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TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

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MEMORANDUM

TO: M. L. HYDER

FROM: J. R. WILEY

Sodium Oxalate Solubility in Simulated SRP Waste Solutions

INTRODUCTION AND SUMMARY

Oxalic acid ($H_2C_2O_4$) has been selected for dissolving the residual sludge in SRP waste tanks after most sludge has been removed by hydraulic slurring.[1] One option for disposing of the spent oxalic acid is to neutralize it with NaOH and to process the resulting sodium oxalate along with waste sludge and supernate through the Defense Waste Processing Facility (DWP). About 3 million lbs of sodium oxalate could be generated by tank cleaning,[2] so this material can have a significant effect on DWP operation.

Because of its low solubility, sodium oxalate will be distributed between sludge and supernate streams, and this distribution will depend primarily on the sodium concentration in the supernate. To determine this distribution the solubility of $Na_2C_2O_4$ in series of $NaNO_3$-NaOH solutions was measured. The apparent solubility product calculated from molar concentrations of Na^+ and $C_2O_4^{2-}$ at saturation ($Kc = [Na]^2[C_2O_4]$) increased from 0.07 to 0.5 $(\text{moles/liter})^3$ as the Na concentration increased from 0.5 to 6M. When the activity coefficients for Na and oxalate were included in the calculation, the solubility product was constant at $\sim 2.5 \times 10^{-3}$ $(\text{moles}/\ell)^3$. In simulated supernate the equilibrium oxalate concentration is about 75% of that in a $NaNO_3$-NaOH solution with the same total Na concentration as the supernate.

RESULT AND DISCUSSION

Sodium oxalate solubility was measured in a series of $NaNO_3$-NaOH solutions (Table 1) because $NaNO_3$ and NaOH are the principal soluble components in SRP sludge. Sodium oxalate solubility in solutions of 50% and 100% simulated supernate* was also measured. Excess $Na_2C_2O_4$ powder was added to these solutions and the mixtures were shaken overnight at ambient temperature (~21°C). Undissolved $Na_2C_2O_4$ was allowed to settle and oxalate remaining in the saturated solutions was determined by $KMnO_4$ titration.

Results of the tests are summarized in Table 2. As expected, the molar amount of sodium oxalate in solution decreased as the concentration of sodium increased. In solutions initially containing equal concentrations of sodium (numbered 3 and 4; 6 and 7; 9 and 10 in the Tables) the equilibrium oxalate concentration was increased by about 25% when OH^- was omitted and NO_3^- was the only anion present (Figure 1). Hydrolysis of $C_2O_4^{2-}$ to $HC_2O_4^-$ occurs at the lower pH of the pure $NaNO_3$ solutions and this would increase the total amount of dissolved oxalate. In simulated supernate the oxalate concentration was about 25% lower than in the $NaNO_3$-NaOH solutions. This is probably due to the increased ionic strength (next section) of the simulated supernate.

The apparent solubility product, Kc, should be adequate for DWP flowsheet calculations; however, it is clearly not a constant (Table 2). The chemically correct solubility constant, Ks, calculated from estimates of the sodium and oxalate ionic activities was included in Table 2 to show that no unusual factors affected the sodium oxalate solubility.

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* Simulated supernate contained 3.3M $NaNO_3$, 0.75M NaOH, 0.5M $NaAlO_2$, 0.3M Na_2CO_3, 0.3M Na_2SO_4.

Calculation of Ks

The solubility constant Ks is given by

$$Ks = (a_{Na})^2 (a_{C_2O_4}) \tag{1}$$

where the ionic activity, a, is related to measured concentration, C, of each ion by the activity coefficient, γ.

$$a = \gamma C \tag{2}$$

The solubility products Kc and Ks are therefore related by

$$Ks = Kc\ \gamma_{Na}^2\ \gamma_{C_2O_4}. \tag{3}$$

For $NaNO_3$ and NaOH solutions γ_{Na} can be found in the literature.[3] However, $\gamma_{C_2O_4}$ must be estimated from Debye-Huckel theory. This theory assumes that the activity coefficient depends on the ionic charge, Z, and is a function of the ionic strength of the solution, μ. ($\mu = \sum_i C_i Z_i^2$)

$$\log \gamma = Z^2 f(\mu) \tag{4}$$

This expression can be written as

$$\gamma = e^{Z^2 f(\mu)} = e^{f(\mu)}\ ^{Z^2} \tag{5}$$

For univalent ions this reduces to

$$\gamma = e^{f(\mu)} \tag{6}$$

Comparing equation 5 and 6 shows that for a given solution the activity coefficient of a polyvalent ion can be related to that of a univalent ion by

$$\gamma_{Z>1} = (\gamma_{Z=1})^{Z^2} \tag{7}$$

Hence for the $Na_2C_2O_4$ solutions in Table 2

$$\gamma_{C_2O_4{}^{2-}} = (\gamma_{Na})^4 \tag{8}$$

From equation 2, the expression for Ks becomes

$$Ks = Kc\ \gamma_{Na}^{2}\ \gamma_{C_2O_4{}^{2-}} = Kc\gamma_{Na}^{2}\gamma_{Na}^{4} = Kc\gamma_{Na}^{6} \qquad (9)$$

This is the relation between Kc and Ks used in Table 2.

REFERENCES

1. R. F. Bradley and A. J. Hill, "Chemical Dissolving of Sludge from a High Level Waste Tank at Savannah River Plant, USDOE Report DP-1471 (Nov. 1977).
2. M. L. Hyder, "Recommended Oxalic Acid Concentration for Chemical Dissolving of Tank 16H Sludge," DPST-78-436 (July, 1978).
3. W. M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, 2nd ed., Prentice-Hall (New York) 1952, p. 354.

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TABLE 1

INITIAL COMPOSITION OF SOLUTIONS FOR MEASURING $Na_2C_2O_4$ SOLUBILITY

Solution	Initial Concentration, molar		
	Na	NO_3	OH
1	(water)		
2	1.0	1.0	0
3	2.0	1.0	1.0
4	2.0	2.0	0
5	3.0	3.0	0
6	4.0	3.0	1.0
7	4.0	4.0	0
8	5.0	5.0	0
9	6.0	5.0	1.0
10	6.0	6.0	0
11	(Simulated Supernate + water, 1:1)		
12	(Simulated Supernate)		

TABLE 2

RESULTS OF $Na_2C_2O_4$ SOLUBILITY TESTS

Solution	[Na] moles/ℓ	$[C_2O_4]$ moles/ℓ	$Kc = [Na]^2[C_2O_4]$	γ_{NaNO_3} [a]	$Ks = Kc\ \gamma^6$
1	0.53	0.263	0.074	0.58	0.0028
2	1.23	0.119	0.181	0.52	0.0036
3	2.08	0.044	0.192	0.48	0.0023
4	2.12	0.058	0.262	0.48	0.0032
5	3.08	0.039	0.370	0.44	0.0027
6	4.04	0.020	0.326	0.44	0.0024
7	4.05	0.026	0.426	0.41	0.0020
8	5.04	0.020	0.508	0.41	0.0024
9	6.03	0.011	0.400	0.41	0.0019
10	6.03	0.015	0.545	0.41	0.0026
11	2.93	0.026	0.223		
12	5.77	0.008	0.266		

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a. Values from Reference 3.

FIGURE 1. Effect of Solution Composition on $Na_2C_2O_4$ Solubility