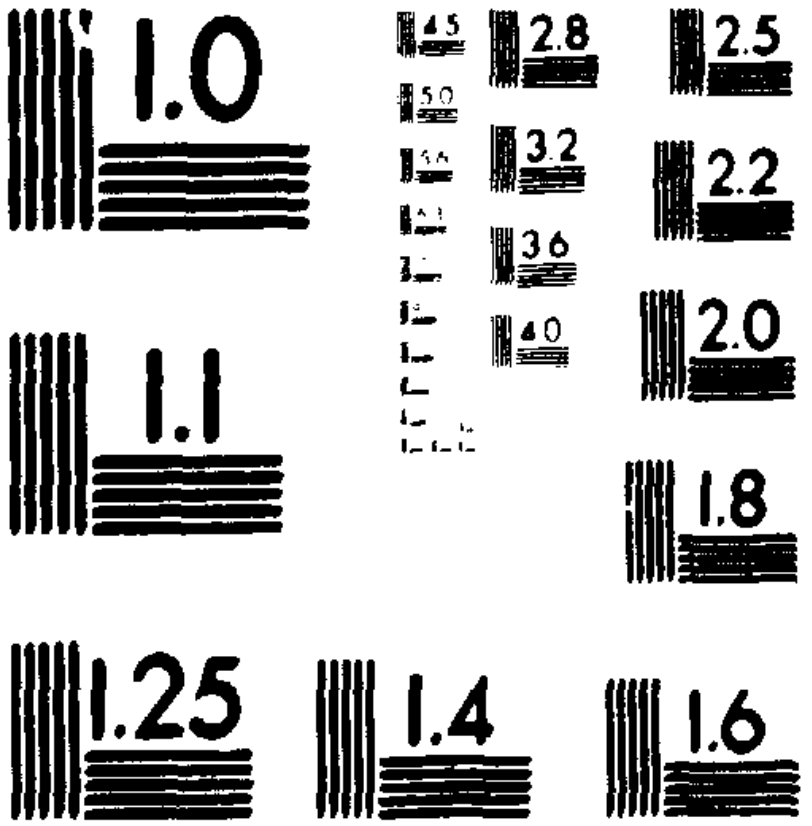
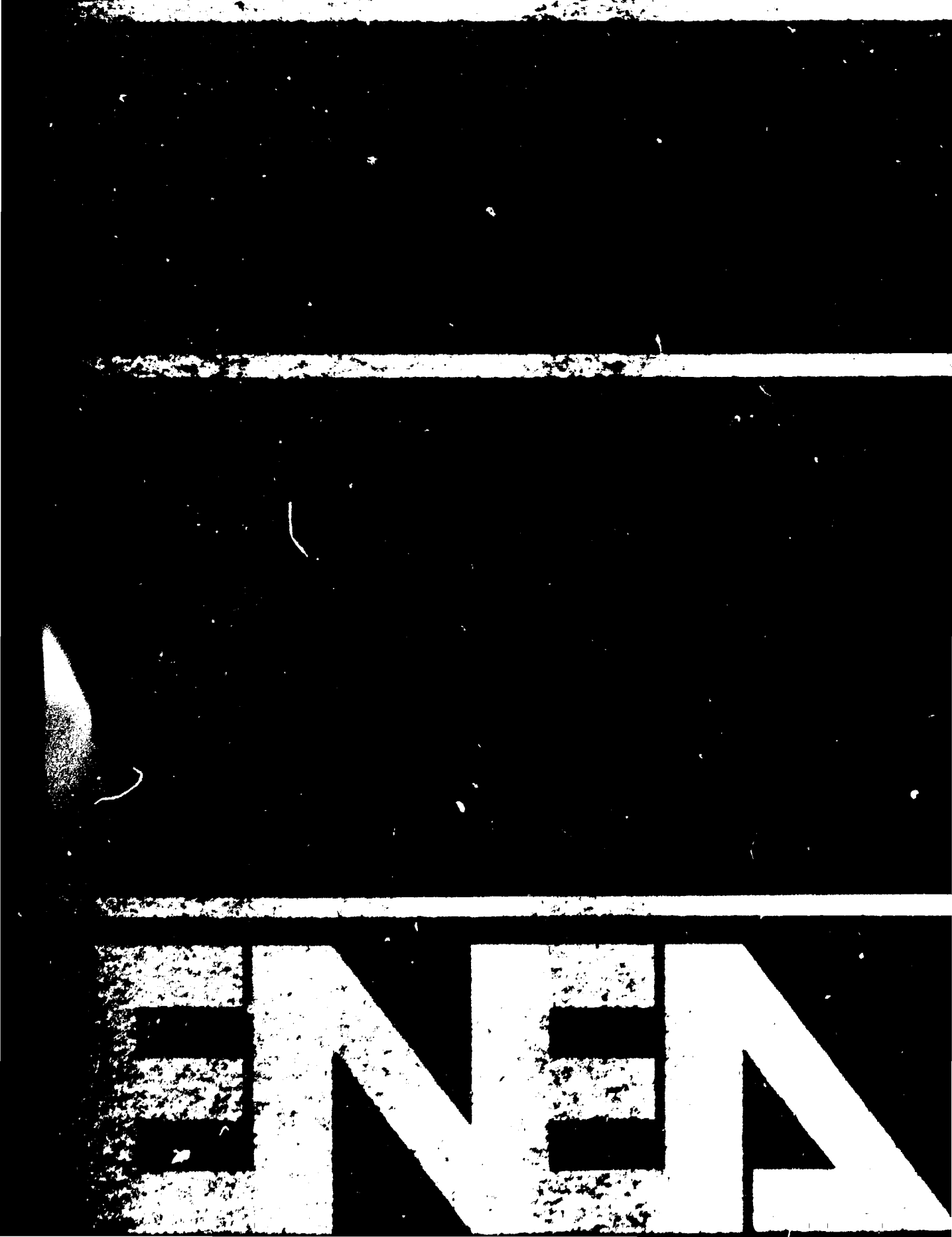




ISSN/0393-6252

COMITATO NAZIONALE PER LA RICERCA E PER LO SVILUPPO
DELL'ENERGIA NUCLEARE E DELLE ENERGIE ALTERNATIVE

# THE R & D ACTIVITIES CARRIED OUT IN ISPRA, ACCORDING TO A COOPERATION BETWEEN ENEA COMB AND JRC-ISPRA IN THE FIELD OF RADIOACTIVE WASTE MANAGEMENT

R. NANNICINI, H. DWORSCHAK, F. DANIELE
ENEA - Dipartimento Ciclo del Combustibile, Attività Enea presso il centro di Ispra

RT/COMB/87/7

*Testo pervenuto nel giugno 1987*

Progetto ENEA: Trattamento - condizionamento
residui radioattivi (CH)

Summary

The R & D activities carried out in Ispra since 1984 in the frame of a collaboration contract ENEA-COMB/ CCR- ISPRA, concerned the HLW vitrification in real conditions of activity, using the ESTER minipilot plant, the decommissioning of this plant, the characterization of the active glasses produced, and, finally, the starting of the PETRA experience (design and construction), which is more complete than the ESTER one, but also more complex.

RIASSUNTO

Le attività di R.e S svolte a Ispra dal 1984 nell'ambito di un contratto di collaborazione tra l'ENEA-COMB e il CCR-ISPRA sono consistite nella vetrificazione dei residui ad alta attività, in condizioni reali di attività, utilizzando l'impianto minipilota ESTER, nel decommissioning dell'impianto stesso, nella caratterizzazione dei vetri attivi prodotti, ed, infine, nell' avvio dell'esperienza PETRA, che é più completa della precedente ESTER, ma anche più complessa.

## ABSTRACT

The R and D activities, carried out in Ispra since 1984, in the field of radioactive waste management, according to a cooperation agreement between ENEA-COMB (Technological Development Laboratory) and JRC, concerned final hot tests of the ENEA owned ESTER mini-pilot plant for HLW vitrification, the decommissioning of this plant and the transportation of 3 of the active glass containing crucibles from the Ispra to the Karlsruhe (Transuranium Institute) establishment of JRC for the characterization of radioactive glasses produced by the ESTER plant.

While the ESTER experience is being successfully finished, contemporarily the basis has been established to start the PETRA experience, more complete than the previous one, but also more complex.

The PETRA experimental infrastructure will be particularly useful for studying, developing and verifying, in real activity conditions, advanced chemical extracting agents and mainly new matrices for the immobilisation of HLWs, or their fractions, and of mixtures of various aqueous waste streams.


## INTRODUCTION

The cooperation between ENEA COMB MEPIS SVITE and JRC ISPRA started in 1984 with final hot tests of the ENEA owned ESTER minipilot plant for the HLW vitrification. The decommissioning of the ESTER plant started by the second half of 1984 with the rinsing of the circuit and was carried on with the plant dismantling and the final decontamination of the cell from November 1985 to June 1986.

It was also provided for the transportation of 3 of the active glass containing crucibles from the Ispra to the Karlsruhe (Transuranium Institute) establishment of the JRC for the characterization of the radioactive glasses produced by the ESTER plant.

The design of a new hot cell facility named PETRA plant for the generation, treatment and conditioning of typical radioactive wastes from reprocessing plants started in February 1984 and was finished by mid-1985. The construction is being carried out during 1986.

## THE ESTER PLANT

The ESTER plant (1,2) installed in one of the hot cells of the ADECO laboratories of JRC Ispra was built and operated by ENEA, Department of Fuel Cycle. It was operated with real radioactive waste from February 1983 to August 1984 incorporating a total of 759 Ci of Fission Products into 7.53 kg equal to 2.8 litres of borosilicate glass (table 1).

The block diagram and layout of the ESTER plant are shown in the figures 1 and 2 respectively.

A total of 5 hot vitrification campaigns were carried out, during which samples of liquid and gaseous streams were taken and anlysed. A radioactivity balance in the plant has been established together with the DFs and the volatilization percentages of $^{137}Cs$ and $^{106}Ru$.

The average values (table 2) of Ru and $^{137}Cs$ DFs obtained in the first 4 campaigns are based on the crucible feeding to crucible off gas filtration and condensation activity ratios. The results are comparable with those obtained in previous cold tests (3, 4, 5).

Two types of HLW solutions have been treated:

a) The first one was generated at JRC Ispra from Obrigheim power station fuel (2). The most relevant chemical and radiochemical data of these 2 litres of HLW are reported in table 3.

b) The second type came from the Belgian Eurochemic facility and was transported to Ispra by a "Cendrillon" HLW transport container (LEMER, mod. LROS 15/8), from which the HLW was fed into the plant (see figure 3). The chemical and radiochemical composition (LEWC-203-1a) is shown in table 3.

Three types of borosilicate glass adjusted and studied at ENEA Casaccia Italy were produced, the main constituents of which are shown in table 4 (2).

The active glasses were produced in crucibles (B) heated by an electrical resistance kiln (R2) with 3 heating zones and a total power of 3 KW.

The crucible was built of 4mm thick AISI 310S with an inner diameter = 52 mm and a height = 600 mm corresponding to a volume of 1270cc.

The in-pot vitrification tests were carried out by feeding the crucible in a batch procedure (2) as illustrated in figure 4.

Three of the active glass containing crucibles have been transported from Ispra to the Karlsruhe JRC establishment by the TN6/3 transport container.

## DECOMMISSIONING OF THE ESTER PLANT

The decommissioning of the ESTER plant was carried out in 4 main operating phases, as follows:

1. The first phase is related to the circuit and components rinsing carried out in order to reduce the total activity in the plant. The condensate from vitrification (MAW) was transferred from the collecting tank (T3) to the HLW tank (T4) in successive fractions in order to dilute the activity of the residual solution and, then the progressively diluted liquids from the latter tank were sent to the crucible (B) for vitrification after a previous concentration in the evaporator (E).

At the end of this operating phase, the final activity of the liquid in the tank (T4) was reduced to about 1.85 GBq/l.

Unfortunately a mal-operation caused active liquid to escape from the cell when a special procedure was applied for a quicker liquid transfer from the HLW tank (T4) to the evaporator (E) by pressurizing slightly the former.

The working area in front of the cell was contaminated and the necessary decontamination operations delayed the successive plant dismantling and the cell decontamination steps.

In the new PETRA plant similar events will be excluded by appropriate design provisions e.g. excluding any piping penetrations on the front wall of the cells.

2. The second phase is related to the plant dismantling by remotized components removing as far as feasible and to the preliminary decontamination of the plant externals and of the cell walls.

The decontamination operations were carried out by the FRIGO SOLVER procedure based on a closed cycle cleaning system making use of FREON TF (see figure 5).

3. The third phase is related to the complete dismantling of the plant by means of a cutting device (see figure 6), that was introduced into the cell and remotely operated from the cell roof through an alpha-tight penetration (SAS) prepared for this purpose.

4. The fourth phase is related to the final decontamination of the cell by means of the FRIGO SOLVER apparatus and finally, by directly operating inside the cell (manual cleaning).

In this FRIGO SOLVER procedure (see figure 5) liquid FREON TF has been pumped at high pressure (10 MPa) against the components and walls in the cell by a suitable spray device. The FREON TF liquid fraction, containing the radioactive particles was collected on the cell floor and completely evaporated inside the cell. The FREON TF vapors were sucked back from the cell to a recovery unit operating at -24°C in order to freeze the water out before recycling. The active sludge was remotely sucked from the cell floor into suitable shielded containers for the final conditioning.

FREON TF is one of the fluorurated solvents produced by DUPONT and its main characteristics are as follows:

- high resistivity ($2.10^{15}$ ohm/cm at 25°C), that makes it particularly suitable for the cleaning of electric parts.;
- low boiling point (47,6°C);
- non-inflammable, non-explosive, practically non-toxic and remaining exceptionally pure and stable during its use.

The only disadvantage encountered with this procedure was the heavy dust formation that resulted in a high dispersion of the contamination not easy to contain.

However the cleaning operation by FREON TF was really effective, considering that decontamination factors higher than 100 were reached in a very quick and simple way.

## THE PETRA PLANT

PETRA will operate at a pre-industrial, fully-active scale on LWR high-burnup (33000 MWd/t) or other non-standard fuel material with a fundamental aim to implement various treatment and conditioning processes on the waste streams generated during the Purex type operations (6).

PETRA can be defined as an experimental tool for verifying and eventually validating at real activity levels various waste management approaches.

In particular, it will be possible to face the safety aspects related to the management of long-lived fractions of radioactive waste like the transuranium actinide or technitium (7).

The facility has been designed to treat 6 kg U batches with a maximum annual throughput of 10 such batches.

The process units will be installed on a surface area of 43 $m^2$ in the existing hot cell (4305, 4306, 4307) located in the ADECO Complex.

Four windows equipped with 8 heavy duty telemanipulators are available as working places.

Another shielded area is available for the installation of the hot analytical support. Pneumatic systems are used to transfer the samples from the process cells and, after appropriate dilution or extraction, to the Radiochemistry building for radiometric assay (see figure 7).

Already two other hot cells are operational and available for performing mechanical operations on either irradiated fuel material or conditioned waste specimens.

These cells could also be available for setting up experimental systems for conditioned waste "near field" interaction studies and leach tests.

For a more detailed characterization of the matrix structures, use will be made of the facilities available at the Transuranium Institute of the JRC at Karlsruhe.

On a photo, taken from a 1:5 model, prepared for layout

optimisation, the arrangement of the components in the 3 cells of the plant is shown (see figure 8).

Construction material is basically AISI 316L SS except the evaporators or reactors, which are built in Incoloy 825.

The simplified flowsheet is shown in figure 9 according to the following single unit operations to be performed mostly in a sequential operating mode:

- dissolution and feed clarification (by filtration);
- HA codecontamination cycle for U+Pu separation;
- exhaust solvent regeneration;
- U/Pu concentration;
- U/Pu calcination;
- HAW concentration;
- MAW concentration;
- denitration and eventually oxalates precipation;
- purification of actinides-RE fraction (by extraction);
- drying and vitrification;
- off-gas treatment.

This operation mode implies, of course, a limitation also in the overall throughput. A simple operational cycle from fuel dissolution to vitrification will require about 4 weeks; half of this time will go into the generation of the waste streams. Alternatively, provisions have been taken to receive in PETRA waste solutions transported by a "cendrillon" from other facilities.

In order to minimise the risk of fire, all units in which organic solvent is involved have been placed in the first cell, from which on the contrary any unit requiring heating is excluded. The HAW raffinate stream and the U/Pu product stream, before being transferred to the reception vessels and then to the evaporators or reactors, are treated at the outlet from the mixer settler batteries on columns filled with special sorbing resin, for the separation of dissolved and entrained solvent.

This system has been kindly made available by the "Institut fuer Heisse Chemie" of KFK Karlsruhe, where it has been applied successfully in hot operation.

The single units of the in-cell equipment are interconnected with metal to metal couplings, which can be handled remotely. Accordingly, to an order of priority established on operational requirements (e.g. filters and crucibles), on

forecasted maintenance frequencies (e.g. dosimetric pump and eventually on process scheme variations, the units ha

been placed in positions accessible for the remotely handled exchange, in order to assure a high degree of flexibility whilst at the same time minimizing exposure to operators.

It has been assured that in stand-by conditions, no active liquid is in contact with these connections.

Filters are drainable before being removed. At the points where such "dirty" pieces must be handled, special drainable driptrays are installed. All transfer systems, either air-lifts or dosimetric pumps are installed above the static liquid head of the vessels and can drain back to the latter. In stand-by conditions there are therefore no dead-liquid volumes in the pipe work.

The general level of instrumentation will be similar to that applied in other facilities of this kind, except the measurement of liquid levels, where time domain reflectometry (TDR) is foreseen. This is a tight "static" system (no dip-tubes) with purge air and capable of detecting the presence of two immiscible liquid phases in a vessel, allowing thus to control efficiently any unexpected presence of solvent for example.

In order to alleviate start-up and down procedures between the single process sequencies and to minimise at the same time the possibility of errors, a computerised process control system is to be installed including also the verification of positioning of all "manual" valves equipped with appropriate position feelers. This system will perform of course also the acquisition of the process data. Such an unusually high degree of design safety for an installation of this type and scale is motivated by the anticipated high variability in operation.

It will facilitate furthermore to exploit the in-built flexibility of the PETRA facility allowing for components replacement and even addition, in order to perform in the future, also other unit operations e.g. the application of inorganic ion exchanger material for waste streams treatment and radioactive products immobilisation. In principle hot testing of on-line analytical process control instrumentation is also applicable.

The PETRA plant is expected to become operational on a fully active scale during 1988.

## REFERENCES

1) BOCOLA,W., "The pot-vitrification of fully radioactive fuel reprocessing wastes - Planning of hot-cell experiments", Management of Radioactive Wastes from the Nuclear Fuel Cycle (IAEA, Vienna 1976).

2) NANNICINI,R., STRAZZER,A., CANTALE,C., DONATO,A., GROSSI,G., L'Impianto Minipilota Remotizzato ESTER per la Vetrificatione dei Residui Radioattivi di Alta Attivita: Rapporto sulla prima campagna di vetrificazione. ENEA, RT/COMB/84/8, August (1984).

3) BOCOLA, W., DONATO., The ESTER Programme - High-level radioactive waste solidification. Bench-sale phosphate glass vitrification tests with simulated fission product solutions, Energ. Nucl. 19.6 (1972)390.

4) DONATO,A., BOCOLA,W., The ESTER Programme - High-level radioactive waste solidication. Borosilicate glass experimental evaluation and bench scale vitrification with simulated fission product solutions, Energ. Nucl. 19.7 (1972) 459.

5) BOCOLA,W., DONATO,A., SGALAMBRO,G., "Survey of the present state of studies on the solidification of fission product solutions in Italy", Management of Radioactive Wastes from Fuel Reprocessing (Proc. IAEA/NEA Symp. Paris, 1972), OECD/NEA, Paris (1973) 449.

6) DWORSCHAK,H., GIRARDI,F., "PETRA, a hot cell facility for waste management studies". Proc. of the 2nd European Community Conf. on Rad. Waste Management and Disposal. Luxembourg, 22-26 April 1985. pp. 71-84, report EUR - 10163, Cambridge University Press, (1986).

7) GIRARDI,F., DWORSCHAK,H. "Optimization studies on radioactive waste management at a pre-industrial scale". Presented at the Int. Topical Meeting of the Amer. Nucl. Soc. on High-level Nuclear Waste Disposal. Pasco (USA), Sept. 24-26 (1985).

TABLE 1 - GLASS AND ACTIVITIES EMPLOYED IN THE CAMPAIGNS

| Campaign | 1 | 2 | 3 | 4a | 4b | 5a | 5b |
|---|---|---|---|---|---|---|---|
| Glass (g) | 2015 | 1010 | 1085 | 1055 | 1265 | 400 | 700 |
| Activity (TBq) | 0,37 | 2,1 | 2,13 | 9,22 | 13,8 | 0,17 | 0,28 |

TABLE 2 - DECONTAMINATION FACTORS IN THE VITRIFICATION CAMPAIGNS

| Campaign | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $^{137}$Cs (x $10^3$) | 1,4 | 6 | 0,5 | 4 |
| Ru | 161 | 35 | 5 | 150 |

TABLE 3 - COMPOSITION OF HLW USED FOR VITRIFICATION

| COMPONENT | JRC | EUROCHEMIC |
|---|---|---|
| $HNO_3$ M | 2,5 | 2,89 |
| Nitrates (total)M | - | 5,28 |
| Sulfate M | - | 0,08 |
| Iron g/dm$^3$ | - | 5,87 |
| Uranium g/dm$^3$ | 1 | 0,79 |
| Alpha GBq/dm$^3$ | - | 11,85 |
| Beta-gamma GBq/dm$^3$ | 3330 | 5291 |
| $^{137}$Cs GBq/dm$^3$ | 481 | 1395 |
| $^{134}$Cs GBq/dm$^3$ | - | 125,8 |
| $^{144}$Ce GBq/dm$^3$ | 8,51 | 296 |
| $^{106}$Ru GBq/dm$^3$ | 4,81 | 214,6 |
| $^{151}$Eu GBq/dm$^3$ | 18,5 | 33,3 |
| $^{125}$Sb GBq/dm$^3$ | 3,33 | - |

TABLE 4 - COMPOSITION OF GLASSES

| Component | Percentage in weight in Glass 1 | Glass 2 | Glass 3 |
|---|---|---|---|
| $SiO_2$ | 50,9 | 36 | 43,4 |
| $B_2O_3$ | 11,2 | 9 | 17 |
| $Al_2O_3$ | 2,13 | 2 | 12,75 |
| $Na_2O$ | 12,67 | 5 | 10,67 |
| $Li_2O$ | 6,7 | 2 | 5 |
| $K_2O$ | - | 3 | - |
| CaO | - | 1 | 8,93 |
| $TiO_2$ | 0,33 | 6 | - |
| CuO | - | 3 | - |
| $Fe_2O_3$ | 12,43 | - | 0,79 |
| $WO_x$ | 3,64 (•) | 33 | 0,01 (•) |
| $SO_3$ | - | - | 1,45 |
| density g/cc | 2,66 | 3,13 | 2,57 |
| melting point °C | 760 | 900 | 1050 |
| soxhlet leach rate $g/cm^2.day$ | 0,004 | - | 0,0009 |

(•) The value refers to Fission Products only.

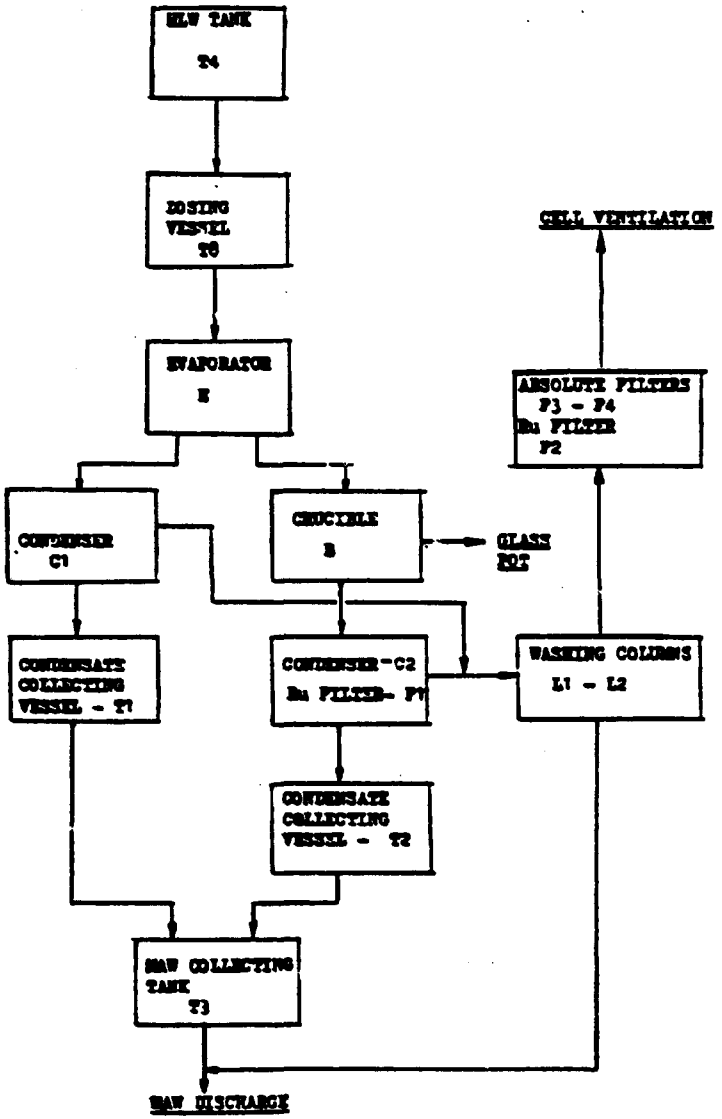



Fig. 1. Block diagram of the ESTER plant

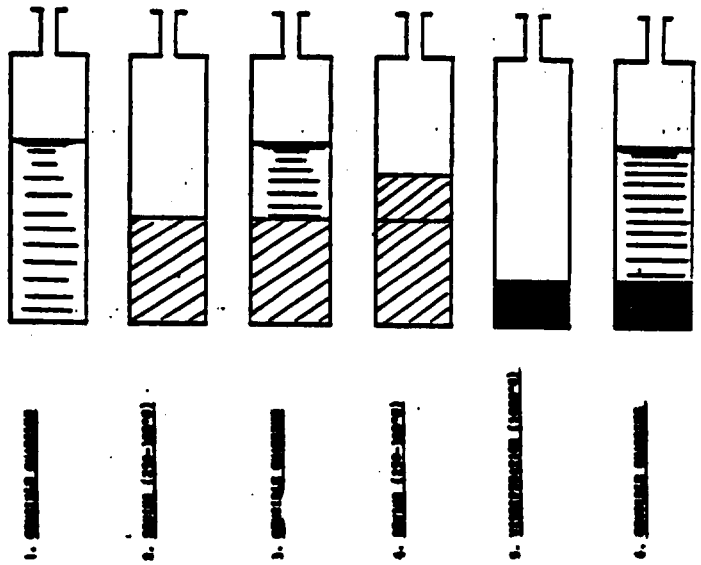


Fig. 4. Batch procedure for crucible feeding

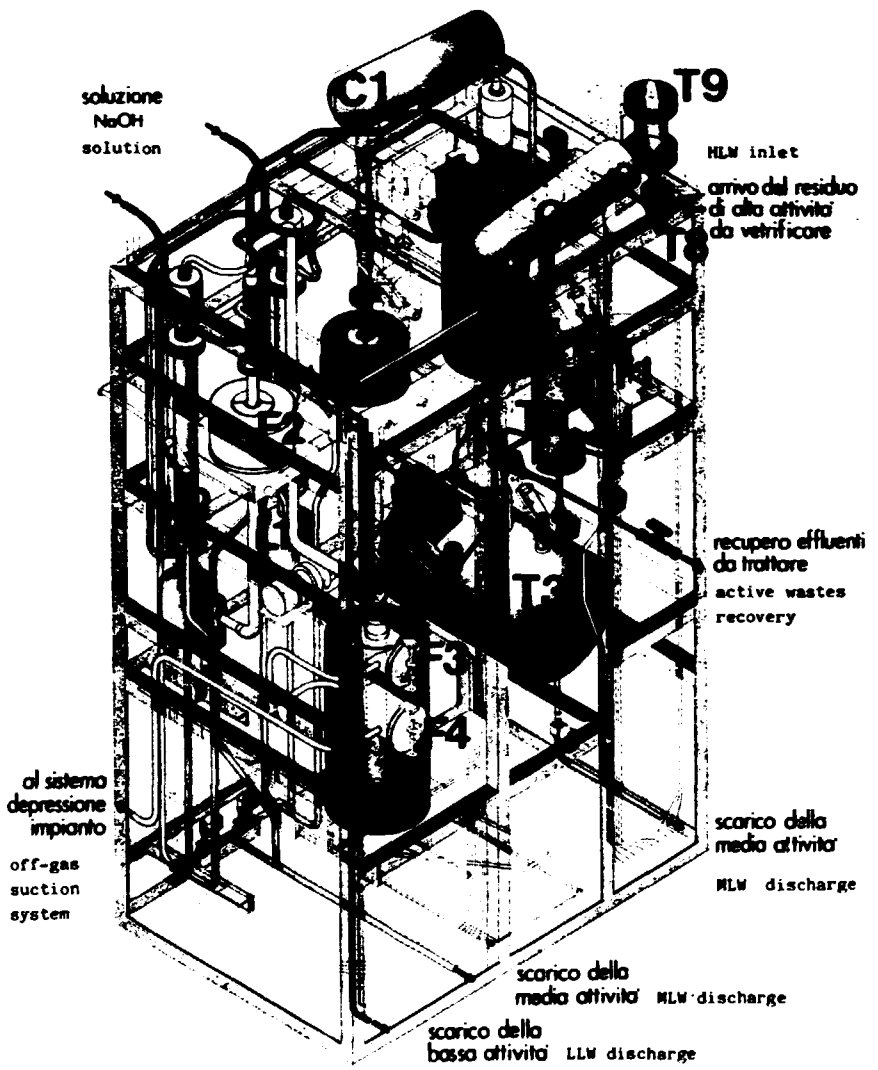



Fig. 2. Lay-out of the ESTER plant

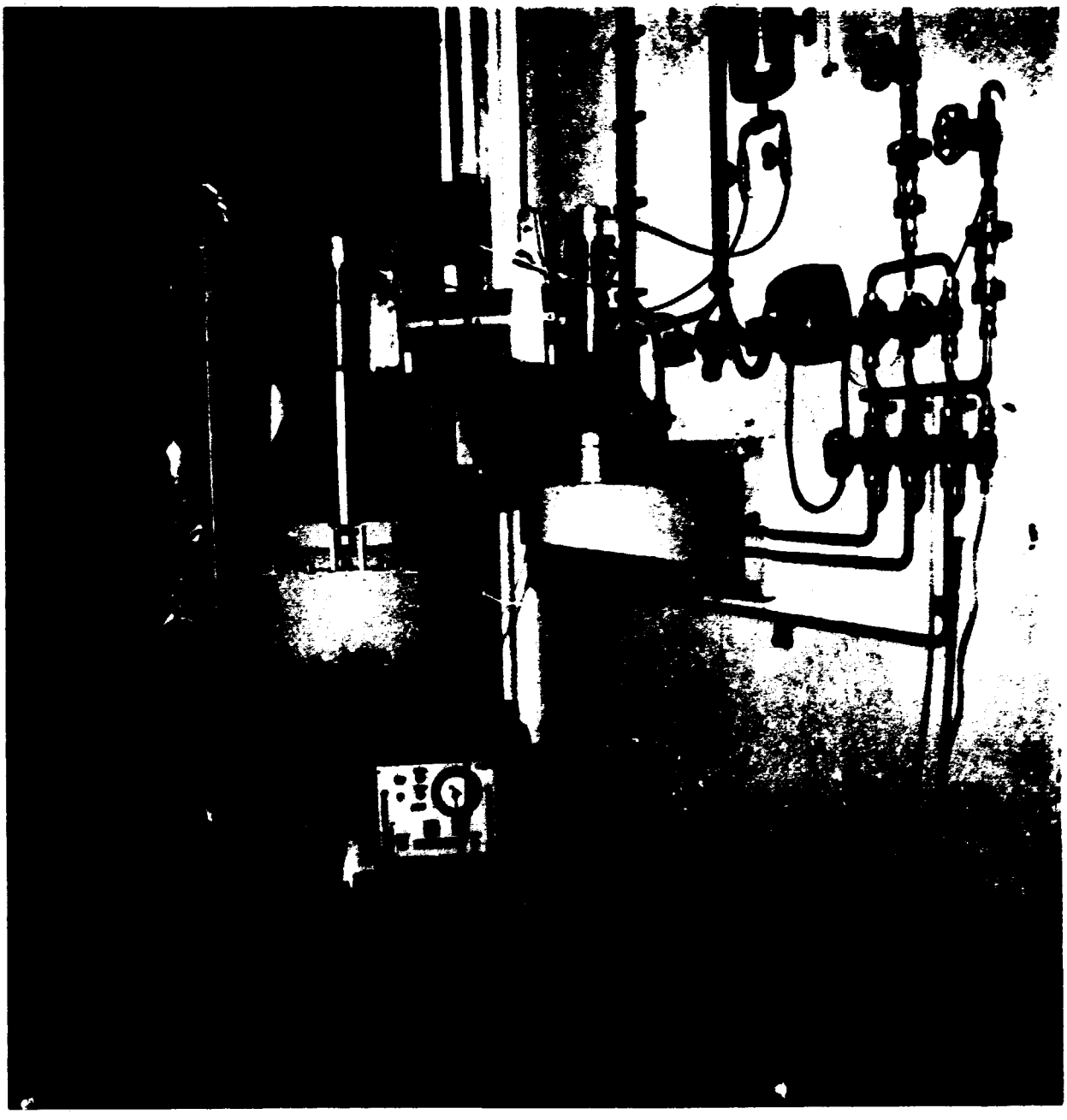


Fig. 3. The HLW feeding system into the plant.

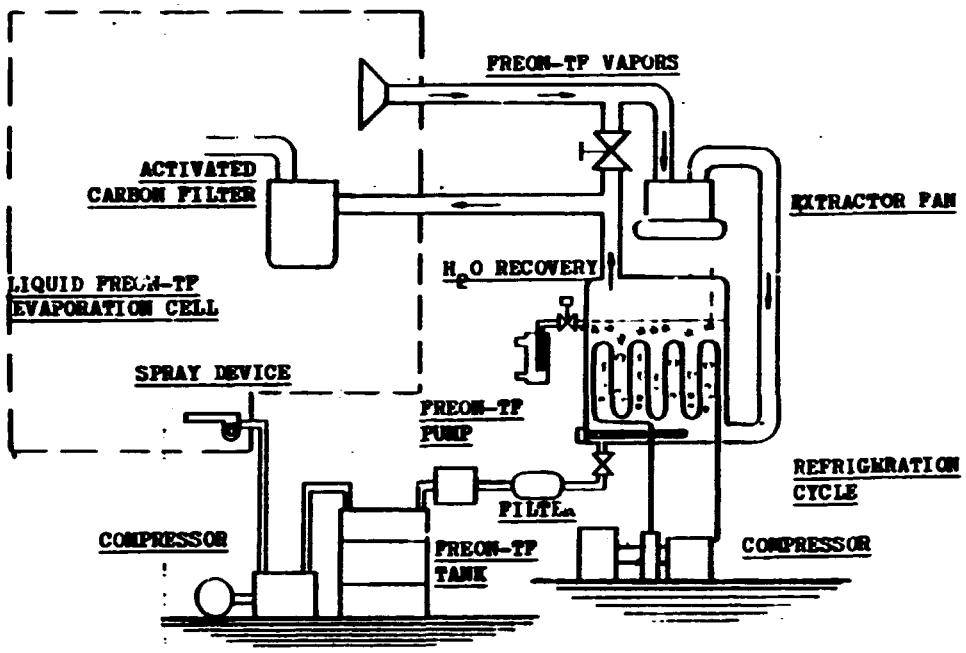



Fig. 5. Frigosolver procedure

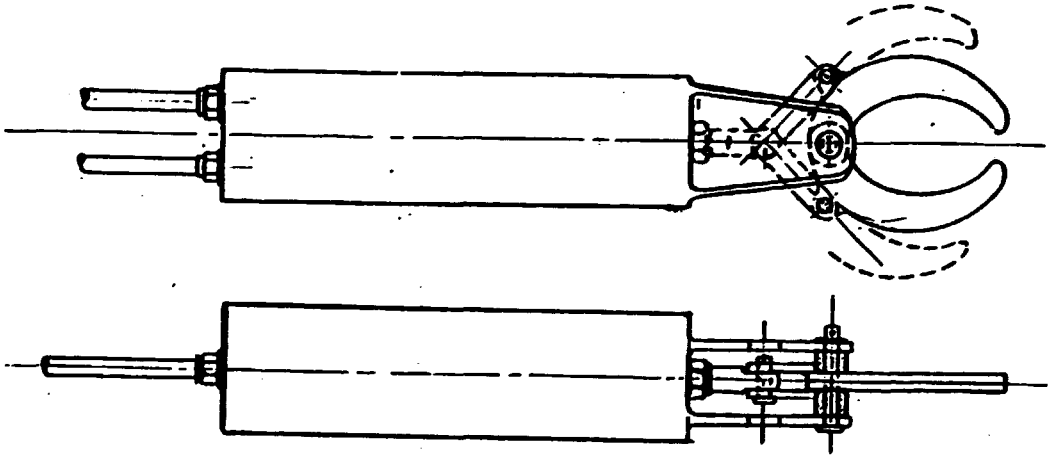


Fig. 6. Cutting device for dismantling

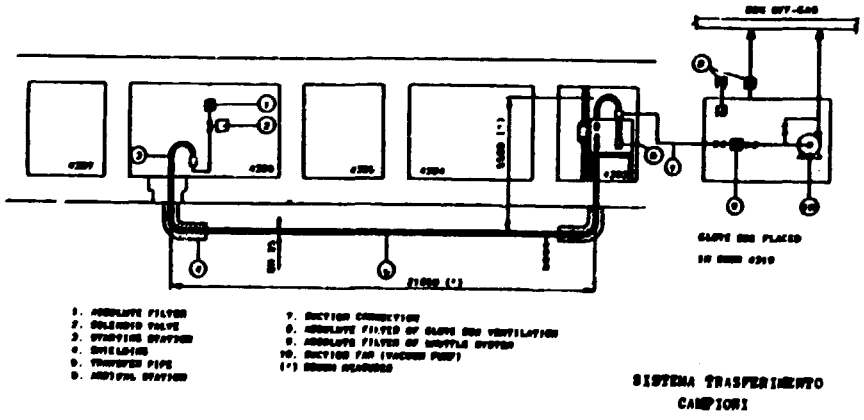
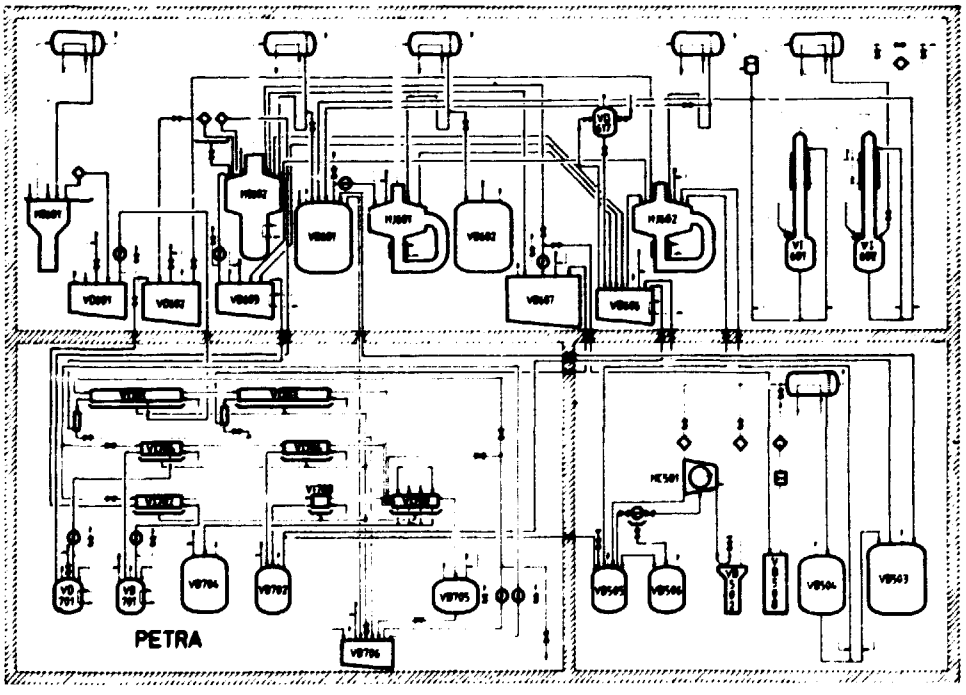



Fig. 7. Pneumatic sample transfer system.

Fig. 9. Simplified PETRA flow-sheet.




G
T 2
88 02 15
AD 88 11