Abstract
The highest achievable accelerating field in Superconducting Radiofrequency (SCRF) cavities is proportional to the maximum surface magnetic field on the cavity wall, the so-called superheating critical field $B_{sh}$. The highest experimental field ever obtained on actual cavities made from bulk niobium material exceeds 170 mT, very close to the estimated theoretical $B_{sh}$ of 200 mT. Other superconducting materials exhibit lower critical fields while thin film technology suffers from high losses exhibiting a quality factor $Q$ strongly degraded at high fields.

However, the niobium cavity behavior at high fields is not yet fully understood. Anomalous losses may appear at fields higher than 100 mT, even upon taking a high purity niobium with extremely low impurities contents (high RRR). That indicates a degradation of the superconducting properties at high fields in the very first 50 nm of the metal surface. Experimental evidence is given here for the great importance to this regard of the final preparation of the cavity including chemistry and temperature. In particular, the possible major role of the first layers of niobium oxides and sub-oxides during and after chemistry is pointed out.

1 INTRODUCTION
An important R&D work on SCRF cavities worldwide is trying to further increase the accelerating gradient, a major figure in the design and cost of future high-energy accelerators. It is well known that the highest RF field experimentally achieved uses bulk niobium cavities, as it will be again shown in this paper. Pure niobium is still the most appropriate metal for building SCRF cavities. Up to now, any trial to replace it by another higher critical temperature material has failed. Even thin film technology has ended up using pure niobium films[1], with results however significantly lower than for thick metal. Therefore, this paper will focus on the behavior of bulk niobium cavities at magnetic surface fields exceeding 100 mT. This is called high fields, corresponding to the state-of-the-art accelerating gradient $E_{acc}$ of 25 MV/m in $\beta=1$ cavities (like those for electron accelerators).

The critical magnetic field in RF is assumed to be the superheating field $H_{sh}$ [2], generally exceeding the critical thermodynamic field $H_c$. It is believed that the nucleation time for creating and moving a vortex in the material is higher than the RF period [3]. But the experience fails to confirm this hypothesis [4], especially at low temperatures ($T = 0K$).

After describing what are the limitations preventing a superconducting cavity to sustain high fields, a set of crucial experimental facts are described. Then some explanation and hints are proposed that may bring some light to what could be done in order to reach the ultimate field limit in bulk niobium cavities.

2 LIMITATIONS

2.1 Field Emission (FE)
The two main limitations for achieving high gradients in SCRF cavities are the quench and field emission. Important progress has been made over the last ten years to nail down the reason of low FE threshold fields in some cryogenic RF tests. It has now been established that particle contamination is the first cause of FE in cavities [5,6]. Moreover, the protrusion on protrusion model [7,8] explains quite well the electric field enhancement observed experimentally. As a result, a thorough fight against particle contamination has led many labs to install effective high pressure rinsing (HPR) systems together with extremely careful assembly in clean room area [9]. Combining all these procedures result in a net gain in FE threshold. As an example, Figure 1 shows a cavity where the surface peak electric field exceeds 70 MV/m without any FE sign (no X-ray emission, no electron signal on the biased pick-up probe). Therefore, although FE is still a major burden for actual multicell cavities in a real accelerator environment, at least the problem is understood and ways to overcome it are found. While most laboratory tests on cavities were FE limited a few years ago, the statistical fraction of FE limited tests has considerably dropped since then.

![Figure 1- FE free cavity.](image)
2.2 The Quench

The Quench is a sudden loss of superconductivity in the niobium cavity wall. Transition to the normal state can occur if the surface magnetic field exceeds a given critical field. This critical field is called superheating field $B_{sh}$ in the radiofrequency regime and may be different from the static critical fields $B_{c1}$ and $B_{c2}$ of a type II superconductor like niobium or from the thermodynamic critical field $B_c = 199 \text{ mT}$ [10,11]. Many theoreticians and experimentalists are debating since a long time about what is the actual value of the superheating field $B_{sh}$ compared to the critical field $B_c$. Some specific experiments have shown that while close to $T_c$, $B_{sh}$ can exceed $B_c$, it falls down even below $B_{c1}$ at $T = 0 \text{ K}$ [4]. At magnetic fields over $B_{c1}$, magnetic flux penetration inside the material in vortex form may induce additional power losses leading to the quench. On top of that, the quench is not a purely magnetic phenomenon. It is a thermo-magnetic process involving thermal instability due to power dissipation in RF field. Heat flux generated at the inner surface ($Q = \frac{1}{2} R_s H^2$) has to be conducted through the niobium wall to be removed by the helium bath. Given the wall thickness $t$, the thermal conductivity $\Lambda$ and the Kapitza conductance $h_k$, the inner surface temperature $T$ will be solution of the equation:

$$T - T_{\text{bath}} = \frac{1}{Q} \left[ \frac{t}{\Lambda} + \frac{1}{h_k} \right]$$

Both the surface resistance $R_s$ and the thermal conductivity $\Lambda$ are rapidly varying with temperature and the above equation might give no solution in the superconducting state above a given field. This defines the “uniform” quench field level, which may vary according to the heat properties of the material. For example, the quench field is much higher in the superfluid regime ($T_{\text{bath}} < T_s = 2.17 \text{ K}$) than in the boiling helium regime due to the excellent heat removal of a superfluid bath. Accordingly, the quench may also vary with the niobium purity (as determined by the RRR or Residual Resistivity Ratio), the heat treatment (under vacuum at $800^\circ \text{C}$ for hydrogen removal or from $1000^\circ \text{C}$ to $1400^\circ \text{C}$ for post purification) or the chemistry and preparation as it will be demonstrated later on.

However, the observed quench field of cavities is usually lower than the expected calculated one assuming the uniform heating case. At the same time, a localized heating spot is detected by temperature mapping indicating that a thermal instability is occurring driven by a micron-size defect. More complete thermal analysis confirm that this is indeed the case and can explain why the quench changes with the heat properties of the helium bath [12,13,14,15].

It will be shown here that purifying the niobium from its impurities and reducing the defects during the sheet production has led to tremendous improvement in the average maximum field limit. It will also be described how the quench field value vary with the niobium purity (RRR), the heat treatment and the cavity preparation (chemistry and temperature). Quench fields exceeding 170 mT have been measured on several electropolished single-cell cavities, closely approaching the thermodynamic critical field of niobium $B_c = 199 \text{ mT}$. It should be also emphasized that extremely low residual resistance can be reproducibly achieved on actual superconducting cavities. Figure 2 shows an example of such a high Q0 cavity obtained after a specific chemistry preparation using a very high RRR niobium.

Figure 2 – Residual resistance as low as 0.5 $\text{n}\Omega$ is actually measured on large area cavities, giving an intrinsic quality factor $Q_0$ exceeding $2.10^{11}$.

3 EXPERIMENTAL FACTS

3.1 RRR

It has been experimentally observed quite early in SRF community [16,17] that the quench field improves when one uses higher RRR material sheet for cavity fabrication. Figure 3 shows $Q$ vs. $E_{\text{acc}}$ curves obtained for different RRR cavities having the same cavity shape at the same frequency (1.3 GHz). The quench field definitely increases with the RRR. A low RRR cavity (reactor grade RRR30) quenches at 9 MV/m. Whereas for the highest RRR (> 500), the quench value could not be reached even at the maximum field exceeding 30 MV/m. Note also that the $Q$ value at low field steadily increases with the RRR as pointed out in previous observations [18]. For low RRR values, the $Q$ curve starts showing a rather strong slope at low field. This slope indicates a non-quadratic loss increase with field and can be observed whenever the superconductor surface is degraded. For example, a cavity as received after fabrication will exhibit that behavior due to the damage layer obtained following the mechanical cold work during forming. Only a heavy chemistry removal (over 100 $\mu\text{m}$) will get rid of that slope. In the same manner, thin film deposited superconductors (like niobium on copper) or seamless cavities (hydroformed or spun) will almost always exhibit that kind of slope starting at low fields.
Figure 3- The quench limit strongly depend on the niobium RRR value.

3.2 Heat Treatment

Two different types of heat treatment of the niobium cavity in a vacuum furnace have been extensively used. The "medium temperature" heat treatment (typically 800°C, 2 hours) is generally used to get rid of the Q-disease [19]. Over 600°C, hydrogen starts getting out fast from the metal. Lowering the hydrogen concentration avoids the formation of the hydride thermodynamic phase during cool down at temperatures between 160 K and 100 K. The result of this heat treatment on the quench value is not established. Surprisingly, some cavities do show an increase in performance while most of the time, the quench does not change. The second "high temperature" heat treatment is used to purify the niobium from its light impurities (O, C and N) using an evaporated getter (for example Ti). Heating temperature range from 1000°C to 1400°C depending on the available time. After that treatment, the RRR is higher (actually very high RRR can be achieved [20]) and consequently the quench field increases. Significant improvement in field value can be obtained following that heat treatment like shown in Figure 4.

Unfortunately, that high temperature treatment has a major drawback. The grain growth is so important at those temperatures that the mechanical properties of the niobium are seriously degraded. The yield strength decreases, the cavity soften and that induces additional problems mainly in pulsed operation due to the frequency shift with field (so-called Lorentz force detuning). The large grain size (a few mm) will also induce uneven etching upon using the standard buffered chemical bath (called BCP or FNP 112 after fluorhydric, nitric and phosphoric acids). Because different grains have different crystallographic orientations, the grain structure is highly revealed, their boundaries are quite well marked showing sharp edges and steps from one grain to another. That is the reason why one would prefer the lower temperature (1000°C) treatment to minimize this drawback. It is also the reason why a study of a new type of chemical etching bath have been started to minimize the uneven etch among grains on heat treated cavities.

Although the field was improved, a Q-slope appears at high field without any sign of field emission or X-ray signal [21]. These anomalous losses at high fields have been shown to be more or less uniformly distributed on the cavity wall.

3.3 Electropolishing

A surprising experimental result came from KEK in the mid 90's: Accelerating gradients as high as 40 MV/m have been obtained on electropolished (EP) cavities even with "moderate" RRR values of around 200 [22,23]. Electropolishing have been used since long time in Japan and have also been investigated elsewhere [24], but other limiting factors at that time were inhibiting the high field capability of this chemical preparation. The Q-slope at high fields on EP cavities happened to be much less of a problem than on the standard BCP chemistry used in most other labs. In fact, it turned out that the cavity preparation procedure used at KEK usually includes a final baking at a temperature around 85°C.

The KEK results have been since widely confirmed, particularly through crosscheck laboratory measurements at KEK, Saclay, DESY or CERN [25]. A specific DESY/CERN/Saclay collaboration has been setup to evaluate the benefit of electropolishing with a large number of single-cell cavity tests. Detailed description of the procedure used and the different results obtained can be found elsewhere [26]. Some typical results are plotted in Figure 5 and can be summarized as follows: The average quench field exceeds 150 mT, significantly higher than the fields obtained with any usual BCP chemistry. Also the reduction in Q-slope at high fields after a 120°C baking under vacuum is much more effective.

Figure 4- A high temperature heat treatment improves the quench field value.
Electropolished Single-Cell Cavities, Test at CEA/Saclay, CERN or DESY
Collaboration DESY/CERN/Saclay, F = 1300 MHz

Figure 5 – Results of four different electropolished single-cell cavities. The average quench field value is around \(E_{acc} = 40 \text{ MV/m}\).

3.4 Baking

As the effectiveness of baking on electropolished cavities was demonstrated [27], this simple treatment after chemistry and high pressure rinsing has been investigated more thoroughly. The cavity is mounted in the clean room, evacuated, then baked on the vertical cryostat insert either outside or inside the cryostat. Baking temperature is typically 120°C for a couple of days. As stated previously, baking is much more effective on an EP cavity. The Q-slope at high field is significantly lowered (Figure 6).

Figure 6 - Effect of baking on an electropolished niobium cavity. Baking a standard BCP cavity would result in an almost negligible change in field performance.

In conjunction with the reduction of Q-slope, one can notice that the surface resistance at 4.2 K (boiling helium at atmospheric pressure) is lower after baking, indicating a lower BCS resistance at that temperature. At the same time, the residual resistance at low field is increased and the corresponding quality factor \(Q_0\) degraded. Also, while the cryogenic test was generally power limited before baking, the quench is always hit after baking, although the RF power injected in the cavity is lower. That is even more striking when the baking temperature is increased.

Figure 7 shows the cavity quench field degradation with increasing baking temperature. The higher the baking temperature, the lower the final quench field.

Figure 7 - The quench field of a SCRF cavity is degraded when the baking temperature is increased. Note that the no baked curve is just power limited (no quench).

3.5 Chemistry

Since a few years, other type of chemical baths, different from the standard FNP112, have been investigated, mainly at CEA Saclay [28]. Many different acid mixtures or preparation have been tried first on samples and then eventually on single-cell cavities. Very interesting results have been published elsewhere or are currently under publication, but the main feature that needs to be stressed here is the fact that the quench field value of a SCRF cavity can be moved if the chemistry is changed. This is not quite surprising though because electropolishing is after all a different chemical etching procedure. But it is worthwhile to point out that this statement is also true for a non-EP cavity as well. As a striking illustration, a cavity has been successively prepared using three different chemical baths. And the corresponding quench field have been measured each time to be different for each different chemistry preparation (Figure 8).

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Figure 8 - The quench field of a cavity may vary with the chemical bath preparation; That particular cavity was not heat treated at high temperature.
4 DISCUSSION

In this section, some explanation or hints are derived, synthesized from the accumulated knowledge and the experimental facts described above. The quench field value and the Q-slope at high fields are deliberately discussed separately because the experimentally mixing behavior sometimes observed has previously misled to quite confusing interpretation.

4.1 Quench

Although the real issue is far more complex, the RRR ratio, related to impurities contents, especially light ones (O, C, N), is obviously an important parameter. Generally speaking, a poor RRR material exhibits poor superconducting properties. Major superconducting parameters can be affected like the critical temperature $T_c$ (loosing for example -1 K/at. % of oxygen [29,30]), the critical field $H_c$ or even the residual resistance [18]. Hence, one needs to get very high RRR material to approach the pure niobium theoretical limits. And the purer is the better. Also, the high RRR material favors the heat conduction through the cavity wall as the thermal conductivity steadily increases with the purity. So the temperature drop between the helium bath and the inner surface is lower for high RRR metal, helping to thermally stabilize local defects at high fields.

That explains the experimental facts observed in both Figure 3 and Figure 4. However, these general statements, while always true, have to be evaluated for each specific case. For example, the critical temperature reduction is very small for all RRR higher than 200 ($\Delta T < 0.01$ K) and can only be measured by extremely precise experiments. In the same manner, the defect stabilization is for example frequency dependent as stated and calculated previously [31]. This is also supported by some experimental results. Q-curves and quench field values are different at different frequencies even for cavities made from the very same RRR sheets and prepared in the same manner (identical chemistry – see Figure 9). Although a low frequency cavity has a much bigger area, and consequently, has a much higher probability to include larger defects, the defect stabilization is more effective at lower frequency, and hence the quench field is higher, as expected from simulations. In a similar way, baking will diffuse some light impurities from the very outer niobium surface inside the material, as shall be seen in the following discussion (§ 4.2). The layer where the diffusion take place will exhibit a degraded RRR and consequently its superconducting properties will be degraded. That is why the quench value, the BCS resistance at 4.2 K and the $Q_o$ value at low field are all three lowered after baking. Baking at higher temperature (or for longer time duration) will also result in additional degradation of the RRR in the diffused layer and is completely consistent with the observation from Figure 7.

Finally, the last major effect on the quench field value of a cavity is the chemical preparation. Each chemical etching should in principle lead to a different quench value, like shown in Figure 8 where quench fields from 70 mT to 130 mT are obtained on the same cavity using different chemistry. However, the largest difference is observed when comparing the standard FNP 112 chemistry (70 mT) with the EP one (over 150 mT) on a non-heat treated cavity. A simple and straightforward explanation can be found here when looking at the micrographic pictures of two niobium samples etched with the two different chemistries [28]. The EP sample is very bright and show no grain boundaries while the heavily etched BCP sample has very pronounced grain boundaries with extremely sharp edges (Figure 10). RF calculations [32] do show that in this case a magnetic field enhancement is expected right on the edges, with the right order of magnitude (factor 1.8). If this theory is confirmed, that reduces the difference in quench field to a mere geometrical feature as the local magnetic field should be probably the same for any chemistry. Due to the difference in the enhancement factor, the ratio between the macroscopic field and the local field is lower for the BCP cavities, leading to a lower accelerating quench field. That explanation may also apply for the different bath mixtures (Figure 8). As a matter of fact, the microscopic observations made on samples etched with these different baths are also quite different (grain boundaries, step heights, shining and roughness are quite different).

At this point, a partial conclusion can be drawn. Ways for achieving the highest possible quench field in niobium may be recommended. The material should have the highest possible purity (highest RRR), the chemistry should be the smoothest possible (no step edges) and the cavity should not be baked after preparation (avoiding impurity diffusion).
Standard BCP Chemistry on niobium: Sharp boundary edges are clearly visible. Figure 10 - Micrographic picture of a BCP etched niobium sample [from 28] and magnetic field enhancement calculation at the edge of a step in a RF cavity [from 32].

4.2 Q-slope

Unfortunately, when trying to apply the above recipe, the Q-slope at high field will limit the cavity performance. The origin of these anomalous non-quadratic losses is still quite mysterious but some hints can be given here. First of all, Q-slope in many cavities is observed even at low field whenever superconductivity is degraded. This is the case for low RRR material (Figure 3) but also for thin films [33] or seamless cavities [34]. This slope is generally attributed to defects (impurities, dislocations from cold work, grain boundaries [35]) in the very first 50 nm from the inner surface. The fact that only a mild baking (at 100°C) may affect the high field Q-slope is also pointing towards a surface effect. In addition, while after baking a high pressure rinsing have no effect, a pure HF bath only a small one, a 1 µm chemistry is enough to remove all the baking effect and brings back the cavity to a similar state where it was prior to baking.

On the other hand, while studying the very first oxide layer growth on a single crystal niobium, I. Arfaoui [36] have shown using UV-ray photon spectroscopy that the two first layers of the niobium metal on the surface right underneath the oxide, are heavily charged in oxygen dissolved atoms. He calculated that the upper two first layers of the niobium metal contain over 10% of oxygen (Figure 11). If now one considers a very thin layer (for example 2 nm) of a heavily degraded superconductor on top of an extremely pure niobium, one can analyze the overall behavior as a two-layer superconductor model. Because of the non-uniformity in the material depth, the order parameter \( \Omega \) has to be calculated [18] following the equation:

\[
\lambda \frac{\partial Y}{\partial z} + Y^2 = \chi, \quad \text{where } \chi = \Omega + i\sigma (1 - \Omega).
\]

\( Y \) is the admittance giving the corresponding surface resistance by \( R_s = \text{Re} \left\{ \frac{i\Omega Y}{\lambda} \right\} \).

Due to the fact that the first heavily degraded layer thickness is much smaller than the coherence length, the proximity effect makes Cooper pairs survive even in the bad layer. That is true up to a given magnetic field, \( B_{c1} \), much lower than the superheating field in the pure niobium region and this is most probably the value at which the Q-slope starts showing up.

Now the baking effect. When heating at relatively low temperatures (100°C), and apart from hydrogen (which is mobile even at room temperature), only the light impurities embedded in the niobium metal may very slightly diffuse. For example, oxygen can travel up to 50 nm in distance after heating at 120°C for 48 hours (Figure 12). But that is enough to affect the superconducting properties of the cavity.

As a consequence of baking, the "bad" superconducting thin layer is spread over the whole bulk niobium at distances of the order of the London penetration depth (50 nm). Instead of having a very good and pure superconductor covered by a "bad" layer, one ends up with a more or less homogeneous superconductor with an "averaged" impurity content in the electromagnetic field penetration region of interest. The Q-slope is therefore decreased, at the expense of a reduced quench field and a higher residual resistance. An optimum in the "pollution"
can be found in order to reach the maximum achievable quench field. This picture is summarized in the next figure (Figure 13) and is consistent with all the experimental observations described above.

![Diagram of quench field and Q-slope behavior](image)

**Figure 13 - Schematic of the thin "polluted" layer explaining the Q-slope behavior. After baking, the pollution is diluted up to a depth of the order of the London penetration.**

If this scheme is confirmed, the oxide growth on the niobium metal has to be of great importance. The polluted layer underneath the oxide is connected to the sub-oxides appearing at the interface metal-oxide (Nb$_3$O and Nb$_5$O). The chemistry used should also affect the amount of dissolved oxygen, together with the preparation right after removing the cavity from the chemical bath. One must remember that after removing the cavity from the bath, an acid film is still lying on its surface. After rinsing in ultrapure water, the very first oxide layer is growing quite rapidly in just a few minutes. These steps may be crucial for the formation of the polluted layer.

The question of how to reduce (if not suppress) this polluted layer is now open. If one cannot avoid having an oxide at the niobium surface (pure metallic surface could not withstand air exposure), is it possible at least to grow a "good" oxide, free from any polluted layer? The answer to this question will ask for further fundamental studies concerning surface treatments, highly precise surface analysis and many chemistry development and most probably long time.

**5 CONCLUSION**

After solving the 100 K effect and considerably reducing the field emission limitation in SCRF cavities, light is brought up to understand what affects the quench field and the Q-slope at high fields in superconducting bulk niobium cavities. It is shown that the quench is mainly driven by local defects, impurity contents and geometrical consideration (sharp grain boundary edges). While the Q-slope seems to be connected to a very thin polluted layer at the metal/oxide interface. The best preparation presently available is to perform electropolishing chemistry, then to dilute the contaminated pollution in the material bulk by baking barely enough to avoid too much quench degradation. But this is a kind of makeshift. The ideal preparation would be to try to suppress surface pollution by growing a proper oxide on a very high RRR niobium.

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