Description of the Material Balance Model and Spreadsheet for Salt Dissolution

by

B. J. Wiersma

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

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October 12, 1994

To: B. L. Lewis, 703-8C

From: B. J. Wiersma, 773-A *Bruce J. Wiersma*

Technical Reviewer: *D.T. Hobbs* 10/13/94
D. T. Hobbs, Interim Waste Technology

Approved by: *N. C. Iyer* 10/18/94
N. C. Iyer, Manager
Materials Applications and Corrosion Technology

Description of the Material Balance Model and Spreadsheet for Salt Dissolution (U)

Summary

The model employed to estimate the amount of inhibitors necessary for bearing water and dissolution water during the salt dissolution process is described. The assumptions and equations in the model, and the input and output cells for the spreadsheet are documented. Two case studies are also shown as examples of how the model may be applied to a tank. Copies of the spreadsheet (in both IBM and Macintosh formats) will be distributed to Waste Removal and High Level Waste Engineering personnel.

Introduction

Saltcake in waste storage tanks will be dissolved and then transferred to Tank 48 for the In-Tank Precipitation (ITP) process. Recommendations for inhibitor additions that will be necessary during the salt dissolution process were recently made[1]. The inhibitor requirements for bearing and dissolution water added to the tank were calculated from a material balance model. This model was inputted on a spreadsheet which allowed many different case studies to be performed. This memo describes the assumptions and equations which are used in the model, and documents the input and output cells of the spreadsheet. Two case studies are shown as examples of how the model may be employed.

Definitions and Assumptions Included in the Material Balance Model

Four different types of water will be referred to in the discussion of the model: bearing water, residual supernate, dissolution water and total volume. A brief definition of each is given below.

Bearing water is used to lubricate and cool the bearings and seals in the Bingham slurry pumps. An amount that may range from a few ml/min to 5 gpm may leak through the seals. Leakage at the higher rate would significantly impact the salt dissolution process. Typically the composition of the bearing water is 0.01 M sodium hydroxide and 0.011 M sodium nitrite. A recommendation was made that the bearing water composition be the same as that of the dissolution water that is added to the tank [1]. This composition may

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range from 0.01M sodium hydroxide with 0.011 M sodium nitrite to 1 M sodium hydroxide depending on the leak rate and the salt dissolution rate.

Supernate is the liquid phase in the tank that is in equilibrium with the undissolved saltcake. Supernate compositions vary from tank to tank. Supernate samples are taken and analyzed on a regularly scheduled basis. The results are reported in the Tank Chemistry Report [2]. Two approaches have been recommended for handling the supernate during waste removal operations. The first method is to remove all the supernate above the crystals and then dissolve the salt with inhibited water. An alternative means is to leave a fraction of the supernate above the salt and then add the inhibited water to the tank. The latter approach may prevent the dissolution water from being out of technical standards at the low nitrate concentrations. A comparison between these two approaches will be given later in the report.

Dissolution water is added to the tank to dissolve the saltcake. Since the salt is predominantly sodium nitrate, the water must contain either sodium hydroxide or a combination of sodium hydroxide and sodium nitrite to ensure that the dissolution water is not corrosive to the tank walls. The recommended composition of the dissolution water will depend on the bearing water leak rate, the salt dissolution rate, the amount of supernate left in the tank and the composition of the saltcake.

Total volume is the total volume of solution upon dissolution of the saltcake. This volume includes bearing water leakage, supernate left in the tank, inhibited water added to the tank, and dissolved salt. The Excel spreadsheet tracks the concentration of sodium hydroxide, sodium nitrite and sodium nitrate in the dissolution water as a function of time and determines whether or not its composition meets the corrosion technical standards.

The spreadsheet also utilizes the parameter R, which is the ratio between the molar concentration of the inhibitor anions and the molar concentration of the aggressive anions. The ratio provides a means for determining appropriate temperature limits for the total volume during salt dissolution.

Several assumptions were made when developing the model. These include:

- the bearing water, dissolution water, supernate and saltcake are completely mixed during the dissolution process;
- the volume of salt includes the saltcake and the interstitial liquid in the saltcake;
- the volumes of saltcake, dissolution water, bearing water and supernate are additive [3];
- hydroxide, nitrite and nitrate dissolve at an independent rate (i.e., no common ion effect);
- the saltcake dissolution rate is constant with time and does not vary within the tank;
- the most significant species from a corrosion standpoint are nitrate (aggressive anion) and hydroxide and nitrite (inhibitor anions);
- the time necessary to pump the dissolution water into the tank is negligible;

- 3500 gallons of saturated dissolution water occupy one inch of the waste tank. This assumption allows conversion from inches of salt to gallons of salt; and
- the specific gravity of the saltcake was 1.9.

The assumption that the components dissolve at a constant rate likely produces some error in the model. A mass transfer model that was developed for salt dissolution utilized a similar assumption [4]. This model also assumed that the only component dissolving was sodium nitrate. The results from this model showed that initially the composition and dissolution rate are comparable with the Tank 19 test [5]. However, during later stages of salt dissolution the actual rate decreases, while the model predicts an increase in the dissolution rate. The likely cause of this discrepancy is the different solubilities of saltcake constituents (e.g., sodium hydroxide dissolves more readily than sodium sulfate). An alternative to this model would be to experimentally determine the saltcake dissolution rates for a given saltcake concentration. This dissolution rate may then be inserted directly into the mass balance model.

In addition, there were two process limitations that were placed on the model results. The volume of total volume can not exceed two times the initial total volume. For example, if the initial total volume is 200,000 gallons, the point at which the total volume reaches 400,000 gallons is the final time step in the model. This limitation assumes that the total volume does not reach saturation before this condition occurs. If saturation of the total volume is achieved, the time at which it occurred would be the final time step. The second limitation is that the inhibitor concentration in the total volume had to be less than the level specified in DPSTS 241-5.01 [6] for longer than 5 days in order to be considered outside technical standards. This time period was selected as a conservative limit after which a significant amount of pitting or stress corrosion cracking could initiate [7].

Equations in the Excel Spreadsheet

This section shows the equations that are employed in the spreadsheet:

Initial total volume concentration of component i:

$$C_{io_{tw}} = \frac{C_{dw}^{i} V_{dw} + C_{rs}^{i} V_{rs}}{V_{tw}^{o}} \quad (1)$$

where $C_{io_{tw}}$ is the concentration of component i in the initial total volume, C_{dw}^{i} is the concentration of component i in the dissolution water, C_{rs}^{i} is the concentration of component i in the residual supernate, V_{dw} is the volume of the dissolution water, V_{rs} is the volume of the residual supernate, and V_{tw}^{o} is the initial total volume.

To prevent pitting corrosion in dilute solutions a critical concentration of sodium nitrite must be present. An equation for this concentration which depends on the nitrate concentration and the temperature has been developed. The temperature dependent coefficient for this equation in standard DPSTS-241-5.01-4d is:

$$C_1 = 0.038 * 10^{(0.041 * T)} \quad (2)$$

where C_1 is the coefficient and T is the temperature in °C.

The temperature dependent coefficient for standard DPSTS-241-5.01-4e is:

$$C_2 = 0.00076 * 10^{(0.041 * T)} \quad (3)$$

where C_2 is the coefficient.

Volume of total volume:

$$V_{tw} = V_{tw}^0 + (Q_{bw} + Q_{sd}) * t \quad (4)$$

where V_{tw} is the volume of total volume, Q_{bw} is the volumetric flow rate of the bearing water, Q_{sd} is the volumetric dissolution rate of the salt, and t is time. The salt dissolution rate maybe modeled [4] or determined experimentally. Saltcake dissolution rates determined in feet/hr are converted to gallons per minute using the assumption that the saltcake profile is flat and that 1 inch of salt is equivalent to 3500 gallons. Concentration of component i in the total dissolution water at time t :

$$C_{i_{tw}} = \frac{C_{i_{tw}}^0 V_{tw}^0 + Q_{bw} C_{i_{bw}} t + Q_{sd} C_{i_{sd}} t}{V_{tw}^0 + (Q_{bw} + Q_{sd}) * t} \quad (5)$$

where $C_{i_{tw}}$ is the concentration of component i in the total dissolution water at time t , $C_{i_{bw}}$ is the concentration of component i in the bearing water, and $C_{i_{sd}}$ is the concentration of component i in the saltcake.

Reclaimed Tank Space:

$$V_{rt} = Q_{sd} * t \quad (6)$$

where V_{rt} is the volume of tank space that is reclaimed.

Ratio:

$$R = \frac{[NO_2^-] + [OH^-]}{[NO_3^-]} \quad (7)$$

where R is the ratio.

Description of Excel Spreadsheet - Input and Output Cells

This section documents the contents of each of the cells in the EXCEL spreadsheet.

Input Cells	Variable Name	Description
C1	Q1	Volumetric flow rate of bearing water leaking from all the pumps into the tank (gpm).
C2	Q2	Volumetric saltcake dissolution rate (gpm).
C3	V0	Initial volume of total volume including residual supernate and additional inhibited water (gallons).
C4	V3	Fraction of initial total volume that is residual supernate (gallons).
C5	V4	Fraction of initial total volume that is inhibited water (gallons).
C6	Cb4	Hydroxide concentration in dissolution water (moles/liter).

C7	Cd4	Nitrite concentration in dissolution water (moles/liter).
C8	Ca2	Nitrate concentration in saltcake. Wt.% data from Fowler reports [8,9] is converted to moles/liter. This value may be adjusted to reflect different saltcake composition in different tanks.
C9	Cb2	Hydroxide concentration in saltcake. Wt.% data from Fowler reports [8,9] is converted to moles/liter. This value may be adjusted to reflect different saltcake composition in different tanks.
C10	Cd2	Nitrite concentration in saltcake. Wt.% data from Fowler reports [8,9] is converted to moles/liter. This value may be adjusted to reflect different saltcake composition in different tanks.
C11	Ca3	Nitrate concentration in supernate (moles/liter). This data can be obtained for individual tanks from the Tank Chemistry Monthly Report.
C12	Cb3	Hydroxide concentration in supernate (moles/liter). This data can be obtained for individual tanks from the Tank Chemistry Monthly Report.
C13	Cd3	Nitrite concentration in supernate (moles/liter). This data can be obtained for individual tanks from the Tank Chemistry Monthly Report.
C14	Ca0	Nitrate concentration in initial total volume (moles/liter). Value is calculated from supernate and inhibited water inputs.
C15	Cb0	Hydroxide concentration in initial total volume (moles/liter). Value is calculated from supernate and inhibited water inputs.
C16	Cd0	Nitrite concentration in initial total volume (moles/liter). Value is calculated from supernate and inhibited water inputs.
C17	Cb1	Hydroxide concentration in bearing water (moles/liter). Per earlier recommendation [1], the concentration is the same as the inhibited water, however this can be altered.
C18	Cd1	Nitrite concentration in bearing water (moles/liter). Per earlier recommendation [1], the concentration is the same as the inhibited water, however this can be altered.
C19	SpG	Specific gravity of the saltcake.
C20	Temp.	Temperature of the dissolution water (°C).
C21	Exp. 1	Coefficient used to calculate required nitrite inhibitor for standard DPST-241-5.01-4d.
C22	Exp. 2	Coefficient used to calculate required nitrite inhibitor for standard DPST-241-5.01-4e.
H15:H20; I15:I20		H15:H20 lists the corrosion technical standards in DPST-241-5.01 section 4. I15:I20 correlates a number to each standard. These numbers will indicate which technical standard was evaluated at a given time step.
A25:A85		Time step (days).

Output Cells:

Input
Cells

Description

B25:B85	Volume of total volume added to the tank. This total includes the dissolution water, residual supernate, bearing water leaked into the tank, and salt dissolved into the dissolution water.
C25:C85	Hydroxide concentration in total volume at a given time (moles/liter). The calculation was made with the material balance equation.

D25:D85	Nitrate concentration in total volume at a given time (moles/liter). The calculation was made with the material balance equation.
E25:E85	Nitrite concentration in total volume at a given time (moles/liter). The calculation was made with the material balance equation.
F25:F85	The sum of the nitrite and hydroxide concentrations. This parameter is useful to determine whether the total volume is within technical standard limits.
G25:G85	A set of logical statements (i.e., IF, AND, OR) which determine the technical standard that applies and whether the inhibitor amounts present are adequate. The number identifies the appropriate technical standard. A "yes" signifies that the inhibitor amounts are adequate, while "no" indicates that they are inadequate.
H25:H85	Amount of tank space reclaimed due to salt dissolution (gallons).
I25:I85	Ratio of the nitrate concentration to hydroxide plus nitrite concentrations. This ratio may be used to determine the temperature limits for the dissolution water [10].
J25:J85	A set of logical statements which identify the ratio and set the appropriate temperature limits.

Applications of the Model

There are several input variables for the model which need to be chosen. Two case studies are presented to show the effects of the two of these variables on the inhibitor requirements for the bearing water and the dissolution water. The first case will look at the effect of salt dissolution rate on the inhibitor requirements, while the second case will look at the influence of leaving a "heel" of residual supernate above the saltcake. There are many other case studies that can be performed with this spreadsheet, however, these two cases will illustrate the importance of a) determining the salt dissolution rate and b) the potential advantages of leaving residual supernate.

Case 1: Effect of Salt Dissolution Rate

This case study compares the inhibitor requirements for a saltcake that dissolves at 4 gallons per minute (gpm) with that of a saltcake that dissolves at 12 gpm. Table 1 is a copy of the EXCEL spreadsheet for the 4 gpm case. The figure shows the input values and the concentration of the various anions in the total volume for the first 12 days. Column G25:G37 shows that the total volume is not within technical standards during this time. The inhibitor concentration in the bearing water and the dissolution water (0.01 M sodium hydroxide and 0.011 M sodium nitrite) would have to be increased to meet technical standards. Table 2 is a copy of the EXCEL spreadsheet for the 12 gpm case. Given that all other input values are the same as that for the 4 gpm case, the results show that after three days the total dissolution water remains within the technical standards requirements. This situation meets the requirement that the total volume can not be outside of technical standards for longer than five days. Thus, for this case less inhibitor may be used at higher salt dissolution rates.

Case 2: Effect of Residual Supernate

In this study 5000 gallons of residual supernate is left in the tank before dissolution water is added. For example purposes the supernate composition of Tank 29 is assumed [2]. Other input variables are the same as those used for the 4 gpm case. Table 3 is a copy of the EXCEL spreadsheet for this case. After three days the total volume remains within

the technical standards requirements for the remainder of the dissolution process. Thus leaving a small amount of supernate may allow for a lower inhibitor concentrations in the bearing and dissolution waters even when the salt dissolution rate is relatively low.

These cases are two examples of the types of comparisons that can be made with this spreadsheet. As mentioned above there are several other variables which impact on the inhibitor requirements: salt composition, total volume, bearing water leak rate, supernate composition etc. The large number of input variables allow this spreadsheet flexibility so that it may be applied to an individual tank. Copies of the spreadsheet will be given to Waste Removal and High Level Waste Engineering personnel for application.

Conclusions

The EXCEL spreadsheet provides a flexible tool for case studies of the salt dissolution process. The equations used are based on a simple material balance of the salt dissolution process. Two examples were given which show how the spreadsheet may be utilized to make comparisons between different conditions.

References

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Table 1. Case study with no residual supernate and a salt dissolution rate of 4 gpm.

	A	B	C	D	E	F	G	H	I	J
1		Q1	2	gpm	bearing leak rate					
2		Q2	4	gpm	salt dissolution rate					
3		V0	200000	gallons	Initial total water					
4		V3	0	gallons	Initial supernate					
5		V4	200000	gallons	Initial dissolution water					
6		Cb4	0.1	mole/l OH	initial dissolution water					
7		Cd4	0.011	mole/l NO2	initial dissolution water					
8		Ca2	11.556471	mole/l NO3	Saltcake concentration					
9		Cb2	1.31575	mole/l OH	Saltcake concentration					
10		Cd2	3.1115942	mole/l NO2	Saltcake concentration					
11		Ca3	1.66	mole/l NO3	Initial supernate concentration					
12		Cb3	6.5	mole/l OH	Initial supernate concentration					
13		Cd3	2.38	mole/l NO2	Initial supernate concentration					
14		Ca0	0	mole/l NO3	Initial total water concentration		TS	ID		
15		Cb0	0.1	mole/l OH	Initial total water concentration		4c	1		
16		Cd0	0.011	mole/l NO2	Initial total water concentration		4b	2		
17		Cb1	0.1	mole/l OH	Bearing water concentration		4a	3		
18		Cd1	0.011	mole/l NO2	Bearing water concentration		4d	4		
19		SpG	1.9	Salt Slurry			4e	5		
20		Temperature	70	C						
21		Exponent 1	28.169789							
22		Exponent 2	0.5633958							
23	Time	Volume	OH	NO3	NO2	OH+NO2	Technical	Reclaimed Tank Space	Aggressor/Inhibitor	Temperature
24	Days	Gallons	Molar	Molar	Molar	Molar	Standard	gallons	Ratio	Limit
25	0	200000	0.100	0.000	0.011	0.111	no 5	0		
26	1	208640	0.134	0.319	0.097	0.2301629	no 4	5760	0.721	70° C
27	2	217280	0.164	0.613	0.175	0.3398489	no 4	11520	0.555	70° C
28	3	225920	0.193	0.884	0.248	0.4411453	no 4	17280	0.499	70° C
29	4	234560	0.219	1.135	0.316	0.5349792	yes1	23040	0.471	70° C
30	5	243200	0.244	1.369	0.378	0.622146	yes1	28800	0.455	70° C
31	6	251840	0.267	1.586	0.436	0.7033319	yes1	34560	0.443	70° C
32	7	260480	0.288	1.789	0.491	0.7791319	yes1	40320	0.436	70° C
33	8	269120	0.308	1.979	0.542	0.8500649	yes1	46080	0.430	70° C
34	9	277760	0.327	2.157	0.590	0.916585	yes1	51840	0.425	70° C
35	10	286400	0.345	2.324	0.635	0.9790916	yes1	57600	0.421	70° C
36	11	295040	0.361	2.482	0.677	1.0379373	yes1	63360	0.418	70° C
37	12	303680	0.377	2.630	0.717	1.0934345	yes1	69120	0.416	70° C

Table 2. Case study with no residual supernate and a salt dissolution rate of 12 gpm.

	A	B	C	D	E	F	G	H	I	J
1		Q1	2	gpm	bearing leak rate					
2		Q2	12	gpm	salt dissolution rate					
3		V0	200000	gallons	initial total water					
4		V3	0	gallons	initial supernate					
5		V4	200000	gallons	initial dissolution water					
6		Cb4	0.1	mole/l OH	initial dissolution water					
7		Cd4	0.011	mole/l NO2	initial dissolution water					
8		Ca2	11.556471	mole/l NO3	Saltcake concentration					
9		Cb2	1.31575	mole/l OH	Saltcake concentration					
10		Cd2	3.1115942	mole/l NO2	Saltcake concentration					
11		Ca3	1.66	mole/l NO3	Initial supernate concentration					
12		Cb3	6.5	mole/l OH	Initial supernate concentration					
13		Cd3	2.38	mole/l NO2	Initial supernate concentration					
14		Ca0	0	mole/l NO3	Initial total water concentration		TS	ID		
15		Cb0	0.1	mole/l OH	Initial total water concentration		4c	1		
16		Cd0	0.011	mole/l NO2	Initial total water concentration		4b	2		
17		Cb1	0.1	mole/l OH	Bearing water concentration		4a	3		
18		Cd1	0.011	mole/l NO2	Bearing water concentration		4d	4		
19		SpG	1.9	Salt Slurry			4e	5		
20		Temperature	70	C						
21		Exponent 1	28.169789							
22		Exponent 2	0.5633958							
23	Time	Volume	OH	NO3	NO2	OH+NO2	Technical	Reclaimed	Aggressor/	
24	Days	Gallons	Molar	Molar	Molar	Molar	Standard	Tank Space	Inhibitor	Temperature
25	0	200000	0.100	0.000	0.011	0.111	no 5	gallons	Ratio	Limit
26	1	220160	0.195	0.907	0.254	0.4497828	no 4	17280	0.496	70° C
27	2	240320	0.275	1.662	0.457	0.7317259	yes1	34560	0.440	70° C
28	3	260480	0.342	2.300	0.628	0.9700267	yes1	51840	0.422	70° C
29	4	280640	0.399	2.846	0.775	1.1740905	yes 2	69120	0.412	BP
30	5	300800	0.449	3.319	0.902	1.350801	yes 2	86400	0.407	BP
31	6	320960	0.493	3.733	1.013	1.5053126	yes 2	103680	0.403	BP
32	7	341120	0.531	4.098	1.110	1.6415611	yes 2	120960	0.401	BP
33	8	361280	0.565	4.422	1.197	1.7626038	yes 2	138240	0.399	BP
34	9	381440	0.596	4.712	1.275	1.8708517	yes 2	155520	0.397	BP
35	10	401600	0.623	4.973	1.345	1.9682318	yes 2	172800	0.396	BP
36	11	421760	0.648	5.208	1.408	2.0563023	yes 2	190080	0.395	BP
37	12	441920	0.670	5.423	1.466	2.1363375	yes 2	207360	0.394	BP

Table 3. Case study with residual supernate and a salt dissolution rate of 4 gpm.

	A	B	C	D	E	F	G	H	I	J
1		Q1	2	gpm	bearing leak rate					
2		Q2	4	gpm	salt dissolution rate					
3		V0	200000	gallons	Initial total water					
4		V3	5000	gallons	Initial supernate					
5		V4	195000	gallons	Initial dissolution water					
6		Cb4	0.1	mole/l OH	initial dissolution water					
7		Cd4	0.011	mole/l NO2	Initial dissolution water					
8		Ca2	11.556471	mole/l NO3	Saltcake concentration					
9		Cb2	1.31575	mole/l OH	Saltcake concentration					
10		Cd2	3.1115942	mole/l NO2	Saltcake concentration					
11		Ca3	1.66	mole/l NO3	Initial supernate concentration					
12		Cb3	6.5	mole/l OH	Initial supernate concentration					
13		Cd3	2.38	mole/l NO2	Initial supernate concentration					
14		Ca0	0.0415	mole/l NO3	Initial total water concentration		TS	ID		
15		Cb0	0.26	mole/l OH	Initial total water concentration		4c	1		
16		Cd0	0.070225	mole/l NO2	Initial total water concentration		4b	2		
17		Cb1	0.1	mole/l OH	Bearing water concentration		4a	3		
18		Cd1	0.011	mole/l NO2	Bearing water concentration		4d	4		
19		SpG	1.9	Salt Slurry			4e	5		
20		Temperature	70	C						
21		Exponent 1	28.169789							
22		Exponent 2	0.5633958							
23	Time	Volume	OH	NO3	NO2	OH+NO2	Technical	Reclaimed Tank Space	Aggressor/Inhibitor	Temperature
24	Days	Gallons	Molar	Molar	Molar	Molar	Standard	gallons	Ratio	Limit
25	0	200000	0.260	0.042	0.070	0.330225	no 4	0		
26	1	208640	0.287	0.359	0.153	0.4403095	no 4	5760	1.227	70° C
27	2	217280	0.312	0.651	0.230	0.5416392	no 4	11520	0.832	70° C
28	3	225920	0.335	0.921	0.301	0.6352184	no 4	17280	0.690	70° C
29	4	234560	0.356	1.171	0.366	0.7219037	yes1	23040	0.617	70° C
30	5	243200	0.376	1.403	0.427	0.8024297	yes1	28800	0.572	70° C
31	6	251840	0.394	1.619	0.484	0.8774305	yes1	34560	0.542	70° C
32	7	260480	0.411	1.821	0.536	0.9474558	yes1	40320	0.520	70° C
33	8	269120	0.427	2.010	0.586	1.0129848	yes1	46080	0.504	70° C
34	9	277760	0.442	2.187	0.632	1.0744371	yes1	51840	0.491	70° C
35	10	286400	0.456	2.353	0.676	1.1321817	yes1	57600	0.481	70° C
36	11	295040	0.470	2.510	0.717	1.1865442	yes1	63360	0.473	70° C
37	12	303680	0.482	2.658	0.756	1.2378135	yes1	69120	0.466	70° C