Water Content of Dried
INFARM2 Top Simulant

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WATER CONTENT OF DRIED INFARM2 TOP SIMULANT

Pacific Northwest Laboratory^(a) received six simulated ferrocyanide sludge samples, INFARM2 top (INFARM2-REV-17), from the Plutonium Process Support Laboratory (PPSL) in mid 1993 for analysis of water content by Thermogravimetric Analysis (TGA) coupled to Fourier Transform Infrared (FTIR) for identification of the thermally evolved gases. The samples were dried by the PPSL prior to delivery according to three methods listed below. Two samples were provided for each drying method, samples 1-6. One additional sample prepared using drying method 3 was received in May of 1994 to check for possible reabsorption of water during storage, sample 7. The light green samples, sealed in clear glass screw cap vials, appeared uniform in color.

DRYING METHODS

1. 60°C for 24 hours under a vacuum of 20"
2. 105°C for 24 hours in air
3. 120°C for 18 hours in air

The samples were analyzed for water content by TGA. The heating program used for the analysis started between 30°C and 50°C and increased at a fixed rate of 5°C per minute up to 320°C or 550°C. During the sample analyses 1A-7A and 1B-7B, an FTIR was connected to the TGA exhaust port to identify the evolved gases. Analyses 1A-6A were performed using purified air scrubbed for CO₂ as a cover gas, however, variations in the efficiency of CO₂ removal by the scrubber during the analyses precluded accurate FTIR identification of CO₂ in the off gas. Analyses 1B-7B, 1C-6C and 7A were performed with Argon as a cover/purge gas.

Table 1 lists the mass loss data from the TGA analysis from 50°C to 275°C. Quantification of the different evolved gases was not performed. The TGA plots are provided in Figures 1 through 20 at the end of this report.

Two mass losses are observed by TGA. The first, between approximately 50°C and 150°C, which has been designated by the PPSL as "weakly-bound" water. We observed the evolution of both H₂O and CO₂ in this temperature range as shown in Figure 20, however, quantification of the two components is not possible. Carbon dioxide could be a small portion of the total loss. The second mass loss is observed between approximately 150°C and 275°C and has been designated by the PPSL as a combination of "strongly-bound" water and NO. The FTIR data for samples 1A-6A and 1B-6B showed only water loss.

To determine if NO is evolved in this temperature range, we used a larger sample mass and limited the test temperatures to prevent damaging the equipment due to an explosion. Sample analyses 7A and 7B used much larger sample masses, 25 mg compared to 5 mg for samples 1A-6A and 1B-6B. The FTIR data for sample 7A indicated the evolution of H₂O, NO, NO₂, N₂O and

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Table 1. Water Content of Dried Sludge Samples by TGA Analysis
Followed by FTIR of the Evolved Gases

Sample	Drying Method	H ₂ O Loss, wt%		
		50-150 °C	150-275 °C	Total
1A	60°C, 24 hrs, Vac	4.3	4.6	8.9
1B	60°C, 24 hrs, Vac	5.1	4.7	9.8
1C	60°C, 24 hrs, Vac	4.7	4.6	9.3
2A	60°C, 24 hrs, Vac	4.1	3.9	8.0
2B	60°C, 24 hrs, Vac	4.2	4.1	8.3
2C	60°C, 24 hrs, Vac	4.2	4.1	8.3
3A	105°C, 24 hrs, Air	4.2	4.1	8.3
3B	105°C, 24 hrs, Air	8.0	3.9	11.9
3C	105°C, 24 hrs, Air	5.2	4.1	9.3
4A	105°C, 24 hrs, Air	3.3	3.7	7.0
4B	105°C, 24 hrs, Air	6.6	4.0	10.6
4C	105°C, 24 hrs, Air	5.0	4.8	9.8
5A	120°C, 18 hrs, Air	2.0	4.0	6.0
5B	120°C, 18 hrs, Air	4.8	4.3	9.1
5C	120°C, 18 hrs, Air	2.9	4.3	7.2
6A	120°C, 18 hrs, Air	2.0	5.5	7.5
6B	120°C, 18 hrs, Air	4.0	4.0	8.0
6C	120°C, 18 hrs, Air	3.6	4.0	7.6
7A	60°C, 24 hrs, Vac	4.6	4.4	9.0
7B	60°C, 24 hrs, Vac	4.4	4.5	8.9

CO₂, see Figure 22. The instrument developed an air leak after this sample, which we have been unable to eliminate preventing a duplicate gas analysis. Analysis 7B was performed to confirm the mass losses observed in analysis 7A.

We believe that the variability in water losses observed between duplicate analyses arose due to variability in the building's humidity. Samples 1A-6A were analyzed during cool weather while the lab's relative humidity was low. Samples 1B-6B were analyzed during the summer months while the building's evaporative cooling system was operating, which raised the humidity levels. We performed sample analyses 1C-6C, 7A, and 7B after the building switched to a low humidity air conditioning system to test our humidity hypothesis.

The results of our experiments support our hypothesis that building humidity affected the water content. Samples 3B-6B, analyzed under humid conditions, show higher losses of "weakly-bound" water compared to samples 3A-6A and 3C-6C (2 wt% to 4 wt%). In addition, samples 3C-6C have slightly higher "weakly-bound" water than samples 3A-6A (≈ 1 wt%). This suggests samples 3-6 readily reabsorbed "weakly-bound" water. Samples 1, 2, and 7, dried by method 1, showed no change in "weakly-bound" water.

Since reabsorption of "weakly-bound" water is noted in samples 3B-6B and 3C-6C, trends in weakly-bound water may only be identified from samples 1A-7A, 1B, 2B, 1C, 2C, and 7B. From these sample analyses, the loss of "weakly-bound" water appears dependent on the drying method used with samples dried at lower temperatures having a greater "weakly-bound" water content. The greatest loss of "weakly-bound" water noted in the samples dried at 60°C under vacuum (≈ 4.1 weight percent, wt%) and the smallest loss in the samples dried at 120°C in air (≈ 2.0 wt%). It should be noted that no reabsorption of "strongly-bound" water was observed between samples A, B, and C in the temperature range 150°C and 275°C. All drying methods, samples and analyses showed a mass loss of 4.3 wt% (± 0.4 wt%) in this temperature range.

Fourier Transform Infrared analysis shows CO₂, H₂O and N₂O as the major components of the evolved gas for samples 1A-6A and 1B-6B, see Table 2. In its current application, the TGA/IR is used only for qualitative analysis of the evolved gases; setting the FTIR up for quantitative use would require extensive development and testing.

The mass losses given in Table 1 are higher than the water losses reported by the PPSL by approximately 2 wt% for samples 1A-7A, 1B, 2B, 1C, 2C, and 7B. This is the result of the PPSL's assignment of 1-2 wt% of the mass loss to NO production. Our study of the TGA data found approximately the same total mass loss as the PPSL study (6-9 wt% for samples 1A-6A, 5.4-10.9 wt% by the PPSL); however, our gas analyses, with one exception, indicates that water is the only gas evolved in this region and we have assigned this mass loss solely to water. Using the PPSL assignment of 1-2 wt% of the "strongly-bound" water as NO loss would put our data in agreement with PPSL.

Table 2. Mass Losses Observed During TGA Analysis Listed by Temperature Range
(Speciation of the mass loss in this table is the result of FTIR analysis on the exhaust gas.)

Sample	Drying Method	T Range, °C	Mass Loss, Wt%	ID Gases
1	60°C, 24hrs, Vac			
		50-139	4.29	CO ₂ H ₂ O
		158-273	4.62	H ₂ O
		350-416	18.60	N ₂ O CO ₂ H ₂ O
1 Dup	60°C, 24 hrs, Vac			
		50-155	5.05	CO ₂ H ₂ O
		155-275	4.69	H ₂ O
		275-410	18.05	N ₂ O CO ₂ H ₂ O
2	60°C, 24 hrs, Vac			
		50-125	4.06	CO ₂ H ₂ O
		167-256	3.87	H ₂ O
		353-419	17.45	CO ₂ N ₂ O H ₂ O
2 Dup.	60°C, 24hrs, Vac			
		50-155	4.17	CO ₂ H ₂ O
		155-275	4.14	H ₂ O
		275-410	19.43	CO ₂ N ₂ O H ₂ O

Table 2. (contd)

Sample	Drying Method	T range, °C	Mass Loss, wt%	ID Gases
3	105°C, 24hrs			
		50-105	1.07	CO ₂ H ₂ O
		106-181	3.12	H ₂ O
		181-275	4.10	H ₂ O
		313-406	22.79	N ₂ O CO ₂ H ₂ O
3 Dup.	105°C, 24hrs			
		50-165	8.04	CO ₂ H ₂ O
		165-275	3.93	H ₂ O
		275-410	16.33	N ₂ O CO ₂ H ₂ O
4	105°C, 24hrs			
		50-115	1.0	CO ₂ H ₂ O
		116-174	2.27	H ₂ O
		174-270	3.67	H ₂ O
		313-356	15.91	N ₂ O CO ₂ H ₂ O
4 Dup.	105°C, 24hrs			
		50-172	6.60	CO ₂ H ₂ O
		172-285	4.02	H ₂ O
		285-410	14.76	CO ₂ N ₂ O H ₂ O

Table 2. (contd)

Sample	Drying Method	T range, °C	Mass Loss, wt%	ID Gases
5	120°C, 18hrs			
		30-165	2.0	CO ₂ H ₂ O
		165-264	4.00	CO ₂ H ₂ O
		312-420	15.73	CO ₂ N ₂ O H ₂ O
5 Dup	120°C, 18hrs			
		50-184	4.80	CO ₂ H ₂ O
		184-275	4.31	H ₂ O
		275-410	17.58	CO ₂ N ₂ O H ₂ O
6	120°C, 18hrs			
		50-125	1.97	CO ₂ H ₂ O
		125-260	5.47	H ₂ O
		312-416	17.15	CO ₂ N ₂ O H ₂ O
6 Dup.	120°C, 18hrs			
		50-155	4.04	CO ₂ H ₂ O
		155-275	3.97	H ₂ O
		275-410	16.55	CO ₂ N ₂ O H ₂ O

Table 2. (contd)

Sample	Drying Method	T Range, °C	Mass Loss, wt%	ID Gases
7	60°C, 24hrs, Vac	30-150	4.62	CO ₂ H ₂ O
		150-275	4.35	H ₂ O NO NO ₂ N ₂ O CO ₂
7 Dup.	60°C, 24hrs, Vac	30-150	4.35	No Data
		150-275	4.46	No Data

Figure 1. TGA data for sample 1A, dried at 60°C under vacuum for 24 hours.

Figure 2. TGA data for sample 1B, dried at 60°C under vacuum for 24 hours.

Figure 3. TGA data for sample 1C, dried at 60°C under vacuum for 24 hours.

Figure 4. TGA data for sample 2A, dried at 60°C under vacuum for 24 hours.

Figure 5. TGA data for sample 2B, dried at 60°C under vacuum for 24 hours.

Figure 6. TGA data for sample 2C, dried at 60°C under vacuum for 24 hours.

Figure 7. TGA data for sample 3A, dried at 105°C under air for 24 hours.

Figure 8. TGA data for sample 3B, dried at 105°C under air for 24 hours.

Figure 9. TGA data for sample 3C, dried at 105°C under air for 24 hours.

Figure 10. TGA data for sample 4A, dried at 105°C under air for 24 hours.

Figure 11. TGA data for sample 4B, dried at 105°C under air for 24 hours.

Figure 12. TGA data for sample 4C, dried at 105°C under air for 24 hours.

Figure 13. TGA data for sample 5A, dried at 120°C under air for 18 hours.

Figure 14. TGA data for sample 5B; dried at 120°C under air for 18 hours.

Figure 15. TGA data for sample 5C, dried at 120°C under air for 18 hours.

Figure 16. TGA data for sample 6A, dried at 120°C under air for 18 hours.

Figure 17. TGA data for sample 6B, dried at 120°C under air for 18 hours.

Figure 18. TGA data for sample 6C, dried at 120°C under air for 18 hours.

Figure 19. TGA data for sample 7A, dried at 60°C under vacuum for 24 hours.

Figure 20. TGA data for sample 7B, dried at 60°C under vacuum for 24 hours.

Figure 21. FTIR data for sample 7A averaged over the low temperature loss (50°C to 150°C).

Figure 22. FTIR data for sample 7A averaged over the high temperature loss (150°C to 275°C).