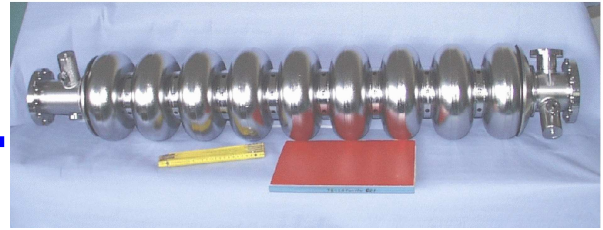SRF

WP 5.1.5.2 : EP Parameters Fixed

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Abstract

In the previous CARE report CARE-Report-06-010-SRF were described preliminary experiments on niobium samples aimed at guiding the program with the single-cell Electro-Polishing (EP) set-up. The influence of fluorine content in the mixture was put forward. Moreover, possible electrochemical mechanisms responsible for EP were investigated.

Complementary studies explained in this final report have shown that the EP of niobium is likely to be limited by fluorine diffusion and have also proved that the HF/H_2O ratio was the relevant parameter to evaluate the aging of the bath and the sulphur generation. Spectrums obtained with impedance spectroscopy confirm that point. Once the EP bench commissioned, we focused on the reproducibility of RF tests after EP when rinsing of cavities with ethanol is used to remove particulate contamination. Repetitive excellent gradient above 40 MV/m with low field emission confirm that this protocol is a good candidate for the large scale cavity production.

Alternative parameters (low voltage, diluted mixture) were also investigated with this set-up.

SYNOPSIS

Introduction

The aim of the Work Package 5.1 is to find a new set of parameters for single-cell niobium cavities electro-polishing (EP). This set of parameters should be tested on 9-cell cavities at DESY before a possible transfer to industry (goal of the Work Package 5.) In a previous CARE-Report-06-010-SRF [1], results were given concerning a preliminary study on samples. Different parameters have been tested (new mixtures' composition, different voltages) and the promising sets of parameters have been chosen to be tested on cavity. At the same time, an electro-polishing set-up for single-cell cavity has been installed in our laboratory at CEA Saclay and we were able to electro-polish cavities on October 2006.
With this new facility on hand, the parameters found on samples can be transferred to cavity preparation and will be crosschecked on their benefit on the surface during RF impact.
Moreover, the modelling of the EP process in 2D with the computer code COMSOL was investigated. In the case of single-cell or multi-cell cavities electro-polishing some imperfections of the systems and optimization of the electrode shape have been pointed out and possible improvements proposed are presented in [2].
A drawback of most of the computer codes in use like COMSOL is that they are not able to simulate easily and precisely the impact of all parameters like rotation speed of the cavity, flow rate, temperature, etc. As a consequence, we decided to focus on the composition of the electrolyte (made of sulphuric and hydrofluoric acids, with a possible addition of water) and on the influence of the voltage. However, some results concerning the effect of cavity rotation speed and of temperature will be given in that report.

Previous experiments on samples will briefly be reminded and completed by last results concerning new mixtures tested, especially "diluted" mixtures. We will then describe the experimental single-cell cavity electro-polishing device, and the results we obtained during one year of continuous operation. Ethanol rinsing has been investigated as a rinsing step prior to final HPR and reproducible results above 40 MV/m were achieved.

PART A. Last results on samples to guide tests on single cell cavities

I Importance of fluorine concentration in the bath

1) Previous experiments and influence of water

Experiments on samples have been made to investigate different sets of parameters. We focused on tests with "new mixtures" composition, prepared with sulphuric acid, hydrofluoric acid, and possibility of addition of water. Percentages related to source acid concentrations are given in weight percentage. For example, most of the acid mixtures are prepared with HF at 40 or 48% (weight percents), H_2SO_4 at 95% and possible additional water. Concentrations are quoted in square brackets.

Notation for mixtures' composition: proportions are given in volume, and H_2SO_4 is marked HS. Example for a mixture prepared with 1 volume of HF (40%) for 9 volumes of H_2SO_4 (95%) and 1 volume of additional water: 1vol $HF_{40\%}$ − 9vol $HS_{95\%}$ − 1vol H_2O.

Previous results in CARE report [1] highlighted the fluorine influence on the electro-polishing process. A higher concentration leads to a longer lifetime of the bath, but also to a loss of the plateau on I(V) curves. The mixture with higher fluorine concentration 3vol $HF_{40\%}$ − 6.72vol $HS_{95\%}$ − 0.28vol H_2O should be considered has a promising electrolyte for single-cell electro-polishing. Moreover, the undesirable effect of water on highly concentrated acid solutions has

also been proved (decreased removal rate, fast deterioration of the surface probably due to the growth of a porous oxide layer).

More precisions concerning aging of the bath will be given in § A-I-2). They have also been presented elsewhere [3].

2) Importance of the [HF]/[H$_2$O] ratio

Thus, the ratio [HF]/[H$_2$O] could be a relevant item to be characteristic of the efficiency of the mixture. To confirm this assumption, EP experiments were carried out with "1-9" mixtures prepared with two different concentrations for the HF source solution (40% and 48%). We have the following ratios:
For a 1vol HF$_{48\%}$ − 9 vol HS$_{95\%}$:
[HF]/[H$_2$O] ~ 0.35
For a 1vol HF$_{40\%}$ − 9 vol HS$_{95\%}$:
[HF]/[H$_2$O] ~ 0.27
In both cases, [H$_2$SO$_4$] is the same: ~ 16 mol/L

Furthermore, EP was carried out at 3 different voltages displayed in Figure 1 as dark/light blue line for 8 volts, orange-red line for 14 volts and green line for 17 volts applied. We use circle/triangle dots to respectively represent results for mixtures prepared with 48%/ 40% hydrofluoric acid. A good surface is attributed to its high brightness. Gloss is then measured as a function of time for successive EP sequences.
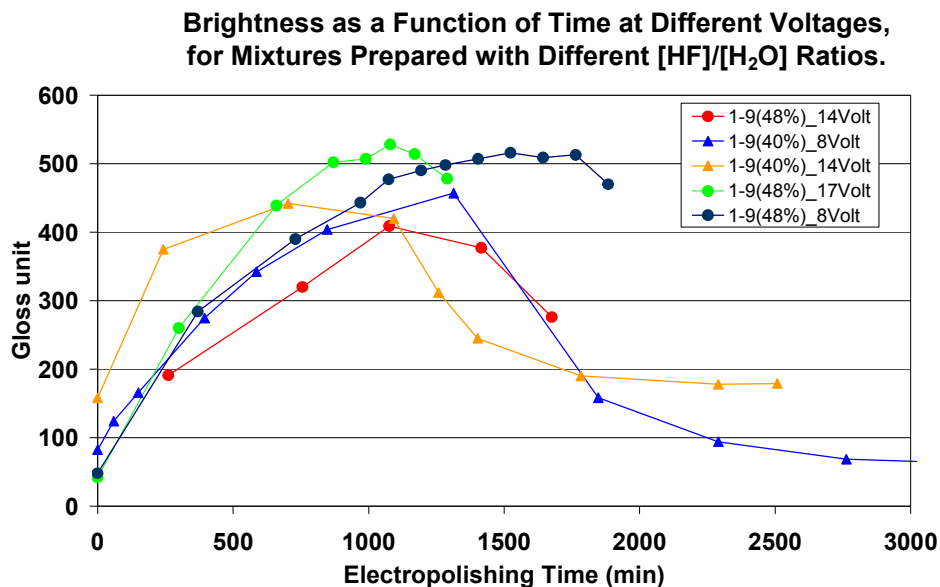

Figure 1: Evolution of gloss during EP at different voltages for 'standard' 1-9 mixtures prepared with different HF concentrations. The lifetime of the mixture is longer for higher [HF]/[H$_2$O] ratios and lower voltages.

It is found that for EP at 8 volts, brightness decreases after longer EP time (and larger amount of dissolved niobium) for the curve lined out with circle-dots. That is to say, the lifetime is longer for the bath with the higher [HF]/[H$_2$O] ratio. This point is confirmed by sequences at 14 volts. Moreover, experiments give some hints concerning influence of the potential. If one considers a mixture with a 48 % content of HF, it can be stated that the higher the voltage, the lower the lifetime of the bath will be. This statement is confirmed by experiments with mixtures prepared with HF at 40% content. The shorter lifetime of the mixture at high

potential could be correlated to a higher continuous local vaporization of the hydrofluoric acid in the mixture (high niobium sample temperatures are measured during experiments).

3) [HF]/[H$_2$O] ratio more relevant than niobium dissolved in solution to explain aging?

We explained in the previous paragraph that a water concentration increase provoked a premature deterioration of the samples' surface. However, amount of dissolved niobium is the retained parameter for the renewal of the acid. For niobium concentrations of up to 9g/L no performance loss is found so far [4]. In this part, we will strive to distinguish influence of one parameter from the other to explain aging of the bath. We will compare 3 experiments with niobium samples electro-polished for long periods in 3 different mixtures.

A   900 mL of a fresh 1vol HF$_{40\%}$ - 9vol HS$_{95\%}$ mixture
B   11.59 g of Nb$_2$O$_5$ dissolved in 900 mL of a fresh 1vol HF$_{40\%}$ − 9vol HS$_{95\%}$ mixture
C   11.59 g of Nb$_2$O$_5$ dissolved in 900 mL of a fresh 1vol HF$_{48\%}$ − 9vol HS$_{95\%}$ mixture

Characteristic concentrations of the 3 mixtures are summed up in the following Table 1.

Mixture	A	B	C
[HF] mol/L	2.26	2.16	2.69
[H$_2$O] mol/L	8.34	8.58	8.17
[HF]/[H$_2$O]	0.27	0.25	0.33
Dissolved Nb g/L	0	9	9

Table 1: Initial amount of dissolved niobium and fluorine content in A, B and C mixtures.

Gloss evolution of a niobium sample during EP in the different mixtures at 8 volts is given in Figure 2. With the 'standard' mixture A, brightness increases up to 1300 minutes and then deteriorates. B and C mixtures include similar amounts of dissolved niobium. Mixture B has the lowest [HF]/[H$_2$O] ratio and does not provide smoothening conditions as in C (with the highest ratio) where the sample is electro-polished during a long period, which is superior or equal to the one obtained for the mixture A.

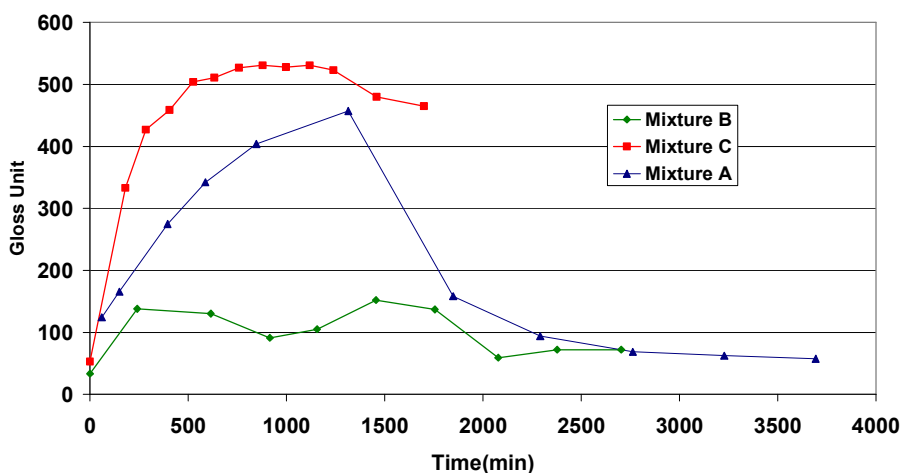**Brightness As a Function of Time. A, B and C Mixtures. 30°C, 8V**

Figure 2: Gloss evolution during EP at 8 volts for A, B and C mixtures. A low [HF]/[H$_2$O] ratio is believed to be the main cause of the deterioration of the surface.

Regarding these observations, we might foresee that water content is more relevant in the causes of the deterioration of the surface during EP. Furthermore, experiments carried out with A, B and C mixtures might provide some understanding concerning EP mechanisms: In the niobium case, it should be considered between the acceptor mechanism where the limiting step is the diffusion of reactive species from solution to surface (F^- or FSO_3^- in our case) and a Metallic Ion Diffusion limiting step (in our case, diffusion of Nb^{5+} ions from anode surface to bulk phase would be the slowest mechanism) [5]. Let us consider I(V) curves plotted (between anode and cathode) in Figure 3 for A and C mixtures. The plateau is found at similar current densities although the niobium contents, and consequently Nb^{5+} concentration gradients in the mixtures are substantially different. On the contrary, an increase in HF concentration leads to increased current densities [1]. An F^- diffusion limited mechanism should be then considered as the most probable possibility.
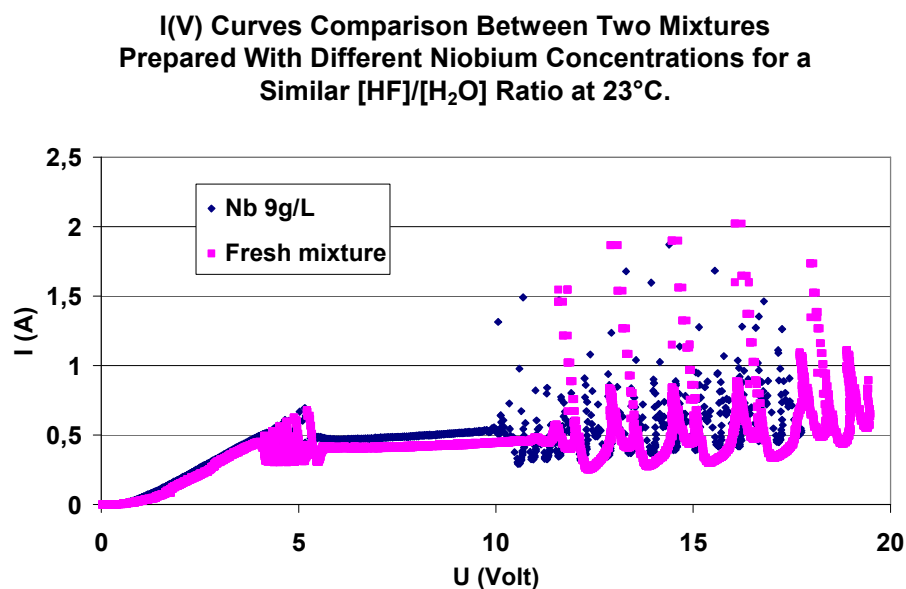
I(V) Curves Comparison Between Two Mixtures Prepared With Different Niobium Concentrations for a Similar [HF]/[H$_2$O] Ratio at 23°C.

Figure 3: Similar I(V) curves at 23°C for mixtures having a similar [HF]/[H$_2$O] ratio, but different niobium concentrations. Niobium concentration has no influence on current density. Electro-polishing mechanisms should not be governed by niobium ions diffusion.

II Use of Electrochemical Impedance Spectroscopy

We discussed in the previous paragraph of the importance of [HF]/[H$_2$O] ratio on aging. If a F^- diffusion must be kept in mind, we shall not forget that a too high fluorine concentration is an origin of the destruction of the viscous layer at the niobium's surface and a too high water concentration provokes a deterioration of the surface, even if the I(V) curve shows a plateau [1].

We will investigate in this paragraph if Electrochemical Impedance Spectroscopy (EIS) is a method that we might apply to niobium EP, and if the [HF]/[H$_2$O] ratios mentioned above would influence the response. In EIS, the impedance Z of the electrochemical system [6] is studied as a function of the frequency: A potential $E_0+\delta E*\sin(\omega t)$ is applied to the working electrode at a stationary state. The response $Z=U/I$ might be considered in Nyquist Diagrams. We worked with an Ag/AgCl reference electrode and niobium samples were mechanically polished under the same protocol, prior to EIS. Potentials were chosen on the "plateau" of the I(V) curve previously plotted with the reference electrode.

Five mixtures have been tested (see Figure 4):

- 1vol $HF_{48\%}$ − 9 vol $HS_{95\%}$ [HF]/[H_2O] ~ 0.35
- 1vol $HF_{40\%}$ − 9 vol $HS_{95\%}$: [HF]/[H_2O] ~ 0.27
- 1vol $HF_{48\%}$ − 9 vol $HS_{95\%}$ with 9g/L of dissolved niobium [HF]/[H_2O] ~ 0.33
- 1vol $HF_{40\%}$ − 9 vol $HS_{95\%}$ − 2 vol H_2O [HF]/[H_2O] ~ 0.13
- 1vol $HF_{48\%}$ − 9 vol $HS_{95\%}$ mixture used during ~ 1300 min of EP at 17 volts. Niobium content > 10 g/L. [HF]/[H_2O] unknown, but very low because of the huge loss of HF by vaporization during the experiment.

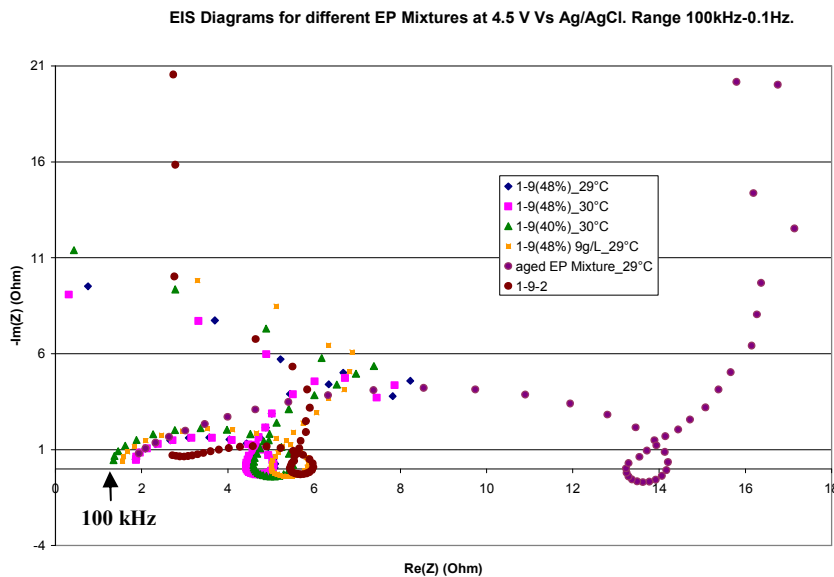EIS Diagrams for different EP Mixtures at 4.5 V Vs Ag/AgCl. Range 100kHz-0.1Hz.

Figure 4: EIS diagrams for potentials on the plateau obtained for mixtures with different water concentrations. Features of the diagrams depend on the mixture's composition.

We notice that the diagram from the aged mixture differs significantly from the others prepared with fresh acid. However, the diagrams exhibit the same shape for all mixtures: a semi-circle starting at the right of the origin. The diameter makes it possible to exhibit 3 characteristics of the system [7]:
- R_0: the limit of the circle at high frequencies (Ω)
- R_1: the diameter of the circle (polarisation resistance in Ω)
- C_1: effective capacity (double layer capacitance in F) calculated from the angular frequency ω at the top of the semi circle: ω =1/(R_1C_1)

R_0 is the signature of the resistance of the electrolyte with a possible contribution of a porous film whose thickness is depending on the applied potential.

We plotted in Figure 5 R_0 as a function of the potential for the different mixtures. Some studies rule out the presence of a porous film at the surface with the standard mixture because of R_0 found as independent of the potential [8]. Our measurements with the mixture 1vol $HF_{48\%}$ − 9 vol $HS_{95\%}$ (pink curve in Figure 5) confirm that point.

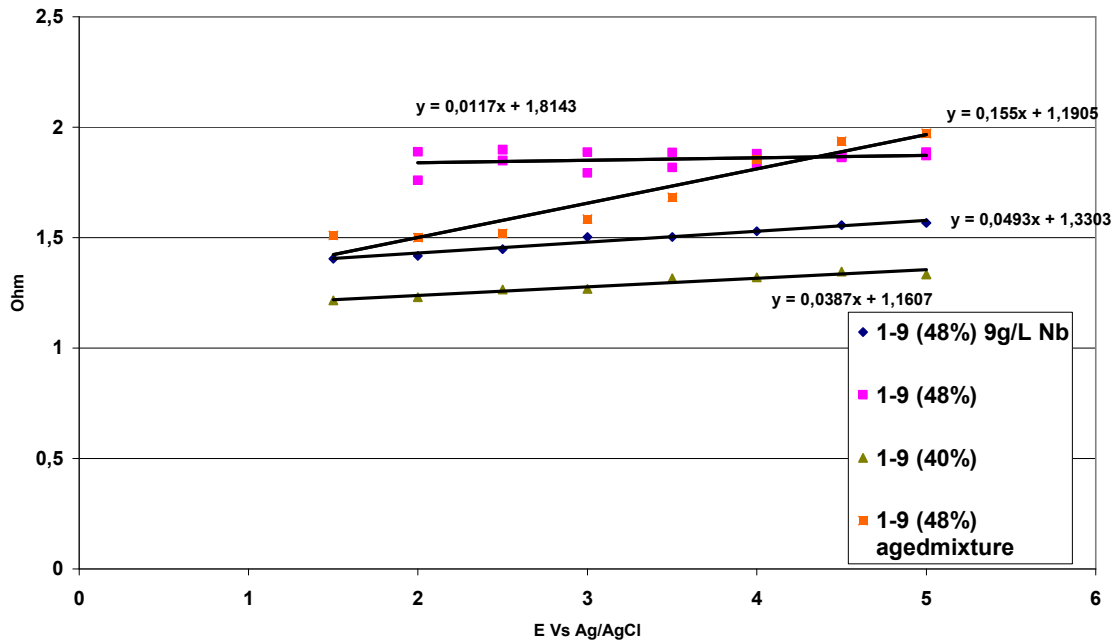**R₀ Resistance as a Function of the Potential for Different Mixtures.**

Figure 5: R_0 resistance as a function of the potential for different mixtures. The slope of the $R_0=f(V)$ extrapolated straight line increases with a decreasing $[HF]/[H_2O]$ ratio.

Nevertheless, we notice that with a decreasing $[HF]/[H_2O]$ ratio, the $R_0=f(V)$ plot exhibits an increasing slope, probably due to the presence of a porous oxide on the surface of the niobium, whose thickness increases with the potential.

These measurements confirm the statements presented in [1]. Degradation of the niobium surface in aged mixture is probably due to the presence of a porous oxide layer at the niobium surface. The forming of this layer is attributed to a decreasing $[HF]/[H_2O]$ ratio.
In that way, EIS could be used at a method to check fluorine content in the EP mixtures.

III Electro-polishing with diluted mixtures

In § A-I-3) it is explained, that high water concentrations would lead to premature aging of the bath. However, contradictory results (increased removal rate) have been noticed during EP on samples with diluted mixtures at Saclay [9]. It is worth clearing up that point, because EP in diluted mixtures could then be of great interest. In fact, some advantages are foreseen:
- higher removal rate
- "safer" mixture (HF concentration is decreased)
- possible decreased sulphur generation
- cheaper process
- less Joule effect during the process
- possible higher lifetime of the bath

In that way we investigated electro-polishing on samples with $1 vol\ HF_{48\%} - 2 vol\ HS_{95\%} - 7 vol$ H_2O mixture. I(V) curve for the mixture is plotted in Figure 6. Results presented in [9] are confirmed. High water content leads to high current density. This characteristic should be attributed to a better acid dissociation in "diluted" mixtures. Electrolyte conductivity happens

8

to be increased. We then had long time EP sequences on sample with this mixture. We used during this experiment a copper cathode because aluminium is corroded in diluted acid mixtures. An 8 volt potential was chosen. It corresponds to the middle of the plateau in Figure 6. Evolution of the brightness as a function of time is shown in Figure 7 (brightness is measured after each sequence of EP). After 2155 min of EP, we had to change the sample because the first one was almost completely dissolved in the mixture.
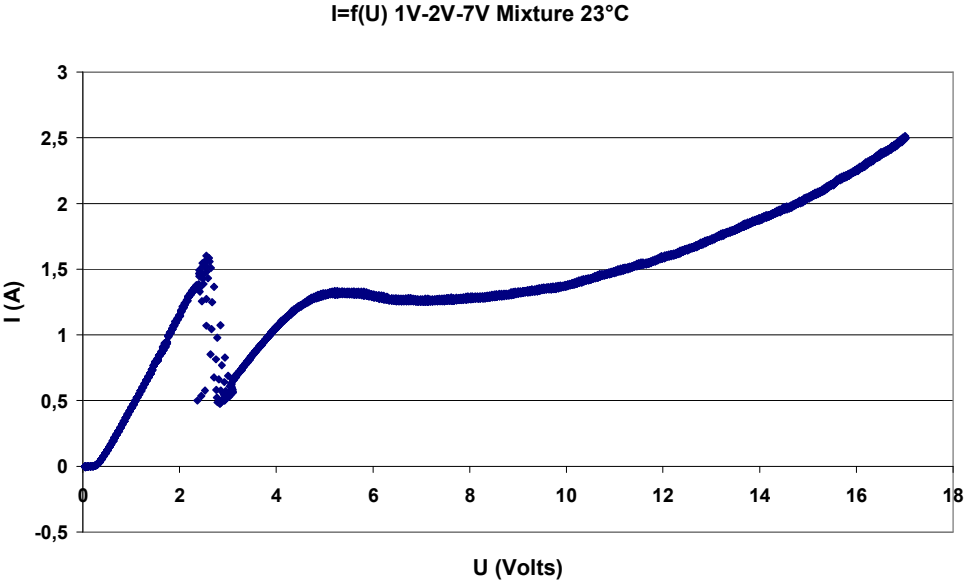
I=f(U) 1V-2V-7V Mixture 23°C

Figure 6: I(V) curve on a niobium sample, for a mixture prepared with $HF_{48\%}$, $HS_{95\%}$ and H_2O in proportions (volumes) 1-2-7.
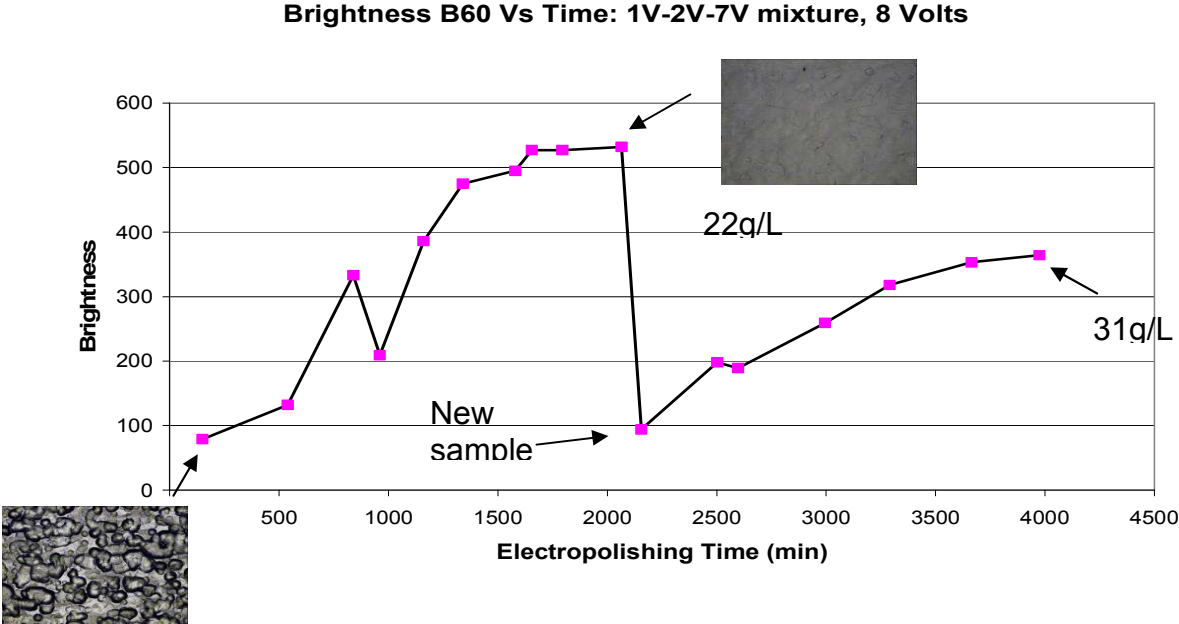
Brightness B60 Vs Time: 1V-2V-7V mixture, 8 Volts

Figure 7: Brightness as a function of time, for a sample electro-polished at 8 volts with a mixture prepared with $HF_{48\%}$, $HS_{95\%}$ and H_2O in proportions (volumes) 1-2-7. Surface becomes smooth after 1500 min electro-polishing. The life time of the bath is long.

9

PART B. Technical description of the set-up

In order to electro-polish single-cell cavities, a bench was installed at CEA Saclay (see Figures 8a and 8b). Technical choices for this set-up are described in this part.

I Set-up presentation

Cavities are polished in horizontal position, half filled (more precisely, at 60%) in a set-up similar to the one used at DESY or KEK. In the present study, a steady voltage is applied between the cathode (tube made of aluminium inside the cavity) and the anode (the cavity). Electrolyte circulates in a close circuit from the tank containing the acid to the cavity. Two pumps are used. The first one drives the acid in the cavity and a second one forces the acid to return to the tank. The layout is described in Figure 9. Acid goes through filters (10 µm mesh) used to prevent particulate contamination. The set-up is under a ventilated cabinet and the upper part of the tank of the cavity is swept by a nitrogen flow during the process.

Figure 8a : The EP facility bench with set-up with remote control for pneumatic valves.

Figure 8b : Saclay EP set-up during a cavity treatment.

Nota: We encountered repetitive failures with the cooling device due to the jamming of its pump. This specific failure is attributed to an inhomogeneous pressure distribution in the cooling pipes. A by-pass to control pressure will be installed in order to improve reliability.

Fluid circulation is controlled by both manual and pneumatic valves. Pneumatic valves are safely operated through a remote control (see Fig 8a.). The cavity is continuously rotated thanks to a motor whose speed is controlled outside the cabinet.
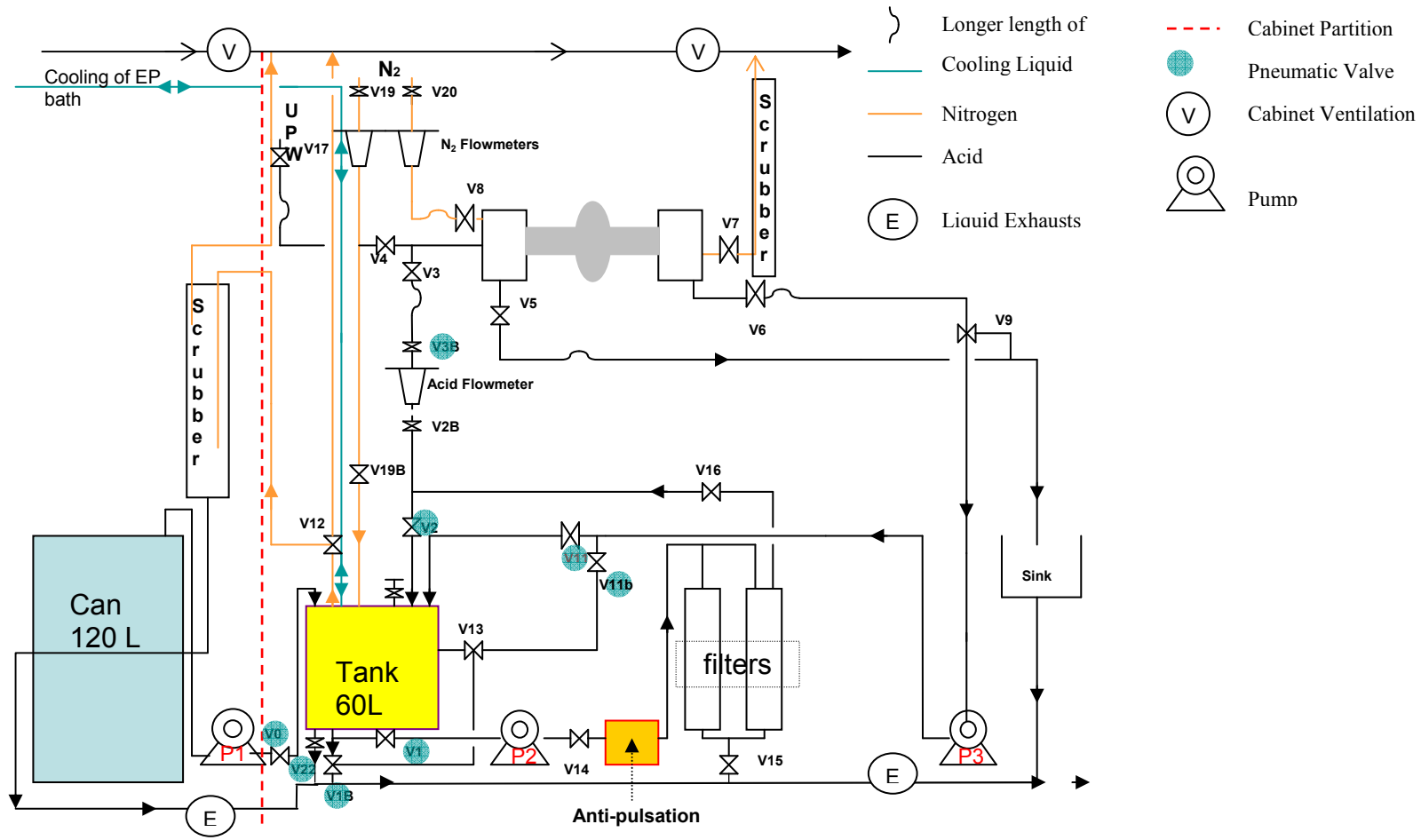
Figure 9: Layout of the electro-polishing set-up.

II Materials in use

The tank is built in PVCC. A coil made from PVDF is connected to a cooling system and fits into the tank (see Figure 10).

**Figure 10: The tank is in PVCC (grey) and coil in PVDF.**

Some parts of the system have been taken from a device that was used at CERN:
- end-blocks in PVDF with flanges to fix the cavity and the cathode
- electric contacts for the anodic part with copper rollers and springs

The piping is made in PFA from Saint-Gobain ASTI.

III Environment concern

The nitrogen flow through the tank is contaminated with acid vapours (HF is a volatile compound). It is necessary to neutralize the resulting acidic vapours. Gaseous exhausts from the process undergo two treatment stages: A scrubber (Figures 11a and 11b) in the cabinet is filled with a known amount of sodium hydroxide NaOH and some drops of Bromo-Thymol Blue (BTB). OH⁻ ions neutralize the acid:

$$NaOH + HF = H_2O + NaF \ (1)$$
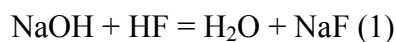
And BTB turns yellow when the solution in the scrubber becomes acidic. The change in colour is a way to estimate amounts of HF that have been vaporised.

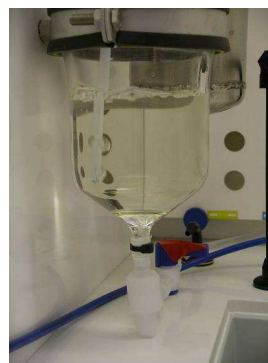**Figure 11a : Scrubber filled with BTB.**

Figure 11b : When the solution becomes acidic, it turns yellow. It must then be changed.

We notice with this scrubber that the amount of degassed acid is higher when the mixture is fresh. During the continuous treatment of single cell cavities (see § C-III), 40 g of NaOH were consumed during 3 h of EP with fresh acid. Additional 20 g of NaOH were put in the scrubber and consumed within the next 7 h of treatment. It confirms results obtained with ionic chromatography analysis during experiments on samples [1].

A complementary gas scrubber outside the laboratory (Figure 12) neutralizes exhausts from the different cabinets of the laboratory.

Figure 12: Gas scrubber outside the laboratory.

IV Data monitoring and control of the process

A program has been developed with Labview to control the process and monitor data. The synoptic diagram of the command is given in Figure 13. The hardware involves: a PC, digital-analogical and analogical-digital converters, a rack (Figure 14a) with electronics to switch measurements between cavity and sample and to control the alarm. The parameter that drives the process is voltage provided by a power supply.

Parameters that are recorded are (see Figure 14b):
- current intensity
- voltage between anode and cathode
- temperature in the acid tank
- temperature in the cavity

Two modes are programmed (Figures 15a and 15b):
- Mod1 to plot polarization curves where intensity I is monitored as a function of voltage V between anode and cathode. For this mode, it is possible to choose the scan rate in voltage, the acquisition frequency, both lower and upper boundaries for voltage, and if the polarization curve should be plotted for decreasing potentials.
- Mod2 to control an electro-polishing sequence. The operator has to choose the potential, the frequency of monitoring, and the value in the temperature activating the alarm.

V Safety aspects

The EP process is dangerous because of different aspects (aggressive chemicals, hydrogen production, warming of the acid etc.). The EP system must integrate technical aspects for a safe use by the operator:

❖ The voltage is shut off (with in addition a sound alarm) if an insufficient nitrogen flow is detected. Furthermore, a warning is displayed on the screen if temperature in the tank or in the cavity exceeds a value chosen by the operator.
❖ In case of a sudden rise in temperature, a pneumatic valve has been installed in the tank to drain it quickly. Liquid exhausts are collected in three containers in the lower ground floor outside the laboratory.
❖ A study has shown that risks of explosion were not consistent since the amount of hydrogen produced is low compared to the dilution with nitrogen and with the ventilation of the cabinet. As a consequence, we decided to not use equipment with ATEX (ATmosphere EXplosive) specifications.
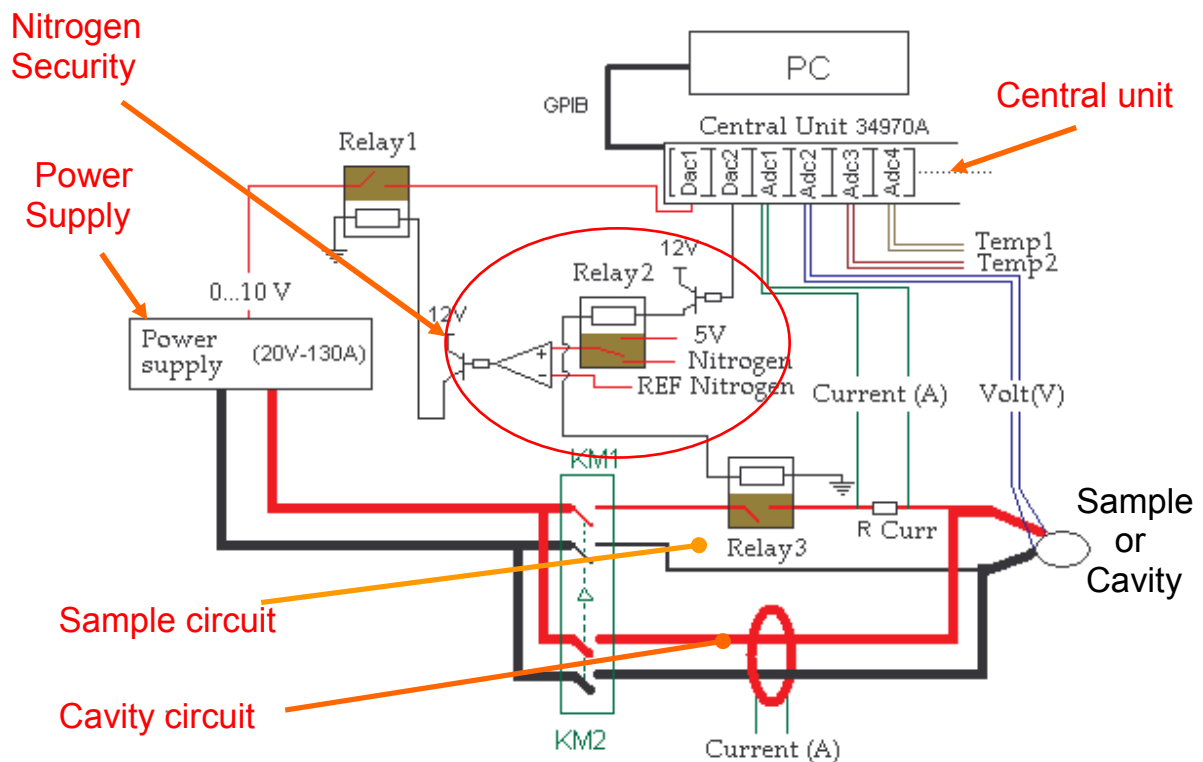

Figure 13: synoptic diagram of the command of the set-up.

Figure 14a : Central unit located on top , rack with electronics located in the middle and power supply located on bottom of the setup view.
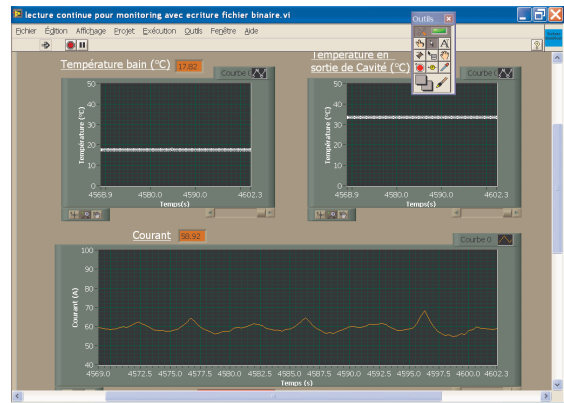

Figure 14b : Temperatures and intensity monitoring during a cavity electro-polishing sequence.

Figure 15a : Parameters chosen for I(V) curves plotting: voltage boundaries, frequency, scan rate, possible reverse scan.
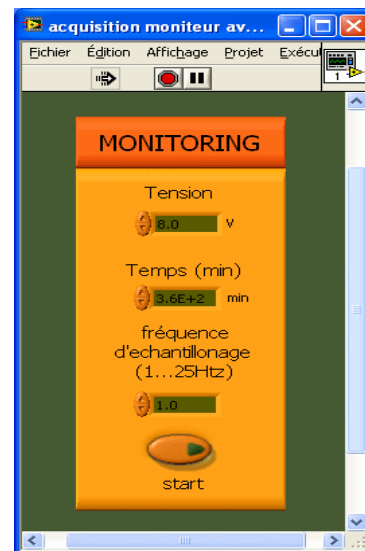

Figure 15b : Parameters chosen for monitoring: voltage, frequency, duration. It is also possible to drive the voltage manually.

PART C. Results achieved on single-cell electro-polishing

I Continuous operation of the set-up

The goal of the Work Package 5.1 is to evaluate impact on the process of change in parameters. In that way, it is crucial to have a reliable process to achieve continuous operation (Task 5.1.4). Electro-polishing on cavity started on October 2006 after successful tests with water and final agreement of the safety comity. Since that time, 8 different cavities have been electro-polished during 23 sequences, and no crippling failure has been encountered.

Drawbacks experienced with the experimental set up:
We might quote some malfunctions of the set-up during early sequences:
  - deterioration of a part of the scrubber made of glass
  - acid condensation in pipes disturbing nitrogen flow
  - momentary loss of electrical contact

The more prejudicial encountered problem was the failure of the cooling system due to the jamming of its internal pump. It delayed some experiments but we were able to process cavities at low voltage (see § C-V)

II Validation of the set-up: standard mixture

Electro-polishing of single cell niobium cavities is a well known process. Many results have been-published at DESY and KEK. For example: [10,11]. With standard mixtures (hydrofluoric and sulphuric acid), achieved gradients between 37 MV/m and 44 MV/m are satisfactory for Tesla shape cavities. Reminder: for ILC specification, gradients above 31.5 MV/m are required for 9-cell cavities.

To qualify the Saclay EP set-up, a single cell cavity from DESY was in use. The cavity 1DE1 has undergone several electro-polishing sequences at Henkel before. For analysis of data, the RF results of vertical tests can be compared with the data published in the DESY cavity database [12]. Before the electro-polishing at Saclay, the gradient of the cavity was 36 MV/m and the best achieved 36.8 MV/m. 1DE1 was electro polished at 17 volts with fresh EP mixture. More details concerning the sequence:
  - 42 μm were removed.
  - A strong sulphur odour was smelt after the EP sequence.
  - The surface was shinier after this treatment compared to the Henkel one.

It is necessary to have more quantitative data to investigate correlations between EP parameters, surface consideration, and RF performance. Some investigations have been carried out [13] suggesting that sharp local surface might provoke a thermal quench. Some printings of the surface have been made on 1DE1 and other ones: 1DE3 (see § C-III) and 1C11 cavity (see § C-IV and § C-V) before and after EP. We do not have results of roughness measurements at the present time. Intensity and temperature evolution during the EP are shown in Figure 16, and $Q = f(E_{acc})$ curve before and after baking are shown in Figure 17.

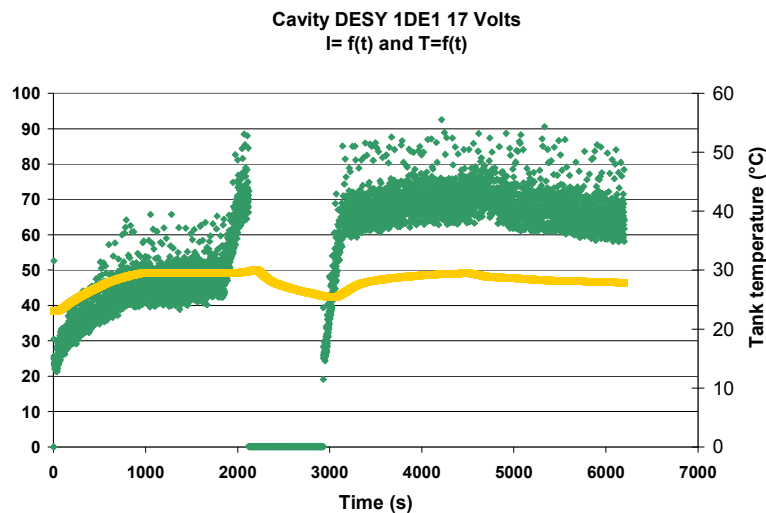**Cavity DESY 1DE1 17 Volts**
I= f(t) and T=f(t)

Figure 16: Evolution of intensity and temperature during electro-polishing of 1DE1 cavity at Saclay. Intensity oscillates. A loss of an electric contact occurred between 2000 and 3000s.
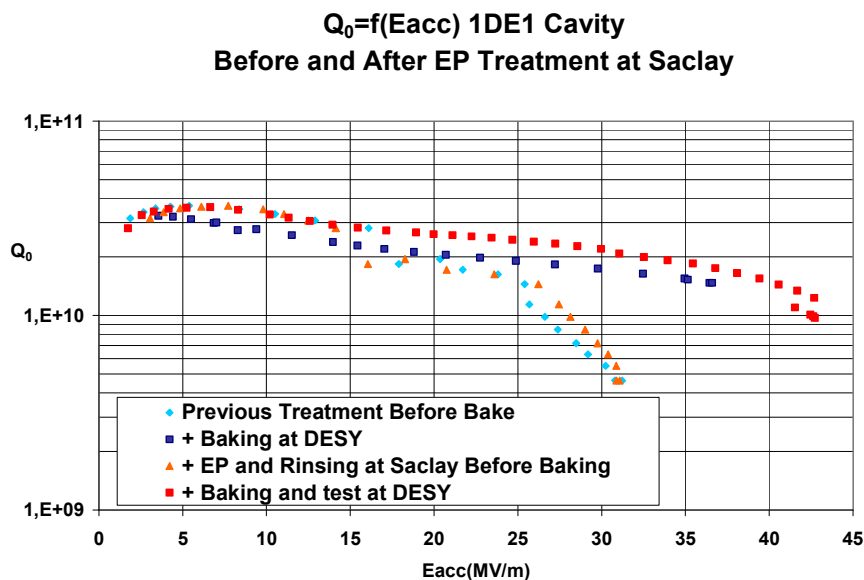
Q_0=f(Eacc) 1DE1 Cavity
Before and After EP Treatment at Saclay

- Previous Treatment Before Bake
- + Baking at DESY
- + EP and Rinsing at Saclay Before Baking
- + Baking and test at DESY

Figure 17: Q=f(Eacc) curves for 1DE1 cavity before and after electro-polishing at Saclay. It reached 31MV/m (orange) before and 42.5 MV/m red) after ultra high vacuum baking

The high gradient above 42 MV/m achieved is very satisfactory. The set-up is qualified and the next results achieved will then be reliable. The strong sulphur odour which was noticed during process reminds us that sulphur compounds are formed during the EP process [14]. This point is well understood and this pollution of the mixture could be a cause of the discrepancy in gradients noticed for 9-cell cavities [15]. R&D efforts have to be made in order to reach high and reproducible gradients. Different repetitive sequences are tested in different laboratories: 3 µm EP with fresh acid (KEK), rinsing of cavities with soap (Jefferson Lab). Ethanol rinsing is also used with large benefits at DESY for 9-cell cavities production. This excellent gradient achieved at Saclay tends to confirm that ethanol rinsing is a promising method. Additional results are presented below.

III Re-evaluation of goals of WP 5.1: evaluation of ethanol rinsing

During the annual JRA meeting at Warsaw in September 2007, achievement of reproducible gradients and focus on rinsing procedures was suggested as a high priority by the advisory committee [16]. In that way, we went on electro-polishing cavities with regards to DESY EP process and including an ethanol rinsing step prior to HPR in clean room. DESY lent us a second cavity, 1DE3 in order to achieve additional results. Treatments were repeated and different RF tests took place at DESY (D) and Saclay (S). Results are presented in Figures 18 and 19.
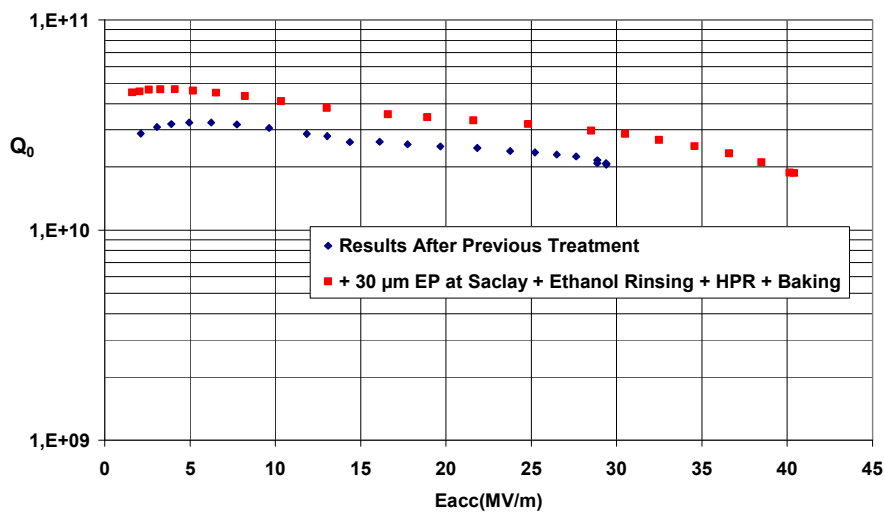
Q_0=f(Eacc) After Baking. 1DE3 Cavity

Figure 18: Q=f(Eacc) curves for 1DE3 cavity before and after electro-polishing at Saclay.

Best Results for Q_0 = f(Eacc) Curves Obtained for S0 program.
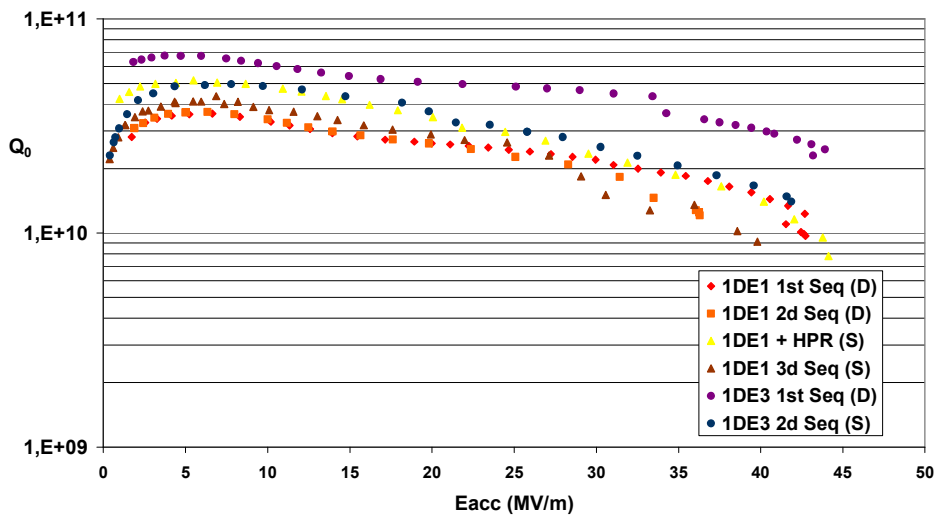**Recipe: EP 30 µm + 30' Ethanol Rinsing. 1DE1 and 1DE3 Cavities.**

Figure 19: Q=f(Eacc) curves for 1DE1 and 1DE3 cavities after treatment at Saclay. Recipe: 30 µm EP + Ethanol Rinsing + HPR.

These results permit us to make statistics for the ILC GDE S0 program on single cell cavities. Within the framework of this program, six tests are made with the same rinsing recipe. We also decided to treat 1C03, a cavity which showed good performance (40MV/m) before EP at Saclay. It was treated under the same preparation sequence (30 μm EP + 30' Ethanol rinsing + HPR). Unfortunately, strong Field Emission at low onset (<15 MV/m) deteriorated the cavity performance (See Figure 20).
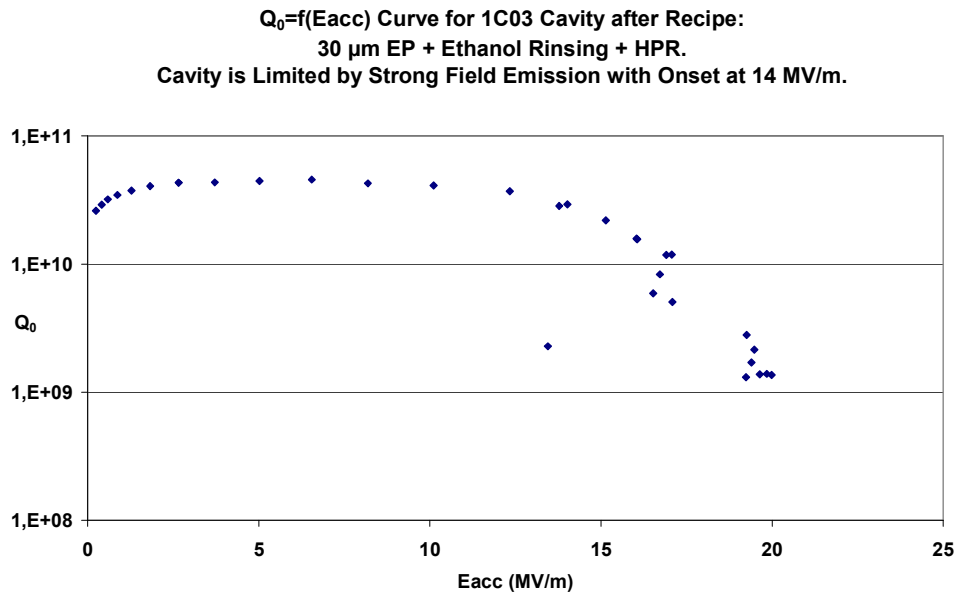
Q_0=f(Eacc) Curve for 1C03 Cavity after Recipe:
30 μm EP + Ethanol Rinsing + HPR.
Cavity is Limited by Strong Field Emission with Onset at 14 MV/m.

Figure 20: Q=f(Eacc) curves for 1C03 cavity after recipe: 30 μm EP + Ethanol Rinsing + HPR. E_{acc} is limited by strong field emission.

After excellent results with 1DE1 and 1DE3 cavities, this poor performance with 1C03 cavity should not be attributed to the rinsing recipe with ethanol. A problem during assembly in Clean Room was firstly suspected. However, a strong oil odour was smelt during disassembling of the cavity. It suggests that a problem has probably occurred during the pumping of the cavity. It also confirms the complexity of the technical steps involved in the cavity treatment/assembling. Different mistakes might jeopardize the cavity performance, even if the chemical treatment is successful.

Different tests took place after each treatment and the gradient distribution of all the tests is described in Figure 21. We also calculated the average gradient after each chemical treatment and obtained the gradient distribution presented in Figure 22. Results are summed up in Table 2. As the performance for 1C03 does not match specifications, it is not taken into account for statistics. An additional sequence will be added on 1DE1 or 1DE3 to complete 6 tests.

**Global Gradient Distribution for the Tests on 1DE1, 1DE3 and 1C03 Cavities
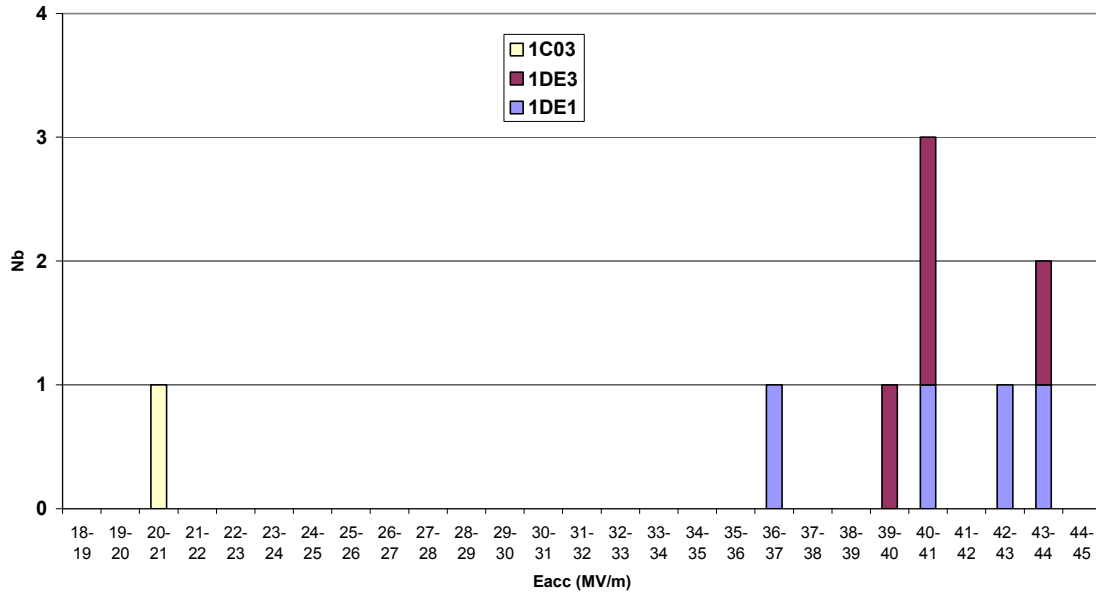after Treatment "30 μm EP + Ethanol Rinsing"**

**Figure 21: Gradient distribution of all tests for 1DE1, 1DE3 and 1C03 cavities after treatment at Saclay:
Recipe: 30 μm EP + Ethanol Rinsing + HPR.**

**Average Gradient Distribution on 1DE1, 1DE3 and 1C03
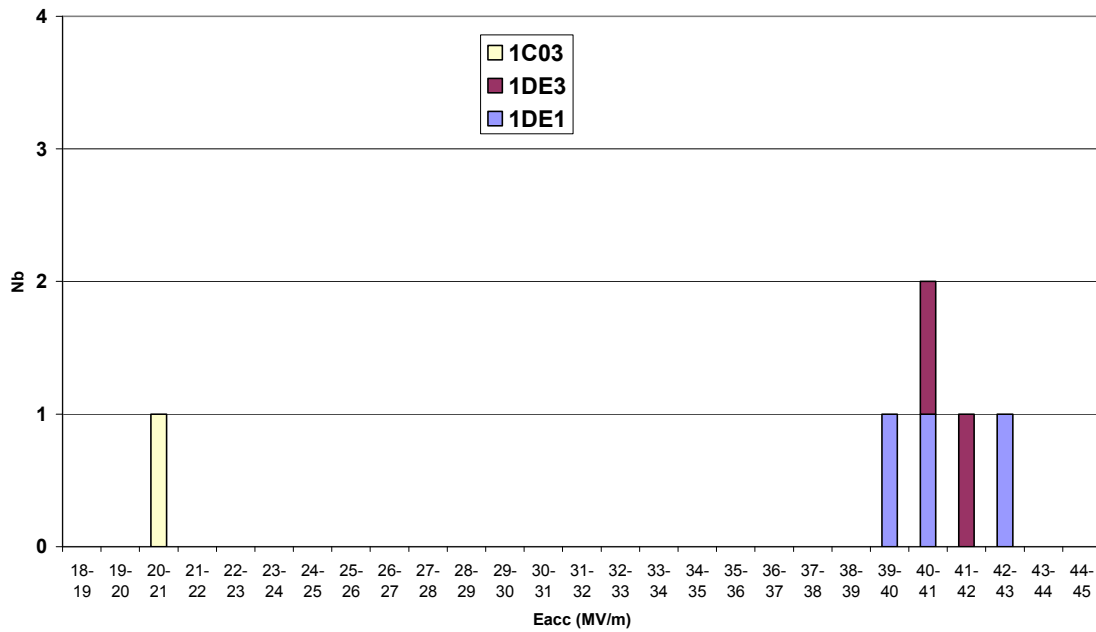After Each Sequence: "30 μm EP + 30' Ethanol Rinsing + HPR"**

**Figure 22: Average Gradient distribution for 1DE1, 1DE3 and 1C03 cavities after each EP sequence at
Saclay. Recipe: 30 μm EP + Ethanol Rinsing + HPR.**

20

Recipe	R#1	R#2		R#3	R#4		R#5	R#6
Test	T#1	T#1	T#2*	T#1	T#1	T#2	T#1	T#1
Cavity	1DE1	1DE1	1DE1	1DE1	1DE3	1DE3	1DE3	1C03
EP @	S	S	S	S	S		S	S
Baking @	D	D	D	S	D		S	S
Test @	D	D	S	S	D		S	S
Eacc Max	42,73	36,30	44,13	39,80	43,92	40,41	41,87	20,00
Average Eacc	**42,70**	**40,21**		**39,80**	**42,16**		**41,87**	**< SPEC**
Q0 @ EaccMax	9,70E+09	1,21E+10	7,82E+09	9,11E+09	2,46E+10	1,87E+10	1,40E+10	
Average Q0	**9,70E+09**	**9,96E+09**		**9,11E+09**	**2,16E+10**		**1,40E+10**	

Eacc=   **41,35**   MV/m   *additional HPR at Saclay
+/-   **1,27**   MV/m

Q_0=   **1,29E+10**
+/-   **5,27E+09**

Table 2: Results obtained with 1DE1, 1DE3, and 1C03 cavities. The average gradient after 5 sequences is 41.35 MV/m for 1DE1 and 1DE3 cavities with a low scatter: ~ 3%.

IV Diluted mixtures

We brought to the fore in § A-IV that electro-polishing with diluted mixture involves positive characteristics. After these preliminary tests on samples, we decided to test it on cavity. The mixture 1vol $HF_{40\%}$ – 9volHS $_{95\%}$ – 7vol H_2O was used to electro-polish the "dummy" cavity 1C11. Evolution of intensity as a function of time during the EP at 8 volts is shown in Figure 23.

Intensity and Tank Temperature as a Function of Time. 1C-11 Cavity. 1-2-7 Mixture. 8.6 Volt. 1 rot/min
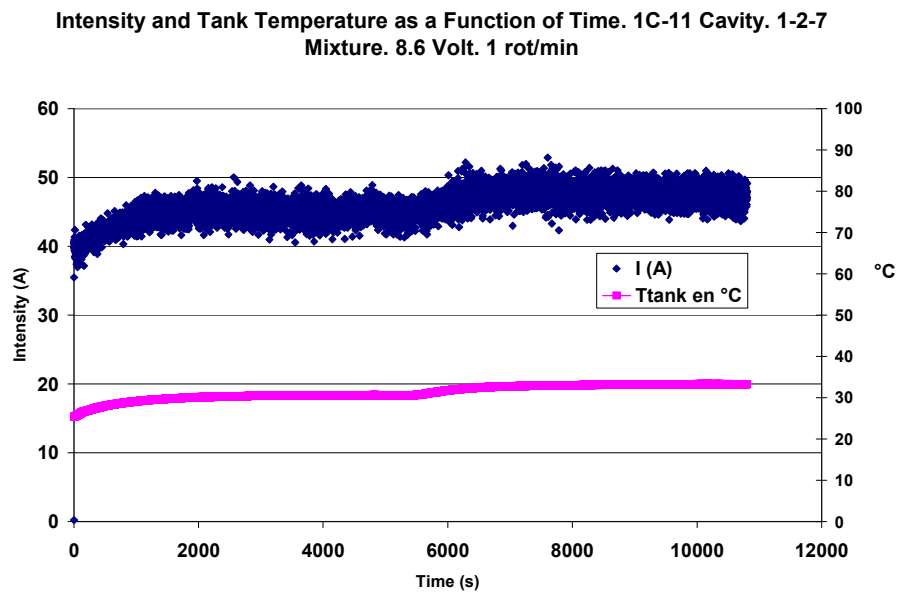
Figure 23: Temperature and intensity monitoring during EP with 1-2-7 mixture at 8 volts.

The surface after the treatment seems satisfactory. Printings of the surface have been made. Some positive aspects might be put forward:
- fast removal rate,
- removal at iris and equator of the cavity more uniform.

This point could be attributed to a diffusion phenomenon: the higher removal rate at the equator would be induced by the higher local velocity of the cavity.

Nevertheless, we have to point out some drawbacks:
- Sulphur is generated: it deposits on the inner surface of the PFA pipes when the mixture is aging (see Figure 24).
- Some copper from the cathode deposits on the cavity inner surface (Figure 25). It would be necessary to use a less reactive metal.
- The final surface state after EP depends on the initial surface state.

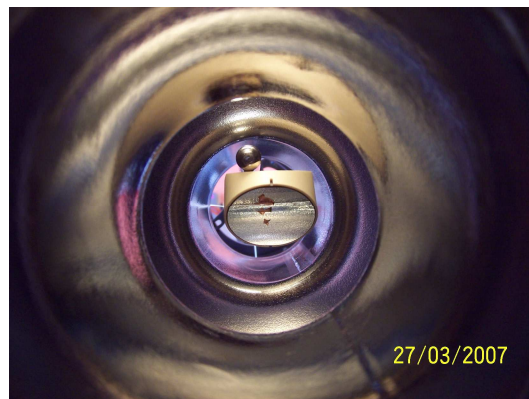**Figure 24: Distinct sulphur deposition on the pipe at the outlet of the cavity.**

Figure 25: Copper deposition on the surface of the cavity. Origin from the copper cathode.

The most prejudicial drawback is induced by a measurement on sample: a sample electro-polished with such a mixture was sent at DESY for hydrogen measurement. It showed heavy contamination: 13-15 µg/g that should lead to Q-disease. As a consequence, we stopped experimentations on cavity with diluted mixtures to focus on other parameters. Diluted mixtures can not be used as a final electro-polishing step because of hydrogen contamination. Nevertheless, due to the high removal rate, long lifetime of the bath and a hint for more uniform removal rate, it could represent a promising alternative for the first stage of electro-polishing, before heat treatment of the cavity.

V Low-Voltage Electro-polishing

Results on samples and literature [17] attribute good surface finishing to an oscillating current regime at constant voltage. Some researchers are more sceptical. As we discussed it in § C-II, promising results are obtained at high voltages, in an oscillation regime. Furthermore, I(V) curves with standard EP mixtures show two oscillation areas at high and low voltages. See Figure 26a and the following curve on Figure 26b obtained using an Ag/AgCl reference electrode.
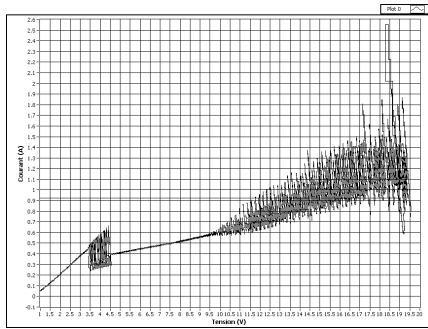

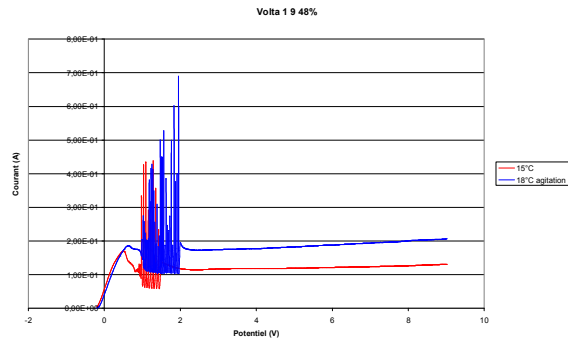**Figure 26a: I(V) curve for standard mixture without reference electrode.**

Figure 26b: I(V) curves for standard mixture with the use of a Ag/AgCl reference electrode.

We aimed to investigate electro-polishing in this regime, because it could induce several advantages:
- decreased consumed electrical power
- no need for heat exchanger (reduced Joule effect)?
- removal rate unchanged compared to the standard process
- probable decreased sulphur generation
- probable higher lifetime of the bath (as explained in § A-I-2))
- possible decreased hydrogen contamination in niobium.
- process easy to control (characteristic oscillation regime).

1C11 "dummy" cavity was EP during long sequences. After 100 μm removal, surface was very shiny, but with a quite different aspect compared to cavities electro-polished at higher voltage: the surface is granular (grain boundaries slightly appear). Printings of the surface have been made in order to measure precisely resulting roughness (roughness measurements are missing at the present time). Motivated by this interesting result, we removed 80 μm on 1C21 cavity at 5 volts. Shininess was improved, even if it was not as impressive at the one noticed on 1C11 and the cavity was baked (120°C) and tested at Saclay. It reached 30 MV/m before and 32 MV/m after baking. $Q_0 = f(E_{acc})$ curve is presented in Figure 27.

Q$_0$=f(Eacc) 1C21 Cavity.
70 µm Standard EP + 80 µm EP at 5 V + Ethanol Rinse + HPR.
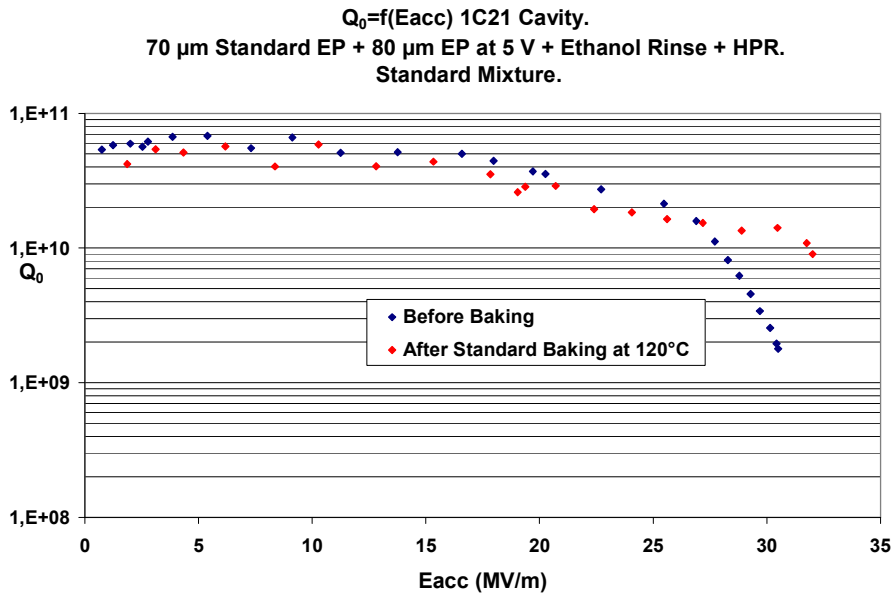**Standard Mixture.**

Figure 27: RF Results after the first sequence at low voltage. It reaches 32 MV/m after baking.

This cavity has been electro-polished a second time at 5 volts to confirm that result. The additional removal is 50 µm. The cavity was rinsed with ethanol prior to HPR in clean room. The shininess of the cavity was improved (see Figure 28) and no sulphur odour was noticed after the EP of the cavity. The cavity then reached 28 MV/m before, and 35 MV/m after baking (110°C – 48h). Results of RF tests after EP at 5 volts are presented in the graph in Figure 29.

Figure 28: Internal surface of 1C21 cavity after 130 µm removal with EP at 5 volts.

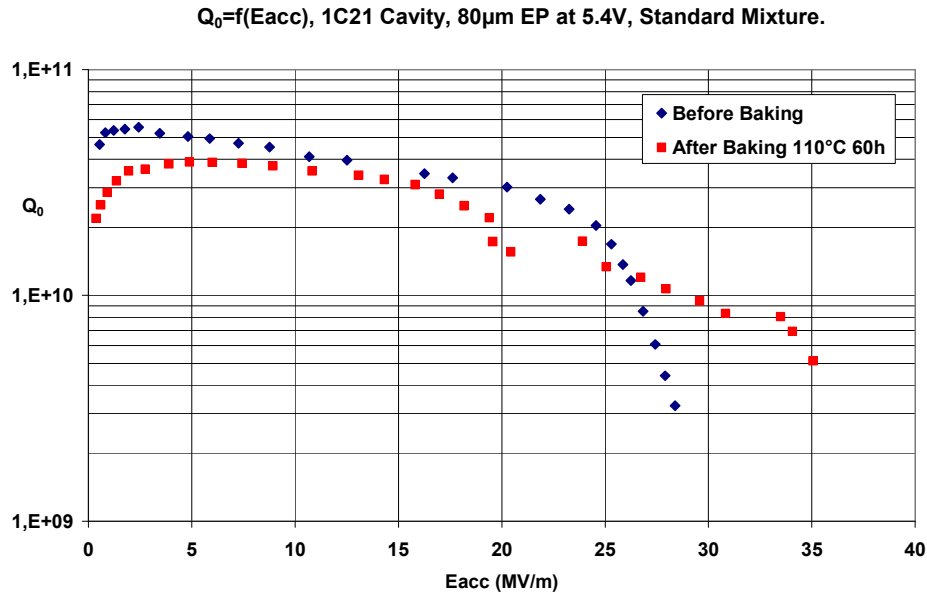**Q$_0$=f(Eacc), 1C21 Cavity, 80µm EP at 5.4V, Standard Mixture.**

Figure 29: RF Results after the second sequence at low voltage. 130 µm were removed at low voltage. 1C21 reaches 35 MV/m.

This additional EP treatment enables to improve the achieved accelerating field. The gradient above 35 MV/m is quite encouraging since this cavity belongs to a series which gave poor results after BCP treatment (no gradient above 25 MV/m with 1C19 and 1C20 cavities). A light "standard" EP at 17 volts will be carried out in order to precisely apprehend the impact of applied potential on EP. If similar performance is observed, low voltage EP could then be considered as a possible candidate for large scale cavity treatment. Moreover, this result would question the postulate that EP must be carried out in presence of a viscous layer. In fact no viscous layer is expected at low voltage since the process is not driven by diffusion (the chosen voltage is not on the "plateau"). This point might also be illustrated in Figure 30 where we notice that an increase in rotation speed of the cavity does not result in an increase of the current density.

The absence of viscous layer is probably the origin of the grainy surface at low voltage. At that point, it is challenging to know if this characteristic surface at low voltage is responsible for a possible lowered performance compared to high voltage EP. In that way, we also intend to remove 80 µm at low voltage on 1DE1 cavity that showed excellent and repetitive gradients at 17 volts.

Furthermore, intensity and temperature monitoring during second treatment of 1C21 cavity are shown in Figure 31. We might see that the temperature increase in the cavity compared to the temperature in the tank where the acid is stored is not consequent. We did not cool the acid in the tank for this experiment. We intend to have experiments at higher temperature with the same potential to investigate heating of the bath (intensity and Joule effect will increase) and influence in term of RF performance.

Intensity and Temperature as a Function of Time.
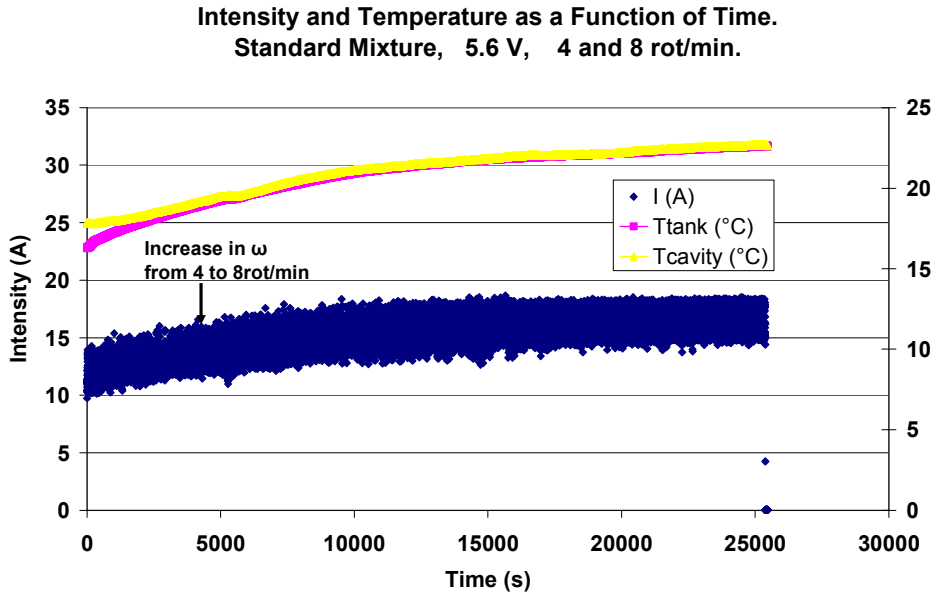**Standard Mixture, 5.6 V,   4 and 8 rot/min.**

Figure 30: Temperature and intensity monitoring during EP at low voltage. An increase in the cavity rotation speed does not result in an increase in current. The process is not driven by diffusion.

Intensity and Temperature as a Function of Time, C1-21 cavity, 5.4V,
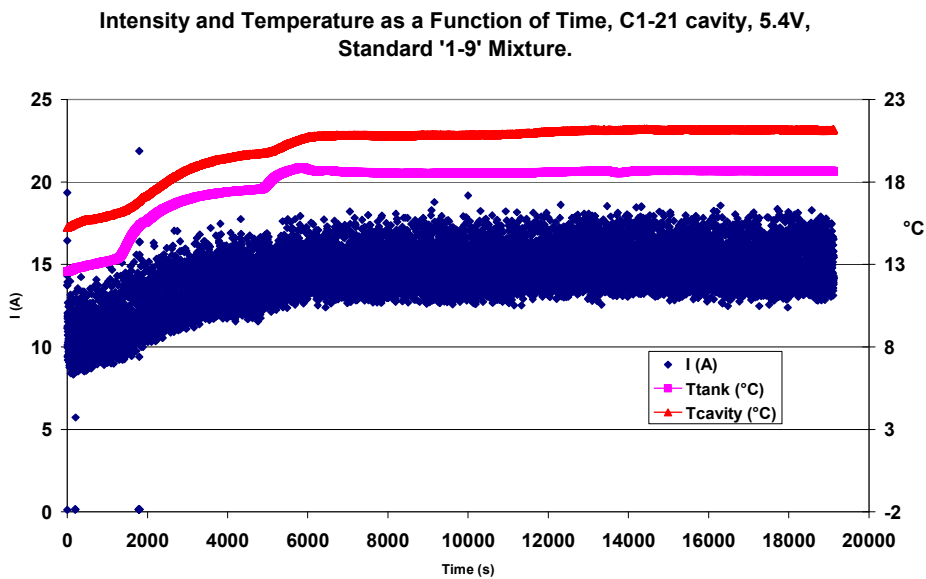**Standard '1-9' Mixture.**

Figure 31: Temperature and intensity monitoring during second EP at low voltage of 1C21 cavity. The temperature increase is lowered compared to the standard EP. Lower voltage results in decreased power consumption by Joule effect.

VI Influence of complementary parameters

a) Temperature

Because of the numbers of additional experiments that would have resulted from, we have decided in a first approach to not make temperature vary during our experimentation program. For example, during EP at 17 volts, temperature was close to 30°C and for low voltage experiments, it was lower (20 – 25°C). However, the strong influence of temperature on

current density is obvious during all sequences (see for example graphs in Figures 16 and 31). We have also to report that temperature was not controlled during a sequence at 17 volts. It went over 40°C. We noticed a strong degassing of the acid mixture, and a loss of the oscillations' regime. The resulting surface of the cavity was tern but it did not affect the performance, since E_{acc} reached 44 MV/m at 1.5 K after additional HPR and test at Saclay.

We intend to analyse the possible relation that could exist between surface state of the cavity and RF performance. This contemplated study is included in a larger program described in the § C-VIII and in the conclusion of this report.

b) Rotation speed of the cavity

We punctually made vary the rotation speed of the cavity during some experiments. As we explained in paragraph § C-V and in Figure 30, the cavity rotation speed has no influence on current density for low voltage experiments. As it is not a viscous layer regime, it should also have no impact on the inner surface of the cavity. Experiments carried out with 1C11 dummy cavity are along the same lines.

On the contrary, at higher voltage, the current increase with rotation speed suggests that the electro-polishing is governed by diffusion. During the EP at 12.5 volts presented in Figure 32, when the rotation speed is multiplied by four, intensity is increased by 25%. If such a rotation speed does not deteriorate cavity performance, it could be used to improve the removal rate.
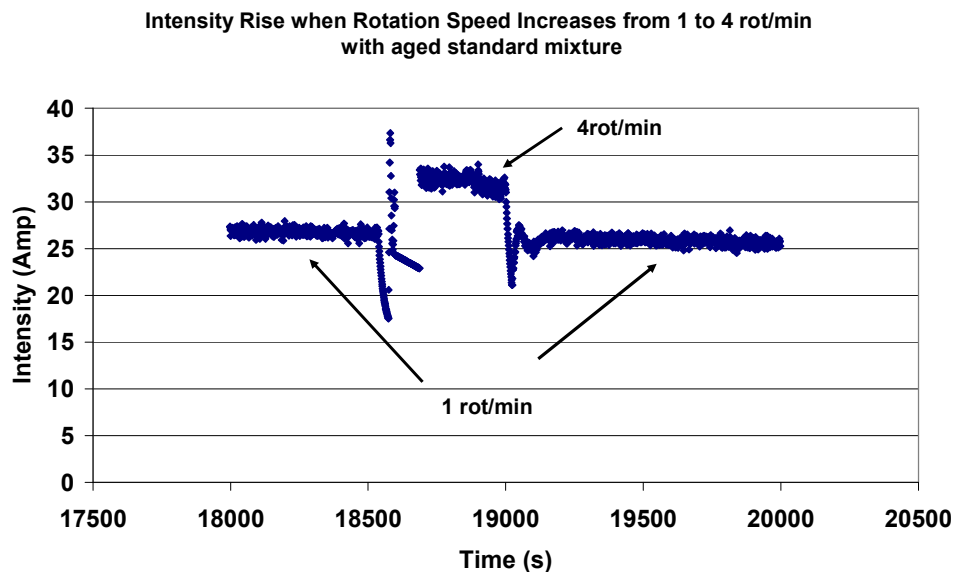

Intensity Rise when Rotation Speed Increases from 1 to 4 rot/min with aged standard mixture

Figure 32: Evolution of the intensity during EP at 12.5 volts after an increase in rotation speed. The electrolyte is an aged 1vol HF$_{40\%}$ - 9vol HS$_{95\%}$ mixture.

VII A process that should be improved

During experiments, we notice (pointing for example a laser sensor on the surface along the cavity) that the temperature is not uniform. This is due to the fluid distribution in the cavity: the acid is injected in the middle of the cathode and goes out at the right side of the cavity. As a result, the left side of the cathode constitutes a dead end, where acid is badly renewed. This point is of paramount importance because we noticed some surface deterioration at the left part of the cavity during some EP sequences, especially when the acid was old.

Modelling with COMSOL software enables to traduce this non homogeneous fluid distribution in the cavity. Some results are presented in Figures 33a, 33b and 33c. This software has been used to investigate new configurations that would lead to better EP. For example, the acid coming by the left side of the cavity and the presence of a protuberant cathode forcing the acid to sweep the equator of the cavity should make the EP more efficient. This study is presented in [18] and must be pursued.
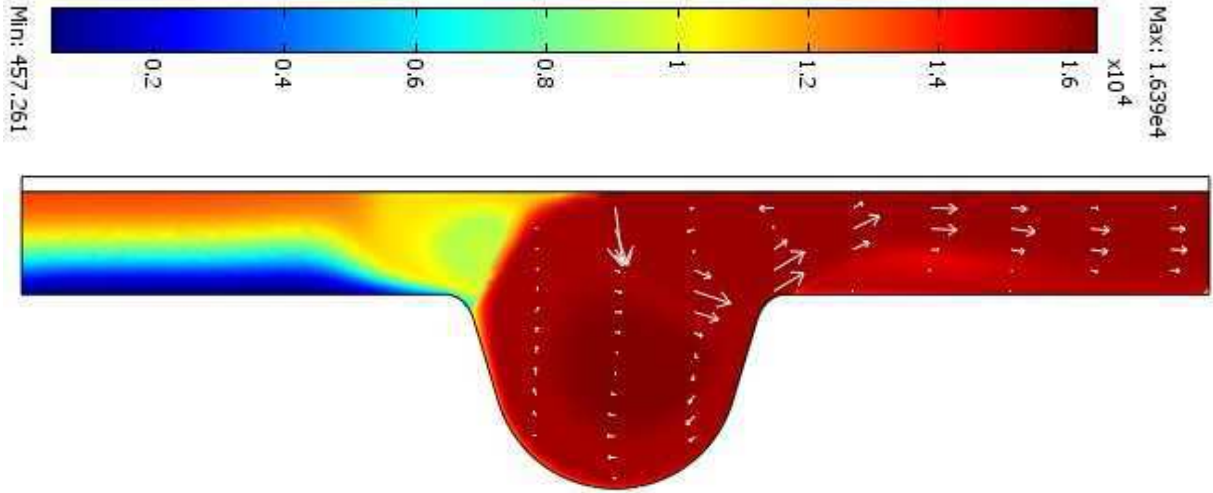

Figure 33a: HF concentration (mol.m^{-3}) in the cavity when the acid is injected through the middle of the cathode. There is a dead end in the left part of the cavity where the acid is badly renewed.
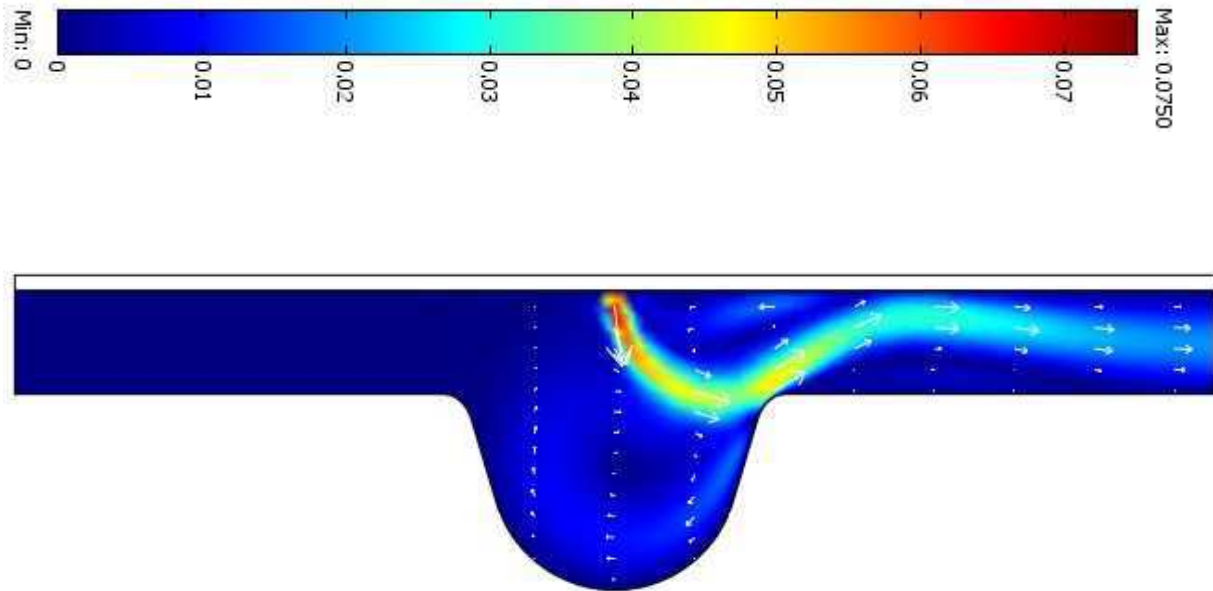

Figure 33b: Flow rate (m.s^{-1}) in the cavity when acid is injected through the middle of the cathode.
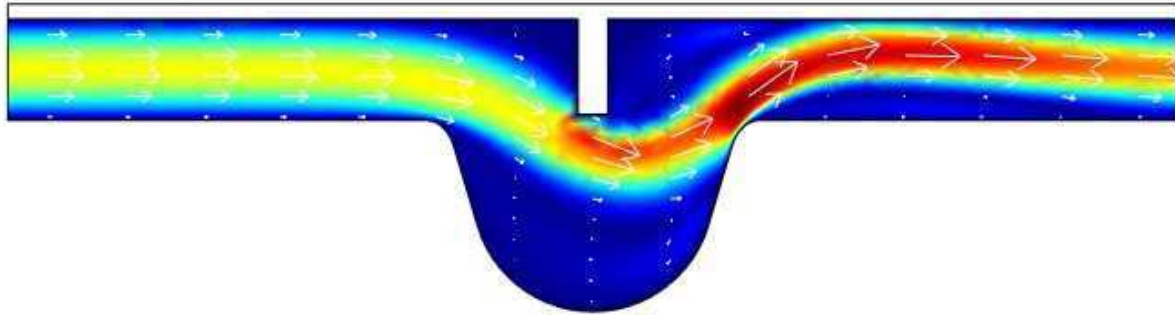
Figure 33c: Flow rate (m.s⁻¹) in the cavity when the acid is injected in the left side of the cavity and when a protuberance forces the acid to sweep the equator of the cavity.

VIII Outlook and proposal for a new program

The results obtained within Work Package 5.1 of CARE-SRF Program are very encouraging. In fact:
- The understanding of the EP process in the niobium case has been improved.
- Alternative parameters have been proposed resulting from studies on samples and first results on single-cell cavities.
- Excellent gradients have been obtained with the EP bench.

In that way, this set-up constitutes a useful tool for R&D experimentation which is worth going on. Unfortunately, we did not have the possibility during this program to test with RF cavities prepared with some alternative parameters. For example, results with concentrated and diluted mixtures are missing. We then intend to pursue R&D investigations under the following scheme:

❖ Different electrolyte's compositions, partially investigated during CARE-SRF program, will be tested. Cavities will be treated and tested several times in order to make statistic and precisely evaluate reproducibility of the process. Cathodes with modified shape should be considered as a fundamental criterion to improve EP by making the removal more uniform in the cavity. Such cathodes will be used during these treatments. New cathode materials should also be investigated in order to reduce impurities forming during Electro-Polishing.

❖ It is not clear if the performance of the EP is due to the lower roughness achieved by this process. The treatments described above will generate surfaces with different profiles, making possible to map the performance has a function of the roughness. We also intend to broaden this research:

❖ We will be able to pursue a former study carried out at Saclay and that completes the previous one [19, 20]: Does the quench occur at a location in the cavity where the magnetic field is enhanced by the morphology of the surface? The quench location will be determined during RF tests by the use of a temperature mapping system. COMSOL Software will be used advisedly in order to model the morphology of the quench area and evaluate the magnetic field enhancement at the grain boundaries.

Conclusions

- ❖ Standard mixture has been tested with success on single-cell cavities. Ethanol rinsing enables to achieve high reproducible gradients.
- ❖ Electro-Polishing at low potential, characterized by regular current oscillations enables to reach gradients above 35 MV/m. It is worth going on with that process that involves some benefit compared to the 'standard' process:
  - process easy to control
  - less power consumed
  - no need for heat exchanger
  - less vaporization of hydrofluoric acid and longer lifetime of the bath
- ❖ Diluted mixtures are also promising, but as a preliminary EP step for fast heavy removal. A new material should be tested in order to replace copper generating copper deposition on the cavity surface. Graphite will be tested as a possible material for cathode.

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