

HYDROFLUORIC ACID SAFETY GUIDELINES

Hydrofluoric acid (HF) is an extremely corrosive substances used in the production of organic or inorganic fluorine compounds, in the treatment of metals (aluminum, steel), glass and crystal (etching and polishing), in the petroleum industry (refining), in the electronics industry for the surface treatment of electronic components and in biological staining. Hydrofluoric acid usually comes in solution of 47-51% concentration. It is significantly more hazardous than any other acids. This document discusses the properties, health and safety hazards of HF and how to appropriately protect yourself from potential HF exposures. Also included are emergency procedures for dealing with accidental HF contact, including first aid treatment information.

⚠WARNING⚠: Hydrofluoric acid is a contact poison. Contact may not be noticed until long after serious damage has been done. HF can cause serious burns to the skin with significant complications due to the fluoride toxicity. Deaths have been reported from concentrated acid burns involving as little as 2.5% Body Surface Area (BSA), an area roughly the size of your hand is sufficient to cause death.

1. Properties

Names: gaseous state: hydrogen fluoride or anhydrous hydrofluoric acid
 aqueous solution: hydrofluoric acid, fluorhydric acid, fluoric acid

Chemical Formula: HF

CAS #:

7664-39-3

Physical aspect (Hydrofluoric acid, 47-51%):

colorless liquid

mineral acid

irritating odor at low concentrations (3 ppm)

Table 1. Physical and Toxicological Properties of HF

Molar Mass	20,006 g.mol-1
Boiling point	112,2°C
Melting point	-83,36°C
Vapor pressure	13,3 kPa at -28,2°C 53,3 kPa at 2,5°C 150 kPa at 30°C
Density at 0°C	1,002
pKa (water)	3.20
PEL (TWA)	3 ppm (2,5 mg/m ³)
IDHL	30 ppm (25 mg/m ³)

2. Hazard Classification (Hydrofluoric acid, 47-51%)

WHMIS 1988



D1A Very Toxic Material Causing Immediate and Serious Toxic Effects:

Highly toxic by ingestion

D2B Toxic Material Causing Other Toxic Effects:

Highly toxic by skin absorption

E Corrosive Material Highly toxic by inhalation:

Severe eye irritant

Corrosive to skin

WHMIS 2015



Acute toxicity, Oral (Category 2)

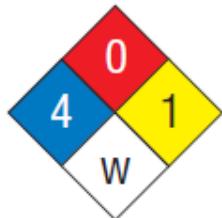
Acute toxicity, Inhalation (Category 2)

Acute toxicity, Dermal (Category 1)

Skin corrosion/irritation (Sub-category 1A)

Serious eye damage/eye irritation (Category 1)

NFPA



Flammability: non-flammable/will not burn.

Health hazard: very short exposure could cause death or major residual injury (liquid and gas)

Instability/Reactivity: normally stable, but can become unstable at elevated temperatures and pressures

Anhydrous HF reacts strongly with water

3. Health Hazards

a) Toxicity Mechanism

The mechanism of HF burns is linked to the dual corrosive and toxic effects of the hydrofluoric acid. HF toxicity originates from a combination of its acidic properties and its ability to release toxic fluoride anions inside cells. The reason for this toxicity is the high electronegativity of the fluoride ion which holds onto the hydrogen cation tightly. The result is a weak acid that exists predominantly in the undissociated state compared to other acids (1000 times less dissociated versus HCl). The pKa (the logarithmic measure of the acid dissociation constant) of HF is 3.20 (Table 1). The larger the value of pKa, the smaller the extent of dissociation (a weak acid has a pKa value in the approximate range -2 to 12 in water). In the undissociated state, the HF molecule is able to penetrate deeply into the skin and soft tissues by non-ionic diffusion, resulting in destruction of nerves, blood vessels, tendons and bone. Once in the tissue, the F⁻ anion is able to dissociate and cause liquefactive necrosis of soft tissue, bony erosion, as well as extensive electrolyte abnormalities by binding the cations Ca⁺² and Mg⁺² (Fig. 1). This leads to conditions known as hypocalcaemia (low calcium levels), hyperkalemia (high potassium levels), hypomagnesaemia (low magnesium levels) which can result in a sudden death.

A systemic risk may arise because of a high concentration of HF or/and an extended time of contact.

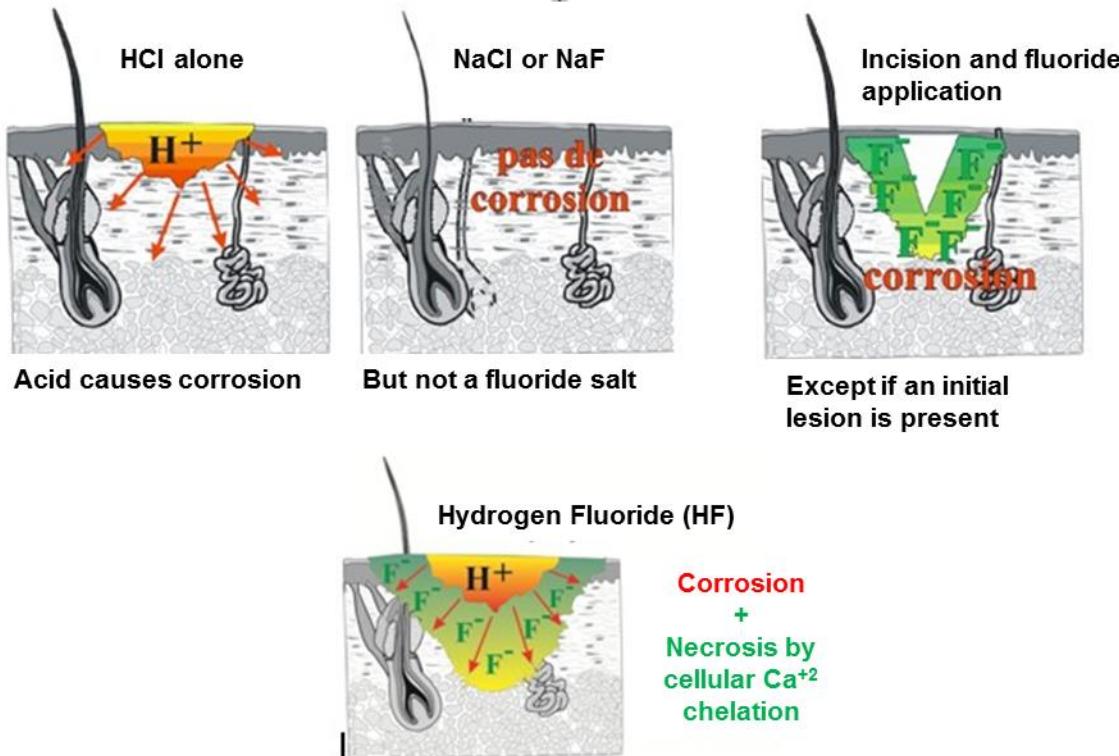
Figure 1: Toxicity Mechanism of HF


Table 2 reports, in relation with the body surface area, the minimal concentration of HF able to generate a lethal risk, for the different exposure routes.

Table 2: Fatal systemic risk in relation to the HF concentration and the damaged body area

TYPE OF CONTACT	BODY SURFACE AREA	HF CONCENTRATION
Skin	1 %	Anhydre
	> 70 %	
	50-70 %	
	20-50 %	
	< 20 %	
Ingestion		> 5 %
Inhalation		

b) Skin Exposure

The most common route of exposure is dermal. Symptoms are often delayed, particularly with exposure to diluted solutions. The delay likely reflects the time required for penetration of the fluoride ion into the tissue (Table 3). Depending on the concentration of a dermal exposure, affected skin can initially look completely normal, but often will become painful and appear pale or white, possibly leading to necrosis.

Damage to the skin develops over several hours or days, starting with erythema and followed by deep and painful lesions.

Table 3. Concentration–response relationship

Concentration (wt/v)	Pain
<20%	Delayed by 24 hours or more (with erythema developing with same time)
20-50%	Delayed by 1 to 8 hours after contact (with erythema developing with same delay)
>50%	Immediate, associated with a rapidly visible destruction of tissues

The damaged area of skin discolors and becomes whitish or grayish at the centre, surrounded by a purplish crown. If the time of contact increases, the damaged skin turns to red then to grayish purple/black purple, with a significant oedema and intense pain. Serious skin damage and tissue loss may result if not treated early and properly. Cutaneous exposure to HF vapors may cause similar lesions.

c) Eye exposure

At the ocular level, exposure to HF will generate a severe burn with corneal opacification that may lead to necrosis of the structures of the anterior chamber of the eye. Blindness may result from severe or untreated exposure. Immediate first aid is required.

d) Inhalation

Due to its strong irritant nature, someone who inhales HF vapors or fumes will usually experience upper respiratory injury, with mucous membrane irritation (including eyes and nose), inflammation and cough. Inhalation exposure may result in dyspnea, chest pain, airway obstruction and wheezing. Large amounts can damage the lungs. Delayed reactions, up to and including fatal pulmonary oedema, may not be apparent for hours after the initial exposure. The Permissible Exposure Limit (PEL) set by the U.S. Occupational Safety and Health Administration (OSHA) is a time weight average (TWA) exposure for 8h of 3 ppm (Table 1). The National Institute for Occupational Safety and Health (NIOSH) has established a concentration that is immediately dangerous to life and death (IDLH) at 30 ppm (Table 1).

e) Ingestion

Oral exposure may result in severe burns to the mouth, esophagus and stomach which can lead to vomiting (possibly bloody), abdominal pain and bloody diarrhea. Ingestion of even small amount of diluted HF can result systemic poisoning. Systemic signs and symptoms include hypocalcemia and hyperkalemia, which may lead to seizures and possibly death.

4. Safety Precautions for HF Use

a) Training

Students and employees who handle HF must have read the Safety Data Sheet (SDS) and receive training on the hazards of HF from their respective department. They must know what to do in the event of a spill or an exposure incident. The SDS must always be kept the immediate vicinity of the working area along with the Standard Operating Procedure (SOP) developed by the student / employee's department. Special training can also be offered by EHS.

b) Ventilation

HF MUST be handled in a well-ventilated area. Concentrated HF and solution with concentrations greater than 5% HF wt/v MUST be handled inside a certified chemical fume hood.

c) Eye Protection

Chemical goggles along with a face shield MUST be worn when handling HF at concentrations greater than 20% wt/v. Safety glasses may not provide adequate eye protection.

d) Gloves

Always consult the manufacturer's glove selection guide when selecting gloves for working with HF (Table 4). Thin disposable gloves (such as 4, 6, or 8 mm blue Nitrile glove) provide a contact barrier only. Thicker (10-20 mm) PVC or neoprene gloves provide good resistance to HF. If gloves become contaminated with HF, remove them immediately, wash your hands and check for any sign of contamination. Contaminated gloves must be disposed of as HF waste.

e) Protection Clothing

A lab coat or chemical smock along with a chemically-resistant apron (natural rubber, neoprene or Viton) MUST be worn when handling HF at concentrations greater than 5% wt/v. **No exposed skin is allowed;** long pants, sleeves, and closed toe shoes/boots must be worn. Disposable sleeve covers should be worn for added protection.

f) Safe Work Practice

- **Never work alone when using HF.**
- HF MUST be slowly poured into an aqueous solution while stirring the mixture. Anhydrous hydrofluoric acid reacts strongly with water and its dilution in water is associated with the emission of white fumes and a significant heat release.
- The area must be equipped with an emergency shower, an eyewash station and a first aid kit
- **The first-aid kit MUST contain calcium gluconate gel.** This gel must be inspected before each use of HF or at least monthly to ensure the gel has not been removed or has not reached the expiration date. If a tube of the gel has been opened, a new container must be purchased and the old container discarded. **No work with HF can be done with an expired tube of calcium gluconate gel.**

Table 4. Glove compatibility chart for Hydrofluoric Acid 48%

Glove Description	Material	Overall Rating	Degradation Rating (@30min)
Ansell AlphaTEC Nitrile Gloves	Nitrile	G	E
Ansell Canners and Handlers Unsupported Latex Gloves	Latex	G	E
Ansell Chemi-Pro Flock-Lined Neoprene-Over-Latex Gloves	Neoprene	G	E
Ansell Sol-Vex Nitrile Gloves	Nitrile	G	E
ANSELL Unsupported Neoprene Gloves	Neoprene	G	E
Best Butyl II Gloves	Butyl	G	E
Best N-DEX Laboratory Grade Nitrile Gloves	Nitrile	G	G
Best N-DEX Medical Grade Nitrile Gloves	Nitrile	G	G
Best N-DEX Plus Industrial Grade Nitrile Gloves	Nitrile	G	G
Best Nitri-Solv Knit Chemical-Resistant Gloves	Nitrile	G	E
Best Viton Gloves	Viton	G	E
KleenGuard G80 Chemical Resistant Gloves	Neoprene	G	E
Microflex Color Touch Latex Gloves	Latex	F	
Microflex ComfortGrip Latex Exam Gloves	Latex	F	
Microflex Diamond Grip Plus Latex Gloves	Latex	F	
Microflex Diamond Grip Latex Gloves	Latex	F	
Microflex Evolution One Latex Gloves	Latex	F	
Microflex FreeForm SE Nitrile Gloves	Nitrile	F	
Microflex Micro One Latex Gloves	Latex	F	
Microflex Nitron One Nitrile Gloves	Nitrile	F	

E = excellent, G = good, F = fair

5. Storage, Spill and Waste Issues

a) Storage

HF solutions must be stored in a cool, dry place away from incompatible materials. Avoid contact with glass, concrete, metals, water, other acids, oxidizers, reducers, alkalis, combustibles, organics and ceramics. Store in compatible containers made of polyethylene or fluorocarbon plastic, lead, or platinum. The storage bottles in should also be placed in secondary polyethylene containment trays. **NEVER store HF in glass containers.**

b) Spills

i. Information and special precautions for Hydrofluoric Acid:

ALL SPILLS OF HYDROFLUORIC ACID MUST BE CLEANED BY THE HAZMAT SPILL RESPONSE TEAM.

The immediate area of the HF spill must be cleared of all non-response personnel. Depending on the concentration of the HF solution and location of the spill, an EVACUATION must be considered.

An **HF incident** is defined as involving **ANY** of the following HF release scenarios:

1. DOES NOT INVOLVE ACTUAL OR SUSPECTED HUMAN EXPOSURE;
2. ANY spill of less than 10 ml of concentrated HF outside of a fume hood environment;
3. ANY spill of less than 100 ml of concentrated HF inside a fume hood;
4. ANY spill of less than 100 ml of any HF concentration outside a fume hood environment.

Notify Security at **ext. 3717** of all releases meeting **incident** criteria and request the Hazmat Spill Response Team.

An **HF emergency** is defined as involving **ANY** of the following situations:

1. ANY ACTUAL EXPOSURE TO LIQUID HF, regardless of its quantity or concentration;
2. ANY spill of greater than 10 ml of concentrated HF outside of a fume hood environment;
3. ANY spill of greater than 100 ml of concentrated HF inside a fume hood;
4. ANY spill of greater than 100 ml of any HF concentration outside a fume hood environment.

Notify Security at **ext. 3717** of all releases meeting **emergency** criteria.

ii. HF spill clean-up procedure:

For NON-HAZMAT Team Members (students, lab technicians, workers)

1. Advise and warn co-workers.
2. Evacuate and secure the area immediately.
3. Do not touch the hazardous material.
4. Call Security at **ext. 3717** or **514-848-3717**, providing them with the following information:
 - a. Name of hazardous material.
 - b. Quantity involved.
 - c. Related health risks and precautions to be taken.
5. Provide Safety Data Sheet (SDS) or appropriate documentation.
6. Wait for the arrival of Hazmat clean-up team; remain available to provide them with details about spill.

For HAZMAT Spill Response Team:

Evaporation rate calculations for a 20% HF bottle broken on floor demonstrate that the time required to reach vapor steady (plateau) concentration value is about 20-30 min, depending on the volume spilled. Table 5 shows a summary of the estimated values. These values represent good estimates in terms of how big of a spill can be handled. Always consider that surrounding conditions (e.g. ventilation) can change rapidly which can make the spill even more hazardous than what it looks like.

Table 5. Evaporation estimates of 20% HF spill

HF spilled volume (L)	Evaporation (ppm)
5.0	~4.3
1.25	~1.7
0.5	~1.0

The minimum PPE for HF response should include:

- Full NEOPRENE boots with over boots
- KAPPLER CPF 2 or higher suits, with hoods up
- NEOPRENE gloves with SOLVEX™ gloves and N-DEX™ under liners
- SCBA
- Hard Hat with Face Shield

Spill response information and special precautions for Hydrofluoric Acid

1. Concentrated HF (70%) solutions may be diluted with water before clean-up to reduce hazards. However, the water must be added slowly and carefully to prevent boiling of HF solution due to exothermic reaction of water and HF. Contain spill before adding water to prevent spread of contamination.
2. HF reacts with all silicon containing materials such as glass, concrete **AND CHEMICAL SPILL SORBENTS SUCHA AS VERMICULITE AND MAGICCORB™**. This reaction will cause the generation of the highly **TOXIC GAS – Silicon Tetrafluoride**. Hazmat responders must BE AWARE and PREPARED for this possibility.

Using Liquid Neutralizer Methods

The HF will be absorbed on polypropylene pads, which will be placed in the appropriate container (5 Gal plastic pails or lined drums), secured and then transported to the hazardous waste storage area for disposal.

The remaining acid residue will be neutralized using a liquid neutralizer. The neutralized residue will be absorbed on pads and placed in appropriate containers. This material will be treated as a hazardous waste until determined otherwise.

This neutralization treatment will be done at least three times, after which the contaminated site will be analyzed using pH paper. Additional treatment will continue until all acid residues are neutralized.

Final clean-up will be performed using normal and appropriate maintenance procedures for the contaminated area.

Using Solid Sodium Bicarbonate

Free liquid will be diked and contained with the solid neutralizer. Sufficient material will be spread over the spill to just cover the surface with a light coating. The solid will be thoroughly mixed to effect absorption of all the free liquid. If necessary, a small quantity of water may be added to cool the slurry or increase the rate of neutralization. If a color indicator is not present to monitor the pH, then the pH paper

should be used. The responder should attempt to maintain the final pH in the range of 6 to 10. This material will be treated as a hazardous waste until determined otherwise.

After all free liquid is absorbed and the residue is containerized, the area should be rinsed at least twice with water to remove residual contamination and excess solid neutralizer.

Clean-up procedure

This procedure should be followed by ALL members of the HAZMAT Spill Response Team who respond to an HF spill.

All areas where HF is used must have proper spill control kit. Small spills can be neutralized by covering with acid neutralizer/sodium bicarbonate, and absorbed with spill control pads/absorbents. Once the spill is contained isolate the room and leave the area immediately. Call Security for help

1. After completion of the above SITUATIONAL RESPONSE requirements, assess the release area for HF CLEAN-UP utilizing a team of Hazmat responders within EHS.
2. Develop a lab-specific clean-up plan for each spill for use once incident or emergency dangers are no longer present and any victim(s) exposure needs have been addressed;
3. Wear applicable PPE determined to be protective to you during an HF clean-up operation;
4. Apply an HF neutralizing substance such as slaked lime for larger quantities or high concentrations or HF Acid Eater liquid for smaller quantities or dilute concentrations of HF to an area 3-5 times larger than the spill area;
5. Allow at least 15 minutes for the neutralizing materials to react with the HF and form insoluble salt fluoride, a white water insoluble substance;
6. Test any remaining liquid for the presence of HF. Use HF test paper (see next point for details) to confirm that there is no free HF in the reacted materials above the detection limit of the test paper (typically 10-20ppm);
7. Using a plastic or Teflon scoop for solid waste created during this operation, place the solid materials in a plastic bucket and label it as hazardous waste;
8. Using Paper Towel, absorb any remaining free liquid and place spent paper into plastic bucket designated as hazardous waste.
9. Dry the damp release area with Paper Towel and place them in normal solid trash.

iii. Fluoride Test Paper:

Fluoride Test Paper can be used to confirm a spill or to assess clean-up levels. This test paper has the capability of determining fluoride ions and gaseous hydrogen fluoride. The pinkish-red paper turns yellowish-white in the presence of fluorides. The limit of sensitivity is 20 ppm of fluoride. Laboratory workers must be familiar with the proper use of this monitoring paper before using it. Do not use the Fluoride Test Paper to determine direct human exposure. The time to perform the test may delay decontamination and potentially worsen the exposure.

c) Waste Handling

HF waste should be placed in a chemically compatible container with a sealed lid. **Never** put HF contaminated material in regular waste. Furthermore, HF waste is treated differently than other types of hazardous waste. All waste containers must be labeled with a hazardous waste label with the full chemical

name written out (hydrofluoric acid - NOT HF!). Contact EHS (hazardouswaste@concordia.ca) for waste pick-up.

6. Fire and Explosion Hazard

HF is non-combustible, but may create irritating and corrosive fumes of fluorides when heated or in combination with steam or water. Since HF does not burn, use an extinguishing agent suitable for surrounding fire. Use water to absorb fumes and keep containers cool. Heat released when water or steam combines with hydrogen fluoride or hydrofluoric acid could be hazardous. For fires involving hydrofluoric acid, apply water in flooding quantities. Hydrofluoric acid and various metals may form hydrogen (extremely flammable gas) creating a fire hazard.

7. Emergency Procedures

All exposure to HF must receive immediate first aid and subsequent medical evaluation even if the injury appears minor and no pain is felt. Rapid treatment of the injury is essential since HF can produce delayed effects and serious tissue damages. **If untreated, permanent damage, disability or even death may result.** A first aid kit containing calcium gluconate must be present if HF is to be handled. Always make sure that the calcium gluconate is not expired.

a) Skin Contact

1. Evacuate and secure the immediate area where contamination occurred.
2. Carefully remove contaminated clothing as not to contaminate non-affected areas. Place contaminated clothing in a bag, waste container or fume hood.
3. Immediately rinse the affected area with copious amounts of water for 15 minutes
4. If Calcium Gluconate gel is readily available, limit rinsing to 5 minutes and apply gel.
5. Using Nitrile gloves, apply the gel to the affected area, spreading it to ensure adequate coverage.
6. Call Security at ext. 3717 or 514-848-3717 stating that you require an ambulance for a person(s) who has been exposed to hydrofluoric acid.
7. Provide the SDS and the Calcium Gluconate gel to security/paramedics
8. Calcium Gluconate gel should be reapplied into affected area of skin every 15 minutes.

b) Eye Contact

1. Evacuate and secure the immediate area where contamination occurred.
2. Immediately irrigate eyes at eyewash for at least 15 minutes with copious quantities of water keeping eyelids apart and away from eyeballs.
3. **Do not apply Calcium Gluconate gel to eyes.**
4. Calling Security at ext. 3717 or 514-848-3717 stating that you require an ambulance for a person(s) who has been exposed to hydrofluoric acid.
5. Provide the SDS to security/paramedics.

c) Inhalation

1. Evacuate and secure the immediate area where contamination occurred.
2. Move victim to fresh air.
3. Call Security at ext. 3717 or 514-848-3717 stating that you require an ambulance for a person(s) who has been exposed to hydrofluoric acid.
4. Provide the SSDS to security/paramedics
5. Inhalation of HF fumes may cause swelling in the respiratory tract up to 24 hours after exposure.

d) Ingestion

1. Evacuate and secure the immediate area where contamination occurred.
2. Give the victim large amounts of water to drink to dilute the chemical.
3. Several glasses of milk or several ounces of milk of magnesia may also be given.
4. Do not induce vomiting.
5. Call Security at ext. 3717 or 514-848-3717 stating that you require an ambulance for a person(s) who has been exposed to hydrofluoric acid.
6. Provide the SDS to security/paramedics.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) must be brought to the emergency room as the treating physician might be unaware of the treatment measures for HF. All HF incidents and exposures must be reported to your Supervisor and to Environmental Health & Safety (EHS). An [injury/near-miss report](#) must be filled for any incident involving HF spill or exposure.

If you have any concerns about the use of hydrofluoric acid at Concordia University, please email EHS at ehs@concordia.ca

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References:

- Recommended Medical Treatment for Hydrofluoric Acid Exposure, Honeywell Specialty Materials, Honeywell Chemicals
- Product File: Hydrofluoric Acid: Management of eye and skin chemical splashes, Prevor Toxicology Laboratory and Chemical Risk Management, 2010 Edition
- *Hydrogen Fluoride – The Protoplasmic Poison*; I. Makarovsky, T. Dushnitsky and A. Eisenkraft, *IMAJ* **2008**, 10, pp.381–385
- *Vapor generation and mist evaporation during Buffered Chemical Polish (BCP) operations at the Material Development Testing Laboratory (MDTL)*, D. Baird, C. Boffo, C. Cooper, R. Ruthe, Fermilab, January 17, **2007**