

Effects of Ball Milling on Zeolite powders for use in Additively Manufactured Solid Sorbents

Tiago F. Costa¹, Nichole Carder² and Tane Boghozian³
AMA, NASA Ames Research Center, Moffett Field, CA 94035

and

Tra-My Justine Richardson⁴
NASA Ames research Center, Moffett Field, CA 94035

Zeolite is used as an adsorbent in carbon dioxide (CO₂) removal systems in spacecraft cabins. Reducing the size of zeolite powder particles may provide uniform particle size distribution and increase the materials manufacturability as a paste for additive manufacturing (AM) or slip casting. This paper will describe the zeolite powder ball milling process and the analysis methods used in characterizing the materials particle size, particle size distribution, surface area, and CO₂ gas adsorption. Multi-variable dry ball milling in a planetary ball mill was used as the process for this experiment: the amount of time powder was milled, rotational speed of the milling machine, ball to powder ratio, and ball to jar volume ratio where considered. Virgin powder was compared to milled powder through laser diffraction and SEM imaging techniques.

Nomenclature

<i>CO₂</i>	= Carbon Dioxide	<i>AC-TSAC</i>	= Air-Cooled Temperature Swing Adsorption Compression
<i>AM</i>	= Additive Manufacturing	<i>ISS</i>	= International Space Station
<i>NASA</i>	= National Aeronautics and Space Administration	<i>XRD</i>	= X-Ray Diffraction
<i>ARC</i>	= Ames Research Center	<i>SEM</i>	= Scanning Electron Microscopy
<i>CAD</i>	= Computer Aided Design	<i>BM</i>	= Ball Milling
<i>4BCO₂</i>	= Four-Bed Carbon Dioxide	<i>RPM</i>	= Rotation Per Minute
<i>4BMS</i>	= Four-Bed Molecular Sieve	<i>ECLSS</i>	= Environmental Control and Life Support System
<i>LD</i>	= Laser Diffraction		

¹ Materials Scientist/Engineer JRSE, Thermal Protection Materials Branch, and MailStop 234, Moffett Field, CA 94043

² Ceramic Engineer, Thermal Protection Materials Branch, and MailStop 234, Moffett Field, CA 94043

³ Chemist, Thermal Protection Materials Branch, and MailStop 223- , Moffett Field, CA 94043

⁴ Research Physical Scientist, Bioengineering Branch, and MailStop 239-15, Moffett Field, CA 94043

I. Introduction

Solid sorbent beds are used to remove contaminants from air in closed-loop life support systems such as those on spacecrafts. Spacecraft regenerative sorbent beds were designed to operate for over three years and in the cast of the Carbon Dioxide Removal Assembly (CDRA)¹, and have been in operation since 2001. Over the years, the CDRA has encountered many technical challenges. One of which includes the degradation of the sorbent materials due to contamination. As such, the sorbent materials were replaced, but these materials are no longer fabricated by the manufacturer. Therefore, new sorbent selection campaign was completed to select new materials for the upgraded system, the 4BCO₂. The 4BCO₂ performs the same function as the CDRA, but with improvements in heater designs and different sorbent materials. As NASA plans to travel further into space and to support life for longer missions, systems must be designed for longer life cycles. Therefore, it is recommended that future system designs consider material selections that are independent of the manufacturer, if possible, to reduce both risk and cost to the program.

To reduce risk and cost to the design of solid sorbent beds, the traditional methods of using solid sorbent pellets from the manufacturer and designing systems based on the provided material properties must be improved. One approach is making the pellets from the base powders themselves. The Multifunctional Sorbent (MultiSORB) project funded by the Advanced Exploration System (AES) Habitation System aims to establish methods to fabricate solid sorbents bed through either robocasting or slip/freeze casting. Robocasting is a type of Additive Manufacturing (AM) where, instead of printing a melted polymer, robocasting involves printing a paste from a syringe at room temperature. This approach has multiple advantages such as tailored contaminant removal capacities, tailored air flow paths, and improved solid sorbent thermal conductivity. These approaches will improve the Equivalent System Mass (ESM) and ensure long term access to solid sorbents.

A. MultiSORB

The MultiSORB project involves the parallel and iterative development of three major areas: paste formulation, lattice designs, and heater designs. Figure 1 shows the various components of the project. Lattice design and heater designs are independent, but will rely on data from the paste formulation process. Paste formulation covers the development of the zeolite paste from the raw materials to the printing and post processing. The zeolite paste is made up of the zeolite powders, inorganic and organic binders, and water. First the powder components are mixed (zeolite and binders) and then water is added to the desired viscosity. The amount of water to be added depends on the equipment used to produce the lattice. That is, some equipment is able to print thicker paste than other. The lattice designs are limited in the printability of the paste such as the ability to form desired shapes and edges. Therefore, efforts are made to improve the rheology of the paste. One approach is to ensure that the powder components are of similar size. Components of similar size and density will mix better². This research work will focus on evaluating the different size of paste formulation powder components and ball milling the components to reduce the size of the particle. Ball milling will maximize the surface area to volume ratio of the particles and may also improve adsorption kinetics.

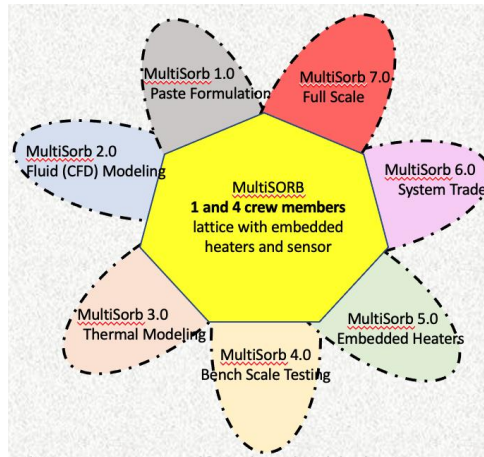


Figure 1: The various MultiSORB parallel development areas.

B. Zeolite Overview

A zeolite is a crystalline aluminosilicate with a three-dimensional framework structure that forms uniformly sized pores of molecular dimensions¹. Because of this structure, zeolites are preferred as molecular sieves – their pores will adsorb molecules smaller than that of the diameter of their pores and exclude any molecules that are larger than their pore size. This allows for zeolites to adsorb and immobilize several particles, liquids, and gasses – in the use case of the ISS, zeolite is used to adsorb CO₂ from a stream of cabin air.

Zeolite 13X and 5A were specifically chosen for this research due to their current usage in the noted systems. Zeolite 13X is being used in the Environmental Control and Life Support System (ECLSS), while zeolite 5A is used in the Air-Cooled Temperature Swing Adsorption Compressor (AC-TSAC). The MultiSORB project will utilize the past and present information of zeolite 13X and 5A that is presented from these two systems in order to optimize CO₂ removal.

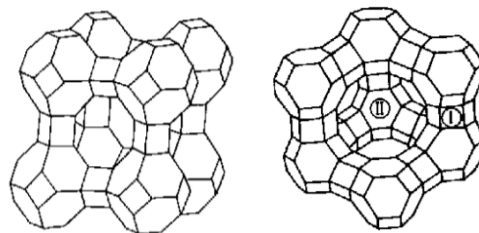


Figure 2: Molecular structure of (left) zeolite 13X and (right) zeolite 5A¹

C. Ball Milling

Ball milling (BM) is a process of comminution, which refers to the reduction of solid materials from one average particle size to a smaller average particle size. This can be done in many ways, including crushing, grinding, cutting, and vibrating. BM is used when the desired

particle size distribution cannot be achieved by other means, such as elutriating, classifying, or screening. The process used in this experiment, planetary ball milling, uses grinding media that is encapsulated within a jar on the ball mill to impact the material needing to be reduced. The grinding media cascades from the top of the jar as the jar rotates on the mill, transferring its energy to the material through collision, and in turn breaking down the individual particles of the material. The energy required for this size reduction to occur can be characterized by the following equation, which can be thought of as essentially a simplified version of Rittinger's Law:

$$E = \gamma * \Delta S \quad (1)$$

Where γ is the specific surface energy of the material and ΔS is the increase of surface area of the material over time. This equation especially applies to zeolites, as zeolite's already large surface area is continuously increased with the process of ball milling.

Due to the properties of smaller zeolite particles, it has started to become of increasing interest to scientist and engineers to ball mill zeolites. The reduction of zeolite particle size leads to a larger external surface area, allowing for shorter diffusion path lengths, reduction of mass and heat transfer resistances in catalytic and adsorption application, decreasing side reactions, and lowering tendencies of coke formulation in some catalytic reactions². It is also thought that the increase of zeolite surface area will increase zeolites capacity when adsorbing CO₂. Having a specific particle size is also favorable when using zeolite in a paste for AM. To achieve maximum particle packing, multiple particle sizes are required. BM allows the zeolites particle size and distribution to be tailored to each paste formulation that will be used for additive manufacturing (AM) or slip casting – this is important to allow part densification, strength, and porosity requirements to be met after sintering.

All mentioned characteristics are related to reactivity, which is a function of particle size distribution. Typically, the finer the powder and the greater its surface area, the lower are the temperatures and time at temperature needed for densification³. This has an important effect on strength, as longer times at temperature result in increased grain growth and lower part strength.

Particle shape also plays a role in the pastes packing density – the more oblong a particle is the more difficult it will be to pack amongst other materials that have a more uniform shape. BM may create unwanted shape characteristics of the zeolite particles, which would be unfavorable for usage in AM and slip casting techniques.

II. Materials & Methodology

A. Materials

Commercial zeolite 13X and 5A were purchased from Advanced Specialty Gas Equipment (Downers Grove, IL). Methylcellulose, polyvinyl alcohol (PVA), bentonite and kaolin nano clay powders were purchased from Sigma-Aldrich (Saint Louis, USA). Table 1 shows the supplied material properties from both Advanced Specialty Gas Equipment (ASGE). Sigma Aldrich did not provide nominal pore diameter nor average particle size for bentonite, PVA, or methyl cellulose. The average particle size will be later characterized alongside both 13X and 5A, in order to compare between all materials.

Table 1: Material properties as listed by supplier

Material	Nominal Pore Diameter (Å)	Average Particle Size (um)
13X (ASGE)	8	< 10
5A (ASGE)	5	< 10

B. Experimental Methods & Matrix

Ball milling was performed in the Materials Processing lab at NASA Ames Research Center with the use of a U.S Stoneware (Mahwah, NJ) mill. The grinding media used were 6.35 mm (¼”) by 6.35 mm (¼”) cylindrical zirconia milling media (Cole-Parmer) for both the 13X and 5A powder. Two 0.3 L roalox jars (Gilson Co.) were used during ball milling – one jar being used for only 13X powder and the other only for 5A powder to prevent cross-contamination. Grinding media was loaded with two different parameters. It was first chosen to load 5 volume% (75 grams) of the jar with media to analyze preliminary results of BM. It was then chosen to do one run at 35 volume% of the jar (547 grams), in order to provide a larger sample size for BET analysis and observe the effects of volume percentage changes on processed characteristics. Zeolite 13X and 5A were then loaded at 8 mass% of the media (44 grams for a 35 volume% of media, and 6 grams for a 5 volume% of media). The zeolite was then milled for 12 hours at 45 RPM and 100 RPM, respectively. These parameters were chosen mostly due to the current limitations of the U.S. Stoneware milling machine. The limiting factor was the RPM of the machine, maxing out at 100 RPM. Due to this limitation, it was thought that the best approach would be to start at roughly half the maximum RPM, monitoring the results, then try the maximum RPM in case the particle size was not adequate. The time of 12 hours was chosen to give a broad spectrum of samples, allowing us to monitor the break down rate per hour, and test each sample for particle size, particle size distribution and gas adsorption. It is important to note that BM can destroy the crystallinity of zeolite, which is another reason for the multiple samples taken – being able to see if there is a drop off in crystallinity at a certain time and RPM of BM was important. A small sample, ranging from 0.09 to 0.1 grams was taken every hour. Sample size was limited by the starting amount of powder – as more samples are taken, the powder to media ratio is altered, which has the potential to lead to a faster break down rate of particle size and crystallinity.

Table 2: Experimental Matrix

Material	Time Milled	Ball Diameter (mm)	Speed (RPM)	Powder to Ball Ratio (mass %)	Ball to Jar Ratio (volume %)
13X (ASGE)	1 to 12 hours	6.35 (cylindrical)	45	8%	5%
5A (ASGE)	1 to 12 hours	6.35 (cylindrical)	45	8%	5%
13X (ASGE)	1 to 12 hours	6.35 (cylindrical)	100	8%	35%

C. Characterization

Each sample had been placed in a small bag, that was used to transport the powder. Initially, SEM images were taken, using the Philips XL 30. The powder was placed on a SEM stage that was prepared with double sided adhesive tape – the powder was cautiously sprinkled and lightly spread out with a small scraper on the tape to ensure that there were no agglomerations induced by this method. Each sample used magnifications of multiple ranges to better determine the effects of BM. “Water mode” was used due to charging, which is an occurrence that causes an anomalous contrast in SEM images when observing non-conductive materials. Measurements were taken of particle sizes in the Scandium (ResAlta Research Technologies) software environment on top of the SEM image.

Laser diffraction (LD) measurements were taken on a Mastersizer 2000 Hydro (Malvern Instruments) to characterize both particle size, particle size distribution, and surface area of the virgin and milled powders. Each sample was run at 3500 RPM, 30% sonication and with a 2-minute dispersion period. These settings were chosen based off of iterative testing of raw 13X and 5A powder. The samples were run at different settings to compare consistency between results – it was found that the mentioned settings were the most consistent in both particle size and particle size distribution measurements. Laser intensity for each measurement averaged at 79.5%.

Brunauer-Emmett-Teller (BET) analysis was done using an ASAP 2020 (Micromeritics) on nitrogen and carbon dioxide as the analysis gas. Isotherms were completed on the raw materials – unfortunately, due to calibration issues on the ASAP 2020, the team was unable to pull data that we felt was accurate for the processed powder, so this data was omitted. Future work will be done in order using this technique to validate the processed powders.

III. Results and Discussion

A. Particle Size & Particle Size Distribution

To analyze the effects of milling on virgin powder, the average particle size, as well as the span (S) and range of each sample where compared. The span (S) of the sample can be defined as:

$$S = \frac{d(0.9) - d(0.1)}{d(0.5)} \quad (2)$$

In this equation $d(0.1)$, $d(0.5)$, and $d(0.9)$ represent the sizes for which 10, 50, and 90% by volume of particles are in each sample. The value given for span can be used as a representation of the width of the particle size distribution graph. Table 3 below shows the measured particle sizes and span of the 13X and 5A powders, with the milling different milling conditions. Due to a high number of agglomerations in the samples of the 100 RPM, 35vol% run, average particle size analysis was omitted. It is believed that the sample loading was much too high for that given RPM, causing the zeolite to cake against the walls of the jar, forming a thin layer circumferentially. This layer become so dense, that the impacts from the media within the jar did not have any effect on the powder – it was even found that some of the media had actually been

lodged within the thing layer of zeolite. These observations were made at 3 hours in to the 12-hour run, which, at that point, the experiment was halted, and no data was taken. Further work is needed in order to optimize a high percentage of powder loading in order to have adequate powder for not only characterization but manufacturing of the final AM or slip casted parts.

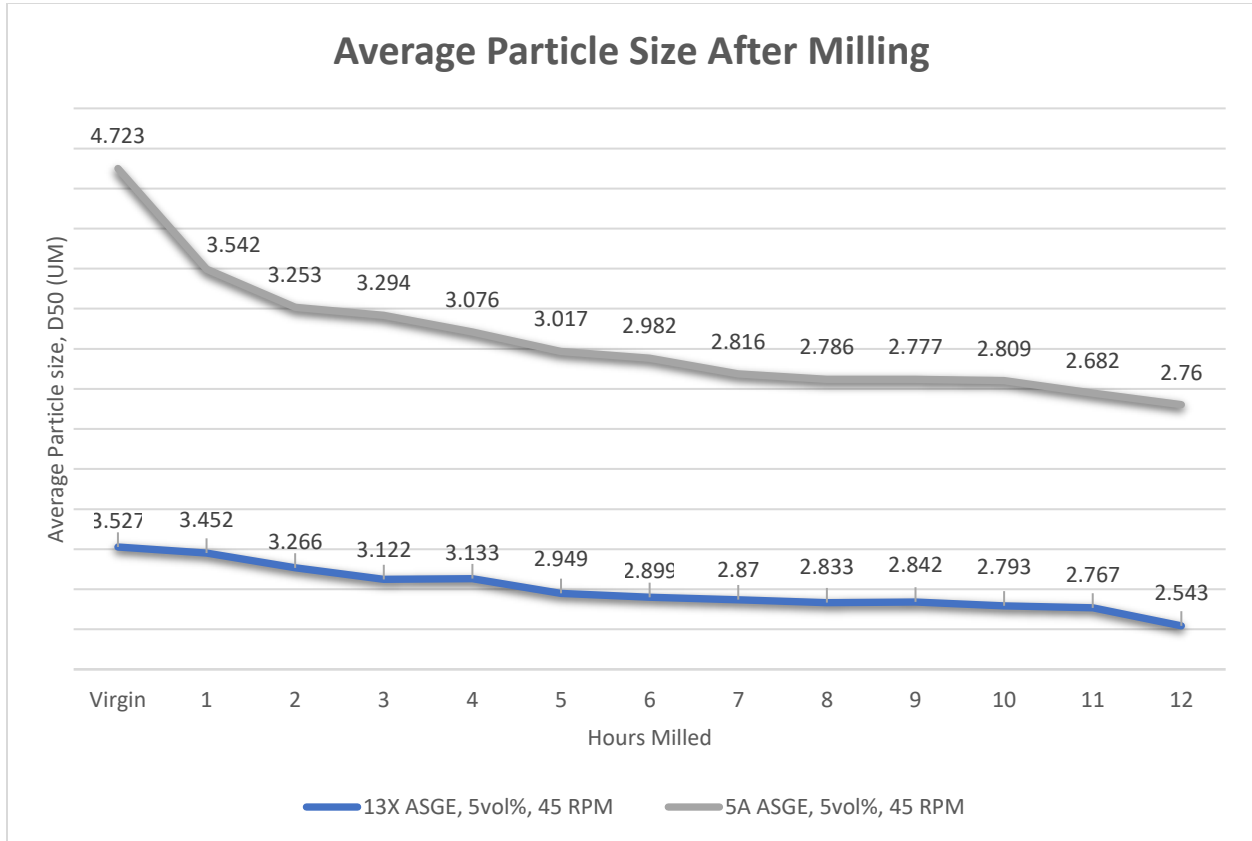


Figure 3. Average particle size measurements for zeolite 13X and 5A.

Notably, we can see a large range and span reduction between the virgin powders and their 12-hour samples after milling, with the average particle size, span, and range being reduced by the percentages shown in Table 3.

Table 3. Average particle size, span, and range reduction percentages between zeolite 13X and 5A virgin powders, and their respective 12-hour samples.

Material	Media loading (volume%)	RPM	Average Particle Size Reduction	Span Reduction	Range Reduction
5A(ASGE)	5%	45	41.6%	27.3%	57.5%
13X (ASGE)	5%	45	32.4%	79.5%	105.1%

Specific surface areas of each sample were found through the same techniques as particle size and particle size distribution (LD). Table 4 shows the effects of BM on specific surface area of both zeolite 13X and 5A powders.

Table 4. Specific surface area measurements using Mastersizer 2000.

Material	Media loading (volume%)	RPM	Virgin Specific Surface Area (m ² /g)	Specific Surface Area after 12 hr. BM (m ² /g)	% Increase
5A(ASGE)	5%	45	1.69	2.63	55.6%
13X (ASGE)	5%	45	1.92	2.31	20.3%

B. SEM Imaging

As shown in Figure 3, the particle shapes between the virgin powders and 12hr. BM powder samples had similar shapes. Some agglomerations were seen when analyzing the powder and were apparent throughout all samples. It was difficult to note if these agglomerations were due to the handling of the powder before analysis, or due to the process of BM itself. Further work will be needed in order to narrow down the effects of all processes on agglomerations. As noted, it was initially seen that in the 35vol% media loading samples, the powder will cake up against the wall, forming a layer of zeolite that has to be scrapped off. The higher percentage of media and powder loading may see a disadvantage in terms of agglomerations due to the little amount of space the particles have to move compared to the 5vol% media loaded samples. It is thought that the centrifugal force of the larger mass of the 35vol% loading at 100 RPM caused all of the material and media to stay close to the walls of the jar, not allowing for the media to mix with the loaded zeolite. In order to reduce this mass, smaller media could be used at the same higher RPM to potentially achieve particle break down similar to the 5vol% loading case, with a larger amount of processed powder being produced.

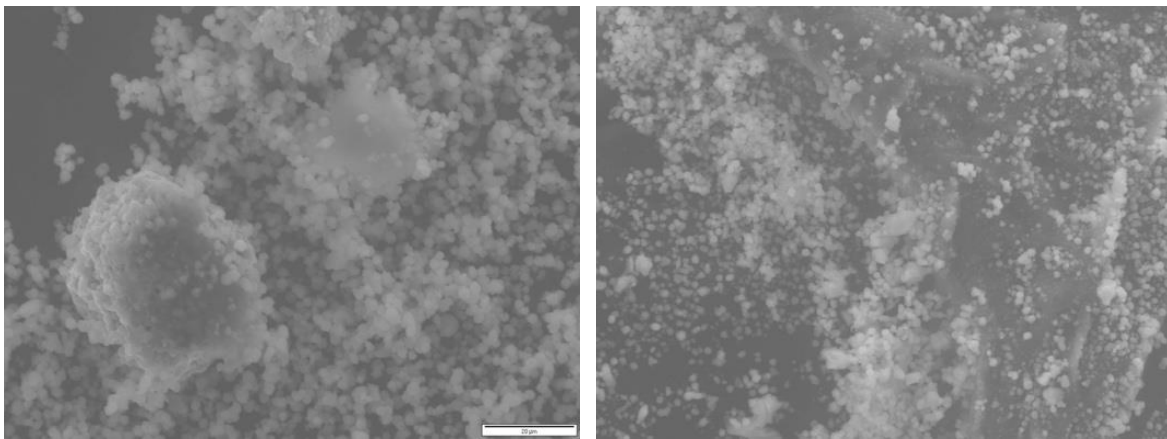


Figure 2: SEM images of the ball mill samples. (left) Virgin 13X powder (right) 13X powder after 12 hours of BM.

IV. Future Work

It has been shown that BM does indeed reduce particle size and the particle size distribution span of both zeolite 13X and 5A, in a quite considerable amount. This initial analysis is ideal in terms of what is wanted for the paste formulation for the MultiSORB project. While size reduction of zeolite was accomplished, the technique of size reduction still requires optimization. Ideally, the particle size of both the zeolite 5A and 13X should be determined by characterizing the particle size of all other organic and inorganic binders, and finally finding the optimal packing density based on these particle sizes and distributions. Of course, each materials size and distributions can be tailored for packing density but will require experimentation to find optimal packing density given the initial characteristics of the purchased materials. Nanoscale particle sizes may be achievable with these materials and may pose an advantage for AM as the smaller particles could allow for a smaller diameter nozzle, which would be able to print much more fine rod diameters. A 40-hour trial was run on zeolite 13X with 5 volume% of media loaded, at 45 RPM, to indicate whether zeolite particles could be brought down to the nanoscale. It was shown that between 12 hours and 40 hours, the size reduction was minimal.

The results of 35vol% media samples were seen to not have much effect on the breakdown of zeolite powders. With the current hardware available (media and jar sizes), 100 RPM led to many agglomerations of the materials – at 3 hours the zeolite powder had completely caked against the wall of the jar, forming a $\sim 1/8$ " thick layer of zeolite. It is thought that the reasoning behind this is the size and shape of the media, and speed of the jar. At this higher RPM, the cylindrical media likely centrifuged around the jar, rolling the zeolite powder into this thin layered agglomeration. The ball milling media was even found to be stuck inside of this layer of zeolite. Due to this initial observation at 3 hours, samples were not taken until the 12-hour mark, as it was obvious this process was not optimal for the milling of zeolite. This observation led to further investigation of the choice of milling media – smaller media of spherical shape was chosen as an attempt to optimize the process given the current parameters and will be used in future work.

Reducing the particle size of zeolite to the nanoscale, and not disrupting the crystalline structure of the material is a difficult task. Development of a technique to achieve this goal will likely take many iterations, but preliminary ideas have been presented below.

One potential way of addressing this issue is by filtering out the smallest particles from the virgin zeolite powder before milling the powder. This should theoretically allow the starting particle size to be around 1.6 μm (13X), which is about 1 μm smaller than the average particle size of the 12-hour sample of 13X. The issue with this is the amount of powder needed to achieve the given powder ratios of the experiment, and the filtering or sieving system that would have to be used. A possible way of doing this would be to create a slurry with the zeolite powder and run the slurry through a 1 μm syringe filter (or any filter with small enough aperture) to capture the larger particles. You would end up with a slurry that is populated with the smallest particle sizes of the zeolite powder, which could then be ball milled to the ideal size, using a wet ball milling technique.

Another way to address this issue would be to use a dampening material in conjunction with the zeolite as it is milled, as addressed by Zhuman⁵. The authors of this paper discuss the usage of carbon nanostructures in their process, which allow for the crystalline structure of zeolite to stay more intact throughout the ball milling process. The technique is novel, and to be

reproduced would require equipment that is not in hand, such as centrifuge, which makes this option more difficult to be tested.

Although further consideration is needed, synthesizing zeolite in the lab is possible. With the ability of controlling every aspect of the synthesizing process, nano sized zeolites with an intact crystalline structure may be able to be obtained. This may not be optimal in terms of large volumes – but batch sizes currently needed are small enough for this option to be viable.

The limiting factor at this point is having equipment that can produce enough energy to reduce the size of zeolite to the nanoscale, as the current ball mill is only able to rotate at a maximum of 100 RPM and the grinding media size and shape were limited to one option. It is possible to optimize the variables given the current parameters of the equipment, which is the reasoning for trying different RPM's and ratio percentages – there is still further work needed to optimize these parameters for the current setup. To overcome the obstacle of what can be considered “low energy” equipment, a ball mill that has a tunable RPM range between 0 and 3500 RPM is being designed. Once this ball mill is manufactured, the parameters of this experiment can be further optimized at higher RPM ranges, using a combination of the techniques listed, to potentially produce an average particle of zeolite size in the nano range without the loss of crystallinity to compliment the particle sizes of the organic and inorganic binders of the MultiSORB paste.

V. Conclusion

It was shown that ball milling was able to reduce the average particle size, tighten the particle size distribution curve, and increase the surface area of zeolite 13X and 5A, all of which may allow for the optimization of MultiSORB paste formulations. Further optimization of the ball milling parameters and techniques is needed in order to achieve a particle size of zeolite that is closer to the particle sizes of the organic and inorganic binders of the MultiSORB paste formulation, but the reduction in the range of particles and distribution, or span, was quite impressive and alone should allow for an improvement of the paste formulation packing density.

References

¹ Introduction to zeolite science and practice, 2nd edition, H.van Bekkum, EM Flanigen, PA Jacobs s

² Amir Charkhi, Hossein kazemian, Mohammad Kazemeini (2010). Optimized experimental design for natural clinoptilolite zeolite ball milling to produce nano powders, Powder Technology 203 (2010) 389-396.

³ Modern Ceramic Engineering, Properties, Processing and use in design, David W. Richerson

⁴ Jeng, F.F., et al., Analyses of the Integration of Carbon Dioxide Removal Assembly, Compressor, Accumulator and Sabatier Carbon Dioxide Reduction Assembly. 2004, SAE Technical Paper.

⁵Zhuman, Botagoz & , Sepurahman & Anis, Shaheen & Hashaikeh, Raed. (2018). Obtaining high crystalline ball milled H-Y zeolite particles with carbon nanostructures as a damping material. Microporous and Mesoporous Materials. 273. 10.1016/j.micromeso.2018.06.041.