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7. Abstract To be categorized as conditionally safe, ferrocyanide tanks containing ≥ 8 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ on an energy equivalent basis (i.e., ≥ 115 cal/g) are required to contain some amount of water. These tests were conducted to determine the equilibrium moisture content of waste simulant at the conditions of 30% relative humidity and 25°C. This test report was prepared to disseminate data collected from these tests. These data are used to model the waste tank moisture contents and transport. These models can determine if the moisture in these tanks will drop below the defined safety limits.		
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CONTENTS

1.0 BACKGROUND	1
2.0 SCOPE	1
3.0 TEST PROCEDURE	1
4.0 TEST EQUIPMENT AND MATERIALS	2
5.0 TEST DOCUMENTATION AND DATA	6
6.0 CONCLUSIONS	8
7.0 REFERENCES	11

LIST OF FIGURES

1 Detailed Sketch of the Samples as of September 15, 1994.	5
2 Percent Moisture Versus Time of the Simulants in the 30% Relative Humidity Environment Through September 15, 1994.	7

LIST OF TABLES

1 U-Plant-1 Simulant Feed Solution Based Upon 77 L of Total Solution	2
2 In-Farm-1 Bottom Fraction Simulant Feed Solution Based Upon 150 L Batch	3
3 Tank BY-104 Simulant Composition	4
4 Initial Moisture Analysis Data	6
5 Moisture Weight Loss Data as of September 15, 1994	9

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1.0 BACKGROUND

To be categorized as conditionally safe, ferrocyanide tanks containing ≥ 8 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ on an energy equivalent basis (i.e., ≥ 115 cal/g) are required to contain some amount of water. Tests are necessary to determine if a minimum water concentration could be maintained in the waste at equilibrium if the waste were allowed to dry. It is also important to determine the rate of drying that could be reasonably expected in a tank.

The moisture content of the saltcake or sludge found in the waste tanks will have a water concentration at equilibrium that is related to the moisture in the atmosphere above the saltcake. Because of the complex nature of the waste, the rate of drying and the equilibrium moisture concentrations are not available through the normal scientific literature. Tests were conducted to obtain these data and the results are outlined in this report.

2.0 SCOPE

Samples of saltcake and sludge simulants were placed in a moisture and temperature controlled environment. The moisture loss rate of these samples was measured by weighing the samples periodically during the test. These data were tabulated and are presented in this report.

3.0 TEST PROCEDURE

The following is an outline of the test procedures used to support the identified scope (King 1994).

- Previously prepared samples of U-Plant-1 mixed, In-Farm-1 bottom, and tank BY-104 saltcake simulant were obtained and placed in previously weighed 20 ml sample bottles.
- A saturated solution of NaNO_3 in deionized water was prepared and placed in a previously weighed 20 ml sample bottle. This solution was prepared as a standard.
- An infrared moisture analyzer was used to obtain the starting moisture content of each of the simulant samples.

- A saturated solution of CaCl_2 was placed in the bottom of a glass desiccator. The CaCl_2 solution had undissolved crystals to ensure the saturation was maintained.
- Each of the labeled sample bottles containing simulant was weighed and placed into the prepared desiccator. The desiccator was then placed into an oven and held at a constant temperature of 25°C .
- Sample weight, oven temperature and relative humidity of the desiccator were periodically measured. Data were recorded in project notebook WHC-N-9151.

4.0 TEST EQUIPMENT AND MATERIALS

Equipment and materials used in this test are listed below.

- The U-Plant-1 mixed sample was obtained from sample N231N-19 as identified in the controlled notebook RHO-RE-NB-199. This simulant was prepared using the ingredients shown in Table 1 and using the techniques identified in Section 3 of *Ferrocyanide Waste Simulant Characterization* (Jeppson and Wong 1993). Sample N231N-19 was a centrifuged portion of the simulant.

Table 1. U-Plant-1 Simulant Feed Solution Based Upon 77 L of Total Solution.

Molarity	Constituent
0.19	sodium sulfate (Na_2SO_4)
0.15	sodium phosphate (Na_3PO_4)
1.55	sodium nitrate (NaNO_3)
2.07	nitric acid (HNO_3)
0.033	sulfamic acid ($\text{NH}_2\text{SO}_3\text{H}$)
0.017	ferrous ammonium sulfate [$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$]
0.002	sodium ferrocyanide [$\text{Na}_4\text{Fe}(\text{CN})_6$]
0.004	strontium nitrate [$\text{Sr}(\text{NO}_3)_2$]
2.01	sodium hydroxide (NaOH)
0.002	nickel sulfate (NiSO_4)

- The In-Farm-1 bottom fraction sample was obtained from the simulant sample 1-Rev-29 as identified in controlled notebook RHO-RE-NB-199. This simulant was prepared using the ingredients shown in Table 2 and using the techniques identified in Section 3 of *Ferrocyanide Waste Simulant Characterization* (Jeppson and Wong 1993). This sample came from the centrifuged bottom portion of the simulant.

Table 2. In-Farm-1 Bottom Fraction Simulant Feed Solution Based Upon 150 L Batch.

Molarity	Constituent
4.2334	sodium nitrate (NaNO_3)
0.00037	cesium nitrate (CsNO_3)
1.5	sodium nitrite (NaNO_2)
0.23	sodium sulfate (NaSO_4)
0.27	sodium phosphate (Na_3PO_4)
0.2666	nitric acid (HNO_3)
0.08	sodium hydroxide (NaOH)
0.01	nickel sulfate (NiSO_4)
0.003	sodium sulfide (Na_2S)
0.0075	sodium ferrocyanide [$\text{Na}_4\text{Fe}(\text{CN})_6$]

- Tank BY-104 saltcake was obtained from the simulant sample prepared as indicated in *Justification of Salt Cake Simulants* (Wanner 1993). Table 3 identifies the simulant composition.
- A 250 mm inner diameter glass desiccator was used in this application. The bottom of the desiccator was filled with a saturated solution of CaCl_2 with excess CaCl_2 to ensure continued saturation. The vapor pressure of this saturated solution maintained relative humidity of 30% at a temperature of 25 °C within the closed desiccator system.
- The test samples were placed in glass sample bottles as shown in Figure 1. The sample material was filled to the top leaving no air space. Screw cap lids were not used for these tests.

Table 3. Tank BY-104 Simulant Composition.

WT%	Constituent
81.4	sodium nitrate (Na_2NO_3)
2.2	sodium hydroxide (NaOH)
7.5	sodium aluminate (NaAlO_2)
0.6	sodium phosphate (Na_3PO_4)
1.5	sodium silicate (Na_2SiO_3)
0.4	calcium nitrate [$\text{Ca}(\text{NO}_3)_2$]
0.2	magnesium nitrate [$\text{Mg}(\text{NO}_3)_2$]
0.2	manganese nitrate [$\text{Mn}(\text{NO}_3)_3$]
1.0	iron (III) nitrate [$\text{Fe}(\text{NO}_3)_3$]
~ 5.0	water (H_2O)

- All samples and containers were weighed on a calibrated AE261 balance with a readability of 0.1 mg and a reproducibility of ± 0.2 mg.
- The humidity of the desiccator was measured using a digital humidity/temperature precision psychrometer. The range of the psychrometer is 10 to 100% relative humidity, with an accuracy of $\pm 2\%$. A fan in the psychrometer draws air across two matched temperature sensors; one of the sensors measures the dry bulb temperature, the other, which is fitted with a moistened wick, measures wet bulb temperature. The psychrometric chart is programmed into the meter for a direct reading of relative humidity. The dry bulb and wet bulb temperatures were also recorded for this test using this meter. The meter was factory calibrated. This was acceptable because the normal calibration method is to use a saturated salt solution with a known relative humidity at a given temperature. In this application, a saturated salt solution is the relative humidity controller. The measurement is used to verify that the relative humidity is correct.

Figure 1. Detailed Sketch of the Samples as of September 15, 1994.

- An IR 100 moisture analyzer was used to measure the moisture content of the original samples. The analyzer is a balance that operates by heating the sample using an infrared quartz heater and monitors the weight change during the heating cycle. The instrument was set to operate at a temperature of 105°C with a cutoff when the change in weight was less than 5% over a 1 minute period. The analyzer contains a printer that provides a hard copy of the data collected. The analyzer has a resolution of 0.001 g and is calibrated using the manufactures' recommendations.

5.0 TEST DOCUMENTATION AND DATA

All data were recorded in project notebook WHC-N-9151. The starting weight of the simulants was measured using the moisture analyzer. The starting simulant moisture data and set points are shown in Table 4. These data provide a starting point to calculate the change in moisture percentage of the samples with time. This calculation is shown in the following equation:

$$PM_t = \frac{M_o - S_o + S_t}{S_t} * 100$$

Table 4. Initial Moisture Analysis Data.

	104-BY	U-Plant-1	In-Farm-1
Initial Sample Weight	8.095g	2.016g	2.639g
Elapsed Time	40.3 min	37.6 min	38.3 min
Final Sample Weight	7.377g	0.993g	1.559g
Initial Percent Moisture	8.76%	50.74%	40.92%

Where PM_t is the percent moisture in the sample at time t , M_o is the original moisture content of the sample at $t=0$, S_o is the initial total sample weight at $t=0$, and S_t is the sample weight measured at time t .

Moisture weight loss data were collected from March 3, 1994 through September 15, 1994 and are tabulated and recorded in Table 5. The data are plotted in Figure 2. A visual description of the samples is shown in Figure 1.

Figure 2. Percent Moisture Verses Time of the Simulants in the 30% Relative Humidity Environment Through September 15, 1994.

6.0 CONCLUSIONS

The objective of this test (which is still continuing) was to determine the rate of drying that could be reasonably expected in the waste tanks and the associated minimum water content equilibrium. Weight loss for the BY-104 saltcake simulant diminished quickly and is at approximately 7 wt% moisture as of September 15, 1994. However, some drying continues to occur at a slow rate. The U-Plant-1 sample reached a negative moisture content. This is probably the result of offgassing of some of the nitrogen in the salts. Equilibrium was not achieved in this sample. Weight loss for In-Farm-1 bottom fraction sample appears to have slowed at a moisture of approximately 3%. However, it appears that drying is continuing to occur. The rate of drying can be obtained from data gathered thus far. It is not clear when equilibrium will be reached. It is recommended that the tests continue, and that data continue to be taken in order to determine the equilibrium concentration.

It appears that salt migration has occurred in the samples, as shown in Figure 1. The migration occurred early in the test, as would be expected. The larger quantities of moisture would have the hydraulic ability to carry with them small amounts of dissolved salts. It could also be assumed that this migration was dramatic enough to affect the drying action of the samples.

In summary, enough data were collected to allow modeling of water evaporation from waste simulants. These data will help eliminate some of the assumptions now being used for this purpose. Data will continue to be gathered to determine the equilibrium moisture concentration in the salt samples. This will further substantiate the information that has already been gathered.

It is recommended that the moisture content for each sample be measured at the end of the test (using an agreed upon method) to verify the final moisture results. This is particularly critical when interpreting the data from the U-Plant-1 sample which shows a negative percent moisture number (this number is probably the result of offgassing of nitrogen during the drying process).

Table 5. Moisture Weight Loss Data as of September 15, 1994.

Time (hrs)	RH (%)	Dry Bulb Temp (°C)	U-Plant-1		In-Farm-1 Bottom Fraction		104-BY		Sodium Nitrate Standard	
			Sample Weight (gms)	Percent Moisture (%)	Sample Weight (gms)	Percent Moisture (%)	Sample Weight (gms)	Percent Moisture (%)	Sample Weight (gms)	Percent Moisture (%)
0.0	*	29.0	30.2531	50.7400	32.4307	40.9200	42.8738	8.7600	30.0874	54.5454
25.0	*	29.0	29.5741	49.6089	32.0625	40.2420	42.7958	8.5938	29.0909	52.9884
90.8	*	29.0	28.0823	46.9321	31.3078	38.8015	42.7098	8.4098	28.4326	51.8999
113.8	*	29.0	27.5836	45.9726	31.0412	38.2759	42.6648	8.3132	28.1438	51.4063
142.8	*	25.6	26.5768	43.9259	30.5412	37.2654	42.6017	8.1774	27.6198	50.4844
161.8	*	25.0	26.2654	43.2610	30.3937	36.9609	42.5860	8.1435	27.4592	50.1948
234.5	*	25.0	25.4350	41.4086	29.9421	36.0102	42.5510	8.0680	27.0125	49.3712
257.3	*	26.0	25.1749	40.8034	29.7730	35.6467	42.5300	8.0226	26.8379	49.0418
281.8	*	22.8	24.9125	40.1798	29.5983	35.2669	42.5118	7.9832	26.6738	48.7283
315.3	*	*	24.3157	38.7116	29.1600	34.2939	42.4686	7.8896	26.2558	47.9121
376.3	32	23.7	23.8058	37.3989	28.7381	33.3293	42.4290	7.8036	25.8460	47.0862
398.3	32	23.9	23.6243	36.9179	28.5831	32.9677	42.4168	7.7771	25.6885	46.7618
423.0	31	23.7	23.4432	36.4306	28.4257	32.5966	42.4028	7.7467	25.5207	46.429
448.3	33	24.2	23.2429	35.8828	28.2461	32.1680	42.3882	7.7149	25.3392	46.0291
471.3	31	24.2	23.0941	35.4697	28.1113	31.8427	42.3779	7.6925	25.1990	45.7276
546.3	32	24.1	22.6210	34.1201	27.6682	30.7512	42.3490	7.6295	24.7150	44.6648

Table 5. Moisture Weight Loss Data as of September 15, 1994.

Time (hrs)	RH (%)	Dry Bulb Temp (°C)	U-Plant-1		In-Farm-1 Bottom Fraction		104-BY		Sodium Nitrate Standard	
			Sample Weight (gms)	Percent Moisture (%)	Sample Weight (gms)	Percent Moisture (%)	Sample Weight (gms)	Percent Moisture (%)	Sample Weight (gms)	Percent Moisture (%)
566.3	32	23.9	22.4978	33.7593	27.5497	30.4533	42.3415	7.6131	24.5765	44.3529
596.3	32	24.5	22.3344	33.2747	27.3906	30.0494	42.3359	7.6009	24.3956	43.9403
615.8	33	24.4	22.2268	32.9517	27.2841	29.7763	42.3313	7.5908	24.2712	43.6530
639.0	33	24.7	22.0837	32.5172	27.1419	29.4084	42.3279	7.5834	24.1036	43.2612
742.0	32	24.6	21.6063	31.0261	26.6611	28.1354	42.3196	7.5653	23.5146	41.8400
880.0	33	24.5	20.9970	29.0246	26.0186	26.3608	42.3125	7.5498	22.6597	39.6457
1049	33	25.4	20.3692	26.8371	25.3018	24.2745	42.3084	7.5408	21.6666	36.8793
1288	33	24.9	19.5368	23.7199	24.2785	21.0829	42.2968	7.5155	20.1913	32.2674
1576	33	24.9	18.6746	20.1980	23.2201	17.4857	42.2853	7.4903	17.6110	22.3434
1892	34	25.0	17.6835	15.7254	22.1086	13.3373	42.2677	7.4518	16.6396	17.8099
2584	36	23.2	16.1594	7.7769	20.8849	8.2596	42.2253	7.3589	16.6186	17.7060
2992	36	22.8	15.6817	4.9676	20.6429	7.1841	42.2031	7.3101	16.6141	17.6838
3334	35	23.8	15.4439	3.5043	20.5041	6.5558	42.1843	7.2688	16.6134	17.6803
3453	35	24.1	15.3421	2.8640	20.4375	6.2513	42.1764	7.2514	16.6122	17.6744
4509	33	31.5	14.7699	-0.8991	19.9294	3.8611	42.0554	6.9846	16.6064	17.6456
4648	30	27.8	14.7075	-1.3272	19.8930	3.6852	42.0386	6.9474	16.6029	17.6282

*Data unavailable or were measured using damaged equipment.

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