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**NITRIC ACID - FORMIC ACID COMPATIBILITY IN DWPF
(U)**

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by R. E. Eibling
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

DE93 006878

Other Authors:

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SAVANNAH RIVER TECHNOLOGY CENTER

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CC: L. F. Landon, 704-T
J. T. Carter, 704-1T
C. T. Randall, 704-T
M. J. Plodinec, 773-A
M. D. Boersma, 704-T
C. W. Hsu, 704-1T
J. R. Zamecnik, 704-1T
SRTC Records (4)

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TO: E. W. HOLTZSCHEITER, 773-A

FROM: R. E. EIBLING, 704-T *Russell E. Eibling*

Nitric Acid - Formic Acid Compatibility in DWPF(U)

Introduction

The addition of the Nitric Acid Flowsheet to the DWPF feed preparation process introduces nitric acid into a vessel which will subsequently receive a formic acid solution. The combination of these two acids suggests that a denitration reaction might occur. This memorandum reviews the conditions under which a denitration reaction is possible and compares these conditions to DWPF operating conditions.

Summary and Conclusion

The DWPF will not produce any significant denitration of nitric acid under the planned operating conditions. For denitration reactions to occur, sufficient nitric acid to reduce the pH to less than 3 would have to be added to the Slurry Receipt Adjustment Tank (SRAT). The normal operating condition for the SRAT is pH>4. Results from IDMS and bench-scale testing suggest no net consumption of nitrate during aqueous hydrolysis product (PHA) addition. The only significant NOx generating reaction observed has been the destruction of nitrite at elevated temperatures under acidic conditions.

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Nitric Acid - Formic Acid Denitration Reactions

The reaction of formic acid with concentrated nitric acid solutions has been applied as a means of reducing the nitrate concentration fuel cycle solutions. ^{1,2,3} Previous studies have demonstrated that the reactions are autocatalytic with an induction period while a critical intermediate is produced. The intermediate is nitrous acid. Depending on the nitric acid concentration and the amount of formic acid (or formate) present, the following reactions can occur:

All of these reactions occur at relatively (compared to DWPF) high nitric acid concentrations and the rate expressions empirically derived for these reactions have the nitric acid concentration cubed.³ As the nitric acid concentration is significantly reduced to pH greater than 3 no further denitration has been observed in a previous study on denitration of waste solutions.² Therefore, for pH < 3 denitration reactions are possible and NO or N₂O are the observed products. For pH > 3 only decomposition of nitrite (nitrous acid) would be observed.

SRAT Conditions

Under the normal DWPF operating conditions, only sufficient nitric acid is added to give a pH between 4 and 6. Under these conditions the net nitric acid concentration is 10⁻⁴ molar or less since the rest of the acid was consumed in neutralizing basic compounds. Based upon the references cited previously, no net denitration should occur under these conditions. Denitration has not been observed in development of the nitric acid flowsheet. Analysis of when NO_x has been observed correlates well with destruction of the nitrite present in the sludge. Only an excessively high addition of nitric acid could lead to denitration.

References

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2. E. G. Orebaugh, "Denitration of Savannah River Plant Waste Streams", DP-1417, July 1976.
3. L. Cecille and M. Kelm, "Chemical Reactions Involved in the Denitration Process with HCOOH and HCHO", Denitration of Radioactive Liquid Waste, Edited by L. Cecille and S. Halaszovich, 1986, p 11-31.

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