selected based on the test with the shortest run time. Three of the tests ran longer than 444 min and would have resulted in inflated H_2 values if the area was calculated over the entire length of the test. The data was also normalized with respect to slurry volume. Figure 8 shows that the amount of H_2 produced increases with increasing noble metal concentration and, like the peak generation rate, reaches a threshold value. A possible explanation of this behavior may be that at low noble metal concentrations, $HCOOH$ decomposition is limited by the amount of catalyst (noble metals) present. As the amount of catalyst increases, the reaction reaches a point where it becomes reaction rate limited. Increasing the catalyst at this point will no longer increase the reaction rate. It should be noted that the amount of $HCOOH$ was in excess and therefore not a limiting factor.

Experiments performed by King et al. (1993 and 1994) found that H_2 increased linearly with respect to Rh concentration. Langowski et al. (1993)* also noted an increase in measured H_2 with respect to noble metal concentration while performing studies on radioactive NCAW simulant.

It was observed that the behavior of the 10% nominal noble metal test was very different than the other tests. The off gas profile shapes were similar in the 25%, 50%, and 100% test for all the gases measured, while the off gas profile shapes of the gases in the 10% test were different. Specifically, the H_2 peak was significantly smaller, broader, and lagged behind the peaks of the other tests. This behavior may have resulted from the reduction in noble metal concentration and a higher NO_2^- concentration (Table II) before H_2 evolution. The catalytic behavior of the noble metals is sensitive to the NO_2^- concentration. At high and low concentrations of NO_2^- , the catalyst is inhibited (Smith et

* Langowski, M.H., E.V. Morrey, J.M. Tingey, M.R. Beckett. 1993. *Offgas Characterization from the Radioactive NCAW Core Samples (102-AZ-C1) and Simulant During HWVP Feed Preparation Testing*. PHTD-C93-03.08A, Pacific Northwest Laboratory, Richland, Washington.

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al. 1993). The initial NO_2^- concentrations of slurries were the same for all the tests. However, the NO_2^- consumption in the 10% nominal noble metal test was less than in the other tests. A repeat of the 10% test is necessary because of the emphasis place on this point in identifying data trends.

Table II. Slurry NO_2^- Concentration Measured During Tests

Noble Metal Concentration (% of Nominal)	Initial NO_2^- Concentration (g/L)	Post Formating NO_2^- Concentration (g/L)	Post Digestion NO_2^- Concentration (g/L)
10%	25.3	10.3	<0.2
25%	23.2	0.63	<0.2
50%	23.1	<0.2	<0.2
100%	21.1	<0.2	<0.2

Ammonia is produced during stage III by a decomposition of NO_3^- and HCOOH (Reaction 6). Figure 9 shows that the total NH_3 measured increases linearly as noble metal concentration increases. H_2 promotes NH_3 production (Reactions 8 and 9), which explains the dependence of NH_3 on noble metal concentration.

Reactions 8 and 9 are intermediate reactions for Reaction 6. The reduction of NO_3^- by HCOOH to form NH_3 during NCAW melter feed preparation was first predicted by Wiemers et al. in 1990*. Subsequent experiments in 1991** and 1992*** observed the

* Wiemers, K.D. 1990. *The Effect of HWVP feed Nitrate and Carbonate Content on Glass Redox Adjustment*. HWVP-90-1.2.2.03.03A, Pacific Northwest Laboratory, Richland, Washington.

** Wiemers, K.D., M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an*

relationship between NH_3 and H_2 production but the mechanism of the reaction is not clearly understood and needs further study.

CONCLUSION

This study has shown the relationship between the concentration of noble metals (Pd, Rh, and Ru) in a simulated NCAW waste slurry and the production of H_2 gas and NH_3 . The noble metals catalyze the production of H_2 , which in turn promotes NH_3 production. Within the concentration range tested, decreasing the noble metal concentration will decrease the amount of H_2 produced. A decrease in noble metal concentration does not have a significant effect on the H_2 generation rate until the noble metal concentration is reduced to below 25% of its nominal value. The observed relationship between noble metal concentration and the H_2 generation rate may be coupled to a higher NO_2^- concentration at the initiation of the H_2 peak in the 10% nominal noble metals test as compared to the 25%, 50% and 100% tests. Higher NO_2^- would be expected to reduce H_2 generation. These observations are significant to mitigation efforts, which focus on reducing the H_2 generation rate and NH_3 production. NH_3 increases as the noble metal concentration increases, which is expected since NH_3 is related to H_2 production.

These experiments suggest general trends that may be expected as a result of modifying noble metal concentration. The data is limited and repeat experiments are necessary to confirm the findings of these experiments. Other noble metal concentrations should be tested as well. If differences in observed H_2 generation rates between the tests are determined by plant design

NCAW Simulant--Fiscal Year 1991: Evaluation of Off gas Generation, Reductant Requirements and Thermal Stability.
PHTD-93-K899, Rev. 0, Pacific Northwest Laboratory,
Richland, Washington.

*** Smith, H.D., K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal Year 1992: Evaluation of Off gas Generation and Ammonia Production.* PHTD-C93-03.02, Pacific Northwest Laboratory, Richland, Washington.

criteria to be significant, then additional tests must be conducted before relying on the current data. Work is continuing on understanding the mechanisms involved in this complex system.

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Figure 1. Off gas Reaction Vessel in Which Tests Were Performed

Figure 2. Offgas Measurement Apparatus

(a) 10% Nominal Noble Metals

(b) 25% Nominal Noble Metals

Figure 3. Gas Generation Data for Experiments with 10% and 25% Nominal Noble Metals Concentration

Figure 4. Gas Generation Data for Experiments with 50% and 100% Nominal Noble Metals Concentration

Figure 5. Hydrogen Generation Rates as a Function of Time for Four Noble Metals Concentrations

Figure 6. Maximum H₂ Generation Rate for Four Tests

Figure 7. Maximum Slope for Four Tests

Figure 8. Hydrogen Measured During the Time Interval 0-444 min

Figure 9. Ammonia Measured During Digestion

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