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ETF Grout Expansion: Evaluation of MgO Additions and Struvite Precipitation Protocol for Potential Expansion

K. A. Hill

C. L. Langton

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REVIEWS AND APPROVALS

AUTHORS:

K. A. Hill, SRNL Applied Materials Research Date

C. L. Langton, SRNL Materials Technology & Energy Date

TECHNICAL REVIEW:

A. D. Cozzi, SRNL Materials Technology & Energy, Manager, Reviewed per E7 2.60 Date

APPROVAL:

J. Manna, Director Date
SRNL Materials Technology & Energy Science Division

G. Chen, Washington River Protection Services Date

D. J. Swanberg, Manager Date
Washington River Protection Services

EXECUTIVE SUMMARY

The ETF ammonia tolerant grout waste form was developed by the Vitreous State Laboratory (VSL) to stabilize ammonium and thereby prevent emission of ammonia vapor during solidification of an ammonium-rich, concentrated sulfate aqueous waste stream generated at the Hanford Effluent Treatment Facility (ETF). VSL did not observe expansion in samples prepared during the waste form development work. However, Savannah River National Laboratory (SRNL) personnel did encounter expansion, in some cases up to 20+ volume percent expansion in ETF grout samples while preforming work scope to evaluate compositional ranges for ETF brine and of the precipitation and solidification reagent. The work requests can be found in Washington River Protection Services (WRPS) Statement of Work (SOW), Requisitions #: 339922 Revisions 0 and 1, March 11, 2021, and November 2021.

Additional evaluation was requested by WRPS SOW Requisitions #: 356730, Revision 1, February 1, 2022, to determine whether differences in the slags or differences in sample preparation protocols used by VSL and SRNL were the cause of the expansion observed in the SRNL samples. G. Chen, WRPS, arranged a materials exchange between VSL and SRNL and coordinated the VSL protocol for grouting and curing 1L of Base Case ETF simulant. Materials were exchanged between VSL and SRNL and both laboratories performed the VSL struvite precipitation-solidification protocol and cured samples for at least 28 days. VSL and SRNL encountered expansion, at varying degrees, in all samples prepared under the material exchange and grouting protocol.

Additional material exchange testing between VSL and SRNL and alternative materials evaluation to further investigate the causes of grout expansion and differentiate the effects of various dry materials, grouting procedures, and curing containers was requested by WRPS SOW Requisitions #: 356730, Revision 2, January 10, 2023. Pacific Northwest National Laboratory (PNNL) assembled and distributed materials to both laboratories for testing.

Observations from this study indicated variations in MgO additions, water-to-dry mix (dm) ratios and curing containers did not correlate to ETF ammonia grout expansion. In comparison to previous work, SRNL observed the addition rate of NaOH to be a potential factor for the final pH in the struvite precipitation step.
In the current testing NaOH was added in bulk (5-10 mL at one time) during the precipitation step. The resulting pH was 7.57-9.15 which is slightly higher than pH observed at a slower addition rate. Additional testing is needed to identify the presence and/or struvite stability in high-pH struvite precipitant ETF ammonia grout samples. Therefore, based on current data, it is unknown if NaOH addition rate is the fundamental cause of grout expansion.

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LIST OF ABBREVIATIONS

BFS	Blast Furnace Slag
ETF	Effluent Treatment Facility
FY21	Fiscal Year 2021
FY22	Fiscal Year 2022
FY23	Fiscal Year 2023
MC	Moisture Content
MgO	Magnesium Oxide
PNNL	Pacific Northwest National Laboratory
PSAL	Process Science Analytical Laboratory
SAS	Sulfate Activated Slag
SOW	Statement of Work
SRNL	Savannah River National Laboratory
VSL	Vitreous State Laboratory
WRPS	Washington River Protection Services

1.0 Introduction

The Vitreous State Laboratory (VSL) conducted lab-scale development of cementitious waste forms to prevent evolution of significant ammonia vapor during solidification of ammonia-rich sulfate waste solutions generated at the Effluent Treatment Facility (ETF) at the Hanford site.[1, 2] From this testing, struvite precipitation followed by immobilization in a sulfate activated slag (SAS) grout was recommended as the preferred alternative. In Fiscal Year 2021 (FY21), SRNL was requested to test the waste formulation, struvite precipitation, and reagent addition strategy proposed for a future grouting facility with three ETF waste simulants that span the range of brine feed compositions expected to be processed.[3] In Fiscal Year 2022 (FY22), an evaluation of the effects of variation in reagent addition was requested because using the materials and sample preparation protocol provided by WRPS, all the FY21 samples expanded.[4] Consequently, additional testing was requested by Washington River Protection Services (WRPS) Statement of Work (SOW) Requisitions # 356730, Revision 1, February 1, 2022,[5] to determine whether differences in the slags or differences in sample preparation protocols used by VSL and SRNL were the cause of the expansion observed in the SRNL samples. G. Chen, WRPS, arranged a materials exchange between VSL and SRNL and coordinated the VSL protocol for grouting and curing 1L of Base Case ETF simulant. Materials were exchanged between VSL and SRNL and both laboratories performed the VSL struvite precipitation-solidification protocol and cured samples for at least 28 days.[5] Both VSL and SRNL encountered expansion, at varying degrees, in all samples prepared under the material exchange and grouting protocol.[6]

This report addresses work performed for FY23 scope, WRPS SOW 356730, Revision 2, Task 1.[7] The objective for this task was to continue investigating the potential cause(s) of grout expansion observed by VSL and SRNL in FY22.[6] The work scope requested for Task 1 is identified below:

> **Task 1: Evaluate the Effects of Different Reagent Batches –** All grouts made by both SRNL and VSL in the first round of material exchange testing in FY22 expanded to varying degrees. Grouts made with SRNL dry materials expanded more than those made with VSL dry materials. Differences in the direction of expansion were also observed between the SRNL versus VSL curing containers. Work is now requested in Fiscal Year 2023 (FY23) for additional material exchange testing between SRNL and VSL and alternative materials evaluation to further investigate the causes(s) of grout expansion and differentiate the effects of various dry materials, grouting procedures, and curing containers. Materials in this round of testing will be assembled by PNNL and distributed to SRNL and VSL. A protocol for sample preparation and evaluation has been reviewed and agreed upon by SRNL, VSL, PNNL and WRPS.

2.0 Experimental Procedure

2.1 Sample Preparation

The protocols for mixing, casting, and curing for SOW 356730, Revision 2, Task 1[8] were provided by G. Chen, WRPS, and are provided in Appendix, Attachment, A-1.[9] Batch sheets were developed by SRNL and reviewed by G. Chen, WRPS, and can be found in Appendix, Attachment, A-2.[10]

2.1.1 Base Case Simulant

The composition of the Base Case Simulant and chemicals used to prepare the 1-L batches of ETF grout are listed in Table 2-1.[9] The simulants were prepared with SRNL reagent chemicals and deionized water. Fresh 1-L solutions of simulant were prepared for each waste form and batch sheets are provided in Appendix 1, Attachment, A-2.[10]

Table 2-1. Recipe for 1-Liter of Hanford ETF Brine Simulant

Analyte	Target		Reagent	Molecular Weight	Assay	Target
	g/L	Molar				Mass (g)
NH_4^+	6.075	0.3368	$(NH_4)_2SO_4$	132.14	0.990	22.48
Na^+	72.772	3.1654	-	-	-	-
SO_4^{2-}	160.014	1.6657	Na_2SO_4	142.04	0.998	213.11
Cl^-	0.265	0.0075	NaCl	58.44	0.990	0.414
NO_3	9.248	0.1491	$NaNO_3$	84.99	0.997	12.72
HCO_3-	1.058	0.0173	$NaHCO_3$	84.01	0.990	1.47
H_2O	-	-	DI H_2O	18.02	1.000	938.21
Total, g/L						1188.43

2.1.2 ETF Ammonia Grout Precipitation

The first step in the ammonium grout waste form protocol[9] was to precipitate struvite in the Base Case simulant by adding $MgSO_4 \cdot 7H_2O$ and $NaH_2PO_4 \cdot H_2O$ then adjust the pH to about 7 with a 50 wt. % NaOH solution. Reagents and the target additions for precipitating struvite in a 1-L batch of Base Case simulant are provided in Table 2-2. The target amount of caustic solution was used as a guide. Per protocol[9] provided by WRPS, the bulk mass of 50 wt. % NaOH solution was added during the first 10 minutes to reach the pH of about 7. The resulting slurry was then mixed for an additional 20 minutes to reach equilibrium. If needed, additional addition of 50 wt. % NaOH solution was added to reach pH of about 7. The second step of the precipitation process was to stir the struvite mixture for an additional 2 hours. The pH and temperature were measured once per minute throughout the entire struvite precipitation process.

Table 2-2. Recipe for Struvite Precipitation

Order Addition	Chemicals	Target Weight (g)	Assay
1	ETF Base Case Simulant (1L)	1188.43	1.000
2	$MgSO_4 \cdot 7H_2O$	83.85	0.990
3	$NaH_2PO_4 \cdot H_2O$	46.47	1.000
4	NaOH 50 % w/w	54.193	0.506

2.1.3 ETF Ammonia Grout: Solidification / Stabilization

The next step in the ammonium grout preparation was to add various water to dry mix ratios of Lafarge blast furnace slag, and SIKA Control SC (MgO) to the precipitated slurry in in a Hobart planetary mixer for 5 to 10 minutes. A test matrix was provided by G. Chen, WRPS, and can be found in Table 2-3.[9] For grout batches with both solidification reagents, the Lafarge blast furnace slag, and SIKA Control SC (MgO) was blended resulting in a mixture referred to as “Dry Mix”.

Table 2-3. Test Matrix for VSL, SRNL, and PNNL 1-Liter Grout Samples

Test #	Wt.% MgO in dry mix	Water to dry mix ratio (w/dm)	Target weight BFS (g)	Target weight MgO (g)
1	None	0.4	2344.66	0
2	None	0.5	1876.57	0
3	None	0.6	1565.05	0
4	3%	0.4	2274.32	70.34
5	3%	0.5	1820.27	56.30
6	3%	0.6	1518.10	46.95
7	8%	0.4	2157.09	187.57
8	8%	0.5	1726.44	150.13
9	8%	0.6	1439.84	125.20

2.1.4 Grout Sample Preparation

Plastic cylinders used by SRNL and VSL were noticeably different in FY22 testing. Therefore, casting cylinders for FY23 work were procured by PNNL and provided to SRNL and VSL. The ammonia grout slurry was cast into 2 X 4-inch curing containers provided by PNNL and into SRNL containers, 2 mm below the top. A spatula was used to tap the side of cylinders to remove any air entrapment. The containers were capped after filling and placed into a zip lock bag and left to cure at room temperature. Per WRPS protocol[9], room temperature at sample storage location was monitored and recorded periodically. See Table 2-4. Samples were observed for bleed water and any visual expansion every couple days. Photographs were taken at 7, 14, 21 and 28 days.[10]

Table 2-4. Grout Laboratory Room Temperature Variation

Date / Time	Temperature	
	°F	°C
3/29/23	70.5	21.4
3/30/23	67.9	19.9
3/31/23	72.1	22.3
4/3/23	68.8	20.4
4/4/23	68.6	20.3
4/4/23	68.2	20.1
4/10/23	67.4	19.7
4/11/23	70.6	21.4
4/12/23	68.7	20.4
4/12/23	71.7	22.1
4/14/23	68.2	20.1
4/17/23	69.0	20.6
4/18/23	69.9	21.1
4/20/23	69.4	20.8
4/24/23	71.2	21.8
4/25/23	68.2	20.1
4/26/23	68.7	20.4
4/26/23	69.0	20.6
4/27/23	67.7	19.8
4/28/23	68.5	20.3
4/29/23	67.8	19.9

2.2 Expansion Determination

Characterization to document whether the ETF grout in the cylinders filled to the top and to within 2 mm of the top expanded over 28 days was limited to visual observation. Evidence for expansion included mold lids popping off, vertical or horizontal growth of sample, visible/measurable bulging of cast mold, and/or cylinder wobble. Approximate expansion change was also measured by a standard wooden ruler.

2.3 Moisture Content of Dry Materials

Moisture content measurements were performed on Lafarge blast furnace slag (BFS), and SIKA Control SC (MgO) upon arrival from PNNL and after 28 days. The weight loss measurements were performed per, WRPS protocol provided by G. Chen.[9] The purpose of this test was to identify any differences of material storage between laboratories.

2.4 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Revision 2.[11]

3.0 Results

The work performed for SOW 356730, Revision 2, Task 1[7], focused on ammonia grout expansion in various water to dry mix ratios of BFS and MgO. Results for ammonia grout without MgO, 3% MgO and 8% MgO at various water to dry mix ratios are presented in Table 3-1, Table 3-2, and Table 3-3, respectively.[10] Photographs of the samples were taken at 7, 14, 21 and 28 days. Sample photos at 28 days cured are presented in Figure 3-10 to Figure 3-19. SRNL did not observe/measure expansion in any of the ammonia grout samples that cured for 28 days.

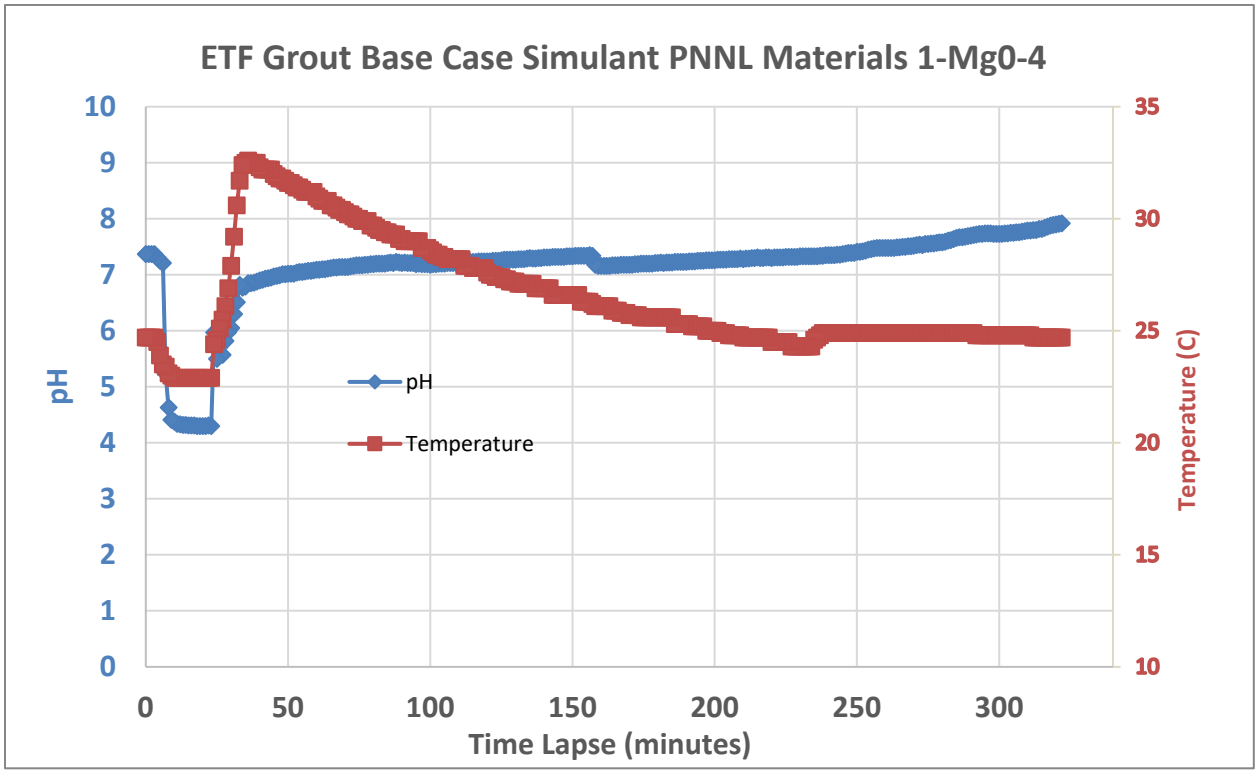
3.1 ETF Grout Preparation

Fresh 1-L solutions of the Base Case Simulant were prepared for each grout batch. The first step in the ammonium grout waste form protocol[9] was to precipitate struvite in the Base Case simulant. The $MgSO_4 \cdot 7H_2O$ and $NaH_2PO_4 \cdot H_2O$ was added and stirred until reagents were dissolved. Then the pH was adjusted to approximately 7 with a 50 wt. % NaOH solution. Per protocol provided by WRPS[9], the bulk mass of 50 wt. % NaOH solution was added during the first 10 minutes to reach the pH of about 7. During this step the total target weight of 54.19 grams of 50 wt. % NaOH solution was needed. The precipitant then mixed for an additional 20 minutes to reach equilibrium. As shown in Table 3-1, the pH and temperature after equilibrium resulted in a pH range of 7.01 to 7.75. Additional 50 wt. % NaOH solution was not needed to reach pH 7.1 ± 0.2. After the struvite reached equilibrium, the mixture stirred for an additional 2 hours.

The pH and temperature were measured once per minute throughout the entire struvite precipitation process for each batch and can be found in Figures 3-1 to 3-9. The final struvite precipitation resulted in a pH range of 7.57 to 9.15. At this time the cause of pH rise has not been identified. The final step of the WRPS protocol[9], the struvite mixture was poured into a Hobart planetary mixer with pre-weighed dry feed material and mixed for 5 minutes. Table 2-3 shows the process variable investigated in dry materials was Magnesium Oxide (MgO) and proportion of dm. Various water-dm ratios ranging from 0.4 to 0.6 and MgO additions ranging from 0-8% of the solidification recipe were used. The grout was then cast into 2 X 4-inch cylinders approximately 2 mm below the top. Cylinders were lightly tapped on sides with a spatula to release any entrapped air, none was observed. Samples were placed into a zip lock bag and left to cure on the laboratory benchtop. Data for each grout batch can be found below in Table 3-1.[10]

Table 3-1. ETF Ammonia Grout Data[10]

Grout Batch	Final ETF Brine Simulant pH & Temp (°C)	Caustic Addition to pH 7.1 ± 0.2 over ~ 10 m (°C)	Caustic Addition after ~30 mins pH & Temp (°C)	Final Amount of NaOH 50 % w/w added (g)	2-hr Stir Struvite Precipitant pH & Temp (°C)	Final Grout pH and Temp (°C)
1-Mg0-4	7.34 @ 24.9	6.90 @ 32.2	7.19 @ 29.6	54.20	7.92 @ 24.6	12.26 @ 23.7
2-Mg0-5	7.30 @ 24.8	6.80 @ 32.3	7.01 @ 30.3	54.19	7.57 @ 24.4	12.14 @ 24.0
3-Mg0-6	7.29 @ 25.5	6.99 @ 32.4	7.19 @ 30.0	54.19	7.64 @ 24.4	12.10 @ 23.6
4-Mg3-4	7.32 @ 24.9	6.88 @ 31.5	7.31 @ 28.7	54.19	8.78 @ 24.2	12.32 @ 23.6
5-Mg3-5	7.29 @ 25.3	6.99 @ 32.5	7.38 @ 29.6	54.19	8.18 @ 24.6	12.13 @ 23.2
6-Mg3-6	7.32 @ 25.8	6.97 @ 33.9	7.15 @ 31.2	54.18	7.68 @ 24.8	12.14 @ 23.8
7-Mg8-4	7.28 @ 26.3	6.98 @ 32.9	7.75 @ 30.1	54.19	9.15 @ 24.9	12.13 @ 24.7
8-Mg8-5	7.32 @ 24.6	6.85 @ 32.3	7.28 @ 29.6	54.20	8.71 @ 24.6	12.11 @ 24.4
9-Mg8-6	7.31 @ 24.9	6.93 @ 32.1	7.26 @ 29.1	54.19	8.10 @ 24.7	12.18 @ 24.5



3-9

Figure 3-1. Grout Batch 1 Struvite Precipitation time-temperature-pH

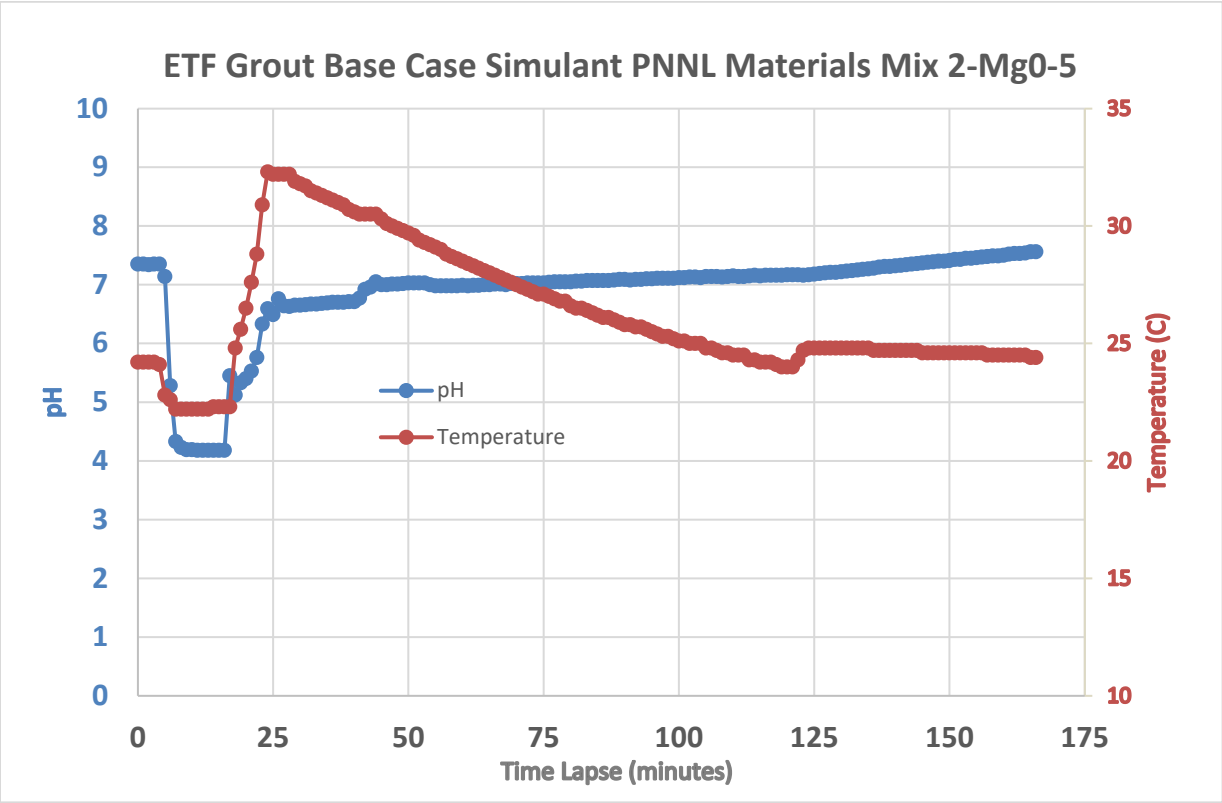


Figure 3-2. Grout Batch 2 Struvite Precipitation time-temperature-pH

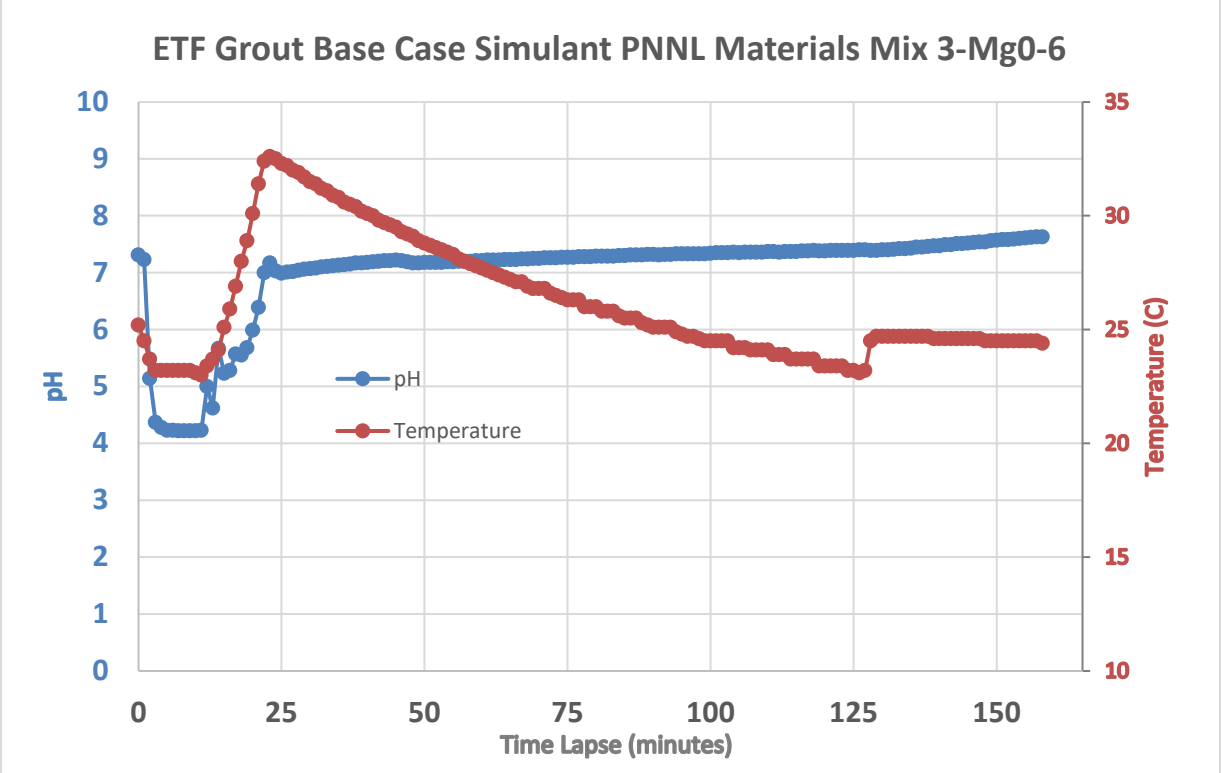


Figure 3-3. Grout Batch 3 Struvite Precipitation time-temperature-pH

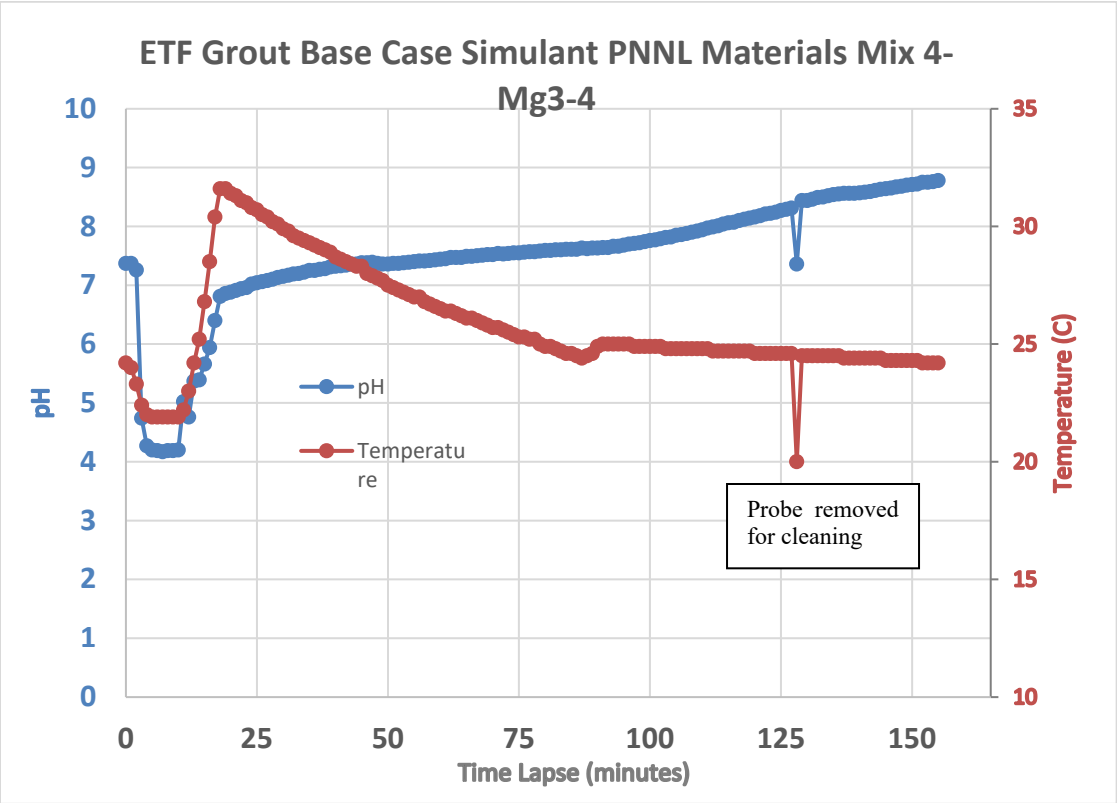


Figure 3-4. Grout Batch 4 Struvite Precipitation time-temperature-pH

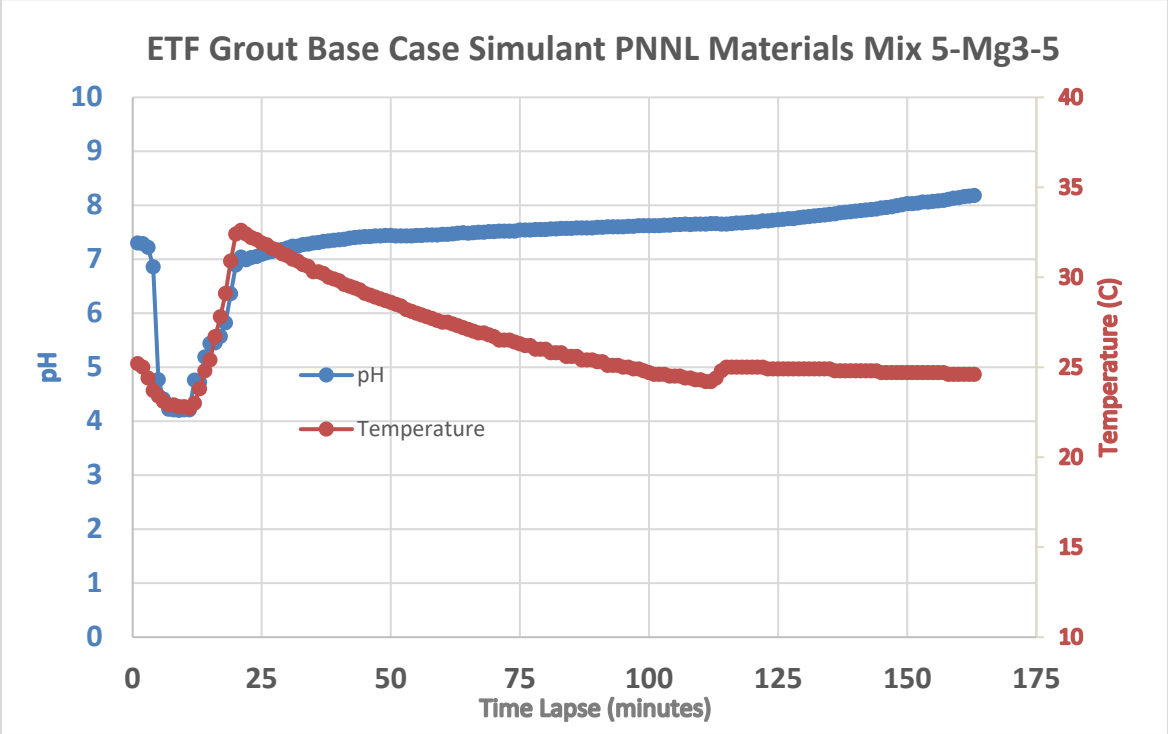


Figure 3-5. Grout Batch 5 Struvite Precipitation time-temperature-pH

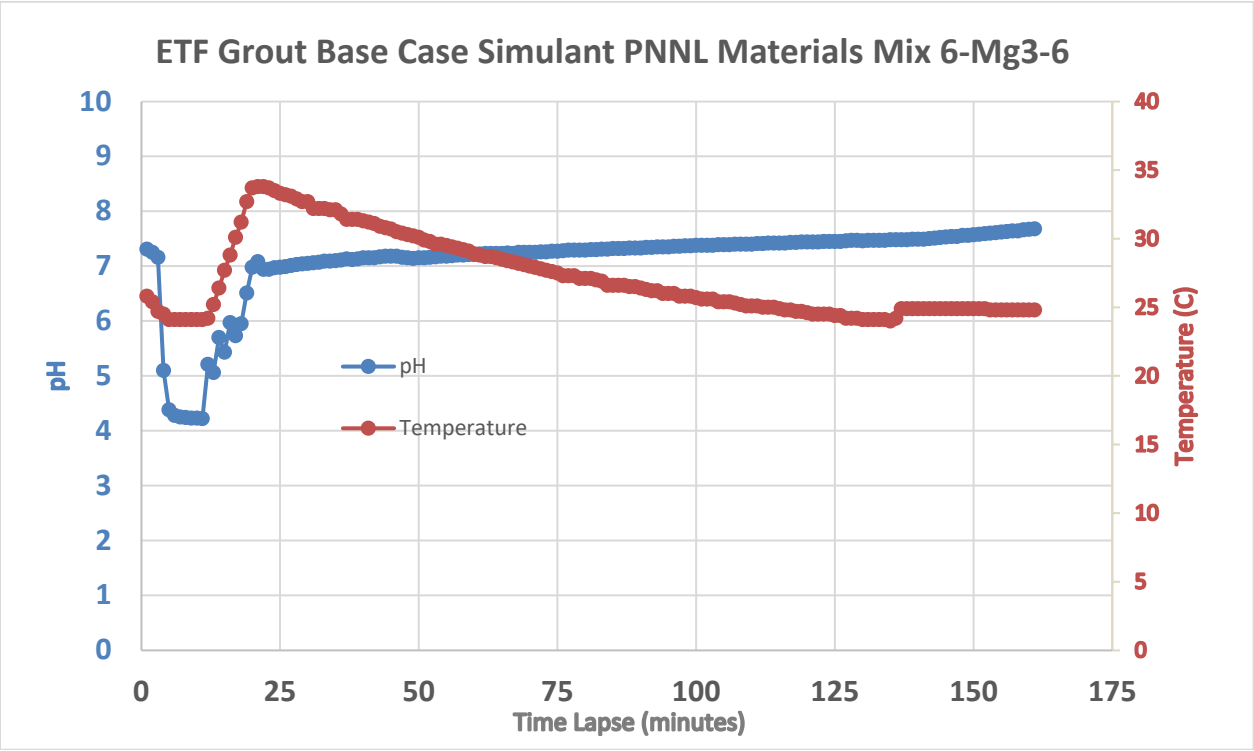


Figure 3-6. Grout Batch 6 Struvite Precipitation time-temperature-pH

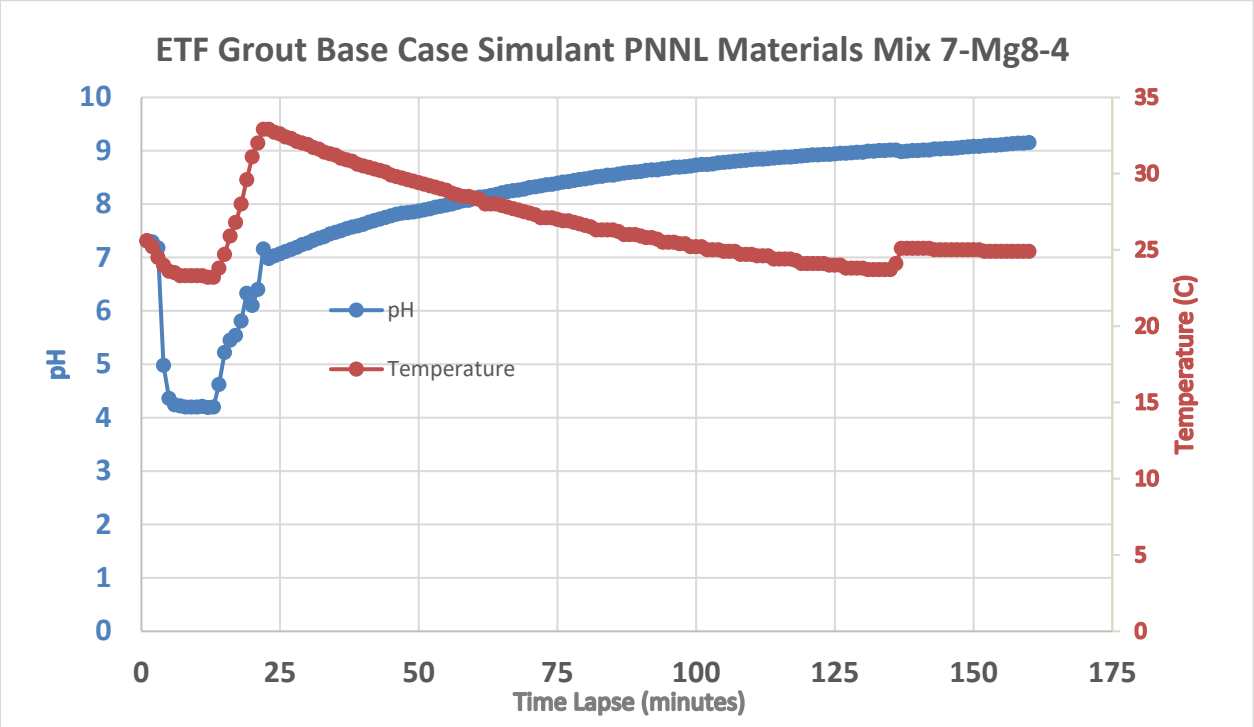


Figure 3-7. Grout Batch 7 Struvite Precipitation time-temperature-pH

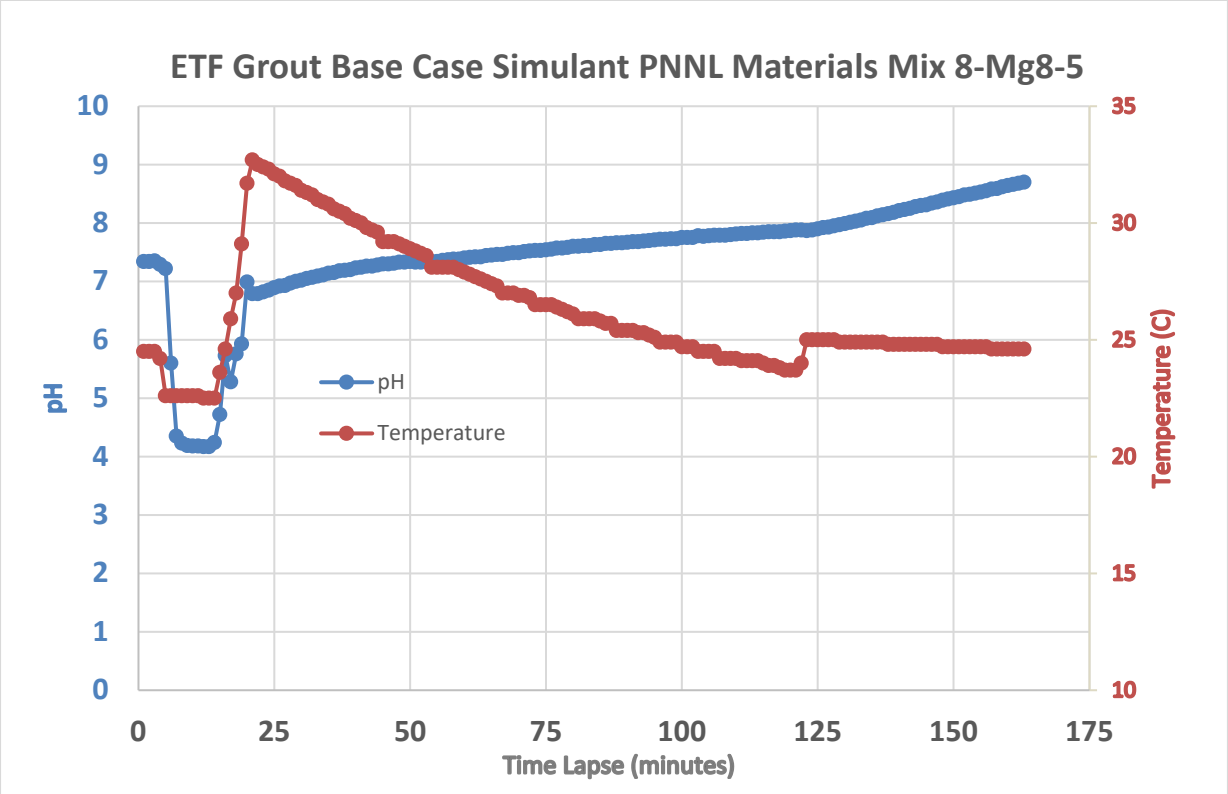


Figure 3-8. Grout Batch 8 Struvite Precipitation time-temperature-pH

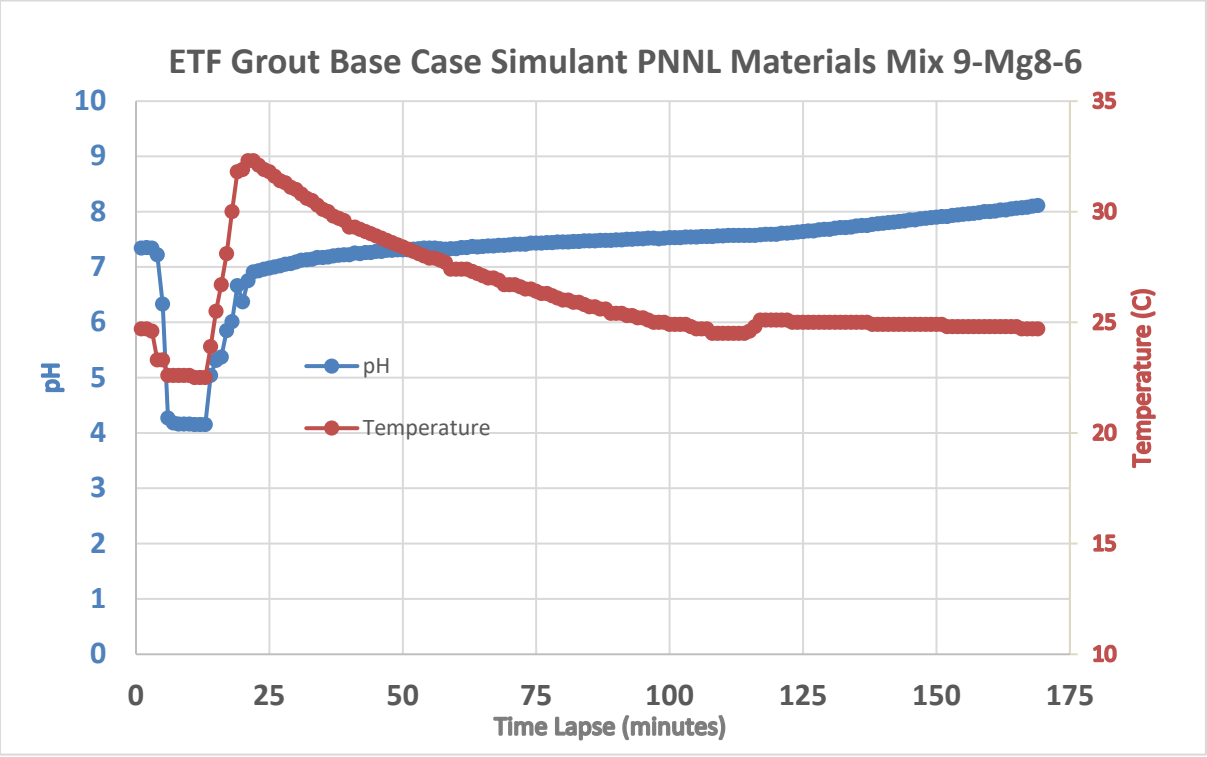


Figure 3-9. Grout Batch 9 Struvite Precipitation time-temperature-pH

3.2 ETF Grout Monitoring

Samples were prepared, capped, and placed in a zip-lock bag to cure on the laboratory benchtop at room temperature. All samples were checked for bleed water and monitored for grout expansion.

3.2.1 Ammonia Grout 0% MgO

Expansion results for the 0% MgO mixes at 0.4 to 0.6 water-to-dry mix ratios are shown in Table 3-2. Photographs of each sample at 28 days cure time are shown in Figures 3-10 to 3-12. SRNL did not observe any bleed water or expansion in the ETF ammonia grout samples without MgO.

Table 3-2. Preparation /Observation of 1-Mg0-4, 2-Mg0-5, 3-Mg0-6

1-Mg0-4 ***0% MgO w/dm=0.4***	**2-Mg0-5** ***0% MgO w/dm=0.5***	**3-Mg0-6** ***0% MgO w/dm=0.6***	**Bleed Water**	**Observation and Curing time** **NE-**No expansion			
Prepared: 3/30/23	Prepared: 3/31/23	Prepared: 4/4/23		7 days	14 days	21 days	28 days
1A	2A	3A	NONE	NE	NE	NE	NE
1B	2B	3B	NONE	NE	NE	NE	NE
1C	2C	3C	NONE	NE	NE	NE	NE
1D	2D	3D	NONE	NE	NE	NE	NE
1E	2E	3E	NONE	NE	NE	NE	NE
1F	2F	3F	NONE	NE	NE	NE	NE
1G	2G	3G	NONE	NE	NE	NE	NE

Figure 3-10. 1-Mg0-4 cured for 28 days

Figure 3-11. 2-Mg0-5 cured for 28 days

Figure 3-12. 3-Mg0-6 cured for 28 days

3.2.2 Ammonia Grout 3% MgO

Bleed water was not observed in any samples containing 3% MgO. Expansion results for the 3% MgO mixes are shown in Table3-2. Samples at the 28-day cure time were photographed and shown Figures 3-10 to 3-12. SRNL did not observe any expansion in the 3% MgO ETF ammonia grout samples.

Table 3-3. Preparation/ Observation of 4-Mg3-4, 5-Mg3-5, 6-Mg3-6

4-Mg3-4 ***3% MgO w/dm=0.4***	**5-Mg3-5** ***3% MgO w/dm=0.5***	**6-Mg3-6** ***3% MgO w/dm=0.6***	**Bleed Water**	**Observation and Curing time** **NE-**No expansion			
Prepared: 4/10/23	Prepared: 4/12/23	Prepared: 4/12/23		7 days	14 days	21 days	28 days
4A	5A	6A	NONE	NE	NE	NE	NE
4B	5B	6B	NONE	NE	NE	NE	NE
4C	5C	6C	NONE	NE	NE	NE	NE
4D	5D	6D	NONE	NE	NE	NE	NE
4E	5E	6E	NONE	NE	NE	NE	NE
4F	5F	6F	NONE	NE	NE	NE	NE
4G	5G	6G	NONE	NE	NE	NE	NE

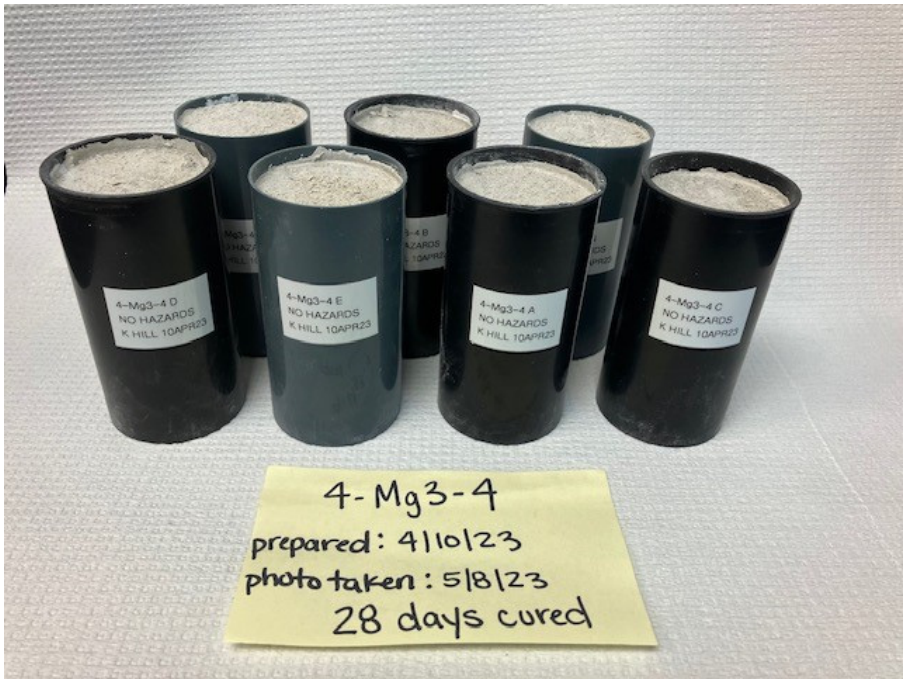


Figure 3-13. 4-Mg3-4 cured for 28 days

Figure 3-14. 5-Mg3-5 cured for 28 days

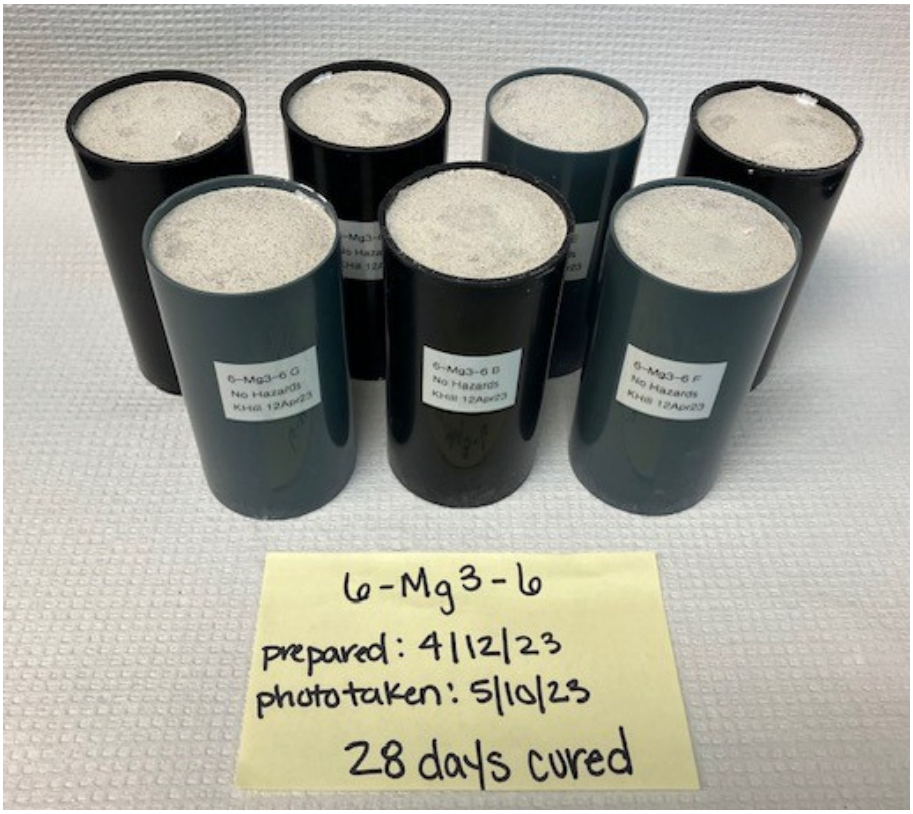


Figure 3-15. 6-Mg3-6 cured for 28 days

3.2.3 Ammonia Grout 8% MgO

Expansion results for the 8% MgO mixes are shown in Table 3-2. Bleed water was not observed in any samples containing 8% MgO. Photographs of the 28 day cured samples are shown in Figures 3-10 to 3-12. SRNL did not observe any expansion in the 8% MgO ETF ammonia grout samples.

Table 3-4. Preparation/ Observation of 7-Mg8-4, 8-Mg8-5, 9-Mg8-6

7-Mg8-4 ***8% MgO w/dm=0.4***	**8-Mg8-5** ***8% MgO w/dm=0.5***	**9-Mg8-6** ***8% MgO w/dm=0.6***	**Bleed Water**	**Observation and Curing time** **NE-**No expansion			
Prepared: 4/14/23	Prepared: 4/17/23	Prepared: 4/18/23		7 days	14 days	21 days	28 days
7A	8A	9A	NONE	NE	NE	NE	NE
7B	8B	9B	NONE	NE	NE	NE	NE
7C	8C	9C	NONE	NE	NE	NE	NE
7D	8D	9D	NONE	NE	NE	NE	NE
7E	8E	9E	NONE	NE	NE	NE	NE
7F	8F	9F	NONE	NE	NE	NE	NE
7G	8G	9G	NONE	NE	NE	NE	NE

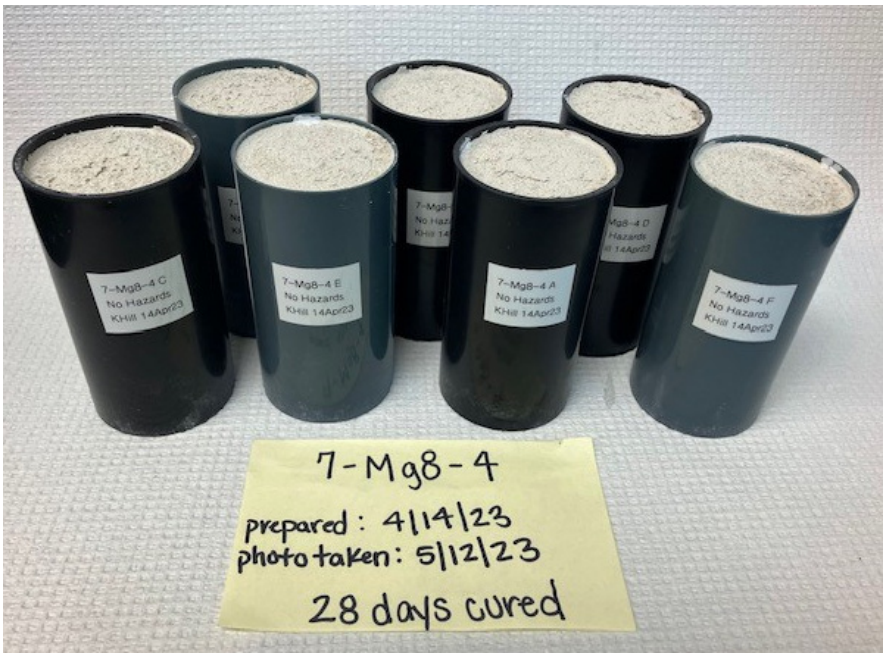


Figure 3-16. 7-Mg8-4 cured for 28 days

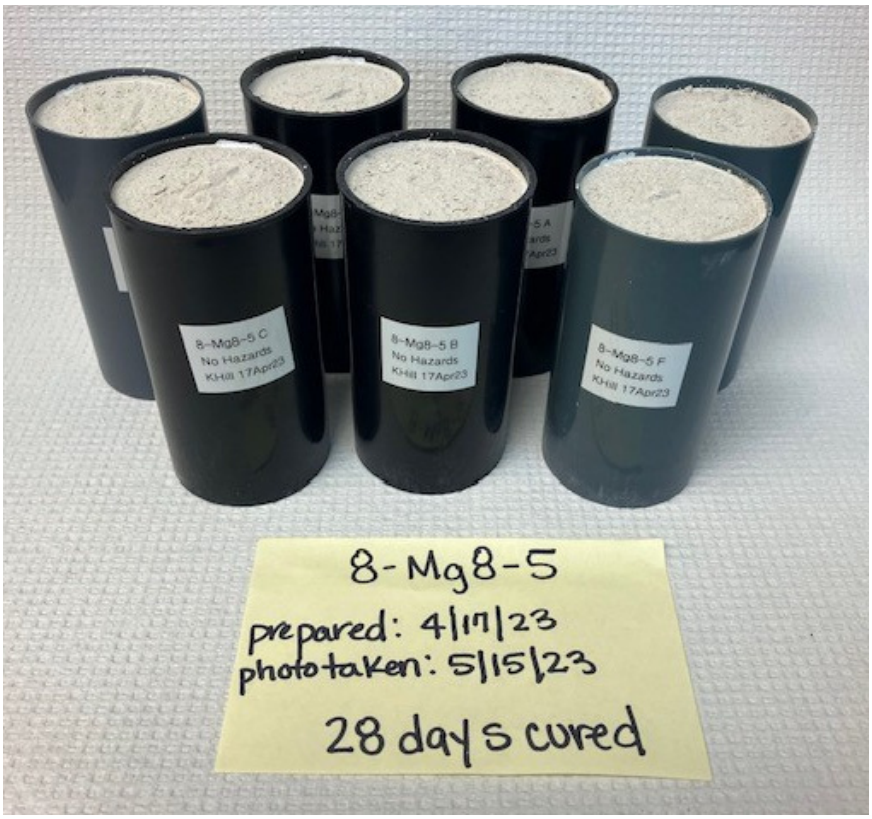


Figure 3-17. 8-Mg8-5 cured for 28 days

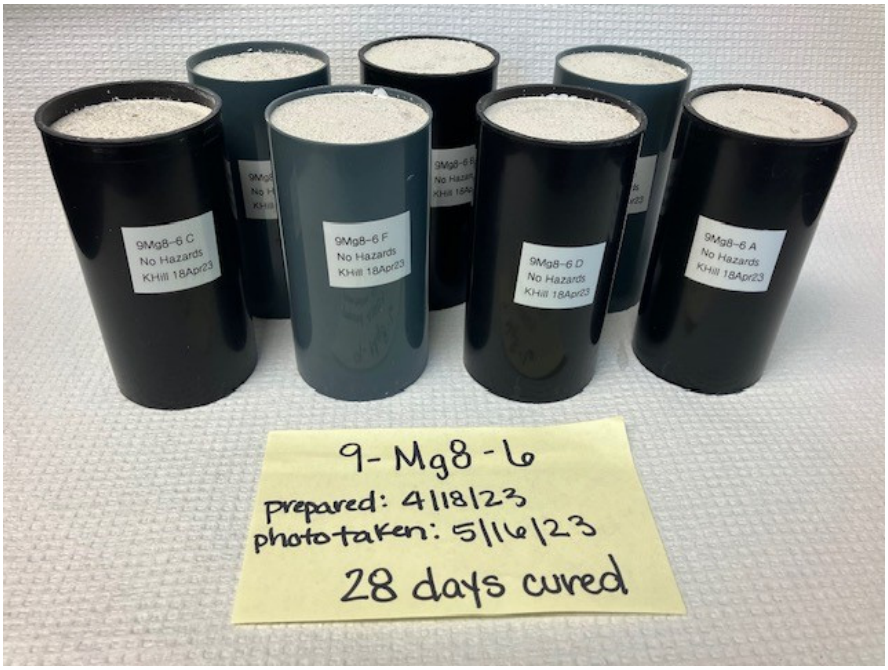


Figure 3-18. 9-Mg8-6 cured for 28 days

3.3 Sample Curing Conditions Data

3.3.1 Grout Laboratory Curing Conditions

Room temperature at the sample storage area was monitored and recorded until all samples reached a cure time of 28 days, see Table 3-4. All samples were cured in a sample storage area where temperature remained between 67°F-72°F and 19°C-22°C**.**

Table 3-5. Grout Laboratory Temperature Variation

Date / Time	Temperature	
	°F	°C
3/29/23	70.5	21.4
3/30/23	67.9	19.9
3/31/23	72.1	22.3
4/3/23	68.8	20.4
4/4/23	68.6	20.3
4/4/23	68.2	20.1
4/10/23	67.4	19.7
4/11/23	70.6	21.4
4/12/23	68.7	20.4
4/12/23	71.7	22.1
4/14/23	68.2	20.1
4/17/23	69.0	20.6
4/18/23	69.9	21.1
4/20/23	69.4	20.8
4/24/23	71.2	21.8
4/25/23	68.2	20.1
4/26/23	68.7	20.4
4/26/23	69.0	20.6
4/27/23	67.7	19.8
4/28/23	68.5	20.3
4/29/23	67.8	19.9
5/1/23	67.9	19.9
5/2/23	69.2	20.7
5/3/23	70.1	21.2
5/4/23	70.4	21.3
5/5/23	69.5	20.8
5/8/23	70.2	21.2
5/9/23	70.3	21.3
5/10/23	68.7	20.4
5/11/23	68.5	20.3
5/12/23	68.3	20.2
5/15/23	68.4	20.2
5/16/23	68.2	20.1
5/17/23	67.5	19.7
5/18/23	67.9	19.9
5/19/23	68.8	20.4

3.3.2 Grout Laboratory Material Storage Evaluation

Weight loss measurements were performed at two different time variables on BFS and MgO from SRNL and PNNL. SRNL material was received on April 22, 2021, in 5-gallon buckets. PNNL material was shipped and received at SRNL on January 2, 2023. The BFS from PNNL was packaged in a 5-gallon bucket. The MgO from PNNL was packaged in a 2-L plastic poly bottle, double-bagged with desiccant. All material was stored in the same laboratory until use. This test was to identify any differences of material storage between laboratories. Weight loss measurements were performed per G. Chen, WRPS, protocol[9]. Samples of each material were prepared in triplicate and then placed into an oven at 110°C for 24 hours. The samples were removed from oven and weighed. Samples continued to be dried and weighed until change in mass was less than 0.05 grams. Moisture content was determined when material was received and then repeated 28 days later. Results for moisture content can be found in Table 3-6.[10] SRNL did not find any significant difference in materials stored at different laboratories.

Table 3-6. Moisture Content of Solidification Reagents

Material	Laboratory	Average MC%	
		As Received	Stored in SRNL Lab 28 days
Blast Furnace Slag	PNNL	1.00	0.83
Blast Furnace Slag	SRNL	0.58	0.37
Magnesium Oxide	PNNL	2.38	2.74
Magnesium Oxide	SRNL	3.97	3.52

4.0 Discussion

WRPS requested PNNL to obtain, characterize, and distribute new samples of BFS and MgO. These materials were sent to VSL and SRNL for additional round robin testing to determine whether some feature of the dry mix was responsible for the expansion observed by SRNL and VSL in FY22 ETF grout testing. In addition, WRPS provided a test matrix[7] for the PNNL supplied materials that included the following variables:

- NaOH addition method and rate for struvite precipitation step
- Struvite slurry stir time after NaOH addition (120 minutes)
- ETF water to dry mix ratio (0.4 to 0.6)
- Dry mix composition (0 to 8 mass % MgO + slag)
- Curing conditions (monitor room temperature)
- Curing containers

Details of the ETF grout samples prepared according to the test matrix provided by WRPS are discussed below.

4.1 Struvite Precipitation and NaOH Addition

In FY22, previous work was done to evaluate ETF grout expansion through struvite precipitation stir times at 30, 60, 90, and 120-minutes.[6] This work resulted in a 2-hour struvite precipitation stir time for the FY23 grouting procedure.[9] During the struvite precipitation, as shown in Table 3-1 and Figures 3-1 to 3-9, the 50

wt. % NaOH solution was added several ml at a time by pipette in the first 5-10 minutes to reach a pH of approximately 7. The total weight of 54.19 grams of 50 wt. % NaOH solution was needed. The pH values met the target of 7.1 ± 0.2. SRNL observed **c**lumping of struvite crystals during this process. After the additional 20 minutes of stirring to reach equilibrium, some pH values increased by 0.4. Per WRPS protocol[9], the struvite mixture continued to stir for an additional 2-hours. During which time the small clumps of precipitated struvite separated into individual crystals. The pH values for each batch of the final struvite precipitation step ranged from 7.57 to 9.15.

4.2 Magnesium Oxide Additions

The dry mix compositional variable investigated was magnesium oxide (MgO). The proportion in the dry mix blend ranged from 0 to8% in the solidification step shown in Table 2-3.[9] All samples were monitored for at least 28 days. SRNL did not observe expansion in the FY23 ETF ammonia grout samples. Bleed water was not observed in the 9 grout batches prepared.

4.3 Water-to-Dry mix

The ETF ammonia grout base case was also investigated in water-to-dry mix ratios ranging from 0.4 to 0.6. SRNL did not observe a significant difference in slurry for the 9 grout batches prepared. All samples were monitored for at least 28 days. SRNL did not observe bleed water or expansion in the FY23 ETF ammonia grout samples.

4.4 Curing Conditions and Moisture Content

After filling, the containers were capped and placed into a zip lock bag. They were placed on the laboratory benchtop to cure at room temperature. Room temperature at sample storage location was monitored and recorded periodically as shown in Table 2-4. Significant variance in the room temperatures was not recorded at the sample location.

The moisture contents of the BFS and MgO were also measured to determine if moisture absorption during storage at PNNL and SRNL was a factor in expansion. The moisture content of SRNL and PNNL materials differed by approximately 1-1.5%. Sorbed moisture on the dry mix ingredients was consequently determined not to be a factor in the observed expansion of the previous samples prepared at SRNL.

5.0 Summary

The ETF ammonia tolerant grout waste form was developed by the Vitreous State Laboratory (VSL) to stabilize ammonium and thereby prevent emission of ammonia vapor during solidification of an ammonium-rich, concentrated sulfate aqueous waste stream generated at the Hanford ETF).[1, 2] VSL did not observe expansion in samples prepared during the waste form development work. However, Savannah River National Laboratory (SRNL) personnel detected expansion, in a few cases up to ~ 20 volume percent expansion, in ETF grout samples while preforming work scope to evaluate grout prepared with a range of ETF brine compositions.

In Fiscal Year 2021 (FY21), WRPS requested SRNL to test the waste formulation, struvite precipitation, and reagent addition strategy proposed for a future grouting facility with three ETF waste simulants that span the range of brine feed compositions expected to be processed.[3] In Fiscal Year 2022 (FY22), an

evaluation of the effects of variation in reagent addition was requested because using the materials and sample preparation protocol provided by WRPS, all the FY21 samples expanded.[4] Consequently, additional testing was requested by Washington River Protection Services (WRPS) Statement of Work (SOW) Requisitions # 356730, Revision 1, February 1, 2022[8], to determine whether differences in the slags or differences in sample preparation protocols used by VSL and SRNL were the cause of the expansion observed in the SRNL samples. G. Chen, WRPS, arranged a materials exchange between VSL and SRNL and coordinated the VSL protocol for grouting and curing 1L of Base Case ETF simulant. VSL and SRNL encountered expansion, at varying degrees, in all samples prepared under the material exchange and grouting protocol.[6]

This report summarizes work SRNL performed to identify the cause of ETF grout expansion by an additional material exchange testing between SRNL and VSL.[7] The effects of a new set of dry materials were supplied by PNNL and grouting procedures and curing containers were provided by WRPS. A protocol[9] was followed by all laboratories for sample preparation.

Observations from this study indicated variations in MgO additions, water-to-dry mix ratios and curing containers did not result in or correlate to ETF ammonia grout expansion. In comparison to previous work, SRNL observed the addition rate of NaOH to be an important factor for achieving the final target pH in the struvite precipitation step. In the current testing NaOH was added in bulk (5-10 mL at one time) during the precipitation step. The resulting pH was 7.57-9.15 which is slightly higher than pH observed for slower addition. (Previously NaOH was added over 30 minutes at a slower addition rate). Additional testing is needed to identify the presence and stability of struvite slurry and in then ETF ammonia grout. **B**ased on the current data, it is unknown if NaOH addition rate is the fundamental cause of grout expansion.

6.0 References

1. W. Gong, H. Abramowitz and I. L. Pegg, "Formulation Development and Testing of Ammonia Tolerant Grout," Vitreous State Laboratory The Catholic University of America, Washington, DC, VSL-19R4630-1, August 2019.

2. H. Abramowitz, W. Gong, M. Brandys, D. A. McKeown and I. L. Pegg, "Maturation of Grout Formulation and Immobilization Technology for Effluent Treatment Facility High-Ammonia Waster," Vitreous State Laboratory, Washington, DC, VSL-21R4950-1, Revision 0, January 2021.

3. "Evaluate ETF Brine Range and Reagent Addition," Washington River Protection Services, Hanford, WA, Statement of Work Requisition # 339922, March 2021.

4. "Evaluate ETF Brine Range and Reagent Addition," Washington River Protection Services, Hanford, WA, Statement of Work Requisition # 339922, Revision 1, November 2021.

5. "Evaluate ETF Grout Expansion," Washington River Protection Services, Hanford, WA, Statement of Work Requisition # 356730, Revision 1, February 2022.

6. K. A. Hill and C. A. Langton, "ETF Grout Expansion: Effects of Different Slags and Struvite Precipitation Protocols (Stirring Time)," Savannah River Nationa Laboratory Aiken, SC, SRNL-STI-2022-00268, Revision 0, October 2022.

7. "Evaluate ETF Grout Expansion " Washington River Protection Services, Hanford, WA, Statement of Work Requisition # 356730, Revision 2, January 2023.

8. C. A. Langton, K. A. Hill and J. Manna, "SRNL Response to WRPS CTO to Address Requisition # 356730 Statement of Work Revision 2," Savannah River National Laboratory Aiken, SC, SRNL-L3300-2023-00002, Revision 0, February 2023.

9. K. A. Hill and C. A. Langton, "Task Technical and Quality Assurance Plan to Evaluate Hanford Effluent Treatment Facility Grout Expansion and Struvite Stability " Savannah River National Laboratory Aiken, SC, SRNL-RP-2023-00013, Revision 0, March 2023.

10. K. A. Hill, "ETF Ammonia Grout SOW Revision 2 Round Robin Testing," Savannah River National Laboratory Aiken, SC, i7557-00151-46, SRNL E-Notebook (Production), 2023.

11. "Technical Reviews," Savannah River Site, Manual E7, Procedure 2.60, Latest Revision.,

Appendix A.

Attachment 1. WRPS Protocol

Proposed ETF Grout FY23 Test Plans – VSL, SRNL, PNNL – 11/16/22 All Labs Meeting

- Round-robin style testing between all 3 labs (VSL, SRNL, PNNL) using same material batches, curing containers, procedure. A total of nine 1-liter lab scale tests should be performed by each lab as detailed in the procedure below.
- PNNL will order all dry reagent materials and curing containers (based on VSL-21S5070-1, Rev. 1) and prepare packages to send to VSL and SRNL. PNNL will measure water content of BFS and MgO prior to preparing batches for shipping. Add a desiccant to the package and seal tightly.

Simulant Preparation:

- Start at 24ºC
- Add water to container first
- Impeller speed 120-160 rpm
- Add solid chemicals in Table 1 below one-by-one while mixing. Add ammonium sulfate last, otherwise add solids in order listed in Table 1 starting with Na_2SO_4 first.
- Continue mixing with lid on until all chemicals are dissolved
- Do not adjust pH of resulting solution
- Measure and record pH after ingredients are added and dissolved (visually) at 24ºC
- Measure ammonium ion content after simulant is prepared
- Use the simulant for struvite precipitation and grouting on the same day. Do not wait overnight in between struvite precipitation and grouting steps.

Table 6-1. Recipe for 1 Liter of Hanford ETF Brine Simulant

Analyte	Target		Reagent	Molecular Weight	Assay	Target
	g/L	Molar				Mass (g)
NH_4^+	6.075	0.3368	$(NH_4)_2SO_4$	132.14	0.990	22.48
Na^+	72.772	3.1654	-	-	-	-
SO_4^{2-}	160.014	1.6657	Na_2SO_4	142.04	0.998	213.11
Cl^-	0.265	0.0075	NaCl	58.44	0.990	0.44
NO_3^-	9.248	0.1491	$NaNO_3$	84.99	0.997	12.72
HCO_3^-	1.058	0.0173	$NaHCO_3$	84.01	0.990	1.47
H_2O	-	-	DI H_2O	18.02	1.000	938.21
Total, g/L						1188.43

- Empty data field

Struvite Precipitation:

- Use the same container, mixer, and impeller as was used for simulant preparation above
- Use dry materials sent from PNNL with target weights in Table 2 below
- Add MgSO4•7H2O and NaH2PO4•H2O sequentially over ~10 minutes. Stir until all solids are dissolved.

- Add 50 wt.% NaOH solution (by weight) slowly while stirring to achieve a final pH of 7.1 ± 0.2 over ~30 minutes. Try to get as close to 7.0 as possible. Record the final weight of NaOH added.
    - Use pipette to add the bulk of NaOH in first 5-10 minutes to 7.0, then wait ~20 minutes for pH equilibration, check pH (solution pH may drift over time) and make small adjustments (adding more NaOH) as necessary to reach as close to 7.0 as possible.
- Measure and record pH and temperature ~once per minute throughout entire struvite precipitation process
- Stir struvite mixture for 2 hours with container lid on before proceeding to the grouting step

Table 6-2. Recipe for Struvite Precipitation

Order of Addition	Chemicals	Target Weight (g)	Assay
1	EMF simulant (1 liter)	1188.43	1.000
2	$MgSO_4 \cdot 7H_2O$ [$]	83.85	0.990
3	$NaH_2PO_4 \cdot H_2O$	46.47	1.000
4	NaOH 50% w/w	54.193	0.506

NOTE FROM PNNL: *We are seeing some evaporation when we need to heat it to get the first part to go into solution (<40 C), losing up to 30 mL volume. So, we check the mass balance of the struvite + simulant before batching and add water to get back up to the target mass of ETF + struvite (1372.94 g)*

Grout Formulation and Curing:

- Add requisite quantity of BFS and MgO following Table 3 below into 7-quart planetary mixer. If MgO is added, mix BFS and MgO together with mixer or by hand for ~5 minutes until visually homogenous.
- Pour struvite mixture into the 7-quart mixer with BFS/MgO mixture and mix at ~100 revolutions per minute for ~5 minutes
- Measure final pH and temperature
- Pour fresh grout into 2”x4” cylindrical (uncut) curing containers sent by PNNL (from Deslauriers) and into 2 SRNL containers. Pour grout to ~2mm below the top of the container.
- Air bubbles may be removed by tapping the sides of the curing cylinders with a spatula.
- Note any bleed water and grout consistency (especially any flowability issues at the lower w/dm ratios).
    - If there is bleed water, pull it off, measure the amount, and put it back on. Note any reabsorption (or not) of the bleed water over the next weeks of curing. Note when it is reabsorbed or not.
- Place lids tightly on containers. Place the full and capped containers in a plastic zip lock bag (or similar) and seal the bag. Cure at room temperature on a laboratory shelf. **Do not** place wet towels inside of plastic bag or place samples in a cooler.
- Record room temperature at sample storage location, check for bleed water, and visually observe grout for any changes or expansion starting at 5 days cure time. Use a simple ruler for measuring vertical expansion, if any. Continue checking samples based on sample activity.
- Photograph grout for any changes or expansion every 7 days during curing for at least 28 days.
- Save samples for any potential future characterization (under the same conditions as described in curing step above)

Table 6-3. Test Matrix for VSL, SRNL, and PNNL 1-liter Grout Samples

Test #	wt.% MgO in dry mix	Water to dry mix ratio (w/dm)	Target weight BFS (g)	Target weight MgO (g)
1	None	0.4	2344.66	0
2	None	0.5	1876.57	0
3	None	0.6	1565.05	0
4	3%	0.4	2274.32	70.34
5	3%	0.5	1820.27	56.30
6	3%	0.6	1518.10	46.95
7	8%	0.4	2157.09	187.57
8	8%	0.5	1726.44	150.13
9	8%	0.6	1439.84	125.20

Other notes:

- At the end of Table 3 tests, all labs will perform 110C weight loss measurement to check for moisture content in MgO and BFS again to check for any differences in the materials stored at each lab
- VSL and SRNL to perform 110C weight loss measurement on current batches of dry materials to see if moisture loss is different between same batches stored at different labs.

Attachment 2. Data Sheets for Grout Batches

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 1 : 1-MgO-4	M&TE: 33074/36119 DATE: 3/30/23

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% more for subsample

Order of Addition	Reagent	Target Mass (g)	Actual Mass (g)
~~6~~	$(NH_4)_2SO_4$	22.48 26.98	26.9
~~2~~	Na_2SO_4	213.11 255.73	255.7
~~3~~	NaCl	0.44 0.53	0.533
~~4~~	$NaNO_3$	12.72 15.26	15.2
~~5~~	$NaHCO_3$	1.47 1.76	1.763
~~1~~	DI H_2O	938.21 1125.85	1125.8
	Total, g/L (VSL target: 1188.43)		
	Ammonium ion :		
	Final pH/temp : 7.34 @ 24.9°C	Wt%: 20.7	Density: 1.1893 g/cm^3

NOTES:
Remove from Heat & subsample * sent to BAT

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43	1188.43	-
~~2~~	$MgSO_4 \bullet 7H_2O$	83.85	83.8	~ 10 minutes
~~3~~	$NaH_2PO_4 \bullet H_2O$	46.47	46.4	
4	NaOH 50% w/w	54.193	54.20	~ 30 minutes
Struvite mixture				~ 2 hours

NOTES: Start time 10:17am
$MgSO_4$ all in @ 10:19am
NaH_2PO_4 all in @ 10:21am
4.30 @ 22.9°C After 10min of mix time
After adding NaOH for 10min pH 6.90 32.2°C
After 20mins of NaOH 7.19 29.6°C

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION.

RECORD **starting** pH and temperature & time: 7.37 @ 24.7°C

RECORD **Final** pH and temperature & time: 7.92 24.6°C 12:59pm
(After 2 hours)

* export data logger to computer - save file as pH "Test #"

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 2-MgO-5	M&TE: 33074/36119 DATE: 3/31/23

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New* Target Mass (g)	Actual Mass (g)
6	$(NH_4)_2SO_4$	22.48	**26.98**	27.0
2	Na_2SO_4	213.11	**255.73**	255.7
3	NaCl	0.44	**0.53**	0.53
4	$NaNO_3$	12.72	**15.26**	15.3
5	$NaHCO_3$	1.47	**1.76**	1.76
1	DI H_2O	938.21	**1125.85**	1125.9
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : 7.30 24.8°C	Wt%:		Density:
	NOTES: SubSample removed			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43	1188.4	-
2	$MgSO_4 \bullet 7H_2O$	83.85	83.8	~ 10 minutes
3	$NaH_2PO_4 \bullet H_2O$	46.47	46.5	
4	NaOH 50% w/w	54.193	54.19	~ 30 minutes
Struvite mixture				~ 2 hours

NOTES: 9:15am $MgSO_4$ & NaH_2PO_4 added all in. pH: 4.19 @ 22.2°C
After 10min Stirring pH 4.17 22.3°C 9:25am
After adding NaOH (about 90% of it) pH: 6.80 32.3°C (stopped after 8 min). Added Rest at the Restart

RECORD **starting** pH and temperature & time: 7.35 24.1°C 9:13am

After 2 hour mixing time, RECORD **Final** pH and temperature & time: 7.57 @ 24.4°C pH: 6.64 32.2°C 9:36am

pH 7.01 @ 30.3°C time After 30mins. (9:53am)

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 3-MgO-6	M&TE: 33074 36119 DATE: 4/4/2023

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
✓6	$(NH_4)_2SO_4$	22.48	**26.98**	27.0
✓2	Na_2SO_4	213.11	**255.73**	255.7
✓3	NaCl	0.44	**0.53**	0.532
✓4	$NaNO_3$	12.72	**15.26**	15.3
✓5	$NaHCO_3$	1.47	**1.76**	1.763
✓1	DI H_2O	938.21	**1125.85**	1125.8
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : 7.29 @ 25.5°C	Wt%:		Density:
	NOTES: subsample/submit to PSAL			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43	1188.4	-
2	$MgSO_4 \bullet 7H_2O$	83.85	83.9	~ 10 minutes
3	$NaH_2PO_4 \bullet H_2O$	46.47	46.5	
4	NaOH 50% w/w	54.193	54.19	~ 30 minutes
Struvite mixture				~ 2 hours

NOTES: MgSO4/NaPO4 all in @ 9:21am → pH: 4.34 @ 23.2°C
NaOH → all in @ 9:42 pH: 6.99 @ 32.4°C

RECORD **starting** pH and temperature & time: 7.32 @ 25.1°C Start time 9:18am

After 2 hour mixing time, RECORD **Final** pH and temperature & time: 7.64 @ 24.4°C

after 30 minutes: 7.19 @ 30.0°C

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 4-Mg3-4	M&TE: 33074/36119 DATE: 4/10/2023

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
6	$(NH_4)_2SO_4$	22.48	**26.98**	27.0
✓2	Na_2SO_4	213.11	**255.73**	255.8
✓3	NaCl	0.44	**0.53**	0.532
✓4	$NaNO_3$	12.72	**15.26**	15.3
✓5	$NaHCO_3$	1.47	**1.76**	1.76
✓1	DI H_2O	938.21	**1125.85**	1125.9
Total, g/L (VSL target: 1188.43)				
Ammonium ion :				
Final pH/temp : 7.32 @ 24.9 °C		Wt%:		Density:
NOTES: Subsampled * for PSAL Heated to 24°C				

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
✓1	EMF Simulant	1188.43	1188.4	-
✓2	$MgSO_4 \bullet 7H_2O$	83.85	83.8 – 9:45am	~ 10 minutes > pH: 4.18 @ 21.9°C
✓3	$NaH_2PO_4 \bullet H_2O$	46.47	46.4 – 9:47am	
4	NaOH 50% w/w	54.193	~~54.1515~~ * KH	~ 30 minutes All NaOH in @ 1004 pH: 6.88 31.5°
Struvite mixture			54.1915	~ 2 hours
NOTES: After 20mins of Stirring pH: 7.31 28.7°C @ 1025				

RECORD **starting** pH and temperature & time: 7.37 pH 24.2°C @ 0944

After 2 hour mixing time, RECORD **Final** pH and temperature & time: 8.78 @ 24.2°C

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 5 - $Mg3$ -5	M&TE: 36119 33074 56412 DATE: 04-12-23

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
✓6	$(NH_4)_2SO_4$	22.48	**26.98**	26.9
✓2	Na_2SO_4	213.11	**255.73**	255.7
✓3	NaCl	0.44	**0.53**	0.53
✓4	$NaNO_3$	12.72	**15.26**	15.2
✓5	$NaHCO_3$	1.47	**1.76**	1.76
✓1	DI H_2O	938.21	**1125.85**	1125.9
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : 7.29 @ 25.3	Wt%:		Density:
	NOTES: Heated DI H2O to 24°C subsampled for PSAL			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43	1188.4	-
2	$MgSO_4 \bullet 7H_2O$	83.85	83.8	- Started @ 9:25am → All in @ 9:27 ~ 10 minutes
3	$NaH_2PO_4 \bullet H_2O$	46.47	46.5	- Started @ 9:27am → All in @ 9:30 ~ 30 minutes
4	NaOH 50% w/w	54.193	~~54.1996~~ * KH	- Started @ ~~9:35am~~ → 9:44am all in
Struvite mixture			54.1996 KH	~ 2 hours
NOTES: step 2&3: pH 4.23 @ 22.9°C → precipant reagents				

RECORD **starting** pH and temperature & time: 7.31 @ 25.2°C

After 2 hour mixing time, RECORD **Final** pH and temperature & time: pH: 8.18 24.6°C @ 12:07

pH after 30mins of step ~~3~~ KH 4: 7.38 29.6°C 10:05am

pH after 10mins of Step 4: 6.99 32.5°C @ 9:44am

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 6-Mg3-6	M&TE: 330174/360119 DATE: 4/12/2023

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% ~~larger~~ more simulant batch ~~for~~ prepped for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
✓6	$(NH_4)_2SO_4$	22.48	**26.98**	27.0
✓2	Na_2SO_4	213.11	**255.73**	255.7
✓3	NaCl	0.44	**0.53**	0.53
✓4	$NaNO_3$	12.72	**15.26**	15.26
✓5	$NaHCO_3$	1.47	**1.76**	1.76
✓1	DI H_2O	938.21	**1125.85**	1125.9
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : pH: 7.32 25.8°C	Wt%:		Density:
	NOTES: Finish adding @ 1255 Heated DI H_2O to 24°C Subsampled for PSAL			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43	1188.4	-
2	$MgSO_4 \bullet 7H_2O$	83.85	83.9	Start @ 1302 → end at 1303 ~ 10 minutes
3	$NaH_2PO_4 \bullet H_2O$	46.47	46.4	Start @ 1304 → end at 1305
4	NaOH 50% w/w	54.193	54.18	~30 minutes Started @ 1312 → end at 1322
Struvite mixture				~ 2 hours
NOTES:				

all in at 1305
pH 4.33
24.1°C

1301 7.30

RECORD **starting** pH and temperature & time: ~~pH~~ pH 25.8°C

After 2 hour mixing time, RECORD **Final** pH and temperature & time: 7.08 @ 24.8 °C @ 15:42

After 10 mins of all NaOH added Step 4: pH: 6.97 33.9°C @1322

After 30 mins of NaOH added Step 4: pH: 7.15 31.2°C @1342

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 7-Mg8-4	M&TE: 330741361119 DATE: 4-14-23

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
✓6	$(NH_4)_2SO_4$	22.48	**26.98**	26.9
✓2	Na_2SO_4	213.11	**255.73**	255.7
✓3	NaCl	0.44	**0.53**	0.53
✓4	$NaNO_3$	12.72	**15.26**	15.3
✓5	$NaHCO_3$	1.47	**1.76**	1.76
✓1	DI H_2O	938.21	**1125.85**	1125.8
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : pH 7.28 26.3°C	Wt%:		Density:
	NOTES: ~~finished~~ 9:23am Heated DI H_2O to 24°C Subsampled for PSAL			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
✓1	EMF Simulant	1188.43	1188.4	
✓2	$MgSO_4 \bullet 7H_2O$	83.85	83.8	Adding → started @ 0933 → end 0935 ~ 10 minutes
✓3	$NaH_2PO_4 \bullet H_2O$	46.47	46.5	Started @ 0935 → end 0936
✓4	NaOH 50% w/w	54.193	54.19	~30 minutes Started @ 0945 → end 0954
Struvite mixture				~ 2 hours
NOTES:				

After 10 min: pH 4.20 0943 23.2°C

RECORD **starting** pH and temperature & time: pH: 7.31 25.7°C 9:32

After 2 hour mixing time, RECORD **Final** pH and temperature & time: 9.15 @ 24.9°C time: 12:17 PM

After 10 mins of adding NaOH in Step 4 : pH: 6.98 32.9°C 9:55

After 30 mins of NaOH in Step 4 : pH: 7.75 30.1°C 1016

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 8-Mg8-5	M&TE: 330741361119 DATE: 4-17-23

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
✓6	$(NH_4)_2SO_4$	22.48	**26.98**	26.9
✓2	Na_2SO_4	213.11	**255.73**	255.7
✓3	NaCl	0.44	**0.53**	0.53
✓4	$NaNO_3$	12.72	**15.26**	15.3
✓5	$NaHCO_3$	1.47	**1.76**	1.76
✓1	DI H_2O	938.21	**1125.85**	1125.8
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : 7.32 @ 24.6°C Wt%:			Density:
	NOTES: Heated to 24°C subsampled for ammonia/wt%/spg.			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43		-
2	$MgSO_4 \bullet 7H_2O$	83.85	83.9	start @ 1035 → end 1038 ~ 10 minutes
3	$NaH_2PO_4 \bullet H_2O$	46.47	46.4	start @ 1038 → end 1039 ~ 30 minutes
4	NaOH 50% w/w	54.193	54.20	start @ ~1045 → 1053
Struvite mixture				~ 2 hours
NOTES:				

After 10min pH: 4.17 @22.5 1045

RECORD **starting** pH and temperature & time: @ 10:35am 7.35@24.5°C

After 2 hour mixing time, RECORD **Final** pH and temperature & time: 1315pm pH 8.71 @ 24.6°C

After 10 mins of adding NaOH in Step 4 : pH 6.85 32.3°C 1051 Lean

After 30 mins of Step 4 : pH 7.28 29.6°C 11:16am

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Test #: 9-Mg8-6	M&TE: 330114/326119 DATE: 4/18/23

Prepare simulant at 24°C per Table 1.

Table 1. Recipe for 1 Liter of Hanford Base Case ETF Brine Simulant

NOTE: 20% larger simulant batch for subsampling

Order of Addition	Reagent	Target Mass (g)	*New Target Mass (g)	Actual Mass (g)
✓6	$(NH_4)_2SO_4$	22.48	**26.98**	27.0
✓2	Na_2SO_4	213.11	**255.73**	255.73
✓3	NaCl	0.44	**0.53**	0.53
✓4	$NaNO_3$	12.72	**15.26**	15.3
✓5	$NaHCO_3$	1.47	**1.76**	1.76
✓1	DI H_2O	938.21	**1125.85**	1125.85
	Total, g/L (VSL target: 1188.43)			
	Ammonium ion :			
	Final pH/temp : 7.31 @24.9°C	Wt%:		Density:
	NOTES: Heated to 24°C Subsampled (PSAL)			

Struvite Precipitation

Table 2. Recipe for Struvite Precipitation for Base Case Simulant

START DATA LOGGER ON pH METER BEFORE STARTING PRECIPITATION

Order of Addition	Chemicals	Target Mass (g)	Actual Mass (g)	Mixing Time
1	EMF Simulant	1188.43	1188.4	
2	$MgSO_4 \bullet 7H_2O$	83.85	83.9	Start @ 1126 end @ 1128 (~ 10 minutes)
3	$NaH_2PO_4 \bullet H_2O$	46.47	46.5	Start @ 1129 end @ 1129
4	NaOH 50% w/w	54.193	54.19	Start @ 1131 end @ 1145 (~ 30 minutes)
Struvite mixture				~ 2 hours
NOTES:				

After 10 mins pH: 4.16 22.5°C 1137 am

RECORD **starting** pH and temperature & time: 7.31 24.9°C

After 2 hour mixing time, RECORD **Final** pH and temperature & time: pH: 8.10 24.7°C @ 14:13 pm

After 10 mins of adding NaOH in Step 4 : pH: 6.93 32.1°C @ 11:47 am

After 30 mins of Step 4 : pH: 7.26 29.1°C 12:07 pm

DATA SHEET for preparing ETF GROUT from 1L of BASE CASE SIMULANT

Grout Formulation scale: 33074

Table 1. Grout Test Matrix for VSL, SRNL, and PNNL for Batch prepared with 1L Base Case Simulant

Grout Batch	Grout Preparation Date	wt% MgO in dry mix	Water to dry mix ratio (w/dm)	Target weight BFS (g)	Actual weight BFS (g)	Target weight MgO (g)	Actual weight MgO (g)	Grout Final pH and Temp
1-Mg0-4	3-30-23	None	0.4	2344.66	2344.6	0	0	23.7°C 12.26
2-Mg0-5	3-31-23	None	0.5	1876.57	1876.6	0	0	24.0°C 12.14
3-Mg0-6	4-4-23	None	0.6	1565.05	1565.0	0	0	23.6 12.10
4-Mg3-4 (calcined)	4-10-23	3%	0.4	2274.32	2274.3	70.34	70.34	23.6 12.32
5-Mg3-5	4-12-23	3%	0.5	1820.27	1820.2	56.30	56.3	23.2°C 12.13
6-Mg3-6	4-12-23	3%	0.6	1518.10	1518.1	46.95	47.0	23.8°C 12.14
7-Mg8-4	4-14-23	8%	0.4	2157.09	2157.0	187.57	187.5	24.7°C 12.13
8-Mg8-5	4-17-23	8%	0.5	1726.44	1726.4	150.13	150.1	24.4°C 12.11
9-Mg8-6	4-18-23	8%	0.6	1439.84	1439.8	125.20	125.2	24.5°C 12.18

Distribution:

Name:	Location:	Name:	Location:
G. Chen	Grace_chen@rl.gov		
R. Skeen	Rodney_s_skeen@rl.gov		
D. Swanberg	David_j_swanberg@rl.gov		
J. Manna	999-2W		
A.D. Cozzi	999-W		
C.A. Langton	773-42A		
K.A. Hill	999-W		
S. Hodges (records)	773-A		