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A CHEMICAL DECRUDDING TECHNIQUE APPLIED UPON FUEL PINS  
FOR CHEMICAL IDENTIFICATION OF THE CRUD

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### *Abstract*

*A procedure has been developed for chemical decrudding and analysis of the crud deposited upon semi-industrial fuel pins of the S.C.K./C.E.N. BR3 thermal power reactor. The whole pins are individually immersed in boiling 6M HCl of super pure quality. This treatment is carried out while the fuel pin is inclined at about 20°. The container in which the decrudding takes place is made of quartz and precleaned with boiling 6M HCl blank solution.*

*At the end of the chemical decrudding procedure, the solutions are collected and weighed.*

*The radioactive solutions are then analysed to determine the chemical composition of the crud. It seems to be mainly elements arising from stainless steel reactor components and boron.*

## 1. Introduction

In order to perform non-destructively dimensional measurements and the detection of defects in the cladding by eddy current techniques, a cleaning of the fuel pins is in many cases necessary.

Chemical decrudding is generally preferred above mechanical techniques as it presents the possibility of collecting in a quantitative manner the whole crud layer, deposited upon the fuel pins. This quantitative sampling enables a complete analysis of the deposits.

The chemical treatment of the crud takes place in 6M HCl and is performed in a quartz apparatus. The blanco solutions and the process solutions are collected in polyethylene flasks ; these flasks are transferred from the hot cell into a glove-box in order to take the necessary samples of the dissolved crud. The analytical examinations are then performed upon those samples.

The pretreatment of the quartz equipment and the other necessary material (polyethylene flasks, reagents, etc.) is performed according to the ASTM-E267 standard method.

## 2. Description of the apparatus

The apparatus (Fig. 1) consists of a quartz tube (diameter : 30 mm, wall thickness : 2 mm, length : 1400 mm) with at the front side a spherical enlargement upon which two conical ground joints have been welded. The conical joint R1 has been tightened with a quartz stopper while the second conical joint R2 has been welded for connecting a quartz cooler (the joints are made without tightening material). The quartz tube is mounted in a metallic frame in such a way that it can be tilted from a horizontal position to about an angle of 20° (working position) so that then the cooler takes a vertical position. The apparatus is equipped with a heating element which is mounted at the back of the quartz tube (adjustable power up to 300 W)(Fig. 2).

### 3. Procedure

#### 3.1. *Chemical pretreatment of the equipment*

Before introducing the equipment in the appropriate hot cell, a preparatory treatment has been applied upon the internal parts of the quartz tube according to the above-mentioned ASTM standard method. Concretely this means that the following treatment has been applied :

- washing with demineralized or bidistilled water
- boiling with 6M HNO<sub>3</sub> pro analysis
- washing with demineralized or bidistilled water
- boiling with 6M HCl pro analysis
- washing with demineralized or bidistilled water
- boiling with 6M HCl ULTREX

Samples from this last solution are taken for chemical analysis (blanc. solution B). During boiling, the quartz tube is tilted over 20° vis à vis the horizontal, while the quartz cooler was mounted upon the joint R2.

#### 3.2. *Chemical pretreatment of the polyethylene material*

For the collection of the blanco and process solutions, only polyethylene flasks were used ; this material was pretreated in an analogous way as the quartz equipment according to the same ASTM procedure :

- washing with demineralized or bidistilled water
- washing with 6M HCl pro analysis
- washing with demineralized or bidistilled water
- washing with 6M HCl ULTREX

Then all the polyethylene material was packed to be introduced in the hot cell.

The flasks for the solutions which have to be treated in a glove-box later on, are first weighed and equipped with a double plastic packing in order to avoid contamination.

### 3.3. Reagents

A very important element in this procedure is the use of very pure reagents. For the real chemical decrudding and also for the last preliminary treatment (see 3.1 and 3.2) a solution of 6M HCl was diluted from a concentrated HCl ULTREX solution ( $\sim 38\%$ ) of the J.T. BAKER CHEMICAL COMPANY. The chemical impurities of this concentrated HCl solution is given in Table I. For the dilution, demineralized water (conductivity :  $1.7 \mu\text{Mho cm}^{-1}$ ) was used. The 6M HCl solution was prepared in different badges, each badge has been made of a 38% HCl ULTREX supply having different batch numbers. According to this, all the later analyses could be retraced up to the batch number of the used HCl and thus chemical contaminations, introduced with the reagent, could be accounted for.

The 6M HCl solution was then subdivided in quantities of 700 ml in pretreated polyethylene flasks.

### 4. Mounting of the equipment in the hot cell

As the whole mounting operation had to be performed in a used and contaminated hot cell, all the equipment had to be introduced by means of La Calhène type transfer boxes (maximum diameter 270 mm and a length of 350 or 700 mm). For this purpose the metallic frame sustaining the quartz apparatus has been developed in such a way (Fig. 3) that this frame could be introduced in the hot cell by the above-mentioned boxes.

The mounting itself was carried out by using the classical manipulators type MA11 La Calhène (Fig. 4).

For the quartz tube, with a full length of 1400 mm, a specially adapted transfer box of sufficient length has been used.

Apart from the quartz tube, a second tube in pyrex glass had to be introduced, in which the fuel pin could be washed and stored after the chemical treatment.

This tube was introduced into the hot cell in the same way as the quartz tube and could be stored on a simple support (Fig. 5).

## 5. Chemical decrudding

### 5.1. Procedure performed in the hot cell

At first the chemical contamination level of the quartz apparatus as it has been set up in the hot cell was determined. For that purpose, the quartz tube was filled with 700 ml 6M HCl ULTREX through the joint R2 and boiled during 1 hour. This has been performed with the apparatus in the "working position", which means tilted over an angle of 20° and equipped with the cooler (Fig. 2). In order to stimulate the boiling and generate the vapour in a more regular way, "boiling stones" were added.

These were small pieces of quartz which received the same preparatory treatment as the quartz tube.

After sufficient cooling, the solution (blanc B1) was transferred from the quartz tube into a preconditioned and numbered polyethylene flask.

This was carried out in the following way :

- the quartz tube was positioned in a horizontal position and blocked ;
- the cooler has been discarded ;
- the quartz tube has now been slowly rotated (according to the horizontal axis) up to 180° and the solution was collected through the conical joint R2 in the preconditioned polyethylene flask.

The apparatus was turned back in the loading position and has been prepared for receiving the fuel pin. Therefore the stopper is discarded from the joint R1 and the fuel pin is introduced from the container directly into the quartz tube. This is done after identification of the fuel pin. The quartz apparatus was then tilted again over 20° and

has been refilled with 700 ml 6M HCl ULTREX ; the joint R1 is closed and the cooler is replaced ; the heating was started and during 1 hour the solution was boiled. After cooling the solution (process solution P1) has been transferred in a numbered, weighed and preconditioned polyethylene flask in the same manner as described above for the blanco solution. The fuel pin was then transferred in the pyrex tube and washed with about 15 l demineralized water (Fig. 6), dried and replaced in the transport container. Meanwhile, the quartz apparatus is washed with 700 ml 6M HCl during 1 hour and the wash solution is also collected in a preconditioned polyethylene flask (Wash solution S1). Finally a last blanco experiment is performed by boiling again 700 ml 6M HCl ULTREX during 1 hour in the quartz tube, what results in a blanco solution B2. The treatment of a single fuel pin has now come to an end and the equipment is ready for the chemical decrudding of a possible second fuel pin.

### *5.2. Discarding of the analytical solutions from the hot cell*

For the treatment of one single fuel pin the above-described method produced the following solutions :

- B1 blanc solution = 60 mRh<sup>-1</sup>
- P1 process solution = 1.8 Rh<sup>-1</sup>
- S1 wash solution = 70 mRh<sup>-1</sup>
- B2 blanc. solution = 60 mRh<sup>-1</sup>

The radiation levels have been mentioned meanwhile for a typical analytical experiment, measured in the transfer box, while coupled at the hot cell.

These solutions in the polyethylene flasks have to be transferred to a glove-box in which the distribution and sampling will take place. The flasks with the different solutions have been controlled on radiation-dosis as they have to be handled manually. Above-mentioned values for a typical case, measured by a background of 60 mRh<sup>-1</sup> demonstrate that only



the process solution P1 has to be treated with the necessary attention during the sampling. The transfer of the solutions to the glove-box has been made by means of the La Calhène type Ø 270 transfer boxes.

### 5.3. Sampling

Before the samples of the different solutions have been taken, the exact weight of each solution has been determined. This is realised by weighing the flasks after discarding the plastic packing material.

About 30 ml of each solution has been transferred in a small polyethylene flask which is of course also preconditioned.

Beside the four above-mentioned solutions originating from the chemical decrudding, there are other samples to be analysed which are taken during the conditioning of the quartz apparatus and during preparation of the 6M HCl ULTREX solutions (par. 3.1, 3.2, 3.3).

From all the solutions mentioned hereafter, an analysis has been requested of the present cations and anions :

1. HCl pro analysis concentrated
2. 6M HCl pro analysis
3. Demineralized water used for the dilutions
- 4-5-6. 6M HCl ULTREX - batches
- B0. Blanc : 6M HCl ULTREX - boiling during 1 hour - quartz tube outside  
the cell
- B1. Blanc : 6M HCl ULTREX - boiling during 1 hour - quartz tube in the cell
- P1. Process solution : 6M HCl ULTREX - boiling during 1 hour of the  
fuel pin
- S1. Wash solution : 6M HCl ULTREX
- B2. Blanc : 6M HCl ULTREX - boiling during 1 hour - quartz tube in the  
cell

## 6. Analytical results

The analytical results of the different solutions have been co-ordinated in Table 2 and Table 3. Table 2 provides the analytical results of the used solutions before decrudding, while Table 3 resumes the results of the solutions involved, after the decrudding procedure.

Knowing the weights and the specific mass of the B1, P1, S1 and B2 solutions as tabulated in Table 4, the total volumes of those solutions which have been evacuated from the hot cell have been determined.

In order to estimate the total weight of each identified element in the oxide crud deposition, the following algebraic sum of the results mentioned in Tables 3 and 4 has been applied.

$$\text{Net weight} = P1 + S1 - \frac{(B1 + B2)}{2}.$$

The outcome of this computation is presented in Table 5. At the mean time the weights of the representative oxides have been calculated using the theoretical densities of the oxides.

The predominant deposit is clearly boron oxide.

The total weight and volume of the mixed oxides deduced from summation of the individual values, are respectively 6,100.58 g and

3,228.87 cm<sup>3</sup>, which leads to a mean theoretical specific mass of 1,885 g/cm<sup>3</sup>.

This value is very near to the theoretical boron oxide density.

An attempt has been made for estimating the layer thickness, accepting the computed oxide volume.

A fuel pin of 339 cm<sup>2</sup> upon which 3.22 cm<sup>3</sup> oxide crud is spread creates a mean layer thickness of 0.095 mm.

The value of the measured oxide thickness, by means of a contact eddy current probe, has been detected, being never higher than 0.09 mm (Fig. 7).

## 7. Conclusions

The oxide thickness measurements before and after decrudding by means of the eddy current technique (Fig. 7) permits to conclude that the chemical decrudding was quantitative. The distribution was non homogeneous, the deposits remain mainly in the centre of the fuel pin. The thickest layer of the deposited oxide was by electric measurement 0.09 mm, but the macroscopic observations reveal a much larger thickness, as the tip of the eddy current probe, left a deep trace into the oxide layer.

Thus the mean calculated thickness based upon chemical analysis could be in the region of the actual oxide layer thickness.

The experience which has been acquired will permit to study in more depth the problems of contamination during sampling and analysis.

The acquired experience permits now to develop a new quartz instrument in order to be able to decrud fuel pins, with a total length of up to 4,600 metres.

## 8. Acknowledgment

The authors are indebted to Messrs Lievens and L. Van de Velde of the Analytical Service, Mr Gys of LHMA who performed the eddy current examinations and Mr L. Vandecruys which took care of the technical aspects of the chemical decrudding.

## 9. Literature

### 1. ASTM - Designation E267-70

Preparation of equipment and reagents.

TABLE 1

Chemical impurities of a typical concentrated (38%) HCl ULTREX solution

Element	Concentration (ppb)
As	1
Al	20
B	30
Ca	20
Cr	< 1
Fe	20
K	< 10
Mg	7
Mn	0.3
Na	100
Ni	< 1
Pb	1
Si	40
Zn	< 1
Zr	-

TABLE 2

Analytical results of chemical contaminants in the different used solutions (expressed in microgram per litre)

Element	1	2	3	4	5	6
As	82		< 0.6	< 0.6	3.5	< 0.6
Al	79	15	< 0.2	24	28	26
B	60	30	< 0.6	400	820	370
Ca	346	35	9	57	27	17
Cr	5	201	< 0.2	0.8	0.4	0.4
Fe	92	2	0.6	54	45	49
K	1.6	1300	0.7	0.4	< 0.4	< 0.4
Mg	27	< 0.4	2	6.6	5.4	4.5
Mn	14	47	2.7	2.5	1.2	0.8
Na	286	11	< 0.2	49	91	93
Ni	5	156	< 0.2	0.7	0.5	< 0.2
Pb	7	1.4	< 0.6	< 0.6	< 0.6	< 0.6
Si	15	21	0.7	14	2.7	8
Zn	70	34	< 4	4	< 4	< 4

TABLE 3

Analytical results of the solutions directly connected  
to the decrudding operation of a specific fuel pin  
(expressed in milligram per litre)

Element	B0	B1	P1	S1	B2
As	0.005	< 0.030	< 0.030	< 0.030	< 0.030
Al	0.063	0.070	1.24	< 0.010	< 0.010
B	0.050	54.2	2640	39	10.7
Ca	0.060	0.053	0.24	0.030	0.022
Cr	0.001	0.080	3.6	0.025	0.014
Fe	0.035	0.24	204	0.29	0.090
K	0.001	0.002	0.003	0.002	0.001
Mg	0.015	0.017	0.90	0.020	0.014
Mn	0.001	0.010	5.00	0.023	< 0.010
Na	0.051	0.065	0.097	0.060	0.065
Ni	0.002	0.045	23.0	0.055	0.010
Pb	0.004	< 0.010	< 0.60	< 0.010	< 0.010
Si	0.065	0.015	19.0	0.027	0.025
Zn	0.720	0.80	< 0.50	< 0.50	< 0.50
Zr	< 0.010	< 0.010	0.40	< 0.010	< 0.010

$$P1 + S1 - \frac{(B1+B2)}{2} = \text{An. Res.}$$

TABLE 4

Specimens and total volume of the solution

	Mass	Specific mass	Total computed volume (ml)
B1	742.9 g	1.1068	671.1
P1	763.6 g	1.1033	692.1
S1	764.2 g	1.1100	694.7
B2	764.4 g	1.1083	689.7



TABLE 5

Calculated total oxide weights

Element	Total weight of the element	Oxide formula	Total oxide weights	Specific mass of oxides	Calculated volumes of the deposited oxides
As	0.02095	As <sub>2</sub> O <sub>3</sub>	0.0276	3.86	0.0071
Al	0.084125	Al <sub>2</sub> O <sub>3</sub>	1.5891	3.5	0.454
B	1,812.58	B <sub>2</sub> O <sub>3</sub>	5,838.32	1.84	3,173
Ca	0.1558	CaO	0.2165	3.34	0.0648
Cr	2.4695	Cr <sub>2</sub> O <sub>3</sub>	3.6104	5.21	0.6929
Fe	141.138	Fe <sub>2</sub> O <sub>3</sub>	201.813	5.24	38.5139
K	0.00165	K <sub>2</sub> O	0.00198	2.32	0.00085
Mg	0.6219	MgO	1.0251	3.58	0.2863
Mn	3.4605	MnO	4.4640	5.43	0.8220
Na	0.0675	Na <sub>2</sub> O	0.1815	2.27	0.0799
Ni	15.9001	NiO	20.193	7.45	2.7104
Pb	0.41525	PbO	0.4442	9.53	0.0466
Si	13.1534	SiO <sub>2</sub>	28.015	2.32	12.075
Zn	0.2497	ZnO	0.3096	5.47	0.0569
Zr	0.2769	ZrO <sub>2</sub>	0.3738	5.49	0.0680

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Fig. 1. Chemical decrudding apparatus : Quartz-tube

Fig. 2. Chemical decrudding apparatus

- Loading position

- Working position

Fig. 3. Chemical decrudding : metallic frame

Fig. 4. Chemical decrudding : installation in the hot cell

Fig. 5.

Fig. 6. Chemical decrudding : rinsing apparatus

Fig. 7. Eddy current oxide thickness measurements before and after chemical decrudding

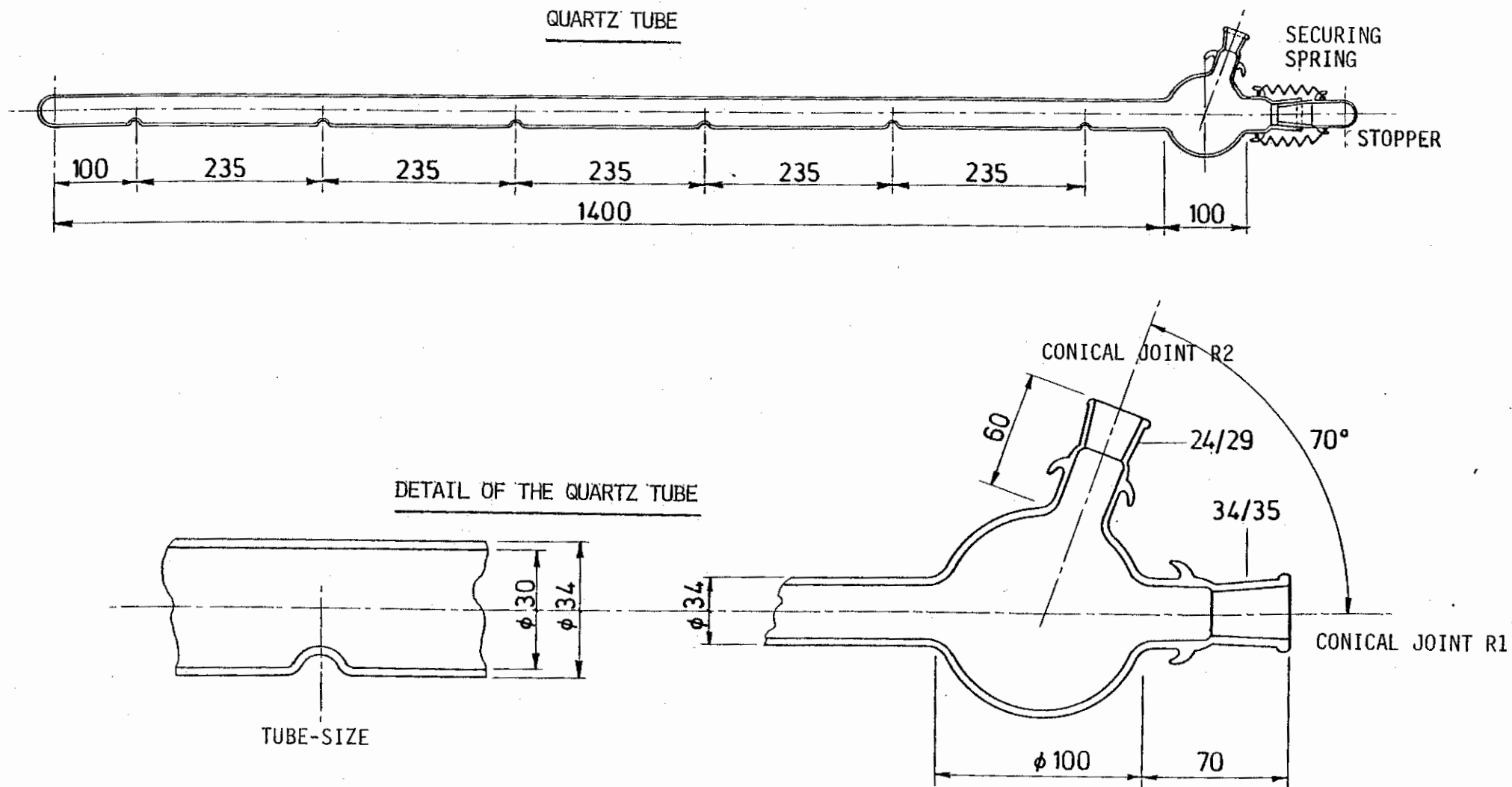


FIG. 1 CHEMICAL DECRUDDING APPARATUS - QUARTZ TUBE.

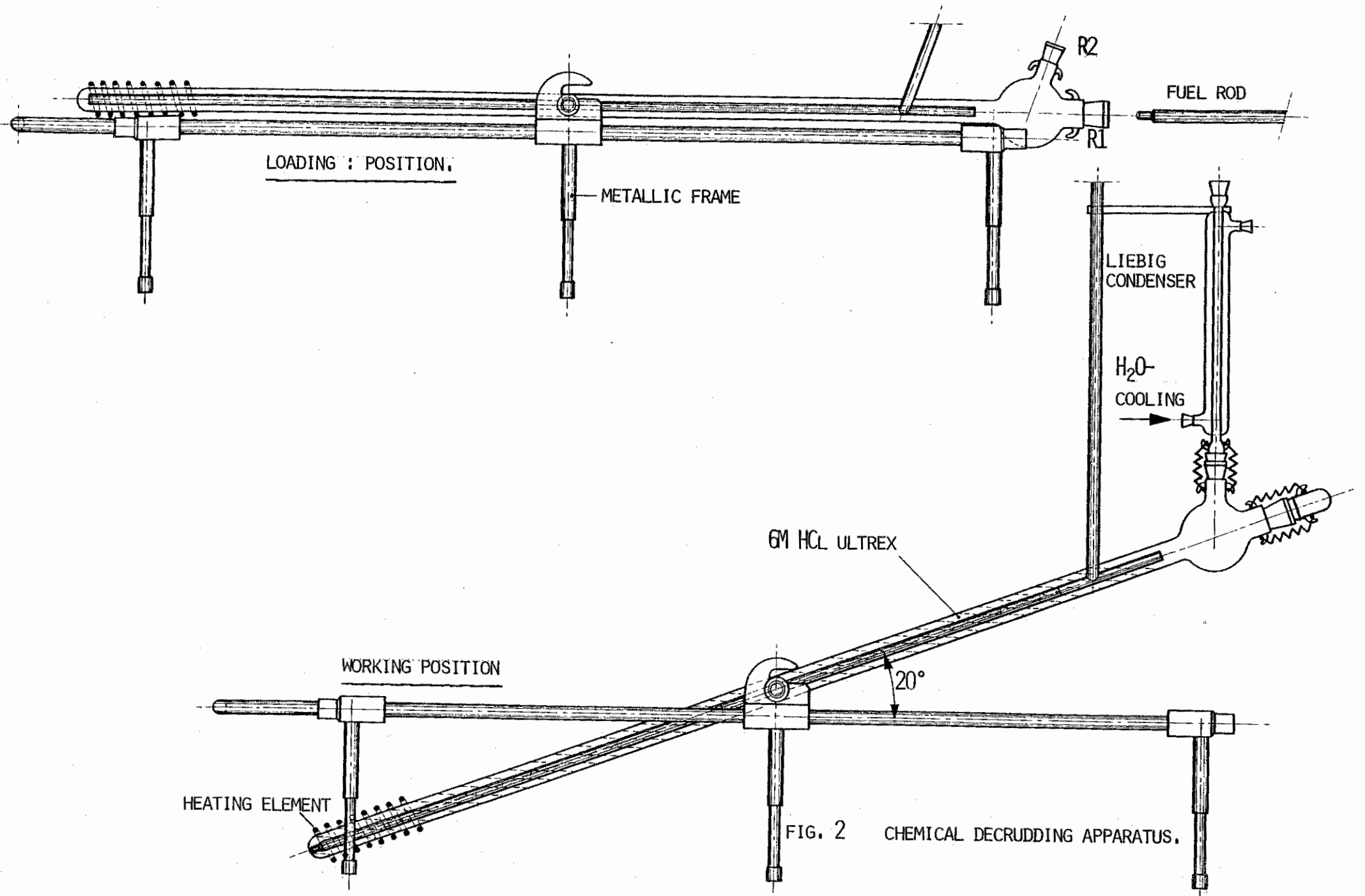


FIG. 2 CHEMICAL DECRUDDING APPARATUS.

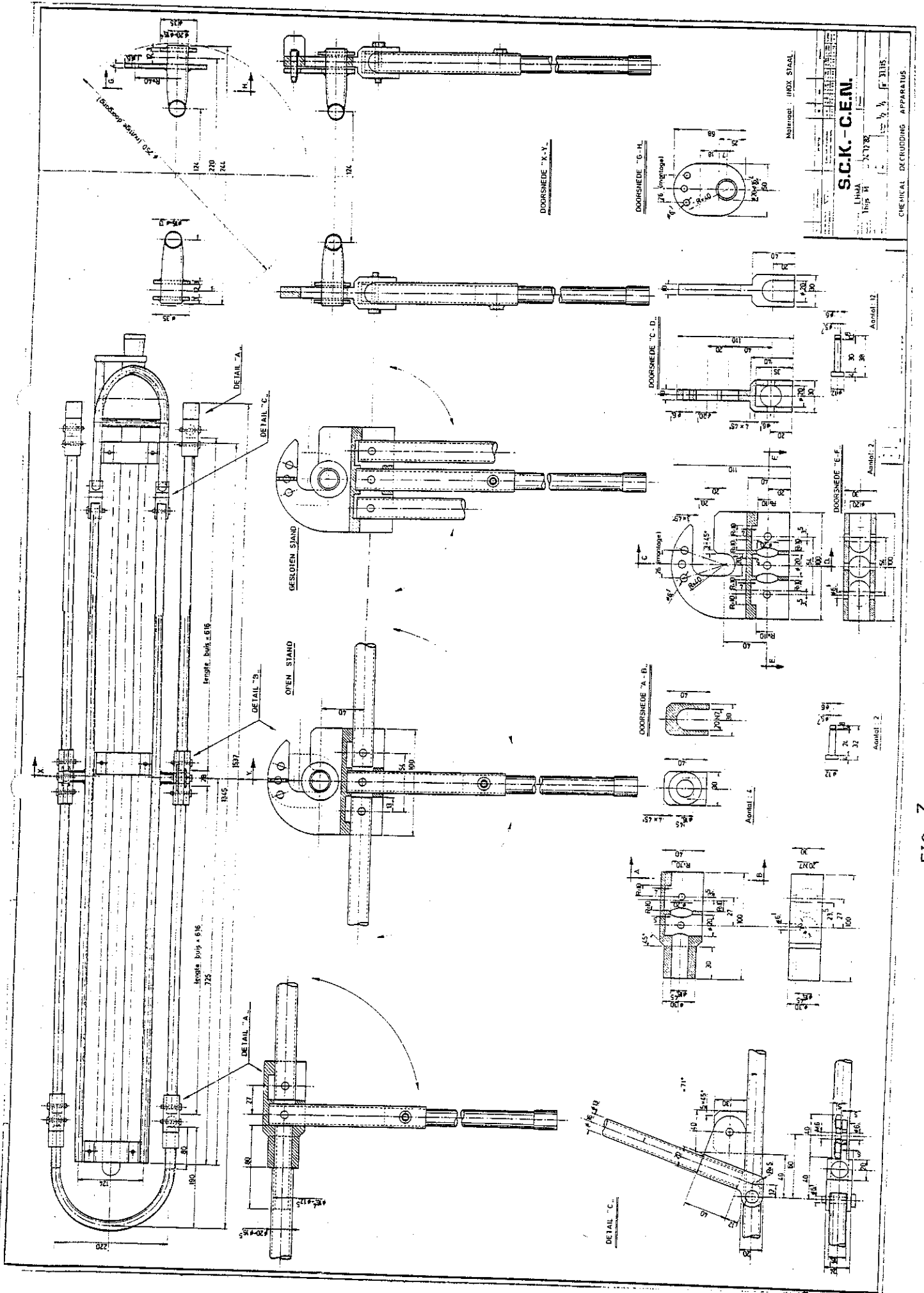


FIG. 3 CHEMICAL DECRUDDING : METALLIC FRAME.

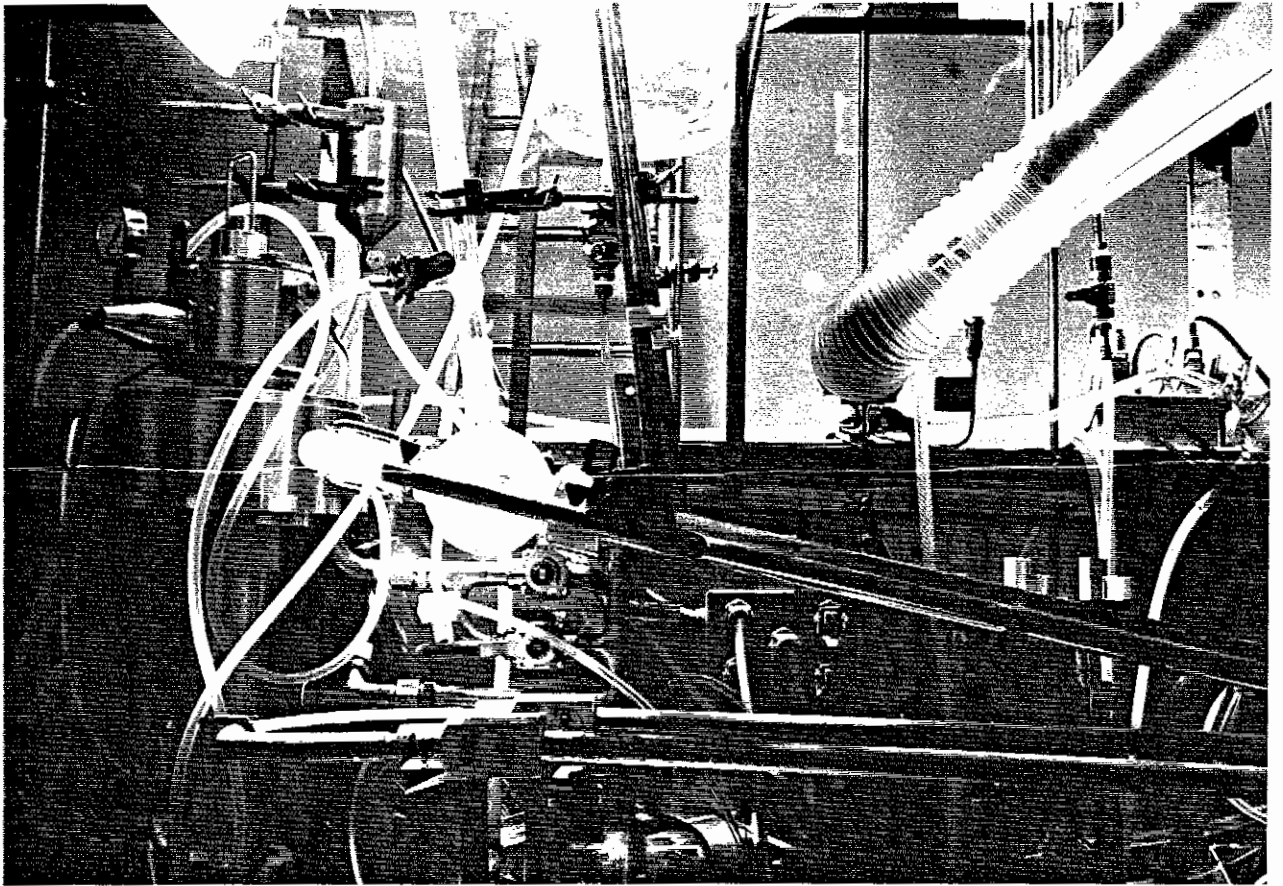


FIG. 4.

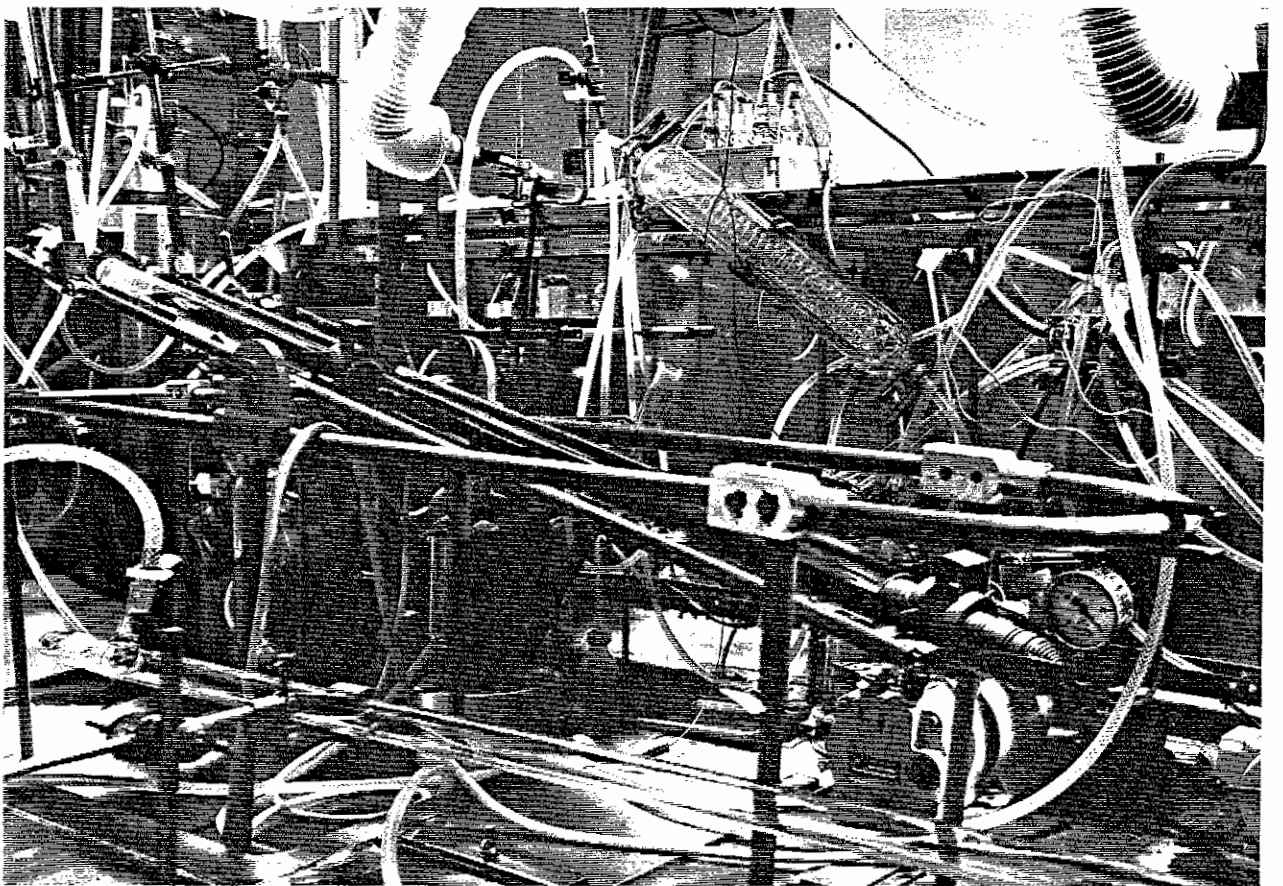


FIG. 5.

INSTALLATION IN THE HOT CELL.

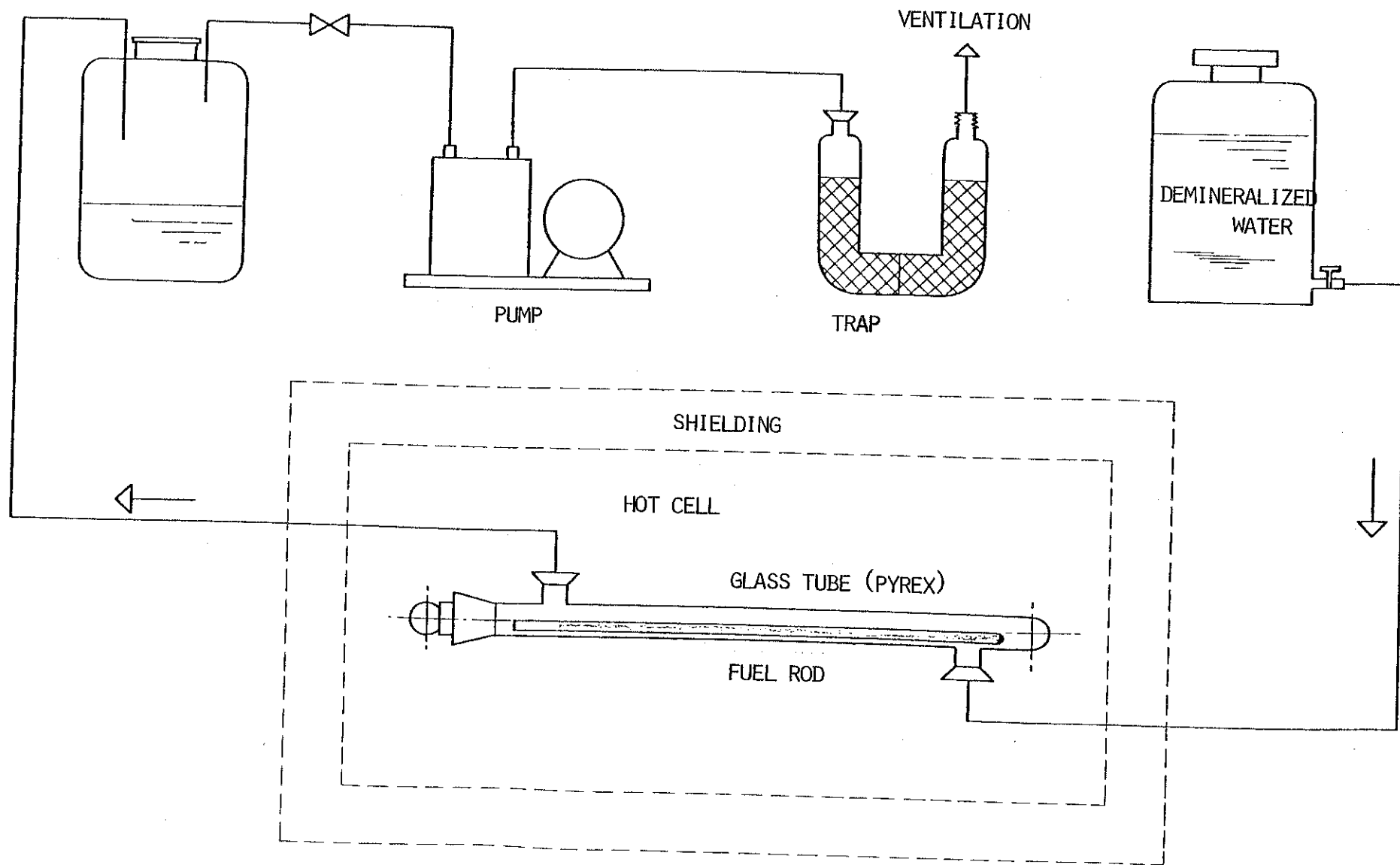


FIG. 6 CHEMICAL DECRUDDING : RINSING APPARATUS.

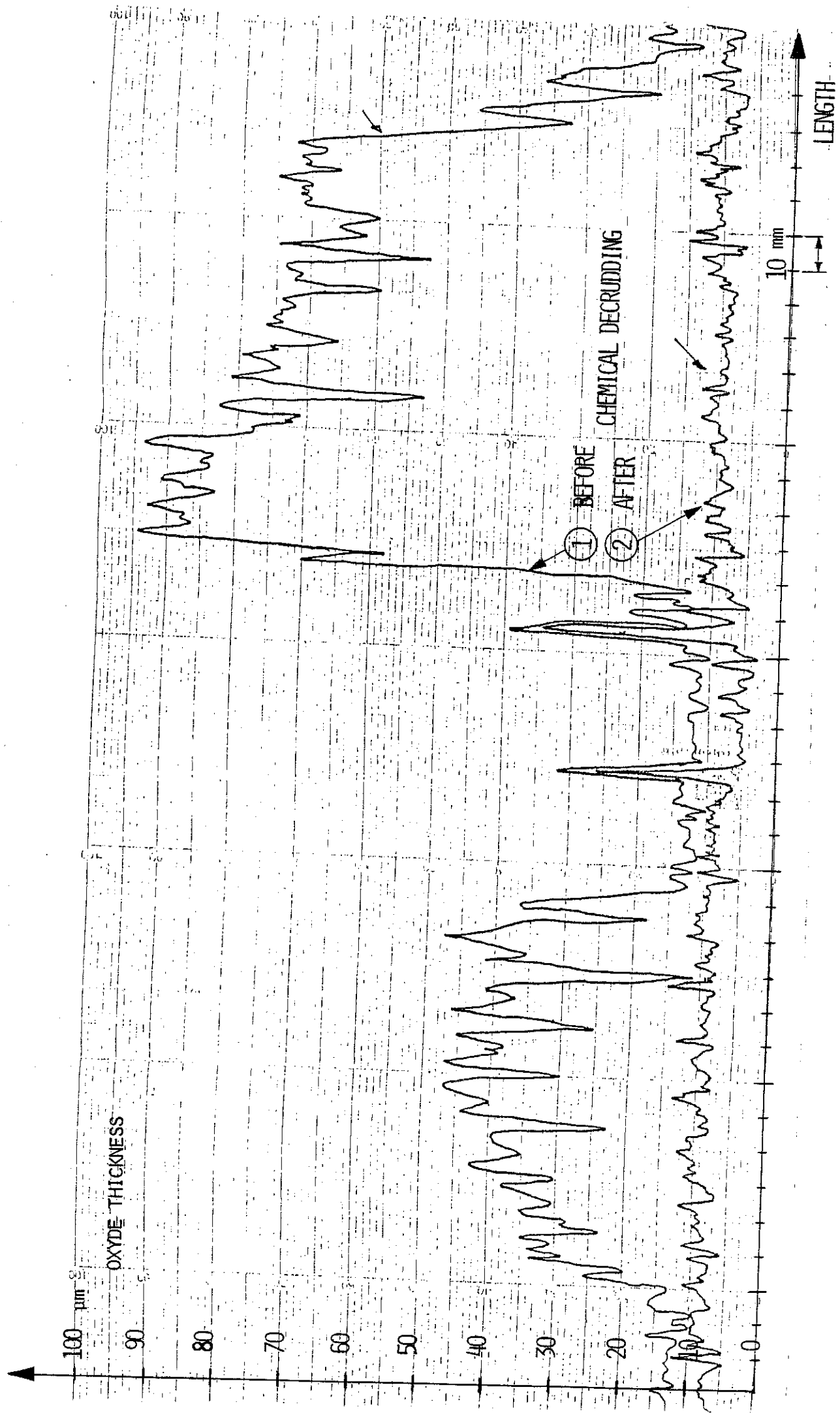


FIG. 7 OXYDE THICKNESS MEASUREMENTS BEFORE AND AFTER CHEMICAL DECRUDDING.