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Elimination of Catalytic Hydrogen Generation in Defense Waste Processing Facility Slurries

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EXECUTIVE SUMMARY

Based on lab-scale simulations of Defense Waste Processing Facility (DWPF) slurry chemistry, the addition of sodium nitrite and sodium hydroxide to waste slurries at concentrations sufficient to take the aqueous phase into the alkaline region ($\text{pH} > 7$) with approximately 500 mg nitrite ion/kg slurry (assuming <25 wt% total solids, or equivalently 2,000 mg nitrite/kg total solids) is sufficient to effectively deactivate the noble metal catalysts at temperatures between room temperature and boiling. This is a potential strategy for eliminating catalytic hydrogen generation from the list of concerns for sludge carried over into the DWPF Slurry Mix Evaporator Condensate Tank (SMECT) or Recycle Collection Tank (RCT).

These conclusions are drawn in large part from the various phases of the DWPF catalytic hydrogen generation program conducted between 2005 and 2009. The findings could apply to various situations, including a solids carry-over from either the Sludge Receipt and Adjustment Tank (SRAT) or Slurry Mix Evaporator (SME) into the SMECT with subsequent transfer to the RCT, as well as a spill of formic acid into the sump system and transfer into an RCT that already contains sludge solids.

There are other potential mitigating factors for the SMECT and RCT, since these vessels are typically operated at temperatures close to the minimum temperatures that catalytic hydrogen has been observed to occur in either the SRAT or SME (pure slurry case), and these vessels are also likely to be considerably more dilute in both noble metals and formate ion (the two essential components to catalytic hydrogen generation) than the two primary process vessels. Rhodium certainly, and ruthenium likely, are present as metal-ligand complexes that are favored under certain concentrations of the surrounding species. Therefore, in the SMECT or RCT, where a small volume of SRAT or SME material would be significantly diluted, conditions would be less optimal for forming or sustaining the catalytic ligand species. Such conditions are likely to adversely impact the ability of the transferred mass to produce hydrogen at the same rate (per unit mass SRAT or SME slurry) as in the SRAT or SME vessels.

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LIST OF ABBREVIATIONS

ACTL	Aiken County Technology Laboratory
CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
E&CPT	Environmental and Chemical Process Technology
FAVC	Formic Acid Vent Condenser
GC	Gas Chromatograph
LWO	Liquid Waste Organization
MWWT	Mercury Water Wash Tank
PSAL	Process Science Analytical Laboratory
SB	Sludge Batch
SME	Slurry Mix Evaporator
SMECT	Slurry Mix Evaporator Condensate Tank
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions, LLC
TR	Technical Report
TT&QAP	Task Technical and Quality Assurance Plan
TTR	Task Technical Request
WSRC	Washington Savannah River Company

1.0 Introduction

Catalytic hydrogen generation is a potential flammability issue that must be mitigated in the DWPF. The major CPC process equipment is air-purged to mitigate accumulation of potentially hazardous gases like hydrogen in the off-gas system and to prevent formation of flammable gas mixtures. DWPF avoids hydrogen generation rates in the Sludge Receipt and Adjustment Tank (SRAT) and Slurry Mix Evaporator (SME) from exceeding 0.65 lbs/hr and 0.223 lbs/hr respectively by controlling air purges and acid addition levels. The DWPF limits correspond to 25% of the lower flammability limit at design purge rates. Hydrogen generation initiates during or after acidification of the waste sludge in the SRAT or SME once formic acid has been added to achieve sufficiently acidic conditions and once sufficient nitrite ion has been destroyed for the noble metals (rhodium and ruthenium) to activate for hydrogen generation. The combination of noble metals and excess formic acid has been identified as the major cause of catalytic hydrogen generation in DWPF. The catalytic hydrogen generation is in addition to that generated by radiolysis of water. Radiolytic hydrogen typically contributes less than 1% to the SRAT or SME limits for hydrogen generation.

The work presented in this technical report was originally identified as a result of Savannah River National Laboratory/Liquid Waste Organization (SRNL/LWO) meetings to define potential causes of catalytic hydrogen generation as well as from an external technical review panel commissioned to evaluate SRNL hydrogen related data and programs.¹ The work scope was covered under the technical task request: HLW-DWPF-TTR-2007-0016.² A task technical and quality assurance plan (TT&QAP³) was issued to address the needs of the TTR which included potential contributing mechanisms identified in meetings with LWO plus some of the recommendations made by the review panel. Work on the TT&QAP scope concluded in 2009. This report reviewed the data developed during the above test programs for applicability to the potential for catalytic hydrogen generation in the DWPF Recycle Collection Tank (RCT). No new testing was necessary or performed to provide the information requested in the current Technical Assistance Request (HLW-DWPF-TAR-2013-00005).⁴

2.0 Discussion

2.1 Overview

This section summarizes technical work related to processing chemistry within DWPF. Several features are relevant to the RCT and Slurry Mix Evaporator Condensate Tank (SMECT) and will be discussed in turn. First, extensive elimination of nitrite ion from the SRAT slurry was necessary for rhodium to become catalytically active for hydrogen generation. Second, near total elimination of nitrite ion was necessary in the SRAT for ruthenium to become catalytically active in the SRAT. Third, palladium activity for hydrogen generation was weak and short-lived. These three areas are discussed in section 2.2. Fourth, significant excess formic acid was necessary to produce DWPF bounding levels of hydrogen as will be discussed in section 2.3. Fifth, nitrite destruction occurs under acidic conditions and is not a rapid reaction as discussed in section 2.4. Sixth, introducing nitrite to a SRAT cycle producing hydrogen will deactivate the catalysts responsible once a sufficient concentration is developed even in the presence of excess acid as discussed in section 2.5. Finally, section 2.6 addresses the relevance of this information to the RCT and SMECT.

2.2 Nitrite and Noble Metals

A series of tests with individual noble metals and combinations of noble metals was performed to develop a better understanding of catalytic hydrogen generation in the DWPF SRAT and SME. Several technical reports based on these data have already been written. The report titled Noble Metal Chemistry and Hydrogen Generation During Simulated DWPF Melter Feed Preparation contains data and analysis related to noble metal catalysis.⁵

The experimental study, based on eighteen SRAT/SME simulations, showed that ruthenium was inactive for hydrogen generation in the presence of excess nitrite ion. The inference is that nitrite ion complexes with ruthenium to form a species that is catalytically inactive for hydrogen generation. Ruthenium is the species with the most sustained catalytic activity for hydrogen generation during SRAT/SME processing (which occurs under essentially nitrite-free conditions during the final stages of the SRAT and the entire SME cycle).

The same study showed that rhodium took on its maximum activity for hydrogen generation when the nitrite ion concentration was small enough to favor formation of partial nitro-rhodium complexes. During nitrite destruction, rhodium appears to be present as a hexa-nitro-rhodium complex, $\text{Rh}(\text{NO}_2)_6^{3-}$, that is a good catalyst for destruction of nitrite by formic acid reduction, but is unable to produce hydrogen. As nitrite is destroyed, some of the ligand nitrite groups are replaced by water permitting an interaction with formate and formic acid to produce CO_2 and hydrogen. The reaction sequence is laid out in a later technical report (page 35 of 48).⁶ High concentrations of nitrite ion prevent the ligand exchange and prevent hydrogen generation. At 0.2 wt.% Rh in the total slurry solids (higher than in any DWPF sludge batch to date), nitrite had to fall to <200 mg/kg slurry before detectable evidence for hydrogen generation was found. These tests were conducted with a large excess of formic acid, so that the catalytic chemistry would be exaggerated, or more visible, than in normal DWPF processing.

Finally, this study showed that palladium was substantially poorer for catalytic hydrogen generation than either rhodium or ruthenium when present at the same concentration.⁵ Peak rates were less than 1% of those found with rhodium with equal amounts of excess acid. Actual waste has typically had 10-25% as much palladium as rhodium rather than equal amounts. Therefore,

palladium is responsible for only a tiny fraction of the catalytic hydrogen made during SRAT/SME processing. There was a suggestion in the data (see section 3.6.3 of the hydrogen-noble metal summary report⁵) that palladium might actually inhibit catalytic hydrogen generation by rhodium and ruthenium when all three were present together. The active form of palladium appeared to go through several transitions during the period where hydrogen was evolved suggesting there might be several different complex forms that had activity. Palladium behaved more like rhodium than ruthenium, in that hydrogen generation was possible when small concentrations of nitrite ion were still present (again, suggesting a partially nitrated palladium complex species was responsible).

2.3 Formic Acid and Catalytic Hydrogen

Catalytic hydrogen has not been seen during either lab-scale simulations or in DWPF during caustic boiling or nitric acid addition (which is in the caustic pH range prior to formic acid addition). This report cannot summarize DWPF process data but will point out that previously active catalysts are present in the SRAT heel and formate ion is present in the SRAT heel, so the ingredients for catalytic hydrogen generation are present during caustic pre-concentration of sludge in the SRAT vessel, but it has not been seen. This further supports earlier observations that excess formic acid is an essential component of catalytic hydrogen generation.

Lab-scale simulations of the SRAT have been performed for a wide range of unusual scenarios. At least one simulation was performed where only nitric acid was used (no formic acid) under stoichiometric conditions that would have led to significant hydrogen generation for the traditional sludge-only flowsheet (nitric plus formic acids). No hydrogen was detected in the absence of formate ions and/or molecular formic acid. This is consistent with outside literature as summarized in the first catalytic hydrogen generation review report.⁷ The literature indicates that catalytic hydrogen generation from formic acid depends on formic acid concentration, and that it is a much faster reaction under acidic conditions (when molecular formic acid is available) than it is under basic conditions (when dissociated sodium formate provides the reactant).

2.4 Stability of nitrite ion

The panel that reviewed hydrogen generation research recommended that a timeline of reactions be developed for the SRAT. The results of this effort were summarized in a technical report.⁸ Sludge containing about 18,000 mg/kg of nitrite was fed 90 wt.% formic acid at the equivalent of two gallons per minute DWPF scale. Nitrite destruction, other than what could be attributed to short-lived local regions of low pH where the formic acid was added into the slurry, did not occur until the bulk slurry pH was below five in processing at 93° C. These data come from many tests using many different pH probes, so the identified pH region where this reaction occurs is not due to an abnormal equipment performance during a test. The pH probes are calibrated prior to tests with NIST traceable standard solutions, and rechecked following the tests for abnormal drift.

The molar rate of nitrite destruction was slower than the relevant molar rate of formic acid addition (several parallel reactions occur requiring 2/3, 3/2, and 2 moles acid per mole nitrite ion). The significant conclusion is that nitrite destruction, even at elevated temperatures, is not a rapid reaction, i.e. not a reaction like strong acid-base neutralization which occurs as fast as mixing can bring the components together. The molar rate of nitrite destruction was determined by pulling many samples of SRAT slurry and immediately quenching the reaction with an addition of strong caustic solution. This permitted determination of nitrite concentration and, through mass balance, nitrate moles present as a function of time. This was compared to the molar rate of formic acid

addition. The molar rate of nitrite destruction at lower temperatures is expected to be much slower under acidic conditions. There is no evidence that nitrite ion is destroyed by DWPF process chemistry under caustic conditions. (Sodium nitrite is an important component of the Tank Farm corrosion control strategy, and some slow erosion of nitrite probably occurs over long periods of time, but those reactions are not relevant on a time scale of days or weeks.)

2.5 Catalyst deactivation by nitrite

Removal of all but a little nitrite ion was seen to be a pre-requisite for activating the noble metals in DWPF waste for hydrogen generation catalysis (sections above). It was postulated that addition of sodium nitrite to a SRAT vessel producing hydrogen would potentially poison the catalysts and stop the hydrogen generation. A lab-scale SRAT demonstration was performed under conditions that had previously produced considerable catalytic hydrogen with a modification that sodium nitrite solution was metered into the SRAT slurry slowly once formic acid addition was complete.⁹

Because of the acid stoichiometry, hydrogen generation began before formic acid addition was complete (implying nearly complete sludge nitrite destruction) and was on-going when sodium nitrite addition began. Consequently, the sodium nitrite addition was not sustaining an existing non-zero concentration of nitrite in the slurry initially, while excess acid accumulated in the SRAT slurry was destroying the majority of what was being added at nearly the rate it was going in (ultimately, two-thirds of the nitrite added was destroyed before the test ended). In spite of being at <100 mg nitrite/kg slurry, there was an order of magnitude reduction in hydrogen generation compared to the baseline test without sodium nitrite addition.

Once SRAT slurry nitrite concentration exceeded ~1,000 mg/kg, hydrogen generation fell to the detection limit of the gas chromatograph (on that day, 0.006 vol%). The slurry pH was still acidic throughout the test. Furthermore, there are regions in the lab-scale SRAT glassware that are potential reservoirs for hydrogen-enriched air and that are not well purged by the SRAT air purge. Presumably, any accumulated hydrogen (from an earlier period of hydrogen generation) would diffuse from these volumes into the flowing purge whenever the hydrogen concentration in the relatively stagnant zones exceeded that in the fresh gas coming off of the SRAT vessel. Because the concentration seen at the GC was so small, it is difficult to distinguish between hydrogen being made versus accumulated hydrogen being slowly bled from the system. The rate being observed at this time was less than 0.0065 lb hydrogen/hour at DWPF scale, or less than 1% of the DWPF SRAT limit (while still at a SRAT slurry temperature of 100-101° C).

Nitrite concentration was not known precisely as a function of time during the above SRAT cycle above. A concentration of 500 mg/kg slurry would have been a large excess relative to the moles of rhodium and ruthenium present. The slurry was at about 25 wt.% total solids. Therefore, a nitrite concentration of 2,000 mg nitrite/kg total solids would be an equivalent statement of the quantity present as hydrogen generation fell to the detection limit. For the SMECT or RCT, the wt.% total solids would presumably be much lower than in the SRAT, so the nitrite ion concentration could be decreased from 500 mg/kg slurry such that the 2,000 mg nitrite/kg total solids ratio was maintained.

If catalytic hydrogen generation was in fact still occurring in this SRAT test (versus bleeding out residual hydrogen from earlier in the test), then several scenarios are possible. One is that the nitrite poisoning of the catalysts (which was overwhelmingly indicated by the data) was not instantaneous, and a small fraction of the catalyst species had not yet been deactivated. A second

possibility is that competition for ligand sites was permitting a small fraction to continue to be active for hydrogen generation (competing equilibrium conditions leading to a steady-state balance between poisoned and unpoisoned states). A third possibility is that the hydrogen was being made by palladium catalysis (roughly correct order of magnitude), but that the rhodium and ruthenium had been completely poisoned by the nitrite. In any case, the SRAT slurry with added nitrite could not be compared to any sort of normally bounding SRAT slurry with respect to catalytic hydrogen generation (system without added sodium nitrite) even at boiling and with excess formic acid present.

2.6 Implications for the DWPF RCT

It is possible to carry sludge solids (including noble metal catalyst species) overhead into the Slurry Mix Evaporator Condensate Tank (SMECT). From there the solids are moved forward to the RCT. The question has been asked as to what is the catalytic hydrogen generation rate in the RCT, and what is the rate if the contents of the RCT have been adjusted to be caustic and contain nitrite ion. Assuming a maximum observed temperature of 42° C for the RCT, SRNL has no data saying that the SRAT or SME will produce measurable catalytic hydrogen below 42° C. In some SRAT/SME tests, catalytic hydrogen has gone below detection limits (0.002-0.008 vol% depending on the condition of the gas chromatograph) at 60° C or above, while in other tests there is still a small concentration (typically <0.03 vol%) of hydrogen at 50° C, as measured downstream of the formic acid vent condenser. The hydrogen generation rate is consistently observed to fall exponentially with decreasing absolute temperature in both the SRAT and SME slurries. Off-gas composition data are rarely taken below 50° C during lab-scale tests, because the values are at or near the detection limit.

As discussed above for the test with added sodium nitrite, Section 2.5, it becomes problematic at these low gas concentrations to differentiate between the bleed off of accumulated hydrogen in the system versus formation of fresh hydrogen. Data of this type have been used to estimate the temperature dependence of catalytic hydrogen generation¹⁰, and such correlations must be seen as very conservative for this reason when applied at the low temperature end of the data or extrapolated to temperature below those where hydrogen could be detected in the experiments.

A kinetic rate expression for catalytic hydrogen generation has not been developed, in part due to the complex nature of the phenomenon. Consequently, the dependence of rate on concentration has not been quantified, but likely depends on the concentration of active species and the concentration of formic acid and of formate ion (the split of which is a function of pH). It is quite likely for such a system that the dilution of all species by an order of magnitude, such as would happen in the SMECT, would lead to more than an order of magnitude reduction in hydrogen generation even if temperature were maintained at boiling.

The above results, in and of themselves, do not eliminate the possibility of forming a negligible amount of catalytic hydrogen in the RCT if sludge is present. SRNL has assumed for estimation purposes that the DWPF SRAT hydrogen generation rate limit of 0.65 lb/hr is roughly three orders of magnitude greater than the radiolytic rate.

It should be pointed out that the SRAT/SME slurry cannot sustain the peak generation rate for any length of time (it will either increase or fall, but it doesn't remain constant). Catalytic hydrogen generation is a dynamic process consuming formate while the catalysts are either becoming active or going inactive based on the relevant reactions. This feature of catalytic hydrogen generation has been documented and used in prior safety analyses.¹¹ Assuming rhodium catalyzed hydrogen would continue at the same rate, e.g. 0.65 lb/hr per 6,000 gallons

sludge, following a transfer of 400 gallons of SRAT slurry into 4000 gallons of SMECT condensate, even if the temperature stayed at boiling, is not defensible. The ligand exchange reactions controlling the hydrogen generation rate would be significantly disrupted by the dilution into the SMECT condensate.

Based on what is known about the catalysts, the best way to minimize their activity is to add nitrite ion and take the pH into the alkaline region ($\text{pH} > 7$). Rhodium and ruthenium are virtually insoluble in alkaline solutions, and palladium is fairly insoluble as well. It takes some time to break down any metal complex catalysts following pH adjustment, but the noble metals should eventually precipitate in alkaline solutions like they did when the waste was first treated with caustic coming out of the separation canyons. The precipitated noble metal hydroxides (or hydrous oxides) have not been observed to be catalytically active for hydrogen generation in SRS waste systems.

Shorter term, the addition of nitrite ion under conditions where nitrite will not be destroyed, for example in the alkaline pH region, has also been shown to deactivate the noble metals (even when still mildly acidic and at elevated temperatures). Deactivation is defined here as hydrogen production is below detectable limits of the measuring equipment under the test conditions. Processing conditions such as the found in the RCT with added caustic and sodium nitrite would be expected to have hydrogen generation rates that were below detection limits for multiple reasons including poisoning of the catalysts by nitrite ion, low temperature (42°C), high pH (>7), and dilution (compared to the SRAT or SME slurries).

3.0 Conclusions

Studies of sludge processing chemistry with nitric and formic acids have shown that nitrite ion concentration is one of the key factors controlling hydrogen generation in the presence of formic acid (or formate ion). Hydrogen generation is not seen until after nitrite ion in the SRAT feed has been nearly destroyed. The rate of hydrogen generation has been shown to be directly related to the concentration of formate in the system. Nitrite ion has also been shown to poison noble metal catalysts after they have become active. A strategy for preventing catalytic hydrogen generation in the DWPF RCT is to provide sufficient nitrite ion ($>2,000$ mg nitrite/kg total solids) to effectively overwhelm the available noble metals (at least an order of magnitude more moles of nitrite than noble metals, and preferably several times that or more) and to keep the pH in the alkaline range ($\text{pH} > 7$) which prevents destruction of nitrite ion.

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