Attrition Resistance of Supports for Iron Fischer-Tropsch Catalysts

Hien N. Pham[†], Alec Klinghoffer[‡], Lech Nowicki[‡], Jian Xu[*], Abhaya K. Datye[†], Dragomir Bukur[‡], Calvin Bartholomew[*]

[†]Center for Microengineered Materials and Department of Chemical & Nuclear Engineering, University of New Mexico, Albuquerque, NM 87131
[‡]Department of Chemical Engineering, Texas A&M University, College Station, TX 77843
[*]Department of Chemical Engineering, Brigham Young University, Provo, UT 84602

Abstract

Seven commercially available aluminas and silicas were screened for their use as supports for preparing attrition resistant iron Fischer-Tropsch (F-T) catalysts. We used ultrasonic fragmentation to determine the attrition resistance of these supports. Among the supports tested, one alumina support and two silica supports were found to possess adequate attrition resistance. These supports were then tested in a stirred tank slurry reactor (STSR) under non-reactive conditions, using either N_2 gas or syngas as the feed. Particle size distributions of these supports provided a measure of attrition as these supports were used for the simulated F-T synthesis runs. Particle size distributions allow us to infer the extent of fracture and erosion during attrition tests. Our work showed that ultrasonic fragmentation was less severe than stirring of the supports in the STSR for causing erosion of particles from these supports.

Introduction

The Fischer Tropsch synthesis reaction is attracting increasing attention as a possible route for conversion of natural gas and coal into liquid fuels. Fe is an active catalyst for this reaction, however, attrition of Fe Fischer Tropsch catalysts has been identified as a major problem in commercial implementation of slurry bubble column reactors [1]. It is also recognized that precipitated Fe catalysts, while possessing high activity for F-T synthesis may not possess the optimal morphology for slurry bubble column reactors. Our work is directed at supported Fe catalysts, and as a first step, we have studied commercially available silica and alumina materials for their suitability for preparing attrition resistant iron Fischer-Tropsch (F-T) catalysts. The attrition resistance of these supports was studied via ultrasonic fragmentation, a method we have shown to be useful for rapid screening of attrition behavior [2,3]. The more promising supports from this initial screening were then tested in a stirred tank slurry reactor (STSR), where either nitrogen gas or syngas ($CO + H_2$) was bubbled during stirring to simulate the mechanical forces that would be encountered during slurry reactor operation. In subsequent work, catalyst supports of adequate stability will be used to prepare supported Fe F-T catalysts.

Previous Work

In a previous study, Pham et al. [4] reported on the synthesis of attrition resistant Fe catalysts for F-T synthesis, a reaction that allows conversion of coal or natural gas into liquid fuels. These catalysts were prepared using a spray dryer, and the processing steps were examined to correlate the microstructure with the attrition resistance of the catalysts [5]. Other researchers have also used spray drying to prepare Fe F-T catalysts [6,7].

Recently, Zhao et al. [8] investigated in greater detail the catalyst properties affecting the attrition resistance of spray-dried Fe catalysts. They found that particle density, among all of the particle properties, was most significant in determining the catalyst attrition resistance. A higher particle density resulted in a more compact catalyst structure that provided better mechanical strength. In addition, the silica type and concentration were critical in the improvement of the attrition resistance of the spray-dried Fe catalysts.

It is important to improve the attrition resistance of the Fe F-T catalysts without sacrificing both the activity and selectivity of the catalysts. Previously, precipitated Fe catalysts were found to have higher activities [9-12] compared to supported Fe catalysts, which were attrition resistant but had lower catalytic activities [13,14]. Recently, O' Brien et al. [15] characterized the activity, selectivity and attrition of several supported Fe catalysts. They found that the Fe catalysts supported on alumina (commercial) or magnesium aluminate (prepared) had higher activity after running the catalysts in a CSTR than the Fe catalysts supported with silica or magnesium silicate (both commercial). On the other hand, the silica and magnesium silicate based catalysts were more attrition resistant than the alumina and magnesium aluminate based catalysts during the CSTR runs.

O' Brien et al. [15] reported the range of particle sizes for the alumina- and aluminate-containing catalysts before and after attrition, presumably derived from scanning electron microscope (SEM) images. The SEM images of the silica- and silicate-containing catalysts before and after the CSTR runs suggest that there was little sign of attrition during use. However, it is difficult to derive accurate particle size distributions from SEM images because weakly agglomerated particles will not clearly show up in these images. In order to provide better insight into the relative extent of fracture and erosion, we have used a sedigraph particle size analyzer that directly measures particle size distribution. By following particle size distributions as function of time on stream in a slurry reactor we gain insight into the extent of attrition during STSR runs. In this work, we present an evaluation of commercially available silica and alumina supports for their suitability in preparing attrition resistant Fe F-T catalysts. We used ultrasonic fragmentation because it can evaluate, in a very short time, the attrition behavior of these catalysts. However, ultrasonic fragmentation is performed in an aqueous suspension while F-T synthesis is carried out in an organic wax medium. There is some concern about the suitability of the ultrasonic fragmentation approach for predicted performance in a slurry reactor. We therefore present a comparison of the ultrasonic tests with the behavior of supports subjected to long-term tests in a stirred tank slurry reactor.

Experimental

Four silica supports and three alumina supports were used for the attrition tests: Grace Davison 644, 654, 948, 952 silicas and Condea Vista B, HP 14, HP 14-150 aluminas. Tables 1 and 2 show the properties of the alumina and silica supports, respectively. For the ultrasonic fragmentation tests, 1 g of support was added to 50 ml of a 0.05 wt.% sodium hexametaphosphate solution, which was used as a dispersant. A Micromeritics Sedigraph 5100 analyzer was used to measure the particle size distribution at time 0 min. The suspension was then subjected to ultrasonic energy at an amplitude setting of 20 (100 W) at 5 min intervals using a Tekmar 501 ultrasonic disrupter (20 kHz $\pm$ 50 Hz) equipped with a V1A horn and a ½" probe tip. After different extents of ultrasonic irradiation, the particle size distribution was analyzed to detect the mode of particle fragmentation.

After screening, the more promising supports were tested in a STSR. Under non-reacting conditions, N_2 gas was used as the feed gas, while under reacting F-T conditions, syngas was used as the feed gas. A hydrogenated 1-decene homopolymer (Durasyn-164 oil) was used as the slurry liquid medium. The samples were collected at various times on stream, after which particle size distributions were measured after the hydrocarbons were removed from the support by repeated washing in a solvent.

Results

Ultrasonic Fragmentation Runs

Fig. 1 shows cumulative mass distribution plots of Vista HP 14 and Vista HP 14-150 aluminas, respectively. These plots show the mass % of the sample that is finer than a given size as a function of ultrasonic irradiation. The shift in the median particle size to smaller particles is indicative of the fracture of larger particles into smaller fragments. Smaller fragments are seen with Vista HP 14-150 than with Vista HP 14, after ultrasonic irradiation. However, neither alumina leads to generation of fine particles below 6 μm suggesting very little erosion of the primary agglomerates during ultrasonic irradiation. SEM images (Fig. 2) show that these alumina particles are roughly spherical in shape, a shape that would be more suitable for a slurry reactor.

Fig. 3 shows a cumulative particle size distribution plot for Vista B alumina. In our previous work [16], this alumina was used as a test sample for comparing the strength of other slurry phase heterogeneous catalysts. In this figure, we see that the extent of particle fracture is much less pronounced than in Fig. 2. However, unlike Vista HP 14 and HP 14-150, fine particles smaller than 3 μm are generated throughout the ultrasonic fragmentation process for the Vista B alumina. These results suggest that this support is not as resistant to erosion as the Vista HP 14 and HP 14-150 supports. The SEM image (Fig. 4) shows that the Vista B particles are irregularly-shaped, suggesting that this alumina may not be as suitable as the HP-14 for a slurry phase reactor.

Fig. 5 shows cumulative particle size distribution plots of Davison 644 and Davison 654 silicas, respectively. The median particle size for Davison 644 and 654 are 38 μm and 42 μm, respectively. For Davison 644, there is fracture of particles after 5 min of ultrasonic irradiation, but little fracture occurs thereafter. There also appears to be very little generation of fine particles below 8 μm, suggesting that Davison 644 is attrition resistant to erosion. On the other hand, Davison 654 is not attrition resistant either to fracture and erosion after 25 min of ultrasonic irradiation. SEM images (Fig. 6) show that Davison 644 particles are irregular-shaped, similar to those seen for Vista B alumina by SEM.

Fig. 7 shows cumulative particle size distribution plots of Davison 948 and 952 silicas, respectively. For Davison 948, very little attrition of particles due to fracture is seen after 25 min of ultrasonic irradiation. Also, little generation of fine particles due to erosion is seen below 6 μm. Fracture of particles is also seen for Davison 952. Generation of fine particles suggests that it is not attrition resistant to erosion. The median particle sizes for Davison 948 and 952 are 33 μm and 44 μm, respectively. SEM images (Fig. 8) show that Davison 948 particles are roughly spherical, whereas Davison 952 particles are irregularly-shaped.

Of the alumina supports we have studied, Vista B alumina is more resistant to fracture than Vista HP 14 or HP 14-150. However, Vista B alumina is not resistant to erosion. The generation of particles smaller than 5 μm occurs for Vista HP 14-150, whereas no particles smaller than 5 μm are observed with Vista HP 14, both after 25 min of ultrasonic irradiation. The generation of fine particles due to erosion below 5 μm may not be acceptable for slurry F-T reactors based on the work reported in U.S. Pat. No. 5,348,928. This patent discloses a process for optimally operating a three-phase slurry bubble column where the inventors find that although smaller catalyst particles improve fluidization, these particles also increase the difficulty in separating them from the liquid product stream. Thus, particle diameters less than 5 μm should be avoided. Since no generation of particles below 5 μm has been observed for Vista HP 14, this alumina may be more suitable as a support for preparing the attrition-resistant Fe F-T catalysts.

Of the silica supports we have studied, Davison 654 is the least attrition resistant to fracture, while Davison 952 is the least attrition resistant to erosion, during the ultrasonic fragmentation runs. Very little generation of fine particles below 5 μm due to erosion was observed for Davison 644 and 948. Furthermore, these silicas are attrition resistant to fracture throughout the ultrasonic fragmentation process, even though fracture of particles for Davison 644 is initially observed after 5 min of ultrasonic irradiation. Thus, Davison 644 and 948 may also be suitable for preparing attrition resistant Fe catalysts.

Simulated F-T synthesis runs

Two of the alumina and two silica supports were processed in a STSR under non-reacting (N_2) conditions, using Durasyn-164 oil as the slurry liquid medium. The particle size distributions were measured with the same sedigraph analyzer as used for the ultrasonic fragmentation runs with all other experimental conditions being maintained the same. The setup for the STSR runs has been described elsewhere [9]. Fig. 9 shows cumulative particle size distribution plots of Vista HP 14 alumina and Davison 948 silica. In this case, Vista HP 14 shows no significant fracture, but there is generation of fine particles in the 1-10 μm range after use in the STSR for 168 h. In contrast, the generation of fine particles is less pronounced in Davison 948. Fig. 10 shows cumulative particle size distribution plots for Vista B alumina and Davison 952 silica after being processed in the STSR under non-reacting conditions. The Vista B alumina appears to be resistant to fracture, since the median particle size does not increase with time on stream, but there is evidence for erosion since small particles start to appear after stirring in oil. Davison 952 is clearly not very attrition resistant since the particles seem to fracture with stirring time in the STSR. This behavior confirms the trend seen in ultrasonic fragmentation tests.

Discussion

Table 3 provides a summary of the attrition resistance as determined by ultrasonic fragmentation and the simulated F-T synthesis runs. These two methods rely on different mechanisms to cause attrition of the support agglomerates. Ultrasonic fragmentation relies on cavitation caused by collapse of bubbles in solution, while it is the shear forces that cause fragmentation during mixing in a STSR. The behavior of the supports with respect to their attrition resistance was similar despite the different approaches to fragmentation. For example, the Vista B alumina and Davison 952 show similar extents of particle break up during ultrasonic fragmentation or during stirring in a CSTR. In the case of Vista HP 14 and Davison 948 more erosion is seen after the STSR runs than during ultrasonic fragmentation. We would expect to see more erosion with irregular shaped, non-spherical particles. Since Vista B alumina and Davison 952 particles are irregularly-shaped compared to Vista HP 14 and Davison 948, more erosion is observed for Vista B alumina and Davison 952 via ultrasonic fragmentation and STSR runs. However, significant erosion is also observed for Vista HP 14 and Davison 948 after the STSR runs, while both supports have roughly spherical particles, with more erosion seen for Vista HP 14 than for Davison 948. This means that having nearly spherical, smooth shapes is not sufficient to prevent erosion during F-T synthesis runs. In fact, the supports with irregular particles seemed to be more resistant to fracture than those with nearly spherical shapes.

One variable that needs to be considered is the extent of residual oil present on the support particles. Residual oil may cause the fine particles generated during CSTR runs to stick to the larger particles so that the Sedigraph analyzer may not be able to detect them. Residual oil could therefore interfere with the accuracy of the particle size analysis, which is performed in an aqueous solution. To avoid this artifact, we used a consistent washing procedure to remove the hydrocarbon oils, and do not expect to see major differences among the supports. Since some of the supports clearly show the generation of fine particles after long term tests in the CSTR, we feel confident that the results are indicative of the extent of attrition resistance of these particles.

Summary

We have investigated several commercially available aluminas and silicas for use as a suitable support in preparing attrition resistant Fe F-T catalysts. After initially screening these supports by the ultrasonic fragmentation method, it was found that alumina supports were generally less attrition resistant than the silica. Among the alumina supports we tested, Vista HP 14 alumina, showed evidence for fracture and erosion. In contrast, there was no fracture of the particles in Vista B alumina, but erosion was observed both during ultrasonic fragmentation as well as during STSR runs. Among the silica supports, Davison 644 and 948 silicas were more attrition resistant than either of the aluminas we tested: Vista B and HP 14-150 alumina. Davison 654 and 952 silica showed considerable fracture and particle erosion. Results also showed that the STSR runs were more severe on the particles and led to increased erosion compared to the ultrasonic irradiation approach.

In future work, the attrition resistant supports will be used to load iron onto them. The prepared catalysts will then be tested in the STSR under actual F-T conditions, after which the reactivities of these catalysts will be evaluated to see which of the supports will provide optimal catalytic performance. These tests will be long term, hence slurry supports will be periodically withdrawn from the STSR in an inert atmosphere for particle size distribution measurements and catalyst characterization. Also, experimental data will be analyzed to calculate catalyst activity and selectivity as a function of process and/or pretreatment conditions and time on stream.

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Table 1. Properties of commercially available alumina supports.

Name	Condea Vista HP14		Condea Vista B	Condea Vista HP14-150	
Type	Boehmite			γ-Alumina	
	Uncalc.	Calc.[a]	Uncalc.	Uncalc.	Calc.[a]
Density (g/cm^3)	2.71	2.68	-------------	3.07	3.07
Pore Volume (cm^3/g)	0.94	------	0.47	0.97	------
Surface Area (m^2/g)	150	156	243	153	157

[a]500°C for 5 hours

Vista HP14 and HP14-150 microspherical particles (spray drying)

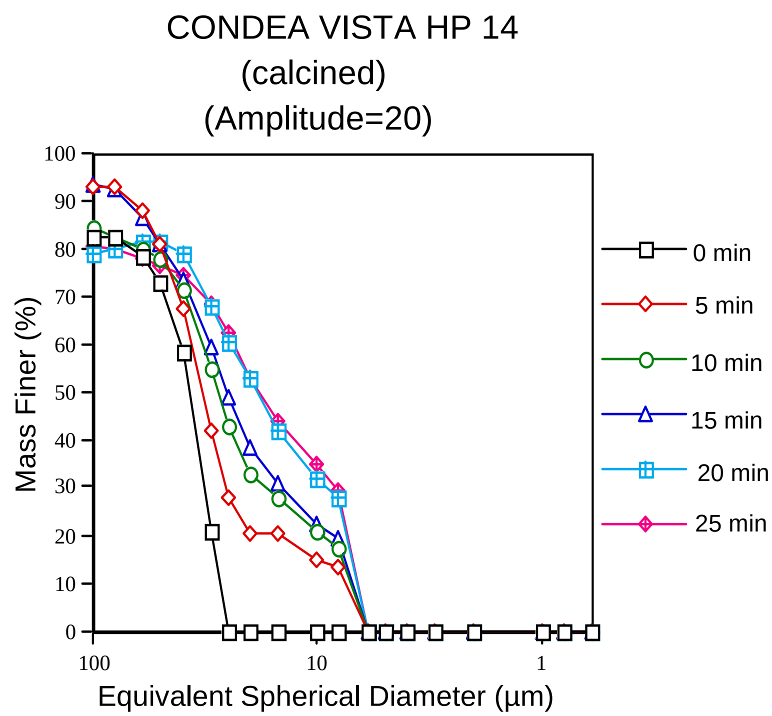
Table 2. Properties of commercially available silica supports.

Name	Grace Davison 644	Grace Davison 654	Grace Davison 948		Grace Davison 952
Type	Silica Gel				
	Uncalc.	Uncalc.	Uncalc.	Calc.[a]	Uncalc.
Density (g/cm^3)	2.29	2.23	2.09	2.08	2.32
Pore Volume (cm^3/g)	1.10	1.70	1.62	------	1.61
Surface Area (m^2/g)	268	272	279	304	309

[a]500°C for 5 hours

Table 3 Extent of Attrition Via After Ultrasonic Fragmentation and Simulated STSR runs

Support	Morphology	Ultrasonic Fragmentation		STSR tests	
		Fracture	Erosion	Fracture	Erosion
		Alumina			
Vista HP-14	Smooth, rounded	Pronounced	None	Modest	Pronounced
Vista HP-14-150	Smooth, rounded	Pronounced	Some	---	---
Vista B-965	Irregular, fines visible	None	Significant	None	Some
		Silica			
Davison 644	Irregular, fines visible	Significant	None	---	---
Davison 654		Pronounced	Pronounced	---	---
Davison 948	Smooth, rounded	Very small	None	Some	None
Davison 952	Irregular, fines visible	Pronounced	Pronounced	Pronounced	Pronounced



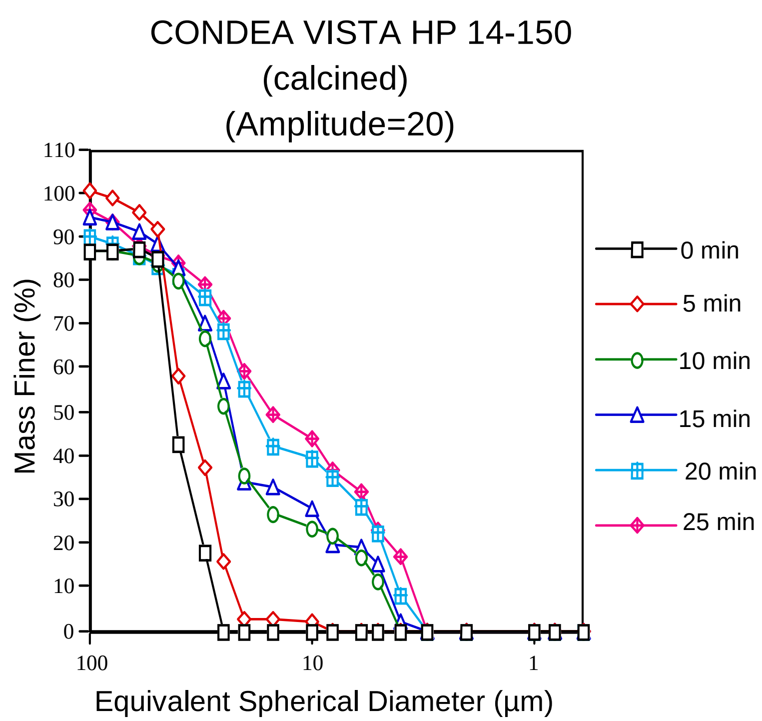
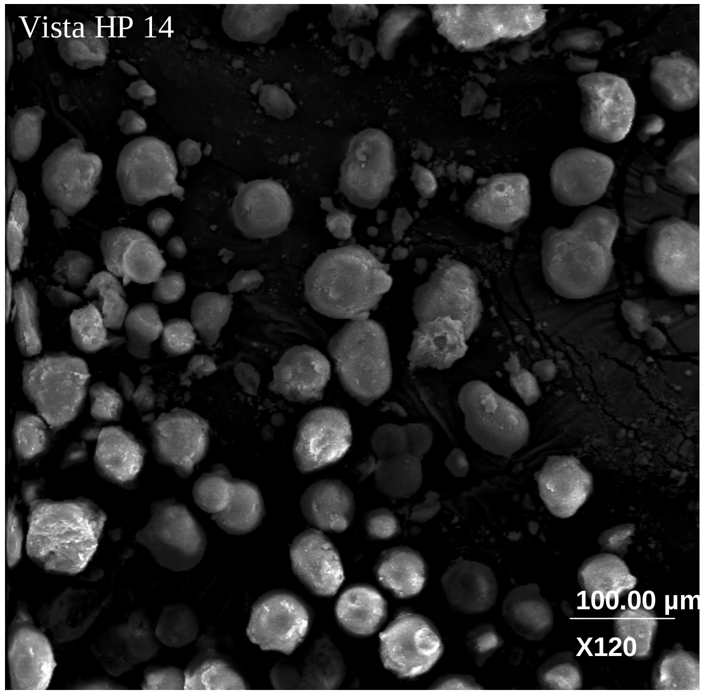


Fig. 1. Sedigraph particle size distributions of Vista HP 14 and HP 14-150 alumina supports. The shift in the median particle size to smaller particles indicates fracture of the primary agglomerates, which occurs more readily with Vista HP 14-150 than with Vista HP 14.



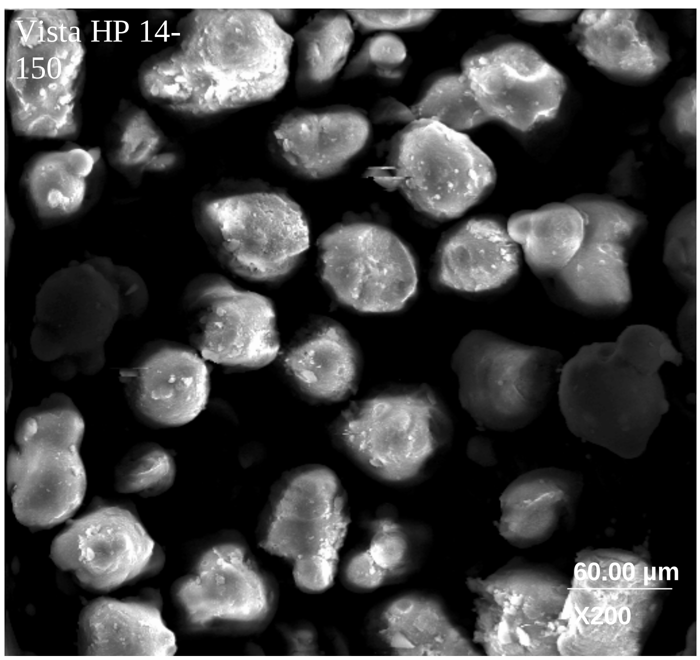


Fig. 2. SEM images of Vista HP 14 and HP 14-150 alumina supports. These particles are roughly spherical, as expected from a spray drying process.

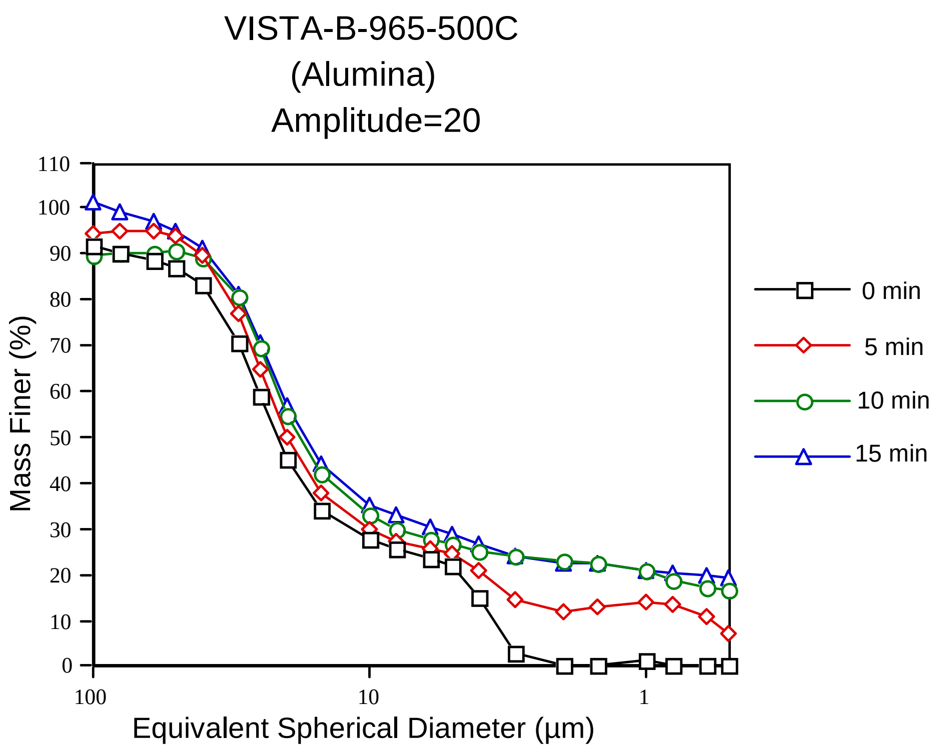


Fig. 3. Sedigraph particle size distribution for Vista B alumina as a function of ultrasonic irradiation time. The starting alumina from VISTA was sieved and calcined in air at 500°C before use in this test.

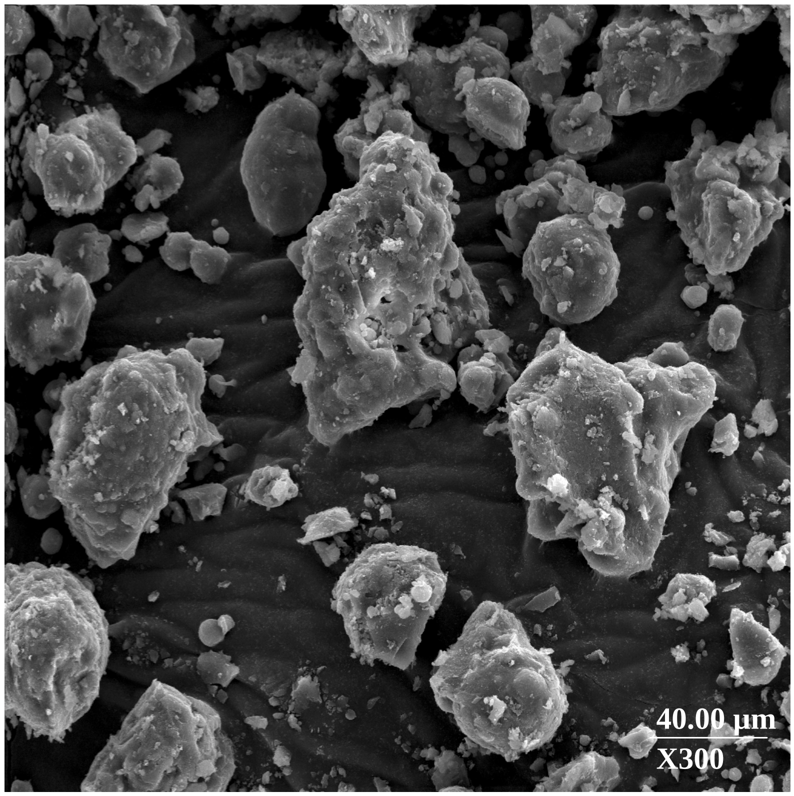


Fig. 4. SEM picture of Vista B alumina. This alumina shows particles that are considerable more irregular when compared to Vista HP 14 and Vista HP 14-150.

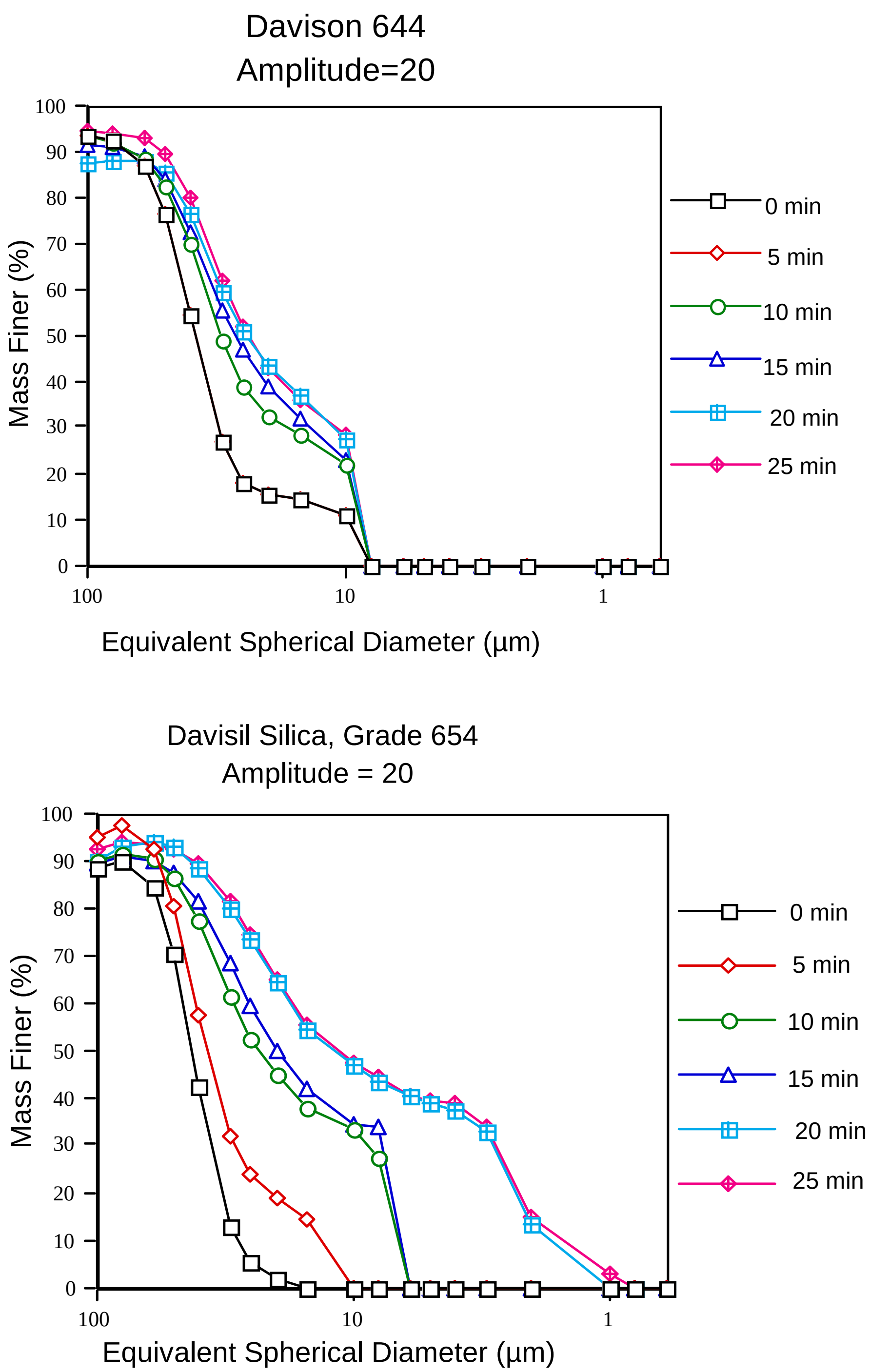


Fig. 5. Sedigraph particle size distributions of Davison 644 and 654 silica supports. Davison 644 appears to be more attrition resistant to fracture and erosion than Davison 654.

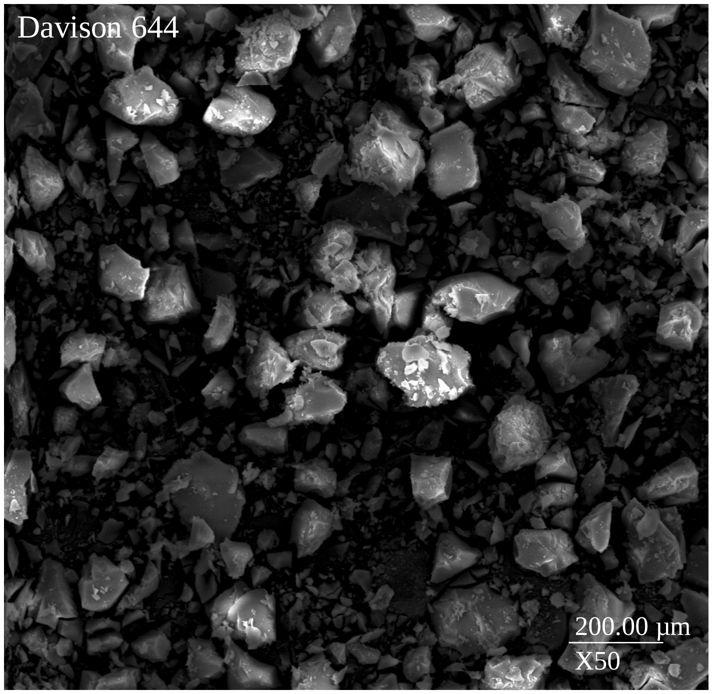
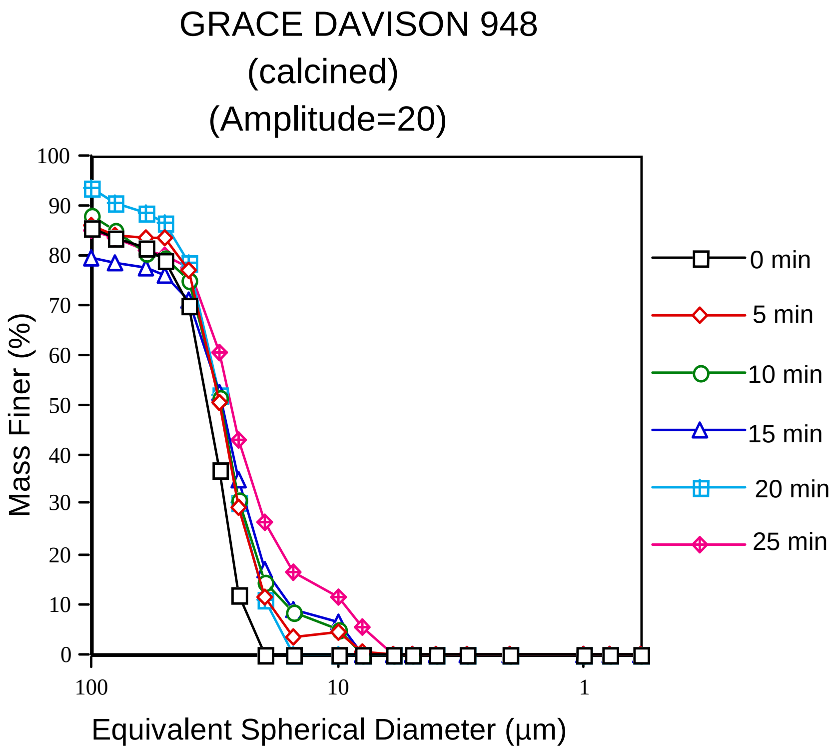


Fig. 6. SEM image of Davison 644. These particles are irregularly shaped, similar to those seen for Vista B alumina.



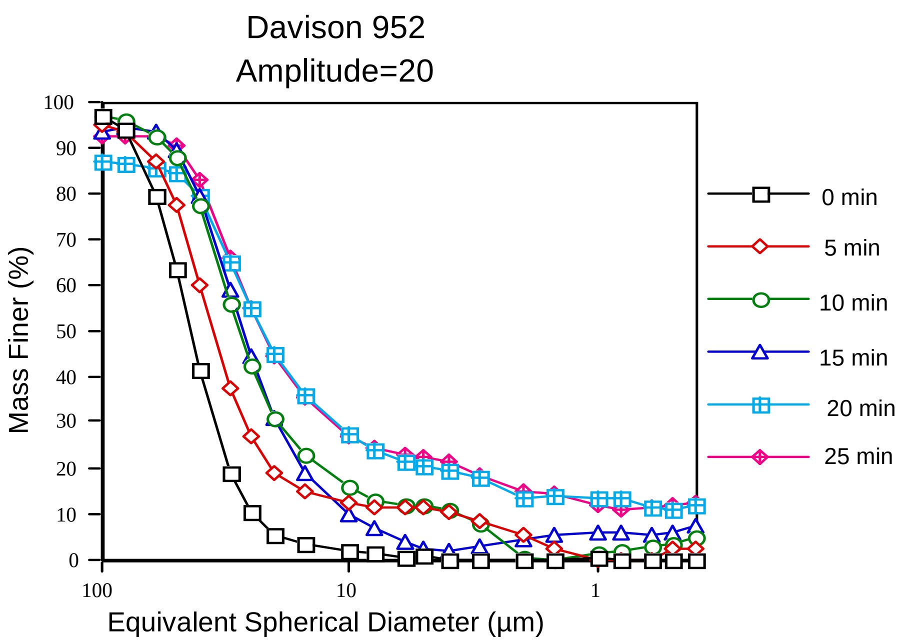
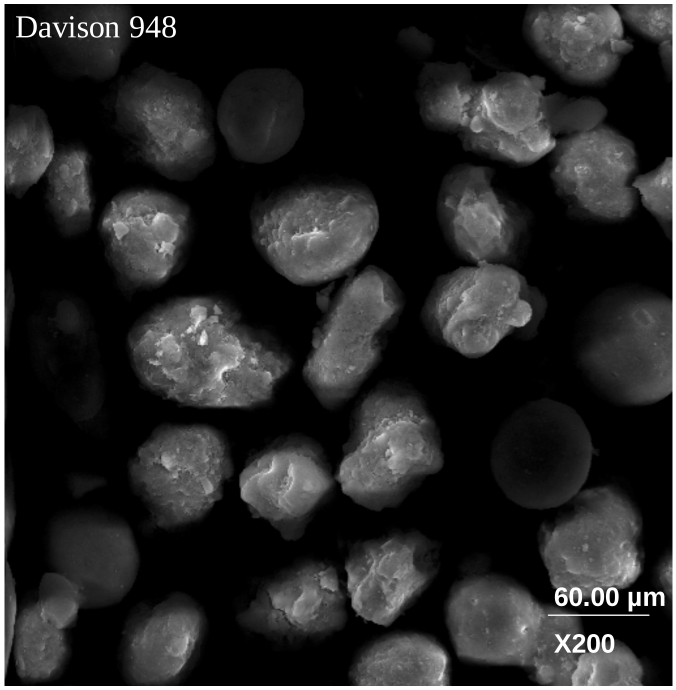


Fig. 7. Sedigraph particle size distributions of Davison 948 and 952 silica supports. Davison 948 appears to be more attrition resistant to fracture and erosion than Davison 952.



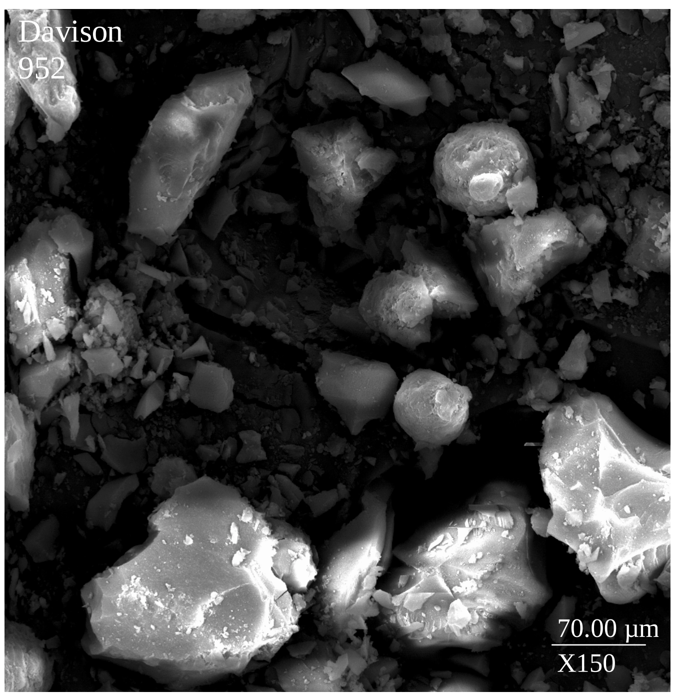
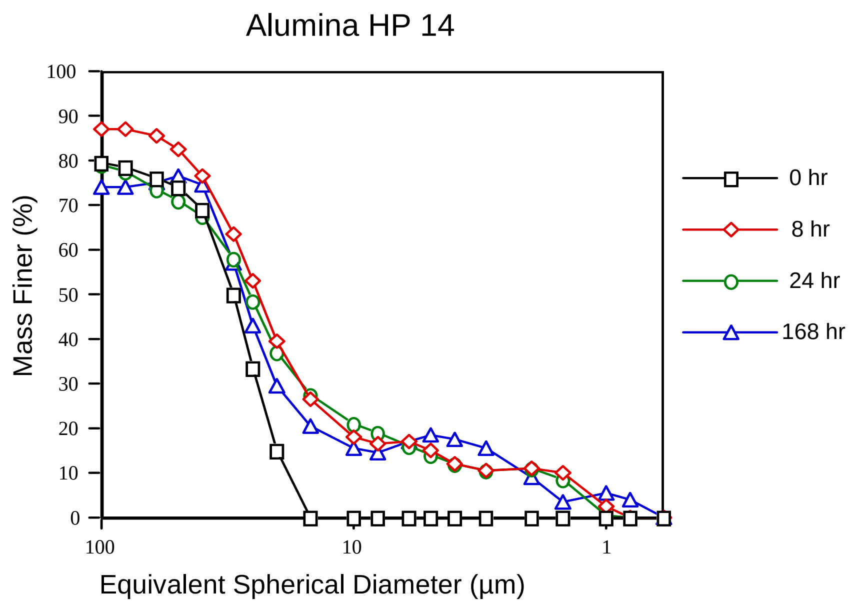


Fig. 8. SEM images of Davison 948 and Davison 952 silica supports. Davison 948 is roughly spherical in shape, while Davison 952 is irregularly shaped.



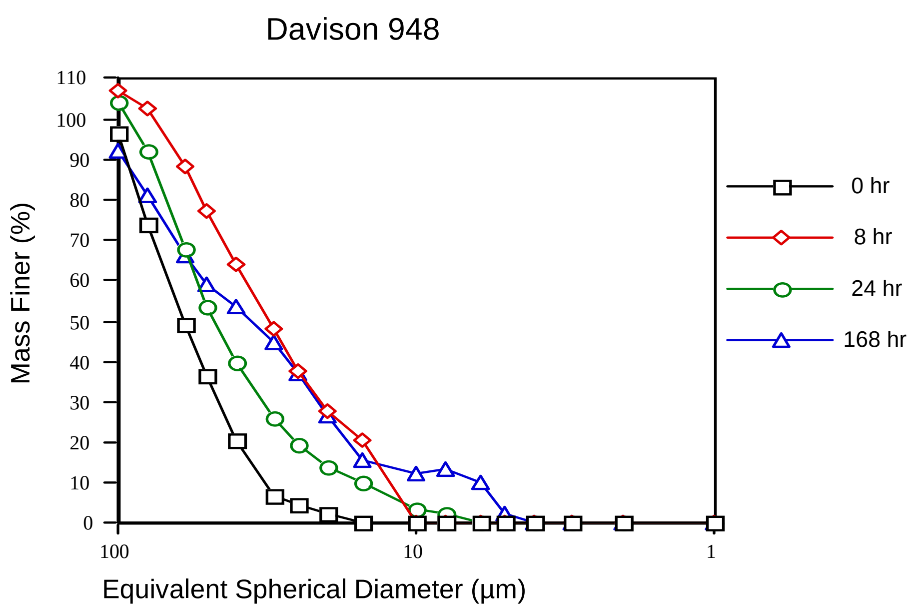
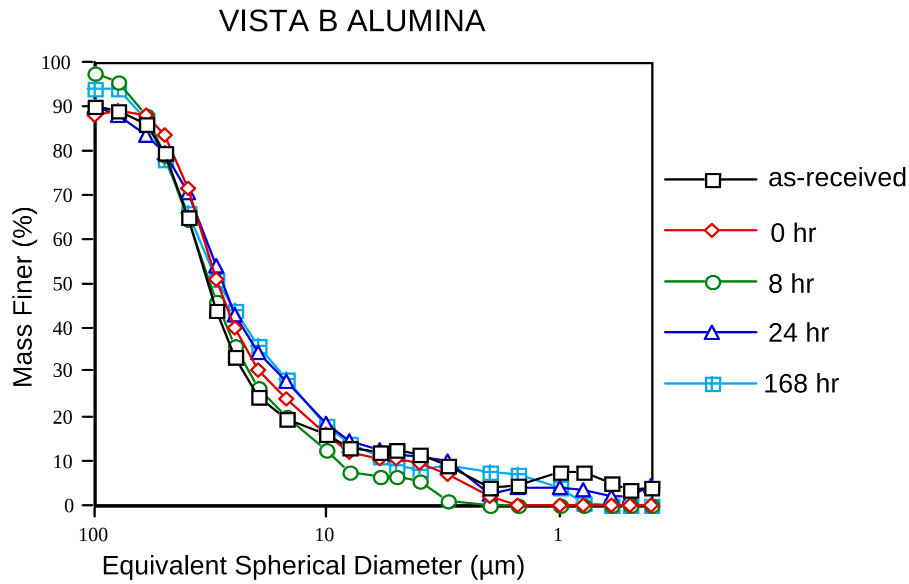


Fig. 9. Sedigraph particle size distributions of Vista HP 14 and Davison 948, performed in a STSR under non-reactive F-T conditions. The production of fines is not as pronounced in the silica support. In both cases, this seems to be a result of erosion of these particles as they are subjected to agitation in the STSR.



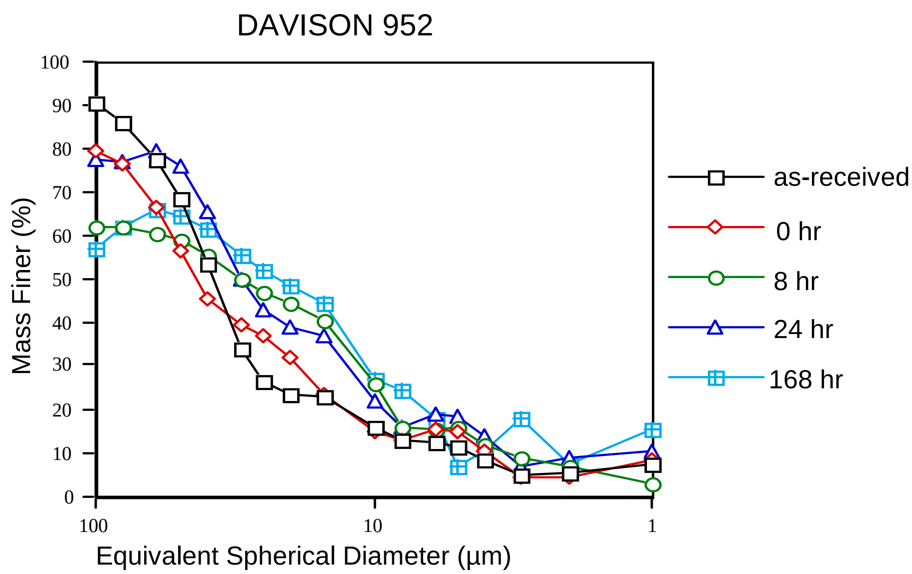


Fig. 10. Sedigraph particle size distributions of Vista B alumina and Davison 952 silica, performed in a STSR under non-reacting conditions. These supports appear to be more attrition resistant after the STSR runs than after the ultrasonic fragmentation runs.