a place of mind
THE UNIVERSITY OF BRITISH COLUMBIA
School of Engineering
Okanagan Campus

All users *must* get permission from the School of Engineering Safety Committee before Hydrofluoric Acid is purchased or used

1.0 Introduction to Hydrofluoric Acid ($HF_{(aq)}$).

This hydrofluoric ($HF_{(aq)}$) acid standard operating procedure outlines the significant hazards associated with the handling of this chemical. This is not a comprehensive guide to handling this chemical, and it assumes that the users of this guide have basic experience in handling chemicals, mixing chemicals, and working with acids. The user should also refer to the following document from the Health, Safety and Environment (HSE) office at the University of British Columbia's Okanagan campus:
https://hse.ok.ubc.ca/wp-content/uploads/sites/72/2021/01/HSE-Working-with-HF.pdf

Hydrofluoric acid can cause serious injury or even death from skin exposure. The mechanism for the local tissue corrosion is caused by the active hydrogen cation (H^+) of the acid. Hydrofluoric acid will also cause local injuries; however, it does not stop there. The fluoride anion (F^-) that dissociates from its hydrogen counterpart readily absorbs through the skin, damage tissues, and causes systemic injury. The fluoride ion also has an affinity for calcium and magnesium, two minerals that are essential for the body. As the fluoride ion binds with calcium, it consumes the body's supply of this mineral in the blood and attacks bone, forming calcium fluoride salts.

As serum calcium levels are depleted in the blood, a condition known as hypocalcaemia, or organ failure, begins to occur, with heart functioning becoming erratic. This can cause the heart to fail, resulting in death.

1.1 Introduction to acid etching

Etching aluminum can be a pre-treatment step for anodizing, chemical conversion coating, metal-to-rubber bonding, and a host of other processes. Chemical etching using either alkaline or acid solutions produces a matte finish on aluminum products.

2.0 Pre-Etching check list

2.1 Hydrofluoric ($HF_{(aq)}$) acid first aid kit

Referred to the University of British Columbia's document "Working safely with HF acid (document 1), section 5. Material /equipment".

2.2 Acid glove test

Neoprene gloves should be used for handling $HF_{(aq)}$. This should be worn on top of regular nitrile gloves. Various sizes of acid gloves are also available for users in EME 1207. All the gloves should be checked for compatibility with hydrofluoric acid with the manufacturer’s documentation (not all the gloves available in EME1207 are rated for use with hydrofluoric acid). Note that the specific model must be checked; not all gloves of the same material or brand are created equal. All the gloves should be leak tested prior to use. Gloves should be blown with air (at 20 psi) until they are inflated, and then they should be submerged in a bucket of water to ensure that there are no leaks. This is usually done with the portable air tank and bucket in EME 1207A.

As a preventative measure, prepare a second pair of gloves for the principle $HF_{(aq)}$ handler and keep in on a nearby bench. If there is major contamination of the handler's gloves during processing, the contaminated gloves can be removed into the solid waste container and the second gloves can be used.

2.3 Visual inspection of gown and boot covers

Visually inspect all the personal protective equipment (PPE), including face shield, gown, and boot covers. Duct tape can be used to form a good seal on open areas, e.g., gloves and sleeves.

2.4 Calcium Gluconate eye drops.

Researchers are required to have calcium gluconate eye drops handy from a pharmacy. It is available from Dyck's Pharmacy, on 3039 Pandosy street, Kelowna, BC, with but a prescription is typically required and at least four days notice must be given. The drops should be stored in a refrigerator. Note that the drops expire two weeks after being produced. The prescription is for 1% calcium gluconate in a saline eye drop solution. Previous eye drops were ordered in a 30 mL volume.

In the case of $HF_{(aq)}$ splash to the eye area, an alternating cycle of drops and eye wash station flushing is recommended. Apply some drops, then flush for 5 minutes, and repeat at least two more times.

2.5 Neutralising base

Calcium carbonate ($CaCO_3$) powder is used as a neutralising base for HF acid. Is can be used for small spill cleanups and for wiping down face shields and gowns. Used calcium carbonate should be disposed of in a polyethylene bag that is tagged as hazardous waste. Lime or calcium hydroxide can also be used as a neutraliser. The neutralizer should be added slowly, as the reaction can be vigorous. It is also prudent to dilute acids into water prior to adding the neutralizer. Have a large container of water available in the fumehood throughout etching to use as a diluent.

2.6 Beakers and disposing bottles

Only polyethylene or polypropylene beakers and containers should be used for storing as well as disposing $HF_{(aq)}$. Do not store or dispose of $HF_{(aq)}$ in glass containers, as hydrofluoric acid attacks all silica containing materials.

2.7 Microscope for analysis

The microscope to be used should be brought to a safe location that is close to the etching area, if possible.

3.0 Etching procedure

3.1 Etchant preparation

The most common $HF_{(aq)}$-based etchants for aluminum alloys are Keller's and Kroll's reagents. The composition of these reagents and the appropriate etching conditions are provided in Table 1.

Etchant	Components	Concentration	Conditions	Comments
Keller's reagent	Distilled water Nitric acid (HNO_3) Hydrochloric acid (HCl) Hydrofluoric acid ($HF_{(aq)}$) Note: $HF_{(aq)}$ comes as ~50% solution; use 1 mL of the provided concentration.	95 mL 2.5 mL 1.5 mL 1 mL	Immerse the sample for 10–30 seconds	Use only fresh etchant; Suitable for most Al alloys It is normal to see brown discolouration/ gas in the nitric acid (small amounts of Nitrogen dioxide [NO_2] gas)
Kroll's reagent	Distilled (DI) water Nitric acid (HNO_3) Hydrofluoric acid ($HF_{(aq)}$)	92 mL 6 mL 2 mL	Swab the sample for 10–20 seconds or immerse 10–30 seconds	Suitable for Al-Cu alloys

Table 1: Common $HF_{(aq)}$-based etchants for aluminum alloys.

The various steps in the etchant preparation are as follows:
1. Take 95 mL/92 mL (as appropriate) distilled water in a clean polyethylene or polypropylene beaker (Do not use glass, hydrofluoric acid dissolves glass) and add 1 mL of $HF_{(aq)}$ in water using a micropipette.
2. Gently mix the $HF_{(aq)}$ solution with the pipette tip. Then, eject the pipette tip into the large beaker of water.
3. Add the required amount of other acids (e.g., HNO_3, HCl) to the $HF_{(aq)}$ solution (by always adding acids to the solvent). Use a fresh pipette tip for each acid.

3.2 Etching

Before starting the etching, keep three large beakers of water in the fumehood to clean the etched sample via dipping. The beakers should be large enough for the samples to be fully dipped into the water and then shaken off to remove excess water. The sample should then be placed in the fumehood on a paper towel with the polished face up.

Etching can then be performed either by immersion or swabbing:
· **Immersion**: The sample is immersed for an appropriate time in a small beaker containing 100 mL of etchant (using tongs).
· **Swabbing**: The sample is held with tongs using one hand and swabbed with cotton (or Q-tips) using tongs in the other hand.

The steps for etching are as follows:
1. Hold the sample with tongs and immerse it into the etchant for an appropriate time. (Have a second person time the immersion for the set time.) Gently move the sample in the etchant to provide agitation (and thus give better uniformity of etching).
2. Next, remove the sample from the etchant and its beaker and dip it into the three beakers of water. Gently shake the sample to remove excess water after each dipping.
3. Check the sample with a pH strip prior to drying it off.
4. Place the sample on a fresh paper towel for drying (etched face up) within the fumehood. Then, gently wipe the sample surface with a paper towel.

5. Once the sample is completely dried, the second person can check the microstructure under the microscope to ensure that the surface is not under- or over-etched. If the surface is under-etched, the etching time can be increased; if it is over-etched, the sample must be repolished.
6. After finding the correct etching time, repeat the above steps for the remaining samples.
7. The beakers should have their pH tested after every five samples and their water should be replaced if it is acidic (pH <7).

3.3 Inspection of the samples using the optical microscope

The etched samples can be inspected under a microscope, ideally located within the lab. After examining all of the samples, the microscope should be cleaned with alcohol and Kimwipes.

4.0 Disposal procedure

The $HF_{(aq)}$ etchant and the surfaces that could have been exposed are to be neutralised with calcium carbonate. The fumehood surfaces, face shields, etc., should be wiped with calcium carbonate and wipes. These consumables should be disposed of in a polyethylene bag tagged as hazardous waste.

The etchant, dip solution, and water + $CaCO_3$ (used for neutralising the accessories) should be stored separately in a polyethelene/polypropelyne containers and tagged respectively for HSE waste pickup. These should be stored and locked in the hydrofluoric acid cabinet. Glass bottles should not be used to hold hydroflouric acid.

6.0 Emergency Procedures

For any accidents or near-misses, contact Campus Security at 250-807-8111 (or 78111 from an on-campus phone). Otherwise, dial 911 for emergency services. When contacting emergency services, state that hydrofluoric acid is involved.

6.1 Spills

Do not attempt to clean up a spill volume larger than 200 mL of > 20% $HF_{(aq)}$ — contact Health, Safety & Environment or Campus Security for assistance.

Spill on an individual

- Immediately remove contaminated PPE items and/or contaminated clothing.
- If, during the spill, the skin or eye(s) came into contact with HF, follow the specific emergency procedures below.
- Ask for assistance with clean-up and proceed to decontamination.
- Any clothes contaminated with $HF_{(aq)}$ should be disposed of as hazardous waste.
- Contaminated PVC gloves can be decontaminated as per procedure below.

Spill on equipment or surfaces

- Alert supervisor and personnel in the immediate area and ask a co-worker to bring the spill kit.
- Isolate spill area (caution tape, signage).
- Put on PPE (face shield over safety googles, disposable gloves, neoprene gloves on top, PVC apron over lab coat, rubber boots — if necessary).
- Contain spill by spreading $HF_{(aq)}$ neutralizing powder outside spill area, working inwards
- Allow sufficient contact time as recommended by the manufacturer.
- Verify that neutralization is complete by using pH strips or observing the color change for the specific neutralizer used.
- Collect $HF_{(aq)}$ clean-up waste and all materials used in the clean-up in a sealed plastic container. Label the container "Hydrofluoric acid clean-up waste" and arrange for disposal as hazardous waste through the Hazardous Waste Inventory System.
- Decontaminate the PVC gloves, face shield and googles for re-use (if not heavily contaminated); other contaminated PPE should be disposed of as hazardous waste.

6.2 Emergency First Aid

Skin contact

- Wash the affected area immediately under running water under the safety shower and flush affected area thoroughly with cool running water for at least 5 minutes. Remove all contaminated clothing while flushing.
- Apply a generous amount of calcium gluconate gel to the affected area wearing gloves so as to not spread the acid to a new person; the gel will turn white upon reaction with the acid. Massage the 2.5% calcium gluconate gel into the burn site. Apply every 15 minutes and massage continuously until more definitive medical care is given.
- Seek immediate medical attention at a hospital; continue applying gel during transport to the medical facility.

Eye contact

- If $HF_{(aq)}$ liquid or vapor has contacted the eyes, immediately flush for at least 15–20 minutes. Hold upper and lower eyelids open and away from the eye during irrigation.
- Do not apply calcium gluconate gel to the eye
- Avoid rubbing of the eyes
- Seek immediate medical attention.

Inhalation

- Vapor exposures can cause skin and mucous membrane burns as well as damage to pulmonary tissue

Ingestion

- Have victim drink large amounts of room temperature water as quickly as possible
- Drink several glasses of milk or several ounces of Mylanta, Maalox, or antacid tablets (all contain calcium or magnesium which may act as antidote)
- Do not induce vomiting, do not give emetics or baking soda or any bicarbonate

Seek immediate medical attention; ingestion of HF is a life-threatening emergency

7.0 References

1. Safe Handling of HF — Princeton University.
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3. Safe Handling of HF — University of Regina:
https://www.uregina.ca/hr/hsw/hazardous-materials-equipment-safety/procedures.html

4. Safe Use of HF— Harvard University:
https://chemistry.harvard.edu/files/chemistry/files/safe_use_of_hf_0.pdf

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