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

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Derivative Classifier_____

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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 $NaNO_2$ solutions[7] 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 /liter
			scale factor	1E+05					
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	0.04	0.91
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	Liters		0.096	Liters	95.63	mL		
Total volume	10245	Liters		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 CO_2 gas, via the reaction

$$OH^- + CO_2 \rightarrow HCO_3^-$$
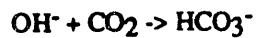
The apparatus for bubbling CO_2 through the solution is shown in Fig. 1. Dry ice (solid CO_2) was placed in a stainless steel tube that could be capped on both ends. The dry ice was allowed to sublime at room temperature, providing a flow of CO_2 gas. This CO_2 gas escaped through a side arm fitted with 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 CO_2 flow were allowed to continue, it is possible to over-neutralize to a pH of 8-9, the pH of a HCO_2^- solution. In actual plant operation it may be preferable to use CO_2 from a gas cylinder rather than subliming dry ice.
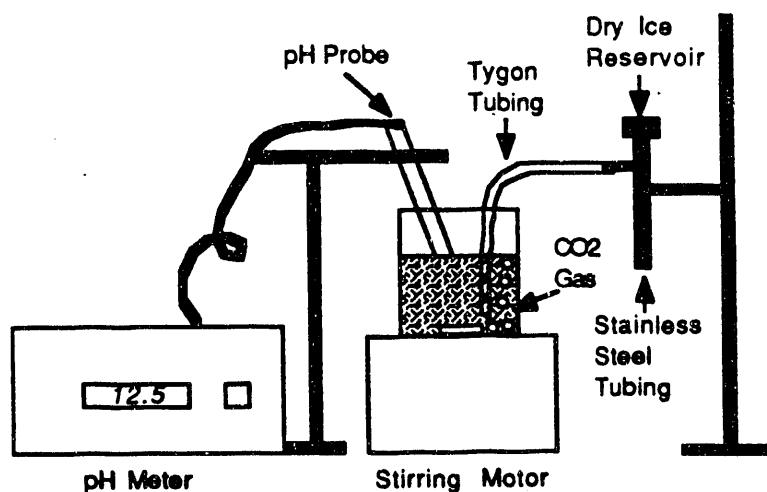

Fig. 1.

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.

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