

*Technology to Facilitate the Use of Impaired Waters in Cooling Towers*

DE-NT0005961

Dr. Robert Colborn

GE Global Research

1 Research Circle

Niskayuna, NY 12309

July 31, 2012

Final Report

## Executive Summary:

The project goal was to develop an effective silica removal technology and couple that with existing electro-dialysis reversal (EDR) technology to achieve a cost effective treatment for impaired waters to allow for their use in the cooling towers of coal fired power plants. A quantitative target of the program was a 50% reduction in the fresh water withdrawal at a levelized cost of water of \$3.90/Kgal.

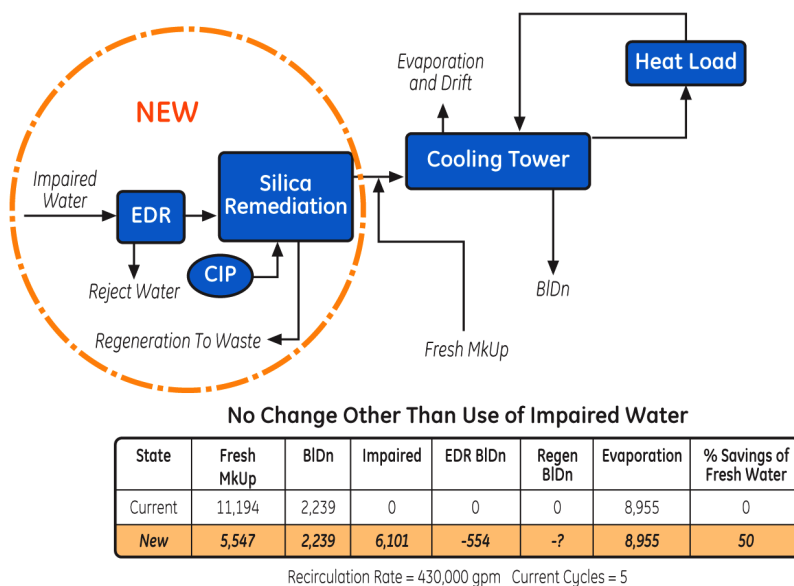
Over the course of the program, a new molybdenum-modified alumina was developed that significantly outperforms existing alumina materials in silica removal both kinetically and thermodynamically. The Langmuir capacity is 0.11g silica/g adsorbent. Moreover, a low cost recycle/regeneration process was discovered to allow for multiple recycles with minimal loss in activity. On the lab scale, five runs were carried out with no drop in performance between the second and fifth run in ability to absorb the silica from water. The Mo-modified alumina was successfully prepared on a multiple kilogram scale and a bench scale model column was used to remove 100 ppm of silica from 400 liters of simulated impaired water. Significant water savings would result from such a process and the regeneration process could be further optimized to reduce water requirements.

Current barriers to implementation are the base cost of the adsorbent material and the fine powder form that would lead to back pressure on a large column. If mesoporous materials become more commonly used in other areas and the price drops from volume and process improvements, then our material would also lower in price because the amount of molybdenum needed is low and no additional processing is required. There may well be engineering solutions to the fine powder issue; in a simple concept experiment, we were able to pelletize our material with Boehmite, but lost performance due to a dramatic decrease in surface area.

## Final Report

### Introduction

The objective of this program was to develop a silica removal technology that when used in concert with commercial electro-dialysis reversal (EDR) technology would provide a cost effective way to treat impaired waters for use as cooling tower water in coal fired power plants (See Figure 1).



**Figure 1. Proposed GE solution for the use of impaired water for cooling tower applications. EDR (Electrodialysis reversal), CIP (clean in place)**

In order to use impaired water in this application the silica must be below 20 ppm, ideally closer to 10 ppm. The technology under development here will take the EDR effluent and reduce the silica levels by 90% (from 100 ppm to 10 ppm). This will enable a 50% reduction in the withdrawal of fresh water for the cooling tower. The intermediate cost target for this process is \$3.90/Kgal of water with a final goal of \$3.00.

The issue of dissolved silica in cooling towers has continued to receive attention since the project was started<sup>1,2</sup>. The approaches have included electrocoagulation and hybrid ion exchange resins. From a more general perspective, Ning has written a review on reactive silica in natural waters<sup>3</sup>. There have also been several reports dealing with the issue of silica in geothermal waters<sup>4-6</sup> and in fouling of membranes<sup>2,3,6-15</sup>. It is unfortunately beyond the scope of this report to make an economic comparison between some of these different approaches to silica removal. However, it should be noted that in many cases the pH of the fouled water is changed to take advantage of the different solubility and reactivity properties of the silica<sup>16</sup>. It was our intent to treat the water at near neutral pH and only use an acid or base treatment in the recycle or regeneration steps which would entail a small percentage of the total water usage.

Our early experiments were directed toward an approach of ligand functionalized particles such that the ligand would capture the silica. The silica chelation would be followed by separation of the bound particles and lastly regeneration of particles for reuse (See Figure 2). During the first year of the program, there was extensive preparation and testing of modified silica gels, including two-step syntheses and modification of both commercially sourced and in-house produced silica particles. However, due to variable results and inability to achieve more than ~30% removal of silica, work was suspended. We also studied a variety of other metal oxides including Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, TiO<sub>2</sub> and MnO<sub>2</sub> but there was no advantage compared to alumina.

Additional work on modification of commercial resins with amines and other compounds of interest was also discontinued because they were not effective at removing silica from water. Attempts to use the ligand fragments or low molecular weight species as a way to screen for functionalities of interest were generally unsuccessful; the interactions are too weak to compete with the acidic reaction with the molybdenum complex. Similarly, chromatography and mass spectrometry methods were unable to detect interactions between the small molecules and the dissolved silica under the dilute conditions of 100 ppm silica.

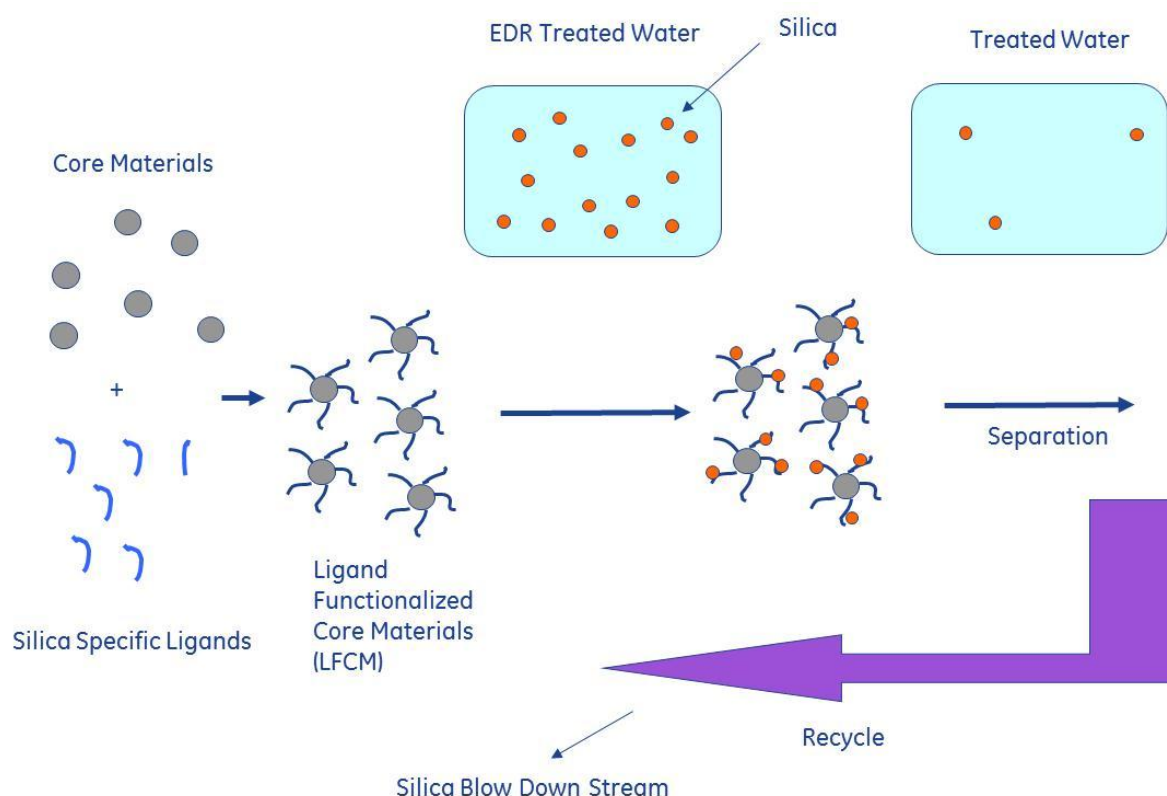


Figure 2. Schematic of original concept to remove silica with particles.

While carrying out the preliminary studies with modified particles and ligand fragments, we wanted to benchmark the removal of silica with some known materials such as alumina<sup>17-20</sup>. In particular, we evaluated the ability of a variety of commercially available alumina materials and some in-house prepared materials. The excellent performance of some of the aluminas as silica adsorbents became the primary focus of our work.

## Results and Discussion

### Synthesis

In the course of our benchmarking data with commercial alumina as an adsorbent for silica, we discovered that some of our in-house alumina materials were also very active in the removal of silica

(See Figure 3). Specifically, these materials were able to very rapidly remove almost 100% of the silica from the water in a bottle test with the adsorbent sitting on the bottom of the bottle and gentle magnetic stirring at room temperature. While there was a general trend that high surface area materials are able to perform better (see Figure 4), we have determined subsequently that neither pore size nor surface area are able to predict the adsorbent properties. It is also not surprising that the exact conditions for calcination can make a significant difference in the ultimate characteristics of the material.

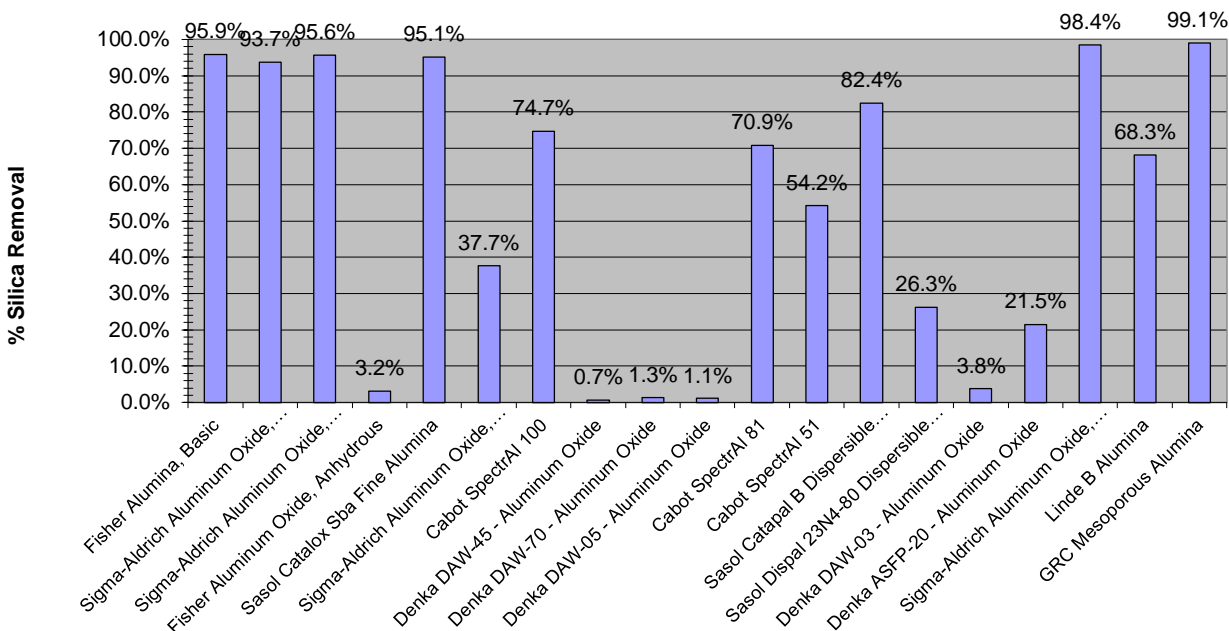


Figure 3. Bottle test results with 2g alumina in 125 mL water for 30 minutes

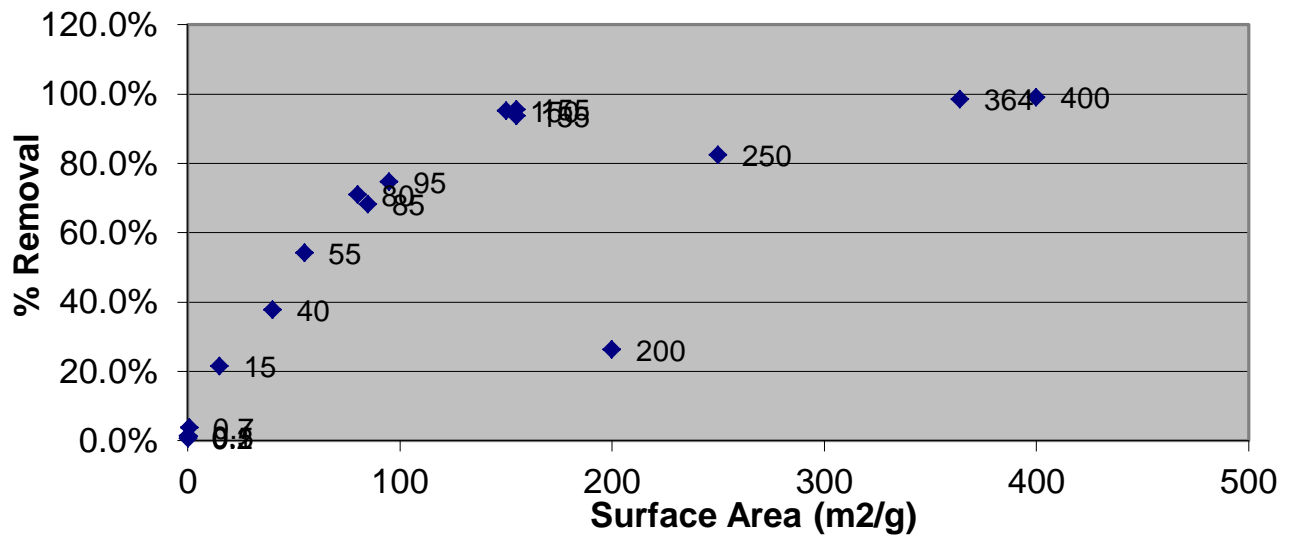
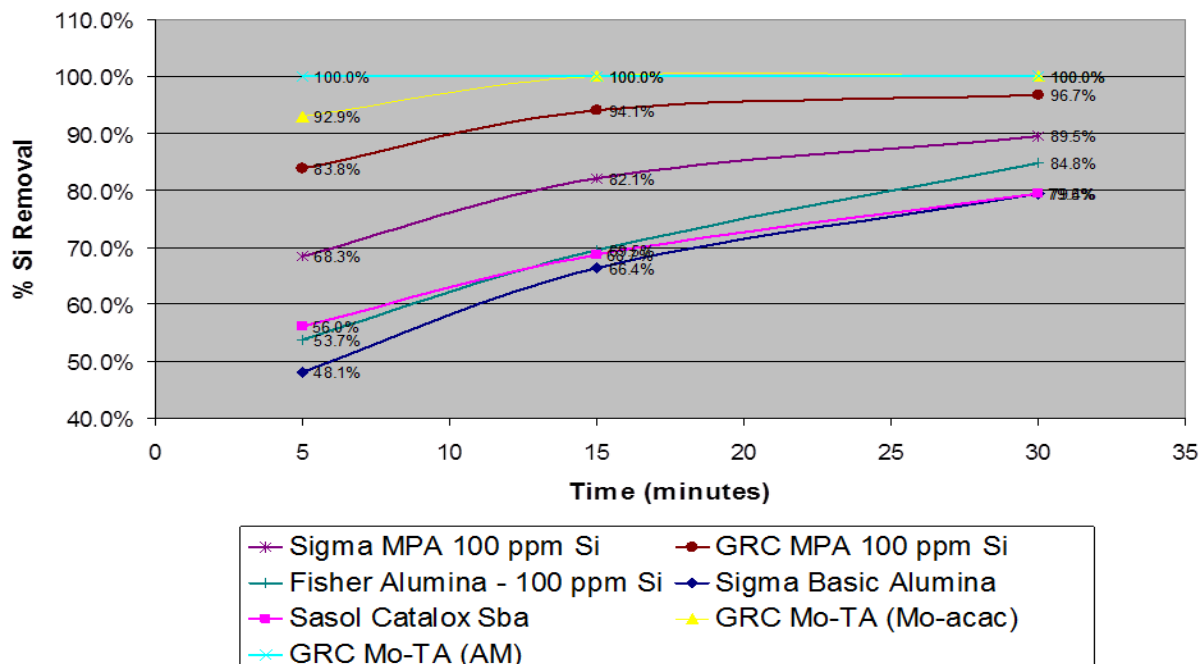


Figure 4. Correlation of alumina surface area with 30 minute bottle test adsorption

One of our early ideas in the program was to think about ways to use the strong binding ability of molybdenum that is used in standard tests to quantify dissolved silica<sup>21</sup>. Thus, we prepared an alumina with molybdenum incorporated inside the material at different loadings and with different sources of molybdenum. We used both ammonium molybdate and bis(acetylacetonate)dioxomolybdenum as precursors and likewise varied loadings from 0-5% molybdenum compared to aluminum. The presence of the molybdenum did have a beneficial effect upon the performance both from a kinetic (speed of absorption) and thermodynamic (capacity of absorbance) effect and became the focus of our efforts in the second year of the program. A graphic of the kinetic benefit is shown in Figure 5 with the Mo-modified aluminas able to remove greater than 90% of the dissolved silica in 5 minutes in a bottle test.



#### Figure 5. Kinetic effects with different aluminas in bottle test

Additional bottle test results showed that 1% Mo was preferable to 5% Mo and the results were largely independent of the precursor type. Therefore, for reasons of cost and performance, the lead candidate employs ammonium molybdate with a 1% Mo loading. Additionally, we sieved the calcined powders into fine (25-45  $\mu\text{M}$ ), medium and large (>150  $\mu\text{M}$ ) sizes. Though there was a modest benefit to the smaller size materials, even the largest size performed well in bottle tests. We have filed an application for a US patent based on the characteristics of the molybdenum-modified alumina<sup>22</sup>.

We have prepared the Mo-modified aluminas in several different ways with the goal of lowering the cost to obtain the final material. The basic reaction is an emulsion approach to the alumina using surfactants as templates that are removed subsequently by calcination<sup>22</sup>. In that aspect some of the variables included concentration of the reagents, length of time for the reaction and methods of drying prior to calcination. There have only been limited studies on the use of alternative surfactants for this material, but previous work at GE Global Research has shown that the Triton X114 is an excellent choice for making the mesoporous aluminas. One aspect that is important to the performance is the controlled hydrolysis of the aluminum butoxide; if that reaction is too rapid, the product material is unable to absorb the silica as well even with fine tuning of the calcination. The reaction as currently practiced generates a powder that is somewhat fine. In practice, such a material becomes undesirable for use in a column configuration due to the high back pressures that will develop. One area that might be appropriate for future research is to induce coagulation into larger particles at the end of the reaction.

We have carried out several experiments to probe effects during calcination. One study tested whether the loading in the furnace had any influence on the performance of the material. To that end, from a single reaction batch, loadings of 25g, 100g, and 500g were all calcined according to the standard protocol with two heat cycles to 550C. As described in the figure below, the 25g and 100g batch performed nearly equally, but the 500g batch was less effective at all three loadings. Such a result is consistent with our earlier data when the multiple kilogram batch was calcined at an outside vendor; the performance was inferior to that obtained in our own furnace. Similarly the performance of our second scale-up reaction was about 20% below the expected result based on the 100g lab scale reactions when

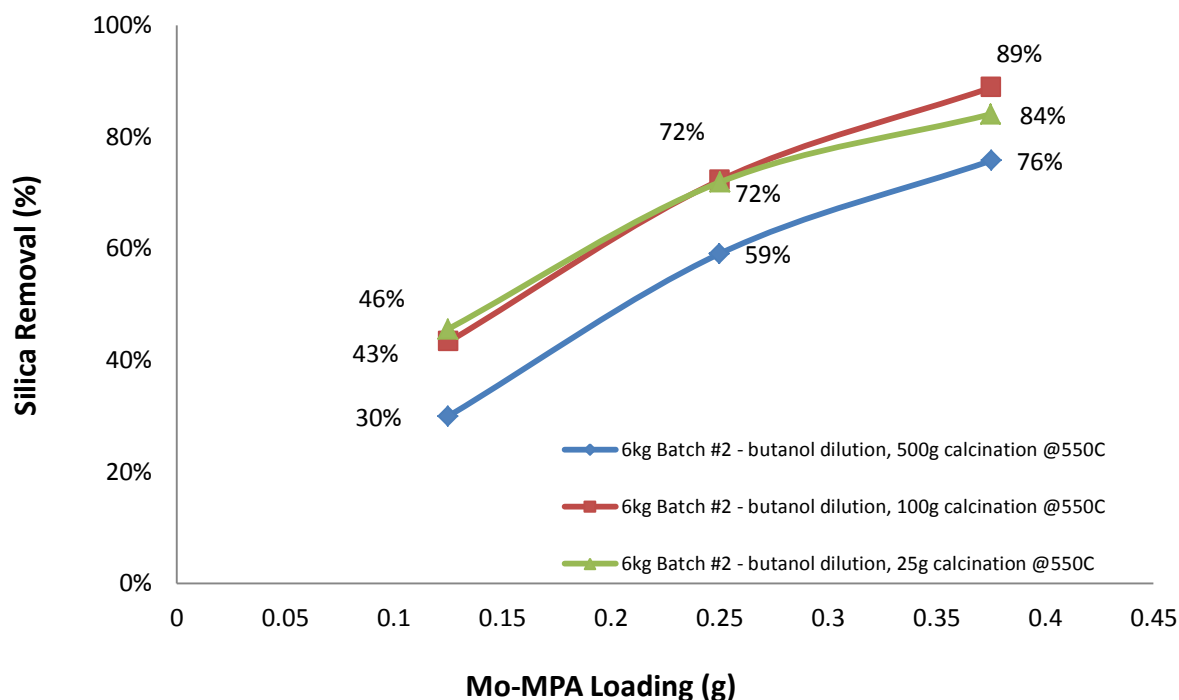


Figure 6. Effect of loading capacity in furnace on bottle test performance.

we calcined 500g in one operation. The exact scientific explanation for this is not entirely clear, but is apparently related to the ability of the surfactant to be burned out in a concentrated solid versus one that is more dispersed.

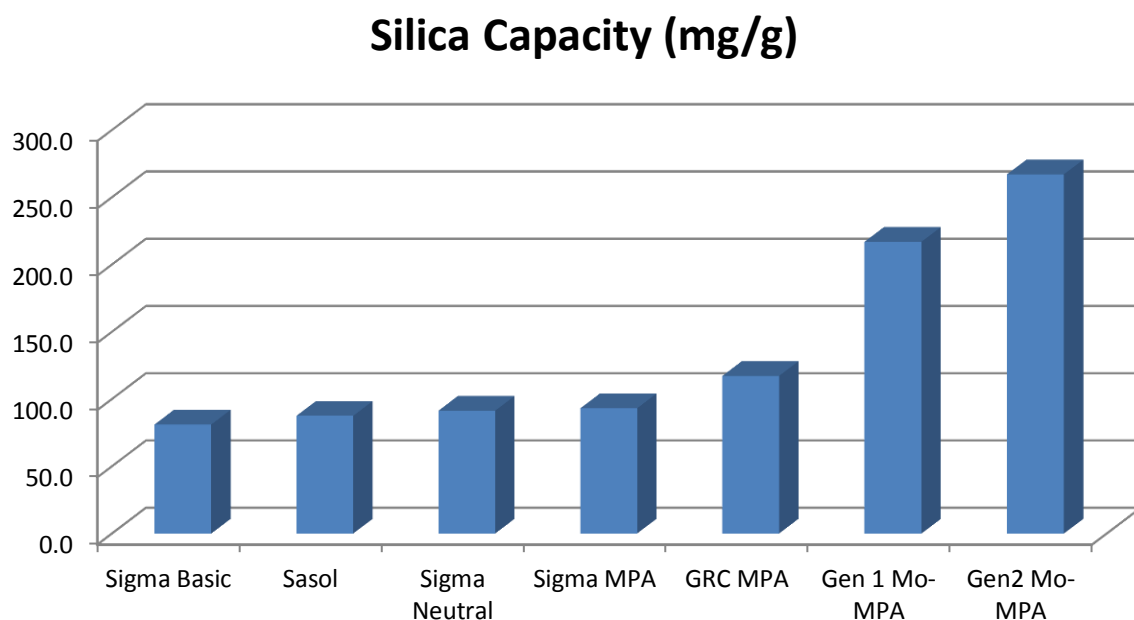
In a related experiment, one adsorbent was calcined at two temperatures (550C and 650C) in two ovens both to look at temperature effects and consistency across the different furnaces. Weight loss across the four samples was quite consistent ranging from 35.6-38.7% with no trends. The greatest spread in performance was at the lowest adsorbent loading in the bottle test (7.2%, at 0.1g adsorbent) while at the highest loading the range was reduced to 5% (at 0.4g adsorbent). At five out of the six conditions, the materials treated at 550C performed better (3-7%). Similarly at five out of six conditions one furnace generated improved data over the other by 0.5-5.1%.

### Capacity Experiments

While preliminary capacity tests in the bottle test configuration suggested that the capacity of the modified aluminas would be over 0.1g silica/g adsorbent, some of the early column tests demonstrated uptake on the order of 15 wt.% silica. Since we felt that a bottle test should be a better measure for ultimate capacity, a second set of experiments were carried out with only 0.05g of adsorbent and 500 mL of 100 ppm silica water with hardness for 24h. Under such conditions, our modified aluminas



showed absorptions of over 20%. To our knowledge, this is the highest capacity material known for silica. Results in comparison with other aluminas are shown in the figure below.



**Figure 7. Silica capacity as measured by absorption of 0.05g adsorbent from 500 mL of 100 ppm silica water**

During the course of column experiments, we observed an interesting behavior after breakthrough of the silica into the filtrate. The curve showed a steep breakthrough initially and then a more gradual slope later on. We carried out some long term experiments in bottle tests with loading of 0.05g to 3.0 g of material. The results indicated that some samples were taking up silica even after 3 weeks. Thus, one can not assume an equilibrium during the short duration of a column. The good news was that this data continued to support that our material was substantially better than a commercial mesoporous material with a Langmuir capacity of 0.11g/g compared to 0.06g/g. A final set of data confirmed that shaking the samples does slightly enhance the rate to equilibrium.

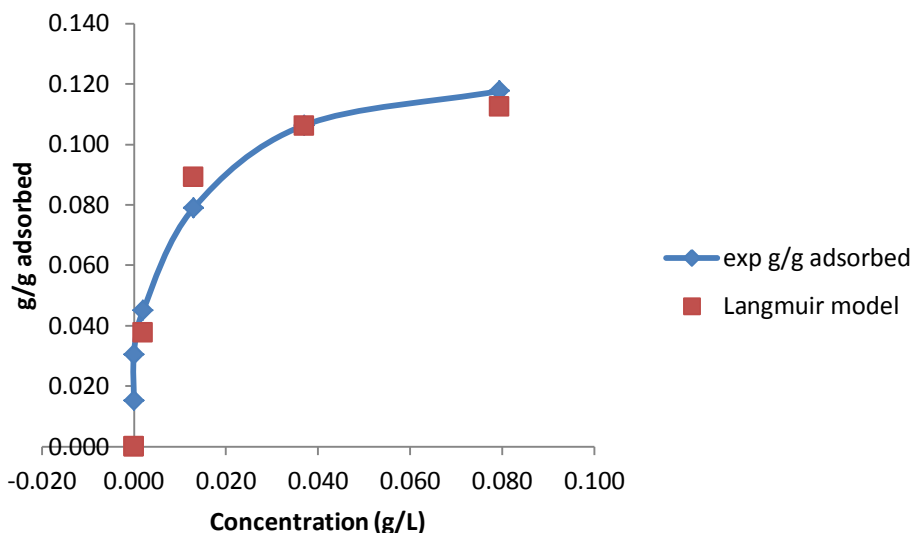


Figure 8. Observed data compared to Langmuir model for Mo-modified alumina

### High throughput testing

During the course of the work on this project, there were many occasions when a large number of samples needed to be evaluated either for screening or longitudinal studies. As a result, we developed an automated method using 96 well plates to analyze for the silica using the standard molybdate colorimetric test. In the automated test, the overall volume is 250-400 uL as compared to 1.5 mL in the typical lab test. A robotic program was used to load the well with both samples and reagents. In a typical experiment, samples were run at least in duplicate and silica standards were included for internal calibration. The optical measurement was done with a commercial multi-well plate reader (Molecular Devices SpectraMax M5) and calibration to silica concentration at times over 18 minutes yielded excellent linear plots with R2 typically greater than 0.999. Data was available in an Excel format.

### Characterization

It would be important to understand the details of how the Mo-modified alumina works better as a possible route to even more active materials. Thus we carried out quite an extensive study in comparison of standard mesoporous alumina and the Mo-modified material both prior to treatment with silica water and afterward. These studies included solid state NMR, Raman spectroscopy and EXAFS. In analysis of the solid state  $^{27}\text{Al}$  NMR, the Mo-modified material appears to have an increased signal associated with 5-coordinate aluminum. When the material is loaded with silica, the 5-coordinate peak diminishes and the 6-coordinate peak sharpens. In the  $^{29}\text{Si}$  spectra of the same samples, a downfield shift is observed in the Mo-modified alumina consistent with an effect from the presence of the molybdenum. In the Raman spectroscopy, most of the spectra were generally featureless although a peak at  $930\text{ cm}^{-1}$  was seen in some of the Mo-templated samples prior to treatment with silica.

We were hopeful that direct observation of the molybdenum atoms from extended X-ray fine structure (EXAFS) would provide key understanding, but the results were not sufficient to understand a mechanism. In all samples, whether with silica or not, the molybdenum is present as Mo(VI) and is surrounded by a first layer of oxygen atoms (1.8 Å on average) either in a tetrahedral or octahedral environment. The second order of atoms which might contain silicon or aluminum is too disordered to specify bonding arrangements. There is, however, a tendency of the silica loaded samples to increase the symmetry at molybdenum toward octahedral; again this would be consistent with interaction of the silica oxygen atoms.

Routine characterization of calcined materials would include a BET measurement. Average pore size was generally in the range of 60 Å and the surface area typically was near 350 m<sup>2</sup>/g or above. In the early experiments, the Mo loading was determined by ICP analysis and was typically on the order of 85% of theoretical. Our experiments with silica removal may be compared to those by Kim who focused on the importance of pore size in a process to remove arseni<sup>23</sup>c.

### Regeneration and Reuse

Since the Mo-modified alumina performed well in both bottle test and column test, the next critical problem to solve was to regenerate the material by removal of the silica and reuse. The schematic for this process is illustrated below (Figure 9) as a contrast to Figure 2.

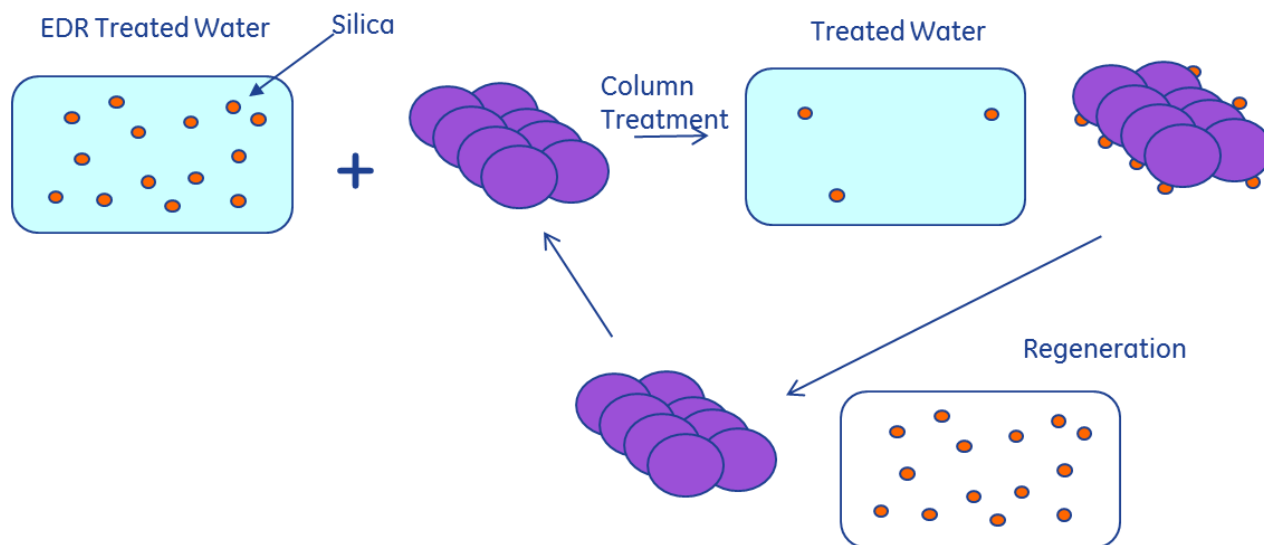


Figure 9. Schematic for use of Mo-modified alumina (purple spheres) to remove silica (red dots)

The schematic nicely illustrates that the problem of recycle can largely be separated into distinct steps: the removal of the bound silica from the adsorbent and the subsequent re-use of the material with a

fresh batch of impaired water. Thus, we often would test the two portions separately so that we would understand if a given treatment had issues with regeneration (silica removal) or reuse. One of the early experiments in this regime was to treat a silica loaded sample with a broad spectrum of aqueous pH conditions at room temperature. It is well known that silica becomes much more soluble at both strongly acidic and basic conditions<sup>16</sup>. The results of this study are shown graphically in Figure 10. If the silica loaded sample is re-exposed to impaired water, it is still able to remove over 50% of the dissolved silica because it was not loaded to capacity. Samples exposed to strong base were able to recover most of the bound silica and after the pH was returned to 7.0, the material was able to perform on a comparable basis with the unused sample. With less base present, there was not as complete removal of the silica and a corresponding decrease in performance on re-use. As an interesting contrast, the acidic samples were able to generally recover more of the bound silica, e.g., 0.1M HNO<sub>3</sub> achieved over 60% recovery of the silica compared to just over 40% for the same volume of 0.1M NaOH. However, the re-use performance of the acidic treated materials also suffered such that under the conditions just described, the base treated material removed 93% of the silica in a second bottle test while the acid treated material was only able to achieve 69%. The magnitude of this difference is further highlighted when compared to the control as the base treated material improved by 41% while the acid material only gained 17%. These results strongly supported the use of base for regeneration as compared to acid. We also examined counterion effects, but there was typically not much difference when making such changes as sulfuric acid compared to nitric acid or ammonium hydroxide compared to sodium hydroxide. All of these reasons combined with the lost cost of caustic made it the most attractive agent for regeneration by simple manipulation of pH.

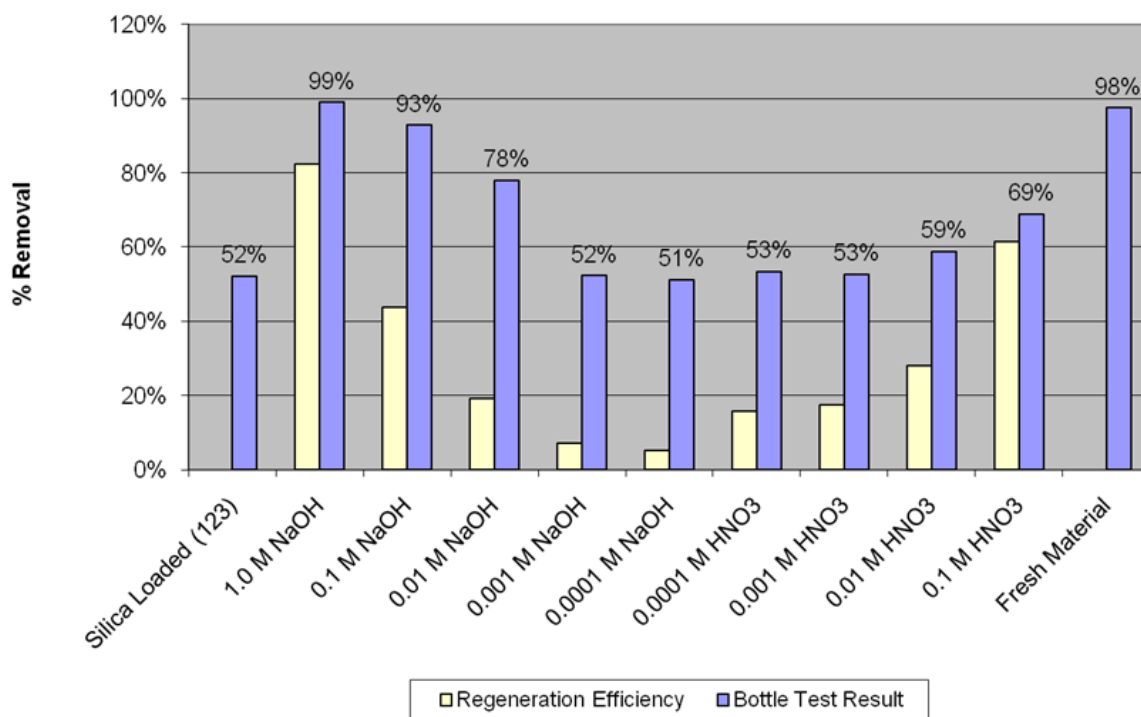


Figure 10. Effects of acid and base on silica removal and re-use

There remained, however, a significant problem in the use of caustic to remove the silica followed by neutralization for additional water treatment. The problem was that strong base has a tendency to dissolve the alumina itself as well as to cleave the bonds that are associated with the bonding of the silica to the alumina. We could monitor this effect either by analysis of the dissolved aluminum ions in the water or by measuring weight changes in the adsorbent after various treatments. Experiments to probe the effect of silica versus alumina dissolution were carried out with additional pH points in the basic range and also probed the effect of 5 minute treatment compared to 30 minute treatment or two rinses at a more dilute concentration compared to one. The bad news was that the conditions which allowed for comparable performance for fresh material resulted in a weight loss of between 10-20%; such conditions would obviously not be practical for a commercial scale. Another experiment that was carried out was to simulate a gradient treatment of base by sequential treatment with weaker base in each rinse. Under one such set of conditions, a 90% removal of silica in re-use was obtained while a total weight loss of the alumina was 6%. Such a result was generally somewhat encouraging. The first rinse generally contained the best Al: Si ratio though often that was still in the range of 4:1. As a result of this issue, significant work was carried out looking for materials that might be more selective in stripping the silica from the alumina.

A large number of materials were tested for their ability to selectively remove the silica from the Mo-modified alumina. Probably the largest set of compounds was tested with pH adjustment to 11 using ammonium hydroxide at loadings of 5000 ppm and 10000 ppm. Some of the molecules were tested based on literature results<sup>24</sup> while other followed from structures similar to compounds that looked interesting in a preliminary screen. Out of the additives tested, only one compound, tropolone, both increased the selectivity to silica and decreased selectivity to aluminum yielding a Si: Al ratio over one. The other compounds that showed improved selectivity generally also contained chelating hydroxyl groups as can be seen in the structures in Figure 11; however, the other four compounds only improved the Si: Al ratio by a factor of two while tropolone suggested more than an order of magnitude effect.

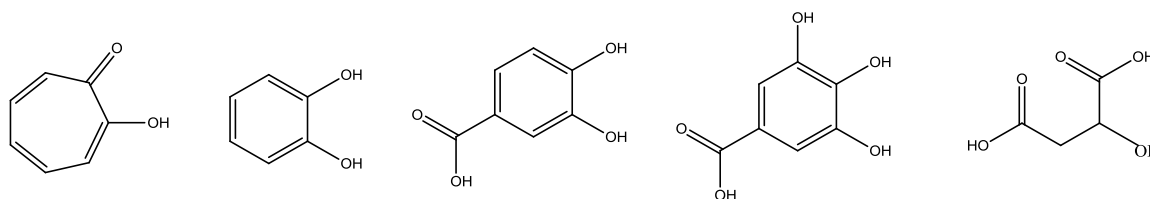


Figure 11. Structures of tropolone, catechol, 3,4-dihydroxybenzoic acid, gallic acid and malic acid

A small design of experiments was carried out around the processing conditions for regeneration with tropolone. The factors included residence time, loading of tropolone and pH. ICP analysis was used to measure levels of Al, Mo and Si in the rinse water. The optimal conditions were with pH at 4.5, loading of 5000ppm and an intermediate time (12.5 min). Under such conditions, Si was measured at 62 ppm, Mo at 2 ppm and Al less than 0.4 ppm. These results appeared to be highly promising for regeneration of the material. When the solid was rinsed back to neutral pH and subjected to a re-use experiment, the performance was very poor (55% removal) which was even below the activity of the untreated loaded

adsorbent. Subsequent analysis of the tropolone washed solid showed significant absorption of the tropolone as measured by carbon analysis and consistent with a residual color. Although re-use was better at pH 7 (approximately 80% silica removal), the performance dropped dramatically after a second recycle (16% removal). The final conclusion was that while tropolone would be an excellent choice for silica removal, it was not an acceptable candidate because the tropolone itself blocks active sites on the adsorbent.

An additional set of compounds were screened for regeneration based on their structural similarity to siliicatin or other biological molecules with a known affinity for silica<sup>25</sup>. Unlike the previous set of materials which relied on hydroxyl groups, these often used amines or polyamines as potential chelates (ethanolamine, propylamine, and polyallylamine). Some of the compounds like mimosa tannin and papain did generate favorable Si: Al ratios but suffered from the same issue as the tropolone in re-use performance.

Since the general approach of regeneration with selective agents was proving to be highly challenging, a fairly broad class of simple acids and bases were screened with the notion that return to pH of 7 would also eliminate the species from the adsorbent. The two species that were studied the most were probably phosphoric acid and ammonium hydroxide. As suggested above, ammonium hydroxide did perform quite well in the bottle tests, but subsequent experiments on a column at lab scale indicated problems compared to the sodium hydroxide treatment. With the acid treatments, even at low loadings of acid (0.01N) it was difficult to get high reuse numbers so the acid work was abandoned.

Thermal regeneration was also tested as a means to release the bound silica from the alumina. In particular, experiments were carried out at 30C, 60C and near reflux with times ranging from 1h to 24h. The best results were for 60C at 24h and near reflux for 1h. Under such conditions about 7-8% of the bound silica was removed; the resulting materials showed slightly enhanced performance in re-use experiments with silica removal at about 67% and 70% compared to the loaded sample at 59%, but far short of the fresh alumina. Thus any thermal methodology could only be used for a slight enhancement, but could not be a key element in regeneration.

### Column Experiments

While the bottle tests were a standard approach to screening large numbers of adsorbents, the test in a column was always going to be a more realistic test of the ability of a material to remove silica from impaired water. Thus, we began to run column experiments with alumina before we understood very much about the regeneration or recycle of the material. In our typical lab experiment, 2g of adsorbent were placed in the column and a slow feed of approximately 1 mL/min was used. Samples were taken over 10 minute intervals. The figure below shows the comparison of our modified alumina with several other commercial materials as well as the unmodified mesoporous alumina.

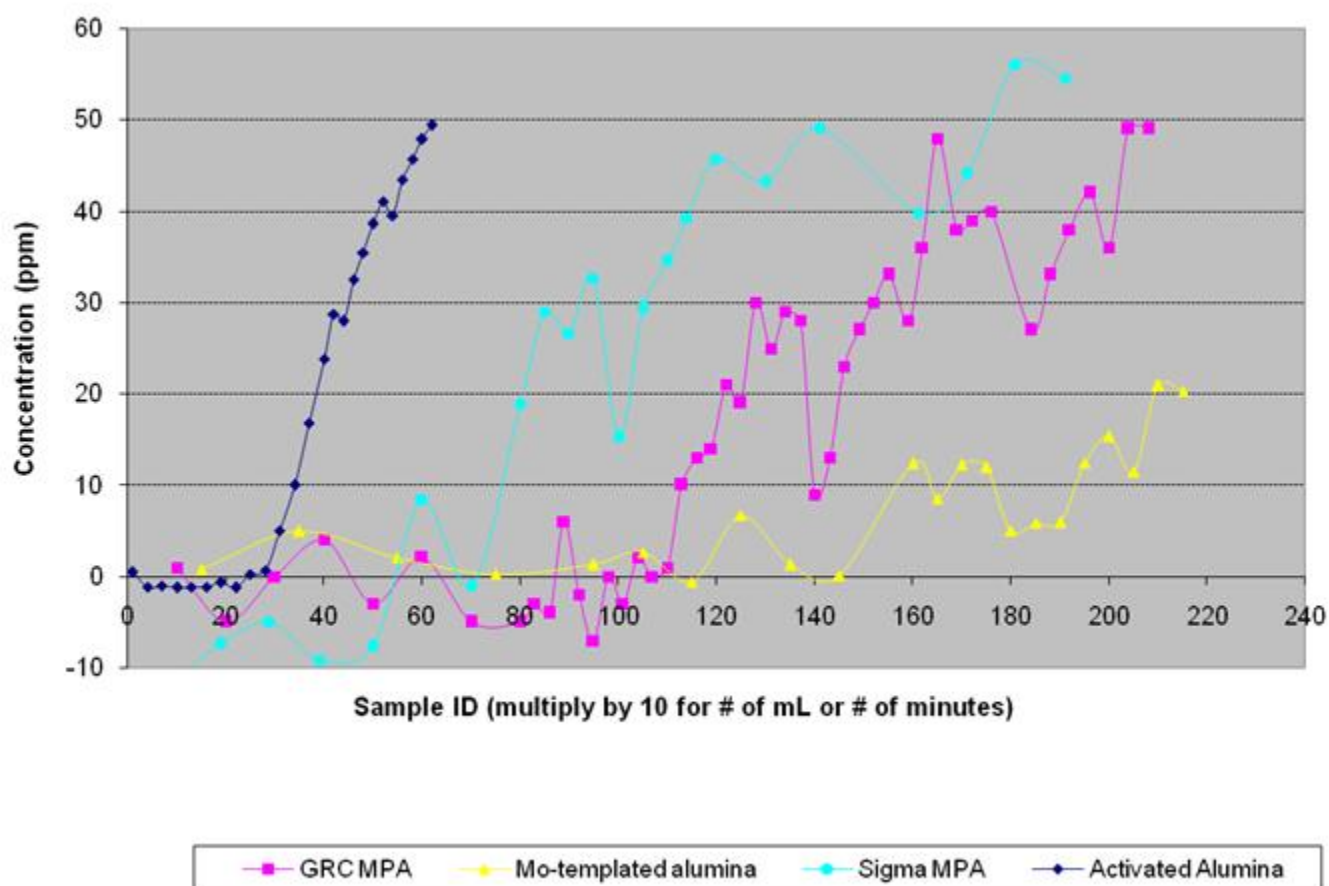


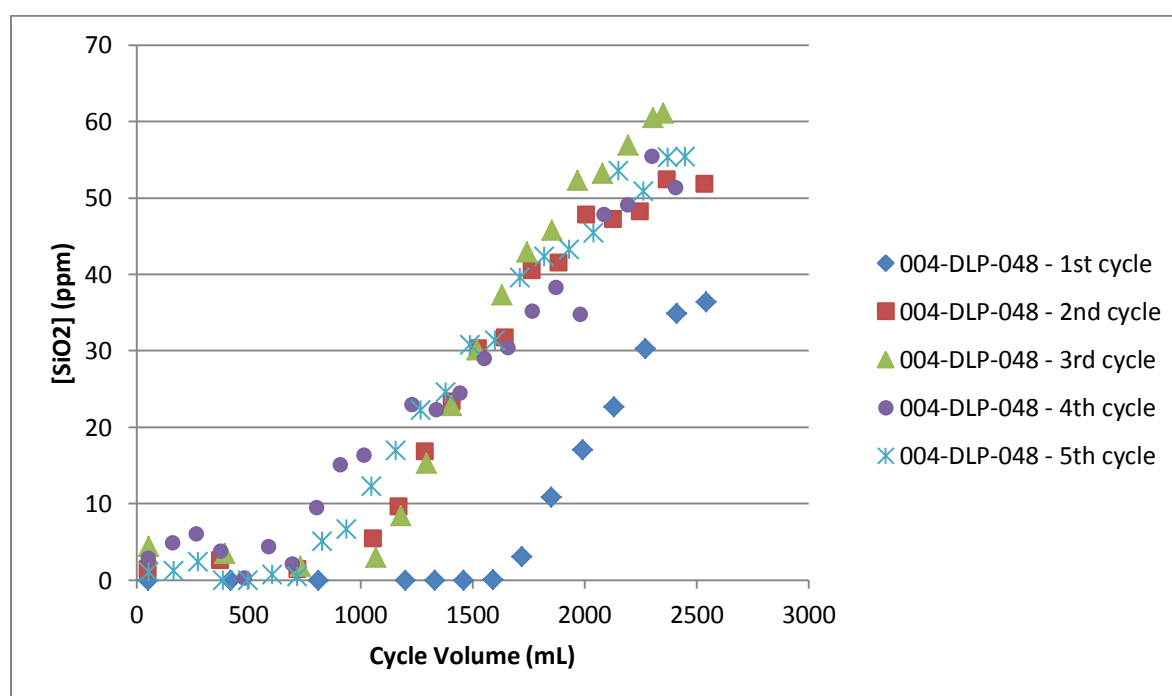
Figure 12. Tracking of column outflow with time for different adsorbents on 2g column with 1mL/min flow of 100 ppm Silica

It can readily be seen that activated alumina only absorbs about 300 mL of silica until breakthrough while our materials lasted through about 1500 mL and were still under 20 ppm after 2000 ml through the column. These results were naturally encouraging and strongly supported the results from the bottle testing. However, it was apparent that the cost of our material was sufficiently high that multiple recycles would be necessary so we started to work on the column regeneration.

In the first few attempt to regenerate the column, we treated the column with base and then used additional pH 7 water to bring the column back to neutral conditions. We observed that the back pressure stayed low during the column run and the base treatment but tended to spike up when we brought the pH down. Indeed, in some instances, the pressure rose to the point that we could no longer add more silica loaded water. Eventually, we found that the key to stable pressure was to *gradually* lower the pH by steps so that there is no shock to the system. We speculate that the cause of the problem is that the silica or sodium silicate is soluble at the higher pH of 10 or above, but when abruptly exposed to pH 7 water, there is precipitation that causes the column to plug. In practice, we used step changes from 0.01N NaOH to 0.001N to pH 10 to pH8 and neutral. For most of the experiments in lab, at least a 2x level of base was added compared to what theoretically would be necessary based on the

silica absorption. Obviously this procedure could be automated and optimized to reduce both the amount of base necessary and the amount of water necessary for the regeneration.

Once a set of conditions for the regeneration of the column with weak base were determined, we went ahead and measured the column outflow for a series of recycles. Data including the amount of silica absorbed is presented in Figure 13 below. Although there is a drop-off in performance between the first and second runs, the additional runs do not show further decrease in activity. The data below are very encouraging for the potential of this adsorbent since it shows enhanced activity for multiple runs. As the cost of the system is roughly inversely proportional to the number of runs one can do, the benefit of multiple runs is very critical to a commercial system.



	mg silica/g removed	mg silica/g removed through 20 ppm
1 <sup>st</sup> cycle	105.7	91.6
2 <sup>nd</sup> cycle	83.9	53.7
3 <sup>rd</sup> cycle	75.4	52.5
4 <sup>th</sup> cycle	83.4	48.7
5 <sup>th</sup> cycle	80.7	51.6

Figure 13. Analysis of filtrate from 2g column with 5 treatments of 100 ppm silica and 4 regenerations



Later experiments demonstrated that it was possible to achieve good regeneration with initial base treatments as concentrated as 0.05N. Such a result is important because it allows for a much lower total volume of water necessary in the regeneration step. Since one of the key goals of the project is lower water usage, minimizing the water requirement for the regeneration step is important.

### **Large Scale Column and Simulated Cooling Tower Experiments**

After the successful demonstration of multiple recycles on a lab scale unit, it was important to demonstrate the ability to carry out the process at a larger scale. Moreover, it was important to demonstrate the viability of column regeneration on a large scale without issues due to plugging or complications in starting and stopping of the water flow. To this end, the material that was generated in the pilot facility in Niskayuna in the fall of 2011 was sent to the GE Water facility in Trevose. It was loaded into a large column (see Figure 16 below) suitable for treatment of water. A simulated water composition was used as the feed for the experiment; in addition to 100 ppm SiO<sub>2</sub>, the water contained significant amounts of magnesium and calcium salts. The water was pushed through the column with the aid of a pump. During the initial hydration of the column, some of the hardness was removed along with the silica, but over the course of the entire run, more than 90% of the salts passed through while no silica breakthrough was observed. The amount of silica in the permeate tank was 0 ppm which is equivalent to 0 g of silica in the 154L collected. As the silica level in the make-up water was 98 ppm or 19.6 grams of Silica, it can be estimated that about 15g of silica was adsorbed on the column.

After the completion of the first passage of water through the column, it was subjected to a regeneration treatment as outlined in Table 4 below. The strategy of this protocol is to remove the silica as sodium silicate early in the process and then gradually return the pH to neutral so that high concentrations of silica do not precipitate. Although this is far from an optimized procedure, it can readily be seen that only 55 L of water were used to regenerate the column for an additional 200 L. Indeed it is apparent that the column can absorb more than 200 L at 100 ppm silica. The regeneration process was carried out smoothly and no pressure spikes were observed during the process.

The run was repeated as described above with identical water composition. The water composition obtained from the ICP analysis of the make-up water, water sampled every hour and the final water permeate reported in Table 5. Although a small amount of silica is observed in the first sample, the silica quickly settles down to a number of about 2.2 ppm that represents about 98% removal of the dissolved silica. The final permeate sample analysis showed that approximately 0.4g of silica passed through the column while over 15 g were retained on the column.

As the saturation limit of silica in waters at neutral pH is about 200 ppm, only two cycles of concentration can be achieved in a cooling tower using the untreated water as make-up (100 ppm) with silica as the limiting factor. However, the treated water or permeate water obtained above can be cycled up 10 times, though hardness actually becomes a limiting factor beyond 6 cycles with the appropriate scaling chemical treatment. To test this, the permeate water collected above was fed into a bench top testing cooling tower to see how high the water can

be cycled up and compare it to the number of cycles that can be obtained using the untreated water.

Bench top testing of the Silica removal program at GEWPT's Trevose laboratory is carried out in a Controlled Evaporation Research Tower (CERT) that simulates a Cooling tower. The CERT system allows us to accurately predict field performance on a range of metallurgies and water velocities according to specific customer application conditions. The CERT utilizes un-cycled make-up water that is circulated through a heat transfer tube so that corrosion and fouling potential can be assessed. The CERT mimics a real cooling tower operation by including a tower segment to effect evaporation and a pre-heater to affect a " $\Delta T$ " across the tower. The evaporation leads to increasing cycles of concentration and a requirement for make-up water to be added so that system volume is maintained. The number of cycles is measured for total hardness (TH) and silica (ratio of the concentration ions at a particular point to that of the make-up water). A close agreement of the two numbers indicates a stable system with no loss of salts to precipitation or scaling.

Figure 14 below shows the number of cycles of concentration obtained when using the untreated water (control) and the treated water as the make-up water over an eleven day period with a flow rate of 30 ml/min. The control was cycled up briefly to 3 though we can see an immediate gap between the TH and silica levels with the silica levels dropping to approximately 2.5 cycles. The treated water is cycled up steadily to 6 cycles without any gap between the TH and silica levels indicating a stable system with no loss of salts to scaling.

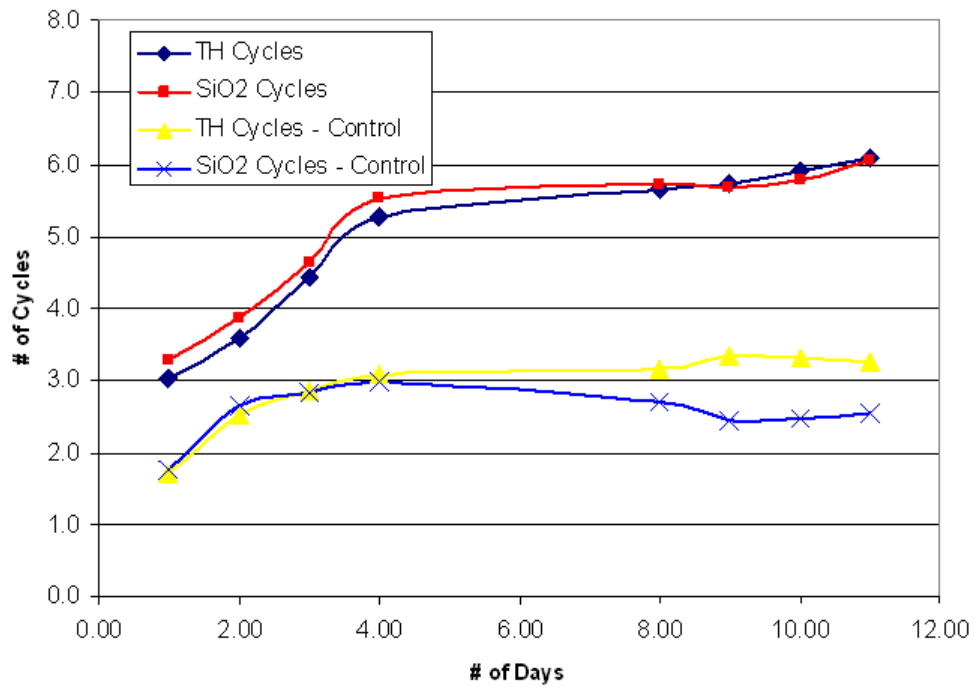


Figure 14. Number of cycles of concentration based on total hardness and silica levels for both treated and untreated (control) water

The water saved by the cooling tower by increasing the cycles of concentration from 2.5 to 6 is 8.4 ml/min or 28% which is calculated using the following formula:

Equation 1

$$\Delta V = \frac{M*(C2-C1)}{C1(C2-1)}$$

In Equation 1,  $\Delta V$  is the volume of water saved,  $C1$  and  $C2$  are the initial and final number of cycles of concentrations achieved in the cooling tower respectively and  $M$  is the make-up water flow which in this case is 30 mL/min. Such a savings is consistent with the original intent of our proposal to decrease fresh water usage by removal of the silica impurities.

### Cost Scenarios

At early stages in a development project it is difficult to accurately assess the cost of a given process. For the proposal outlined above, we have focused almost exclusively on the silica removal portion since there was no low cost process for that. Today, there are still some lime softening approaches practiced<sup>4,17,26,27</sup>. Estimation for the Electrodialysis portion of the process using the DOE model would

be \$2.06/1000 gallons. If the goal is for the entire process to cost \$3.00/1000 gallons, then there is only about \$1 available for the silica removal process.

We have employed a fairly simple model that looks at the cost of adsorbent, performance of the adsorbent and cost of the recycle process. It is not surprising that the cost is dominated by the cost of the adsorbent especially since we are using a dilute caustic as the key reagent of the recycle. If we make the assumption that the cost of the adsorbent is fairly high at \$40/kg, then the amount of adsorbent that will be necessary per day will depend on the flow rate and the concentration of dissolved silica. If the dissolved silica concentration is 100 ppm and we desire to lower the output to 20 ppm, then it requires four times more silica absorption than starting at 40 ppm dissolved silica and lowering to the same 20 ppm. Based on the Langmuir absorption of 0.11g/g, one can calculate how much water a given mass of adsorbent can treat. Then the cost becomes factored by the number of recycles to a first approximation so 10 recycles would lower the cost by a factor of ten. Naturally there is some cost for the caustic treatments, disposal and so on, but these are typically small compared to the adsorbent cost. In our hypothetical example of \$40/kg adsorbent, the cost of alumina per 1000 gallons would be approximately \$27 for a 40 ppm silica water and \$105 for 100 ppm silica. As we have demonstrated 5 recycles in the lab, then we can assume perhaps 10 recycles which drops the prices to \$2.70 and \$10.50 for 1000 gallons. Obviously if the cost of the adsorbent itself could be dropped by a factor of two, then all the costs would drop correspondingly. Caustic and disposal costs are probably under \$0.30 per 1000 gallons. In reality, there would be capital expenses, energy costs and non-chemical consumables to be included in a more complete cost analysis. In summary, although there may be a pathway to low cost treatment of the impaired water, we have not yet demonstrated the target cost suggested in the original proposal of this project.

## Conclusion

Over the course of the program, a new molybdenum-modified alumina was developed that significantly outperforms any existing adsorbents, including alumina materials, in silica removal both kinetically and thermodynamically. The Langmuir capacity is 0.11g silica/g adsorbent. Moreover, a low cost recycle/regeneration process was discovered based on a gradient treatment with dilute caustic to allow for multiple recycles with minimal loss in activity. On the lab scale, five runs were carried out with no drop in performance between the second and fifth run in ability to absorb the silica from water. The Mo-modified alumina was successfully prepared on a multiple kilogram scale and a bench scale model column was used to remove 100 ppm of silica from 400 liters of simulated impaired water including a regeneration/recycle step. Significant water savings would result from such a process and the regeneration process could be further optimized to reduce water requirements.

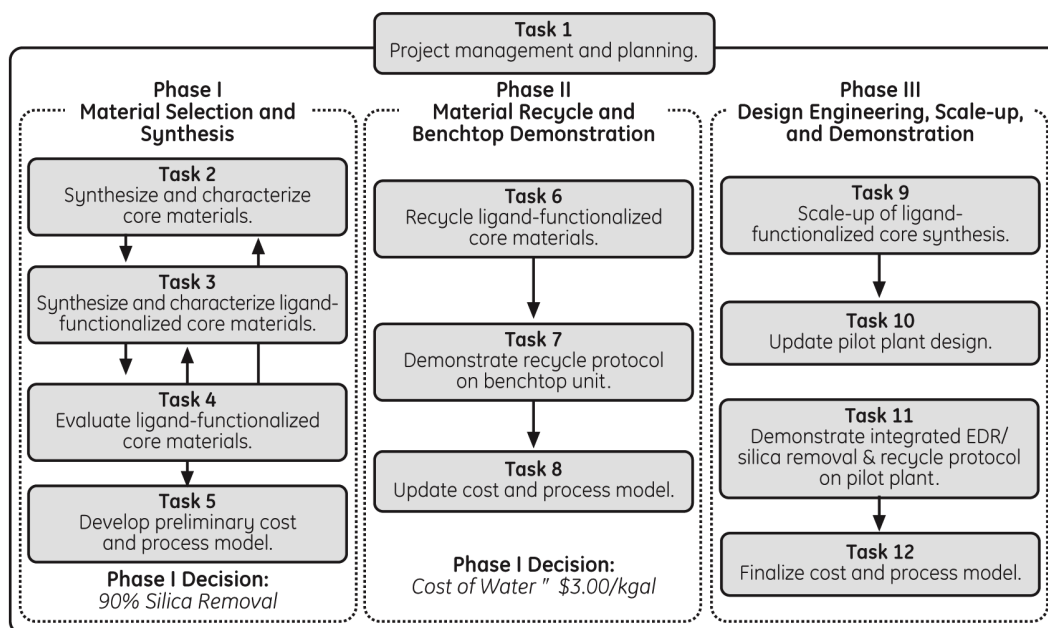


Figure 15. Project Outline by task

## Experimental

### Experimental

#### Test Water

At this point three water formulations are being used to baseline the performance of materials. The first is simply silica (sodium silicate -- usually 100ppm) dissolved in Millipore 18mega-ohm deionized water and neutralized with hydrochloric acid. The second is the same sodium silicate in deionized water with added hardness prepared as described below and the third is a 180 ppm silica make-up.

#### Procedure for the preparation of 100 ppm silica make-up water with hardness

100 ppm silica make-up water is prepared using two solutions. The first, Make-Up A, is prepared by combining 199.6 mg anhydrous calcium chloride ( $\text{CaCl}_2$ ) and 144.3 mg anhydrous magnesium sulfate ( $\text{MgSO}_4$ ) in a 500 mL volumetric flask. The flask is filled to the line with deionized water. Make-Up B is prepared by combining 353.1 mg sodium metasilicate pentahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ), 55.4 mg sodium bicarbonate, and 333  $\mu\text{L}$  10 N sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and in a 500 mL volumetric flask, which is filled to the line with deionized water. Make-Up A and B should be combined in equal amounts prior to use.

#### Procedure for the preparation of 180 ppm silica make-up water

180 ppm silica make-up water was prepared in 4 L batches. For one batch, 2.5434 g sodium metasilicate pentahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) was added to 3 L water (deionized) while stirring. 1.0 M and

0.1 N HCl were used to adjust the pH to neutral. The solution was then diluted 3900 mL and the pH was rechecked. The volume was then brought to 4 L.

### **Original Column studies – revised downflow**

2 g of alumina was added to a stainless steel column. 100 ppm silica water with hardness was run through the column downflow at a rate of 60 mL/hour. A fraction collector was used to collect samples continuously, every 10 minutes. Samples were tested for silica concentration using the automated silicomolybdate method. In some instances, the samples may also be analyzed by ICP for residual aluminum or other metals derived from the modified alumina.

### **Bottle Test Procedure**

Bottle tests are performed by weighing out a predetermined amount of adsorbent into a 125 mL Nalgene bottle, 15 dram plastic vial, 7 dram plastic vial, or 12 mL plastic test tube depending on scale. A magnetic stir bar and either 125 mL, 45 mL, 20 mL, or 12 mL of the make-up water is added to the bottle, vial, or test tube. The mixture is stirred for 5 minutes to 24 hours (in a standard test, stir for 30 minutes). The adsorbent is then filtered off using a 0.02  $\mu\text{m}$  syringe filter (in a standard test) or Whatman 50 filter paper. Silica content can be determined using the silicomolybdate colorimetric method.

### **True maximum capacity protocol**

0.05 g of various aluminas was added to 500 mL Nalgene bottles with 500 mL 100 ppm silica water with hardness. The mixture was stirred for 24 hours before being filtered using 0.1  $\mu\text{m}$  syringe filters. The water was then analyzed using the silicomolybdate method.

### **Silicomolybdate Test Procedure for Determination of Silica Content**

Silica content is determined via a colorimetric method using a molybdate reagent comprised of 4.84 g sodium molybdate, 13.86 mL concentrated nitric acid, and 1.72 g sodium dodecyl sulfate in deionized water (total volume = 1 L). 1 mL of reagent is added to 0.5 mL of sample and is allowed to sit for 5 minutes prior to taking the UV measurement. The absorbance is recorded at 410 nm.

### **Gen2 Procedure for MPA impregnated with 1 wt.% Mo- Direct Addition of Al to water, Triton, and Cyclohexane emulsion**

A 3-neck, 5L round bottom flask equipped with a mechanical stirrer, condenser and  $\text{Al}(\text{OBU})_3$  addition apparatus was charged with 300mL of water, 1L of Cyclohexane and Triton X114 (140g). The flask was stirred vigorously and a white suspension was formed.  $\text{Al}(\text{OBU})_3$  (500g, 2.03 mol) was added by charging a 1L polyethylene jar whose cap was equipped with a gas inlet and a dip-tube outlet. Using a 2-3psi nitrogen purge, a feed of approximately 4-5 mL/min was achieved. Total addition time should be

155min. After the addition of  $\text{Al}(\text{O}i\text{Bu})_3$  is completed, 1.766 g of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , dissolved in 25ml of water, was added to the flask. The mixture was allowed to stir for 30 minutes at room temperature before being aged at reflux with stirring for 24 hours. The solid was recovered by filtration and washed with approximately 1L of cyclohexane. The obtained solid was then subjected to pyrolysis at  $550^\circ\text{C}$  under nitrogen and then calcination in air at  $550^\circ\text{C}$  in each case with heating ramps of  $2^\circ\text{C}/\text{min}$  followed by a 3h soak at temperature and rapid cooling.

### Scale-up Reaction of Modified Alumina

A large scale preparation of the modified alumina was undertaken in a 100 gallon stirred reactor. The reactor was initially charged with 15L of DI water, 4L of 2-butanol, 50L of cyclohexane and 7kg of Triton X114. These contents were stirred to generate a white suspension. Then a mixture of aluminum isobutoxide (25kg) and an additive (1.3kg) were added over a period of about 2.5h. After completion of the aluminum compound, a solution of ammonium molybdate (88.3g) in 1.25L of water is added to the reactor. The contents were allowed to mix for approximately 0.5h and then the reactor was heated to  $68^\circ\text{C}$  for 24h. The reaction was then allowed to cool to room temperature and filtered into a centrifuge bag in 2 portions. The solid was washed with isopropanol and then dried in a vacuum oven over several days gradually ramping the temperature from 60- $105^\circ\text{C}$ . Calcination was carried out on small portions of this material (125g per run) as described above.

### Full-scale column study

2.0 g of molybdenum templated alumina from batch CME\_121610 was loaded into the column and deionized water was run through to hydrate. 100 ppm silica water with hardness was then run through the column, and pump speed was adjusted periodically to adjust the flow rate. A total of approximately 5.92 L 100 ppm silica water with hardness was run through the column in the first cycle.

To complete regeneration, the amount of required NaOH was first calculated by determining the mol of silica removed during the column run. This number was then multiplied by 2 to determine the mol of NaOH required for regeneration, and then multiplied by 2 again to determine the amount with excess. For the first regeneration, 0.0056 mol of silica were adsorbed to the column. This translated to a necessary 450 mL of 0.05 N NaOH to perform the regeneration with excess. After regeneration had been completed, the pH was gradually reduced using dilute NaOH (0.01 N NaOH, 0.001 N NaOH, to pH 10 NaOH, pH 8 NaOH, and neutral water).

This process was repeated for four additional cycles.

### Bottle tests for regeneration model

The silica saturated alumina was prepared by charging a polypropylene container with 16 grams of modified alumina and 2.0 liters D.I. water containing 2.118 grams of sodium silicate pentahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) which is a 300 ppm solution of " $\text{SiO}_2$ ", after acidification with HCl to pH 7.0 prior to adding the alumina. This mixture was shaken for 24 hours collected by filtration and the procedure repeated with a fresh silica solution as just described. This alumina

was collected and determined to be 7.25 wt.% SiO<sub>2</sub> by difference from the original silica solution as determined by the colorimetric molybdate test for soluble silica. This alumina was used as common feedstock for subsequent experiments. Two grams of the alumina was slurried in the regeneration solution with samples of the solution collected and filtered for analysis and the ultimate alumina sample was isolated by filtration and dried for 24 hours under vacuum. All samples were submitted for ICP analysis

### Large Scale Column Study

500g of GRC Molybdenum impregnated Mesoporous alumina (F925-78) was packed into a steel column 120 cm long with a 2 cm diameter.

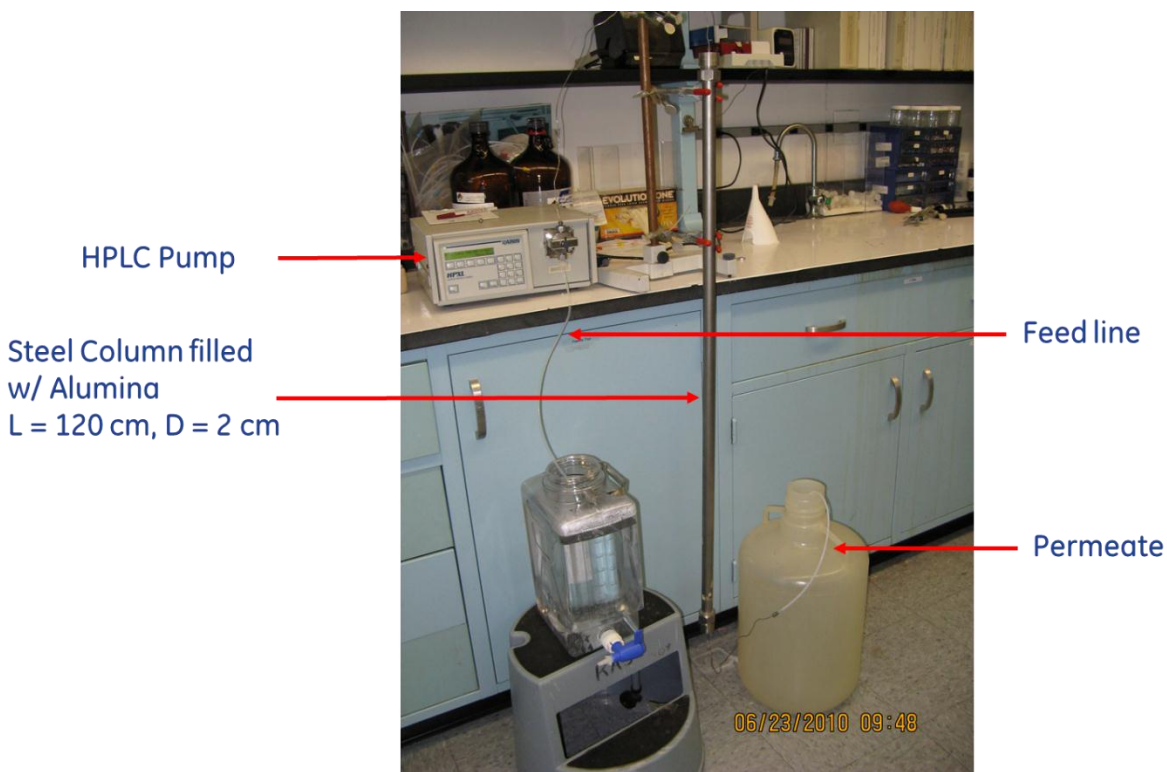


Figure 16 Large scale column for treatment of impaired water

200 Liters of water with the chemical composition shown in Table 1 was prepared by dissolving the salts shown in Table 2 in distilled water. The resulting make-up water was pumped using a HPLC pump through the column in a downward flow at a rate of 100 mL/min and collected in a 200L plastic tank. A backpressure of 500 psi was noted.



Table 1. Make-up Water Composition

Water Chemistry	
Ca as CaCO <sub>3</sub> (ppm)	180
Mg as CaCO <sub>4</sub> (ppm)	120
Silica as SiO <sub>2</sub> (ppm)	100
MAIk as CaCO <sub>3</sub> (ppm)	33

Table 2 Salts dissolve in Make-up water

Treatment (Salts)	
CaCl <sub>2</sub> *2H <sub>2</sub> O (g)	52.876
MgSO <sub>4</sub> *7H <sub>2</sub> O (g)	59.100
Na <sub>2</sub> SiO <sub>3</sub> *5H <sub>2</sub> O (g)	70.619
NaHCO <sub>3</sub> (g)	11.079
10 N H <sub>2</sub> SO <sub>4</sub>	66.58 ml

The permeate water was collected in a 100 mL plastic bottle suspended near the top inside wall of the permeate tank and allowed to overflow into the tank. An automatic sampler collected water from the bottle every 180 minutes. This simple set-up ensured that water from the last minute of the 180 minute interval (with a 25 mL/min flow rate) was being sampled hence giving us the snapshot of the water composition at the end of the 180 minute interval.

At the end of the experiment, the permeate water in the tank was mixed and sampled (final water permeate). The water composition obtained from the ICP analysis of the make-up water, water sampled every hour and the final water permeate reported in Table 3.

Table 3 . Water composition of make-up, final permeate in tank and at regular 180 minute intervals for pass 1.

	SiO <sub>2</sub>	Ca	Mg	Total Hardness
<b>Make Up</b>	<b>98</b>	<b>175</b>	<b>121</b>	<b>296</b>
<b>Hours</b>				
0	0	0	0	0
4	0	0	0	0
8	0	163	27	190
12	0	172	108	280
16	0	168	120	288
20	0	164	125	289
24	0	170	124	294
28	0	171	124	295
32	0	171	128	299
36	0	171	125	296
40	0	175	125	300
44	0	168	123	291
48	0	173	129	302
52	0	171	126	297
56	0	169	128	297
60	0	175	125	300
64	0	179	130	309
68	0	170	128	298
72	0	171	127	298
76	0	173	125	298
80	0	178	128	306
84	0	174	126	300
88	0	171	127	298
92	0	170	129	299
96	0	169	127	296
<b>FINAL Permeate Composition</b>	<b>0</b>	<b>155</b>	<b>110</b>	<b>265</b>

## Column Regeneration

The column was rinsed with Caustic and DI water as described below. The NaOH concentration was steadily reduced in sequence to prevent precipitation of silica and alumina in the column thereby plugging the filter. This problem was observed in smaller test columns when the pH was rapidly dropped.

Table 4 Experimental Protocol for Large Scale Column Regeneration

1	10L of 0.05N NaOH at 25 mL/min
2	10L of 0.01N NaOH at 10 mL/min
3	10L of 0.001N NaOH at 25 mL/min
4	10L of water at pH 10 at 2.5 mL/min
5	15L of DI water 10 mL/min

Table 5 Water composition of make-up, final permeate in tank and at regular 180 minute intervals after column regeneration

	SiO <sub>2</sub>	Ca	Mg	Total Hardness
<b>Make Up</b>	<b>92</b>	<b>170</b>	<b>121</b>	<b>291</b>
<b>Hours</b>				
0	11.1	0	0	0
4	3.5	8.2	6.9	15.1
8	2	51	24	75
12	2.4	155	102	257
16	2.3	165	116	281
20	2.3	169	117	286
24	2.2	166	119	285
28	2.3	171	119	290
32	2.2	173	123	296
36	2.3	173	121	294
40	2.2	173	125	298
44	2.2	173	121	294
48	2.1	170	121	291
52	2.2	172	121	293
56	2.2	174	123	297
60	2.1	169	123	292
64	2.1	173	125	298
68	2.2	170	121	291
72	2.2	175	125	300
76	2.2	174	124	298
80	2.3	179	120	299
84	2.2	171	121	292
88	2.1	170	125	295
92	1.9	167	127	294
96	2	172	129	301
100	1.9	171	132	303
104	1.9	167	124	291
<b>FINAL Permeate Composition</b>	<b>2.4</b>	<b>157</b>	<b>109</b>	<b>266</b>

ACKNOWLEDGMENT: "The material is based upon work supported by the Department of Energy under award number DE-NT0005961. A large number of people allowed for this work to be completed. I would like to thank Donald Whisenhunt as the first primary investigator. Chemistry contributions were made by Danielle Petko, Chris Eastman, Ron Wroczynski, Sheldon Shafer and Pat McCloskey. Engineering support was provided by Pierre Bui and Hrishikesh Keshavan. Larry Lewis was invaluable for his discussions on the mesoporous alumina. We also had excellent support from the analyst at Global Research in a variety of characterization techniques. I would like to thank my key collaborators at GE Water, Jeff Melzer and Ashok Shetty for their support.

*DISCLAIMER: "This report was prepared as an account of work sponsored by the agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation or favoring by the United States Government or an agency thereof. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."*

### Milestone Status Report

		Project Duration - Start: Oct 1, 2008 End: Sept 30, 2011												Planned Start Date:	Planned End Date:	Actual Start Date:
		Project Year (PY) 1				Project Year (PY) 2				Project Year (PY) 3						
Task #	Project Milestone Description	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12			
1	Updated PMP	X												4Q08	4Q08	4Q08
2	Core Materials selected/synthesized			X										4Q08	2Q09	1Q09
3	Ligands selected/synthesized				X									4Q08	3Q09	1Q09
3a	LFCM synthesized				X									4Q08	3Q09	1Q09
4	Evaluation of LFCM				X									2Q09	3Q09	2Q09
5	Initial cost/process model				X									4Q08	3Q09	1Q09
6	Recycle protocol developed							X						4Q09	3Q10	1Q10
7	Bench top unit demo								X					2Q10	3Q10	2Q10
8	updated cost model								X					2Q10	3Q10	3Q10
9	LFCM synthesis scale up											X		4Q10	2Q11	2Q10
10	Pilot plant updated											X		4Q10	2Q11	3Q10
11	EDR/silica removal process demo												X	2Q11	3Q11	1Q12
12	Cost model finalized												X	1Q11	3Q11	1Q12

\*In agreement with DOE program manager actual technical work started 1Q09

1. Liao Z, Gu Z, Schulz MC, Davis JR, Baygents JC, Farrell J. Treatment of cooling tower blowdown water containing silica, calcium and magnesium by electrocoagulation. *Water Sci. Technol.* 2009;60(Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved.):2345-2352.
2. Meyers P. Selective silica removal. *Off. Proc. - Int. Water Conf.* 2009;70th(Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved.):862-873.
3. Ning RY. Reactive silica in natural waters -A review. *Desalination and Water Treatment.* 2010;21(1-3):79-86.
4. Gallup DL, Hinrichsen CJ. Control of silicate scales in steam flood operations. Paper presented at: Society of Petroleum Engineers - 9th International Conference on Oilfield Scale 2008 - "Managing Scale Through the Field Lifetime"2008.
5. Borrmann T, Johnston JH, McFarlane AJ, McBrearty R. Realizing complete silica removal - Moving technology from the laboratory to pilot scale. Paper presented at: Geothermal Resources Council2010.
6. Öner ŞG, Kabay N, Güler E, Kitiş M, Yüksel M. A comparative study for the removal of boron and silica from geothermal water by cross-flow flat sheet reverse osmosis method. *Desalination.* 2011;283(0):10-15.
7. Mavredaki E, Stathouloupoulou A, Neofotistou E, Demadis KD. Environmentally benign chemical additives in the treatment and chemical cleaning of process water systems: Implications for green chemical technology. *Desalination.* 2007;210(1-3):257-265.
8. Ning RY, Troyer TL. Colloidal fouling of RO membranes following MF/UF in the reclamation of municipal wastewater. *Desalination.* 2007;208(1-3):232-237.
9. Den W, Wang C-J. Removal of silica from brackish water by electrocoagulation pretreatment to prevent fouling of reverse osmosis membranes. *Sep. Purif. Technol.* 2008;59(3):318-325.
10. Singh G, Song L. Impact of feed water acidification with weak and strong acids on colloidal silica fouling in ultrafiltration membrane processes. *Water Res.* 2008;42(3):707-713.
11. Cheng H-H, Chen S-S, Yang S-R. In-line coagulation/ultrafiltration for silica removal from brackish water as RO membrane pretreatment. *Sep. Purif. Technol.* 2009;70(Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved.):112-117.
12. Acevedo CR, Gardea-Torresdey JL, Tarquin AJ. Silica removal from brine by using ion exchange2010.
13. Al-Samadi R, Inventor; Can. . assignee. Enhanced high water recovery membrane process. US patent AU2009210363A12010.
14. Kang GC, Cho JR, Nam HS, Choi CH, Kwon TH, Inventors; Hansu Ltd., S. Korea . assignee. Method for removing silica in membrane pretreatment process. US patent KR2011087512A2011.
15. Manabe A, Inventor; Miura Co., Ltd., Japan . assignee. Pure water production system having membrane separation modules in two or more stages. US patent JP2011189298A2011.
16. Iler RK. *The Chemistry of Silica*: John-Wiley and Sons, Inc.; 1979.
17. Al-Rehaili AM. Comparative chemical clarification for silica removal from RO groundwater feed. *. Desalination.* 2003;159(1):21-31.
18. Bell GR, Leineweber JP, Yang JC, Hunter JA, Savage WF. Characterization and removal of silica from Webster, South Dakota, and Roswell, New Mexico, well waters. Removal of iodide from Webster, South Dakota, well water. . *U.S. Clearinghouse Fed. Sci. Tech. Inform., PB Rep.* . 1968;No. 189716.

19. Park Ho S, Lee Y-C, Choi Bong G, Hong Won H, Yang J-W. Clean and Facile Solution Synthesis of Iron(III)-Entrapped gamma-Alumina Nanosorbents for Arsenic Removal. *ChemSusChem*. 2008;1(4):356-362.
20. Wohlberg C, Buchholz JR. *Silica in water in relation to cooling tower operation*: Los Alamos Sci. Lab.;1973.
21. Zini Q, Buldini PL, Morettini L. Rapid determination of dissolved silica in natural waters. *Microchem. J.* 1985;32(2):148-152.
22. Zhang H, Cooper AI. Synthesis and applications of emulsion-templated porous materials. *Soft Matter*. 2005;1(2):107-113.
23. Kim Y, Kim C, Choi I, Rengaraj S, Yi J. Arsenic Removal Using Mesoporous Alumina Prepared via a Templating Method. *Environ. Sci. Technol.* 2004;38(3):924-931.
24. Mavredaki E, Neofotistou E, Demadis KD. Inhibition and Dissolution as Dual Mitigation Approaches for Colloidal Silica Fouling and Deposition in Process Water Systems: Functional Synergies. *Ind. Eng. Chem. Res.* 2005;44(17):7019-7026.
25. Fairhead M, Johnson KA, Kowatz T, et al. Crystal structure and silica condensing activities of silicatein [small alpha]-cathepsin L chimeras. *Chemical Communications*. 2008(15):1765-1767.
26. Samuel PCDG. Significant silica reduction in cold lime process. *Proc. - Int. Water Conf., Eng. Soc. West. Pa.* 1986;47th(Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved.):451-458.
27. Sheikholeslami R, Bright J. Silica and metals removal by pretreatment to prevent fouling of reverse osmosis membranes. *Desalination*. 2002;143(3):255-267.