SYSTEM FOR THE COLLECTION, PURIFICATION AND RE-DRUMMING OF THE HEAVY WATER AT THE JRC ISPRA: DESIGN, OPERATION AND IMPLEMENTATIONS.

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Abstract

JRC Ispra has about 46.000 kg of slightly tritiated heavy water that no longer serves research activities. As the site has no suitable plant to process this liquid, a contract was signed for the transfer of ownership and its transport to the establishment of the future owner.

The heavy water has been stored for about twenty years in drums not more qualified for transportation, so that the transfer of the liquid into new IP-3 qualified drums must be performed before its shipment, in order to comply with international and future owner's Regulations.

In addition, as the acceptance of the heavy water by the future owner is conditioned to the respect of some quality parameters: title, electrical conductivity, pH, oil, TOC, turbidity, activity, the quality control of the D_2O during all operating phases plays an important role. For this reason on-line measurements and a sample taking system for subsequent lab tests have been considered.

Taking into account the above, the JRC has developed an operating system for the collection, purification, sampling and re-drumming the various stocks of D_2O.
A further implementation of the system has been carried out, after discovering an undesired high level of acetone in the heavy water. With the aim to reduce its concentration within the specified limits, a new equipment containing activated carbon has been added.

The details and most relevant aspects of the system are presented in this paper, while the results of the operating experience are given in another paper.

1. HISTORICAL BACKGROUND

JRC Ispra had about 46.000 kg of slightly tritiated heavy water that no longer served research activities.
The water has four degrees and has been safely stored for more than twenty years at the ESSOR Reactor (Figg. 1 and 2) in:

- 1 tank, called VB01 tank, located at level –11m in room 1120 containing about 10 m^3 of heavy water;
- 154 stainless steel drums, each containing about 200 litres liquid, located in a bunker at level –11m.

Hereafter are summarised the total inventory and the quality of the heavy water, according to the analysis of 1985:

Table 1 – Inventory of heavy water

STOCK	200-litre DRUMS	LOCATION	MASS ($x10^3$ kg)	Average D_2O Isotopic Concentration (%) weight	Max H_3 Activity (MBq/g) **
A	119	Bunker 1103	26.77	99.55	66.1 (28.4)
A	Tank VB01*	Room 1120	11.39	99.67	16.3 (7.02)
B	10	Bunker 1103	2.06	99.78	0.1 (0.04)
C	11	Bunker 1103	2.39	95.38	63.8 (27.4)
D	14	Bunker 1103	3.12	62.17	23.5 (10.1)
Total	**205**		**45.74**		

***** Tank VB01 contents is about 10.000 kg D2O, theoretically equivalent to 51 200-litre drums.
** According to 1985 analysis; updated values are indicated in parenthesis.

Table 2 – Characteristics of stored heavy water
(According to 1985 analysis)

Turbidity	< 5	Equivalent ppm SiO_2
Conductivity	< 2	µS/cm
Chemical Oxygen Demand	< 10	ppm $KMnO_4$
pH	5.5 – 8	
Chloride	<< 0.05	ppm
Nitrate	<< 0.05	ppm
Nitrite	<< 0.005	ppm
Ammonia	<< 0.05	ppm
Peroxide	<< 0.05	ppm
Aluminium	<< 0.05	ppm
Iron	<< 0.05	ppm
Chromium	<< 0.005	ppm
Sodium	<< 0.01	ppm
Mercury	<< 2	ppm
Copper	<< 0.005	ppm
Boron	<< 0.05	ppm
Fluoride	<< 0.5	ppm
Sulphate	<< 0.5	ppm
Nickel	<< 0.01	ppm
Nuclear poison	Absent	

2. ENDEAVOURS TO SELL THE HEAVY WATER

As the site has no suitable plant to process this liquid, a contract for the transfer of ownership and its transport to the establishment of the future owner was highly pursued during the collection period. There have been three attempts to sale the heavy water:

- *First endeavour in 1985*: publication of sale notice on the OJ, five selected candidate contractors, all declined to make an offer.
- *Second endeavour in 1990*: publication of sale notice on the OJ, three selected candidate contractors, one offer was accepted, seven years of negotiations brought to a "Nulla di Fatto" and formal discussions ended in 1998.

Meanwhile, the poor market conditions made the heavy water a **"no value"** object. It was considered a liability rather than an asset, therefore it was classified as a **waste** and

appropriately managed. In 1999, as part of the development of Ispra site D&WM Programme, the removal of the D_2O was identified as one of the 26 D&WM Projects.

- *Third endeavour in 2000*: publication of sale notice on the OJ, three selected candidate contractors, one of them submitted an offer, contract awarded to a Canadian Company.

  The Canadian Company required severe conditions, but it was very likely that the JRC Ispra would not have had another opportunity to transfer the ownership of the heavy water.

3. CONDITIONS FOR THE TRANSFER OF TITLE

3.1 General contractual requirements

Among others, the Canadian Contractor imposed the following technical conditions to the JRC Ispra to get the ownership of the D_2O:

a) Prior to shipment, a sample of each of the four heavy water lots (A, B, C and D) must be sent to the Contractor's chemical laboratory for acceptance testing, accompanied by a copy of the JRC Ispra analysis results for each drum.

Following its characterisation in 1985, the heavy water has been stored in its present locations, since when neither movements nor additional analyses ware carried out. So a new analysis campaign on all lots of heavy water had to be taken into consideration.

b) Upon confirmation of the acceptance testing, the heavy water is to be shipped in 200-litre stainless steel certified drums and appropriate overpack.

The heavy water has been stored for about twenty years in DOT 5B stainless steel drums supplied by DOE in the sixties. They are not more qualified for transportation, so that the transfer of the liquid into new IP-3 qualified drums had to be performed before shipment, in order to comply with international Regulations and future owner's requirements.

c) The contractor assumes the title of the D_2O at point of delivery.

From a legal point of view this means that the JRC Ispra is responsible on the D_2O for all activities indicated in point d), from on-site handling and preparation of drums and overpacks to the overseas transport up to the delivery point.

d) Handling, transportation and liability insurance up to the delivery point will be arranged by the JRC Ispra.

Together with point c) this implies that the JRC Ispra had to carry out activities such as re-drumming of water, analysis, handling, arrangement of drums into the overpacks and these latter into the sea containers, overseas transportation up to the delivery point.

3.2 Requirements on heavy water quality

According to the customer's requirement at point a) of the previous paragraph, a new characterisation analysis campaign on the heavy water before its shipment to Canada had to be taken into consideration, in order to ensure full compliance of physical and chemical characteristics with the Customer's requirements.

As a first set of measurements, the following characteristics had to be measured and their values compared with the acceptance limits set by the customer:

Table 3 – Customer's required quality for heavy water

	CHARACTERISTIC TO MEASURE	ACCEPTANCE LIMITS
1	D_2O isotopic abundance	99.5%
2	Electrical Conductivity	2 ìSiemens/cm
3	pH(a)	6.5 – 9.5
4	Total Organic Carbon	1.1 mg/l
5	Oil	1.1 mg/l
6	Turbidity	2 NTU
7	Tritium activity	11 Ci/l (407 MBq/cm^3)

According to the customer's requirements, if the subject heavy water does not pass the above test, then the JRC would have to perform a second set of chemical analyses, in an effort to determine the source of impurities, which shall consist on testing for:

- Nuclear poisons (Gadolinium, Lithium and Boron);
- Nitrate, Ammonia, Chloride;
- Chemical Oxygen Demand (COD).

4. THE DEVELOPMENT OF THE PURIFICATION SYSTEM: CONCEPTUAL DESIGN, MANUFACTURE AND OPERATION

Taking into account the requirements listed above, the whole project for heavy water transfer came to light, starting from the conceptual design, developed with the scope to optimise the re-drumming and purification process, up to the transportation scheme.
The following operational hypotheses were done and subsequent actions undertaken:

1. The tank VB01 would have been used as a "temporary tank" for mixing, homogenising and eventual purification of all heavy water stocks.
   In fact, the requirement to have each drum analysed was considered too tough from the financial point of view, so it was decided to mix up the heavy water of drums from the same lot into tank VB01 up to its filling, in order to have a homogeneous lot.
   This solution presented several advantages:

   - only one sample, or a limited number of samples per lot, could have been taken for analysis;
   - reduced duration of the whole process of purification and re-drumming if compared with that for each single drum;
   - only one final drainage of tank VB01 would have been required.

2. As a consequence of the previous point, all 154 drums stored in bunker 1103 must be transferred to the working room 1138.
   Such operation will be carried out by means of the 50Mg bridge crane of the ESSOR Reactor, following a well defined path: bunker → reactor hall → working room 1138.

3. The homogenised water in tank VB01 should have been transferred into new IP3 certified 200-litre drums, following a decreasing order of quality of water, from stock A to stock D.
   This ensures that a high quality stock would not have been contaminated with heavy water at a lower level of isotopic abundance.

4. For the transfer of the D_2O into the 200-litre drums, JRC will utilise a new mobile purification equipment, located in the working area at level –11m, whose realisation will be based on an already existing equipment, suitably implemented to take into account the design and the operating inputs.

   The choice of a mobile system was determined by the fact that the equipment could be used in other installations of the Centre for liquid treatment.
   The same equipment should have been "reversible", in order to allow not only the transfer of the liquid from the tank into the new 200-litre IP3 certified drums, but also the reverse operation from old drums to tank, in order to meet the requirement set in point 2.

5. The equipment should have been "multi-purpose" equipment with the following functions:

   - Circulating, mixing and homogenising the heavy water present at each stage in the tank VB01;
   - Purifying the D_2O by means of ion exchange resins, in order to lower the electrical conductivity of the liquid to the required value (2 ìSiemens/cm). With regard to this, two conductivity meters would have been mounted on the equipment, to monitor and measure inlet and outlet values;
   - Re-drumming the D_2O into the new IP3 drums;
   - As the acceptance of the heavy water by the future owner was conditioned to the respect of the seven physical and chemical characteristics listed in the previous paragraph, the quality control of the D_2O during all operating phases played an important role.
     For this reason a sample taking system, with water drainage both on the inlet and outlet side, for subsequent lab tests has been taken into consideration.

6. The equipment should be equipped with a mechanical filter for impurity removal.

7. Before starting the circulation and purification of the liquid, the resins had to be properly conditioned with high quality D_2O, in order to avoid any undesired lowering of its title. For this reason the appropriate procedure to deuterise the ion exchange resins had to be set up.

The above hypotheses led to the following design and operating schemes:

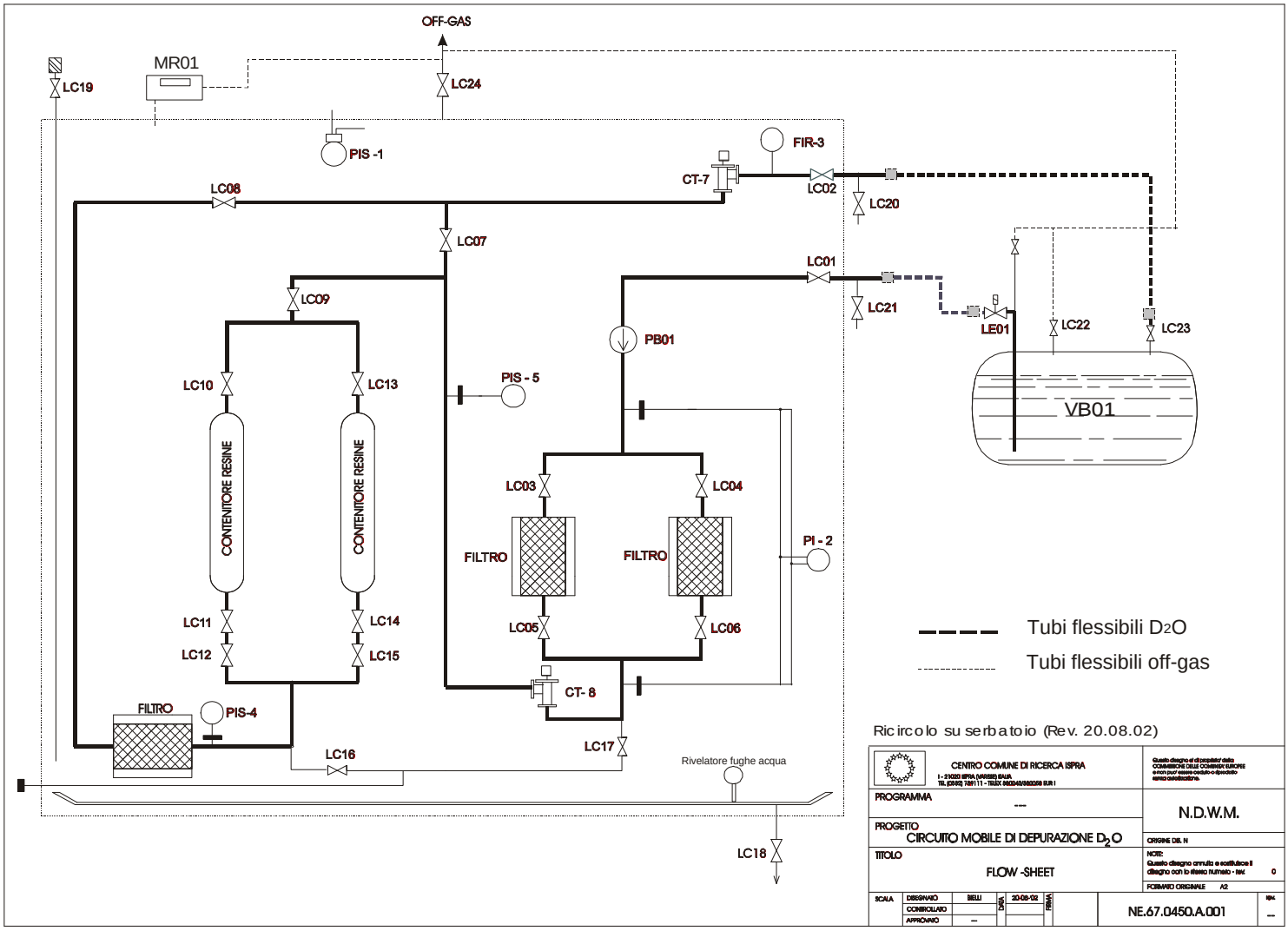


Fig. 1 – The mobile purification equipment recirculating the D_2O into tank VB01

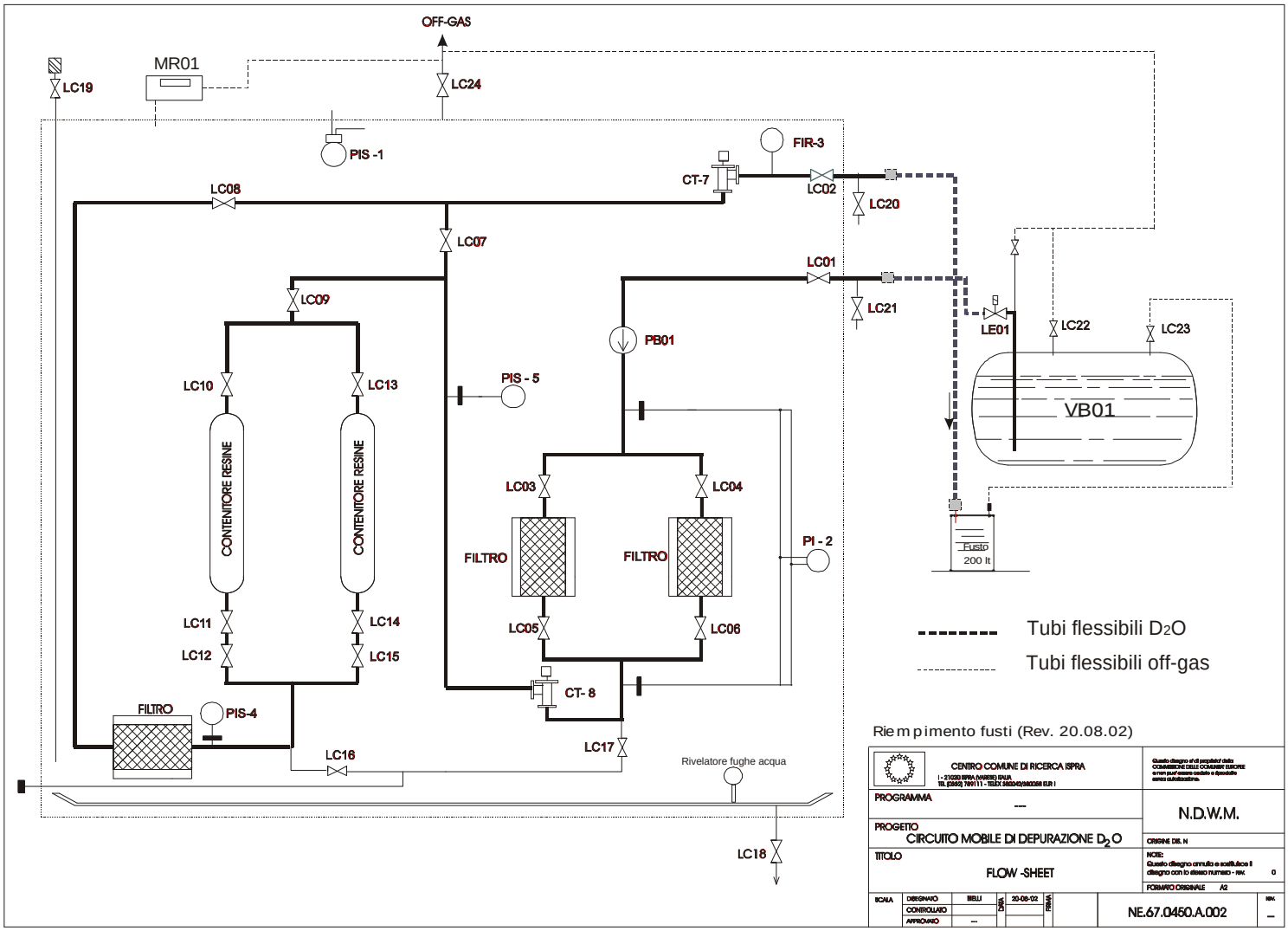


Fig. 2 – The mobile purification equipment filling the new drums with purified D_2O

5. THE MOBILE PURIFICATION EQUIPMENT

The equipment has been designed and manufactured with the aim to allow transferring the heavy water from its current location to the new drums and, if necessary, its treatment for purification, so to reach the contractual value for the characteristics listed in point 2.2.
Such a result has been achieved by means of the mobile purification equipment in a close circuit circulation (see Figures 1 and 2). The connection between the equipment and the tank/drum is carried out by means of flexible pipes in Teflon with external stainless steel reinforcement (up to pressures of 140 bar).

The circulation of the heavy water is ensured by means of a peristaltic pump, with a maximum pressure drop of 5 bar and two different liquid flows of 500-1000 litre/min, to take into account the different conditions for purification and liquid transfer.
The purification of the heavy water has been achieved with liquid flow through a mechanical filter and a fluid bed with ion exchange resins (Amberlite IRN Nuclear Grade Mixed Bed).

The instrumentation mounted on the equipment includes:

- Two conductivity analysers/controllers: the first on the inlet side, the second one on the outlet side of the equipment.
- A flow-meter with integral counter;
- A differential pressure gauge, for monitoring the efficiency of the filter.
- A pressure gauge to measure the inlet pressure.
- A differential pressure gauge, for monitoring the efficiency of the filter downstream of resins.

The equipment with all its instrumentation has been installed within an airtight box, connected to the off-gas system with the double function of keeping the box underpressure with respect to the ambient pressure and safely evacuating the tritium through the proper ventilation network.
A small fan has been mounted in order to ensure a reasonable value of negative pressure inside the box.

All valves in the box are driven from outside by means of airtight gloves.
The sidewalls and the cover of the box, in Plexiglas, are demountable, to allow resins and filters replacement and equipment maintenance.

Both on the inlet and outlet liquid flow of the circuit two pipe fittings with plug valve (cock) have been foreseen for sample taking.

The equipment is remotely driven and controlled by means of a control board (see Fig. 5).

An ion chamber with double threshold set at 10^6 Bq/m^3 and 2Ì10^6 Bq/m^3 for in-air tritium monitoring is installed on the connection between the equipment and the off-gas line.

Figure 3 shows the mobile purification equipment in its “as built” state, while Fig. 4 shows the same equipment in working conditions (sample taking procedure).

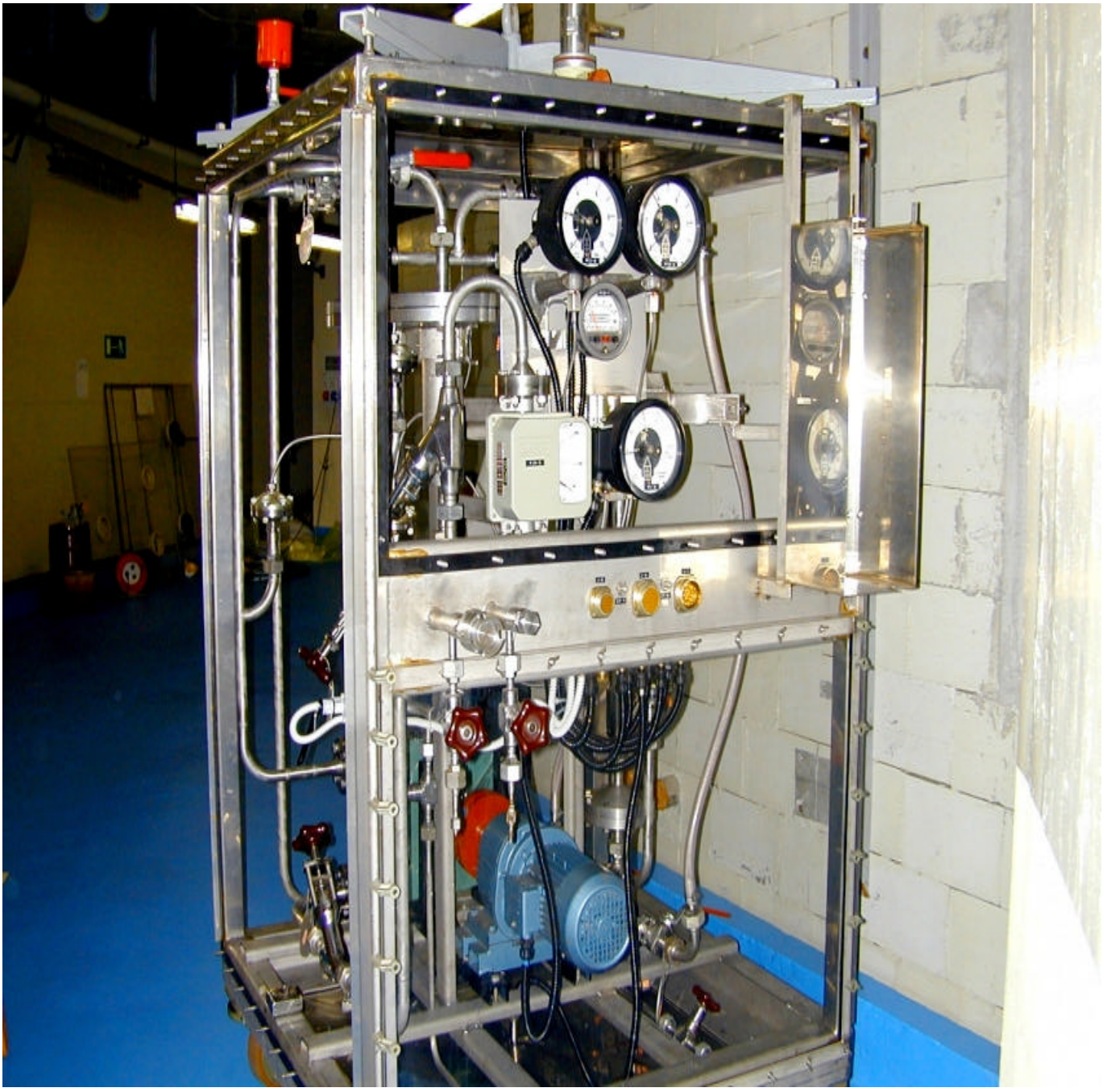


Fig. 3 – The mobile purification equipment

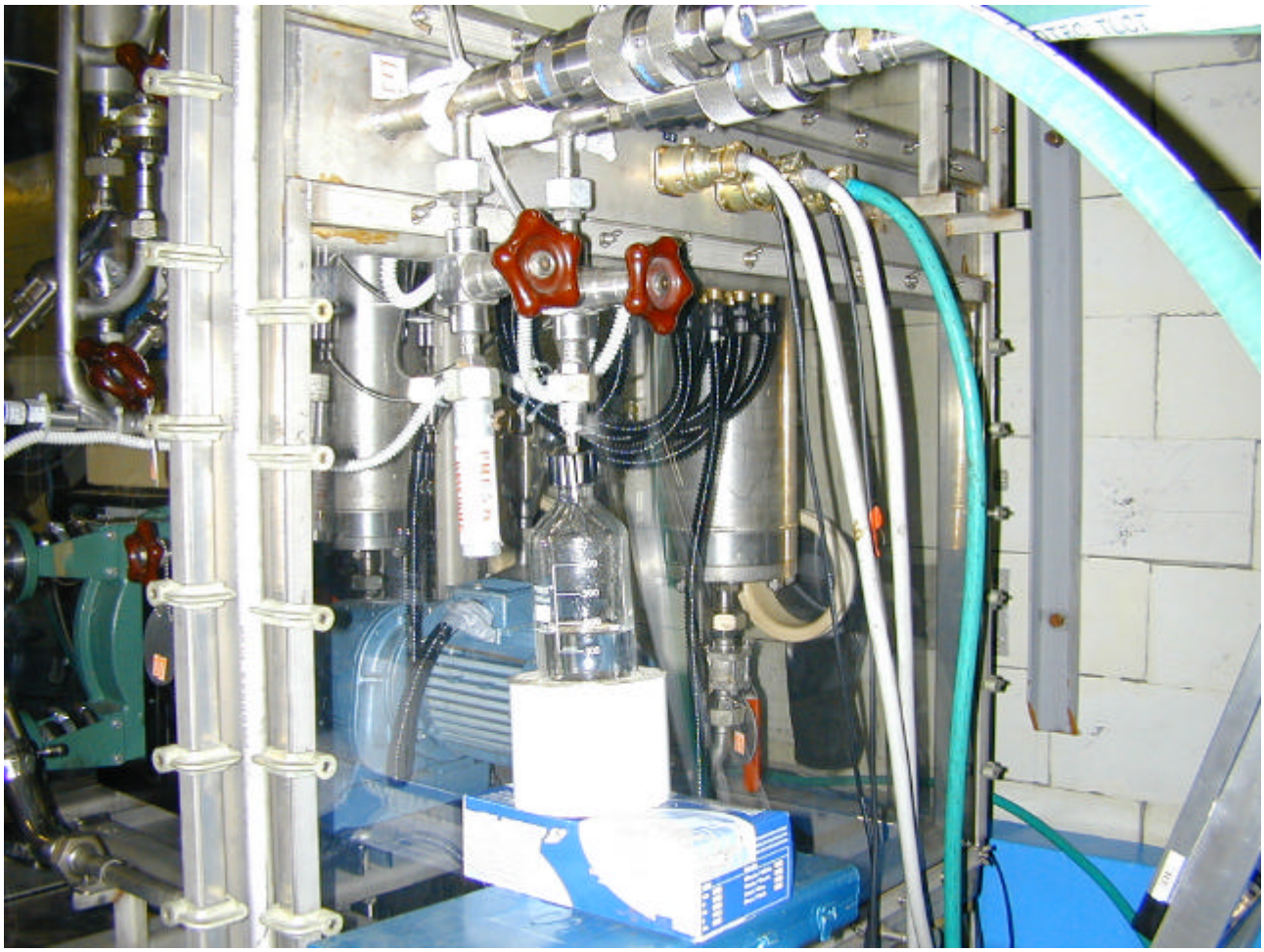


Fig. 4 – Sample taking in progress

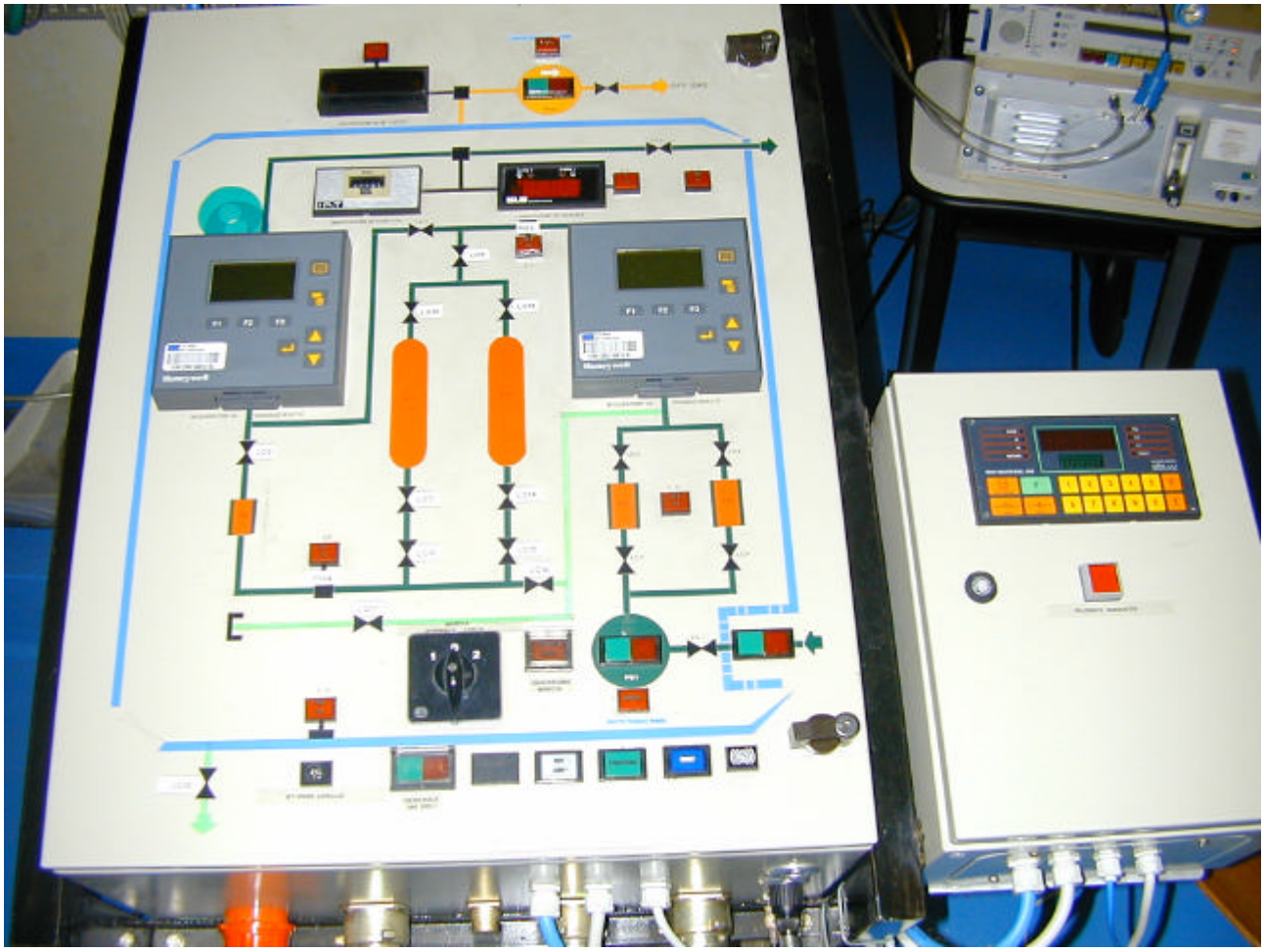


Fig. 5 – The control panel of the mobile purification equipment

6. WORKING AREAS AND FACILITIES

The working area chosen to install the mobile equipment is room 1130 located at level – 11m, where there is sufficient space for equipment arrangement and drums handling.
This choice has been dictated by the fact that the tank VB01 is located in a room adjacent to room 1138, very easy to reach with flexible pipes from the mobile equipment.
Moreover, the same room is served by the bridge crane for the transfer of the old and the new drums from the storage bunker to room 1138 and viceversa, from the latter to the reactor hall for drum loading into the overpacks.

7. THE PURIFICATION AND RE-DRUMMING PROCEDURE

7.1 Purification and re-drumming procedure of D_2O from tank VB01

Check of heavy water quality and eventual purification

- Connecting the tank VB01 to the mobile purification equipment by means of flexible pipes and electro-pneumatic safety valve (see Fig. 1);

- A pressure test for leaks is carried out with helium at a pressure test of 0,1 bar;

- Circulation of heavy water through the filters with instantaneous measurement and check of electrical conductivity value (outlet side). At this stage the resins are by-passed and therefore excluded from the circulation of liquid;

- In case of measured values of conductivity too high when compared to those required, the circuit layout is modified by inserting the resins, closing valve LC7 and opening at the same time the valve LC11 and LC25.

- Purification of the heavy water begins and continues purifying until the target value of 2 μS/cm is reached.

- During the phase of purification the following parameters are monitored and kept under control:
  - ΔP of filters
  - MF for evaluating the liquid flow and the pressure drops in the circuit.
  - The measured values of the conductivity, with the double scope of assessing the effectiveness of the purification process and the reach of the saturation limits for resins.
  - Presence of tritium inside and outside the box equipment.

Liquid transfer from tank VB01 to the new IP3 certified drums (see Fig. 2)

- Keeping the suction pipe connected to the VB01 tank, connect the runback pipe of the mobile equipment to an empty drum;

- The drum, located on the automatic balance, is then connected to the off-gas system by means of a drop vent plug;

- Drum filling with the mobile equipment on the basis of the litre counter FIR-3 connected to the flow meter and the weight on the balance scale.

- The amount of D_2O let into the drums is controlled by means of an on-line electronic balance, with adjustable set point and automatic intervention stop the filling of drums. The balance is connected to a PC in which all measured data are stored in a database. The

system output is an adhesive bar code label with all information related to the drum, its content, weight and characteristics of the liquid.

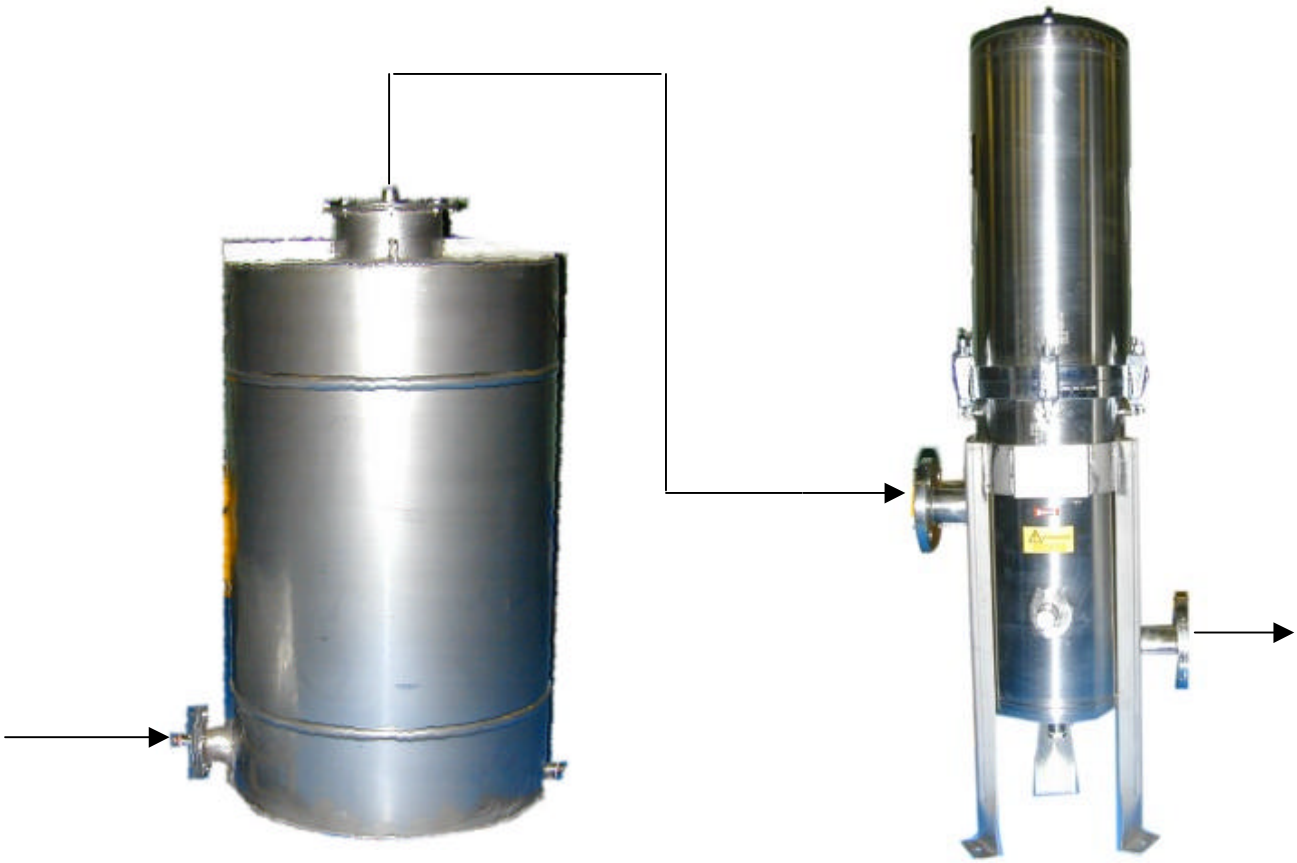
- At the end of the filling operation, all connections are removed, the cover plugs inserted and the weighing of the filled drum performed.

- The drums are then transferred to the interim storage area, waiting to be inserted into the overpacks.

- A new drum is connected and the same procedure repeated.

8. IMPLEMENTATION OF THE SYSTEM

A further implementation of the system has been carried out, after measuring a very high TOC level in the heavy water contained in the old DOT 5B drums. After deep investigation, whose results are reported in another paper, it was evident that the undesired high level of TOC was attributable to acetone.
In order to reduce its concentration within the specified limits, a new filtering equipment containing activated charcoal has been added. This has led to the modification to the previous circuit as indicated in Fig. 5.



Charcoal filters for acetone removal

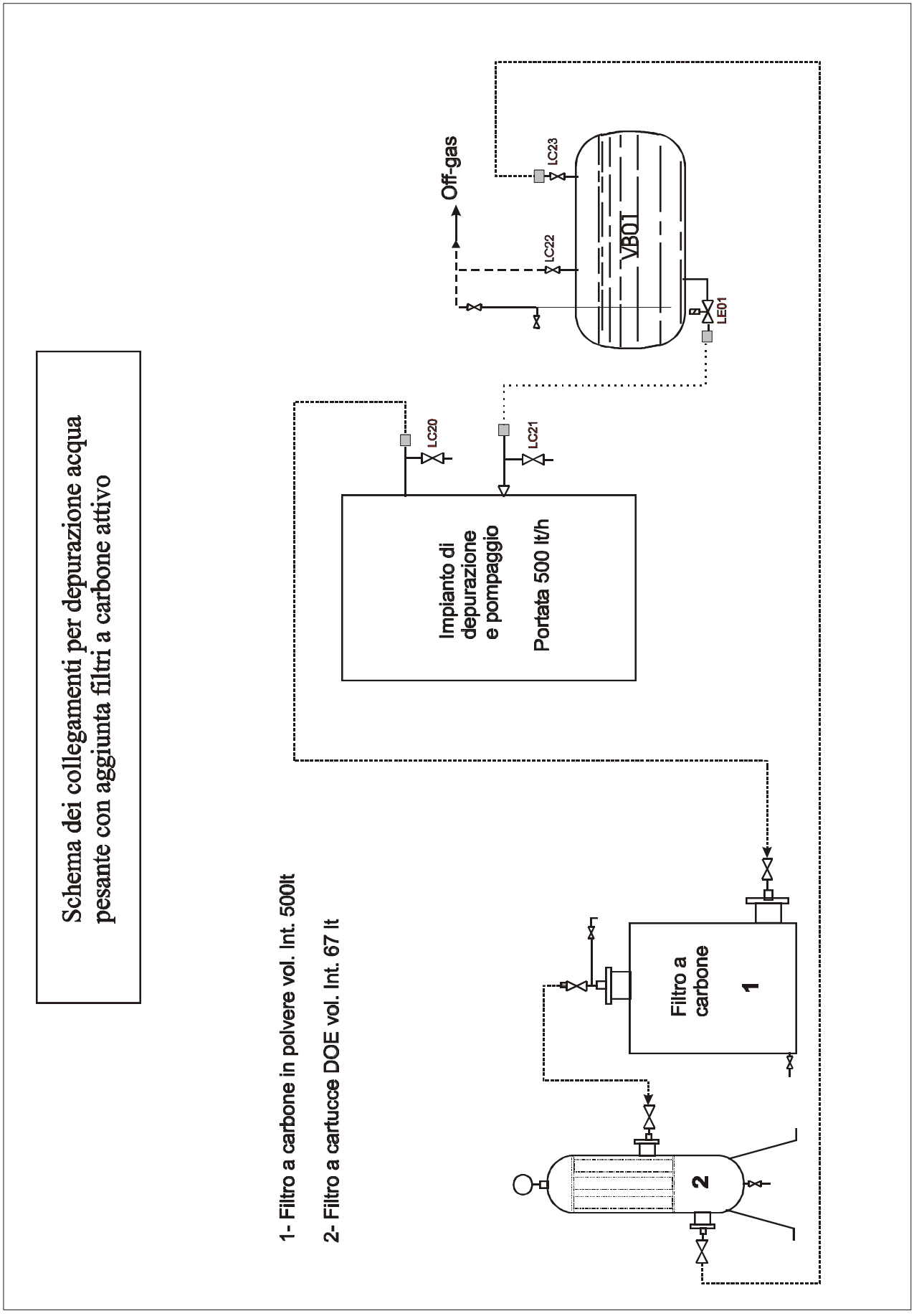


Fig. 5 – The circuit of purification with the charcoal filters