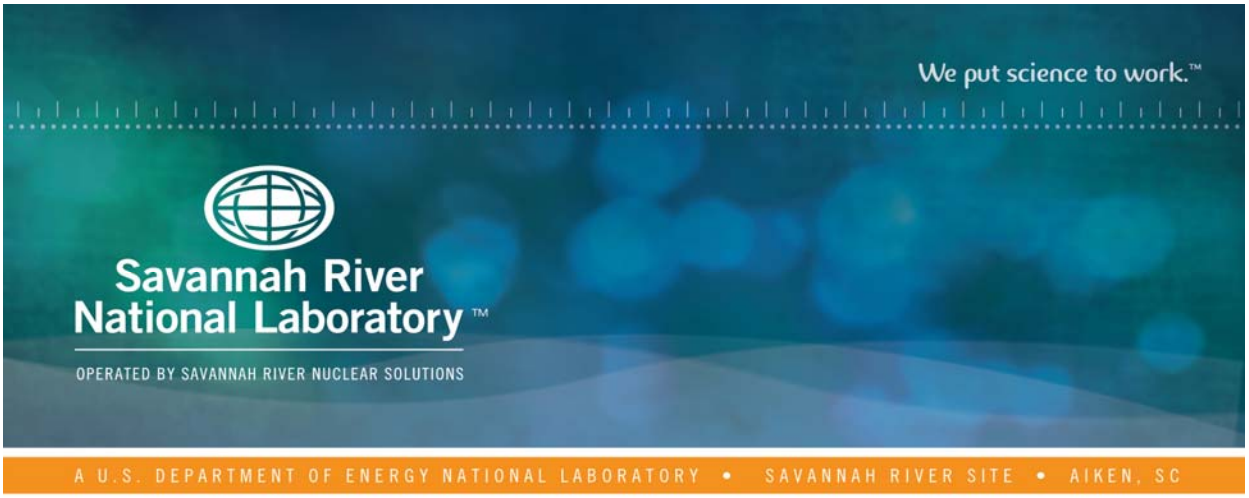

Analysis of Harrell Monosodium Titanate Lot # 46000824120

K. M. L. Taylor-Pashow

April 2014

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EXECUTIVE SUMMARY

Monosodium titanate (MST) for use in the Actinide Removal Process (ARP) must be qualified and verified in advance. A single qualification sample for each batch of material is sent to SRNL for analysis, as well as a statistical sampling of verification samples. The original Harrell Industries Lot #46000824120 qualification and 16 verification samples received in September 2012 failed to meet the specification for weight percent solids. All of the pails sampled and tested contained less than 15 wt % MST solids. The lot was returned to the vendor, and in February 2014 a new qualification sample and set of 14 verification samples were received from this lot. The new lot met each of the selected specification requirements that were tested and, consequently, the material is acceptable for use in the ARP process.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
MST	monosodium titanate
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TTQAP	Technical Task and Quality Assurance Plan
VOA	volatile organic analysis

1.0 Introduction

Harrell Industries is under contract with Savannah River Remediation (SRR) to provide MST for use in the Actinide Removal Process (ARP). In September 2012 a 1-L qualification sample from Lot #46000824120 was sent to the Savannah River National Laboratory (SRNL) to confirm the material meets certain requirements specified in the purchase specification.[1]

The vendor is also obligated to send verification samples from ~10% or more of the pails of MST product for each lot. The verification samples are selected from the entire inventory of pails so that the set of verification samples represents pails filled from the beginning to the end of the pail-filling operation for the entire lot of MST. For the verification of this lot, Harrell Industries sent 16 samples in September 2012, one each from pails #10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, and 155 of 155 total pails.

SRR requested analysis of the qualification sample for weight percent MST, density, pH, volatile organics, and particle size. They also requested analysis of the verification samples for weight percent solids, density, and pH.[2] The work was controlled by a Task Technical and Quality Assurance Plan (TTQAP).[3]

Original analysis of the samples received in September 2012 showed the material did not meet the weight percent solids specification. The lot was returned to Harrell Industries. In February 2014 a 1-L qualification sample and 14 verification samples, one each from pails #1, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, and 127 of 127 total pails, were received. These samples represent the reworked lot of material previously returned to Harrell.

2.0 Experimental Procedure

2.1 Analyses

SRNL analyzed the qualification and verification samples for density, pH, and weight percent solids. Density was measured using an electronic pipette in triplicate. The pH was measured by colorimetric pH strips, and the weight percent solids were measured in triplicate using a Mettler-Toledo Halogen Moisture Analyzer HG63 instrument.

Weight percent solids measurements performed on the samples received in September 2012 at SRNL were lower than the value reported by Harrell Industries for this lot. Therefore, the weight percent solids measurements were confirmed for the qualification sample using the method provided by Harrell Industries. This procedure is provided in Appendix A.

Aliquots of the qualification sample were removed under well mixed conditions to provide sub-samples for each of the analyses. SRNL performed the following analyses: volatile organic analysis (VOA) and particle size using a Microtrac® S3500 analyzer.

2.2 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, Rev. 2.

3.0 Results and Discussion

The results of the weight percent, pH, and density measurements for the September 2012 samples are reported in Table 3-1, while the results of the additional qualification sample analyses are reported in Table 3-2. The weight percent, pH, and density measurements for the February 2014 samples are reported in Table 3-3, while the results of the additional qualification sample analyses are reported in Table 3-4.

As seen in Table 3-1, all of the samples tested from the September 2012 set of samples contained less than 15 wt % MST solids and, therefore, failed to meet the purchase specification. Pail #s 1 – 150 were marginally below the lower weight percent limit, while Pail #155 was significantly below the limit, containing only ~ 14 wt % solids. The measured density of Pail #155 was also lower than the remainder of the lot. There has been a declining trend in the most recent batches of MST received from Harrell Industries, with respect to the weight percent MST in the slurries. The three previous lots (#46000706120, 46000722120, and 46000808120) were very near the 15 wt % lower limit, but were accepted.[4]

Harrell reported a weight percent solids of 15.7 wt % for this lot of material. Using the method provided by Harrell (Appendix A), SRNL obtained a value of 14.53 wt % solids, consistent with the low values obtained using the normal SRNL method (Mettler-Toledo Halogen Moisture Analyzer). During performance of the Harrell method, it was found that it required approximately 3 hours of drying to reach a constant weight. This is a possible source of the discrepancy between the SRNL and Harrell reported values. If the samples are not completely dry the weight percent solids will be reported high.

As seen in Table 3-3, the new lot of qualification and verification samples received in February 2014 had higher weight percent solids. All samples fell within the 15-17 wt % acceptable range. The results for the remaining analyses (pH, density, particles size, VOA) were similar to the September 2012 samples, and were within the acceptable range.

Table 3-1. Weight Percent, pH, and Density Results for All Samples (September 2012)

Sample ID	Weight % Solids (Standard Deviation)	pH[a]	Density[b] (g/mL) (%RSD)
Qualification	14.92 (±0.112) %	11.5	1.116 (0.10%)
Pail #10	14.82 (±0.137) %	12.0	1.116 (0.04%)
Pail #20	14.75 (±0.076) %	11.5	1.115 (0.04%)
Pail #30	14.63 (±0.178) %	12.0	1.115 (0.06%)
Pail #40	14.61 (±0.159) %	12.0	1.117 (0.36%)
Pail #50	14.80 (±0.106) %	12.0	1.111 (0.15%)
Pail #60	14.67 (±0.056) %	12.0	1.119 (0.12%)
Pail #70	14.81 (±0.273) %	12.0	1.114 (0.26%)
Pail #80	14.85 (±0.082) %	12.0	1.115 (0.02%)
Pail #90	14.73 (±0.122) %	12.0	1.116 (0.02%)
Pail #100	14.82 (±0.191) %	12.0	1.116 (0.07%)
Pail #110	14.81 (±0.047) %	12.0	1.113 (0.05%)
Pail #120	14.81 (±0.068) %	12.0	1.115 (0.05%)
Pail #130	14.80 (±0.026) %	12.0	1.115 (0.16%)
Pail #140	14.64 (±0.104) %	12.0	1.115 (0.04%)
Pail #150	14.70 (±0.329) %	12.0	1.113 (0.23%)
Pail #155	14.05 (±0.050) %	12.0	1.108 (0.09%)
Average	14.72 (±0.192) %	12.0	1.115 (0.23%)
Acceptable Range[1]	15-17 %	> 10	no requirement
Harrell Method[c]	14.53%	n/a	n/a

a) The uncertainty of the pH measurement is 0.5 pH units.

b) Density measurements taken at 23 °C.

c) Performed at SRNL using the qualification sample from this lot and the method provided by Harrell. Note total drying time to reach the constant weight was approximately 3 hours.

Table 3-2. Results of the Qualification Sample Analyses (September 2012 sample)

Property	Method	Result	Specification	Pass ?
Volatile Organics	VOA	17 ppm[1]	n/a[2]	n/a
Particle Size, < 0.8 μm	Microtrac®	4.60 vol %	<10 vol %	YES
Particle Size, > 37 μm	Microtrac®	0 vol %	<1 vol %	YES
Particle Size, geometric standard deviation (absorbance mode)	Microtrac®	3.22	≤3.5	YES

The "Particle Size, geometric standard deviation" is defined as the 50th percentile result divided by the 16th percentile result. Microtrac® results have a 10% analytical uncertainty. VOA results have a 20% analytical uncertainty.

[1] Isopropanol = 17 ppm, all other analytes = < 0.25 ppm

[2] Purchase specification does not include a specification for volatile organics, only total alcohol content of < 500 ppm.

Table 3-3. Weight Percent, pH, and Density Results for All Samples (February 2014)

Sample ID	Weight % Solids (Standard Deviation)	pH[a]	Density[b] (g/mL) (%RSD)
Qualification	16.05 (±0.056) %	12.5	1.105 (0.65%)
Pail #1	16.10 ((±0.058) %	12.5	1.113 (0.11%)
Pail #10	15.95 (±0.023) %	12.5	1.112 (0.33%)
Pail #20	15.90 (±0.065) %	12.5	1.110 (0.14%)
Pail #30	15.79 (±0.129) %	12.5	1.118 (0.40%)
Pail #40	15.79 (±0.055) %	12.5	1.119 (0.27%)
Pail #50	16.01 (±0.116) %	12.0	1.116 (0.21%)
Pail #60	15.92 (±0.060) %	12.0	1.120 (0.30%)
Pail #70	15.85 (±0.104) %	12.0	1.101 (0.15%)
Pail #80	15.94 (±0.081) %	12.5	1.116 (0.10%)
Pail #90	15.92 (±0.111) %	12.5	1.112 (0.39%)
Pail #100	15.81 (±0.049) %	12.5	1.109 (0.25%)
Pail #110	15.83 (±0.026) %	12.5	1.106 (0.12%)
Pail #120	15.90 (±0.083) %	12.5	1.111 (0.02%)
Pail #127	15.55 (±0.122) %	12.0	1.108 (0.20%)
Average	15.89 (±0.130) %	12.5	1.112 (0.49%)
Acceptable Range[1]	15-17 %	> 10	no requirement

a) The uncertainty of the pH measurement is 0.5 pH units.
b) Density measurements taken at 25 °C.

Table 3-4. Results of the Qualification Sample Analyses (February 2014 sample)

Property	Method	Result	Specification	Pass ?
Volatile Organics	VOA	2.5 ppm[3]	n/a[4]	n/a
Particle Size, < 0.8 µm	Microtrac®	4.26 vol %	<10 vol %	YES
Particle Size, > 37 µm	Microtrac®	0 vol %	<1 vol %	YES
Particle Size, geometric standard deviation (absorbance mode)	Microtrac®	3.17	≤3.5	YES

4.0 Conclusions

Initial analyses of the Harrell Lot #46000824120 MST material received in September 2012 indicated the material met the specifications, with the exception of weight percent solids. The pails all contained less than 15 wt % solids (the lower limit of the specification). The material from this lot was returned to Harrell, and a new set of qualification and verification samples were received in February 2014. Analyses of the new samples from this lot indicate the material falls within the specifications required for use at ARP.

[3] Isopropanol = 2.5 ppm, all other analytes = < 0.25 ppm
[4] Purchase specification does not include a specification for volatile organics, only total alcohol content of < 500 ppm.

5.0 References

1. Specification for Purchase of 15 wt % Monosodium Titanate (MST) for 96-H ARP, Specification No. X-SPP-H-00012, Rev. 6, November 2010.
2. C. Duffey, "MST Qualification and Verification", X-TTR-H-00017, Rev. 0, February 2012.
3. K. M. L. Taylor-Pashow, "Task Technical and Quality Assurance Plan for Monosodium Titanate (MST) Qualification and Verification", SRNL-RP-2012-00094, Rev. 0, March 2012.
4. K. M. L. Taylor-Pashow, "Analysis of Harrell Monosodium Titanate Lot #s 46000706120, 46000722120, and 46000808120", SRNL-STI-2012-00629, Rev. 0, October 2012.

Appendix A. Harrell Weight Percent Solids Procedure

PROCEDURE: WEIGHT PERCENT

PURPOSE: To determine the weight percent of monosodium titanate in an aqueous slurry

EQUIPMENT: Oven
Analytical balance
Porcelain crucible

METHOD:

1. Thoroughly clean a porcelain crucible and dry in a 105 ^{o}C oven. Cool to room temperature in a desiccator. Weigh crucible and record weight to 0.0001 g.

2. Thoroughly suspend the MST slurry by shaking the sample bottle. Open the bottle and stir with a glass rod to make sure no chunks of MST remain unsuspended. Add approximately 1 g monosodium titanate slurry to crucible and record weight to 0.0001g.

3. Place crucible in 105 ^{o}C oven for one hour. Remove from oven and cool to room temperature in desiccator.

4. Weigh dish and record weight to 0.0001g.

5. Place crucible back in oven for 30 minutes, remove to desiccator, cool, and reweigh. Continue until weight percent does not change from one measurement to the next.

CALCULATION:

$$\text{Weight \%} = \frac{\text{(weight dried slurry – weight dish)}}{\text{(weight wet slurry – weight dish)}} \times 100$$

SPECIFICATION: 15 – 17 wt %

Distribution:

S. L. Marra, 773-A
T. B. Brown, 773-A
D. H. McGuire, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)

C. K. Chiu, 704-30S
B. A. Gifford, 704-56H
M. T. Keefer, 766-H
T. A. Le, 766-H
D. J. Martin, 241-152H
A. R. Shafer, 766-H

P. R. Jackson, DOE-SR, 703-46A
J. A. Crenshaw, DOE-SR, 703-46A

K. M. L. Taylor-Pashow, 773-A
T. C. Shehee, 773-A
T. B. Peters, 773-42A
M. R. Poirier, 773-42A
F. F. Fondeur, 773-A
D. T. Hobbs, 773-A
D. J. McCabe, 773-42A