

The removal of neutron poisons,
in particular ^{135}Xe and ^{135}I , from an aqueous
homogeneous suspension reactor

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
TECHNISCHE WETENSCHAP AAN DE TECHNISCHE HOGESCHOOL TE DELFT
OP GEZAG VAN DE RECTOR MAGNIFICUS DR. R. KRONIG,
HOGLERAAR IN DE AFDELING DER TECHNISCHE NATUURKUNDE,
VOOR EEN COMMISSIE UIT DE SENAAAT TE VERDEDIGEN
OP WOENSDAG 13 JUNI 1962 DES NAMIDDAGS TE 4 UUR DOOR

PIETER JOB KREIJGER

NATUURKUNDIG INGENIEUR
GEBOREN TE SOERAKARTA

BIBLIOTHEEK
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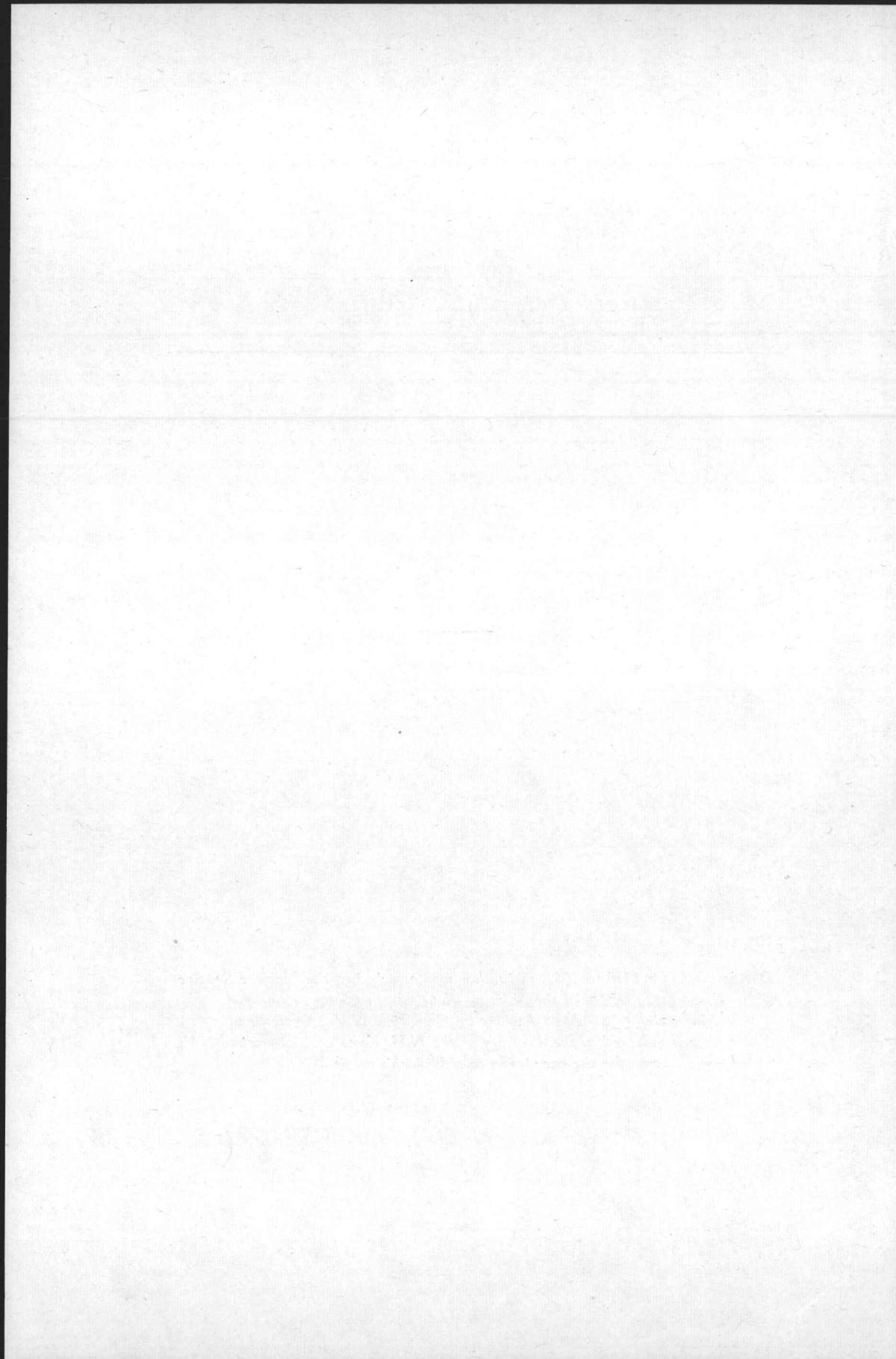
1962

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Dit proefschrift is goedgekeurd door de promotoren
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*During the years 1956 to 1961, the author was attached to the Nuclear Reactor Laboratory (KRL) of the N.V. tot Keuring van Electrotechnische Materialen (KEMA) at Arnhem by Comprimo N.V., Amsterdam.
The author is indebted to the directors of the N.V. Kema and Comprimo N.V. for the permission to publish this thesis.*



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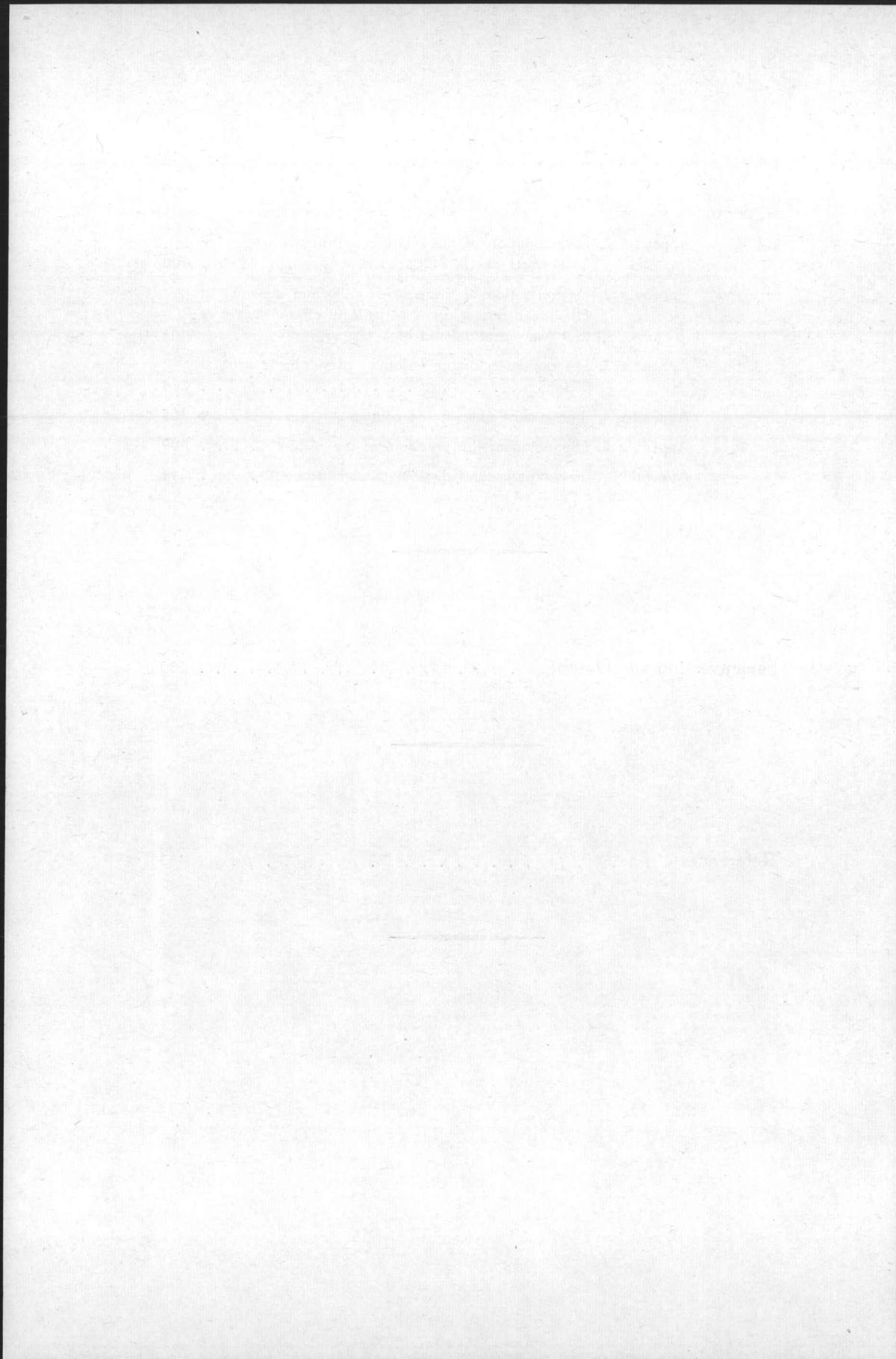
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PART I

General considerations on the purification of aqueous homogeneous suspension reactors

1. Introduction

Though homogeneous liquid fuel reactors are as yet in an experimental stage only, such reactors have been under consideration already from the beginning. *Urey* [1] described in 1943 a proposal for a heavy water slurry pile. The absence of construction materials in a homogeneous reactor (e.g. canning of fuel elements) opens the possibility to obtain a high conversion with a thermal reactor. The conversion factor can be put at about one or even more than one by using heavy water as a moderator, ^{233}U as fissionable material and ^{232}Th as fertile material. During reactor operation the mixture of fuel and moderator should then be processed to a certain extent so as to remove neutron absorbing materials viz. corrosion and fission products. This is the subject of the present thesis.

Reactors using a liquid fuel can be purified during operation and the concentration of parasitic neutron absorbing materials (poisons) can be maintained at a sufficiently low level. These neutron absorbing materials can be classified into the following categories:

- a) erosion and corrosion products (from the materials of construction);
- b) $^{135}\text{Xe}^*$ (and its precursor in the decay chain $^{135}\text{I}^{**}$);
- c) $^{149}\text{Sm}^*$;
- d) other fission products.

* ^{135}Xe is a fission product with a relatively high yield and extremely high cross section for the thermal neutron capture.

The Samarium isotope, ^{149}Sm , is a fission product with lower yield and cross section for neutron capture.

** The greater part of ^{135}Xe is formed by ^{135}I decay.

Several authors (*Wells and Lofthouse* [2], *Tongue and Jenkins* [3], *Bruce* [4]) discussed the removal of these poisons and its results for aqueous homogeneous two region reactors with a fissile fuel solution of UO_2SO_4 in D_2O in the inner region. *Robinson* [5] studied the removal of xenon from a molten salt reactor.

2. Reasons behind the purification of a one region aqueous homogeneous suspension reactor

Here, we shall restrict ourselves to a one region aqueous homogeneous suspension reactor with circulating fuel. The specific properties and advantages of this type of reactor have been described by *Went* [6]. The suspension is composed of ThO_2 — UO_2 particles in heavy water. The particles have such dimensions that the recoil range of the fission products is larger than the particle diameter. Furthermore, the particles have to be uniformly dispersed in the liquid phase during the hold-up of the suspension in the reactor. The fission products will then, for the greater part, leave the particles and accumulate in the continuous liquid phase. By purification of this liquid phase alone, the concentration of the neutron absorbing material in the reactor can be reduced to a lower limit, which is then determined by the amount of fission products left in the fuel particles, i.e. by the recoil efficiency. However, measures have to be taken to prevent the agglomeration of the particles resulting in apparently larger particles and the precipitation of the poisons already present in the water phase on the fuel particles by which the advantages of the recoil effect would be reduced. This precipitation can be prevented by adding a second adsorbent to the slurry with a large competing surface with respect to the fuel particle surface. *Hermans* and *Van der Plas* [7] suggested to use active coal as a second adsorbent.

The energy liberated on fission is not entirely available in the form of immediate heat production. Part of the fission energy is delayed and it is produced in the form γ - and β -radiation of the fission products. If the reactor has produced power during a long time, for instance 1000 hours, then approximately 6 % of the power originates from delayed radiation of the radioactive fission products. Thus, at the moment of a reactor shut-down, still 6 % of the power is

generated. This delayed power production decreases in course of time after shut-down as indicated in table I.1.

TABLE I.1

Decay heat from fission products after a reactor shut-down

% of initial power	time after shut-down
6.0	0
5.2	10 sec.
2.5	10 min.
0.9	10 hours
0.05	10 days

The relatively heavy fuel particles can easily be separated from the continuous phase by using a hydrocyclone. The fuel can then be collected in a small storage vessel which is in open connection with the heavy phase outlet of the cyclone. At a low recoil efficiency the greater part of the fission products is left in the particles and consequently the delayed heat is produced within the particles. In that case the application of a hydrocyclone and storage vessel as a device for fuel concentration control becomes practically impossible due to the high specific power produced in the settled bed of fuel particles in the storage vessel. Since this specific power is of the same order of magnitude as that produced in the reactor, this is another reason for using a high value of the recoil efficiency.

The effect of a poison on the operation of a reactor can be expressed by means of the poisoning factor W . It is defined as the ratio between the number of thermal neutrons absorbed by the poison and the number absorbed in fissionable material. When it is small, W is practically equal to the negative reactivity introduced by the poison [8]. The poisoning factor is proportional to the concentration of specific poison. The concentration of the erosion and corrosion products will depend on the rate at which these products are formed. It is supposed that the corrosion of construction material is introduced by the erosion of the protecting oxide layer on stainless steel. It

seems possible to limit this erosion to an acceptable value by applying a good hydrodynamical design of the system. However, in several components e.g. pumps, hydrocyclone and valves some erosion by slurry particles can not be avoided. In these cases the selection of special materials such as for instance stellite can be of advantage. In general, however, the concentration of the erosion and corrosion products will increase as the ratio between the wall surface of the slurry system and the volume increases. The wall surface of the slurry system is mainly located in the heat exchanger, while the volume of the system is for the greater part located in the reactor core. The ratio between the core volume and the volume of the

TABLE I.2

Properties of a 600 MW (th) one region aqueous homogeneous suspension reactor

Reactor power	600 MW (thermal)
Power density	25 MW/m ³
Reactor vessel diameter	3.6 m
Reactor vessel volume	24 m ³
Total slurry volume	50 m ³
Heat flux in the heat exchanger	0.2 MW/m ²
Concentration of fissile material ²³³ UO ₂	4.5 kg/m ³
Concentration of fertile material ThO ₂	300 kg/m ³
Average thermal neutron flux	1.4 × 10 ¹⁴ n/sec cm ²
UO ₂ — ThO ₂ particle size	5 μ
Recoil efficiency	90 %
Maximum temperature	300° C
Temperature drop over the reactor	27° C
Slurry flow rate	5.7 m ³ /sec
Linear flow velocity in piping and heat exchanger	4.5 m/sec

system outside the reactor should be small so as to minimize fuel investment. A ratio of 1:1 seems acceptable and possible in this respect. As the heat exchanger surface is determined by the heat flux applied and the core volume is proportional to the power; the wall surface to volume ratio or the surface to power ratio can be considered to be more or less constant for suspension reactors, when the same power density is applied.

As an example we now wish to consider a one region aqueous homogeneous suspension reactor which is supposed to have the properties as listed in table I. 2.

In fig. I. 1 the poisoning due to the said poisons is plotted against the duration of reactor operation if no purification at all exists. The mean erosion and corrosion rate (decrease in wall thickness) is assumed to show an average of approx. 0.1 mm/year of stainless steel. This rate of erosion and corrosion may be expected for aqueous ThO_2 slurries [9, 10, 11]. The curves in fig. I. 1 show clearly that, under these assumptions, after a relatively short time the poisoning

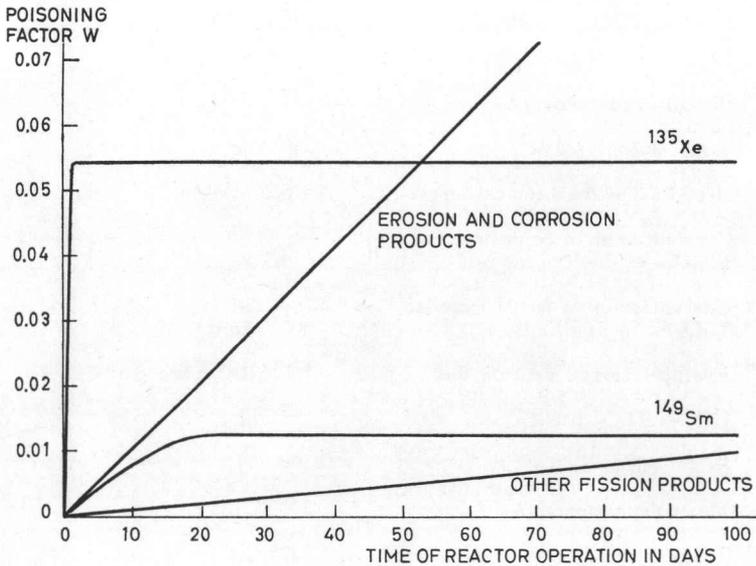


Fig. I. 1

The poisoning of a 600 MW aqueous homogeneous one region slurry reactor. No purification.

due to erosion and corrosion products reaches such a value that the fuel has to be reprocessed. After 100 days of reactor operation the poisoning factor W is approx. 0.15 and a proper operation becomes difficult.

The amount of energy, which can be extracted from the nuclear fuel before replacement must take place, is expressed in the number of mega-watt-days produced by one ton of fuel and is called "burn-up". If it is possible to split all the UO_2 and ThO_2 initially present, the burn-up is 9×10^5 MWd/ton. Replacement of the fissionable material (including fertile material) after 100 days is equivalent to a burn-up of 4000 MWd/ton, so that less than 0.5 % of the fuel atoms is used. With gas cooled reactors a burn-up of 1200 MWd/ton has been reached and a burn-up of 3000 MWd/ton is expected with modern gas-cooled reactors. In a present-day pressurized water reactor a burn-up of 2000 MWd/ton has been reached and a figure of at least 10,000 MWd/ton is considered in future.

The fuel cost is for a great deal determined by the burn-up because both the reprocessing and refabrication of the fuel elements are expensive. For an advanced type of reactor e.g. the aqueous slurry reactor, anyhow a high burn-up of at least many thousands MWd/ton seems desirable, presuming that the reprocessing cost of the fuel is not low. At this time no figures are available for the reprocessing costs of a slurry fuel. In contrast to the assumption made above, it might be that the reprocessing costs of a slurry are only a small figure when compared to that of fuel elements for heterogeneous reactors. Reasons for this are the possibility for remote production of the particles, which avoids the necessity of a long cooling time (i.e. six month for fuel elements) and a high decontamination factor of the spent fuel. If the refabrication of the fuel is cheap, the argument for purification of the liquid fuel during reactor operation for obtaining a high value for the burn-up becomes less dominant.

A small rate of liquid purification will decrease the poisoning due to erosion and corrosion to an acceptable low value. If the fuel particles can withstand a sufficient dose and, for the greater part, keep their original size, this liquid flow can be taken off from a suspension reactor without the entrainment of particles by using a device for phase separation, thus minimizing the entrainment of fuel

from the reactor. In fig. I.2 the poisoning factor of the specific poisons is plotted against the duration of reactor operation when a liquid flow of 2 % of the slurry volume per hour is continuously taken off from the reactor and completely purified before recycling. The poisoning due to erosion and corrosion is now of minor importance. The ^{149}Sm poisoning has been decreased to 1/3 of the value without purification. However, the ^{135}Xe poisoning shows only a small decrease at this rate of purification. A further step for improving neutron economy must than be the depression of ^{135}Xe concentration.

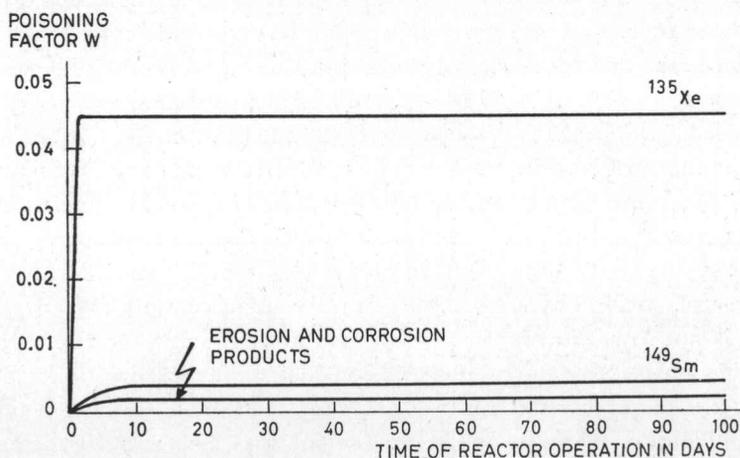


Fig. I. 2

The poisoning of a 600 MW aqueous homogeneous one region slurry reactor. Purification of 2 % of the liquid phase of the slurry per hour.

Another reason which makes a further decrease of the ^{135}Xe concentration necessary in the rise in the ^{135}Xe concentration after a power drop. This build-up of ^{135}Xe occurs, because at the moment the neutron flux is diminished, the absorption of neutrons by ^{135}Xe decreases and the ^{135}Xe removal only takes place by its radioactive decay which has a half-life of 9.7 h. On the other hand, the production of the ^{135}Xe , formed for the greater part by ^{135}I decay (half-life 6.7 h), is only slowly decreased. So, after a power drop the

production of ^{135}Xe initially exceeds the removal rate by decay to ^{135}Cs . Since after a power reduction the ^{135}I concentration decreases with time and the removal of ^{135}Xe is proportional to its concentration, at a certain moment the ^{135}Xe concentration will pass through a maximum after which it will decrease to zero. The maximum ^{135}Xe concentration is highly dependent on the neutron flux. In fig. I. 3 the poisoning factor for ^{135}Xe after a reactor shut-down is plotted against time. At a neutron flux of 1.4×10^{14} n/cm² sec and a volume of the system outside the reactor equal to the reactor volume, the maximum value of W is approximately 0.23 and it takes about 50 hours before the poisoning is lowered to the initial value. Even if 2 % per hour of the liquid phase of the suspension is cleaned during operation and after shut-down, the increase in poisoning is still considerable. Without further removal of ^{135}Xe from the reactor this build-up will lead, after a reduction of power, to a complete shut-down during more than one day. In a nuclear power plant such an intermission in the power production may be intolerable and hence a more complete removal of ^{135}Xe and (or) ^{135}I is necessary.

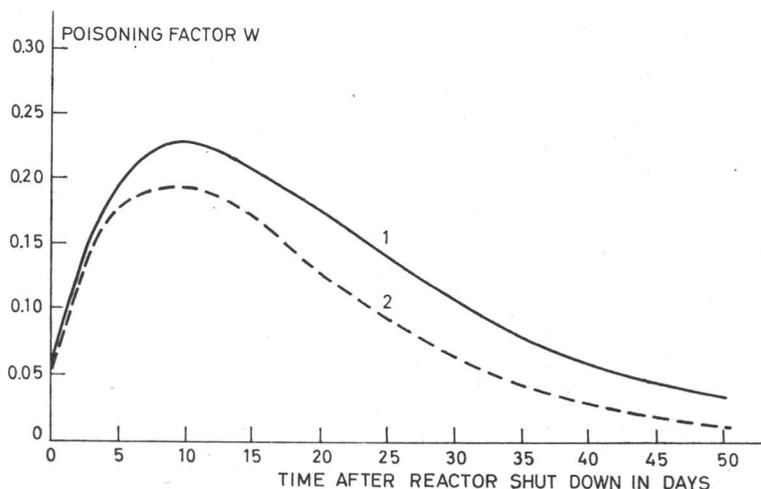


Fig. I. 3

^{135}Xe build-up after shut down of the 600 MW reactor;

1) Without purification,

2) with purification of 2 % of the slurry before and after shut down.

Summarizing, it can be concluded that the removal of erosion and corrosion products is primarily necessary to obtain a high burn-up and conversion. The removal of ^{135}Xe has to be carried out for further increasing of the conversion and to eliminate ^{135}Xe build-up after a power reduction. In order to diminish the production of decay heat at undesirable locations and to decrease the content of radioactivity of the system after a reactor stop, other fission products have to be removed as well.

3. Aim of this study

The reasons outlined in the preceding section have led to the design of a processing system, capable of reducing the poisoning in an aqueous homogeneous suspension reactor. The purification process should preferably be based on simple physical principles rather than on chemical ones, which would require an intricate system of control.

The medium which has to be decontaminated is heavy water. To limit the investment of this expensive material, the hold-up outside the reactor must be kept as small as possible. The rate of decontamination is small compared with that applied in reprocessing of conventional solid fuel elements. As a consequence, the processed heavy water is, even after removal of the relevant poisons, highly radioactive and thus difficult to handle. Therefore, it is desirable to carry out the purification under system pressure, permitting a simple recycling of the processed heavy water into the reactor system.

The poison can be present in several forms:

- a) Volatile and thus removable via the gas phase (xenon, krypton, while also iodine and bromine can be volatile if in the molecular form).
- b) Non-volatile and insoluble; some of these will be adsorbed on the second adsorbent, others will form separate particles.
- c) Non-volatile and soluble.

The iodine can be present in several chemical forms e.g. the volatile form I_2 and the non-volatile forms I^- and IO_3^- . The volatile form is predominant in the presence of excess of oxygen [9], e.g. due to a high rate of water decomposition.

Xenon can be removed directly by processing the gas phase of the system, or by removing iodine, its precursor in the decay chain. The

latter can be achieved by processing the gas or liquid, depending upon the volatility of iodine.

The system to be installed for purifying the liquid phase should be able to remove primarily the erosion and corrosion products. However, also non-volatile iodine, samarium and other fission products should be eliminated.

In part II of this thesis the ^{135}Xe removal by purification of the gas phase and the removal of ^{135}I by purification of the liquid- or gas phase will be discussed. General relationships will be derived for describing the behaviour of the purification system. The required rate of elimination and the corresponding value of the poisoning factor will not be considered since this is a matter of optimization of the reactor design and has to be considered for each case separately.

The proposed purification systems will be worked out for the 250 kW aqueous homogeneous experimental suspension reactor K.S.T.R., (Kema Suspension Test Reactor), which has already been described elsewhere [12]. This is a one region aqueous homogeneous suspension test reactor, designed for supplying information on the behaviour of the suspension and on a number of process variables such as power density limit, power fluctuations, power control, efficiency of continuous removal of neutron poisons, rate of radiolytic water decomposition, erosion and corrosion under radiation conditions. For reasons of neutron physics, in this small reactor light water will be used as a moderator instead of heavy water. In order to prevent boiling inside the reactor a hydrogen overpressure will be applied.

It will appear that the rate of liquid to be purified is entirely determined by the necessity of ^{135}I removal; the elimination of the other poisons in the liquid being a problem of secondary importance (see part II. 5).

Whereas the measures to be taken for the removal of ^{135}Xe can be based on the well-known properties of xenon, the information needed for the separation of iodine from the liquid phase is insufficient. In this respect it is important to know whether the iodine is in the volatile form or not. As was already mentioned, the volatile form of iodine, e.g. I_2 , can only exist under oxidizing circumstances. Because the reactor is kept under overpressure with hydrogen gas, the presence of I_2 in the reactor seems less probable.

Therefore, iodine can be removed from the reactor simultaneous with the removal of other non-volatile products by processing a small liquid flow from the reactor system. During this processing these products have to be concentrated before they are discharged from the system. As will be discussed in part II. 4, this concentration can be best realized by evaporation. In the evaporator a high level of radioactivity will exist and water decomposition may then lead to oxidizing circumstances in the absence of hydrogen. In this case volatile iodine may be formed as a consequence of which I_2 is swept out from the evaporator together with the steam. Therefore, a study was carried out on the separation by distillation of trace amounts of iodine from water in a rectifying column at a temperature of 270—275° C. This work will be reported in part III of the present thesis.

PART II

Discussion of the possible purification processes for the removal of poisons, particularly ^{135}Xe and its precursor ^{135}I

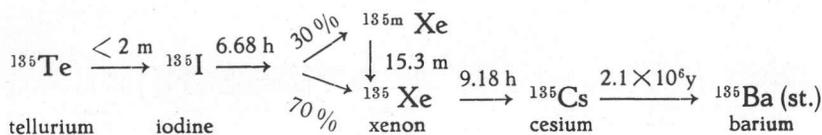
1. Derivation of the general equation for the elimination of ^{135}Xe

The purpose of this chapter is to calculate the amounts of the ^{135}I and ^{135}Xe present in the primary circuit of the reactor system under steady operation with ^{135}I and ^{135}Xe removal from the liquid phase.

Due to the recoil effect, part of these fission products will remain in the solid particles and thus in the system. Expressions for the ^{135}I and ^{135}Xe concentrations in the solids are derived in 1.1. The concentrations in the liquid phase are calculated in 1.2 where the continuous removal of a part of these substances is taken into consideration (1.2). Finally the results of 1.1 and 1.2 are combined to give the overall average concentration of ^{135}I and ^{135}Xe in the primary circuit, among other things as a function of the purification constants. From this study it is in principle possible to determine the values of these parameters desired for proper operation of the reactor.

Before we proceed to these calculations, the decay process leading to ^{135}Xe and the corresponding physical data will be reviewed.

The ^{135}Xe isotope is partly formed from fissions and partly formed by decay of its precursors in the decay chain. The decay chain of the fission products with an atomic mass of 135 for ^{235}U fission according to *Prawitz* [13] is shown below with the corresponding half-lives:



Cumulative yield: ${}^{135}\text{I}$, $\gamma_1 = 6.1\%$; ${}^{135}\text{Xe}$, $\gamma_1 + \gamma_2 = 6.4\%$.

Thermal neutron cross section for ${}^{135}\text{Xe}$: $\sigma_2 = 2.7 \times 10^{-18} \text{ cm}^2$.

Only 70 % of the ${}^{135}\text{I}$ decays directly to ${}^{135}\text{Xe}$, 30 % decays firstly to the excited state of the ${}^{135}\text{Xe}$ nucleus: ${}^{135\text{m}}\text{Xe}$.

However, in the following discussion it will be assumed that all the iodine is transferred directly to the non-excited state of ${}^{135}\text{Xe}$ because the half-life of the excited state is small as compared to that of the non-excited state. The cumulative yield, giving the percentage of a certain isotope formed from one fission, is for ${}^{135}\text{I}$: $\gamma_1 = 6.1\%$. The direct yield of ${}^{135}\text{Xe}$, i.e. the fraction of ${}^{135}\text{Xe}$ formed directly from fissions, is: $\gamma_2 = 0.3\%$. Thus, the cumulative yield of ${}^{135}\text{Xe}$ is: $\gamma_1 + \gamma_2 = 6.4\%$. For ${}^{238}\text{U}$ fissions, the cumulative yield of ${}^{135}\text{Xe}$ is slightly different; according to *Ivanov et al.* [14] it is: $\gamma_1 + \gamma_2 = 5.8\%$.

Due to the recoil effect, a fission product present in the suspension reactor is supposed to be distributed over:

- the solid phase for a fraction $1 - \beta$,
- the liquid phase for a fraction β .

1.1. ${}^{135}\text{I}$ and ${}^{135}\text{Xe}$ in the solid phase of the suspension

${}^{135}\text{I}$ in the solid phase

In the steady state the material balance for ${}^{135}\text{I}$, which expresses that the rate of production of ${}^{135}\text{I}$ is equal to its decay rate, becomes:

$$(1 - \beta) \gamma_1 N - \lambda_1 J_s = 0, \quad 1.1$$

or:

$$J_s = (1 - \beta) \frac{\gamma_1 N}{\lambda_1}. \quad 1.2$$

J_s is the total number of ${}^{135}\text{I}$ atoms present in the solid phase in the primary system; λ_1 is the decay constant of ${}^{135}\text{I}$ and N the total number of fissions per second in the reactor; the latter is given by:

$$N = \Sigma_f \varphi V_R, \quad 1.3$$

where Σ_f is the macroscopic cross section for fissions, φ the average thermal neutron flux and V_R the volume of the reactor. The solid phase, present in the primary system with a total volume V_T , occupies a volume of $a V_T$, where a is the volume fraction of solids. Thus the concentration of ^{135}I in the solid phase expressed as the number of nuclei per unit of solids volume is:

$$I_s = \frac{J_s}{a V_T}, \quad 1.4$$

and from 1.2:

$$I_s = \frac{(1 - \beta) \gamma_1 N}{a \lambda_1 V_T}. \quad 1.5$$

If φ' is defined by:

$$\varphi' = \varphi \frac{V_R}{V_T}, \quad 1.6$$

we can write for I_s :

$$I_s = \frac{(1 - \beta) \gamma_1 \Sigma_f \varphi'}{a \lambda_1}. \quad 1.7$$

^{135}Xe in the solid phase

In the steady state the production of ^{135}Xe by fissioning and by ^{135}I decay is equal to the ^{135}Xe decay rate and the rate of conversion of ^{135}Xe by neutron absorption. Thus the material balance gives:

$$(1 - \beta) \gamma_2 N + \lambda_1 J_s - \left(\lambda_2 + \sigma_2 \varphi \frac{V_R}{V_T} \right) Y_s = 0, \quad 1.8$$

or:

$$Y_s = (1 - \beta) \frac{(\gamma_1 + \gamma_2) N}{\lambda_2 + \sigma_2 \varphi'}. \quad 1.9$$

Y_s is the total number of ^{135}Xe atoms present in the solid phase of the primary circuit, λ_2 is the decay constant of ^{135}Xe , σ_2 is the cross section for thermal neutrons of ^{135}Xe . For X_s , the amount of ^{135}Xe present in the solid phase per unit volume of solids, we have:

$$X_s = \frac{Y_s}{a V_T}. \quad 1.10$$

Substitution of 1.9, 1.3 and 1.6 into 1.10 gives:

$$X_s = \frac{(1 - \beta)(\gamma_1 + \gamma_2) \Sigma_f \varphi'}{a(\lambda_2 + \sigma_2 \varphi')}. \quad 1.11$$

1.2. ^{135}I and ^{135}Xe in the liquid phase of the suspension

In analogy to the decay constant, λ , a purification constant, λ^+ , is defined as the ratio of the amount of material removed per second by purification and the amount of material present.

^{135}I in the liquid phase

In the steady state the production is equal to the decay rate and the removal by purification.

Hence:

$$\beta \gamma_1 N - \lambda_1 J_l - \lambda_1^+ J_l = 0, \quad 1.12$$

or:

$$J_l = \frac{\beta \gamma_1 N}{\lambda_1 + \lambda_1^+}. \quad 1.13$$

J_l is the amount of ^{135}I present in the liquid phase; $\lambda_1^+ J_l$ is the amount of ^{135}I that is removed per second by purification. The ^{135}I concentration in the liquid phase is:

$$I_l = \frac{J_l}{(1 - a) V_T}, \quad 1.14$$

which can be written as:

$$I_l = \frac{\beta \gamma_1 \Sigma_f \varphi'}{(1 - a)(\lambda_1 + \lambda_1^+)}. \quad 1.15$$

^{135}Xe in the liquid phase

The production of ^{135}Xe is equal to the sum of the decay rate, the

rate of removal by purification and the rate of conversion of ^{135}Xe by neutron absorption:

$$\beta \gamma_2 N + \lambda_1 J_l - (\lambda_2 + \lambda_2^+ + \sigma_2 \varphi') Y_l = 0. \quad 1.16$$

Substitution of 1.13 into 1.16 leads to:

$$Y_l = \beta \frac{(\gamma_1 + \gamma_2) N}{\lambda_2 + \lambda_2^+ + \sigma_2 \varphi'} \left(\frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\lambda_1}{\lambda_1 + \lambda_1^+} \right). \quad 1.17$$

The concentration of ^{135}Xe in the liquid phase is:

$$X_l = \frac{Y_l}{(1 - a) V_T}. \quad 1.18$$

Substitution of 1.17 into 1.18 gives with 1.3:

$$X_l = \frac{\beta}{1 - a} \cdot \frac{(\gamma_1 + \gamma_2) \Sigma_f \varphi'}{\lambda_2 + \lambda_2^+ + \sigma_2 \varphi'} \left(\frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\lambda_1}{\lambda_1 + \lambda_1^+} \right). \quad 1.19$$

1.3. The average ^{135}Xe concentration in the suspension and the purification factor

The average ^{135}Xe concentration is given by:

$$X = aX_s + (1 - a) X_l. \quad 1.20$$

This gives with 1.11 and 1.19:

$$X = \frac{(\gamma_1 + \gamma_2) \Sigma_f \varphi'}{\lambda_2 + \sigma_2 \varphi'} \left\{ 1 - \beta + \beta \frac{\lambda_2 + \sigma_2 \varphi'}{\lambda_2 + \lambda_2^+ + \sigma_2 \varphi'} \left(\frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\lambda_1}{\lambda_1 + \lambda_1^+} \right) \right\}, \quad 1.21$$

or:

$$X = X_o \{\xi\}. \quad 1.22$$

The factor ξ defined above will be called the purification factor; without purification ($\lambda_1^+ = \lambda_2^+ = 0$) its value is 1 and $X = X_o$.

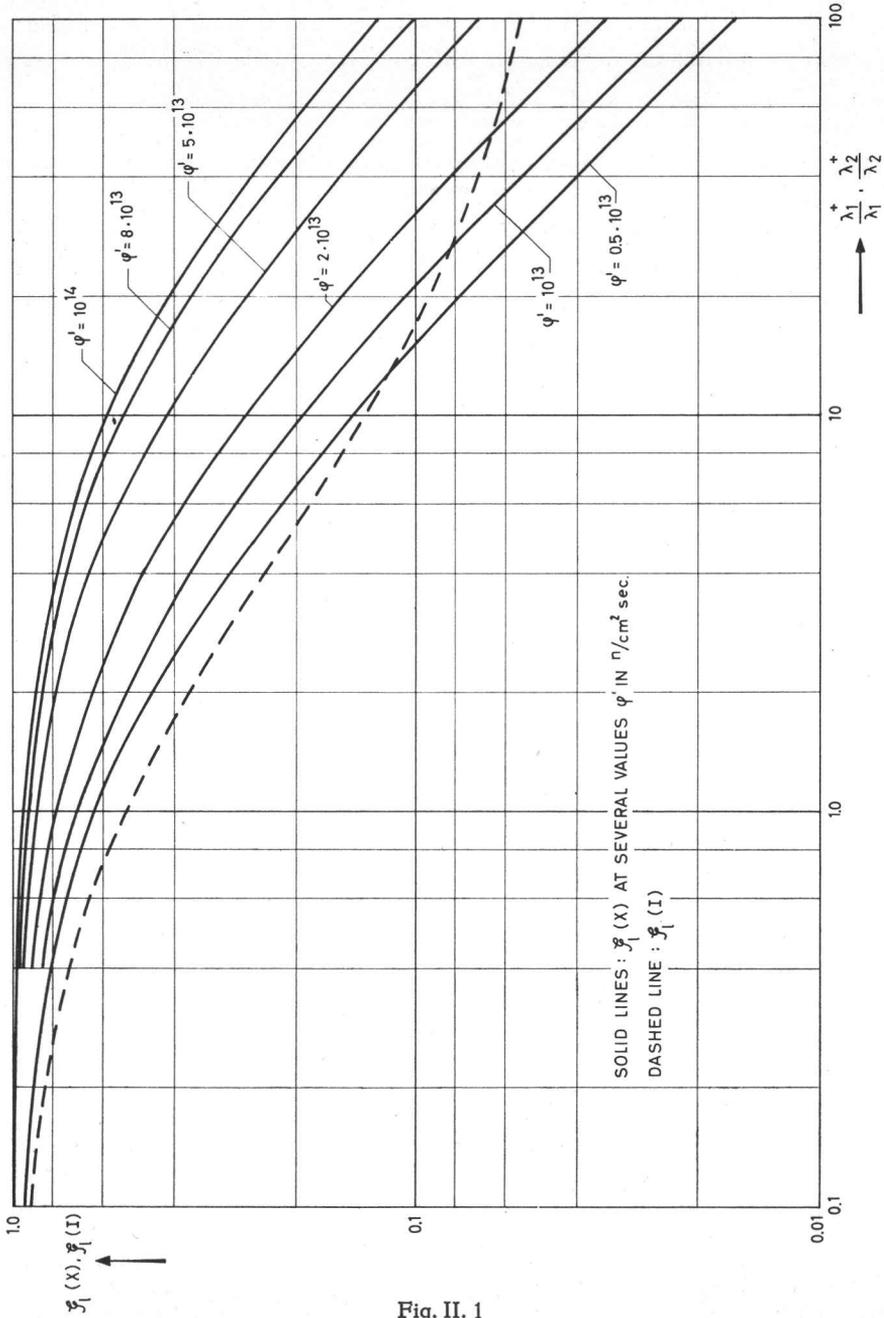


Fig. II. 1

The purification factors, $\xi_i(X)$ and $\xi_i(I)$, for ^{135}Xe in the liquid phase as a function of the purification constants of ^{135}Xe , λ_2^+ , and ^{135}I , λ_1^+ .

As can be seen from 1.21, ξ is composed of the term $1 - \beta$ and a term proportional to β ; we will call the proportionality factor of the latter term ξ_l , the purification factor of the liquid phase.

Thus:

$$\xi = (1 - \beta) + \beta \xi_l, \quad 1.23$$

ξ_l can be regarded as the product of the purification factors $\xi_l(X)$ and $\xi_l(I)$ for the removal of ^{135}Xe and ^{135}I respectively:

$$\xi_l(X) = \frac{\lambda_2 + \sigma_2 \varphi'}{\lambda_2 + \lambda_2^+ + \sigma_2 \varphi'}, \quad 1.24$$

$$\xi_l(I) = \frac{\gamma_2}{\gamma_1 + \gamma_2} + \frac{\gamma_1}{\gamma_1 + \gamma_2} \cdot \frac{\lambda_1}{\lambda_1 + \lambda_1^+}. \quad 1.25$$

As could be expected the limit of the removal of ^{135}Xe from the reactor is determined by the fraction $(1 - \beta)$ of ^{135}Xe left in the particle. This effect is shown clearly in equation 1.23.

From 1.24 and 1.25 it can be seen that $\xi_l(X) \rightarrow 0$, if $\lambda_2^+ \rightarrow \infty$; while $\xi_l(I) \rightarrow \frac{\gamma_2}{\gamma_1 + \gamma_2}$ ($= 0.047$) if $\lambda_1^+ \rightarrow \infty$. This lower limit of $\xi_l(I)$ is to be expected because the ^{135}Xe concentration is determined by its direct fission yield if all the ^{135}I is removed from the reactor before it has formed ^{135}Xe by decay.

With the aid of equations 1.24 and 1.25 a number of cases has been worked out in fig. II.1. As can be observed from this figure $\frac{\lambda^+}{\lambda}$ has to be an order of magnitude greater than 1 if an appreciable reduction in the ^{135}Xe concentration in the liquid is to be obtained.

In the next chapters the several processes will be discussed by which the ^{135}Xe concentration in the liquid phase of the reactor may be reduced both by ^{135}Xe and by ^{135}I removal.

2. The removal of ^{135}Xe from the suspension reactor by means of an auxiliary gas and subsequent decay in the gas phase

Now that the relationships between the purification factor, ξ , and the purification constants, λ_1^+ and λ_2^+ , has been established, the possibilities for removing ^{135}Xe and ^{135}I have to be considered more in detail. It is evident that the gas xenon can best be removed by desorption by means of an auxiliary gas stream after which ^{135}Xe can decay. This purification method will be discussed in this chapter.

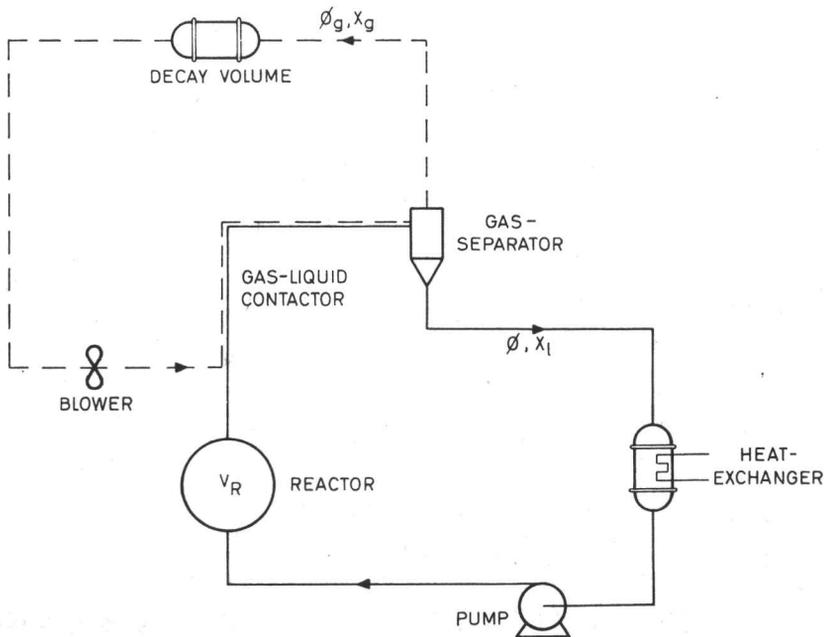


Fig. II. 2

Flow diagram for ^{135}Xe removal with decay in the gas phase.

We shall consider a primary circuit with circulating suspension of fissile material in water. This suspension is successively circulated through the reactor core, a gas-liquid contactor, a gas separator, a heat exchanger and a pump (compare fig. II.2). For the removal of the (volatile) ^{135}Xe , a carrier gas is introduced into the gas-liquid contactor. Depending on the efficiency of the contactor, the gas picks up a certain amount of ^{135}Xe and is recirculated through a decay volume by means of a blower (see fig. II.2).

If the ^{135}Xe concentration of the carrier gas is in equilibrium with the ^{135}Xe concentration in the liquid phase, the following equilibrium relationship between the ^{135}Xe concentration in atoms per m^3 in the gas, X_g , and liquid, X_l , at the outlet of the contactor may be used:

$$X_l = h_x X_g, \quad 2.1$$

h_x is the dimensionless solubility coefficient of Ostwald* in l (xenon gas) per 1 (water).

If ϕ_g m^3/sec carrier gas is circulated through the gas-liquid contactor, $\phi_g X_g$ xenon atoms are removed per second from the primary circuit. In the decay volume the ^{135}Xe concentration decreases by natural decay. The ^{135}Xe concentration at the outlet of the decay volume is given by:

$$\int_0^{\infty} X_g e^{-\lambda_2 t} E(t) dt, \quad 2.2$$

where $E(t)$ is the residence time distribution function which gives the fraction $E(t)dt$ of the fluid at the outlet with a residence time between t and $t + dt$. From the definition of $E(t)$ it follows that:

* For low concentrations of the gas in water, the coefficient of Ostwald can be expressed in the more familiar Henry constant, \mathcal{H} , according to:

$$h = \frac{1.244 \rho_l}{\mathcal{H}} \cdot \frac{T}{273},$$

where \mathcal{H} is expressed in moles of xenon per mole water per atmosphere of xenon pressure at the temperature T ($^{\circ}\text{K}$) and ρ_l is the density of water in kg/m^3 . At 250°C $h = 1/7$. The solubility of xenon in heavy water is practically equal to the solubility in light water [20].

$$\int_0^{\infty} E(t) dt = 1. \quad 2.3$$

The amount of ^{135}Xe that has decayed during the hold-up of the circulating gas in the decay volume is:

$$m = \phi_g X_g (1 - \int_0^{\infty} e^{-\lambda_2 t} E(t) dt). \quad 2.4$$

The amount of ^{135}Xe that is removed by decay is proportional to the amount ^{135}Xe that is present in the decay volume. The latter amount is large if the time during which decay takes place is short. For this reason we will only consider small values of $\lambda_2 t$ so that 2.4 can be written as:

$$m \approx \phi_g X_g (1 - \int_0^{\infty} E(t) dt + \lambda_2 \int_0^{\infty} t E(t) dt). \quad 2.5$$

Substitution of 2.3 into 2.5 gives:

$$m \approx \lambda_2 \phi_g X_g \int_0^{\infty} t E(t) dt. \quad 2.6$$

The mean time of residence, τ_g , is defined by:

$$\tau_g = \frac{V_g}{\phi_g} = \int_0^{\infty} t E(t) dt. \quad 2.7$$

ϕ_g being the flow through the decay volume V_g .

Substitution of 2.7 into 2.6 results in:

$$m \approx \lambda_2 V_g X_g, \quad 2.8$$

for $\lambda_2 \tau_g \ll 1$.

We see that the amount of ^{135}Xe removed by decay is independent of the type of flow in the decay volume, i.e. independent of its residence time distribution, if relatively small times of residence are applied. In order to obtain an upper limit for the time of residence at which the decay volume possesses an acceptable difference from its

minimum value at infinitely large values of the throughput, we will take into consideration the third term of the expansion of 2.4.

Then:

$$m \approx \lambda_2 V_g X_g \left(1 - \frac{1}{2} \frac{\lambda_2}{\tau_g} \int_0^{\infty} t^2 E(t) dt \right). \quad 2.9$$

The term $\frac{1}{2} \frac{\lambda_2}{\tau_g} \int_0^{\infty} t^2 E(t) dt$ is the correction, ε , to be considered.

We will investigate its value for two different cases:

- a) The decay volume behaves like a perfect mixer.
- b) The decay volume is a tube with pure piston flow.

Ad a) In a perfect mixer the contents of the vessel is supposed to be so well mixed that the concentration in the vessel is equal to the outlet concentration. The distribution function is given by:

$$E(t) = \frac{1}{\tau_g} e^{-\frac{t}{\tau_g}}, \quad 2.10$$

and the correction is:

$$\varepsilon = \frac{1}{2} \lambda_2 \tau_g \int_0^{\infty} \left(\frac{t}{\tau_g} \right)^2 e^{-\frac{t}{\tau_g}} d \frac{t}{\tau_g} = \lambda_2 \tau_g. \quad 2.11$$

Ad b) A piston flow is characterised by the residence time distribution:

$$E(t) = 0, \quad t \neq \tau_g; \quad 2.12$$

$$\int_0^{\infty} E(t) dt = 1.$$

The correction becomes in this case:

$$\varepsilon = \frac{1}{2} \lambda_2 \tau_g. \quad 2.13$$

Thus, the correction on the minimum decay volume is of the same order of magnitude, irrespective of the type of flow through the decay volume. In practice a deviation of 1 % will be acceptable, thus:

$$\lambda_2 \tau_g = 10^{-2}; \quad 2.14$$

with $\lambda_2 = 2.1 \times 10^{-5} \text{ sec}^{-1}$, the decay volume is only 1 % larger than its capacity at an infinitely large throughput if $\tau_g \approx 500 \text{ sec}$.

Equation 2.8 provides a relation for the rate m , which ^{135}Xe is removed from the primary circuit and the ^{135}Xe concentration in the gasphase, X_g . This rate of ^{135}Xe removal can be expressed in terms of the ^{135}Xe concentration of the liquid phase of the suspension in the gas-liquid contactor, X_l , with the aid of 2.1. If the rate of ^{135}Xe removal from the primary circuit by decay in the gas volume, decay in the primary circuit and neutron capture is small compared to the rate of ^{135}Xe circulated through the primary circuit, the ^{135}Xe concentration in the gas-liquid contactor can be considered to be equal to that in the other parts of the primary circuit. According to the definition of the purification constant for ^{135}Xe , λ_2^+ , (see Ch. 1) the relationship between m and λ_2^+ is:

$$m = \lambda_2^+ X_l V_T (1 - a). \quad 2.15$$

Substitution of 2.1 and 2.8 into 2.15 gives the dependence of the purification constant of ^{135}Xe on the process variables:

$$\lambda_2^+ \approx \frac{\lambda_2 V_g}{h_x V_T (1 - a)}. \quad 2.16$$

As an example, the reduction in the ^{135}Xe poisoning is calculated for the 600 MW(th) aqueous homogeneous suspension reactor that was introduced in part I.2 when discussing the importance of the various poisons. If in that case a decay volume is applied, having a volume of twice the volume of the primary circuit (slurry volume), the ^{135}Xe concentration in the liquid will be reduced to 40 % of the ^{135}Xe concentration without purification. This can be calculated using equation 2.16 and 1.24.

3. The reduction of the ^{135}Xe concentration in the reactor by simultaneous removal of xenon and iodine

Although in principle a considerable reduction in the ^{135}Xe concentration can be obtained by applying desorption of xenon and subsequent decay of ^{135}Xe in the gas phase (compare Ch. 2), it appears to be desirable that also ^{135}I is removed from the liquid phase. This removal has to be carried out by fixation of iodine in some form with a subsequent decay of ^{135}Xe resulting from ^{135}I .

In this chapter the reduction of the ^{135}Xe concentration will be treated by considering the removal of ^{135}I and ^{135}Xe from both the gas and the liquid. The purification process must be capable of concentrating these isotopes outside the reactor in order that a sufficiently large decay rate is obtained in a volume of acceptable dimensions. A flow diagram of the primary system with the gas- and liquid purification system is shown in fig. II.3.

In the core ^{135}Xe and ^{135}I are produced by fissions. The fraction m of the iodine is volatile and the fraction $1-m$ is non-volatile. The rate of ^{135}Xe that is transferred from the liquid phase into the gas phase is small when compared to the rate of ^{135}Xe present in both phases being circulated through the gas-liquid contactor. Therefore, the gases present in the gas phase are assumed to be in equilibrium with the gases in the liquid phase. The flow of circulating carrier gas, ϕ_{g1} enters the gas purification system via the gas separator (with gas volume V_u). Here, the flow is split into two parts viz. ϕ_{g2} and ϕ_{g3} . The latter flow is lead through a condenser where steam is condensed, after which the non condensed gas flows through the decay volume V_{g1} and is returned to the gas-liquid contactor. The flow rate through the decay vessel is ϕ_{g4} .

The gas flow ϕ_{g2} is lead through an iodine adsorption column e.g. a bed of active coal or of silvered pellets. It is assumed that

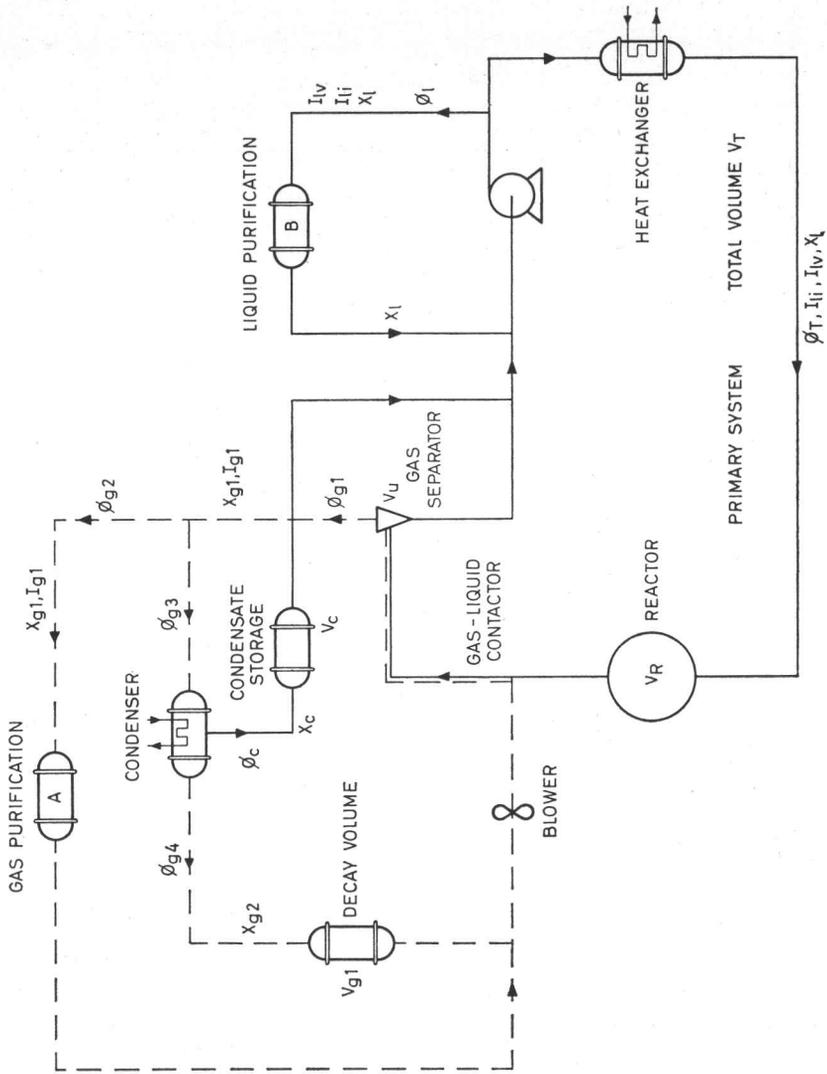


Fig. II. 3

Flow diagram of a one region aqueous homogeneous suspension reactor. A and B: fixation of volatile iodine, followed by complete decay of ^{135}Xe produced from ^{135}I .

the ^{135}Xe which is produced here from ^{135}I is held up for a sufficient period of time, so that the flow returned to the gas-liquid contactor is practically free of ^{135}Xe . The condensate is assumed to be returned to the primary circuit via storage volume V_c . In practice, the condensate can be used for purging purposes. The liquid purification system is fed from the main circuit by a bypass flow, ϕ_b , of liquid free from suspended particles. It is supposed that in the system the iodine is fixed and that no ^{135}Xe from ^{135}I decay is returned to the primary circuit. However, for the sake of simplicity, it is assumed that the ^{135}Xe concentration in the return flow of the liquid purification system is the same as the ^{135}Xe concentration in the feed. Furthermore, it is postulated in this chapter that the times of residence in the volumes of V_{g1} , V_u , V_c and of the primary circuit are so small with respect to the half-lives of ^{135}Xe and ^{135}I that the concentration of these isotopes are constant within these volumes.

3.1. The determination of the purification constant for ^{135}I

The iodine present in the liquid phase is partly in the volatile form I_2 . The concentration of the volatile ^{135}I in the liquid of the suspension is I_{lv} , that of the non-volatile iodine I_{li} . The fraction m of the total ^{135}I concentration is volatile and the fraction $1-m$ is non-volatile.

Thus:

$$I_{lv} = mI_l, \quad 3.1$$

and

$$I_{li} = (1 - m) I_l. \quad 3.2$$

Iodine is removed from the primary circuit by two ways, viz. to the liquid purification ϕI_l and to the gas purification $\phi_{g2} I_{g1}$. According to the definition of the purification constant (compare 1.2.1):

$$\lambda_1 + I_l V_T (1 - a) = \phi_l I_l + \phi_{g2} I_{g1}. \quad 3.3$$

If the Ostwald solubility coefficient for the volatile iodine is h_i , we have:

$$I_{lv} = h_i I_{g1}. \quad 3.4$$

Substitution of 3.4 and 3.1 into 3.3 gives:

$$\lambda_1^+ = \frac{\phi_l + m h_l^{-1} \phi_{g2}}{V_T (1 - a)}. \quad 3.5$$

3.2. The determination of the purification constant for ^{135}Xe

The removal rate of ^{135}Xe has the following contribution:

a) decay in the gas separator volume:

$$\lambda_2 X_{g1} V_u.$$

b) decay in the condensate storage tank:

$$\lambda_2 X_c V_c.$$

c) decay in the decay volume:

$$\lambda_2 X_{g2} V_{g1}.$$

d) removal via the iodine purification facility:

$$\phi_{g2} X_{g1}$$

According to the definition of the purification constant the total rate of ^{135}Xe removed is:

$$\lambda_2^+ X_l V_T (1 - a) = \lambda_2 X_{g1} V_u + \lambda_2 X_c V_c + \lambda_2 X_{g2} V_{g1} + \phi_{g2} X_{g1}. \quad 3.6$$

X_{g1} can be expressed in terms of X_l by:

$$X_{g1} = h_{xp}^{-1} X_l, \quad 3.7$$

h_{xp} being the value of h_x at the conditions of the primary circuit in the gas-liquid contactor. The concentration of xenon in the gas phase of the condenser can be considered to be in phase equilibrium with the condensate. Thus:

$$X_{g2} = h_{xc}^{-1} X_c, \quad 3.8$$

where h_{xc} is the solubility coefficient at the temperature of the condenser.

The material balance of the condenser is:

$$\phi_{g3} X_{g1} = \phi_{g4} X_{g2} + \phi_c X_c. \quad 3.9$$

Substitution of 3.8 into 3.9 gives:

$$X_c = \frac{\phi_{g3}}{h_{xc}^{-1} \phi_{g4} + \phi_c} X_{g1}, \quad 3.10$$

and:

$$X_{g2} = \frac{\phi_{g3}}{\phi_{g4} + h_{xc} \phi_c} X_{g1}. \quad 3.11$$

Substitution of 3.10 and 3.11 into 3.6 gives:

$$\lambda_2^+ X_l V_T (1 - a) = \left\{ \lambda_2 V_u + \frac{\phi_{g3}}{h_{xc}^{-1} \phi_{g4} + \phi_c} \cdot \lambda_2 V_c + \frac{\phi_{g3}}{\phi_{g4} + h_{xc} \phi_c} \cdot \lambda_2 V_{g1} + \phi_{g2} \right\} X_{g1}, \quad 3.12$$

or with 3.7:

$$\lambda_2^+ = h_{xp}^{-1} \left\{ \frac{\lambda_2 V_u}{V_T (1 - a)} + \frac{\phi_{g3}}{h_{xc}^{-1} \phi_{g4} + \phi_c} \cdot \frac{\lambda_2 V_c}{V_T (1 - a)} + \frac{\phi_{g3}}{\phi_{g4} + h_{xc} \phi_c} \cdot \frac{\lambda_2 V_{g1}}{V_T (1 - a)} + \frac{\phi_{g2}}{V_T (1 - a)} \right\}. \quad 3.13$$

The equations 3.5 and 3.13 give the expression of the purification constants, λ_1^+ and λ_2^+ , for the system shown in fig. II.3. The quantities determining these purification constants are process variables. With the values of these constants the purification factor of ^{135}Xe in the liquid phase is easily found from equations 1.24 and 1.25. The purification factor, ξ , for the suspension is then found from 1.23. With this quantity and equation 1.22 the actual ^{135}Xe concentration can be calculated. Finally, the poisoning factor can be calculated from the actual ^{135}Xe concentration. The advantage of the application

of the purification constants in describing the purification process is, that these constants are independent on the average thermal neutron flux. It is difficult to determine this flux exactly. However, with the purification constants the quality of the purification process can be determined unequivocally.

The purification constant, λ_2^+ , according to 3.13, is the same as was already arrived at in chapter 2. If $\phi_{g2} = 0$ and no condensation is applied ($V_c = 0$, $\phi_c = 0$), the equations 3.13 and 2.16 become identical.

As a consequence of the condensation, the decay volume is decreased by a factor:

$$\frac{\phi_{g3}}{\phi_{g4} + h_{xc} \phi_c}$$

The factor h_{xc} is less than unity and also ϕ_c is small as well with respect to ϕ_{g4} . If the temperature of the primary circuit is 250° C, the steam pressure is 40 atm. and if the excess gas pressure is 20 atm., the factor:

$$\frac{\phi_{g3}}{\phi_{g4}} = 3.$$

thus by condensation the decay volume can be reduced by factor 3 in this case.

4. The removal of ^{135}I from the primary circuit

The purification constant λ_1^+ for the removal of ^{135}I , which was defined in Ch. 3, depends on the form in which the iodine is present. Until now, it has not been established whether in a real suspension reactor the iodine will be mainly volatile or mainly non-volatile. As was mentioned in part I.3, the volatile form of iodine, I_2 , will exist if excess oxygen is present*.

However, in the primary system the probability of volatile iodine seems to be small because a hydrogen or deuterium overpressure will be applied, resulting in reducing circumstances. Therefore we will confine ourselves in this chapter to the case where the primary circuit only contains non-volatile iodine.

In this case, the expression for λ_1^+ (see 3.5) can be simplified to:

$$\lambda_1^+ = \frac{\phi_i}{V_T(1-a)}, \quad 4.1$$

where ϕ_i is the flow of liquid, free of suspension particles, fed to a facility where iodine is held-up until it decays to ^{135}Xe . In the steady state the same amount of ^{135}Xe is leaving this facility as ^{135}I is fed, assuming that 100 % of the iodine feed is fixed. The ^{135}Xe must be removed from the outlet flow of this facility before it is returned to the primary circuit. Thus, in the liquid purification system two processes should be carried out, viz: fixation of iodine, and subsequent removal of ^{135}Xe .

* In part III. 1 the behaviour of iodine in water at elevated temperatures is discussed more in detail.

4.1. Two methods for the removal of ^{135}I

Two possibilities for the ^{135}I removal have been considered. In fig. II.4 a flow diagram is given of a system in which iodine is fixed in a suitable adsorber, while ^{135}Xe resulting from the decay of ^{135}I is stripped from the liquid leaving the adsorber. The stripping gas is circulated over a decay volume, where ^{135}Xe decays. The alternative system is given in fig. II.5. In this case, iodine is held-up in an evaporator and xenon is stripped from the condensate by steam. Xenon and other non-condensable gases from the condenser are led

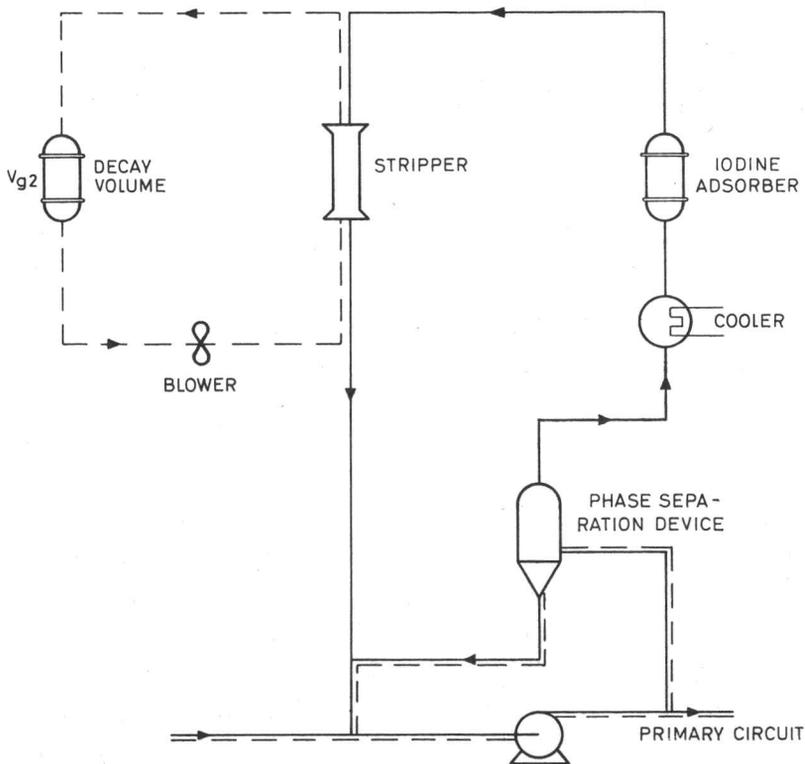


Fig. II. 4

Flow diagram for the removal of non-volatile iodine based on adsorption of iodine and subsequent xenon stripping and decay.

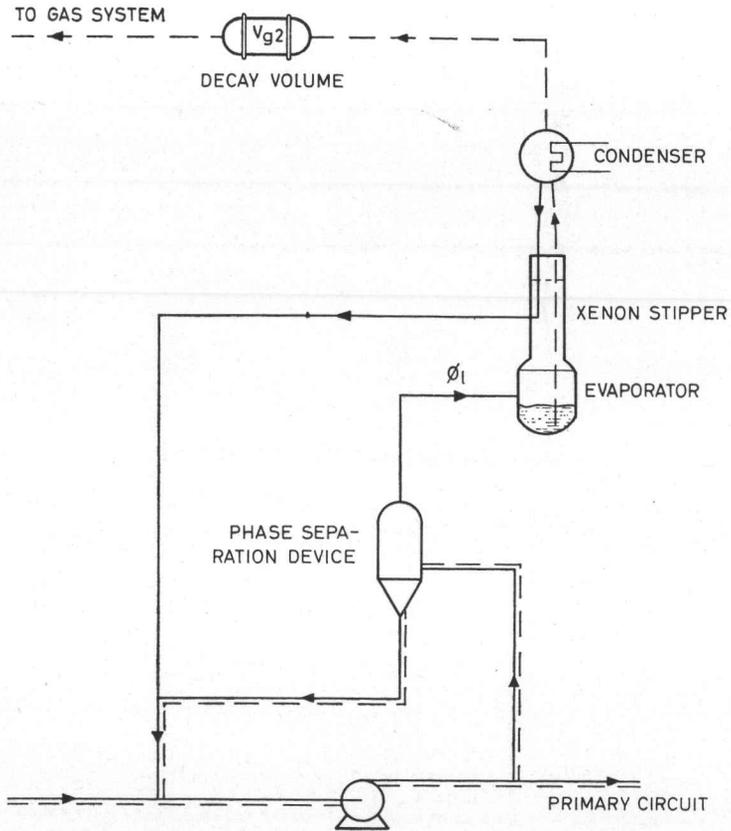


Fig. II. 5

Flow diagram for the removal of non-volatile iodine based on the concentration of iodine in an evaporator and subsequent xenon stripping and decay.

through a decay volume, where ^{135}Xe decays. Several arguments have lead to the choice of the evaporator system. These are:

- a) In the evaporator all the non-volatile neutron poisons are concentrated irrespective of their chemical properties. Several products will be adsorbed on the second adsorbent which will be added to the suspension (e.g. active coal, see part I.2). Since this adsorbent has a small density in comparison to the fuel material, the separation between fuel and adsorbent is simple

and consequently the second adsorbent can also be fed to the evaporator, carrying products to be removed from the primary circuit.

- b) The decay volume, V_{g2} , in the system of fig. II.5 is much smaller than that in the system given in fig. II.4. This is due to the fact that the ^{135}Xe concentration in the gas leaving the condenser is considerably higher than in the gas leaving the stripper of fig. II.4. The values of the decay volumes for both systems have been calculated. In table II.1 the result of this calculation is given, for the condition that the ^{135}Xe concentration in the liquid phase of the primary circuit is decreased to 20 % of the concentration obtained when no purification is carried out.

TABLE II.1

The decay volume, V_{g2} , to be applied in the liquid purification systems.

$\xi_l(X) = 1.0$, thus $\frac{\lambda_2^+}{\lambda_2} = 0$ and $\xi_l(I) = 0.2$, thus $\frac{\lambda_1^+}{\lambda_1} = 5$. (See for relation between ξ and λ^+ fig. II.1)

	Iodine fixation in adsorber	Iodine fixation in evaporator
Temperature	Stripper: 100° C	Stripper: 275° C Condenser: 100° C
Number of theoretical plates in the stripper	$n = 2$	$n = 2$
Decay volume	$\frac{V_{g2}}{V_T} = 2.6 (1 - a)$	$\frac{V_{g2}}{V_T} = 0.31 (1 - a)$

As can be seen from table II.1 the decay volume in the system according to fig. II.5 is only 1/9 of the volume to be used in the system of fig. II.4.

As has been indicated before, in the evaporator the greater part of the fission products are concentrated. Due to the ionizing radiation from these radioactive products, probably oxygen in a reactive state is produced by water decomposition. This oxygen might cause the oxidation of non-volatile iodine, present originally in the ionic form

(I⁻), giving volatile molecular iodine (I₂). This volatile iodine will be stripped from the bottom by steam and returned to the primary circuit, either by the condensate (reflux take off from the stripper in fig. II.5) or by the gas flow from the top condenser. If the relative volatility of iodine with respect to water at high temperature is smaller than one, the iodine is returned with the reflux take off, whilst a relative volatility of more than one brings the iodine in the gas flow from the condenser. The latter situation is not so serious because the dimensions of the decay volume could be chosen such that both gaseous ¹³⁵I and ¹³⁵Xe can decay. However, as will be discussed in part III of this work, the volatility of iodine in water is less than one at elevated temperature. In that case, the carry-over of iodine from the bottom can be decreased by washing iodine back into the still by the use of some excess condensate as partial reflux in the lower part of the column. In the next section this process will be considered more in detail.

4.2. Calculation of the iodine washer

In fig. II.6 a diagram of the rectifying column is shown. In the lower part, iodine is washed from the steam; in the upper part xenon is stripped from the condensate. The reflux is partially taken off at a place where it is free from both xenon and iodine.

In the following calculations, mass fractions are used instead of concentration; x denotes the iodine mass fraction in the liquid and y the iodine mass fraction in the vapour. L and V are the liquid and vapour flows in mass per unit time. D is the rate of liquid take off, F is the liquid feed rate. M is the mass of water present in the still. It is assumed that no iodine is removed through the condenser vent and that the iodine hold-up in the column is small when compared to that in the bottom. Furthermore, the temperature of the condenser is so low that the amount of water vapour leaving through the vent is negligible.

The overall ¹³⁵I balance is:

$$x_f F = x_o D + \lambda_1 x_{n+1} M. \quad 4.2$$

The overall water balance is:

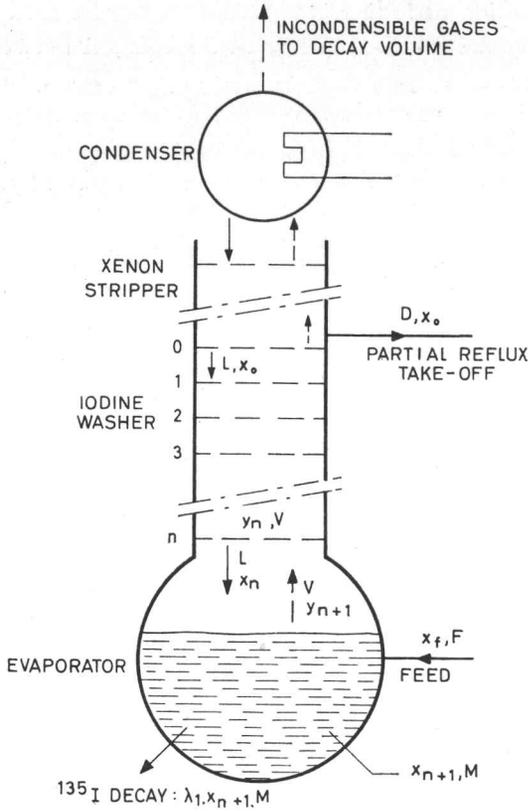


Fig. II. 6

Schematic diagram of the rectifying column.

$$F = D.$$

4.3

The column is isothermal. The temperature is equal to the boiling point of water at the system pressure due to the low iodine concentration. This means that L and V are constant. Furthermore, it is assumed that y_n/x_n is constant for all plates. The separation factor for an actual plate, S , is:

$$S = \frac{yV}{xL}.$$

4.4

The distribution of iodine in the column can be easily calculated by considering the mass balance and the relation between the concentrations in the two phases leaving each plate. As this derivation is well known, it will not be given here. In our case the vapour flow, the liquid flow and the stripping factor are constant and the concentration of ^{135}I in the steam leaving the still is given by:

$$S^n y_{n+1} V = x_o D \frac{S^{n+1} - 1}{S - 1} + x_o L. \quad 4.5$$

It can be assumed that the vapour leaving the bottom is in phase equilibrium with the liquid in the bottom:

$$y_{n+1} = K_i x_{n+1}, \quad 4.6$$

K_i is the phase equilibrium constant for iodine in water. Because L and V are constant the water balance in the column can be written as:

$$L = V - D. \quad 4.7$$

Substitution of L according to 4.7 and y_{n+1} according to 4.6 into 4.5 gives:

$$\frac{x_{n+1}}{x_o} = \frac{D \frac{S(S^n - 1)}{S - 1} + V}{S^n K_i V}, \quad 4.8$$

or with 4.3:

$$\frac{x_{n+1}}{x_o} = \frac{F \frac{S(S^n - 1)}{S - 1} + V}{S^n K_i V}. \quad 4.9$$

From 4.2 and 4.3 it follows that:

$$\frac{x_f}{x_o} = 1 + \frac{x_{n+1}}{x_o} \frac{\lambda_1 M}{F}. \quad 4.10$$

Substitution of 4.9 into 4.10 gives:

$$\frac{x_f}{x_o} = 1 + \frac{\lambda_1 M \left\{ F \frac{S(S^n - 1)}{S - 1} + V \right\}}{S^n K_i V F}, \quad 4.11$$

Equation 4.11 gives the relation between the process variables and the permitted concentration in the return flow to the primary circuit. This concentration can be chosen rather arbitrary because the same net removal of ^{135}I from the reactor is achieved if $(x_f - x_o)F$ is kept constant. The purification constant for ^{135}I is in this case (see 4.1):

$$\lambda_1^+ = \frac{\phi_I}{V_T (1 - a)} \left(1 - \frac{x_o}{x_f} \right). \quad 4.12$$

Therefore, it is a matter of optimization to decide which solution is the better one, using more plates and decreasing L/V , or using a higher feed rate to the evaporator.

The derivation given here is not restricted to a column with plates, it can also be used for determining the relevant variables in other types of gas-liquid contacting devices, e.g. a packed bed. However, the decontamination of a packed bed is difficult. For this reason it seems preferable to apply rectification in a plate column, which is more easily decontaminated.

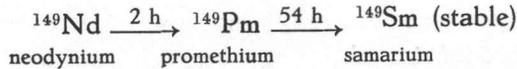
Apart from an iodine washer an iodine adsorber can probably be used as well (e.g. bed of silvered pellets). However, an important drawback of such a device is the possible loss of activity for adsorption. In such a case a replacement is necessary and the facility has therefore to be duplicated.

The applicability of this method for ^{135}I removal depends on the S value. In part III of this work the results are reported of an experiment to determine this value at elevated temperatures in stainless steel equipment.

5. Derivation of the general equation for the elimination of ^{149}Sm

As has already been discussed in part I.2, also ^{149}Sm is an important neutron absorber. In this chapter we will consider briefly the properties of this isotope. In analogy with the ^{135}Xe poisoning, a purification factor, $\xi_l(S)$, for ^{149}Sm can be defined, which factor determines the decrease of the ^{149}Sm concentration due to purification. The rate of fluid from the primary system to be processed in order to obtain a sufficient decrease in the ^{149}Sm concentration will be compared with that necessary to reduce the ^{135}I concentration in the primary system.

The decay chain for ^{149}Sm is [13]:



The cross section for thermal neutrons of ^{149}Sm : $\sigma_5 = 6.6 \times 10^{-20} \text{ cm}^2$. The cumulative yield is for ^{235}U fissions $\gamma_5 = 1.13\%$ [13] and for ^{233}U fissions $\gamma_5 = 1.8\%$ [14].

Application of the same treatment for these isotopes, as has been carried out in Ch. 1 for ^{135}I and ^{135}Xe , gives the following purification factor of ^{149}Sm for the liquid phase viz.:

$$\xi_l(S) = \left(1 + \frac{\lambda_3^+}{\lambda_3}\right)^{-1} \cdot \left(1 + \frac{\lambda_4^+}{\lambda_4}\right)^{-1} \cdot \left(1 + \frac{\lambda_5^+}{\sigma_5 \phi'}\right)^{-1}, \quad 5.1$$

λ_3^+ , λ_4^+ , λ_5^+ are the purification constants of ^{149}Nd , ^{149}Pm and ^{149}Sm respectively. These isotopes are non-volatile and thus have to be removed via the liquid phase. If a liquid flow ϕ_l is continuously taken off from the primary circuit as a by-pass stream and these three isotopes are removed by a purification device in this by-pass

(e.g. the evaporator circuit discussed in Ch. 4), the purification constants are:

$$\lambda_{3,4,5}^+ = \frac{\phi_l}{(1-a) V_T} \quad 5.2$$

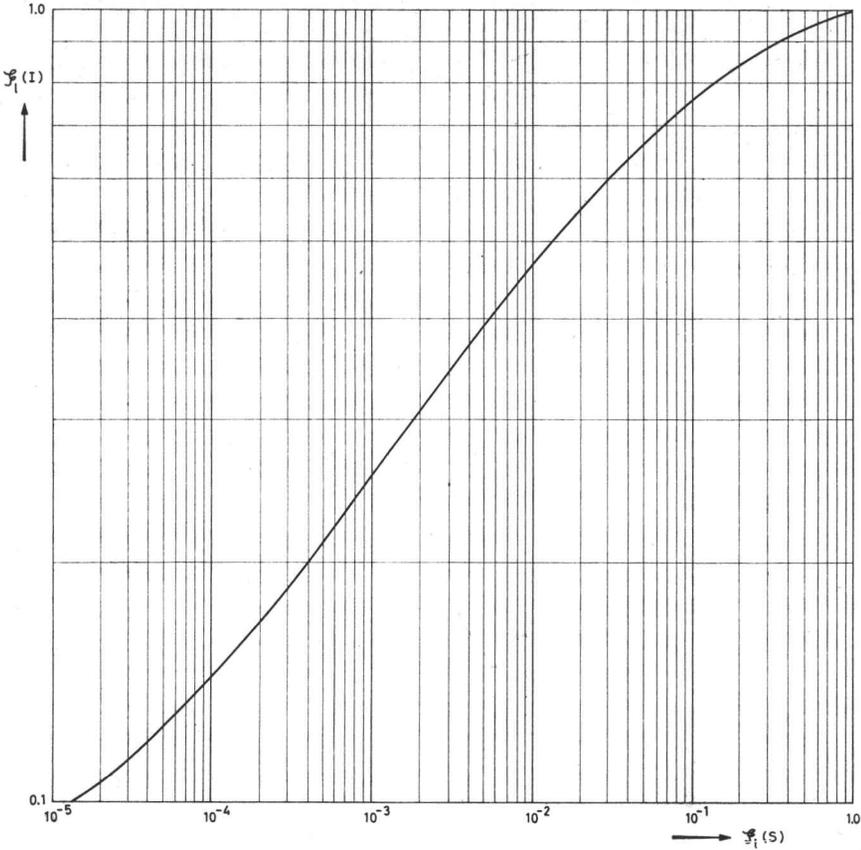


Fig. II. 7

Comparison between the purification factor ^{149}Sm , $\xi_l(S)$, at a flux of; $\varphi' = 10^{14}$ n/sec cm^2 and the purification factor of ^{135}Xe , $\xi_l(I)$. It is assumed that a certain by-pass flow is completely purified from ^{149}Sm , its precursors and ^{135}I .

In this case the purification constants $\lambda_{3,4,5}^+$ are equal to that for ^{135}I , thus $\lambda_{3,4,5}^+ = \lambda_1^+$. In fig. II.7 the purification factor for ^{149}Sm

is plotted against the purification factor for ^{135}Xe , if ^{135}I is removed. It is shown that even at high values of the neutron flux; $\xi_l(\text{S}) < \xi_l(\text{I})$.

The total reduction of the ^{149}Sm concentration is given by:

$$\xi(\text{S}) = (1 - \beta) + \beta \xi_l(\text{S}). \quad 5.3$$

This relation is the same as was derived in Ch. 1 for ^{135}Xe .

Thus, if the non-volatile components present in the feed to the liquid purification system are separated from water by means of an evaporator, the feed rate to this evaporator is completely determined by the required ^{135}I removal and not by the ^{149}Sm removal. The feed could be appreciably smaller if only a sufficient ^{149}Sm elimination would be required.

6. A proposal for the purification systems of a small experimental suspension reactor

In this chapter the purification of a small scale experimental suspension reactor will be calculated. As has already been discussed in Ch. 2, the purification system has primarily to be adapted for ^{135}Xe and ^{135}I removal. Before giving the results of this calculation, a short description of the reactor system will be given.

In Fig. II.8 a flow diagram of the purification systems for ^{135}Xe removal from a 250 kW experimental suspension reactor is shown. A description of the objectives of this reactor has already been given in [12]. Here, we will confine ourselves to a short description of the simplified flow scheme. This is based on the method of the direct removal of ^{135}Xe from the liquid phase of the suspension as it was discussed in Ch. 2 and the removal of ^{135}I by means of an evaporator according to Ch. 4.

In the primary system a slurry of fuel particles (i.e. $\text{ThO}_2 - \text{UO}_2$) and second adsorbent (e.g. small particles of active coal) in light water is circulated through the reactor core, a gas-liquid contactor, a gas separator, a heat exchanger and a pump. The fuel particles should have such dimensions that a sufficient recoil efficiency (90 %) is obtained. This condition gives the upper limit of the particle size (i.e. $d_{\text{particle}} \approx 5 \mu$). A flow of hydrogen gas, ϕ_{g2} , is injected into the gas-liquid contactor and is separated from the slurry in a gas separator. The outlet gas flow, ϕ_{g1} , of the gas separator is led to a condenser where steam is condensed. The condensate and the flow of non-condensable hydrogen gas and fission gases are displaced by means of a water jet compressor. This water jet is fed by particle-free water in a separate circulation system having a volume V_c , to which the condensate is added. This condensate is returned to the primary system as purge water, for instance to purge

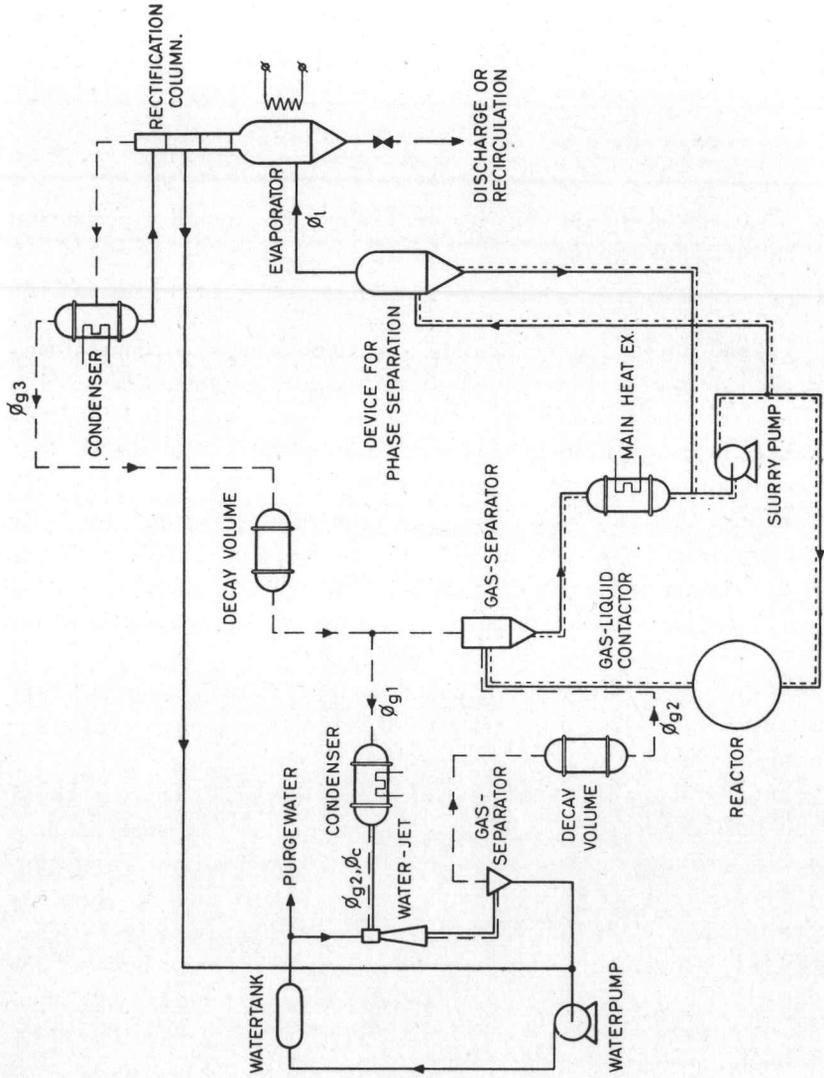


Fig. II. 8

Flow diagram of the purification systems for ^{135}Xe removal from a 250 kW experimental suspension reactor.

the bearings of the canned rotor slurry pump. The flow of particle-free water, to be returned to the primary system, is controlled in such a way, that the fuel concentration in the reactor is kept constant. After separation of the gas from the circulating water, this gas is returned to the gas-liquid contactor via a decay volume, V_{g1} .

From a device for phase separation (hydraulic cyclone or elutriator) a flow, ϕ_1 , of water, free of particles of the right size but containing second adsorbent carrying fission products, is fed to an evaporator. The efficiency for particle separation of the phase separation device dictates the lower limit of the fuel particle size (i.e. $d_{\text{particle}} > 1 \mu$). In the evaporator more water is evaporated than fed. The excess steam is, after condensation, used as a partial reflux in the lower part of a rectification column to wash out volatile iodine (compare Ch. 4). In the upper part of the column, xenon is stripped from the condensate, which is used as a total reflux here. The ^{135}Xe originated from ^{135}I decay in the evaporator, is allowed to decay in a decay volume V_{g2} , through which a flow, ϕ_{g3} , of non-condensable gases is returned from the condenser to the gas phase of the primary circuit. The same amount of water fed to the evaporator is returned to the primary circuit by partially taking off the reflux in the column in a place where the reflux is both xenon- and iodine free.

The purification constant for ^{135}Xe is given by equation 3.13 which here is written as:

$$\frac{\lambda_2^+}{\lambda_2} = \frac{\phi_{g1}}{\phi_{g2} + h_{xc} \phi_c} \cdot h_{xp}^{-1} \left(\frac{V_{g1}}{V_T(1-a)} + \frac{V_c}{h_{xc}^{-1} V_T(1-a)} \right) + h_{xp}^{-1} \frac{V_u}{V_T(1-a)} \quad 6.1$$

The following values are used to calculate λ_2^+ :

reactor volume: $V_R = 1.7 \times 10^{-2} \text{ m}^3$,

primary circuit: $V_T = 3.5 \times 10^{-2} \text{ m}^3$,

condensate hold-up: $V_c = 20 \times 10^{-2} \text{ m}^3$,

gas phase gas separator: $V_u = 10^{-2} \text{ m}^3$,

gas separator outlet flow $\phi_{g1} = 1.5 \times 10^{-3} \text{ m}^3/\text{sec}$ (250° C, 60 atm.),

gas feed to the gas-liquid contactor: $\phi_{g2} = 3.8 \times 10^{-4} \text{ m}^3/\text{sec}$ (100° C, 60 atm.),

condensate flow: $\phi_c = 2.8 \times 10^{-5} \text{ m}^3/\text{sec}$,

temperature gas-liquid contactor: $T_p = 250^\circ \text{ C}$,

temperature of the condensate: $T_c = 100^\circ \text{ C}$.

The solubility coefficient for xenon in water at T_p : $h_{xp} = 0.14$, [20] and at T_c : $h_{xc} = 0.049$, [20].

Inserting these values into 6.1 gives, when the volume fraction of the solids in the slurry is neglected ($a = 0.04$):

$$\frac{\lambda_2^+}{\lambda_2} = 0.81 (V_{g1} + 1) + 2.1. \quad 6.2$$

In fig. II.9 λ_2^+/λ_2 is plotted against V_{g1} .

With the aid of fig. II.1, the relation between the decay volume and the purification factor for ^{135}Xe , $\xi_l (X)$, is also known.

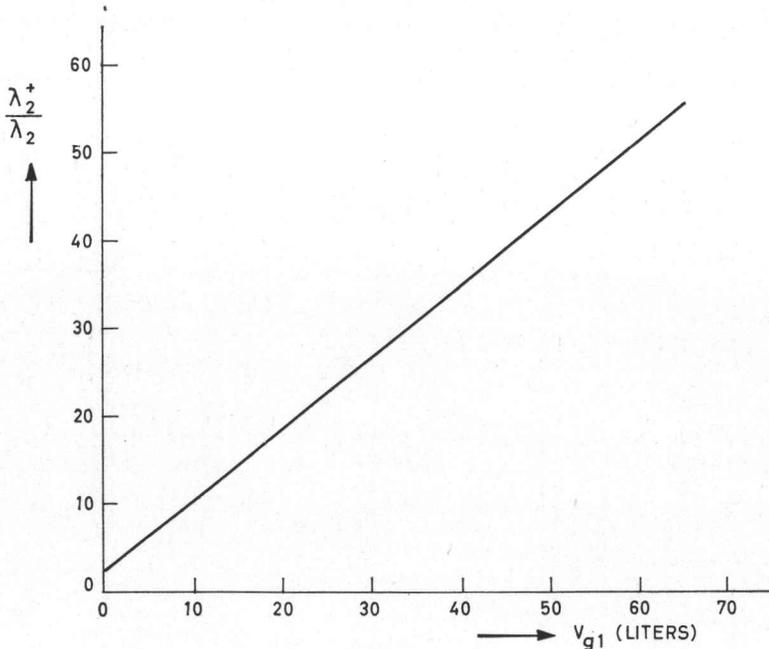


Fig. II. 9

The purification constant, λ_2^+ , as a function of the decay volume in the gas purification system of a 250 kW experimental suspension reactor.

The purification constant for ^{135}I removal is given by 4.12:

$$\lambda_1^+ = \frac{\phi_l}{V_T(1-a)} \left(1 - \frac{x_o}{x_f}\right). \quad 4.12$$

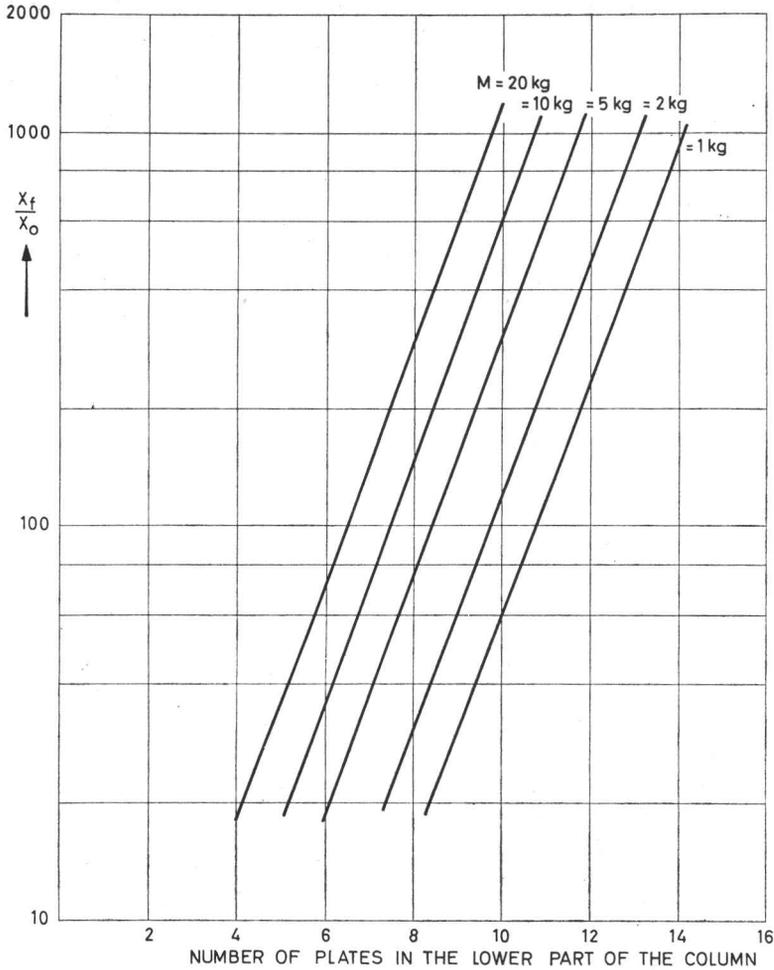


Fig. II. 10

The ^{135}I concentration in the partial reflux take off as a function of the evaporator water contents, M , and the number of actual plates in the lower part of the column (below the reflux take off).

In fig. II.10, x_f/x_o according to 4.11 is plotted against the number of actual plates, n , and the evaporator water contents, M , for the following values of the variables:

decay constant ^{135}I : $\lambda_1 = 2.9 \times 10^{-5} \text{ sec}^{-1}$,

evaporator feed: $F = 12 \text{ kg/h}$ (thus; $\phi_l = 4.2 \times 10^{-6} \text{ m}^3/\text{sec}$),

vapour flow: $V = 15.5 \text{ kg/h}$,

reflux flow: $L = 3.5 \text{ kg/h}$

and $y/x = 0.12$ (see experimental results in part III). As is shown, x_o/x_f can be made much smaller than unity; e.g. for $M = 20 \text{ kg}$ and 6 plates ($n = 6$), the value of x_f/x_o becomes 70.

Thus:

$$\frac{\lambda_1^+}{\lambda_1} = 4.6. \quad 6.3$$

With this value of λ_1^+ we can calculate the size of the decay volume V_{g2} , by using table II.1 in Ch. 4. It is shown there, that the decay volume is given by equation 6.4, when $\lambda_1^+/\lambda_1 = 5$ and two theoretical plates are used in the upper part of the column (xenon stripping section);

$$V_{g2} = 0.3 V_T (1-a). \quad 6.4$$

Inserting the value for V_T into 6.4 and neglecting a , we obtain:

$$V_{g2} = 10^{-2} \text{ m}^3. \quad 6.5$$

We can now calculate the purification factor ξ . If we accept a decay volume V_{g2} of approximately 35 liters, then we can find from fig. II.9: $\lambda_2^+/\lambda_2 = 30$.

With this value for λ_2^+/λ_2 and $\lambda_1^+/\lambda_1 = 5$, we find from fig. II.1: $\xi_l(\text{X}) = 0.11$ (when it is supposed that: $\varphi' = 2 \times 10^{13} \text{ n/cm}^2\text{sec}$) and $\xi_l(\text{I}) = 0.2$. Assuming a recoil efficiency of 90 %, we obtain with equation 1.23:

$$\xi = 0.12. \quad 6.6$$

Thus, the ^{135}Xe concentration has been reduced to 12 % of the value which is reached when no purification is present.

List of symbols used in part II

Symbol	Description	Dimension
D	Partial water take off from the column	kg/sec
$E(t)$	Distribution function of residence times	—
F	Evaporator feed	kg/sec
\mathcal{H}	Henry coefficient	atm
I	^{135}I concentration	atoms/m ³
J	Total amount of ^{135}I present in the primary circuit	atoms
K	Phase equilibrium constant; $K = \frac{y}{x}$	—
L	Water reflux in the column	kg/sec
M	Evaporator water contents	kg
N	Rate of fission	sec ⁻¹
S	Stripping or separation factor; $S = \frac{yV}{xL}$	—
T	Temperature	°K, °C
V	Volume	m ³
V	Water vapour flow	kg/sec
X	^{135}Xe concentration	atoms/m ³
Y	Total amount of ^{135}Xe present in the primary circuit	atoms
a	Volume fraction of solids in the suspension	—
h	Coefficient of Ostwald	—
m	Mass transfer rate	atoms/sec
m	Fraction of volatile ^{135}I in the core	—
n	Number of plates	—
t	Time	sec
x	Concentration of a component in liquid; $\frac{\text{mass comp.}}{\text{mass liquid}}$	—
y	Concentration of a component in vapour; $\frac{\text{mass comp.}}{\text{mass vapour}}$	—

Symbol	Description	Dimension
Φ	Flow rate	m ³ /sec
Σ_f	Macroscopic cross section for fission	cm ⁻¹
β	Recoil efficiency	—
γ_1	Cumulative fission yield of ¹³⁵ I	—
γ_2	Direct fission yield of ¹³⁵ Xe	—
γ_3	Fission yield of ¹⁴⁹ Sm	—
ε	Correction number	—
λ_1	Decay constant of ¹³⁵ I	sec ⁻¹
λ_2	Decay constant of ¹³⁵ Xe	sec ⁻¹
$\lambda_{3,4,5}$	Decay constant of ¹⁴⁹ Nd, ¹⁴⁹ Pm and ¹⁴⁹ Sm	sec ⁻¹
λ_1^+	Purification constant of ¹³⁵ I	sec ⁻¹
λ_2^+	Purification constant of ¹³⁵ Xe	sec ⁻¹
$\lambda_{3,4,5}^+$	Purification constant of ¹⁴⁹ Nd, ¹⁴⁹ Pm and ¹⁴⁹ Sm	sec ⁻¹
μ	10 ⁻⁶ m	—
ξ	Purification factor	—
$\xi(X)$	Purification factor for ¹³⁵ Xe	—
$\xi(I)$	Purification factor for ¹³⁵ I	—
$\xi(S)$	Purification factor for ¹⁴⁹ Sm	—
ρ	Density	kg/m ³
σ_2	Microscopic thermal neutron cross section ¹³⁵ Xe	cm ²
σ_3	Microscopic thermal neutron cross section ¹⁴⁹ Sm	cm ²
τ	Mean time of residence	sec
φ	Mean thermal neutron flux in the reactor	n/sec cm ²
φ^1	Mean reduced thermal neutron flux in the primary circuit	n/sec cm ²

Index	Description
<i>R</i>	Reactor core
<i>T</i>	Total primary circuit
<i>c</i>	Condenser
<i>f</i>	Feed
<i>g</i>	Gas
<i>i</i>	Iodine, non-volatile
<i>l</i>	Liquid
<i>n</i>	Plate number
<i>o</i>	Without purification
<i>p</i>	Primary circuit
<i>s</i>	Solid phase
<i>u</i>	Gas separator
<i>v</i>	Volatile, vapour
<i>x</i>	Xenon

The numerical suffixes are generally used to indicate the different locations in the same phase.



PART III

The separation of iodine from steam by rectification at high temperature and low concentrations

1. Introductory

1.1. Statement of the problem

In part II of this work the removal of ^{135}I from a suspension reactor was discussed. It was indicated, that the most promising and simple system for realizing this purification is an evaporator-condenser combination (see part II.4). In the evaporator all non-volatile products to be removed from the primary system can be concentrated, whereas clean water is returned to the primary system as condensate. As was already indicated, this system fails in isolating iodine when this element is partly present in a volatile form (I_2). Due to the fact that the evaporator content is highly radioactive (10 kC/l), oxygen is produced by water decomposition. This oxygen might cause the oxidation of the initially non-volatile ionic iodine form (I^-) into the volatile form (I_2). This argument has lead us to consider the application of a rectifying column between the evaporator and the condenser in order to prevent the carry over of iodine from the still (see part II.4.2). Therefore, a test circuit was built for the investigation of the separation of iodine from steam at elevated temperatures by rectification. This experimental facility will be described in section 3.1. The concentration of iodine in the column was measured by using as a tracer ^{131}I , a radioactive isotope with a half-life of 8 days. Samples were taken from various points in the column and the concentration in these samples was determined by counting the ^{131}I radioactivity. The sampling and counting procedure will be described in 3.3. The oxidizing circumstances in the still were simulated by

the addition of sulphuric acid and potassium bichromate to the aqueous iodine solution in the evaporator.

We shall first review the properties of iodine in aqueous solution (1.2). In 1.3 the conditions in the column will be examined from which it is concluded that on the column trays a combination of distillation and chemical reaction takes place. This mechanism will be treated theoretically in chapter 2. Thereafter, the experimental apparatus and procedure are described in chapter 3. The results of the experiments will be discussed in chapter 4.

1.2. *The behaviour of iodine in water*

The properties of iodine in aqueous solutions at high temperature ($> 100^{\circ}\text{C}$) are not well known. This is probably due to the fact that the determination of the chemical state of iodine at high temperatures is difficult. In principle, it should imply chemical analysis under system conditions. In practice this is, of course, not possible. Therefore, in most cases it is attempted to cool down the sample to room temperature as rapidly as possible, after which follows a rapid separation or analysis of the various forms of iodine. However, due to the change of the equilibrium between the various iodine forms with temperature, the results obtained give a partial picture only of the real situation at high temperatures. Most experience at high temperature has been obtained at Oak Ridge National Laboratory in the U.S.A. This work was carried out in connection with the Homogeneous Reactor Project. *Peterson* gave a survey of this work in [9].

Iodine in aqueous solution at room temperature can exist in several oxidation states. These are: iodide ion (I^-), molecular iodine (I_2), iodate (IO_3^-) and periodate (IO_4^-). The latter exists only under strongly oxidizing conditions. Iodine vapour (I_2) in air can be considered as an ideal gas at low concentration [15]. At room temperature and pH values of 6 and lower the degree of hydrolysis of iodine is small. According to the equilibrium constant for hydrolysis reported by *Morgan* [16] at $\text{pH} = 6$ approximately 10 % of I_2 is hydrolysed, when the iodine concentration is of the order of magnitude of that in a suspension reactor ($[\text{I}_2] \approx 10^{-5}\text{N}$). Molecular iodine in aqueous solution is reduced to iodide in stainless steel equipment [9].

The volatility of I_2 in water at low temperatures ($\leq 100^\circ\text{C}$) has been measured by several investigators. *Taylor* [17] measured the distribution of I_2 over the gas phase and water at 20°C . *Van der Plas* * [18] has measured the phase equilibrium constant, K^{**} , for I_2 in water at 100°C , while *Keeler et al.* [19] measured the value of K at high temperatures ($200^\circ\text{C}-300^\circ\text{C}$).

A convenient quantity for comparing solubilities of other gases is the Henry coefficient, \mathcal{H} . At low concentrations of the solute, the Henry coefficient is given by the proportionality factor between the partial vapour pressure of the solute above the solution, p , and the mole fraction of the solute in the solution, x , thus:

$$p = \mathcal{H} x, \quad 1.1$$

\mathcal{H} has the dimension of pressure.

In table III.1 the values for the Henry coefficient of I_2 in water are given, calculated from the data of *Taylor* and *van der Plas*.

TABLE III.1

The Henry coefficient, \mathcal{H} , of I_2 in water

Temp. $^\circ\text{C}$	\mathcal{H} (atm)	Reference
20	11.3	<i>Taylor</i> [17]
100	38	<i>van der Plas</i> [18]

Water vapour of temperatures below 100°C can be considered as an ideal gas. The relative volatility of I_2 with respect to water, α , can then be given by:

* The measurements of *van der Plas* are described in the appendix 1.

** K is the mole fraction of I_2 in the vapour divided by the mole fraction of I_2 in the liquid. At low concentrations of the solute, the relation between K and \mathcal{H} is:

$$K = \frac{273 M_l \mathcal{H}}{22.4 T \rho_v},$$

M_l is the molecular weight of the solvent and ρ_v is the density of the saturated vapour of the solvent in kg/m^3 .

$$\alpha = \frac{\mathcal{H}}{p^\circ}$$

1.2

where p° is the saturated water vapour pressure. It is observed that $\alpha > 1$ for $T \leq 100^\circ\text{C}$, so that in this temperature region I_2 is more volatile than water. In order to extrapolate \mathcal{H} to higher tempera-

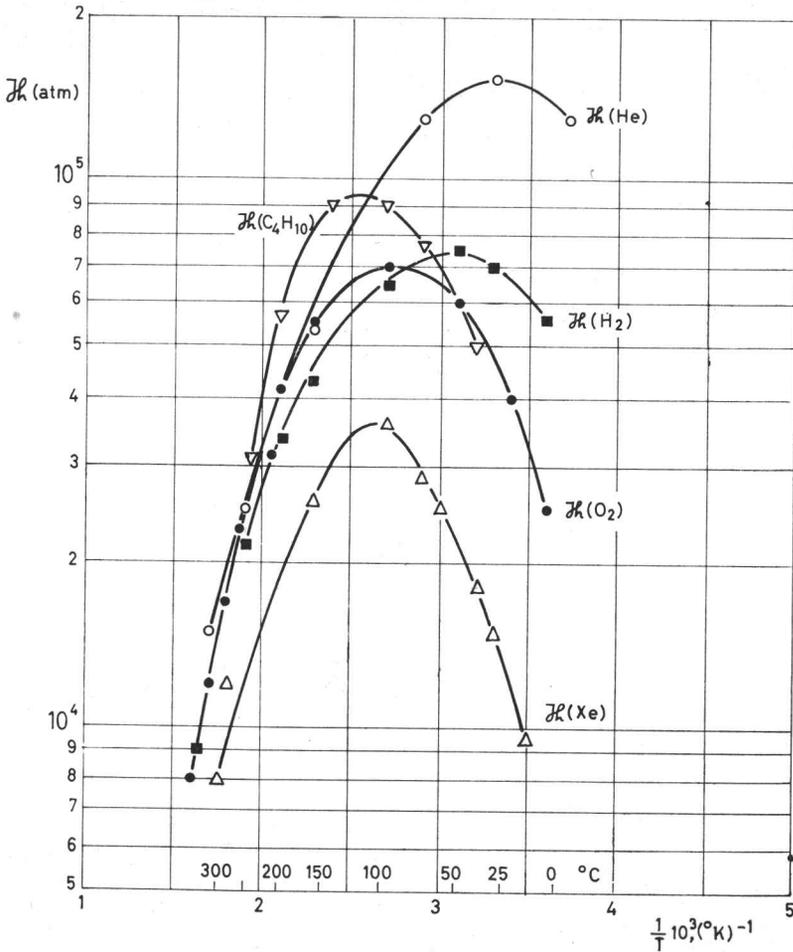


Fig. III. 1

The Henry coefficient of several gases in water.

tures, we have to rely on the behaviour of the value of \mathcal{H} of other gases in water and assume a certain degree of analogy between the course of the value of \mathcal{H} for iodine in water with that of other gases.

In fig. III.1 the Henry coefficient of several gases in water has been plotted against temperature. These values of \mathcal{H} have been taken from *Himmelblau* and *Arends* [20] who have summarized the volatility data of gases in water of several investigators. It appears that above about 100°C the value of \mathcal{H} drops rapidly with increasing temperature. In analogy with this behaviour, it may be expected that also the value of \mathcal{H} for I_2 in water will decrease at higher temperatures. Since the saturated steam pressure rapidly increases with increasing temperature, above a certain temperature I_2 may become less volatile than water. This trend of the volatility is confirmed by the value of $K \approx 0.29$ * at temperatures between 200°C and 330° C which has been reported by *Keeler et al.* [19]. This would give a \mathcal{H} value at 275°C of ≈ 15 atm. These experiments were carried out in a stainless steel autoclave. Oxygen overpressure was maintained to prevent the reduction of I_2 . Probably due to the difficult experimental technique, the K values measured by these authors scatter rather badly. Therefore, the value of K shows no significant dependence on temperature and pH. An average value of $K = 0.29$ is reported for the pH range: 3.7–9.9 and the temperature range: 200°C–330°C.

1.3. The conditions in the column

In the former section the properties of iodine in aqueous solution have been discussed. We will now consider what the conditions in the column are and what behaviour of the iodine is to be expected.

The separation is carried out in stainless steel equipment and consequently a reduction of I_2 to I^- will take place in the absence of oxygen. In the evaporator an oxidizing agent is added in the form of

* The relative volatility:

$$a = \frac{K(I_2)}{K(H_2O)} \approx K(I_2)$$

at low iodine concentrations.

a potassium bichromate-sulphuric acid solution. Thus, in the bottom only a small fraction of I^- may be expected. The volatile I_2 is swept with steam into the column, where no oxidizing circumstances are present*. Thus, in the column I_2 is reduced to I^- , due to presence of stainless steel. Because the volatility of I^- is low**, the apparent volatility of iodine is reduced due to this chemical reaction. Since very probably the volatility of I_2 at high temperature is already small, an efficient reduction of iodine concentration in the top of the column can be expected. A separation carried out at lower temperatures (e.g. 100°C) may become difficult, because the volatility of I_2 can be higher than that of water; however, due to the reduction of I_2 the apparent volatility of iodine can become very near to that of water.

* The volatility of H_2SO_4 is negligible (see appendix 3).

** $K(\text{HI}) \approx 1.4 \times 10^{-3}$ at 272°C (see appendix 2).

2. Theory of the separation of free iodine from water by distillation with chemical reaction

2.1. The ratio y/x for one tray

On a tray in a distillation column, steam and I_2 are brought into contact with solution present on the tray. I_2 will be absorbed to a certain extent and the dissolved I_2 is partially converted into non-volatile I^- .

Using this model, we will derive the material balance for one tray and a relationship for the ratio between the mass fraction of I_2 in the steam leaving the tray, y , and the total iodine mass fraction (I_2 and I^-) in the liquid leaving the tray, x . This ratio is called ζ , so that for tray number n :

$$\zeta_n = \frac{y_n}{x_n}. \quad 2.1$$

The liquid present on the tray is well mixed by the vapour bubbles rising through it. It is assumed that the mixing time (i.e. the time necessary for reaching a homogeneous distribution of material introduced at a certain point of the tray) is small compared with the time of residence of the liquid in one tray*.

In that case the concentration in the liquid is the same at all points of the tray (i.e. a perfectly mixed continuous flow reactor). Fig. III.2 shows a schematic drawing of a tray.

The material balance for iodine for tray nr. n is given by:

$$x_{n-1} L + y_{n+1} V = x_n L + y_n V, \quad 2.2$$

* The minimum time of residence used in the experiments was about 1 minute.

where L = liquid flow (kg/sec),
 V = vapour flow (kg/sec).

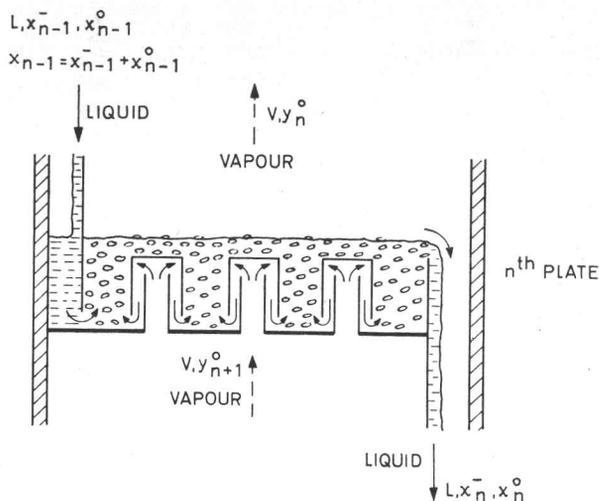


Fig. III. 2

Schematic drawing of a tray.

In this case of low iodine concentrations the temperature in the column is determined by the boiling point of water at the working pressure. The temperature is constant and no condensation occurs on the trays*. Consequently, L and V are constant throughout the column. All trays are of identical construction so that the hold-up of solution is constant and equal for each tray.

From 2.2 it can be easily derived that (see fig: III.3):

$$y_{n+1} V - x_n L = D, \quad 2.3$$

where D = rate at which iodine is taken off at the top of the column (kg/sec).

We will restrict now the derivation of a relation for ζ to those cases where the amount of iodine taken from the top is small.

* Heat losses are small and are neglected.

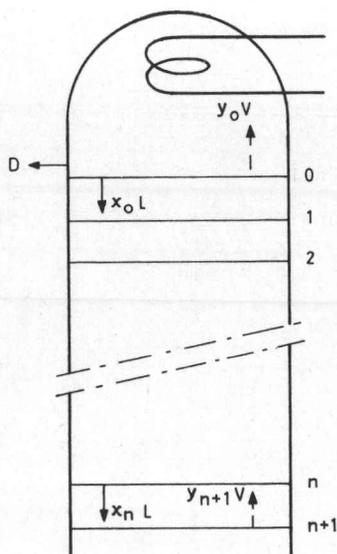


Fig. III. 3

Schematic drawing of the column.

Then $D \ll x_n L$ and 2.3 becomes:

$$y_{n+1} V \approx x_n L. \quad 2.4$$

Substitution of 2.4 into 2.1 gives:

$$\zeta_n \approx \frac{y_n L}{y_{n+1} V}. \quad 2.5$$

Now an additional relationship between y_n and y_{n+1} must be available. To this end we make use of the Murphree [21] tray efficiency, E , which is defined as:

$$E = \frac{y_{n+1} - y_n}{y_{n+1} - K x_n^o}. \quad 2.6$$

where x_n^o = the mass fraction of I_2 in the liquid,
 K = the phase equilibrium constant:

$$K = \frac{y_n}{x_n} \text{ for equilibrium.}$$

It must be noted that the iodine present in the vapour is only in the form of I_2 , thus $y_n^\circ = y_n$. Equation 2.6 will be put now in the following form i.e.:

$$\frac{y_n}{y_{n+1}} = (1 - E) + KE \frac{x_n^\circ}{y_{n+1}}. \quad 2.7$$

In order to eliminate $\frac{x_n^\circ}{y_{n+1}}$ we will use 2.4 and write this equation in the form:

$$y_{n+1} V = (x_n^\circ + x_n^-) L \text{ or} \\ \frac{y_{n+1}}{x_n^\circ} = \frac{L}{V} \left(1 + \frac{x_n^-}{x_n^\circ} \right), \quad 2.8$$

where x_n^- = the mass fraction of iodide in the liquid. Substitution of 2.8 and 2.7 into 2.5 gives:

$$\zeta_n \approx (1 - E) \frac{L}{V} + \frac{KE}{1 + x_n^-/x_n^\circ}. \quad 2.9$$

We will now consider the relationship between the mass fraction of I^- in the liquid, x_n^- , and the mass fraction of I_2 in the liquid, x_n° . It has already been mentioned that I_2 is reduced to I^- in stainless steel equipment and we will assume that the conversion rate can be expressed by:

$$r_n = k x_{n,x}^\circ, \quad 2.10$$

where r_n = mass of I_2 converted per unit mass of mixture and per unit of time,

k = reaction velocity constant (sec^{-1}).

The material balance for the non-volatile iodide on tray nr. n is:

$$x_{n-1}^- L + r_n m = x_n^- L, \quad 2.11$$

where m = the hold-up of solution on the tray (kg).

The increase of the mass fraction of iodide on the tray can be written as:

$$x_n^- - x_{n-1}^- = \frac{m}{L} r_n, \text{ or with 2.10:}$$

$$x_n^- - x_{n-1}^- = \frac{m}{L} k x_n^\circ. \quad 2.12$$

Because in this derivation it has been assumed that the amount of iodine taken from the top can be neglected, the mass fraction of I^- on tray nr. n , x_n^- , is the sum of the converted I_2 on the preceding trays. Therefore, x_n^- can be expressed by:

$$x_n^- = \frac{m}{L} k \sum_{i=0}^n x_i^\circ, \quad 2.13$$

where k is assumed to be constant over the column. Substitution of 2.13 into 2.9 gives:

$$\zeta_n \approx (1 - E) \frac{L}{V} + \frac{KE}{1 + \frac{m}{L} k \sum_{i=0}^n \frac{x_i^\circ}{x_n^\circ}}. \quad 2.14$$

From the definition of E (2.6) and if y_{n-1}/y_n is much smaller than unity we have:

$$\frac{x_{n-1}^\circ}{x_n^\circ} = \frac{y_{n-1} - y_n(1 - E)}{y_n - y_{n+1}(1 - E)} \approx \frac{y_{n-1}}{y_n}, \quad 2.15$$

and we may make the approximation:

$$\sum_{i=0}^n \frac{x_i^\circ}{x_n^\circ} \approx 1 + \frac{x_{n-1}^\circ}{x_n^\circ}. \quad 2.16$$

From 2.5, provided $D \ll x_n L$, we have:

$$\frac{y_{n-1}}{y_n} \approx \zeta_{n-1} \frac{V}{L}. \quad 2.17$$

Hence, for $\frac{y_{n-1}}{y_n} \ll 1$ or $\zeta_{n-1} \frac{V}{L} \ll 1$, eq. 2.14 can be approximated by:

$$\zeta_n \approx (1 - E) \frac{L}{V} + \frac{KE}{1 + \frac{m}{L} k \left(1 + \zeta_{n-1} \frac{V}{L}\right)}. \quad 2.18$$

Since L , V , E , K , m and k are constant through the column, we see from 2.18 that if

$$\zeta_n \frac{V}{L} < 1,$$

ζ_n must be independent of the tray number. Therefore, we may put for ζ :

$$\zeta \approx (1 - E) \frac{L}{V} + \frac{KE}{1 + \frac{m}{L} k \left(1 + \zeta \frac{V}{L}\right)}. \quad 2.19$$

Equation 2.19 is restricted to those plates, where the throughput of the iodine is large compared with the amount of product taken off at the top. It is shown by 2.19 that by chemical conversion of the volatile iodine the phase equilibrium constant, K , is apparently lowered and has become dependent on the liquid reflux L . It is also seen that if the liquid reflux becomes very small at a constant vapour flow, ζ will equally diminish; due to the long time of residence relatively much I_2 is converted on the tray so that x_n° and y_n are lowered.

2.2. The distribution of iodine in the column

In section 2.1 a relationship for y/x (on each tray) was derived and it appeared that under certain conditions its value can be considered constant. These conditions are:

- a) The throughput of the component is large compared with the product take off at the top.
- b) The separation factor, $S = \frac{yV}{xL}$, is smaller than unity.

The distribution of iodine in the column is, for a constant value of the separation factor, given by:

$$S^n y_{n+1} V = D \frac{S^{n+1} - 1}{S - 1} + x_0 L, \quad 2.20$$

or:

$$S^n x_n L = D \frac{S^n - 1}{S - 1} + x_0 L. \quad 2.21$$

The relationships 2.20 and 2.21 are used to determine the value of S or ζ from the measured iodine concentration in the experimental column.

3. Experimental part

In order to demonstrate the separation of volatile iodine and steam in a rectifying column, a test circuit was built. This system will be described in section 3.1. In 3.2 the experimental procedure will be treated; in 3.3 a description is given of the sampling procedure and concentration measurement.

3.1. The experimental apparatus

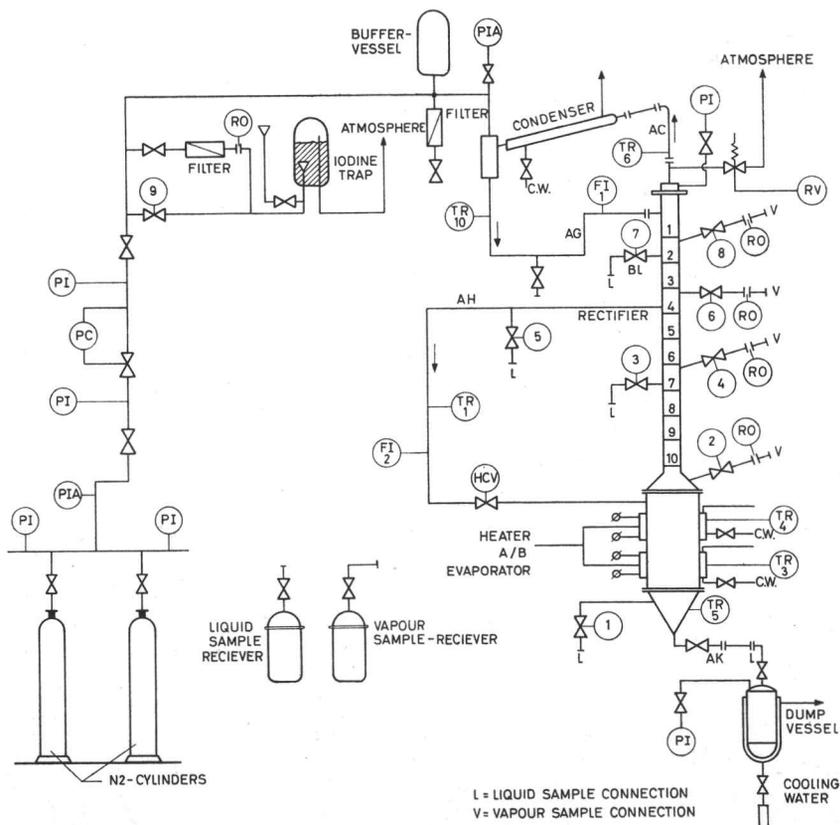


Fig. III. 4

Diagram of the experimental circuit.

In fig. III.4 a diagram is shown of the evaporator, the column and the part of the test circuit which is essential for carrying out the iodine tests. This test circuit is a full scale model of a proposed liquid purification system of a 250 kW experimental aqueous homogeneous suspension reactor. A photograph of the test circuit is shown in fig. III.5.

The maximum pressure and temperature are 60 atmospheres and 275°C. All the equipment parts are made of stainless steel of the AISI-300 series.

The evaporator is an empty vessel which can contain 36.7 l of liquid at normal level. The heat for evaporation is supplied by low frequency induction heating of the wall. For that purpose the cylindrical section of the evaporator wall is composed of two layers, an inner layer of stainless steel with a thickness of 3 mm and an outer layer of carbon steel with a thickness of 10 mm. The heat is mainly generated in the carbon steel part of the wall and it flows through the stainless steel layer to the evaporator contents. The total heat transferring surface is 0.31 m².

The electromagnetic field is produced by two coils wound around the cylindrical evaporator in two separate sections. These induction coils are thermally insulated from the evaporator wall and are cooled with water. Each coil is fed with a low frequency alternating current (50 cycles) from a 15 kVA transformer. The heat generation can be varied by means of a stepwise adjustment of the secondary voltage of the transformer and of a continuous regulation between the steps by means of a variable transformer. The maximum secondary voltage of the transformers is 23 V. The maximum net heat input in the evaporator is approximately 15 kW.

On top of the evaporator vessel a rectifying section is built. This column contains ten bubble cap trays, containing three bubble caps each. Vertical and horizontal cross section of these are shown in figs. III.6 and 7. The trays have been mounted on a central rod so that the tray assembly can be easily removed from the column. The liquid reflux flows tangentially over the plate from downcomer to overflow, passing successively the three bubble caps.

The trays are fitted in the column by means of a high temperature resistant teflon asbestos sealing. In the downcomer at the level of the tray bottom a 1 mm hole is drilled, enabling the complete drainage

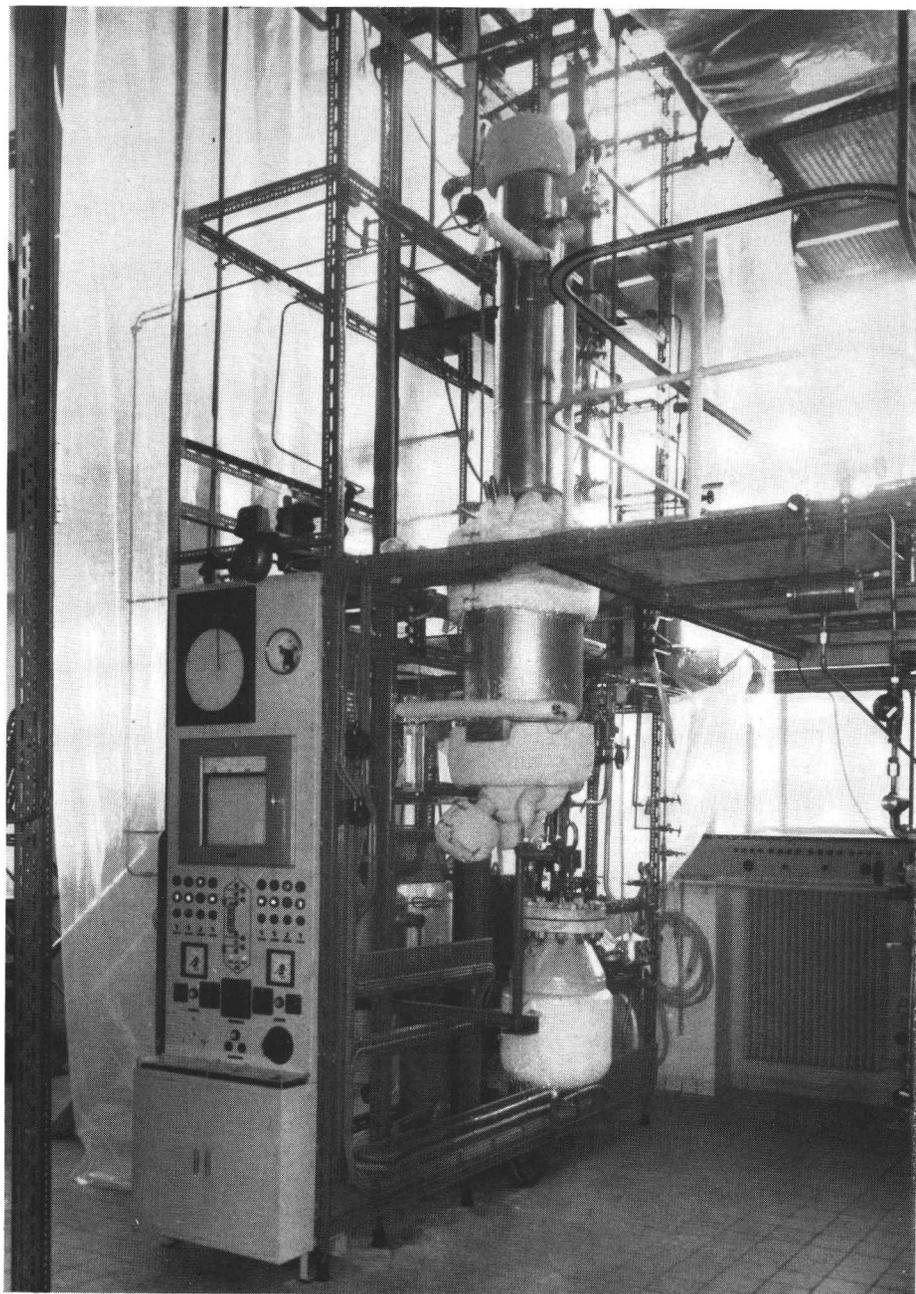
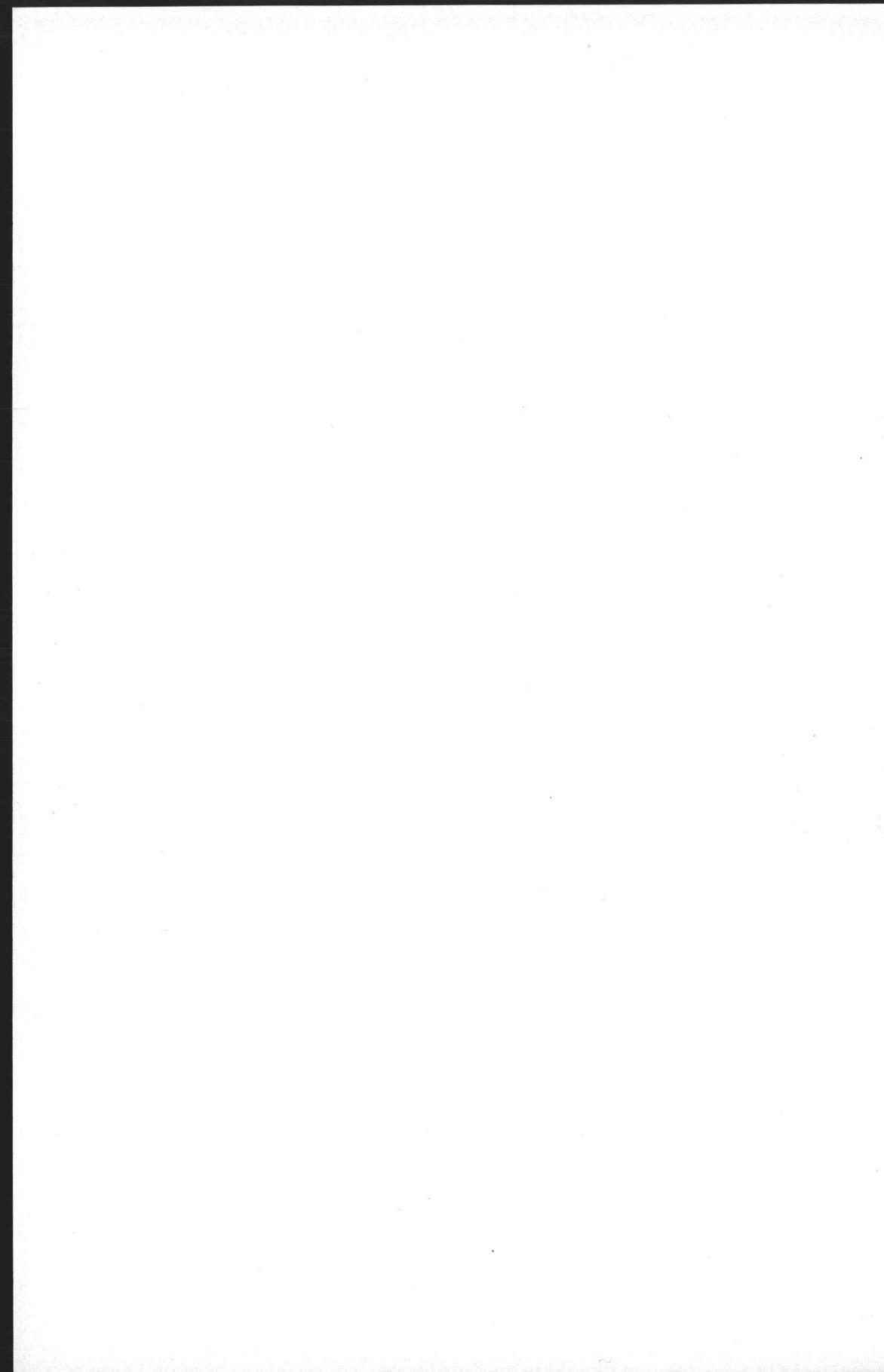


Fig. III. 5

Picture of the experimental circuit.



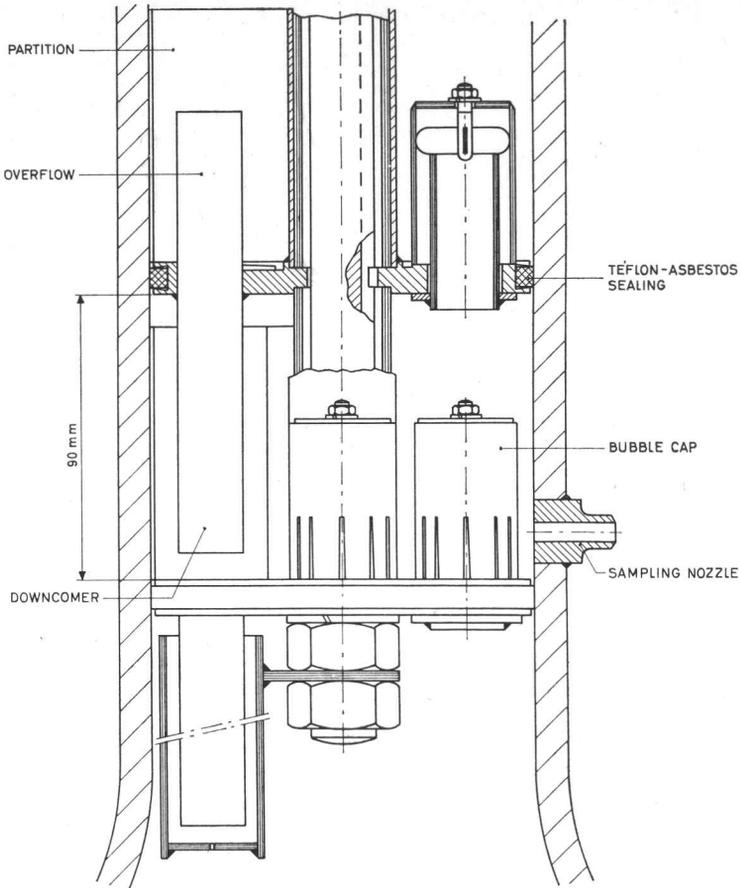


Fig. III. 6

The bubble cap trays in the column (vertical cross section).

of the plate at the end of an experiment. Fig. III.8 shows a photograph of the trays mounted on the central rod.

Above the column a condenser is mounted from which the condensed steam is returned by gravity through the line AG* and a

* The symbols in this section refer to fig. III. 4.

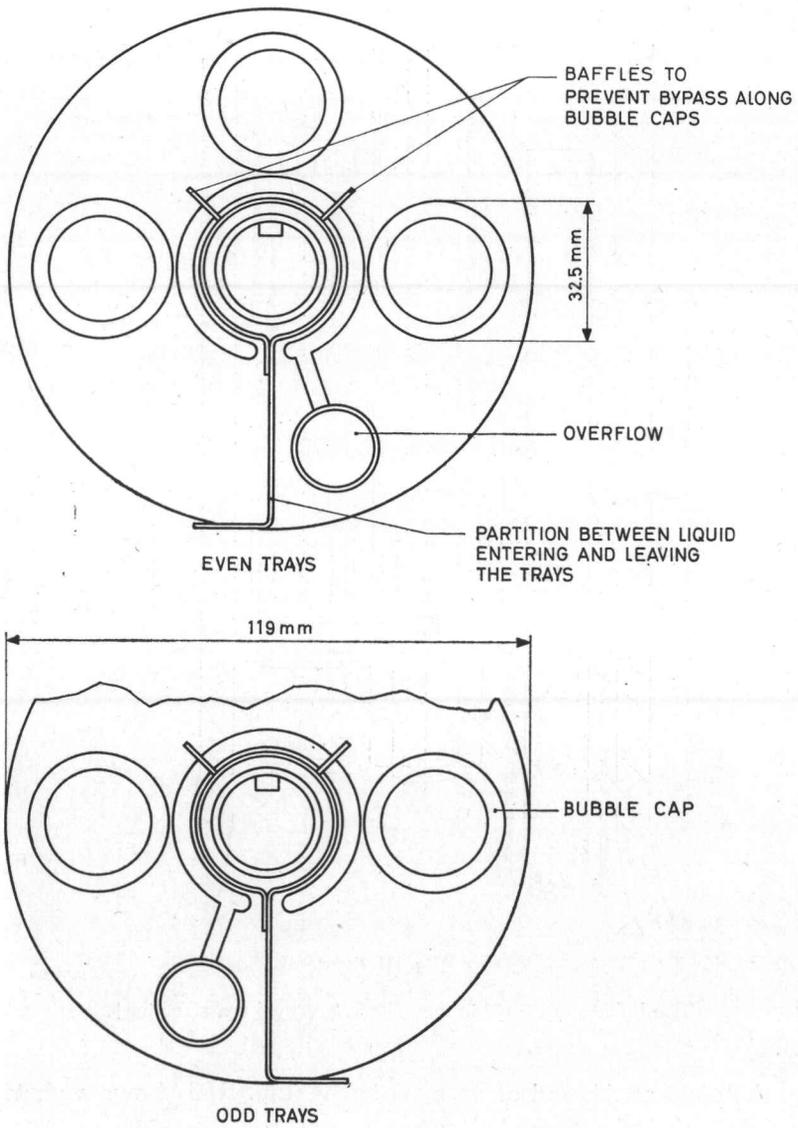


Fig. III. 7

Horizontal cross section of a bubble cap tray.

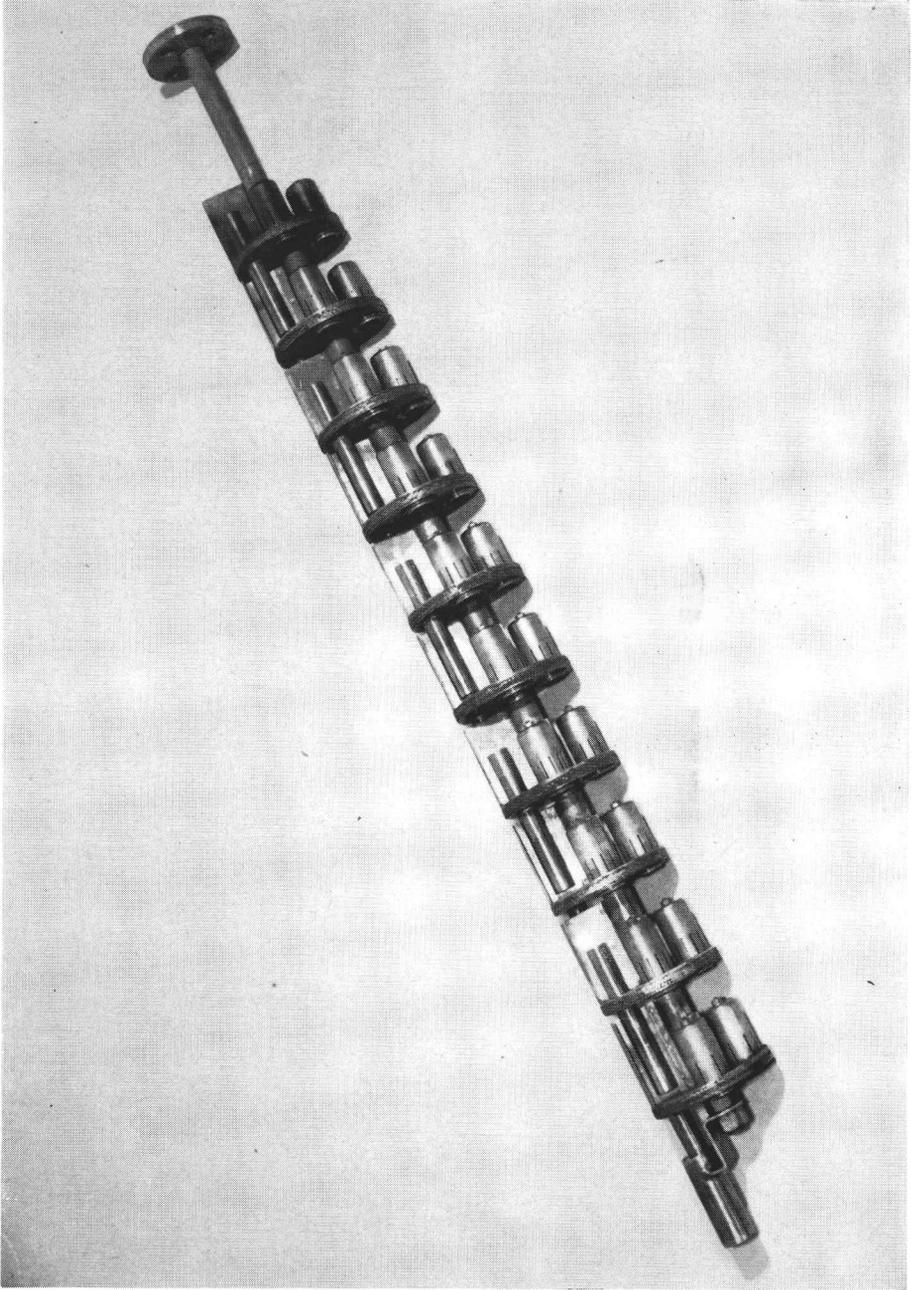
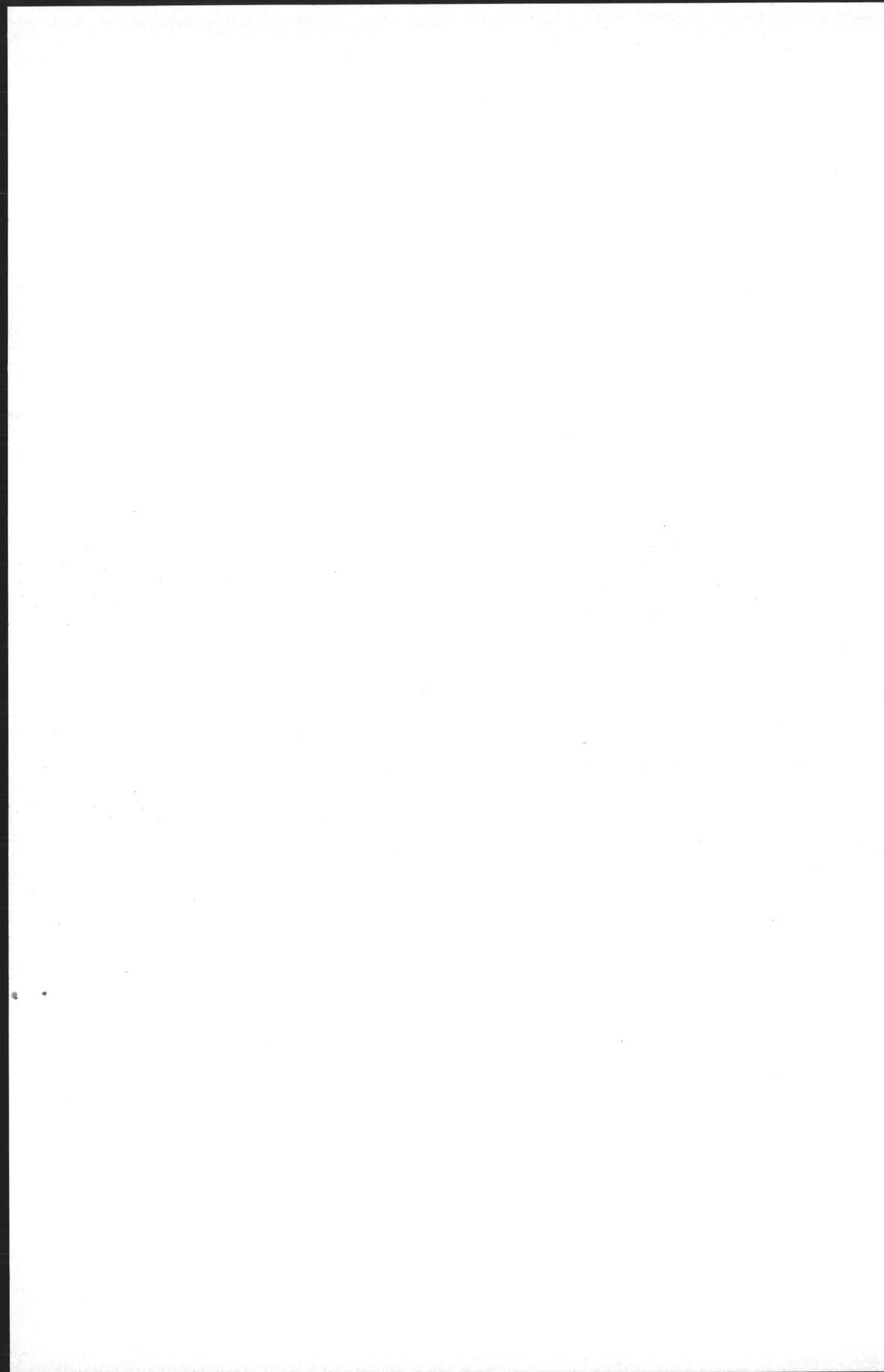


Fig. III. 8

Photograph of the trays mounted on a central bar.



rotameter FI-1 (Fischer flowrator 2—25 l/h) to the top of the column, where it is used as a reflux.

Means are provided for taking off a part of the reflux from the fourth tray and returning it directly to the evaporator bottom through line AH. For the adjustment of this liquid flow, a hand controlled valve (HCV) and a rotameter FI-2 (Fischer flowrator 2—25 l/h) are mounted. This by-pass line makes it possible to adjust a partial reflux in the bottom section of the column from the fourth to the tenth plate.

The outlet of the condenser is connected to a buffer vessel in order to eliminate pressure fluctuations. The system is pressurized by means of N₂ gas from high pressure N₂ cylinders.

At the bottom of the evaporator a dump vessel is installed, which is kept at low pressure. It is provided with external water cooling in order to maintain the temperature and consequently the pressure in the dump vessel at a low level during the discharge of the evaporator contents through line AK.

The column is provided with several sample connections. There are four vapour sample connections above trays nr. 2, 4 and 7 and at the top of the evaporator vessel. In order to prevent a too rapid removal of steam during the first moments of sampling, the restrictions indicated as RO are used. The steam is condensed by expansion and the heat capacity of the receiver.

Liquid samples can be taken from the 2nd tray, the by-pass line AH, the 7th tray and the evaporator bottom.

The sample receivers have a volume of 50 ml. The lid and the receiver are joined by means of a screwed connection and sealed with a copper ring. On the lids valves with cone joints are present to permit the attachment to the sample connections of the system.

The thermal insulation of the column and the evaporator, except for the heater sections, consists of 5 cm asbestos.

The whole installation is surrounded by a plastic foil to prevent the contamination of the laboratory with radioactive iodine in the case of a leakage.

The pressures at various places are measured by conventional means. The temperatures are measured with chromel-alumel thermocouples at several points indicated in fig. III.4 by TR. They are recorded on a Philips 12-point recorder (type PR-3210-A/00).

3.2. Experimental procedure

The evaporator is filled with water (about 20 kg) through valve 1 (see fig. III.4). Successively 1 l of a radioactive iodine solution (activity approx. 0.6 mC ^{131}I), 1 l non-active iodine solution (total amount of iodine in active and non-active solutions together is approx. 2×10^{-4} mole I_2 or 5×10^{-2} gram), a solution containing 0.12 mole H_2SO_4 and 0.06 mole $\text{K}_2\text{Cr}_2\text{O}_7$ are added. Then water is supplied until the evaporator contains 33 to 40 kg water. The amount of iodine used in the experiment is comparable with that present in the evaporator at reactor conditions. Sulphuric acid and potassium bichromate are used in order to provide for oxidizing conditions in the evaporator.

After the evaporator has been charged the cooling water valves of the condenser and of the heater coils are opened and the electric heater is switched on. As the temperature rises, the pressure is increased by adding N_2 to the system (at such a rate that the liquid in the evaporator stays near its boiling point). This procedure is continued till the desired working pressure and temperature have been reached.

The power of the heaters is adjusted at a value corresponding to the desired steam production. This steam production is determined by measuring the condensate flow (FI-1), the condensate temperature (TR-10) and the steam temperature (TR-6).

If the experiment is to be carried out at partial reflux the hand control valve in line AH is opened and the reflux take off is adjusted. Temperature, pressure, flowmeter and power readings are noted every quarter of an hour.

Once the installation is thermally stationary (approx. 4 h after the temperature in the evaporator has reached the value of 275°C) the sample receivers are connected to the column and evaporator. Then the samples from the various plates and evaporator are taken. During one experiment the sampling is repeated once in every two hours.

At the end of the run, the power supply to the evaporator heater is switched off. Then the pressure is decreased by opening valve 9. The rate of pressure decrease is adjusted in such a way that the steam production by evaporation, due to the supersaturated state of

the liquid, is adapted to the cooling capacity of the condenser. This is done by observation of flowmeter FI-1 and manipulation with valve 9. In approximately two hours the temperature of the system contents is decreased from 275°C to 100°C. Then valve 9 is closed and the cooling water supply to the heating coils is maintained during several hours in order to remove residual heat from the wall and insulation.

The duration of one experimental run is approximately 14 hours: during this period about 30—40 samples are collected.

3.3. *Sampling procedure and concentration measurement*

An important part of the experimental procedure is the determination of the iodine distribution in the column. The concentration of iodine at several points of the column is determined by sampling and subsequent measurement of ^{131}I radioactivity with the aid of a scintillation counter. We shall first describe the sampling procedure. Thereafter, the counting apparatus and the counting procedure will be treated.

The sampling procedure

Before the sampling can be carried out, the sample receivers and lids are cleaned and dried. Then 5 ml 0.1 N KI solution is added to them, except for the one which is to be used for sampling the evaporator contents. The purpose of the addition of KI solution to the sample vessels is to prevent adsorption of the iodine present in low concentrations on the steel wall of the receiver. The concentration in the top of the column is often very low and approximately 2×10^{-6} g/l. Moreover, the KI solution strongly dilutes the radioactive ^{131}I in the vapour phase, if volatile iodine is present. The addition of a KI solution to the bottom sample is of no use because of the oxidant present in the evaporator contents.

After they have been closed, the sample receivers are connected to the corresponding sampling connections of the evaporator and the column. Since the sampling procedure has a certain influence on the operating of the column, the samples are taken in such a sequence that each is taken upstream the preceding one.

The mass of the liquid sample (ca. 40 g) is rather small com-

pared with the mass present on the tray (ca. 250 g). The liquid sampling connection is situated near the overflow of the tray, so that it can be considered to be representative of the liquid leaving the plate. The vapour sample, however, contains more material (ca. 40 g) than there is vapour present over a tray (ca. 15 g). This means that the vapour sample may not be representative unless it is drawn off at a very low rate. An exception can be made for the vapour sample taken from the vapour over the boiling liquid in the evaporator. Thus, apart from the latter, the vapour samples are much less reliable than the liquid ones.

First the liquid samples are taken, starting with the lowest sample (valve 3 in fig. III.4) and continuing successively with the higher liquid samples of the column (valves 5 and 7). The time required for taking a liquid sample is short, only 1–2 sec. per sample. Thereupon, the vapour samples are taken starting with valve 8, and continuing with valves 6, 4 and 2. The time taken for vapour sampling is 20 to 30 seconds per sample.

Once the samples have been taken, the receivers are disconnected and cooled in a tank with water. The valves on the lids are opened in order to let off pressure. In the case of the liquid sample of the evaporator, this is done via a filter containing cotton wool soaked in a KI solution by which the escape of volatile active iodine is prevented.

To avoid inhalation, the sample receivers are opened in a hood. The loss of activity proved to be only small during the manipulation with the sample and does not seriously affect the determination of the concentration. After opening the samples are put into 100 ml flasks. The sample vessels are rinsed with 0.01 N KI solution which, after rinsing, is also added to the flasks. Then the flasks are filled with water to the calibration mark. After cleaning and drying, the receivers and lids are ready for use again.

Several samples are taken with the purpose of isolating I_2 as rapidly as possible. To this end, instead of a KI solution, 5 ml decaline is put into the receiver before sampling, in which I_2 from the sample is to be preferentially dissolved. After closing and before sampling, these receivers are evacuated by means of a water jet pump in order to prevent a pressure higher than one atmosphere after sampling and cooling. These samples are emptied into a burette

to check the amount of decaline left. Sometimes, if the quantity of sampled liquid is too large, some decaline is left in the tubing on the lids of the sample receivers. A correction for the decaline lost can be made. The sample vessel is rinsed with toluene which is also put into the burette. Then the water phase of the sample is put into a 100 ml volumetric flask and the flask is filled with some KI solution and water to the calibration mark. The decaline-toluene mixture is put into a 50 ml volumetric flask and the flask is filled to the calibration mark with toluene. The sample vessels are cleaned with acetone.

The radioactivity from ^{131}I of the liquids in the flasks is measured by pipetting 50 ml liquid into a counting vessel followed by counting with a scintillation counter. Then the counting vessels are emptied and thoroughly rinsed either with acetone followed by rinsing with a 0.01 N KI solution, or only rinsed with the KI solution depending on whether decaline or an aqueous solution was put into the vessels.

Then the counting vessels are washed in water, dried and ready for use again. The activity of the counting vessel itself after this procedure is less than 0.2 counts/sec.

The concentration measurement

The iodine concentration in the counting vessels is determined by measurement of the ^{131}I activity with a scintillation counter. A scintillation crystal (NaI-Tl) with the dimensions of 1.5×1.5 inches is placed on a photomultiplier tube EMI-6260. The crystal and tube are surrounded by an aluminium canning.

As is shown in fig. III.9 the counting vessel, containing a sample of 50 ml liquid, has such a shape that the crystal is surrounded by the liquid layer of constant thickness as well as possible. These counting vessels are made of glass and have a wall thickness of 2 mm. Several counting vessels are used. Due to small deviations in the dimensions it proved to be necessary to calibrate the position of the individual counting vessels on the crystal.

The counting equipment further consists of a high tension source, a cathode follower (mounted in the multiplier container), an impulse amplifier, a channel discriminator and a counter.

The voltage over the multiplier is 808 V. The amplification is 840 times. The channel width is 10 V (24 V—34 V). The γ -line of

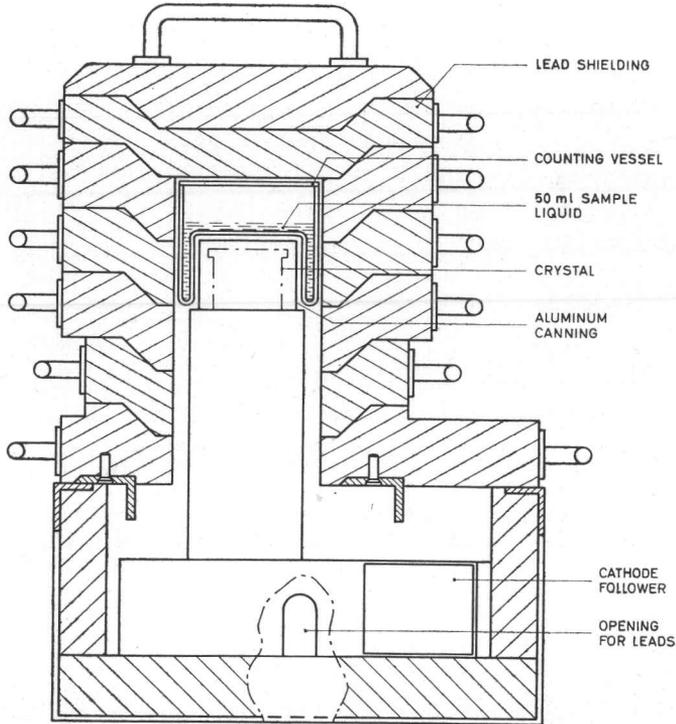


Fig. III. 9

Cross section of the lead castle.

0.36 MeV corresponds to a height of 29 V. The sensitivity is 1 n Curie at a counting rate of 1 count/sec and the background counting rate is 0.4 counts/sec. Incidentally the background is higher due to contamination of the canning of the crystal, but it never exceeds 1 count/sec.

The measured count rate is first corrected for the background count rate. This correction is relevant only for the samples with a low activity. The measurements of the activity of the several samples of one experiment takes two days. Thus a correction is necessary for the decay of ^{131}I . The various samples are not equal in weight. Therefore, all activities are calculated per 50 grams of sample at a certain reference time. The accuracy of the measured iodine concentration will be discussed in appendix 4.

4. Results

The experiments for determining the distribution of iodine in the column were carried out at several values of the total and partial reflux (26 kg/h—1 kg/h) and several temperatures (275°C—120°C). The results are given in the tables of appendix 6 and will be discussed in the following sections.

In section 4.1 the results at total reflux and in section 4.2 those at partial reflux will be treated. An estimation of the numerical values of the Murphree plate efficiency, E , the phase equilibrium constant for I_2 in water, K , and the reaction velocity constant for the reduction of I_2 , k , is carried out in section 4.3.

From the results presented here it is concluded that rectification at 275°C is an efficient method to separate volatile iodine from water.

However, at lower temperatures this separation becomes more difficult whereas at approximately 120°C the separation is not possible at all. Above this temperature, the apparent volatility of iodine in water is smaller than one; below this temperature the opposite appears to be the case.

4.1. *The experiments with total reflux*

In tabel III.2 the ζ values for total reflux are given for several values of this reflux and temperatures. The accuracy of the ζ value is given by an upper and a lower limit with a probability of 70 % that the true value of ζ is between these limits. A discussion of the precision of the measurements is given in appendix 5.

The ζ value is calculated from each possible combination of two concentrations. It has been assumed that ζ has the same value for all plates. In principle this assumption is not correct, because it is to be expected that the upper plates have a somewhat higher value.

TABEL III.2

Values of ζ for total reflux, at different values of the reflux flow L and temperature T

Experiment	Temperature °C	Reflux L kg/h	$\zeta = \frac{y}{x}$ for one tray. The precision is indicated by the 70% confidence					
			y_{11} and x_7	y_{11} and y_7	y_{11} and y_4	y_{11} and x_2	y_{11} and y_2	x_7 and y_7
15	270	26.4	0.54 ± 0.10	0.52 ± 0.02		0.59 ± 0.01	0.54 ± 0.04	0.5 ± 0.0
14	270	19.9 ± 0.4	0.48 ± 0.04	0.44 ± 0.14		0.50 ± 0.08	0.53 ± 0.08	0.38 ± 0.0
21	273	19.4 ± 0.7	0.55 ± 0.06	0.54 ± 0.05		0.48 ± 0.03	0.52 ± 0.04	0.43 ± 0.0
24	271	12.9 ± 0.2	0.44 ± 0.04	0.34 ± 0.06	0.39 ± 0.07	0.40 ± 0.03		0.16 ± 0.0
22	270	3.7	0.36 ± 0.01	0.32 ± 0.07		0.45 ± 0.03	0.47 ± 0.06	0.25 ± 0.0
27	200	14.5 ± 1.5	0.90 ± 0.02	0.93 ± 0.06	0.95 ± 0.04	0.91 ± 0.03	0.95 ± 0.06	1.02 ± 0.0
28—05	200	6.5	0.88	0.88	0.85	0.81	0.77	0.90
29	121	3.1 ± 0.1	1.11 ± 0.12	0.94 ± 0.05	0.96 ± 0.05	0.98 ± 0.05	0.99 ± 0.03	0.62 ± 0.0

This can easily be concluded from an examination of eq. 2.14. As was already discussed in section 3.3, the most representative samples are the liquid samples and the vapour sample from the evaporator (y_{11}). The conditions in the lower part of the column are best in agreement with the assumption of a constant ζ value. Therefore, the ζ value calculated from y_{11} and x_7 (iodine concentration in the liquid of the 7th tray) are used to compare the experimental results with the theoretical relation between ζ and the other variables which was derived in section 2.1 and given in equation 2.19.

From table III.2 it appears that at a temperature of 270°C ζ decreases with decreasing reflux. This is in accordance with the relationship between ζ and L given in eq. 2.19. This will be discussed more amply in section 4.3.

A comparison of the ζ value calculated from y_{11} and x_7 , $\zeta(y_{11}, x_7)$,

limits								
x_7 and y_4	x_7 and x_2	x_7 and y_2	y_7 and y_4	y_7 and x_2	y_7 and y_2	y_4 and x_2	y_4 and y_2	x_2 and y_2
	0.62 ± 0.10	0.55 ± 0.02		0.66 ± 0.02	0.57 ± 0.12			0.31 ± 0.24
	0.55 ± 0.11	0.53 ± 0.03		0.58 ± 0.06	0.62 ± 0.17			0.9 ± 0.4
	0.44 ± 0.02	0.50 ± 0.12		0.45 ± 0.06				0.79 ± 0.16
0.35 ± 0.08	0.38 ± 0.02			0.48 ± 0.08		0.36 ± 0.08		
	0.52 ± 0.05	0.52 ± 0.14		0.62 ± 0.19				0.4 ± 0.6
0.93 ± 0.02	0.91 ± 0.03	0.92 ± 0.02	0.92 ± 0.07	0.89 ± 0.02	0.91 ± 0.06	0.72 ± 0.05	0.87 ± 0.04	1.07 ± 0.06
0.84	0.77	0.72	0.82	0.75	0.69	0.57	0.54	0.50
0.87 ± 0.06	0.92 ± 0.05	0.95 ± 0.04	0.98 ± 0.03	1.03 ± 0.13	1.04 ± 0.03	1.14 ± 0.20	1.13 ± 0.04	1.15 ± 0.20

and that calculated from x_7 and x_2 , $\zeta(x_7, x_2)$, can teach us whether the ζ values for plates in the top of the column are higher than those for plates in the lower part of the column. The experiments 15, 14 and 22 give $\zeta(y_{11}, x_7) < \zeta(x_7, x_2)$, however, the experiments 21 and 24 show the opposite case. As a consequence of the rather poor precision in the ζ values it can be concluded that there is no reason to expect a higher value of ζ in the top from these results.

The ζ values determined from the vapour and liquid concentrations measured on one tray show in some cases a large deviation from the ζ values derived from measurements on two different trays. This supports the opinion that the vapour samples are less reliable.

No influence of the iodine concentration on the iodine distribution in the column is observed. Experiment 15 is carried out with an iodine concentration 200 times higher than for the other experiments. The

deviation of the ζ value of this experiment and the other experiments can be explained by the fact that a high value of the reflux is applied.

From table III.2 it is observed that ζ increases at decreasing temperature. At 200°C separation of iodine from steam can only be realized by the application of a large number of trays whilst at 120°C no separation is possible. The increase of ζ with decreasing temperature can be explained qualitatively by the decrease of reaction velocity constant for the conversion of I_2 into I^- , and the increase of the phase equilibrium constant, K , with decreasing temperature. The latter is in accordance with the behaviour of K as a function of temperature (see section 1.2).

In order to obtain some information on the fraction of molecular iodine present in the vapour and liquid in the column, some samples were taken where some decaline had been put into the sample vessels beforehand. Indeed some iodine was found in the decaline, but not more than 30 % of the total amount present in the vapour and 5 % of the total amount present in the liquid. Due to the low volatility of the iodide, all the iodine present in the vapour must be molecular form. That not more iodine is found in decaline in the case of a vapour sample, is probably due to some reduction already taking place before extraction of I_2 in the decaline. Furthermore, some reduction of I_2 present in decaline can also occur. Though no numerical values about the fraction of molecular iodine present in the column can be given because of the poor reproducibility, it has been shown that the molecular iodine concentration in the vapour is higher than in the liquid.

4.2. *The experiments with partial reflux*

The ζ values obtained from the experiments with partial reflux are collected in table III.3. Here too, the values of ζ calculated from y_{11} and x_7 are considered to be the most reliable.

From these results it appears that ζ decreases with decreasing reflux. The value of ζ calculated from x_7 and y_7 in some cases deviates appreciably from the value calculated from y_{11} and x_7 . As is already pointed out in section 4.1, this was probably due to the

TABEL III.3

Values of ζ for partial reflux, at different values of the vapour flow V and the reflux L

Experiment	Temperature °C	Vapour flow V kg/h	Reflux L kg/h	$\zeta = \frac{y}{x}$ for one tray. The precision is indicated by the 70 % confidence limits			
				y_{11} and x_7	x_7 and x_4	y_7 and x_4	x_7 and y_7
15-05	275	17.0	0.9	0.017			0.023
18-08/10	273	11.2 ± 0.6	1.8 ± 0.4	0.053 ± 0.008			
18-10	273	10.9	1.4		0.063	0.031	0.22
18-09	273	12.0	2.3		0.070	0.038	0.20
18-07	273	11.9	3.6				0.083
26-02/05	275	15.5 ± 0.4	3.5 ± 0.3	0.12 ± 0.02	0.12 ± 0.01	0.10 ± 0.01	0.18 ± 0.10
25-02/08	271	15.9 ± 0.2	3.8 ± 0.2	0.13 ± 0.02			
16-04/05	274	14.1 ± 0.8	4.5 ± 0.5	0.15 ± 0.02			
16-05	273	14.5	4.8		0.10	0.13	0.15
14-04/06	275	15.5 ± 0.6	5.2 ± 0.3	0.11 ± 0.02			
16-01/03	274	16.1 ± 0.2	6.3 ± 0.2	0.21 ± 0.01			
17-01	268	15.6	6.9				0.23
17-04	270	15.4	7.3				0.08
17-01/05	270	16.6 ± 0.8	8.3 ± 0.7	0.24 ± 0.03			
17-05	270	17.0	8.7		0.17		
17-02	268	18.4	10.3				0.15
15-03/04	275	24.6 ± 0.1	11.2 ± 0.1	0.23 ± 0.02			0.13 ± 0.1

unreliability of y_7 . The ζ value calculated from x_7 and x_4 and from y_{11} and x_7 are rather in good agreement. This leads to the conclusion that ζ is in fact independent on the tray number.

Experiment 26 was carried out under the conditions that are close to those to be applied in the liquid purification system of an experimental suspension reactor (see part II.6). It is shown in table III.3 that all the ζ values calculated from the several combinations of two samples of experiment 26 are in good agreement with each other. Also the ζ value for tray 2, where we have total reflux, is in good agreement with the value of ζ obtained in other experiments with total reflux (see in Appendix 6 the list of results of experiments 26, $\zeta(x_2, y_2) = 0.45$ at $L = 15.5$ kg/h).

It is useful to check whether the assumption made in section 2.1 $D \ll x_n L$ is valid in the case of experiment 26. This can be done by calculating the deviation introduced by this simplification. Without neglectation of D , equation 2.5 in section 2.1 has to be written as:

$$\frac{y_n}{y_{n+1}} = \zeta_n \left(\frac{L}{V} + \frac{D}{x_n V} \right)^{-1}. \quad 4.1$$

Considering the first tray with partial reflux, this equation becomes:

$$\frac{y_5}{y_6} = \frac{\zeta_5 V x_5}{L x_5 + D}. \quad 4.2$$

With:

$$D = x_4 (V - L) \text{ and } x_4 = \zeta_5 x_5,$$

eq. 4.2 becomes:

$$\frac{y_5}{y_6} = \zeta_5 \frac{V}{L} \frac{1}{1 + \frac{V-L}{L} \zeta_5},$$

or:

$$\frac{y_5}{y_6} = \zeta_5 \frac{V}{L} \left(1 - \frac{\frac{V-L}{L} \zeta_5}{1 + \frac{V-L}{L} \zeta_5} \right). \quad 4.3$$

Thus the correction to be applied to ζ , under the assumption that

$$\frac{y_5}{y_6} \approx \zeta \frac{V}{L}$$

is:

$$\frac{\zeta}{\zeta_5} - 1 \approx - \frac{(V-L)\zeta}{(1-\zeta)L + V\zeta} \quad 4.4$$

During experiments 26 the following figures were obtained:

$$\zeta = 0.12, \quad \bar{V} = 15.5 \text{ kg/h}, \quad \bar{L} = 3.5 \text{ kg/h},$$

thus:

$$\frac{\zeta}{\zeta_5} \approx 0.7.$$

Along the same lines it can be found that

$$\frac{\zeta}{\zeta_6} \approx 0.85 \text{ and } \frac{\zeta}{\zeta_7} \approx 0.92.$$

From these figures and from the approximated relation for ζ , determined by the iodine concentrations in the liquid on the 4th and 7th tray i.e.

$$\zeta(x_4, x_7) \approx (\zeta_5 \cdot \zeta_6 \cdot \zeta_7)^{1/3}, \quad 4.5$$

we find $\zeta \approx 0.8 \zeta(x_4, x_7)$.

Thus, in the upper part of the column with partial reflux an underestimation of approximately 20 % in is made when D is neglected with respect to $x_n L$. This error is of the same order as the confidence limits of the measurements of experiment 26.

4.3. The estimation of Murphree plate efficiency, E , the rate of conversion of I_2 to I^- and the phase equilibrium constant, K , of I_2 in water at 273°C.

In fig. III.10 the ζ 's calculated from y_{11} and x_7 have been plotted against the reflux L . It is of interest to determine whether the results are in agreement with the theoretical relationship between the variables and to estimate the numerical values of E , K and k .

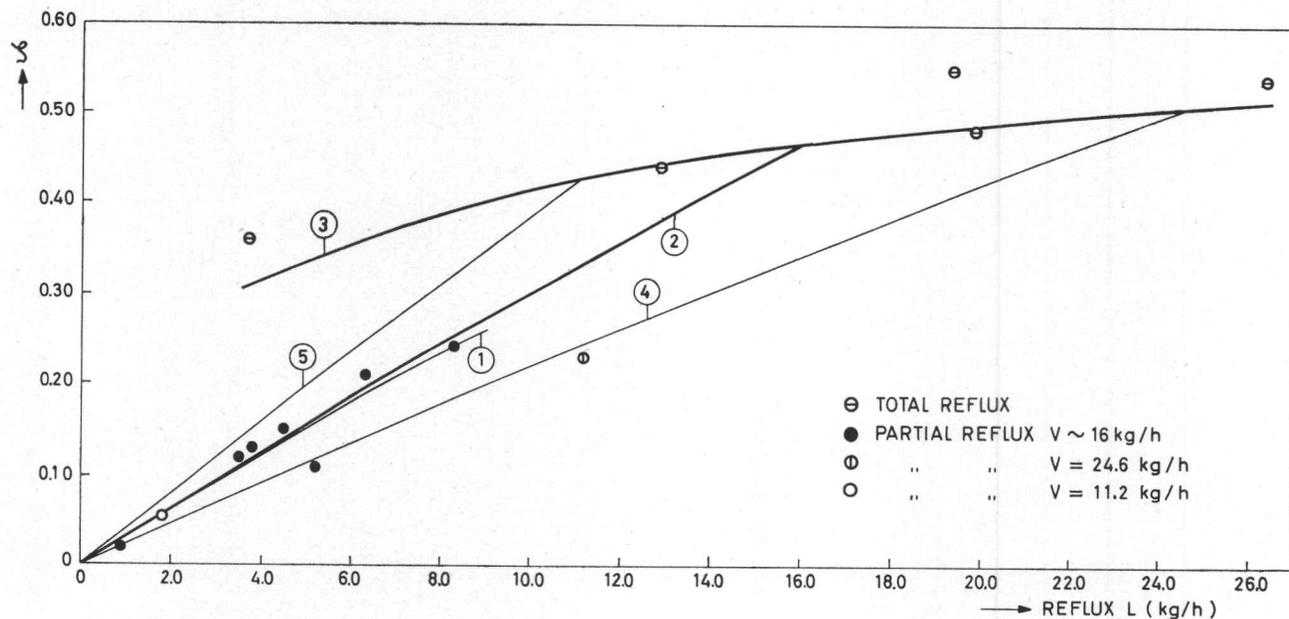


Fig. III. 10

The ratio $\zeta = \frac{y}{x}$ for one plate calculated y_{11} and x_7 as a function of the reflux, L . ① $\zeta = 3.3 \times 10^{-2} L - 4.3 \times 10^{-4} L^2$ (eq. 4.9). ② $\zeta = \zeta(L)$ according to 4.6 with $E = 0.62$, $K = 0.29$ and $k = 36 \text{ h}^{-1}$. ③ $\zeta = \zeta(L)$ according to 4.6 with $E = 1 - \exp(-1.73 V^{-0.21})$, $K = 0.29$ and $k = 36 \text{ h}^{-1}$. ④ $\zeta = \zeta(L)$ according to 4.6 with $E = 0.59$, $K = 0.29$, $k = 0.36 \text{ h}^{-1}$ and $V = 24.6 \text{ kg/h}$. ⑤ $\zeta = \zeta(L)$ according to 4.6 with $E = 0.65$, $K = 0.29$, $k = 0.36 \text{ h}^{-1}$ and $V = 11.2 \text{ kg/h}$.

The relationship derived in section 2.1 was:

$$\zeta \approx (1 - E) \frac{L}{V} + \frac{KE}{1 + \frac{mk}{L} \left(1 + \zeta \frac{V}{L}\right)}. \quad 4.6$$

The results for partial reflux show that ζ is almost proportional to L ; this indicates that the second term on the right hand side of 4.6 is small compared with the first term.

Because ζ is not linear in the variables E , K and k a direct determination of the numerical values of these quantities by applying the method of least squares is impossible. Therefore, we shall try to

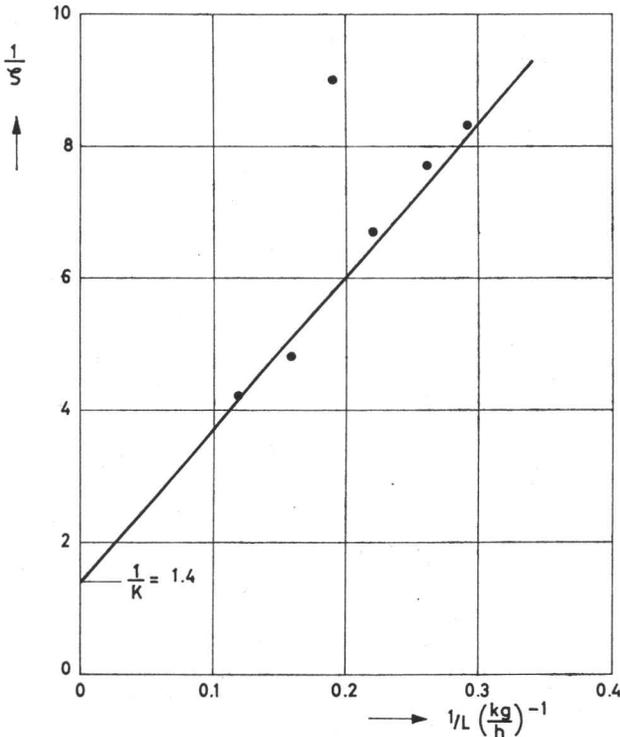


Fig. III.11

The estimation of K from a linear extrapolation of $\frac{1}{\xi}$ to $\frac{1}{L} = 0$ if $E = 100\%$.

find the limits between which the values of E , K and k can lie according to the experimental results.

The upper value of the tray efficiency, E , is 100%. We will assume that E has this value, we may write for $1/\zeta$:

$$\frac{1}{\zeta} \approx \frac{1}{K} + \frac{\frac{m}{L} k \left(1 + \zeta \frac{V}{L}\right)}{K} \quad 4.7$$

From this relationship we can estimate the value of K by plotting $1/\zeta$ against $1/L$ from which $1/K$ is found by extrapolation to $1/L = 0$. This has been done in fig. III.11 for $V = 16$ kg/h. In this way we obtain; $1/K \approx 1.4$ or $K \approx 0.7$. Because $\zeta V/L \approx 0.5$, we can calculate from the slope of the curve in fig. III.11 that:

$$\frac{mk}{K} \approx 15 \text{ kg/h.}$$

With $K \approx 0.7$ we obtain: $mk \approx 11$ kg/h.

We can also assume that $K = 0$ or that mk is infinitely large. In that case 4.6 is reduced to:

$$\zeta \approx (1 - E) \frac{L}{V}.$$

For $V = 16$ kg/h the value $\zeta V/L \approx 0.5$, hence $E \approx 0.5$. Thus, from the measurements at partial reflux with a vapour flow of 16 kg/h the results can be summarized by:

$$\begin{aligned} 0.5 &\leq E \leq 1; \\ E &= 1 \text{ if } K = 0.7 \text{ and } mk = 11 \text{ kg/h,} \\ E &= 0.5 \text{ if } K = 0 \text{ and } mk > 11 \text{ kg/h or} \\ &mk = \infty \text{ and } K < 0.7. \end{aligned}$$

From the measurements at total reflux comparable conclusions can be drawn. All these experiments give $\zeta \approx 0.5$.

Thus:

$$0.5 \approx (1 - E) + \frac{KE}{1 + 1.5 \frac{mk}{L}}.$$

We can now consider two different cases:

a) $K \ll 1$ or/and $\frac{mk}{L} \gg 1$, gives $E \approx 0.5$.

b) If $E = 1$, then $K = 0.5$ if $\frac{mk}{L} \ll 1$ or

$$K = \frac{3}{4} \frac{m}{L} k \text{ if } \frac{m}{L} k \gg 1.$$

Both possibilities of situation *b* are improbable because we expect that $\frac{mk}{L}$ is not small and K has not a high value. This means that E is smaller than one.

The conclusion of this reasoning is that a value of K between 0 and 0.7 has to be expected. The value reported by Keeler i.e. $K \approx 0.29$ (see section 1.2) is not in contradiction with this result, whereas also the hypothesis made in section 1.2 i.e. that $K < 1$ is confirmed. The results of the experiments can only be understood if $k > 0$; it can be concluded, therefore, that a reduction of I_2 takes place. Of the value of E we can say that the expected value between 0.5 and 1 is in good agreement with other experience with bubble cap trays.

We will now calculate the values of E and k which belong to $K \approx 0.29$. Because E is a function of the vapour flow, V , we will use ζ at a vapour flow of about 16 kg/h:

Therefore, we develop the right-hand side of 4.6 into a power series of L ,

$$\zeta \approx \left\{ \frac{1-E}{V} + \frac{KE}{mk \left(1 + \zeta \frac{V}{L}\right)} \right\} L - \frac{KE}{\left\{ mk \left(1 + \zeta \frac{V}{L}\right) \right\}^2} L^2 \dots \quad 4.8$$

For the values of L where $\frac{L}{mk} \ll 1$, this series is converging; we shall break it off after the second term. For the experiments at partial reflux with a vapour flow of 16 kg/h the value of $\zeta \frac{V}{L} \approx 0.5$. This value is introduced into the right-hand side of 4.8 and from

the experimental values of ζ at partial reflux with $V = 16$ kg/h, the following form of eq. 4.8 was found by application of the method of the least squares:

$$\zeta \approx 3.3 \times 10^{-2} L - 4.3 \times 10^{-4} L^2. \quad 4.9$$

This relationship is shown in fig. III.10 as curve ①. With $K \approx 0.29$ we obtain: $E \approx 0.62$ and $mk \approx 13.7$ kg/h. The amount of water present on one tray, m , is approximately 0.38 kg at a temperature of 275°C. Hence: $k \approx 36$ h⁻¹. This means that each minute approximately half the amount of I₂ initially present on the tray is reduced.

Because 4.8 and 4.9 are only valid for those values of L where $L < mk$, these equations can not be used to calculate the value of ζ at total reflux, i.e. $L = 16$ kg/h. In that case we have to use eq. 4.6 and curve ② in fig. III.10 represents this relationship for $V \approx 16$ kg/h with $K \approx 0.29$, $E \approx 0.62$ and $mk \approx 13.7$ kg/h. At $L = V$, a value $\zeta \approx 0.46$ is found. This value is in good agreement with the other values of ζ measured at total reflux.

Examination of the experimental values at total reflux shows that ζ is only to a minor extent dependent on L . This is in accordance with 4.6, because only the second term is decreasing with L . At very small values of the reflux: $\zeta \approx 1 - E$. If E does not depend on V , a value of $\zeta \approx 0.38$ has to be expected at $L = 0$. Although the experimental ζ values have a rather poor precision, this value of ζ seems positively to high. This result is in agreement with the general experience according to which the tray efficiency somewhat decreases with increasing vapour load. *Frank and Schulte Vieting* [22, 23] have measured the Murphree point efficiency for the vapour in a model of a bubble cap plate as a function of the vapour flow. In our case there is no difference between the local and overall plate efficiency since the liquid on the plates is well mixed. From these references it is derived with $E = 0.62$ at $L = 16$ kg/h:

$$E = 1 - \exp(-1.73 V^{-0.21}). \quad 4.10$$

Curve ③ shows the relationship between ζ and L for total reflux according to 4.6 and 4.10 with $K \approx 0.29$ and $mk \approx 13.7$ kg/h. This curve shows a reasonable agreement with the experimental results.

Finally we shall examine whether the two values of ζ at partial reflux under the conditions of respectively $L = 11.2$ kg/h with $V = 24.6$ kg/h and $L = 1.8$ kg/h at $V = 11.2$ kg/h are in agreement with the other results. Curve (4) in fig. III.10 gives $\zeta(L)$ according to 4.6 with $V = 24.6$ kg/h and $E = 0.59$ from 4.10. It is observed that the measured value of ζ at $L = 11.2$ kg/h and $V = 24.6$ kg/h does not deviate much from curve (4). The measured value of ζ for $L = 1.8$ kg/h and $V = 11.2$ kg/h is lower than is expected from curve (5) which is the relationship between ζ and L according to 4.6 with $E = 0.65$. It is, however, to be noted that at this low reflux the precision of L is poor and that the observed difference is within the confidence limits.

The conclusion of the above considerations is that, due to the rather large error, the experimental results do not lead to an exact determination of the numerical value of E , K and k . However, an estimate of the numerical values can be given and the relative position of the experimentally determined ζ values in fig. III.10 can be explained by the theory of a combined effect of diffusion of I_2 into the water followed by a conversion of I_2 into I^- due to the presence of iron.

The practical result of this investigation is that under the experimental conditions at high temperature (273°C) a nearly complete separation between iodine and water can be obtained.

List of symbols used in part III

Symbol	Description	Dimension
D	Iodine take off from the 4th plate	kg/sec
E	Murphree plate efficiency on the vapour side	—
\mathcal{H}	Henri coefficient	atm
K	Phase equilibrium constant; $\frac{\text{mass fraction comp. in vapour}}{\text{mass fraction comp. in liquid}}$	—
L	Liquid reflux	kg/sec
M	Molecular weight	—
S	Separation factor; $S = \zeta \frac{V}{L}$	—
T	Temperature	°C
V	Vapour flow	kg/sec
k	Reaction velocity	sec ⁻¹
m	Mass of liquid on a tray	kg
m	Number of trays	—
n	Number of trays, number of experiments	—
p	Partial pressure	atm
p	Number of trays between two points in the column where samples are taken	—
p°	Saturated vapour pressure	atm
r	Conversion rate; $\frac{\text{kg I}_2}{\text{kg liquid} \cdot \text{sec}}$	sec. ⁻¹
s	Estimated standard deviation of the distribution of a single stochastic variable: $s = \sqrt{\frac{\sum (z - z_i)^2}{n - 1}}$	—
t	Parameter of Student	—
x	Iodine concentration in the liquid; $\frac{\text{kg iodine}}{\text{kg liquid}}$	—
x°	Molecular iodine concentration in the liquid; $\frac{\text{kg I}_2}{\text{kg liquid}}$	—

Symbol	Description	Dimension
x	Iodide concentration in the liquid; $\frac{\text{kg I}^-}{\text{kg liquid}}$	—
y	Iodine concentration in the vapour; $\frac{\text{kg iodine}}{\text{kg vapour}}$	—
y°	Molecular iodine concentration in the vapour; $\frac{\text{kg I}_2}{\text{kg vapour}}$	—
z	Stochastic variable, e.g. $\frac{y}{x}$ for one plate from one measurement	—
Δ	Small value or difference	—
Σ	Summation operator	—
α	Relative volatility	—
α	Probability that the true value of ζ is not between the confidence limits of the experimentally determined value; $\alpha = 0.3$	—
ζ	Ratio of the iodine concentration in the vapour and in the liquid for one plate $\zeta = \frac{y}{x}$	—
ρ	Density	kg/m^3

Index	Description
i	Index for indicating a certain experiment or certain plate
l	Liquid
v	Water vapour
—	A bar above a value indicates a mean value
2 etc.	The numbers indicate a specific plate in the column

APPENDICES

Appendix 1

Determination of the phase equilibrium constant of I_2 in water at $100^\circ C$ [18].

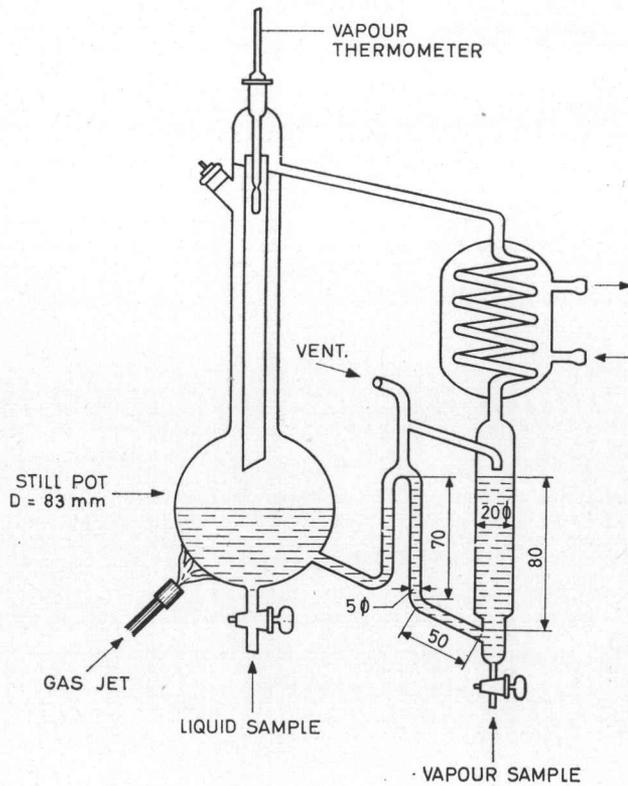


Fig. 1 of appendix 1

Modified Othmer Still.

A modified Othmer apparatus made of Pyrex glass as shown in fig. 1 has been used. In the still pot the iodine solution is boiled and superheated on its way to the condenser to prevent reflux. For this purpose the connection between the still pot and the condenser is wrapped with a heating wire. The condensate passes through an overflow and is returned to the still pot. In this way a circulation is obtained and after due time a steady state is reached. It is assumed that the vapour produced in the still is in phase equilibrium with the boiling liquid. Since the vapour is completely condensed, the composition of the condensate is equal to that of the vapour. The K value is determined by sampling the contents of the still pot and condensate receiver contents in the steady state and measuring the concentrations of these samples (x and y respectively), after which the ratio of y/x yields the value of K .

Before starting an experiment the apparatus is thoroughly cleaned in order to remove all organic contamination. The solution of iodine is introduced by charging the condensate receiver with a solution of iodine whereas the still pot is filled with water. Then the still pot contents are brought to boiling with a Bunsen burner. During boiling the vent opening is filled with a wad of glass wool with the purpose of damping oscillations in the left-hand side of the syphon leg resulting from the boiling in the still pot. Due to these oscillations iodine vapour might escape from the system through the vent.

After this the steady state is allowed to reach. The circulation rate applied is 60 ml/h. This means that every 2 hours the entire contents are circulated.

For the purpose of sampling, first the condensate receiver is drained. Then the apparatus is tilted at such a slope that the liquid present in the left-hand side leg of the siphon is driven out by liquid from the still pot. After this the sample from the still pot is taken. During and after sampling care is taken to prevent the escape of iodine from the samples.

The experiments are carried out with an iodine concentration in the condensate of 10^{-3} moles/mole water. The iodine is entirely in the form I_2 . The I_2 concentrations in the samples are determined by adding an excess of sodium thio-sulphate and back titration with standard potassium iodate, using an amperometric end point [24].

Results: y = iodine concentration in condensate.
 x = iodine concentration in still pot.
 $T = 100^\circ \text{C}$.

time of operation before sampling, hours	$K = \frac{y}{x}$
2	10.0
2	11.2
4	16.5
5	28.9
7	31.2
7	32.2
7	33.4
7	26.1
16	38.4
16	37.5
16	38.2

It can be assumed that after 16 hours the steady state has been reached.

Appendix 2

Determination of the phase equilibrium constant of HI in aqueous solution under acid circumstances at low concentration and high temperature

The experimental evaporator (see chapter 3) was used for this experiment.

Iodine concentration: $\approx 6 \times 10^{-6}$ mole KJ/kg water.

Sulphuric acid concentration: $\approx 3.7 \times 10^{-3}$ mole H_2SO_4 /kg water.

Exp. — 20 Run	Activity of sample, counts per sec. per 50 ml		$K = \frac{y}{x}$	Temp. °C	H_2SO_4 conc. $\frac{\text{m mole}}{\text{kg water}}$
	y valve 2	x valve 1			
01	0.65	525	1.2×10^{-3}	270	2.36
02	0.53	685	0.8×10^{-3}	272	—
03	1.36	982	1.4×10^{-3}	272	3.76

Note 1: The background count rate was 0.4 counts/sec. The error in y is relatively high (relative standard deviation approximately 10 %).

Note 2: The specific concentration in the bottom of iodine and sulphuric acid increased during this experiment. This is due to an initial inhomogeneous mixture of the solution. During the boiling the mixture is homogenised. Therefore, the K value of run 03 is considered to be the most reliable. However, this experiment clearly shows that HI in aqueous solution is less volatile than I_2 .

Appendix 3

Determination of the volatility of sulphuric acid at 274° C

The experimental evaporator (see chapter 3) was used for this experiment.

Temp. °C	H ₂ SO ₄ concentration in sample in mole/kg H ₂ O	
	liquid (valve 1)	vapour (valve 2)
274	4.0×10^{-3}	$< 5 \times 10^{-7}$

Appendix 4

The steady state in the column

It appeared to be impossible to reach a true steady state in the column. Due to the presence of sulphuric acid, corrosion products were formed in the evaporator. Iodine was partially chemically bound or adsorbed by the corrosion products; these were present in the form of solid particles which partially settled on the bottom. As a consequence, no homogeneous distribution of iodine in the reboiler existed, whereas also the form in which the iodine was present (initially as a I_2 solution) may have changed during the experiment. Especially if an experiment was carried out with a solution in the evaporator which had already been used in a former experiment, the decrease in activity of the sample of the evaporator liquid during one experiment was appreciable.

In chapter 2 the influence of iron on the distribution of iodine in the column was discussed. It was to be expected that due to iron I_2 was reduced to I^- and it was open to question whether iodine would be fixed on the wall or not. Therefore, experiment number 19 was carried out with pure water. Subsequently the evaporator and column were filled with a 0.01 N KI solution for desorption.

Next, the column was opened and the trays were removed. The activity on the inner wall of the evaporator, column and trays were then measured with a G.M. counter.

In table 1 the results of experiment 19 have been collected, whereas also the activities of the preceding experiment are given, so as to facilitate comparison.

TABLE 1

Activities present in the column and evaporator when operated with pure water after an experiment with active iodine

Number of the experiment	Activity of 50 ml sample in counts/sec				
	vapour in the evaporator, y_{11}	liquid on the 7 th tray, x_7	vapour above the 7 th tray y_7	liquid on the 2 nd tray x_2	vapour above the 2 nd tray, y_2
18	≈ 2200	≈ 600	≈ 100	— *)	—
19-01	41	5	8	2	nil
-02	9	3	—	—	—
-03	9	3	2	nil	—
-04	10	—	—	—	nil
-05	5	2	—	nil	—
-06	—	2	—	—	—
-07	2	2	1	—	—
-08	3	2	—	—	—

*) — means not measured.

It is concluded that the amount of iodine desorbed by the pure water reflux is only small compared with activities in the experiment with iodine. Some activity was measured in the vapour present in the evaporator (y_{11}). This might be caused by activity adsorbed on the inner wall of the tubing to the sampling valve or by volatile iodine produced by small amounts of sulphuric acid, potassium bichromate and iodine still present in the evaporator. Hereafter, the amount of iodine adsorbed on the wall was measured by desorption. The results of this desorption with a KI solution is given in table 2.

TABLE 2

Desorption of iodide from the evaporator and column with a 0.01 N KI solution

Sample location	Activity of 50 ml sample counts/sec	Remarks
evaporator, valve 1	2.6*)	After 3 days desorption at room temp. with 0.01 N KI
" valve 2	2.8	
7 th tray, valve 3	19.3	After 3 days desorption with a second batch of fresh KI solution at room temp.
evaporator, valve 1	1.1	
7 th tray, valve 3	25.4	Same as above after mixing of the desorption solution
evaporator, valve 1	6.5	
7 th tray, valve 3	6.2	After 1 night desorption with a third batch of fresh KI solution at room temp.
evaporator, valve 1	1.6	
7 th tray, valve 3	1.9	

*) The standard deviation of the count rates is 3%.

The amount of solution required to fill completely the evaporator and column was approximately 100 l. The amount of curies desorbed was, with a sensitivity of the counter of 10^{-9} Curie per 1 count/sec per 50 ml liquid, approximately 2.4×10^{-2} mC. After opening the column, the residual activity on the inner walls and trays was estimated to be 3×10^{-3} mC, using a G.M. counter, with an assumed efficiency of the G.M. counter of 3%. Thus the total amount of iodine left on the walls was of the order of 3×10^{-2} mC. The iodine flow through tray 7 during experiment 18 was equivalent to approximately 12×10^{-2} mC per hour. The experiment took 10 hours; hence 120×10^{-2} mC was passed through this tray. The total amount of activity adsorbed on the walls was only small compared with the total amount of activity circulated. Consequently, the conclusion can be drawn that the amount of iodine adsorbed on the walls is negligible and does not seriously affect the material balance of the column.

The decrease of the iodine concentrations in the column during the experiment was less than the decrease of iodine in the samples taken from the evaporator liquid. This equally points to an inhomogeneous distribution of iodine in the evaporator liquid. Since we are only interested in the distribution of iodine in the column and

not in the partition of iodine between the evaporator liquid and vapour, the liquid samples of the evaporator are of minor importance.

The deviation of the steady state in the column is of importance only if the decrease of the amount of iodine present in a certain section of the column is not small compared with the iodine flow to and from that section. In the column approximately 5 kg water was present. Most of the iodine is present on the lower trays. Assume that during one experiment of 9 hours the concentration of iodine in the column decreases continually to 0.1 of the initial value and that the concentrations of iodine at a certain moment are the same throughout the column. If the mass flow through the column is 10 kg/h, then each hour the contents of the column are twice replaced, while 10 % of the amount of iodine originally present is not returned to the column. Hence, from each unit of iodine removed, only 95 % is returned. This means that in the material balance a mistake of 5 % is introduced. From this we may conclude that even under the conditions of a nearly complete disappearance of iodine from the column during an experiment, the error introduced in the material balance, by assuming a steady state, is only small.

The concentration of sulphuric acid and potassium bichomate in the liquid of the evaporator remained constant during the experiments.

Appendix 5

Discussion of the precision of the results

The accuracy of the measured concentrations is mainly determined by the accuracy with which the iodine concentration in the samples is measured. The reproducibility of these concentration measurements was in agreement with the probable error associated with the number of counts. This number was in most cases greater than 1000, hence the relative standard deviation of the concentration of iodine in the calibrated flasks is 3 %. The error introduced by the treatment of the sample before it has been put into the counting vessel (weighing, filling of the calibrated flasks and pipetting etc.) is estimated to be smaller than 3 %.

The greatest inaccuracy associated with the counting is the shift of the 0.36 MeV peak of the ^{131}I spectrum to other voltages of the discrimination which sometimes occurs. Due to this shift, leading to a decrease of the sensitivity of the counter, the difference in the measured counting rate of the same iodine solution can deviate 10 % from one day to the other. This decrease in the sensitivity only takes place in case of an important temperature change of the photomultiplier. To avoid errors owing to this effect, the height of the discriminator voltage was adjusted to the 0.36 MeV peak in cases of an appreciable change in the room temperature.

The measurement of the iodine concentration in the liquid sample taken from the top of the column (tray 2) is less accurate than that of the other samples. Often the concentration in that part of the system is so low (1 to 1.5 counts/sec) that it is not possible to count 1000 impulses without introducing an appreciable delay in the counting program. Therefore, the relative standard deviation of the counting result is approximately 10 %. Including the error in the

background measurement (background is abt. 0.5 count/sec), the total relative standard deviation of the iodine concentration measurements amounts to some 20 % for the samples of tray 2. Incidentally, the background counting rate increases to 1 count/sec, limiting the lowest activity of the liquid to be counted with a reasonable accuracy to 2 counts/sec.

As was already mentioned before, the variations in the iodine concentration in the system under the same experimental conditions are due to fluctuations occurring in the system itself, mainly owing to deviations from the steady state. For calculating the value of ζ , the numerical values of the vapour flow, V , and the liquid reflux, L , are needed. The vapour flow was determined by measuring the condensate flow by means of a flow meter in the condensate line and by measuring the temperature of the condensate and the vapour. The condensate flow appears to be fluctuating around an average value.

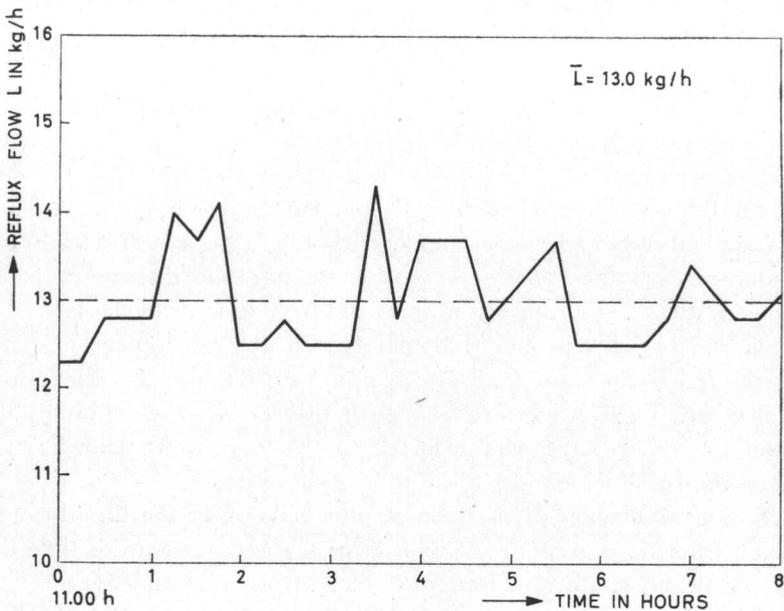


Fig. 1 of appendix 5
Reflux flow during experiment 24.

This probably due to:

- a) fluctuations in the operation of the condenser;
- b) variations in the main voltage resulting in variations in the heat input to the evaporator and thus in the vapour production.

In fig. 1 the reflux flow is given for experiment 24. The partial reflux in the lower part of the column is found by subtraction of the liquid take off flow from the reflux in the top of the column. Especially at low values of the liquid reflux, the precision of L becomes poor. For these reasons, the reliability of ζ was determined by statistical treatment of the available data instead of a priori estimating the precision.

The n values of y/x for one plate ($z_1 \dots z_n$), obtained under the same conditions, are considered to be an independent random test of ζ . It is supposed that the z values are distributed according to a Gaussian or normal distribution. The best estimate of ζ is \bar{z} according to:

$$\bar{z} = \frac{1}{n} \sum_{i=1}^n z_i. \quad 1$$

The left-hand side and right-hand side confidence limits of ζ are given by:

$$\zeta_{1,\alpha} = \bar{z} \pm t_\alpha \frac{s}{\sqrt{n}}. \quad 2$$

in which:

$$s = \sqrt{\frac{\sum_{i=1}^n (\bar{z} - z_i)^2}{n-1}}$$

and t_α is the parameter of Student, which is a function of n ; it is the factor by which $\frac{s}{\sqrt{n}}$ has to be multiplied in order to obtain the confidence limits of ζ if α is the probability to exceed the confidence limits. In this case $\alpha = 0.3$ is used. This means that there is a probability of 70 % that the true value of ζ is found between the two

limits. In general the z_i values are determined from concentrations not belonging to one tray but e.g. from two iodine concentrations on the trays m and n ($m > n$). In that the distribution of x_i depends on the number of plates between m and n . Consequently a correction for the number of plates concerned has to be introduced. This will be done in the following manner.

Suppose that at total reflux the value of ζ for one plate is:

$$\zeta = \bar{z}(1 \pm \Delta), \quad 3$$

where Δ is the relative confidence limit in \bar{z} .

Then according to the definition of ζ :

$$\frac{y}{x} = \bar{z}(1 \pm \Delta). \quad 4$$

At total reflux $y_m = x_{m+1}$, thus:

$$\frac{x_{m+1}}{x_m} = \bar{z}(1 \pm \Delta). \quad 5$$

If we consider the x values on the $m + p^{\text{th}}$ plate and the m^{th} plate, then:

$$\frac{x_{m+p}}{x_m} = \{\bar{z}(1 \pm \Delta)\}^p. \quad 6$$

Assuming that the deviations on each plate are independent of each other, the variances may be added, so that eq. 6 becomes:

$$\frac{x_{m+p}}{x_m} = \bar{z}^p (1 \pm \Delta \sqrt{p}). \quad 7$$

In practice y/x is determined from:

$$\frac{y}{x} = \left(\frac{x_{m+p}}{x_m} \right)^{1/p}. \quad 8$$

or:

$$\frac{y}{x} = \bar{z} (1 \pm \Delta \sqrt{p})^{1/p}, \quad 9$$

or, if $\Delta \sqrt{p} < 1$:

$$\frac{y}{x} = \zeta \approx \bar{z} \left(1 \pm \frac{\Delta}{\sqrt{p}} \right). \quad 10$$

Thus the relative interval of confidence that is calculated according to eq. 2 from z_i values obtained by measuring the decrease in iodine concentration over p plates is greater than the real interval of confidence for \bar{z} by a factor \sqrt{p} . Therefore, the value of $t_{\alpha} \frac{s}{\sqrt{n}}$, calculated from the z_i values, is multiplied by the square root of the number of intermediate plates, \sqrt{p} . The results of these calculations are included in tables III 2 and III 3.

Appendix 6

The experimental data in tabular form

In this appendix the iodine concentrations measured in the evaporator and column are reported. Equally, the values of ζ , calculated from the iodine concentrations at different locations in the column, are shown. However, a figure for ζ is only given for those cases where a steady state in the column was approached. In some cases the ζ value was calculated, but not used for the determination of the average value and its probable error. These figures are indicated by an asterisk. No steady state was then present either.

The experiments 1 up to 13 are not reported here, because they were used to obtain experience and the necessary skill required for carrying out useful experiments. During experiment 23, which is not reported here, no steady state was obtained. However, this experiment, carried out at a small total reflux, confirms experiment 24. Experiment 19 was used for the determination of the amount of iodine adsorbed by the walls in the column (see appendix 4) and experiment 20 for the determination of the volatility of HI (see appendix 2).

In all cases, the vapour flows applied were smaller than the vapour flow at which entrainment occurs. The critical vapour flows were determined according to the method of *Sounders and Brown* [25]. They are shown in table 1 for three temperatures.

TABLE 1

Vapour flows below which no entrainment occurs

Temperature T ($^{\circ}\text{C}$)	Vapour flow V (kg/h)
275	33
200	27
100	9

EXPERIMENT: 14

Composition of the solution in the evaporator :

Start at: 5h 25

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample in counts/second						
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate y_7	Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4	Liquid on the 2 nd plate x_3
01	9h 25	275	20.2	20.2	810	2350	369	268	—	—	28.3
02	11h 30	271	20.2	20.2	795	3240	345	75.7	—	—	8.3
03	12h 45	264	19.3	19.3	875	3170	431	80.3	—	—	10.8
04	15h 30	272	16.2	5.6	720	3200	376	28.8	48.8	5.7	—
05	17h 00	276	15.2	5.0	620	3220	293	21.5	3.2	1.2	—
06	18h 30	275	15.1	5.0	550	3160	328	23.9	4.6	3.3	—

EXPERIMENT: 15

Composition of the solution in the evaporator :

Start at: 5h 20

01	9h 30	270	26.4	26.4	189	1036	134	83	—	—	15.2
02	12h 00	270	26.4	26.4	323	272	50.2	19.6	—	—	3.8
03	14h 15	273	24.5	11.1	356	164	41.1	5.3	31.7	0.5	—
04	16h 00	275	24.6	11.2	357	110	30.0	3.5	2.5	1.1	—
05	17h 15	275	17.0	0.9	359	78	48.5	1.0	2.4	—	—

iodine: $7.5 \cdot 10^{-4}$ g/kg water
 H_2SO_4 : $3.3 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $1.3 \cdot 10^{-3}$ mole/kg water

$\zeta = y/x$ for one plate, calculated from the iodine concentrations as indicated below										
Vapour above the 2nd plate y_2	y_{11} and x_7	y_{11} and y_7	y_{11} and x_2	y_{11} and y_2	x_7 and y_7	x_7 and x_2	x_7 and y_2	y_7 and x_2	y_7 and y_2	x_2 and y_2
10.2	0.47	0.54	0.55	0.53	0.73	0.59	0.73	0.56	0.52	0.36
7.6	0.47	0.39	0.47	0.51	0.22	0.47	0.22	0.56	0.63	0.91
15.5	0.51	0.40	0.49	0.56	0.19	0.58	0.56	0.61	0.72	1.43
—	0.12									
—	0.10									
—	0.11									

iodine: 0.2 g/kg water
 H_2SO_4 : $3.0 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $2.0 \cdot 10^{-3}$ mole/kg water

3.9	0.51	0.53	0.59	0.54	0.62	0.64	0.55	0.65	0.54	0.25
1.4	0.57	0.52	0.58	0.55	0.39	0.60	0.50	0.66	0.59	0.36
—	0.22				0.13					
—	0.23				0.12					
—	0.023									

EXPERIMENT : 16

Composition of the solution in the evaporator :

Start at: 5h 30

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample		
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7
01	9h 30	272	16.3	6.5	972	604	168
02	11h 30	274	15.7	6.0	373	864	386
03	13h 00	276	16.1	6.4	250	1020	412
04	14h 45	275	13.7	4.3	179	964	295
05	17h 00	273	14.5	4.8	148	875	276
06	18h 00	273	13.2	0.4	152	770	407

EXPERIMENT : 17

Composition of the solution in the evaporator :

Start at: 5h 30

01	10h 50	268	15.6	6.9	515	1095	290
02	12h 45	268	18.4	10.3	820	1340	170
03	14h 15	270	15.4	7.3	—	1023	207
04	15h 00	270	16.6	8.5	482	1030	405
05	17h 00	270	17.0	8.7	259	1132	214

iodine: $8 \cdot 10^{-4}$ g/kg water
 H_2SO_4 : $3.3 \cdot 10^{-3}$ mole/kg water
 $K_2Cr_2O_7$: $1.8 \cdot 10^{-3}$ mole/kg water

in counts/second					$\zeta = y/x$ for one plate, calculated from the iodine concentrations as indicated below			
Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4	Liquid on the 2 nd plate x_2	Vapour above the 2 nd plate y_2	y_{11} and x_7	x_7 and y_7	x_7 and x_4	y_7 and x_4
11.9	11.2	3.4	—	—	0.21			
25.2	18.6	1.0	16.0	—	0.22			
44.0	19.1	1.6	—	—	0.21			
60	3.5	1.1	1.5	—	0.14			
40	2.3	—	—	8.0	0.16	0.15	0.10	0.13
44.2	3.1	—	1.7	2.0				

iodine: $8 \cdot 10^{-4}$ g/kg water
 H_2SO_4 : $2.6 \cdot 10^{-3}$ mole/kg water
 $K_2Cr_2O_7$: $1.6 \cdot 10^{-3}$ mole/kg water

67	17.9	4.0	19.9	—	0.22	0.23		
25.2	17.6	2.5	—	—	0.23	0.15		
—	—	—	—	—	0.22			
30.7	3.3	1.4	—	—	0.30	0.08		
—	2.3	1.1	—	—	0.23		0.17	

EXPERIMENT : 18

Composition of the solution in the evaporator :

Start at: 5h 00

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample		
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7
01	8h 45	272	9.1	—	988	2920	1160
02	9h 30	273	7.7	—	797	2435	904
03	10h 30	273	8.9	—	720	1600	925
04	11h 00	273	9.4	—	—	2313	770
05	12h 15	273	11.1	—	770	2215	713
06	13h 00	273	9.7	—	—	—	—
07	14h 30	273	11.9	3.6	844	2124	582
08	16h 00	273	10.6	1.4	—	1908	—
09	18h 00	273	12.0	2.3	594	2280	643
10	19h 00	273	10.9	1.4	378	2470	576

iodine: $1.0 \cdot 10^{-3}$ g/kg water
 H_2SO_4 : $3.5 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $1.4 \cdot 10^{-3}$ mole/kg water

in counts/second					$\xi = y/x$ for one plate, calculated from the iodine concentrations as indicated below			
Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4	Liquid on the 2 nd plate x_2	Vapour above the 2 nd plate y_2	y_{11} and x_7	x_7 and y_7	x_7 and x_4	y_7 and x_4
382	—	170	—	—				
—	—	—	—	—				
129	78	30.7	—	—				
—	—	—	—	—				
58.2	12.8	8.8	—	—				
107	27.2	—	—	—				
48.8	4.1	4.0	—	—	0.13	0.083		
—	20.3	—	—	—				
128	4.7	2.4	—	—	0.060	0.20	0.070	0.038
130	6.2	3.1	—	—	0.050	0.22	0.063	0.031

EXPERIMENT: 21

Composition of the solution in the evaporator:

Start at: 5h 30

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample in counts/second						
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7	Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4	Liquid on the 2 nd plate x_2
01	9h 00	272	15.9*	15.9	721	3050	1460	404	—	—	107
02	10h 00	273	16.4	16.4	—	1680	540	250	—	—	9.0
03	11h 30	273	18.5	18.5	715	1940	333	126	—	—	8.6
04	12h 15	273	19.0	19.0	—	1360	250	—	—	—	3.0
05	13h 30	273	20.0	20.0	682	1412	292	—	—	—	4.6
06	14h 55	273	20.0	20.0	—	1450	209	—	—	—	4.8
07	17h 00	273	21.1	21.1	413	1206	206	98	—	—	2.6
08	18h 45	273	21.1	21.1	—	1390	188	69	—	—	2.4

EXPERIMENT: 22

Composition of the solution in the evaporator:

Start at: 5h 00

01	10h 00	270	4.0	4.0	650	2100	183	44.4	—	—	13.4
02	11h 30	270	3.7	3.7	—	1951	81	41.7	—	—	2.1
03	12h 30	270	3.7	3.7	644	1455	82	20.7	—	—	2.8
04	14h 00	270	3.7	3.7	—	1668	67	21.4	—	—	2.3
05	14h 45	270	3.7	3.7	588	1516	70	—	—	—	2.9
06	16h 15	270	3.7	3.7	—	1310	70	—	—	—	1.8
07	17h 00	270	3.7	3.7	521	1352	80	6.2	—	—	1.6
08	18h 30	270	3.7	3.7	—	847	34	3.3	—	—	2.7

iodine: $8 \cdot 10^{-4}$ g/kg water
 H_2SO_4 : $3.0 \cdot 10^{-3}$ mole/kg water
 $K_2Cr_2O_7$: $1.8 \cdot 10^{-3}$ mole/kg water

second				$\zeta = y/x$ for one plate, calculated from the iodine concentrations as indicated below				
Liquid on the 4th plate x_4	Vapour above the 4th plate y_4	Liquid on the 2nd plate x_2	Vapour above the 2nd plate y_2	y_{11} and x_7	x_7 and x_4	y_7 and x_7	y_7 and x_4	y_2 and x_2
41	68	9.7	3.9			0.08		0.40
50	45	5.6	2.3	0.13	0.12	0.09	0.18	0.41
51	13.1	5.6	2.6	0.10	0.14	0.12	0.30	0.46
20	51	6.0	2.4	0.13	0.12	0.10	0.13	0.40
14	25	6.1	2.8	0.12	0.11	0.11	0.11	0.46

iodine: $6 \cdot 10^{-4}$ g/kg water
 H_2SO_4 : $2.4 \cdot 10^{-3}$ mole/kg water
 $K_2Cr_2O_7$: $1.6 \cdot 10^{-3}$ mole/kg water

y/x for one plate, calculated from the iodine concentration as indicated below

y_{11} and y_7	y_{11} and y_4	y_{11} and x_2	y_{11} and y_2	x_7 and y_7	x_7 and y_4	x_7 and x_2	x_7 and y_2	y_7 and y_4	y_7 and x_2	y_7 and y_2	y_4 and x_2	y_4 and y_2	y_2 and x_2
0.86		0.89		1.04		0.93			0.90				
0.88		0.89							0.90				
0.97		0.93		1.05		0.91			0.89				
0.89		0.89		1.11		0.94			0.90				
0.91	0.93	0.90	0.92	0.86	0.94	0.88	0.92	0.98	0.89	0.94	0.67	0.84	1.16
0.96	0.95	0.93	0.94	0.98	0.94	0.91	0.93	0.92	0.89	0.91	0.81	0.90	0.99
1.05	0.97	0.93	0.98	1.06	0.92	0.88	0.90	0.87	0.83	0.88	0.72	0.88	1.06

EXPERIMENT : 28

Composition of the solution in the evaporator :

Start at : 5h 30

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample in counts/second								$\zeta =$
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7	Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4	Liquid on the 2 nd plate x_2	Vapour above the 2 nd plate y_2	
01	9h 45	191	—	—	102	377	538	488	—	385	345	320	Due
02	12h 00	200	—	—	106	222	326	365	—	305	219	240	—
03	14h 00	200	6.5	6.5	133	1900	1545	1240	—	797	487	380	0.93
04	16h 00	201	6.5	6.5	107	1770	1175	990	—	670	353	215	0.87
05	18h 45	200	6.5	6.5	97	1626	1102	990	—	540	307	155	0.88

EXPERIMENT : 29

Composition of the solution in the evaporator :

Start at : 5h 30

01	9h 45	121	3.2	3.2	182	884	1332	860	—	860	595	1100	1.14
02	12h 00	121	3.1	3.1	80	304	742	222	—	235	642	319	1.35
03	14h 30	121	3.0	3.0	57	554	558	303	—	276	324	390	1.00
04	17h 30	121	3.0	3.0	40	302	405	293	—	298	286	318	1.10
05	19h 45	121	3.0	3.0	39	368	362	298	—	240	280	313	0.99
06	20h 15	121	3.4	3.4	38	379	391	275	—	257	241	279	1.02

iodine: $1.8 \cdot 10^{-3}$ g/kg water
 H_2SO_4 : $2.2 \cdot 10^{-3}$ mole/kg water
 $K_2Cr_2O_7$: $1.3 \cdot 10^{-3}$ mole/kg water

$\zeta = y/x$ for one plate, calculated from the iodine concentrations as indicated below																				
Vapour above the 2 nd plate y_2	y_{11} and x_7		y_{11} and y_7		y_{11} and x_2		y_{11} and y_2		x_7 and y_7		x_7 and x_2		x_7 and y_2		y_7 and x_2		y_7 and y_2		x_2 and y_2	
	—	0.78*	0.60*	0.66*						0.28*	0.52*					0.72*				
—	0.68*	0.62*	0.52						0.46	0.44					0.44					
—	0.56	0.50	0.51						0.38	0.48					0.51					
—	0.57		0.47							0.41										
3.3	0.59		0.49	0.51						0.44	0.47									0.71
4.2	0.52		0.49	0.52						0.47	0.52									0.87
—	0.57	0.53	0.46						0.48	0.42					0.41					
—	0.51	0.47	0.45						0.38	0.42					0.43					

iodine: $1.8 \cdot 10^{-3}$ g/kg water
 H_2SO_4 : $2.1 \cdot 10^{-3}$ mole/kg water
 $K_2Cr_2O_7$: $1.7 \cdot 10^{-3}$ mole/kg water

—	0.44*	0.38*	0.53*						0.24*	0.59*					0.74*					
—	0.35	0.39	0.43						0.51	0.48					0.47					
—	0.38	0.35	0.46						0.25	0.51					0.60					
—	0.34	0.34	0.46						0.32	0.54					0.61					
0.9	0.36		0.45	0.44						0.53	0.49									0.32
1.0	0.34		0.44	0.47						0.51	0.57									0.83
—	0.39	0.26	0.43						0.08	0.46					0.71					
—	0.34	0.25	0.49						0.10	0.60					0.95					

EXPERIMENT: 24

Composition of the solution in the evaporator:

Start at: 5h 30

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample in counts/second					
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7	Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4
01	10h 00	271	10.7*	10.7	836	1695	169	44	—	—
02	11h 00	271	12.1*	12.1	—	1759	191	23	—	—
03	11h 45	271	12.7	12.7	702	1660	176	—	—	3.7
04	12h 45	271	14.1	14.1	—	1643	180	28	—	—
05	13h 45	271	12.4	12.4	770	1485	143	25	—	—
06	15h 45	271	12.6	12.6	—	1825	162	—	—	2.5
07	17h 45	271	12.6	12.6	146	770	50	—	—	0.5
08	19h 00	271	13.1	13.1	—	663	28	5.3	—	—

EXPERIMENT: 25

Composition of the solution in the evaporator:

Start at: 5h 30

01	9h 30	270	11.9*	1.3*	1698	1682	1188	370	60	—
02	10h 45	273	16.1	4.1	—	2395	1880	232	26	—
03	12h 00	273	15.7	3.8	1276	1925	769	—	43	27
04	13h 15	273	16.6	4.4	—	2575	1856	1237	3.3	—
05	14h 00	271	14.8	2.7	542	2058	1698	213	6.0	—
06	15h 30	269	16.0	3.8	—	2414	1594	—	4.2	201*
07	17h 00	271	16.0	3.8	168	1979	2155	—	28	25
08	19h 00	271	16.3	4.1	—	2370	1351	198	11.7	—

EXPERIMENT: 26

Composition of the solution in the evaporator:

Start at: 5h 30

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample in counts/			
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7	Vapour above the 7 th plate y_7
01	9h 15	274	12.6	—	467	2130	2307	185
02	11h 15	274	16.3	3.6	549	1640	1685	156
03	14h 00	275	15.3	3.0	450	1440	990	121
04	16h 30	275	15.7	4.1	321	1280	1010	105
05	18h 45	275	14.8	3.2	176	1165	850	90

EXPERIMENT: 27

Composition of the solution in the evaporator:

Start at: 5h 00

Run	Time of sampling	Temperature T °C	Vapour flow V kg/h	Reflux L kg/h	Activity of 50 gram sample in counts/second								$\zeta =$
					Evaporator liquid x_{11}	Vapour in the evaporator y_{11}	Liquid on the 7 th plate x_7	Vapour above the 7 th plate y_7	Liquid on the 4 th plate x_4	Vapour above the 4 th plate y_4	Liquid on the 2 nd plate x_2	Vapour above the 2 nd plate y_2	
01	9h 00	199	12.6	12.6	538	2665	1390	1445	—	—	960	—	0.80
02	10h 30	202	13.0	13.0	—	2172	—	1331	—	—	868	—	
03	12h 00	200	22.4	22.4	153	1074	965	955	—	—	597	—	0.96
04	13h 30	200	16.2	16.2	—	1359	762	848	—	—	549	—	0.82
05	15h 00	200	13.7	13.7	102	1028	817	700	—	648	437	510	0.92
06	16h 45	200	13.7	13.7	66	637	555	548	—	432	350	349	0.95
07	18h 30	202	10.2	10.2	57	438	494	526	—	352	255	271	1.04

iodine: $8 \cdot 10^{-4}$ g/kg water
 H_2SO_4 : $2.5 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $1.5 \cdot 10^{-3}$ mole/kg water

$\xi = y/x$ for one plate, calculated from the iodine concentrations as indicated below

Liquid on the 2 nd plate x_3	Vapour above the 2 nd plate y_2	$\xi = y/x$ for one plate, calculated from the iodine concentrations as indicated below								
		y_{11} and x_7	y_{11} and y_7	y_{11} and y_4	y_{11} and x_3	x_7 and y_7	x_7 and y_4	x_7 and x_3	y_7 and x_3	y_4 and x_3
5.7	—	0.46	0.40*		0.49*	0.26*		0.51*	0.60*	
0.5	—	0.48	0.34		0.36	0.12		0.30*	0.38*	
1.2	—	0.47		0.42	0.40		0.38	0.37		0.32
1.7	—	0.48	0.36		0.42	0.15		0.37	0.50	
1.0	—	0.46	0.36		0.40	0.18		0.37	0.45	
1.0	—	0.45		0.39	0.39		0.35	0.36		0.40
0.6	—	0.40		0.35	0.41		0.32	0.41		1.2*
—	—	0.35	0.30		0.38	0.19		0.40	0.49	

iodine: 10^{-3} g/kg water
 H_2SO_4 : $2.7 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $1.3 \cdot 10^{-3}$ mole/kg water

—	—	
—	—	0.15
—	—	0.13
—	—	0.15
—	—	0.10
—	—	0.13
—	—	0.15
—	—	0.13

iodine: $1.1 \cdot 10^{-3}$ g/kg water
 H_2SO_4 : $3.2 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $1.6 \cdot 10^{-3}$ mole/kg water

y/x for one plate, calculated from the iodine concentration on indicated below

y_{11} and y_7	y_{11} and y_4	y_{11} and x_2	y_{11} and y_2	x_7 and y_7	x_7 and y_4	x_7 and x_2	x_7 and y_2	y_7 and y_4	y_7 and x_2	y_7 and y_2	y_4 and x_2	y_4 and y_2	y_2 and x_2
—	—	—	—	—	—	—	—	—	—	—	—	—	—
0.90	0.88	0.84	0.84	0.80	0.84	0.79	0.79	0.86	0.79	0.79	0.61	0.69	0.78
0.87	0.87	0.82	0.79	0.84	0.87	0.79	0.75	0.88	0.77	0.74	0.53	0.57	0.61
0.88	0.85	0.81	0.77	0.90	0.84	0.77	0.72	0.82	0.75	0.69	0.57	0.54	0.50

to a wrong position of the condenser the reflux flow was strongly fluctuating

0.90	0.88	0.84	0.84	0.80	0.84	0.79	0.79	0.86	0.79	0.79	0.61	0.69	0.78
0.87	0.87	0.82	0.79	0.84	0.87	0.79	0.75	0.88	0.77	0.74	0.53	0.57	0.61
0.88	0.85	0.81	0.77	0.90	0.84	0.77	0.72	0.82	0.75	0.69	0.57	0.54	0.50

iodine: $1.1 \cdot 10^{-3}$ g/kg water
 H_2SO_4 : $3.2 \cdot 10^{-3}$ mole/kg water
 $\text{K}_2\text{Cr}_2\text{O}_7$: $1.6 \cdot 10^{-3}$ mole/kg water

1.00	1.00	0.95	1.02	0.65	0.90	0.85	0.97	1.00	0.91	1.05	0.69	1.14	1.85
0.92	0.96	1.10	1.00	0.30	0.75	0.97	0.88	1.02	1.30	1.08	1.91	1.16	0.50
0.86	0.90	0.93	0.96	0.54	0.85	0.90	0.94	0.97	1.02	1.05	1.17	1.19	1.20
0.99	1.00	0.99	1.01	0.72	0.93	0.93	0.96	1.00	0.99	1.02	1.00	1.03	1.11
0.95	0.94	0.97	0.98	0.82	0.90	0.95	0.98	0.93	0.98	1.01	1.16	1.14	1.12
0.92	0.95	0.94	0.97	0.70	0.90	0.91	0.95	0.98	0.97	1.00	0.94	1.09	1.15

SAMENVATTING

Dit proefschrift heeft betrekking op de verwijdering van neutronen absorberende stoffen uit een suspensie-kernreactor. De gedachten-gang die tot dit onderzoek heeft geleid wordt in deel I weergegeven. *Went* [6] heeft de eigenschappen van een waterige suspensie-reactor beschreven en gewezen op de mogelijkheid om met dit type thermische reactor evenveel of bijna evenveel nieuwe splijtbare kernen te maken als er worden gebruikt voor de productie van energie. Daarbij wordt het niet splijtbare isotoop ^{232}Th door het in-vangen van een thermisch neutron omgezet in het splijtbare isotoop ^{233}U . Om een zo groot mogelijke opbrengst van nieuwe splijtbare kernen te verkrijgen dienen neutronen absorberende stoffen zoals corrosie- en erosieproducten en splijtingsproducten, vooral ^{135}Xe , ^{135}J (de voorganger van ^{135}Xe in de vervalreeks) en ^{149}Sm , uit de reactor verwijderd te worden.

Andere redenen voor de reiniging van de suspensie zijn: de ver-laging van het in de splijtstofkorrels geproduceerde nagekomen ver-mogen door de radioactiviteit van de splijtingsproducten en het be-perken van de tijdelijke verhoging van de ^{135}Xe concentratie na het plotseling onderbreken van de energieproductie. Deze piek in de ^{135}Xe concentratie zou namelijk het weer in bedrijfstellen van de reactor gedurende een periode van circa 50 uren belemmeren.

Het blijkt dat de vloeistofstroom die gereinigd moet worden om de concentratie van de corrosie- en erosieproducten op een voldoende laag peil te handhaven veel geringer is dan die welke voor het hand-haven van een voldoende lage ^{149}Sm en ^{135}J concentratie nodig is. Daarom wordt, naast de verwijdering van het gasvormige ^{135}Xe , vooral aandacht geschonken aan het verwijderen van de niet-vluchtige splijtingsproducten ^{135}J en ^{149}Sm .

In deel II van dit proefschrift worden algemene betrekkingen af-geleid met behulp waarvan de concentraties van ^{135}Xe en ^{149}Sm in de reactor kunnen worden berekend. In deze betrekkingen komt een reinigingsconstante, λ^+ , voor, die bepalend is voor de hoeveelheid

neutronenvergift welke per tijdseenheid uit de reactor wordt verwijderd. De werking van een reinigingssysteem kan worden beschreven met deze reinigingsconstante.

Het gasvormige ^{135}Xe kan het best worden verwijderd door de suspensiestroom te wassen met een dragergas (H_2); daarna wordt het circulerende gasmengsel door een volume van zodanige grootte geleid dat door het natuurlijke verval van ^{135}Xe (halveringstijd: 9,2 uur) veel ^{135}Xe in de gasfase, dus buiten de reactor, vervalt tot ^{135}Cs .

Het jodium zal in waterig milieu en in apparatuur van roestvrijstaal alleen dan in de vluchtige J_2 vorm zijn, wanneer er voldoende zuurstof aanwezig is. In de suspensiereactor zullen echter de oxyderende omstandigheden onvoldoende zijn om een belangrijke fractie van het jodium in de J_2 vorm te houden. Door middel van een fase-scheiding kan nu een vloeistofstroom, die vrij is van splijtstofdeeltjes, uit de reactor worden afgevoerd naar een vloeistofreinigingssysteem. Dit systeem bestaat uit een verdamper waarin de niet vluchtige componenten worden geconcentreerd. Na condensatie wordt de stoom teruggevoerd naar de reactor. Het residu wordt na zekere tijd afgevoerd en als radioactief afval opgeslagen. In de verdamper wordt, door waterontleding tengevolge van de radioactiviteit van het residu, zuurstof geproduceerd. Hier is niet, zoals in de reactor, een overmaat waterstof aanwezig en het is daardoor mogelijk dat het jodide geheel of gedeeltelijk wordt geoxideerd tot het vluchtige J_2 . Indien geen speciale maatregelen werden genomen zou J_2 met de stoom afgevoerd en met het condensaat teruggeleid worden naar de reactor. Een maatregel die het overdestilleren van J_2 kan voorkomen is het toepassen van rectificatie van het stoom-jodium mengsel in een schotelkolom.

De verlaging van de ^{135}Xe concentratie in de reactor, tengevolge van het ^{135}Xe verval in de gasfase en de ^{135}J verwijdering door middel van gecombineerde verdamping en rectificatie, wordt in deel II berekend voor een kleine homogene waterige suspensiereactor. Deze reactor wordt thans bij de N.V. KEMA in Arnhem ontworpen. Dit ontwerp is reeds eerder beschreven [12].

De maatregelen die genomen moeten worden om het ^{135}Xe uit de reactor te verwijderen konden worden gebaseerd op de bekende eigenschappen van xenon. Daarentegen was het gedrag van jodium

in het vloeistofzuiveringssysteem onzeker. In verband hiermede werden in een semi-technische rectificatiekolom proeven uitgevoerd om na te gaan of jodium door middel van rectificatie bij hoge temperatuur (ca. 275°C) van water kan worden gescheiden. Deze proeven werden uitgevoerd in een roestvrij-stalen kolom bij lage jodiumconcentratie. Hierover wordt in deel III van dit proefschrift verslag uitgebracht.

De eigenschappen van het jodium-water systeem worden besproken, waarbij vooral aandacht wordt besteed aan de vluchtigheid van J_2 ten opzichte van water bij hoge temperatuur. Daarna wordt een theoretische relatie afgeleid voor de verhouding van de jodiumconcentratie in de damp en vloeistof op een schotel in de rectificatiekolom. Daar het vluchtige J_2 in tegenwoordigheid van roestvrijstaal wordt gereduceerd tot het niet-vluchtige jodide, wordt hierbij uitgegaan van het simultaan plaatsvinden van destillatie en een chemische omzetting.

De proeven werden uitgevoerd met jodium waaraan een hoeveelheid ^{131}J was toegevoegd. Dit radioactieve isotoop maakte het mogelijk om de jodiumconcentratie met behulp van een stralingsmeter vast te stellen.

Het is gebleken dat bij 275°C rectificatie een efficiënt proces is om J_2 van water te scheiden, waarbij het jodium onder in de kolom wordt geconcentreerd. De scheiding die in de kolom plaatsvindt kan beschreven worden met de daarvoor opgestelde theorie. Het is niet mogelijk om uit de resultaten de numerieke waarden van het schotelrendement, de vluchtigheid van J_2 ten opzichte van water en de omzettingssnelheid van J_2 tot J^- af te leiden. Wel zijn de gebieden bepaald waarin de waarden van deze grootheden kunnen liggen. Daarbij blijkt dat de relatieve vluchtigheid van J_2 ten opzichte van water bij 275°C kleiner is dan één. Bij temperaturen van 100°C en lager is de relatieve vluchtigheid groter dan één [17, 18]. Deze temperatuurafhankelijkheid van de vluchtigheid van J_2 ten opzichte van water komt overeen met het gedrag van andere, weinig oplosbare gassen in water. Geheel in overeenstemming hiermede is ook dat de scheiding van jodium en water in de schotelkolom slechter wordt naarmate de temperatuur lager is, terwijl bij 120°C geen scheiding meer blijkt op te treden. Bij nog lagere temperaturen is het te verwachten dat jodium boven in de kolom wordt geconcentreerd.

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STELLINGEN

I

De door *Keeler* opgegeven waarde van de verdelingscoëfficiënt van J_2 over stoom en water bij 100°C ($K \approx 0.01$) is 3800 maal te klein.

Keeler, R. A., Anderson, C. J., Klach, S. J., Chappel, R. M.; KLX-10080 (USAEC rapport 1957).

Lane, J. A., Mac Pherson, A. G., Maslan, F.; Fluid Fuel Reactors blz. 320, Addison-Wesley Publishing Comp. Inc. 1958.

II

De Roos vermeldt dat de toegelaten lek van kernreactoren waarin een aanzienlijke hoeveelheid van de splijtingsproducten in het koelmiddel voorkomt slechts enkele malen groter is dan met een heliummassa-spectrometer kan worden gemeten. Indien men echter het criterium waarvan *De Roos* uitgaat juist interpreteert, is de toelaatbare lek ca. 10^4 maal zo groot als de kleinste meetbare lek.

de Roos, J. L.; *De Ingenieur* 69 (1957) 8, W 23.

III

Rietema heeft voor een hydrocycloon een dimensieloze grootheid, Cy_{50} , ingevoerd, die de scheiding van vaste deeltjes uit een vloeistof karakteriseert. Deze grootheid kan ook met vrucht worden gebruikt bij andere toestellen voor fasescheiding, omdat dit kengetal evenredig is met de verhouding tussen de dwarsstroom van die deeltjes welke met een kans van 50 % worden afgescheiden en het totale debiet door het apparaat.

Rietema, K.; *Chem. Eng. Sci.* 15 (1961) 3/4, 310.

IV

Bij de afleiding van de uitdrukking voor Cy_{50} (zie stelling 3) gaat *Rietema* uit van een onjuiste veronderstelling aangaande de radiale snelheidsverdeling in een cycloon.

Rietema, K.; Chem. Eng. Sci. **15** (1961) 3/4, 310.

V

De conclusie die *Steinberg* en *Manowitz* trekken uit de temperatuurafhankelijkheid van de Henry coëfficiënt van Xenon in Amsco 123-15 (de commerciële naam voor een mengsel van organische extractiemiddelen), nl. dat de aantrekkingskrachten tussen de opgeloste xenonmoleculen en de solventmoleculen even groot zijn als de onderlinge aantrekkingskrachten tussen de xenonmoleculen, is onjuist.

Steinberg, M., Manowitz B.; Ind. Eng. Chem. **51** (1959) 1, 47.

VI

De bewering van *Pfleiderer* dat het energetisch rendement van een waterstraalpompe toeneemt naarmate de tegendruk kleiner wordt, is niet algemeen geldig.

Pfleiderer, C.; Zeitschr. Ver. Deutsch. Ing. **58** (1914) 24, 125.

VII

Het is onjuist om, zoals in de onderstaande publicaties wordt gesuggereerd, de gemiddelde snelheid van een gegeven suspensie als de enige bepalende grootte voor de erosie van het oppervlak te beschouwen.

- 1) Johnson, W. E., Fax, D. H., Garber, H. J., Taylor, G. R.; 2nd UN Conf. Geneva 1958 P/2373.
- 2) Staff of Homogeneous Reactor Project at Oak Ridge National Laboratory; 2nd UN Conf. Geneva 1958 P/2391.
- 3) Lane, J. A., Mac Pherson, A. G., Maslan, F.; Fluid Fuel Reactors blz. 258, Addison-Wesley Publishing Comp. Inc. 1958.

VIII

Het door *Bretton* en *McCullogh* gepubliceerde onderzoek naar het afscheiden van met de damp meegesleurde vloeistofdruppels bij verdampers voor het reinigen van radioactief afvalwater is van weinig waarde bij het ontwerpen van dergelijke installaties, omdat men niet heeft gelet op het mechanisme voor het verwijderen van druppels uit de dampstroom.

Bretton, R. H., McCullogh, G. E.; BNL-59, 27-28/3/1950.

IX

Het verdient aanbeveling om verdampers voor het reinigen van radioactief afvalwater bij hoge druk te bedrijven om een zo groot mogelijke zuiverheid van het gereinigde water te bereiken.

X

De bewering van *Fortuin* dat de optimale verlichtingssterkte omstreeks 30.000 à 50.000 lux zou bedragen, is aanvechtbaar.

Fortuin, G. J.; Mens en Onderneming 16 (1962) 1,2.

XI

Door de spiegelende reflectie van het wegdek wordt het waarnemen van kleur- en helderheidscontrasten op het wegdek bij avond moeilijk en onder bepaalde omstandigheden onmogelijk. Daarom is het aan te bevelen om bij zebra-paden een zodanige verlichting aan te brengen dat door diffuse reflectie de zwart-wit markering goed kan worden waargenomen.

XII

De door *Sproull* gegeven verklaring voor de vermindering van de viscositeit van gassen door de aanwezigheid van stofdeeltjes, nl. dat de stofdeeltjes de gemiddelde vrije weglengte van de gasmoleculen verkleinen, is onjuist.

Sproull, W. T.; Nature 190 (1961) 4790,976.