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Analysis of Harrell Monosodium Titanate Lot #081811

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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 Harrell Industries Lot #081811 qualification and 12 verification samples met all the requirements in the specification, with the possible exception of the geometric standard deviation for particle size. Two sub-samples from the qualification sample were analyzed, giving results of 3.82 and 3.28, respectively, for the geometric standard deviation. The specification is ≤3.5. The results for both samples met the remaining particle size specifications, i.e. <10 vol% below 0.8 μm and <1 vol% above 37 μm. Filtration behavior of the current batch is expected to be near that of recent batches. SRNL recommends acceptance of this material. SRNL also recommends performing a statistical review of particle size data for the MST lots from this vendor to assess whether an improved material specification is appropriate.

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LIST OF ABBREVIATIONS

ARP	Actinide Removal Process
CSSX	Caustic Side Solvent Extraction
DF	decontamination factor
IC	ion chromatography
ICP-ES	inductively coupled plasma – emission spectroscopy
MCU	Modular CSSX Unit
MST	monosodium titanate
SRNL	Savannah River National Laboratory
TIC-TOC	total inorganic carbon – total organic carbon
VOA	volatile organic analysis

1.0 Introduction

Harrell Industries is under contract with Savannah River Remediation to provide MST for use in the Actinide Removal Process (ARP). A 500-mL qualification sample for Lot #081811 was sent to the Savannah River National Laboratory (SRNL) to confirm the material meets the 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 (distributed roughly evenly through the entire lot of pails). For the verification of this lot, Harrell Industries sent 12 samples, one each from pails #1, 10, 20, 30, 40, 60, 70, 80, 90, 100, 110, and 116 of 116 total pails.

2.0 Experimental Procedure

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.

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: strontium (Sr) decontamination factor (DF), volatile organic analysis (VOA), total inorganic carbon-total organic carbon (TIC-TOC), ion chromatography (IC) for fluoride, chloride, and bromide, and particle size using a Microtrac® S3500 analyzer.

3.0 Results and Discussion

The results of the weight percent, pH, and density measurements are reported in Table 3-1, while the results of the additional qualification sample analyses are reported in Table 3-2.

Table 3-1. Weight percent, pH and Density Results for All Samples

Sample ID	Weight % Solids (Standard Deviation)	pH[a]	Density[b] (g/mL) (%RSD)
Qualification	15.67 (±0.118) %	12.0	1.125 (0.32%)
Pail #1	15.35 (±0.015) %	12.0	1.121 (0.15%)
Pail #10	15.33 (±0.092) %	12.0	1.128 (0.27%)
Pail #20	15.33 (±0.045) %	12.0	1.123 (0.08%)
Pail #30	15.36 (±0.102) %	12.0	1.123 (0.18%)
Pail #40	15.45 (±0.137) %	12.0	1.123 (0.12%)
Pail #60	15.34 (±0.075) %	12.0	1.124 (0.11%)
Pail #70	15.32 (±0.070) %	12.0	1.121 (0.05%)
Pail #80	15.33 (±0.089) %	12.0	1.121 (0.01%)
Pail #90	15.23 (±0.040) %	12.0	1.116 (0.17%)
Pail #100	15.47 (±0.044) %	12.0	1.121 (0.38%)
Pail #110	15.40 (±0.029) %	12.0	1.118 (0.02%)
Pail #116	15.03 (±0.070) %	12.0	1.111 (0.00%)
Average	15.36 (±0.144) %	12.0	1.121 (0.38%)
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 24 °C.

Table 3-2. Results of the Qualification Sample Analyses

Property	Method	Result	Specification	Pass ?
Sr DF	Sr test	3.11 (±0.152)	>1.79	YES
Alcohol content[a]	VOA	<65.8 mg/L	≤500 mg/L max	YES
Total Inorganic Carbon	TIC	17.7 mg/L	≤100 mg/L max	YES
Total Organic Carbon	TOC	24.3 mg/L	≤300 mg/L max	YES
Total Halides (F+Cl+Br)	IC	<30 mg/L	≤100 mg/L max	YES
Particle Size, <0.8 μm[b]	Microtrac®	5.39 vol % / 4.83 vol%	<10 vol %	YES / YES
Particle Size, >37 μm[ii]	Microtrac®	0 vol % / 0 vol%	<1 vol %	YES / YES
Particle Size, geometric standard deviation (absorbance mode)[ii]	Microtrac®	3.82 / 3.28	≤3.5	NO / YES

[a] The alcohol content is derived from the TOC and VOA data. The VOA result was <1 mg/L isopropanol. Using the conservative case that all of the carbon from the TOC result was from methanol (and knowing methanol is 37.5 wt % carbon), we calculate the MeOH as 64.82 ppm. This gives a total alcohol content of <65.82 ppm.
[b] Two sub-samples of the qualification sample were submitted for particle size analysis. Results from both samples are reported.

Microtrac®, TIC-TOC, and IC results have a 10% analytical uncertainty. VOA results have a 20% analytical uncertainty. The inductively coupled plasma – emission spectroscopy (ICP-ES) results used for measuring the Sr DF have an average analytical uncertainty of 10.5%. Results in parentheses are derived from the standard deviation.

The "Particle Size, geometric standard deviation" is defined as the 50th percentile result divided by the 16th percentile result. The first sub-sample analyzed gave a result of 3.82, so a second sub-sample from the qualification sample was submitted. The results of the second sample were 3.28. The average of the two results, 3.55, is still slightly above the specification limit. The Certificate of Analysis, provided by Harrell Industries, indicates that this lot of MST has a geometric standard deviation of 2.4. With the exception of the geometric standard deviation, the other particle size results reported by Harrell are consistent with SRNL's measurements. Harrell reported 5.4 vol% less than 0.8 μm, and 0 vol% greater than 37 μm.

The bases set used to develop the criterion for geometric standard deviation is sparse, with only a few samples evaluated.[2] The value of 3.5 represented the largest value measured in the MST lots examined at that time. For a change in geometric standard deviation range of 1.9 – 3.5, the filtration rate varied on the order of 26%, but fell within the experimental variance. A larger value in geometric deviation is expected to result in slower filtration. Table 3-3 provides the particle size data for recent lots of MST from this manufacturer. The current measurements are near the maximal values for both geometric standard deviation and fraction of particles smaller than 0.8 μm. Hence, the current batch will likely show filtration performance comparable to the most recent batches of MST.

Table 3-3. Particle size variance in recent lots.

Lot # (date format)	Geometric standard deviation	vol % < 0.8 micron
07/13/11	2.35	4.81
05/25/11	1.87	6.04
05/04/11	3.48	4.98
03/03/11	2.43	4.93
01/28/11	2.23	2.47
01/06/11	2.69	5.84
12/10/10	2.36	3.79

The TIC and TOC results are in terms of mg/L of carbon. If we assume that the entire TIC result is carbonate, this translates to a carbonate concentration of ≤0.0015 M.

4.0 Conclusions

Analyses of the Harrell Lot #081811 MST material indicate the material falls within the specifications required for use at ARP, with the possible exception of the geometric standard deviation of the particle size results.

SRNL recommends performing a statistical review of the particle size data to date from this manufacturer and looking for correlation versus measured filter performance. Such an analysis may provide the bases for refining the procurement specification.

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. M. R. Poirier and D. T. Hobbs, "Development of Monosodium Titanate (MST) Purchase Specifications," WSRC-TR-2006-00039, April 2006.

Distribution:

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