

INVESTIGATION OF BCP PARAMETERS FOR MASTERY OF SRF CAVITY TREATMENT

F. Éozénou, E. Cenni, G. Devanz, T. Percerou, T. Proslie, C. Servouin, M.L.L. Nghiem*
Irfu, CEA, Université Paris-Saclay, F- 91191 Gif-sur-Yvette, France
*Université Pierre et Marie Curie, 4 place Jussieu, F- 75252 Paris, France

Abstract

Mastery of Standard Buffered Chemical Polishing (with mixture of hydrofluoric, nitric and phosphoric acids) is of paramount importance for the treatment of SRF resonators with complex geometry as IFMIF half-wave resonators, in order to control accurately their frequency evolution. Furthermore, strong and unexpected asymmetry in removals has recently been observed after BCP treatment of ESS-medium beta resonators.

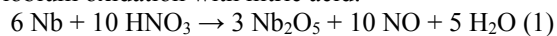
The goal of this study is to investigate accurately influence of parameters such as surface geometry and orientation, acid temperature, agitation and their coupling on the removal rate. We will also focus on the influence of by-products such as NO_x on kinetics. The mixture used is HF(40%)-HNO₃(65%)-H₃PO₄(85%) with ratio 1-1-2.4.

INTRODUCTION

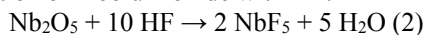
Electropolishing has become the reference surface treatment process for high-gradient elliptical cavities. However, standard chemical process with mixtures of hydrofluoric, nitric and phosphoric acids, also known as Buffered Chemical Polishing (BCP) remains the reference process for the preparation of low-beta resonators.

The main and simplified chemical reactions occurring at the niobium surface are:

Niobium oxidation with nitric acid:



Dissolution of niobium oxide with HF:



The main by-products are fluorinated salts and NO molecules (more generally NO_x with x<3) which is a yellowish toxic gas. Both might be observed during experiments on samples (see later). Applied to the treatment of niobium SRF resonators, this process generates removal rates between 0.5 and 1 μm/min.

We propose in this paper simple experiments on niobium samples to guide the BCP treatments of structures with complex geometries. It is of paramount importance to anticipate the treatment in order to:

- Achieve the required removal all over the surface of the cavity
- Avoid local heating during the cavity treatment
- Control the frequency to maintain it in the tuning range

For example, assuming a uniform removal, the theoretical frequency variation for half-wave IFMIF resonators is -200 Hz/μm. After BCP treatment, we reproducibly achieve -500 Hz/μm because of non-uniform removal.

Furthermore, BCP is useful for this kind of structures to tune the frequency by etching at relevant locations [1]. The goal of the work presented here is to precisely quantify the influence of parameter such as:

- Temperature
- Fluid velocity
- Surface orientation
- Influence of NO_x gases (by-product of the chemical treatment)

Some researchers have modeled chemical treatment with Computational Fluid dynamics (CFD) [2-4]. An accurate knowledge of parameters involved in BCP would make it possible to enrich such codes with relevant data.

The mixture used for experiments on samples was home made. The proportions are 1-1-2.4 in HF-HNO₃-H₃PO₄. This bath composition used at CEA Saclay makes it possible to have HF concentration in mass below 7%, which is required for safety considerations. The higher H₃PO₄ concentration, which acts as buffer, results in a lower removal rate compared to 1-1-2 composition.

MOTIVATION: DIFFERENT REMOVAL RATE FOR SIMILAR CAVITIES

BCP chemical treatments have been recently carried out on 704MHz elliptical ESS resonators, of two different types: β = 0.67 (6 cells) [5] and β = 0.86 (5 cells). The cavities were polished in vertical position, with continuous acid circulation. The cavities are similar (see details in Table 1) and similar parameters were used (T = 15°C, acid flow of 20 L/min) for the chemical treatment (Fig. 1). However, the achieved removal rates differ significantly. The achieved removal rate is 0.5 μm/min for the high beta cavity, where as it is as high as 1 μm/min in the medium-β case.



Figure 1: ESS medium-beta cavity during BCP treatment.

Furthermore, bulk BCP (200 μm) in medium- β case, was responsible for Q-disease during vertical test, and was cured by heat treatment at 600°C for 10 hours [5]. So better comprehension of the chemical process is of paramount importance to possibly avoid such inconvenience.

Table 1: Comparison of Medium- β and high- β ESS Elliptical Cavities

Cavity type	ESS high- β	ESS medium- β
Frequency (MHz)	704.4	704.4
# cells	5	6
Length (mm)	1316	1259
Volume (L)	75	68
Area (m ²)	1.71	1.85
Acid for BCP	FNP 1-1-2.4	FNP 1-1-2.4
Tacid (in tank)	< 15°C	< 15°C
Removal rate	0.5 $\mu\text{m}/\text{min}$	1 $\mu\text{m}/\text{min}$
Removal ratio		
low half cell/top half cell	0.45	0.25

INFLUENCE OF TEMPERATURE AND AGITATION

In a first step, we studied the influence of the temperature and fluid velocity on the chemical process. To simulate the agitation, we evaluated the niobium removal for rotating niobium discs. We used a rotating disc electrode (also known as RDE) device generally used for electrochemical measurements (Fig. 2). In fact, such a system make it possible to control the velocity $V(x)$ of the flow close to the horizontal sample. $V(x)$ is given by:

$$V(x) = -0.510 \cdot \nu^{-1/2} \cdot \omega^{3/2} \cdot x^2 \quad (3)$$

ν : kinematic viscosity in cm^2/s

x : distance from surface

ω : rotation speed in rad/s

And the Reynolds number:

$$\text{Re} = r\omega^2 \cdot \nu \quad (4)$$

With r : radius of the disc

The niobium discs used were 10 mm diameter. They were mechanically polished prior to chemical polishing measurements.

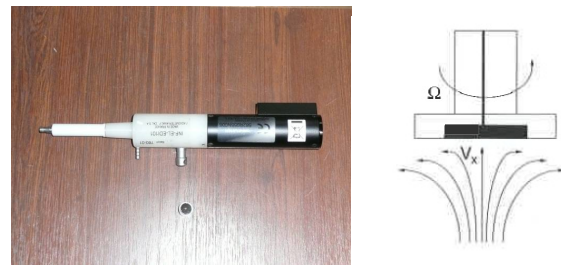


Figure 2: Rotating electrode device and the niobium sample (left) and schematic, from [6] of fluid distribution close to the niobium sample.

For each experiment, we measured the removal of a sample rotating in 900 mL of BCP mixture with controlled temperature. The removal is estimated by weighing the sample after/before the etching sequence. The duration of each sequence was 7 minutes. Measurements were done at 3 different temperatures: 3°C, 19°C and 33°C. For each temperature, the removal rate v (in $\mu\text{m}/\text{min}$) was estimated for rotation speeds between 25 rpm and up to 4500 rpm. The removals rates achieved as a function of the rotation speed are shown in Fig. 3 below:

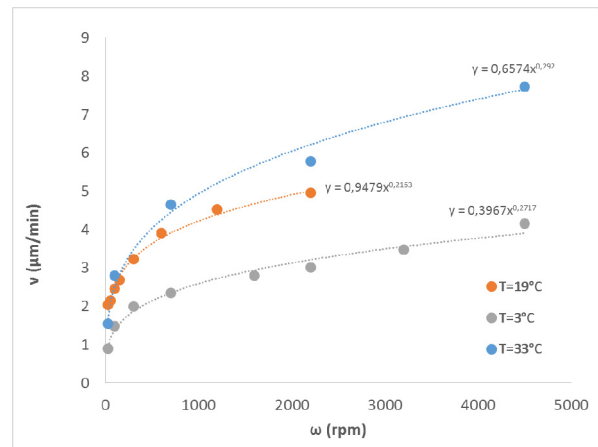


Figure 3: Removal rate v obtained at different rotation speeds and different temperatures.

The plots obtained might be fitted with a power law:

$$v = \alpha \cdot \omega^\sigma \quad (5)$$

with obtained σ between 0.22 and 0.29

We notice that v is strongly correlated to fluid velocity, especially in the range 0 $\mu\text{m}/\text{min}$ – 3 $\mu\text{m}/\text{min}$, which is characteristics of rates observed on cavities. Working at lower temperature promotes uniform removal since the span for v is reduced. For a given rotation speed, the removal rate is proportional to temperature (see Fig.4), similarly to results found in literature [7]. The proportionality coefficient depends on the agitation. For high rotation rates, the niobium removal is more sensitive to temperature. High dependence on temperature should be avoided since significant temperature discrepancy is generally observed during cavity treatment [5].

Content from this work may be used under the terms of the CC BY 3.0 licence (© 2017). Any distribution of this work must maintain attribution to the author(s), title of the work, publisher, and DOI.

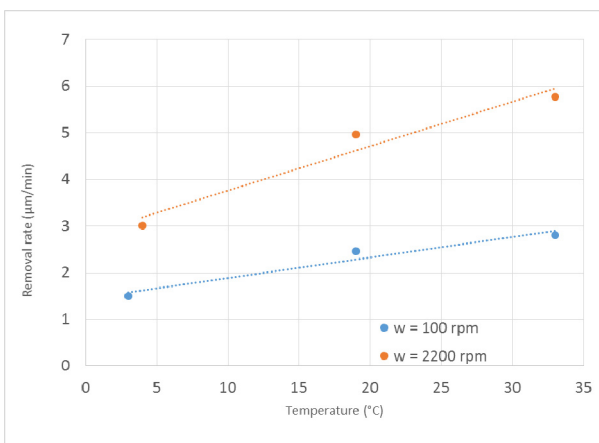


Figure 4: Removal rate as a function of temperature at two different rotation speeds.

We might conclude that low temperature and low agitation promote uniformity of removal.

EFFECT OF SURFACE GEOMETRY

Thickness measurements on elliptical cavities, polished in vertical configuration show strong asymmetry of the process. For upper sides of the cells, the removal is higher. As a result, the 200 µm bulk BCP is carried out in two sequences of 100 µm removal, with flipping of the cavity in-between in order to obtain symmetric removal.

We decided to study more in details the influence of the surface orientation on the removal rate. With this purpose in mind, we used a cylinder in niobium (diameter: 8 mm, height: 2.5 mm), immersed in BCP mixture with precise orientation (Fig. 5), and measured the niobium removal as a function of the location (see Fig. 6). The external surface of the cylinder was wrapped with acid-resistant adhesive, in order to only consider the contribution of the inner surface.

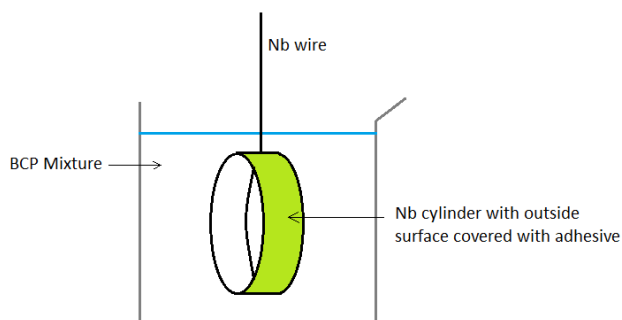


Figure 5: Set-up used for the experiment.

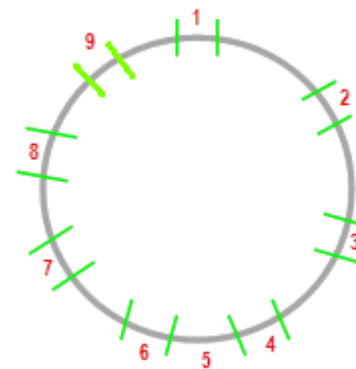


Figure 6: Different locations in the cylinder were the removal was investigated.

The cylinder was polished in two different configurations:

- A: With fresh acid at room temperature (21-23°C)
- B: With aged acid (~10g/L of niobium) and high temperature (30-40°C)

The thickness is measured by using an ultrasonic sensor, at different locations of the cylinder before and after chemical treatment. The obtained results are given in the graph below (Fig. 7).

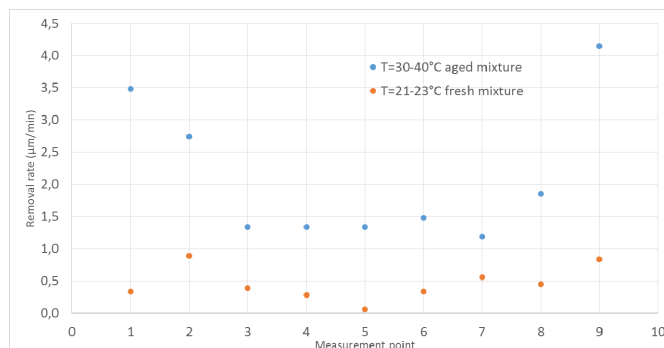


Figure 7: Removal rate in the cylinder in two different configurations: Lower temperature and fresh mixture and High temperature and aged mixture.

We observe that the removing profile varies significantly according to the acid temperature.

Case A: For a cold acid, the removal rate is quite low and the amount of released NO_x does not cause any turbulence. As a consequence:

- NO_x bubbles run along the surface and accumulate at the top of the higher area (location 1) of the cylinder
- Viscous by-products run down the surface and accumulate at the lower area of the cylinder (locations 4-5 and 6).
- In the upper half-cylinder, the surface is 'naked' (locations 2-8 and 9).

In cases a) and b), accumulation of reactions products (see Fig. 8) prevent active molecules from reacting with niobium and the removal rate is low.

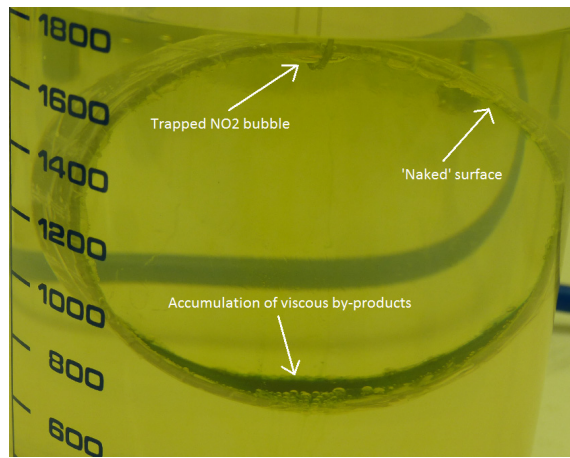


Figure 8: Different areas of a niobium cylinder, when immersed in fresh BCP mixture at room temperature.

Case B: When the acid is hotter, the removal rate is higher and amount of generated NO_x is responsible for turbulences in the acid mixture. As a consequence, we assume that no bubble is trapped in location 1 and that the accumulation of by-products in the lower half-cylinder is decreased. We observe that the removal rate in the lower half cylinder is uniform (locations #3-4-5-6 and 7). The removal rate is the highest at location #9. We assume that this high removal rate is due to faster gaseous flow (compared to location #1) at this location. In fact, after the sequence, clear bubbles stripes were observed at location #9.

If we exclude location #1 and #5, we might conclude that lower acid temperature promotes uniform removal rate along the surface.

EFFECT OF DISSOLVED NO_x

We discussed previously the two different types of elliptical ESS cavities (high and medium-β). For these cavities, the ratio surface/volume is different. So the influence of gaseous byproducts could be increased, in medium-β case, because of the lower volume of the cells. In fact, the difference in removal rates could be correlated to the gas concentration in the cells of the cavity. Furthermore, gaseous nitrogen oxides, also known as NO_x, are by-products of niobium polishing. NO₃⁻ ion is reduced in NO_x form with x<3. Contrary to hydrogen H₂, which is the major gaseous by-product during electropolishing process, NO_x is a strong oxidant, which can impact the kinetic of reaction. So we have carried out preliminary experiments on niobium samples in order to quantify the influence of NO_x on kinetics.

We decided to introduce additional NO_x close to the sample by oxidising copper samples in a closed recipient connected to the beaker with BCP mixture. Please see the set-up in Fig. 9.

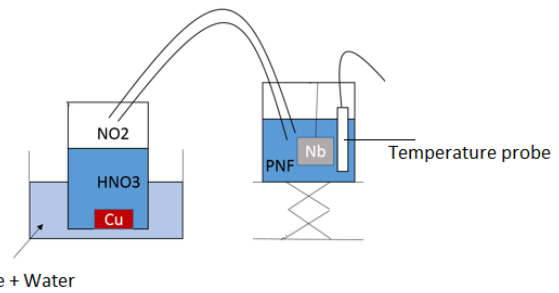


Figure 9: Set-up used for the experiment.

The removal rate for a parallelepiped niobium sample was estimated in different configurations:

- A: 200 mL H₃PO₄(85%) + 100 mL HF(40%) + 100 mL H₂O + NO_x
- B: sample in BCP mixture, no NO_x introduced
- C: 400 mL of BCP mixture, NO_x introduced

The duration of the etching was between 9.5 min and 10 min. The removal rates observed in each configuration are reported in Table 2.

Table 2: Removal Rate as a Function of the Mixture, with or without NO_x Introduced

Experiment	v (μm/min)
A	0,48
B	0,87
C	1,34

The mass removal in A experiment proves that NO_x are molecules which can play a similar role compared to HNO₃: Nb is oxidised into Nb₂O₅ which dissolves with HF. The chemical etching is achieved. Furthermore, experiment C shows that injection of NO_x in the BCP mixture generates an increased removal rate.

So we might anticipate that the higher NO_x concentration achieved during cavity treatment could be responsible for higher removal rate:

- High gaseous concentration will generate higher agitation of the acid mixture, resulting in increased kinetics, especially at the upper half-cell.
- NO_x will promote oxidation of the surface and also speed up the material removal.

We consider these as preliminary investigation and complementary experiments have to be carried out. In fact, the bath agitation resulting from the bubbling modify the fluid velocity and is also responsible for higher removal rate. So we plan additional experiments using dedicated commercial NO₂ bottles with precise amounts injected in the acid mixture. We also intend to inject neutral gas as N₂ in order to precisely evaluate the contribution of NO₂ on the kinetics.

CONCLUSION

Thanks to simple experiments, we have quantified the influence of several parameters on niobium chemical polishing.

- Removal rate is proportional to temperature but the coefficient depends on the fluid velocity.
- Removal rate is strongly correlated to fluid velocity, especially at lower Reynolds values. For higher temperature, the influence of fluid velocity is increased.
- Geometry/orientation of the surface is of paramount importance, because of accumulation of salts (in lower horizontal locations) or gas (in higher horizontal locations). The effect of the geometry depends on the velocity of the fluid.
- NO_x gases are strong oxidizing agents and are likely to locally increase the reaction rate. High local concentration in NO_x could explain the high removal achieved in upper half-cells during treatment of ESS resonators.

REFERENCES

- [1] G. Devanz *et al.*, "Manufacturing and Validation Test of IFMIF Low-Beta HWRS", Proceedings of IPAC2017, Copenhagen, Denmark, MOPVA039, pp. 942-944.
- [2] K. Elliott *et al.*, "SRF cavity Etching Development for FRIB Cavity", Proceedings of PAC2013, Pasadena, CA USA, WEPAC18, pp. 826-828.
- [3] L. Popielarski *et al.*, "Buffered Chemical polishing Development for the Beta=0.53 Half-wave Resonator at Michigan State University", Proceedings of SRF2011, Chicago, IL USA, TUPO057, pp. 526-529.
- [4] T. Tajima *et al.*, "Optimization of Chemical Etching Process in Niobium Cavities", Proceedings of American Society of Mechanical Engineers, International Design Engineering Technical Conference, Salt Lake City, Utah USA, 2004.
- [5] E. Cenni *et al.*, "Vertical Test Results on ESS Medium Beta Elliptical Cavity Prototype", Proceedings of LINAC2016, TUP106006, pp.631-633.
- [6] J-P. Diard, B. Le Gorrec and C. Montella, "Cinétique Electrochimique", editions Hermann, 1996,
- [7] D. Bloess, "Chemistry and Surface Treatment", Proceedings of SRF1984, Geneva, Switzerland, pp.409-426.