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EXPERIENCE GAINED IN THE CRYODISTILLATION UNIT FOR KRYPTON REMOVAL

L. GEENS, G. COLLARD, W.R.A. GOOSSENS, P.J. VAESEN

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E. Plaskylaan 144, 1040 BRUSSEL
(BELGIE)

BLG 547 144, avenue E. Plasky, 1040 BRUXELLES
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- a first packed column working continuously in order to trap krypton and xenon from the process gas by cryogenic distillation;
- a second packed column where the bottom product of the first column is splitted in a krypton and a xenon product by batch distillation.

The installation is provided with the necessary peripherical systems and is highly instrumented to allow an uninterrupted operation with maximal safety and minimal personnel occupation. The most important measurements are treated by a microprocessor for printing-out purposes and for feed-back control.

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Samenvatting. - De cryogene distillatieeenheid ontwikkeld door het S.C.K./C.E.N. bestaat uit:
- twee parallele drie-compartimentswarmtewisselaars, die om beurt ingeschakeld worden;
- een eerste vullingskolom, waarin krypton en xenon afgescheiden worden door continue cryogene distillatie;
- een tweede vullingskolom, waarin het bodemprodukt van de eerste kolom gescheiden wordt in zuiver krypton en xenon door ladingsgewijze distillatie.

De eenheid is voorzien van de nodige randapparatuur en meetinstrumenten om een ononderbroken bedrijfsvoering mogelijk te maken, onder optimale veiligheidsomstandigheden en met een minimale personeelsbezetting. De belangrijkste meetgegevens worden verwerkt door een microprocessor die ze opslaat en gebruikt voor feed-back sturing.

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Résumé. - L'unité de distillation cryogénique développée par le C.E.N./S.C.K. se compose de:
- deux échangeurs de chaleur à trois compartiments, qui sont en opération alternativement;
- une première colonne à garnissage, où le krypton et le xénon sont piégés par distillation cryogénique continue;
- une deuxième colonne à garnissage, travaillant en batch, où le produit liquide de la première colonne est fractionné en krypton et xénon purs.

L'installation est équipée des systèmes d'alimentation et des instruments de mesure nécessaires pour obtenir une opération continue, dans des conditions de sécurité optimales et avec un minimum de personnel. Un microprocesseur collectionne toutes les données de mesure et les transforme afin de les stocker et de les user pour un contrôle feed-back.

This unit with a nominal gas throughput of 8.5 g.s^{-1} has been used to investigate the removal of krypton from reprocessing off-gases under non-radioactive conditions. During the investigation a total operation time of more than 13.000 hours was reached with an average availability factor of 99.36 %. The trapping efficiency for krypton was higher than 99.9 %.

The operational experience acquired indicates some critical aspects for the design of such a unit. The experimental results obtained allow to show the influence of feed pressure and temperature, reflux flow rate and noble gas concentrations on the performance of the unit.

Deze eenheid met een nominale gasdoorvoer van 8,5 g.s^{-1}, werd gebruikt om de kryptonvangst uit afgassen van opwerkingsfabrieken te onderzoeken onder niet-radioaktieve omstandigheden. Tijdens dit onderzoek werd een totale werkingstijd van meer dan 13.000 uren bereikt, met een gemiddelde beschikbaarheidsgraad van 99,36 %. Het vangstrendement voor krypton bedroeg meer dan 99,9 %.

De opgedane bedrijfservaring bracht een aantal belangrijke aspekten voor het ontwerp van een dergelijke eenheid aan het licht. De uitgevoerde experimenten toonden aan hoe de werking van deze cryogene distillatieeenheid beïnvloed wordt door een aantal parameters, zoals druk en temperatuur van de voedingsstroom, refluxverhouding en edelgaskoncentraties.

Cette unité avec un débit gazeux nominal de 8,5 g.s^{-1} a été utilisé pour étudier la rétention de krypton d'effluents gazeux d'une usine de retraitement, dans des conditions non-radioactives. L'installation a été en opération continue pendant plus de 13.000 heures, avec une disponibilité moyenne de 99,36 %. L'efficacité de rétention se montait à plus de 99,9 %.

L'expérience opérationnelle a relevé des éléments importants concernant la conception d'une telle unité. Les résultats des expériments montrent l'influence de certains facteurs comme le taux de reflux et les concentrations en gaz nobles, sur l'opération de l'unité.

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ABSTRACT

The cryogenic distillation unit such as built by the S.C.K./C.E.N. in Mol is technically described. This cryogenic installation consists mainly of :

- two parallel three-compartment heat exchangers working alternatively;
- a first packed column working continuously in order to trap krypton and xenon from the process gas by cryogenic distillation;
- a second packed column where the bottom product of the first column is splitted in a krypton and a xenon product by batch distillation.

These main parts are provided with the necessary peripherical systems. The whole installation is highly instrumented to allow an uninterrupted operation with maximal safety and minimal personnel occupation. The most important measurements are digitally treated by a microprocessor for printing-out purposes and for feed-back control on the basis of preset alarm levels.

This unit with a nominal gas through-put of 8.5 $g \cdot s^{-1}$ (25 STP m^3) has been used to investigate the removal of krypton from reprocessing off-gases in the presence of xenon under non-radioactive conditions. Under the extreme operating conditions of the investigation a total operation time of more than 13 000 hours was reached with an average availability factor of 99.36 %. The trapping efficiency for krypton was higher than 99.9 %.

The operational experience described in this report indicates some critical aspects for the design of the heat exchangers, the first distillation column and the liquid nitrogen supply system. The experimental results obtained allow to show the influence of feed pressure and temperature, reflux flow rate and noble gas concentrations on the performance of the unit.

I. INTRODUCTION

Since several years, the Belgian Nuclear Research Center, S.C.K./C.E.N., initially in association with BelgoNucléaire, BN, has been studying the different steps for the purification of off-gases from reprocessing plants (1). A major part of this study concerns the removal of radioactive krypton by means of cryogenic distillation.

The krypton-85 with its half-live of 10.76 y is produced in a PWR reactor at a rate of 330 $kCi \cdot (GWe \cdot y)^{-1}$. According to the recent USA-EPA recommendation (2), its release to the environment has to be restricted to 50 $kCi \cdot (GWe \cdot y)^{-1}$, implying an over-all decontamination factor of 6.6. Since this krypton-85 is nearly completely set free as noble gas during the head-end operations, a specific decontamination factor of about 7 is needed during the up-cleaning of the head-end off-gases. This radioactive krypton isotope is diluted by stable krypton isotopes and by less volatile noble gas namely xenon. On the average, the head-end off-gas contains about 600 ppm vol. xenon and about 60 ppm vol. krypton of which 6 % is krypton-85. The maximum peak concentrations of noble gases may amount to several thousands ppm vol. of xenon and several hundreds ppm vol. of krypton. In fact, these peak concentration values depend mainly on the shearing process.

The aim of the experimental investigation described in this report is to show the feasibility of the cryogenic distillation technique as a reliable method for removal of krypton in the presence of representative amounts of xenon from simulated head-end off-gas consisting of 99 % nitrogen and 1 % argon. Furthermore, the experimental results obtained should allow the up-scaling to an industrial pilot unit working under real conditions of a reprocessing plant for irradiated nuclear fuel.

The cryodistillation unit such as described here is applicable only when the crude head-end off-gas is freed from various potentially interfering components, the removal of which is not described here. In principle the cryogenic distillation is performed in a column to which the pretreated off-gas is fed at a point located between two packed beds. The upper rectifying sector is designed to obtain a sufficiently hihg decontamination factor for the krypton in the off-gas. The lower stripping section must have enough stages to avoid collection of too large amounts of the more volatile compounds as nitrogen, argon and oxygen. The bottom product, consisting mainly of krypton and xenon is further batchwise treated in a second distillation column in order to get a xenon product as pure as possible and a low volume krypton product.

II. DESCRIPTION OF THE CRYOGENIC DISTILLATION UNIT

2.1. FLOW-SHEET

In figure 1 and figure 2 are respectively shown a simplified flow-sheet and the actual flow-sheet of the cryodistillation unit. One can distinguish here the real distillation installation, the different material supplies and the emergency system.

A constant flow of dry nitrogen, to which argon, krypton and xenon are added, is fed at a pressure of 0.9 MPa into one of two parallel three compartement heat exchangers, which are used alternatively. In the exchanger in use the process gas is cooled countercurrently by the treated gas and by the liquid nitrogen vapours coming from the condenser of the first column. The cooling streams are preheated in such a way that the feed is kept at a constant temperature at the column's entrance and that xenon desublimation in the heat exchanger is prevented.

In the upper section of the first distillation column, which is a packed tower operated at 0.8 MPa, xenon and krypton are continuously washed out with liquid nitrogen, refluxed at the column's condenser. Cooling is performed with liquid nitrogen, which is evaporated inside the coil type condenser at a pressure of about 0.3 MPa. The thermal balance is held in equilibrium by regulating the reflux so that the krypton layers always reach the same height in the lower column packing. This results in an almost constant temperature profile in the column as shown in figure 3. Under these working conditions xenon and krypton accumulate in the kettle, while argon and nitrogen leave the column at the top. In the case of a break-down or of insufficient krypton decontamination, the outlet gas can be diverted either manually, or automatically, to an emergency loop where it can be stored temporarily before being recycled.

The liquid accumulating in the boiling kettle of the first column is transferred batchwise to the second column. In this column, which is also a packed column and operates at a pressure of 0.2 - 0.3 MPa, xenon and krypton are separated by batch distillation. Krypton is distilled off at a high reflux rate until its concentration in the bottom is below 1 ppb. Cooling is performed by a coil type condenser, wherein liquid nitrogen is evaporated at a pressure of 2 MPa. The condenser forms part of a closed high pressure loop. The nitrogen evaporated in the condensor is recondensed in a second coil of the closed loop. This condensation is caused by evaporation of liquid nitrogen at 0.3 MPa outside of this second coil. The top product and the bottom product of this second column are both transferred by manual operation into the storage bottles, except in case the column pressure rises too high. In this case a safety valve will open and will conduct the gas to the emergency loop.

The noble gas products are transferred from the distillation column into the storage bottles in two steps. First, krypton and xenon are pumped by cryogenic vacuum into intermediate storage bottles, which are externally cooled with liquid nitrogen at atmospheric pressure. When this transfer is finished, these bottles are allowed to warm up, so that their pressure increases by evaporation of the condensed gases. Hereafter the gases are transferred into storage bottles, which are directly connected to the noble gas supply installation for the purposes of this study.

The operation of the cryodistillation unit is almost completely controlled by a microprocessor. Alarms are provided as well on this microprocessor, as on other conventional measuring and control systems. Furthermore, in order to guarantee a safe continuous operation, both columns are fitted with suitable safety valves and rupture discs.

2.2. DESCRIPTION OF THE MAIN PARTS OF THE INSTALLATION

In this section a description of the main parts of the installation is given. For a more detailed description of the cryodistillation unit, one is referred to the safety report of the unit (11).

2.2.1. Material supplies

2.2.1.1. Process gas : nitrogen

Nitrogen used as process gas contains about 0.011 mole % water vapor. It is coming from a 5 m^3 liquid nitrogen vessel, which is fitted with an evaporator. The feed pressure is 1 MPa and up to 40 $Nm^3 \cdot h^{-1}$ of gas can be delivered. The gas pressure is reduced to 0.9 MPa before entering the cryogenic installation. According to the needs of the moment the main stream can be divided by means of manually operated valves, e.g. for the regeneration of the heat exchangers.

The process gas flow is measured with a thermal mass flow meter. It is regulated by means of a flow regulator and an electric regulation valve.

2.2.1.2. Noble gases

Argon has to be supplied, since the simulated process gas has to contain 1 % vol argon. Commercial H.P. Ar bottles are used herefore. Its flow is regulated manually and measured with a thermal mass flow meter.

For the krypton supply and for the xenon supply two commercial bottles, of which initially one empty and the other full, are connected with a collector. This collector itself is linked with the intermediate storage-bottles on the other side. So, both bottles serve in turns as

supply and as storage. Xenon and krypton gas flows are adjusted manually and measured either with a dp cell, or with a thermal mass flow meter.

2.2.1.3. Liquid nitrogen for cooling

The cryogenic unit is provided with two nitrogen loops for cooling :
- a low pressure loop for the cooling of the first column, the intermediate bottles and the low temperature coil of the high pressure loop;
- a high pressure loop for the cooling of the second column.

2.2.1.3.a. Low pressure loop

In the low pressure loop, liquid nitrogen is obtained from a 3 m^3 liquid nitrogen vessel. It is delivered to a liquid-gas separator through a manually operated valve and an electromagnetic valve, which is commanded by the liquid level in the separator. This separator supplies liquid nitrogen to the different cooling devices at a pressure up to 0,3 MPa, through electromagnetic valves.

The liquid nitrogen flow to the condensor of the first column is measured in the vapor phase, with a thermal mass flow meter and regulated by means of a flow regulator and an electric regulation valve. The possibility exists to make the liquid nitrogen flow vary with the process gas flow up to a minimum value which can be preset.

The liquid nitrogen flow cooling the high pressure loop is also measured in the vapor phase with a thermal mass flow meter. The flow rate is regulated by means of a pneumatic regulation valve which is controlled by the pressure measurement in the second column.

The liquid nitrogen flow cooling the intermediate storage bottles is controlled by means of an on-off mechanism : both branches open and close automatically by means of electromagnetic valves, that are commanded by level controllers in the dewars.

2.2.1.3.b. High pressure loop

The high pressure loop consists of a closed nitrogen loop with two coils, which is connected with a nitrogen gas bottle and a buffer bottle and wherein the pressure is kept at 2 MPa. The nitrogen gas is condensed in the first coil, that is cooled by the low pressure loop, and it evaporates in the second coil, that is mounted in the top of the second column.

2.2.2. Cryogenic distillation

The cryogenic distillation unit essentially consists of two heat exchangers and two distillation columns, which are all placed in a cold box, and of two intermediate storage bottles, outside the cold box.

2.2.2.1. Cold box

The cold box, containing the heat exchangers and the columns, is filled with isolating perlite powder. Freezing of humidity and condensation of air in contact with the cooling loops, is avoided by rinsing the whole box with nitrogen, in slight underpressure.

2.2.2.2. Heat exchangers

The heat exchangers consist of three concentric copper tubes with a length of 2.7 m. The liquid nitrogen vapors coming from the first column's condenser flow trough the inner tube which has a diameter of 19 mm. The process gas flows through the finned intermediate pipe, which has a diameter of 39 mm. The external tube, with a diameter of 60 mm, is passed through by the treated gas that leaves the first column.

2.2.2.3. First column

The first column consists of four main parts :

- a boiling kettle, which has a 0,219 m diameter and is about 0,28 m high. The kettle is heated by means of a 6 cm broad electrical heating tape, with a maximum power of 400 W.
- a lower packed section consisting of spring type Raschig rings (3 x 3 x 0.4 mm), with a bed height of 0.80 m and a bed diameter of 0.07 m;
- an upper packed section consisting of the same type of Raschig rings, with a bed height of 0.725 m and a bed diameter of 0.10 m;
- a condensor of the coil type, which is fed with low pressure liquid nitrogen. The coil has a diameter of 0.15 m and consists of 11 spires of a 12 mm copper tube with a length of 5.5 m.

The lower packing is equiped with thermoresistances for the measurement of the local temperatures. Pressure drop measurements are foreseen as liquid level indicators or as indicators of potential pluggings caused by crystallization in the packings. The column is also fitted with some gas sampling points. All this is illustrated in figure 4.

The precooled process gas enters the column, that is kept at a pressure of 0.8 MPa, below the packing of the upper section. It rises trough a gas distributor into the upper packing, where the noble gases are absorbed in liquid nitrogen. The gas rises further to the condenser, where it is cooled and partially condensed. The non-condensed gas leaves the column, while the condensed liquid trickles downwards into the upper packing through a liquid distributor. The liquid nitrogen, that has absorbed the noble gases, falls into the lower packing, where the nitrogen evaporates and liquid mixture of noble gases is formed. In the kettle only liquid krypton and xenon is accumulated. This liquid can be transferred to the feed point of the second column, because of the higher pressure in the first column.

2.2.2.4. Second column

The different parts of the second column are analogue to those of the first column :

- a boiling kettle, having the same dimensions, heated by means of a 6 cm broad electric heating tape of 350 W maximum power;
- two identical sections of 0.80 m height and 0.05 m diameter, packed with the same spring type Raschig rings (3 x 3 x 0.4 mm). The liquid from the first column enters the second between these two packed bed-sections.
- a coil type condenser having a diameter of 15 cm and a length of 2.3 m which is formed by 5 spires of 12 mm copper tube. As already mentionned in section 2.1.3.2., this coil makes part of the high pressure cooling loop, wherein nitrogen is evaporated and condensed at a pressure of 2 MPa.

The second column is also provided with thermoresistances, pressure and pressure drop measurements and gas sampling points.

The liquid which enters the column between the two packed beds, trickles into the lower packing. There, the liquid is enriched with xenon by evaporation of the krypton that will rise in the column. In the upper packing the rising gas is washed with liquid krypton coming from the condenser. During the fractionation of the components, the column remains closed. Slowly, equilibrium is attained : the krypton condenses on the cooling coil and evaporates in the upper packing; the xenon is evaporated in the boiling kettle and condenses in the lower packing. When equilibrium is attained, krypton gas is transferred from the top to the intermediated storage bottles by cryogenic pumping. The xenon is transferred afterwards from the bottom as a liquid.

2.2.2.5. Intermediate storage bottles

Krypton and xenon are intermediately stored in the solid state. This occurs in 3.8 dm^3 bottles, that can withstand a pressure of 12 MPa. The transfer is done by cryogenic pumping : the bottles are placed in open

dewars filled with liquid nitrogen, the level of which is controlled automatically by means of electromagnetic valves and thermoresistances. The transfer being finished, the dewars can be lowered so that the bottles can warm up. Hereby the gases will evaporate and can be transferred to the storage bottles of the supply lines.

2.2.3. Recycling system

In the case of a break-down or of insufficient krypton decontamination the gas stream leaving the first column can be diverted to a recycling system. This can be done manually or automatically by pneumatic valves commanded by thermoresistances. The whole content of both columns may also be sent to this recycling system, where cooling ceases.

The recycling system itself consists of four parts : a buffer vessel, a storage vessel and two compressors. When the gas stream is diverted to the recycling system, first it enters a 5 l buffer vessel. The purpose of this vessel is to amortize the shocks when the compressor which empties the vessel starts or stops.

After the buffer vessel, there is a membrane compressor, which pumps the gas in the storage vessel. At its maximum outlet pressure of 1.5 MPa a gas flow of 15 $Nm^3 \cdot h^{-1}$ can be obtained. The compressor automatically starts when the pressure in the buffer vessel rises above a variable preset value and it also automatically stops when the pressure falls below a second variable preset value. The compressor also stops when the pressure in the storage vessel is higher than 1.5 MPa, the gases then being sent to the ventilation.

The gases are pumped into a storage vessel, which has a volume of 3 m^3 and can withstand a maximum pressure of 1.5 MPa. It is fitted with two safety valves.

By means of a two stage membrane compressor, the gases in the storage vessel can be recycled to the head of the cryogenic installation. An outlet pressure of 1 MPa is the only requirement for this compressor.

2.3. PROCESS CONTROL

The operation of the cryogenic installation and particularly of the first column is almost completely managed automatically by a mixed regulation system, in which conventional regulation devices and a microcomputer are combined. A detailed description of all measuring and regulation devices is given in the safety report (11).

All measurements of the different parameters are transmitted to the microprocessor. They can be permanently read off on a video display and they are regularly printed out by a teletype. Under normal working conditions the regulations will be controlled by the microprocessor. Furthermore, alarms are programmed on it and in this case the first necessary operations are controlled by the microcomputer.

2.3.1. Control under normal working conditions

The most important parameters to be controlled under normal working conditions are feed gas flow rate and temperature, column pressure and cooling liquid nitrogen flow rate. These regulations are outlined in figure 5 and will be discussed in this section.

The feed gas flow rate is maintained constant by an electrical regulation valve, that is commanded by a mass flowmeter.

The temperature of the feed gas at the first column's entrance is maintained constant at a preset value by heating the cooling gases by means of electrical heating tapes, before they enter the heat exchangers. The nitrogen vapors coming from the first column's condensor are kept a few degrees above the temperature of the treated gas on which the regulation is applied.

In normal working conditions, the pressure in the first column is held constant by means of a PID-regulator at the outlet of the column. When, in the case of an alarm, the column is working in stand-by, the pressure is regulated by means of the cooling nitrogen flow rate, while the temperature indications (TR 18 or TR 16) no longer are used for regulation of the cooling. The heating power applied to the first column is set manually and remains constant.

The cooling of the first column is regulated so that a constant temperature profile in the column is obtained. In order to obtain this, the cooling nitrogen flow is divided into two streams. The primary stream flow rate automatically follows changes in feed gas flow rate fully and changes in kettle heating power partly. The secondary stream flow rate is adjusted to maintain the upper krypton layers in the vicinity of one of the thermoresistances TR 16 or TR 18 (fig. 4). In practice, the primary stream is continuously supplied to the column and its flow rate lies about 5 % under the required flow rate. The secondary stream flow rate amounts to 10 % of the required flow rate. It is supplied only when the temperature of one of the thermoresistances TR 16 or TR 18 exceeds a certain preset and programmed value and its supply stops when this temperature decreases down to another programmed value. The supply is controlled by means of electromagnetic valves that are commanded by the thermoresistances intermediately through the microprocessor. The required liquid nitrogen flow rate is determined by the thermal equilibrium of the column. In order to keep the column in thermal equilibrium the liquid nitrogen flow must compensate for every heat absorption. Heat is absorbed by the column in three ways : the kettle heating, the entering gases which are warmer than the column's content, and thermal losses, i.e. heat taken up from the isolating material. The following relation applies :

$$L = A_1 \cdot G \cdot \Delta T + A_2 \cdot W + A_3 \cdot V$$

wherein : L = liquid nitrogen flow rate ($Nm^3 \cdot h^{-1}$)

G = feed gas flow rate ($Nm^3 \cdot h^{-1}$)

ΔT = temperature differences between feed gas at the entrance and the temperature in the upper packing = TR 6 - 101(K)

W = heating power (W)
V = thermal losses (W)
A_1, A_2, A_3 = constants

In this formula G, ΔT and W are known, while V, A_1, A_2, A_3 can be determined experimentally so that L may be calculated for every case within the working limits of the installation.

Following values were experimentally found for the constants :

$$V = 88.2\ W,\ A_1 = 0.00899,\ A_2 = A_3 = 0.0145.$$

Control and regulation of the second column are much simpler. The pressure in the high pressure loop is maintained constant by means of a pressure regulator. Again, the heating power is set at a constant value. Column pressure and liquid nitrogen flow rate in the low pressure loop are related to each other in this way that the cooling flow rate is regulated by means of a pneumatic regulation valve that is commanded by a pressure measurement so that the pressure in the column remains constant.

2.3.2. Alarms and resulting automatic operations

For the most important parameters to be controlled, alarm levels are provided on conventional measuring instruments or are programmed on the microprocessor. The first interventions to be made are also programmed on the microprocessor and are executed automatically.

These alarms and the resulting automatic operations are illustrated in figure 6 and will be discussed here.

Perhaps the most important alarms are provided on pressure measurements. As one can see in fig. 6 the pressure of the first column is measured twice. On the first pressure measurement two alarms are adjusted : the first when the pressure falls below 0.75 MPa (abs.), the

second when the pressure rises above 0.9 MPa (abs.). In case the pressure falls below 0.75 MPa, a pneumatic valve will cut off the feed stream; this valve can only be reopened manually. At the same time an electromagnetic valve closes the outlet, but il will reopen when the pressure rises above 0.9 MPa, the feed stream will be cut off by the same pneumatic valve as mentioned before. Futher an electromagnetic valve opens an additional branch in the outlet line. This valve must reclose with delay when the pressure falls below 0.9 MPa. At last two pneumatic valves will switch over so that the outlet gases are diverted to the ventilation through the little buffer vessel of the emergency loop. The switching back of these valves is done manually. On the second pressure measurement also two alarms are provided. When the pressure falls below 0.7 MPa an electromagnetic valve must close the cooling outlet line. This valve must reopen when the pressure rises again above 0.75 MPa.

Temperature alarms without automatic interventions are provided in the lower packing of the column to indicate a too large deviation of the normal temperature profile. Both in the top and in the bottom of this packing a high and a low alarm level are adjusted. Another temperature alarm is provided in the upper packing : when the temperature becomes too high, the pneumatic valves to divert the outlet gases through the emergency loop are switched over.

There is also an alarm provided on the pressure drop measurement over the column. A too high value is an indication for plugging of the column, caused by cristallization of xenon. In this case both inlet and outlet of the column are closed by respectively the pneumatic valve and the electromagnetic valve, already mentioned before.

Some of the alarms mentioned result in the diverting of the outlet gas to the ventilation through the buffer vessel (T2). When the pressure in this vessel becomes too high, the outlet to the ventilation is closed and the gases are sent to the compressor of the emergency loop by the switching over of two pneumatic valves, which can be switched back manually.

The compressor will automatically start when the pressure at the suction side exceeds a certain value which can be preset. When this pressure falls below a second preset value, the compressor stops. Of course, the possibility of manually starting and stopping the compressor remains.

A last alarm is provided on the emergency vessel (T1). When its pressure exceeds 15 bar, the manual operation as well as the automatic operation of the compressor are blocked. Further the pneumatic valves which divert the gases to the compressor instead of to the ventilation are switched back automatically.

III. OPERATIONAL EXPERIENCE AND EXPERIMENTAL RESULTS

The operational experience gained with the cryogenic distillation unit will be discussed in the first part of this chapter. Some important conclusions concerning the design of such a unit will be drawn from it.

In the second part the experimental results obtained in the cryodistillation unit will be given. Here too the interpretation of the results reveals some new design aspects.

3.1. OPERATIONAL EXPERIENCE AND DESIGN ASPECTS

During the operation of the unit, a number of break-downs occurred, while on the other hand also some shortcomings of the installation were revealed.

3.1.1. Break-downs

Some of the necessary interventions to make were caused by ordinary break-downs in electric or electronic circuits like short-circuits or blown fuses. Having the right schemes at his disposal, they do not cause much trouble to be found and repaired.

Defects due to repetitive use of some parts of the unit were another important cause of break-down. Especially valves were subject hereto.

- Bellows of valves on the sampling lines, that were used at most, began to leak internally after some time, so that they had to be sealed between two samples in order to avoid losses of noble gases from the column. By mounting an extra valve between column and sampling valve, which only is closed in case of a leaking sampling valve, this sampling valve can be replaced without excessive losses of gas.

- The regulation valve between the two columns, which is also used repetively for the transfer of krypton and xenon, became blocked in closed position, so that transfers couldn't be done anymore. This problem was solved by connecting the bottoms of the columns outside the cold box. Although much faster, the transfer between the columns went well. From this it can be concluded that the regulation valve for the transfer may be placed outside the box, between two other valves which are only closed for the replacement of the regulation valve.
- The pneumatic valves in the outlet lines that regulate the pressure in the separator, had to be repaired or changed more than once. These reparations caused no trouble at all, but for new installations doubling of these lines would be advisable.

Quite a number of interventions were caused by break-downs in the liquid nitrogen supply system, perhaps the weakest point of the whole installation. In particular the supply of liquid nitrogen from the storage tank to the separator caused numerous troubles. This supply is regulated by an electromagnetic valve which is commanded by a level controller in the separator. Doubling of this line was necessary, because the valve may become blocked or may begin to leak. Besides, this system is placed outside of the building, so that it has to be insulated and screened very carefully in order to avoid condensation and freezing of water with all its disadvantages. In order to assure a continuous operation of the cryogenic installation, in case this supply system might fail, a large dewar has to be provided which can take over the cooling duties for about 5 hours.

3.1.2. Shortcomings and possible improvements

In this section the major shortcomings experienced during operation of the installations will be discussed and possible improvements will be given.

In order to follow the working of the heat exchangers, a sampling point has to be provided between the heat exchanger and the first column. In the existing unit, this could be solved by a provisional connection.

The behaviour of the first column and particularly of the inlet section could be studied much better if some more thermoresistances were provided as well above as under the inlet.

The reflux flow rate in the first column was limited by the cooling flow rate. The liquid nitrogen flow rate could only be regulated up to a value of 7 Nm^3h^{-1} of vapors. Probably this was due to the high gas velocities at this flowrate, which cause entrainment of liquid droplets into the piping after the condenser, where they are evaporated. Since the regulation is based on gas flow measurements and since the measured gas flow rate no longer represents the actual cooling flow rate, regulation becomes impossible. For future units this can be avoided by paying special attention to the mechanical design of the condenser and to its configuration.

In the existing cryodistillation unit, the second column isn't provided of any alarm at all. For future installations an emergency system must be added to it, e.g. in case the pressure becomes too high. Such an emergency system could consist of a container, that is cooled by an independent liquid nitrogen loop and in which the column can be emptied instantaneously. A recycling system from this emergency system to the column must be foreseen. A similar system can also be provided for the first column.

3.2. EXPERIMENTAL RESULTS AND DISCUSSION

3.2.1. Working conditions of the cryodistillation unit

By working conditions of the unit is meant the working conditions of the first column, since this is the hart of the whole installation. The nominal working conditions of the first column are given in table I.

TABLE I : Nominal working conditions of the rectification column

Flow rate	: 2 to 8.6 10^{-3} $kg \cdot s^{-1}$
Pressure	: 0.8 MPa
Inlet temperature	: 124 K
Argon concentration	: 1 % volume
Krypton concentration	: 0 - 200 ppm volume
Xenon concentration	: 0 - 1800 ppm volume
Reflux ratio	: 0.3 to 1

Under these conditions, it was possible to operate the unit for more than 13 000 hours without the need of a permanently present operator. The availability factor for this period was 99,36 %. The main outage (51 h of 84 h total unavailability time) was due to a break-down in the liquid nitrogen supply system. The major part of the rest was due to the nature of the experiments going on : determination of the extreme working limits of the installation.

In table I, flow rate and noble gas concentrations values were design specifications. The inlet temperature was determined by xenon concentration, as will be proved in the next section. As already mentionned before, the reflux ratio is limited by the design of the first column's condenser. At last, the choice of the working pressure was based on the following considerations. The ternary system N_2-Kr-Xe shows zones, in which a solid xenon phase appears (4). In order to increase the xenon concentration in the feed without cyrstallization problems, the pressure of the system has to be higher than 2 MPa. However, such a pressure will not be easily accepted for an installation treating radio-active gases. Besides, increasing the total pressure will cause problems for the operation of the heat-exchangers. As a compromise between these considerations a working pressure of 0.8 MPa has been retained to study the operational limits of the unit.

3.2.2. Performance of the heat exchangers

When the partial pressure of xenon in the gas flow is higher than its vapor pressure at the outlet temperature, a solid xenon phase is formed on the cold walls of the heat exchangers. This has been observed : the outlet xenon concentration remains constant with increasing inlet concentration. In table II these measured outlet concentrations are compared with concentrations calculated by means of its vapor pressure above solid xenon. From this comparison may be concluded that pure xenon crystallizes. For the calculation of the vapor pressure of solid xenon, the equation of Freeman and Halsey has been used (5) :

$$\log_{10} P_s = 9.8563 - \frac{799.1}{T}$$

where P_s is the vapor pressure of solid xenon (Pa)
T is the temperature (K).

By keeping the temperature at the outlet of the heat-exchangers higher than the saturation temperature of xenon under the nominal conditions of total pressure and xenon concentration, crystallization can be prevented. Furthermore, by appropriate heating of both cooling gas streams wall temperatures will not go far below the saturation temperature. Temporary crystallization, due to short time peaks of xenon concentration, can be allowed by choosing the cross-sections of the exchanger tubes large enough in order to avoid complete plugging.

TABLE II : Maximum concentration of xenon at the outlet of the heat exchangers

Gas flow rate ($kg.s^{-1}$)	Temperature (K)	Concentration of xenon (ppm volume)	
		experimental	F & H
$2.1 \cdot 10^{-3}$	112	653	658
$2.1 \cdot 10^{-3}$	113	763	761
$2.1 \cdot 10^{-3}$	116	1076	1160
5.2 to $6.2 \cdot 10^{-3}$	120	2066	1968
$2.1 \cdot 10^{-3}$	121	1980	2234
5.2 to $6.2 \cdot 10^{-3}$	125	3780	3634
$2.1 \cdot 10^{-3}$	126	3897	4084

TABEL III : Working limits of the column

Gas feed rate ($g.s^{-1}$)	Inlet gaseous Xe concentr. (vol. ppm)	Kettle heating power (W)	Reflux flow rate ($g.s^{-1}$)	Calculated liq. Xe concentr. (mol %)	Working time (h)
2.08	2634	100	0.63	0.87	15.25*
	5506	200	1.26	0.92	16.60*
	7206	250	1.58	0.95	10.50*
4.17	1869	100	0.63	1.22	> 23
	2643	150	0.95	1.14	> 17
6.25	1296	100	0.63	1.27	> 23
	1826	150	0.95	1.19	> 23.5
	2665	175	1.10	1.49	> 19
8.33	1264	100	0.63	1.64	> 24
	1164	150	0.93	1.03	> 23

* Plugging caused by crystallization took place in the column after this time

3.2.3. Performance of the rectification column

As already mentioned in section IV.1, a solid Xe phase may appear in the column, at a pressure of 0.8 MPa. At this pressure the boiling point of nitrogen is 100.38 K. The xenon vapor pressure at this temperature equals 78 Pa which corresponds of 97,5 ppm vol. Gosset (8), who applied the Peng-Robinson equation of state (6) on the experimental results of Mastera (7), showed that binary mixtures of nitrogen and xenon at 0.8 MPa have a triple point at 100.59 K, corresponding to a liquid phase xenon concentration of 1.14 mol % and a gas phase xenon concentration of 48.56 ppm vol. Both gas phase concentrations lie far below the 1000 ppm vol, the xenon concentration expected in dissolver off-gases and accepted as design base for the installation. When instantaneous equilibrium between the phases at the inlet of the column is assumed, the liquid phase xenon concentration has to be kept below the triple point concentration in order to avoid crystallization. This liquid phase xenon concentration is determined by the xenon supply (feed gas flow rate x xenon feed concentration) and by the reflux rate. Thus for a given xenon feed concentration, the occurrence of a solid xenon phase can be avoided by regulation of the reflux rate.

Dynamical working conditions have an important influence on the behaviour of the column, as can be seen in table III. There, the xenon concentration in the refluxing liquid below the feed point was calculated under the following assumptions :

- instantaneous equilibrium between the phases,
- negligeable xenon concentration in the gas phase rising from the lower column packing,
- reflux flow rate in this lower packing only depending on the heating power of the kettle.

These results show that the solubility of xenon in the liquid phase falling down in the column might probably be higher than 1.14 mole %, the value calculated by Gosset. At low feed rates the calculated liquid xenon concentration is obviously lower than at higher feed rates. This indicates that in these conditions mass transfer is slower than heat transfer and that xenon crystallization will occur directly form the

gas phase. Due to its too low dissolution rate, the solid xenon formed accumulates in the column. In order to avoid this, mass transfer must be improved in the inlet section. This can be done by decreasing the empty space between the feed point and the support plate of the upper packing.

3.2.4. Influence of traces of oxygen on the column's operation

Gases like oxygen and methane, the boiling point of which lies between those of xenon and nitrogen and that might be present in trace amounts in the feed gas, will - depending on their boiling point - accumulate at determined points in the column. The oxygen enrichment is of special importance since in the presence of radioactive krypton ozone will be formed, which represents a real explosion hazard. In order to determine the place where and the amount to which oxygen may accumulate, the following experiments were carried out :

Experiment	I	II
gas flow rate ($g.s^{-1}$)	4.17	4.17
Ar-concentration (% vol.)	1	1
O_2-concentration (ppm vol.)	5	100
Time (days)	12	12

In neither of the two experiments a change in the temperature profile could be detected. Since no sampling point was available in the argon and krypton layers, this was the only mean to detect and estimate oxygen accumulations. These results seem to confirm what von Ammon had found (4) : with 10 ppm vol. oxygen concentration a maximum oxygen concentration is found which practically coïncides with the argon maximum and which amounts to 3 % vol. Obviously, the temperature change corresponding to such a small concentration of oxygen in argon cannot be detected with the available instruments.

Because of the low accumulation rate and the low concentration of oxygen in the column, ozone formation will be limited and regularly stripping of the oxygen layer may further reduce the hazard.

3.2.5. Efficiency of krypton removal

Assuming ideal solutions, perfect gases and a constant relative volatility of 50 in the N_2-K_2 system between 90 and 110 K, it can be calculated that krypton decontamination factors of 100 and 1000 can be achieved by respectively 4 and 5 transfer units for a reflux ratio of 0.25 at a gas feed rate of 8.3 $g \cdot s^{-1}$ at a temperature of 130 K (9). Since the spiral rashig rings used as packing material have a height of a transfer unit of about 3 cm in these working conditions (10), decontamination factors of 100 and 1000 can be achieved with packing heights of respectively 12 and 15 cm. However, the lowest layers of the upper packing are used for heat transfer so that the liquid flow rate in them varies from a lower value corresponding to the reflux rate in the stripping section to the desired value.

In tabel IV results of krypton measurements in the feed (AP_0), in the column at the feed level (AP_2) and for packing heights of 25 cm (AP_4) and 72 cm (AP_1) are summarized. It can be seen that DF's higher than 500 are already obtained with a packing heigth of 25 cm. Nevertheless, it has been shown that such performance can only be achieved if the regulation of the cooling maintains a rather constant liquid flow rate in the column. This means that in practice the variations in the cooling power must be lower than 10 % of the value corresponding to the desired reflux rate. Furthermore the lowest value of the cooling power must remain between 90 and 99 % of the kettle heating power.

TABLE IV : Krypton concentration at different points

Feed ($g \cdot s^{-1}$)	Heating power (W)	Feed temperature (K)	Cooling nitrogen ($g \cdot s^{-1}$)	Krypton concentration (vol. ppm)			
				AP_0	AP_2	AP_4	AP_1
2.1	100	121	1.5	148	149	< 0.2	< 0.2
2.1	200	124	2.1	225	223	< 0.2	< 0.2
2.9	100	120	2.1	63.5	n.m.	n.m.	< 0.2
2.9	100	120	1.8	900	n.m.	n.m.	< 0.2
4.13	100	120	2.0	760	n.m.	n.m.	< 0.2
6.25	102	120	2.1	1000	n.m.	n.m.	< 0.2
6.25	102	120	2.1	2100	n.m.	n.m.	< 0.2
6.25	102	116	1.6	90	140	< 0.2	n.m.
6.25	101	126	2.3	90	139	< 0.2	n.m.
6.25	200	116	2.4	97	96	< 0.2	< 0.2
10.5	100	120	2.7	873	n.m.	n.m.	< 0.2

n.m. = not measured.

IV. CONCLUSION

The feasibility of cryogenic distillation for the removal and separation of krypton and xenon from reprocessing plant off-gases has been demonstrated with cold simulated off-gas in the cryodistillation unit existing at S.C.K./C.E.N. Critical points in the design of such a unit have been revealed from operational experience and experimental results. The experience gained will be applied in the design of a new radioactive unit for the project HERMES.

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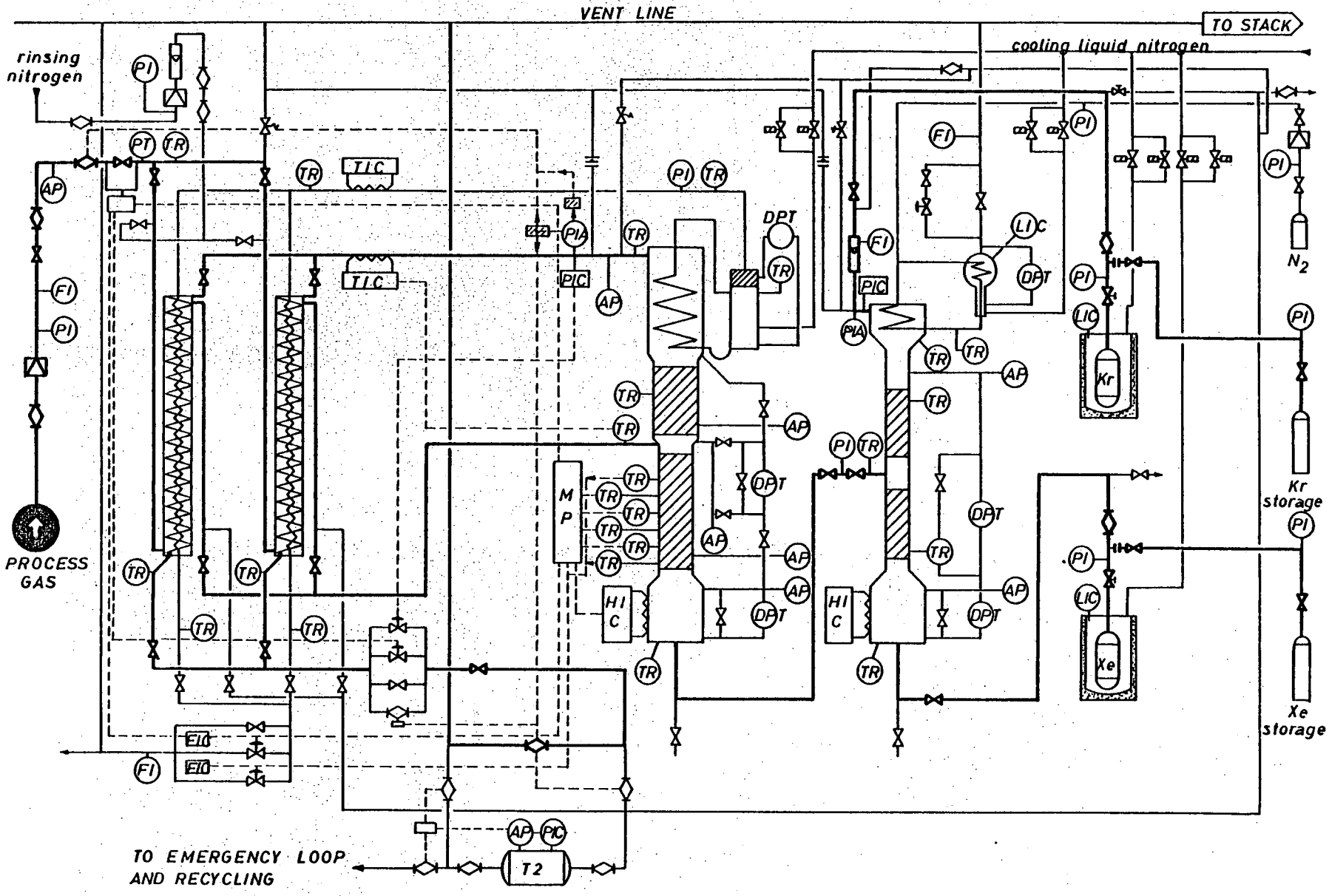

FIG.1: KRYPTON REMOVAL BY CRYOGENIC DISTILLATION

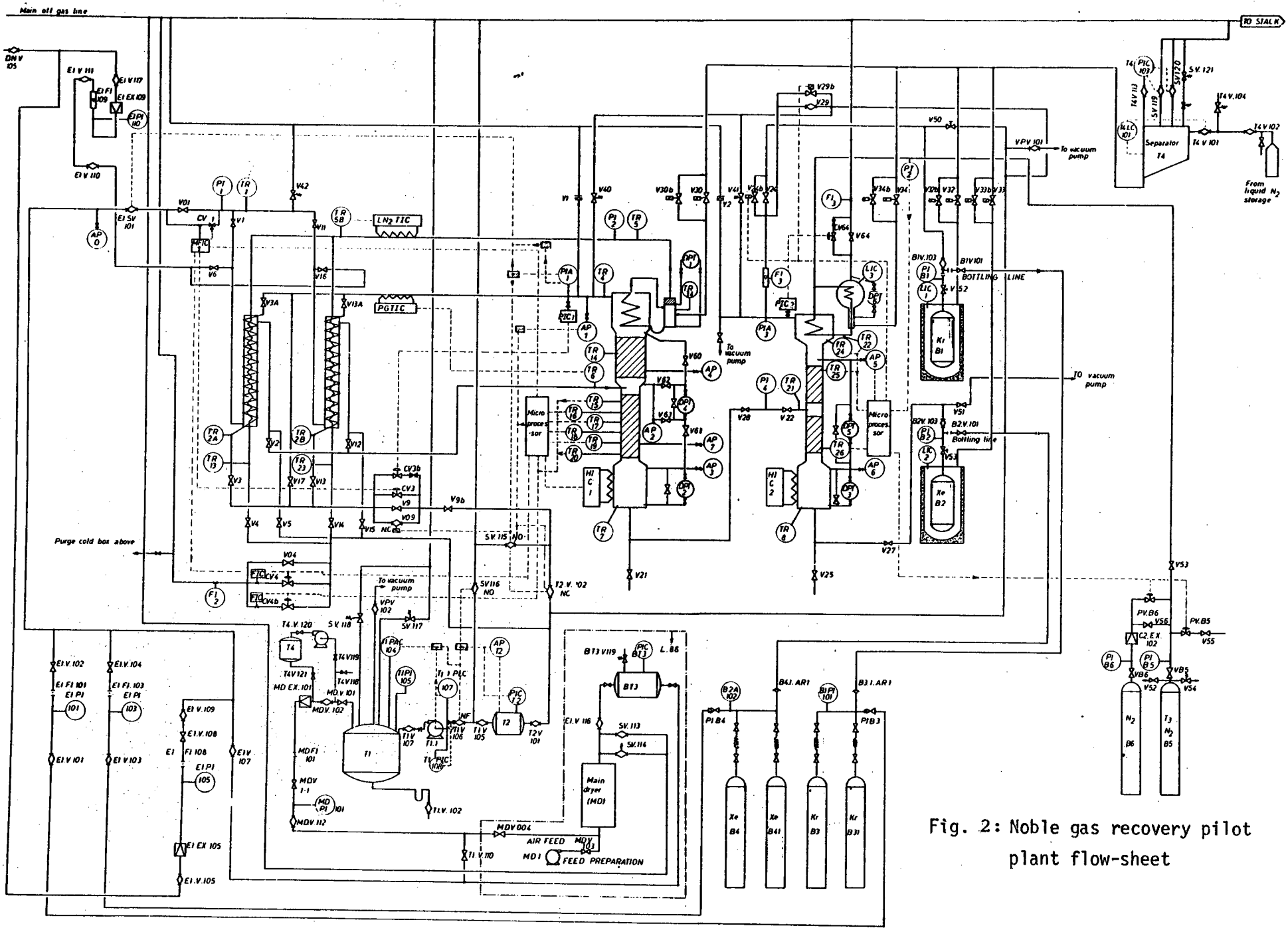

Fig. 2: Noble gas recovery pilot plant flow-sheet

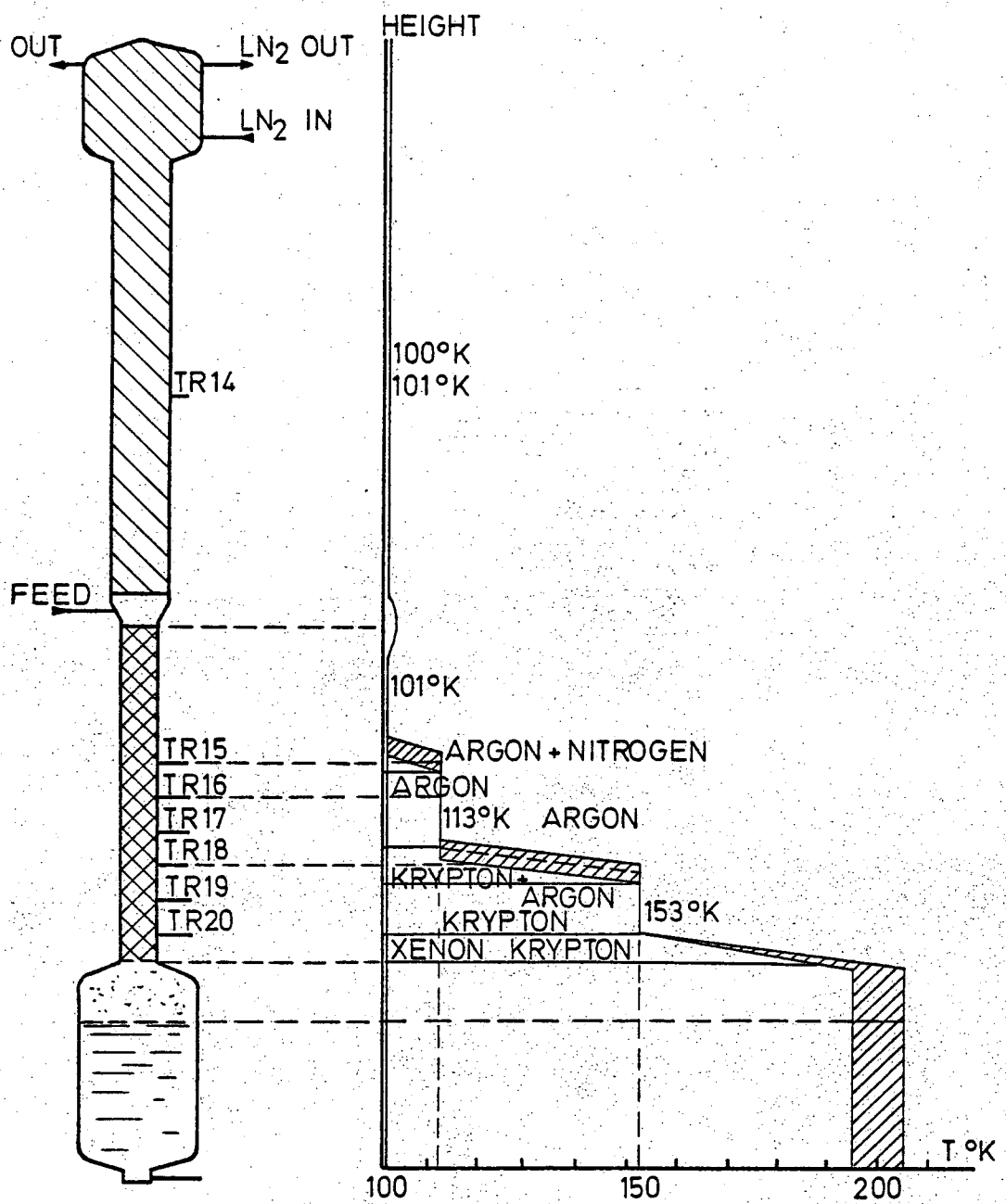

FIG. 3: TEMPERATURE PROFILE IN THE FIRST COLUMN

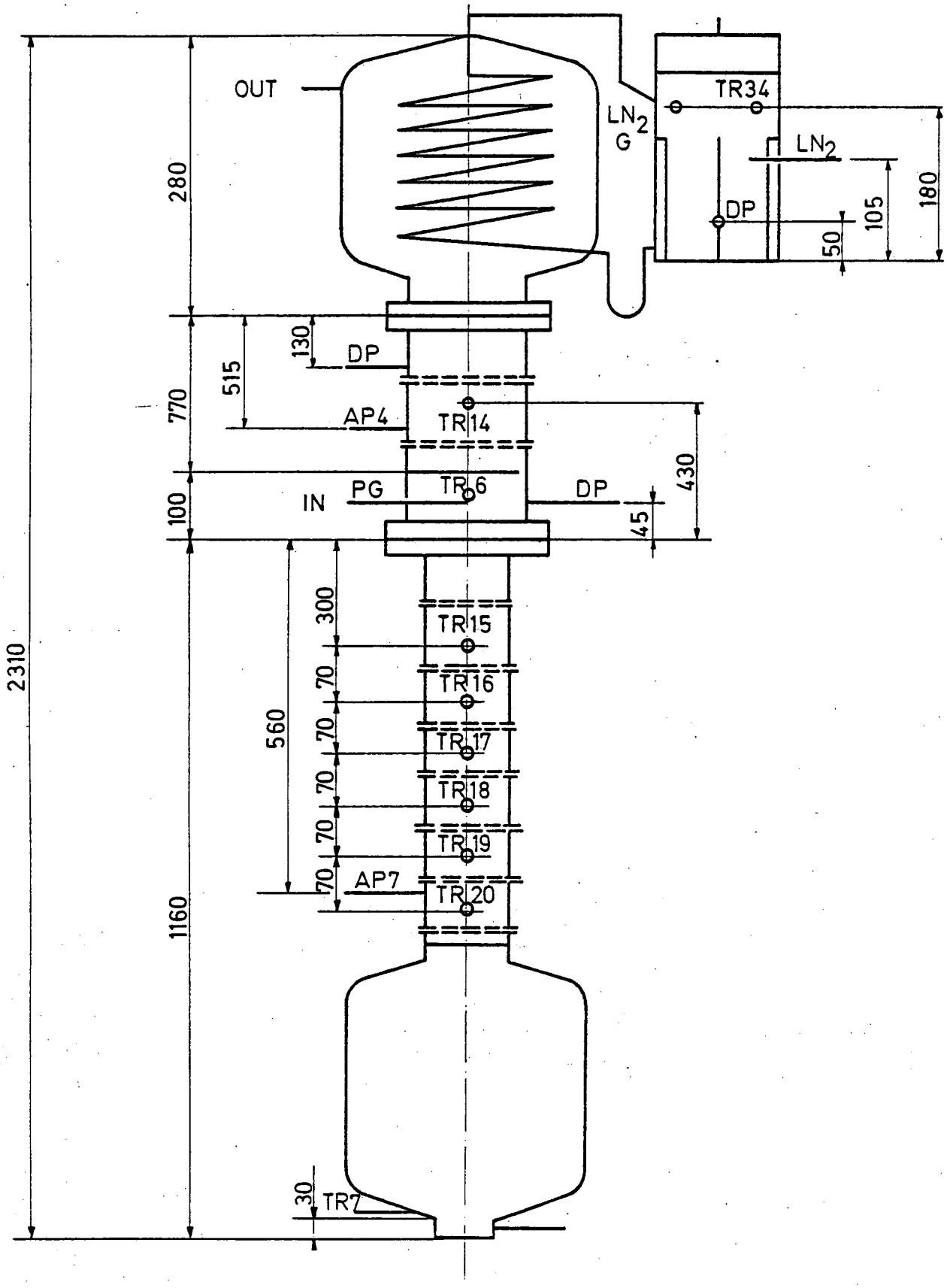

FIG.4 : MAIN DIMENSIONS OF THE FIRST COLUMN

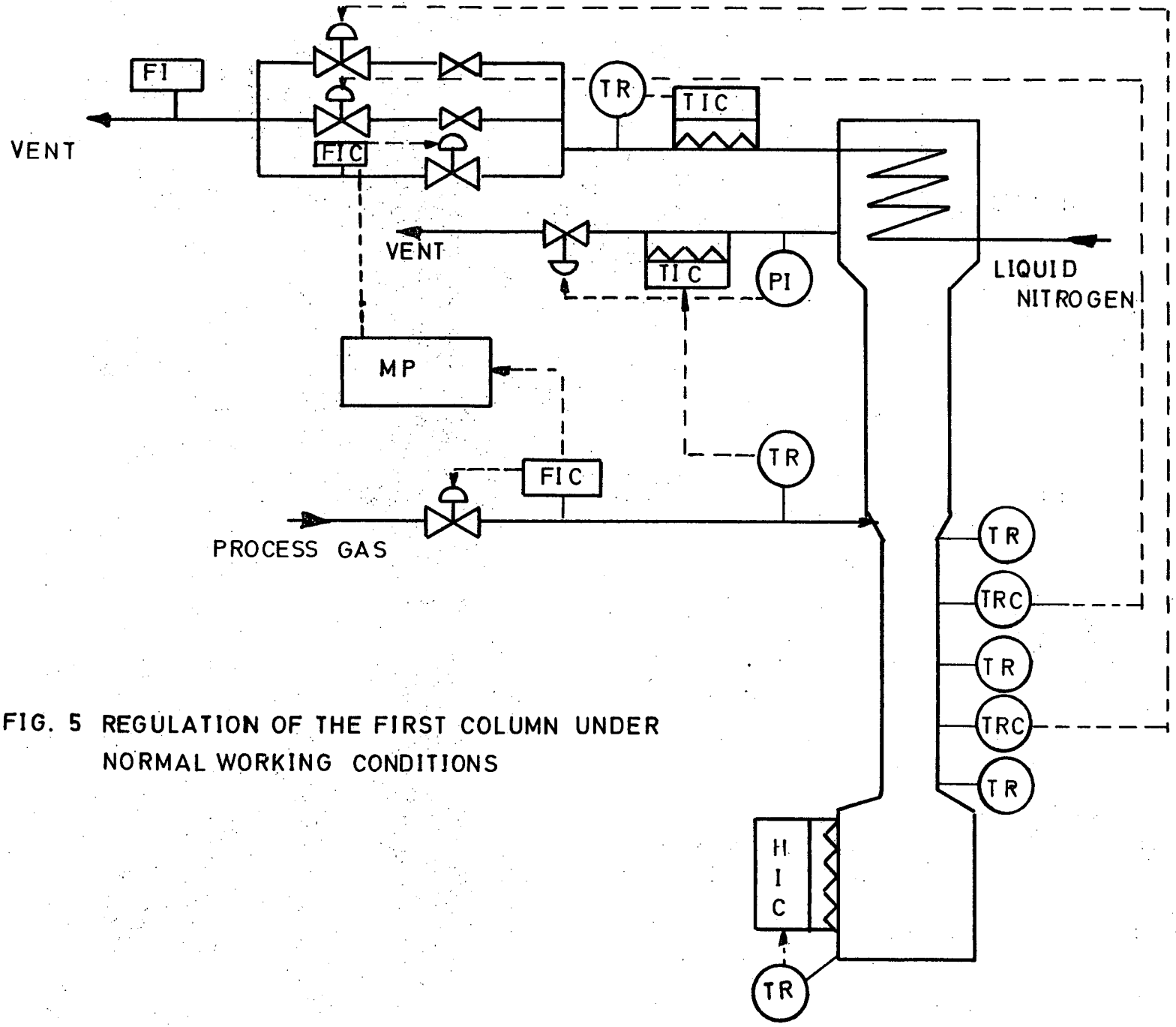

FIG. 5 REGULATION OF THE FIRST COLUMN UNDER NORMAL WORKING CONDITIONS

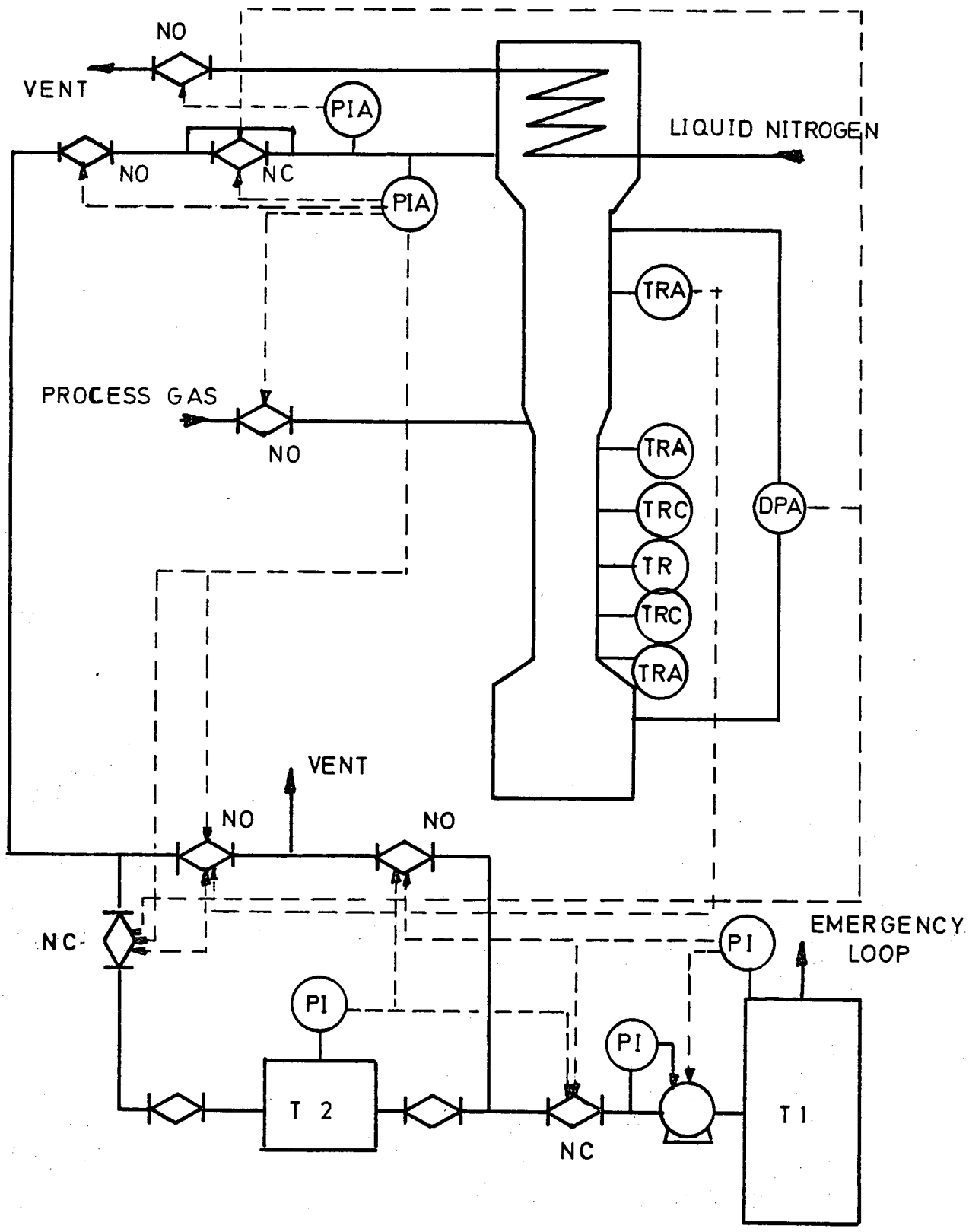

FIG. 6 ALARMS AND AUTOMATIC OPERATIONS

APPENDIX I : Start-up procedure

A. FIRST COLUMN

- Nitrogen gas at a flow rate of 0-3 Nm^3h^{-1} and liquid nitrogen at a flow rate of 7-8 Nm^3h^{-1} are fed to the column, so that nitrogen is liquefied.
- As the N_2 liquid level in the column approaches 150 mm W.H., the liquid nitrogen flow rate is lowered to 2-3 Nm^3h^{-1}.
- Krypton is fed to the bottom of the column until its liquid level approaches 100 mm W.H.
- Gas flow rate, heating power and temperature of the cold outlet gases are adjusted at the desired values.
- The liquid nitrogen flow rate is calculated in function of gas flow rate, gas inlet temperature and kettle heating power and the cooling regulation is put in operation with the N_2-Kr separation zone at TR16 or TR18.

B. SECOND COLUMN

- The column is put under vacumm.
- Krypton at pressure slightly above the normal column pressure is continuously supplied to the bottom and the cooling system is put in operation.
- As the krypton liquid level reaches 100 mm W.H., the krypton supply is cut off and the kettle heating power is adjusted at the desired value.

APPENDIX II : Close-down procedure

A. FIRST COLUMN

- As much Kr and Xe as possible are transferred to the second column, taking care that no Ar, O_2 or N_2 is entrained. This transfer might need a few steps.
- Heating power and liquid nitrogen supply are cut off.
- The column is rinsed with nitrogen gas, that is sent to the emergency loop, where it is stored.

B. SECOND COLUMN

- The Kr-Xe separation is pushed as far as possible and both compounds are drawn off, taking care that they aren't contaminated with the other.
- Heating power and liquid nitrogen supply are cut off.
- The mixture remaining in the column is collected in one of the intermediate storage bottles where it is stored, by means of cryogenic pumping.

APPENDIX III : Review of 13 000 hours campaign

The long duration campaign of more than 13 000 hours lasted from November, 1978 until April, 1980. The total outage time amounted to only 84 hours, which represents an over-all availability factor of 99.36 %. The major part of this outage, 51 hours, was caused by the reparation of a break-down in the liquid nitrogen supply system. However, here must be mentioned that the reparations were carried out only during daytime working hours. A large part of the remaining outage time was due to the nature of the experiments going on : the determination of the extreme working limits of the installation. Here, plugging of the heat exchanger and of the first column were the causes for the outage.

In this appendix the outage times, their causes and eventually the necessary repairs are tabulated.

TABLE 1 : Outage caused by experiments

Month	04-79	05-79	06-79	09-79	11-79	12-79	01-80	03-80	04-80
Outage time (h)	1	2	2	4	2	4	1	1	1

sum : 18 h
additional : 2 h (sum of the outage time of all the other months)

Total : 20 h

TABLE II : Outage caused by break-down

Date	Time (h)	Cause, Problem	Repair, Solution
16/04/79	7	Out of liquid nitrogen feed tank empty.	- Immediate supply of liquid nitrogen. - An emergency dewar must be provided, which can take over cooling duties for 5-6 hours.
19/10/79	1	Separator too full, caused by leaking electromagnetic valve in one (of two) liquid nitrogen supply line.	- Cut off manually the defect line (temporarily). - Alarm on liquid nitrogen supply connected to the microprocessor. - The use of the emergency dewar limited the outage time.
26/10/79	1	Separator too full again (vide infra).	- Cut off the defect line. - Change the e.m. valve, but left it unconnected until operation is necessary. - Use of emergency dewar.
23/11/79	0	Blocking of valve used for transfer from the first to the second column.	- Connection between the bottoms of both columns, outside the cold box.
09/12/79	0	Short-circuit in control rack of liquid nitrogen supply.	- Replacement of fuse. - Emergency dewar used, no outage.
25-26/1/80	1	Short-circuit in connection line of e.m. valve between liquid nitrogen tank and separator.	- Change of supply line. - Emergency dewar used.
6-8/2/80	51		- Repair of the liquid nitrogen supply lines : new e.m. valves. - Installation of a new isolation for the supply lines.

sum : 61 h
additional : 3 h (sum of outage time caused by less important break-downs).

Total : 64 h

APPENDIX IV : Analytical methods

The analytical method used for the determination of noble gases in nitrogen was gas chromatography (GLC). The components to be separated and measured are argon, krypton and xenon respectively in a concentration of 0-1 % vol, 0-2000 ppm vol, 0-8000 vpm vol.

INSTRUMENTS

Gas chromatograph : "Tracor MT 150 G",
Detector : "Tracor V9" ultrasonic detector and phasemeter,
Integrator : "Infotronic CR S-204",
Printer : "Teletype",
Recorder : "Texas Instruments Inc. Servoriter II".

EXPERIMENTAL WORKING CONDITIONS

Column : Porapak Q, 100-120 mesh, 61 cm L, 1/8 in OD,
Column temperature : 28°C,
Detector temperature : 120°C,
Carrier gas : N_2, 14 ml/min, inlet pressure 6.2 bar,
Sampling : 8 port gas sampling valve "Tracor", fitted with two loops of variable volume,
Sampling gas pressure : 1-3 bar.

X