OZONE PROCESSING AND COMPARISON WITH PLASMA PROCESSING

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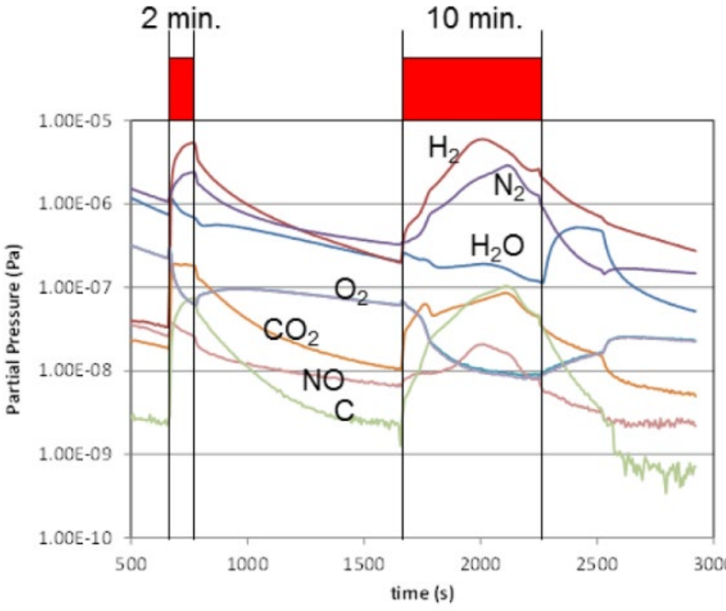
Plasma Processing

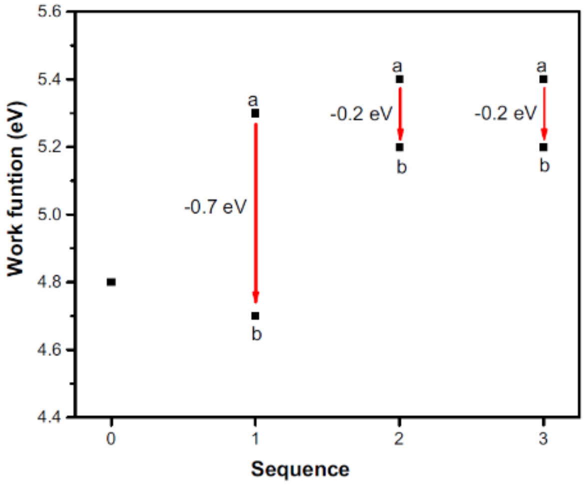
- **Established technique** for removing hydrocarbons
- Increases Nb work function by 0.5 to 1.0eV (Ar/O_2)
  - after 15 min in vacuum,
    - hydrocarbon concentration on surface increases to initial level before processing
    - hydrocarbon concentration below top surface decreases
- Confirmed using methane plasma as artificial contamination
  - P.V. Tyagi et al., *Improving the work function of the niobium surface of SRF cavities by plasma processing*, Appl. Surf. Sci. 369 (2016) 29.
  - T. Powers, et al., *In Situ Plasma Processing of Superconducting Cavities at JLab*, Proc. NAPAC, Albuquerque, USA, (2022) 22–25.
- Oxidizes niobium surface
  - Nb_2O_5 ratio increases from 25% to 79%
  - Z. Zhang et al., *The mechanism study of mixed Ar/O_2 plasma-cleaning treatment on niobium surface for work function improvement*, Appl. Surf. Sci. 475 (2019) 143-150.
- **Conclusions**
  - effective hydrocarbon cleaning method
  - hydrocarbons migrate to top surface over time
  - mitigate by longer and more processing cycles



S.H. Kim et al., *R&D Status for in-situ plasma cleaning of SRF cavities at SNS*, Proc. NAPAC (2011) 2124.

Table 1
Summary of the experimental conditions for work function studies experiments after subsequent cycles of plasma processing.

Sequence		Experimental details	Work function (eV)
0		Initial condition	4.8
1	a	8 min of active plasma over 1.5 h total plasma	5.3
	b	15 h waiting in vacuum	4.7
2	a	Additional 17 min of active plasma over 3.5 h total plasma	5.4
	b	15 h waiting in vacuum	5.2
3	a	Additional 8 min of active plasma over 1.5 h total plasma	5.4
	b	24 h waiting in vacuum	5.2



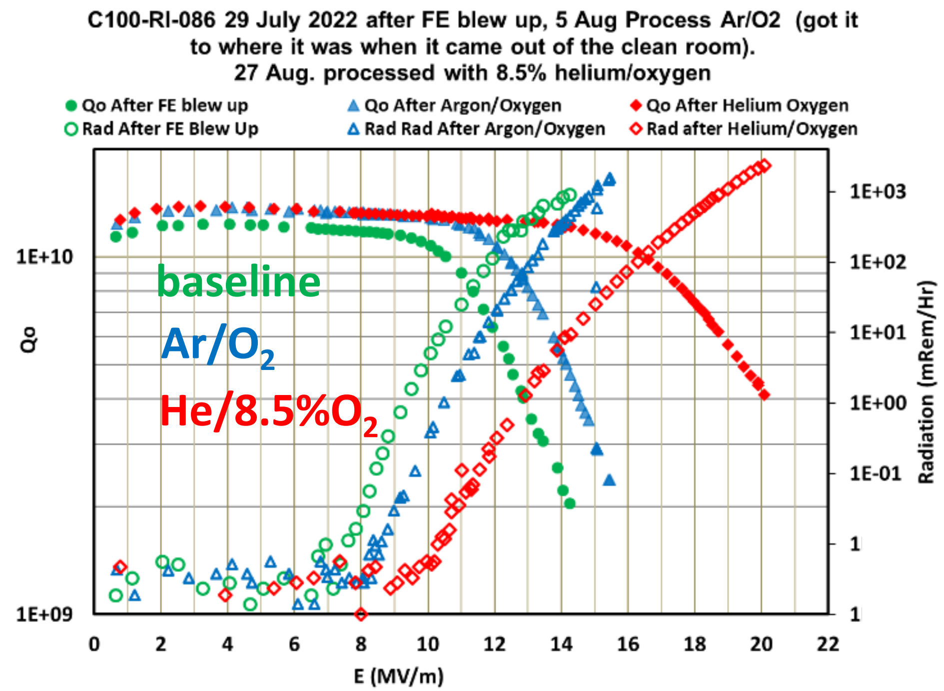
P.V. Tyagi et al., *Improving the work function of the niobium surface of SRF cavities by plasma processing*, Appl. Surf. Sci. 369 (2016) 29.

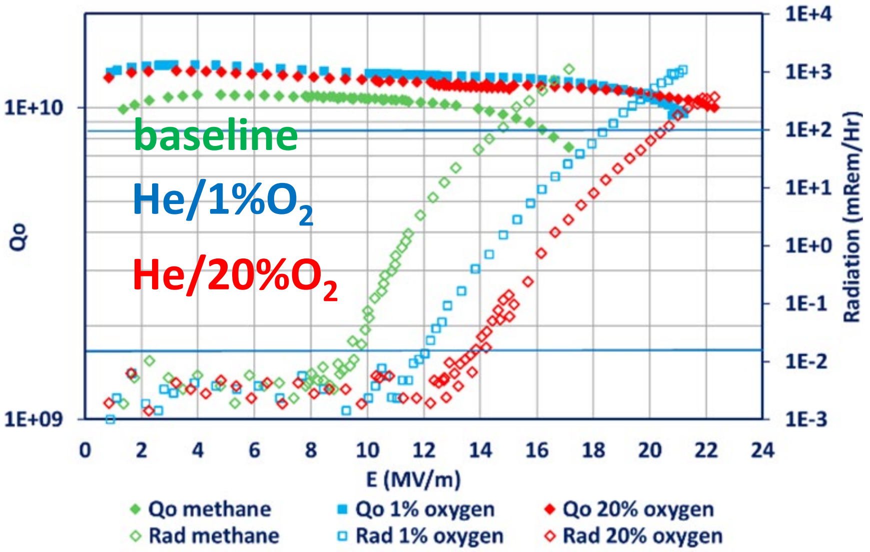
Plasma Processing

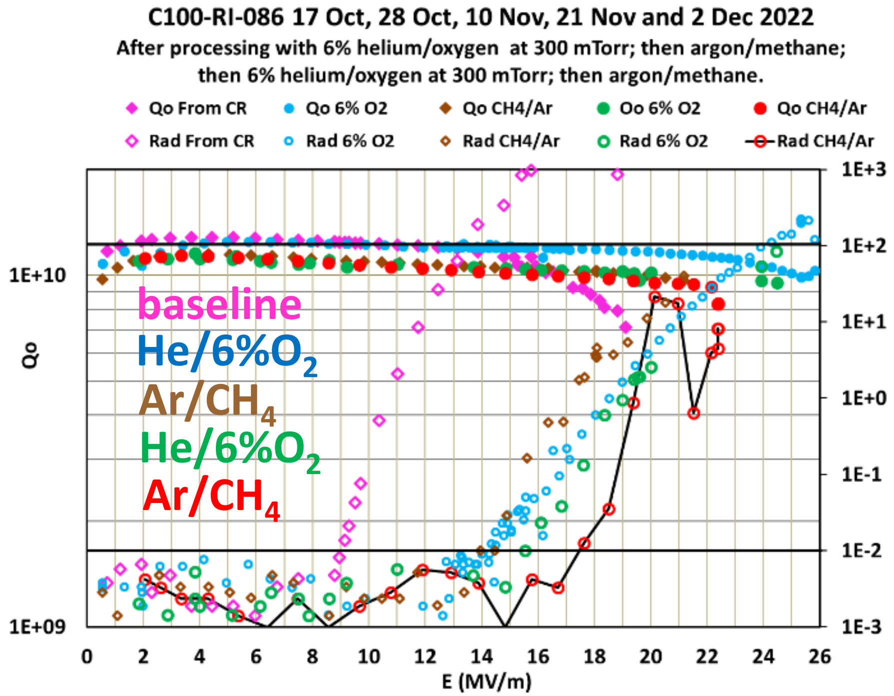
Courtesy Tom Powers

T. Powers, et. al., *"An overview of Plasma Processing of SRF cavities at JLAB"*. IPAC2024.
https://doi.org/10.18429/JACoW-LINAC2024-THXA005

- **C100-RI-086**
  - 1.5 GHz 7-cell elliptical
  - **Ne/O_2 mix**
    - not used
  - **Ar/O_2 mix** processing
    - standard 1-2% O_2
    - improved FE onset
  - **He/O_2 mix**
    - standard 6% O_2
    - further improved FE onset
  - **Ar/CH_4 methane mix**
    - artificial contamination

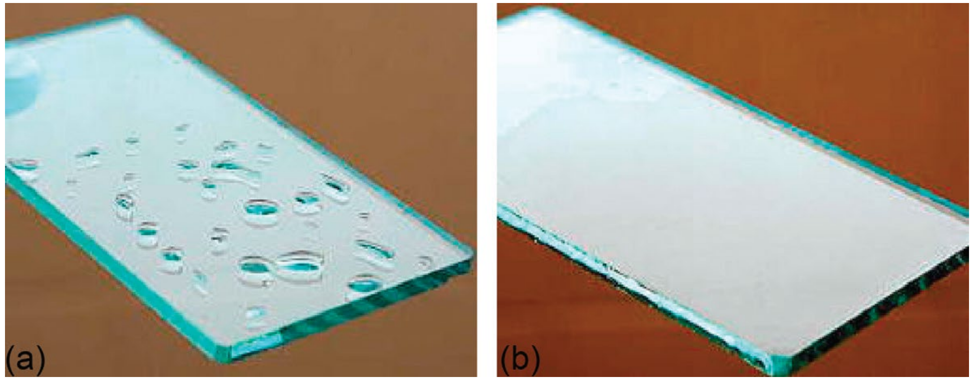






Ozone Cleaning

- **Well-established technique** to use ozone for removing biological material, hydrocarbons
- **UV/ozone cleaning of surfaces** mentioned in the 1970's
  - using UV radiation in air or low-pressure oxygen (<mTorr)
    - R.R. Sowell et al., *Surface cleaning by ultraviolet radiation*, J. Vac. Sci. Technol. 11, 474 (1974)
    - during cleaning, the partial pressure of O_2 decreased, while that of CO_2 and H_2O increased.
  - UV also desorbed gases from the vacuum chamber walls
    - J. Vig, *UV/ozone cleaning of surfaces*, J. Vac. Sci. Technol. A3, 1027 (1985)
  - *used at Brookhaven Nat. Lab. for NSLS-2 vacuum chambers*
    - H. Hseuh, private communication; K. Wilson, private communication.
- **Ozonized water cleaning** used in semiconductor industry since 1990's
  - remove organic impurities from the wafer surface, 1–2 ppm O_3 concentration
    - T. Ohmi et al., *Native oxide growth and organic impurity removal on Si surface with ozone-injected ultrapure water*, J. Electrochem. Soc. 140, 804 (1993)



Glass plate before (a) and after (b) UV-ozone cleaning for 1 min. No water beads on cleaned surface.
R. Kohli, *UV-Ozone Cleaning for Removal of Surface Contaminants,* In Developments in Surface Contamination and Cleaning, Vol. 8 (2015).

H_2O_2 and Ozonized Water Cleaning at KEK

- Mid 1990's, Asano et al. at KEK **copy technique from semiconductor industry**
  - experimenting first with H_2O_2 later also test O_3 rinsing
- Superconducting niobium single cell 508 MHz for KEK-B, electro-polished
  - rinse with H_2O_2 or ozonized water: fill cavity and empty after 10, 20 or 30 minutes
  - observed reduced field emission and improved accelerating gradient
  - O_3 rinsing has stronger effect than H_2O_2 rinsing

Field Emission after H_2O_2 rinsing

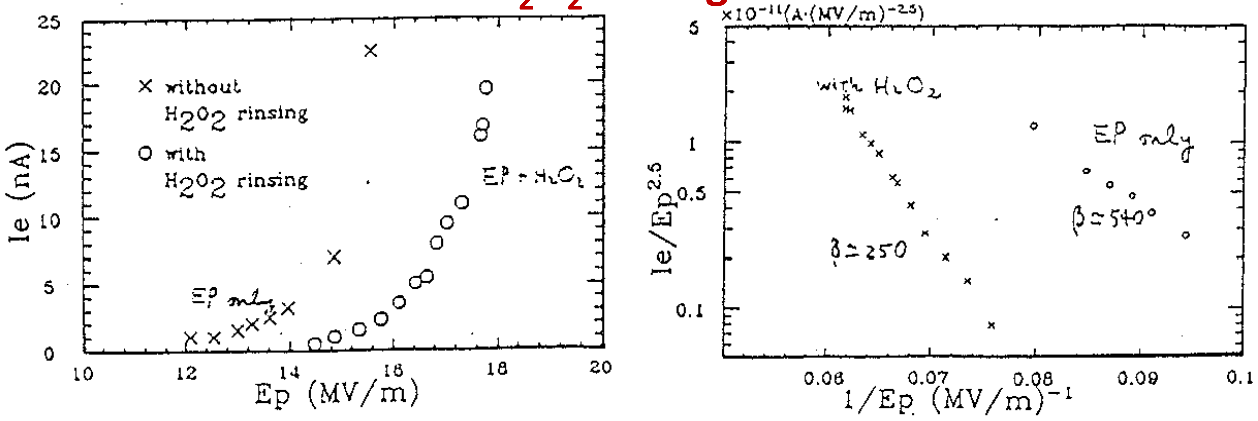


Fig.3 Field emissions for 508 MHz single cell Nb cavities with and without H_2O_2 rinsing after EP.

K. Asano, *Ozonized Ultrapure Water Treatment of Nb Surfaces for Superconducting RF Cavities*, KEK Preprint 93-216 (1993).

Recovery after O_3 rinsing

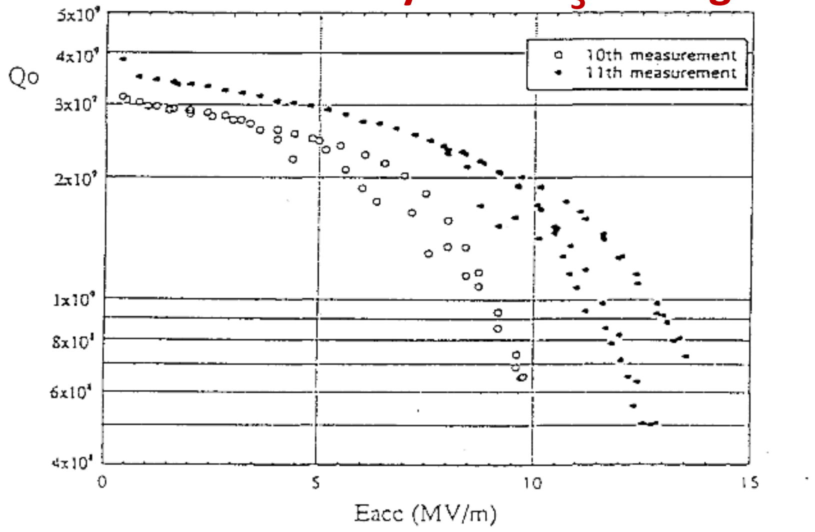


Fig. 4 Performance recovery of the 508 MHz Nb cavity with Cu plated SUS extended beam pipes, SUS flanges sealed by In ribbons and Al_2O_3 ceramics. 10th and 11th measurements show before and after ozonized ultrapure water rinsing, respectively.

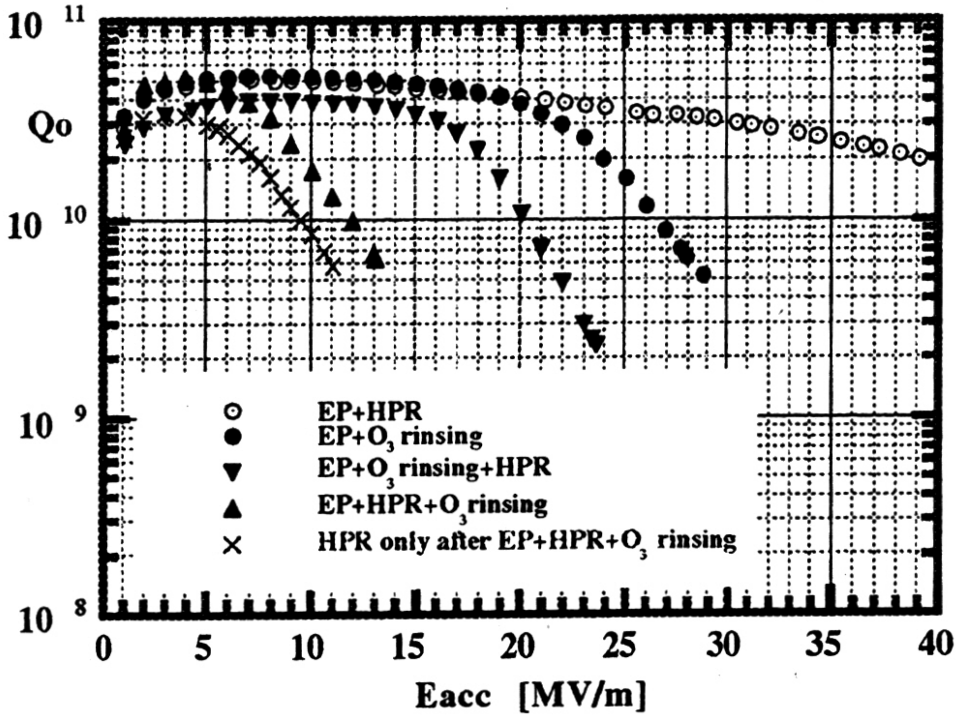
K. Asano et al., *Stable Performance of 508 MHz Superconducting RF Cavities for KEKB*, Proc. 1995 Workshop on SRF (1995) 419.

Follow-up Experiments at KEK

- **Fails on high-gradient 1300 MHz single cell cavity**
  - electro-polished (EP) *but no heat-treatment*
  - high-pressure rinsed (HPR)
  - ozone (O_3) rinsing
  - multipacting around 15 MV/m
  - field emission onset around 18 MV/m

- **Method abolished**
  - kept for cleaning KEK-B cavities and for power couplers, overflow with ozonized water for 5 minutes
  - used for Taiwan Photon Source vacuum chambers
    - C. Chan et al., *Cleaning of aluminium alloy chambers with ozonized water*, J. Phys. Conf. Ser. 100, 092025 (2008)

- Built prototype system to produce clean ozone ice
  - can reach 150 ppm ozone in water
  - idea to use for in-situ cleaning of vacuum systems



K. Saito, *Recent Developments in SRF Cavity Cleaning Techniques at KEK*, Proc. 1999 Workshop on RF Superc. (1999) 118.

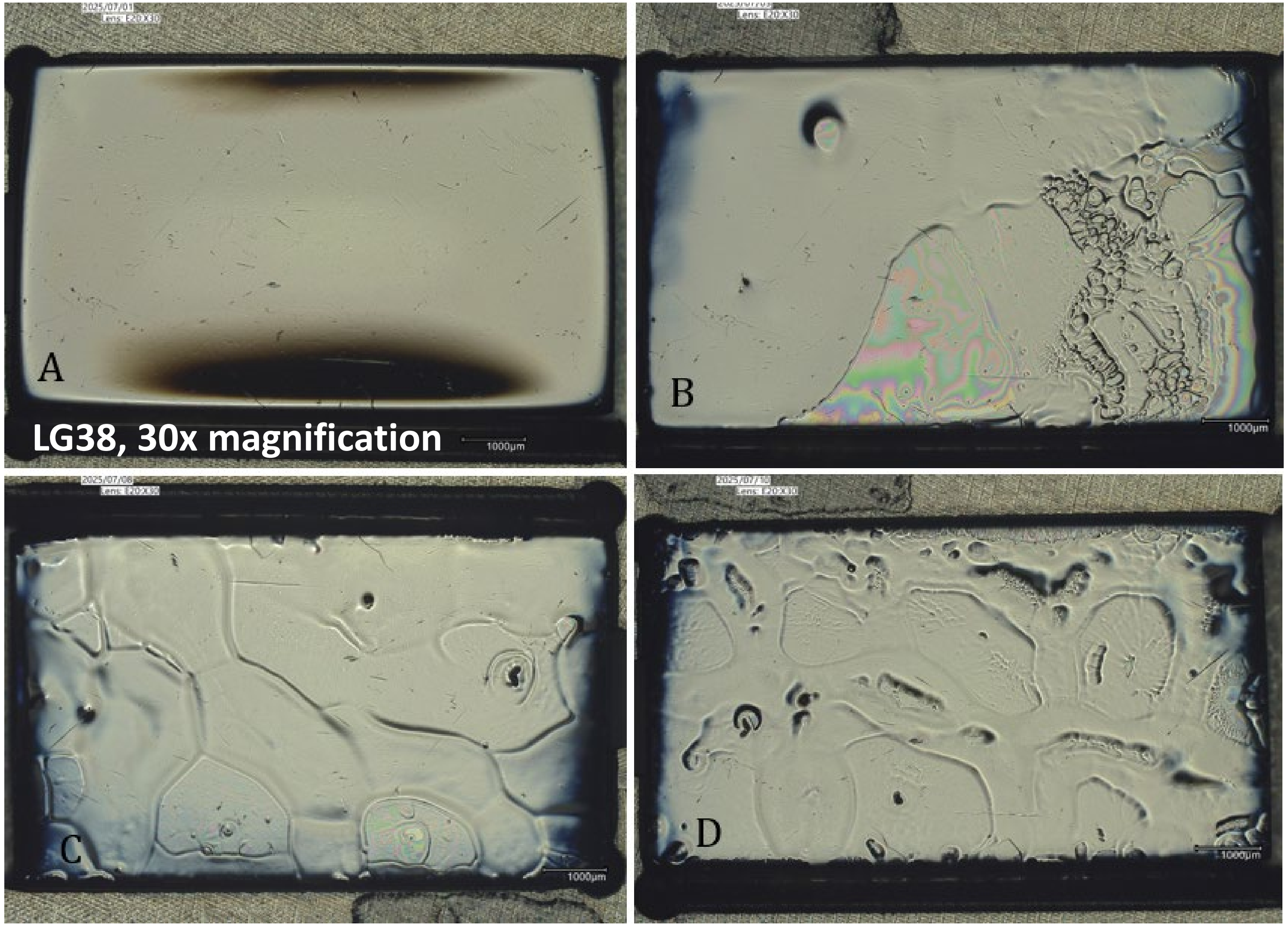
Niobium Sample Processing

Courtesy Carol Quinones Sanchez

- Contaminated with mixture of acetone and low viscosity oil as used in vacuum pumps
- **In situ O_3 processing**
  - 10 wt%, 0.2 l/min ozone
  - A = before
  - B = 2 hours
  - C = 10 h
  - D = 34 h

Pronounced change

Duration not sufficient to completely remove the oil film



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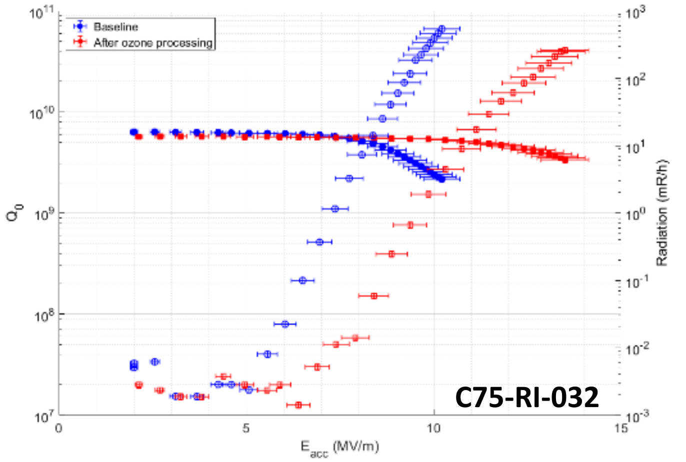
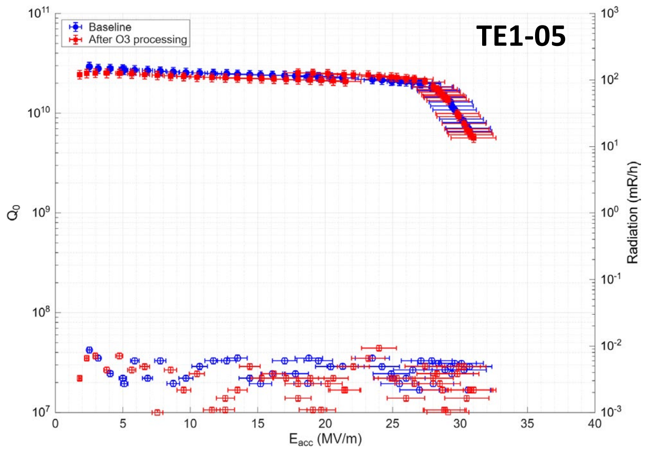
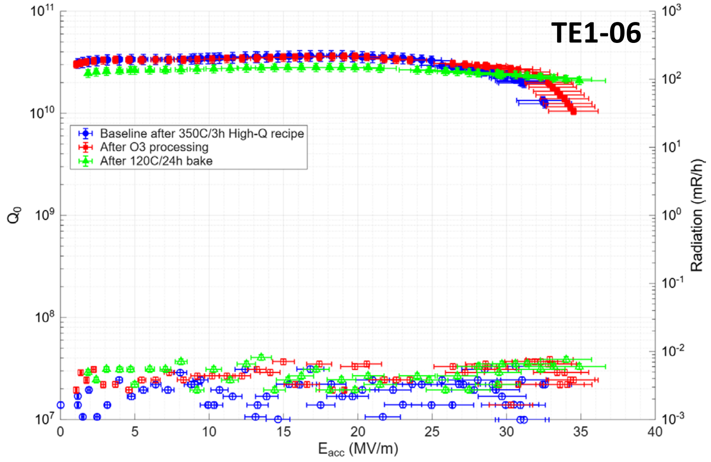
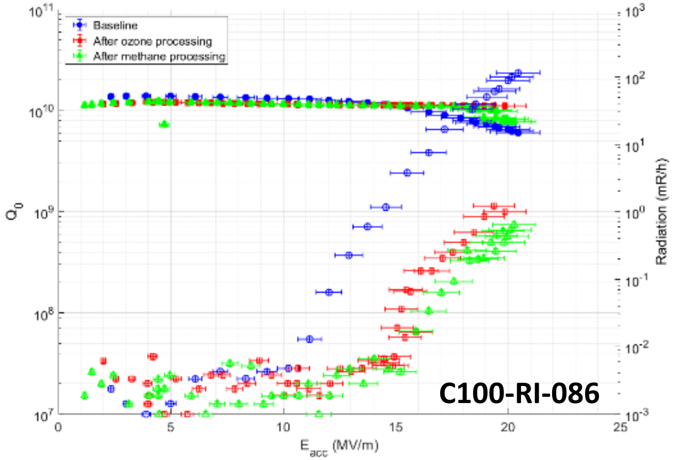
In Situ Ozone Processing – SRF Cavity

- **C75-RI-032**
  - 1.5 GHz 5-cell elliptical
  - 16 h at 84 °C, 7 wt%, 0.7 l/min ozone
- **TE1-05**
  - 1.3 GHz single cell elliptical
  - 10+8 h at RT, 6 wt%, 0.2 l/min ozone
- **TE1-06 high-gradient, high-Q**
  - 1.3 GHz single cell elliptical
  - 350 °C / 3 h high-Q treatment
  - 18 h at RT, 6.2 wt%, 0.2 l/min ozone
  - 120 °C / 24 h bake
    - Q_0 decrease but improve at high field
- **C100-RI-086**
  - 1.5 GHz 7-cell elliptical
  - 2.5 + 3.25 h at RT, 6 wt%, 1 l/min ozone
  - Ar/CH_4 methane plasma processing









P. Dhakal, High-Q_0 treatment of CEBAF 1.5 GHz SRF cavities, Eur. Phys. J. Plus **141**, 464 (2026). https://doi.org/10.1140/epjp/s13360-026-07702-9

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Effects of Ozone Processing (1/2)

Surface Characteristics Measurements at KEK after ozonized water rinsing

- Superconducting niobium cavity
  - **The carbon contamination on the electropolished Nb surfaces, … , was removed completely by this ozone treatment**
- Aluminium and copper samples
  - The ozonized surface was exposed to synchrotron radiation with a critical energy (e_c) of 26 keV.
    - **photo-desorption coefficient was two orders of magnitude lower than non-treated and oxygen-plasma treated samples**
    - suggests low desorption coefficient of the ozonized surface.

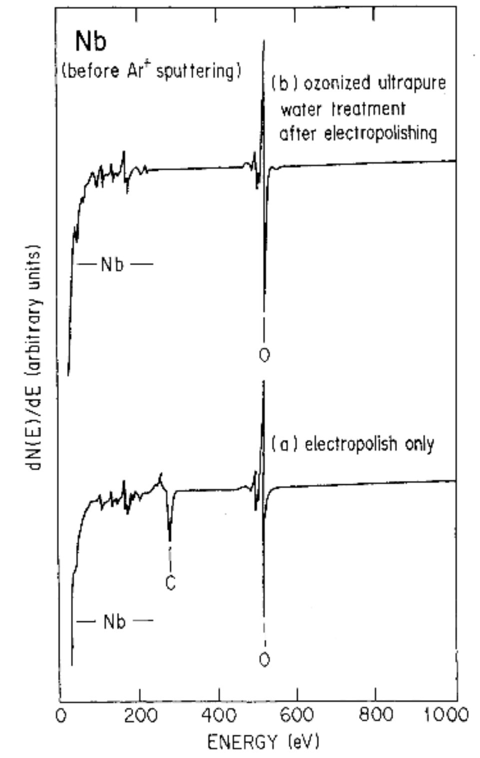
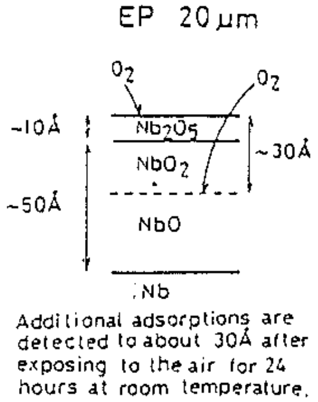
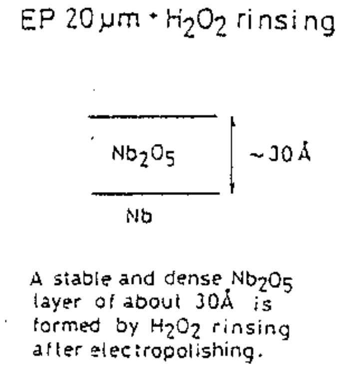


Fig. 5 Auger spectrum of Nb surfaces (a) electropolish only (b) ozonized ultrapure water treatment after electropolishing.

- Niobium-oxide XPS spectra for electropolished (left) and electropolished plus H_2O_2 rinsed (right).
  (X-ray photoelectron spectroscopy)





S. Mitsunobu et al., *Activities of Superconducting Cavity for KEK-B Factory*, Proc. SRF (1993) J05.
T. Momose et al., *Surface characteristics of aluminium and of several metals from view point to reduce dynamic gas desorption*, Vacuum 47(4) (1996) 319.
N. Ota et al., *Reduction of photodesorption yield by oxygen discharge cleaning*, J. Vac. Sci. Technol. A12(3) (1994) 826.
K. Asano, *Ozonized Ultrapure Water Treatment of Nb Surfaces for Superconducting RF Cavities*, KEK Preprint 93-216 (1994).

Effects of Ozone Processing (2/2)

- Asano et al. report
  relatively stable performance after ozonized water rinsing and subsequent exposure to air
- Successfully applied to 508 MHz KEK-B niobium cavities
  - 3 ppm ozone in water at 5 l/min for 20 min
  - O_3 rinsing has stronger and cleaner effect than H_2O_2 rinsing
  - cavity performance was not degraded by air exposure for **4 days**
    - attributed to formation of a stable and clean Nb_2O_5 layer
    - Nb_2O_5 formed acts passively and is not able to absorb water or hydrocarbons

Q_0 vs. Eacc after air exposure

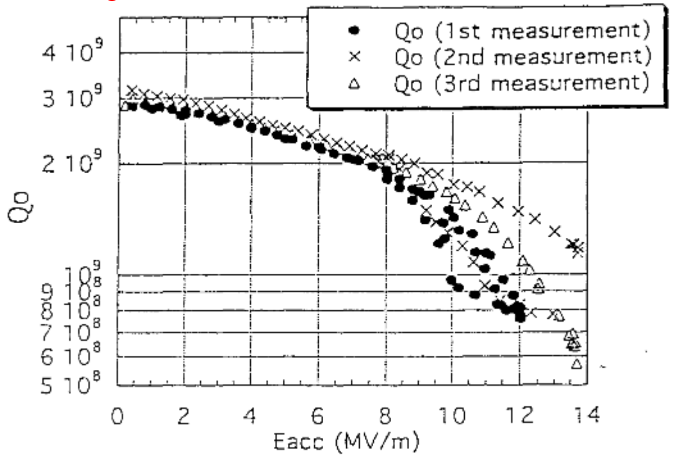


Fig. 1 Stable performance of the 508 MHz Nb cavity rinsed by ozonized ultrapure water. The 2nd and 3rd tests were measured after 1 atm air exposures for 23 hours and 69 hours, respectively.

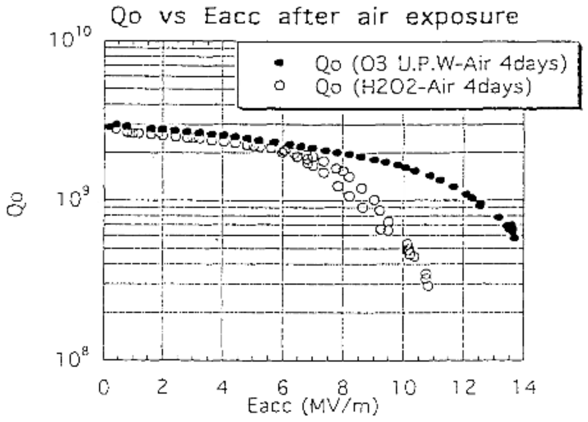


Fig. 2 The comparison of the effect of air exposures on cavity performance rinsed by ozonized water and H_2O_2. The clean and stable oxide layers on Nb surfaces formed by ozonized water can keep the cavity performance after air exposures.

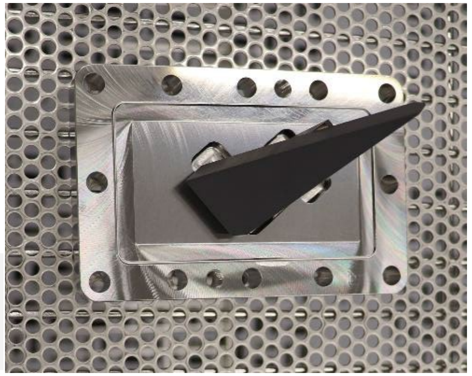
Table1 The comparison of weak superconductors (NbO+NbO2) and hydrides of Nb for ozonized ultrapure water rinsed and H2O2 rinsed Nb surfaces after electropolishing

	$\frac{NbO_x}{Nb + NbO_x}$	$\frac{Nb(OH)_x}{Nb_xO_y + Nb(OH)_x}$
EP + O_3	0.9 %	24 %
EP + H_2O_2	4.0 %	53 %

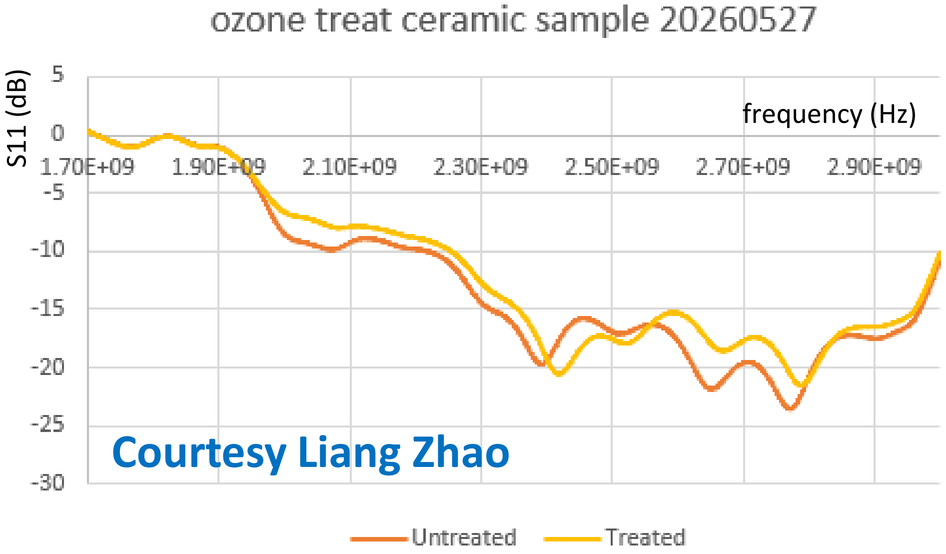
K. Asano et al., *Stable Performance of 508 MHz Superconducting RF Cavities for KEKB*, Proc. 1995 Workshop on SRF (1995) 419.

Preparation for Cryomodule Processing

- **CEBAF HOM RF load**
  - from JLab FEL cryomodule
  - aluminium-nitride glassy carbon (AlN/GC) ceramic absorber
- **In situ O_3 processing**
  - 12 h at room temperature
  - 10 wt%, 0.5 l/min ozone

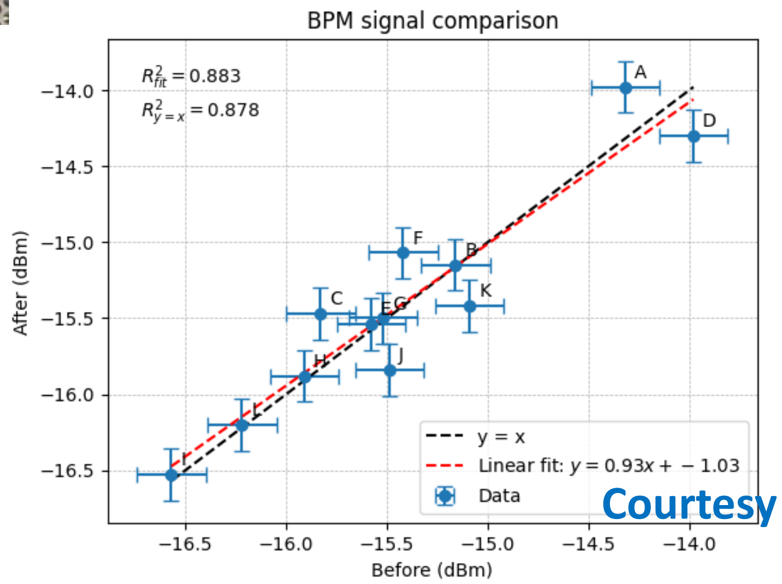


I.E. Campisi et al., *Artificial Dielectric Ceramics for CEBAF's Higher-Oder-Mode Loads*, SRF 1993, https://proceedings.jacow.org/SRF93/papers/srf93i05.pdf

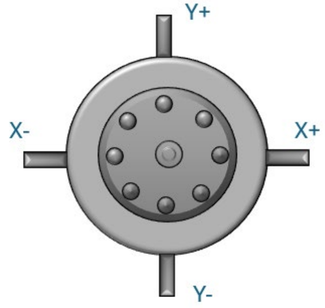


Courtesy Liang Zhao

- **CEBAF antenna type BPM**
- **In situ O_3 processing**
  - 24 h at room temperature
  - 10 wt%, 0.2 l/min ozone
- Measurement RMS 0.17 dBm
- No significant negative effect on signal response



	$X+$	$X-$	$Y+$	$Y-$
$X+$		D	G	J
$X-$	A		H	K
$Y+$	B	E		L
$Y-$	C	F	I	



Courtesy Carol Quinones Sanchez

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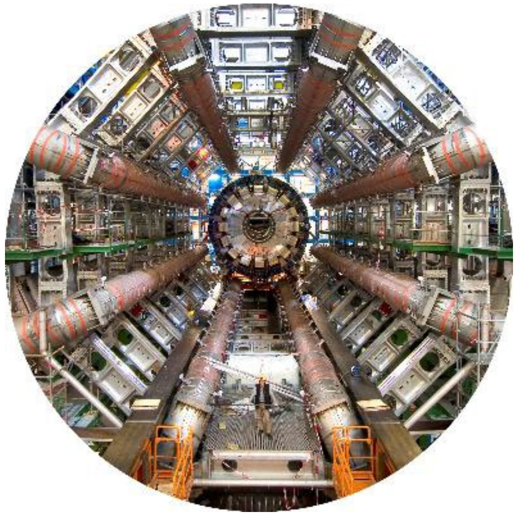
Conclusions

- **Ozone is as effective as plasma processing**
  - removes organic, hydrocarbons, and some inorganic, e.g. sulfur contaminants
  - no negative effect seen on high-Q high-gradient cavities
  - global effect on cavity's interior
- **Ozone is simple method for all cavity shapes**
  - and other (beam line) vacuum chambers



- **Stabilizing the upper surface layer**
  - oxidizing Nb surface layer to Nb_2O_5
  - increases the work function value and
  - immunizes the surface layer against adsorption of contaminants

Acknowledgements

- **JLab** staff, especially SRF Ops, SRF S&T, ES&H; **CERN**, and **KEK**
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