Ing. G. Orsello
Elettrochimica Marco Ginatta

INDUSTRIAL PLANT FOR THE PRODUCTION OF ELECTROLYTIC TITANIUM. GINATTA TECHNOLOGY

Summary

Electrowon titanium has reached industrial commercialization.
In this paper we review the development stages which permitted the realization of the electrowinning plant.
Our first electrolytic industrial pilot plant ("Modex I") was built in 1980. It was succeeded by a second plant (Modex II) in 1983, and in 1986 we constructed the plant presently in operation (Modex III), which has a nominal capacity of 70 ton of titanium per year.
The core of the plant is its extraction module ("Modex") which comprises a chamber and a pre-chamber with controlled atmospheres and ancillary equipment. The interior of the chamber is horizontally divided by removable covers into two parts. The lower part contains the electrolytic cells operating at temperatures up to 950°C and with current intensities attaining 50,000 A. In the upper part, operating at temperatures of 100 to 120°C, an hydraulic manipulator handles the electrodes and allows a continuous mode of production.
The overall operation of the plant has a simplicity comparable to that of aqueous solution tankhouses.
In comparison with other present processes and plants for the production of titanium, the metal produced by a Ginatta plant has the advantages of lower costs and higher quality.
Costs are lower mostly because of: a) lower overall energy consumption; b) lower labour requirements due to the continuous character of the process and its high degree of automation; c) high rate of throughput; d) lower capital costs.

Introduction

The literature on electrolytic cells for the production of titanium from molten salts is quite extensive.
Although some of the associated developments reached the pilot plant stage, the lack of specifically designed hardware has not allowed their full exploitation at the commercial scale. Important examples of this state of affairs are provided by the activities of the U.S. Bureau of Mines (1-2), and of Companies such as New Jersey Zinc (3), Timet (4), Cezus (5) and D-H Titanium (6).
The Ginatta electrolytic plant was specifically designed and constructed for titanium.
Our development work started from experimental studies (7-9) in prototype cells. The results confirmed that the electrolytic production of reactive metals is difficult to maintain in small, closed cells for any length of time of industrial significance. Clearly, too many tasks and functions were assigned to too few general-purpose components, often with conflicting specifications.

The main recurring problems were:

- mechanical strength of the equipment at working temperature;
- corrosion of materials;
- handling of the cathodes for the continuous operation of the process;
- accurate data logging for all process parameters.

Our goal was to design a plant which overcomes these problems. In this paper we describe and illustrate the hardware which allows an easy operation of the process.

Description of the process

The raw material fed into the electrolytic plant is titanium tetrachloride.

It dissolves in the electrolyte in the Dissolution Cell (10) according to the reaction :

$$TiCl_4 \rightarrow TiCl_2 + Cl_2$$

The electrolytic titanium is deposited on cathodes in the Extraction Cell according to the reaction:

$$TiCl_2 \rightarrow Ti + Cl_2$$

The Dissolution Cell is separated from the Extraction Cell. Their common electrolyte (Sodium-Titanium-Chloride) circulates in closed circuit.

The cells have Heterogeneous Bipolar Electrodes, generating a high titanium tetrachloride dissolution rate in the electrolyte and a low average valence of the titanium species dissolved. They maintain, at a steady state, a very low activity of titanium chlorides in the insoluble anodes electrolyte volume (anolyte).

The operating temperature (830°C) results in:

- Low drag out.
- High current density.
- High titanium concentration in the electrolyte.

The electrolyte is inexpensive (NaCl technical grade) and easy to handle.

Description of the plant

The present design of our electrolytic plant (11) has enabled us to achieve the ease of operation of an aqueous solution tankhouse.

The plant we needed was to be characterized by high versatility and was to enable us to make electrochemical measurements and obtain samples under reproducible and steady state conditions of real industrial conditions.

Our Modex III plant has the flexibility required for the performance of long runs and for the rapid changes of many key parameters: cell configurations, types of electrodes, electrolyte chemistry, working temperatures, pressures and compositions of the gas atmosphere, current densities and voltages.
The plant is the result of a design integrating many components, each one specializing in a specific function.
The main tasks of the Modex plant are:

- providing an inert atmosphere in the electrolytic cell;
- melting the electrolyte and keeping the electrolytic cell at the working temperature;
- allowing energy and mass transfer between the electrolytic process and the exterior;
- controlling the process.

The Modex plant comprises:

- the external shell, formed by a chamber and a pre-chamber;
- the electrolytic cell, inside the chamber;
- the removable covers of the cell;
- a structure for supporting the electrodes and feeding electric current to them;
- the electrodes;
- the hydraulic manipulator, which performs the handling of the electrodes as well as maintenance and ancillary operations.

The Shell

The shell provides a protected environment in which the titanium electrolytic process can be operated in open cells.
The pre-chamber has the purpose of transferring material from the Modex to the exterior under a controlled atmosphere.
Windows allow vision inside the chamber and into the cells. Consequently, the electrodes can be photographed during the operation, and reference and standard electrodes can be exactly positioned for accurate measurements.

The Cell

Departing from the traditional designs, the Cell here has only one function, i.e. to contain the molten electrolyte. Gas tightness is assured by the shell.

This results in two very important operative advantages; the process can be run:

- at higher temperatures, and
- under negative pressure.

The Cell has been entirely built with carbon steel, the latter being quite compatible with the electrolytes of titanium production. The structural weakness of the cell at operating temperature has been overcome by refractories supporting the outside of the Cell.

The Cell is rectangular, a geometry typical of aqueous electrolytic plants (such as Pb, Zn, Cu...) and placed inside an electric furnace. To avoid corrosion and impurities, heaters and refractories are not in contact with the gases generated by the electrolysis. On start-up of the plant, the furnace melts the electrolyte. The current for electrolysis keeps the Cell at the operating temperature, but the furnace allows to test other working temperatures.

The Electrodes

The assembly of the electrodes is such that each one has an independent electric control and can be easily replaced.

The harvesting of the cathodes allows for the production to be continuous. In the Modex III Extraction Cell there are six cathodes, each one having a total immersed surface of two square meters.

Good electric contact is provided by the weight of the electrode on the couple of feeding bars; the shape of the contact ensures its cleanliness and a negligibly small junction voltage drop.

Bearing bars are fed by high intensity-low voltage electric feedthroughs, across the shell.
Busbars connect the feedthroughs to rectifiers.

Ancillary Equipment

All power-mechanisms of our Modex III use proportional hydraulics, that proved to be very reliable.
The main movements are associated with the two pre-chamber ports, the removable covers of the cell which thermally insulate the upper zone of the chamber, the manipulator which handles the electrodes and performs various maintenance tasks inside the module.
The inert atmosphere in the Modex is created by producing a vacuum (by means of pumps) at the plant start-up phase, and then by filling it with argon. The anodic gas is recovered with a chlorine pump continuously.
The rectifiers can be current or voltage controlled; reference electrodes can be used to pilot energy feeding.
$TiCl_4$ feed is introduced either by argon gas pressure, by metering pump or by negative pressure intake.
Various thermocouples measure the temperature at several strategic points of electrolysis, while linear piezo-resistive transducers monitor the pressure.
Logging and control equipments (PC and PLC) are located in a Control Room.

Materials

The Modex plant has been designed with the goal of cost effectiveness; consequently, low cost materials have been used. Low carbon steel has been selected for the equipment in contact with the electrolyte or with cell atmosphere: since iron reacts with the electrolyte and forms a highly stable and protective intermetallic compound.

That reaction is accelerated by means of a pre-electrolysis period in which the steel operates as a cathode, at low current density.
The steel is protected from anodic gas corrosion, at operating temperatures, because of the formation of a compact, high-melting compound (of the type Fe-Ti-O-Cl), which adheres to the metal and is generated by the reaction of iron with the atmosphere of the cell at the start-up of operation.
Low-cost refractories have been used, since they are not in contact with either the electrolyte or the cell atmosphere. The electrical insulators of the electrodes feedthroughs are the only high quality materials.

Operation of the plant

The continuous steady state production is obtained by supplying $TiCl_4$ to the Dissolution Cell housed in the shell.
The electrodes of this Cell are supplied with direct current from a specific section of the rectifier.
The electrolyte is composed of a mixture of sodium and titanium chlorides at a temperature of about 830°C. That temperature is maintained by the Joule effect of electrolytic current.
The titanium in solution is then deposited on the cathodes of the Electrowinning Cell, while chlorine gas is simultaneously evolved on the graphite anodes.
The electrodes of the Cell are supplied with direct current from a section of the rectifier which is independent of that for the Dissolution.
The electrolyte, containing a high concentration of titanium, progresses from the Dissolution Cell to the Extraction Compartment through convection movements in the electrolyte.
Samples of the electrolyte are periodically taken on a scheduled program and sent to the analytical laboratory in order to determine the concentration of titanium and its average valence state.
The chlorine produced is pumped to a plant for its recovery.

When the titanium metal deposited on a cathode has reached a predetermined mass, this cathode is removed from the bath by the manipulator. The "mature" cathodes are individually taken to the stripping machine, in order to harvest the product, and then immediately repositioned in the Extraction Cell to continue the electrowinning process.
To remove the harvested titanium, the pre-chamber is set in communication with the pre-chamber through an intermediate door. Before starting the operation an inert atmosphere in the pre-chamber is provided at the same pressure as that of the chamber.
The product is loaded in the crusher, and then treated in the leaching plant.
The titanium crystals are dried at low temperature and packed under argon.

Conclusion

The operating experience we gained through the Modex III plant allows us to conclude that:

- the positioning and handling of electrodes is very efficient;
- the equipment is reliable. Present hydraulic components ensure a very low probability of failure; furthermore maintenance do not interfere with production;
- the molten-salt electrolytic cell can be operated with the same simplicity as that of an aqueous solution electrolytic tankhouse. It is possible to pull up the electrodes, examine visually the deposit, take truly representative samples, without affecting the electrolytic system, and immerse them again;
- the inert gas volume above the cell has seal surfaces which are at room temperature;
- energy losses associated with the electrolytic process (i.e. ohmic potential drops and heath losses) or with ancillary equipment (i.e. manipulator) are very low.

Consequently, the overall energy consumption is also very low;

- the design of the plant permits the operation to be carried at high temperature, thus allowing:
  - the use of pure and inexpensive NaCl as electrolyte;
  - high density currents with reduced voltages;
  - low metal-values in drag-out salt;
- the design of the plant also allows a high level of automation.

The process and equipment yields an excellent quality of titanium metal. Typically, the impurities are in the following range: O, 200 to 400ppm; N, 30 to 50ppm; H, 200ppm; C, 50ppm; Cl, 200 to 400ppm; Fe, 50ppm.

In comparison with the titanium produced by thermochemical process (Kroll or Hunter) plants, only the core of the cake attains such a high quality.

Our work has demonstrated that this new design of electrolytic plant is cost effective on an industrial scale (12), because of significantly lower capital and operating costs.

We are presently installing at RMI Co. in U.S.A. a larger plant (Modex IV) with a rated capacity of 140 tons of titanium sponge per year. It is scheduled to start operations in the Fall of this year 1988 (13).

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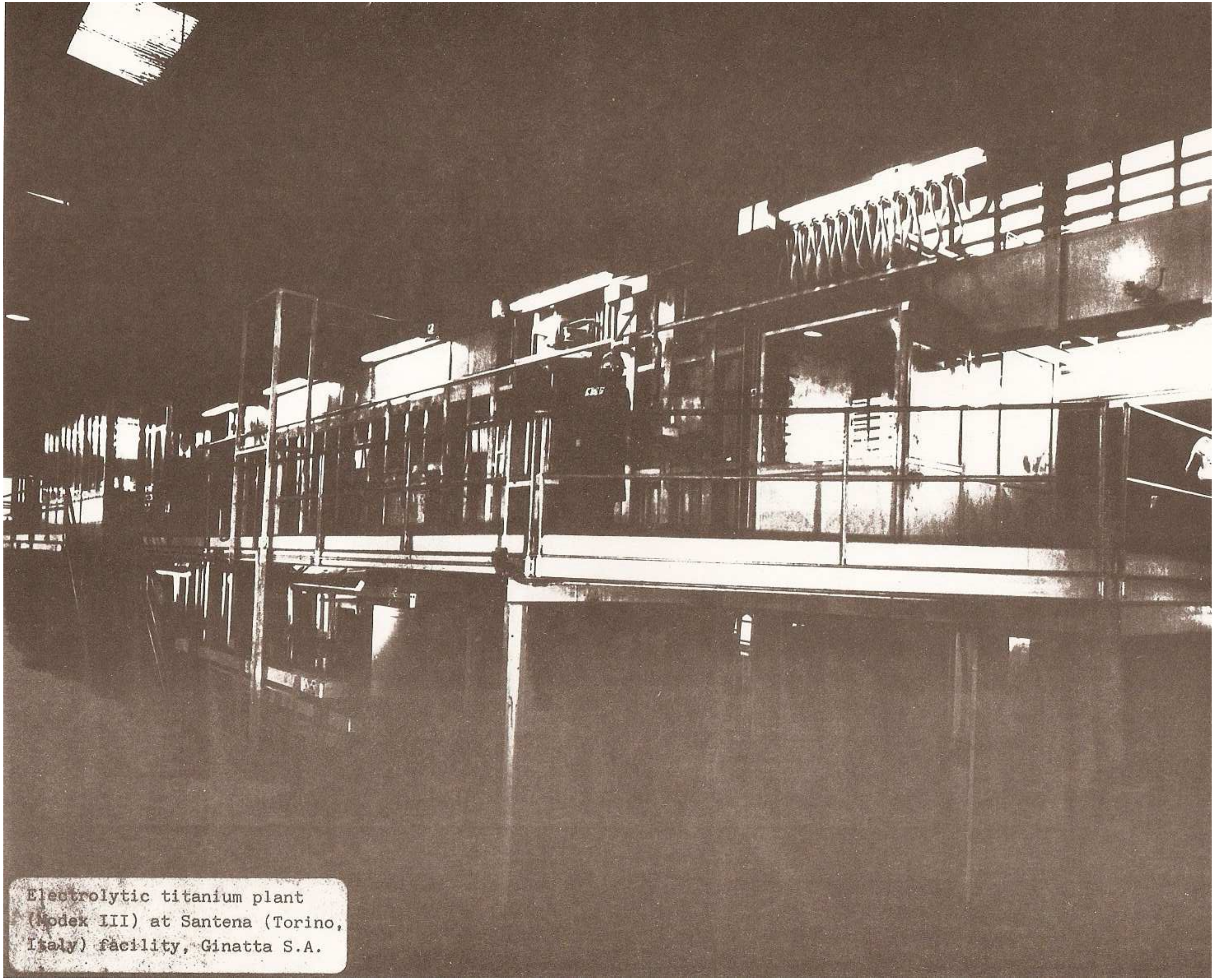
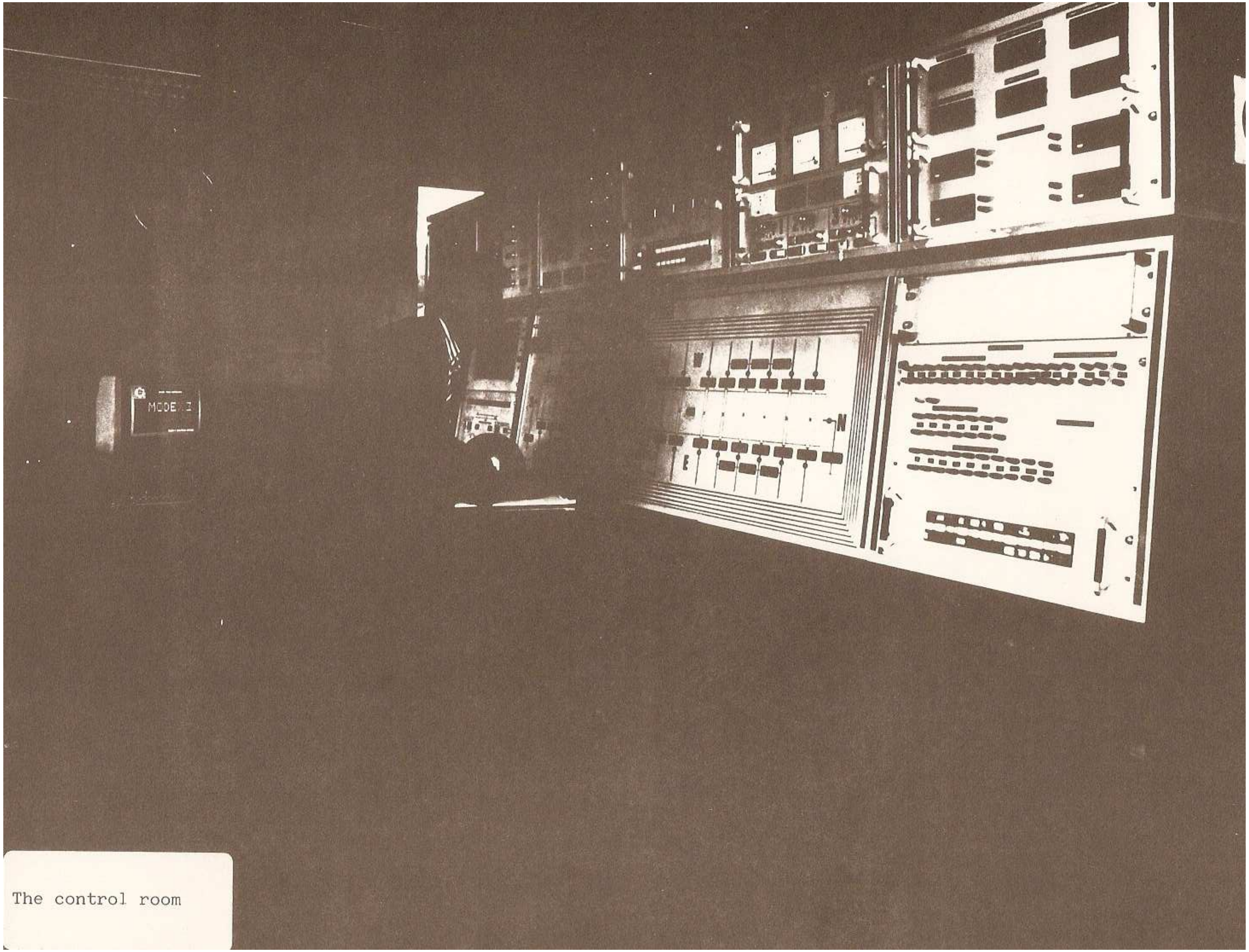
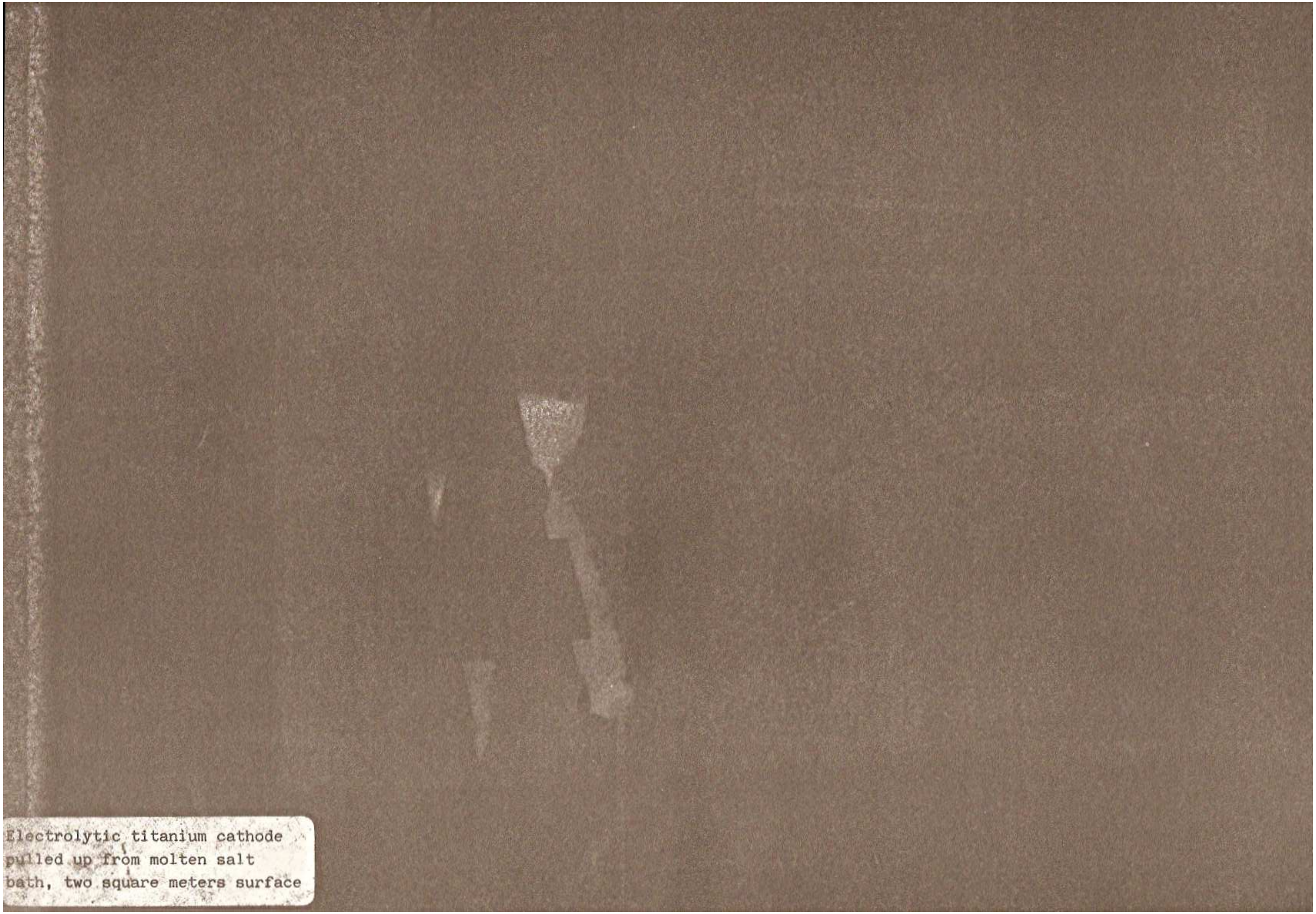


Electrolytic titanium plant (Modek III) at Santena (Torino, Italy) facility, Ginatta S.A.

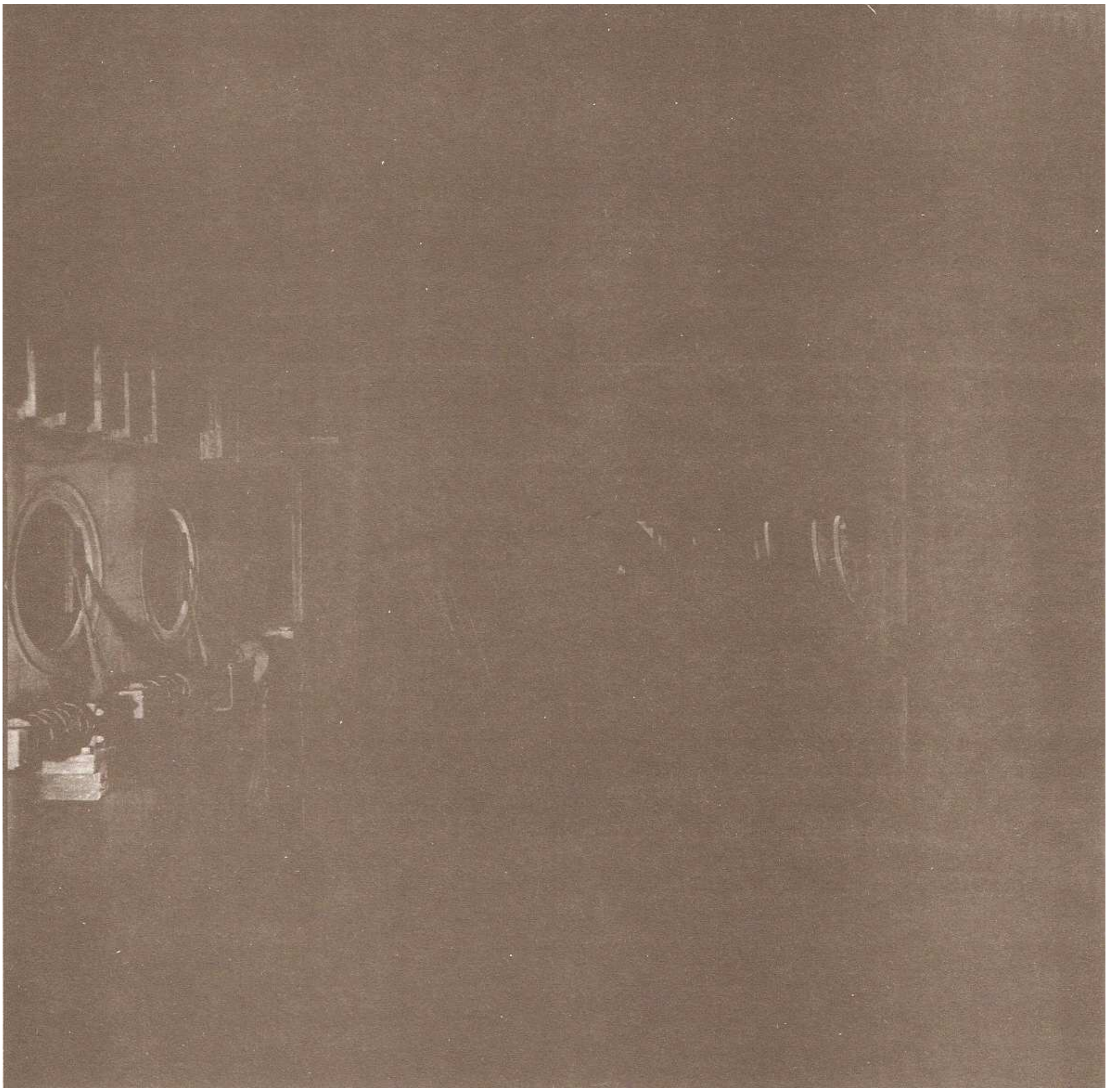


The control room



Electrolytic titanium cathode
pulled up from molten salt
bath, two square meters surface

Electrolytic titanium sponge



The Hydraulic manipulator
which handles the electrodes
inside the Modex