WSRC-TR-94-0250

RECOMMENDED NITRITE LIMITS FOR CHLORIDE AND SULFATE IN ESP SLURRIES

by

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WESTINGHOUSE SAVANNAH RIVER COMPANY
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WSRC-TR-94-0250

INTER-OFFICE MEMORANDUM

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FROM: P. E. Zapp, 773-A *P.E. Zapp*

Approved by: *[signature]*
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RECOMMENDED NITRITE LIMITS FOR CHLORIDE AND SULFATE IN ESP SLURRIES (U)

SUMMARY

Two additional nitrite limits are developed and recommended for Extended Sludge Processing slurries. These limits apply to slurries in which the chloride or sulfate concentrations exceed specified percentages of the nitrate concentration.

DISCUSSION

In a previous report additional nitrite limits were developed and recommended for inclusion in the In-Tank Precipitation (ITP) Operational Safety Requirements.[1] These limits specify nitrite concentrations which prevent pitting corrosion of carbon steel exposed to waste solutions which contain high chloride or sulfate concentrations. Such additional limits cover the conditions in which a specified percentage of the concentration of nitrate, which is normally the principal corrosive anion, is exceeded by the chloride or sulfate concentration. The new limits are based on previously obtained laboratory corrosion data on the corrosivity of simulated washed precipitate solutions. They permit the inhibition of pitting with nitrite additions to the ITP tanks rather than caustic additions to raise the hydroxide level to > 1 M.

Nitrite concentrations based on chloride and sulfate can be developed also for Extended Sludge Processing (ESP) operations. The approach to developing these was identical to that followed for the ITP limits. In previously conducted electrochemical corrosion tests, the nitrite concentration which is required to inhibit pitting was established in a simulated fully washed ESP solution with varied chloride or sulfate levels.[2] The fixed concentrations of the various ions in the simulant were those reported in the "Basic

Data Report Defense Waste Processing Facility Sludge Plant, DPST-80-1033, Vol. 2, Rev. 90", except for the nitrate, sulfate, and fluoride concentrations, which were calculated under the assumption of the complete solubility of these species. This assumption yielded, for example, a nitrate concentration in the simulant solution of 0.063 M, rather than 0.022 M. Pitting susceptibility or immunity was assessed with cyclic potentiodynamic polarization scans on specimens of ASTM A537 Class 1 carbon steel. Testing was conducted at 40°C only.

The tests revealed that, as with the ITP test results, the logarithm of the inhibiting nitrite concentration is independent of the logarithm of the corrosive anion below a certain critical value and then linearly dependent upon it above that value. The general form of the linearly dependent relationship is

$$\log [NO_2^-] = a + b*\log[CA] \qquad (1)$$

where CA stands for any corrosive anion, and a and b are constants, which are dependent upon the composition of the simulant under test.

The equation for nitrite to prevent chloride-induced pitting in the washed sludge is

$$\log [NO_2^-] = 2.25 + 1.34*\log[Cl^-] \qquad (2)$$

obtained at 40°C. Equation 2 applies when the chloride concentration exceeds 3% of the nitrate concentration.

In order to provide a temperature dependence to the nitrite concentration, one can adopt the temperature dependence expressed in the equation developed for the minimum nitrite equation as a function of the nitrate concentration in ESP solutions:

$$[NO_2^-] = 0.025*10^{0.041T}*[NO_3^-]^{0.98} \qquad (3)$$

where T is in °C.[3] Equation 3 was developed from laboratory data obtained at 23, 30, 40, 50, and 60°C, and is applicable over that range only. Equation 3 incorporates the increase in corrosivity with temperature due to nitrate in ESP solutions. With a change in temperature T away from 40°C, the nitrite requirement changes by a factor of $10^{0.041T}/10^{0.041*40}$, or $10^{0.041*(T-40)}$, from the 40°C nitrite level. Based on the thermal activation of corrosion reactions and the relatively small differences between 40°C and temperatures of interest, it is reasonable to apply the same temperature factor to Equation 2. Thus Equation 2 becomes, with the antilogarithmic transformation and the inclusion of the temperature dependence and a safety factor of 1.5,

$$[NO_2^-] = 1.5 * 10^{0.041*(T-40)} * 10^{(2.25 + 1.34*\log[Cl^-])} \qquad (4)$$

The equation for the minimum nitrite concentration required to inhibit pitting caused by sulfate is

$$\log [NO_2^-] = -0.0675 + 0.835*\log[SO_4^{=}] \qquad (5)$$

Equation 5 applies when the sulfate concentration exceeds 30% of the nitrate concentration. After the antilogarithmic transformation, the same temperature dependence and safety factor may be introduced to the nitrite-sulfate relationship to give

$$[NO_2^-] = 1.5 * 10^{0.041*(T-40)} * 10^{(0.0675 + 0.835*\log[SO_4^=])} \quad (6)$$

It has been shown that corrosive anions act independently, not additively.[4] Pitting corrosion is prevented, when the highest nitrite concentration required by any corrosive anion is present in the waste. Thus the minimum nitrite limit is the highest of the three nitrite concentrations calculated from the nitrate (see Reference 3), chloride, or sulfate concentration.

RECOMMENDED ESP PROCESS REQUIREMENT LIMITS

Equations 4 and 6 may be inserted as additional limits in the Requirements for Corrosion Control of Waste Tank Contents in the ESP Process Requirements. The new limits may take the form

Applicability	Parameter	Minimum	Maximum	Units
$[NO_3^-] \leq 1.0$ Molar and $[OH^-] < 1.0$ Molar and $[Cl^-] > 0.03\ [NO_3^-]$	$[NO_2^-]$	A	-	Molar
	Temperature	-	60	°C
	pH	10.3		pH units

where $A = 1.5 * 10^{0.041*(T-40)} * 10^{(2.25 + 1.34*\log[Cl^-])}$

Applicability	Parameter	Minimum	Maximum	Units
$[NO_3^-] \leq 1.0$ Molar and $[OH^-] < 1.0$ Molar and $[SO_4^=] > 0.3\ [NO_3^-]$	$[NO_2^-]$	B	-	Molar
	Temperature	-	60	°C
	pH	10.3		pH units

where $B = 1.5 * 10^{0.041*(T-40)} * 10^{(0.0675 + 0.835*\log[SO_4^=])}$

For these limits the pH has been changed to 10.3, so that the limits are valid at any ESP dilution.

REFERENCES

1. P. E. Zapp, "Effect of Chloride and Sulfate on Nitrite Requirements for ITP (U)," WSRC-TR-94-0217, May 5, 1994.

2. J. W. Congdon and J. S. Lozier, "Inhibition of Washed Sludge with Sodium Nitrite," DPST-87-379, April 7 1987.

3. P. E. Zapp, "Effect of Temperature on the Nitrite Requirement to Inhibit Washed Sludge (U)," WSRC-TR-90-292, September 18, 1990.

4. J. W. Congdon, "Inhibition of Nuclear Waste Solutions Containing Multiple Aggressive Anions," Materials Performance 22, 34 (1988).

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August 9, 1999

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