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Revision 0

FILTERABILITY OF MONOSODIUM TITANATE SUPPLIED BY BLUE GRASS CHEMICAL SPECIALTIES

Michael R. Poirier
David T. Hobbs

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Summary

The design specification for monosodium titanate (MST) requires that less than 1% of the particles are larger than 35 micron and that less than 1% of the particles are smaller than 1 micron. Blue Grass Chemical Specialties produced two batches of MST for the Defense Waste Processing Facility (DWPF) that do not meet the particle size specification. The material has more than 1% of the particles smaller than 1 micron. This increase in the fraction of particles less than 1 micron could adversely affect filtration within the Actinide Removal Project (ARP).

The authors conducted dead-end filtration testing with 0.45 micron polymeric filter media, 0.5 micron Mott sintered stainless steel filter media, and 0.1 micron Mott sintered stainless steel filter media. The conclusions from this test follow.

- If a 0.5 micron Mott filter is used for the ARP process, the Blue Grass Chemical Specialties MST will filter more slowly than the Optima 00-QAB-417 MST.
- If a 0.1 micron Mott filter is used for the ARP process, there is no difference between the filterability of the Blue Grass Chemical Specialties MST and the Optima 00-QAB-417 MST.
- The reason for the differing conclusions with the different filters is that the Blue Grass MST contains more fine particles (< 0.6 micron). The fines become trapped in the pores of the 0.5 micron filter media, but not in the pores of the 0.1 micron filter.

The authors make the following recommendations for MST particle size.

- If a 0.5 micron Mott filter is used for the ARP process, the existing particle size specification (less than 1% of particles less than 1 micron and less than 1% of particles greater than 35 micron) should be maintained.
- If a 0.1 micron Mott filter is used for the ARP process and the existing particle size specification is not met, DWPF personnel should arrange for filter tests, such as those described in this report, to be performed to evaluate the filterability of the MST.
- DWPF personnel should consider revising the particle size specification, because technology improvements allow better resolution of particles less than 1 micron. The limited data collected during this testing is not sufficient to change the particle size specification. Limited additional testing similar to that performed here would provide sufficient technical bases.

Introduction

The Savannah River Site (SRS) is developing a process to treat radioactive waste that is low in cesium-137, but high in strontium-90, plutonium, uranium, and neptunium. The process is the Actinide Removal Process located in Building 512-S.

This process adds MST to high level waste supernate. The MST sorbs soluble strontium, plutonium, uranium, and neptunium. The process then filters the resulting slurry, which contains entrained metal hydroxide sludge and MST, to remove the insoluble solids. Operations next washes the concentrated solids to reduce the sodium and nitrite concentrations, and transports the slurry to the DWPF for vitrification. The filtrate flows to Z-area for disposal in a cement-based waste form.

The design specification for MST requires that less than 1 volume % of the particles are larger than 35 micron and less than 1 volume % of the particles are smaller than 1 micron. Blue Grass Chemical Specialties (New Albany, IN) produced two batches of MST that do not meet the particle size specification (see Appendix A). The material has more than 1% of the particles smaller than 1 micron. This increase in the fraction of particles less than 1 micron could adversely affect filtration within the ARP. The Blue Grass MST did meet the strontium decontamination factor specification.

The particle size data in Appendix A also shows that the Optima batch# 00-QAB-417 MST did not meet the particle size specification. That sample had 12 volume % of its particles less than 1 micron. The MST particle size specification derives in part from measurements performed with earlier Microtrac instruments that have no resolution below 1 micron. The measurements described in Appendix A came from a Microtrac S3000, which can measure particles as small as 0.34 micron. Previous measurements of this batch with a Microtrac showed ~ 2 volume % of the particles less than 1 micron. In addition, SRTC conducted a number of filtration tests with the Optima batch# 00-QAB-417 MST, with the results used to calculate throughput for the 512-S filter.[8-12] Thus, Optima MST is viewed as acceptable for Operations.

The Kozeny-Carman model provides a simple description of colloidal fouling of microfilters.[1,2] The model is described by equation [1]

$$J = (-\Delta P/L)[d_p^2\ \varepsilon^3/150\ \mu(1-\varepsilon)^2] \quad [1]$$

where J is the filter flux, ΔP is the transmembrane pressure, L is the cake thickness plus the filter thickness, d_p is the particle diameter, ε is the filter cake porosity, and μ is viscosity. According to equation [1], if all other parameters remain constant, a decrease in particle diameter will decrease the filter flux. Therefore, MST with more fines will likely produce lower filter flux than MST that meets the particle size specification.

DWPF personnel requested the authors to conduct bench-scale dead-end filtration tests with the following batches of MST to determine whether the Blue Grass MST will produce adequate filter flux:[3]

- Optima Batch# 00-QAB-417
- Blue Grass Lot# 2753
- Blue Grass Lot# 2753 reworked
- Optima batch 33180 (control used in previous MST filtration tests)[4]

The authors conducted dead-end filtration testing with 0.45 micron polymeric filter media, 0.5 micron Mott sintered stainless steel filter media, and 0.1 micron Mott sintered stainless steel filter media. The results of the dead-end filtration testing provide insight into the expected performance from cross flow filtration. They have used this approach in previous SRTC work.[5,6]

Based on the testing results, SRTC will recommend a procurement specification for acceptable MST particle size range for use with both 0.5 micron and 0.1 micron stainless steel filter media.

Testing

Table 1 shows the feed solution for these tests. SRTC personnel have used this feed recipe in previous tests to mimic the expected SRS high level waste supernate composition.[7] The feed contains 5.6 M sodium salt solution with 0.55 g/L MST added.

Table 1. Feed Composition[7]

Component	Concentration
NaOH	1.33 M
$NaNO_3$	2.60 M
$NaAl(OH)_4$	0.43 M
$NaNO_2$	0.13 M
Na_2SO_4	0.52 M
Na_2CO_3	0.026 M
MST	0.55 g/L

The authors performed the tests with a bench-scale dead-end vacuum filter, a bench-scale dead-end filter, and a stirred cell filtration unit. The dead-end vacuum filter (see Figure 1) tests were conducted as follows. Personnel placed a sample of 5.6 M Na salt solution containing MST in a carboy and stirred it with a magnetic stirrer. Personnel then poured the salt solution (~100 mL) into the top of a graduated 115 mL capacity, 0.45 μm pore-size Nalgene disposable dead-end filter (Cat. No. 245-0045) connected to a vacuum pump. They started the pump (620 mm Hg vacuum) and measured the filtrate volume as a function of time.

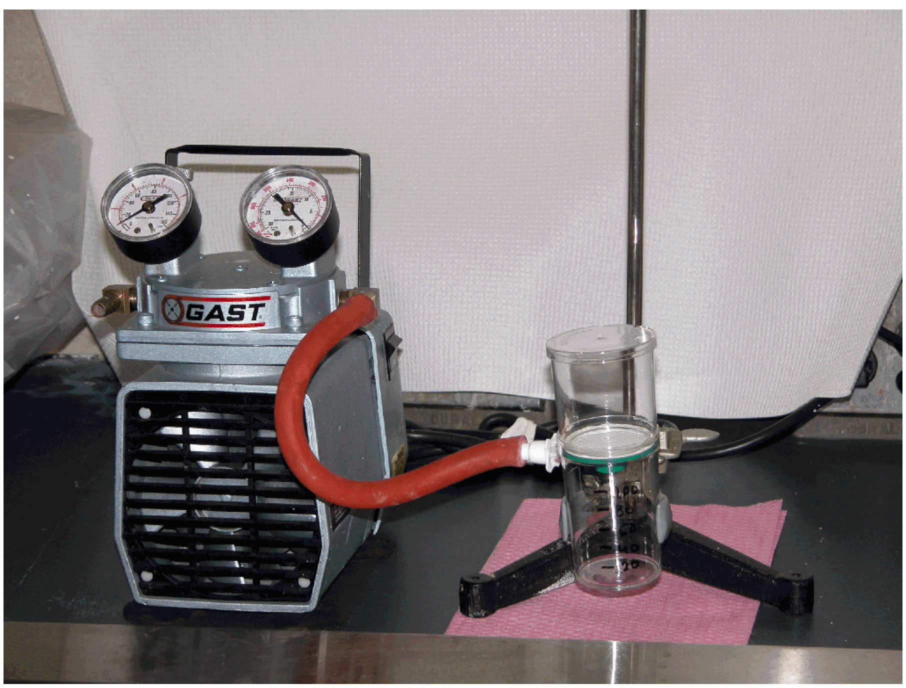

Figure 1. Dead-End Nalgene Vacuum Filter

The bench-scale dead-end filter (see Figure 2) tests were conducted as follows. Personnel placed a sample of 5.6 M Na salt solution containing MST in a carboy and stirred it with a magnetic stirrer. Personnel then poured the salt solution (~100 mL) into the filter unit connected to a vacuum pump. They started the pump (620 mm Hg vacuum) and measured the filtrate volume as a function of time. The media for these tests was 0.5 micron Mott sintered stainless steel filters.

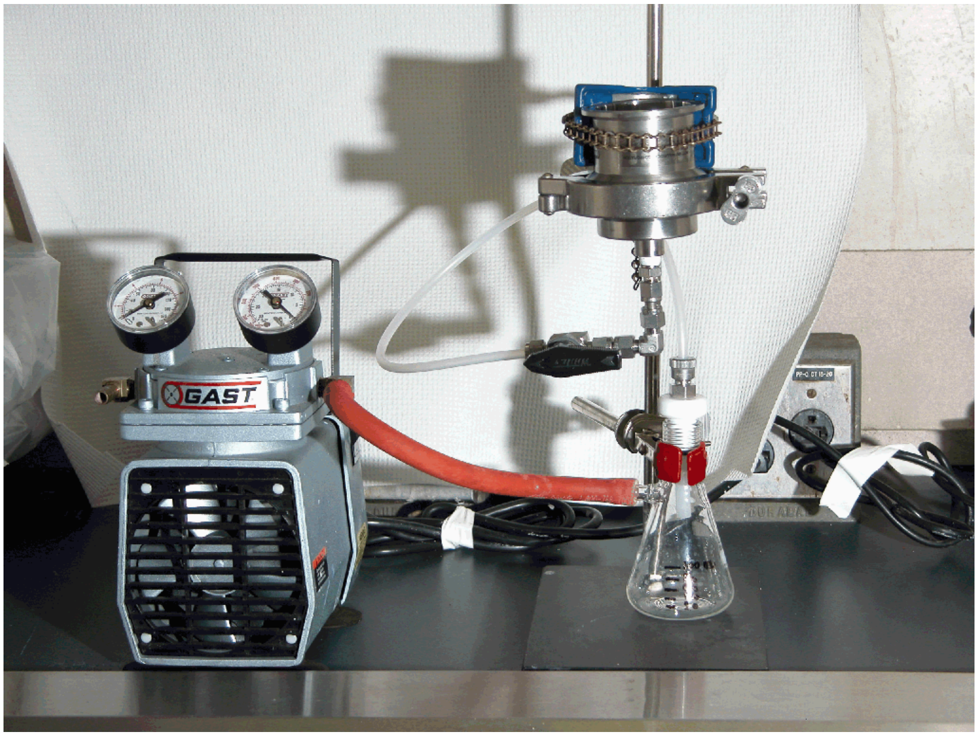

Figure 2. Dead-End Mott Filter

The stirred cell (see Figure 3) tests were conducted as follows. Personnel placed a sample of 5.6 M Na salt solution containing MST in a carboy and stirred it with a magnetic stirrer. Personnel then poured the salt solution (~60 mL) into the stirred cell. They agitated the cell contents, pressurized the cell (~ 30 psi), and measured the filtrate volume as a function of time. The media for these tests was 0.1 micron Mott sintered stainless steel filters.

Table 2 shows results from previous filter tests, which filtered feed slurries with 0.45 micron Nalgene dead-end vacuum filters and with a 0.5 micron Mott crossflow filter.[5,6] The results show the dead-end filter fluxes correlate well with crossflow filter fluxes, and the dead-end filter serves as a useful screening tool to evaluate the impact of changes in feed composition on crossflow filter flux.

Figure 3. Stirred Cell Filter Unit

Table 2. Comparison of Dead-End Filter Results with Crossflow Filter Results[5,6]

Feed	Relative Filtration Rate Dead-End Filter	Relative Filtration Rate Crossflow Filter
Baseline (6.4 M Na, 0.6 g/L sludge, 0.55 g/L MST)	1.0	1.0
Baseline + Bentonite	1.0	0.9
Baseline + SRTC1*	0.7	0.9
Baseline + SRTC2*	1.5	1.4
KTPB* (4 wt.%)	3.2	2.8
KTPB* (10 wt.%)	1.3	1.3

* SRTC1 and SRTC2 are proprietary flocculating agents. KTPB is potassium tetraphenylborate

Results

Figures 4 – 6 and Table 3 show the test results. The different colors represent repeat measurements. The filtrate rate was approximately the same in all tests with the 0.45 micron Nalgene filters. Statistical analyses performed showed no correlation between MST source and filtrate rate (see Appendix B).

The filtrate rate was approximately the same in all tests with the 0.1 micron Mott filters. Statistical analyses performed showed no correlation between MST source and filtrate rate (see Appendix B).

In all tests with the 0.5 micron Mott filters, statistical analyses performed showed a correlation between MST source and filtrate rate (see Appendix B). The Blue Grass MST filtered more slowly than the Optima 00-QAB-417 MST, but filtered at approximately the same rate as the Optima 33180 MST.

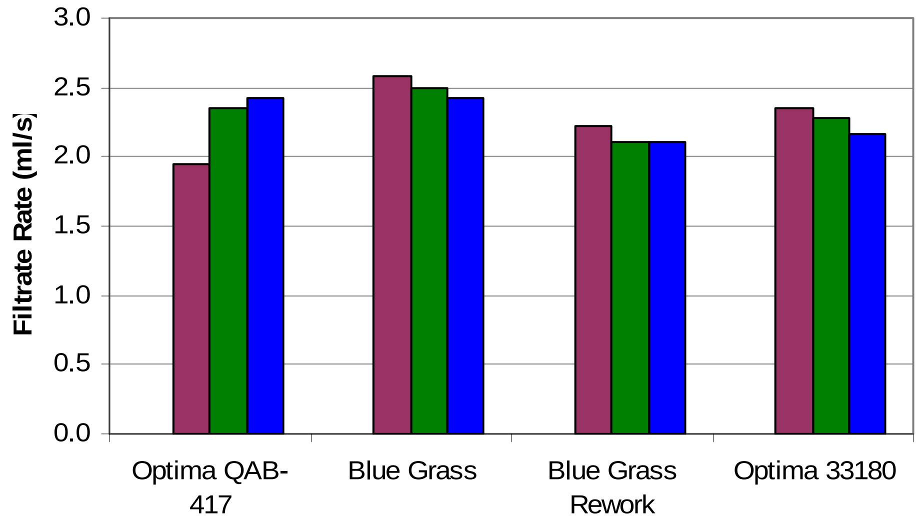

Figure 4. 0.45 Micron Nalgene Filter Test Results

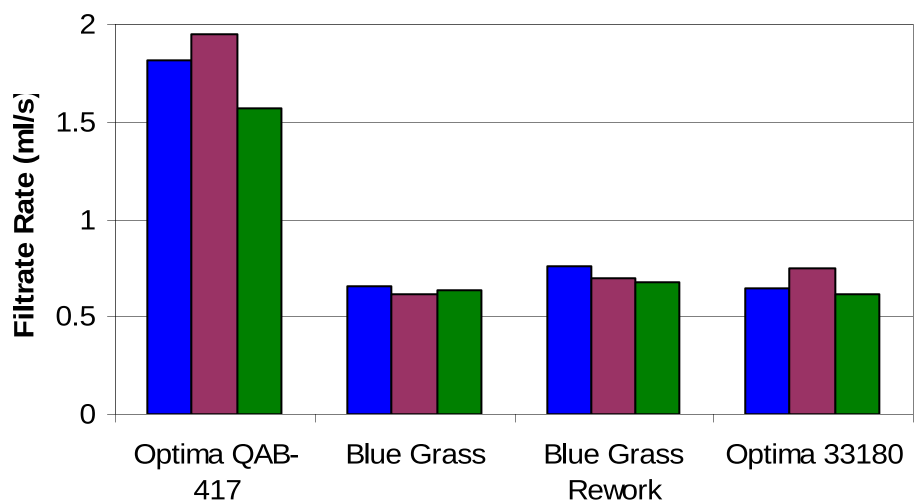

Figure 5. 0.5 Micron Mott Filter Test Results

The results appear to give conflicting conclusions. With the 0.45 micron Nalgene filters and the 0.1 micron Mott filters, no difference was observed in the filtration rates with the Optima and Blue Grass MST. With the 0.5 micron Mott filters, a significant difference was observed in the filtration rates with the Optima and Blue Grass MST.

The reason for the difference is the Blue Grass MST contains more fines than the Optima MST. The Optima 00-QAB-417 sample had 0.18 volume % of its particles less 0.5 micron, 0.80 volume % less than 0.6 micron, and 2.2 volume % less than 0.7 micron. The original Blue Grass MST had 0.51 volume % of its particles less 0.5 micron, 1.2 volume % less than 0.6 micron, and

2.3 volume % less than 0.7 micron. The reworked Blue Grass MST had 0.34 volume % of its particles less 0.5 micron, 2.2 volume % less than 0.6 micron, and 6.1 volume % less than 0.7 micron. The Blue Grass MST samples contain a larger fraction of particles less than 0.5 micron and 0.6 micron than the Optima 00-QAB-417 sample. The fine particles become trapped in the pores of the 0.5 micron filter, but not in the pores of the 0.1 micron filter.

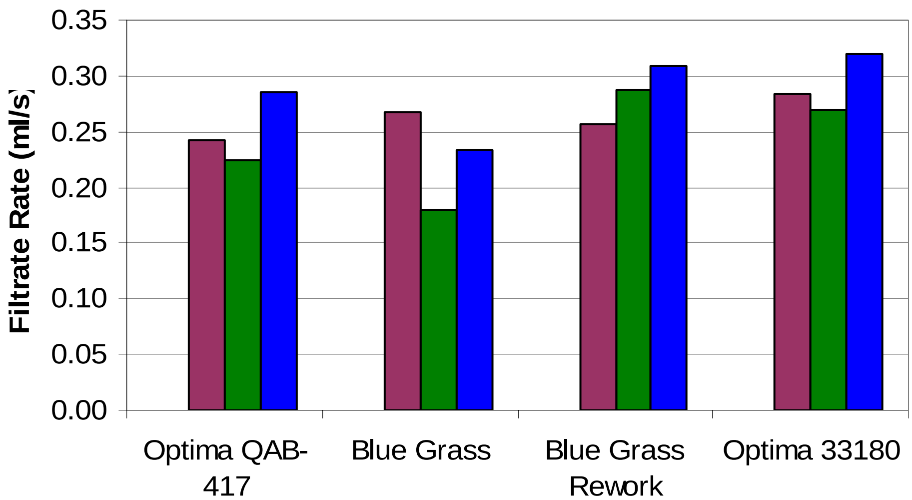

Figure 6. 0.1 Micron Mott Filter Test Results

Table 3. Filtration Test Results

Nalgene Filter	Optima QAB-417	Blue Grass	Blue Grass Rework	Optima 33180
Avg. Filtrate Rate (ml/s)	2.24	2.50	2.15	2.27
Standard Deviation (%)	11%	3%	3%	4%
0.5 Micron Mott	Optima QAB-417	Blue Grass	Blue Grass Rework	Optima 33180
Avg. Filtrate Rate (ml/s)	1.78	0.64	0.71	0.67
Standard Deviation (%)	11%	3%	6%	10%
0.1 Micron Mott	Optima QAB-417	Blue Grass	Blue Grass Rework	Optima 33180
Avg. Filtrate Rate (ml/s)	0.25	0.23	0.28	0.29
Standard Deviation (%)	13%	19%	9%	9%

The Optima 33180 sample has the same fraction of fines (< 1 μ, < 0.7 μ, 0.6 μ, 0.5 μ) as the Optima 00-QAB-417 MST, but performs similarly to the Blue Grass MST with the 0.5 μ filter. The 33180 sample has more particle size variability and a stronger bimodal distribution than the 00-QAB-417 sample. This difference could produce a cake with lower permeability than the 00-QAB-417 sample, but one would expect to observe this effect with all of the filters tests. We are uncertain of the reason the 33180 filtered more slowly that the 00-QAB-417 sample, and this result remains an open issue.

Conclusions

The conclusions from this test follow.

- If a 0.5 micron Mott filter is used for the ARP process, the Blue Grass Chemical Specialties MST will filter more slowly than the Optima 00-QAB-417 MST.
- If a 0.1 micron Mott filter is used for the ARP process, there is no difference between the filterability of the Blue Grass Chemical Specialties MST and the Optima 00-QAB-417 MST.
- The reason for the differing conclusions with the different filters is that the Blue Grass MST contains more fine particles (< 0.6 micron). The fines become trapped in the pores of the 0.5 micron filter media, but not in the pores of the 0.1 micron filter.

References

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Appendix A
MST Decontamination Factor and Particle Size

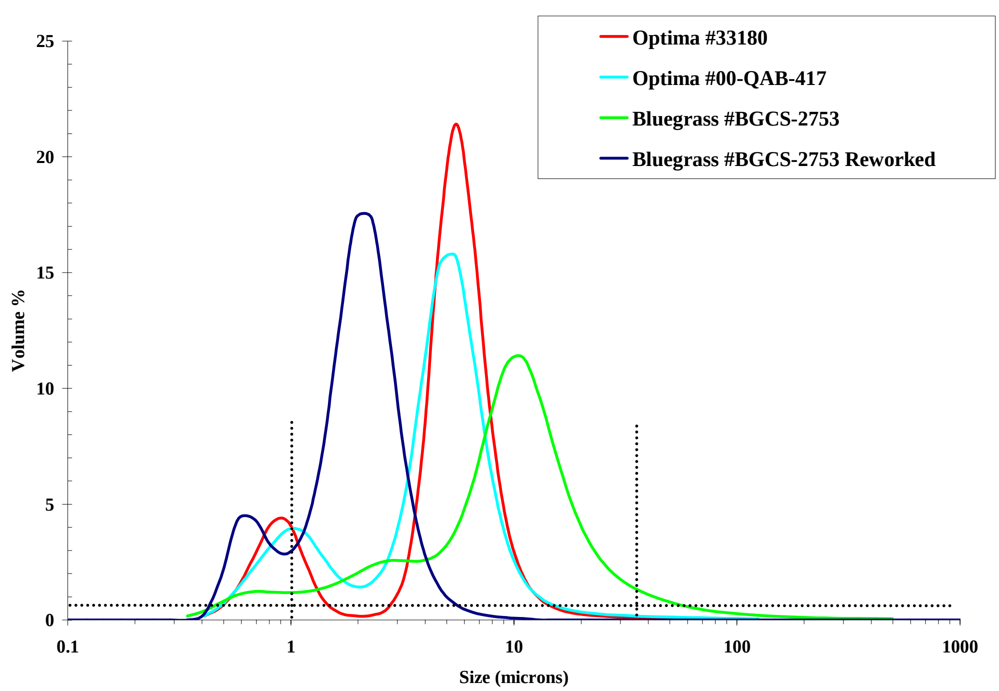
Table A.1 Characterization of MST Samples[13,14]

Sample ID	**Optima #33180**	**Optima #00-QAB-417**	**Bluegrass Original**	**Bluegrass Reworked**
Sr DF[a]	212 (31)	186 (2.8)	236 (25)	nd
Particle Size[b]: < 1 um	13 (0.028)	12 (0.071)	6.1 (0.049)	16 (1.0)
Particle Size[b]: > 35.5 um	0.46 (0.16)	0.84 (0.085	3.5 (0.89)	0
Particle Size[b]: < 0.5 um	0.17	0.18	0.51	0.34
Particle Size[b]: < 0.6 um	0.73	0.80	1.22	2.16
Particle Size[b]: < 0.7 um	2.15	2.22	2.28	6.06

[a] DF = decontamination factor = Initial Solution Concentration/Final Solution Concentration numbers in parenthesis are single standard deviation of duplicate sample results.
nd = not determined
[b] measured in deionized distilled water using Microtrac™ analyzer Model #S3000. Units are vol. %.

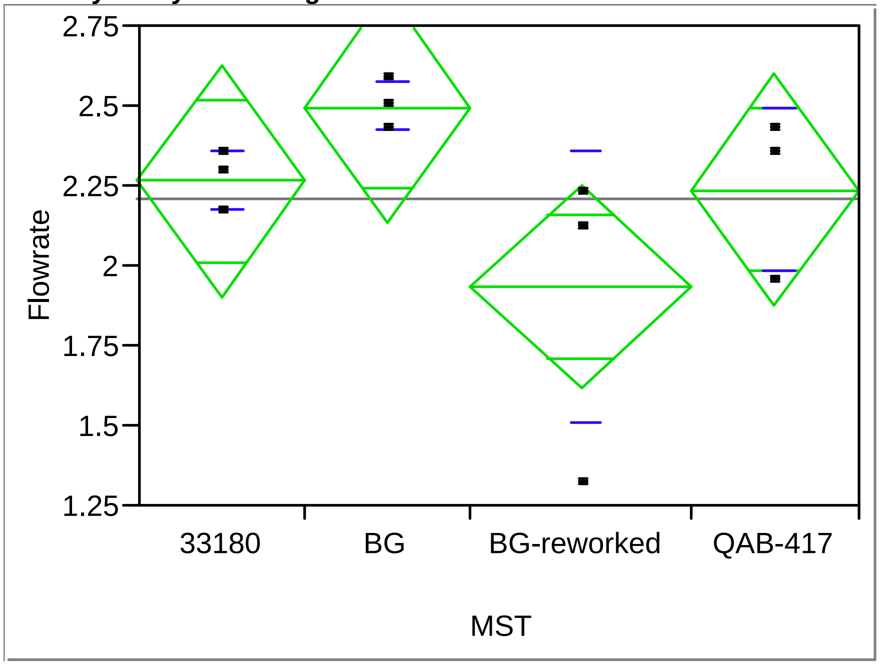
Figure A.1 provides plots of the volume % versus particle size for the Optima and Bluegrass samples reported in Table A.1. For clarity the graph shows only one of the two measurements performed using a Microtrac™ Model #S3000 unit.

Figure A.1 Particle Size of MST Samples



Appendix B
Statistics

Oneway Analysis of Nalgene Filter Data



Oneway Anova

Summary of Fit

Rsquare	0.447482
Adj Rsquare	0.26331
Root Mean Square Error	0.277557
Mean of Response	2.213077
Observations (or Sum Wgts)	13

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
MST	3	0.5615353	0.187178	2.4297	0.1323
Error	9	0.6933417	0.077038		
C. Total	12	1.2548769			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
33180	3	2.26667	0.16025	1.9042	2.6292
BG	3	2.50000	0.16025	2.1375	2.8625
BG-reworked	4	1.93750	0.13878	1.6236	2.2514
QAB-417	3	2.24000	0.16025	1.8775	2.6025

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

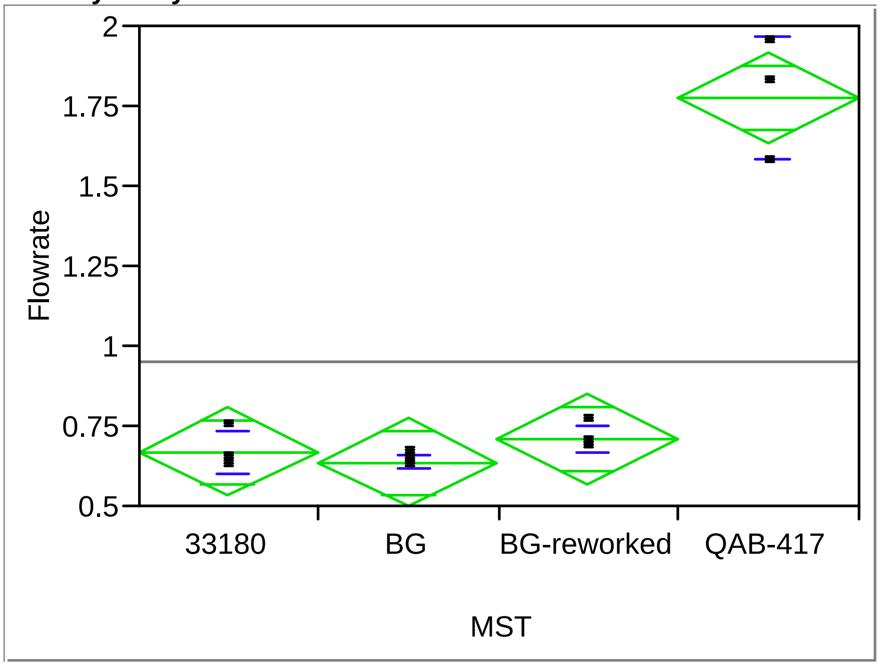
Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
33180	3	0.0971253	0.0711111	0.0833333
BG	3	0.0800000	0.0533333	0.0800000
BG-reworked	4	0.4215349	0.3137500	0.2275000
QAB-417	3	0.2535744	0.1933333	0.1800000

Test	F Ratio	DFNum	DFDen	Prob>F
O'Brien[.5]	0.7712	3	9	0.5386
Brown-Forsythe	0.3153	3	9	0.8141
Levene	2.8298	3	9	0.0988
Bartlett	1.9670	3	.	0.1165

Warning: Small sample sizes. Use Caution.
Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob>F
4.1922	3	4.7046	0.0839

Oneway Analysis of 0.5 Micron Mott Filter Data



Oneway Anova

Summary of Fit

Rsquare	0.968976
Adj Rsquare	0.957341
Root Mean Square Error	0.10496
Mean of Response	0.951667
Observations (or Sum Wgts)	12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
MST	3	2.7526333	0.917544	83.2869	<.0001
Error	8	0.0881333	0.011017		
C. Total	11	2.8407667			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
33180	3	0.67333	0.06060	0.5336	0.8131
BG	3	0.64000	0.06060	0.5003	0.7797
BG-reworked	3	0.71333	0.06060	0.5736	0.8531
QAB-417	3	1.78000	0.06060	1.6403	1.9197

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

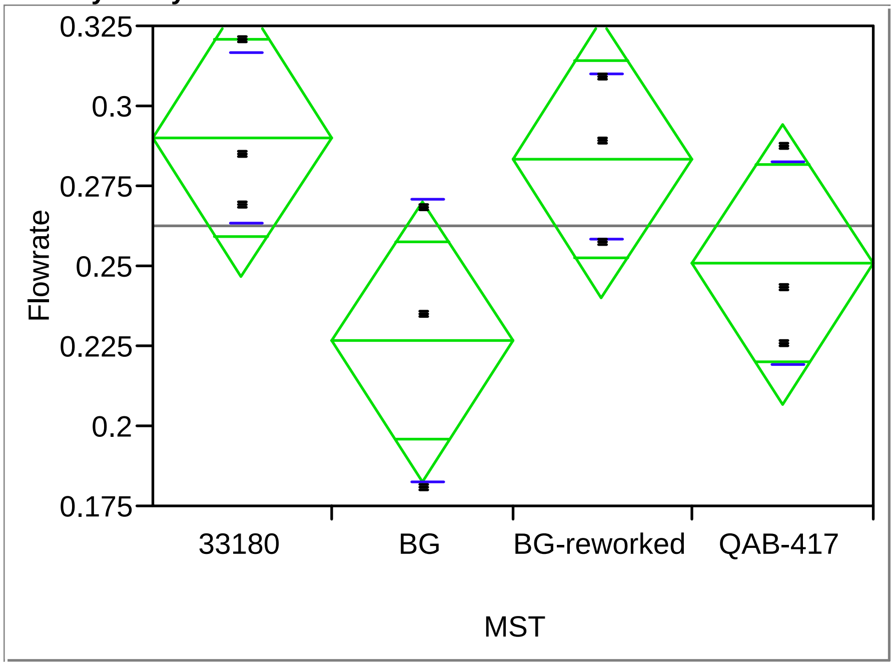
Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
33180	3	0.0680686	0.0511111	0.0533333
BG	3	0.0200000	0.0133333	0.0200000
BG-reworked	3	0.0416333	0.0311111	0.0333333
QAB-417	3	0.1931321	0.1400000	0.1700000

Test	F Ratio	DFNum	DFDen	Prob>F
O'Brien[.5]	1.5577	3	8	0.2736
Brown-Forsythe	8.1069	3	8	0.0083
Levene	4.2024	3	8	0.0464
Bartlett	2.6547	3	.	0.0468

Warning: Small sample sizes. Use Caution.
Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob>F
26.9162	3	3.8437	0.0048

Oneway Analysis of 0.1 Micron Mott Filter Data



Oneway Anova

Summary of Fit

Rsquare	0.479013
Adj Rsquare	0.283643
Root Mean Square Error	0.032853
Mean of Response	0.263167
Observations (or Sum Wgts)	12

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
MST	3	0.00793900	0.002646	2.4518	0.1381
Error	8	0.00863467	0.001079		
C. Total	11	0.01657367			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
33180	3	0.290667	0.01897	0.24693	0.33441
BG	3	0.227000	0.01897	0.18326	0.27074
BG-reworked	3	0.284000	0.01897	0.24026	0.32774
QAB-417	3	0.251000	0.01897	0.20726	0.29474

Std Error uses a pooled estimate of error variance

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
33180	3	0.0266333	0.0195556	0.0226667
BG	3	0.0439204	0.0313333	0.0400000
BG-reworked	3	0.0262298	0.0186667	0.0240000
QAB-417	3	0.0314802	0.0233333	0.0260000

Test	F Ratio	DFNum	DFDen	Prob>F
O'Brien[.5]	0.4256	3	8	0.7401
Brown-Forsythe	1.3466	3	8	0.3263
Levene	0.4293	3	8	0.7376
Bartlett	0.2068	3	.	0.8918

Warning: Small sample sizes. Use Caution.

Welch Anova testing Means Equal, allowing Std Devs Not Equal

F Ratio	DFNum	DFDen	Prob>F
1.6835	3	4.3871	0.2973