

WSRC-RP-92-340

**METHOD FOR KEEPING RBOF WASTE WITHIN EPA pH
LIMITS FOR NONHAZARDOUS WASTE (U)**

by C. L. Cobb, et al.
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

WSRC-RP--92-340

DE93 008506

E. W. Baumann

RECEIVED
FEB 01 1993
DOTI

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ep*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

**WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER LABORATORY**

WSRC-RP-92-340

February 18, 1992

To: A. L. Blancett, 773-A

From: C. L. Cobb, 773-A
W. N. Wilson, 773-A

E. W. Baumann, 773-41A
J. E. Young, 773-A

Distribution: F. R. Graham, 773-A
S. W. Stump, 244-2H
D. K. Parkman, 221-H
M. F. Herlihy, 221-H
A. N. Holloway, 244-2H

T. R. Cowlam, 244-2H
D.R. Johnson, 707-H
P. F. Cloessner, 773-A
S. W. O'Rear, Jr., 244-2H
S. A. Yano, 221-H

Derivative Classifier

JG Kanaker

Method for Keeping RBOF Waste within EPA pH Limits for Nonhazardous Waste (U)

Conclusion

A system to control corrosion, while reducing the amount of hazardous waste generated, is proposed for the RBOF receiving basin. Details of the chemistry, experimental setup, and methods for monitoring pH are included.

Summary

Solutions with a pH of > 12.5 are considered RCRA hazardous waste (characteristic corrosive). The Receiving Basin for Offsite Fuel (RBOF) currently adjusts its waste to a pH > 12.5 to inhibit corrosion of the waste tanks. As of May 8, 1992 this waste will be banned from land disposal (third-third) and will exceed Waste Management acceptance criteria. RBOF proposed, as a solution to this problem,¹ to buffer the waste with a carbonate/bicarbonate buffer to a pH > 10 , then use nitrite as the corrosion inhibitor. A pH of ≥ 10 is necessary for corrosion inhibition at a NO_2^- concentration of 0.86 M .² RBOF proposed to monitor the pH with a pH meter, backed up by Alizarin Yellow indicator. A worst-case scenario in which the caustic feed blocked and only acid was released into the tank was used to determine the amount of buffer salts needed.

We tested this approach and found that the amounts of carbonate/bicarbonate salts required would be insoluble. We have demonstrated that CO_2 gas could be bubbled through the solution to lower the pH without adding additional salts.³ We also suggested an alternative indicator, Azoviolet^{4,5} and an inexpensive, commercially available instrument for reading the indicator.⁶ The colormetric pH reading would serve as a supplement and confirmation of a pH meter reading. From the literature we found that the NaNO_2 solution would have to be used within 24 hours due to the instability of neutral NaNO_2 solutions⁷ and that the concentration of the NaNO_2 solution would have to be greater than the standard 30% plant solution.

Experimental Details

Two indicators, Alizarin Yellow and Azoviolet, were tested by noting the color in solutions with pH in the range 7-13. Azoviolet seemed to have the most distinctive color change in the desired range, pH 10 to 12.5 (i.e., yellow at pH \leq 11 and purple at pH \geq 13)..

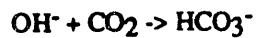
Using information provided by RBOF (Table I), we mixed a simulated waste and a waste adjustment solution containing the buffer. The original proposal was to add the anion regeneration solution (caustic) and cation regeneration solution (acid) to the waste adjustment solution.

Table I

Recipe as given		Scaled Recipe		moles	moles
		scale factor	1E+05		/liter
Anion Solution					
3066	L H2O	0.03066	L H2O	30.66	mL H2O
273	L 50% NaOH	0.00273	L 50% NaOH	2.73	mL 50% NaOH
				0.05	1.58
Cation Solution					
4087	L H2O	0.04087	L H2O	40.87	mL H2O
409	L 50% HNO3	0.00409	L 50% HNO3	4.09	mL 50% HNO3
Final soln.				OH =	0.01 0.15
Rinse Water				pOH =	0.82
Acid				pH =	13.1
1362	L H2O	0.01362	L H2O	13.62	mL H2O
Base					
1048	L H2O	0.01048	L H2O	10.48	mL H2O
Final soln.				pH =	13.0
Total water	9563	Liter s	0.096	Liters	95.63 mL
Total volume	10245	Liter s	0.102	Liters	102.45 mL
Waste Adjustment					
1892	L H2O	0.01892	L H2O	18.92	mL H2O
NaHCO3					
445	kg	0.00445	kg	4.45	g
Na2CO3					
563.2	kg	0.005632	kg	5.632	g
NaNO2					
719.6	kg	0.007196	kg	7.196	g

However the amount of salts required for the waste adjustment solution proved to be insoluble.

We then proposed adjusting the pH of the solution with CO₂ gas, via the reaction



The apparatus for bubbling CO₂ through the solution is shown in Fig. 1. Dry ice (solid CO₂) was placed in a stainless steel tube that could be capped on both ends. The dry ice was allowed to sublime at room temperature, providing a flow of CO₂ gas. This CO₂ gas escaped through a side arm fitted with Tygon tubing and bubbled through the solution. The rate of gas evolution was not measured, but it appeared vigorous and was sufficient to lower the pH of our initial pH 12.5 solution to pH 10 within a few minutes. If the CO₂ flow were allowed to continue, it is possible to over-neutralize to a pH of 8-9, the pH of a HCO₃⁻ solution. In actual plant operation it may be preferable to use CO₂ from a gas cylinder rather than subliming dry ice.

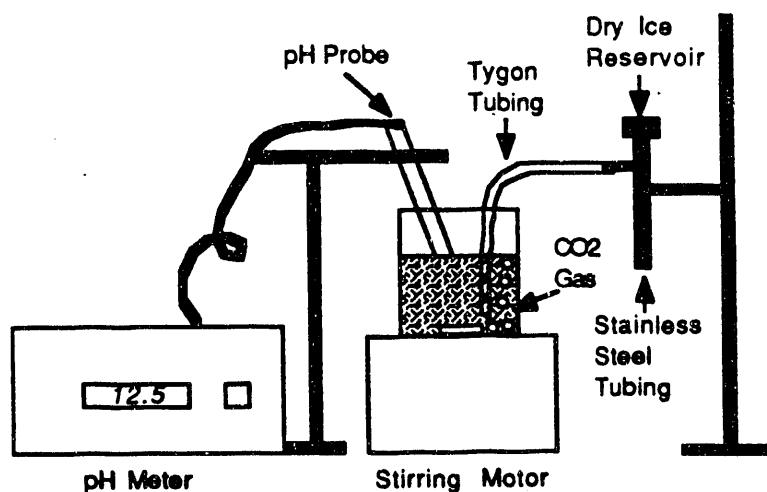


Fig. 1.

The solution was allowed to sit in an open beaker. The pH appeared to drop by 0.2 pH units over 48 hours. It is not known if this change is outside expected experimental error.

- 1 Personal communication, S. W. Stump, 244-2H.
- 2 "Limitations on Waste Tank Contents," DPSTS-241-5.01; "Limitations on Waste Tank Contents During Sludge Processing and Storage," DPSTS-241-5.03.
- 3 Young, J. E. "Treatment of "MAGNUSPRAY 205" Hazardous Waste," SRL-ADS-91-0622.
- 4 Baumann, E. W. "Colorimetric Determination of High pH with Azoviolet Indicator," WSRC-TR-90-12.
- 5 Baumann, E. W. and Buchanan, B. R. "Colorimetric pH Determination with Computer Modeling," *Applied Spectroscopy*, 45, 1991, 632.
- 6 For instance HACH model DR/3000 spectrophotometer.
- 7 Hyder, M. L.; Perkins, W. C.; Thompson, M. C.; Burney, G. A.; Russell, E. R.; Holcomb, H. P.; and Landon, L. F.; "Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant," DP-1500, p 7.25.

END

**DATE
FILMED**

5/05/93

