HF

Preamble:

This document serves to cover as completely as possible the chemical materials that KSU LCI has in the Prototyping Facility that either contain directly or generate indirectly, HF. Also, this document covers alternative materials to HF reagents that have been substituted for HF reagents under the incorrect assumption that these materials are a nonhazardous 'form' of HF. MSDS data will be reviewed from multiple sources. Safety hazards will be discussed. Recommended Personal Protection Equipment (PPE) will be covered. Standard use protocols will be outlined. Emergency exposure response will be detailed. HF and its cousins are potentially very dangerous to your physical health. No one should perform any processes using any HF or HF-like chemicals, without complete understanding of the use of these materials, without complete training being completed, without all proper work environment safety guards being in place at all times, and without having one other person equally well-trained standing by to assist in case of unexpected emergency. There is a reason that HF chemical reagents are locked up in a separate cabinet. Do not buy your own and bring into the facility. If you do, you will be banned from working in the facility.

Introduction:

Hydrofluoric acid (HF aq) is a chemical that is present in the KSU-LCI Prototyping facility. You will see from its name that it is an acid. To simply think of this chemical as an acid similar to your experiences with HCl, HNO_3 or H_2SO_4 is a gross underestimation of your opponent. From WebMD: "Acids can cause injury, depending on the type, the strength, and the length of time the acid is in contact with the body. The damage is usually kept to the area of contact and does not usually cause damage deep in the tissue." Also, "Most chemical burns are treated first by rinsing (flushing) the chemical off your body with a large amount of cool water." Anyone who has worked in a chemical lab environment for any length of time will know these things to be true. Therefore, one might read those to imply, "No big deal. Rinse it off. All good." In the case of the standard lab acids, at lower concentrations and short exposures to skin, this is usually fairly true. But change to nontypical acids or get exposure to the eyes, mouth or lungs and this situation becomes much more of a "big deal." This document will not branch out to describe the proper response for all chemical acids, just HF. The main message here is that if you have experience with acids and feel very comfortable around them, you should NOT allow yourself to think of HF as an acid in the same way. In fact, if you look it up and discover that it is technically considered a *weak* acid, you could lull yourself into thinking that it is even less dangerous than the typical lab mineral acid reagents. However, you must not think of HF as simply an 'acid' but think of it as HF, and the special considerations that working with this specific material requires you to know.

A weak acid simply means that in aqueous solution the parent compound (HF in this case) does not completely dissociate and the solution is not all H_30+ and F- ions. There is some HF still in the water. The labels *weak acid* and *strong acid* have very little to do with some perception of the chemical's ability to cause damage or chemical reaction, and merely state something about the extent of its ability to ionize in solution. We all know what the labels hardwood and softwood mean right? Hardwoods are typically the deciduous trees, hard, dense, strong. Softwoods are typically the conifers, soft, flexible, not as dense. Would it then surprise you to find out that wood from the Balsa tree is categorized as a hardwood? Balsa is one of the lowest density wood materials. It is used for all those little engineering projects where things are built to be structurally strong with minimal weight. Clearly the term hardwood is misleading at the level that most people understand it to imply hard, dense wood. Spider webbing has a higher tensile strength than steel. So, which is 'stronger'? Would you cross a bridge that was made out of spider webbing, purely based on the knowledge that spider webbing is "stronger" than steel? Anyway, the point is, do not be fooled by what you think acid implies as a working hazard, or what weak acid may imply as a chemical strength. Let us learn about HF, and treat this material as HF and not make the mistake of equating labels HF may technically have with things that we know from some experience to be relatively safe.

HF is hazardous for reasons that other acids are hazardous, but also hazardous in its own special way. HF is an acid and it will attack organic tissue. More generally, HF is corrosive, meaning it can damage materials with which it comes into contact. But this is the 'lesser' hazard, at least for skin. Rinse most acids (and corrosives) off right away with water, and most acid contact problems will be relatively resolved. That is because most lab acids attack the top layer of organic tissue, which in the case of skin, is dead anyway. From a good wikipedia reference: "Their action on living tissue (e.g. skin, flesh and cornea) is mainly based on acid-base reactions of amide hydrolysis and ester hydrolysis. Proteins (chemically composed of amide bonds) are destroyed via amide hydrolysis while lipids (many of which have ester bonds) are decomposed by ester hydrolysis. These reactions lead to chemical burns and are the mechanism of the destruction posed by corrosives."

But the reason that HF is more dangerous than typical lab acids is due to its ability to penetrate skin and move to deeper layers of tissue. Not only can it do this, but it can do this without any immediate indication that this is occurring. During even short contact exposure times, HF does not simply sit on top and digest away at the first layer of tissue. It penetrates the skin and becomes a hazard to the body's biological processes. With its capability to disrupt biological processes, HF is listed as a poison as well as being corrosive. Insidiously, it is the weak acid character of HF that gives it the ability to penetrate deep into tissues so much more rapidly than mineral acids. The HF molecule is fat soluble and moves readily through the fat layer under the skin to depths that are far too deep for it to be simply rinsed off.

Also, the mechanism of chemical action that HF has on the body is to interfere with nerve function. This means that pain normally associated with a corrosive action on a tissue may not be felt. Not feeling pain at the site of exposure may cause accidental contact exposures to go unnoticed, and thus, proper response and treatments delayed. Prolonging exposure and delaying response and treatment, can cause the extent of exposure and subsequent damage to be higher in magnitude.

The final action that HF can exert on the body is that once it has penetrated into the bloodstream through a skin contact exposure (or by any other entry route), HF chemically reacts with serum calcium and binds it up to form the insoluble calcium fluoride. A relatively small exposure contact area of approximately 25 square inches (just larger than the palm of your hand) with concentrated HF solutions can bind up enough serum calcium to interfere with the ion pumps of the nervous system, and most notably, cause cardiac arrest. Even if someone has not received what will ultimately be a fatal exposure level, permanent damage can result if the exposure is the eyes, and permanent nerve damage can occur to areas of the skin that get exposed. If nonfatal, but repeated doses are encountered, HF can begin to secure Calcium from bones, taking the calcium away from the calcium phosphate compounds they are normally made of, and form calcium fluoride instead. This makes the bones weak and subject to fracture.

So, HF is scary stuff. We get it. But we have to use it anyway. So how do we do it?

The only endorsed reason to use an HF reagent in the prototyping facility is to etch SiO_2 depositions. Since our in-house processes generate SiO_2 layers of approximately a few hundred Angstroms, this is a good thing. What this means is that the concentration of the HF solutions we use are from 1-2% in water. The good thing is that any accidental exposure to this reagent has very little HF in it. It is mostly water. But, even at 1% HF can permanently damage the cornea of your eyes. Prolonged exposure to skin can still cause deep tissue burns. The problem is that in weak concentration the symptoms of such a burn may not show up for 24 hours or more, long past the time when you thought you might have a problem. Therefore, even though a weak concentration is more safe on some level, it is still a serious hazard to your safety and to those around you. With this in mind, here is how we approach the use of our HF reagent:

1. Request training on the use of this chemical reagent from facility staff

2. Read, understand and follow all material related to the HF reagent, including the MSDS, the use protocols, and the emergency response protocols.

3. Set up a protected work area for the carrying out of the HF SiO_2 etching process. This means, find an empty hood to use where no one else is working. Put up a sign that indicates you are working with HF. Place a square plastic tray on the hood chemical counter and sprinkle some calcium carbonate on the bottom. Place four vial caps in the tray enough to support your plate to be etched. Mark the back

4. Place the substrate SiO2 side face up on top of the vial caps.

5. Use a plastic eye dropper to dispense HF reagent onto necessary areas of the plate.

6. Wait for the desired amount of time for complete etching to occur.

7. Rinse the plate off with water, into the plastic lid/tray.

8. Send the plate through a full cleaning process.

9. Collect all the water/reagent in the lid using a plastic funnel into an appropriate “HF solution waste” bottle (plastic).

10. Thoroughly clean the work area and rinse down all materials used, funnel, tray, bottles, vial caps.

11. Discard vial caps in regular trash. Allow all materials to dry in the hood before returning to storage.

12. Place HF reagents back into the locked HF storage cabinet.