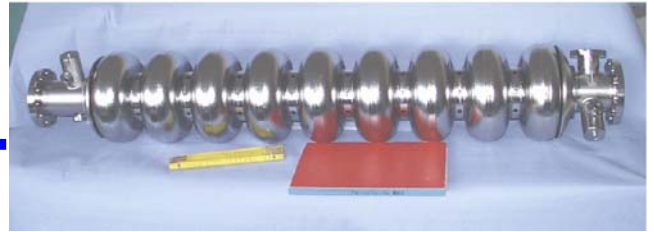




# SRF



## **Deliverable 5.2.3.9: “Evaluate oxipolishing experiments”**

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### **Abstract**

Thorough cleaning of the surface of Niobium resonators is crucial for high gradient superconducting performance. The standard procedure consists of electropolishing and high pressure pure water cleaning. One typical example of contaminations are drying spots. Oxipolishing is a simplified method of electro-polishing. The aim of this investigation is to explore the feasibility of oxipolishing as simple method to remove drying spots. It could be shown that this procedure is a promising option as additional cleaning method of Niobium surfaces.

### **Acknowledgements**

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## I Introduction

For the cleaning of superconducting niobium surfaces destructive and non destructive treatments are applied. Buffered Chemical Polishing (BCP) and Electropolishing (EP) acid mixtures are in use for removal of the so called damage layer. According to experience this damaged layer has a thickness of about 100  $\mu\text{m}$ . As first cleaning step this layer is removed by BCP or EP. As second cleaning step possible contaminations by drying spots, chemical residues or particulates are removed by non destructive methods like High Pressure Rinsing (HPR) and / or ultrasonic cleaning with specialized detergents are applied. Non destructive methods are limited by the forces that can be transferred on to the surface areas to overcome the binding forces of contaminations. The destructive methods EP and BCP make use of the chemical reaction. These wet chemical treatments allow to undermine embedded and chemical resistant material by removing the Niobium carrier layer. In the case of conducting cavities this material removal leads to changes of the resonant frequencies and the Radio Frequency (RF) field profile due to the volume change related to that removal.

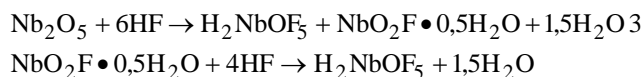
## II Material removal by Oxy-polishing

The EP process consists of two simultaneous chemical reactions: oxidization of Niobium and dissolving the Niobium oxide in the electrolyte. Oxipolishing separates these electro chemical reactions:

1. Step one of the chemical reaction leads to an oxidation of the niobium and the build up of a thick  $\text{Nb}_2\text{O}_5$  layer on the surface.
2. In step two Hydro fluoride (HF) acid is applied to remove of the  $\text{Nb}_2\text{O}_5$  layer and dilute the NB fluorides build up during this reaction in rinsing water.

In step 1 of the oxy polishing process chemical component like  $\text{HN03} + \text{H}_2\text{O}$  (1/10) or  $\text{HNO}_3$  14- 25% or  $\text{H}_2\text{SO}_4$  (10%) are in use. A DC voltage is applied during this oxidizing part of the OP. The thickness of the  $\text{Nb}_2\text{O}_5$  layer is proportional to the voltage with a rate of 20 Angstrom per 1 Volt. .. The  $\text{Nb}_2\text{O}_5$  layer is an electrical insulator in the region of up to 100 V DC voltages. The oxidation of the Niobium stops automatically when the whole surface is covered with a  $\text{Nb}_2\text{O}_5$  Oxide film of a thickness according to applied DC voltage.

In step 2 HF acid transfers the oxide into Nb fluoride which can be diluted in water:



Mixtures from 40% down to <1% concentration of the Hydro fluoride acid are reported. High concentration of HF leads to a fast removal while low concentrated HF removes the oxide in the same effective way but at longer treatment time.

## III Process parameters

The Nb surface is a conductor and reacts as an electric short circuit until some Angstrom of oxide is built up. In this phase high current densities appear on the surface. This results in the formation of unfavorable higher oxides ( $\text{Nb}_2\text{O}_x$ ). These oxides, mostly visible as white or

grey surface layers are of ceramic like nature and can not be removed by Hydrofluoric acid or other standard chemical etching mixtures. To prevent the build up of Nb<sub>2</sub>O<sub>x</sub> the start up current has to be limited to a maximum current density of about 5A/m<sup>2</sup>. The oxidation process is stopped when the current is reduced to 0, or as pragmatic limit to 1/e of the start up current.

#### **IV Application of Oxipolishing for quality control of Niobium material**

The oxipolishing process also was applied as quality control during cavity fabrication. The thin Niobium pentoxide layers shows up in a color related to the interference mechanism of a  $\lambda/4$  thin optical film. Therefore a “clean” surface has a uniform color. But any foreign inclusion or material contamination will be visible as a (local) discolored spot. This contrast allows an easy optical surface control.

Based on this experience it is proposed to make use of the oxipolishing (OP) for final or post test surface investigation and / or cleaning process. Due to the small amount of material removal the resulting frequency shift of 1, 3 GHz resonators is of the order of -10.6 kHz/ $\mu$ . This small frequency shift and the homogenous removal allow to apply this cleaning to remove damages on resonators as a repair method after evidential contamination with particulates and as a final treatment for resonators. This is especially applicable for resonators where the excess for a chemical treatment is limited due to geometry (Gun Cavities) and for cavities which are already welded into their helium container.

#### **V Test setup for samples**

To test the efficiency of oxy polishing on RF surfaces, some test were carried out on samples and on a single cell resonator. In the test set up we tried to simulate the reality of multicell processing as close as possible. A test set was adapted to the existing infrastructure at DESY. For testing of the efficiency of the oxipolishing process for application as surface cleaning and test preparation, reproducible and known surface contaminations have to be placed onto samples and have to be analyzed before and after the OP treatment.

In the past it was found that during the preparation of resonators the removal of chemical residues and rinsing in water of less than 12 MOhm cm resistances leads to so called drying stains. These residues are known as field emitters and stick very strongly on the Niobium surface after drying. During inappropriate or accident-like venting of resonators or storage in normal air, the surfaces are covered by particulates of different material and origin. These contaminations are correlated with the environment they are origin from and therefore are of different nature. For the sample investigations the reproducible drying stains are chosen as reference contaminations. The areas of the sample contaminated with drying stains were analyzed and marked under a light microscope available inside the DESY cleanroom.

##### **V.1 Sample preparation and measurements**

The samples are fabricated from standard niobium sheet from the cavity production. Cleaning was done by BCP (1/1/2) inside a class 10 ASTM cleanroom. These are the same cleaning conditions as for Niobium resonators after chemical surface treatment. After rinsing in ultra pure water the samples are dried in a class 10 (ASTM) airflow. We did not find any residues or contaminations during visual inspection under a microscope located inside the class 10000 (ASTM) cleanroom at DESY

**Test sequence 1: Cross check of removal by the pure water rinsing.**

After inspection the clean surface was rinsed by tap water of nominal hardness of 7 -10 deg German scale. The samples dried in clean atmospheres and were inspected under the microscope again. It was obvious that these residues can not be removed by a standard washing/ rinsing procedure. The ultra pure water rinsing took place in the cavity preparation area inside the DESY cleanroom with the same infrastructure in use for cavity preparation.

**Test sequence 2: Cross check of removal by the acid components.**

For this test the contaminated sample is immersed in high and low concentrated acid to crosscheck that the removal is not due to the chemical reactions of the drying stains and chemicals in use. The microscopic investigation showed that the pure chemical treatment has no cleaning effect.

**Test sequence 3: Test of the Oxy polishing treatment.**

A sample polluted with drying marks is anodized in a mixture of water and HNO (8 %) at a voltage of 35V DC corresponding to a light blue coloration. After the Anodisation the oxide is removed in a hydro fluoride mixture with 4,5 % HF concentration. Details of this test sequence are given in the following sections:

**1. Test set up**

A const voltage / current source with current controller and limiter is connected to the sample. The sample is fabricated from Niobium and the electrode is made from aluminum (Figure 1). The voltage is set to the value to be tested. During start up of the OP process the current is limited to a value below  $5A/m^2$ . After the current has dropped to  $1/e$  of the start up current the voltage is switched off. The Niobium sample is removed from the Teflon ® acid container and rinsed in ultra pure water until all residues of the HNO<sub>3</sub> are totally removed.



Figure 1: Test set up for oxidation of Niobium Samples Left side: power supply Right side: Teflon® container filled with HNO<sub>3</sub> (8% concentration)

For removal of the Niobium pentoxide layer the sample is inserted into a container filled with HF acid of 4,8 % concentration. To improve the homogeneity of the removal an agitation unit (Figure 2) moved the acid during that part of the OP process. A rinse with ultra pure water and drying in a class 10 to 100 environment is done before the sample is analyzed under the light microscope again.



Figure 2: PVDF container filled with HF acid (4,8 % concentration). At the bottom the agitation driving unit can be seen

## V.2 Test results

### 2a) Pollution of samples

After drying of the sample the surface was inspected by a microscope. The residues on the surface of the sample looked like those which were observed in resonators with non adequate cleaning and rinsing. The borderline of these drying stains are identified and marked under a microscope with a 5 times magnification factor (Figure 3).

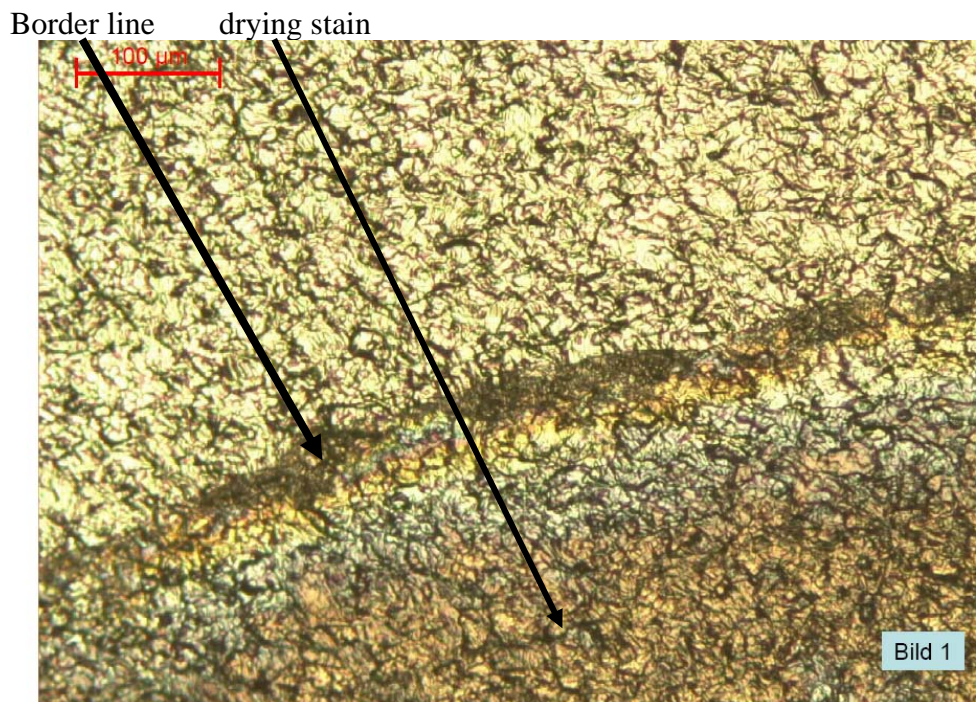


Figure 3: Typical surface of a sample which is polluted by drying stains (light microscope with a magnification of factor 5).

*2b) Test to remove drying marks by only rinsing in ultra pure water*

The sample was rinsed in ultra pure water of 18,2 M Ohm cm resistance inside the ultra pure water rinsing basin of the DESY cleanroom. The drying mark is cross checked under the microscope before and after rinsing. It is found that parts of the drying stains are dissolved by the ultra pure water. The borderlines of the defect are still visible and clearly be identified. (Figure 4).

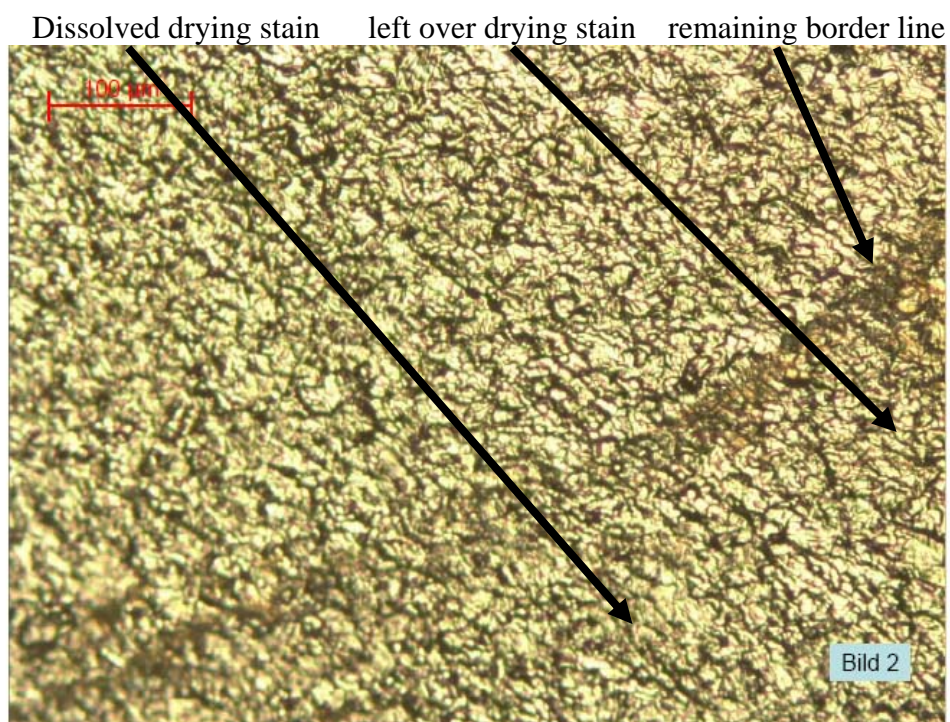


Figure 4: Border lines of the drying marks after exposure to ultra pure water.

*2c) Treatment of polluted sample with HF rinsing, but without external current source*

For the Oxy polishing process an acid mixture with less than 5% HF content is preferred (because of safety aspects). The sample was exposed to a 4,5 % HF and a 8% HNO<sub>3</sub> acid for 1 hour. It was found that either the 4,5 % HF or the 8% HNO<sub>3</sub> mixture removed the defects significantly (see Figure 5).

remaining border line left over drying stain

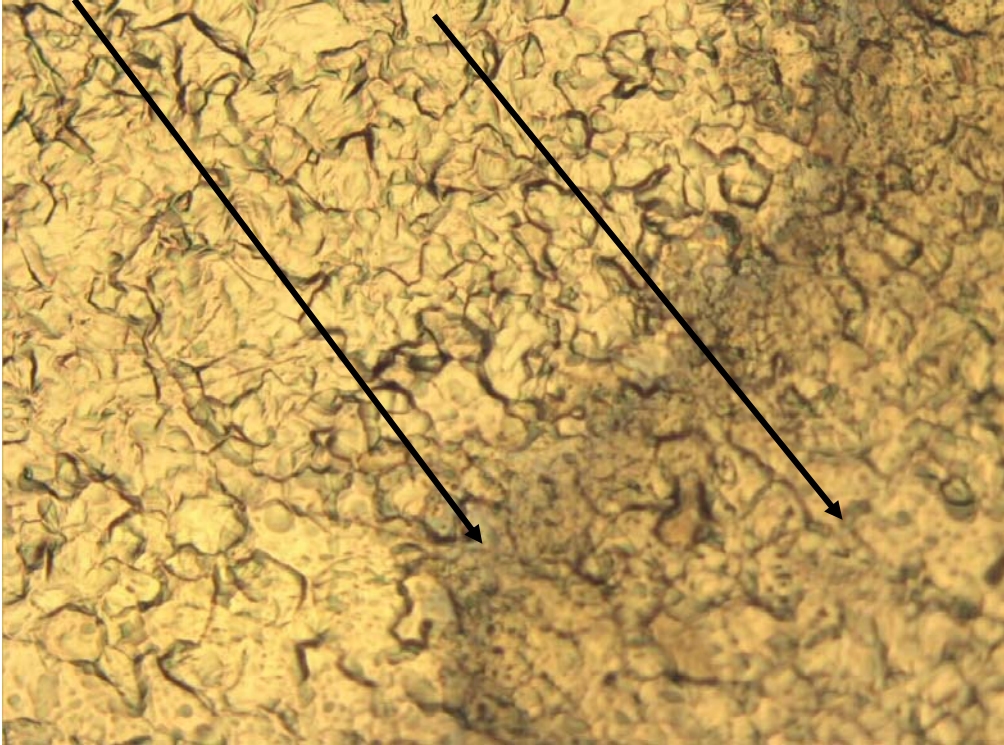


Figure 5: Microscopic view of drying marks after exposure of one hour to 4,5 % HF acid.

*2d) Removal of drying marks by oxy polishing*

A sample polluted with drying marks is anodized in a mixture of water and HNO<sub>3</sub> (8 %) at a voltage of 35V DC corresponding to a light blue coloration. After anodisation and rinsing the oxide is removed in 4,5 % HF acid. The sample surface was examined under a light microscope and a magnification of 5-50 times before and after the oxipolishing process. The optical as well as the microscope inspection showed that no residues of the drying marks are left over after oxipolishing.

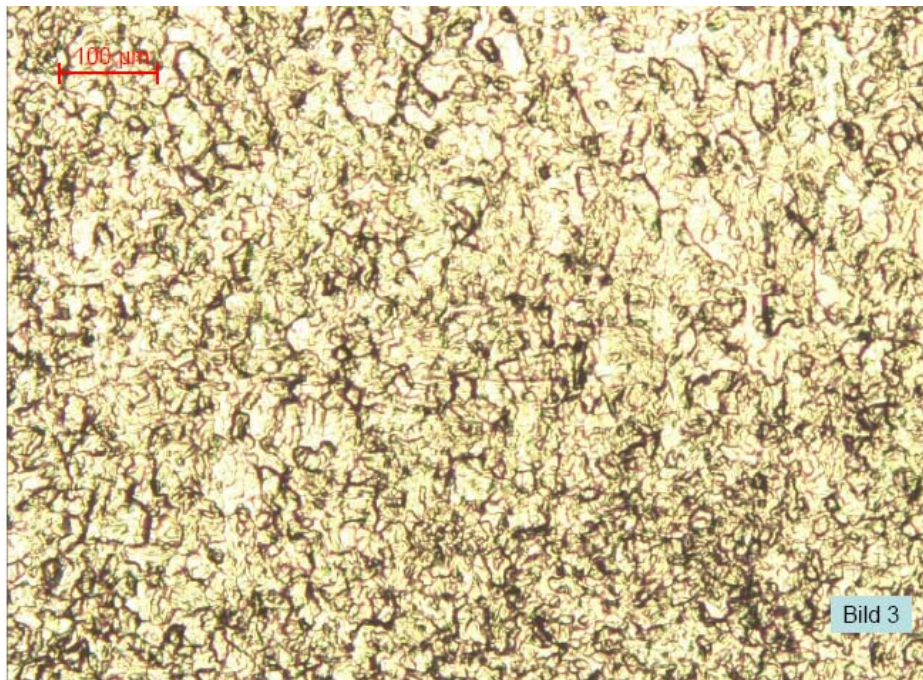


Figure 6: Light microscope picture of the area of drying mark after oxy polishing. It is obvious that the contaminations by drying marks were completely removed.

## VI Test on single cell

Within a test series of single cell experiments, related to the XFEL preparation test sequences, the single cell resonator 1B8 was oxipolished. The OP was done in a chemistry laboratory in normal atmosphere. After transportation back to the cleanroom the resonator was high pressure rinsed and measured at 1,9 K. The superconducting performance of this resonator before and after the oxipolishing cleaning is shown in figure 7. Within the measurement errors the performance of this resonator is not changed. Therefore it can be concluded that the oxipolishing process itself has no negative effect on the superconducting resonator performance even if the oxipolishing process is done in conditions of normal atmosphere.

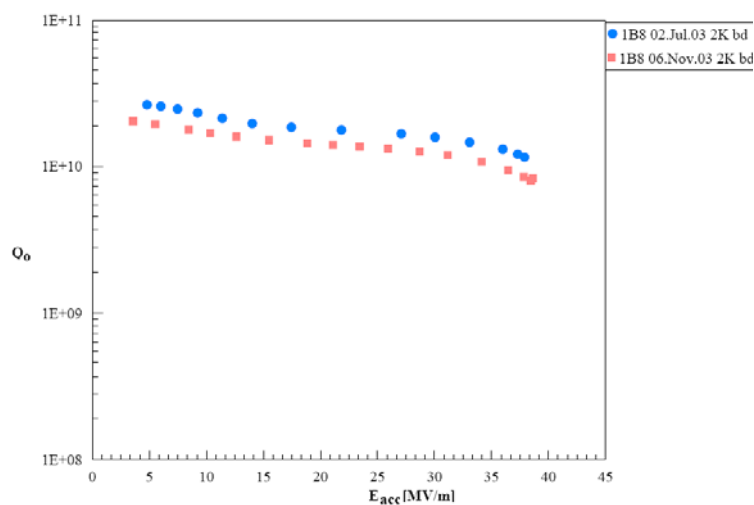


Figure 7: RF test results of the single cell resonator 1B8 before (red squares) and after oxy polishing (blue dots).



## VII Proposal for a multi cell set up at DESY

For safety reasons the application of chemical treatments is not allowed in the DESY cleanroom. Chemical cleaning of cavities by BCP or EP are done in a special closed loop circuit. In both cases the cleaning apparatus is installed in special areas outside the cleanroom. Therefore a test of multi-cell oxipolishing has to be performed outside of the existing DESY clean room. The oxipolishing process is split into two operations: anodizing and oxide removal.

- The anodisation process uses  $\text{HNO}_3$  with a concentration of only 5 %. This acid does not need to be moved or exchanged during the operation. The total amount of reactive  $\text{HNO}_3$  inside the superconducting resonator volume is about 1,5 liter and will not be used up during the chemical reaction.

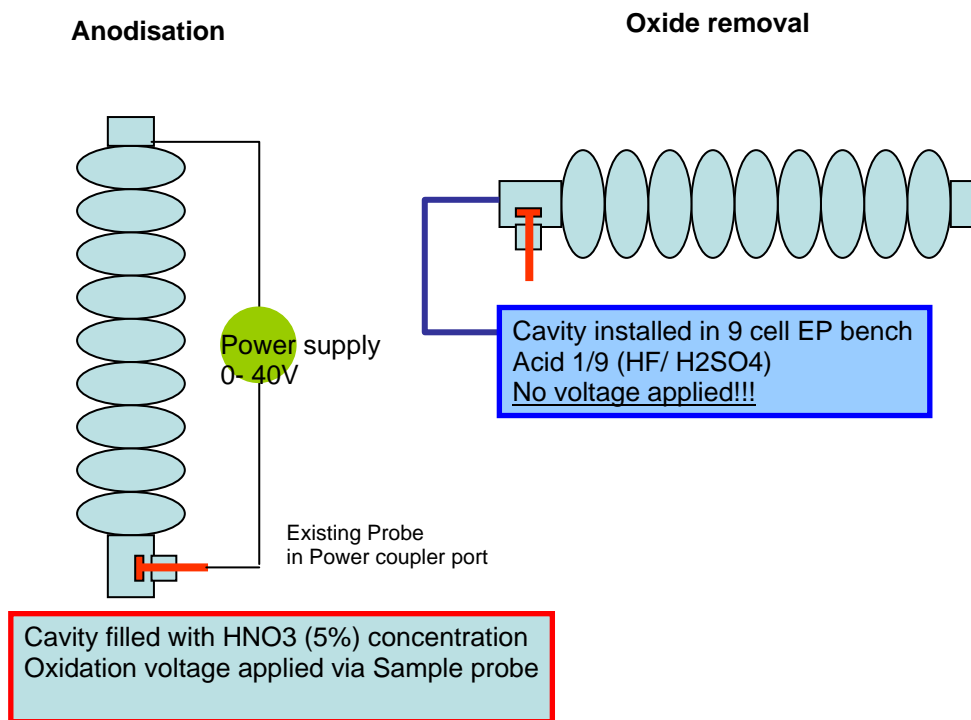


Figure 8: Schematics of the oxipolishing apparatus as proposed for application for multi-cell cavities at DESY. Left picture shows the vertical anodizing of a 9-cell Niobium cavity; the right picture is a sketch of the oxide removal step.

The out gassing of Nitric acid during the anodizing process was measured to be very low. This is a consequence of the low acid concentration of the anodizing chemistry. Furthermore the time of the anodizing process is short, only about 10-20 minutes. Therefore a safety analysis concluded that the anodisation process can be done using the gas exhaust system of the BCP installation at DESY (see figure 9).



Figure 9: Test set up for anodisation of nine cell resonator inside the DESY cleanroom

For the more critical operation of reduction of the  $\text{Nb}_2\text{O}_5$  layer by Hydro fluoric acid the out gassing is too strong, even with the low concentrated mixture tested on the samples. It is foreseen to use the existing EP infrastructure at DESY where the acid is circulates in a closed loop (see figure 10)

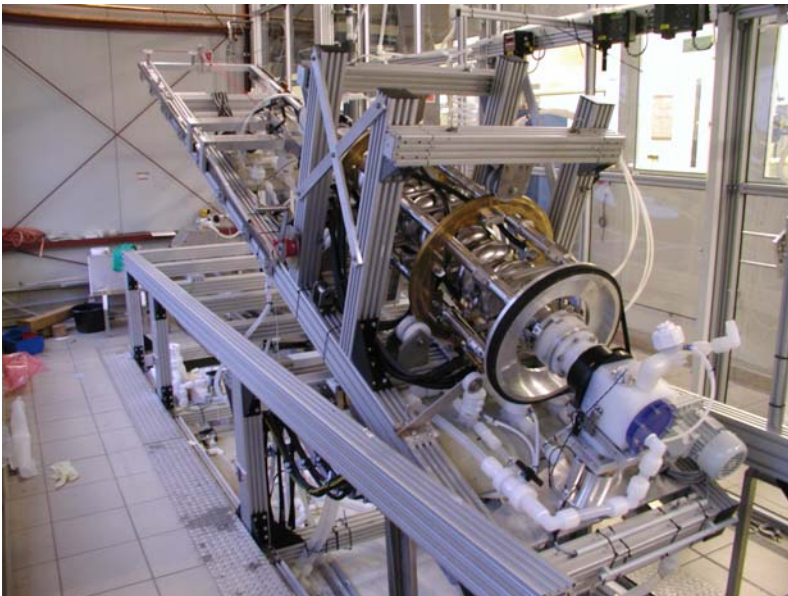


Figure 10: Removal of the  $\text{Nb}_2\text{O}_5$  layer inside the DESY EP installation.  
The applied EP mixture in use at DESY consist of a total of 5,5 % pure HF in the acid liquid.  
The set up allows to circulate EP mixture through the 1,3 GHz 9 cell cavities without applied

voltage (see figure 10). It is well known that the EP mixture does not remove Niobium in the absence of voltage so that this procedure can be applied for removal of the oxidized surface layer without additional chemical reactions.

## VIII Conclusion

The effect of oxipolishing has been tested on niobium samples. The samples were contaminated with drying spots or residues which are typical for insufficient wet cleaning of the surface of superconducting niobium resonators. It could be shown that these defects can be removed by an oxipolishing cycle. The cleaning cannot be explained by the pure action of the chemistry. The electro-chemical process is the essential ingredient for successful cleaning. Tests on single cell cavities proved that the oxipolishing treatment itself does not deteriorate the superconducting properties. The parameters of oxipolishing treatment are defined and the equipment for oxipolishing multi-cell cavities is described. It is important that existing installations for electro-polishing can be used for stripping the oxide film as second step of the oxipolishing treatment.