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WSRC STI Program

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Author <u>L. F. Landon</u>	
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**DWPF INTEGRATED COLD RUNS
REVISED TECHNICAL BASES FOR PRECIPITATE HYDROLYSIS (U)**

The attached document defines new precipitate hydrolysis process operating parameters for DWPF Chemical Runs assuming the precipitate feed simulants to be processed reflect the decision to implement a final wash of the tetraphenylborate slurry before transfer to DWPF (i.e. the Late Wash Facility).

Control of the nitrite content of the tetraphenylborate slurry to 0.01M or less has eliminated the need for hydroxylamine nitrate (HAN) during hydrolysis. Consequently, the oxidant nitrous oxide (N₂O) will not be generated. However, nitric oxide (NO) is expected to be generated (reaction of formic acid with nitrite) and some fraction of the NO can be expected to be oxidized to nitrogen dioxide (NO₂). The rate of NO generation with low nitrite feed has not been quantified at this time nor is the extent to which the NO is oxidized to NO₂ known. A mass spectrometer is being installed in the Precipitate Hydrolysis Experimental Facility (PHEF) which will enable the NO generation rate to be defined as well as the extent to which the NO is oxidized to NO₂. There is some undocumented data available for C₆H₆/NO and C₆H₆/NO₂ with N₂ as the diluent but no similar data for CO₂. Development of test data in the required time frame is not possible.

However, MOC's will be estimated for benzene/NO/NO₂/CO₂ gas mixtures (the MOC is expected to be approximately 60% less than for the HAN process). Once these data are obtained, and NO/NO₂ concentration profiles are obtained from PHEF hydrolysis process demonstrations, a flammability control strategy for the DWPF Salt Processing Cell will be developed. Implementation of the HAN process purge strategy upon startup of the SPC with the late wash process would be conservative.

Questions regarding the contents of the attached document should be referred to L. F. Landon (Ext. 56403) or J. C. Marek (Ext. 56349).




E. W. Holzscheiter, Manager, SRTC-DWPT Section

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**DWPF INTEGRATED COLD RUNS
REVISED TECHNICAL BASES FOR PRECIPITATE HYDROLYSIS (U)**

INTRODUCTION

On 5/15/92, a formal recommendation was made to DOE-SR that a final wash of the tetraphenylborate precipitate slurry produced during In-Tank Precipitation Operations be performed to reduce the nitrite content of the slurry to 0.01M or less prior to transfer to DWPF. Previous laboratory studies demonstrated that if the nitrite content of the precipitate slurry could be reduced to 0.01M or less the need for the reductant hydroxylamine nitrate (HAN) during hydrolysis could be eliminated (the principal source of ammonium ion flow to the Chemical Process Cell) and that the non-polar organic content of the aqueous product from hydrolysis (PHA) can be reduced by at least a factor of 10 compared to previous products produced in the 1/5th-scale Precipitate Hydrolysis Experimental Facility (PHEF).

Hydrolysis process operating parameters were redefined for low nitrite feed to ensure all applicable process operating constraints were attainable both during DWPF Chemical Runs and during radioactive operation. The process operating parameter changes during hydrolysis include (1) a greater formic acid requirement, (2) higher feed temperature, (3) greater catalyst requirement (and a change in the timing of the catalyst addition) and (4) the addition of a hold period prior to initiating aqueous boil.

SUMMARY

This report defines the new precipitate hydrolysis process operating parameters that DWPF should implement for Chemical Runs with precipitate feeds having $\leq 0.01M$ nitrite. These parameters are also applicable for radioactive operation with a final wash of the precipitate slurry to be produced during In-Tank Precipitation operations. WSRC-TM-90-11, "Defense Waste Processing Facility: Technical Bases for the Precipitate Hydrolysis Process - DWPF Integrated Cold Runs (U)" will be updated accordingly after the technical reports detailing the results of the research and development effort are issued.

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PROCESS OPERATING CONSTRAINTS

The precipitate hydrolysis process operating parameters must produce an aqueous product and an organic product that meet the following constraints:

- o Remove >90% of the aromatic carbon from the tetraphenylborate slurry
- o Limit total mercury content of recovered organic to <260 ppm
- o Limit phenylboric acid content of aqueous product to <53 ppm

Precipitate hydrolysis, performed within the process operating parameters specified in the following section, will meet these constraints. The mercury limit was not exceeded with irradiated tetraphenylborate precipitate feed simulants containing 3X the reference DWPF material balance diphenylmercury concentration.

REVISED PRECIPITATE PROCESS OPERATING PARAMETERS

PHA Target Acidity - 0.25M

Acceptable Operating Range - 0.20M to 0.30M

Copper Catalyst Target Concentration in PHA - 950 ppm

Acceptable Operating Range - 850 ppm to 1050 ppm

Timing of Catalyst Addition - in pre-reaction heel

Precipitate Reactor Temperature During Feed Cycle - $90^{\circ}\text{C} \pm 5^{\circ}\text{C}$

Post-Feed Reaction Period Prior to Heatup to Aqueous Boil - 5 hours @ $90^{\circ}\text{C} \pm 5^{\circ}\text{C}$

Total Aqueous Boilup - 10,000 lbs minimum

Aqueous Boilup Period - 5 hours minimum

HCOOH REQUIREMENT

See attachment for methodology to calculate formic acid requirement.

FLAMMABILITY CONTROL

Limiting the nitrite content of the slurry feed to 0.01M has eliminated the need for HAN; consequently, no nitrous oxide (N₂O) will be generated during hydrolysis. However, nitric oxide (NO) will be produced by the reaction of formic acid with the nitrite content of the precipitate slurry and some fraction of the NO will be oxidized to nitrogen dioxide (NO₂). The minimum oxidant for combustion (MOC) will depend on the amount of NO generated and the extent to which it is oxidized to NO₂. This information is not known at this time. A mass spectrometer is being installed in the Precipitate Hydrolysis Experimental Facility (PHEF) to measure the composition of the off-gas during precipitate hydrolysis with low nitrite feed. Once these data are obtained, a MOC for the revised hydrolysis process will be defined and an inerting strategy recommended to DWPF.

The NO generation rate will be at least a factor of 20 less than the generation rate of N₂O with the previous HAN process. Assuming all the NO is converted to NO₂, the MOC will be approximately 60% less than for the HAN process (~8 vol% vs ~21 vol %). If less NO is oxidized, the MOC will be higher. Consequently, a reduction in inertant requirement should be realized and a corresponding reduction in benzene emissions to the atmosphere should result.

There is currently no on-line instrumentation specified for the Salt Processing Cell to monitor for NO and NO₂ (the existing IR detector can only be converted to monitor for NO). Unless appropriate instrumentation is installed to monitor for NO and NO₂, DWPF may have to set the feed rate to inertant flow ratio to control at $\leq 25\%$ of the MOC.

COPPER ANALYSIS

Copper analyses will be performed by Atomic Absorption (AA). It was recently observed that copper concentrations determined by AA of samples of aqueous product were consistently lower than predicted. Investigation revealed that the cause for the erroneous results was the acidity of the sample (following dilution to reduce the anticipated copper content to within the calibration range of the instrument) was sufficiently low that a fraction of the copper had hydrolyzed which interfered in the AA measurement of the copper ion. It is recommended that the sample prep procedure specify the samples be diluted with a nitric acid diluent such that the pH of the diluted sample is ≤ 2 .

SAMPLE AND ANALYTICAL SCHEDULE

The DWPF Sample and Analytical Schedule should be altered as follows:

<u>Analyses</u>	<u>Location</u>	<u>Purpose</u>
Total copper in pre-reaction heel (post formic acid/copper addition)	PR	Confirm accuracy of copper addition
Total copper in aqueous product (post PR cycle)	PR	Required in order that the catalyst requirement for the subsequent PR cycle accounts for the copper content of the heel in the Precipitate Reactor
Total copper in aqueous product	PRBT	Required for batching strategy to meet copper constraint in the waste glass

Delete all analyses for HAN

**PROCEDURE FOR DETERMINING
 THE FORMIC ACID REQUIREMENT FOR HYDROLYSIS**

- 1) Calculate the Mass and Volume of Organic Product After Completion of the PR Cycle

$$\text{Organic Mass, lbs} = (\text{PR Feed Batch, gal})(8.345)(\text{PRFT Slurry SpG})(\text{wt\% TPB}/100)(\text{lb-mol TPB}/\text{lb TPB})(\text{lb-mol C}_6\text{H}_6/\text{lb-mol TPB})(\text{lb C}_6\text{H}_6/\text{lb-mol C}_6\text{H}_6)$$

where, $\text{lb-mol TPB}/\text{lb TPB} = 0.0031328$
 $\text{lb-mol C}_6\text{H}_6/\text{lb-mol TPB} = 4.0$
 $\text{lb C}_6\text{H}_6/\text{lb-mol C}_6\text{H}_6 = 78.11$

$$= (0.081682)(\text{PR Feed Batch, gal})(\text{PRFT Slurry SpG})(\text{wt\% TPB})$$

$$\text{Organic Vol, gal} = (\text{Organic Mass, lbs})/(8.345 \times \text{Organic SpG})$$

$$= (0.1362)(\text{Organic Mass, lbs})$$

where, a SpG of 0.88 is assumed for the organic product. The SpG of the organic batch in the Organic Evaporator from the previous PR cycle could be used

- 2) Calculate the Final Mass and Volume of Aqueous Product in the Precipitate Reactor After PR Cycle

$$\text{Aq Product, lbs} = (\text{Pre-Reaction Heel, gal})(8.345)(\text{Pre-Reaction Heel SpG}) + (\text{PR Feed Batch, gal})(8.345)(\text{PRFT SpG}) - \text{Organic Product, lbs}$$

$$= (\text{Pre-Reaction Heel, gal})(8.4285) + (\text{PR Feed Batch, gal})(8.345)(\text{PRFT SpG}) - \text{Organic Product, lbs}$$

where, a SpG of 1.01 is assumed for the pre-reaction heel. The SpG of the pre-reaction heel from the previous cycle could be used

$$\text{Aq Product, gal} = (\text{Aq Product, lbs})/(8.345)(\text{Aq Prod SpG})$$

where, the SpG of the aqueous product is that measured for the aqueous product produced in the previous cycle

- 3) Calculate the Copper Requirement (target - 950 ppm in aqueous product)

$$\text{Cu Req't, lbs} = (\text{Aq Product, lbs})(950/1.0\text{E-}06)$$

$$= (0.00095)(\text{Aq Product, lbs})$$

- 4) Calculate Quantity of Catalyst Solution Required

$$\text{Catalyst Sol'n, lbs} = (\text{Cu Req't, lbs})/(\text{wt\% Cu in Catalyst Cold Feed Solution}/100)$$

$$\text{Catalyst Sol'n, gal} = (\text{Catalyst Sol'n, lbs})/(8.345)(\text{SpG of Catalyst Cold Feed Solution})$$

5) Calculate Formic Acid Requirement for Zero Excess Acid

$$\text{HCOOH, g-mol} = \text{HCOOH Req't for Base Equivalences} + \text{HCOOH Req't for TPB}$$

where,

$$\begin{aligned} \text{HCOOH Req't for Base Equivalences, g-mol} &= (\text{PR Feed Batch, gal})(3.785) [1.0 - (\text{wt\% Ins Solids}/100)](\text{Base Equiv., M}) \\ &\text{where, Base Equiv. determined by titration of feed slurry to pH 5.5} \end{aligned}$$

$$\begin{aligned} \text{HCOOH Req't for TPB, g-mol} &= (\text{PR Feed Batch, gal})(8.345)(\text{Feed Slurry SpG})(\text{wt\% TPB}/100)(0.0031328 \\ &\text{lb-mol TPB/lb TBP})(453.59) \\ &- (0.1186)(\text{PR Feed Batch, gal})(\text{Feed Slurry SpG})(\text{wt\% TPB}) \end{aligned}$$

6) Calculate Excess HCOOH Requirement (Target - 0.25M)

$$\begin{aligned} \text{Excess HCOOH Req't, g-mol} &= (\text{Aq Product, gal})(3.785)(0.25) \\ &= (\text{Aq Product, gal})(0.9463) \end{aligned}$$

$$\begin{aligned} \text{7) Total HCOOH Req't, gal} &= [\text{HCOOH Req't for Base Equiv, g-mol} + \text{HCOOH Req't for TPB, g-mol} + \\ &\text{Excess HCOOH Req't, g-mol}] / [(\text{Cold Feed Formic Acid Concentration, M})(3.785)] \end{aligned}$$

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