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# MERCURY-NITRITE-RHODIUM-RUTHENIUM INTERACTIONS IN NOBLE METAL CATALYZED HYDROGEN GENERATION FROM FORMIC ACID DURING NUCLEAR WASTE PROCESSING AT THE SAVANNAH RIVER SITE – 136c

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## ABSTRACT

Chemical pre-treatment of radioactive waste at the Savannah River Site is performed to prepare the waste for vitrification into a stable waste glass form. During pre-treatment, compounds in the waste become catalytically active. Mercury, rhodium, and palladium become active for nitrite destruction by formic acid, while rhodium and ruthenium become active for catalytic conversion of formic acid into hydrogen and carbon dioxide. Nitrite ion is present during the maximum activity of rhodium, but is consumed prior to the activation of ruthenium. Catalytic hydrogen generation during pre-treatment can exceed radiolytic hydrogen generation by several orders of magnitude. Palladium and mercury impact the maximum catalytic hydrogen generation rates of rhodium and ruthenium by altering the kinetics of nitrite ion decomposition. New data are presented that illustrate the interactions of these various species.

## INTRODUCTION

Legacy radioactive high-level waste (HLW) generated at the Savannah River Site (SRS) during production of enriched uranium and plutonium during the Cold War is currently being processed in the Defense Waste Processing Facility (DWPF) into a stable borosilicate glass waste form for long term storage. Generally radionuclides account for less than 10% of the solid waste mass. Hydrous oxides of iron, aluminum, manganese, nickel and calcium are some of the main components. The majority of the legacy waste is stored in large cylindrical storage tanks at SRS. These 3.5-4.9 thousand cubic meter (900,000-1,300,000 gallon) carbon steel storage tanks also contain 5-7M sodium solutions rich in hydroxide, nitrate, and nitrite anions. Most SRS tank farm processes involve the transport of two phase slurries between tanks and the decanting of excess aqueous phases for processing in the tank farm evaporators. Batch feed preparation for DWPF involves washing the aqueous phase of slurries obtained from one or two waste tanks to about a 1M sodium concentration. A DWPF feed batch is typically about 1-2 thousand cubic meters of washed slurry.

The DWPF brings the washed sludge slurry into the Sludge Receipt and Adjustment Tank (SRAT) to begin batch processing. About 25 dm<sup>3</sup> are processed at a time. The SRAT is the primary chemical pretreatment vessel in the DWPF. The SRAT is operated like a batch reactor. Acids are added to adjust the rheology, dissolve some of the alkaline earth and transition metal compounds, convert HgO to elemental mercury for steam stripping, destroy some of the existing anions such as carbonate and nitrite, and chemically reduce a portion of the MnO<sub>2</sub> to Mn<sup>2+</sup>. (Chemical reduction is desirable since thermal reduction of Hg and Mn in the DWPF melter can lead to reduced melter throughput foam formation.) Optimal

performance of the DWPF waste glass melter requires a balance of chemical oxidizers and reductants in the feed in order to avoid foaming and prevent precipitation of metals. The balance is achieved by dividing the SRAT acid demand between nitric acid (oxidizer) and formic acid (reductant).

The legacy HLW contains small concentrations (1-200 ppm) of noble metals formed from  $^{235}\text{U}$  thermal neutron fission product decay chains. In particular, the HLW contains Ru, Rh, and Pd in the approximate relative proportions of 3.75 to 1 to 0.52. These species become catalytically active during formic acid addition at 93 °C. HgO also reduces to elemental Hg once formic acid becomes available under acidic conditions. Catalytic activity was originally identified during lab-scale nuclear waste processing over fifteen years ago (1), and the potential for catalytic hydrogen generation was studied just prior to completion of the DWPF design. The chemical reaction catalyzed by the noble metals is given by:



The planned DWPF air purge system, used to keep the process equipment under slight negative pressure, was redesigned to permit a large flow of purge air through the SRAT in order to dilute hydrogen below the lower flammable limit (LFL). Much subsequent experimental work was performed with the goal of ensuring that operating conditions would be selected that produced hydrogen concentrations below the LFL in the available air purge.

Catalytic hydrogen generation can be three or more orders of magnitude greater than radiolytic hydrogen generation when noble metals are at their most active state. This creates the potential for the formation of flammable or explosive air-hydrogen mixtures in the SRAT off-gas system. The DWPF analyzes the hydrogen concentration of the off-gas once per minute using a pair of redundant gas chromatographs. Catalytic hydrogen generation, however, can effectively be interrupted by dropping the temperature from 93-103 °C to less than 60 °C, whereas radiolytic hydrogen generation is not impacted by temperature.

Changes in the preparation of the legacy HLW sludges have been made to reduce the amount of decanted wash water. These less washed feeds have resulted in DWPF SRAT cycles that require proportionately more acid to process (more hydroxide, carbonate, nitrite per unit volume). This evolution in operating doctrine has constrained the quantity of acid that can be added during pre-treatment relative to the minimum required to accomplish various processing controls in the DWPF. This in turn has brought a renewed interest in understanding the nature of catalytic hydrogen generation and in seeking means to better control and/or eliminate it. Consequently, several new rounds of experimental work were authorized to better understand the process chemistry.

## EXPERIMENTAL PROGRAM

The need to produce a large volume of melter feed simulant that would require many lab-scale SRAT cycles provided an opportunity to design a matrix of tests that contained individual noble metals in the bulk sludge solids. These tests confirmed some earlier hypotheses about catalytic hydrogen generation. These tests, however, required the exclusion of mercury. Two subsequent tests were performed at smaller scale using a single noble metal combined with mercury in the bulk sludge solids. The results were used to design a statistical

matrix of testing at smaller scale focused on the three most significant elemental species: Rh, Ru, and Hg. A full factorial design was conducted with each factor at either a high or low level (8 tests), plus three tests at the matrix midpoint. The same bulk sludge solids were available for all of these tests, in other words many factors that normally vary from test program to test program were held constant throughout these studies. The starting concentration of nitrite ion in the feed was the same during a series of over forty tests.

New data for the Ru-sludge system show that ruthenium does not become catalytically active for hydrogen generation in the presence of an excess of nitrite ion, but that ruthenium does become catalytically active once nitrite ion is brought to concentrations below that of ruthenium, Figure 1.

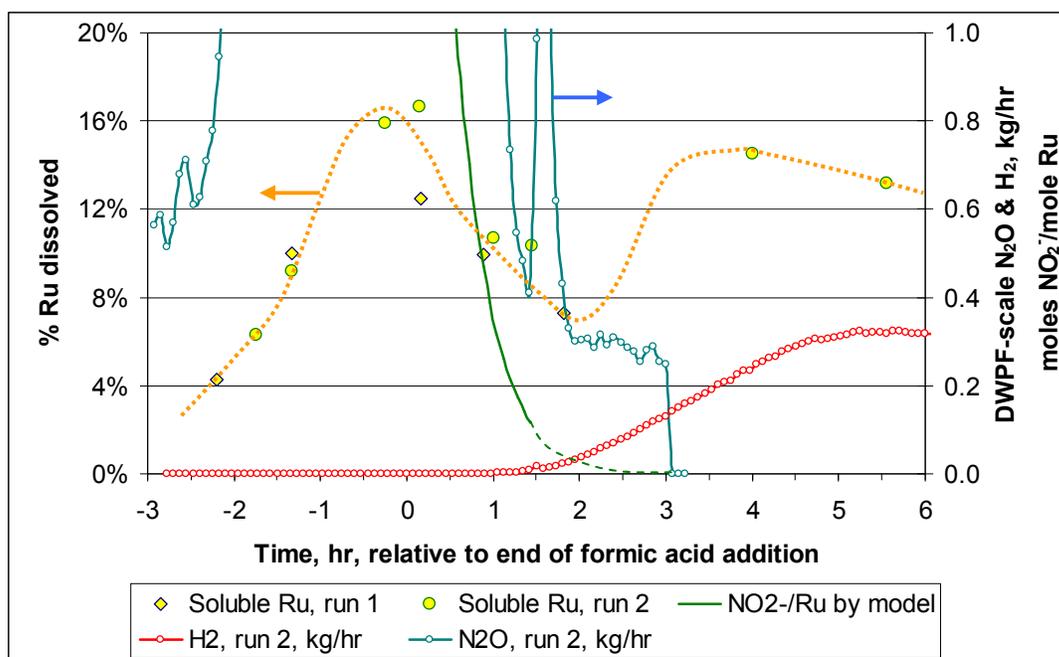


Figure 1. Relative timing of events related to Ru-catalyzed hydrogen generation in the absence of mercury, including nitrite destruction and associated  $N_2O$  generation.

The nitrite ion concentration data correlate well with the  $N_2O$  off-gas data with respect to the timing of complete nitrite destruction at about three hours after formic acid addition. The amount of nitrite ion present at the onset of hydrogen generation at one hour past formic acid addition is less than 0.5 mole nitrite ion per mole Ru, indicating that nitrite is losing its potential effectiveness as an inhibitor for Ru catalyzed hydrogen generation.

The addition of mercury to the single noble metal system with Ru produced several effects, Figure 2. The first was the accelerated conversion of nitrite to NO at the expense of  $N_2O$  that was observed in the off-gas data. This shift was most obvious in the  $N_2O$  data, but it was supported by additional evidence of  $O_2$  depletion from the conversion of NO to  $NO_2$ . Second, nitrite destruction finished nearly an hour earlier in the Hg-Ru-sludge system than in the Ru-sludge system. As shown in Figure 2, the  $N_2O$  peak ended about an hour earlier, and the onset of hydrogen generation coincided with the end of nitrite destruction in both cases.

The impact of an earlier onset of hydrogen generation had a minimal impact on the peak rate or the timing of the peak rate at about 5.5 hours after formic acid addition.

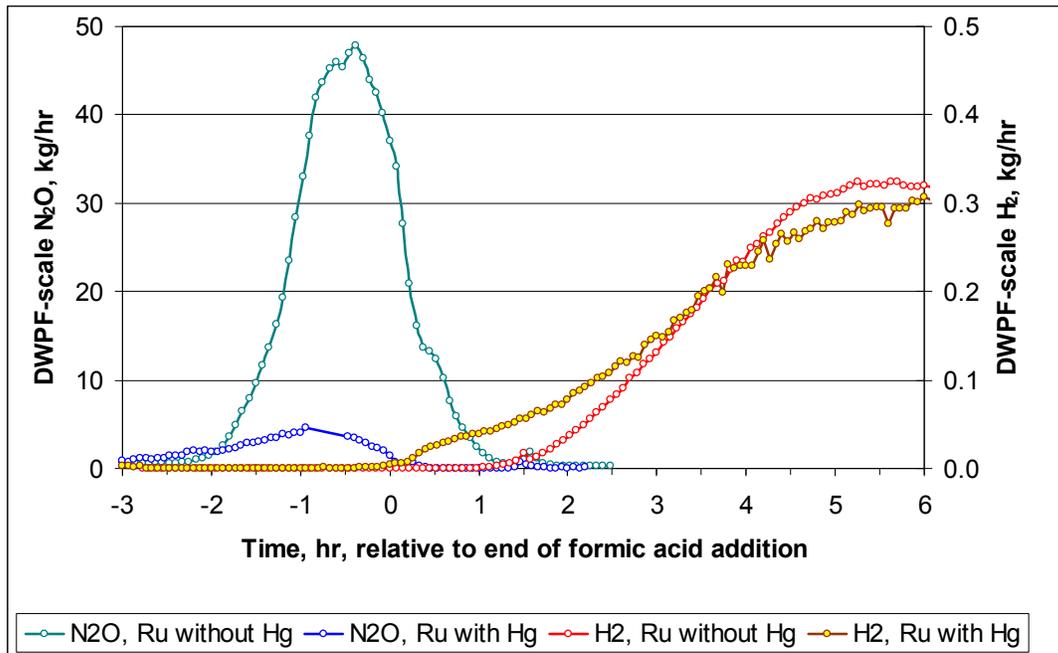


Figure 2. Impact of Hg on Ru catalysis of formic acid to produce hydrogen

Data on Ru in the supernate were obtained only after the onset of hydrogen in the Hg-Ru-sludge test, but the data overlaid the data from the two runs using Ru-sludge during this period. No evidence for a direct impact of Hg on the partitioning of the Ru between the supernate and insoluble solids was seen.

The most active catalytic form of Rh during the SRAT cycle appears to be a nitro-Rh complex. Such a complex was first proposed by King and Bhattacharyya during 1992-3 testing under contract to SRS and also in (2). Rh has now been identified as also catalyzing the destruction of nitrite ion to nitrous oxide and carbon dioxide during formic acid addition. This reaction probably involves one form of a nitro-Rh complex,  $\text{Rh}(\text{NO}_2)_n^{3-n}$ . The presence of Rh at 0.2 wt% in the total solids caused the production rate of  $\text{N}_2\text{O}$  to more than double compared to tests with no noble metals. At high nitrite ion concentrations the Rh is believed to be present as a hexanitro-Rh complex,  $\text{Rh}(\text{NO}_2)_6^{3-}$ . Gradual destruction of nitrite ion leads to eventual substitution of one or more of the nitrite ligands with other species ( $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , formate, etc.).

New data show that it is during the period near the end of nitrite destruction that Rh becomes an excellent catalyst for converting formic acid into hydrogen and carbon dioxide. Figure 3 shows, however, that the Rh catalyzed hydrogen generation period occurs before the nitrite is entirely destroyed.

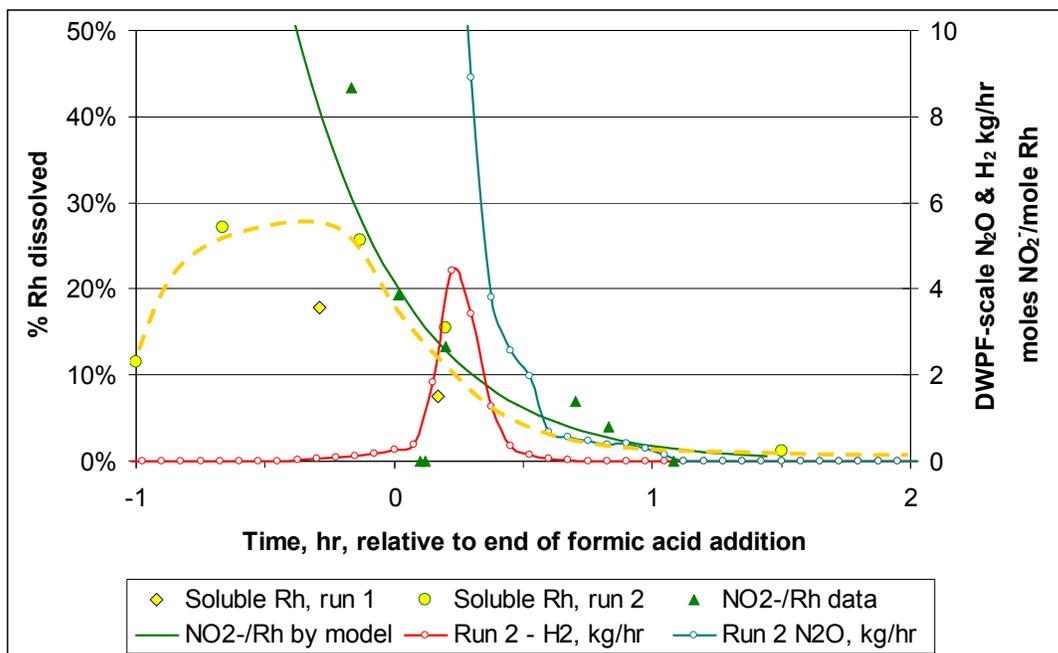


Figure 3. Hydrogen generation goes through a maximum near the time when the ratio of total nitrite to total Rh is between two and four.

The Rh is partitioned between the aqueous and insoluble solid phases, but it is not clear whether or not the nitro-Rh complex is stable and active adsorbed onto the insoluble solid surfaces or is only active in the aqueous phase. The ratio of nitrite to Rh in the aqueous phase alone could be as high as twenty to one at the maximum hydrogen generation rate based on the available data. In any case, a condition is reached where one or more of the ligands can be substituted with formate and/or other ions to permit the conversion of formic acid to hydrogen. One unresolved analytical issue is whether or not the nitrite ions complexed onto the Rh can be detected by ion chromatography (the nitrite ion has to be solubilized for detection).  $N_2O$  data are included in Figure 3 to show that nitrite destruction was not completed prior to the hydrogen generation rate maximum at about ten minutes after formic acid addition.

The virtual completion of nitrite destruction (by the  $N_2O$  trace) about 30-35 minutes after formic acid addition corresponds with the end of the peak in the hydrogen generation rate. This indicates that the initial deactivation mechanism for the nitro-Rh complex is the elimination of the nitrite ligands and simultaneous destruction of the nitro-Rh complex. The kinetics of nitrite destruction appears to be controlling both the activation and the deactivation of the nitro-Rh complex form that catalyzes hydrogen generation. The nitro-Rh complex is currently the catalyst of primary concern. Although there is more Ru than Rh in HLW, the activity of the nitro-Rh species exceeds that of whatever Ru species catalyzes hydrogen generation (suspected to be either a Ru-carbonyl complex or a hydrolyzed Ru complex).

Adding Hg to the Rh-sludge system caused some adjustments to the nitrite destruction and hydrogen generation as it did in the Ru-sludge system, Figure 4.

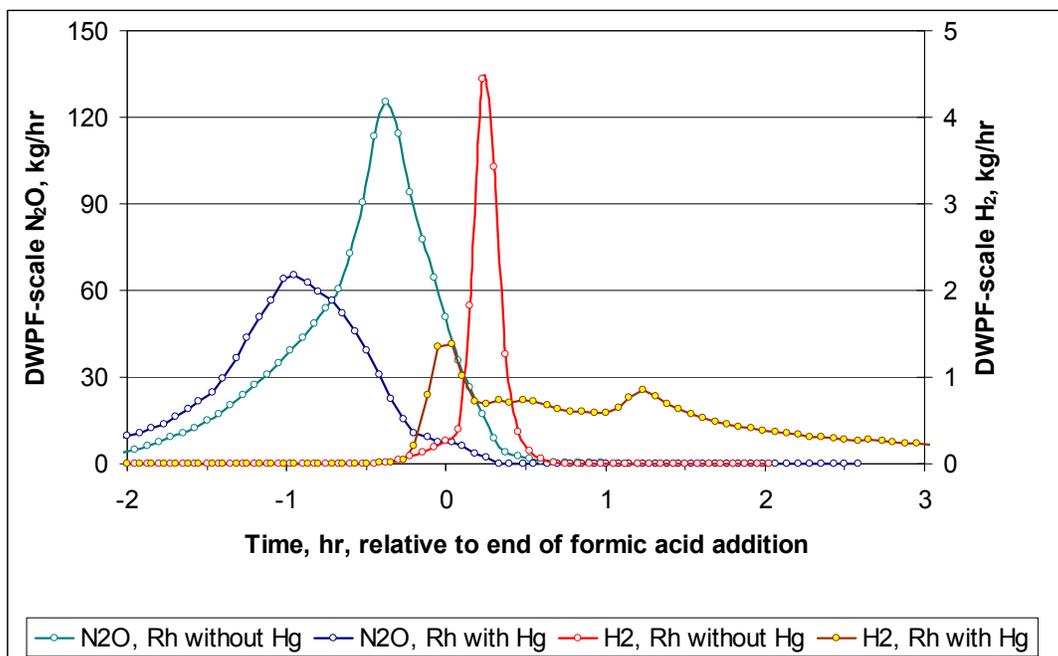


Figure 4. Impact of Hg on the Rh-sludge system including accelerated nitrite destruction and earlier hydrogen generation.

Nitrite destruction was accelerated by the addition of HgO to the starting sludge simulant. A reduction in N<sub>2</sub>O formation was seen, but not as much as in the Ru-sludge case. Other testing has shown the Rh is a catalyst for N<sub>2</sub>O production. In the Hg-Rh-sludge system, Rh and Hg were competing to catalytically convert nitrite to either N<sub>2</sub>O or NO, while in the Hg-Ru-sludge system Hg was the only catalyst appreciably active during nitrite destruction.

Accelerated nitrite destruction in the Hg-Rh-sludge system caused initiation of the Rh catalyzed hydrogen generation reaction to occur sooner. In this case, the initiation came before all of the formic acid had been added. In other words, less of the reactant was present when Rh activated for hydrogen generation. This may explain why the maximum hydrogen generation rate obtained with Hg present was only a third that obtained when Hg was absent. The Hg-Rh-sludge system retained significant catalytic activity for hydrogen generation after nitrite destruction. The Rh-sludge system destroyed enough formic acid that the pH rose above seven about four hours after formic acid addition, but the Hg-Rh-sludge system retained enough formic acid that it stayed below pH six for fifteen hours after formic acid addition. The sustained catalytic activity in the Hg-Rh-sludge system may be due to the presence of much more formic acid relative to sodium formate.

The presence of nitrite ion during the period of maximum Rh activity coupled with the absence of nitrite ion during the period of Ru activity for hydrogen generation indicate that the two catalysts are unlikely to combine to produce an enhanced maximum generation rate. The slower activation of Ru for catalytic hydrogen generation often correlates with lower hydrogen generation rates than occurred during the period of maximum Rh activity, but this is not always true.

Rh retains some activity after destruction of the nitro-Rh complex. A number of lab-scale process simulations have shown continued lower levels of hydrogen generation after complete nitrite destruction. A primary deactivation mechanism for either Ru catalysis or the post-complex Rh species has not been fully identified, but adsorption and/or precipitation of both soluble Rh and soluble Ru onto the insoluble solids correlates linearly with reductions in the observed catalytic hydrogen generation rate. Falling hydrogen generation rates in both cases are observed to coincide with decreasing concentrations of the soluble form(s), but the soluble forms are typically only 1-5% of the total Rh or Ru during this period.

Palladium has been found to be relatively ineffective at converting formic acid into hydrogen in SRAT simulations, which, coupled with its lower concentrations, makes it a minor factor for hydrogen generation. Tests of Pd at 0.2 wt% compared to Rh at 0.2 wt% in the total solids produced maximum hydrogen generation rates that differed by over a factor of 1000. Pd has been found, however, to be a fairly effective catalyst for formic acid conversion of nitrite ion to nitrous oxide, carbon dioxide, and water, in other words Pd acts like Rh during nitrite destruction and with comparable catalytic activity. Therefore, Pd influences the Rh and Ru catalysis of formic acid to hydrogen via its impact on the nitrite ion.

The new data on the individual roles of Rh, Ru, Pd, Hg and nitrite ion presented in this talk represent a considerable advance in the understanding of the reaction sequences and the interplay of the significant species during processing of the legacy waste slurry upstream of the DWPF melter. Testing on systems with all species present simultaneously exhibit all of the above effects. The new data have identified the causes for the effects that were previously observed but only poorly understood.

## REFERENCES

1. Noble Metal Catalyzed Hydrogen Generation from Formic Acid in Nitrite-Containing Simulated Nuclear Waste Media, R. B. King, N. K. Bhattacharyya, and K. D. Wiemers, *Environmental Science and Technology*, Vol. 30, No. 4, (1996) 1292-1299.
2. Catalytic reactions of formate 4. A nitrite-promoted rhodium(III) catalyst for hydrogen generation from formic acid in aqueous solution, R. B. King and N. K. Bhattacharyya, *Inorganica Chimica Acta*, 237 (1995) 65-69.
3. Koopman, D., B. Pickenheim, D. Lambert, J. Newell, and M. Stone, "Characterization of Individual Chemical Reactions Consuming Acid during Nuclear Waste Processing at the Savannah River Site", Proceedings of the 2009 Annual AIChE Meeting, New York, NY: AIChE. 2009.