

Vapor generation and mist evaporation during Buffered Chemical Polish (BCP) operations at the Material Development Testing Laboratory (MDTL)

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1. Introduction

As part of the refurbishing of the chemistry facility within the TD-MDTL, vapor generation and mist evaporation both during normal BCP operations and in the case of floor spill have been evaluated. In terms of hydrofluoric (HF) concentration, BCP is clearly the most dangerous procedure performed in the lab and the total amount of acid allowed during a single process is 5 liters in order to etch up to a 1-cell 3.9 GHz cavity. In addition the electropolish (EP) process on small samples and 1-cell cavities will be performed as well. For this process the amount of HF acid used is limited to a smaller amount and nitric acid is substituted by sulfuric acid, which is less volatile.

2. Concentration limits

Estimated steady state room concentration levels using evaporation models were compared to the 2005 American Conference of Industrial Hygiene (ACGIH) limits. As part of the newly promulgated Department of Energy (DOE) Worker Safety and Health Standard 10 Code of Federal Regulations (CFR) 851 Fermilab is required to adopt the lower limits imposed by either the ACGIH or the Occupational Safety and Health Administration (OSHA).

2.1. Prolonged exposure

When dealing with prolonged exposure one should consider the OSHA PEL (permissible exposure limits), ACGIH TLV (threshold limit values) and the 1/10 IDLH (immediately dangerous to life and health) limits in terms of ppm (molar) for a time weighted average (TWA) exposure corresponding to the working life time of a person.

Below are listed the limits for the species involved in chemical etching of niobium [1].

CHEMICAL	TLV - TWA	TLV-STEL	TLV-ceiling
HF	0.5 ppm (molar)		2.0 ppm (molar)
HNO ₃	2.0 ppm (molar)	4.0 ppm (molar)	
H ₃ PO ₄	1.0 mg/m ³	3.0 mg/m ³	
H ₂ SO ₄	0.2 mg/m ³		
NO ₂	3.0 ppm (molar)	5.0 ppm (molar)	

Table 1 Concentration limits for chemical species involved in etching of niobium

These values define the tolerated limits of exposure for normal operation that is performed under a hood. The exposure limits in case of short time exposure (STEL) can be higher with respect to TLV-TWA for a maximum of 15 minutes as long as the TLV-TWA for the day is not exceeded. A ceiling limit establish a definitive boundary that exposure concentrations shall not exceed.

2.2 Acute exposure (spill)

In addition to the normal operation hours accepted exposure, one should take into account the possibility of acute exposure in the case of a spill. Depending on the chemical species and duration of exposure the limits are very different and the vapor and gas evolution can be different, for example nitrogen dioxide is heavier than air thus limiting

the possibility of inhalation in case of spill on a used BCP solution on the floor (no nitrogen dioxide will evolve if the solution was not put in contact with niobium).

2.3. Fume Stack emission

During the process, gasses and vapors are collected in the hood and emitted to the atmosphere through a 27' tall 12" diameter chimney. In this case the total amount in grams of pollutant per year shall be estimated to clarify if any special permit should be issued to the lab.

Considering that, under the present safety limitations, the laboratory will be allowed to use up to 10 liters of BCP per month and that the total amount of Nb permitted in solution (for process optimization) is 10 g/liter; 100 g will be the maximum monthly Nb etchable amount corresponding to 1.08 moles. Such processing upper limit will develop a total amount of 5.38 moles per month of **nitric oxide** corresponding to **~3.0 Kg per year**. This number is independent from the total amount of samples etched since is simply based on maximum material removal.

Different is the evaluation of the evaporation rate of HF and HNO₃ which greatly depends of the environmental conditions during operations. In this case the condition of largest open surface shall be adopted as the one producing the largest amount of evaporation for one and half hour per day. Taking into account the results shown in 4.1.4 the total evaporation would be **~ 0.287 Kg per year of HF and ~1.163 Kg of nitric acid per year**

3. Reproducing ANL Calculations

The following calculations have been performed on the basis of previous work completed for the BCP facility at ANL in collaboration with the ANL ESH group [2].

3.1. Assumptions:

1. For NO₂ generation it was assumed that the largest BCP process to be performed at MDTL should be limited to a 1-cell 1.3 GHz cavity. The estimated cavity surface is 0.1m² and the etching rate 1 um/minute at 15 C.
2. For HF and HNO₃ evaporation it was considered the case of an open container 0.25 m in diameter and an air speed of 1 m/s at 20 C.
3. Standard 1:1:2 BCP presents a total concentration in weight of HF equal to 12% and 17% for HNO₃.

3.2. Fume generation

Given the surface and the removal rate, during the process there would be a removal of 51 g/hr of Nb which corresponds to ~0.56 moles. For each mole of Nb etched one generates 5 moles of NO₂. So the rate of generation of NO₂ is ~2.8 mol/hr corresponding to 128 g/hr (2.14 g/min). If the hood is capable of 1600 cfm (45 m³/min) and assuming that the air density is 1.29 kg/m³ one can calculate the NO₂ concentration in the exhaust to be ~37 ppm.

3.3. Mist evaporation

The evaporation rates for Nitric acid (HNO₃) and HF were calculated using standard software named ALOHA provided by NOAA and EPA [3]. Given the maximum surface exposed to the ventilation and the air speed at the given temperature of 20 C, one can obtain the evaporation rate of the two acids:

HF 5.6 mg/min

HNO₃ 9.0 mg/min

The two values correspond to a concentration in the exhaust of :

HF 0.148 ppm (molar)

HNO₃ 0.076 ppm (molar).

4. Additional investigations

Along with the calculations, at ANL a wet scrubber was fabricated and installed in order to drastically decrease the total amount of contaminants introduced in the atmosphere. The ANL facility was designed to handle large cavities and for rather extended use since it was planned to support both the 3.9 GHz cavity program at FNAL and the RIA project at ANL.

Since, given the smaller scale of the MDTL scope, a scrubbing system will not be adopted, it was decided to crosscheck the results obtained with the NOAA software with more “controllable” calculations.

4.1. HF and Nitric acid in BCP evaporation in hood

In order to perform the evaporation calculation, a spill model developed in [4] has been adopted. This model is based on the mass and energy balance of the acid pool where the evaporation is occurring. Several simplifications of the evaporation process had to be adopted in our specific case, in particular due to the fact that we are using a mixture of 3 acids diluted in water. This condition affects the evaporation rate of each single species due to different binding forces with the other components of the mixture. Nevertheless it is known that the presence of other components in solution decreases the evaporation rate putting us on the safe side when neglecting this factor.

4.1.1 Model assumptions

For the case of normal operation in the hood the following considerations apply:

- The acid temperature is constant at 20 C (safe assumption since the acid is kept at 15 C during the process) as opposed to a standard evaporation process where the temperature of the pool decreases due to the latent heat of evaporation.
- The area of the pool is constant since the acid is held in a container.
- The air velocity at the acid surface is decreased due to the fact that the acid is held in a container and the free surface is at least 4 inch within the container. A simplified finite element model of the airflow in the hood is discussed in 4.1.2.
- The total surface of the single acid (both HF and HNO₃) is one quarter of the total surface.
- Fully open sash was considered (maximized flowrate).
- No shortcut of air is considered.
- The input air is free of contaminants.

4.1.2. Air flow in the hood

A simple 2D finite model in Comsol has been developed to simulate the steady state airflow in the hood. This model allowed correlating the velocity of air measured at the sash of the hood with respect to the one at the free surface of the acid stored in a 25 cm diameter container.

For this model a standard air velocity of 0.5 m/s equivalent to ~100 fpm at the hood sash was adopted. Results are shown in figure 1 and 2. The ratio between the velocity of air at the inlet of the hood fully open compared to the one 1 inch above the acid free surface is 50:1.

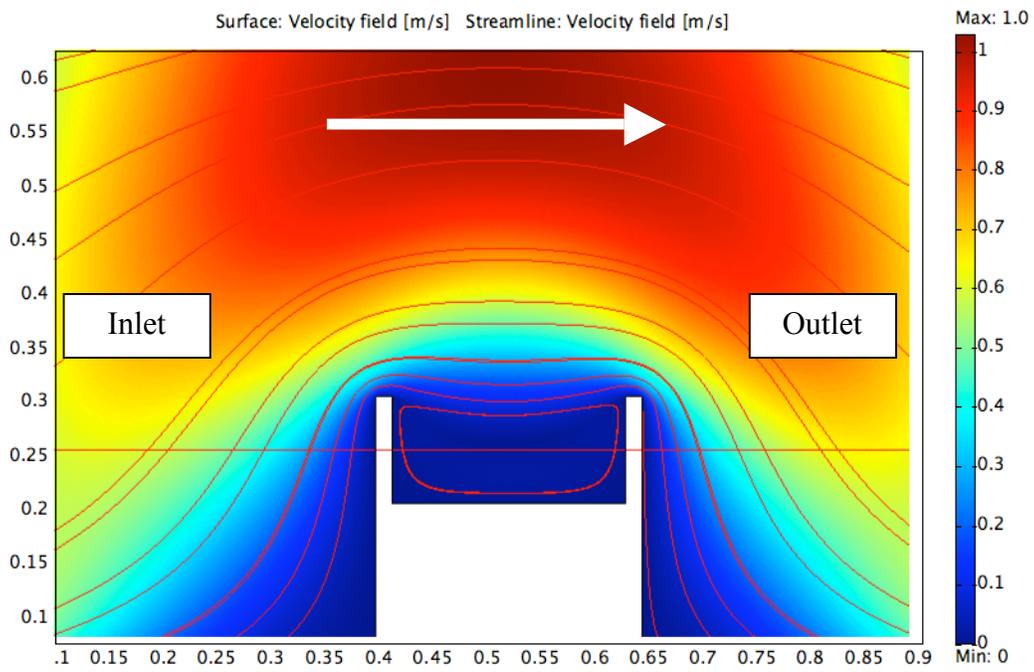


Figure 1 Velocity field on hood cross-section.

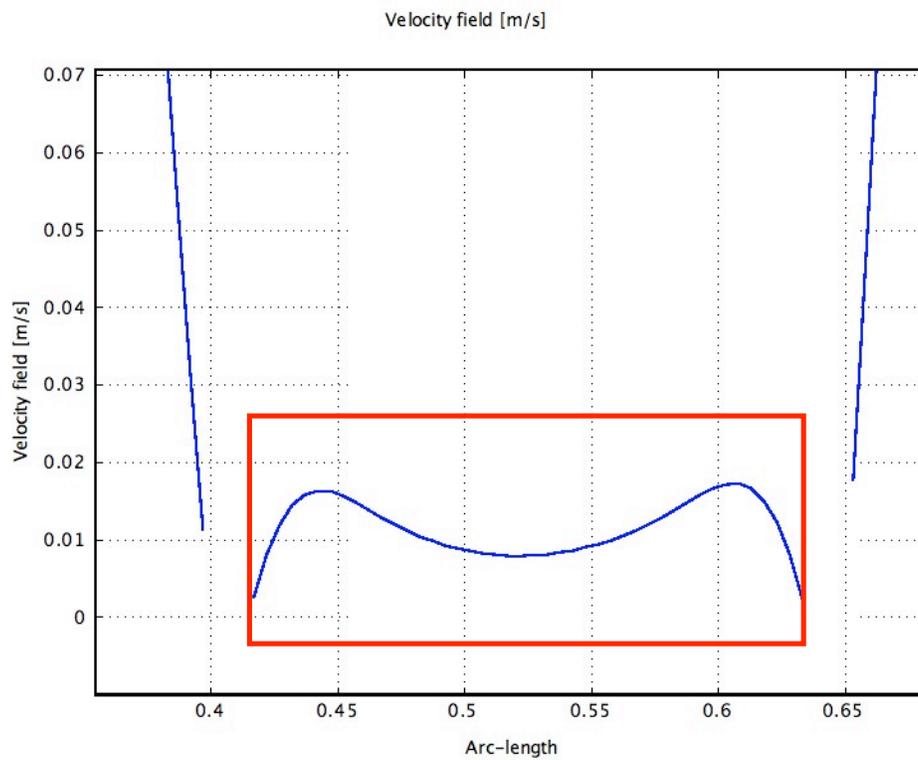


Figure 2 Velocity profile in the acid container.

4.1.3. Input data

The model input data are the following:

air properties

```
rhoa      = 1.22      ; % kg/m3   air density
mua       = 1.83e-5  ; % N s /m2 air viscosity
vpair     = 760      ; % mmHg    air pressure
Tair      = 20       ; % C       air temperature
Q         = 0.757    ; % m3/s   air flow 1600 scfm
S         = 0        ; %         short circuit factor
Vroom     = 2        ; % m3     hood volume
V         = 24.05    ; % m3(K mol)-1 Spec. volume
u         = 0.01     ; % m/s     air speed
```

spill data

```
Ts        = 20       ; % C       spill temperature
MWA       = 20       ; % kg/kmol HF molar mass (63 nitric)
b0        = 0.01     ; % m       pool thickness (irrelevant)
d         = 0.25     ; % m       container diameter
As0       = (3.141/4*d^2)/4; % m2 container area
Vs0       = As0*b0   ; % m3     acid volume
rho1      = 1150     ; % kg/m3 HF density (1400 nitric)
vphf     = 25       ; % mmHg    vapor pressure (48 nitric)
Dair      = 0.2e-4   ; % m2s    diffusivity (0.115e-4 HNO3)[5]
```

4.1.4 Results

The result of the calculation are:

HF 0.338 ppm

HNO₃ 0.456 ppm

4.2. HF evaporation when a bottle is broken on floor

4.2.1. Model assumptions

This case is a little different with respect to the one described above since each single species is considered separately allowing for more accurate evaporation rate calculation at least in terms of partial pressure calculation. Below are listed the main assumptions of this model:

- The area of the spill reduces in time due to evaporation
- The temperature of the acid pool reduces in time due to the evaporation heat
- The presence of safety mats with grid reduce the total surface of acid exposed to air
- Air re-circulation in the building shall be stopped
- The air velocity is measured in the existing MDTL configuration
- The spill area is measured experimentally by dropping a full 1 gallon bottle of water on the floor of the lab
- Short-circuit coefficients are assumed from standard configurations of HVAC systems described in ASHRAE documents

4.2.2. Input data

The model input data are the following:

```
air properties
rhoa      = 1.22      ; % kg/m3 air density
mua       = 1.83e-5   ; % N s /m2 air viscosity
vpair     = 760       ; % mmHg air pressure
Tair      = 293       ; % K air temperature
kair      = 0.0257    ; % W(mK)-1 air thermal conductivity
cpair     = 1005      ; % J(Kg K)-1 air heat capacity
Q         = 0.757     ; % m3/s air flow in the hood 1600 scfm
S         = 0.2       ; % short circuit factor
Vroom     = 220       ; % m3 room volume
V         = 24.05     ; % m3(k mol)-1 Spec. volume
u         = 0.001     ; % m/s air speed

spill data
Ts        = 293       ; % K Spill initial temperature
MWA       = 20        ; % kg/kmol HF molar mass (63 nitric)
b0        = 0.0064    ; % m pool thickness (irrelevant)
d         = 1.00      ; % m container diameter
As0       = (3.141/4*d^2) ; % m2 container area
Vs0       = As0*b0    ; % m3 acid volume
rho1      = 1175      ; % kg/m3 HF density
vphf     =
0.000182*(Tspill1)^3+0.014927*(Tspill1)^2+0.554014*(Tspill1
)+9.141143; % mmHg vapor pressure
Dair      = 0.2e-4    ; % m2s diffusivity (0.115e-4 nitric)[4]
```

$$H_{vapR} = 1000 \cdot (40.193 \cdot (T_{spill1}) + 6839.7); \text{ \% J(kmol)}^{-1} \text{ latent heat of vap.}$$

$$c_p = 27000; \text{ \% J(Kg K)}^{-1} \text{ heat capacity}$$

4.2.3 Results

Preliminary results show that in case of a 5 liters spill the maximum level of HF contamination close to the source is **4.27 ppm** and that it takes 30 minutes to reach this value. In 15 minutes the contaminant level is already above 4 ppm as shown in figure 3.

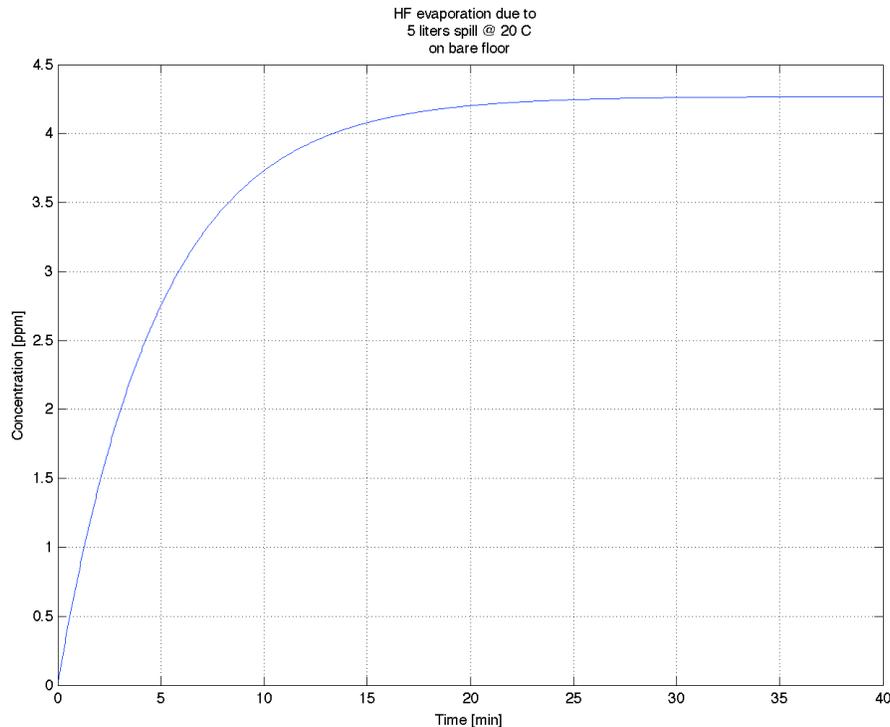


Figure 3 HF spill 5 liters on floor evolution

The same calculations have been performed in the case of a 1.25 liters bottle, which corresponds to the amount of HF present in the maximum allowed volume of BCP (5 liters). If it would be possible to buy such containers the largest spill would be contained in an equivalent 0.5 m in diameter puddle and the maximum release of HF due to evaporation would be **~1.7 ppm** as shown in figure 4. A further step can be accomplished by limiting the bottle dimensions to 0.5 liters, which would additionally decrease the maximum HF release to less than **1 ppm** in case of spill on the floor as shown in figure 5. In the same graph is shown the expected fully mixed concentration of HF assuming a floor mat coverage of the spill of about 50% of its area. In this last case the average evaporation is **~0.5 ppm**. Table 2 summarizes the results described above.

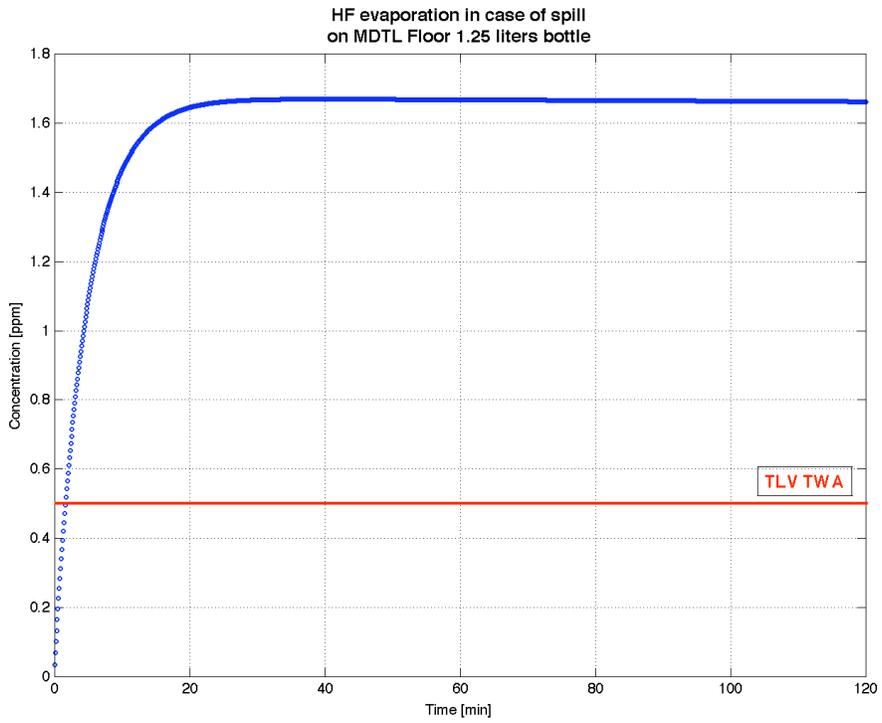


Figure 4 HF spill 1.25 liters on floor evolution

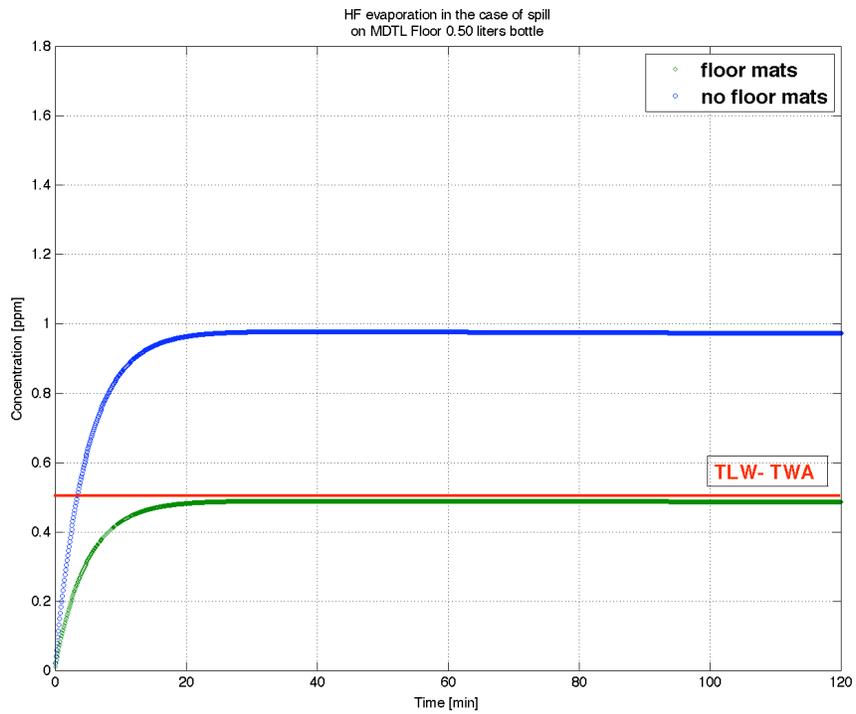


Figure 5 HF spill 0.5 liters on floor evolution

HF Amount	evaporation ppm
5.00 liters	~4.3
1.25 liters	~1.7
0.50 liters	~1.0
0.50 liters + mats	~0.5

Table 2 Calculation summary

4.2.4. Aloha Results

The case of aqueous HF spill, compared to a mixture of several acids, can be simulated with good precision by the NOAA software. For this reason the case of a 5 liters spill on the bare floor of MDTL was considered.

The main assumptions are:

- According to the software a maximum surface of $\sim 1 \text{ m}^2$ would be covered by the acid.
- The minimum air speed at 3 meters high from the spill surface allowed by the software is 0.676 m/s which is higher than expected.
- The ventilation flow rate taken into consideration is the one provided by the hood assuming that this is the only stream pulling air out of the building.
- The total surface covered by the acid is exposed to the air stream (in reality a safety floor mat system will lower this number)

The result is that the full building would be filled by HF vapors with concentration higher than 0.5 ppm. Additional calculations should be performed to have a more realistic number: in particular, several air speed measurements should be performed.

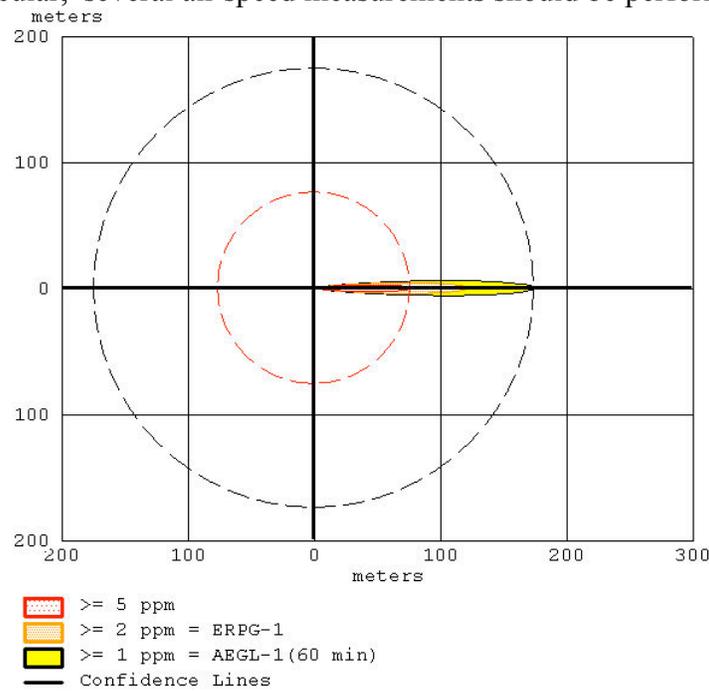


Figure 6 HF dispersion due to evaporation in case of 5 liters spill.

5. Conclusions

During normal operations in the hood the amount of HF and HNO₃ evaporation is below the TLV-TWA limits. On the contrary the evolution of NO₂ (NOX) is above the limits. In case of hood blower failure the sash shall be immediately closed to avoid exposure of the operation and if possible the niobium removed from the acid bath to stop the chemical reaction.

The calculations presented in section 4 show that the evaporation of HF due to a spill on the floor can be limited if smaller bottles are utilized. The numbers stated in section 4 shall be considered a worse case scenario and can be additionally lowered by adopting the following actions:

- Use grid mats which decrease the surface of the spill exposed to the air stream as showed in the last case
- Use acid adsorbent right below the grid mats to decrease the acid evaporation rate
- In case of spill the amount of NO₂ evolution is limited due to the fact that the reaction is stopped.

Any acid spill outside the hood environment larger than a “drip drip” condition shall be treated as a large spill. In the case of large spill on the floor, the suggested actions are:

- Leave the building as soon as possible
- Do not attempt to remove the Nb from the bath if the reaction is still ongoing
- Stop the HVAC recirculation and let the hood be the exhaust of the building
- Use portable devices to monitor the air quality during a spill.

6. Reference

[1] National Institute for Occupational Safety and Health
www.cdc.gov/niosh/idlh/intrid14.html

[2] G. Barrett (ANL), D. Baird, Y. Terechkine (FNAL), *ANL-FNAL SRF cavity treatment facility, air pollution issues*, TD-03-056 June 2003.

[3] Software available at <http://archive.orr.noaa.gov/cameo/> as part of the NOAA chemical spill treatment tools.

[4] P.H. Reinke, L. M. Brosseau, *Development of a model to predict air contaminant concentrations following indoor spills of volatile liquids*, Ann. Occup. Hyg.. Vol. 41 no. 4 pp 415-435 1997

[5] J. P. Monat, *Estimating Gaseous Diffusion Coefficients from passive Dosimeter Sampling Rates, with Application to HF*, Ind. Eng. Chem. Fundam. 1982, 21, 413-416

Appendix A Matlab Code

```

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% evaporation a spill HF on floor case %
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%% INPUT %%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

% air properties
rhoair = 1.22          ; % kg/m3 densita' aria
muair  = 1.83e-5      ; % N s /m2 viscosita aria
vpair  = 760          ; % mmHg
Tair   = 293         ; % C temperatura aria
kair   = 0.0257      ; % W(mK)-1 air thermal conductivity
cpair  = 1005        ; % J(Kg K)-1 air heat capacity
Q      = 0.757       ; % m3/s 1600 scfm
S      = 0.2         ; % short circuit factor
Vroom  = 220         ; % building volume m3
V      = 1/(101300/(8314*Tair)); % m3 (k mol)-1
u      = 0.001       ; % m/s velocita' aria

% spill data
Ts     = 293         ; % C initial temperature
MWA    = 20          ; % kg/kmol molar amss
b0     = 0.0064      ; % m
d      = 1           ; % m
As0    = (3.141/4*d^2); % m2
Vs0    = As0*b0      ; % m3
rho1   = 1175        ; % kg/m3
cp     = 27000       ; % J(Kg K)-1 heat capacity
Tc     = 461         ; % K

%%%%%%%% Initial conditions %%%%%%%%%
As1    = As0
yroom1 = 0
t      = 6
t1     = 0
Tspill1 = Ts

data1  = []          ;
data2  = []          ;
data3  = []          ;

%%%%%%%% Cycle %%%%%%%%%

Re     = d*u*rhoair/muair ; % Reynolds number
Sc     = muair/(rhoair*Dair) ; % Schmidt number
Pr     = cpair*muair/kair ; % Prantl number
Nu     = 0.0366*(Re^0.8)*(Pr^0.33) ; % Nusselt number

if Re > 15000
    kfp = 0.036*(Re^-0.2)*u*(Sc^(-2/3)) ;

```

```

else
    kfp = 0.664*(Re^-0.5)*u*(Sc^(-2/3))          ;
end

for i=1:t:3600*t

    vphf    = 0.000182*(Tspill1-273)^3+0.014927*(Tspill1-
273)^2+0.554014*(Tspill1-273)+9.141143; % mmHg
    Dair    = 0.200e-4          ; % m2 s diffusivity
    Hvap    = 1000*(40.193*(Tspill1-273)+6839.7); % J(kmol)-1 latent
heat of vap

    hair    = Nu*kair/d          ;
    uk      = 5.8                ;
    ya      = vphf/vpair        ;

    Na      = (kfp/V)*log((1-yaroom1)/(1-ya))    ;
    X       = -(Na*MWA*As0)/(Vs0*rhol)          ;
    Y       = (Na*V*As1)/((1-S)*Vroom)         ;
    Z       = Q/Vroom                          ;
    alfa    = (uk+hair)/(cp*b0*rhol)           ;
    beta    = (Na*Hvap)/(cp*b0*rhol)          ;

    yaroom  = (Y/(Z+X))*exp(X*(t-t1))+(yaroom1-(Y/(Z+X)))*exp(Z*(t1-t))
;
    As      = As1*exp(X*(t-t1))                ;
    Tspill  = Tair-(beta/alfa)-(Tair-Tspill1-(beta/alfa))*exp((-alfa*t-
t1));

    data1   = [data1 yaroom*1000000];          ;
    data2   = [data2 As      ]                ;
    data3   = [data3 Tspill]                  ;
    yaroom1 = yaroom                          ;
    As1     = As                              ;
    Tspill1 = Tspill                          ;

end

plot([1:t:3600*t]/60,data1); hold on; grid on;
xlabel('Time [min]')
ylabel('Concentration [ppm]')
title('HF evaporation')

```