PART II

EXPERIMENTS

IRRADIATIONS PERFORMED AT CEN– SACLAY
CONDITIONS AND METHODOLOGY DEVELOPED

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ABSTRACT

In this paper the irradiation facilities used to irradiate salt samples at CEN–SACLAY are described. With these facilities salt samples could be irradiated at temperatures upto 400 °C and dose rates upto 10^5 Gy.h^{-1}.

1.   INTRODUCTION

The Osiris nuclear experimental reactor is capable of supplying γ radiation, which spectrum is similar to that of waste, using its own fuel as it undergoes deactivation while simultaneously allowing to speed up the production of radiolytic gases by an increase in the dose rate level (by way of example, an total dose of 10^8 Gy corresponds to the first one hundred years of disposal).

The selection of an irradiation installation inside a reactor to conduct the program offers several advantages, such as :

a)   the best cost–effectiveness : the gamma sources are already available and do not have to be fabricated or shipped ; and

b)   the best availability : the installation was dedicated to the research program and available sources had a wide range of activity, facilitating the achievement of high dose rate levels.

The existing irradiation installation as well as the operating procedures were gradually adapted to the evolution of program needs, especially for the parameters of dose rate, total dose and temperature.
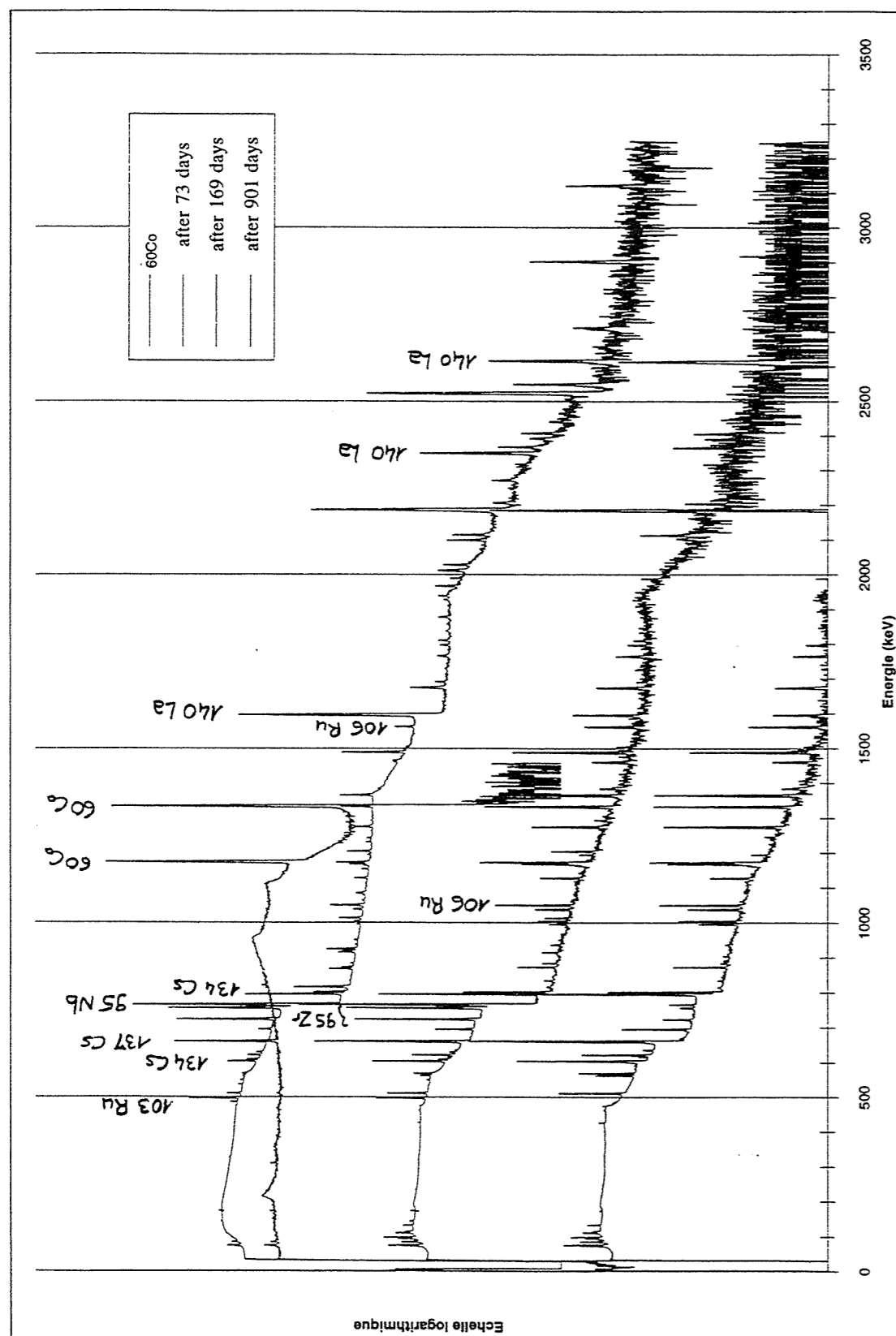
Figure 1: *Gamma spectrum emitted by Osiris fuel element and ^{60}Co*

2. THE USED RADIATION SOURCES

2.1. Gamma radiation

The γ radiation sources are primarily fuel elements unloaded from the Osiris reactor core and transferred underwater to the irradiator designed to accommodate them. The radiation spectrum is therefore determined by the fission products and daughter products present; its complexity diminishes as cooling increases (Fig. 1).

Low dose rates are achieved with elements that have been cooled for at least a few months (and that are no longer returned to the reactor core) and are positioned at a rather large distance from the samples (Fig. 4a).

High dose rates are achieved with elements unloaded from the core specifically for the purpose of γ irradiation. These elements are transferred into the irradiator after a reduced cooling time and are positioned close to the samples.

For a given activity, the ratio between the dose rate obtained when the elements are placed in the innermost positions and the dose rate obtained when the elements are placed in the outermost position, is 10

Few other γ radiation sources consisted of piles of small ^{60}Co plates with a very high specific activity prepared in Osiris by the activation of metallic cobalt. While the geometry of the baskets of ^{60}Co is not strictly identical to that of the fuel elements (Fig. 4b), the overall configuration remains the same. Only the energy spectrum of the ^{60}Co plates is different from that of the fuel elements.

Figure 1 illustrates the spectral differences of the two types of γ sources (the results were achieved with a γ spectrometry bench in the Osiris reactor pool).

AIR INTAKE AIR OUTLET

INSTRUMENTATION CHANNELS

ELECTRIC HEATERS

GUIDE-ROD

SAMPLE HOLDER

FUEL ELEMENT

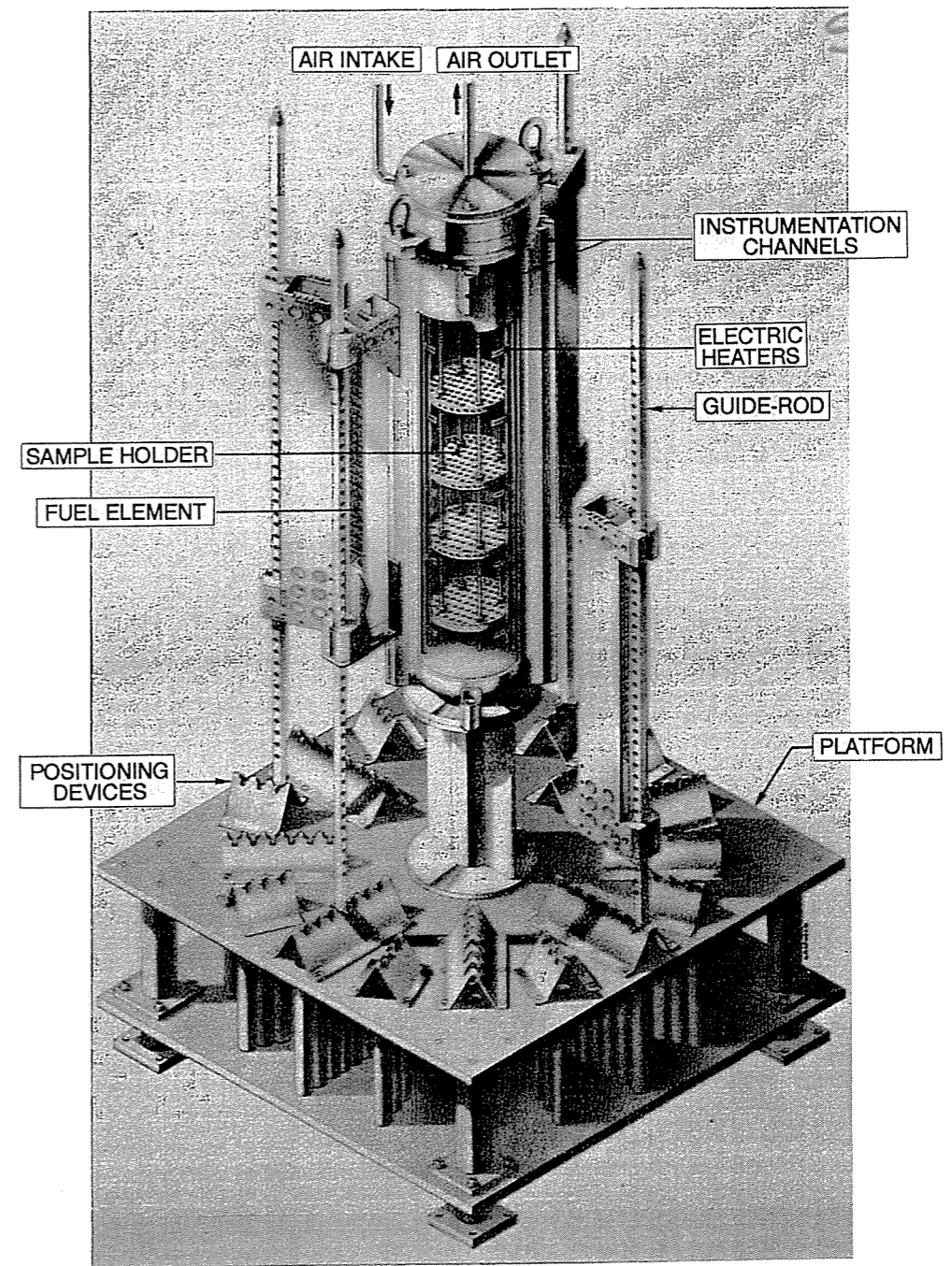POSITIONING DEVICES

PLATFORM

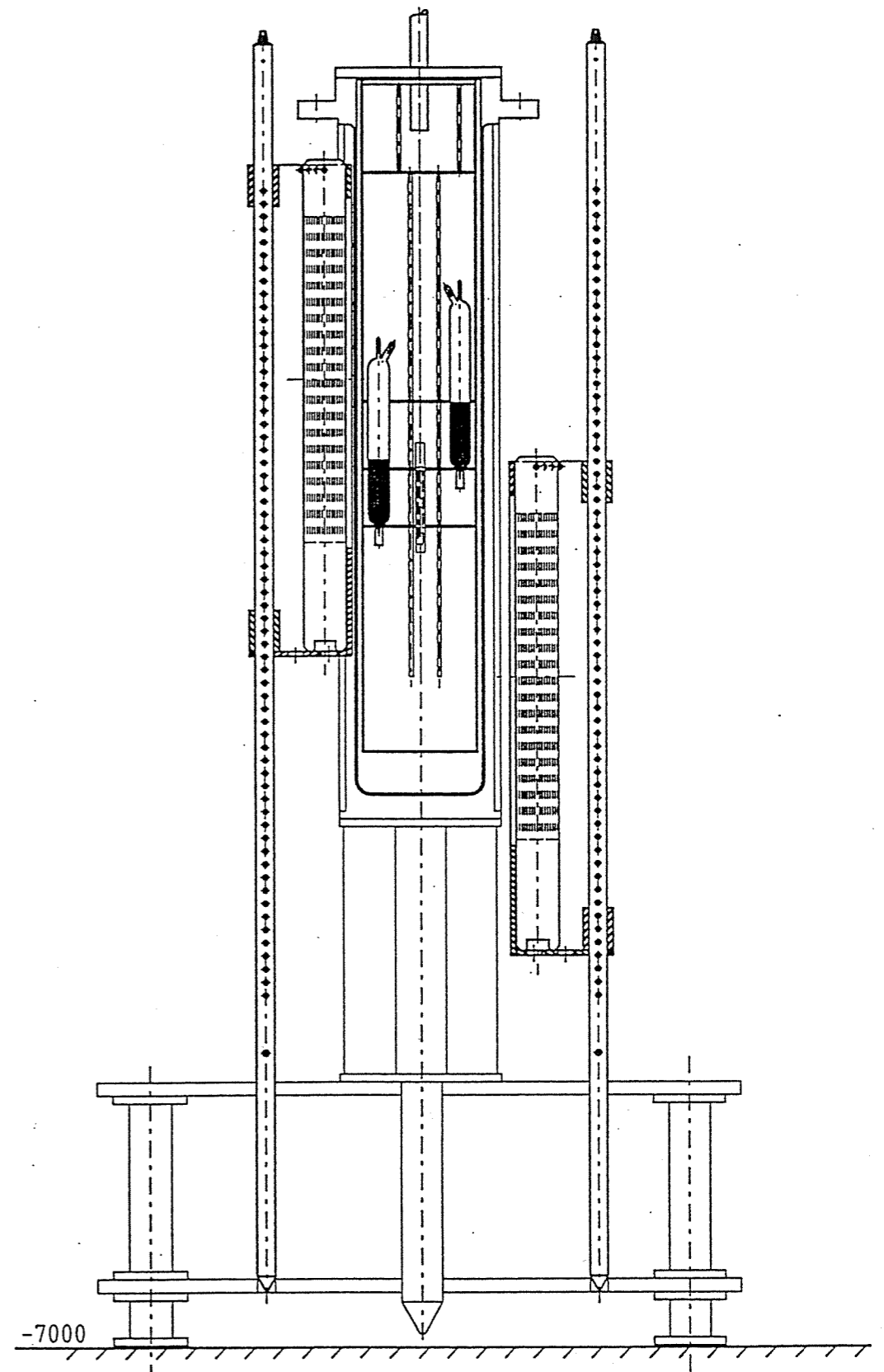Figure 2:   *View of the main irradiator*

−7000

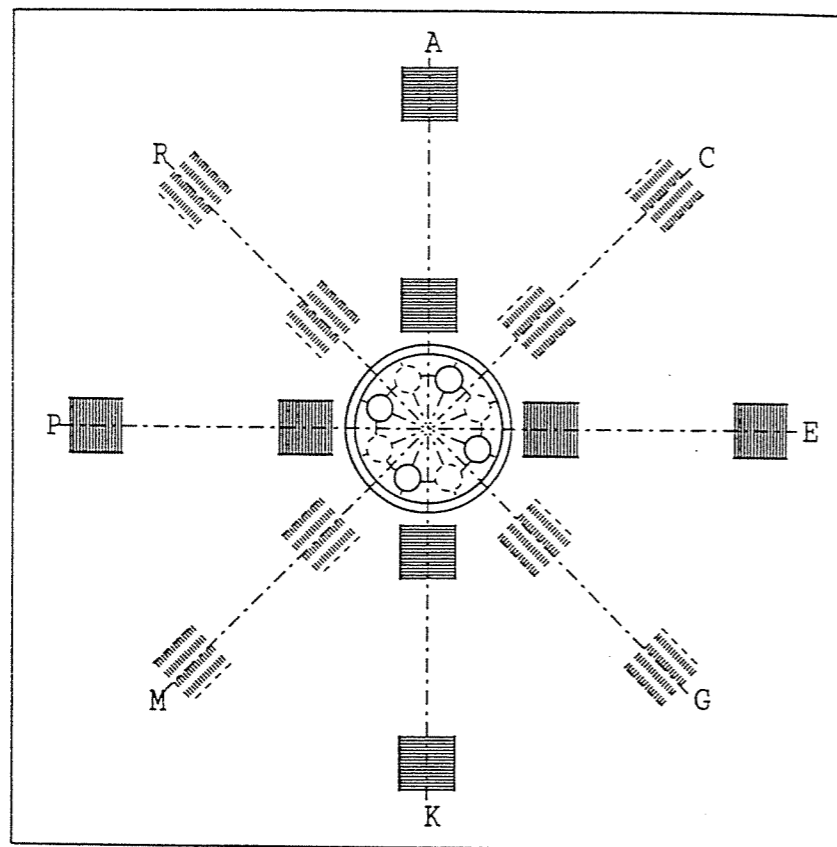Figure 3:   *Main irradiator (vertical cross section)*

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Figure 4a: *Horizontal cross section of gamma irradiator. Fuel elements are represented at the two extreme possible radial distances from the samples. Dashed lines = lower position, full = higher position.*
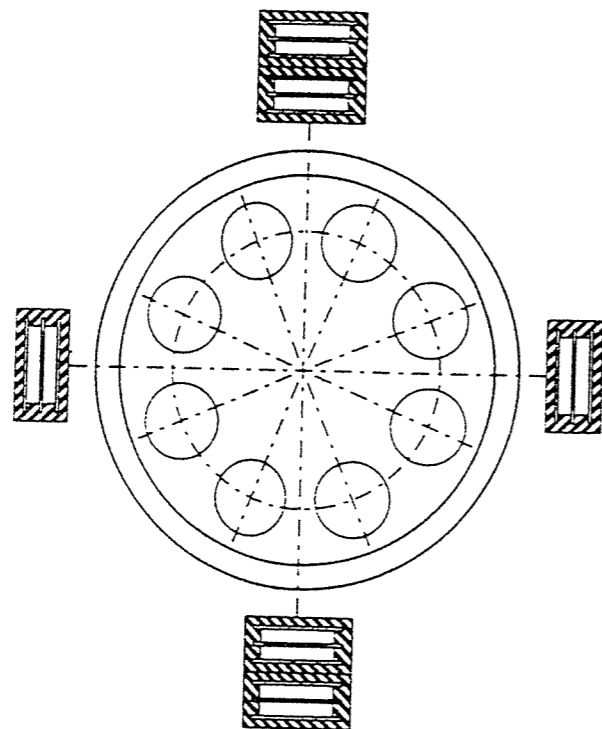

Figure 4 b: *Horizontal cross section of gamma irradiator with six ^{60}Co elements (sources are here located as close as possible to the samples)*
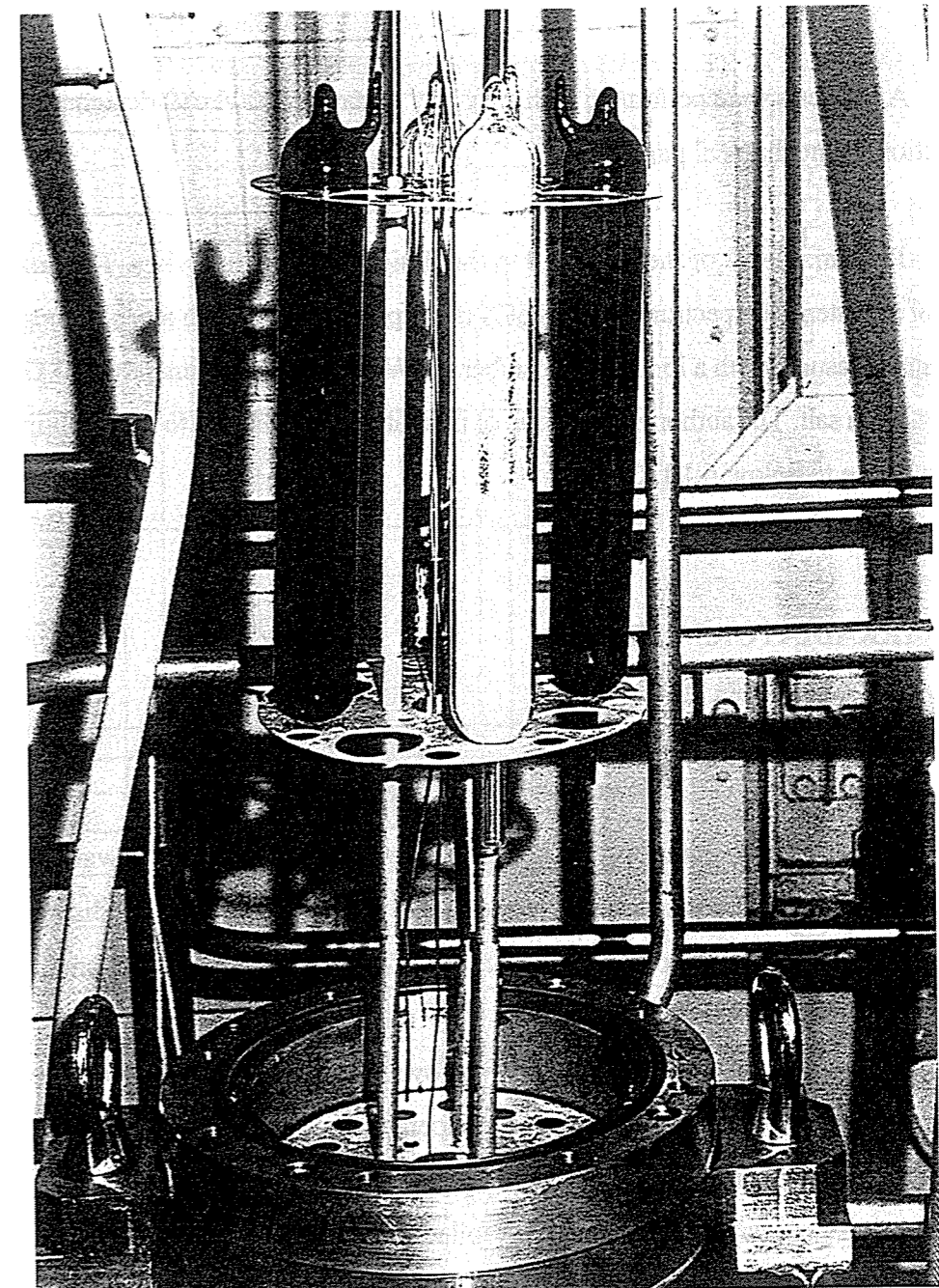

Figure 5: *Salt samples, sample holder and instrumentation*

2.2. X– Rays

A few tests were performed with an X–ray generator (300 keV) designed for radiographic inspection of mechanical parts.

The small size of the beam led to the design of small size vials. The anticathode being made of tungsten, the spectrum consists of X rays up to 300 keV with a peak around 72 keV. The dose rate, measured with a ionization chamber (PTW type), is approximately 600 Gy.h^{-1} in air and 200 Gy.h^{-1} in salt. The authorized duration of irradiations was limited to some hours, thus limiting the total dose to below 6.10^3 Gy.

3. IRRADIATORS USED

3.1. Principal irradiator

The irradiator is placed on a floor submerged beneath 7 meters of water in the n°3 canal of the Osiris reactor. It consists of a cylindrical irradiation chamber (useful diameter ~ 220 mm), weighted, submersible, surrounded by 8 supports for fuel elements (Fig. 2 and 3).

The irradiation chamber is sealed by a moveable cover which supports the sample carrier structure (Fig. 5). Electric furnaces enable a temperature of several hundred °C to be reached. To homogenize the temperature and evacuate any gases from radiolysis, the volume of the chamber is constantly swept with dry, dedusted, de–oiled air.

The chamber is instrumented with:
a)   chromel–alumel thermocouples to monitor and regulate the temperature,
b)   a central ionization chamber to monitor and regulate the dose rate (type CRGA11 manufactured by RTC). Its response vs. energy of the gammas is given in Fig. 6.

The measurement chain is periodically calibrated by a certified laboratory (LMRI). The total dose is calculated every minute using the measured dose rate values.
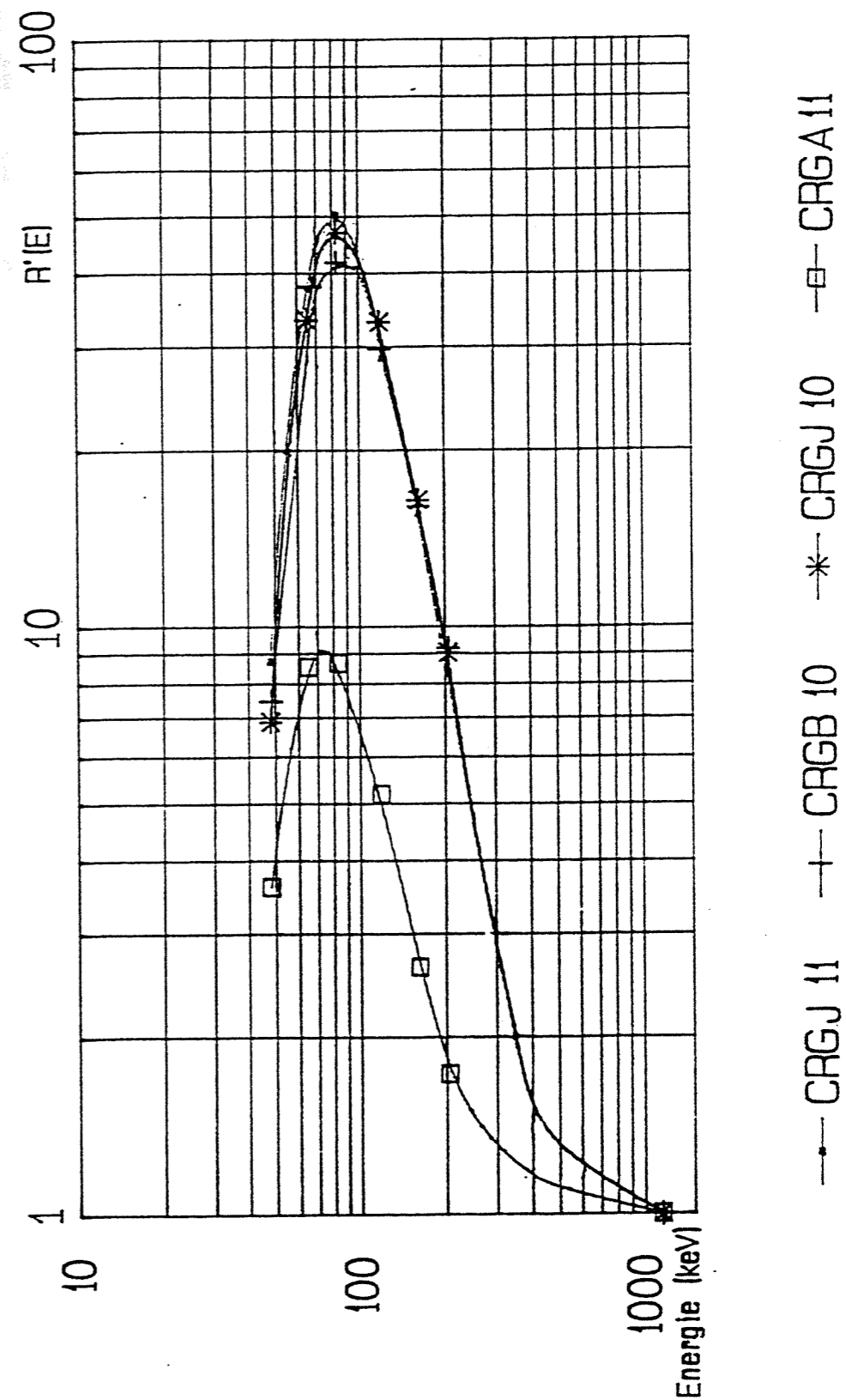

Figure 6:   Ion chambers for irradiation monitoring : response vs. energy of the gammas for 4 types of ion chambers
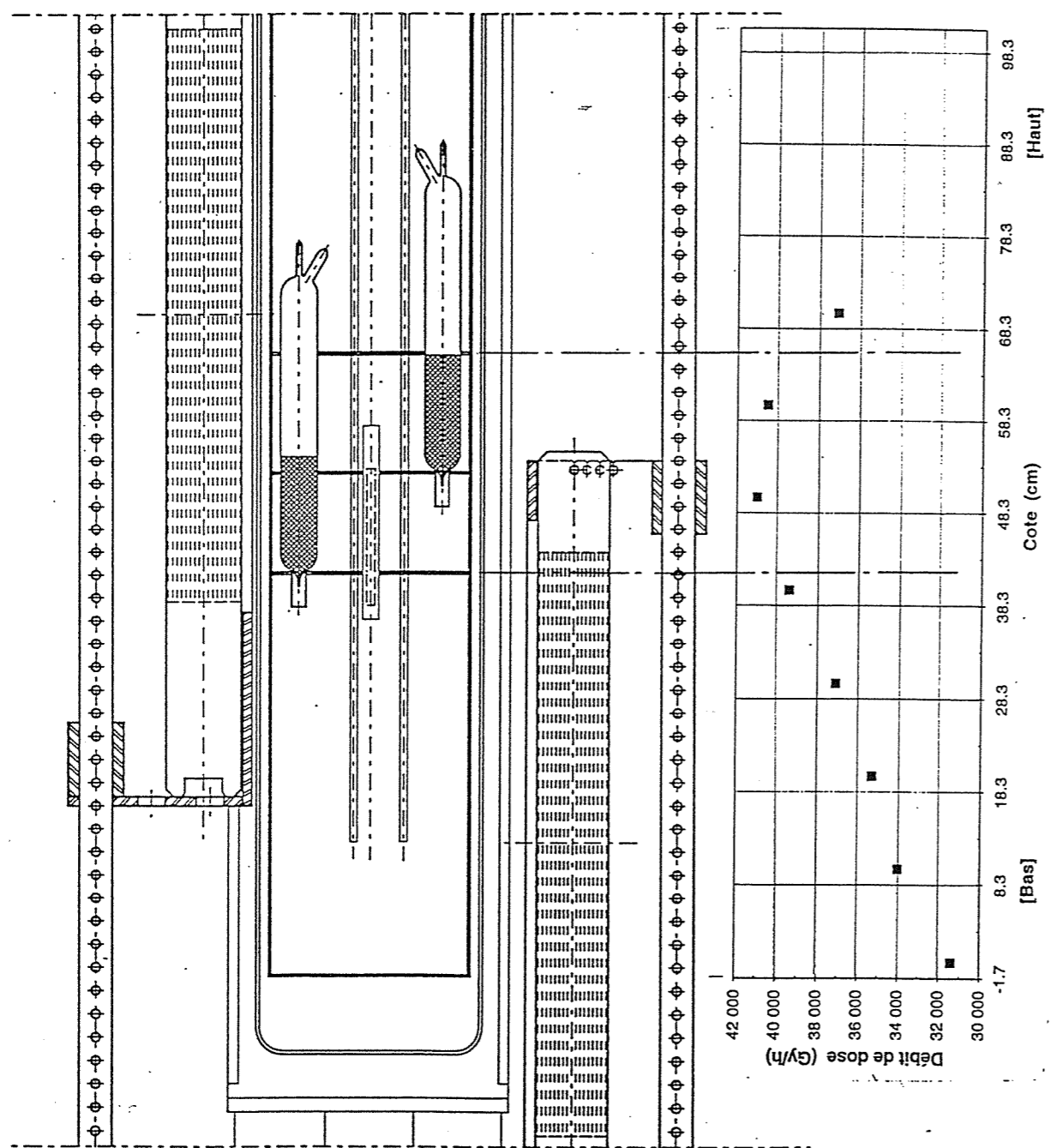
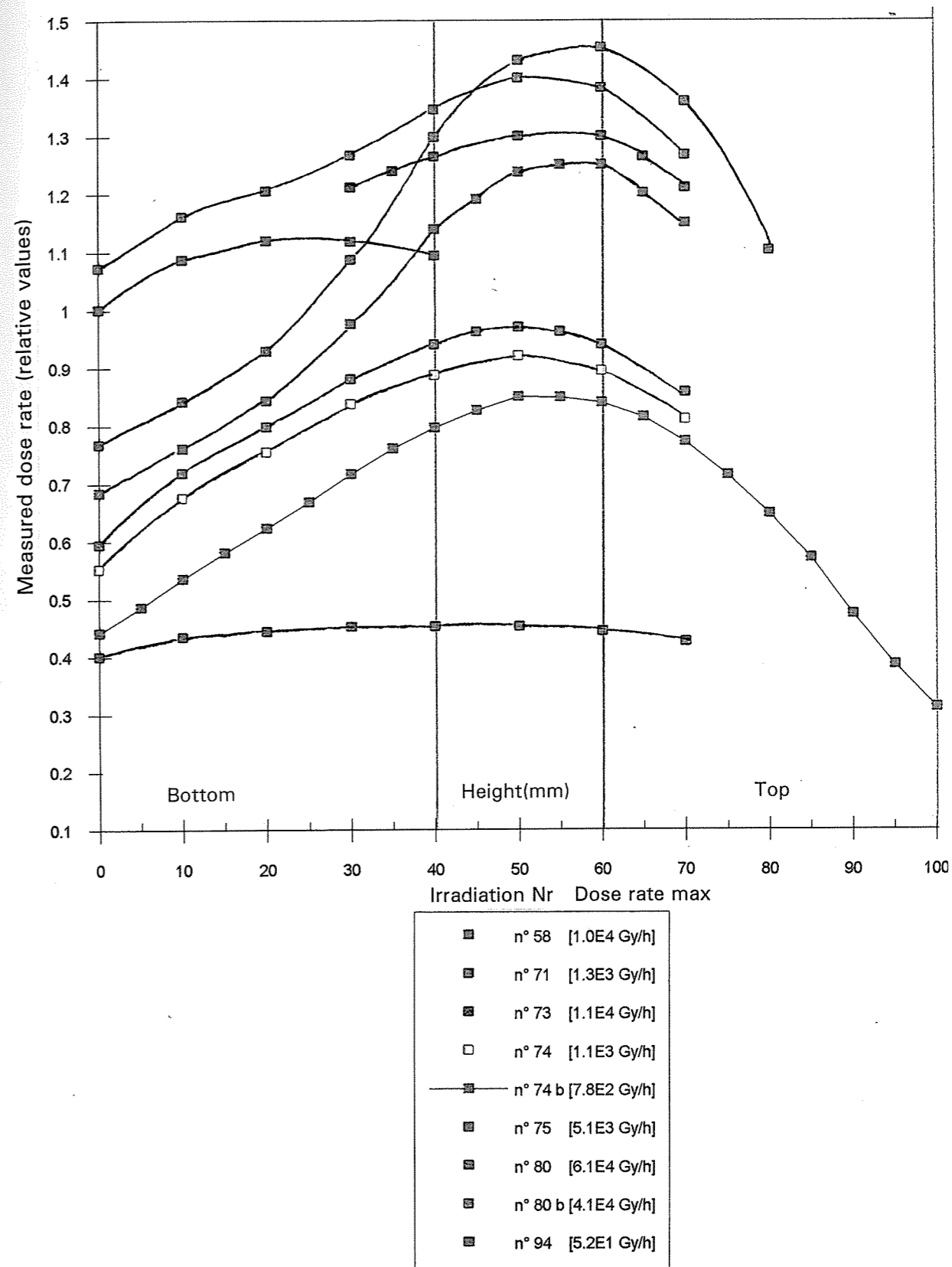Figure 7: *Flux distribution in the irradiation chamber (irradiation Nr 79)*

Figure 8: *Axial gamma flux distribution in the irradiator without salt (relative values). The samples are located between 40 and 60 cm.*

The homogeneity of the resulting gamma flux is a function of:

a)   the number of γ sources;

b)   the activity dispersion between the sources, which is minimized during selection; and

c)   differences in radial position between the sources.

The volume where the dose rate is homogeneous may be increased along the vertical dimension by alternately dividing the γ sources between two levels. In addition, the temporal decrease in activity, and therefore of the dose rate, may be compensated by bringing the sources slightly closer together radially.

3.2.   Additional irradiators

Three small size irradiators were constructed to be able to perform low dose irradiations of long duration at ambient temperature simultaneously with other experiments in the principal irradiator. An instrumented irradiation chamber capable of accommodating two vials is placed between two fuel elements in a structure adapted from fuel storage racks.

4.   PROCEDURES DEVELOPED

Irradiations procedures aimed at complying as much as possible with the contractually fixed values of the following parameters: temperature, dose rate and total dose. According to these procedures, before each irradiation with a new configuration of γ sources, the gamma flux in the empty irradiation chamber is mapped (Fig. 7 and 8), enabling:

a)   pre–adjustment of the radial position of the sources in relation to the nominal dose rate level and therefore reduction of the transient experienced by the samples when they are placed in or removed from the furnace;

b)   verification of the central axial gradient of the dose rate and therefore of the setting of the sample carrier and the instrumentation.
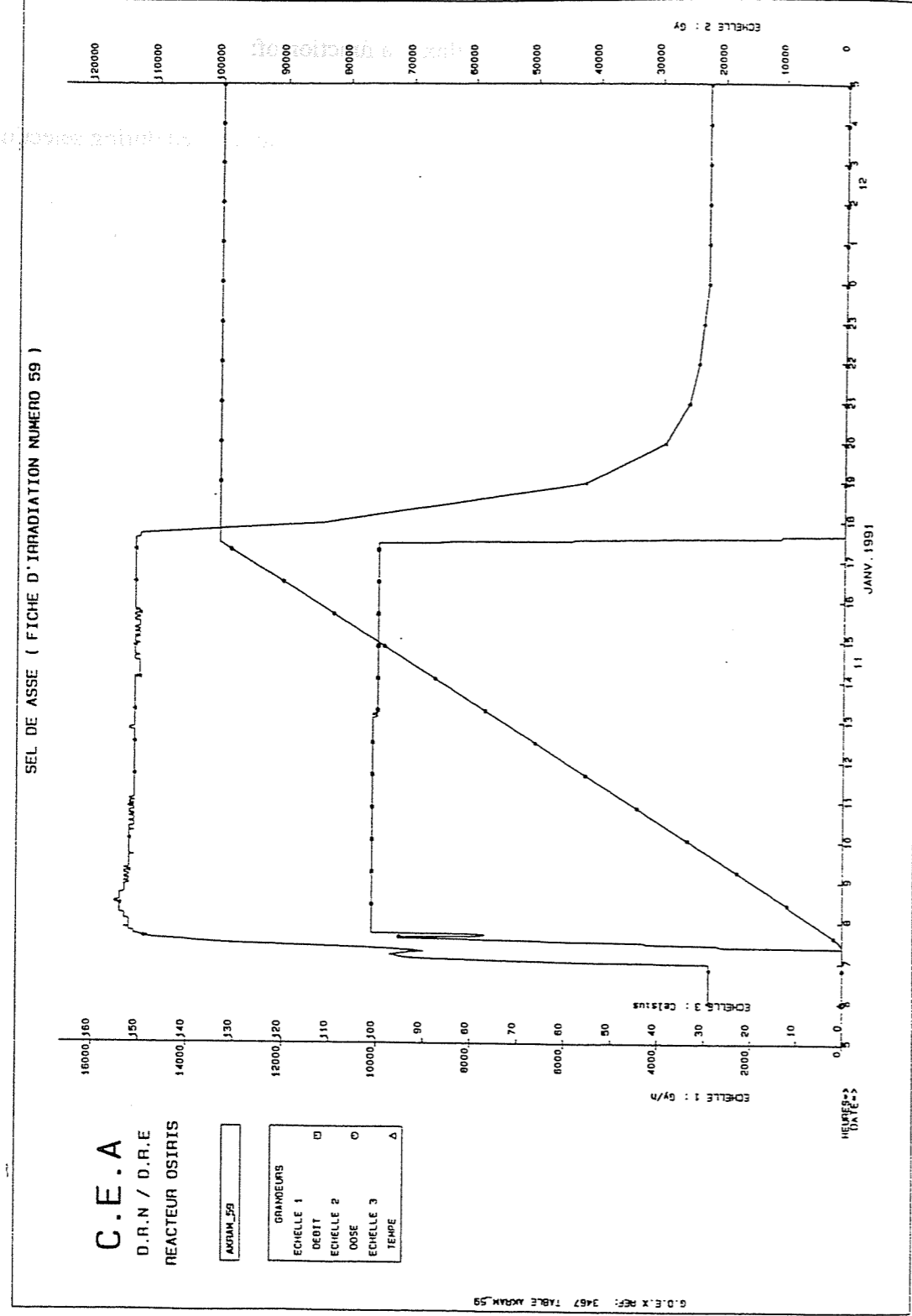
Figure 9a: *Example of graphic data report for an irradiation (Irr. nr 59) : dose rate, total dose and temperature vs. time*
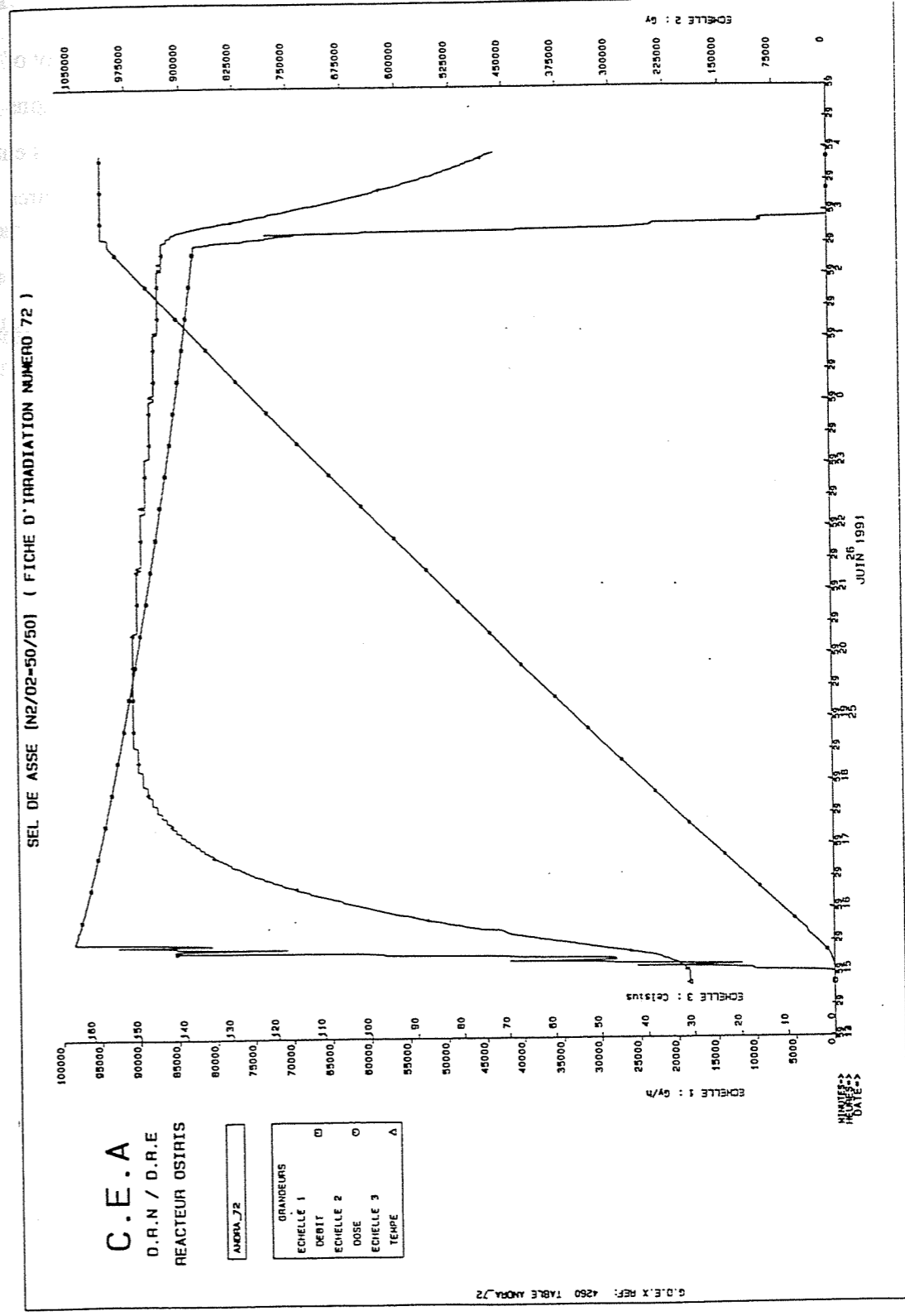
Figure 9b: *Example of graphic data report for an irradiation (Irr. nr 72) : dose rate, total dose and temperature vs. time*

From a safety standpoint, the gamma irradiation installation is the responsibility of the Nuclear Facility Safety Division of the Ministry of Industry; the various authorizations for operation and operating amendments (high dose rates, etc.) had to be procured from this entity following examination of the various design, construction and operation procedures by commissions of experts.

Installation and operating procedures were discussed and approved by the reactor operator.

5. RESULTS OBTAINED

The records in Fig. 9a to 9b show the evolution of the mean temperature of the air surrounding the vials, of the dose rate measured by the ionization chamber and of the resulting total dose during irradiation.

The time to establish or to stop irradiation was kept as brief as possible. However, the return to ambient temperature is not as rapid due to the thermal inertia of the irradiation chamber, a consequence of its design allowing the achievement of high temperatures ($400°C$).

In the absence of additional electrical heating, the temperature level is determined by that of canal water (measurably constant at some $30°C$) and by the absorbed γ energy; In this way, the temperature rises with the dose rate to reach $110°C$ at 10^5 Gy.h^{-1}. For the same reason, temperature fluctuations are correlated to the small radial displacements that are applied to the fuel elements to regulate the dose rate.

The evolution of spatial and temporal gradients has already been mentioned during the description of the irradiators. It may nonetheless be specified that the maximum dose rate level that can be achieved, taking into account the diameter of the irradiation chamber and the duration of cooling required before the transfer of the elements can take place (radiation protection requirement), is 10^5 Gy.h^{-1}. Since the sources are closest as possible to the samples, it is not possible to maintain a constant rate and their natural decay is observed.

5.1. Accuracy of the results

Temperatures

Ambient air temperatures in the irradiation chamber are measured and appear homogeneous regardless of the temperature and dose rate levels. However, the existence of spatial and temporal temperature gradients in the samples is not to be excluded; they could be estimated through calculations performed using computer simulation of the irradiation chamber and instrumentation of the samples.

Dose Rates and Total Doses

The dose rate levels are estimated by application of the calibration factors determined by irradiation of the ^{60}Co in a range of a few Gy.h^{-1} to some 20 Gy.h^{-1}.

Two additional dosimetries performed at 10^4 Gy.h^{-1} with the alanine at around 10^4 Gy and $35°C$ (CEA–DTA–DAMRI–LMRI Laboratory) and with calcium sulfate (approximately 10^6–10^5 Gy and 45–$200°C$) (CEA–IPSN–DPHD–SDOS Laboratory). They show an apparent gross difference of less than 30% with the monitoring system of the irradiator.

A better concordance could be achieved by a better understanding of the spatial gradients of the dose rate, but also of temperature, which can influence sensor response. However, irradiations performed in the framework of the HAW program show that the response of ion chambers type CRGA11 is not influenced by a variation in the level of ambient air temperature, whether the amplitude is low (less than $10°C$) or high (greater than $100°C$).

One notes that the central axial gradient in the absence of samples is less than 15% over a height of 30 centimetres (Fig. 8); the horizontal gradient is much lower (Fig. 7).

In the framework of another irradiation program, a discordance was noted between the CRGA chambers on the one hand and the PTW–type chambers and alanine dosimeters on the other; the latter estimated a rate and a dose of about a factor two lower than the CRGA chambers, at a dose rate level of on the order of 40 to 70 Gy.h^{-1}.

At these low dose rate levels, the contribution of the radiation diffused may no longer be insignificant and the sensor may be more sensitive to low energies (Fig. 5); it was not possible to determine the energy response of the PTW chambers, nor to go into more depth on the various factors involved.

We note, however, that although there may be a relative uncertainty of a few tenths of a percent in the dose rate level and hence of the dose, the relative values are correct. In fact, measurements have shown the right response of chamber CRGA in the dose rate range : 10^2 to 4.10^3 Gy.h^{-1}.

The approach undertaken nonetheless enabled several causes of systematic uncertainties to be identified. To reduce these uncertainties, the following must be done:

a) modification of the irradiator to reduce the flux gradients (rotation of sample carrier, coordinated displacement of fuel elements) and to better understand them (improved instrumentation of the irradiation chamber, filing the data of position of fuel elements and samples, etc.);

b) identification and implementation of other dosimetric processes;

c) performance of several irradiations dedicated to dosimeter under increased surveillance;

d) performance of more irradiations to increase the level of confidence.

6. FURTHER STRATEGIES

The entire salt research program was conducted from 1988 to 1993. Aside from the preliminary preparation of test facilities and their gradual adaptation during the implementation of the program, a large volume of samples was subjected to γ radiation under various spectrum, dose rate, total dose and temperature conditions. The irradiation program went well overall. Good mastery of irradiation planning, preparation and operation was acquired, allowing the principal objectives of the program to be met.

While the accuracy of knowledge of dose rate levels and, subsequently, of total dose is better than an order of magnitude, error values remain nonetheless greater than the 15% that would have been preferred. It is possible that the doses are overestimated. The relative values are most assuredly correct.

It nonetheless appears that miscellaneous improvements could still be made to reduce the systematic uncertainties identified:

a) establishment of preliminary calibration covering the entire field explored (spectrum, dose rate, temperature);

b) identification and implementation of other dosimetric processes in addition to the coverage of the field explored;

c) modifications to the irradiator to reduce residual flux gradients (rotation of sample carrier, coordinated displacement of γ sources, etc.) and to better understand flux gradients (*in situ* cartography, archiving of position data);

d) characterization of thermal gradients inside the samples;

e) modelling of energy deposits and of the associated thermal behaviour; and

f) performance of several irradiations dedicated to dosimetry under heightened surveillance.

GAMMA IRRADIATION EXPERIMENTS IN NATURAL AND SYNTHETIC HALITE

A. García Celma, A. J. Nolten, W. A. Feliks & H. v. Wees

ABSTRACT

A description is given of the methods, instruments and samples used in gamma-irradiation experiments on salt samples performed in the storage pool of the High Flux Reactor (HFR) at Petten, The Netherlands.

Pre- and post- irradiation analyses and mechanical handling of the samples were planned and performed besides the irradiation experiments themselves and, prior to the irradiation experiments, the instruments needed were designed and constructed.

The developed irradiation instrumentation essentially consists of blocks both impermeable and isothermal which contain eight sample assemblages each. These blocks allow irradiation to take place at constant and homogeneous temperature. They were placed in racks among spent fuel elements in the storage pool of the HFR. The spent fuel elements were used as radiation source. Different combinations of spent fuel elements produce different dose rates due to the different decay time of the fission products contained in them.

The pressure conditions of the experiments were fixed independently for each of the eight sample assemblages contained in a block, and therefore samples irradiated simultaneously could be subject to different pressure conditions. The racks with the spent fuel elements are here called Gamma Irradiation Facility (GIF). Two different types of experiments named GIF A and GIF B were performed. GIF A experiments were performed at high and variable dose rates and non-enhanced pressure. GIF B experiments were performed at low and (quasi) constant dose rate and on two non-pressurized and six pressurized sample assemblages simultaneously. In this way each of the following factors could be varied independently: total dose, dose rate, pressure, and chemical composition and microstructure of the sample.

1. INTRODUCTION

The theories on the radiation damage of rock salt which underlie the models on which nuclear waste repository safety previsions are based, needed revision and countercheck. The purpose of our research was testing some of these theories against the experimental results of irradiation of samples in conditions as near as possible to those of a repository.

Our research was complicated by the existence of two different groups of variables. One group of variables are the physical conditions of the irradiation. The other group of variables are the different sample characteristics.

This required many irradiation experiments to independently vary the intrinsic irradiation parameters, and many samples in each irradiation experiment to vary the sample characteristics independently.

Two different types of experiments have been carried out in the Gamma Irradiation Facility (GIF), GIF A and GIF B experiments.

In chapter 2 we describe the GIF characteristics and the requirements of our experiments. In the subchapters 2.1 and 2.2 the instruments and procedures developed in order to use the GIF to fulfill the experimental requirements are described. The general methodological description of chapter 2 is followed by two chapters (3 and 4) which respectively describe the methodological particularities of GIF A and GIF B types of experiments independently. At the end of this article a chapter (5) of results summarizes the amount of samples of each type which have been irradiated under each set of conditions. The results of the analyses of the samples are not described in this article but can be found in the data report and are worked out and interpreted in different articles of this volume [De las Cuevas and Miralles, 1995; Donker and García Celma 1995 a and 1995 b; García Celma and Donker, 1995 and García Celma et al. 1995 (articles. Nos 15, 17,18, 21 and 20 respectively, in this volume)]

2. GENERAL CHARACTERISTICS OF GIF EXPERIMENTS

The above mentioned Gamma Irradiation Facility (GIF) consists of spent fuel elements in compact storage racks (where they are placed to cool) in the pool of the High Flux Reactor (HFR) at Petten. Figure 1 gives a view of the GIF.

When the spent fuel elements are fresh, (just retrieved from the reactor) their emitted gamma dose rate and heat output are high. The intensity of both emissions decreases with time as shown in Fig. 2 a and 2 b. If the spent fuel elements are old, i.e. have already spent some months in the cooling pool, their emitted gamma dose and temperature are low and quasi-constant.

Our irradiation experiments required three main additional procedural conditions from the irradiation facility which had to be taken into account when building the instrumentation:

a)   possibility to fix and control the temperature of irradiation (at 100°C)

b)   possibility to irradiate simultaneously different samples to be able to guarantee that the samples had been subject to the same dose rate and temperature, and

c)   possibility to identically irradiate identical samples but under different pressure conditions.

2.1. Instrumentation developed

The HEated Irradiation of SAlt instrumentation (HEISA) was designed and constructed to simultaneously irradiate many samples at a constant temperature. A HEISA consists of an external metallic prism containing an inner solid metal block and connected to a computer, a gas system and a temperature regulator. The metallic prism is placed in the racks amongst the fuel elements. The gap between the metallic block and the prism is filled with a gas. Different gases can be used depending on their heat conduction characteristics and on whether cooling or protection against cooling is needed to maintain a constant temperature inside the HEISA. In the metallic block holes have been machined out to place in tight fitting eight sample holders, and slots have been machined as well to fit the heating elements. The heating elements are connected
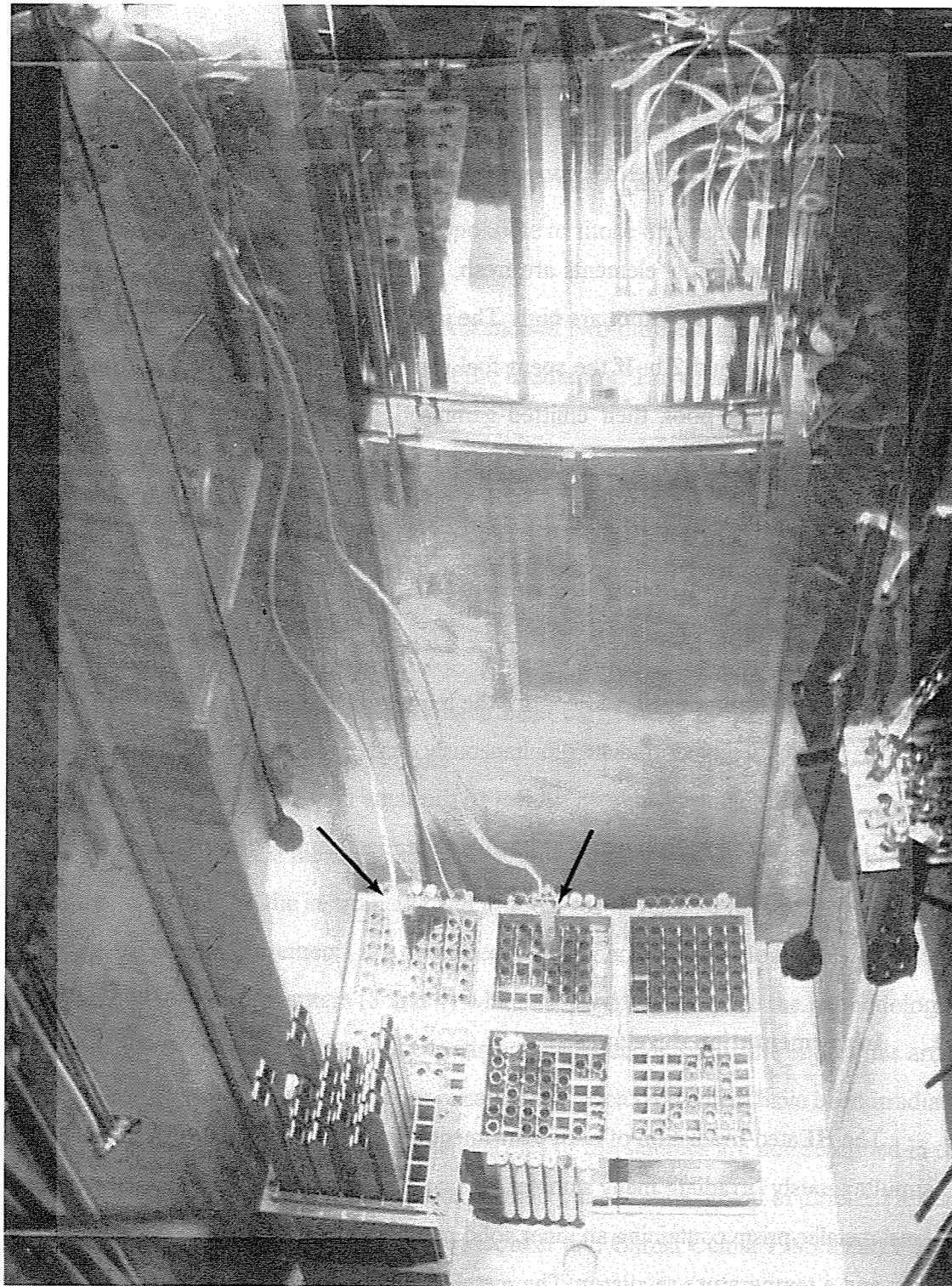
Figure 1 a.   *A view of the compact storage racks with the spent fuel elements at the bottom of the pool where the Gamma Irradiation Facility (GIF) experiments are carried out. Arrows show the HEISA'S where experiments GIF A and GIF B take place.*

new spent
fuel element

older spent
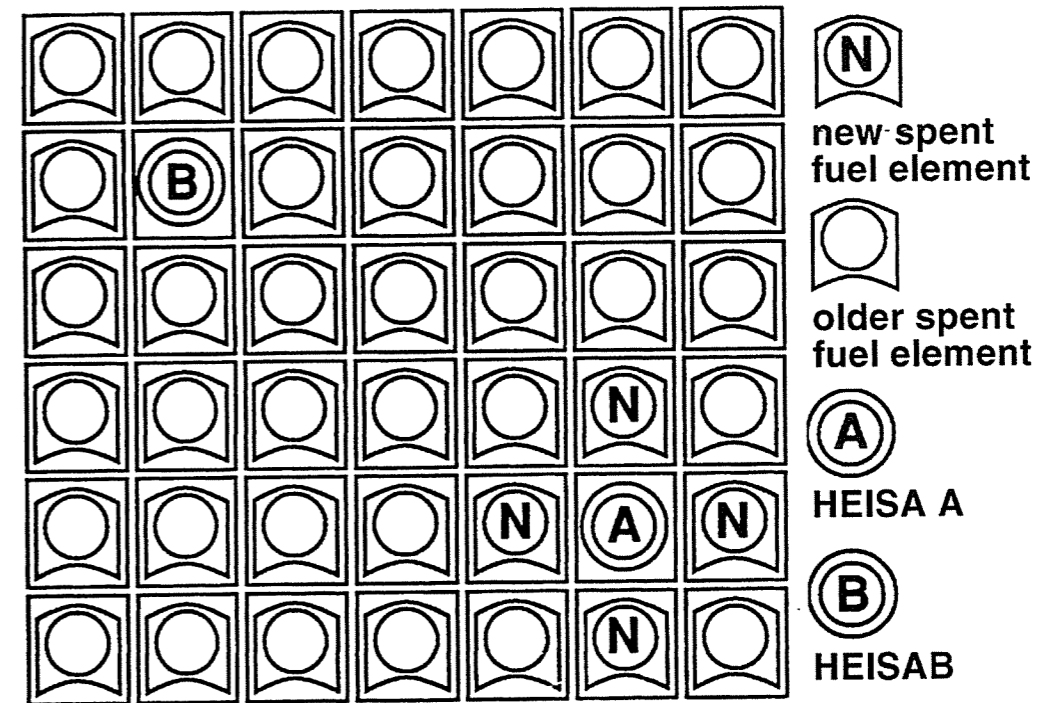fuel element

HEISA A

HEISAB

Figure 1 b: *Storage rack with two HEISAS containing the GIF experiments.*

to a proportional band temperature regulator (outside the pool). There is a minimum of two thermocouples in each HEISA, one produces the reading for the temperature controller and the readings of the other are directly registered by a computer (see Fig.3).

A sample holder consists of a stainless steel cylinder with only part of a basis. The holders are represented in figure 4. A plate of stainless steel is set loose within the holder and rests on the incomplete basis. Within the stainless steel cylinder a second stainless steel cylinder closely fitting the first one is introduced. The third cylinder is a gold jacket containing the samples. Gold jackets were chosen to reduce holder corrosion by the chlorine emitted by the NaCl during irradiation. There have been earlier designs which were used to carry out some of the earlier experiments and which did not use gold jackets by silver wrappings. The old set up of the samples within the various cylinders is described in [García Celma and Van Wees, 1992]

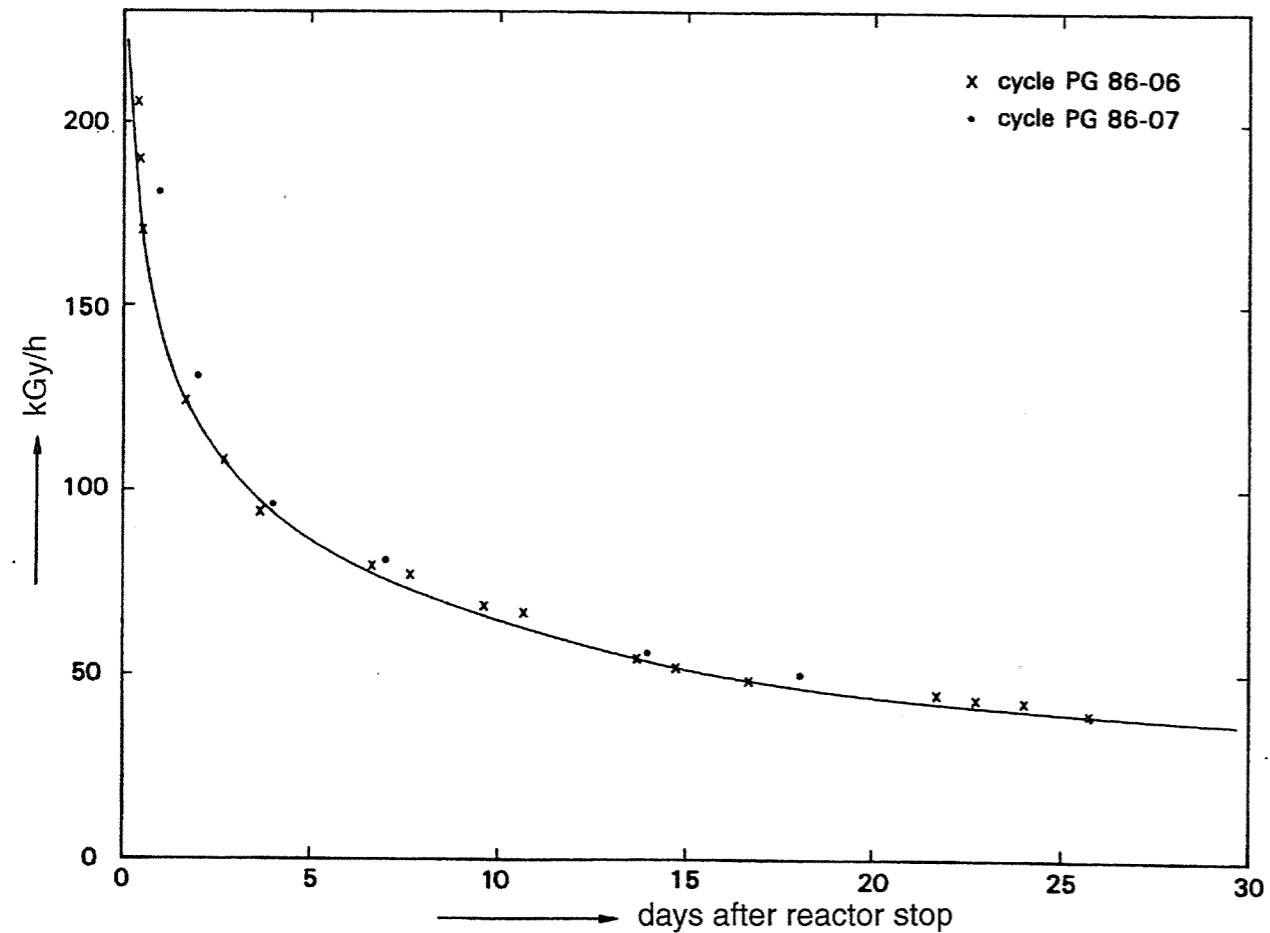**DOSE RATE VARIATION WITH TIME IN THE TARGET LINE OF THE GIF**

Figure 2 a.:   *Dose rate in the target line of a GIF.*

The top of the stainless steel cylinder can be closed in two ways. One way of closing the top of the stainless steel cylinder is a lid in contact with the top of the gold jacket and welded to a gas bellows. The top cover of the gas bellows is, in its turn, welded to the top of the stainless steel cylinder. The gas bellows can be filled in with gas at a high pressure. This holder exerts a pressure of about 200 bar on the inner (gold) cylinder (Fig. 4) [García Celma and Van Wees, 1992, and García Celma, 1992]. This is a *pressurizing sample holder*.

The other way of closing the samples holder is by a lid fixed to the holder by a bayonet fitting and having a spring in the inside with an end piece which contacts the top of the gold jacket keeping it into place. This spring is assumed not to subject the samples to additional pressure this

type of holder is called a *non-pressurizing sample holder*.
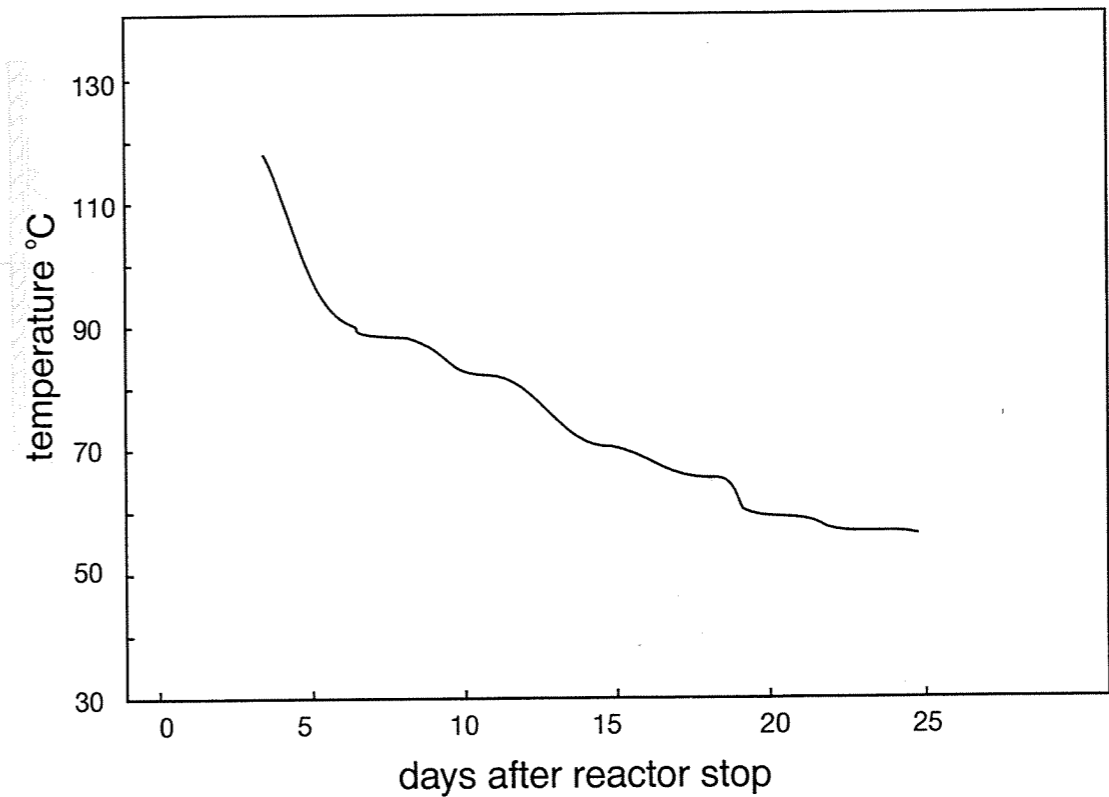
Figure 2 b: *Temperature evolution as registered by a thermocouple in a sample container in the irradiation facility in absence of the HEISA instrumentation.*

There are two types of gold jackets, one of about 52 mm length with an inner diameter of 24.26 mm and one of about 12 mm length and with an inner diameter of 23.76 mm. The holders are assembled with the samples in the following manner. Inside the long jacket a long sample is introduced, on top of it the shortest gold jacket is introduced in the longest. Then a tablet shaped sample is introduced in the shortest jacket and a gold lid is placed on top of it. The lid and the two top ends of the jackets are then welded together. In this way the samples are gastightly packed during irradiation. The gold jackets used in pressurizing sample holders contain as well a ceramic plate of the same diameter as the samples on the top of each of the two samples. This is done to avoid sample fracturing, since the pressure is transmitted by the lower surface of the bellows which is smaller than that of the sample (see Figs. 3 and 4).
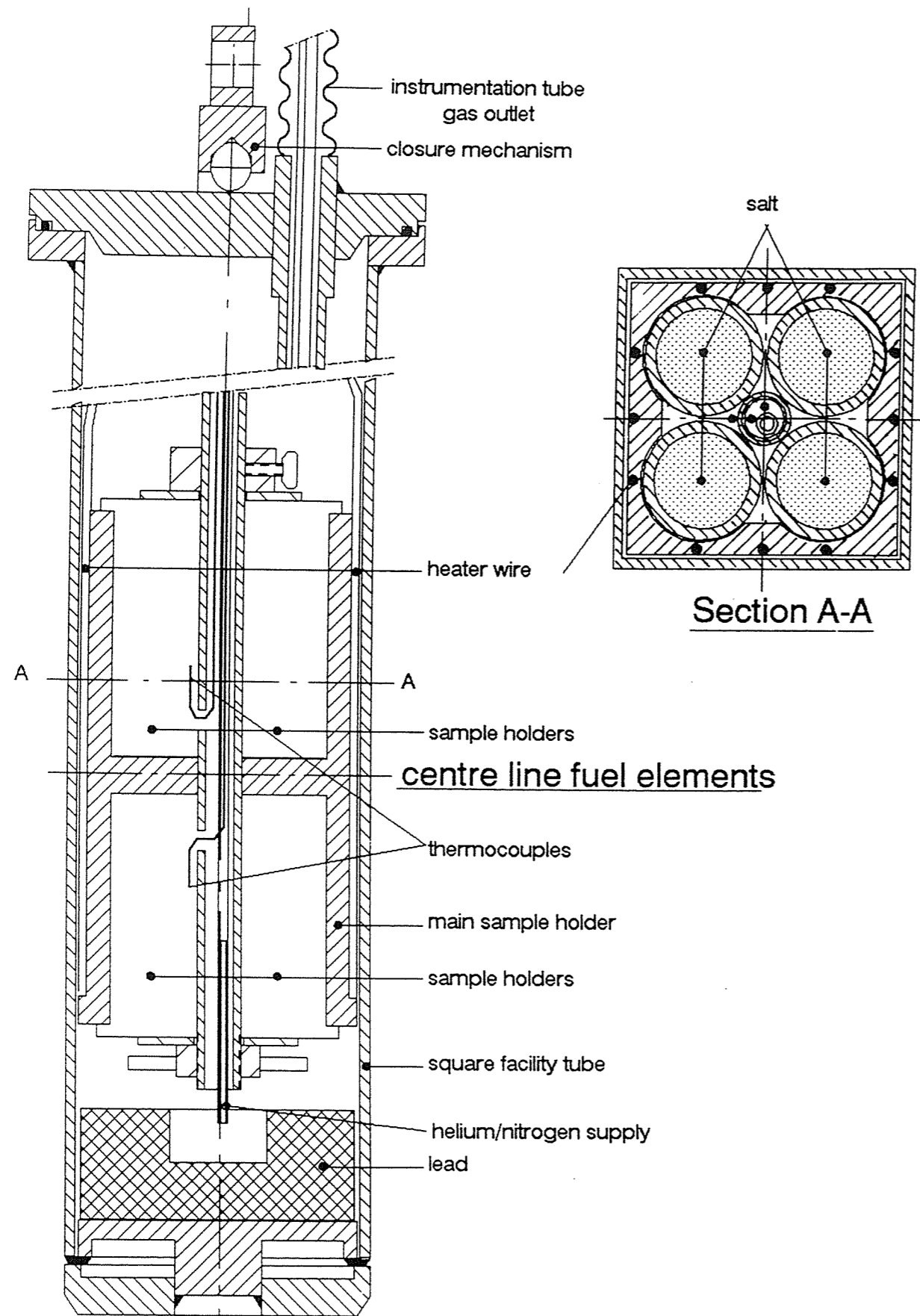
Figure 3: *HEated Irradiation of SAlt (HEISA) instrumentation.*

instrumentation tube
gas outlet

closure mechanism

salt

Section A-A

heater wire

A ——— A

sample holders

centre line fuel elements

thermocouples

main sample holder

sample holders

square facility tube

helium/nitrogen supply

lead
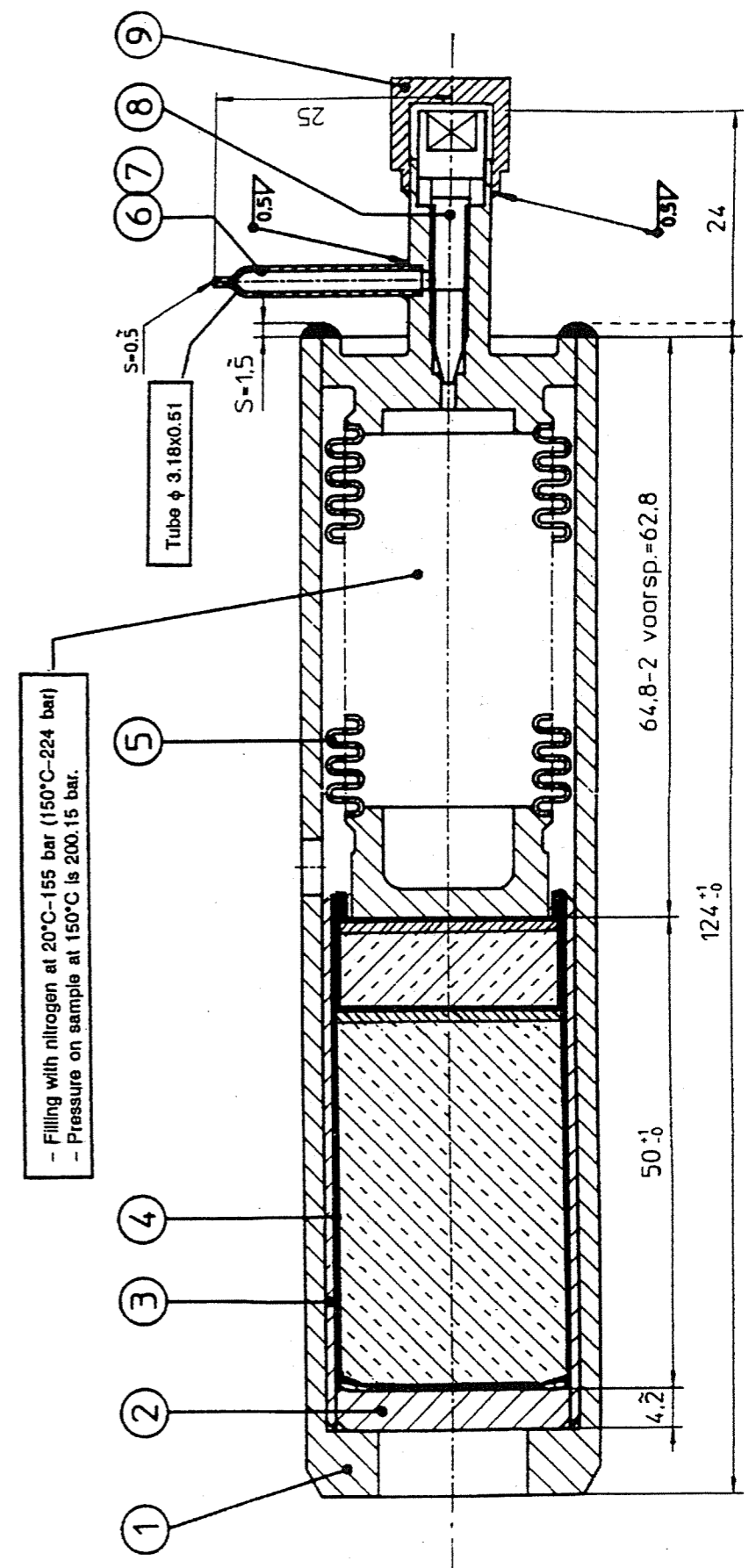
Figure 4: *Design of the pressurizing sample holders.*

- Filling with nitrogen at 20°C-155 bar (150°C-224 bar)
- Pressure on sample at 150°C is 200.15 bar.

Tube φ 3.18x0.51

S=0.5

S=1.5

0.5V

0.5V

25

24

64,8-2 voorsp.=62,8

124 +1 -0

50 +1 -0

4,2

92

93

2.2. Procedures

We will distinguish two types of procedures: handling and analyses. The procedures which we group here under the name handlings imply preparation of the samples for the experiments or for observation, such as sample machining and are described in 2.2.1. The analyses refer only to the observation or measurement, i.e. stored energy analyses, and are described in 2.2.2.

2.2.1. Pre- and post- irradiation handling

The samples are kept in dry drawers or in the "salt room". Both places are dried by a constant flow of compressed air. Handlings took place either in the dry drawers (precision cuts) or in the salt room (machining etc...). Some thin sections of each sample type were made in order to study their general pre-irradiation microstructure. The thin sections were conventional optical microscope preparations.

Prior to irradiation the samples had to be machined to fit the holders into two different sizes, i.e. : tablets and cylinders. The tablets have a diameter of 23.76 mm and a height of 10 mm, while the cylinders have a diameter of 24.26 mm and a height of 40 mm. Before introducing the polycrystalline samples in the gold jackets and acetate replica of the position of the grain boundaries in their top and bottom surfaces was taken. The samples were also weighted and their dimensions measured. To some polycrystalline samples known quantities of brine were added prior to their introduction in the jackets. The gold jackets were sealed by cold welding and placed inside the stainless steel holders and the whole made ready for irradiation. The procedures are described in detail in [García Celma, 1991 and 1992; and García Celma and Van Wees, 1992].

After irradiation the sample dimensions were measured, the samples weighted and new acetate replicas made. Then the samples were cut in two, one piece was sent to the Barcelona University, while the other piece was kept at ECN. With this piece of the sample first a thin section was made, and then pieces were selected for stored energy analyses. The thin section was used for observation in a conventional optical microscope and for Image Analysis measurements.

2.2.2. Pre- and post-irradiation analyses

Most of the planned analyses change the properties of the studied material (e.g. stored energy analysis anneal crystal defects out and dry out the samples) or require cutting the sample. Therefore pre-irradiation analyses are in fact analyses performed on non-enhanced- irradiated samples of the same batch as those being irradiated. Non-enhanced-irradiated samples are subject to the same analysis as irradiated samples in order to know which has been the effect of the irradiation on the sample properties. Not all the analysis were performed with all the samples, and the analytic work was shared between the ECN department at the Utrecht University and the Barcelona University [Mönig et al., 1990; De las Cuevas and Miralles, 1995 and Donker and García Celma, 1995 (this volume art. Nos..15 and 17)]. The pre- and post-irradiation analysis of each sample are always performed at the same laboratory. The different analytic techniques are grouped here below and the information which is obtained from each is summarized. Detailed information on detection limits etc.. can be found elsewhere in this volume [De las Cuevas and Miralles, 1995 and Donker et al., 1995 (this volume art. Nos.15 and 19)].

Light Absorption (LA) analyses were performed on irradiated salt because some of the crystal defects produced by irradiation absorb light of a characteristic wave length. LA analyses consist of registering the transmitted spectra of (originally) white light after traversing the salt samples and analysing which wave lengths have been absorbed. The type of defect, its relative frequency and even the defect size can be inferred from the spectra characteristics. These analyses were performed at the Barcelona University, and the results are reported in [García Celma et al, 1992 and De las Cuevas and Miralles, 1995 (this volume, art. nr.15)].

Differential Thermal Analysis (DTA), consists of heating a sample within a holder included in an isothermal block and measuring the temperature reached by the sample holder and the temperature reached by a reference holder also included in the isothermal block. The two measurements are then compared with each other. If the sample contains energy which is liberated at a given temperature, the temperature of the sample becomes higher than that of the reference. It also can happen that the sample becomes cooler than the reference. These differences are registered. This is what constitutes the "first run" of a measurement. After the first run the sample is allowed to cool down to room temperature (without opening its holder) and the "second run" can start. The second run consists of carrying out again the same heating process as the first run.

The difference between the first and the second run gives the energy balance of the irreversible processes. The irreversible process which interests us most is the anneal of the crystal defects produced by irradiation. These measurements were performed at the Thermodynamisch Centrum Utrecht, and the results can be found in [García Celma and Donker, 1994; Donker and García Celma 1995 a and 1995 b, (this volume , art. nr.17 and 18)] .

ThermoGravimetric analyses (TG), measure the weight changes undergone by a sample that is being heated in much the same way as the DTA does. The sample temperature and weight are registered along with time. Since the heating rate is constant, weight changes with time correspond to weight changes with temperature. Interpretation of these analyses, in our case, gives mostly information on some endothermal (heat consuming) processes, such as vaporization of the brine included in natural samples. The measurements register the weight loss associated with the release of the gases from the samples and the temperature at which this takes place. In our case these analyses give valuable information on the brine contained at grain boundaries and in fluid inclusions, and on the dehydration processes of accessory minerals. These analyses have been performed at the Barcelona University and the results can be found in [De las Cuevas and Teixidor, 1992 and De las Cuevas et al.,1995, (this volume, art. nr. 10 and 12)].

Chemical Analyses produce information on the type and amounts of impurities present in the samples. Combining them with microscopical sample observation it is possible to know whether the halite contains many lattice impurities or not. Intracrystalline impurities influence the radiation damage development in the NaCl crystal while the intercrystalline accessory minerals can only influence intercrystalline processes. Chemical analyses also measure the nature and amount of gases contained before irradiation and heating and those contained after irradiation [De las Cuevas et al., 1995, (this volume, art. nr. 12)]. Mainly the amount of hydrogen and of chlorine produced during irradiation are very important. Another relevant chemical analysis result is the determination of the amount of Na-metal produced by irradiation. This determination is done indirectly, by dissolving the salt samples in water and measuring the amount of hydrogen which is obtained $(2\ Na + 2\ H_2O = 2\ OHNa + H_2)$. These analyses have been performed at the Barcelona University, and also at Braunschweig by the GSF with other samples. The results can be found in [De las Cuevas et al., 1995, and Mönig et al., 1995 (this volume, art. Nos. 12 and 16)].

Microscopic analysis, consisted of conventional optical microscope observation of the thin

sections made from irradiated and non-enhanced-irradiated samples. Microscopic analyses help interpretation of other analyses, e.g. the presence of hydrated minerals can justify endothermal signals in the DTA record of a sample. A particular type of microscopic analysis is the microstructural analysis which gives information on the mechanisms by which mono- and poly-crystals adapt to stressing situations, in our case to radiation damage. The microstructural analyses of irradiated salt samples are eased by the fact many microstructures can be coloured by irradiation [García Celma and Donker, 1994]. Damaged parts of crystals, when observed by transparency under the microscope, tend to be yellow, brown, red and blue, while non-enhanced damaged parts are colourless. The amounts of colourless versus coloured material can be measured using a conventional image analysis system [García Celma et al., 1988].

3.   PARTICULARITIES OF GIF A EXPERIMENTS

It has been postulated that, by continuous irradiation with gamma rays, the energy stored in radiation damage defects in natural rock salt will not reach a saturation level through gradual anneal of the defects but will steadily grow until a very high concentration of defects is reached at which a spontaneous (and explosive) back reaction would take place [Den Hartog et al., 1990]. In the GIF A experiments we were looking for a possible saturation of radiation damage in natural rock salts at concentration values of defects inferior to those needed for the postulated back reaction. Therefore these experiments required a single type of natural sample to be progressively irradiated up to very high doses.

A couple of pure single crystals were as well irradiated in this facility to produce samples for experiments in which we intend to determine the size and size distribution of radiation damage defects (Na-colloids in particular) by Small Angle Neutron Scattering (SANS). However, the SANS method and/or the installation used were inadequate for this purpose. Anyway the pure samples could be used to check the radiation damage theory on other points.

3.1.   Samples used in GIF A experiments

Most samples used in GIF A experiments were of a rather pure natural rock salt, but also

pure synthetic single crystals have been used.

The *pure single crystals,* also poor in OH⁻ contents, were purchased from *Harshaw* Ltd. They are frequently used as standard crystals in radiation damage experiments. They were all machined into tablets, and labelled "SANS + number" when used in GIF A.

Harshaw crystals, as received, contain a stored energy of between less that 1 J/g and up to 14 J/g [García Celma and Donker, 1994]. This energy disappears by anneal at 500°C in an open canister in an argon atmosphere during one hour. Schutjens [1991] showed that the random distribution of free dislocation lines found in the Harshaw crystals is substituted by an organized structure during anneal. The annealed Harshaw crystals do not give any endo- or exothermal signal. In the first experiments (GIF A1 and GIF B1) non-enhanced-annealed Harshaw crystals were used. Annealed crystals have been used in the second set of experiments of the GIF A (GIF A2).

The *natural samples* used in GIF A were samples of the *Speisesalz* from the 800 meter depth level of the Asse Mine, Remlingen, Germany. This is a very pure (99,9 % halite) rock salt which is also very dry (0.05 % weight of brine), has a granular structure with grain diameters varying between 3 and 10 mm. The composition and characteristics of this salt and salt formation are described in [Jockwer, 1981; Peach, 1991; Spiers et al., 1986; Urai et al., 1986; García Celma et al. 1988 and Gies et al.,1994]. The Speisesalz samples used in this experiment were all tablets and their code is " TSp + a number".

3.2. Procedures of GIF A experiments

Tablets of Sp-800 were machined, introduced in golden jackets and sealed. Also SANS samples were prepared. Thirty nine Sp-800 samples and sometimes a SANS sample were included in eight non-pressurizing sample holders. The non-pressurizing sample holders were placed into a HEISA. And the HEISA was placed in a GIF between freshly spent fuel elements (GIF A).

The temperature was fixed at 100°C. The dose rate was the highest which could be reached in a GIF, but decayed quickly as show by the dosimetric measurements plotted in Fig.2

a. At about 28 days after irradiation start a sample was taken out of the facility and substituted by a non-enhanced-irradiated sample, and another dosimetry was performed. See Fig. 5. In each experimental cycle a dosimetry was performed before placing the samples in the radiation field and some dosimetries more were performed during the following 28 days.
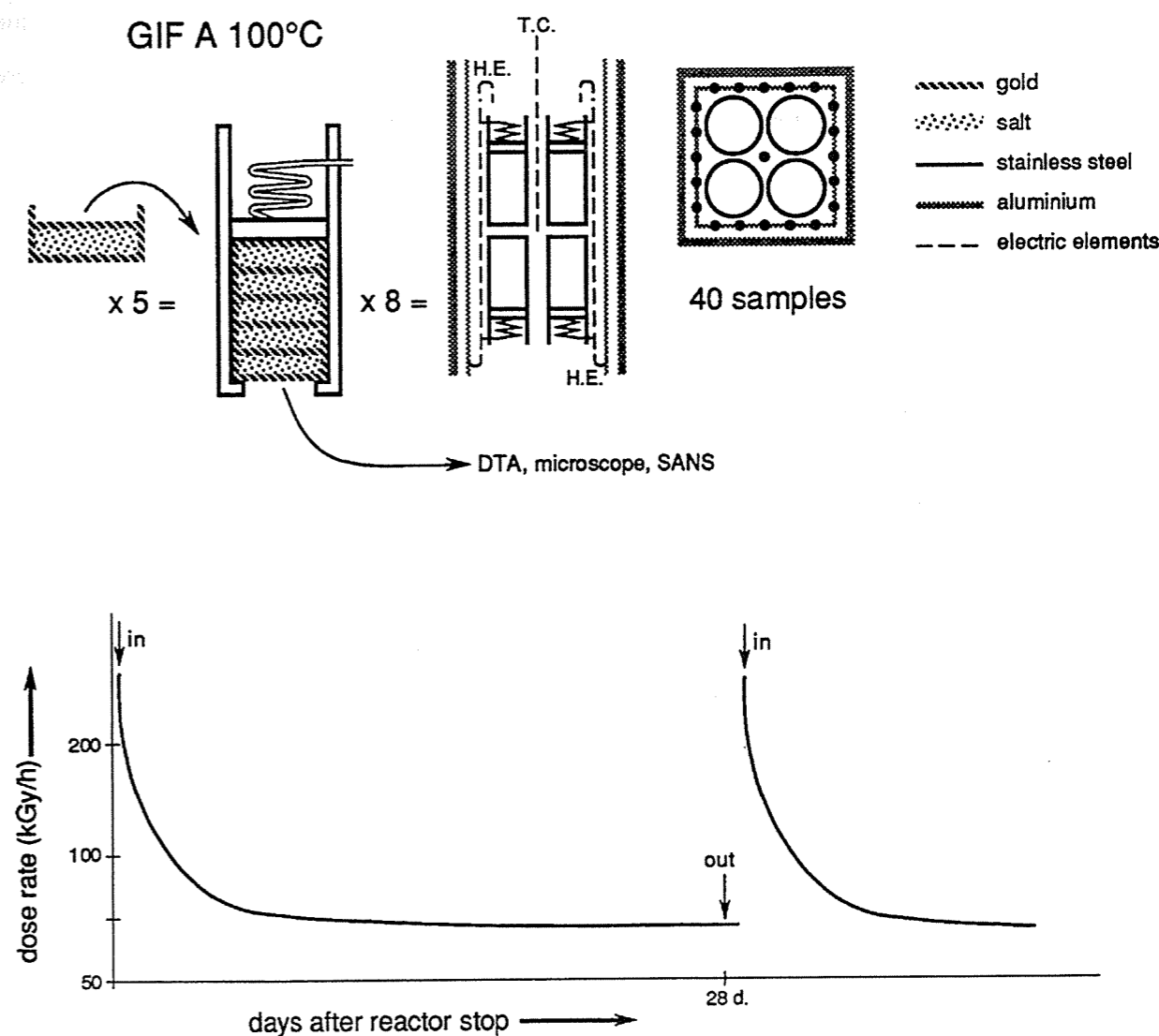

Figure 5:   *Schematic representation of the procedure in GIF A. In the schematic representation of the dose rate evolution* in *and* out *indicate when samples are replaced.*

After each reactor cycle (about 28 days) the new freshly spent fuel elements were placed in the GIF A, a new dosimetry was performed, and the HEISA containing the new sample and the thirty nine samples which had already been irradiated during one month were replaced in GIF A. Repeating this procedure after each reactor cycle gives a somewhat variable dose rate traject for the samples, an example of which is given in Fig 6.

This procedure was repeated each month, from December 1989 until May 1994. Each month the samples which had not been retrieved received an additional dose of about 40 to 30 MGy. The experiment was restarted once, but anyway, at the end of the second experiment some samples which had not yet been retrieved and had received a total dose of 1223 MGy, and there existed at least one sample for each 40 to 30 MGy increment from 40 up to 1223 MGy.
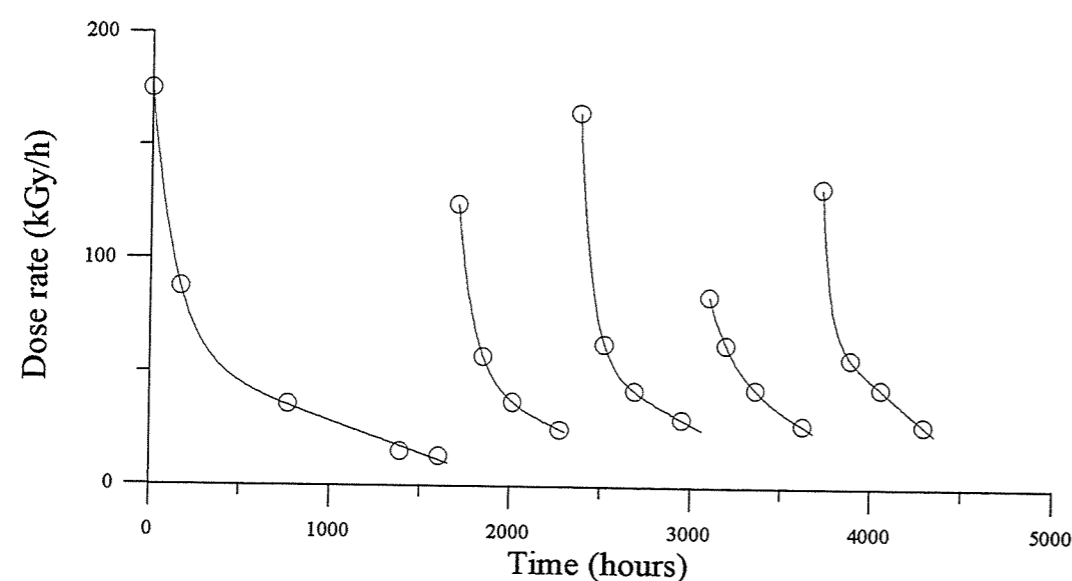

Figure 6:   *An example of the dose rate trajectory in GIF A.*

After retrieval, the samples were cut into two pieces and a thin section was made. One piece of the sample remained at Utrecht and from it we performed DTA analysis, and the other piece was sent to Barcelona where they performed LA, and TG analyses and measured the production of hydrogen by solution in water in order to determine the amount of damage in terms of amount of Na-metal. This is reported in [De las Cuevas and Miralles, 1995, (art. nr.15, this volume].

4.   PARTICULARITIES OF GIF B EXPERIMENTS

GIF B experiments were planned to produce information on the effect of pressure and of impurities on radiation damage development at conditions as near as possible to that of a radioactive waste repository. Therefore various types of samples had to be irradiated up to the same total doses for a whole set of total doses and the effect of (low) dose rates and of (enhanced) pressure had to be studied as well for different total dose (time) increments.

Dose rate had to be as low and as constant as possible in each experiment to approach radioactive waste conditions. The effect of low dose rate in natural samples had to be analyzed (figure 6). This was done by performing different series of experiments at different dose rates. These series were GIF B1, GIF B2 and GIF B3; each series consisted of irradiating up to different total doses 16 samples at a time.

Here we will give some information on the samples, first on the planned differences between them, and the reason for using these samples, and then they will be summarily described in 4.1. The procedures and a résumé of the reasons to adopt them are given in 4.2.

4.1.   Samples used in GIF B experiments

In the GIF B experiments, to compare the effect of identical irradiation in samples differing only in "wetness', 'purity', mono- or poly-crystallinity or degree of deformation samples differing from each other in only one of these factors have been simultaneously irradiated. We irradiated together pure dry and undeformed single crystals of NaCl, pure polycrystals and natural rock salts (neither pure, dry, monocrystalline nor undeformed).

4.1.1.   Pure single crystals

Pure single crystals, purchased from Harshaw Ltd., have been described in 3.1. They were all irradiated as tablets. In the first series of GIF B experiments (GIF B1) they were not annealed prior to irradiation. In the following set of GIF B (GIF B2) experiments they were annealed prior

to irradiation, and in the third set (GIF B3) a combination of annealed and non-enhanced-annealed Harshaw crystals was irradiated. The Harshaw crystals are labelled "H + a number".

4.1.2. Pure polycrystals

Since natural rock salt is always impure, pure polycrystals had to be produced. The starting material from which all the pure polycrystals were produced was the same, namely NaCl powder of "pro-analysis" quality as produced by Merck to which 0.2 % weight bi-distilled water was added. Two types of pure polycrystals were produced differing in their microstructures, the pressed powder and the synthetic salt polycrystals.

The *pressed powder* samples were produced by cold pressing up to 1.7 kbar, maintaining the pressure during 3 min, and slowly taking the pressure away. The thus obtained cylinders were further machined into either cylinders (" PP + number") or tablets (" TPP + number"). Sometimes, brine was added to the finished samples or tablets. The brine was produced using NaCl powder pro-analysis and bi-distilled water.

The individual crystals of the pressed powder samples display brittle deformation structures and have a mean diameter of 60 μm. The poria between crystals in the Pressed powder samples are irregular and therefore grain boundaries are not shared by two grains but consist only of the limits of individual crystals. Fig 7. These samples yield an exothermal stored energy of 4.2 J/g before irradiation [García Celma, 1992; García Celma and Van Wees, 1992; García Celma , 1991; García Celma et al., 1993].

The *synthetic rock salt* was produced by first pressing the starting material cold at 1 kbar during 8 hours, and then annealing it during 30 days at 500 bar and 150°C. During the anneal the salt crystals develop real grain boundaries shared by two grains while the brittle structures of the crystals disappear. The new grain boundaries are straight and meet each other at triple points making angles of 120 degrees. This shows that they migrated until their exterior surfaces reached a very low free energy configuration. These are typical recrystallized granular structures called "foam-textures" by evident morphogenetic reasons. See fig 8. These samples are also machined after production to fit the holders and are labelled " SS + number" or "TSS + number". To some
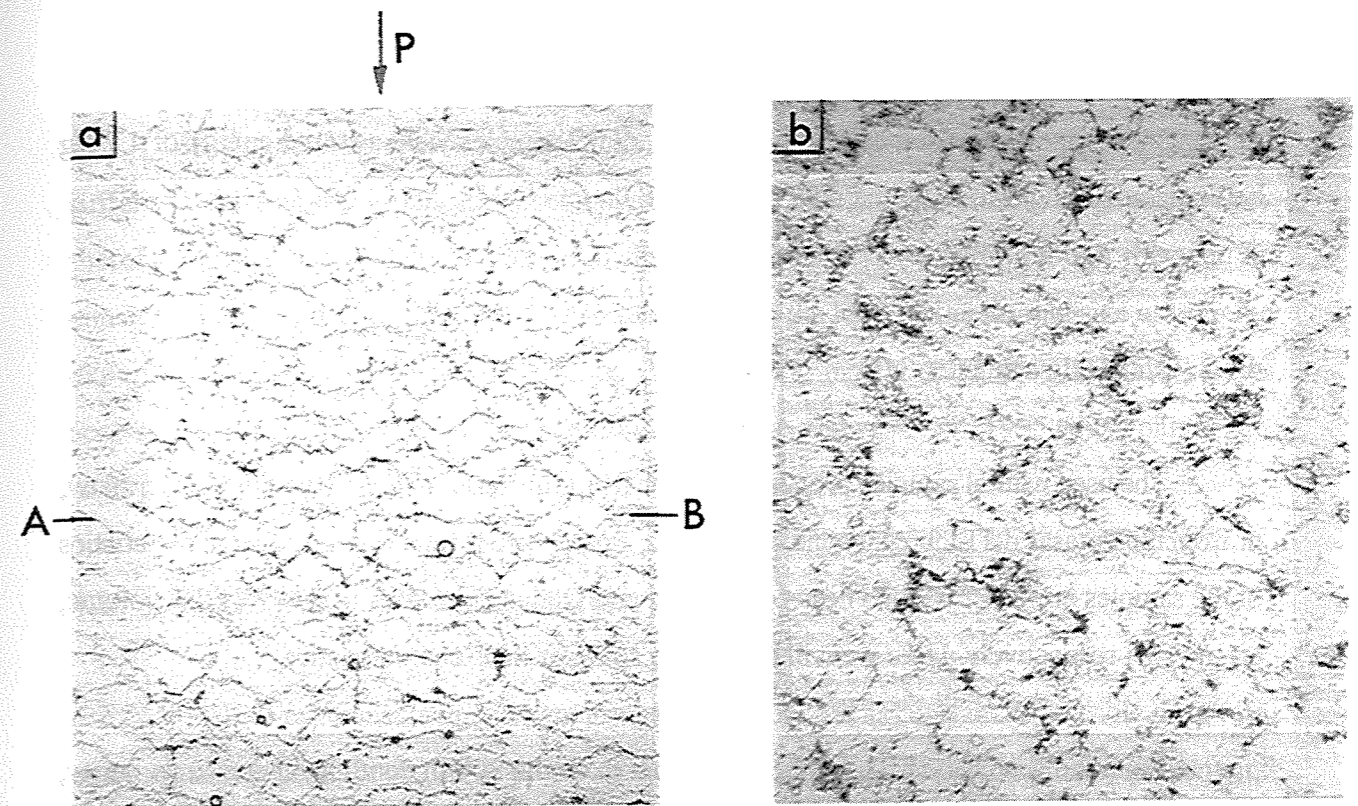
Figure 7 :   *Microstructural aspect of Pressed Powder samples in two perpendicular sections a): section parallel to the direction of the pressure (P) used to produce it. b): section perpendicular to the direction of the pressure (A-B in 7a). Mag. 5x.*
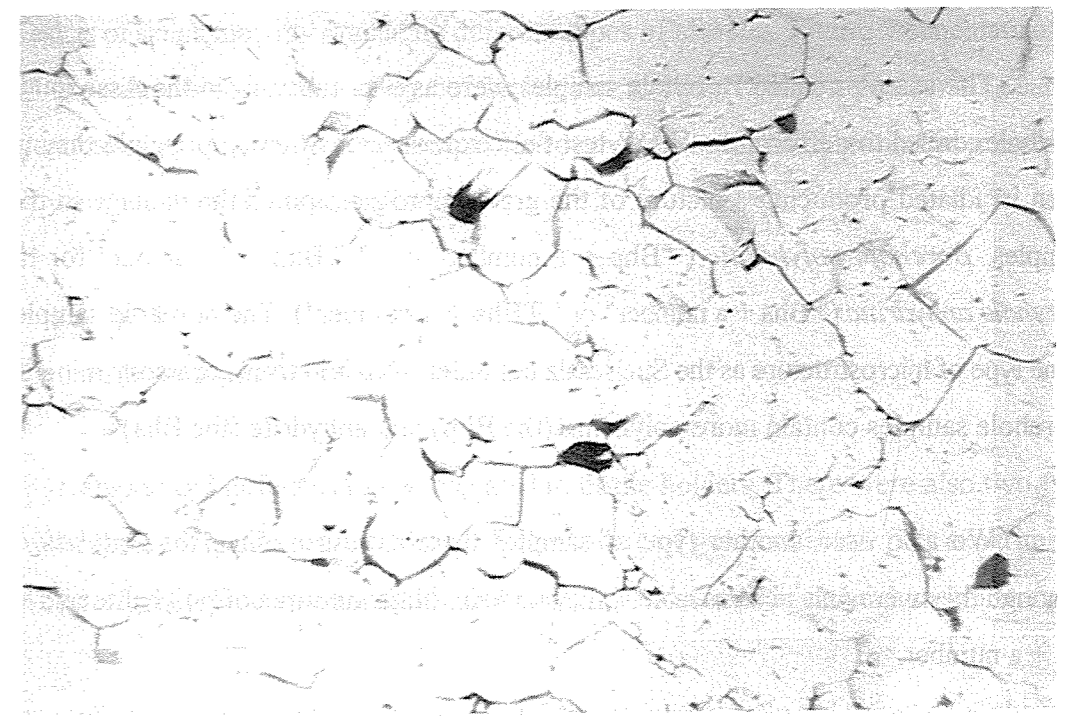

Figure 8 :   *Microscopical aspect of synthetic rock salt. Observe the polygonal shape of the grains. Mag. 5x.*

of them pure brine was added before the irradiation. SS samples yield a stored energy of 4.7 J/g before irradiation [García Celma, 1991 and 1992; García Celma and Van Wees, 1992].

4.1.3. Natural rock salts

The used natural samples proceeded either from the Asse mine, in Remlingen, Germany, or from the Potasas del Llobregat mine, in Cardona, Spain. The formations and the characteristics of the samples are described in Gies et al. [1994] and De las Cuevas et al., [1995, (this volume, art. nr.10)] respectively. Here we will only name some of their characteristics.

From the Asse mine we used the *Speisesalz* from the 800 m depth level due to its purity, and also to the fact that so many studies [Jockwer, 1981; Spiers et al., 1986; Urai et al., 1986; García Celma et al., 1988; Peach, 1991; Gies et al., 1994] have been performed with these rather homogeneous salt that it has almost become a standard for pure natural rock salts (it was also used for GIF A experiments, see chapter 3.1.). These samples are labelled " Sp-800 + number " when long (40 mm) and " TSp800 + number" when in the form of tablets (10 mm high).

The samples called Borehole samples were as well taken from the Asse mine, from the boreholes drilled to perform the HAW-test field experiment, where in principle they would have been irradiated producing a picture of the gradual progression of the damage in the borehole samples. *Borehole polyhalitic* ("Bhp + a number" or " TBhp + a number" for tablets) and *Borehole anhydritic* (" Bha + a number" or " TBha + a number"). The borehole samples have the same type of microstructure as the Speisesalz but differ from it in their accessory mineral contents. Borehole samples contain more polyhalite (the Bhp) and anhydrite (the Bha).

We also used another type of samples from the Asse mine, the *Polyhalitic* samples, although they were only used as tablets, they contain huge amounts of polyhalite and are labelled PS + a number.

The Asse samples have been recrystallized a couple of times during their geological history, therefore they present a granular microstructure from which the original sedimentary structures have been whipped out.

The samples from the *Potasas del Llobregat* mine, contrary to the Asse samples have not suffered complete recrystallization but only developed overgrowths during diagenesis. They therefore display many relics of the originally precipitated crystals and although they can be considered just as pure as those of Asse in their bulk, at the level of the sample size used in the experiments they are rather heterogeneous. They contain mostly anhydrite and some clay as accessory mineral. They are extensively described in [De las Cuevas et al., 1995 (this volume, art. nr.10)],

4.2. Procedures in GIF B experiments

In GIF B experiments samples are irradiated at a low and as constant as possible dose rate, at a constant temperature of 100°C, and up to different integrated doses. The (quasi)constant and low dose rate can be reached by placing the samples amongst old spent fuel elements in the GIF B (see Figs. 1 b and 9).

Through repeating experiments at the same dose rate but during a different length of time different integrated doses are obtained, and since a HEISA can contain eight sample holders the possibility exists of simultaneously irradiating different types of samples. Figure 7 schematizes the way GIF B experiments are operated. By combining pressurizing with non-pressurizing sample holders identical samples were irradiated simultaneously which only differed in the pressure at which they were subjected during irradiation.

4.2.1. Pre-irradiation procedures

Long samples and tablets had to be prepared to fit the holders. There were also two types of holders, pressurizing and non-pressurizing. Jackets were of gold but in the first experimental set (GIF B1) the samples were wrapped in silver foil and introduced in aluminium holders.

The artificial samples had to be produced and the process developed to produce them has been summarily described in 4.1.2. The samples were measured and weighted before irradiation. From the long samples an acetate peeling was made before packing them for irradiation. In a single irradiation experiment up to three identical samples could be irradiated which differed in

the amount of brine added to them prior to irradiation [García Celma and Van Wees, 1992].

4.2.2. Irradiation conditions

First two sets of experiments have been carried out, GIF B1 at 15 kGy/h and GIF B2 at 4 kGy/h. The wished dose rates were obtained by using different combinations of old spent fuel elements. Depending on the time elapsed since they were used in the reactor they emit a higher or lower dose rate (see Fig.9). Different irradiation duration produced samples irradiated up to different total doses. Irradiation took place at a constant temperature of 100°C.

In each experiment two identical samples and two identical tablets were irradiated which differed in the pressure applied to them during irradiation. There were six pressurizing sample holders and two non-pressurizing samples holders in each experiment of GIF B1 and GIF B2. Dosemetries were regularly performed.

In the GIF B3 experiment a smaller quantity of samples and sample types was irradiated at 15 kGy/h up to about the same total doses as in the previous two experiments, and also at 100°C and in pressurized and non-enhanced-pressurized sample holders.

The data of the irradiations are given in a separated data report (in prep) for each sample and irradiation configuration.

4.2.3. Post-irradiation procedures

Post-irradiation procedures consisted of first of all obtaining an acetate replica of the position of the grain boundaries in the circular surfaces of the long samples immediately after irradiation. Once the replicas had been obtained the samples were cut in two halfs one of which was sent to Barcelona and the other was kept by us. With the half of the samples which we kept, first a thin section was made, then a piece was cut from which the darkest pieces were hand picked for stored energy analysis by DTA. With the piece sent to Barcelona where H_2, and Cl_2 determinations and LA and TG analyses were performed.

All samples have always been kept dry and dark and at room temperature.
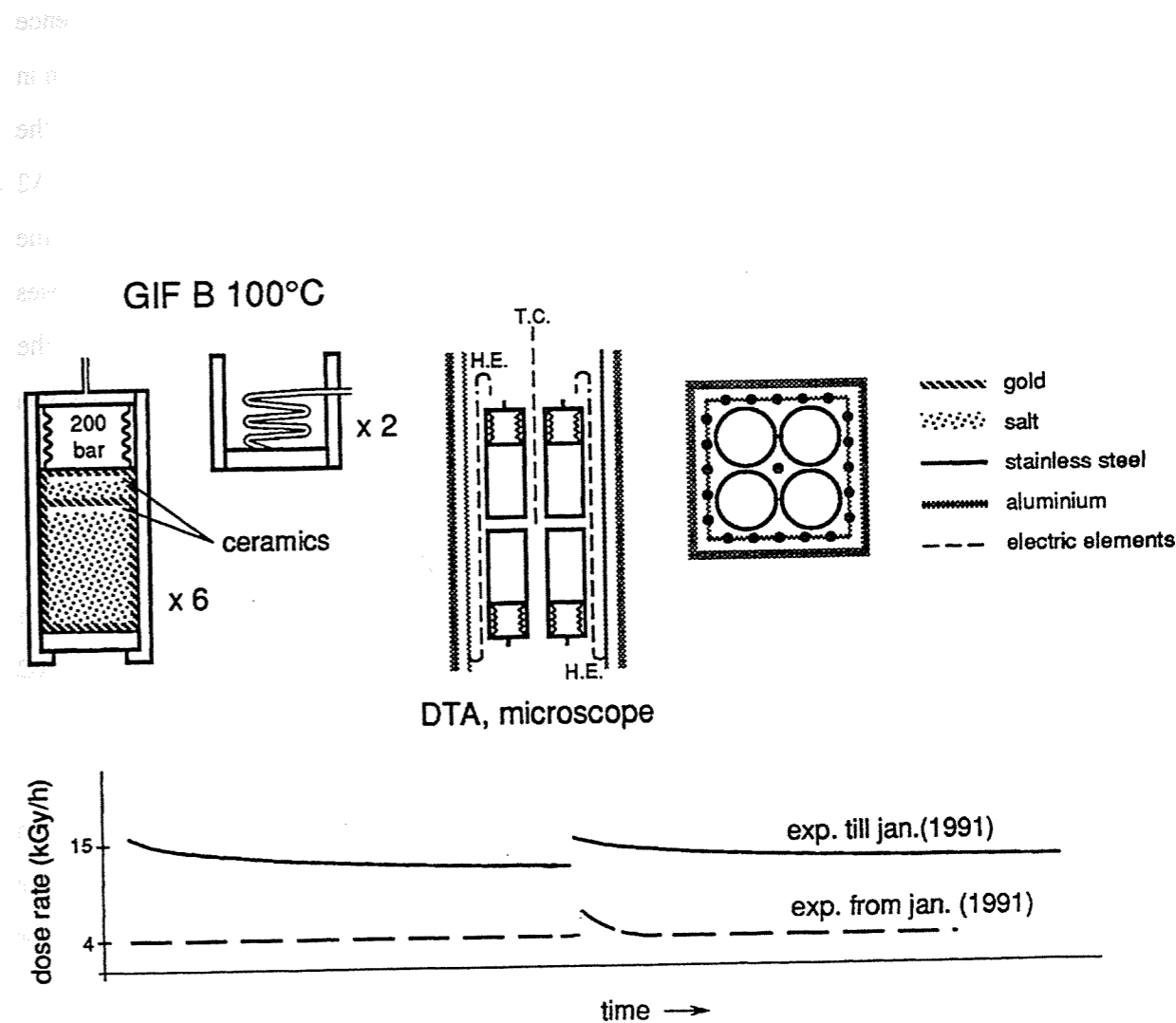
Figure 9:   *Schematic experimental set-up of GIF B experiments. The different dose rates are reached by using different combinations of old spent fuel elements. Time scale is arbitrary. See as well Fig. 1 b.*

5.   RESULTS

All obtained samples were irradiated at a constant temperature of 100°C.

In GIF A1 experiment a set of samples wrapped in silver was irradiated up to a total dose of 567 MGy. In GIF A2 experiment the samples were enclosed in welded golden jackets which

was an improvement in the design regarding eventual leaking of gases or brine. Another difference between GIF A1 and GIF A2 was that the Harshaw crystals were annealed before irradiation in GIF A2 while they were not annealed prior to GIF A1 experiments. Moreover, the quality of the fuel elements had been changed, and as a consequence the highest dose rate was lower in GIF A2 than in GIF A1 experiments. Under these conditions, in GIF A2, we were able to irradiate some samples up to 1223 MGy up to a total of 39 Asse Speisesalz samples which received total doses of between 1223 and 40 MGy in increments of about 40 MGy to 30 MGy, depending on the reactor cycle. All sample composition conditions of irradiation and results of the analysis are given in a separated data report (in prep).

In GIF B, we could perform three sets of experiments and irradiated a total of 400 samples. GIF B1 (160 samples) experiment was performed at a dose rate of approximately 15 kGy/h (decreasing from 20 to 10 kGy/h), 10 different total doses were reached varying from 0.02 to 45 MGy. In this set the Harshaw crystals had not been annealed prior to irradiation.

A second set, GIF B2 (160 samples) was performed with a dose rate of 4 kGy/h, up to 10 different total doses varying from 0.022 to 44 MGy. The sample compositions were the same as in the previous experiment with a few exceptions. The Harshaw samples were annealed prior to irradiation, and all samples were included in gold jackets.

The third set of experiments, GIF B3 (80 samples) was performed at a dose rate of 15 kGy/h, up to 10 different dose rates , also between 0.022 and 41 MGy. In this experiment only PLL, Sp800 and Harshaw samples were irradiated. The Harshaw crystals were annealed and non-enhanced-annealed prior to irradiation and both sorts were irradiated up to the same total doses pressurized and non-enhanced-pressurized.

We wished to perform experiments at yet lower dose rates and for a variety of relevant temperatures and aimed at it in the HAW-field planning, but we had to settle for laboratory experiments which are necessarily shorter (human interference difficults to maintain the factors constant) and we also had to choose to perform the experiments at a constant temperature, that of maximum damage production reported to be 100°C [Den Hartog, 1988]. In spite of these disappointments the agreed extension of the laboratory experiments has produced a unique and very important data base which has substantially modified the theory in most of the points which

constituted questions for the HAW-field experiment on radiation damage.

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THE RECRYSTALLIZATION APPARATUS

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ABSTRACT

A "recrystallization apparatus" has been designed and constructed. The apparatus was meant to allow observation of static recrystallization. It can subject sample slices up to 3 mm thickness to a temperature of 100°C, and to a lithostatic pressure of 200 bar while allowing microscopic observation of the samples and independent control of the intergranular fluid pressure. We meant to observe and photograph the progression of static recrystallization in irradiated rocksalt samples. As a consequence of the use of salt in contact with metals, repeated corrosion of tubes, connectors and devices constantly caused leaking which had to be solved. The apparatus has now reached a state of development where it can be used without leaking. In this article the apparatus design and materials as they are now are described.

1. INTRODUCTION

Within the framework of the studies on radiation damage in rock salt it was important to observe the progression of fluid assisted recrystallization of irradiated rock salt not subject to differential stress. Fluid assisted recrystallization consists of the solution into the grain boundary fluid of species from the grain boundary, and transport and re-precipitation of the dissolved species in another place [Urai, 1983; García Celma et al., 1988]. A driving force for this process is present provided some parts of crystals in contact with the fluid are damaged while others are not. The non-damaged crystal areas then grow to the expense of the damaged. In our case the damage is produced by gamma irradiation prior to the experiment, and the non-damaged rims present in some crystals are the result of diffusion processes [García Celma and Donker, 1995, art. nr. 20 in this volume]. The fluid at the grain boundary void is brine, which is present in natural rock salts in different amounts.

Experiments where irradiated salt samples were set in pressure vessels under enhanced pressure and temperature had previously shown that fluid assisted recrystallization of rock salt takes place [García Celma et al., 1988]. To directly observe the process while it takes place was the reason for building the apparatus.

J. Urai , and W. Means, constructed apparatus where dynamic recrystallization produced by differential stress could be observed. In their apparatus, thin sample slices are observed by transparency under the microscope, while being deformed by the relative displacement of the sample boundaries. In these apparatus recrystallization is made evident by the change of optical orientation of material portions which results in colour and illumination differences when observed between the crossed polarizers of a petrological microscope. The existing apparatus, however, were not adequate to study the effect of lithostatic pressure and of temperature in (static) recrystallization processes driven by the energy stored in lattice defects of the mineral grains.

The exigences to be met by our apparatus were :

a) The temperature of all parts of the apparatus had to be homogeneous (spatially) to hinder transport of species in solution from hot to cold places with reprecipitation in the cold places.

b) The temperature had to be constant or at least not subject to sudden changes to hinder heterogeneous nucleation.

c) The apparatus had to allow for the pressure on the sample to be constant and controlled but vary in different experiments from 0 to 200 bar.

d) The apparatus had to allow for changes, and control of the pressure of the brine in between 0 and 200 bar.

e) The apparatus had to possess good light sources and thus distributed that the samples could be observed and photographed by transmission and by reflection.

Our apparatus did not need polarized light for recrystallization observation because the irradiated salt is blue or black and the recrystallized salt is not irradiated and therefore colourless. Moreover salt is optically isotropic. Nonetheless, if wished, polarized light can be added to the system.

2. THE DESIGN

2.1. The first design

The first design for the apparatus was partly due to Dr. J. Urai and consisted of a nearly cubic block of brass with a vertical cylindric hole in its centre (Fig.1). A glass plate was placed on the bottom of the hole (which is a cylinder with shorter radius). On top of the glass plate a salt sample slice covered by a second glass plate was placed. The whole arrangement is pressed together by a lid which covers the cylindric hole and can be screwed to the hole walls. The lid also has a round hole of a shorter radius. The light can go through the glass plates and the sample thus allowing vertical microscopic observation.

The volume between the glass plates is further closed by two O-rings each surrounding one glass plate. The O-rings contact the metal walls. An horizontal duct drilled in the metal wall brings the space between the glass plates in contact with the exterior. Brine could be added or subtracted through this duct which was in contact with an "oversized brine pump" acting as well as brine reservoir. The very first version of this pump was a clinical syringe. The idea behind this was that the brine would be pumped into the space between the two glass plates and set the sample under pressure. A manometer was placed in the tube which connects the brine pump with the duct in the metal block to measure the brine pressure.

Heating took place by means of two heating elements fitted into two holes made in the metal block. Another horizontal duct was drilled to introduce a thermocouple. The thermocouple was read by a proportional band temperature regulator which regulated the power sent to the heating elements. The hole system was fixed on top of a copper plate and placed within a "pertinax" box for temperature isolation.

A →

A →

SECTION A—A

light   light

④
②
①
brine inlet
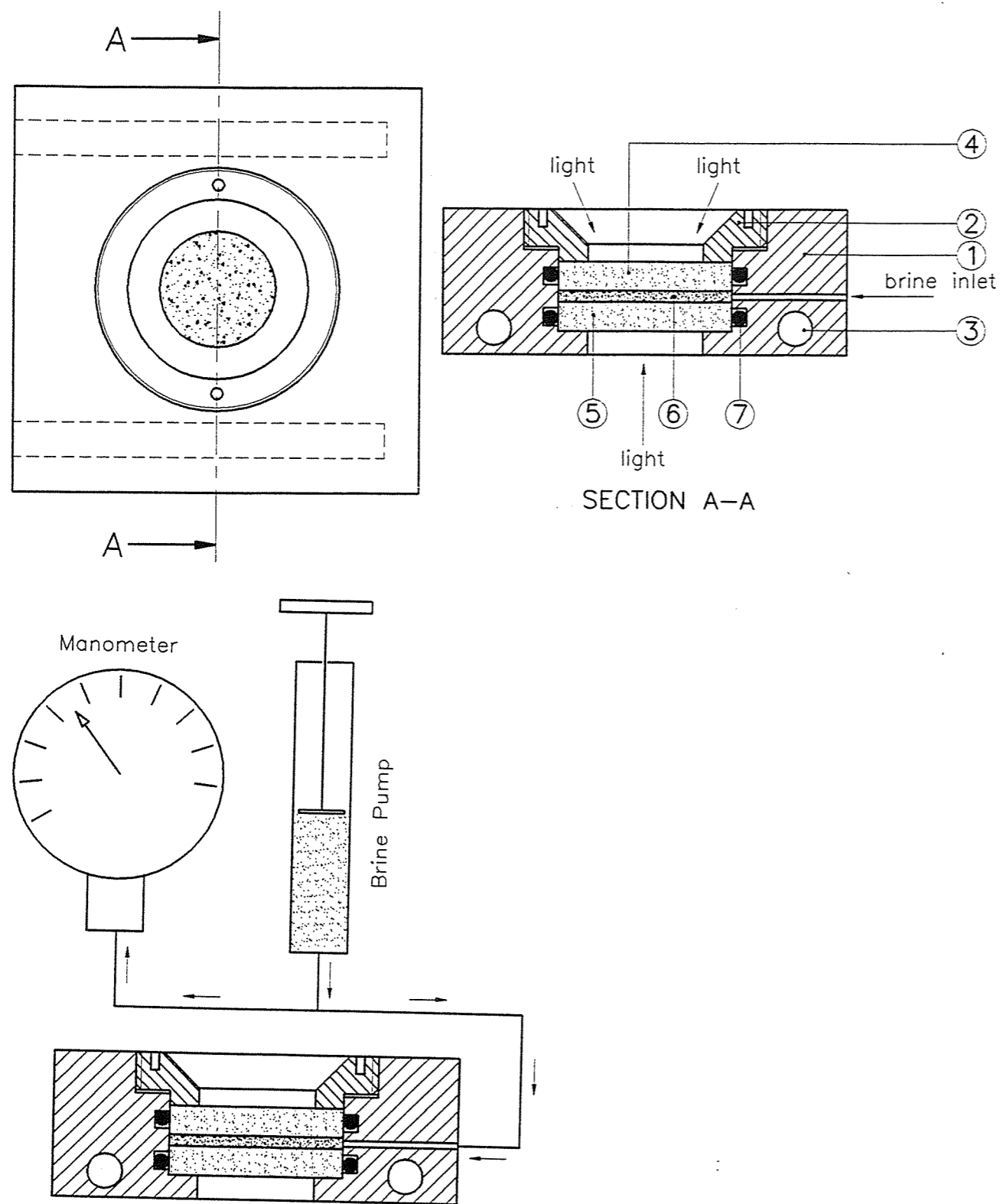③

⑤ ⑥ ⑦

light

Manometer

Brine Pump

Figure 1.   *Schematic views of the old design of the recrystallization apparatus. 1) casing, 2) lid, 3) holes for heating elements, 4) top glass window, 5) bottom glass window, 6) sample slice, 7) O-ring.*

Through progressive mending of all what turned out to disfunction the new design gradually emerged. The main problems of this old design were:

a)   the lack of real control on the pressure imposed on the sample which depended mainly on the tightness with which the lid was screwed,

b)   the poor contact of the glass plates with the O-rings,

c)   the easy corrosion of the material in spite of the electrolytic gold plating,

d)   the high temperature gradient in the system, and

e)   various leaking points.

These problems did not stop the samples from dissolving as expected, but caused the reprecipitation, which ought to take place in the sample producing the recrystallized material, to take place at the leaking points, outside the apparatus, which, moreover, were colder than the sample.

Nonetheless some observations could be made with this apparatus.

2.2.   The new design

Very important in this new design is the choice of materials as discussed in 3. The basis of the new design is a cylindric metallic block which (Fig. 2) contains three glass windows placed between two metallic covers which are attached to each other by studs and nuts.

The casing consists of the cylindric metallic block. The glass windows are circular plates of boronsilicate glass with thin metal rings glued to them. These metallic rings improve the contact of the glass with the O-ring which is otherwise rather poor. The glass windows are on top of each other inside the casing which they divide into two spaces: the sample chamber and the gas chamber.

The space between the two lower glass plates, *the sample chamber*, meant to contain the sample which recrystallization is to be studied, can hold samples of thicknesses up to 3 mm. To introduce brine in the sample chamber two horizontal ducts have been drilled in the metallic walls.
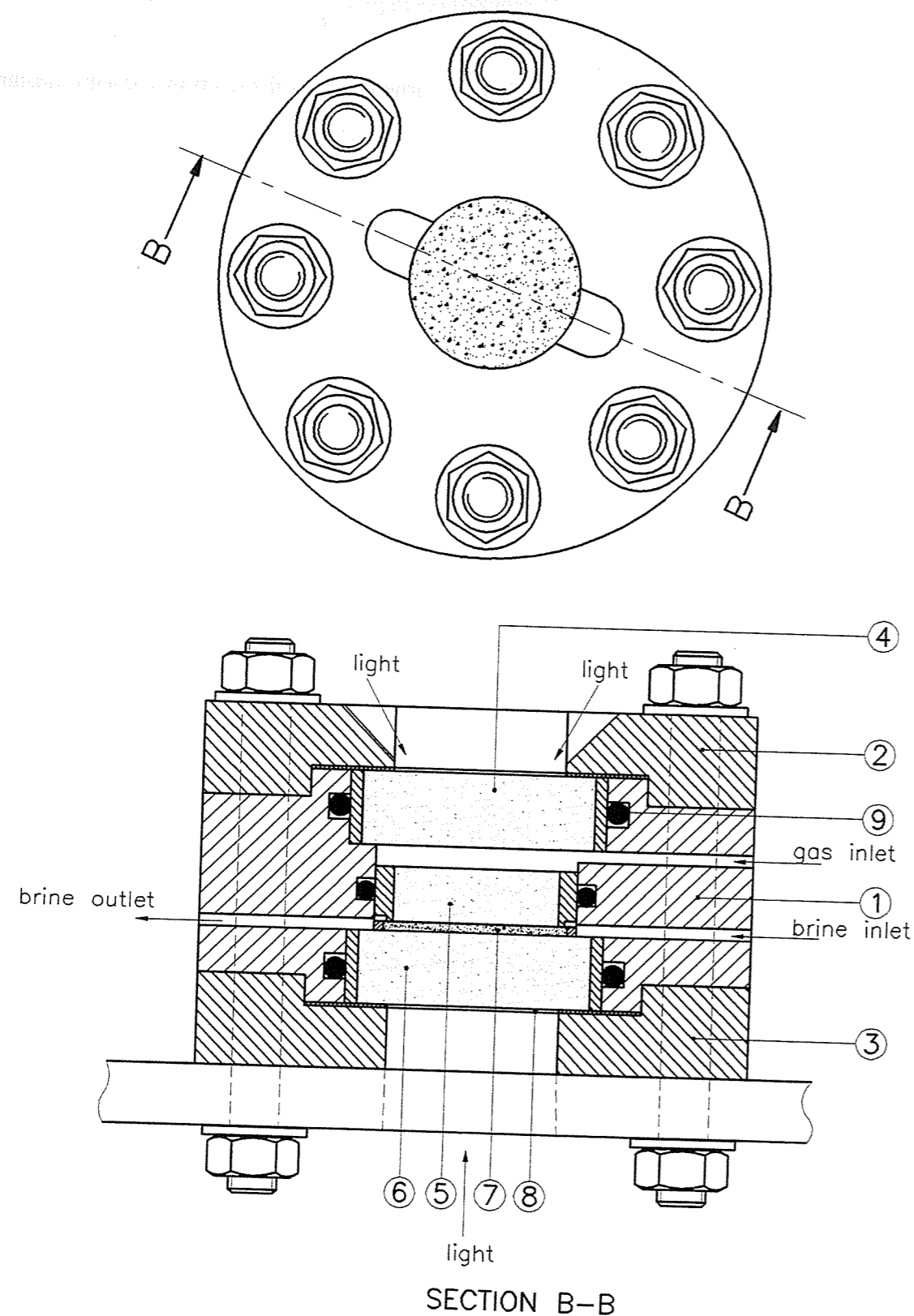
SECTION B—B

Figure 2. *Two sections of the new design of the recrystallization apparatus. 1) casing, 2) top cover, 3) bottom cover, 4) top glass window, 5) mid glass window, 6) bottom glass window, 7) sample slice, 8) Arlon rings, 9) O-ring.*

The samples can be mechanically pressurized by filling the space between the middle and top glass plates, *the gas chamber*, with gas at high pressure. The gas is introduced into the gas chamber through an horizontal duct drilled in the metallic wall (Figs. 2 and 3).

The metallic *covers* which hold together the sample housing and its contents are very stiff to hinder their bending under pressure. Bending of the covers could produce differential stress on the glass windows and break them. Two arlon rings are placed between the glass and the covers. The arlon rings smooth away eventual imperfection in the material flatness which could also produce differential stress and fracturing. The covers are hold together by 8 studs and 16 nuts.

Two circular holes have been cut out from the covers. The holes have a diameter of 28 mm, as planned for the samples which can therefore be observed (except for a rim of 1.5 mm) during the experiment. A lamp shines through the lower cover circular hole. In the top cover two additional slots have been made on the circular hole wall where two additional lamps can be placed and fixed on a good illumination angle. The samples can thus be observed by transparency and by reflexion and photographed through the upper cover circular hole.

There are two independent pressure systems feeding the experimental pile, one for the gas, and one for the brine. The pressure of the brine can be regulated and read independently of that of the gas (Fig. 3). This opens up the possibility of performing another sort of experiment i.e. on the relationship between intergranular fluid pressure and lithostatic load.

The gas pressure system is made up of a tap, a regulable overpressure safety valve, a manometer, connectors and tubes. This system ends on the one side in the gas chamber, and on the other side is attached to the pressure producing installation i.e. a gas bottle.

The brine system is made up of the same elements as the gas pressure system and some other additional devices. At one side of the sample chamber an additional tap for vacuumimg is present, while at the other side a "brine pump" constitutes the equivalent of the gas producing installation. This "brine pump" is a device to supply brine and brine pressure consisting of a reservoir filled with brine which can be pumped by a piston driven by a spindle.
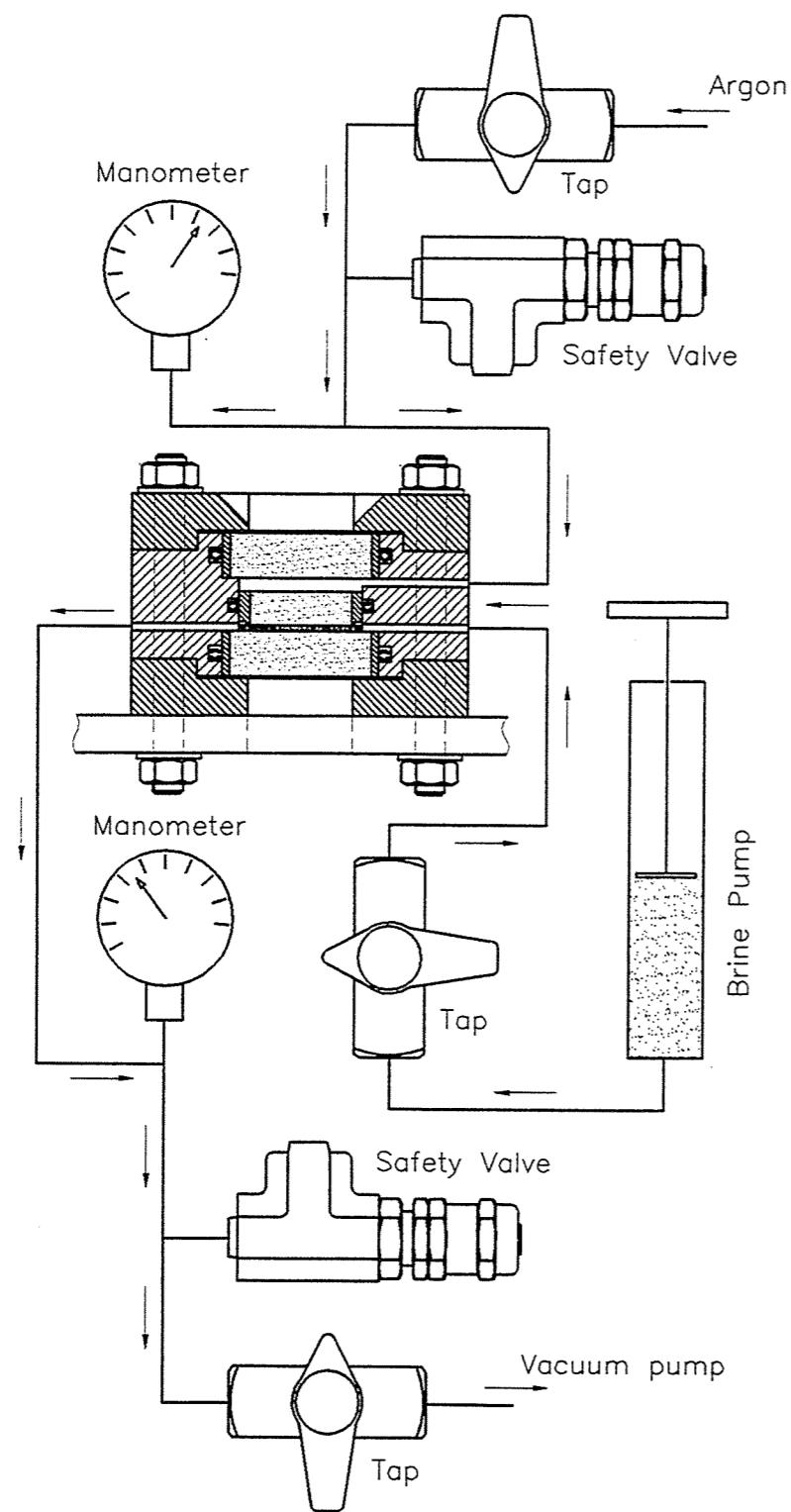
Figure 3. *Schematic representation of the complete recrystallization apparatus including the gas and brine system.*

All connections between system components are made through metal tubes with a diameter of 6 mm and a wall thickness of 1 mm. To link tubes and devices connectors with Swage-Lok tube fittings are used.

The total system as constituted by casing, covers and studs and the two pressure systems is fixed on an aluminium plate measuring 260 x 215 x 10 mm. All the devices and tubes have been fixed as near to each other as possible so as not to loose any heat and not to create heat gradients. To achieve this, parts of the apparatus have been fixed on the down side of the plate. The tubes cross therefore the aluminium plate through a couple of holes. See Fig. 4. The casing and the covers are tightened to the aluminium plate through the same studs and nuts which hold them together, and the other components are fixed using braces and screws.

The sizes and materials have been thus chosen that the hole set up amply accomplishes the safety regulations to work at 200 bar of pressure. This allows for use of the apparatus outside special high pressure laboratories. It has also been repeatedly tested for safety, see 4.

Heat is supplied by four heating elements of 100 W each (at 220 V) which sheaths have been fastened to the aluminium plate (two above and two below) and distributed so as to minimize temperature gradients. Heat power is regulated by a proportional band temperature regulator; the temperature is read from a thermocouple placed near the sample in the casing.

Thermal Isolation is reached by providing the aluminum plate with three legs and placing it all inside an isolation box. The box is 350 x 310 x 210 mm made of stainless steel plate 1 mm thick, covered with a lid, and filled with a 50 mm thick rockwool blanket. The lid on top of the box has three possible openings, one to photograph the sample and/or illuminate it, and two to read the manometers without opening the box. Each of the three holes can be closed with a lid. All exterior lids have a layer of Pertinax in their inner side. There is also a plate of pertinax in the bottom of the box. On the side of the box holes have been perforated for the 220 V electricity cable and its protection, the two jacks for the light plugs and the thermocouple to go through.

Illumination is made through a lamp fixed in the bottom of the box in a position convenient to illuminate the bottom of the sample. On the top lid of the box a holder is positioned to fix the two lamps which have to illuminate the sample from above. All three lamps can be step-

less dimmed.

3.   CHOICE OF MATERIALS

The materials for the casing and pressure systems had to be metals due to the thermal conductivity and mechanical properties required. However, sodium chloride in the presence of water easily corrodes and oxidates metals, and therefore the choice of metals was limited by their resistance to corrosion. Most resistant to corrosion by salt are Ni alloys, like Inconel.

The casing is made of Inconel 625 and the rings glued to the glass-windows are made of Inconel 600. Inconel 625 is the most resistant to corrosion by salt. The tubes and the conic parts of the swagelock fittings which join the casing and the brine system are made of Inconel 600. The tubes have been welded to the conic fitting pieces using the Tungsten Inert Gas (TIG) method.

The covers which hold together the casing and glass windows are not in contact with either brine nor salt and therefore could be made of Remanit 4122 which is not resistant to corrosion by salt but can be (and was) hardened up to 48 HRc.

The rings between the glass windows and the metal covers are made of a synthetic material named arlon which can stand the required temperatures remaining elastic. Arlon can deform under high pressure adapting its shape to the eventual small roughnesses in the contacts between glass and metal but does not flow at 100°C and 200 bar.

The tubes and fittings of the gas system are made of stainless steel (316 L).

All fittings, taps and valves of both pressure systems are made of the same type of stainless steel (316 L). In the case of the brine system this material choice is only due to the ease with which fittings, taps and valves could be purchased, but the definitive version of the apparatus was meant to have them made of Inconel 600.
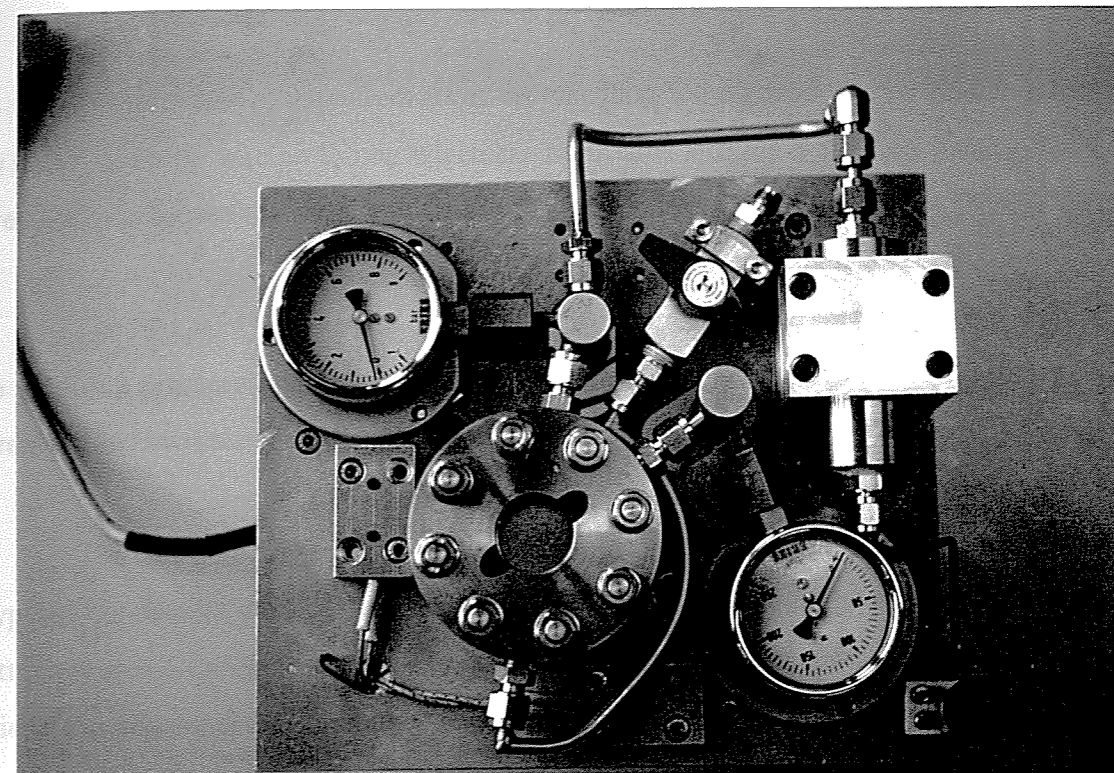

Figure 4a: *Top view of the recrystallization apparatus*
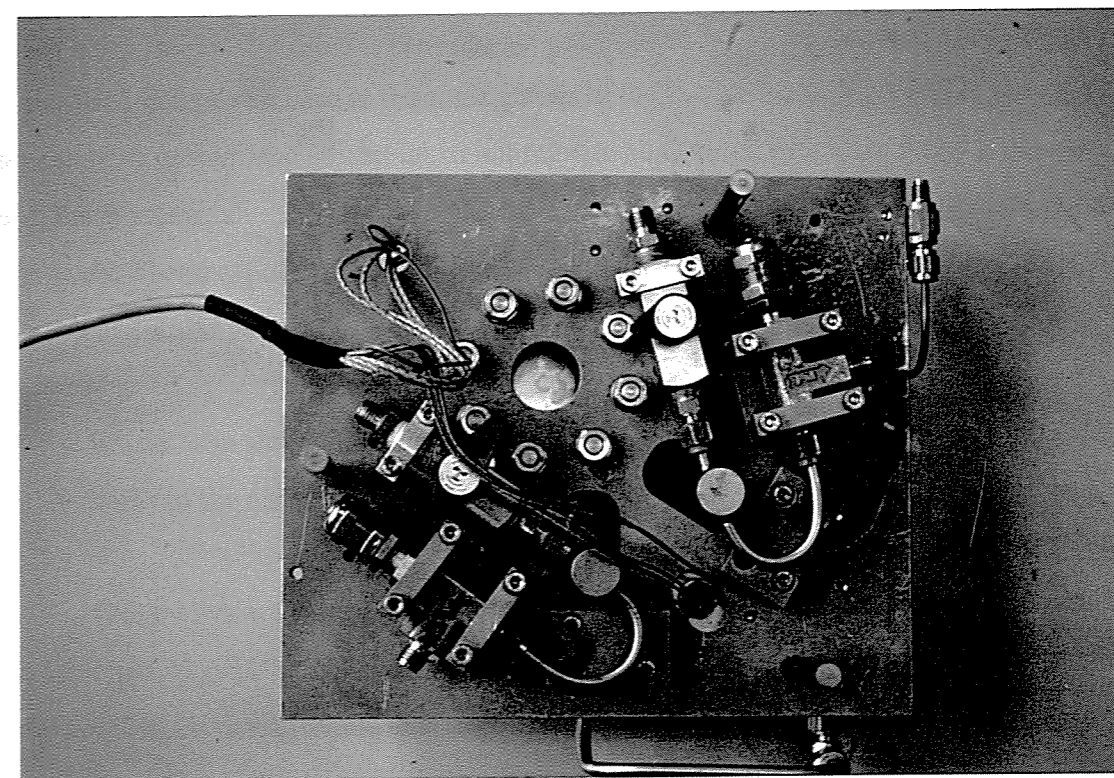

Figure 4b: *View from below of the recrystallization apparatus.*

The three taps of the system are of the type Plug Valves produced by NUPRO, they work by means of a stop with an O-ring which can be twisted into the outlet hole closing it. This taps are chosen because they are simply built and easy to clean.

The two safety valves are of the type R3A from NUPRO, they can be step-less adapted to a chosen pressure. This type of valve has been chosen to allow for a precision release of pressure and increase the safety of the apparatus during the experiments.

The connectors used for the tubes are of the type Swage-Lock for 6 mm diameter. This type of connectors works by means of a conic tube piece which, when a nut is screwed, it is attached to a 6 mm diameter tube constituting a gastight connection. The tube with the conic piece can be connected to another piece with a conic hole and hold together by screwing yet another nut. The contact between the two conic elements is also gastight at the applied temperatures.

We were unable to purchase manometers with inner bourdon of any material more resistant to corrosion than stainless steel (316).

Teflon tape was used at the conic fittings of the Swage-Lock links and at the taps of both gas and brine system and silicon fat to impregnate all O-rings which are found in the casing, the taps, the pressure valves and the fittings of the manometers. The O-rings themselves are made of Viton with a hardness of 70 Shore. This material is nor easily corroded, adequate for vacuum and can be used at temperatures of between -20 and 200°C.

Braces from aluminium and inner hexagonal screw of stainless steel (316) fix all parts of both systems to the aluminium plate.

Glass windows from boronsilicate of 27 mm diameter and 9 mm thickness, and 38 mm diameter and 12 mm thickness, with the following specifications: parallelism deviation less than 0.05 mm, flatness deviation less than 0.01 mm and, between plane and cylindric surfaces a 0.1 mm rounded corner was polished off. For each experiment one small and two big glass -windows are needed.

The glue which attaches the metal rings to the glass windows is one -component epoxy-glue of the Permapox 2032 AB type, which hardens at a temperature of between 90 and 120°C. The glue is gastight and resistant to chemical agents and can be used up to a temperature of 160°C.

Leak fluid not aggressive for the used materials is also used to check on the gas tightness of the system.

4. EXPERIMENTAL METHOD

4.1. Sample preparation

To observe a sample by transparency, a slice of it as thin as possible is needed.

Since it will be impossible to saw and polish a very thin slice of salt without it falling apart, the sample is glued to a support, in this case a metallic ring. It is proceeded as follows: a cylinder of the sample to recrystallize is machined out of a bigger piece in a cylinder adapting to a tube of stainless steel 316 with a precision of 0.4 mm. The sample is introduced in the tube and glued to it using the same glue as for the metal-glass contacts in the apparatus. After hardening of the glue one of the surfaces of the sample is machined flat and polished with a 600 Grit polishing paper. Now, a slot is made in the stainless steel and up to the glue with a width of 0.9 mm, and at a distance of 1 mm from the first flat polished surface. The width of the slot is chosen in relation with the thickness of the diamond saw blade (0.85 mm) with which the salt sample will subsequently be cut, and the distance of 1 mm is the thinnest we could go without the sample falling apart during sawing.

The complete cylinder in which the slot has been cut is now fixed in a precision saw and further cut with the diamond saw into a slice. The slot made in the stainless steel guides now the saw blade very precisely by hindering blade bending. In this way a reasonably flat and plan-parallel slice is obtained.

The obtained slice is fixed in a specially developed holder and further polished with a 600 grit polishing paper into fat shiny surfaces (precision of 0.01 mm) and parallel to each other (within an accuracy of 0.02 mm). The roughnesses and filaments of the stainless steel are polished away with a file, and four small slots are made in the top of the ring to ease brine transport.

4.2. Experimental set up

To prepare an experiment first the sample and the brine have to be prepared, then the safety valves have to be adjusted to the wished pressure taking into account the temperature rises. Assemblage of the apparatus with the sample then takes place.

The order of assemblage of the whole system begins by screwing the 3 legs under the aluminium plate. Then the two tubes connecting the top and down of both systems are made to cross the aluminium plate. Now, in an inverted apparatus, the following pieces and in the following order have to be set within the lower chamber of the sample housing: an O-ring greased with silicon fat, a glass window, an arlon ring and the bottom cover. Now the three connectors with their correspondingly greased O-rings must be screwed into the side wall of the sample housing.

The apparatus is now turned back to a normal upside position, and the whole assemblage is fixed with the 8 bolts which traverse the bottom cover and the aluminium plate and which are fixed at the down side of the aluminium plate by the 8 nuts.

Two of the three connectors are now attached to the connecting tubes which had been made previously to cross the plate. The third connector of the casing is coupled to a tube which on the other side is communicated with a tap which is attached to the plate.

In the top side of the plate the two manometers are coupled to their respective tubes and fixed on top of the aluminium plate, the four heating elements are fastened on the top and down side of the plate and the two remaining taps and security valves are coupled to their corresponding pressure system and further fixed to the plate.

To start an experiment a sample is placed inside the sample housing on top of he lowest glass window, then the mid glass window is placed on top of the sample. This mid window constitutes with the lowest window the lower chamber, and is closed using an O-ring which is greased with silicone fat. On top of this an equally greased O-ring and the top glass window are placed. The complete assemblage is then closed by the synthetic ring (of arlon) and the metallic top cover. Then the nuts are tightened.

In the only tap for the gas system an argon bottle is now placed and the system brought up to the wished pressure. After this, both the bottle of argon and the pressure system are closed and uncoupled. It has to be taken into account that when the temperature of the system rises, the gas pressure will rise as well, and therefore a pressure lower than that desired has to be given to the system.

The brine container with pump has to be coupled now to the upper tap of the brine system and the reservoir has to be filled by about 3/4 of its capacity. The tap has to be closed during this procedure. At the lower side of the plate, the brine tap has to be coupled to a tube which in its turn is coupled through a threeway valve and a Dresler bottle to a vacuum pump.

With the lower tap opened it is now proceeded to vacuum pump the brine system during about 2 minutes, after what the upper tap with the brine reservoir is shortly opened (and closed). As a consequence a little brine appears in the Dresler bottle showing that if any air was present it has been taken out of all the volume between the reservoir and the valve. The brine reservoir can again be filled in up to 3/4 of its capacity.

Now, after 5 minutes more of vacuuming, the top tap is opened and the brine enters the system. When the brine reaches the Dresler bottle the lower tap has to be closed. The system is now full of brine (in spite of the gas pressure) and the vacuum pump with accessories can be taken away.

The complete apparatus, including the brine reservoir is now placed in the stainless steel box, the thermocouple set in the sample casing, the electrical connections for temperature control are made and the apparatus isolated with the rockwool.

The temperature regulator is now set to reach 100°C at the maximum heating speed. When the temperature reaches 60°C the potence of the apparatus is lowered by 40 %, and at 80°C by an additional 20%. These last changes are performed by hand what makes it possible to reach the wished temperature in about 30 min without producing much overshoot. When the temperature reaches 100°C the system can be pressurized using the spindle. The brine reservoir is then taken away and the tip of the tap is cleaned with water. To be able to perform the last handlings, the apparatus has to be taken out of the box. After replacing it in the box and coupling again the electricity connections the two upper lamps are placed and the isolation as well. After 45 min the apparatus has reached the wished temperature.

During the experiment the pressure of the brine and gas systems can be read in the manometers and the state of the sample can be photographed through the holes in the box.

5. TESTS AND MODIFICATIONS

The *temperature gradient* of the apparatus has been measured during a simulation of operation and it has been found that there may be differences of 3°C between different devices. The gradient in the air inside the box near the apparatus is higher. No variation in the gradient could be measured as a consequence of opening the lid of the holes for illumination and reading of the pressure, nor as a consequence of heat produced by the lamps.

Also the *maximum pressure* which can safely be used has been determined with tests. The experiments consisted of filling the system with gas and observing at which pressure the glass windows break. The lower glass window breaks for a pressure on the sample of 195 bar which is reached at a gas pressure of 150 bar and the upper glass window breaks at a gas pressure of 240 bar. The difference in gas pressure which can be withstanded by the glass plates is due to the size and form of the mid plate: the mid plate presses the sample in a surface smaller than its upper surface by a factor 1.3 (see Fig. 2).

The fractures in the glass windows are evidently produced by bending. They pass through the centres of the windows, no pieces are blown apart and the glass remains gastight.

Leakings were repeatedly found when testing the system and they were localized and helped in some different ways. For instance, the *safety valves* for both pressure systems are completely made of stainless steel (316). The closure pin of the valve which is in contact with brine corroded during the tests and leaking appeared at the O-ring of the valve. To avoid this the pin was changed by a self made Arlon pin. The swage-lock fittings also had to be modified.

To be certain that the system is gastight the whole was, before a sample was set together, filled with argon at a pressure of 100 bar through one of the taps of the system while all the other were smeared with leak fluid.

Both systems could be tested together if connected to each other by means of suppressing the mid glass window and O-ring.

We performed many additional tests to know whether the gas from the gas chamber leaks to the sample chamber, this was necessary because there is a drop in the pressure of the gas chamber of about 5 bar within three months.

There were two weak places where leaking could take place, either between the O-rings and the housing or between the glass and the glued metal rings. The last was not the reason, because substituting the glass by a metal plate the "leaking" went on. The only possibility would thus be the O-ring leaking. This was controlled by performing a test on the housing independently with only the upper and mid glass windows. Between these two windows helium was set instead of the usual argon and then an helium leaking test was performed. The measured leaking was very small (2×10^{-9} l/min) en took place after 30 min waiting between each measurement, and yet this leaking, given the size of the sample and gas chamber can justify the pressure drop in the gas system. Therefore experiments with silicon oil instead of with argon were performed since it was expected that less leaking would take place for these bigger molecules but, the changes in pressure remained the same.

The leaking problem has remained unsolved. As a last attempt to solve the problem, an accumulator was made (see red cylinder in the photograph) which was coupled to the communication tube of the brine system. These accumulator is in principle made of a rubber balloon which is coupled to the brine system and will be filled in when the system is filled in with

brine. If the brine pressure in the inner system grows the balloon will increase in volume reducing the pressure in the system. The balloon is surrounded by a stainless steel cylinder where the air is set under pressure by the balloon and which can be let out if needed. It is also possible to increase the pressure of the brine by increasing that of the air in the cylinder. The accumulator did not change anything in the pressure equilibrium, although it certainly increased the system safety.

6.   DISCUSSION

The apparently unnecessary complications in the system of pressurizing and heating are due to the wish of avoiding sudden temperature changes when the temperature of the experiments is set near 100°C. The brine has to be introduced in a previously heated apparatus and at the temperature of the apparatus as well. This is necessary to avoid precipitation of the salt dissolved in the brine in the cold apparatus, what would not only disturb the saturation degree at which the experiment ought to take place, but probably also obstruct the ducts with salt crystals. On the other hand, if the brine is introduced at 100°C, in a system which has been vacuum pumped, it will certainly boil producing gas bubbles which disturb the experiment. Notice that if the system has not been vacuum pumped the brine will not penetrate the apparatus due to the pressure of 200 bar exerted by the gas chamber on the sample chamber.

Although the leaking measured is not really relevant for some experiments (a drop of 5 bar in three months is rather good), there is always the possibility of the gas bubbles influencing the recrystallization by poisoning the grain boundaries : It is known that depending on the size of gas bubbles included in the brine the grain boundaries can advance easily or not. This is why we insisted as much in solving the leaking problem.

7.   RESULTS AND FURTHER SUGGESTIONS

Five experiments have been carried out and photographs of the samples were taken, however, although little could be observed since in each experiment one or another problem would appear, we were able to control the importance of surface tension in driving grain boundary migration. Mostly leaking problems forced the experiments to stop. Now we think that it would