U.S. Army Hand Held Extinguisher Environmentally Acceptable Replacement Agent Development

Dr. J. Douglas Mather - CGI Federal (Stanley Associates, Inc.)
Timothy Helton - U.S. Army Aviation and Missile Command (AMCOM) G-4
Kevin Dowell and Leonard Lombardo – Aberdeen Proving Ground – Aberdeen Test Center
Alivio Mangieri - AGSE PM Technical Branch - Redstone Arsenal

Synopsis

United States (U.S.) Army Program Executive Office (PEO) Aviation sought a replacement for the 2.75 pound Halon Handheld Fire Extinguisher (HHFE) (National Stock Number-NSN: 6830-00-555-8837) currently mounted in/on legacy rotary wing weapon systems. The U.S. Army Aviation Ground Support Equipment (AGSE) Product Manager Office (PMO) was tasked with finding a non-ozone depleting substance (ODS) and environmentally friendly fire suppression agent to replace the 2.75lb. Halon 1301 HHFE for Army rotary wing aircraft. The existing Halon 1301 extinguisher specification (MIL-E-52031D) did not indicate the "B" firefighting performance required and the extinguisher was unrated necessitating baseline performance characterization as an initial project goal. Baseline testing employed Underwriters Laboratories (UL) 711 as did all project related agent fire suppression performance testing. Overall, the HHFE agent development program ran from the summer of 2008 through the fall of 2012. Initially, agent development resulted in optimized agent/hardware configurations for three of the four fluorocarbon candidate agents under test. Subsequent development work provided two blended agents based on nano and ultra-fine sodium bicarbonate (SBC) powders blended with HFC-227ea and the development of a new nozzle design for use with the SBC based blended agents.

The initial agent development work focused on testing of four commercially available clean fluorocarbon agents. Development testing included the following phases: an initial round of fire suppression optimization (testing involving varied extinguisher configurations and nozzles to establish a baseline performance on each commercial candidate), a second round of optimization sought to further improve fire suppression performance through additional changes to nozzles, pressurization, pressurization gas, discharge horn, and extinguisher fill as well as perform initial testing of operational temperature range fire suppression performance. A final characterization check of each optimized agent was performed, this included the following: spray pattern and agent discharge distance characterization, operational temperature range performance verification, storage temperature pressure and leakage checks and final fire suppression performance characterization. A down-selection based on these performance objectives and the maximum safe allowable fire suppressant agent air concentrations for the crew occupied space in the smallest aviation weapons platform resulted in the recommendation of only one of the four fluorocarbon agents for consideration as a replacement for Halon 1301.

As fire suppression performance of the optimized agent selected lagged performance of the current Halon 1301 configuration, a limited series of fire suppression tests utilizing SBC blends was performed with promising results. Subsequent acquisition and development testing of nano- and ultra-fine powders of SBC demonstrated dramatic fire suppression performance enhancement using this strategy.

Extensive testing of available SBC powders from commercial processes occurred but proved unsatisfactory for the HHFE application. The potential to generate nano and ultra-fine SBC powders were investigated and SBC powders were sourced from a commercial vendor and a supplier of research quantities of nano-powders. Both of these powders dramatically improved fire suppression performance of the selected fluorocarbon agent and demonstrated promise of performing as needed in the HHFE application.

New proprietary and non-proprietary processing methods for generation of nanoparticle powders of SBC were identified. Strategies for prevention/reduction of SBC caking, the characterization of the SBC particle sizes, optimizing SBC suspendability in HFC-227ea and maximizing agent fire suppression performance were pursued. The project developed SBC characterization methods (field emission scanning electron microscopy, SBC surface area characterization, particle size distribution characterization, and SBC powder water content). A procurement specification for the process specific types of SBC used in the agent blends was also developed.

The final phase of the blended SBC/fluorocarbon agent development work included extensive testing of alternate sodium bicarbonate processing methods to provide alternative sourcing and potentially identify superior powder processing methods. Processes were sought that yielded the smallest SBC particle sizes, high suspendability SBC powders (in fluorocarbons), minimal required SBC loading in the fluorocarbon, and minimal SBC water content). Testing of long term aging and temperature effects on the SBC/fluorocarbon blend as well as materials compatibility testing were performed with satisfactory results on SBC's from two different sources. The characterization information for these two SBC's was assembled into a now published procurement specification covering both nano and the ultra-fine SBC powders and the blended agents based on these two powders.

The published agent specification is MIL-DTL- 32412 DETAIL SPECIFICATION, "HFC-227ea FIRE EXTINGUISHING AGENT ENHANCED WITH SPECIAL SODIUM BICARBONATE POWDER (HFC-227ea/SBC_S). MIL-DTL-32412 is available for use by all Departments and Agencies of the Department of Defense. This specification established the requirements and verification methods for two HFC-227ea/SBC_S Fire Extinguishing agents based on different SBC powders requiring different weight percent's when mixed with the HFC-227ea. These two Agents when used in the new HHFE hardware, also developed at the direction AGSE PMO, performed equivalently in fire suppression applications compared to the Halon 1301 configuration.

The two Agents are free-flowing slurries of specialized sodium bicarbonate powder (SBC_S) suspended in HFC-227ea that will be used in the non-ODS HHFE. The specialized sodium bicarbonate (SBC_S) powders are designated as SBC-1 and SBC-2.

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Replacement Agent Development

This report covers chronologically the development of the replacement agents. Detailed descriptions will be included where possible and appropriate. Readers needing additional information are urged to contact the authors. An extensive Appendices accompanies this report. The Appendices provide method information for the following SBC and Agent characterization topical areas including: analysis of SBC water content; SBC surface area characterization; sourcing information for the nano-particulate SBC; Agent flow and caking checks; and Jet-Milling procedures for the generation of ultra-fine SBC. No proprietary information or business confidential information is contained in this report.

The authors and the U.S. Army gratefully acknowledge the technical assistance, testing support and fluorocarbon agent and/or SBC powders provided by several suppliers (DuPont, 3M, American Pacific Corporation, Quickfire USA).

The initial project goals were to develop an extinguisher with:

1. Equivalence in form, fit and function to the existing Halon 1301 HHFE. New HHFE was required to be a “Drop In Replacement” i.e., fit in the same space on the rotary wing aircraft with no changes to mounting bracket. No allowance for a larger cylinder size.
2. The replacement HHFE agent combination would meet or exceed the firefighting performance of the existing halon 1301 extinguisher.
3. The agent employed in the replacement HHFE is required to be commercially available, and be environmentally acceptable.

The candidate environmentally acceptable clean agents selected for this developmental effort are all non-brominated, commercially available fluorocarbon fire extinguishants and, other than Halotron-I, are non-chemically active fire suppressants.

Baseline fire suppression testing of the current halon 1301 based extinguisher

Beginning in August 2008 and continuing through February 2009, Aberdeen Test Center (ATC) tested the current halon 1301 HHFE to establish a baseline for its performance by determining its upper limit of performance against both JP-8 and n-heptane fuels. (Note: Limited baseline testing was also performed at Tyndall AFB during the summer of 2008). The rationale for use of both JP-8 and n-heptane fuels in this development is to verify that the extinguisher will handle fire threats that are unique to military aviation weapon systems.

The baseline performance testing was required to facilitate the development and the selection of the replacement extinguisher/agent configurations by providing a qualitative and quantitative reference to gauge each candidate extinguisher/agent’s performance with respect to the existing extinguisher. The baseline testing methods were based on UL-711 and employed pans of intermediate sizes (5, 7.5, 10 and 12.5 square feet, Table 1). Fire extinguishment testing and optimization of all candidate agents were also based on UL-711. Use of the two intermediate sized pans, 7.5 ft^2 and 10 ft^2, along with the UL standard test pans (5 ft^2 and 12.5 ft^2) enabled better assessment of the performance limits of the extinguishing agent/hardware configurations under test and identification and selection of optimal extinguisher modifications.

Table 1. Pan Fire Configurations For All Extinguishment Testing

Pan Size, (ft^2)	**Internal Pan Dimensions (inches)**					**Fuel Depth and Water Depth****
	Length		Width		Depth	
5	26.8	by	26.8	by	10 to 12	2 in. fuel over 2 to 4 in. of water
7.5	32.9	by	32.9	by	10 to 12	2 in. fuel over 2 to 4 in. of water
10	37.9	by	37.9	by	10 to 12	2 in. fuel over 2 to 4 in. of water
12.5	42.4	by	42.4	by	10 to 12	2 in. fuel over 2 to 4 in. of water
15	46.5	by	46.5	by	10 to 12	2 in. fuel over 2 to 4 in. of water

**A custom-size pan used for static fire testing (no fire fighter) during the initial stage of the development work.

UL 711 requires the use of n-heptane for liquid fuel fire tests. However, for experimental reasons and as indicated earlier the HHFE's expected principle use on JP-8 fueled fires, testing was conducted primarily using JP-8-based fires with n-heptane fires performed for comparison on a limited basis. The fire suppression results of the baseline testing of the current 2.75 pound Halon Handheld Fire Extinguisher (HHFE) (NSN: 6830-00-555-8837) are presented Tables 2 and 3.

A single professional fire fighter performed all pan fire tests. Baseline testing predominantly occurred at the Aberdeen Test Center (ATC) in Aberdeen, Md. Limited baseline testing was also performed at United States Air Force fire suppression test facilities located at Tyndall AFB.

Experimental Phase I - optimization of four clean agent candidates and downselect.

Replacement agent development and testing were subsequently initiated at ATC, under the direction of AGSE PMO support personnel. Four commercially available environmentally acceptable clean agents, C6-Fluroketone (3M NOVEC 1230), HFC-236fa (DuPont FE-36), HFC-227ea (DuPont/Great Lakes FM 200), and HCFC Blend B (AMPAC Halotron I) were selected for testing and optimization. HHFE hardware configuration was based on the current halon 1301 extinguisher’s cylinder volume. Modified valve assemblies were employed.

Optimization approach.

As no earlier testing of the four candidate agents had occurred by Army Aviation, the optimization effort was divided into two phases.

Phase I testing provided an initial opportunity to perform a limited evaluation of each agent focused on its extinguishment performance; agent spray characteristics (throw, discharge pattern); pressure effects on spray characteristics, discharge time and fire suppression performance. In the first phase all of the four agents were tested under similar conditions of fill and pressurization in order to obtain comparative performance information and identify any agent specific issues. Agent testing was performed in order of agent ascending boiling points in order to facilitate recognition of the effects on spray and allow time to develop strategies to improve poorly performing agents.

Phase II concentrated on agent pressurization, nozzle and horn refinement, plumbing and agent flow corrections, discharge times were set to 8 to 9 seconds, high and low temperature operational extinguishment performance checks occurred, final pan-fire extinguishment performance on JP-8 and n-heptane was determined, spray discharges were characterized using the Planar laser-induced illumination test fixture and a final data package created for presentation to program management.

Test methods for evaluation of fire suppression performance were supplemented with a laser-induced illumination based characterization of agent discharged spray patterns. Specialized equipment for characterizing extinguisher internal pressure and extinguisher pressure differentials during discharge was developed. Methods for documenting agent throw distance on discharge, SBC/fluorocarbon agent residue post-discharge, video documentation of all pan-fire testing, and water sensitive materials handling were developed.

As with the earlier baseline testing effort, a single professional fire fighter performed all pan-fire tests. For each new agent/hardware configuration, the fire fighter was allowed a sufficient number of practice attempts to become acclimated with the extinguisher/agent under test as well as the pan fire size and fuel. Allowing the fire fighter to become familiar with the extinguisher’s suppression characteristics greatly aided in assessing the agent/hardware combinations maximum performance potential.

The selected extinguishing agents differ greatly in physical properties making it essential that the extinguisher itself be tailored to the agent to optimize fire extinguishing performance. The boiling point of the lowest and highest agent candidates are 2.3 °F (-16 °C) for HFC-227ea and 120 °F (49 °C) for Novec 1230. As a direct result, optimization testing of extinguishing agent/extinguisher cylinder combinations required a systematic approach involving testing of alternative nozzles, a range of cylinder pressures, improvements to agent flow path (dip-tube and valve assembly), and other design changes to improve agent spray dispersion. Hardware components used included parts (with slight modifications) used to manufacture similar extinguisher configurations (for example, NSN 4210-01-519-0942) with special spray nozzle designs.

Each alternative agent required development of spray characteristics and agent delivery rates to optimize fire-suppression performance within the targeted discharge time window for the extinguisher. Commercial as well as experimental extinguisher nozzles, designed and manufactured at ATC, were tested. A wide range of extinguisher pressures and pressurization gases were evaluated to assess potential for improving the performance of higher boiling candidate agents. Development work included characterization of agent flow rates and cylinder pressure drops during discharge. Variations in extinguisher fill-ratio (liquid volume to total extinguisher volume) and decreased discharge times (8 to 10 seconds) were necessitated to allow greater weights of agent to be discharged per second. The liquid volume of 2.75 lbs. of Halon 1301 is approximately 800cc leaving a headspace of 500cc in the developmental extinguisher cylinder. The optimization approach employed alternative agent volumes of 1000cc to maximize performance. Modifications to the extinguisher dip-tube (syphon tube) were evaluated, and hardware valve and swing arm flow restrictions were eliminated. Extinguishers performance characteristics for spray throw-distance, spray angle, cylinder discharge time, and discharged agent dispersion (droplet size) were documented. Fire-suppression tests were done under indoor controlled conditions eliminating environmental effects, allowing greater optimization of fire-fighter technique, improved test repeatability, and a better location for photographic documentation of all testing.

In addition to the use of intermediate pan sizes in fire tests, several experimental fixtures were designed, assembled and employed as aids in characterizing test extinguishers.

- Extinguisher filling station and dedicated pumping equipment for each agent. Figure 1,
- Static discharge test stand for use in evaluating spray effects on pan-fires, Figure 2
- Laser illuminated spray characterization fixture and high speed photographic support
- Pressure transducers and dedicated data collection capability


Figure 1. The extinguisher filling station employed in this testing.

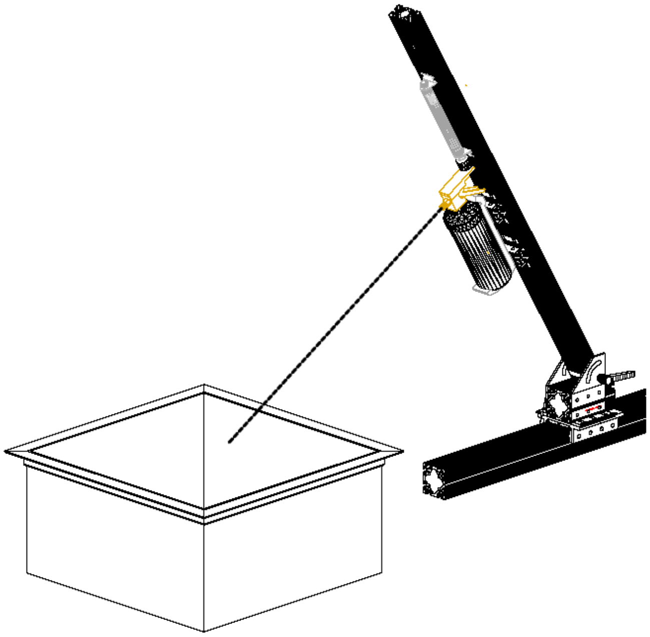


Figure 2. Static discharge test fixture.

Required test fixture set-up and evaluation was performed in early 2009 and limited experimental characterization information obtained from experimental extinguisher discharges. The test fixture provides a laser based planar illumination of spray patterns and throw ranges and employs three green lasers each emitting an individual plane of laser light overlapped to cover the full extent of the spray discharge. In the final test configuration the three lasers were positioned above the spray and on the centerline of the experimental extinguisher's discharge direction. Still (see figures 3 and 4) and video photography methods were developed that allowed capture of still images at a rate of 2 per second as well as continuous video.

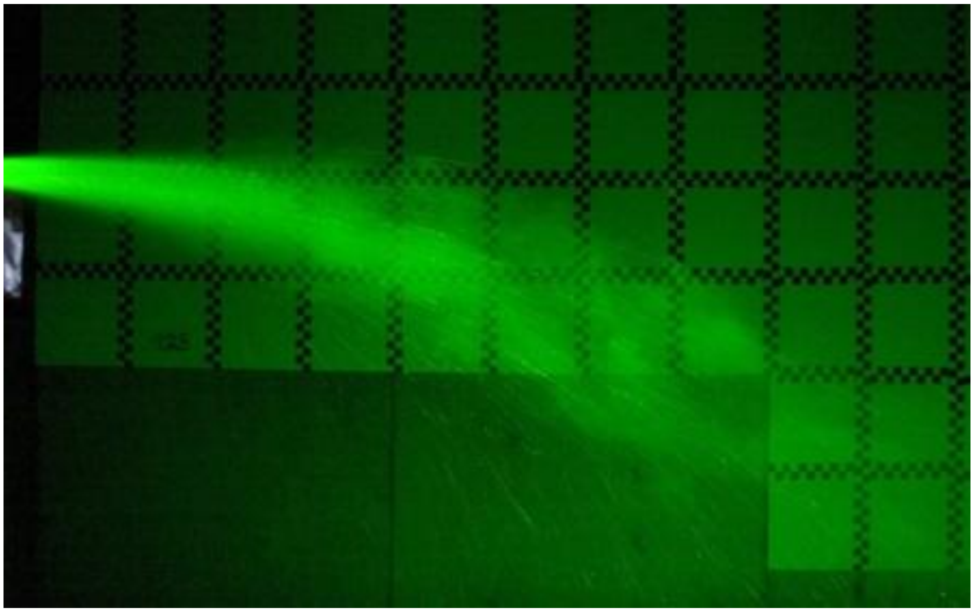


Figure 3. Spray pattern with visible droplets.

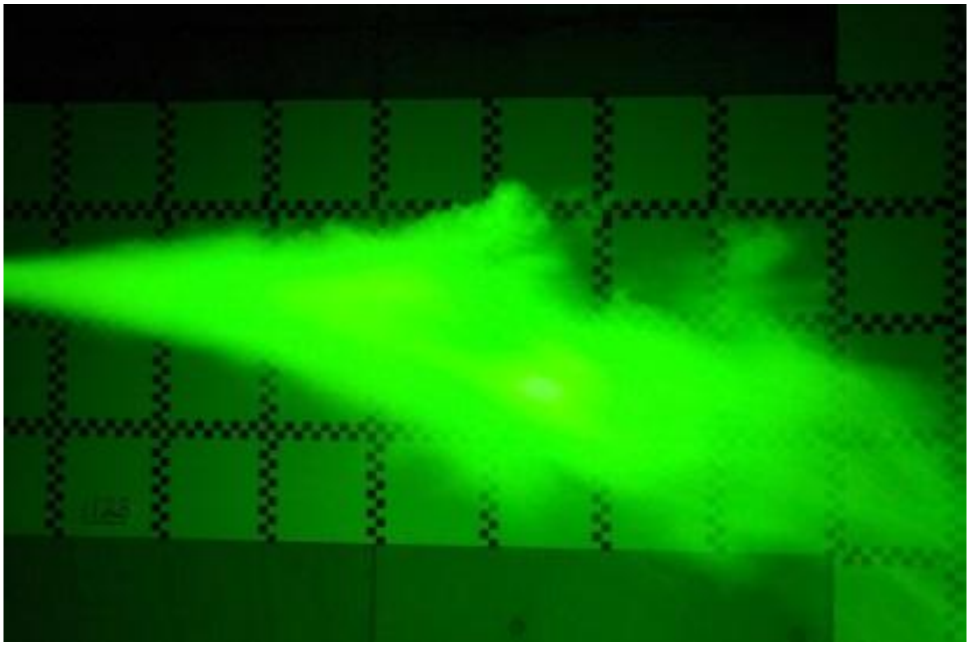


Figure 4. Spray variability.

Extinguisher pressure change data was captured electronically (Chart 1) and proved useful in characterizing extinguisher discharge flow, detecting conditions that may lead to two phase flow conditions and the selection of spray nozzles for test trials. This information initiated efforts to identify methods of moderating early high flow rates.

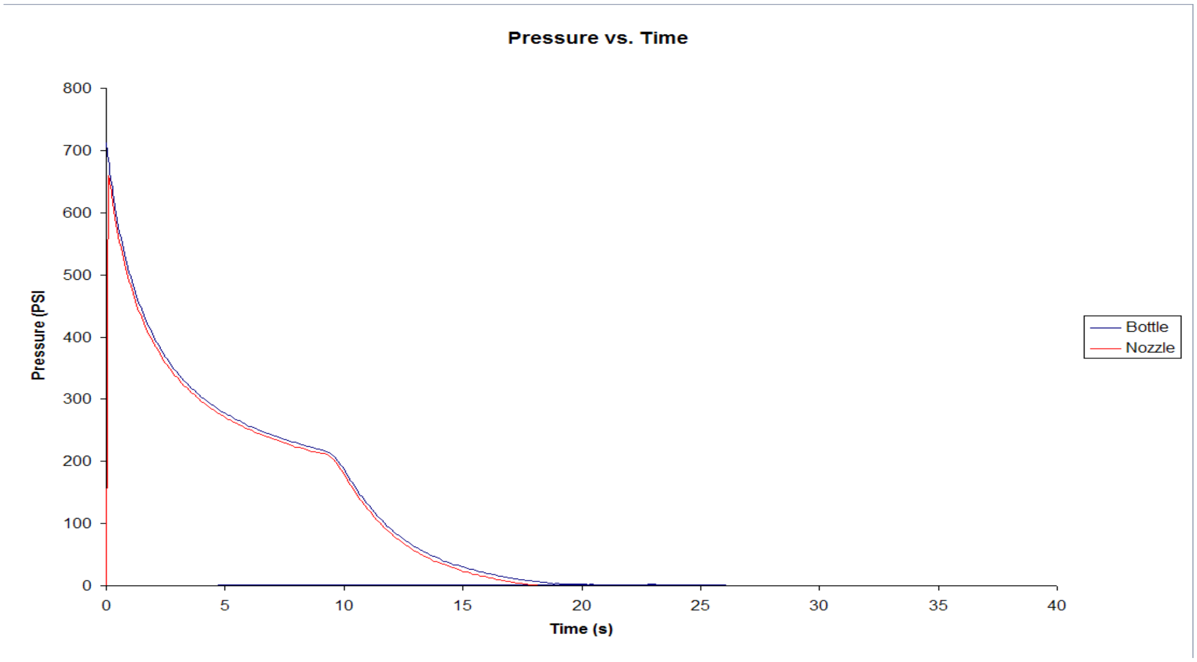


Chart 1. Extinguisher cylinder pressure and nozzle pressure during discharge.

Earlier gas solubility evaluations indicated that the pressurization gas contributes to a pressure "recharge effect" during extinguisher discharge. Pressure recharge helps to maintain a more consistent agent flow rate (Chart 2).

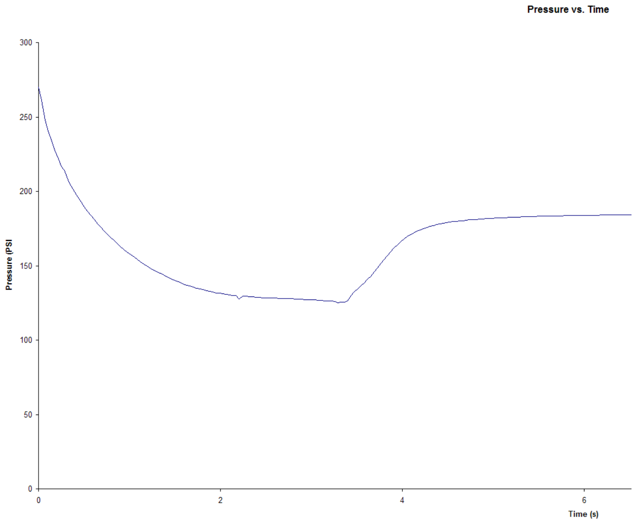


Chart 2. Cylinder pressure during discharge. Discharge stopped at 3.7 sec. observed pressure increase due to dissolved gas coming out of solution.

Pressure studies for all agents were initiated to determine the limitations on extinguisher agent fill ratios and initial cylinder pressurization imposed by high environmental temperatures (185 ºF). Testing was complicated by valve body leakage and occasional failure of burst disks at higher pressures. The pressure limitations of the extinguisher cylinder also prevented data collection at high storage temperatures so this testing was repeated using a higher pressure larger cylinder and alternate filling and pressure monitoring fittings.

Testing of candidate agents included cold operational (-40 ºF) temperature extinguishment performance and high temperature operational extinguishment testing with extinguishers containing 1 liter of agent. The operational range of the extinguisher assembly was established as -54 °C to +71 °C while the non-operational (storage) temperature range of the extinguisher assembly was set to -62 °C to +85 °C. Extinguishers were conditioned to the appropriate temperature and in the case of the operational limits extinguishers were tested to verify acceptable fire suppression capability.

Determination of pressurization gas solubility in each candidate agent employed gravimetric methods. It was determined that carbon dioxide was the most soluble gas for the four agents under test. Argon and nitrogen gases were considerably less soluble in the candidate fluorocarbons, Chart 3. Limited agent solubility testing of single component gases (nitrogen, carbon dioxide and argon) was performed at ambient temperature conditions and limited fire suppression testing of higher boiling agents pressurized with carbon dioxide was performed. Use of carbon dioxide as a means of flash micronization and formation of fine droplets of the higher boiling agents showed some promise. However, because the low temperature solubility of carbon dioxide in the agent increases so dramatically cylinder pressure drops to near ambient reducing extinguisher discharge rates dramatically. Mixed gas options were not attempted.

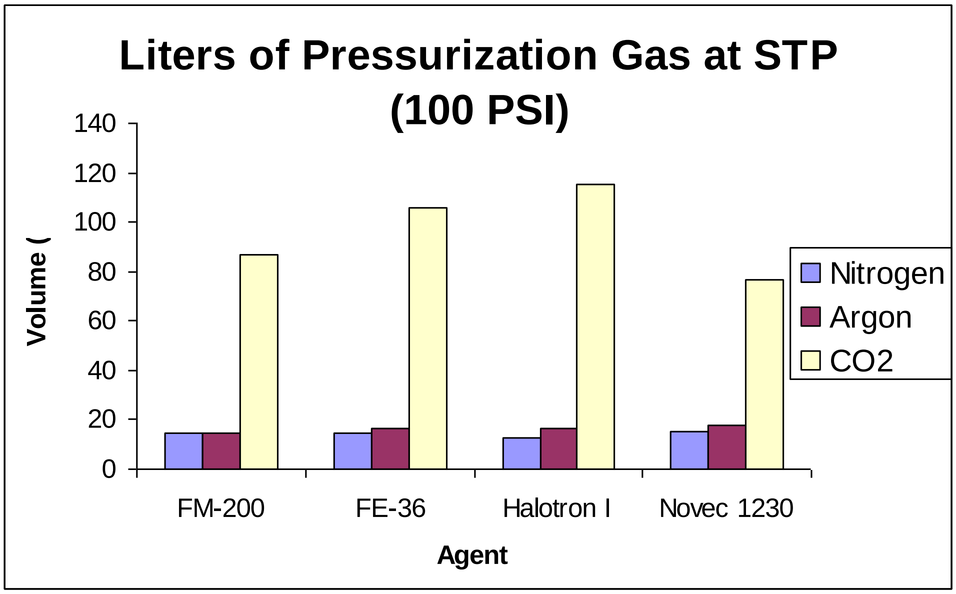


Chart 3. Volume of dissolved gas in 1L of agent at 100 PSI presented adjusted to STP.

At this point the elements of optimized agent extinguisher configurations for each agent had been identified and characterized. These elements include: a reproducible nozzle, agent fill (weight and volume), pressurization gas selection and charging pressure, cylinder and modified swing arm hub assembly. An unique optimized nozzle was developed for Halotron I, Figure 5.

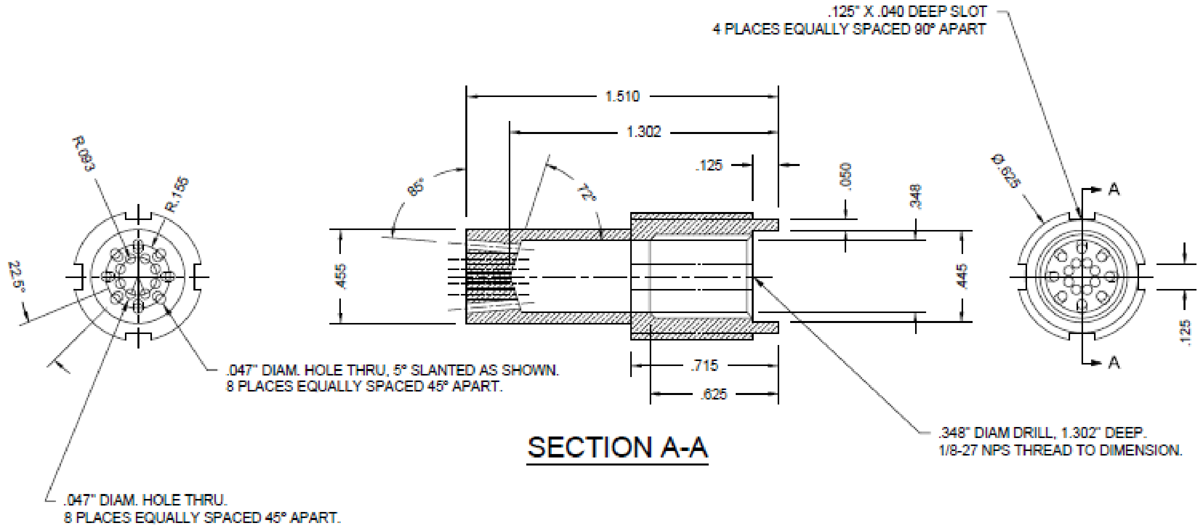


Figure 5. Optimized nozzle developed for Halotron I and also used in optimization of SBC blends with HFC-227ea.

Final operational testing and evaluations were completed in the fall of 2009. Results were summarized and a program review occurred in late 2009. Excerpts from the agent fire suppression performance summary are shown in Tables 2 and 3.

Table 2. Final Optimization Results - JP-8 Fire Suppression Performance (See Note 1)

Agent	**Test Phase**	**Max JP-8 Pan Fire (SQ FT)/attempts**	**Max JP-8 Pan Fire (SQ FT)/Fire out**	**Average Discharge Time Fire Out**
Halon 1301	Baseline	12.5/5	12.5/3	7.53 sec.
FM-200	Final	10/8	10/6 (See Note 2)	4.52 sec.
FE-36	Final	10/7	10/6 (See Note 2)	2.41 sec.
Halotron I	Final	12.5/6	12.5/6	2.97 sec.

Note 1: NOVEC 1230 optimization ceased after round #1.

Note 2: HFC-227ea and FE-36 performed marginally on 12.5 ft^2 JP8 fires

Table 3. Final Optimization Results - n-Heptane Fire Suppression Performance

Agent	Test Phase	Max n-Heptane Pan Fire (SQ FT)/attempts	Max n-Heptane Pan Fire (SQ FT)/Fire out	Average Discharge Time Fire Out
Halon 1301	Baseline	7.5/6	7.5/4 (See Note 1)	7
FM-200	Final	5/2	5/2 (See Note 2)	3.8 sec.
FE-36	Final	5/2	5/0	------
Halotron I	Final	5/2	5/0	------

Note 1: The last three successful attempts were consecutive, none of the attempts on a 10 ft^2. n-Heptane fire were successful.

Note 2: The performance demonstrated n-Heptane on 5 ft^2 was deemed marginal and no 7.5 ft^2 fires were attempted with the final configuration**.**

Clean Agent Final Selection Criteria

The Federal Aviation Administration (FAA) draft circular AC20-42D provided guidance enabling a final down select of optimized agents based on exposure limits for cardiac sensitization. HFC-227ea was ultimately identified as the best alternative clean agent offering the all-round properties for the replacement of Halon 1301 though the agent/extinguisher hardware combination was incapable of matching the performance of the 2.75 pound Halon Handheld Fire Extinguisher (HHFE) (NSN: 6830-00-555-8837) currently mounted in/on legacy rotary wing weapon systems.

- FAA Advisory circular (AC20-42D) gives guidance for the fire-fighting effectiveness, selection and safe-use of hand fire extinguishers in airplanes and rotorcraft.
- Safe-use (*Wt./Vol.)* guidance for various air change times, assuming perfect mixing, is presented in appendix 4, paragraph 2 of AC20-42D

Calculations for an OH-58D weapons platform were based on the Draft FAA Advisory Circular. The variables entered in this calculation are shown below. This approach allows calculation of the allowable agent exposure:

- Crew area volume for smallest rotary wing platform: OH-58D
- S = Specific Volume, agent specific value from FAA AC 20-42D Figure 16
- A Safe (%V/V): Maximum Safe Initial Discharge Concentrations (%v/v) for Ventilated Compartments for 1 minute Air Exchange (From FAA AC 20-42D Figure 14), See Note 1.
- H value 12,500 Ft (Altitude): value used from FAA AC 20-42D Figure 15 for 12,500 ft.)

(Note 1: Cubic Feet/Minute ECU (From CO_2 HHA Addendum Table 6-1) is 140 cu ft./minute)

The allowable weights of each commercially available fluorocarbon agent were calculated at two different ventilation clearance rates (1 minute and 6 minute) of crew area Chart 4 and Chart 5. Allowable cylinder agent amounts for HFC-227ea and FE-36 greatly exceed the actual cylinder agent content (red line on each bar) at both levels of ventilation while Halotron I allowable amounts would be exceeded under this models discharge conditions. The allowable limit calculated using the Draft FAA Advisory Circular for discharge of Halotron I would have restricted the cylinder agent content to an amount less than what was needed to meet basic fire suppression performance needs.

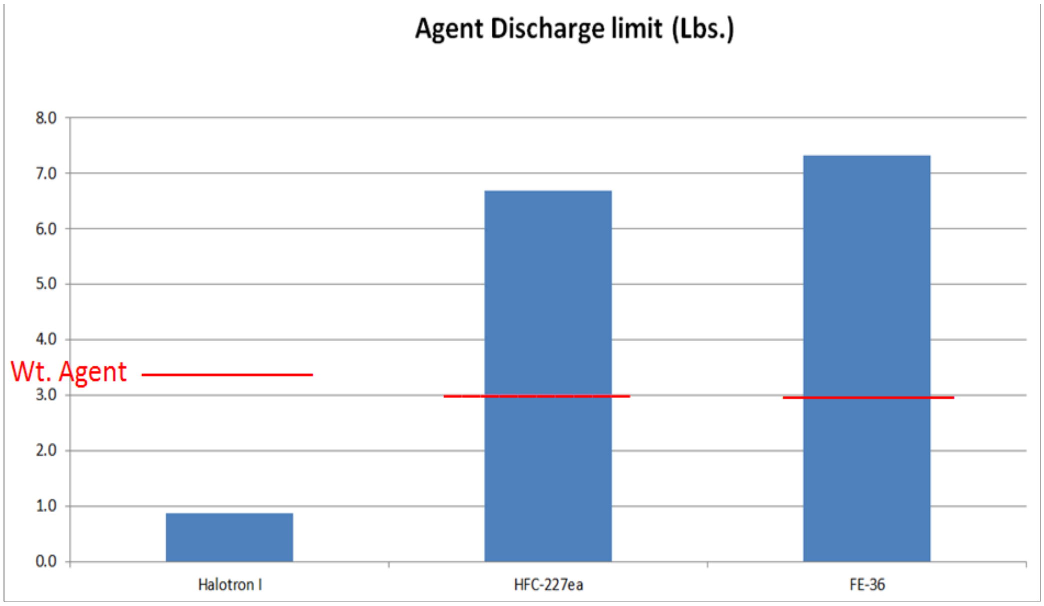


Chart 4. Calculated agent amounts limits for discharge under conditions of 1 minute clearance. Red line indicates approximate weight of each agent in the HHFE.

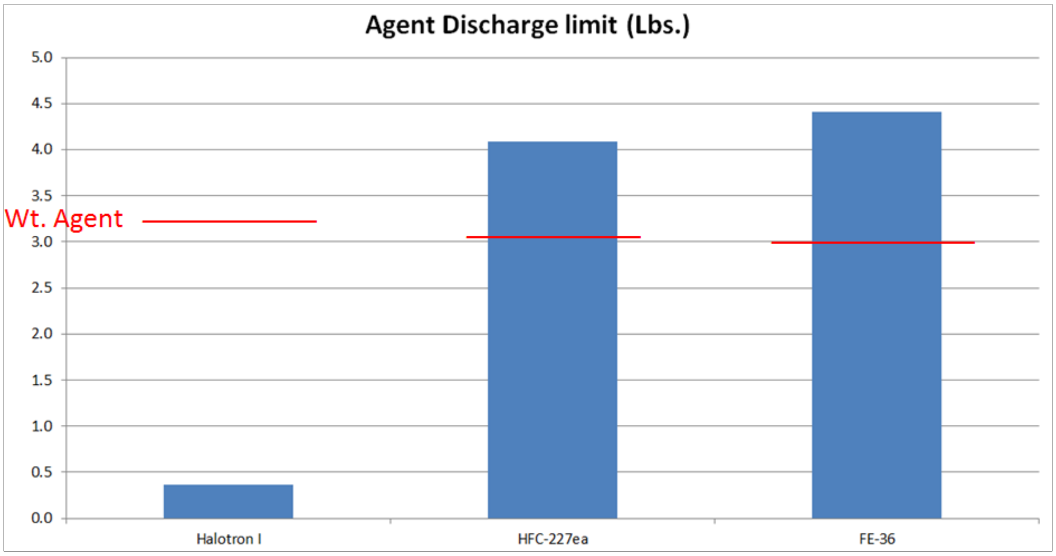


Chart 5. Calculated agent amounts limits for discharge under conditions of 6 minute clearance. Red line indicates approximate weight of agent in the HHFE.

Based on the optimized fire suppression performance results and the calculated allowable exposure limits HFC-227ea was ultimately selected for final consideration as a replacement clean agent.

Final agent discharge characterization information for the selected commercially available clean agent, HFC-227Ea, is shown in Figures 5. The discharge characteristics of the existing halon 1301 discharge are shown in Figure 6.

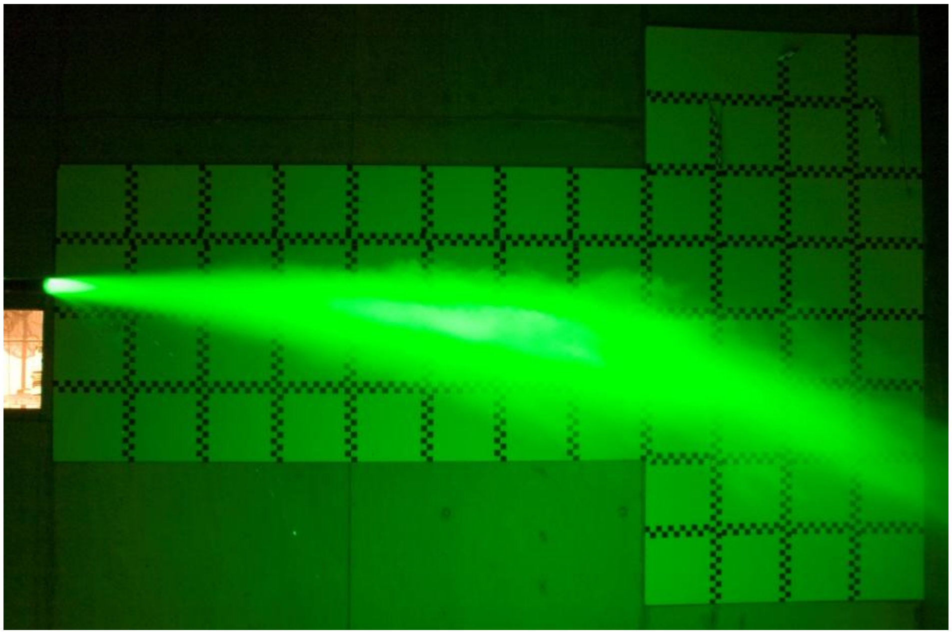


Figure 5. Optimized HFC-227ea discharge pattern (background is a 12 by 12 inch grid).

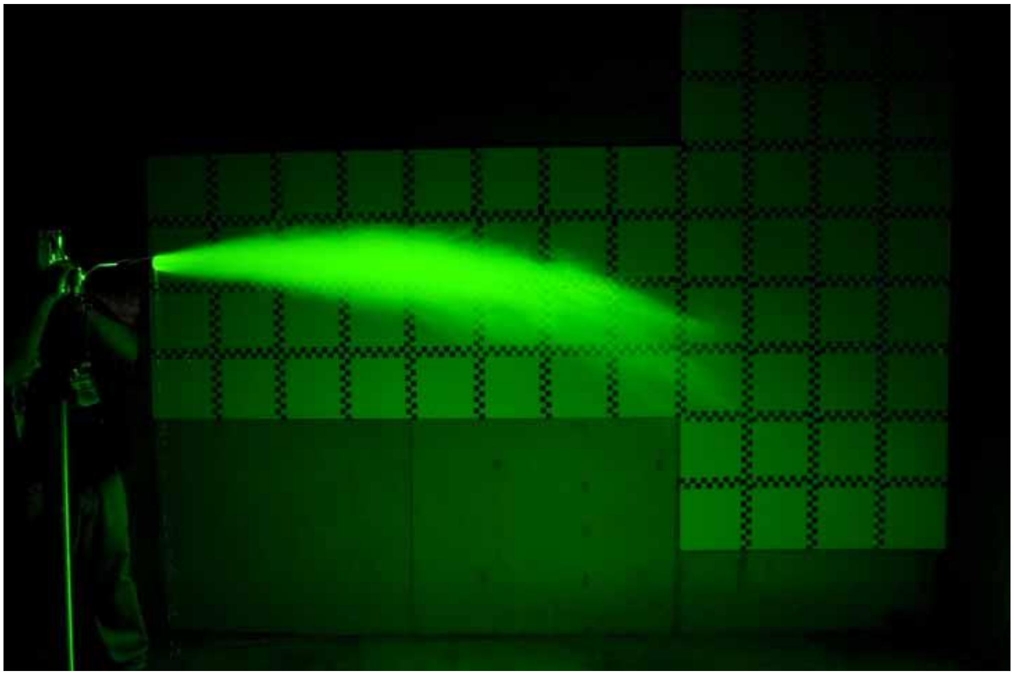


Figure 6. Current HHFE (Halon 1301) discharge pattern. (background is a 12 by 12 inch grid).

Interim assessment of HHFE goals and identification of options

A formal assessment of the performance achieved by the optimized HFC-227ea HHFE configuration concluded that matching the existing Halon 1301 HHFE fire suppression performance had not been achieved. A known strategy for improving fire suppression performance of fluorocarbon agents is the addition of a low weight percent of SBC to the fluorocarbon agent. A series of preliminary tests involving addition of sodium bicarbonate to the HFC-227ea was developed. This list included operational factors such as visual obscuration, SBC residue clean-up and inhalation toxicity assessment. Also recognized as issues to be evaluated were functional considerations inherent in creating a reliable HHFE agent included the creation of a stable suspension of SBC in the liquid HFC-227ea contained in the HHFE, the compositional uniformity of discharged blended agent, agent aging effects and environmental stability concerns. Finally, the chemical stability of SBC and known reversible thermal conversion from the bicarbonate to the carbonate form with release of water on heating were factors requiring assessment.

SBC powders then available from commercial suppliers all employed anticaking agents to deter the formation of particle to particle salt bridges and the resulting caking and clumping which could degrade the fire suppression performance of the HHFE. As inhalation by crew members would likely occur the use of proprietary anti-caking agents was a concern and represented a significant testing and final selection complication.

SBC water content control was recognized as essential for the successful implementation of a blended agent and a possible approach to eliminating the need for anti-caking agents. Use of submicron and micron sized SBC particles potentially offered an opportunity to reduce the required weight percent of SBC required for fire suppression equivalence and possibly gain improved suspendability of SBC powders in the liquid HFC-227ea fluorocarbon. For these reasons the agent developmental effort was directed to evaluate addition of SBC's to the selected clean agent HFC-227ea.

Limited testing of the performance of SBC in HFC-227ea had been performed during the last phase of the clean agent optimization effort. The testing employed the clean agent HFC-227ea blended with low weight percent's of sodium bicarbonate powders. These samples of SBC powder were supplied by Quickfire USA. The testing established that a small weight percent of SBC greatly improved fire suppression effectiveness of the clean agent. While SBC addition to the HFC-227ea was shown to enhance the extinguishing performance of the HFC-227ea the extinguishers required shaking immediately before a test in order to re-suspend the SBC powder in the HFC agent. Tests in small glass pressure tubes confirmed that SBC powders settled quickly and at best occupied less than 25% of the HFC-227ea liquid column. Clearly, if unshaken prior to discharge, the SBC additive would predominantly discharge in the initial moments following the opening of the HHFE valve leaving the remainder of the HFC-227ea still contained in the HHFE deficient in SBC needed to provide the required enhanced fire suppression performance. Discussion with SBC and nanoparticle suppliers regarding liquid suspendability of particles indicated that use of SBC particles of a smaller average size would potentially overcome the rapid settling problem.

Visual obscuration was also recognized as a potential problem for powder containing agents. An assessment of the degree of observable visual obscuration on discharge of blended agent (SBC HFC-227ea) in a fully enclosed light scout helicopter (OH-58) was performed. This test demonstrated that visual obscuration was not likely to be a significant issue for crewmembers. Post discharge clean-up of SBC powder residue in the cab interior of a pick-up truck was also evaluated and found to not present any significant issue.

Experimental Phase II – SBC blended agent development rational.

Sources of smaller particle sized SBC powders were identified and samples of a nano-particulate SBC and ultra-fine particle SBC acquired from Nanomaterials Company and Quickfire USA respectively. These powders were employed in the following proof of concept testing.

Initial 'Proof of Concept" SBC powder experimentation

A short series of tests were planned around the acquired nano and ultra-fine particle SBC powders as a limited "Proof of Concept" with the primary goal being successful demonstration of enhanced fire suppression performance and improved suspendability in HFC-227ea.

The experimental samples obtained for this testing were both dry free-flowing SBC powders. These SBC powders were both evaluated in pan-fire tests. Both SBC powders demonstrated the ability to enhance the fire suppression performance of HFC-227ea with low loadings (5 to 10 weight percent in HFC-227ea) in limited pan-fire testing. Improved suspendability in HFC-227ea was also observed in very limited testing.

Both SBC powders (Quickfire USA and Nanomaterials Company) were handled similarly. The powders were loaded into open extinguisher cylinders under a blanket of dry nitrogen without any further drying or processing. Water content data was not available for the either SBC powder.

Field Emission Scanning Electron Microscopy (FESEM) examination showed that the Nanomaterials Company proprietary powder generation process had created a submicron dimensioned SBC with a clustered needle like morphology, Figure 7. FESEM characterization of the Quickfire USA generated powder indicated that it was comprised of a more regularly shaped crystalline particles, Figure 8.

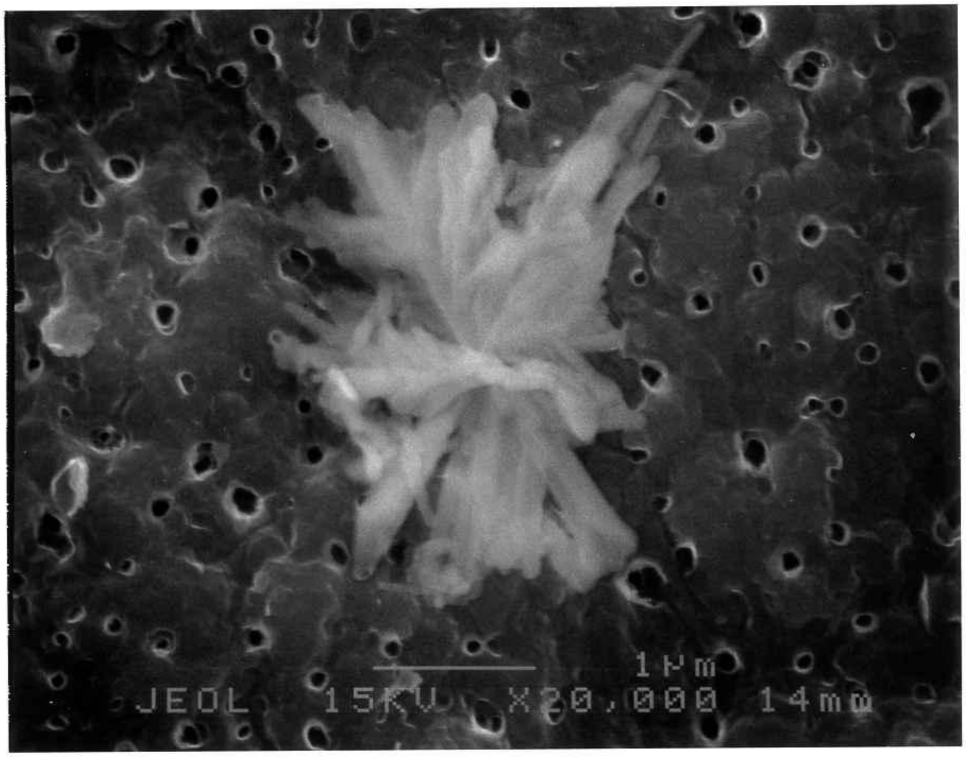
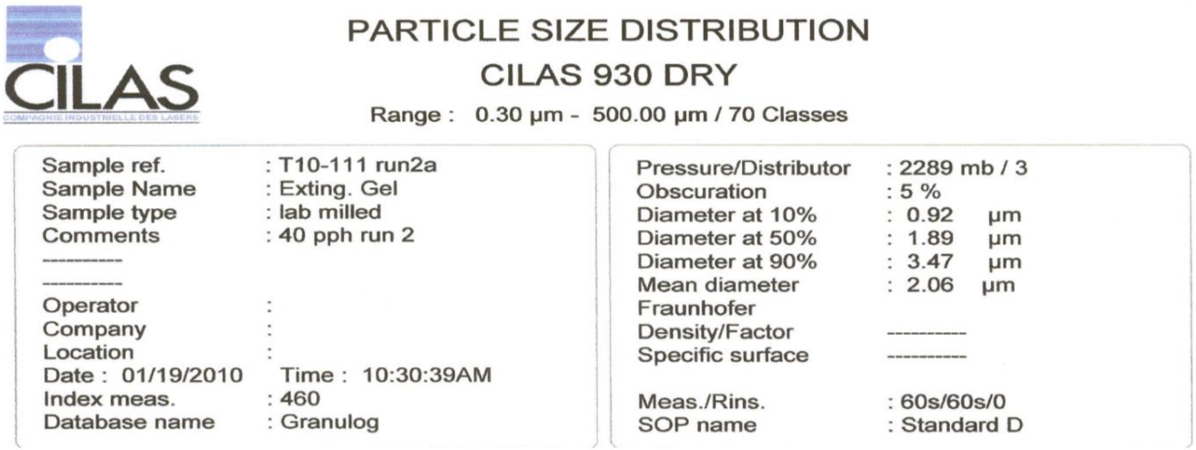


Figure 7. FESEM showing morphology of initial Nanomaterials Company SBC powders.

Figure 8. FESEM showing morphology of Quickfire USA SBC powder

Characterization data supplied by Quickfire USA indicated a mean particle diameter just over 2um, Figure 9. This SBC additive "Proof of Concept" testing occurred in early CY2010.


CILAS

COMPAGNIE INDUSTRIELLE DES LASERS

PARTICLE SIZE DISTRIBUTION

CILAS 930 DRY

Range : 0.30 µm - 500.00 µm / 70 Classes

Sample ref. : T10-111 run2a
Sample Name : Exting. Gel
Sample type : lab milled
Comments : 40 pph run 2

Operator :
Company :
Location :
Date : 01/19/2010 Time : 10:30:39AM
Index meas. : 460
Database name : Granulog

Pressure/Distributor : 2289 mb / 3
Obscuration : 5 %
Diameter at 10% : 0.92 µm
Diameter at 50% : 1.89 µm
Diameter at 90% : 3.47 µm
Mean diameter : 2.06 µm
Fraunhofer
Density/Factor ----------
Specific surface ----------

Meas./Rins. : 60s/60s/0
SOP name : Standard D

Figure 9. Quickfire USA supplied SBC powder characterization data.

Suspendability of the two SBC powders was preliminarily evaluated. In both cases the observed SBC powders suspended and remained free flowing with no signs of caking or clumping.

Fire suppression tests employing the two new SBC powders were performed in February 2010 confirming the near Halon 1301 fire suppression effectiveness of the SBC HFC-227ea suspensions, Table 4.

Table 4. Proof of Concept JP-8 Fire Suppression Performance SBC/HFC-227ea Testing.

Agent	Max Pan Fire (SQ FT)/attempts	Max Pan Fire (SQ FT)/ Fire out	JP-8 Fuel Pan Fire Attempt Success (Y or N)/grams SBC						Average Discharge Time - Fire Out (sec.)
Halon 1301	12.5/5	12.5/3	Y	N	N	Y	Y	-	7.5
HFC-227ea	12.5/6	12.5/1	N	Y	N	N	N	N	4.5
HFC-227ea/SBC (Quickfire USA)	12.5/4	12.5/3	Y/70	Y/35	Y/21	N/21	-	-	3.8
HFC-227ea/SBC (Nanomaterials)	12.5/2	12.5/1	Y/20	N/35*	-	-	-	-	3.2

*Test was compromised

Physical and chemical properties of SBC

SBC (NaHCO3) is a white crystalline solid. Commercial sodium bicarbonate usually is less than 1500ppm of surface bound water distributed on crystal surfaces. SBC crystal to crystal bonding or “Caking” can occur on standing at room temperature and is thought to be due to formation of “salt bridges” between crystals which can occur on standing as a powder or in combined SBC HFC-227ea suspensions. Salt bridge formation is thought to result from SBC particle water evaporation under heating or thermal cycling events with evaporative deposit of dissolved SBC at particle to particle contact points. Repeated water evaporation and condensation in contact areas of two or more powder crystals dissolves additional SBC and with potential of strengthening and extending salt bridges. If sufficient time is available the entire mass of powder can become fused into a single lump.

SBC suspensions in dry fluorocarbons are expected to be relatively stable if particle sizes are small enough that solvent “Brownian Motion” will keep particles from settling and or contacting each other. Discussion with nano-powder producers indicated that particle sizes on the order of 50nm generally might be expected to be susceptible to the effects of solvent Brownian Motion and stay indefinitely in suspension. Physical and chemical characterization of SBC powder under heating was performed to evaluate stability and identify temperatures where decomposition initiates. Initial attempts to gain SBC powder surface water data failed to yield useable data likely due to water generating decomposition processes.

Thermo-gravimetric (weight loss on heating) analysis was performed in late 2011 on both experimental SBC powders and commercial baking soda samples (Arm and Hammer). This testing demonstrating the thermal instability of SBC powders and onset point dependency on particle size. The observed weight loss for all samples was consistent with the known conversion of sodium bicarbonate to the carbonate form with generation of water as a by-product, Figure 10.

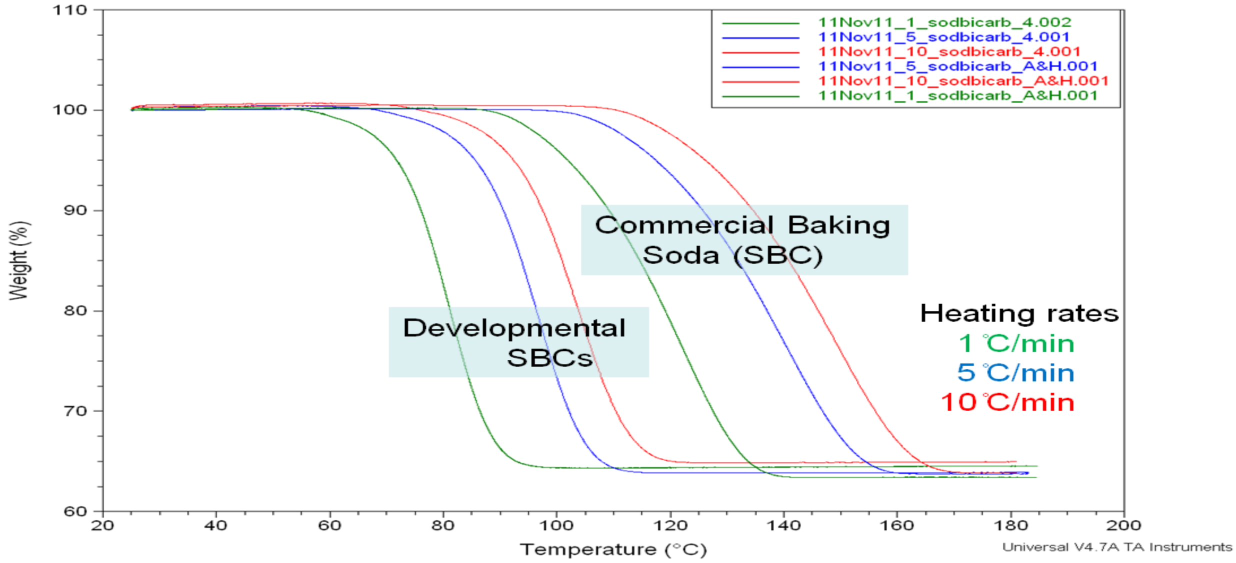


Figure 10. Thermo gravimetric analysis performed at Aberdeen Test Center 14 Nov 2011

In this limited testing the slower sample heating rates and smaller SBC particles appear to undergo this conversion at the lowest temperatures.

Concerns over water generation and the potential for increased caking of suspended SBC particles and or the loss of SBC suspendability were evaluated. The results of this evaluation are described later in this report in the section entitled “Accelerated Aging of SBC Agent”.

SBC powder scale-up approach –SBC sourcing and evaluation

The immediate goal for acquisition of larger SBC production sized samples for further testing focused on the following attributes for two types of SBC powder modeled after the successful SBC acquired in preliminary testing:

Type 1: Bulk Density: < 0.45 g/cc
Particle Size: 90% of particles < 5um
Total Water Content: preferably 100ppm but no more than 400ppm
SBC purity >98% (USP or food grade desired but not required)
Anti-caking agent’s/coatings are acceptable but not preferred

Type 2: Bulk Density: < 0.05 g/cc
Particle Size: 90% of particles < 100 nm
Total Water Content: preferably 100ppm but no more than 400ppm
SBC purity >98% (USP or food grade desired but not required)
Anti-caking agent’s/coatings are acceptable but not preferred

In order to assure the most optimal effectiveness in this application, the two unique types of dry SBC powder were identified for acquisition through the competitive bid process. As a risk mitigation it was determined that sources of both Type 1 and Type II SBC should be sought. A source of commercial nanoparticle SBC was formally selected in early 2011.

A nano-powder vendor (Nanomaterials Company) was selected to provide sufficient Type 2 SBC powder for testing in developmental HHFE hardware. Nanomaterials Company describes its production method as follows: “Sodium bicarbonate nanopowders were manufactured using a proprietary cryogenic technique. Methods employed involve the formation of a molecular dispersion of sodium bicarbonate molecules followed by rapid reformation of sodium bicarbonate particles. The process is stopped prior to the material reaching kinetic equilibrium (large particles). In this processes the sodium bicarbonate particles are managed in a liquid that is removed later. Asymmetrical sodium bicarbonate nanopowders comprised of needle or flattened needle like nano crystals are readily obtained.” Nanomaterials initially produced dry SBC powder but later in the development process produced a suspension of the SBC powder in HFC-227ea.

As no supplier of the Class I SBC was identified and selected a review of potential commercial SBC powder generation technologies was initiated. The search began in FY 2010 and focused on both the generation of generating ultra-fine SBC powders and submicron SBC. These efforts continued into FY 2011. The potential identification of alternative sources and methods of preparing acceptable Class II SBC powder were recognized as contributing to mitigation the risk associated with having a single source for the selected Class II SBC manufacturing method so the scope of alternative SBC powder technologies was expanded to cover both types of SBC.

Desirable SBC powder attributes and development of guidance of SBC alternative SBC processing methods and sources

Efforts were initiated to identify a list of desirable SBCs attributes, develop SBC materials characterization resources (needed to support further materials testing and SBC agent development) as well as fully support tasks geared to eventual procurement of manufactured SBC powders and fielding this new agent technology. Of critical importance was an SBC water-content analysis method with sensitivity to low levels of water content. FESEM sample preparation methods were refined and vendors located. SBC particle size distribution methods were tested. The continuation project area included:

- Developing new or identify existing commercial sources of optimal SBC powders.
- Evaluate long term stability of SBC/HFC-227ea agent (accelerated aging studies based on extended temperature cycling).
- Develop a reliable SBC moisture content characterization method having a low water quantification limit and establish a specification for SBC moisture content.
- Obtain SBC physical characterization information for use in procurement (particle size, morphology & surface area).
- Assist agent SBC/HFC-227ea toxicology evaluations and health hazard assessments

Complete suspension of SBC particles would ensure that a homogenous agent (SBC/HFC-227ea) composition is discharged. In limited testing, smaller particle sizes (Nanomaterials Company SBC) seemed to afford the best suspendability and best fire suppression enhancement while also minimizing the weight percent of SBC required to obtain the desired level of fire suppression.

As FESEM of initial samples of the Nanomaterials Company SBC powders showed a needle like particle morphology it was possible that loosely packed space filling structures would predominantly form in suspension. This seemed to be consistent with the Nanomaterials Company SBC's good suspendability in HFC-227ea.

Experimental studies indicated that dryer SBC powders remained free-flowing in their dry state much longer and also, when evaluated as suspensions, retained a flowable consistency over periods of several months. For this reason SBC's with the lowest water content were to be favored as would particle reduction methods that did not involve water based processing.

Both types of particle morphology and processing appeared to have their advantages. The fine needle-like particles have the highest surface areas and form clusters that are highly space-filling and yield the greatest degree of suspendability. The regular morphology of the micron sized jet-milled SBC had demonstrated its fire suppression enhancement and suspendability. With the experience gained from working with these two new SBC's and HFC-227ea slurry attributes was developed. In summary, optimal SBC powders were expected to:

- Minimize the SBC loading required to improve HFC-227ea pan fire performance to be equivalent with the Halon 1301 HHFE (Selecting those SBC powder with the greatest impact on fire suppression performance enhancement at the low SBC weight percent loadings in HFC-227ea mitigates powder inhalation, cleanup and visual obscuration issues.)
- Result in SBCs that suspend to fill the entire HFC-227ea liquid column
- Minimize visual obscuration potential.
- Minimize any inhalation irritation factors.
- Minimize potential for settling and caking due to possible slow sediment solidification processes by minimizing amount of agent moisture.
- Minimize both post discharge clean-up and potential for corrosion damage to aircraft

A list of desirable SBC attributes was developed following the preliminary testing of SBC HFC-227ea blends. The list was based in part on observations of pressure tube samples and extinguisher discharge tests. Expected functional needs (e.g., a homogeneous and stable suspension) were identified and added to generate the preliminary list of desirable powder and SBC/HFC-227ea slurry attributes:

- SBC powders with a high degree of suspendability in HFC-227ea at the agent loadings needed for acceptable fire suppression performance.
- SBC with resistance to long term settling and caking on standing (storage).

- SBC’s with lowest weight percent loading required to yield fire suppression performance comparable to the existing Halon 1301 HHFE.
- SBC powders with the lowest possible water content.
- SBC powders not needing the addition of anti-caking additives at the loadings anticipated

Alternative production methods evaluated for preparation of SBC powders.

A brief list of the existing commercial methods selected for evaluation follows with general descriptions of the process involved.

- **Jet Milling of SBC:** Initial process development testing and production performed by Sturtevant Inc. (Fluid Energy Corporation did limited process testing early on)
- **Wet Milling of SBC:** This is a potential method for producing very small SBC particles in suspension unfortunately equipment was not available for use during the SBC powder development effort.
- **Spray Drying of SBC dissolved in water:** Early testing was performed at Buchi Instruments. SBC powders produced had excellent suspendability in HFC-227ea. Limited scale up testing occurred at GEA Process Engineering with promising results.
- **Proprietary methods of SBC nano-particle production:** As risk mitigation alternative SBC powder processing to generate SBC powders similar to the Nanomaterials Company yielding SBC powders were sought.

Two commercial methods (jet-milling and spray-drying) for generating small particle size powders were ultimately targeted in order to fulfill the goal of identifying sources of Type 1 SBC powder. While SBC processing using known nanoparticle generation technologies were also sought none were identified. This search also surveyed bulk powder processors, pharmaceutical manufactures (inhalants), bulk powder process developers and powder process laboratories.

Jet-milling testing

Initial jet-milling testing was conducted at Fluid Energy, Inc. This testing resulted in a reduction of SBC particle size from 73 µm to 2.4 µm by use of multiple powder passes through a jet mill. The Fluid Energy process development tests were conducted in an 8” Jet Mill run at several feed rates to establish a correlation between capacity and product fineness.

A second jet-milling developer, Sturtevant, Inc. was identified and employed in more extensive process development and later in production of jet-milled SBCs. Initial tests at Sturtevant facilities (February 2011) identified a single pass process (air flow and SBC feed rate) yielding SBC particles 1.4 µm in mean diameter. Initial suspension tests (SBC in HFC-227ea) results and fire extinguishment pan-fire test confirmed performance and a decision was made to scale up this process to produce an amount of SBC powder sufficient to all anticipated Detailed Test Plan (DTP) related testing.

Sturtevant describes its processing as follows:

> The production tests were conducted in an 8” Micronizer Jet Mill at several feed rates to establish a correlation between capacity and product fineness.
>
> The 8” Micronizer pulverizes powders to low and sub-micron sizes through particle-on-particle impact using centrifugal force and retention time as classifying functions. The Micronizer contains no moving parts and has replaceable liners to minimize wear, contamination or stickiness. One compressed air inlet pneumatically conveys the feed material into the Micronizer chamber through an eductor and one compressed air inlet supplies the grinding energy through a series of tangential grinding jets.
>
> A volumetric screw feeder accurately meters the feed material into the Micronizer funnel and eductor. Higher feed rates result in coarser product particle sizes, while lower feed rates result in finer product particle sizes.
>
> For batch operations, the Micronized product and airflow is conveyed into a loose air filter bag. The upper bag filters the air before it is exhausted into the room. The lower exhaust sleeve connects to a plastic-lined drum, where the Micronizer product is recovered. The upper bag is periodically shaken manually to loosen particles lodged in the pores of the fabric. For continuous production operations, the Micronized product is collected in a self-cleaning process dust collector. Compressed air pulses the powder off the filter bags and various fabrics are selected, in accordance with the fineness and/or stickiness of the product.

The scaled up jet-milling processing was performed in August 2011 generated 4.5 kg of SBC powder. FESEM images of the SBC powders, Figures 11 (initial testing product) and 12 (scaled-up process) were quite similar. Particle Size Distribution analysis of the jet-milled SBC showed narrow particle size distributions with a mean particle diameter of less than 2 µm, Figure 13. The results of particle size distribution analysis were highly dependent on the sample sonication step. Insufficient sonication of SBC samples in the isopropyl alcohol carrier yielded size distributions indicative of agglomerated SBC particles. Particle agglomeration was also seen in FESEM photos of the SBC powders.

The Sturtevant, Inc. jet-milling process laboratory was visited during the processing of the SBC. The developer provided an extensive tour of the process area, processing diagrams (Figure 14) and the outer staging area for the nitrogen tanker, Figure 15, which supplied dry nitrogen to the jet-mill. Also provided was a comprehensive review of the process equipment, Figure 16, and control methods being employed in processing the SBC, such as humidity prevention, feed controls, product handling and storage, and options for shipping of the finished product. Sturtevant also discussed detailed processing and equipment information, analytical capabilities relevant to the production of the SBC powder, and efforts to maintain powder dryness including implemented HVAC modifications.

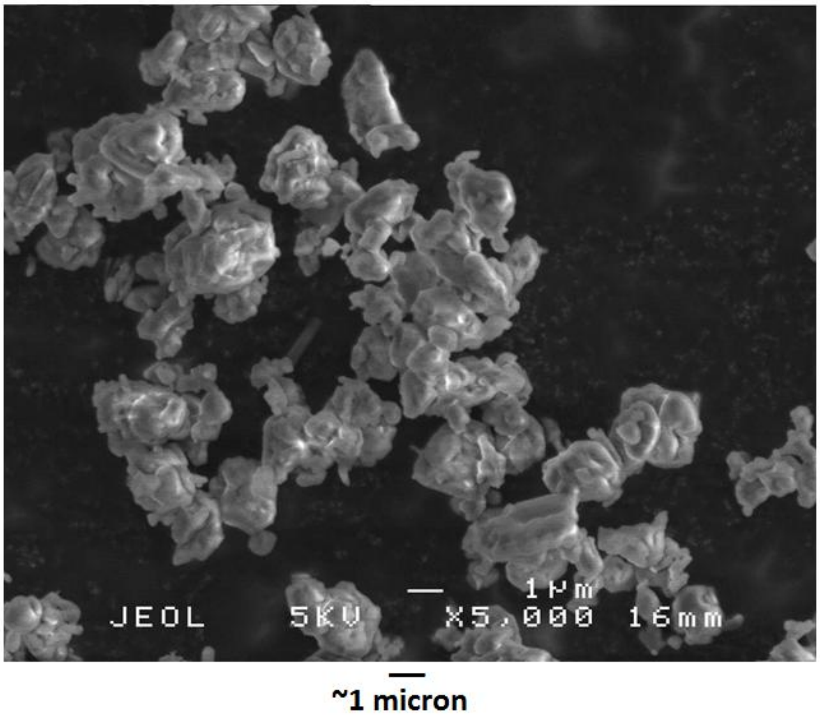


Figure 11. Jet milled SBC sample from initial production

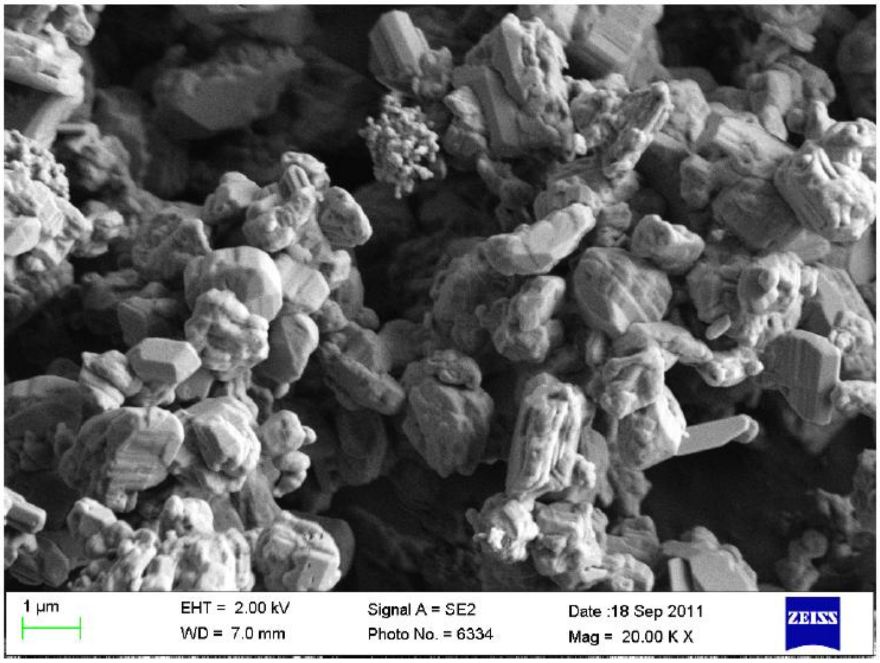


Figure 12. Jet milled SBC sample from scaled-up production

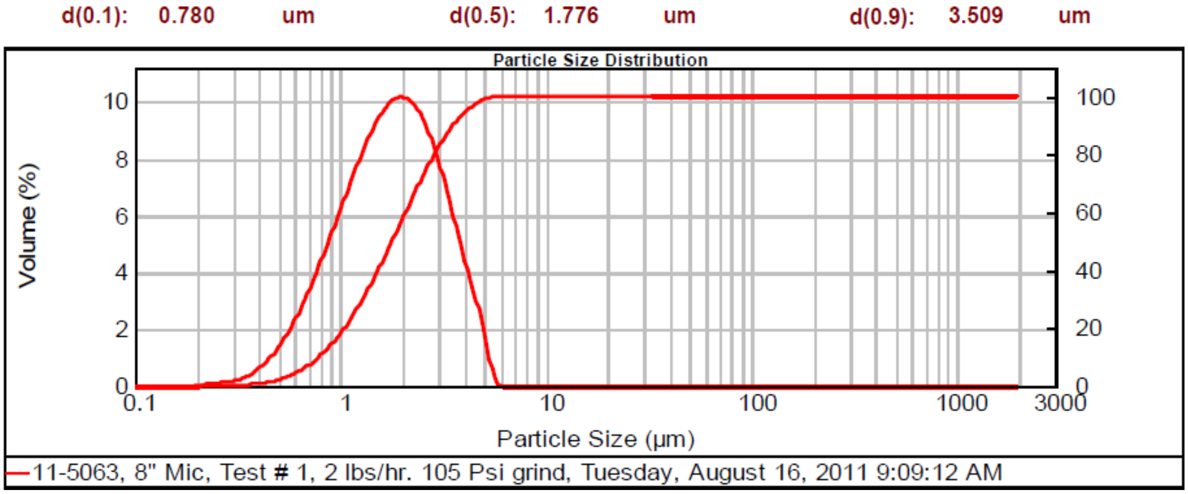


Figure 13. Jet-Milling SBC particle size distribution

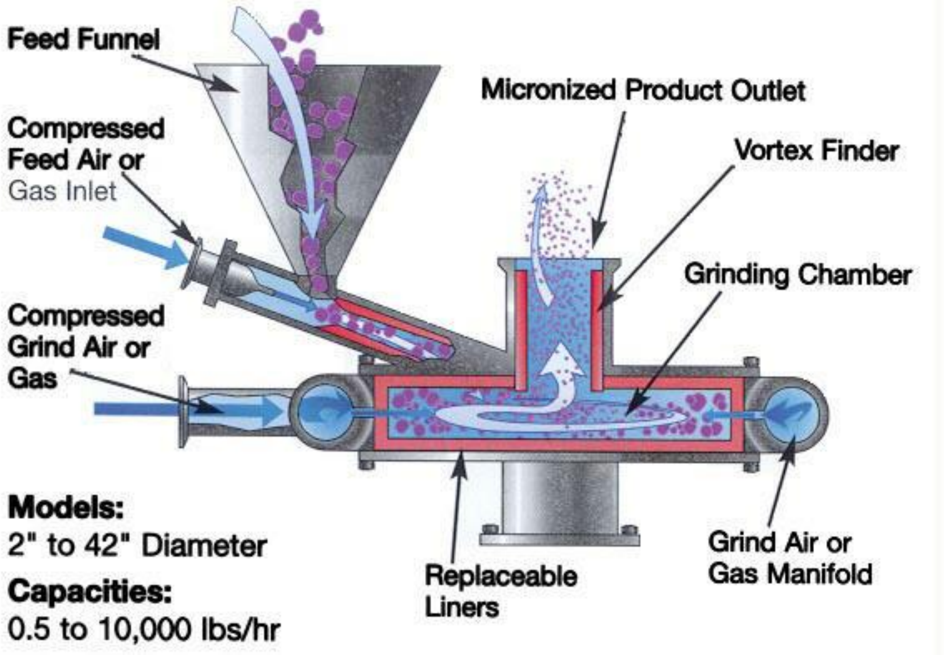


Figure 14. Diagram of jet-milling process flow. Reproduced with permission of STURTEVANT, INC. Hanover, MA

Figure 15. Nitrogen tank source of dry N_2 for the week long production of jet-milled SBC.

Figure 16. Jet-mill used in production of SBC.

The suspendability of jet-milled SBC from the initial testing phase and production phase of development is nearly identical, Figure 15. A suspension of the Nanomaterials Company SBC is shown for comparison. SBC powder suspendability is the total height of SBC layer relative to the top of the HFC-227ea liquid level on a fully settled sample.

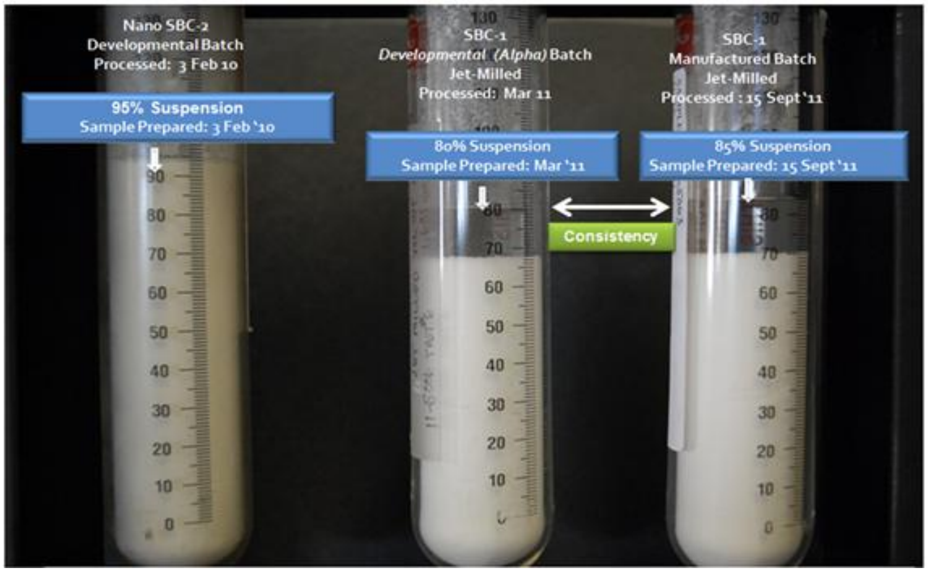


Figure 15. Suspendability of Sturtevant and Nanomaterials Company SBC in high pressure glassware.

The needle like morphology and loose stacking properties, Figures 16 and 17, of Nanomaterials Company SBC powder is thought to make it more “space-filling” giving it the ability to form stable, well suspended SBC powder suspensions in HFC-227ea even at low weight percent loadings.

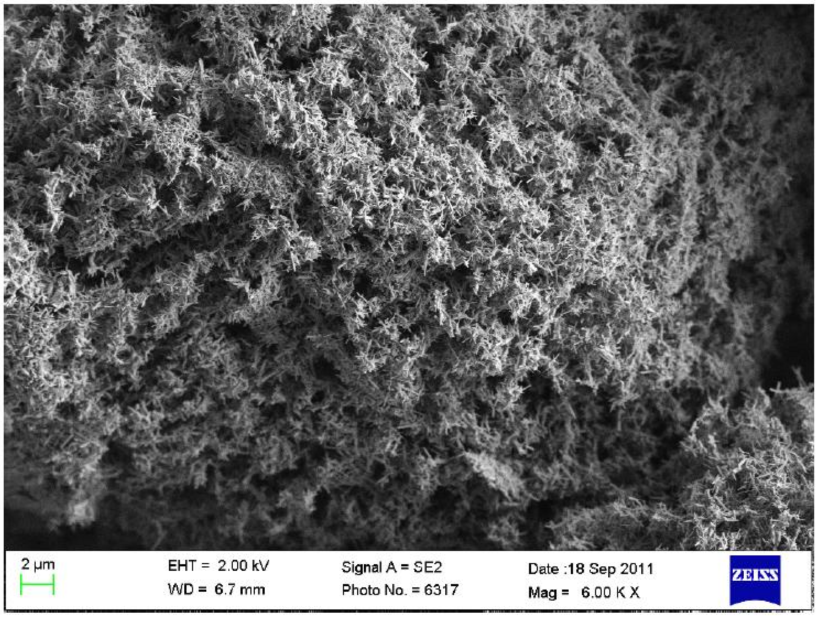


Figure 16. FESEM of Nanomaterials Company SBC product at 6,000 X magnification.

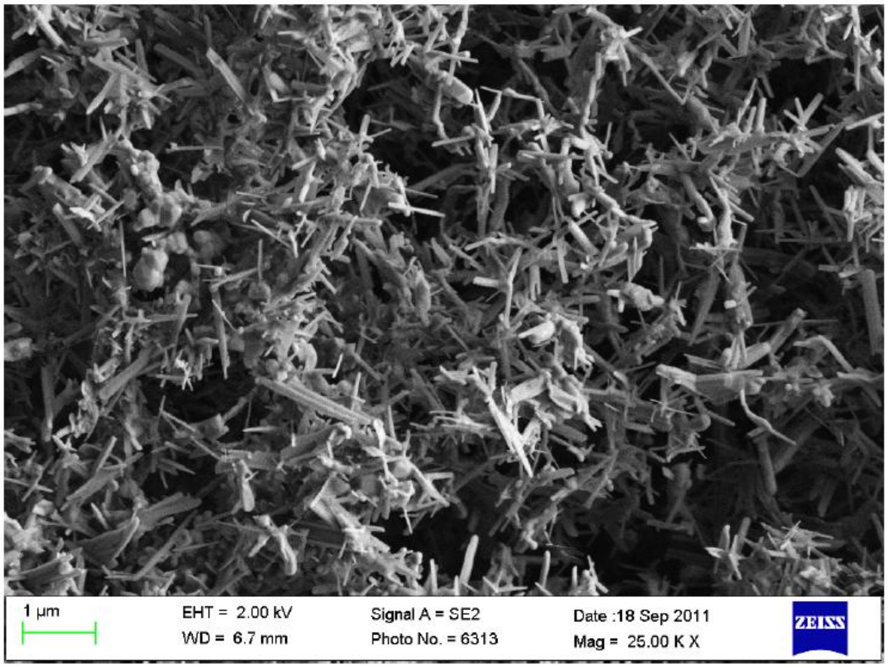


Figure 17. FESEM of Nanomaterials Company SBC product at 25,000 X magnification.

SBC Spray Drying Process Testing

Spray Drying of SBC solutions offered an alternate means of achieving small, highly crystaline particles of SBC. Initial testing was performed by a commercial supplier with the capability to perform "proof of concept" testing using bench-top spray dryers (Buchi Instruments in November 2010). Following the initial tests a commercial full scale spray drying company (GEA Process Engineering in February 2011) performed a scaled up test of spray drying processing based on spraying conditions and process parameters employed in the Buchi testing.

Buchi Instruments SBC Spray Drying Testing (11/04/2010)

Two instruments, the Buchi B290 and B90 spray dryers, were employed in order to evaluate sprayer setting effects and solution feed rates effects on SBC particle size and morphology. Both instruments yielded sufficient SBC powder for use in FESEM particle characterization and suspendability testing.

Solutions of 2% and 10% sodium bicarbonate in water were atomized producing dried SBC powders using both the B290 and B90 bench sized Buchi spray dryers, Figures 18 and 19.

Figure 18. Buchi – B290 bench scale spray dryer used in test of various process flow and heating conditions

Figure 20. Buchi – B90 bench scale spray dryer used in test of various process flow and heating conditions

FESEM of theB90 generated SBC powder showed small SBC particle sizes with a large degree of needle like particle morphology, Figure 20.

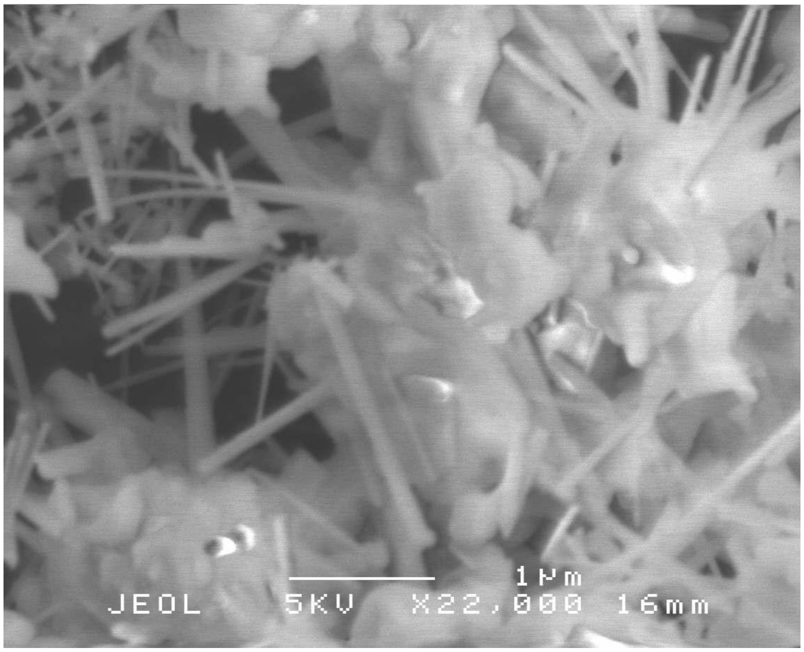


Figure 20. Buchi B90 Powder FESEM (Spray Drying of SBC Solution)

FESEM of the Buchi B290 generated showed particles with a range of morphologies ranging from needles, Figure 20, to fractured spherical structures. The B90 generated fractured spherical particle assemblages whose morphologies evidenced needle like components, Figure 21.

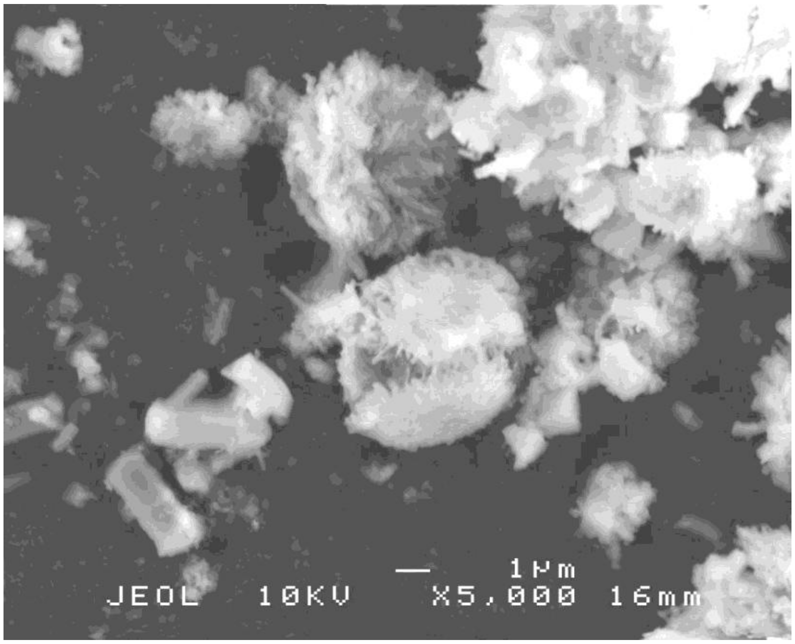


Figure 21. Buchi B290 Powder FESEM (Spray Drying of SBC Solution)

ATC performed FM-200 suspension tests with the spray-dried SBC generated from both instruments with good results. SBC powder suspension test results are shown in Figure 22. Overall the B290 bench scale spray dryer powders generated using 2% SBC solutions had the best suspendability.

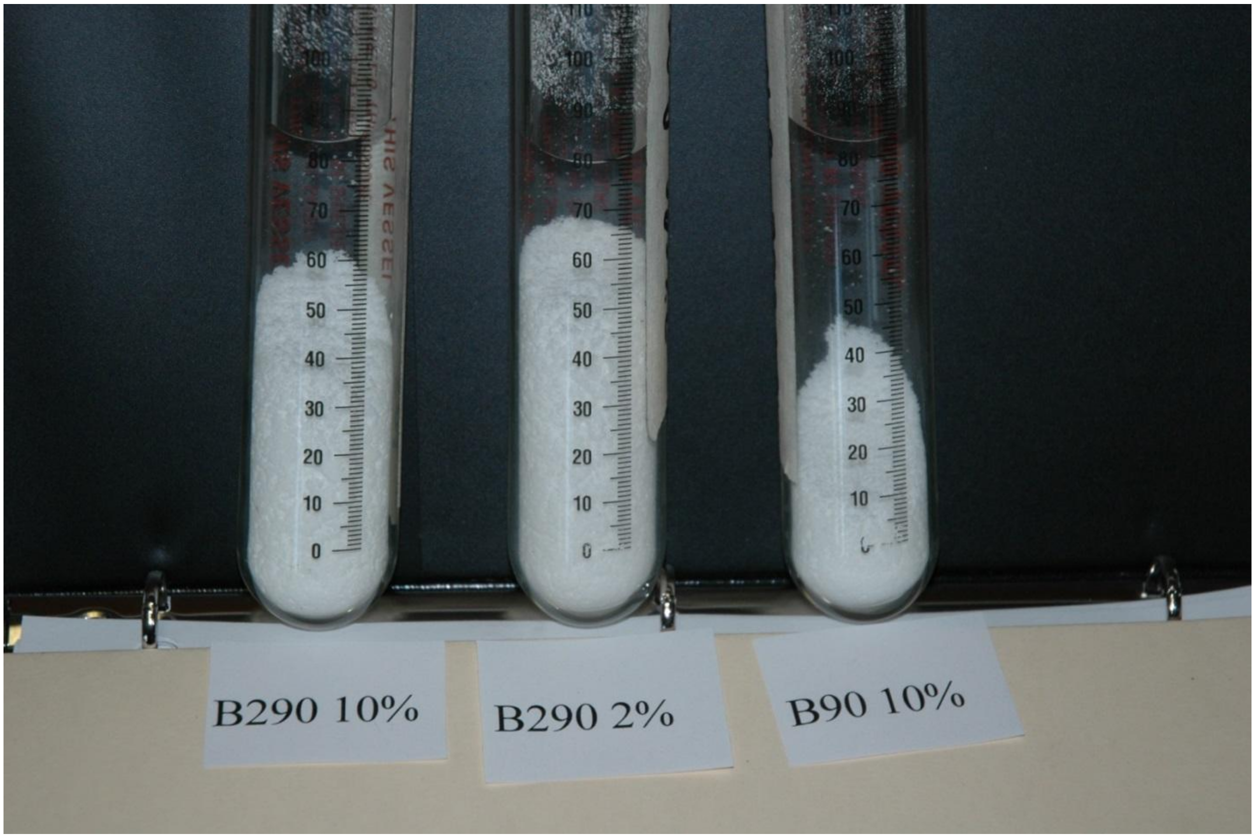


Figure 22. Buchi B290 and B90 spray dryer generated SBC samples suspended in HFC-227ea. (The 2% and 10% shown on sample labels refer to the SBC weight % concentration used in the water solutions use in a specific test.)

Due to the very limited amount of spray dried product only an evaluation SBC_S/HFC-227ea suspensions and FESEM powder examinations could be performed. Fire suppression testing was not an option due to the limited amount of each sample generated using the bench scale equipment. Given this limited but promising spray-drying result, a scale up of the process was needed.

Scaled-Up Spray Drying Process Testing at GEA Process Engineering.

Over a two day period in January 2011 GEA process Engineering conducted process testing for scaled up production of spray-drying SBC powder. The tests employed 2% by weight solutions of SBC in water atomized to a very small droplet size and dried in a spray dryer manufactured by GEA Process Engineering. The use of a 2% SBC concentration meant that each of the very small droplets generated contained only a small weight of SBC. This plus the small droplet size allowed the formation of very fine sodium bicarbonate particles. The SBC powder produced was collected in an attached filter housing. The testing employed a range of sprayer outputs, air temperature and flow conditions. The generated powders were retrieved from the filter housing and samples submitted for FESEM characterization. The particles observed using FESEM covered a broad range morphologies. A large amount of the particles were well under 1 micron in size, some evidenced needle morphologies while others showed the spherical structures seen earlier. The FESEM presented in Figures 23 through 28 cover the range of particle morphologies observed.

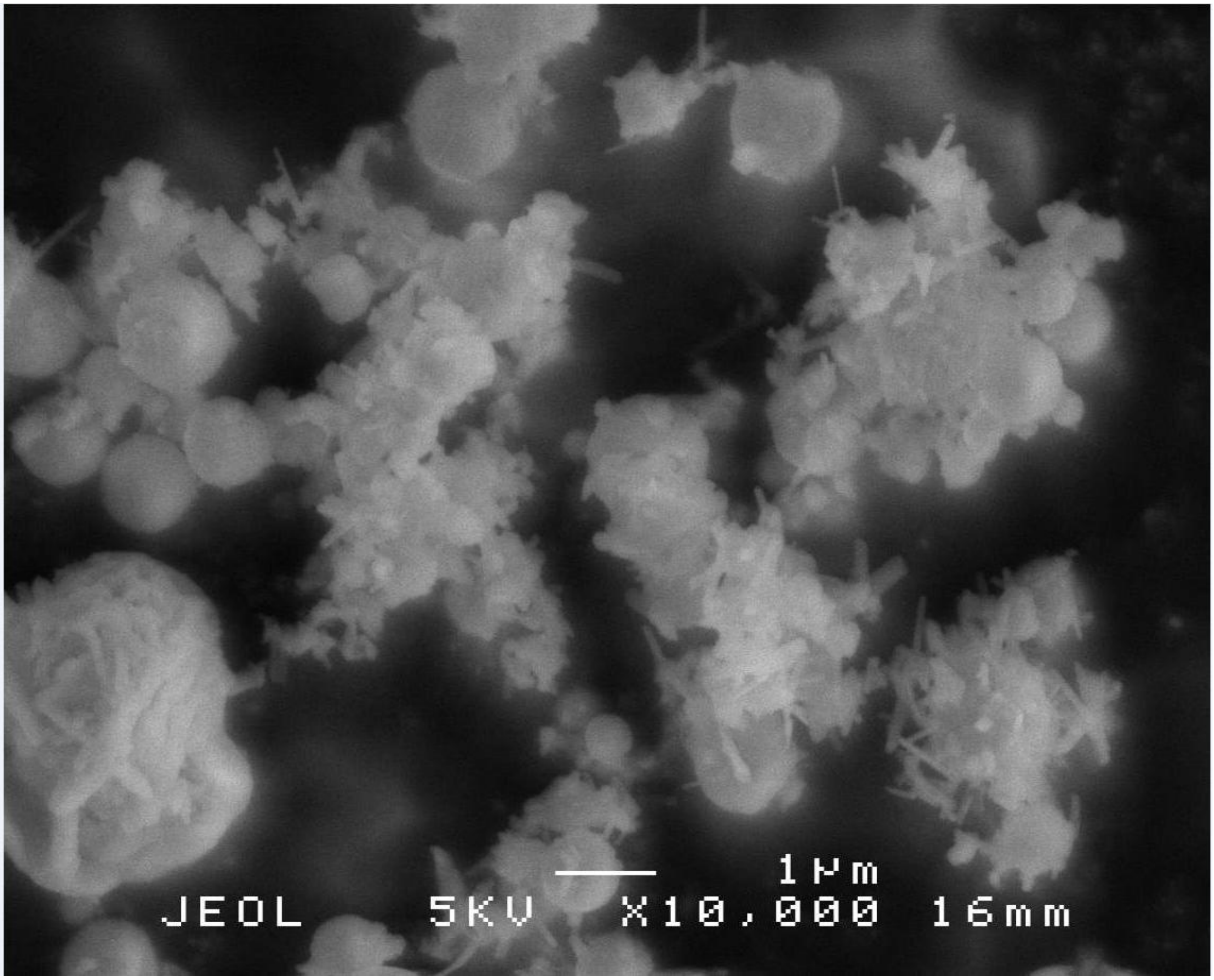


Figure 23. FESEM of GEA produced SBC powders showing small crystalline structures and agglomerates of SBC.

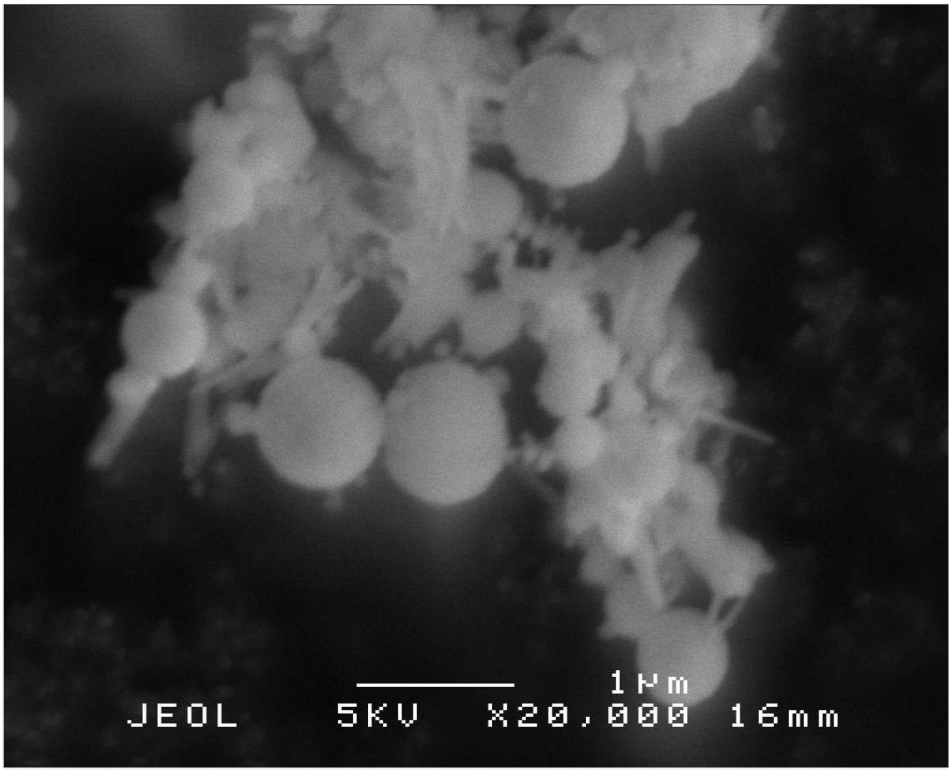


Figure 24. FESEM of GEA produced SBC powders showing small crystalline structures and agglomerates of SBC.

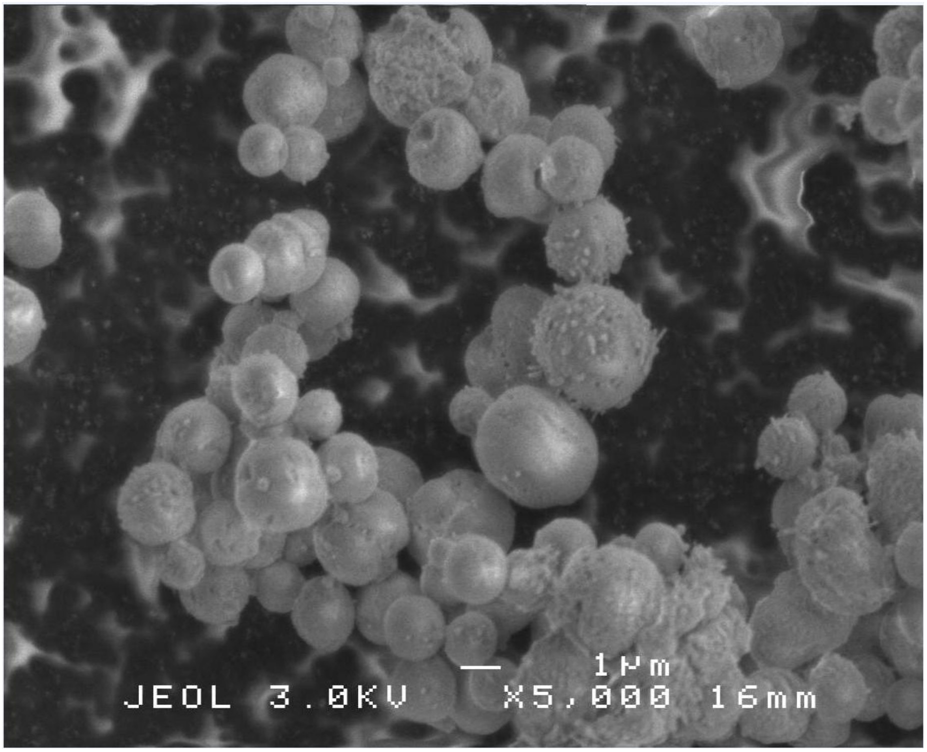


Figure 25. FESEM of GEA produced SBC powders showing small crystalline structures and agglomerates of SBC.

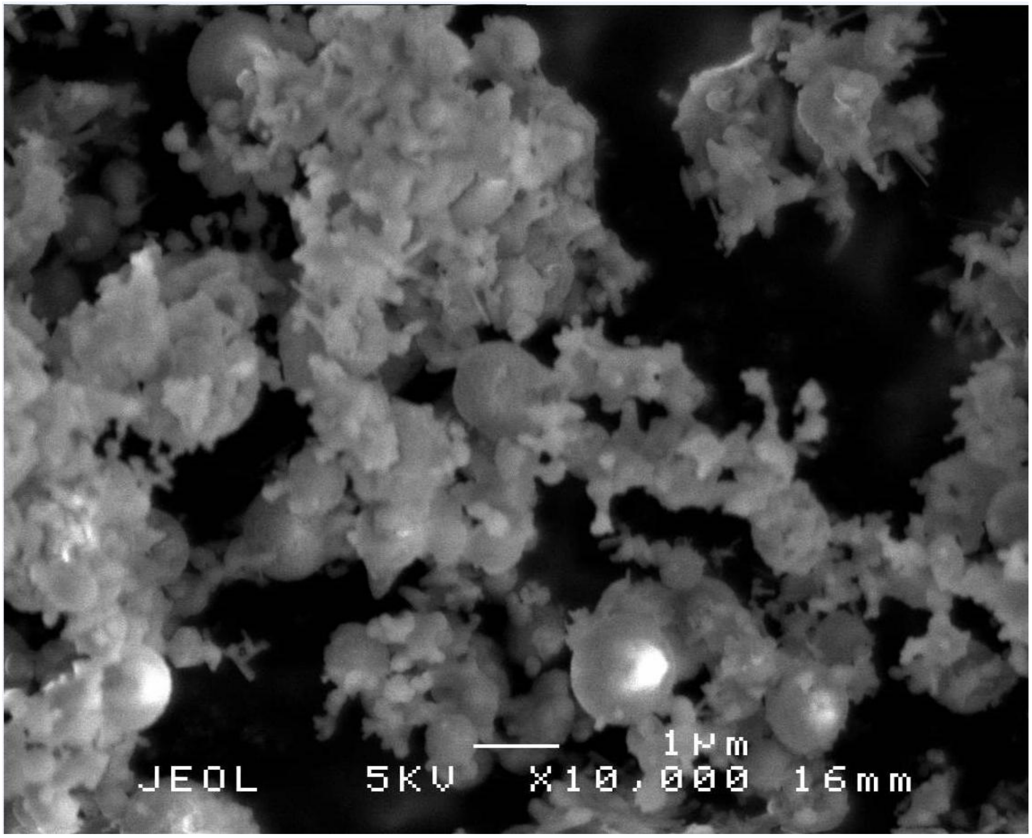


Figure 26. FESEM of GEA produced SBC powders showing small crystalline structures and agglomerates of SBC.

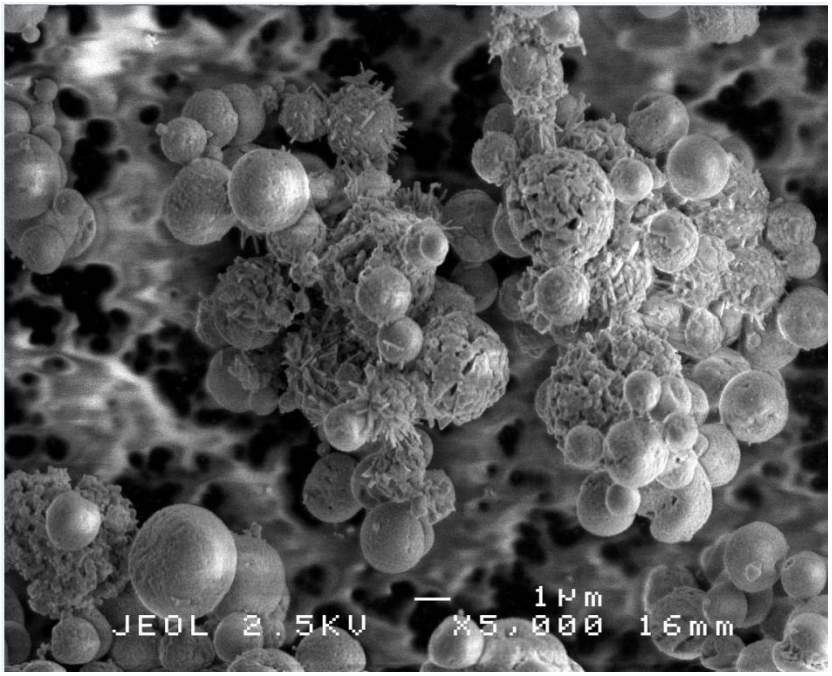
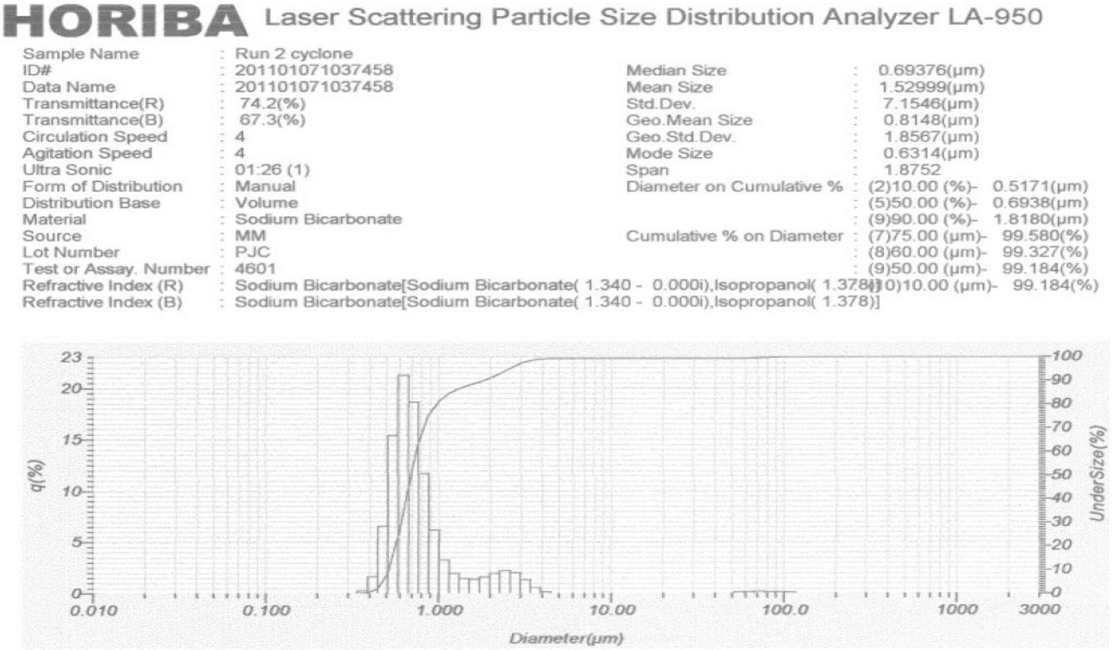


Figure 24. FESEM of GEA produced SBC powders predominantly showing spherical structures and agglomerates of SBC.

Particle size distribution testing was attempted by GEA in the course of the SBC spray drying testing. As stated previously, it was observed that the preparation of SBC powder isopropyl alcohol suspensions used by the particle size distribution test and the use and amount of sample sonication time was a large factor in what was observed. SBC particles of less than 1 micron were observed using this analytical technique. Results of two particle size distribution tests are shown for reference, Figure 25 and 26.

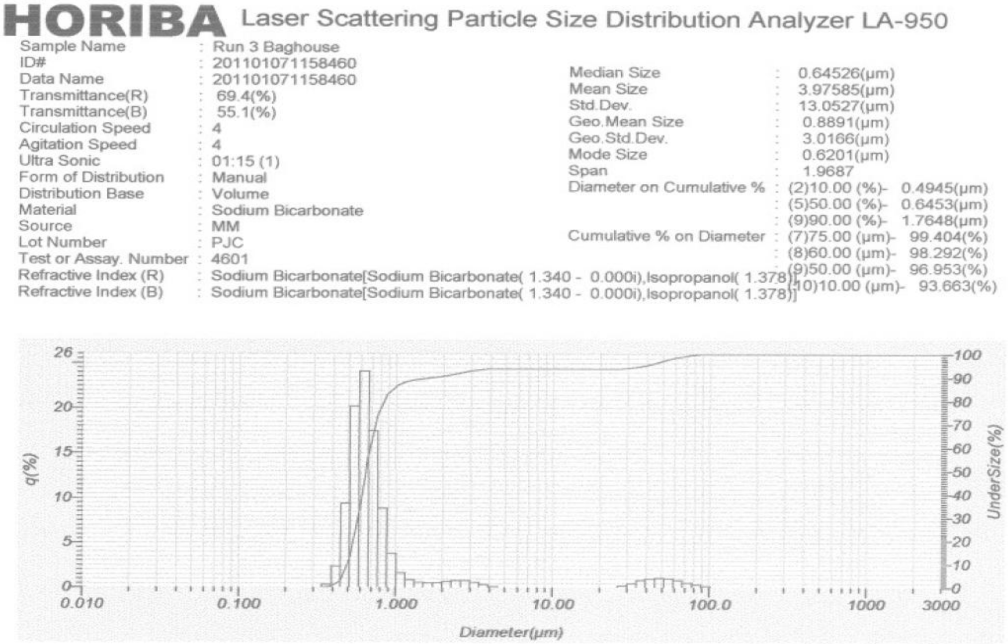


HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name : Run 2 cyclone
ID# : 201101071037458
Data Name : 201101071037458
Transmittance(R) : 74.2(%)
Transmittance(B) : 67.3(%)
Circulation Speed : 4
Agitation Speed : 4
Ultra Sonic : 01:26 (1)
Form of Distribution : Manual
Distribution Base : Volume
Material : Sodium Bicarbonate
Source : MM
Lot Number : PJC
Test or Assay. Number : 4601
Refractive Index (R) : Sodium Bicarbonate[Sodium Bicarbonate(1.340 - 0.000i),Isopropanol(1.378)]
Refractive Index (B) : Sodium Bicarbonate[Sodium Bicarbonate(1.340 - 0.000i),Isopropanol(1.378)]

Median Size : 0.69376(µm)
Mean Size : 1.52999(µm)
Std.Dev. : 7.1546(µm)
Geo.Mean Size : 0.8148(µm)
Geo.Std.Dev. : 1.8567(µm)
Mode Size : 0.6314(µm)
Span : 1.8752
Diameter on Cumulative % : (2)10.00 (%)- 0.5171(µm)
: (5)50.00 (%)- 0.6938(µm)
: (9)90.00 (%)- 1.8180(µm)
Cumulative % on Diameter : (7)75.00 (µm)- 99.580(%)
: (8)60.00 (µm)- 99.327(%)
: (9)50.00 (µm)- 99.184(%)
(10)10.00 (µm)- 99.184(%)

Figure 25. Horiba Particle Size Distribution results for Run 2 of the SBC spray-drying test.



HORIBA Laser Scattering Particle Size Distribution Analyzer LA-950

Sample Name : Run 3 Baghouse
ID# : 201101071158460
Data Name : 201101071158460
Transmittance(R) : 69.4(%)
Transmittance(B) : 55.1(%)
Circulation Speed : 4
Agitation Speed : 4
Ultra Sonic : 01:15 (1)
Form of Distribution : Manual
Distribution Base : Volume
Material : Sodium Bicarbonate
Source : MM
Lot Number : PJC
Test or Assay. Number : 4601
Refractive Index (R) : Sodium Bicarbonate[Sodium Bicarbonate(1.340 - 0.000i),Isopropanol(1.378)]
Refractive Index (B) : Sodium Bicarbonate[Sodium Bicarbonate(1.340 - 0.000i),Isopropanol(1.378)]

Median Size : 0.64526(µm)
Mean Size : 3.97585(µm)
Std.Dev. : 13.0527(µm)
Geo.Mean Size : 0.8891(µm)
Geo.Std.Dev. : 3.0166(µm)
Mode Size : 0.6201(µm)
Span : 1.9687
Diameter on Cumulative % : (2)10.00 (%)- 0.4945(µm)
: (5)50.00 (%)- 0.6453(µm)
: (9)90.00 (%)- 1.7648(µm)
Cumulative % on Diameter : (7)75.00 (µm)- 99.404(%)
: (8)60.00 (µm)- 98.292(%)
(9)50.00 (µm)- 96.953(%)
(10)10.00 (µm)- 93.663(%)

Figure 26. Horiba Particle Size Distribution results for Run 3 of the SBC spray-drying test.

Stability and Compatibility Testing of HHFE Component Materials in the Presence of FM-200 and SBC

The purpose of the testing described below was to investigate any HHFE materials reactivity that may result during storage of HFC-227ea fire extinguishant agent in the presence of SBC. A modified American Society of Heating, Refrigerating and Air-Conditioning Engineers test method, ASHRAE 97, for refrigerant testing was employed. This testing was performed by the DuPont Fluorochemicals Analytical Laboratory.

The test was performed using the different HHFE metal and elastomeric materials loaded into glass tubes with HFC-227ea and SBC and exposed to 85 °C for two weeks. In addition to a visual inspection, the effects on stability and compatibility were determined by measuring acidity and free fluoride ions. For elastomeric materials, physical measurements were made before and after exposure.

Glass tubes were loaded with HFC-227ea fire extinguishing agent and a test piece representative of the cylinder, valve, o-rings, and other components that will be present in the final hardware configuration. To half of the glass tubes, sodium bicarbonate nanoparticle powder was added. Air and moisture were minimized for these studies. The sealed glass tubes were aged in an oven at 85 °C for two weeks. In order to determine if any changes or deterioration had occurred during the oven aging process, the contents were analyzed by several methods and comparisons were made to the original samples. Upon removing the sealed glass tubes from the oven, tubes were first inspected visually. No signs of deterioration or reactivity were observed by visual inspection.

The DuPont Fluorochemicals Analytical Laboratory report on this testing concluded with the following summary paragraph:

> Once visual inspection was complete, the contents of the tubes were extracted for further testing. Chemical decomposition of the FM-200® agent was investigated by ion chromatography, gas chromatography, and acid titration. Some low level fluoride, acidity (as HCl equivalence), and organic byproducts were observed in these studies, as shown in the tables above. In order to investigate the compatibility of the elastomeric test pieces, measurements of weight, dimensions, and hardness were compared before and after testing. Again, slight variations in these properties were observed for some of the test pieces, but the observed changes were well within normal performance. For a highly critical application, further testing at more aggressive test conditions may be needed. However, from the test conditions prescribed herein, signs of significant deterioration were not evident.

SBC HFC-227ea Suspensions Stability Long Term and Estimate of SBC Water Content Upper Limits

The shelf life and sensitivity to thermal conditions of storage and use of HHFE's charged with HFC-227ea suspensions of either the Sturtevant or Nanomaterials SBC powders was unknown and in need of evaluation. This testing also aided in the establishment of SBC and SBC slurry water content limits for use in the agent specification and eventual procurement.

Water content is major factor in SBC particulate clumping and caking but retaining slurry flow ability and the absence of observable caked or clumped SBC would aid in establishing the resistance of the slurried SBC to aging effects. Should significant SBC caking occur in an HHFE the SBC slurry discharge might be slowed or stopped or the SBC weight percent composition of the discharged agent reduced with the result that the HHFE fire suppression effectiveness is compromised.

To assess the SBC slurry shelf life and effects of water content on caking and clumping a range of testing temperatures was selected representing expected extreme conditions and a thermal cycling protocol was established that exposed test SBC HFC-227ea slurries to long periods at each extreme. This test was considered to provide an accelerated aging evaluation of the SBC HFC-227ea agent under a range of water content conditions and allow for an evaluation of post aging slurry changes.

Accelerated Aging Evaluation of SBC/HFC-227ea Suspensions

Using SBC from both sources the accelerated aging process selected exposed slurries to repeated thermal conditioning cycles. The upper temperature selected for this test exceeded the known thermal conversion temperature of SBC from bicarbonate to carbonate while the lower conditioning temperature would favor condensation of any water vapor present in the system. Thermal cycling of the samples was performed in April 2012.

To gain information on the sensitivity of the SBC HFC-227ea slurry to system water content sample water content was varied. In all twelve samples of each dry SBC powder were prepared representing four stages of water content. In addition, as the option of using Nanomaterials Company SBC directly in slurry form (by-passing the need to do the blending of powder and HFC-227ea) samples of the as received slurry as water spiked slurry were included in the testing. The testing objective included:

- Observing the effects on SBC slurries with HFC-227ea of the accelerated aging process through a program of thermal cycling and variation is water content with the focus being slurry flow, SBC caking and clumping and SBC suspendability.

- Establishing, if possible, water content upper limits for the two SBC powders and the Nanomaterials Company SBC HFC-227ea slurry under development.

Experimental Procedure and Equipment

HFC-227ea room temperature (70 °F) vapor pressure is listed in DuPont agent literature as 58 psi. A standard 8 inch glass pressure tube manufactured by Andrews Glass was redesigned as a 24 inch tube for the testing in order to facilitate visualization of the slurry flow and identification of any SBC particle caking. The pressure tubes were rated to 225 psi. As the internal HFC-227ea vapor pressure at the upper extreme of thermal cycling was likely to approach 300psi. use of an external steel sleeve to provide an over-pressurization jacket was required, Figure 27.

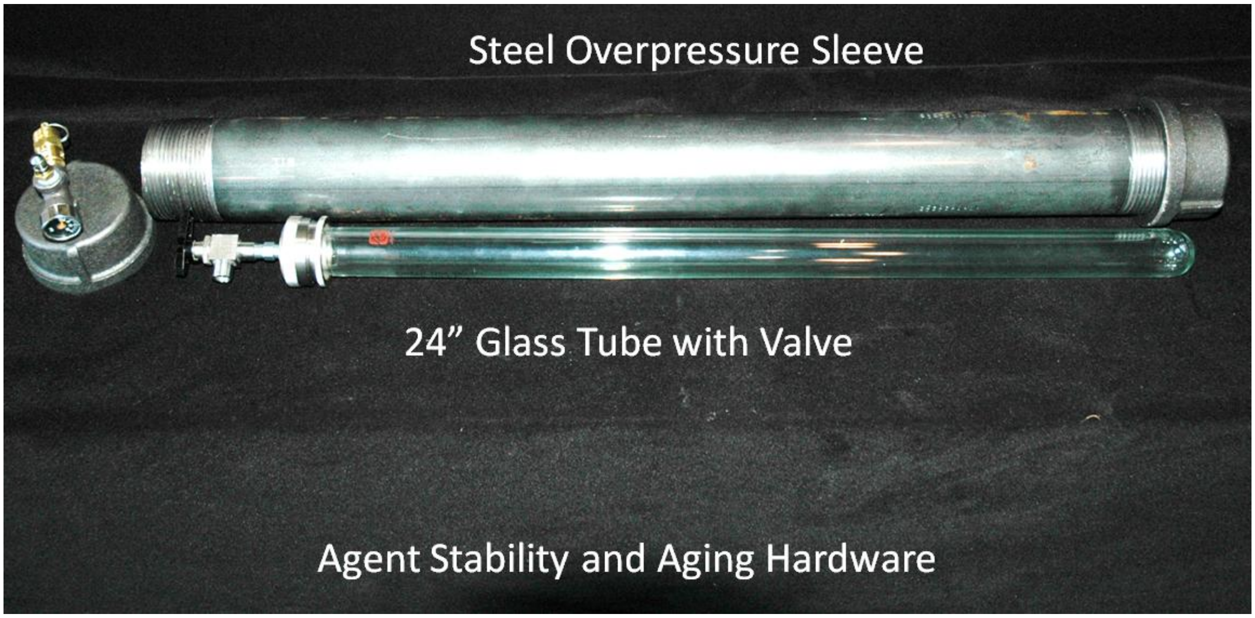


Figure 27. Glass pressure tube with steel overpressure sleeve and closure hardware.

Preparation of Thermal Cycling Sample Tubes

Samples to be prepared are shown in Tables 5 and 6. Sample tubes containing the jet-milled (Sturtevant) SBC-1 were prepared by adding SBC-1 powder to the sample tube until the target weight was reached. Three tubes were prepared using samples of jet-milled SBC-1 that had been “prewashed” using dry HFC-227ea to remove surface water. As received HFC-227ea and HFC-227ea containing two levels of added water (300ppm and 600ppm) were used to fill the glass pressure tubes to set target levels, Table 7.

The Nanomaterials Company SBC samples in tubes 13 through 24 were prepared using SBC-2 isolated from supplied slurry by filtration of “as-supplied” slurry and drying of the isolated SBC-2 powder in a glove box to allow residual HFC-227ea to evaporate. The SBC-2 added to tubes 13 to 15 was pre-rinsed with HFC-227ea to remove any surface water. The SBC-2 added to tubes 16 to 24 was un-rinsed. The amounts of SBC-2 used in each tube are shown in Table 6.

Samples 25 through 29 were created using as delivered SBC-2 HFC-227ea slurry from Nanomaterials Company. Small aliquots of water, 0.3 (1360 ppm) and 0.1ml (450 ppm), were added to samples 28 and 29 respectively. Note that because of the suspendability differences of the SBC-1 and SBC-2 different weight percent's of each SBC were employed in the preparation of samples. Samples of the Nanomaterials Company slurry were used as received (2.5 wt. % SBC) and the Nanomaterials Company dry SBC samples were prepared at a 2 wt. % level. The target weight percent for the Sturtevant jet-milled SBC was 5 wt. %.

Once prepared all sample tubes underwent an SBC resuspension process. The resuspension process was a combination of vigorous shaking, tube inversion, sonication until little change in the suspendability of the SBC was observable. Control samples were then collected separately and placed in vertical holders while the accelerated aging samples (diurnal samples) were assembled into their test group and held vertically.

Once prepared and SBC resuspended all tubes were allowed to stand vertically and undisturbed for 24 hours to allow the SBC suspension to settle whereupon the heights of the column of SBC slurry and the HFC-227ea liquid, Figure 28, were measured and recorded. Once these measurements were recorded the tubes were kept in a vertical orientation for the entire remainder of the thermal cycling testing project.

The prepared samples were separated into control samples which were retained at room temperature in a vertical orientation for the duration of the testing and diurnal testing samples (aka accelerated aging samples) which were loaded into the steel overpressure tubes. Once all overpressure tubes were complete and an overpressure of approximately 95 psi introduced the samples were assembled into vertical holders. The vertical sample holders were placed onto mobile sample racks, Figure 29, and these in turn were placed into the thermal cycling chamber, Figure 30.

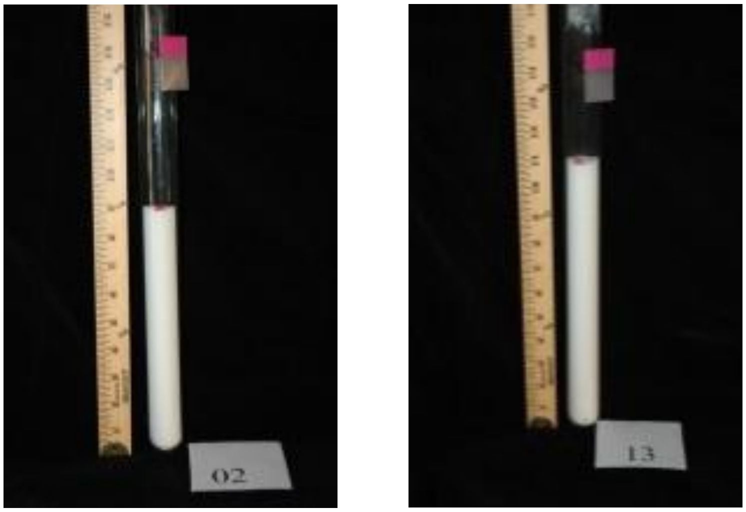


Figure 28. Measurement of SBC suspension and HFC-227ea column heights, samples 2 and 13.

Table 5. Accelerated aging study - Sturtevant SBC-1 sample preparation.

Pressure Tube label #	Sample Description (drying or water addition as indicated)	Sample type	SBC Actual wt. %
1	SBC-1, HFC Dried	Control	4.92
2	SBC-1, HFC Dried	Diurnal sample	4.88
3	SBC-1, HFC Dried	Diurnal sample	4.92
4	SBC-1, As Received	Control	5.06
5	SBC-1, As Received	Diurnal sample	4.93
6	SBC-1, As Received	Diurnal sample	5.02
7	SBC-1, 300 ppm H$_2$0 added	Control	5.10
8	SBC-1, 300 ppm H$_2$0 added	Diurnal sample	5.01
9	SBC-1, 300 ppm H$_2$0 added	Diurnal sample	4.97
10	SBC-1, 600 ppm H20 added	Control	5.11
11	SBC-1, 600 ppm H20 added	Diurnal sample	5.01
12	SBC-1, 600 ppm H$_2$0 added	Diurnal sample	5.10

Table 6. Accelerated aging study - Nanomaterials Company SBC-2 sample preparation.

Pressure Tube label #	Sample Description	Sample type	SBC Actual wt. %
13	SBC-2, HFC Dried	Control	1.94
14	SBC-2, HFC Dried	Diurnal sample	1.94
15	SBC-2, HFC Dried	Diurnal sample	1.98
16	SBC-2, As Received	Control	1.94
17	SBC-2, As Received	Diurnal sample	2.07
18	SBC-2, As Received	Diurnal sample	2.03
19	SBC-2, 300 ppm H20 added	Control	1.98
20	SBC-2, 300 ppm H20 added	Diurnal sample	2.03
21	SBC-2, 300 ppm H20 added	Diurnal sample	2.03
22	SBC-2, 600 ppm H20 added	Control	2.03
23	SBC-2, 600 ppm H20 added	Diurnal sample	2.03
24	SBC-2, 600 ppm H20 added	Diurnal sample	1.98
25	SBC-2 Slurry As Received	Control	2.5*
26	SBC-2 Slurry As Received	Diurnal sample	2.5*
27	SBC-2 Slurry As Received	Diurnal sample	2.5*
28	SBC-2 Slurry 0.3ml water added	Diurnal sample	2.5*
29	SBC-2 Slurry 0.1ml water added	Diurnal sample	2.5*

*Nanomaterials Company weight percent for SBC slurry.

Table 7. HFC-227ea (FM-200) used in sample preparation.

Pressure Tube label #	**Actual stock FM-200 wt (g)**	**Target 300ppm FM-200 Wt (g)**	**Actual 300ppm FM-200 wt (g)**	**Target 600ppm FM-200 Wt (g)**	**Actual 600ppm FM-200 wt (g)**
1	208.5				
2	208.5				
3	208.5				
4	208.4				
5	208.3				
6	208.1				
7		208.3	208.6		
8		208.3	208.5		
9		208.3	208.5		
10				208.3	207.8
11				208.3	208.5
12				208.3	208.4
13	217.2				
14	217.5				
15	217.5				
16	217.5				
17	217.1				
18	217				
19		217.3	217.4		
20		217.3	217.4		
21		217.3	217.1		
22				217.3	216.8
23				217.3	217.6
24				217.3	217.6
25				as rec. slurry	
26				as rec. slurry	
27				as rec. slurry	
28				as rec. slurry	
29				as rec. slurry	

Figure 29. Overpressure tubes in vertical tube holder mounted on mobile rack.

Figure 30. Thermal cycling chamber with rack containing accelerated aging (diurnal) samples.

Actual thermal cycling profile for the chamber containing the twenty SBC HFC-227ea slurries followed the planned chamber temperature profile very closely, Figure 31. The cumulative time at high temperature soak limit of 186 °F is estimated to be 64 hours in 8 hour increments while the cumulative time at the low temperature extreme (23 °F) was approximately 56 hours again in 8 hour increments.

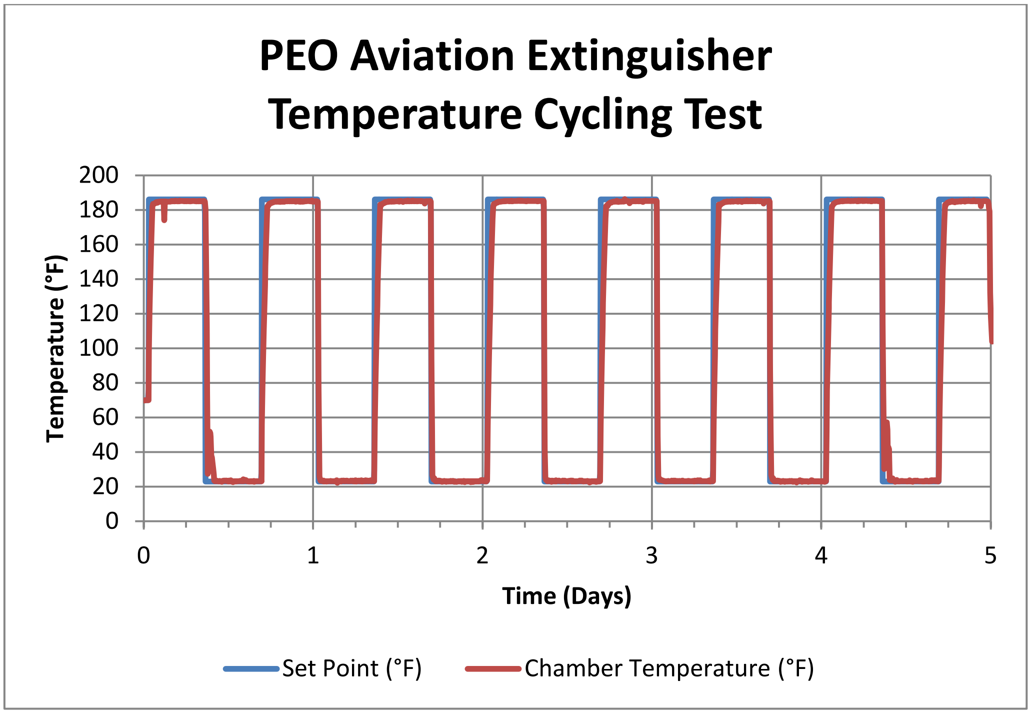


Figure 31. Thermal cycling chamber temperature set points and actual temperature profile.

At the conclusion of the thermal cycling the mobile rack was removed from the chamber. The overpressure tube pressures were noted and found to be not significantly changed from the starting pressures of about 95 psi. Keeping all tubes vertical, each outer pressure sleeve cap was removed. Again keeping the sample tubes vertical each glass pressure tube was removed and the heights of both SBC slurry and HFC-227ea measured and recorded and each tube was photographed. Control samples were handled similarly and the same data collected.

The properties of the settled SBC slurry post thermal cycling reflect accelerated aging and the range of the thermal cycling assured that all the SBC in each tube had ample opportunity to undergo bicarbonate to carbonate interconversion repeatedly.

HFC-227ea (identified as FM-200 in each chart) levels were compared for all tubes, Figure 32 and 33. The charts show initial post accelerated aging and after agitation HFC-227ea (FM-200) levels virtually unchanged indicating that no HFC-227ea leakage had occurred during the long test procedure and post thermal cycling tube handling operations. Control samples, tubes 1, 4, 7 and 10, were not subject to the thermal cycling process.

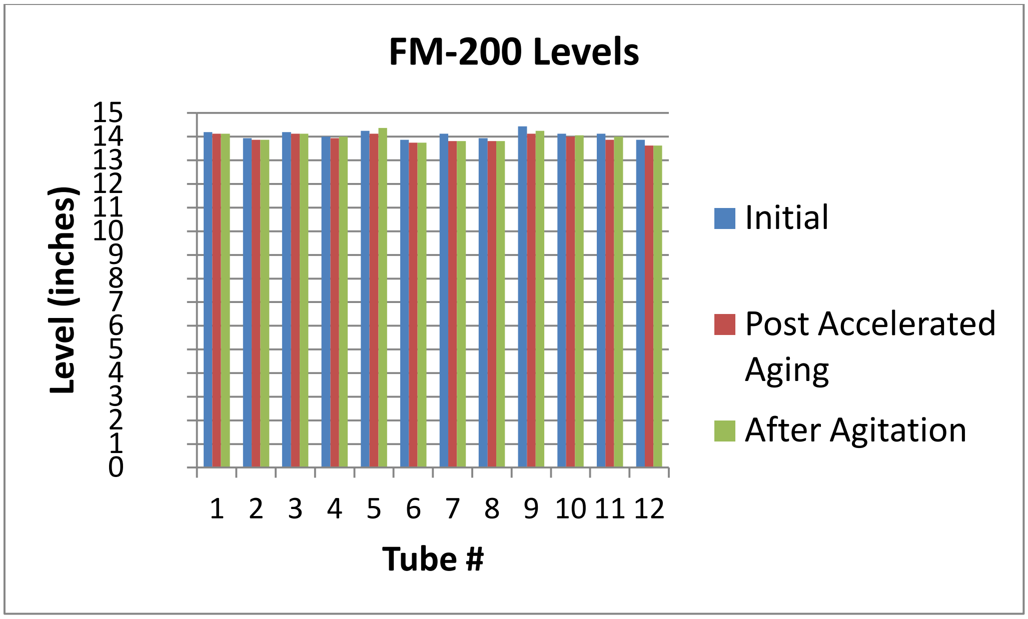


Figure 32. Pressure tube HFC-227ea (FM-200) levels

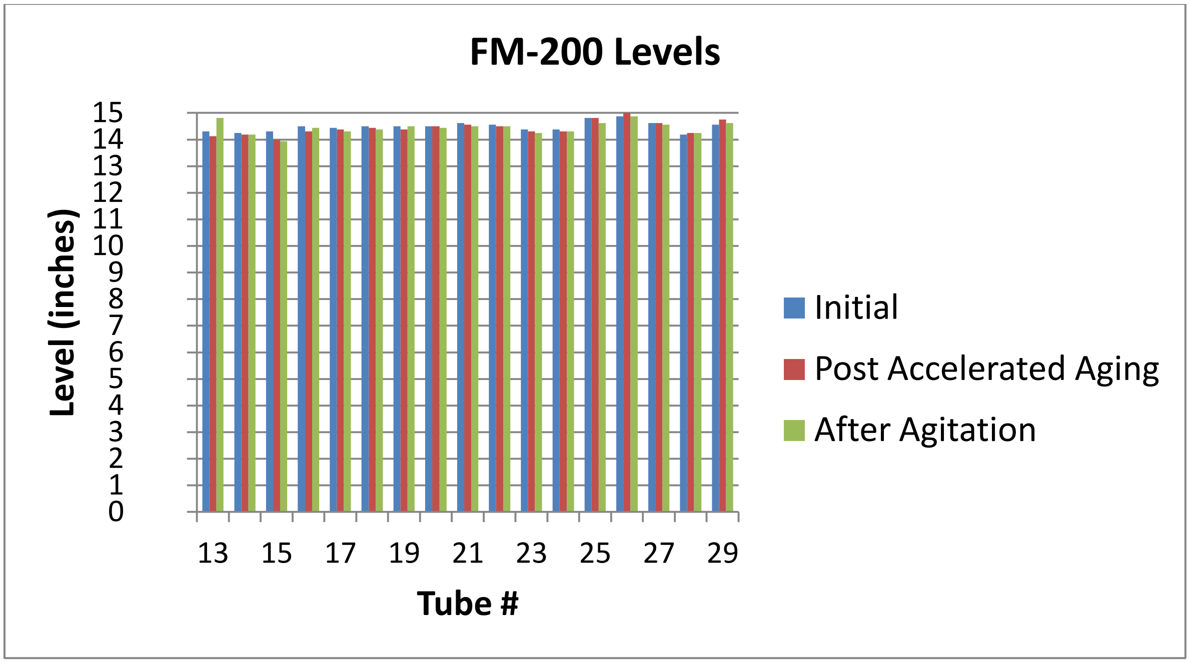


Figure 33. Pressure tube 13 to 29 HFC-227ea (FM-200) levels

SBC-1 suspension levels were compared for all tubes, Figure 34. The chart show initial, post accelerated aging and after agitation settled SBC slurry levels. Control samples are tubes 1, 4, 7 and 10.

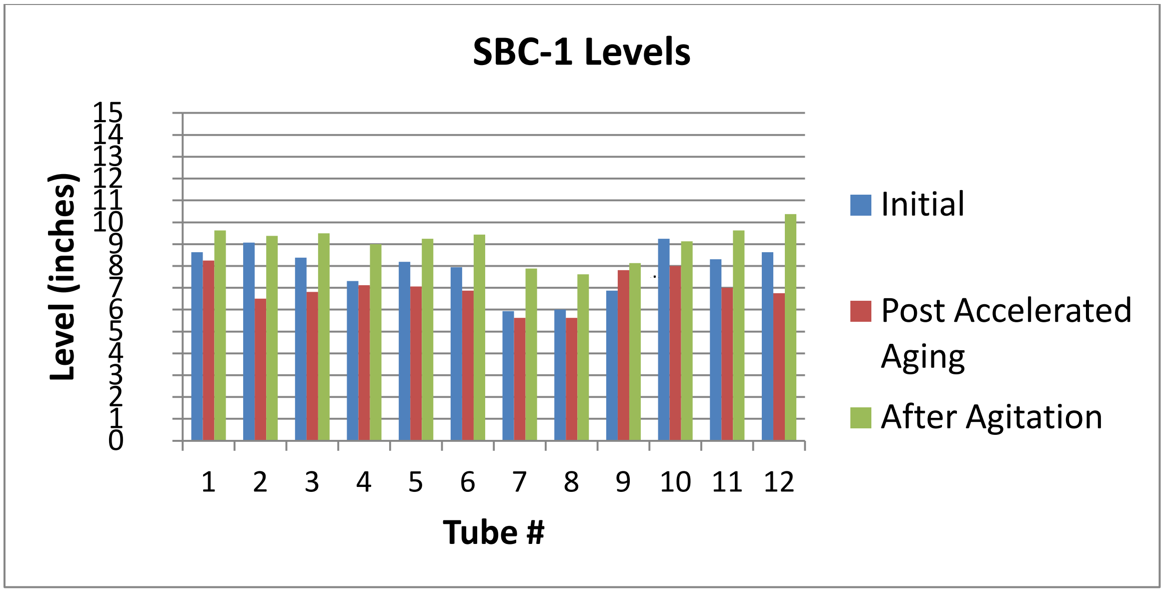


Figure 34. SBC-1 suspendability comparison following thermal cycling.

Evaluating the flowability of each slurry sample post thermal cycling was performed by repeatedly inverting each sample tube sample tubes to see if the SBC slurry would fully resuspend leaving no residue in the heal of the pressure tube. All samples resuspended with no residues remaining in the pressure tube heal. To check for the flowability each sample tube was slowly inverted and the slurry flow closely observed. In each case the tube contents could flow freely, Figure 35. The flowability check was repeated to look for evidence of any clumps or caked SBC and none was observed. Following a 24 hour period in which all sample tubes were held in a vertical orientation a final set of HFC-227ea and SBC resuspension level measurements were taken.

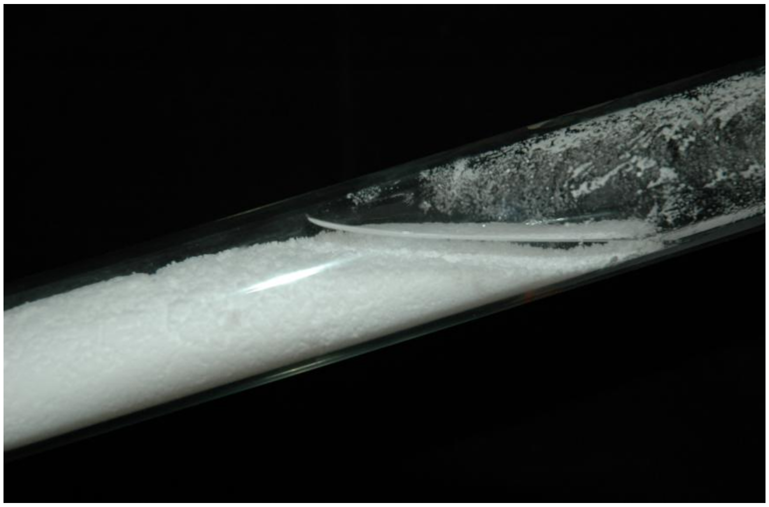


Figure 35. Accelerated aging Tube 4 tilted to show flow and consistency of suspended SBC-1.

Several effects of accelerated aging (diurnal thermal cycling) process on the SBC-1 suspensions were noted:

- In all but one case the thermal cycling accelerated aging process reduced the SBC-1 suspendability level.
- In all but one case the SBC-1 suspendability recovered on shaking of the glass pressure tube with suspendability exceeding the initial SBC-1 suspendability.
- SBC/HFC-227ea slurries after shaking showed no change in their flow characteristics when compared to their respective control sample.
- No SBC clumping or caking was observed in any of the test samples following shaking the glass pressure tube.

In addition it was noted that SBC powder suspendability in the three dried SBC-1 tubes (tubes 1-3) and the three dried SBC-2 tubes (tubes 13-15) exceeded that of the as received SBC-1 and SBC-2 tubes (tubes 4-6 and 16-18 respectively).

SBC-2 suspension levels were compared for all tubes, Figure 36. The chart shows initial, post accelerated aging and after agitation settled SBC slurry levels. The SBC-2 control samples are tubes 13, 16, 19 and 22. Sample 25 is the control for the as received slurry from Nanomaterials Company.

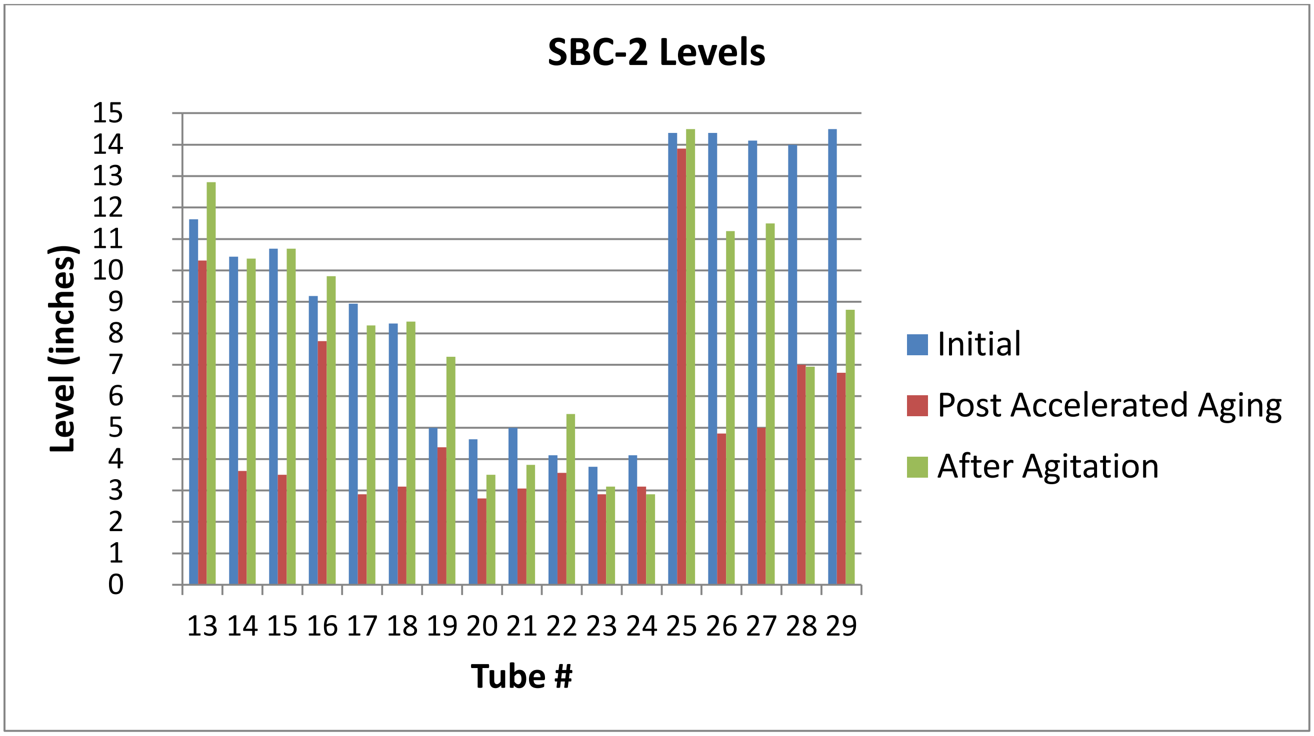


Figure 35. SBC-2 suspendability comparison following thermal cycling.

Evaluation of the flowability of each SBC-2 slurry sample post thermal cycling was performed by repeatedly inverting each sample tube sample tubes to see if the SBC-2 slurry would fully resuspended leaving no residue in the heal of the pressure tube. All samples resuspended with no residues remaining in the pressure tube heal. To check for the flowability each sample tube was slowly inverted and the slurry flow closely observed. In each case the tube contents could flow freely, Figure 36. The flowability check was repeated to look for evidence of any clumps or caked SBC-2 and none was observed. Following a 24 hour period in which all sample tubes were held in a vertical orientation a final set of HFC-227ea and SBC resuspension level measurements were taken.

Figure 36. Thermal Cycling Tube 14 showing flow of suspended SBC-2.

Several effects of accelerated aging (diurnal thermal cycling) process on the tubes loaded with SBC-2 (Nanomaterials Company SBC) powder (tubes 13 to 24) suspensions were noted:

- Average initial SBC-2 suspension levels were greatest for the extra-dry SBC-2 samples.
- Post thermal cycling agent Nanomaterials Company SBC suspension levels had all decreased to nearly the same levels.
- Following repeated inversion (shaking by hand) each tube’s SBC levels recovered to near the control sample SBC suspendability levels.
- SBC/HFC-227ea slurries showed no change in their flow characteristics.
- No SBC clumping or caking was observed in any of the test samples.
- Tubes 13 to 24 decrease in initial SBC-2 suspendability mirrors the added water content increase.

Post diurnal thermal cycle SBC-2 suspendability is approximately equivalent over all samples derived from the initial powder. Post accelerated aging tubes 28 and 29 displayed similar much shrunken and misshapen SBC plugs, Figure 37. Following vigorous shaking of each sample the contained SBC resuspended to free flowing slurries with no observable clumping or caking, Figure 38.

Figure 37. Tube 28 post accelerated aging and before resuspension by shaking and tube inversion.

Figure 38. Tube 28 post accelerated aging and resuspension.

Figure 39. Accelerated aging Tube 28 SBC-2 consistency and flow.

SBC powder was isolated from each of the 29 accelerated aging glass tubes and HFC-227ea residues degas in a dry box. FESEM photos of selected control and sample tube pairs were examined for changes in particle size and changes in morphology, Figures 40 to 59. A summary comparison of visual changes in particles of accelerated aging and control samples is presented in Tables 8 to 10.

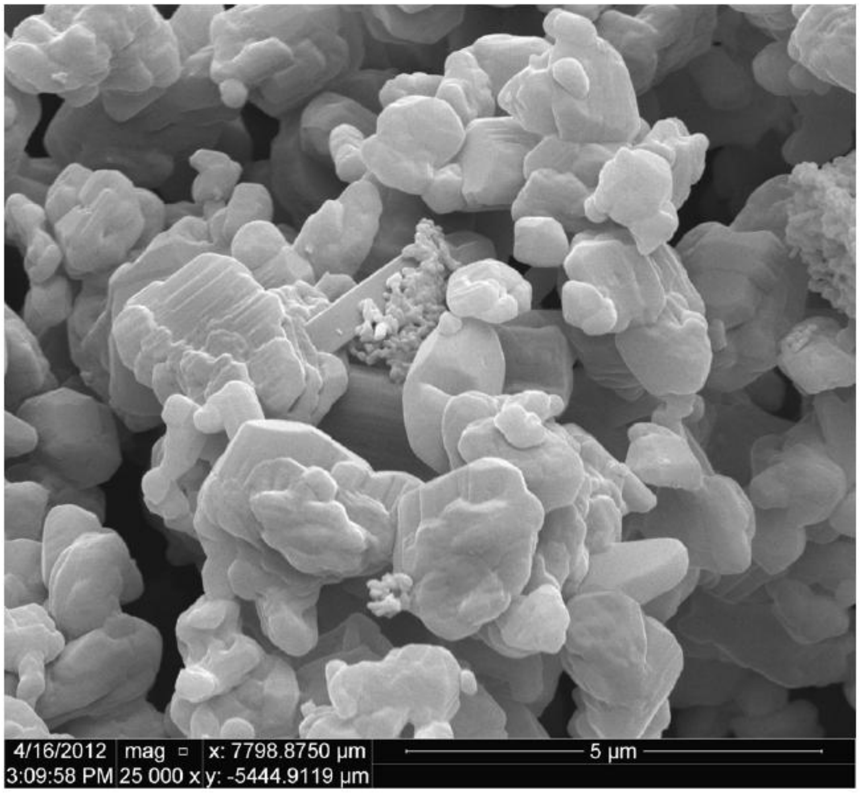


Figure 40. FESEM of SBC-1 from Tube 1 (Nanotech Analytics Report 43104-11, AA-1)

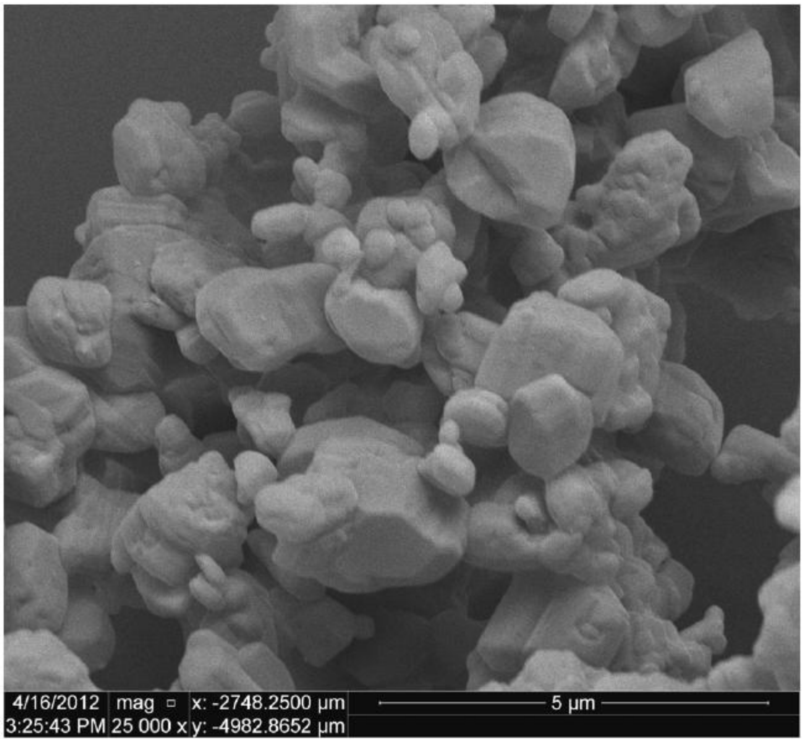


Figure 41. FESEM of SBC-1 from Tube 2 (Nanotech Analytics Report 43104-12, AA-2)

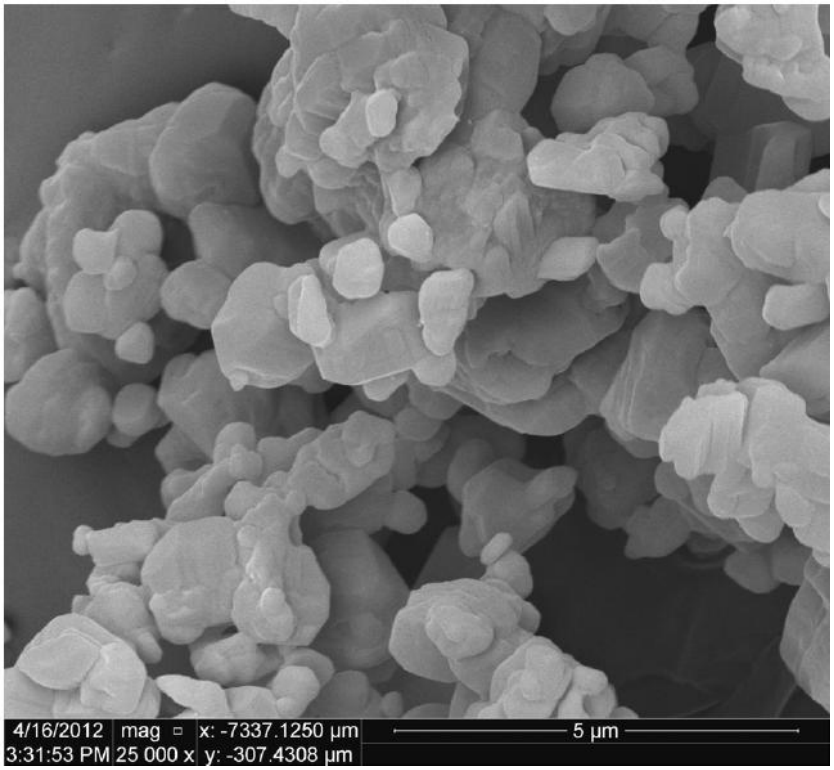


Figure 42. FESEM of SBC-1 from Tube 4 (Nanotech Analytics Report 43104-13, AA-4)

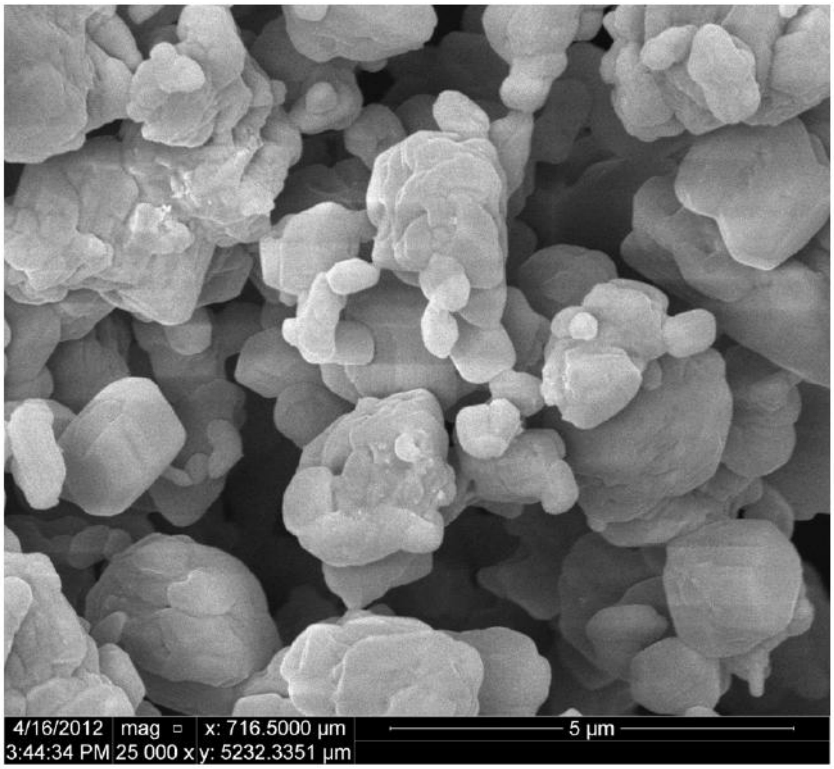


Figure 43. FESEM of SBC-1 from Tube 5 (Nanotech Analytics Report 43104-14, AA-5)

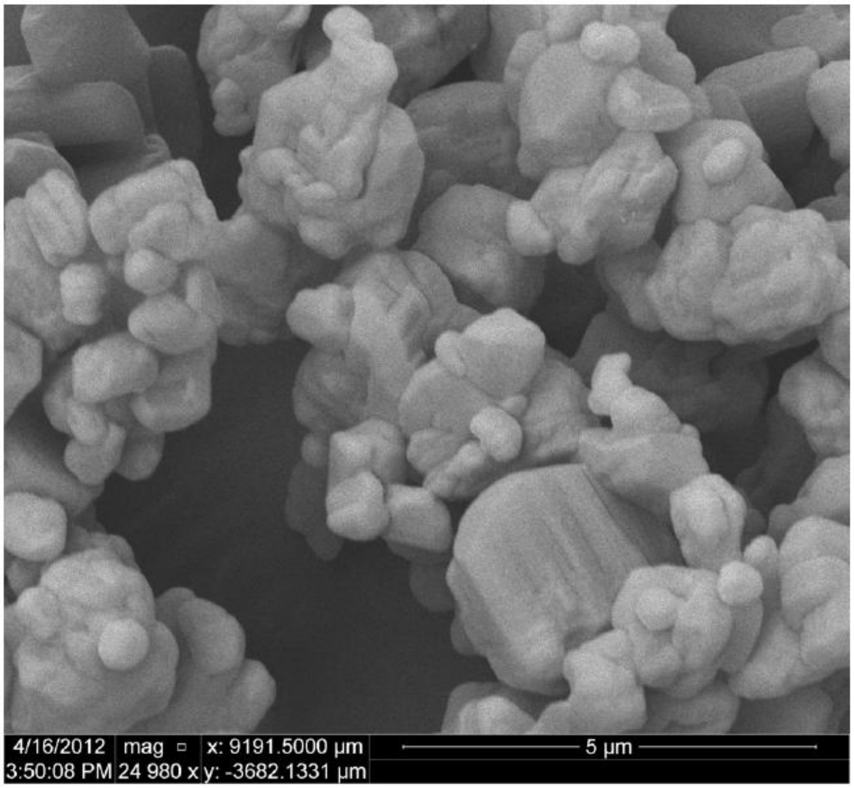


Figure 44. FESEM of SBC-1 from Tube 7 (Nanotech Analytics Report 43104-15, AA-7)

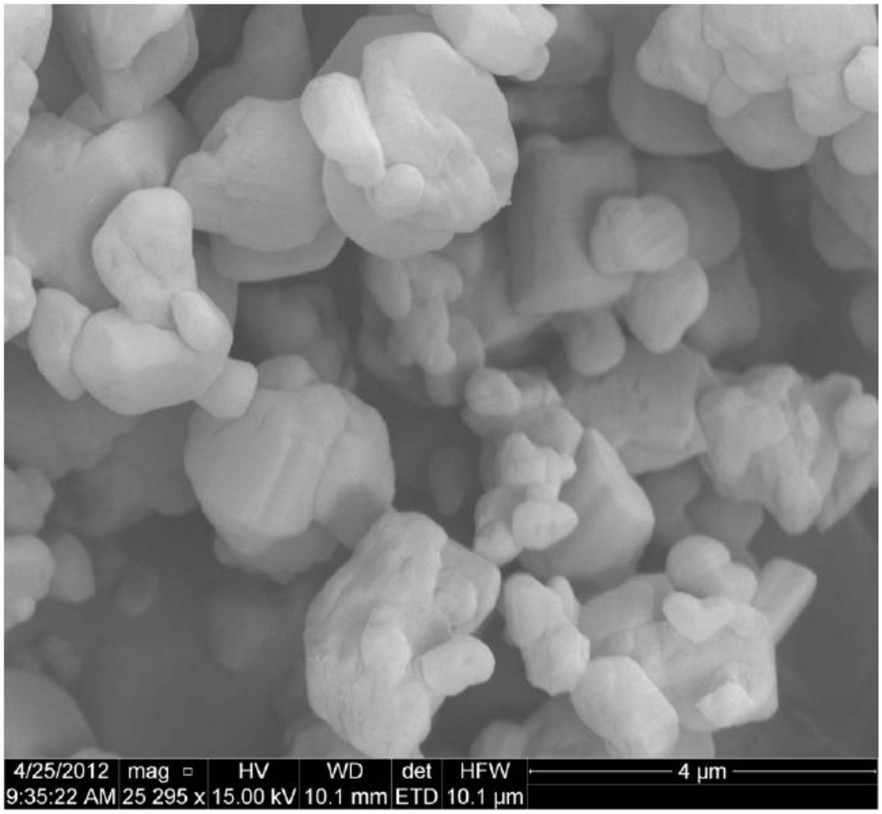


Figure 45. FESEM of SBC-1 from Tube 8 (Nanotech Analytics Report 43104-16, AA-8)

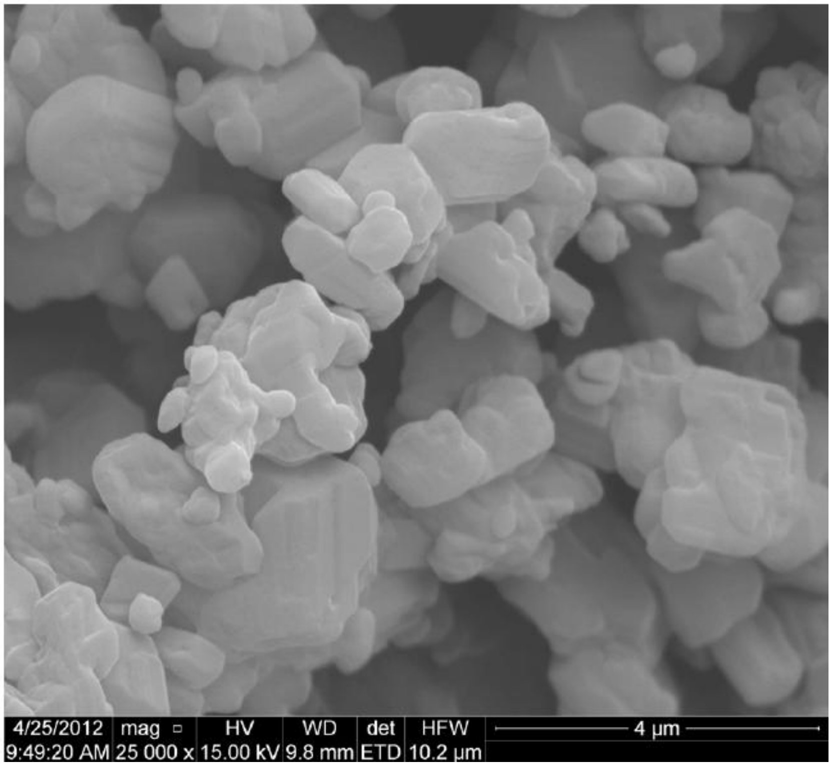


Figure 46. FESEM of SBC-1 from Tube 10 (Nanotech Analytics Report 43104-18, AA-10)

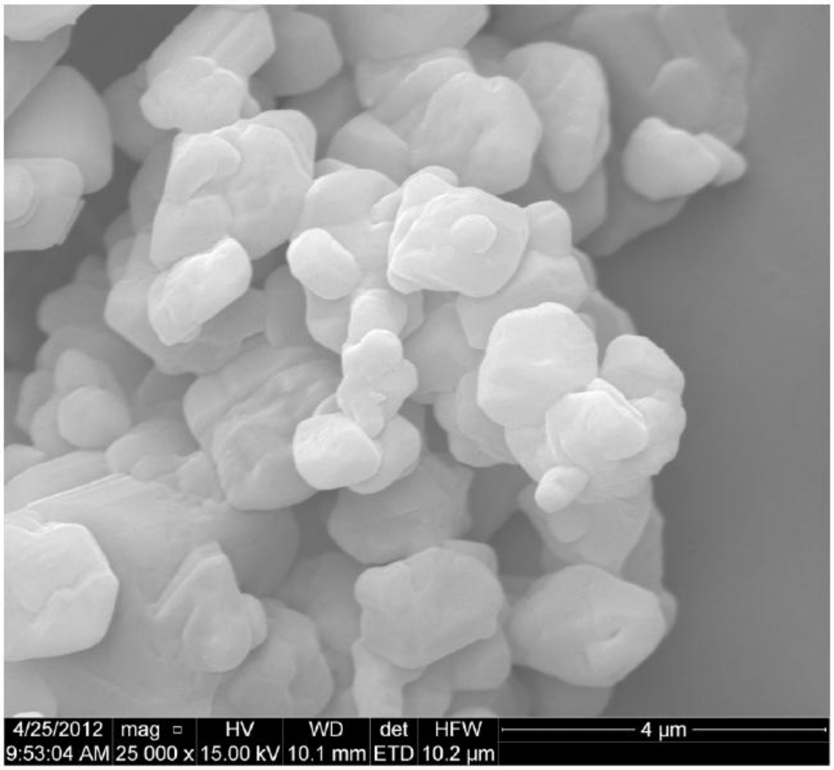


Figure 47. FESEM of SBC-1 from Tube 11 (Nanotech Analytics Report 43104-19, AA-11)

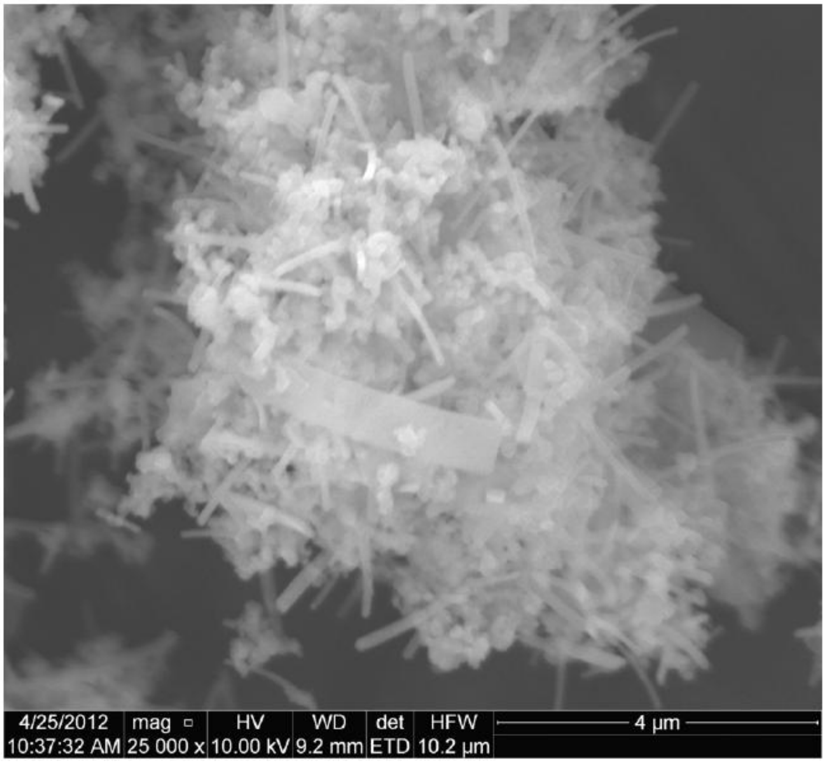


Figure 48. FESEM of SBC-2 from Tube 13 (Nanotech Analytics Report 43104-20, AA-13)

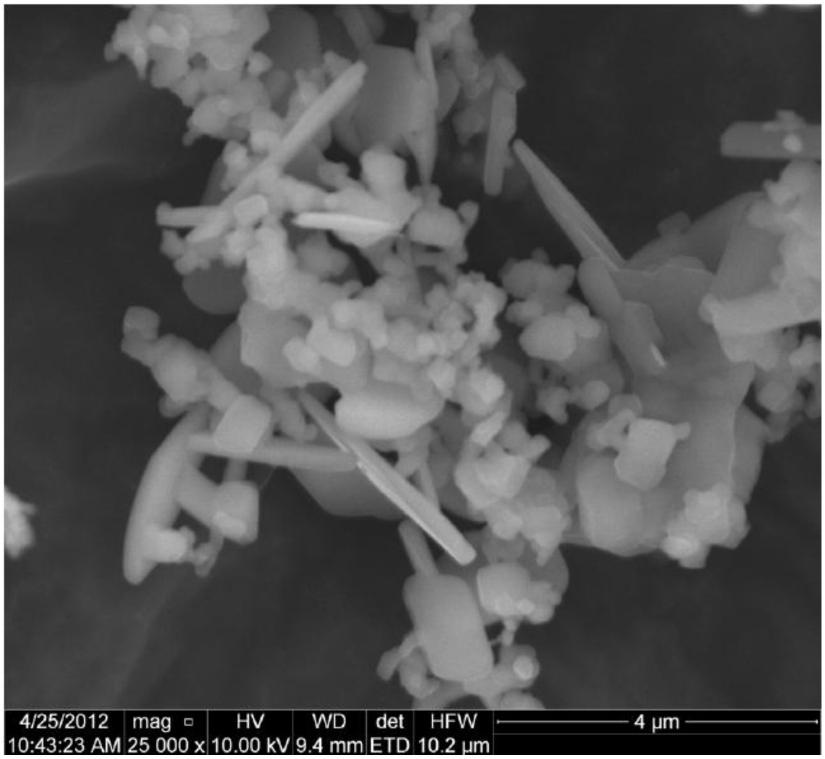


Figure 49. FESEM of SBC-2 from Tube 14 (Nanotech Analytics Report 43104-21, AA-14)

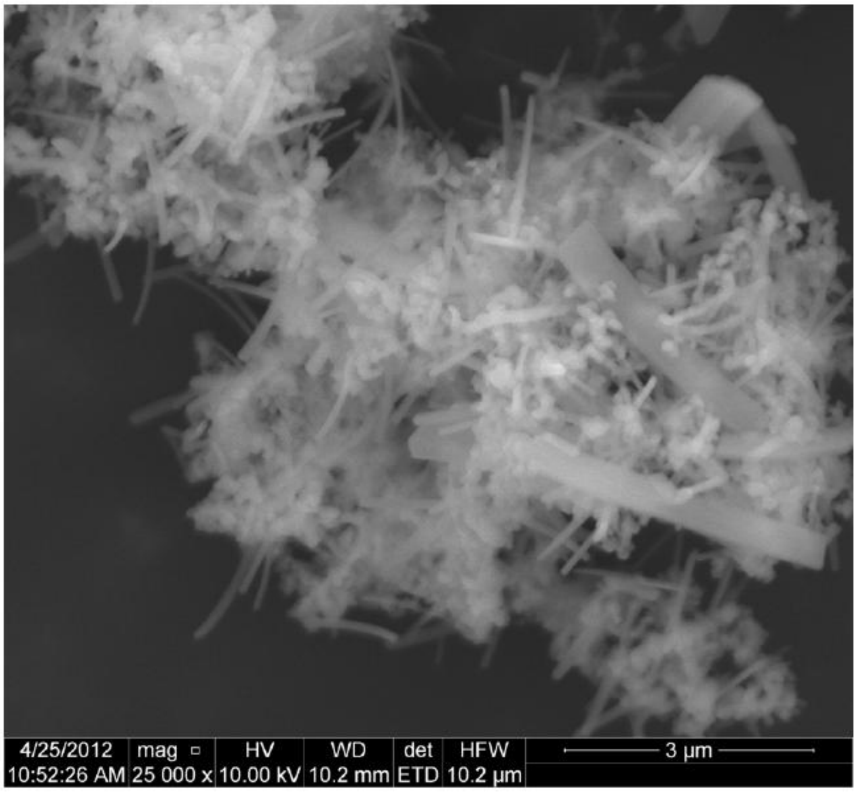


Figure 50. FESEM of SBC-2 from Tube 16 (Nanotech Analytics Report 43104-22, AA-16)

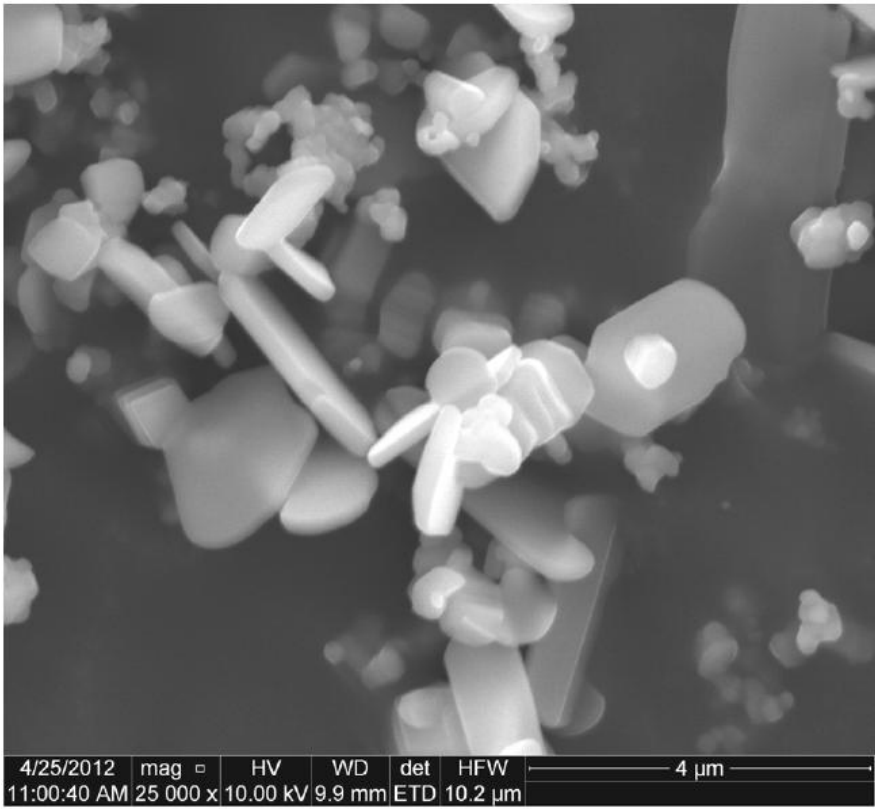


Figure 51. FESEM of SBC-2 from Tube 17 (Nanotech Analytics Report 43104-23, AA-17)

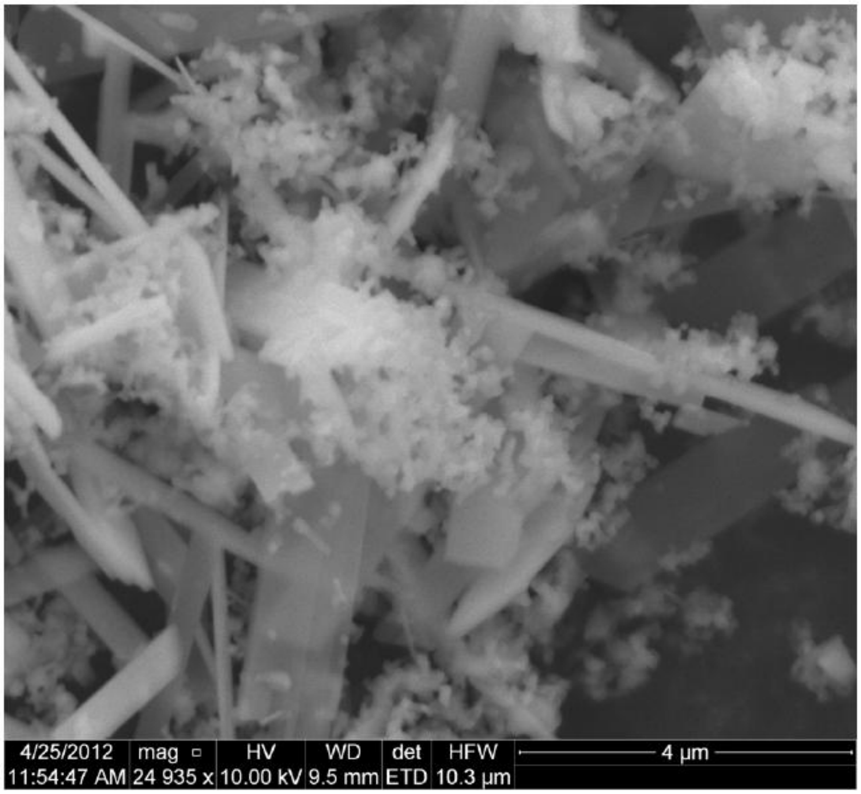


Figure 52. FESEM of SBC-2 from Tube 19 (Nanotech Analytics Report 43104-24, AA-19)

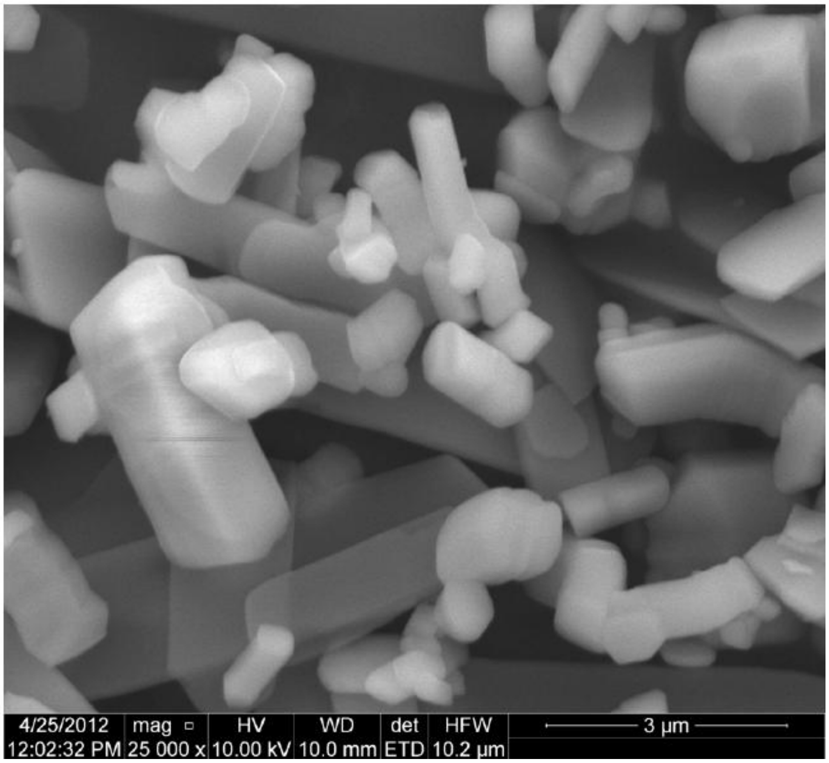


Figure 53. FESEM of SBC-2 from Tube 20 (Nanotech Analytics Report 43104-25, AA-20)

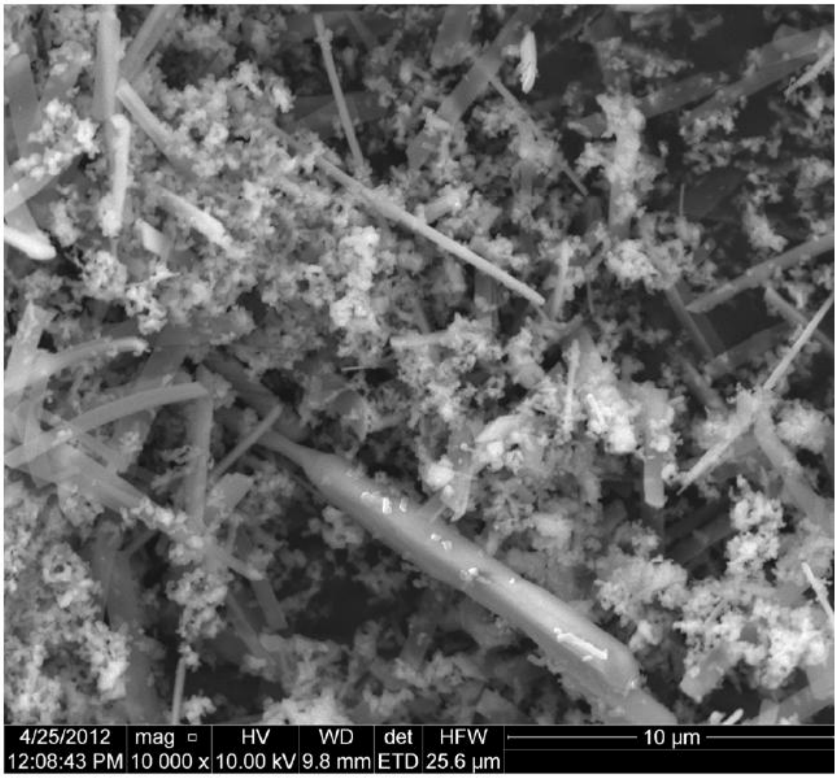


Figure 54. FESEM of SBC-2 from Tube 22 (Nanotech Analytics Report 43104-26, AA-22)

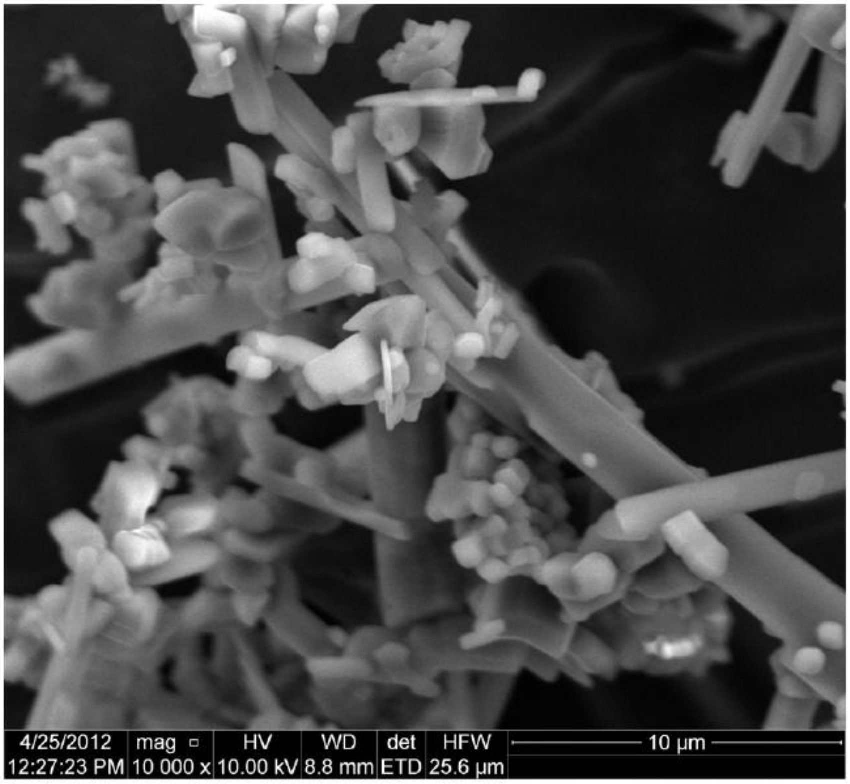


Figure 55. FESEM of SBC-2 from Tube 23 (Nanotech Analytics Report 43104-27, AA-23)

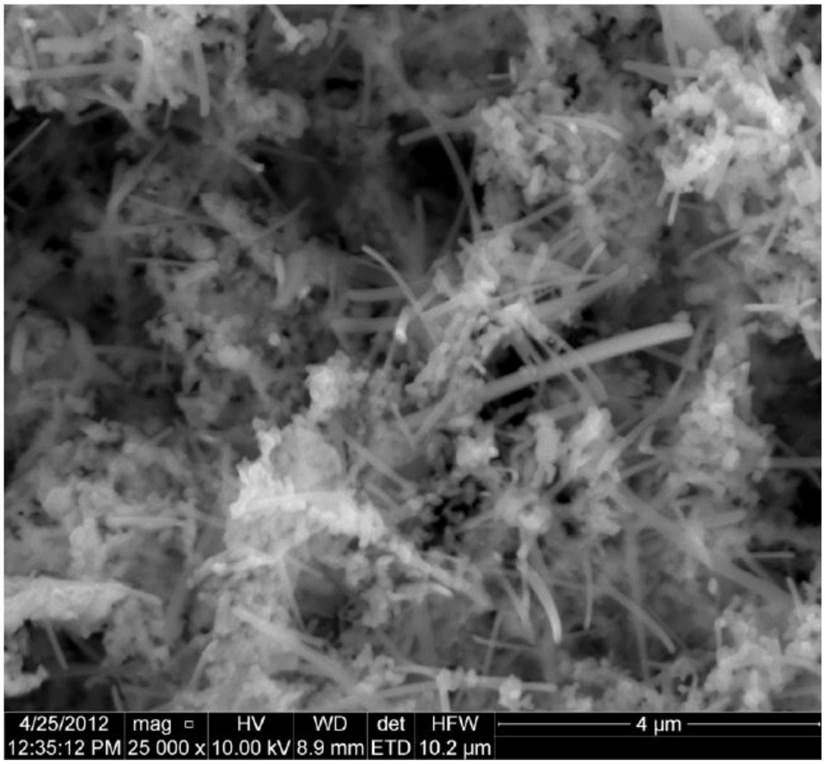


Figure 56. FESEM of SBC-2 from Tube 25 (Nanotech Analytics Report 43104-28, AA-25)

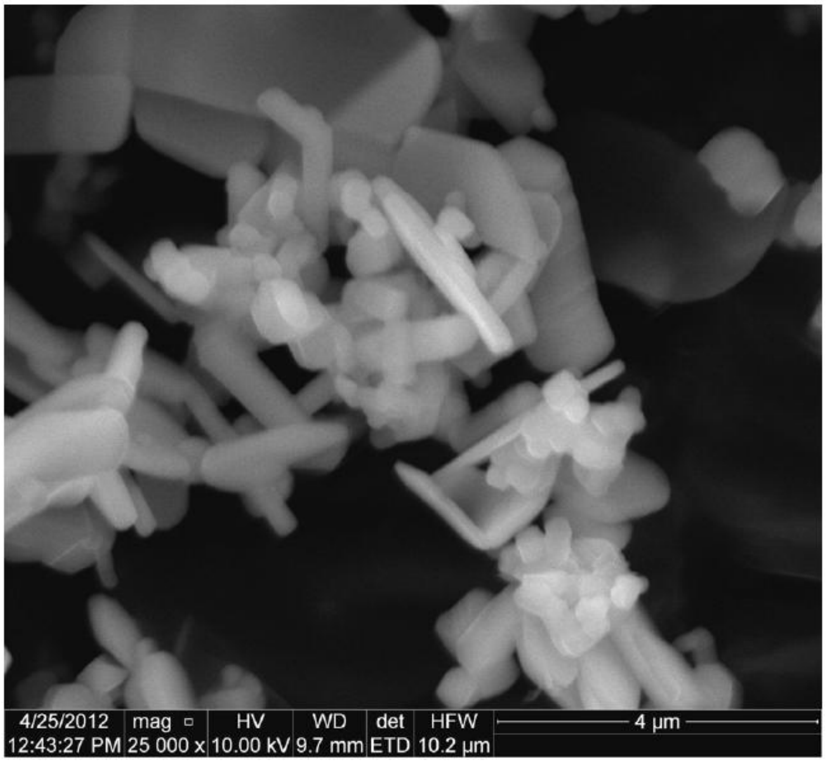


Figure 57. FESEM of SBC-2 from Tube 26 (Nanotech Analytics Report 43104-29, AA-26)

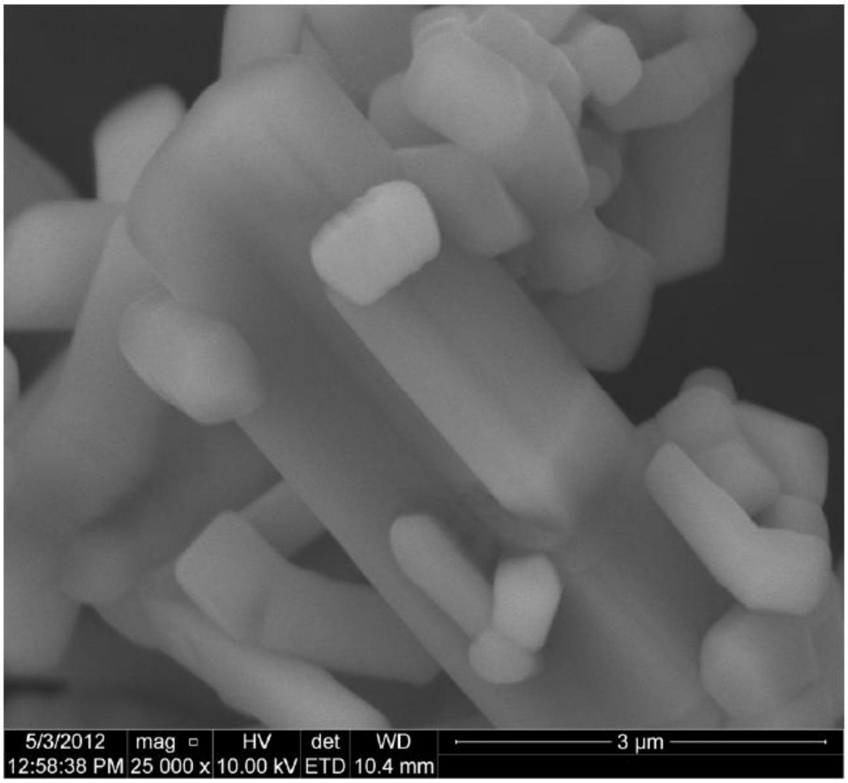


Figure 58. FESEM of SBC-2 from Tube 28 (Nanotech Analytics Report 43104-31, AA-28)

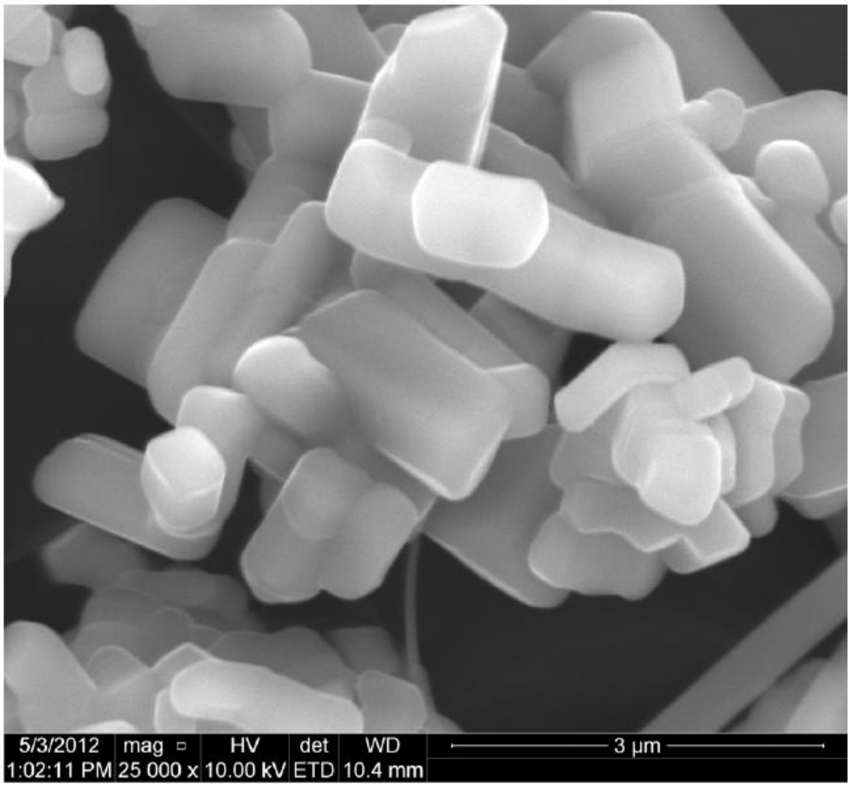


Figure 59. FESEM of SBC-2 from Tube 29 (Nanotech Analytics Report 43104-32, AA-29)

A review of the SBC-1 powder FESEM evidence little accelerated aging effect on the particle sizes of the SBC powder, Table 8.

Table 8. Comparison of FESEM photos of SBC-1 control and accelerated aging pairs.

Control tube # (Figure #)	AA Tube #, (Figure #)	Visual comparison of SBC-1 powders from accelerated aging tubes relative to the control tube - FESEM photos
1 (40)	2 (41)	No observable significant changes in particle sizes or morphology
4 (42)	5 (43)	No observable significant changes in particle sizes or morphology
7 (44)	8 (45)	A slight decrease in number of small particles (< 1 um) in accelerated aging sample
10 (46)	11 (47)	A slight decrease in number of small particles (< 1 um) in accelerated aging sample

A review of SBC-2 powder FESEM evidence progressive loss of smaller needle like particles and increasing prevalence of the larger more regular morphology crystals following accelerated aging of the SBC-2 powder, Table 9.

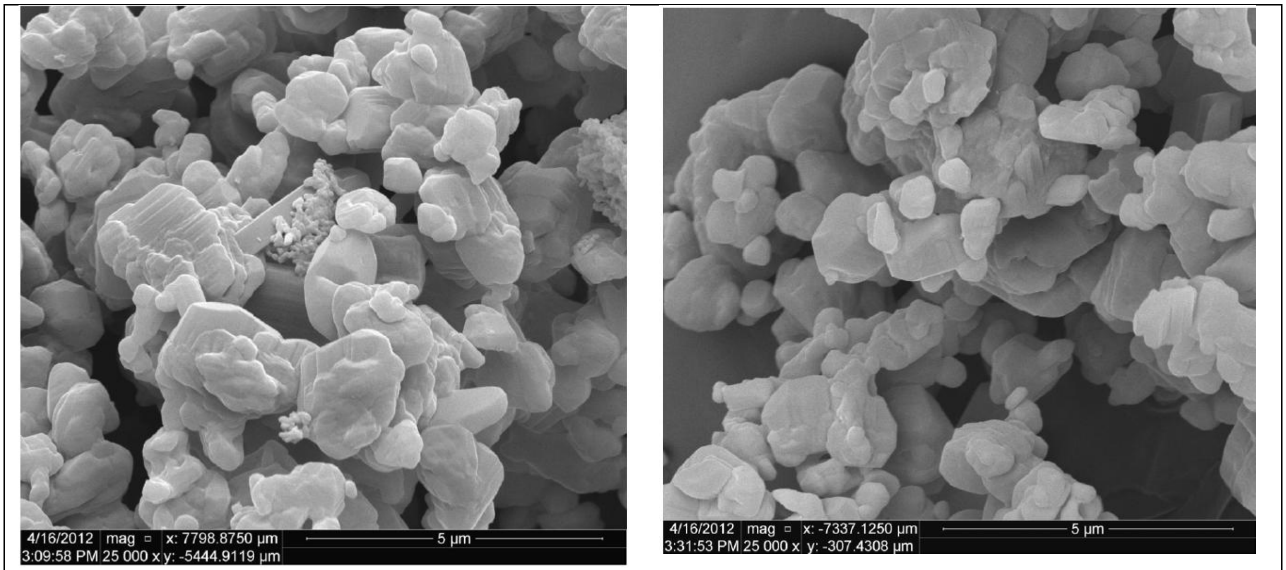
Table 9. Comparison of FESEM photos of SBC-2 control and accelerated aging pairs.

Control tube # (Figure #)	AA Tube # (Figure #)	Visual comparison of SBC-2 powders from accelerated aging tubes relative to the control tube - FESEM photos
13 (48)	14 (49)	Decreased abundance of small fine needles and particles, more regular particles (~ 0.5 um) in accelerated aging sample
16 (50)	17 (51)	No fine needles only flat plates of SBC ~0.2 um thick and 1 to 1.5 um across in the accelerated aging sample.
19 (52)	22 (54)	No fine needles only larger more regularly shaped particles 1 to 2 um in size in the accelerated aging sample.
22 (54)	23 (55)	No fine needles only very large more regularly shaped particles 2 to 4 um (and some >10 um) in size in the accelerated aging sample

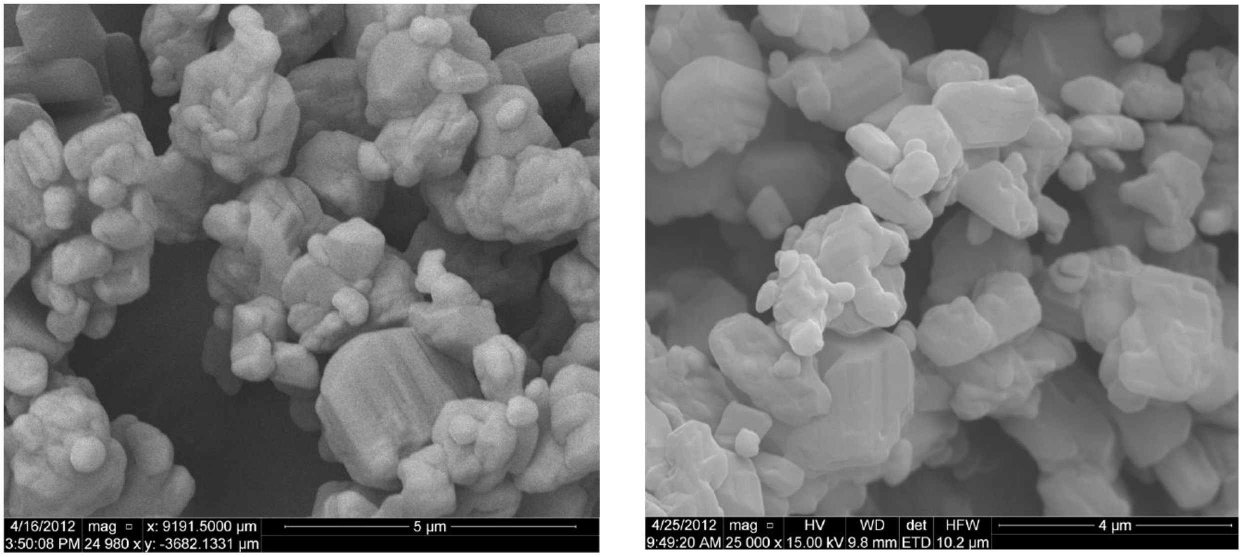
Table 10. Comparison of FESEM photos of SBC-2 (slurry) control and accelerated aging pairs.

Control tube # (Figure #)	AA Tube # (Figure #)	Visual comparison of SBC slurry SBC powders from accelerated aging tubes relative to the control tube - FESEM photos
25 (56)	26 (57)	No fine needles only larger more regularly shaped particles and plates of SBC 1 to 2 um in size in the accelerated aging sample.
25 (56)	28 (58)	No fine needles – only large regularly shaped particles, some plate-like, of SBC 1 um to 3 um.
25 (56)	29 (59)	No fine needles – only large regularly shaped particles (no plate-like particles) of SBC 1 um to 3 um.

The SBC-1 control samples FESEM are collected together for ease of comparison, Figure 60. The assembled photos evidence little if any change in the particle sizes of the SBC-1 powders over the test period of 1 week.



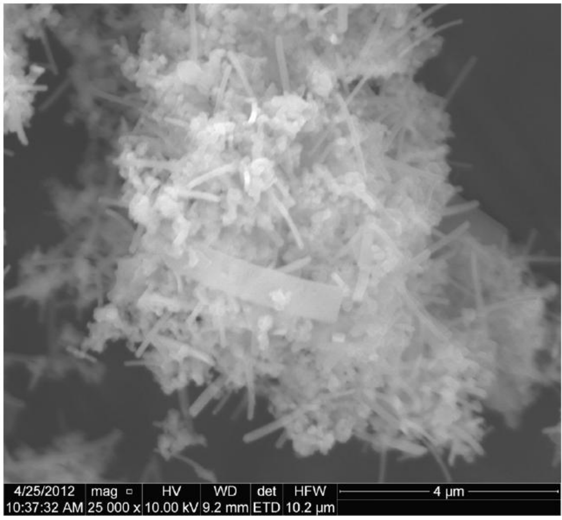
FESEM of SBC-1 dried, (Tube 1) FESEM of SBC-1 as received, (Tube 4)



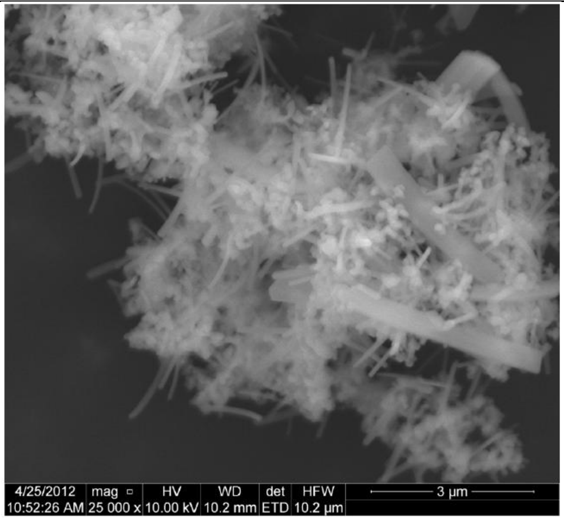
FESEM of SBC-1 300ppm water (Tube 7) FESEM of SBC-1 600ppm water (Tube 10)

Figure 60. SBC-1 control samples FESEM (Tubes 1, 4, 7, 10)

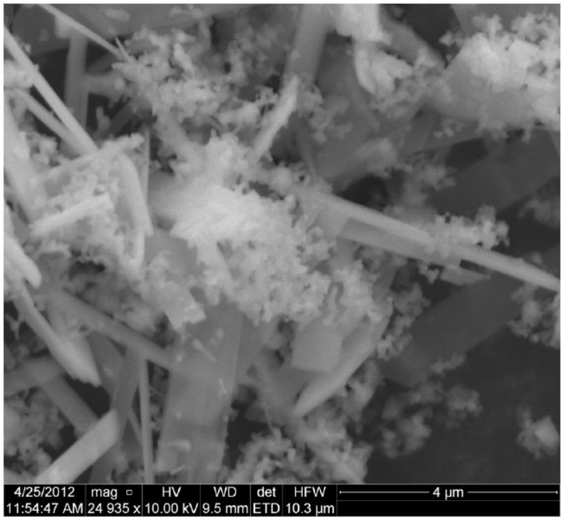
The SBC-2 control samples FESEM are collected together for ease of comparison, Figure 61. The assembled photos evidence a decreasing small needle crystal presence as tube water content is increased. Those tubes in which the water content was the highest have the largest particle sizes of the SBC-2 powders. These photos represent the room temperature aging effects on SBC-2 in the presence of water over a period of approximately 1 week. The driest SBC test samples appear to have changed little or not at all during the one week period.



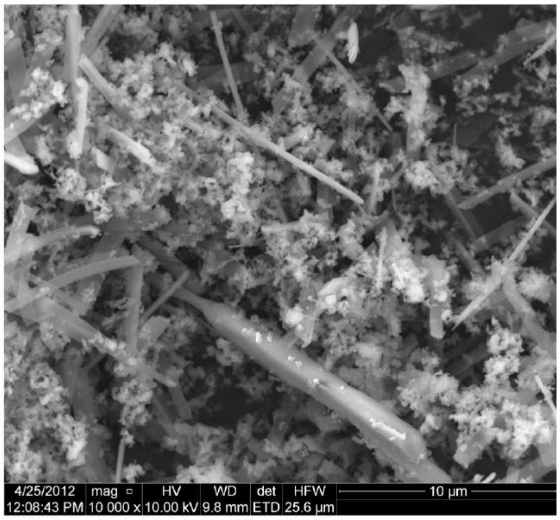
FESEM of SBC-2 dried (Tube 13)



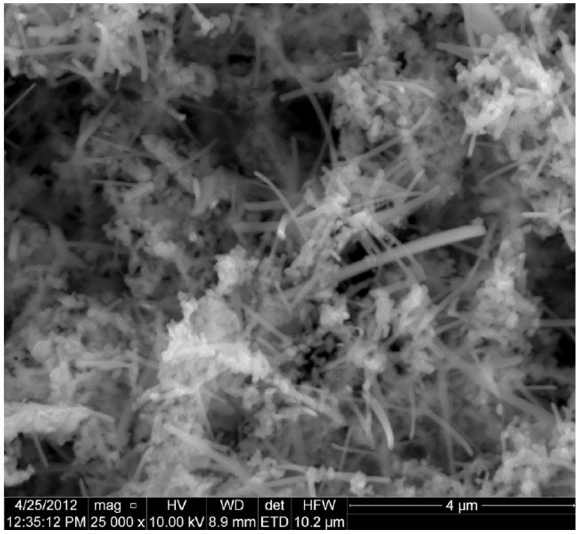
FESEM of SBC-2 as received (Tube 16)



FESEM of SBC-2 300ppm water (Tube 19)



FESEM of SBC-2 600 ppm water (Tube 22)
Note a lower magnification used for Tube 22
SBC FESEM photo



FESEM of SBC-2 slurry (Tube 25)

Figure 61. SBC-2 control samples FESEM (Tubes 13, 16, 19, 22, 25 slurry)

Water content of SBC powders used to prepare accelerated aging tubes was determined using the gas chromatographic method developed by Galbraith Laboratories, Table 11. The drying process used to wash SBC-1 powder reduced the water content by 76ppm while the same process reduced SBC-2 water content by 1558ppm. Even with the potentially large amount of water contained in the HFC_227ea little change in SBC-1 powder particle appearance was noted in the FESEM photos reviewed above. SBC-2 powders were clearly much more affected by the additional water content of the HFC-227ea. The HFC-227ea water content is expected to partition between the SBC powders and the liquid HFC-227ea. The extent of this partition is unknown. Should all the water from the 300ppm and 600ppm HFC-227ea used to prepare samples be completely absorbed or adsorbed the SBC water contents would increase by 31200 and 62400 ppm respectively. As the HFC-227ea washing process is so effective in reducing SBC water content it maybe that the water partitioning equilibrium favors the HFC-227ea.

Table 11. Stock SBC powder water content and HFC-227ea water spike levels

Accelerated aging tube #'s	SBC Water Content (ppm)	Water contained in HFC-227ea (ppm)
1 to 3	433	As delivered stock
4 to 6	509	As delivered stock
7 to 9	509	300
10 to 12	509	600
13 to 15	2029	As delivered stock
16 to 18	3587	As delivered stock
19 to 21	3587	300
22 to 24	3587	600
25 to 27	--	unknown
28	--	*1,500 ppm spike
29	--	500 ppm spike

* This spiked water amount exceeds the 600 ppm limit for water solubility in HFC-227ea.

Water content of both the room temperature particles morphology as seen in the FESEM photos collected in Figures 60 and 61 to a lesser degree than observed in the thermal cycling samples. The driest control samples (tubes 1 and 13) evidenced little morphology change while the wettest sample tubes (those containing HFC-227ea spiked with 600 ppm water) showed FESEM evidence of marked changes in particle morphology. In this limited study of SBC accelerated aging of SBC slurries water content correlates with outcome in terms of particle morphology leading to the specification of conservative limits for SBC water content – less is better. The room temperature aged (control) samples with the highest levels of water did evidence some changes to morphology while the dries showed little evidence of change and appeared to be stable suspensions from a particle appearance point of view. Given that all samples subject to diurnal thermal cycling re-suspended to near original levels and showed no loss of flow or tendency of the SBC particles to form hard clumps or cakes the HHFE discharge would not be compromised. Fire suppression performance could not be evaluated post-test as the amount of material available was insufficient however for the driest and “as received” SBC samples changes in particle morphology post diurnal thermal cycling are slight if any and fire suppression performance would not be affected.

Once the attrition based fielding of the HHFE occurs periodic inspections of fielded extinguishers (including at a minimum HHFE discharges, fire suppression testing and a UL-8 test) would establish a reliable shelf life for the SBC HFC-227ea agent.

Analytical Methods Development and Support to Fielding of SBC HFC-227ea Agents

In the course of SBC powder development a number of characterization needs arose. Some of the methods reflected the particular need to characterize physical and chemical properties of suspensions that are critical to the performance of the HHFE. Others analytical needs were required to adequately characterize both the developmental and final selected SBC powders to be employed in the HHFE. A brief description of each analytical method developed follows. In each case the full method can be found in this report’s appendices.

Suspendability of SBC in HFC-227ea.

The method for evaluating suspendability of SBC in HFC-227ea was developed in order to characterize the level of SBC slurry with respect to the column of HFC-227ea in a cylindrical container. Full suspendability of SBC in HFC-227ea is expected to limit the tendency for formation of a SBC sedimentation layer at the bottom of the cylinder under normal HHFE handling conditions as well as ensure that on discharge of the HHFE the percent composition of SBC in HFC-227ea remains as consistent as possible.

The glass containers employed in this testing are rated to a working pressure of 225psig – well in excess of the 58 psig room temperature vapor pressure of the HFC-227ea. Each tube is coated with a plastic protective coating to prevent scratching of the glass which could lead to failure under pressurization. The tubes are equipped with removable stainless steel closures and valves. The method developed serves to evaluate both dry powders as well as slurries of SBC and HFC-227ea, The method is described more fully in the Appendix and can also be found in MIL-DTL-32412 - Individual Specification Requirements for Class I (SBC1) and Class II (SBC2) Agents and Test Methods which is the published specification.

FESEM SBC Powder Characterization

Characterization of SBC particle sizes and particle morphology was accomplished by field emission scanning electron microscopy (FESEM). This method involves placing prepared dry SBC samples into a high vacuum chamber and illuminating the sample with an electron beam. Because SBC is a non-conductive material and also thermally unstable the electron beam can induce surface charging which affects image quality and slow decomposition which can change particle appearance. To alleviate these two problems SBC prepared samples can be coated with gold in a sputtering process. Regardless, successful evaluation by any laboratory will involve optimizing the imaging by variation in the sample preparation method and FESEM conditions. Due to the tendency of SBC to pick-up water from the atmosphere sample preparation should be performed under dry-box conditions. The method is described more fully in the Appendix and can also be found in MIL-DTL- 32412 - Individual Specification Requirements for Class I (SBC1) and Class II (SBC2) Agents and Test Methods which is the published specification.

SBC Powder Particle Size Distribution

Slight variations in the sample preparation SBC powder/iso-propyl alcohol suspension method proved to have uncontrollable and large impacts on the particle sizing instrumental results. This difficulty could not be resolved satisfactorily and the goal of obtaining particle size distribution information was abandoned. In lieu of particle size distribution an SBC characterization strategy based on particle surface area, FESEM observed particle morphology and particle size upper limits was employed for characterization of SBC powders.

SBC Powder Water Content

Karl Fischer electrochemical water analysis and gas chromatographic (GC) analysis of solvent extracts of SBC samples were evaluated. The Karl Fischer method was reviewed and rejected due to expected degradation of the instruments electrodes which would result in calibration drift, poor sample analysis repeatability and analytical quality control complications. GC analysis of solvent extracts of SBC proved to be the easiest and most reliable water characterization method once effective solvent drying techniques were identified, implemented and optimized. A documented GC analytical procedure was tested and approved. Critical need is a very dry solvent for use in the SBC sample water extraction step. A solvent drying method was found (Williams and Lawton, Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants, J. Org. Chem., 2010, 75(24) pp 8351-4) and provided to Galbraith Laboratories for use in this crucial step. The new SBC water content method is available through Galbraith Laboratories (Knoxville, TN) as method GLI-ARMY-C101. The method is described more fully in the Appendix and can also be found in MIL-DTL- 32412 - Individual Specification

Requirements for Class I (SBC1) and Class II (SBC2) Agents and Test Methods which is the published specification.

Drying of SBC powders

Drying SBC powder was attempted using high vacuum, solvent washing, and desiccants. Of these methods only the desiccant based method showed promise. The vacuum based method is too aggressive and appears to push the room temperature conversion of sodium bicarbonate to the sodium carbonate form with loss of the by-product water. The desiccant based method attempted employed 3A Molecular Sieve in direct contact with the SBC HFC-227ea slurry. The testing employed a cylinder containing 180g of oven dried 3A Molecular Sieve and 1400g of agent slurry. The container was agitated by shaking daily for 2 weeks. At the end of 2 week SBC samples were obtained by filtration and degased to remove residual HFC-227ea in a dry box and submitted for water analysis using the method AP GLI-Army C101. The test was done in duplicate with two dried and two control samples being prepared and submitted for analysis.

The results of the analysis were as follows: Control sample SBC water contents were 2425 and 2211 ppm for an average of 2318ppm of water. The drying test sample water contents were determined to be 1442 and 1332 ppm for an average water content of 1387ppm. This drying process reduced water content by 40%. Should the need arise to achieve dryer SBC HFC-227ea agent slurries this drying method would be a potential approach.

SBC Powder Surface Area characterization

Candidate methods for evaluating SBC powders included BET surface area and Nuclear Magnetic Resonance (NMR) decay time analysis. As the BET method involved an initial sample heating/drying process which could confound the results it was not pursued. The NMR method was tested and it provided repeatable results.

The NMR based surface area method is described more fully in the Appendix and can also be found in MIL-DTL- 32412 - Individual Specification Requirements for Class I (SBC1) and Class II (SBC2) Agents and Test Methods which is the published specification. Several internet sites detailing the theoretical and instrumental design employed in an NMR surface area analysis exist.

SBC powder inhalation health hazard evaluation test support

Support was provided to U.S. Army Public Health Command (USAPHC) health hazard evaluations of SBC-1 powder and SBC-2 HFC-227ea agent. The results of the USAPHC evaluations were:

- A Toxicology Clearance for SBCs (Jet-milled SBC) was obtained.
- A Health Hazard Assessment (HHA) was performed by the U.S. Army Public Health Command (USAPHC) on discharged agent containing the Nanomaterials Company SBC.

SBC and SBC/HFC-227ea Suspension Specification

The test procedures and evaluation criteria employed in evaluation of SBC1 and SBC2 powders and the SBC2 HFC-227ea agent blend were selected and compiled into a material specification document. The document is entitled "**MIL-DTL- 32412 - Individual Specification Requirements for Class I (SBC1) and Class II (SBC2) Agents and Test Methods". This document is available on the internet at:**

http://assistdocs.com/search/document_details.cfm?ident_number=279112&StartRow=4651&PaginatorPageNumber=94&all_words_string=CONTRACT%20PERFORMANCE%20REPORT&search_method=CONTENT

The material specification documents all measurement value ranges of acceptability. It also documents all standard and non-standard test methods, and specialized supplies needed to perform the SBC testing. Included in this document are:

- Moisture Content Limits for SBC
- Caking and Lumping Check Method
- SBC/HFC-227ea Slurry Flow Check
- SBC Suspendability in HFC-227ea Limits
- Average Particle Aspect Ratio (width/length) Limits
- SBC Powder Surface Area Acceptable Range
- Particle Size Requirement (Longest Dimension)
- SBC_S Concentrations in HFC-227ea, Weight % Limits
- Color
- SBC Water Content (ppm) Limits

- Surface Area Characterization - Instrumentation and Method and Limits
- FESEM Sample Preparation and Analysis Technique

Appendix A.
FESEM Method Sample Preparation

Particle characterization using Field Effect Scanning Electron Microscopy

<u>Procedure</u>. Prepare FESEM samples as follows:

For FESEM where a circular, 1 cm, stud is used. Under dry nitrogen, a portion of the SBC_S should be placed into a small jar having an opening Inner Diameter (ID) less than 1 cm and sealed tightly. Keep FESEM laboratory room at 68^o F or lower if possible. Avoid exposing the SBC_S to high humidity and store all samples and preparation materials in desiccators or dry-boxes. Place a piece of carbon tape onto the stud. Open the small jar and place the stud on top of the jar, tape facing the jar opening.

Gently shake the jar/stud. Tap the stud to remove loose SBC_S powder and quickly place into the FESEM sample chamber. Repeat the above but this time place into the sputtering tool for very light coat of gold. Remove and place into the FESEM sample chamber. Note: During sputtering, keep the gold coating to a minimum otherwise decomposition may occur. During analysis, compare the gold coated material to the un-coated material. The uncoated material may only endure a few tens of seconds under focus before the FESEM breaks down the SBC_S into sodium carbonate. Also "charging" for the larger particles is likely. Once in focus, moving to fresh portions of the stud may allow for resolution of detail. The gold coated material should last longer under the beam, but will eventually breakdown as well.

An alternative approach to the preparation of SBC_S is to paint an FESEM stud with a very thin coating of conductive paint and let dry. Using a fine pipette, take a single drop of the dispersion and place it on the painted stud and quickly place into the FESEM sample chamber. The Isopropyl Alcohol (IPA) will evaporate and the particles should stick to the IPA-rewetted paint surface. Repeat the above but this time place into the sputtering tool for very light coat of gold. Remove and place into the FESEM sample chamber. Obtain at least 10 high magnification (20,000 times) non-overlapping photos of the SBC_S sample with the measurement scale shown on the photo. Note: low energy beam currents are needed to avoid decomposing the sample.

Appendix B.

Evaluation of FESEM photos of SBC-1 for characterization of particle morphology (aspect ratio) and dimensions.

Evaluation of the FESEM photos of SBC_S. Equipment needed - needle tipped drafting caliper, steel ruler (inch or centimeter ruling). The procedure shall follow steps 1 through 9, below.

1. Blow up photos to full page size and print out on high contrast printer. Label the printed pages in sequence. Label all printed pages with the lot traceability information, source of sample, and date of characterization.
2. Examine each numbered photo to identify the larger and longer crystals and mark each identified crystal numerically in sequence (1, 2, 3, 4 etc). Note: only select crystals whose boundaries are visible or substantially visible.

3. Using the caliper and ruler measure the scale on each photo and record the length of the scale (in inches or mm) and the scale value (microns).

4. Using the caliper and ruler, obtain length and width information (inches or mm) for the identified larger and or longer crystals.

5. Record all crystal length and width information (in inches or mm).

6. Convert all crystal length and width information to microns using the scale measurement as follows: length = measured length (obtained in step 5) times the scale (usually microns) divided by the length of the scale (determined in step 3)

7. Calculate aspect ratios by dividing width by length values of step 6 for each crystal.

8. Review the data and determine morphology and number of crystals of length exceeding limits for maximum length.

9. Review the data and determine morphology based on aspect ratio (width/length): Needle like samples will exhibit aspect ratios less than 0.2. Granular particles will exhibit aspect ratios (width/length) greater than 0.5.

Appendix C.
SBC Powder Surface Area characterization

Specific surface area test procedure. The method requires use of a Nuclear Magnetic Resonance (NMR) based surface area analyzer. The commercially available Acorn Area -Nuclear Magnetic Resonance (NMR) based surface area analyzer using AreaQuant software version 0.8.3. Manufacturer - Xigo Nanotools, 116 Research Drive Bethlehem, PA 18015 has been successfully employed to characterize both the Class I and Class II agents. The phone number for Xigo Nanotools is (610) 849-5090. See web-page http://www.xigonanotools.com/ for links to additional information.

The Acorn Area measures the wetted surface area of nano particle dispersions using a proton NMR technique. This method relies on the observation that liquid on the particle surface has a relaxation time orders of magnitude smaller than bulk liquid (i.e., liquid far away from the particle surface). The relaxation time of the dispersion is comprised of the response from both bulk and surface liquid, shifted from the bulk liquid in proportion to the quantity of liquid on the particle surface. The method is independent of the particle size distribution, shape, or porosity. However, the calculation of an absolute particle surface area requires a value for ka, a parameter which characterizes the relaxation time shift per unit area for a given particle-liquid combination. A ka value of 0.0026g/m2/ms is to be used in the calculation of surface area.

The suspension fluid is anhydrous n-dodecane (Sigma-Aldrich). Suspensions are prepared at approximately 13 wt% by the simple process of adding a fixed volume of n-dodecane to a known weight of the dry SBC_S powder. The proto-suspensions are then dispersed using a micro-homogenizer. Once prepared, the samples are then diluted by addition of n-dodecane until the “viscosity” is such that the suspension is capable of being the pipette (approximately 0.3 mL) into 4 mm ID glass NMR tubes. At this final concentration, virtually no sedimentation should be observed after 24 hours storage.

A single 0.5 ml aliquot of sample is placed in a 120 mm in length NMR tube, capped and inserted into the Acorn Area. Prior to the actual sample measurement the Xigo Nanotools verification reference solution is used to ensure that the instrument is properly functioning and that the reference frequency is correct. The verification standard is an aqueous solution of a paramagnetic material that replicates the relaxation behavior of a concentrated particulate dispersion without the complications associated with concentrated dispersions, such as settling, flocculation, etc. The verification standard has a relaxation time of approximately 45ms. The surface area is measured using a T2 measurement obtained from a CPMG sequence with 625 echo cycles and $\tau = 0.5$ ms, averaging 8 scans with a recycle delay of 5000 ms. See instrument procedures and operational instruction manual for data entry and sample introduction procedure. Two separate aliquots are taken from each bulk suspension. Each sample is measured 5 times. The specific surface area is calculated from the average T2 value (10 measurements in all) for each sample.

Note that characterizing specific surface area by measuring T2 (spin-spin relaxation time) in 1H-NMR is a well-established, generic technique, not one that requires a specific piece of software or specialized hardware. An online tutorial entitled "Measuring the Specific Surface Area of Nanoparticle Suspensions using NMR" can be viewed at http://cnx.org/content/m34663/latest/ . Alternate instrument vendors with NMR capabilities could adapt their instruments and develop equivalent surface area determination methods if needed.

Appendix D.
Jet-milling method for preparation of SBC-1

PROCESSING of JET-MILLED SODIUM BICARBONATE and HFC-227ea into a SLURRY

SCOPE

Scope. This procedure was prepared for the US Army Aberdeen Proving Ground, to produce a slurry of the Class I Agent. A Class I Agent slurry is the mixture of HFC-227ea and SBC-1. Before the slurry is mixed, the SBC-1 needs to be jet-milled to the micron particle size and, in a separate process, mixed "blended" with the HFC-227ea.

Applicability. The requirements specified in this appendix are required to meet Class I specifications (Table I). However, while this size reduction method was developed for the purpose of this Appendix other equivalent size reduction processes may exist. The purpose of this procedure is to describe a method for producing a slurry of HFC-227ea and SBC-1 where the SBC-1 is jet-milled to the micron particle size and is then blended with the HFC-227ea to produce a slurry of SBC_S suspended in HFC-227ea that will be used in fire extinguishing hardware. The procedure defines the reagents and equipment required for executing the method, the steps for carrying out the analysis, the controls for insuring quality of the results, and the calculation and reporting requirements.

APPLICABLE DOCUMENTS: (Not Applicable)

REQUIREMENTS

Test procedure.

B.3.1.1 Jet-Milling of Sodium Bicarbonate to prepare SBC-1. Start with USP grade sodium bicarbonate. Table B-I contains the parameters used to make the jet-milled material SBC-1. Figure B-1 shows a photograph of the jet-milling equipment employed. Table B-II shows the difference in particle size distributions between the feed material and the processed material for one of the batches. The values given are weight by material volume. The particle size measurement instrumentation used was a Malvern Mastersizer 2000. The particle size values listed in Table B-II were obtained from the Malvern Mastersizer and are not required - they are provided for reference only.

Processing Equipment. Table B-III contains a list of the processing equipment used to process the jet-milled sodium bicarbonate and HFC-227ea into a slurry. The equipment is assembled using chemical resistant build-your-own hoses according to Figure B-2.

TABLE B-I Parameters used to jet-mill the sodium bicarbonate. (for reference only)

PARAMETER	VALUE
Micronizer Size/Type	8" Open Manifold
Liner Type	Stainless Steel
Total Air Flow	130 Scfm @ 100 Psig, dry nitrogen
Grind Pressure	105 Psi
Feed Pressure	80 Psi
Venturi Throat Dia.	1/4" Dia. Al. Oxide
Feed Nozzle Dia.	# 30
Vortex Finder Dia.	2.0" Diameter
Feeder Type/Size	K-Tron Twin / 35 mm
Feeder Setting	Std. CC Screws / 70 - L
Feed Rate	2 lbs/hr.

FIGURE B-1. Photograph of jet-milling equipment.

TABLE B-II. SBC-1 Particle size distribution (for reference only).

FEED	**PROCESSED**
d10 = 39.09µm	d10 = .665µm
d50 = 78.94µm	d50 = 1.421µm
d90 = 139.95µm	d90 = 2.805µm
d100 = 208.93µm	d100 = 5.754µm

Appendix E.
SBC Water Content Analysis Method

THE ANALYSIS of WATER in SODIUM BICARBONATE by GAS CHROMATOGRAPHY
(AP GLI-Army C101)

(Note: Should the GC method not be available, an alternate, potentially more costly and more complicated procedure for the characterization of water in SBC can be found in the following published paper: Karl Fischer based water content determination method: Determination of Moisture in Sodium Bicarbonate, L. N. Gard, R. C. Butler, *Anal. Chem.*, 1954, 26 (8), pp 1367–1368)

SCOPE

1.1 Scope. This procedure was prepared for US Army Aberdeen Proving Ground, Aberdeen, MD to assess the content of water in Sodium Bicarbonate. The method described in this procedure measures water by gas chromatography (GC) using direct injection and thermal conductivity detection (TCD). There are no specifications for water content of sodium bicarbonate. Sample results are reported as <1% or ≥1% based on comparison to a standard. Quantitative results are also reported for reference purposes. The upper range of this analysis may be extended through dilution. The instrument may be calibrated lower to accommodate samples with low moisture content.

1.2 Applicability. The requirements specified in this appendix are required. The purpose of this procedure is to describe a method for the determination of water (moisture) in Sodium Bicarbonate for US Army Aberdeen Proving Ground, Aberdeen, MD. The procedure defines the reagents and equipment required for executing the method, the steps for carrying out the analysis, the controls for insuring quality of the results, and the calculation and reporting requirements.

2 APPLICABLE DOCUMENTS:

The document number for Galbraith Laboratories analytical method procedure outlined below is:

AP GLI-ARMY-C101, Rev. No. 1 - Method to Determine Amount of Water in Sodium Bicarbonate Powder

Galbraith Laboratories, Inc.
Mailing Address: P.O. Box 51610, Knoxville, TN 37950-1610
Physical Address: 2323 Sycamore Drive, Knoxville, TN 37921-1750
Toll Free Telephone: 1-877-449-8797
Telephone: 1-865-546-1335
Fax: 1-865-546-7209 Fax
e-mail: labinfo@galbraith.com

Method: The Analysis of Water in Sodium Bicarbonate by Gas Chromatography

Summary:
A portion of the sample is accurately weighed directly into a centrifuge tube and immediately covered with a volume of isopropyl alcohol (IPA). The vial is closed tightly, mixed well to produce a slurry of the sample in the IPA, and sonicated/shaken to extract moisture from the sodium bicarbonate into the IPA. The extraction solution is filtered and is transferred to a GC vial for analysis. The injector will aspirate a portion of the solution followed by injecting a controlled volume of it into a gas chromatograph. The extracted water from the sample is detected using a thermal conductivity detector (TCD), and the moisture content is determined by comparison of the sample peak area to the areas of external standards using linear regression. Sample results are reported based on comparison to a QC standard prepared to contain 1% water (limit test). Actual sample concentration from the calibration curve is also provided for reference purposes.

Instruments and Materials

- Analytical balance with sensitivity of 0.01 mg
- Assorted Class A volumetric flasks and pipets
- Hamilton, S.G.E., or other equivalent glass microliter syringes
- GC Vials
- 15 or 50 mL Centrifuge Tubes, Fisher, or equivalent
- Nitrogen or Argon glove box
- Syringes, Disposable Polyethylene, Becton-Dickinson or equivalent
- Filters, Disposable Nylon, pore size = 0.2 µm, 30 mm

HP 6890, or equivalent, equipped with the following:

- A temperature controlled inlet with split/splitless capabilities and with a deactivated glass liner and a glass wool plug.
- A RT-U-Bond, or equivalent, capillary column, 15 m x 0.53 mm x 20 µm df, coating as stated above, either with or without a guard column
- Software controlled data system such as HP ChemStation, Dionex Chromeleon, or equivalent

Reagents

- Isopropyl Alcohol, ACS reagent grade, $\geq$99.9%, or equivalent
- Dried Isopropyl Alcohol – Dry IPA over regenerated molecular sieves for at least 72 hours prior to use. Use at least 15% volume ratio of molecular sieves to solvent.

- High purity air, helium and hydrogen, or equivalent
- Molecular Sieves, 3Å, Sigma Aldrich, or equivalent
- Regenerated molecular sieves – Heat molecular sieves for at least 4 hours at 350ºC. Store the regenerated sieves in a closed container within a desiccator.

Reference Standards

- Water, USP purified

Procedure

Note: Moisture is pervasive in the environment. It is present in air, on the surface of laboratory equipment and in reagent solvents, even if they marketed by the manufacturer as “dry.” The technician is required to use sound technique to minimize exposure of blanks, standards and samples to uncontrolled sources of water. Dry all laboratory equipment in an oven at 105ºC for at least 30 minutes prior to use. Handle samples and prepare solutions in a glove box.

1.0 Blank Preparation

1.1 Prepare in the same way as the sample, omitting the addition of the sample material.

1.2 The blank is carried through all sample preparation and analysis steps, and is used to monitor the moisture level of reagents, supplies and the instrument system.

2.0 Standards Preparation

Note: alternate schemes of preparing the following solutions are permissible as long as the final concentration is the same.

2.1 Primary Stock Solutions (prepare each of these solutions fresh)

Primary Stock #1: Fill a 10 mL volumetric flask halfway with dry IPA. Dispense 100 µL of water into the flask and fill the flask to the mark with dry IPA. This solution is 10,000 mg/L.

Primary Stock #2: Prepare as indicated under Primary Stock #1 using a new volume of water.

2.2 Calibration Standards

Transfer 50, 100, 250, 500 and 1000 µL aliquots of the primary stock solutions into separate GC vials. Add enough dry IPA to each of the first 5 vials to make the final volume 1.0 mL, cap each and invert several times to mix. Do not add any dry IPA to the 1000 µL vial. Cap it and use as-is. Also prepare a calibration blank using the dry IPA. These volumes correspond to the following calibration levels: 500, 1000, 2500, 5000 and 10000 µg/mL, respectively. The instrument may be calibrated lower depending on the water content of the samples.

2.3 *Independent Check Standards (ICS)*

This solution is used to verify the calibration curve and is used as a benchmark for comparison to the unknown sample solution.

Transfer 250 µL of Primary Stock #2 into a separate GC vial. Add 750 µL of dry IPA to a vial to make the final volume 1.0 mL. Cap it and invert several times to mix. This solution is 2500 µg/mL.

3.0 Sample Preparation

3.1 Flush a centrifuge tube with gas from the glove box (nitrogen or argon) and cap.
3.2 Obtain the tare mass of the centrifuge tube and return to the glove box.
3.3 Dispense sample into the vial. Note: the product is likely to be fluffy.
3.4 Recap the vial and obtain the gross mass. Calculate the mass of the sample by subtracting the tare mass from the gross mass.
3.5 Return the sample to the glove box. Dispense 4 mL of dry IPA into the tube for every gram of sample. For example, if 2 grams of sample are in the tube, add 8 mL of dry IPA to the vial. Round the volume of IPA to the nearest 0.01 mL.
3.6 Return the cap and shake the tube. If a solution or slurry of the sample is not produced, additional IPA must be added until a solution or slurry is produced. Record the volume of additional IPA added.
3.7 Once a solution or slurry is produced, sonicate the sample for 30 minutes.
3.8 Allow the sample to separate. Remove a portion of the clear supernatant using a syringe and filter the fluid into a GC vial. If desirable, the solution may be centrifuged prior to filtering.
3.9 Cap the vial. This solution is now ready for analysis.

4.0 Matrix Spike (Positive Control)

4.1 Prepare this solution as indicated for the sample, except add the spike during step 3.5 after returning the sample to the glove box but before adding the dry IPA. Make certain to account for the volume of IPA added for the spike in the final volume of dry IPA added to the sample.
4.2 Spike the solution with 375 µL of primary stock #2. This solution is 3750 µg/mL. This concentration corresponds to 1.5% (wt/wt).

5.0 Instrument Set Up

Set up and operate the instrument according to the instrument manufacturer’s instructions for a direct injection analysis.

5.1 GC Conditions

Inlet Settings	
Mode	Splitless
Temperature (ºC)	115
Split flow (mL/min)	50
Purge time (min)	0.5
Column Flow (mL/min)	2.1
Detector Settings	
Makeup Flow (mL/min)	12
Temperature (ºC)	180
Oven Parameters	
Initial (ºC)	100
Initial Hold (min)	6
Ramp (ºC/min)	20
Final Hold (min)	20

Instrument settings may be adjusted according to manufacturer's recommendation or to improve method performance.

6.0 Analysis

6.1 System Suitability

Analyze the working calibration standards, the ICS, and the blank preparation. If the following system suitability acceptance criteria are met, then proceed with the sample analysis. Otherwise, correct any problems that caused the system suitability failure and proceed once the problem has been corrected and confirmed by the system suitability checks.

- The coefficient of determination, r^2, of a plot of the working calibration standards against concentration (in µg of solvent) is not less than (NLT) 0.995 for each analyte.
- The value of the ICS is within 10% of the theoretical value.

6.2 Sample Analysis

Build the analysis queue within the instrument software. Place the set of vials containing the samples into the tray in the autosampler in the same order indicated within the sequence.

6.3 Quality Control

6.3.1 The matrix spike sample (positive control) must read higher than the ICS.

6.3.2 After every 10 samples (or fewer) and at the end of the run, continuing calibration verification checks (CCV) are made. Use these results also as part of the System Suitability checks. For each CCV injection, the criterion for acceptance is +/-15% of the target value. The RSD for all system suitability standards in the sequence must be $\leq$10%.

7.0 Calculations

Calculate the limit test result by comparing the solution concentration for the ICS to the solution concentration for the unknown sample.

Calculate the reference result according to the following:

% (wt/wt) = [(A-B) x C] / (g sample)

Where:

A is the concentration of water in the sample solution

B is the concentration of water in the blank solution

C is the volume of extraction dry IPA added to the sample

"g sample" is the net mass of sample taken for the analysis

8.0 Report

Sample readings below the ICS should be reported as <1%; Sample readings equal to or above the ICS are reported as ≥1%. Also report the actual concentration from the calibration curve for reference purposes.

9.0 References

9.1 *Operating Manuals, Volumes 1 – 3, HP 6890 Series Gas Chromatograph*, Hewlett Packard Company, Revision 1, October 1996.

9.2 Galbraith Laboratories Inc Standard Operating Procedure, GC-100D – Analysis of *Residual Solvents by Gas Chromatography Using Direct Injection and Flame Ionization Detection*, Revision 10, June 2011.

9.3 Williams and Lawton, Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants, J.Org.Chem, 2010, 75(24) pp 8351-4.