THE
AUSTRALIAN
NATIONAL
UNIVERSITY

RESEARCH SCHOOL OF PHYSICAL SCIENCES

ACTIVE GAS DISCHARGE CLEANING FOR SUPERCONDUCTING LEAD-PLATED RESONATORS

Mark D. MALEV and David C. WEISSER

Department of Nuclear Physics
Australian National University,
Canberra, ACT 2601, Australia.

INSTITUTE OF ADVANCED STUDIES

ACTIVE GAS DISCHARGE CLEANING FOR SUPERCONDUCTING

LEAD-PLATED RESONATORS

Mark D. MALEV, David C. WEISSER

Department of Nuclear Physics, Australian National University,

GPO Box 4, Canberra, ACT 2601, Australia.

ABSTRACT

Lead-plating for superconducting RF resonators historically has been directed toward reducing grain size and eliminating spikes on the surface. At present smooth, spike-free, bright lead surface are obtainable, but there is little correlation between appearance and performance. Even the best lead-plated resonators fall short of the BCS limit and exhibit impenetrable low level multipacting barriers. Investigations were made of degassing lead-plated surfaces under RF resonant electron discharge or multipacting. The mass-spectra of the residual atmosphere showed that decomposition of hydrocarbons on the surface took place. Discolouration of the lead surface, due to the formation of a carbon layer, was easily observed.

A method of cleaning surfaces by ion bombardment employing chemically active gases, was proposed and tested. An RF discharge, initiated by multipacting at pressure $10^{-2} - 10^{-1}$ torr was used. The first step, discharge treatment in a CO_2 atmosphere, assures oxidation of carbon and hydrocarbons into gaseous compounds which are removed by pumping. During the second step, discharge treatment in a hydrogen atmosphere, lead oxides are reduced to metal.

1. INTRODUCTION.

There are two kinds of superconducting RF resonators: niobium and lead-plated ones. Each has found its own place in accelerator technology. Niobium assures high performance but it is expensive. Lead-plated resonators are cheaper and simpler to produce for heavy-ion accelerators in most university environments.

The lead tehcnology was developed at CALTECH in the late 70s by combining the standard process of bright lead electroplating with chemical polishing [1]. From the very beginning, the main effort has been directed toward reducing grain size and eliminating spikes on the surface. For that reason, the bright deposition process was taken as a basis. A general aspect of bright electroplating is co-deposition of some organic colloid which supresses the activity of the crystal growth centres on the newly formed cathode surface [2]. A small amount of this brightening agent is added to the electrolyte; 1-3% of peptone, Shinol or other organic liquid is usually used [3].

After some improvement of the electroplating technique [4,5,6], a lead surface could be obtained comparatively easily which had an average grain size as low as 5-10 microns and was practically spike-free. Chemical polishing appears to reduce the grain size to 2-4 μ and eliminates spikes completely. Nevertheless the performance of resonators lead-plated in the above fashion, appears less bright than their surface. The best high β split-ring resonators at Stony Brook had Q's about a factor of three under the BCS limit. The development of lead plated coaxial quarter wave resonators was at first very

encouraging. Resonators were produced with $Q \sim 4 \times 10^8$, which exhibited minor multipacting. Attempts to duplicate their performance stumbled upon stubborn multipacting levels which could only be overcome by re-rinsing the resonator or treatment with wet air. The non-translational invariance of lead plating technology applied to resonators motivated the present investigation.

The factor responsible for inconsistent performance of lead-plated resonators could well be the surface contamination. Lead technology employs hydrocarbons at all stages (electro-plating, polishing, rinsing) without adequate subsequent cleaning procedures. Conclusive illustration of this is shown in Table 1 comparing the main points of lead and niobium technology.

It was shown by R.V. Latham, that the majority of the field-emission sites are associated with oxide and carbide impurities on the surface [7]. Unfortunately, because of the high chemical activity and the low melting point of lead, removing contamin- ation from its surface is a quite non-trivial problem. Neither water rinsing nor vacuum baking can be used effectively. A possible solution is to use ion bombardment. Helium discharge has been employed for conditioning of lead-plated resonators [8], but results of this treatment are rather inconsistent.

It is usually assumed that ion bombardment cleans surfaces by impact sputtering of material. If the chemical interaction between ionized gases and surface is taken into consideration, the cleaning mechanism could be enhanced dramatically. The main emphasis is the chemical conversion of impurities into the gaseous phase and then their removal by pumping. For carbon, hydrocarbon and oxide contaminations, the most suitable

treatment is an oxidizing-reducing cycle, consisting of two stages:

1. Discharge in an oxidizing atmosphere e.g. O_2, H_2O or CO_2 to convert carbon and hydrocarbons into gases.

2. Discharge in a hydrogen atmosphere reducing oxides to pure metal.

In this case, ion sputtering becomes a disadvantage and so has to be minimized by employing RF or arc modes of discharge where ion energy does not exceed a few eV. Luckily, chemical interactions do not need higher energies.

2. EXPERIMENTAL DETAILS

Contamination of lead-plated surface was pursued by studying degassing and surface discoloration under electron bombardment. The secondary electron resonance, multipacting, was used both for electron bombarment and for initiating the RF gas discharge during the cleaning stage.

Copper samples 6 cm in diameter, were lead-plated according to the standard procedure [5]. The experimental setup consisted of the 1/4 - wave resonator line (150 MHz) modelled on a split ring design and located inside the metal bell-jar. The samples and the gap between them, formed the resonator capacitor.

RF power from a 20 W amplifier, was driven into the resonator by conductive coupling. Both RF power and frequency could be set within broad limits. The resonator had a Q of 150-300 and without multipacting, reflected no more than 5% of the incident RF power. At the gap width 14-20 mm and frequency 150-170 MHz, multipacting, commenced for a potential difference across the gap of 200-300 V and terminated for 1000-1500 V. These figures are consistent with numerous published data [9,10].

An omegatron-type mass-spectrometer measured composition of the residual atmosphere. To minimize distortion of the mass-spectra by chemically selective pumping, a turbo pump was used. Measurement of the quantity of gas evolved employed the well-known dynamical method of vacuum impedance. During discharge treatment, gas was supplied through a needle valve and the pumping speed was reduced to 0.1-1 l/s by selectable impedances.

Experimental procedure included the following stages:
1. Baking of the entire vacuum system at $100^{\circ}C$ for 1-2 hours;
2. Multipacting at 10^{-6} torr for 2-5 hours; RF power 2 W;
3. Visual inspection of the surface;
4. Discharge treatment; 0.05-0.1 torr; RF power 2W;
5. Repetition of the steps 1,2,3.

Initiation of multipacting in vacuum, stages 2, was always accompanied by a sharp increase of pressure up to 10^{-5} torr and of reflected RF power up to 20-30%.

The incident RF power during multipacting was maintained at constant level ($\sim$ 2 W) until multipacting had extinguished

spontaneously, usually after 2-5 hours. After that, multi-pacting wou.d only occur at a very low level of RF power ($\sim$0.1 W) and without any observable degassing effect. Leaving the system pumping overnight at 10^{-6} torr, re-established the 2W multipacting level which required another 0.5-1 hour to extinguish. Filling the system with gas similarly re-established the 2 W multipacting as soon as the pressure was reduced to 10^{-4}- 10^{-3} torr.

In none of the more than one hundred samples tested, did an impenetrable multipacting barrier occur. Therefore our test apparatus did not mimic the misbehaviour found in some coaxial quarter wave resonators and so this phenomenon was not available for study.

The samples were inspected through a small glass window. Sometimes, samples were extracted from the system and photographs taken.

Gas discharge initiated by multipacting became luminous at pressure as high as (3-5). 10^{-3} torr; the pale violet glow appeared between the electrodes. The colour did not depend on a type of gas introduced. Only at pressure as high as 0.02-0.05 torr, did the luminescence acquire the characteristic colour of the gas species used. Further increase of pressure led to the continuous expansion of luminescence from the interelectrode space followed by, at pressure of .3 to .6 torr, contraction to small, bright glowing ball in the gap.

3. RESULTS AND DISCUSSION

The typical time dependence of the degassing rate during multipacting is shown on Fig. 1. In the first 10-15 minutes the total gas flow diminished by factor of 10 and subsequently it decreased proportionally to $t^{-1/2}$. The $t^{-1/2}$ shape of the degassing curve shows that desorption is controlled by diffusion process [11]. Similar degassing curves have been observed under D.C. electron bombardment [11].

No substantial difference was found between the total pressure degassing characteristics of copper and lead-plated surface (polished and unpolished). More specific information could be obtained from the degassing curves for partial pressures. For correct interpretation of these curves, the surfaces involved in the different stages of outgassing have to be identified. During multipacting, desorption stimulated by electron impact, takes place from the 60 cm^2 sample surface. The background pressure, without multipacting, is determined by thermal desorption from the whole inner surface of the vacuum system, (about 7000 cm^2).

Commencement of multipacting led to the sharp jump of pressure and its subsequent gradual diminution. Switching the RF power off resulted in a downward jump in the pressure. Different gases exhibit three different patterns of degassing curves (Fig. 2A-4A).

A. Water and Nitrogen

Without multipacting, these two gases comprised 85-90% of the residual atmosphere. Switching the RF power on, decreased them to 50%. The thermal desorption

rate at the room temperature was as high as $(1-5).10^{-10}$ torr.$1/cm^2$.s after baking and 20-40 hours of pumping. Under multipacting, desorption increased initially by factor 10-20 but soon this ratio fell to 2-5. Further outgassing made the difference between stimulated and thermal desorption imperceptible. This pattern shows that electron bombardment does not change the physical mechanism of desorption. This is quite compatible with the low binding energy of H_2O and N_2 to metal surface.

B. <u>Hydrogen and species with M=43-44,56 (CO_2 and hydro-carbon fragments)</u>

Thermal desorption rates of these species, both before and after multipacting, were as low as $10^{-12}-10^{-13}$ torr.$1/cm^2$.s. Stimulated desorption exceeded thermal desorption by a factor 10^3-10^4. The natural explanation of this would be the high binding energy (1-10 eV) so molecules could only be removed from the surface by electron impact. While this might be true for hydrocarbons, it cannot explain the behaviour of hydrogen.

The adsorptive forces between hydrogen and the metal surface are even weaker than those of water and nitrogen. Therefore, there should be no free hydrogen on the lead surface. Evidently the hydrogen observed is released in some chemical reaction initiated by electron bombardment.

C. Oxygen

The partial pressure of oxygen dropped by 30-40% immediately the power was switched on and recovered immediately after termination of multipacting. That is another indication of the existence of some chemical interaction on the surface.

All these desorption patterns could be explained quite naturally assuming that hydrocarbon molecules decompose under electron impact and release hydrogen, carbon and hydrocarbon fragments. Some of these products react with oxygen in the residual atmosphere, some remain on the surface.

Yellow-brown discoloration appeared on the lead-plated surface after first multipacting. The discoloration did not disappear after immersing the sample in the chelating solution which would have removed lead oxide. Formation of a carbon layer on the lead surface also corroborates our hypothesis.

Unsuccessful attempts were made to clean the discoloured surface by RF discharge in He and H_2 atmosphere (2 W, 0.1 torr, 20 hours each). Only successive discharge in CO_2 (0.05 torr, 2-4 hrs) and H_2 atmosphere (0.05-0.1 torr, 20-40 hrs) removed the discolouration.

After treatment in the oxidation-reduction discharges and a second baking, the total degassing rate and duration of multipacting were the same as before, but discoloration did not re-appear. Degassing curves for partial pressures (Fig. 2B-4B) show that, whereas evolution of H_2O and N_2 essentially did not change, the amounts of hydrogen, carbon dioxide and hydrocarbons released were 2-5 times less than they had been before

treatment. The most dramatic change was behaviour of oxygen partial pressure; after an initial drcp, it increased almost to the starting value (Fig. 3B) implying no oxidizing reactions weree now occurring on the surface.

Together with the clear and bright appearance of the lead surface, these facts led one to conclude that the discharge treatment decreased considerably the amount of carbon and hydrocarbons available at the surface.

Chemical interaction between the surface and ionized gases is far from equilibrium: the temperature of the solid is as low as $300^{\circ}K$ and effective ion temperature in discharge is as high as $3000^{\circ}K$ [12]. For this reason, thermodynamics could be applied to analysis of interaction as a crude approximation only. Some indications could be perceived by a comparison of thermodynamical calculations and practical results for the reaction:

$$PbO + H_2 = Pb + H_2O$$
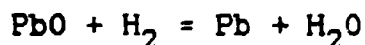
The equilibrium constant for this reaction is shown on Fig. 5. The real conditions in the hydrogen discharge, which observably reduce lead oxide, are:

$$P_{H_2} = 10^{-1} \text{ torr, } P_{H_2O} = 10^{-5}-10^{-4} \text{ torr}$$

Thus the effective temperature for reaction (1) has to be at least $1500 - 2000^{\circ}K$.

On the assumption of this temperature range, the oxidizing action of O_2, H_2O and CO_2 on carbon and lead were calculated. Of three gases, carbon dioxide has a maximum probability to convert carbon into CO leaving lead relatively intact.

4. CONCLUSIONS

One of the reasons for inconsistent performance of lead-plated superconducting resonators could be surface contaminations, particularly hydrocarbons. Surfaces acquire hydrocarbons at every stage of lead technology:; lead-plating, chemical polishing, wet cleaning and rinsing.

At low-field multipacting, hydrocarbons decompose under electron impact and leave carbon patches on the surface which subsequently become field-emission sites.

It is possible to remove carbon, hydrocarbons and oxide from the lead surface in vacuum, by discharge cleaning employing the chemical interaction between the surface and ionized gases.

A procedure of such cleaning was proposed and demonstrated on small samples. First results look quite promising but the work is far from complete. The lack of correlation between treatment and multipacting is a severe disappointment. Only consistent improvement of resonator performance after discharge cleaning could prove its value.

References.

1. G.J. Dick, J.R. Delayen, "A new chemical polishing procedure for lead-plated copper superconducting accelerating resonators"
   IEEE Trans. on Magnetic, Vol. Mag-19, N3, 1315, May 1983

2. E. Raub, K. Müller, "Fundamentals of Metal Deposition", Elsevier Publishing Co., 1967.

3. "Technical Lead-Plating From The Fluoborate Bath", Plating Chemicals TA-38352, Allied Chemical Corporation.

4. W.W. Burt, "Lead Technology for Superconducting Resonant Cavities",
   Proc. of Cryogenic Engineering Conference, 1983.

5. D.W. Storm "Successful Test Of The Prototype Low Beta Quarter-Wave Resonator",
   Univ. of Washington, April 1984.

6. M. Malev, J. Sokolowski, D. Stewart, D. Weisser, "Investigation of Lead Technology for Low Beta Superconducting Resonators",
   Interim report. Research School of Physical Science, Australian National University, Canberra, January 1985.

7. R.V. Latham, "Field-Induced Electron Emission From Localized Sites On Extended-Area Electrodes",
   Proc. of II Workshop on RF Superconductivity, July 1984, Part 2, 533.

8. J. Sokolowski, Private communication, 1984.

9. A.J. Hatch, E.B. Williams, "The Secondary Electron Resonance Mechanism Of Low-Pressure High-Frequency Gas Breakdown" Journ.of Appl.Physics, V.25,No.4, 417, 1954.

10. I.N. Slivkov "Electro-insulation and Discharge in Vacuum" Moscow, Atomizdat, 1972.

11. M. Malev "Gas absorption and outgassing of metals" Vacuum, V.23, No.2, 43, 1972.

12. A. von Engel "Ionized Gases" Oxford, The Clarendon Press, 1955.

TABLE 1

Contamination and cleaning in Lead and Niobium technology

Niobium	Lead
$Q = 10^{10}$	$Q = 5.10^8$
Grain size about 20 μ	Grain size 2-4 μ

Bulk Material

Electron-beam melting during	Lead plating with co-
Nb manufacturing	deposition of organic
Admixture:	colloid
Carbon 0.03%	Hydrocarbons 0.2-2%
Oxygen 0.01%	
Nitrogen 0.003%	

Pre-Vacuum Treatment

1. Chemical polishing in	1. Chemical polishing in
mixture of:	mixture of:
HF, HNO_3, H_3PO_4	HNO_3, CH_3COOH, H_2O_2 and
2. Rinsing in de-ionized water	EDTA (di-sodium salt of
	ethylenediamine tetra-
	acetic acid)
	2. Rinsing in EDTA, NH_4 and
	acetone

Baking

1900-2000°C	100°C
1 hour	20 hours
10^{-6} torr	10^{-6} torr

FIGURE CAPTIONS

Fig.1   Time dependence of the total gas flow from lead-plated
        polished sample under multipacting.

        f = 157 MHz, 1.8 W, 10^{-6} torr.

Fig.2   Partial pressuires of water ($\bullet$——$\bullet$), nitrogen (x——x)
        and hydrogen (o——o) during outgassing of leadplated
        unpolished sample under multipacting.

        f = 172.9 MH, 2 W, 10^{-6} torr

        · A. Before discharge cleaning

        B. after treatment in CO^2 (0.1 torr, 2 W, 2.5 hr)
           and H_2(0.075 torr, 2 W, 50 hrs) discharge.

Fig.3   Partial pressures of Mass 43-44 ($\bullet$——$\bullet$) and oxygen
        (x——x) during multipacting. The same sample as on
        Fig.2.

        A. Before discharge cleaning

        B. After discharge cleaning.

Fig.4   Partial pressure of hydrocarbons with Mass 56 during
        multipacting. The same sample as on Fig.2,3.

        A. Before discharge cleaning

        B. After discharge cleaning.

Fig.5   Temperature dependence of the equilibrium constant for
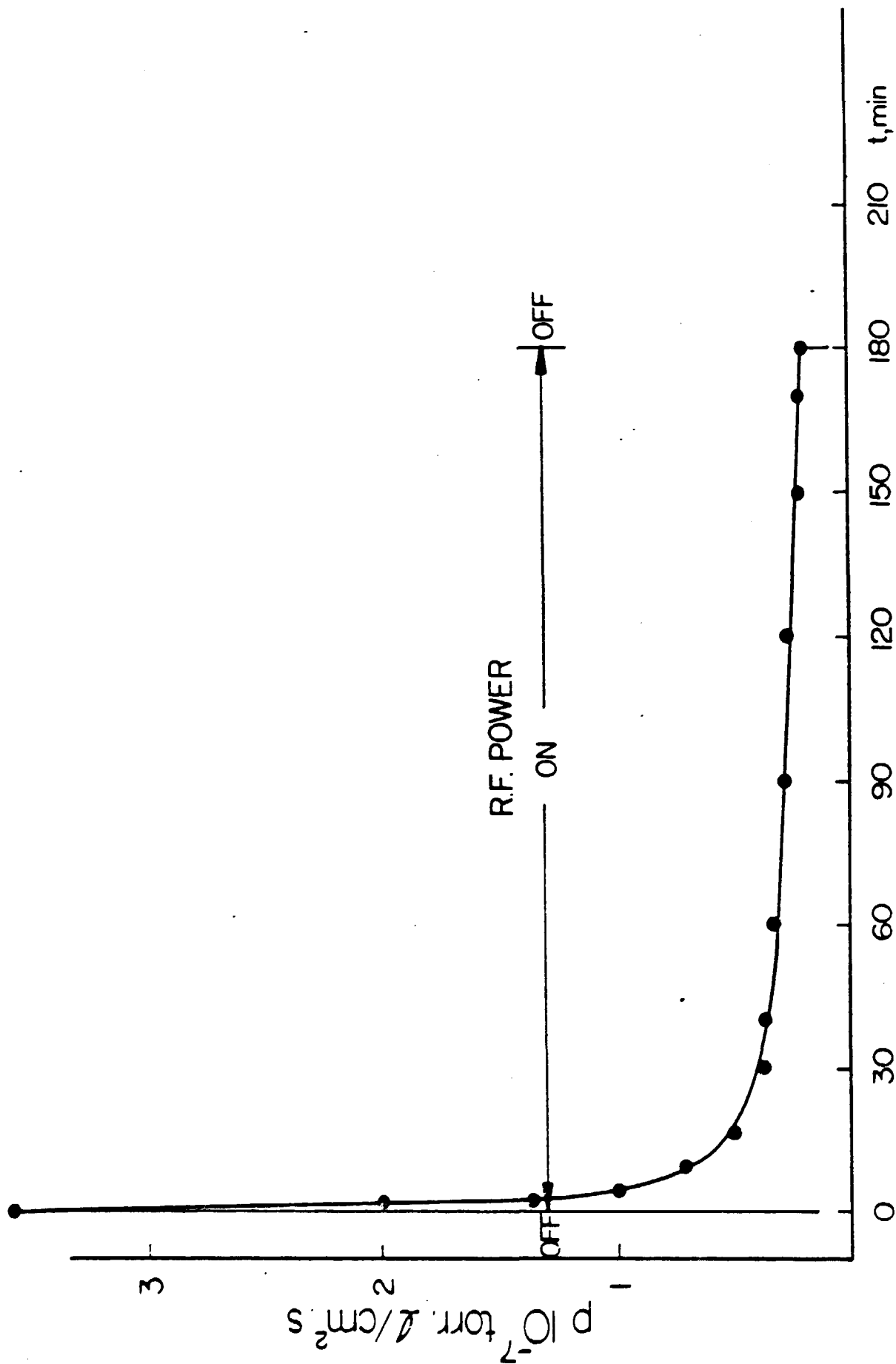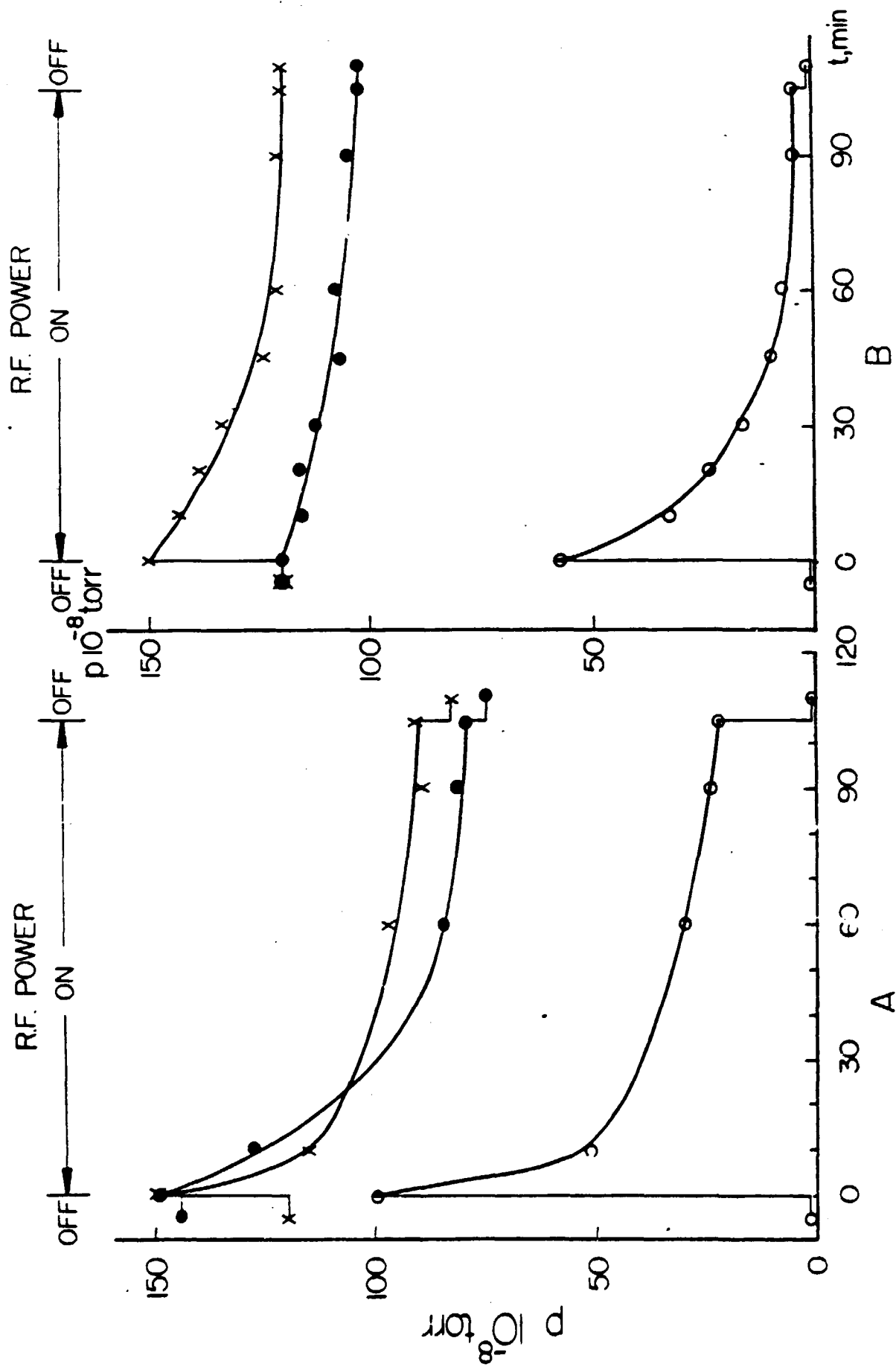   reaction of reducing lead oxide by hydrogen.
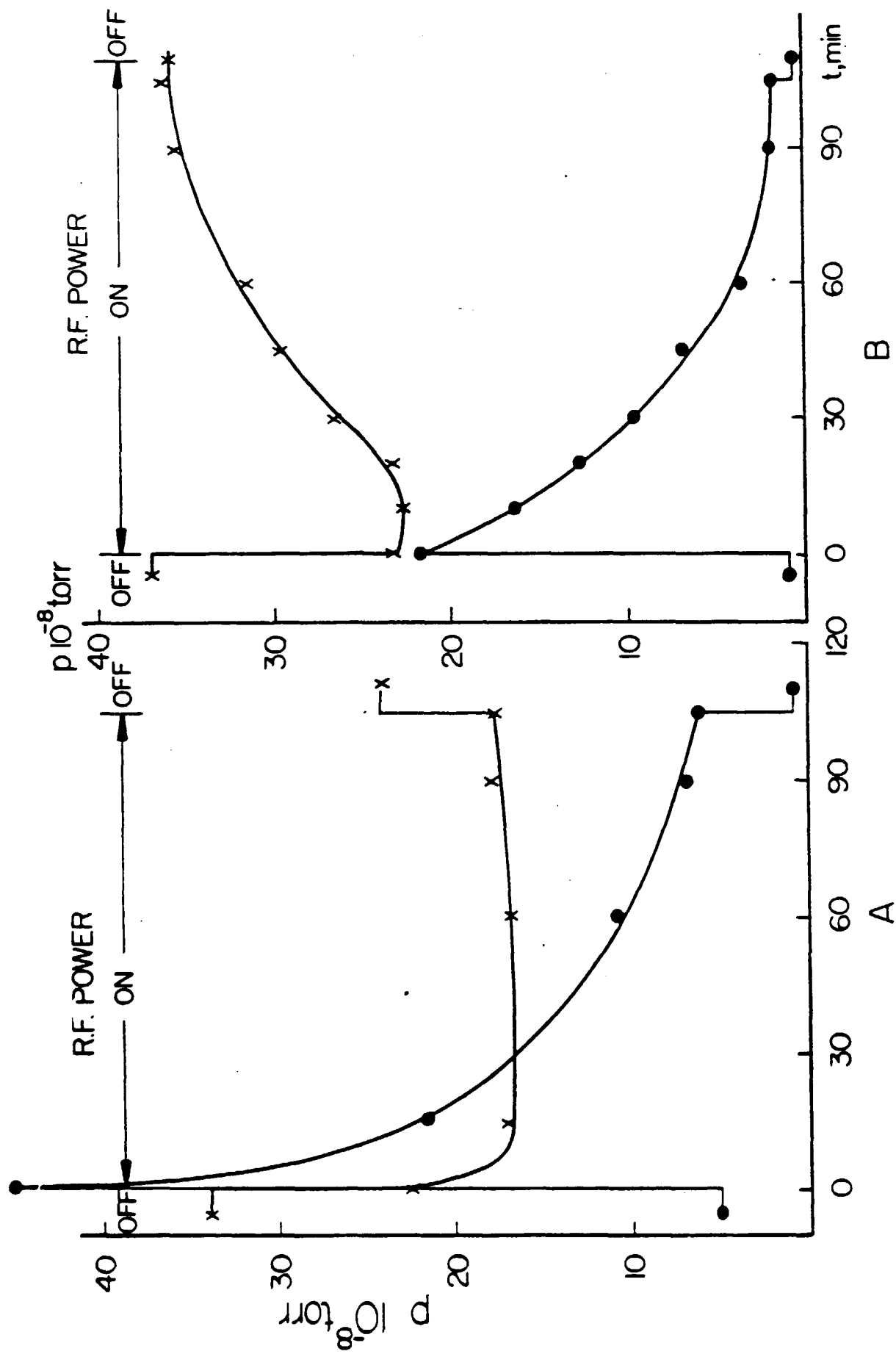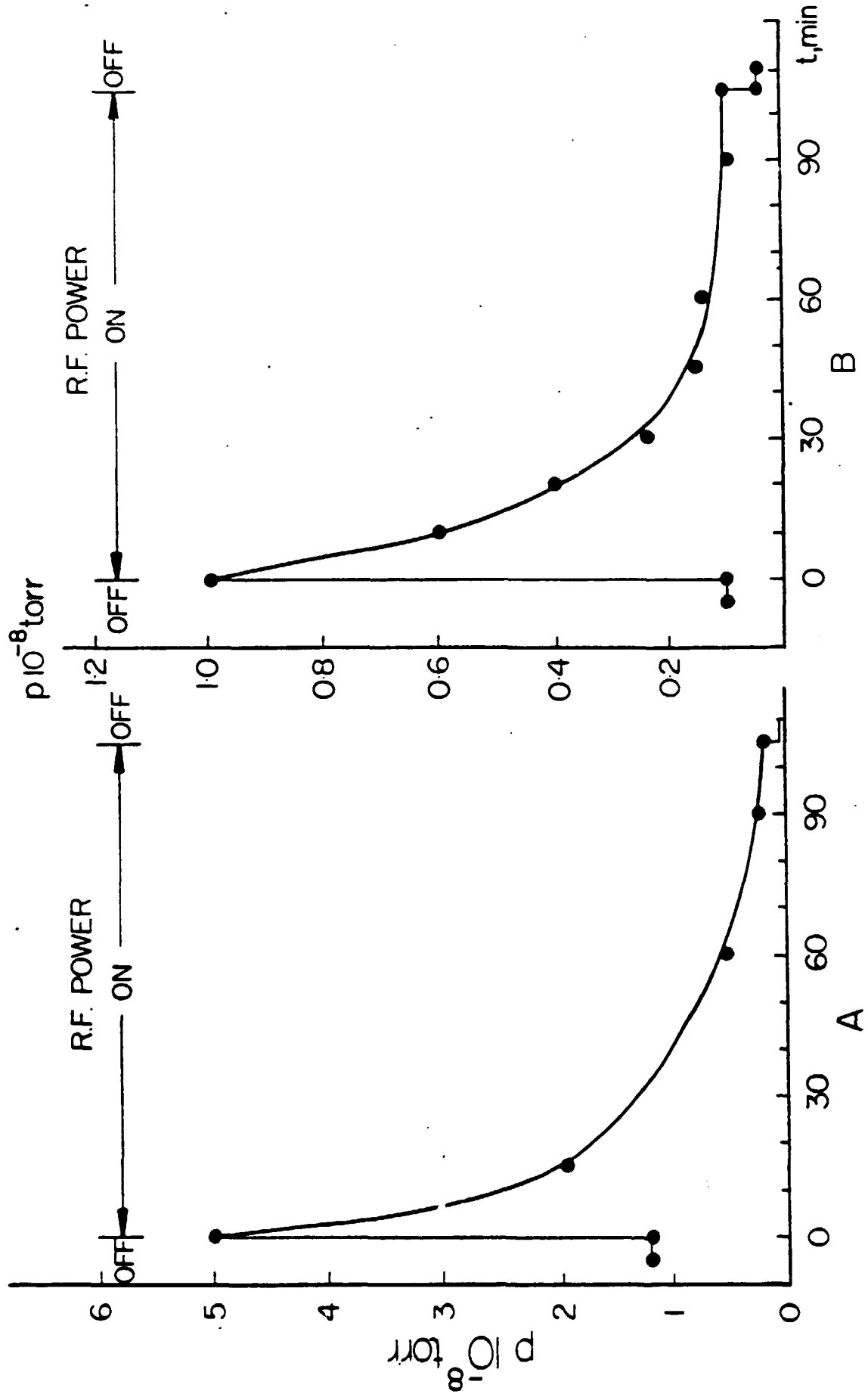
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5