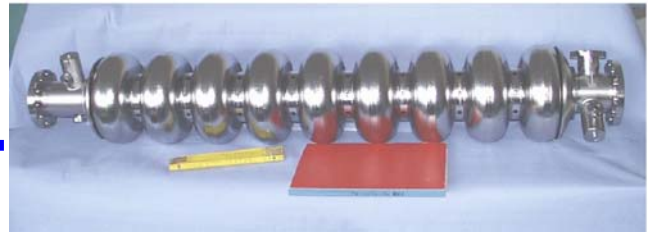




SRF



Deliverable 5.2.4.8: “Final report on industrial electropolishing”

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DESY

Abstract

The standard method to fabricate superconducting cavities for accelerator systems consists of shaping Niobium (Nb) sheets to cups, electron beam welding (EBW) the different Nb parts to a cavity, cleaning the inner surface of the cavity by buffered chemical polishing (BCP) or by electro polishing (EP), final cleaning by high pressure water (HPW), bake at moderate temperature around 140°C and final assembly under clean room conditions. So far the EP treatment has proven to reach higher gradients as compared to BCP. Therefore prototypes of EP installations have been designed and used at different laboratories. At DESY such an EP installation is in operation since several years.

The goal of this task was to explore and optimize the important operating parameters of the DESY EP system and to transfer this technology to industry. Furthermore methods of quality control of the EP acid mixture were investigated in collaboration with the chemical company Henkel.

Acknowledgements

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I Introduction

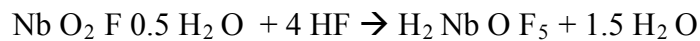
The niobium electropolishing process has evolved from the original Siemens recipe over the last 2 decades. Today electropolishing is considered to be the optimum treatment for cleaning and smoothening the surface of superconducting Niobium cavities for accelerator application.

In the basic electropolishing set-up of Figure 1 for a single cell cavity, the niobium cavity is the anode (+) and the hollow coaxial cathode (-) placed along the cavity beam axis is made from pure aluminum (1100 series). The electrolyte is a mixture of hydrofluoric and sulfuric acid in a volume ratio of 1:9, using typical commercial strengths HF (40%) and H₂SO₄ (98%). As current flows through the electrolytic cell, the niobium surface absorbs electrons and oxygen to convert to niobium pentoxide which subsequently dissolves in the HF present in the electrolyte according to the following equations.

Oxidation



Reduction



Hydrogen evolves at the cathode and rises to the electrolyte surface. Neutral H atoms and the stream of H₂ gas can also be entrained in the electrolyte to reach the anode. By placing the cavity in a horizontal orientation, and filling the cavity with acid (60%), the H gas produced at the cathode can be efficiently swept out from the volume of the cavity with nitrogen gas flow, resulting in minimal exposure to the niobium surface in contact with HF. This minimizes the danger of H absorption into the bulk niobium. A perforated Teflon coaxial tube (or porous Teflon cloth) surrounds the hollow aluminum cathode to further inhibit the evolving hydrogen gas from mixing with the electrolyte and reaching the niobium surface.

Since only about half the cavity surface is immersed in electrolyte the cavity must be rotated to polish the entire surface. Leak tight rotary sleeves at the flanged ends are essential to contain the acid mixture. The acid circulates from the cavity to a large acid barrel cooled with a heat exchanger which maintains the acid temperature. A significant acid chilling system with adequate heat exchangers must be used to maintain the acid temperature during the process.

A membrane pump drives the acid mixture through the cooled barrel to the inlet of the hollow cathode. For some time a 1 μm pore filter was installed at this location, but Sulfur did plug this line in short time. From here the electrolyte fills the center of the cells through openings in the hollow cathode. The acid returns to the storage tank via an overflow. Figure 2 shows a generic scheme of acid flow for a 9-cell EP system.

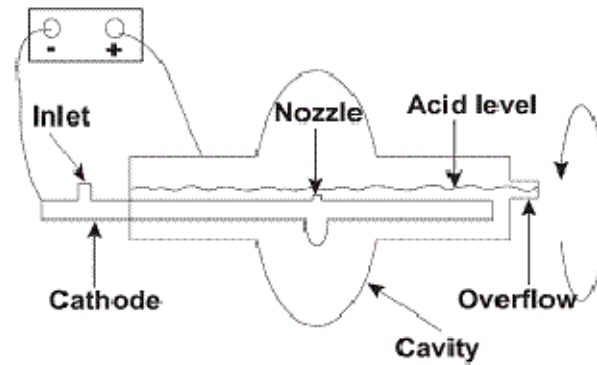


Figure 1: Basic setup for electropolishing

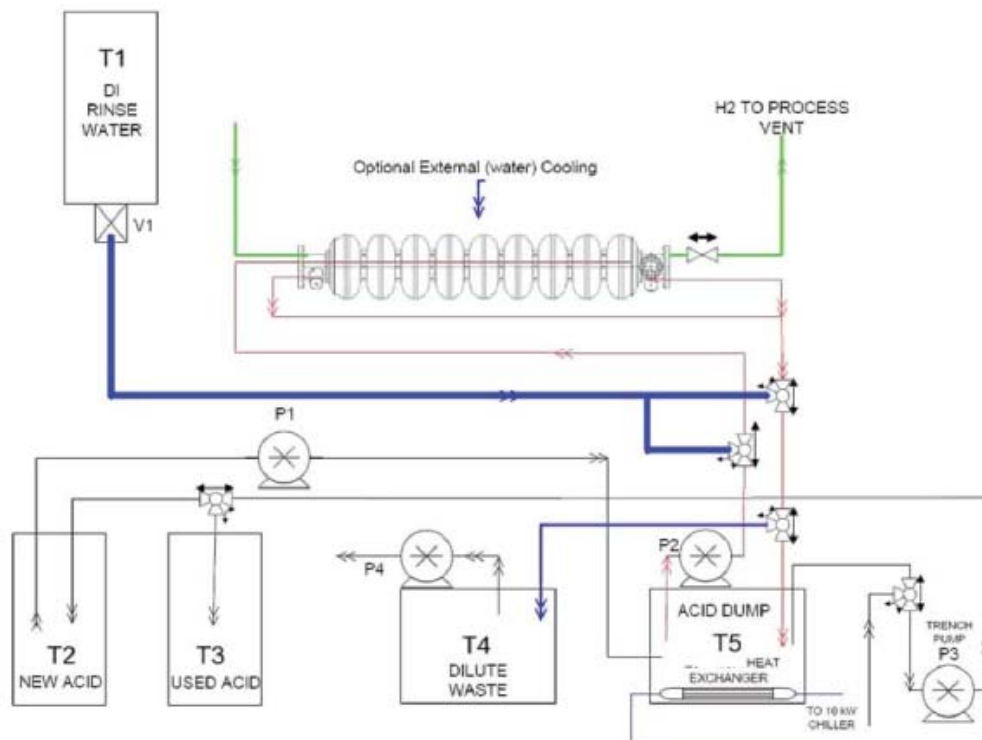


Figure 2 Principle scheme for 9-cell cavity electropolishing

II The DESY 9-cell electropolishing installation

Figure 3 shows the 9-cell EP systems at DESY. The system includes the rotation device, electrode contacts, plumbing connections and diagnostics. All components exposed to acid are made from Teflon (PTFE) material which is inert against corrosive acid. In addition the EP system includes a handling frame which allows lifting the cavity into the vertical position for final acid drainage after EP. The current leads are made from copper. The electrical connections to the cavity are sliding contacts made from a copper carbon alloy.

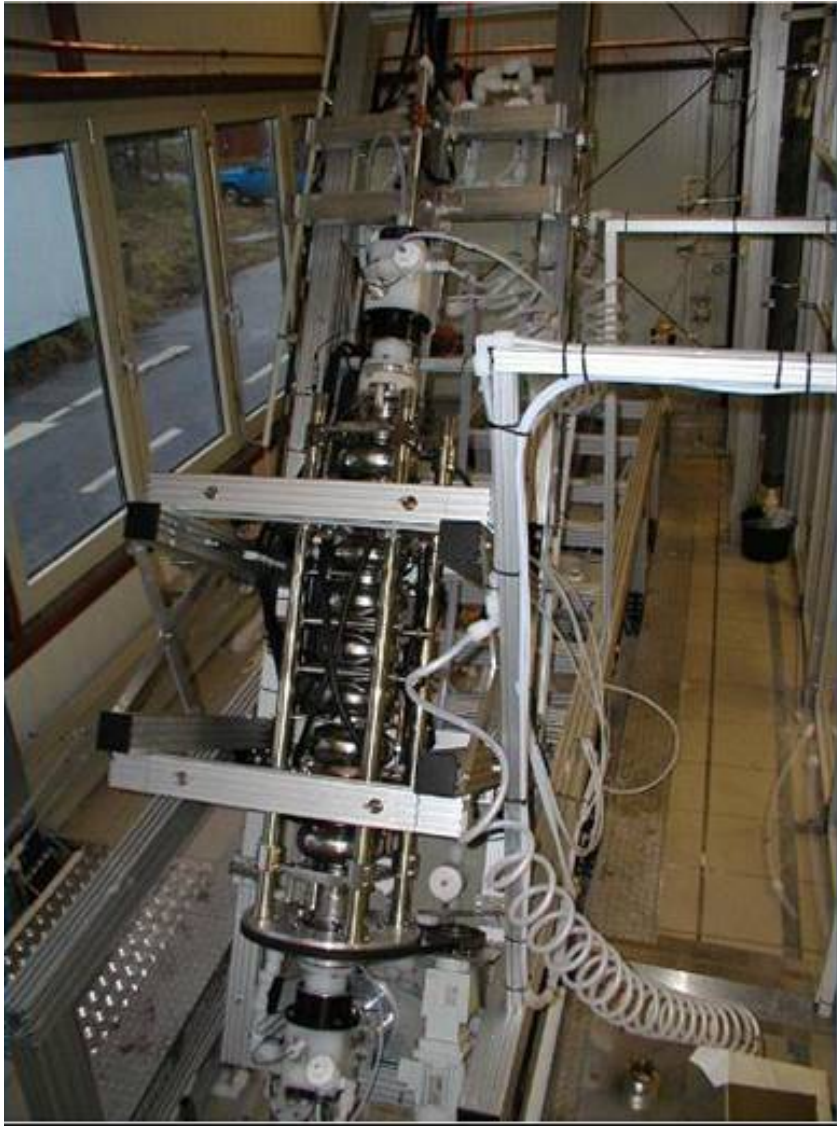


Fig. 3 DESY EP installation during draining the acid

After the assembly of hardware for the rotation device (see figure 4 and figure 7), electrode contacts, plumbing connections and diagnostics the cavity is filled with acid through the circulation system, and the level is maintained at ~60 % volume completely covering the cathode. Electrolyte temperature is adjusted to the appropriate starting temperature. The cavity rotation is switched on and a fluid leak check is done.

DC power is turned on and voltage is set to ~17 (15 to 18) volts constant voltage. The temperature is controlled (equal or below 35° C) by the heat exchanger and / or by changing the acid volume. The cavity is processed for a sufficient time to adequately remove 10-20 μ m from the equator. A typical time for this amount of etching is 75 minutes plus about 45 min for start (heat) up.



Figure 4 Details of the EP mechanical frame at DESY.

- (1) timing belt disc,
- (2) disk for sliding current transmitter)

When the desired amount of niobium material has been removed, the current is switched off. The rotation is stopped and the cavity is put into vertical position to drain the acid mixture. The draining process takes about 1-3 minutes.

The cavity is then filled and drained several times with DI water until the pH of the exiting rinse water is raised to a level of 4 to 5 depending on the system design. This exchange of water on the surface followed by draining is the fastest method to achieve higher pH on the cavity surface. The cavity is then rinsed again by overfilling for ~60 minutes.

III Cathode design

In order to prevent excessive hydrogen from entering the niobium during processing and to reduce etch rates within the end groups, the cathode must have shielding at various places. This shielding is implemented differently at each laboratory, and there is no unique solution. Generically, the shielding is accomplished using a combination of Teflon material or tape and Teflon coated materials and wrapping the cathode at various locations to reduce the current density at those locations. Typically, the cathode has a perforated cloth attached either standing off from the cathode by Teflon blocks or tied around it via a Teflon coated string. The purpose of this cloth is to break up hydrogen bubbles which are formed on the cathode and which will propagate towards the cell walls following the ion movement. Additionally the cathode is shielded at the iris and in the end groups to help reduce the etch rate at those locations.

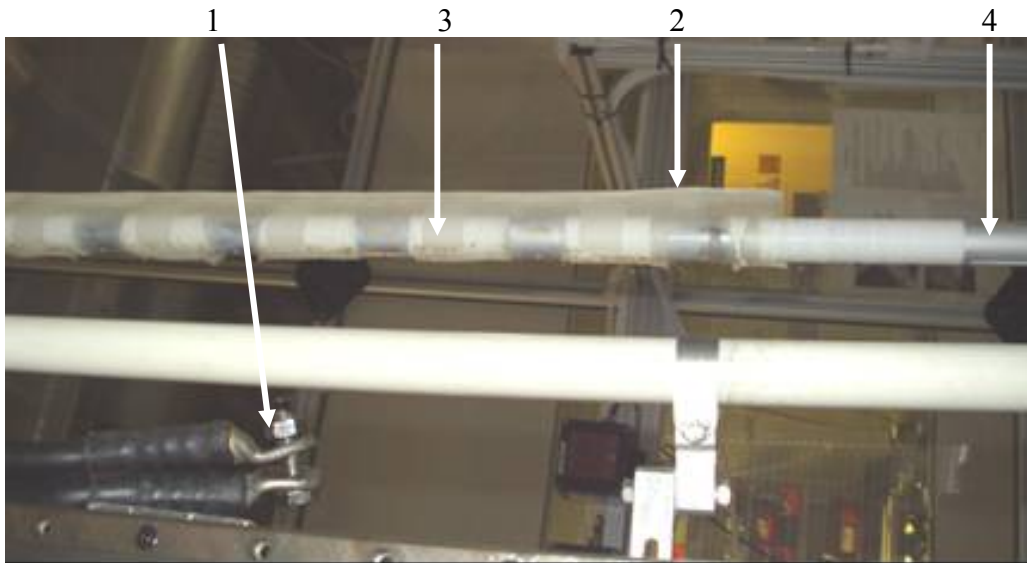


Figure 5: Shielded cathode of the DESY EP installation

- (1) current leads towards sliding connector;
- (2) PTFE net covering the electrode,
- (3) Teflon insulator covering electrode in the iris region)
- (4) Pure alumina electrode

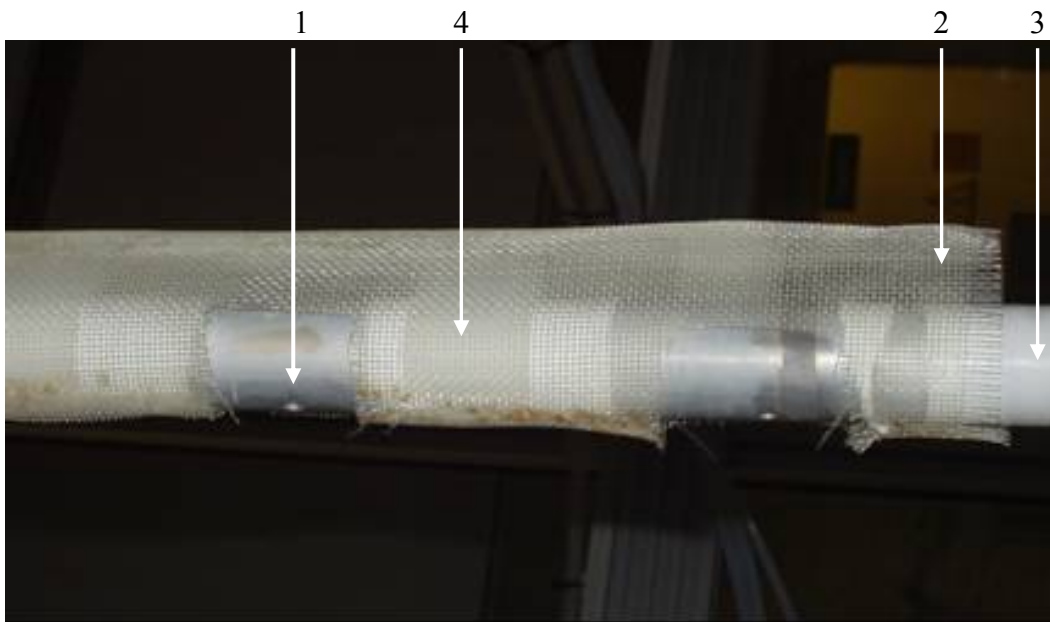


Figure 6 Details of the new EP electrode at DESY

- (1) acid injection hole located on top of cavity equator;
- (2) PTFE net covering the electrodes;
- (3) Teflon insulator covering electrode in the beam tube area,
- (4) PE spacer holding the TEFLON Nitrogen overlay tube)

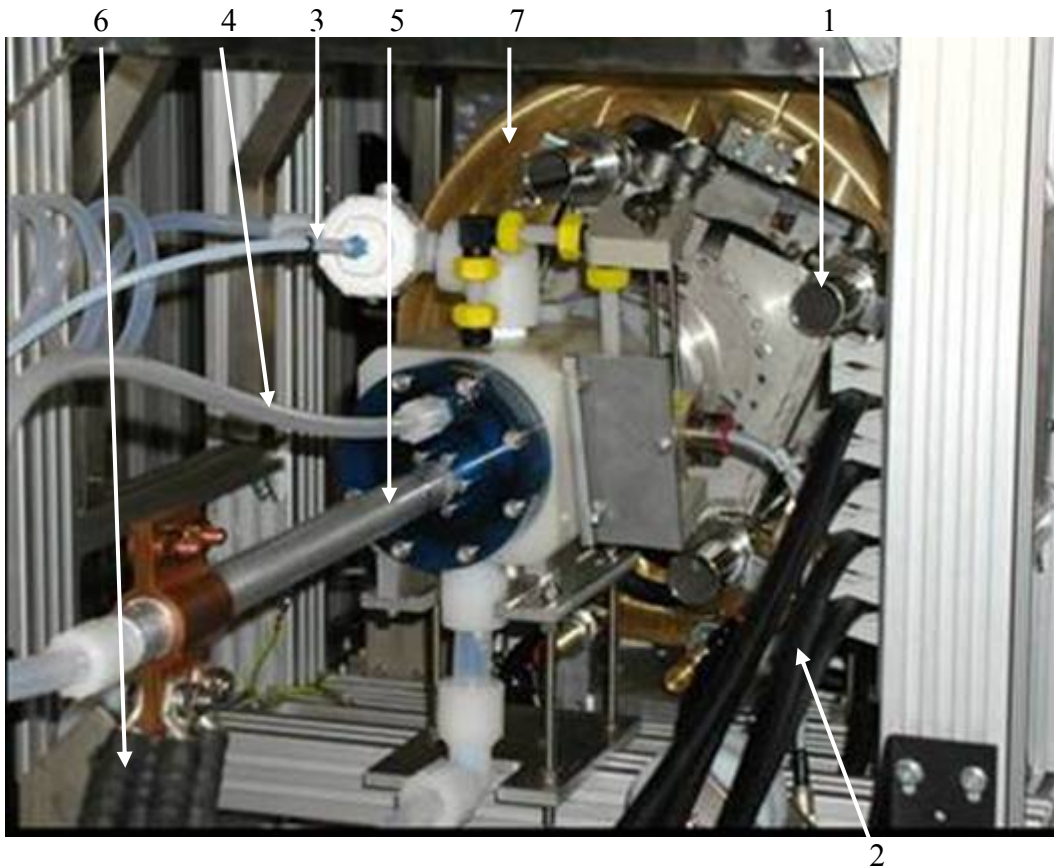


Figure 7 Cathode feed trough at the beam pipe flange

- (1) cavity frame,
- (2) current leads towards sliding connectors;
- (3) gas outlet towards exhaust cleaner for nitrogen, hydrogen and evaporated HF;
- (4) Nitrogen overlay inlet pipe;
- (5) pure alumina electrode,
- (6) current connection to pure alumina electrode;
- (7) disc for sliding current transmitter)

Shaping of cathode geometry

Without shaping the electrode geometry the removal rate at the iris is considerable higher than at the equator region. Therefore the code “Elsy2D” was used to optimize the cathode geometry for a more uniform surface removal rate.

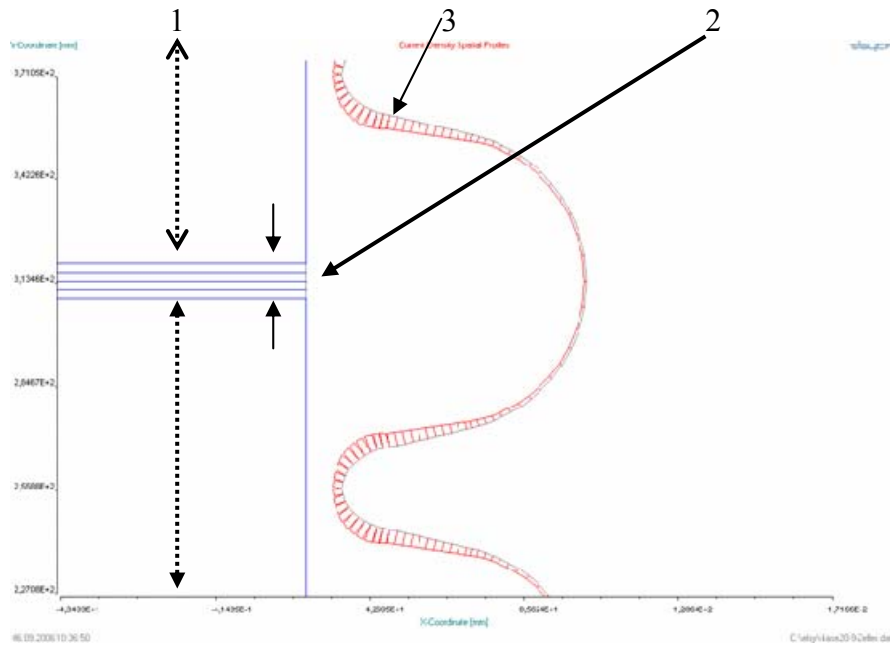


Figure 8 Plane electrode with improved ratio of shielded and unshielded regions (code “Elsy2D”)

- (1) half size electrode shielded region;
- (2) unshielded region with equi-potential lines;
- (3) distribution of current density over the cavity shape

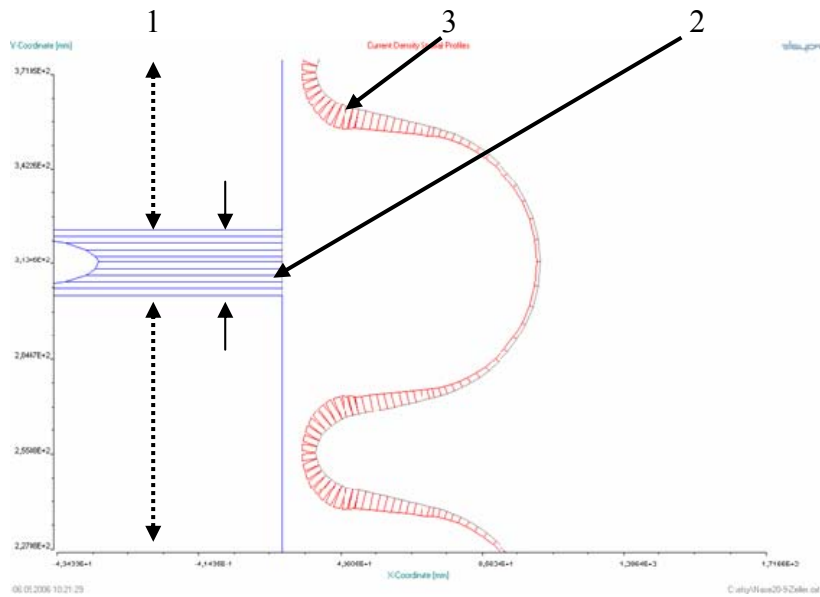


Figure 9 Shaped electrodes: nozzle shaping in the middle of the unshielded region (code “Elsy2D”)

- (1) half size electrode shielded region;
- (2) unshielded region with nozzle shaped center electrode area;
- (3) distribution of current density over the cavity shape)

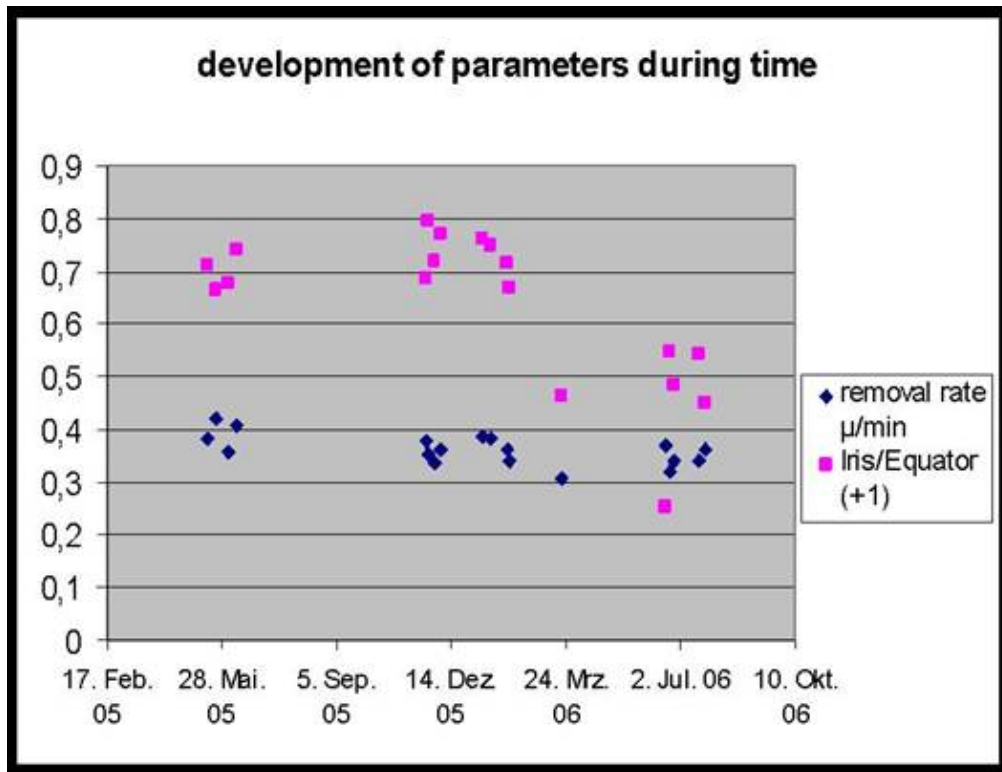


Figure 10. Progress towards uniform removal rate by improved shielding of the electrode during the reporting time. The global removal rate (μm) is displayed as diamonds while the relative removal of iris (smallest distance to electrode) to equator (largest distance to electrode) is displayed as squares. Since March 06 the improved shielding of the electrode is installed and results in a more homogenous removal between iris and equator while the total removal per time unit is nearly unchanged.

V Data logging and controls

The DESY EP system is equipped with passive sensors (as displayed on the operators screen, see picture 11) and active sensors for basic safety loops, e.g. electrical short circuits, cavity position or rotation, filling level (N) and leakage controls (L).

The data of the sensors are displayed on the control panel and are stored on a disk and serve for data logging and process control as well.

Temperature sensors (T) are in use to control the process and to interlock the process. The increase of temperature behind the heat exchanger indicates a leak between cooling water and acid circuit and triggers an emergency shut off.

Flow control sensors (Q) allow checking the right setting of valves for acid flow and Nitrogen overlay. Pressure sensors (P) indicate that supplies like nitrogen and rinsing water are operational and the electrode injection speed at the electrode ejection hole is in the defined regime. Gas sensors (G) are installed for personal safety and ensure that the workspace is free of hydrofluoric gases from possible leakages via gaskets. Also Nitrogen or hydrogen gas might escape from the electro chemical process via leaks in the piping circuit.

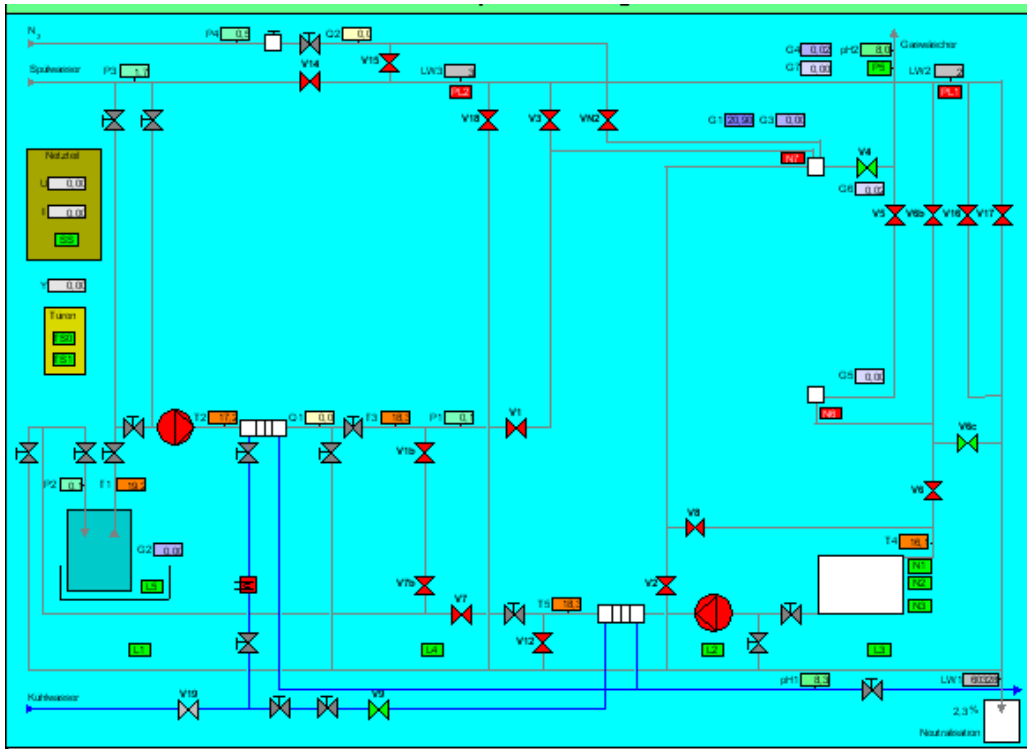


Figure 11 Screen shot of the controls computer for the EP installation at DESY

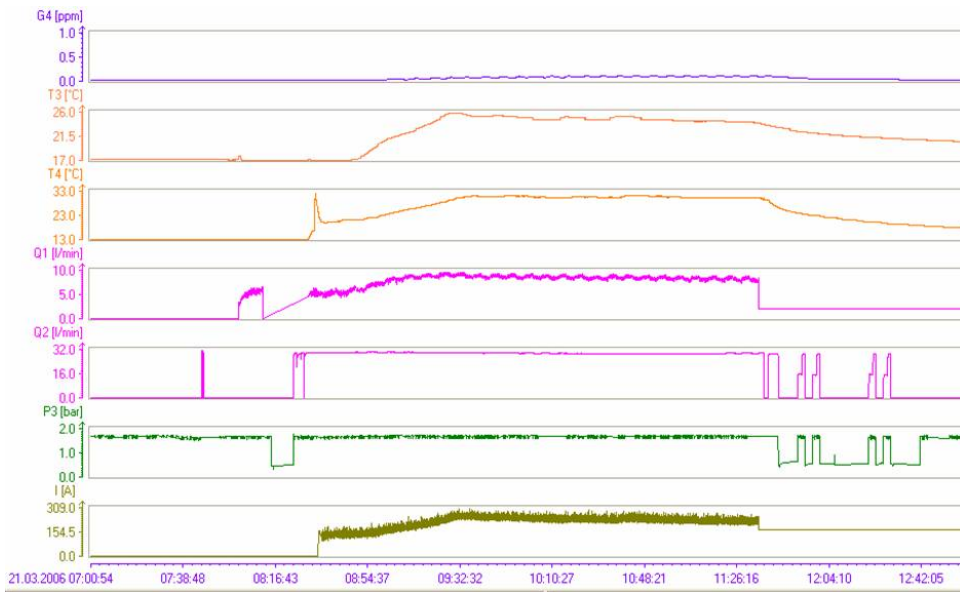


Figure 12 Process parameters recorded during electropolishing, top to bottom:

- (1) G4:HF level exit;
- (2) T3:Acit temperature cavity inlet;
- (3) T4:Acit temperature cavity outlet,
- (4) Q1:Acit volume towards cavity,
- (5) Q2:N2 overlay volume,
- (6) P3:pressure of water inlet line,
- (7) I: current



Figure 12 Online monitoring of U/I function on DESY EP apparatus

- (1) current lead to alumina electrode;
 (2) current lead to Niobium electrode)

| Parameter of EP process at DESY | | | |
|--|------------------------|-------------------------|-------------------|
| | Parameter for new acid | parameter for used acid | Units |
| Time in use | 0 | 600 | minutes |
| Nb content | 0 | 10 - 12 | gr/l |
| HF content | 2,78 | 1,9 | Mol/l |
| Acid volume | 150 | 140 | liter |
| Voltage | 17 | 17 | V |
| Current | 320 | 210 | V |
| Current density | 5,81 | 4,9 | A/dm ² |
| Oscillation | +44 to -66 | +43 to -73 | A |
| Removal rate | 0,44 | 0,36 | µm/min |
| injection speed per cell | 5,3 - 5,6 | 5,9 - 6,5 | m/sec |
| Acid circulation | 9 - 9,5 | 10 - 11 | l/min |

Table 1 Operating parameters of the DESY EP installation



Figure 13 View on to the control cabinet (left side) and power distribution panel (right side) of the DESY EP infrastructure.

- (1) frequency generator for rotational movement of the cavity.
- (2) 2 Siemens S7 PLC
- (3) Ethernet control panel fro Sensors and process
- (4) I/O digital and analogue I/O channel board.
- (5) Hardware interlock for detection of short circuits of sensor and cables to ground.
- (6) Control panel for the power supply control PLC

VI HF Safety

An important aspect of this electropolishing procedure is the safety for personnel from exposure to process chemicals during operation and maintenance of the electropolishing system. The exposure of personnel to the wet cavity and equipment surfaces coupled with the use of HF acid in the electrolyte recipe leads to the possibility of serious personnel safety conditions if the proper procedures for first response to exposures are not in place.



Figure 14 A DESY crew prepares themselves for the repair of the heat exchanger unit. The crew is protected against hazards of the acid and gas from the EP acid by safety overalls (Dräger type Workmaster®)

- (1) safety shower
- (2) Housing of the EP bench
- (3) Storage cabinet of the EP acid
- (4) External air supply for respirators integrated into the safety overall
- (5) EP electrode in hold position after extraction from Cavity

VII Industrialization of the DESY EP installation

In 2007 a call for tender was issued for industrialization of the DESY EP facility. Two companies were contracted (ACCEL and HENKEL) to build, install and operate an EP facility at the companies, based on the design and experience of the DESY EP facility. The installations differ from each other in respect to the physical arrangement of the acid management because of different space constraints. There is also the difference of operating with constant voltage or constant current mode. But the electropolishing set-up of the cavities itself is very similar to the original DESY design. After commissioning these facilities 15 cavities were sent to each company for electro polishing. The good performance of these cavities proved that the technology of EP for Nb cavities was successfully transferred to industry. This is an important progress towards industrial cavity treatment for XFEL or other future superconducting accelerator projects.



Figure 14 EP installation at ACCEL Company

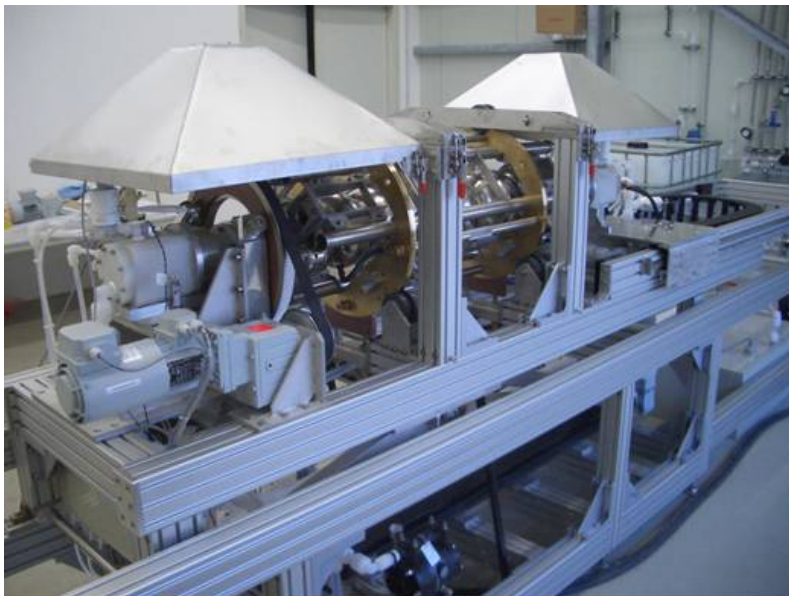


Figure 15 EP installation at Henkel Company (courtesy C. Hartmann)

VIII QA on acid mixture for EP

To ensure the reproducibility and reliability of the EP process for industrial application, a detailed study was carried out. The relation of mixture components, pollutions coming from equipment transport or storage vessels as well as non adequate material installed in the apparatus, have to be analyzed to ensure a continuous and well defined process. To determine the optimal analysis method and to compare different chemical analysis methods the study is split in 3 steps:

- 1) Overview of the commercially available analysis infrastructure and tests of method by standard mixture.
Outcome: list of equipment and test costs
- 2) define and measure the sensitivity and reproducibility of the methods selected
Outcome data base and limits of the different methods
- 3) field test in running processes

1. spectroscopic methods

1.1 molecular spectroscopy

1.1.1 (UV/VIS) ultraviolet spectroscopy

1.1.2 (FT-IR) infrared spectroscopy

1.1.3 Raman spectroscopy

1.1.4 (NMR) nuclear magnetic resonance spectroscopy

1.1.5 (ESR) electron spin resonance spectroscopy

1.1.6 (MS) mass spectrometry

1.1.7 (ICP-MS) inductively coupled plasma mass spectrometry

1.2 atom spectroscopy

1.2.1 (AAS) atom absorption spectrometry

1.2.2 (AES) atom emission spectrometry

1.2.3 (ICP-OES) inductively coupled plasma optical emission spectrometry

1.2.4 (RFA) Roentgen fluorescence spectroscopy

2. Chromatography

(GC) gas chromatography

(HP-LC) liquid chromatography

(IC) ionic chromatography

(CE) capillary electrophoresis

3. electrophoresis

(ISE) ion sensitive / selective electrodes (ISE)

pH electrodes

Karl-Fischer titration

Titration

4. measurement of physical characteristics

determination of density

conductivity measurement

definition index of refraction

Table2 Overview on commercial analysis methods

| Method | Analysis | Investments | Analysis time | applicability |
|-------------------------------|--|-------------|--|----------------|
| AAS | Element analysis | 15-50 k€ | 2 min / Analysis for 10 elements | No |
| ICP-OES | Element analysis all elements in parallel | ca. 60 k€ | 3 min / Analysis for 20 elements | Yes |
| IC Ion chromatography | Ions (SO ₄ , F-, FSO ₃ H) | 15 – 20 k€ | 20 min / Analysis | Yes |
| TOC Total Carbon | Org. contamination | 15 – 25 k€ | ca. 15 min / Analysis | Yes |
| FTIR-ATR (Infrared) | Ions (SO ₄ , F-, FSO ₃ H ?) | 110 k€ | 3 min / analysis | needs studies |
| NMR | Org. contamination | 0.1 – 4 M€ | 15 min / analysis | no |
| CE capillar electrophorese | Ions (SO ₄ , F-, FSO ₃ H) | 25 – 53 k€ | 60 min / analysis | yes CE or ITP |
| ITP Isotachophorese | Ions (SO ₄ , F-, FSO ₃ H) | 26 k€ | 20 min / analysis | yes CE or ITP |
| Titration | total acid content | 10 – 15 k€ | ca. 30 - 45 min / analysis | Should be done |

Table 3 Overview on methods and instruments applicable for the analysis of the EP mixture HF and H₂SO₄

Analysis methods applicable for EP quality control

From the measurement and analysis of QC instruments and equipments, commercially available, the following methods are chosen as best candidates for EP quality control.

- **Titration**
- **ICP-OES** (inductively coupled plasma- optical emission spectroscopy)
- **IC** (ionic-chromatography)
- **TOC** (total organic carbon)
- **NMR** (nuclear magnetic resonance)
- **FTIR-ATR-probe** (Fourier transformation infrared spectroscopy –attenuated total reflection)

None of the analysis instruments allows users to detect the full set of parameters necessary for the overall quality control and quality assurance of the EP acid. Beside the composition of the acid contaminations by oil or softener of PVC tubing's like sometimes in use in industry have to be detected and incorporated in the QC of an acid management

| | |
|-------------------|--|
| Titration | + total acidity |
| ICP-OES | + all elements (Nb, Fe,) |
| IC + distillation | + Ions (SO ₄ , F ⁻ , FSO ₃ H) |
| TOC | + organic impurities |
| NMR | + organic impurities |
| FTIR-ATR-probe | + total overview of components defined by the ATR data base |

Table 4 Applicability of the chosen analysis instruments

IX Conclusion

1). The technology of electropolishing has been successfully transferred to industry. Two companies (ACCEL and Henkel) have designed, built, installed and operated EP installations based on the experience with electropolishing at DESY.

2) Mixing process

Based on the actual knowledge and experiences with the DESY EP apparatus a well defined prescription of the components (H₂SO₄- and HF acid) and the mixing process is now established in industry. Most companies supplying chemicals are able to handle this prescription.

NMR analysis of the basic components

Pre-cooling of the acid basic components

Temperature control and recording during mixing process.

3) Application of EP acid QC instruments

At this stage only the U/I instrumentation allows to determine the acid quality. This analysis is mostly connected to the EP apparatus and a constant process flow in cavity preparation. It is applied at DESY as QC before and during the EP process. A correlation between U/I measurements and RF measurements and test results of superconducting resonators is not apparent up to now. But a detailed calibration and test on application in the cavity preparation will be launched in the near future.