



Hydrofluoric Acid Reduction Project – TURI Grant 2017

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Toxics Use Reduction Institute

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1.0 Executive Summary

Hydrofluoric acid is used in all the glass etching processes at OFS Fitel in Sturbridge, Massachusetts. Due to its (Hydrofluoric Acid, HF) ability to penetrate skin, often without warning symptoms along with subsequent cardiac toxicity and latent corrosiveness, Hydrofluoric Acid presents a significant safety risk to those who handle it.

The Sturbridge facility of OFS was granted funding by the Toxics Use Reduction Institute to investigate possible Hydrofluoric Acid recycling and reduction strategies. Through literature, patent searches and initial experimentation it was quickly discovered that normal acid recycling methods would not be effective with the material etched at OFS. The Silica loading coming from the OFS etch process acts as a poison for most acid recycling systems and that route to a solution was set aside.

Laboratory experiments were run to determine whether other chemicals and Fluoride sources could be added or substituted for HF in the baths and still achieve similar etching performance. The results unexpectedly demonstrated that stronger acids could not be used to significantly accelerate the etching capability of Hydrofluoric Acid, nor activate the Hexafluorosilicic Acid etch byproduct to act once more as an etchant. While there was some increase in Hydrofluoric activity in the presence of a strong acid the increase was fractional and nearly independent of the added acids acid strength or concentration.

Common assumptions about the ability of Fluoride salts to act as active substitute Fluoride sources proved almost completely baseless with little or no activity even at very high strong acid loadings. Sodium and Potassium Fluoride while good at enhancing metal etching baths when used with strong acids, were completely ineffective in forming a Fluoride species that could orient and attack a Silica glass. Assumptions about the active species and forms of Hydrofluoric present in these glass etch baths need to be reexamined, as there are strong hints that coordination chemistry is at work with binuclear and even trinuclear forms of HF functioning as the attacking species. Of all the Fluoride salts trialed in this testing protocol, only Ammonium Bifluoride acted in a manner similar to Hydrofluoric and Ammonium Bifluoride (ABF) is known to exist in such a binuclear complex. Rate constants and etch test results showed that (ABF) while acting like (HF) is not a one to one replacement for the Fluoride in Hydrofluoric Acid on an equimolar basis and in fact acts much more as a complex and not as a free acid source.

Testing showed that Ammonium Bifluoride (ABF) was the most effective Fluoride salt etchant, especially in the presence of Sulfuric Acid. The drawback with substituting ABF for Hydrofluoric Acid, however, is that ABF creates an Ammonium Silica Fluoride

complex in the presence of higher concentrations of Silica. This complex forms a boundary layer on the glass and that can affect the uniformity of the etch. This insolubility of Silica Ammonium Fluoride while complicating use of ABF in glass etching, may also open the door to a recyclable system.

The precipitated Ammonium Silica Fluoride complex has a positive solubility curve to temperature and both Ammonium Bifluoride and Hydrofluoric etch rates follow the square root of the change in energy at higher temperatures, so it may be possible to heat the bath in use to achieve high etch rates and freedom from formation of the boundary layer then cool the bath to precipitate the Silica drawn from the glass. The Silica is precipitating as an Ammonium Silica Fluoride complex, so the possibility exists to quantitatively add back new Fluoride as Ammonium Bifluoride and immortalize the bath. Time became the enemy as this project drew to a close and the discovery regarding the mode of action of the Ammonium Bifluoride happened right at the end of the program. Excitement had to yield to practicality, but it is hoped that the knowledge gained from this study can act as a springboard to further research and a practical solution.

2.0 Background

2.1 Introduction

Hydrofluoric acid is used widely throughout the OFS Fitel manufacturing facility in Sturbridge, Massachusetts. The main purpose of Hydrofluoric Acid is to etch fused quartz at the beginning of the optical fiber manufacturing process. Hydrofluoric Acid is also used in several other industries for etching silicon (Si), glass (SiO₂), and metals due to its ability to dissolve these materials. Although it is extremely effective for etching, Hydrofluoric Acid is a highly corrosive and toxic substance that poses a danger to operators and the environment.

The main danger associated with handling hydrofluoric acid is the possibility of contact with human skin. In addition to being a highly corrosive liquid that can dissolve bone, Hydrofluoric Acid is also a powerful contact poison. Due to the ability of this acid to penetrate tissue, poisoning can occur readily through swallowing, inhaling, or exposure to skin or eyes. Skin contact with aqueous Hydrofluoric Acid could potentially cause deep burns and ensuing tissue death. This acid also interferes with nerve function, meaning that burns may not initially be painful and, as a result, exposed victims may delay medical treatment. Failure to treat a Hydrofluoric Acid spill on the skin can result in serious acid burns and even death. Thus, at OFS in Sturbridge, all tanks containing Hydrofluoric Acid solution are mixed with a small amount of Nitric Acid (HNO₃) so employees can be aware if Hydrofluoric Acid makes contact with their skin. In addition to its skin corrosiveness, Hydrofluoric Acid is quite toxic to water organisms and wildlife. Section 2.2 describes the environmental impacts of Hydrofluoric Acid in further detail.

Due to its extreme toxicity in water and air, as well as its nature as a powerful contact poison, Hydrofluoric Acid is a dangerous chemical to handle and process in a manufacturing facility. Therefore, the Environmental Health and Safety team at OFS applied for a grant through the Toxics Use Reduction Institute (TURI) in the hopes of acquiring funds to conduct a Hydrofluoric Acid reduction project. The goals of this project would be to reduce the use of the toxic chemical, improve worker health and safety, and increase process efficiency. The team was fortunate enough to have the grant application accepted by TURI and work on the project commenced.

To reduce the usage of Hydrofluoric Acid in the etching processes at OFS, two different avenues were considered. The first endeavor was to explore literature and assess the feasibility of implementing some sort of recycling process in order to recover hydrofluoric acid from the current baths. If it were possible to recover the hydrofluoric acid that already exists in the baths, the addition of new hydrofluoric acid could be greatly reduced. The second idea pursued was to change the ratios, temperatures, and

chemicals in the etching baths so each bath contained little to no Hydrofluoric Acid. This concept would require a lot of experimentation but could reduce or even eliminate Hydrofluoric Acid from the etching process. The literary research regarding recycling options was performed first.

2.2 Literature Searches

To determine whether a recycling system would be possible with the current setup at OFS, a variety of different options were taken into consideration. Researching current technologies revealed several plausible recycling methods, including diffusion dialysis, reverse osmosis, and the hydrofluoric acid wastewater recycling method.

2.2.1 Diffusion Dialysis

Diffusion dialysis is a method of separating metals out of an acid waste stream and recycling the purified acid back into a water stream. This process is facilitated through an anion membrane which allows fluorine and hydrogen atoms to diffuse across it but rejects metal ions. In this manner, the diffused atoms can reform as acid in the reclaimed water stream while the rejected metals form another waste stream. Diffusion dialysis is a good option for recycling hydrofluoric acid in a metal etching process, but not in a glass etching process as the silicon in the glass will not be rejected as effectively as the metal ions. Even in a metal etching process, diffusion dialysis suffers from throughput limitations and it creates an additional waste stream. The process is shown in Figure 1 below.¹

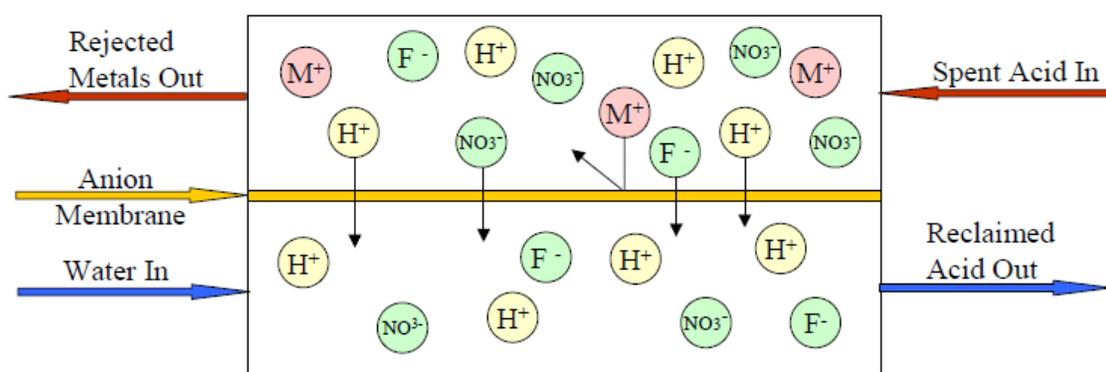


Figure 1: Diffusion Dialysis Separation Process

¹ Bailey, Daniel E. "Acid Purification - Diffusion Dialysis Membrane Technology." AcidRecovery.com, Mech-Chem, www.acidrecovery.com/acid-purification.html.

2.2.2 Reverse Osmosis

Reverse osmosis is the process of using pressure to overcome osmotic pressure, thus forcing desired compounds through a semipermeable membrane while rejecting undesired waste products. As a result, the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. Literature searches revealed that reverse osmosis processes already exist for operations similar to OFS. A process flow diagram for such a patent is pictured in Figure 2 below.

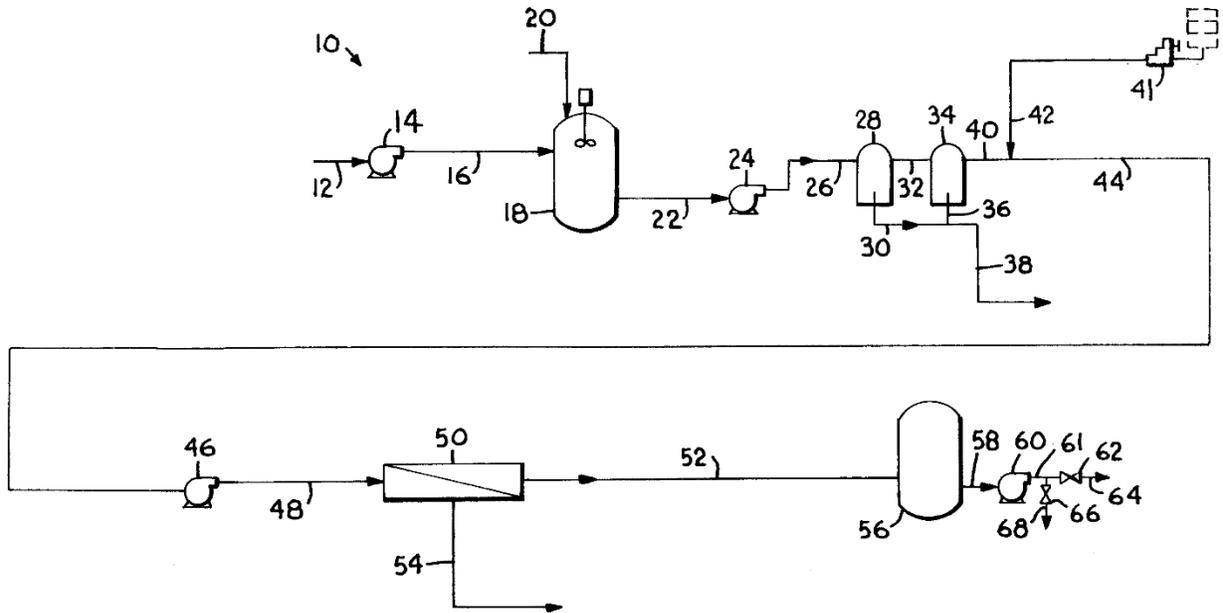


Figure 2: Wastewater treatment system using reverse osmosis (U.S. Patent No. 6,338,803 B1)

In the case of the hydrofluoric acid etch baths at OFS, the entire system shown in Figure 2 would have to be installed. First, the pH of the wastewater would be brought to at least 7, then solid particles would be filtered out of the waste, and finally an anti-scaleant would be added. These steps would prepare the wastewater for passage through the reverse osmosis unit, labeled Unit 50 above. This unit would contain a reverse osmosis membrane to separate the wastewater into a permeate stream (Stream 52) and a reject stream (Stream 54). One of the main issues with this system is the necessity for extensive installation of equipment and instrumentation. The other major problem that eventually steered the team away from the reverse osmosis method is discussed in Section 2.2.4 below.

2.2.3 Hydrofluoric Acid Wastewater Recycling Method

The last feasible option found in the literature was the hydrofluoric acid wastewater recycling method. This method uses the system pictured in Figure 3 below. First, a concentrator (Unit 1) is used to concentrate the wastewater by evaporation to divide it

into liquid and vapor forms. A water contractor (Unit 2) is then used to dissolve the hydrofluoric acid-containing vapor into dissolution water. Next, the residual vapor is fed through an alkali contractor (Unit 3) to produce a neutralized liquid and dehydrofluorinated vapor. This dehydrofluorinated vapor is then condensed in a condenser (Unit 4) to form condensed water. Finally, a separator (Unit 5) is used to separate recovered hydrofluoric acid from desalted water. This system is promising in theory, but has the same flaws as the reverse osmosis system. If this system were to be installed at OFS in Sturbridge, it would require significant installation time and facility space that may not be available. In addition, another major issue exists in regards to the materials being etched at OFS. This issue is discussed in the next section.

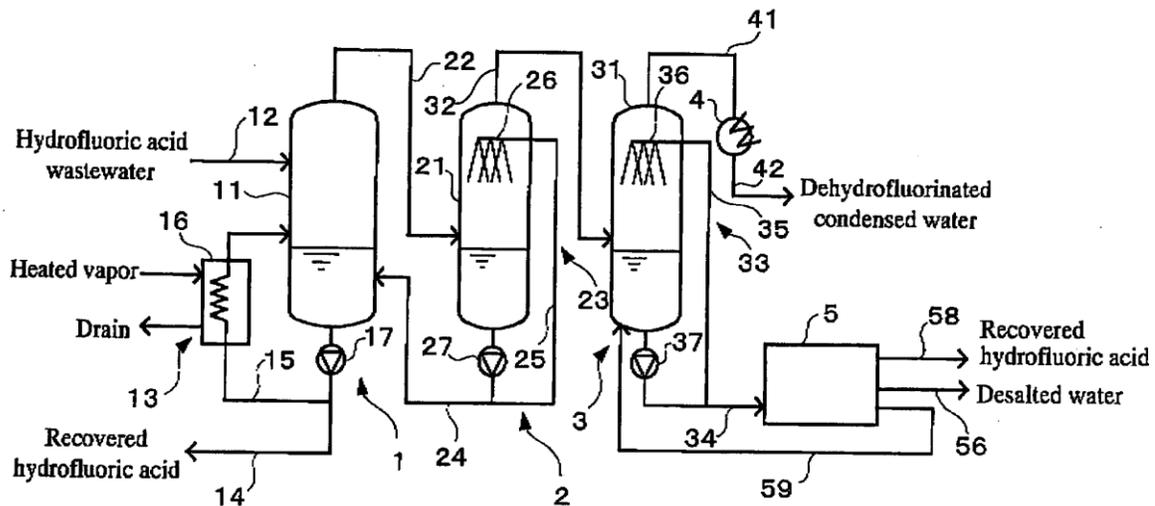


Figure 3: Hydrofluoric acid wastewater recycling method (U.S. Patent No. 7,311,799 B2)

2.2.4 Issues Regarding the Etching of Silicon Dioxide

Consultant David Demarey, one of the lead contributors to this project, voiced his concern about the repercussions of installing a reverse osmosis or Hydrofluoric Acid wastewater recovery system in the etching of Silicon Dioxide. Demarey has enough experience with both glass and metal etching to know that these types of separation or recycling methods are ineffective with glass due to gross membrane contamination and blinding effects from the Silica of the process.

2.3 Alternative Strategies

After it was determined that none of the recycling methods would be feasible, another strategy had to be considered. Besides recycling, the other main way to significantly reduce Hydrofluoric Acid consumption would be to increase the amount of other active

species in the etching baths in an attempt to effectively “substitute” for Hydrofluoric Acid. Fluoride salts, for example, can be used as fluoride sources in a similar fashion to Hydrofluoric Acid, so a few fluoride salts were taken into consideration. All of the chemicals in Figure 1 were selected as possible replacements due to their decreased toxicities and lower potential for environmental harm.

One of the main Hydrofluoric Acid alternatives in industry is Ammonium Bifluoride (ABF). As shown in Figure 4 below, ABF in its natural solid form is less toxic and much easier to handle than Hydrofluoric Acid. Although it is still a hazardous irritant, it is not as corrosive as Hydrofluoric Acid and it is not considered to have potentially fatal outcomes with moderate exposures. According to the Department of Environmental Protection, however, “when dry Ammonium Bifluoride (ABF) contacts water, it generates Hydrofluoric Acid. The Hydrogen Fluoride derived from fluoride salts (such as ABF) is considered “manufactured.”² This newly formed Hydrofluoric Acid will react with the Silicon in the glass rods and remove silica from the outside of the rod. In this manner, ABF or other fluoride salts conceivably could be used as a direct substitute for Hydrofluoric Acid. Ammonium Bifluoride used in this manner while not circumventing the “Manufactured HF” label would dramatically lower the risks to the operators in handling.

When determining chemicals that could be used as possible alternatives to Hydrofluoric Acid, a few aspects needed to be considered. First; is the alternative chemical safer to handle than Hydrofluoric Acid? If so, is it safer for the environment as well? Both of these questions were explored in detail through careful examination of Safety Data Sheets for each chemical.

To determine the relative worker safety of each chemical, the toxicity through skin contact and air concentration were examined. When contacted by skin, none of the chemicals in Figure 4 are considered fatal except for Hydrofluoric Acid. They are all recorded as various levels of “hazardous”, which is still seen as safer than Hydrofluoric Acid. The acute inhalation toxicity of a substance is measured as a factor called LC50 (Lethal Concentration 50%), which specifies the air concentration at which “50% of the animals will be expected to die”³ from inhalation of the substance. Besides Hydrofluoric Acid, the only other substance we used that had a measurable LC50 was Sulfuric Acid. Even so, the LC50 of Hydrofluoric Acid is much lower than the LC50 of Sulfuric Acid, meaning it is lethal at much lower concentrations than the other chemicals.

² United States, Congress, Executive Office of Energy & Environmental Affairs, et al. “Guidance on Reporting Hydrofluoric Acid as a Higher Hazard Substance under the Toxics Use Reduction Act.” 9 May 2016.

³ “Definition of Toxicological Dose Descriptors (LD50, LC50, EC50, NOAEL, LOAEL, etc).” Toxicology and Health Risk Assessment. ChemSafetyPRO, 17 Jun. 2016. Web. 23 May 2018.

As far as environmental impacts are concerned, Hydrofluoric Acid is much more toxic than the other chemicals being considered. A common way to measure this impact is the EC50 (Median Effective Concentration), which measures “the concentration of test substance which results in a 50 percent reduction in either algae growth (EbC50) or algae growth rate (ErC50) or Daphnia immobilization.”⁴ Out of all the substances chosen, Hydrofluoric Acid is the only one with a measurable EC50, indicating a relatively high lethality to plants compared to the other chemicals

	Hydrofluoric Acid	Fluorosilicic Acid	Ammonium Bifluoride	Sodium Fluoride	Potassium Fluoride	Sulfuric Acid	Nitric Acid
NFPA Health Rating	4	3	3	3	3	3	4
Toxicity (skin contact)	Fatal	Hazardous but not a Skin Penetrant	Hazardous but not a Skin Penetrant	Toxic if Ingested	Toxic if Ingested	Very hazardous	Very hazardous
Toxicity (inhalation)	Fatal	Hazardous in Anhydrous Form	Hazardous but not Dusty or Volatile	Possibly Fatal if Inhaled	Possibly Fatal if Inhaled	Very hazardous	Slightly hazardous
LC50 (Ecotoxicity in Water)	660 mg/L (48 hour)	N/A	N/A	N/A	9.3 mg/L (96 hour)	49 mg/L (48 hour)	N/A
LC50	0.5 – 2 mg/L	N/A	N/A	N/A	N/A	320 mg/m ³ (2 hour)	N/A
EC50	270 mg/L (48 hour)	N/A	N/A	N/A	N/A	N/A	N/A
LD50 (Acute Oral Toxicity)	5 – 50 mg/kg	N/A	130 mg/kg	52 mg/kg	245 mg/kg	2140mg/kg (4 hour)	N/A

Figure 4: Safety information regarding hydrofluoric acid and possible alternatives

⁴ Ibid.

3.0 Methodology and Results

3.1 Characterizing the Baths

3.1.1 Fluoride and Nitrate Content by ISE (Ion Specific Electrode)

To characterize the baths, a variety of different analytical techniques needed to be implemented. The first technique was simply testing the etch tank solution with a Fluoride Specific Ion probe. This probe has the ability to measure the voltage across an ion specific membrane, which allows the user to calculate the amount of Fluoride in the solution compared to known standards. The laboratory at OFS is already using 1000 ppm fluoride standard solutions, so a simple dilution was performed to create two solutions to use as lower and upper comparison points for the ISE probe (20 ppm and 200 ppm).

The first step in the process of measuring Fluoride content was to create a solution that could be accurately measured by the probe. The probe could not properly measure the millivolts of the sample straight from the etch tank due to the extremely high Fluoride content. Therefore, it was necessary to dilute the solution with deionized water. A single dilution was not enough to lower the Fluoride content to a measurable level, so it was diluted further, generally to a 1/4000 to 1/8000 dilution.

Using the fluoride probe, the voltage (in mV) of the 20ppm solution was measured and recorded on the spreadsheet below (Figure 5). The same process was carried out for the 200ppm standard solution. The voltage of the actual sample was then measured and recorded in the spreadsheet, which has built-in formulas to calculate the concentration (in ppm) of fluoride in the sample. Consultant David Demarey created the spreadsheet shown.

Specific Ion Analysis by Electrode					
Enter the Ion Analyzed	F				
Enter the Millivolt reading of your "Low" Standard	-25.8	Enter the Concentration of your Low Standard	20	Ionic Species in Sample in Gpl.	360.206
Enter the Millivolt reading of your "High" Standard	-83.4	Enter the Concentration of your High Standard	200	Ionic Species in the Sample in ppm.	360205.7
Enter the Millivolt reading of your "Sample"***	-46.1	Enter the Volume of Your Sample	1	57.6	Millivolts per Decade
Enter the Dilution of your Sample	8000	Enter the Amount of ISA or Buffer added to your sample	0	96.6%	Probe Slope

Figure 5: Spreadsheet used to calculate Fluoride content based on voltages of standard versus the sample

The same Excel spreadsheet was used to calculate the Nitrate content in the samples. To do so, the same process was performed with a Nitrate ISE probe and Nitrate standard solutions instead of Fluoride standards. In the “Enter the Ion Analyzed” box in the spreadsheet, the value was changed to “NO₃” to represent nitrate. Along with the Fluoride and Nitrate concentrations, the samples were evaluated for Silicon and Germanium content using a flame AA.



Figure 6: Atomic Absorption Spectrometer used for measuring Silicon and Germanium content

3.1.2 Testing for Silicon and Germanium Content

The Atomic Absorption Spectrometer, shown in Figure 6, was used to measure the amount of Silicon and Germanium in each sample. Standard solutions with known Silicon content were used to calibrate the spectrometer. Diluted samples from each Hydrofluoric etch bath were then tested for Silicon content. Germanium was tested in the same manner, but the Germanium content in all samples was negligible.

Once the Silicon content was known, the amount of Fluoride likely in the form of Fluorosilicic acid could be determined (Hexafluorosilicic acid, or $(\text{H}_3\text{O})_2[\text{SiF}_6]$, is the main byproduct of etching Silicon with Hydrofluoric Acid). This value was then used to calculate the concentration of remaining “free” Hydrofluoric Acid in the samples. The free Hydrofluoric concentration was found to be the total concentration of Fluoride measured by the probe and expressed as Hydrofluoric Acid minus the concentration of Hexafluorosilicic acid in solution.

In an effort to double-check the concentration of “free” HF in the samples, a pH indicator was used. In this case, a methyl orange indicator was used because it would detect the Nitric Acid in the sample but would not detect the Hydrofluoric Acid.

3.1.3 Predicting Etch Rates

The characterization of the bath by the methods listed above, coupled with observations of the apparent “free acid” as detected by the methyl orange indicator were found to agree within just a few grams per liter of all the components. Further scenario testing of each component and its interactions allowed us to develop a highly predictive algorithm for describing the apparent etch rates under all bath conditions.

This scenario testing rather emphatically demonstrated that the only really correlating variable in regard to the etch rate was the concentration of “free” Hydrofluoric Acid. The etch rates from three of the etch bath samples matched up precisely with the algorithm that assumed only interactions with free Hydrofluoric, as shown in Figure 7 below. The Glass Etching Machine (GEM) etch rate was significantly lower than that predicted by the algorithm, but it was found to be operating eight degrees cooler than the other etch baths. Applying a rate factor to the temperature differential brought the etch rate up to equal the others using the same solely Hydrofluoric based algorithm.

In Figures 7, 8, 9, and 10, the etch rates are displayed in mm/hr. The green highlight represents a very good correlation between predicted and actual etch rates (within 0.003 mm/hr), the orange highlight represents a moderate correlation (within 0.015 mm/hr), and the pink highlight represents a poor correlation (>0.015 mm/hr).

	Etch Rate Predicted By Free HF	Actual Etch Rate	Etch Rate Pred. by Free HF (Temp Corrected)
OC-1 3-29-2018	0.095	0.095	0.095
Saw Room 3-29-18	0.049	0.049	0.049
CRE 4-10-18	0.105	0.102	0.105
GEM 4-10-18	0.089	0.057	0.057

Figure 7: Etch rates predicted by the amount of free HF vs. actual etch rates

All calculations were set to zero off one of the etches called OC-1. This allowed a clear visualization of the impact of the individual bath components on the etch rates. After the free acid comparison, the next correlation established was between the “Nitric Added as Hydrofluoric” and the actual etch rates. The Nitric as Hydrofluoric represents the Nitric Acid in the solution as if it were acting as additional Hydrofluoric Acid (Enhancing the activity of HF). This was essentially a test to see if the Nitric Acid was at least an equal to Hydrofluoric Acid in terms of its contribution to the etch rate; it was not!

Even with temperature correction, predicted etch rates were roughly 0.01 mm/hr different from the actual etch rates, as seen in Figure 8. This showed clearly that the Nitric treated as if it were Hydrofluoric does not seem to affect the etch rate.

	Etch Rate Predicted By Nitric Added as HF	Actual Etch Rate	Etch Rate Pred. By Nitric Added as HF (Temp Corrected)
OC-1 3-29-2018	0.095	0.095	0.095
Saw Room 3-29-18	0.053	0.049	0.053
CRE 4-10-18	0.087	0.102	0.087
GEM 4-10-18	0.074	0.057	0.047

Figure 8: Etch rate predicted by the amount of “Nitric added as HF” vs. actual etch rates

The third method used to predict the etch rates was based solely on the amount of free Nitric Acid in the solution. This was a further effort to see if Nitric Acid was really playing a role in the etch rate. The amount of Nitric Acid in the solution was measured with a Nitrate probe and calculated using the Specific Ion Analysis spreadsheet (just as done previously with the Fluoride concentration). Once the concentration of Nitrate was known, the percent Nitric Acid could be determined with a simple molar calculation. The percent of Nitric Acid in each sample was then zeroed based on the OC-1 value, resulting in the leftmost column in Figure 9.

Even taking into account temperature corrections, the etch rates predicted by the free Nitric concentrations were substantially different from the actual etch rates. Thus, it can be concluded that the free Nitric content of the baths is a poor and irrelevant predictor of the etch rate of the baths.

	Etch Rate Predicted By Free Nitric	Actual Etch Rate	Etch Rate Predicted By Free Nitric (Temp Corrected)
OC-1 3-29-2018	0.095	0.095	0.095
Saw Room 3-29-18	0.083	0.049	0.083
CRE 4-10-18	0.036	0.102	0.036
GEM 4-10-18	0.037	0.057	0.024

Figure 9: Etch rate predicted by the amount of free nitric vs. actual etch rates

These failures to detect any significant impact of either the Nitrate or Nitric Acid level on the resulting etch rates is telling. There is a body of common knowledge that would predict that adding a stronger acid, in this case Nitric to a Hydrofluoric Acid solution, should bring about a dramatic increase in the etch rate. This clearly did not occur, and the invalidation of the common knowledge assumptions derives from something not immediately apparent but nonetheless true: Hexafluorosilicic Acid is a very strong acid. The presence of six fluorine atoms on the silicon imparts a powerful electron withdrawal onto the silicon central atom. The hydrogens attached to the silicon have a hard time holding their electrons and are essentially nearly free protons, making Hexafluorosilicic a powerful acid and much stronger than Nitric. A weaker acid, in this case Nitric, cannot displace a stronger acid. It is still unclear why the Nitric fails to impact the remaining free Hydrofluoric as the pKa of Nitric is much stronger than Hydrofluoric. It is possible this could be the result of complex interactions between the nitrate anion and the Hexafluorosilicic acid or more likely an inability of Nitric to act in concert with a trinuclear attack by Hydrofluoric onto the glass substrate.

The final correlation tested in predicting etch rates was the total Fluoride content of each bath (including both free Hydrofluoric Acid and Silica Fluoride). The fluoride content was measured using the fluoride probe and calculated using the Specific Ion Analysis spreadsheet. Similarly, to the previous methods, the total fluoride values were zeroed based on the value of the OC-1 bath. These values can be seen in Figure 10 below. After temperature correction, the predicted CRE etch rate matches closely with the actual etch rate. The predicted GEM etch rate does not correlate as well, and the saw room prediction is poor.

	Etch Rate Predicted By Total Fluoride	Actual Etch Rate	Etch Rate Pred. By Total Fluoride (Temp Corrected)
OC-1 3-29-2018	0.095	0.095	0.095
Saw Room 3-29-18	0.081	0.049	0.081
CRE 4-10-18	0.105	0.102	0.105
GEM 4-10-18	0.081	0.057	0.051

Figure 10: Etch rate predicted by the total amount of fluoride vs. actual etch rates

This last data set reveals that the total fluoride is a poor predictor of etch rate results. High total fluoride does not necessarily correlate with a high etch rate, meaning that despite the acid strength of Hexafluorosilicic Acid, there is little impact on etch rate when factoring in the Fluorosilicic concentration. This apparent paradox can be explained by the hindrance to reaction of the Hexafluorosilicic Acid's structure. It may be a powerful acid, but it is not labile or easily dissociated so the apparent reactivity is quite low.

These data taken as a whole demonstrate that the most effective value for predicting etch rate is the total amount of free Hydrofluoric Acid in the bath. In these preliminary

experiments, the predicted etch rates based on the free Hydrofluoric Acid were nearly identical to the actual etch rates physically measured by the Chemical Technicians. Therefore, the most effective way to describe the process and control the etch rate of an individual bath is to know the amount of free Hydrofluoric Acid in the solution and to closely monitor the temperature of the bath.

3.2 Laboratory Bath Experiments

3.2.1 Experimental Theory

Once the reactive chemistry in the etch baths at OFS was known, experiments were conducted to assess the feasibility of lowering or eliminating the Hydrofluoric Acid component of the etch. Fifteen scenarios were originally sketched out that utilized different combinations of Hydrofluoric Acid substitutes and other structural changes in the composition of the baths. These experiments fell into two classes, simple substitution or profound composition changes. Many experiments incorporated both substitution and profound composition changes (heat, ultrasonic energy) but not chemical species changes.

The goal with the first category, substitution, was to attempt to stay within the confines of the species that are already in the OFS etch baths; this includes Nitric Acid, Hexafluorosilicic acid and Hydrofluoric acid. By altering the ratio of Nitric Acid to Hydrofluoric Acid and Hexafluorosilicic acid, the Hydrofluoric component might be minimized or even eliminated.

Currently in these (OFS) baths, the ratio of Nitric to Fluoride is very low, so the first step was to bring the Nitric level to molar parity (or beyond) with the Fluoride in both Hydrofluoric and Hexafluorosilicic acid.

In theory, raising the molar ratio of Nitric to Hydrofluoric/Fluoride might allow the Nitric to substitute for and free Fluoride from the Hexafluorosilicic acid or at the least interact more strongly with Hydrofluoric Acid, enhancing the etch rate at lower Hydrofluoric levels. This proved not to be the case.

The goal with the second category; profound compositional changes, was to find another chemical that could be substituted for Hydrofluoric Acid or otherwise added to the baths in order to maintain a suitable etch rate with limited Hydrofluoric Acid present. To do this, the first step was to bring in Sulfuric Acid or another chemical in an attempt again to displace Fluoride from the Hexafluorosilicic acid or to enhance the etching power of low levels of Hydrofluoric Acid.

If this did not work, the last strategy would be to replace the Hydrofluoric Acid with a Fluoride salt like Ammonium Bifluoride (ABF). ABF is known to be a viable substitute for Hydrofluoric Acid in etching processes, but it is thought to “manufacture” Hydrofluoric Acid when contacted with water. Therefore, ABF would improve safety for

the operators, but may still create a “Hydrofluoric Acid” waste.

In addition, it was unknown whether the Hexafluorosilicic Acid buildup would affect the etching performance of ABF in the long term. Thus, the experiments requiring profound compositional changes carry a slightly higher risk factor for OFS as they incorporate substances not present in their current formulations.

3.2.2 Conducting Laboratory Experiments

To conduct these experiments, a miniature bath setup was assembled in one of the hoods at the OFS laboratory. This setup consisted of the following: an ultrasonic cleaner for maintaining a constant bath temperature, several plastic bottles to contain the experimental baths, a lid with holes to prevent the bottles from shifting, and metal stands with clamps to hold the rods vertically in the solutions. After conducting the first few trials with unmixed baths, a small (purple in the picture) air pump was used to induce mixing to ensure the boundary layer on the outside of the glass rods would be broken. Figure 11 depicts two trials being run simultaneously with this setup.

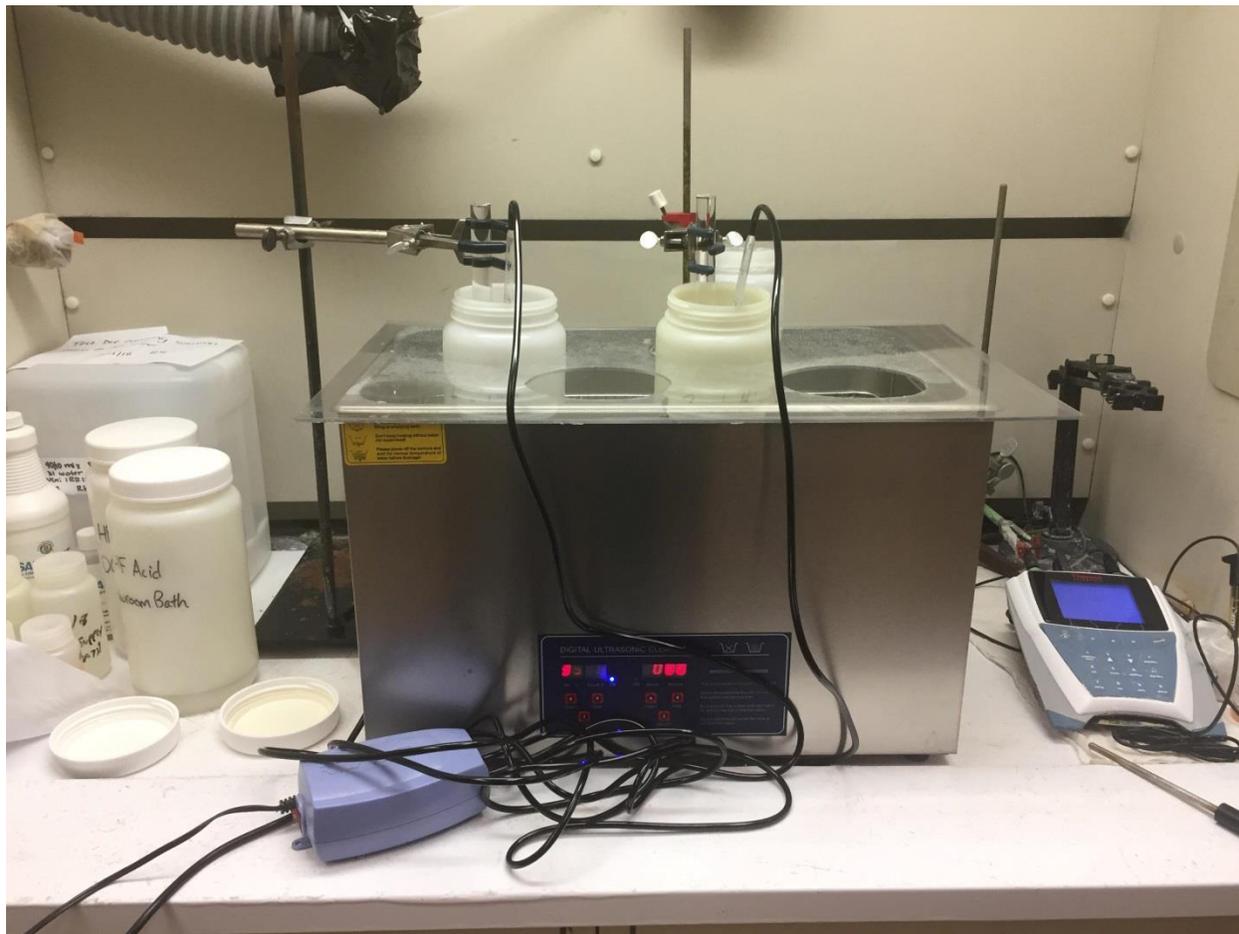


Figure 11: Two simultaneous trials of experimental baths (with mixing)

Besides the first few unmixed trials, the rest of the experimental baths were run with the exact setup above. To measure the etch rate of the test rods, a rigid control procedure was followed. First, a micrometer was used to measure the outer diameter (in mm) of the glass rod. This measurement was performed at least twice in order to get an average and therefore a more accurate value. This original diameter was recorded in an Excel spreadsheet to be referred to later. Next, the ultrasonic cleaner's heat was turned on and the temperature was set to the desired amount for the ensuing tests that day. The large plastic bottles containing the experimental bath solutions were placed in the water and allowed to reach the desired temperature. The rods were then clamped vertically and submerged in their respective baths to begin the etching process. The time was recorded and the rods were removed from the baths exactly four hours after they were submerged. Each rod was rinsed thoroughly with water and the micrometer was used again to measure the new outside diameter of each rod. By dividing the diameter reduction by the time elapsed, an accurate etch rate could be calculated for each trial. A comprehensive summary of the experimental results is laid out in the next section.

4.0 Results and Discussion

The results of all the experiments are displayed in Figure 12 below. The etch rates are color coordinated to convey the relative etching capability for each trial. Red boxes represent poor etching capability (< 0.015 mm/hr.), yellow boxes represent moderate etching capability (between 0.015 and 0.04 mm/hr.), and green boxes represent good etching capability (> 0.04 mm/hr.). As seen with the first two trials, "Sawroom" and "OC-1", the baths at OFS are capable of etching glass at rates between 0.04 and 0.10 mm/hr. Thus, the goal of the experiments was to achieve a similar etch rate with minimal or no Hydrofluoric Acid.

Trial	Components	Temperature (deg C)	Start Diameter (mm)	End Diameter (mm)	Etch Rate (mm/hr)
1	UNMIXED Sawroom	27	18.575	18.391	0.046
2	UNMIXED OC-1	27	18.622	18.297	0.08125
3	UNMIXED 1-1 Molar Nitric to HF	27	18.656	18.586	0.0175
4	UNMIXED 2-1 Molar Nitric to HF	27	18.564	18.488	0.019
5	UNMIXED 1-1 Molar Nitric to HF; spike w/ sulfuric	27	18.526	18.439	0.02175
6	UNMIXED 2-1 Molar Nitric to HF; spike w/ sulfuric	27	18.504	18.397	0.02675
7	1-1 Molar Nitric to HF; spike w/ sulfuric	27	18.521	18.43	0.02275
8	1-1 Molar Nitric to HF; spike w/ sulfuric (high heat)	35	18.509	18.375122	0.0334695
9	2-1 Molar Nitric to HF; spike w/ sulfuric (high heat)	35	18.541	18.39722	0.035945
10	1-1 Molar Nitric to HF; spike w/ sulfuric (higher heat)	45	18.516092	18.3299	0.046548
11	2-1 Molar Nitric to HF; spike w/ sulfuric (higher heat)	45	18.660872	18.474	0.046718
12	1-1 Molar Nitric - 100 gpl equiv. Fluoride as fluorosilicic Acid	27	18.523712	18.523712	0
13	1-1 Molar Nitric - 100 gpl equiv. Fluoride as fluorosilicic Acid; spike w/ sulfuric	27	18.56994	18.56359	0.0015875
14	Double HF 1 Molar Nitric	27	18.504662	18.340832	0.0409575
15	Mg(NO3)2 * 6 H2O + Hexafluorosilicic Acid + HNO3	27	18.6355482	18.6351418	0.0001016
16	Mg(NO3)2 * 6 H2O + Hexafluorosilicic Acid + HNO3 (elevated temp)	45	18.5293	18.5293	0
17	Hexafluorosilicic Acid w/ water (elevated temp)	45	18.55851	18.56232	-0.0009525
18	Nitric / Sodium Fluoride	27	18.506	18.506	0
19	Nitric / AmmoniumBIFluoride	27	18.5175	18.465	0.013125
20	Nitric / Sodium Fluoride; spike with sulfuric	27	18.5375	18.53	0.001875
21	Nitric / AmmoniumBIFluoride; spike with sulfuric	27	18.499	18.413	0.0215
22	Nitric / AmmoniumBIFluoride; spike with sulfuric (higher heat)	35	18.516	18.396	0.03
23	Nitric/ABF/HFSA/Sulfuric	27	18.541	18.488	0.01325
24	Nitric/ABF/HFSA	27	18.53	18.49	0.01
25	Sulfuric/high ABF	27	18.507	18.3	0.05175
26	Sulfuric/high ABF (higher heat)	35	18.541	18.215	0.0815
27	Sulfuric/high ABF (higher heat) ULTRASONIC	41	18.215	18.107	0.108
28	Sulfuric/high ABF (constant higher heat) ULTRASONIC	37	18.584	18.556	0.056
29	Sulfuric / ABF (extremely high heat)	50	18.547	18.359	0.047

Figure 12: Laboratory bath experimental data

4.1 Hypothesis 1: Strong Acid Activation

Throughout these laboratory experiments, several different hypotheses were explored. The first hypothesis; that the addition of a stronger acid would increase the activity of Hydrofluoric Acid is usually accepted as a given in discussions surrounding Hydrofluoric Acid. Our results call that assumption into question.

As seen in Figure 13 below, the first few experiments used Nitric Acid as the “strong acid” in an attempt to accelerate the etching performance of the Hydrofluoric Acid.

Comparing the 1-1 molar Nitric to Hydrofluoric solution to the 2-1 molar solution, it became evident that the Nitric acid was hardly affecting the etch rate at all. Even with something as large as a molar increase of Nitric, the etch rates of the two solutions were so similar (0.0175 mm/hr vs. 0.019 mm/hr) that the Nitric Acid was disregarded as a contributing factor to etch rate.

3	UNMIXED 1-1 Molar Nitric to HF	27	18.656	18.586	0.0175
4	UNMIXED 2-1 Molar Nitric to HF	27	18.564	18.488	0.019
5	UNMIXED 1-1 Molar Nitric to HF; spike w/ sulfuric	27	18.526	18.439	0.02175
6	UNMIXED 2-1 Molar Nitric to HF; spike w/ sulfuric	27	18.504	18.397	0.02675
7	1-1 Molar Nitric to HF; spike w/ sulfuric	27	18.521	18.43	0.02275

Figure 13: Experiments for Hypothesis 1 – Strong Acid Activation

4.2 Hypothesis 2: Strong Acid Liberation

The second hypothesis theorized that the addition of a stronger mineral acid would liberate the Fluoride ions from the Hexafluorosilicic acid. If some of the Fluoride could be pulled away from this molecule, then it could reform Hydrofluoric Acid, then, in theory, the bath could be immortalized.

The strong acid could simply be added to the bath whenever the Fluorosilicic concentration got too high, thus reverting some of it back to Hydrofluoric and causing the etch rate to return to its desired state. This hypothesis was tested with Nitric Acid and Sulfuric Acid, as the “strong acid” agents and Magnesium Nitrate added in an attempt to tie up Silica releasing Hydrofluoric. It quickly became evident that stronger acids had no proportional effect on the etch rate. Figure 14 below shows that relatively little etching was achieved with this method, regardless of the strong acid or its concentration. Even increasing the temperature from 27°C to 45°C had no effect on the etch rate of Hexafluorosilicic Acid. (The “Double HF 1 Molar Nitric” run was not a part of this hypothesis; it was simply a test to determine if doubling the concentration of hydrofluoric acid would double the etch rate.)

12	1-1 Molar Nitric - 100 gpl equiv. Fluoride as fluorosilicic Acid	27	18.523712	18.523712	0
13	1-1 Molar Nitric - 100 gpl equiv. Fluoride as fluorosilicic Acid; spike w/ sulfuric	27	18.56994	18.56359	0.0015875
14	Double HF 1 Molar Nitric	27	18.504662	18.340832	0.0409575
15	Mg(NO ₃) ₂ * 6 H ₂ O + Hexafluorosilicic Acid + HNO ₃	27	18.6355482	18.6351418	0.0001016
16	Mg(NO ₃) ₂ * 6 H ₂ O + Hexafluorosilicic Acid + HNO ₃ (elevated temp)	45	18.5293	18.5293	0
17	Hexafluorosilicic Acid w/ water (elevated temp)	45	18.55851	18.56232	-0.0009525

Figure 14: Experimental data for Hypothesis 2 – Strong Acid Liberation

4.3 Hypothesis 3: Boundary Layer Effects

The third hypothesis that was explored involved boundary layers and how they might affect the etching of the rods. The first few experiments were run without agitation of the baths, so the rods were submerged in stagnant solution. The etch rates for these first few experiments were fairly poor, so it was presumed that the stagnant solution was allowing a boundary layer to form on the outside of the rods. This presumption, coupled with the fact that the current baths at OFS are mixed, prompted the idea that mixing could increase the etch rates of the experimental baths. With this prediction, all trials after Trial 6 were mixed. As seen previously in Figure 13, the same solution (“1-1 Molar Nitric to HF; spike w/ sulfuric”) was tested with and without mixing at the same temperature. The mixing only increased the rate about 4%, which indicated that it was not crucial to achieve a good etch rate. With Hydrofluoric Acid as the main etching

agent, the small boundary layer formed was not enough to significantly affect the etching performance of the bath. Nevertheless, all subsequent trials after Trial 6 were mixed to be consistent with the current baths at OFS.

4.4 Hypothesis 4: Ammonium Bifluoride Substitution

The fourth and final hypothesis was that the use of ammonium bifluoride or another fluoride salt could substitute for hydrofluoric acid. This hypothesis was tested last because it would require changing the contents of the OFS etch bath, as well as likely necessitating different equipment or structure than currently in use.

The fluoride salts tested were Sodium Fluoride (NaF) and Ammonium Bifluoride (ABF). Fluoride salts such as these are “known” by the EPA and MassDEP to “manufacture” Hydrofluoric Acid when contacted by water.⁵ For this reason, both salts were first tested in a solution of water and Nitric Acid to determine whether Nitric would accelerate the etching performance of the salt. As shown in Figure 15 below, the Sodium Fluoride did not etch the glass at all when combined with Nitric Acid. Even when Sulfuric Acid was added to the Sodium Fluoride solution, the etch rate appeared negligible. These results as mentioned before, fly in the face of what is accepted as “common knowledge” in regard to Hydrofluoric Acid etching.

18	Nitric / Sodium Fluoride	27	18.506	18.506	0
19	Nitric / AmmoniumBifluoride	27	18.5175	18.465	0.013125
20	Nitric / Sodium Fluoride; spike with sulfuric	27	18.5375	18.53	0.001875
21	Nitric / AmmoniumBifluoride; spike with sulfuric	27	18.499	18.413	0.0215
22	Nitric / AmmoniumBifluoride; spike with sulfuric (higher heat)	35	18.516	18.396	0.03
23	Nitric/ABF/HFSA/Sulfuric	27	18.541	18.488	0.01325
24	Nitric/ABF/HFSA	27	18.53	18.49	0.01
25	Sulfuric/high ABF	27	18.507	18.3	0.05175
26	Sulfuric/high ABF (higher heat)	35	18.541	18.215	0.0815
27	Sulfuric/high ABF (higher heat) ULTRASONIC	41	18.215	18.107	0.108
28	Sulfuric/high ABF (constant higher heat) ULTRASONIC	37	18.584	18.556	0.056
29	Sulfuric / ABF (extremely high heat)	50	18.547	18.359	0.047

Figure 15: Experimental data for Hypothesis 4 – Ammonium Bifluoride Substitution

Ammonium Bifluoride combined with Nitric Acid, however, produced a measurable etch rate. The solution showed even more promising results when spiked with Sulfuric Acid, nearly doubling the original etch rate. Because the ABF runs were overwhelmingly more successful than the Sodium Fluoride trials, it was decided that Sodium Fluoride and by inference Potassium Fluoride, would no longer be kept as part of the testing protocol. All of the trials after Trial 21 involved the use of ABF.

It was quickly determined that an ABF/Sulfuric Acid solution could achieve very similar etch rates to the current OFS baths, especially at elevated temperatures. Another

⁵ United States, Congress, Executive Office of Energy & Environmental Affairs, et al. “Guidance on Reporting Hydrofluoric Acid as a Higher Hazard Substance under the Toxics Use Reduction Act.” 9 May 2016.

promising sign was that the ABF solutions did not volatilize at higher temperatures as was seen with the Hydrofluoric Acid/Hexafluorosilicic Acid solutions. This means that the baths could be run at higher temperatures without losing fluoride, but it also meant that ABF was not acting like Hydrofluoric Acid in these solutions. Hydrofluoric Acid when it reacts with Silica forms a volatile hydrated complex that distills at low temperatures. Once free of the water solution this hydrated complex decomposes releasing both Hydrofluoric Acid and Silica gel. The Silica Gel made a mess of the inside of the Lab hood leaving a humectant layer of Silica over everything. This was not seen with the use of Ammonium Bifluoride even at highly elevated temperatures.



Figure 16: Raised surface of test rod etched with ammonium bifluoride

Another sign that ABF does not act like Hydrofluoric Acid was the difference in etching quality between the two substances. When the test rods were etched with Hydrofluoric Acid, they were smooth and clear after four hours of etching. The first few trials with Ammonium Bifluoride resulted in similar smoothness, but later trials showed evidence of uneven poor etching. Figure 16. above, depicts the third rod tested in the same Ammonium Bifluoride bath. There is significant buildup on the outside of this rod where some substance prevented etching. The contaminated portion shown in the picture is raised up from the surrounding smooth etched area and it feels bumpy to the touch. This phenomenon did not occur with any of the other Hydrofluoric based acid trials, no matter how often the baths were reused. This observation implies that ABF creates another complex not seen with Hydrofluoric Acid.

An Ammonium Silica Fluoride complex was put forth as the best candidate for the boundary layer forming substance. Silica coming from the glass builds up in the bath reaching a saturation point where a boundary layer of Ammonium Silica Fluoride forms that is only partially soluble in the Acid solution. There is evidence of this effect coming from other work with glass etching from another company where they reported that “after a while you need to put the rods in pure Sulfuric Acid to reactivate the surface”. This observation was noted but not understood in terms of the possible cause.

This buildup occurs even with the Ultrasonic transducers running and at temperatures upwards of 50°C with saturated solutions. Other than this issue, however, the etching capability of Ammonium Bifluoride is just as high as that of Hydrofluoric Acid and the worker health and safety aspects are far more desirable. Thus, if the Ammonium Silica Fluoride complex can be removed from the bath before it starts compromising etching quality, ABF could be the best solution for Hydrofluoric Acid elimination.

5.0 Conclusions

Based on the experiments and results of this project, it seems possible to reduce or eliminate the use of Hydrofluoric Acid in the etching processes at OFS. The best route to achieving this reduction lies with the use of Ammonium Bifluoride, or ABF. ABF can achieve similar etch rates to Hydrofluoric acid at higher concentrations and its use would eliminate the risks inherent with handling Hydrofluoric Acid. That being said; altering the etching process to replace Hydrofluoric Acid with ABF is not as simple as swapping the two substances. The simple use of ABF appears to create a complex that interferes with the etching quality of the rods. To solve this issue, a system for removing this complex would have to be developed and installed at OFS.

If such a system was developed, the Ammonium Bifluoride bath could become “immortalized”. This means that emptying the bath would seldom be required. Simply adding and removing the components would maintain it. A promising aspect of Ammonium Bifluoride is the fact that it possesses two fluorine ions per molecule. The Ammonium Silica Fluoride complex also possesses two Fluorine ions and the Ammonium ions go with the Silica, so the bath could theoretically be maintained by removing the complex and stoichiometrically replacing the reactants. This 1-1 molar ratio of reactants to undesired product would provide for simple bath maintenance. One route to doing this is that the Ammonium Silica Fluoride could be cooled and removed as a salt, while the rest of the bath could then be re-heated, and more ABF could be added as needed. This is one option, but more routes to that end may exist.

It was assumed that the chemistry of Hydrofluoric Acid was well understood going into this project and that knowledge didn't leave many options for substitution on the table. Reclamation by Dialysis, Reverse Osmosis or distillation were all fraught with cost, complexity and membrane poisoning issues, so due diligence was performed looking at those options prior to tabling them at the beginning.

Substitution of other fluoride sources coupled with strong acids became the likeliest routes to success especially in light of the communal knowledge of how strong acids and Fluorides react. But in the end, all that knowledge turned out not to apply to the etching of glass.

Clearly there are coordination effects controlling the interaction of glass with Hydrofluoric Acid. Reaction rates of Hydrofluoric are non-linear at the lower end of concentration ranges used in the etch. Concentrations just below the point where OFS would have dumped a bath due to low activity were found to have a disproportionate drop off in the etch rate. Nonlinearity implies that more than one molecule or atom reacts simultaneously supporting the binuclear approach and showing the effects of diffusion through a boundary layer. Raising the temperature of the etch brought the etching activity up only by the square root of the change in energy, again indicating that it is not a simple mononuclear interaction of HF with the substrate.

It appears that there are two steps involved; one where two or even four Fluorine atoms must coordinate onto the glass surface, followed by a slower reaction where the remaining Silicon bonds to the substrate are broken by charge delocalization onto the Fluoride atoms followed by the formation of Hexafluorosilicic Acid. It is interesting that ABF which exists as a binuclear bi-fluoro complex is the only species showing strong activity over glass.

Simple dissociation of a Fluoride salt by a strong mineral acid should have allowed the generation or "manufacture" of Hydrofluoric Acid in solution. Our research indicates that that is not the case.

6.0 Recommendations

- 1.) Pursue the use of Ammonium Bifluoride as a substitute for Hydrofluoric Acid at OFS.
- 2.) Develop a method for removing the Silica from the solution. Heating and cooling of the solution of ABF appears to offer a simple method.
- 3.) Raise the temperature of the etch solutions to enhance etch at lower chemical concentrations. Heating of the ABF solution is not accompanied by evolution of the Hexafluorosilicic Acid/Silica Gel complex as with Hydrofluoric Acid.

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