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DEVELOPMENT OF A CRYOGENIC KRYPTON-SEPARATION SYSTEM
FOR THE OFFGAS OF REPROCESSING PLANTS

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Abstract

The concept of cryogenic rare gas separation from reprocessing offgas pursued at present at the Kernforschungszentrum Karlsruhe (KfK) is discussed and compared with other offgas purification flowsheets. The KfK concept includes: separation of O_2 and residual NO_x by catalytic reduction with H_2, adsorptive retention of H_2O, CO_2, NH_3 etc. and cryogenic distillation of first N_2-Kr-Xe, then Kr-Xe mixtures. Some features pertinent to this flowsheet which were studied experimentally either on a laboratory or semiworks scale, are described including the following: desublimation of Xe in the first column, coadsorption of Kr at and its selective desorption from the adsorption bed, purification of the Xe product, poisoning of the reduction catalyst and methanization of CO_2. It is shown that all of these features, despite being capable of causing malfunctions of the process, can be controlled by proper process design and operational conditions in a way not to impair with a good Kr decontamination factor.

I. Introduction

Plans for retention of the fission gas Kr from the offgas of the future large German reprocessing plant as well as of the existing small plant WAK (Wiederaufarbeitungsanlage Karlsruhe) prefer a cryogenic distillation scheme. The reason is the long experience with such a process in the industrial production of rare gases in air liquefaction[1].

Two essential differences between the rare gas-oxygen mixtures in air liquefaction plants and reprocessing offgases demand for modifications of the process:

- the mole ratio Kr/Xe in fission gas (0,103) which is almost reciprocal to the ratio in air (13,1); the resulting higher Xe-concentrations enhance the problem of Xe freeze-out;

- the radioactivity of Kr-85 resulting in the radiolytic ozone formation from O_2.

Depending on the risks one places on these differences the existing or planned Kr retention units show different flowsheets (fig. 1)[2]. At the I.N.E.L. (U.S.A.)[3] and at the C.E.A. (France)[4] the complete offgas including O_2 is liquefied in the first column. Here the risk of ozone formation is accepted, but freeze-out of Xe is decreased because of improved solubility in O_2 compared to N_2. Further enrichment of Kr is achieved either by batch distillation of the three-component mixture O_2-Kr-Xe in the second column (I.N.E.L.) or by catalytic reduction of O_2 with H_2 between the two columns and

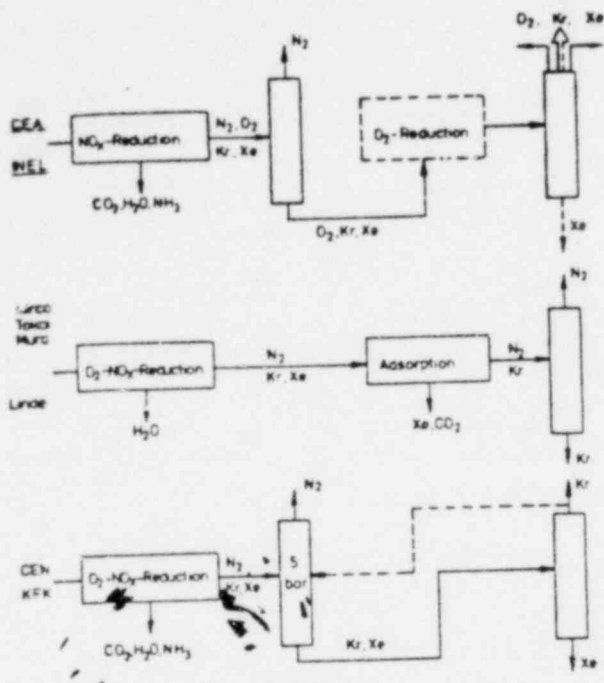subsequent distillation of Kr-Xe (C.E.A.).

FIGURE 1

Different flowsheets for the retention of Krypton
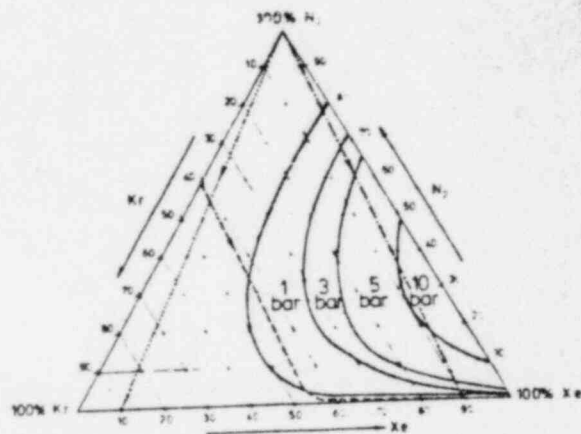from the offgas of LWR-reprocessing plants

FIGURE 2

Pressure dependence (ideal behavior) of the two-phase area
solid-liquid in the phase diagram N_2-Kr-Xe and course of bottom
product concentrations during start-up operation of column.
— without additional Kr
--- additional Kr before operation } Different operation modes
— with Kr recycle

Both risks are circumvented by proposals of Linde (Germany)[5] and by Airco (U.S.A.) for the Japanese Tokai Mura plant[6]: both O_2 and Xe are separated from the offgas before the cryogenic part by catalytic reduction and by adsorption, respectively. Workers at KFA Jülich (Germany) prefer a separation of Xe by freeze-out instead of adsorption[7]. After separation of Xe the cryogenic distillation is simplified to the two-component system N_2-Kr.

In the present concept of KfK[8], similar to the plans of the C.E.N. (Belgium)[9] O_2 is also removed by catalytic reduction, but adsorption of Xe is omitted. Thus the three-component system N_2-Kr-Xe must be distilled in the first column. Whereas N_2 is driven off at the head, Kr and Xe are collected in the bottom of the still. After discontinuous transfer to the second column Kr and Xe are separated into pure products and filled into steel cylinders. The cryogenic part of this concept together with a preceding molecular sieve bed as drying unit was installed on a "cold" semiscale basis (gas through-put 30-50 m^3/h at S.T.P.). These units which bear the names KRETA (Krypton-Entfernungs-Tieftemperatur-Anlage) and ADAMO (Adsorption an Molekularsieben) have been in operation now for 4000 hours. The

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design of these units has been described elsewhere[10]. Some of the results gained are reported in the following sections.

II. Features of the KfK Flowsheet and Results

1. Desublimation of Xenon

1.1 Solid-Liquid Equilibrium

The phase diagram of the three-component system N_2-Kr-Xe has a region of limited solubility on the N_2-Xe side. Solid Xe is in equilibrium with N_2-Kr-Xe liquid (fig. 2). This two-phase area decreases on increasing the pressure and thus the temperature. One could therefore prevent Xe from freezing out completely by operating the column at 17-20 bar[11-13]. Because of safety aspects in plants containing large inventories of radioactivity we chose an intermediate pressure of 5 bar which is also familiar practice in air liquefaction.

Fig. 2 also shows the problem of Xe freeze-out during the start-up period of the column: if the fission gas mixture is fed into the column cooled down with liquid nitrogen (at 95 K) one would pass straight through the critical area (dot-dashed line). This situation can be avoided, if the column is filled with a N_2-Kr mixture before the fission gas feed is opened. In this case the stationary bottom concentration is approached first on a straight line .hen, after opening the bottom product transfer line to the second column, on a curved line (dashed line). The critical area is not intersected. Alternatively, one can also raise the Kr/Xe ratio to or near that of the air by means of an additional Kr feed. In the second Kr separation unit at Karlsruhe being in the planning state now for the offgas of the WAK plant a Kr recycling loop from the top of the second column to the first column possibly will be installed (see fig. 1)[14]. In this case one would be on the safe side in all parts of the column (dotted line in fig. 2).

We have tested all three versions in the KRETA campaigns and confirmed the expectations: whereas in the first version we had serious malfunctions of the column because of Xe freeze-out, we have attained Xe concentrations up to 80 % in the bottom product in the second version without having detected any precipitation of solid Xe.

During unperturbed operation of the column the Kr decontamination factor (DF) at the head was $\geq 10^3$, the upper limit set by the sensitivity of the He ionization detector of our gaschromatographic analysis (100 ppb) and the normal Kr feed concentration of 160 ppm by vol.

1.2 Gas-Solid Equilibrium

More essential than the solid-liquid equilibrium is in our column the gas-solid equilibrium. Due to the construction of the column which is a sieve plate column containing 37 plates with the feed point above the 13th plate (overall height: 8 m) and due to the temperature profile within the column (gas temperature at the feed point: 135 K) we observe desublimation of Xe at the first plate above the feed point (temperature: 95 K) under certain conditions. There solid Xe is not dissolved completely by liquid N_2, but accumu-

lates until the sieve holes are plugged. According to the sublimation pressure curve of Xe (fig. 3) the limiting Xe-concentration in the feed gas at 95 K should be only 80 ppm. In practice we observe a limiting Xe concentration which is higher by almost an order of magnitude. We conclude therefore that the difference is either dissolved by liquid N_2 or carried down the column mechanically in solid form. The aim of our present work is to increase this concentration by increasing the temperature profile in the vicinity of the feed point and by altering the construction of the column interior in that area.

What are the consequences of this result for the rare gas separation from a real offgas ? The offgas most pertinent to our development at the moment is the offgas of the WAK. This offgas consists of 80 - 120 m^3/h at S.T.P. of essentially air containing a maximum of 1600 ppm of Xe at the peak of a dissolution. If continuously fed to a column like ours, it should result in serious plugging after a short time. However, a dissolution of fuel in WAK is essentially completed after two hours followed by a day until the next dissolution starts. We simulated such a feed gas in KRETA (fig. 4) and showed that such a rare gas concentration peak does not lead to any signs of plugging, even if another rare gas peak simulating a dissolution is fed to the column two hours after the end of the first run.
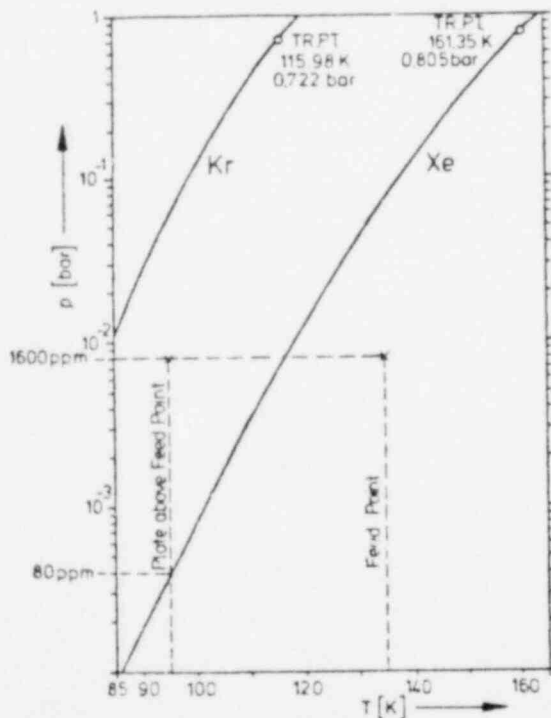

FIGURE 3

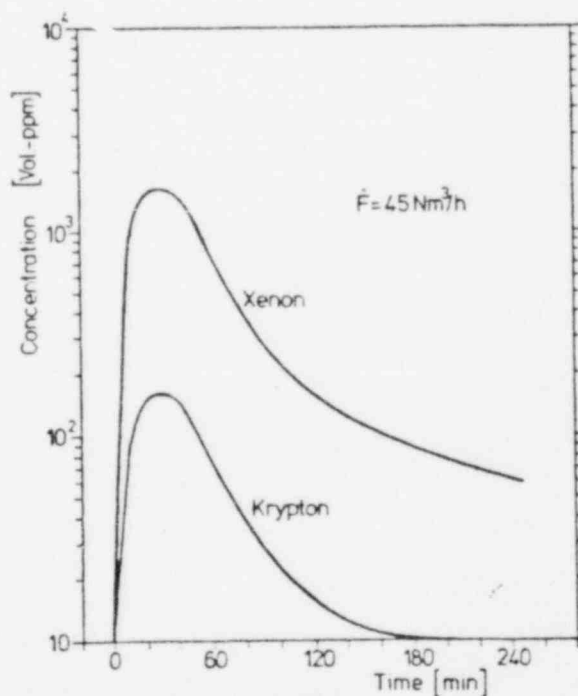Sublimation pressure of Krypton and Xenon

FIGURE 4

Kr- and Xe-concentrations in a simulated offgas of a dissolution at WAK

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In the case of a large reprocessing plant where rare gas concentrations probably will be higher and on a more continuous level, this concept would have to be changed, however, unless we can avoid plugging by desubliming Xe by means of modifying the column structure.

2. Ozone Formation

The primary reason for the separation of O_2 in our concept was to prevent excessive ozone formation. However, even during normal operation, not to speak of malfunction of the reduction catalyst traces of O_2 will reach the cryogenic column. Ozone formation rates therefore have to be known. In addition, use of liquid O_2 as solvent for the rare gases in the first cryogenic column is an interesting process alternative in many respects[3]. If one considers this alternative, the safety risks of ozone formation have to be assessed. We have therefore carried out a calculation of the ozone concentration to be expected in the first column considering three process alternatives (table I):

1) The first case is the alternative presently investigated by us in the KRETA pilot plant; it is assumed that 10 ppm O_2 pass the reduction unit.

2) The second case was proposed for the offgas purification system at the WAK[14], called project AZUR. Here the ratio Kr/Xe is raised to that of air by a Kr recycling loop; O_2 again is reduced down to 10 ppm.

3) In the third case, O_2 which is present in the offgas in air concentration (20 %) is not reduced; it is partially (50 %) liquefied thus acting as solvent for the rare gases; Kr is not recycled.

The O_2 and Kr concentration profiles along the column were calculated by a tridiagonalmatrix method[15]. Stationary column operation has been assumed which is attained 700 hours after startup.

The ozone formation rate was calculated according to the equation shown in fig. 5, where an average G-factor of 10 was assumed [16], where ε_O is the O_2 electron fraction, where the Kr concentration C_{Kr} O_2 takes into account the abundancy of Kr-85 in overall Kr (6 %) and where the radiation dose rate is the product of the specific activity of Kr-85 and its average β-energy. The dimensions of the column considered are typical of the KRETA pilot plant (liquid volume of bottom product: 15 l, and of each of 10 theoretical plates: 1,2 l).

The calculated ozone concentrations in the bottom product are given in table I. Surprisingly the highest value is not obtained in the case of O_2 operation (case 3), but with 10 ppm O_2 in the feed gas (case 1), whereas in the Kr recycle mode (case 2) it is lowest. The explanation is found in the different transfer rates of the bottom product; whenever this rate is high, the residence time of O_2 and Kr in the column is short and thus the ozone formation rate is low. This is particularly true for cases 2 and 3. In case 2 the effect of high Kr concentration is even overcompensated.

Generally, the calculated ozone concentrations are very low and presumably beyond a critical concentration[17,18]. The calculation

Flowsheet	1 "KRETA"	2 Kr-Recycle	3 O$_2$-Liquefaction
Feed Composition (N$_2$ Carrier Gas) Kr	500 Vol.-ppm	5 Vol.-%	500 Vol.-ppm
Xe	5000 Vol.-ppm	5000 Vol.-ppm	5000 Vol.-ppm
O$_2$	10 Vol.-ppm	10 Vol.-ppm	20 Vol.-%
Transfer Rate of Bottom Product [l/h]	0,56	3,98	8,41
Krypton-Inventory [l]	2,24	21,2	0,06
[Ci]	1,14·10^5	1,08·10^6	3,06·10^3
Ozone-Concentration [Mol-ppm] (Bottom)	170	8,2	53

<u>Table I</u>

Ozone formation in the first cryogenic column in different process flowsheets

$$\frac{d[O_3]}{dt} = \frac{G \left[eV^{-1}\right] \cdot \varepsilon_{O_2} [Mol/Mol] \cdot C_{Kr} [Mol/Mol] \cdot \text{dose rate} \quad \left[eV \cdot l^{-1} \cdot s^{-1}\right]}{N_L \left[Mol^{-1}\right]}$$

$$\frac{d[O_3]}{dt} = \frac{10 \cdot 10^{-2} \left[eV^{-1}\right] \cdot \varepsilon_{O_2} \cdot 0,06 \cdot C_{Kr} \cdot 8,51 \cdot 10^5 \left[Ci \cdot l^{-1}\right] \cdot 3,7 \cdot 10^{10} \left[Ci^{-1} \cdot s^{-1}\right] \cdot 2,49 \cdot 10^5 [eV]}{6,02 \cdot 10^{23} \left[Mol^{-1}\right]}$$

$$\frac{d[O_3]}{dt} = 7,8 \cdot 10^{-5} \cdot \varepsilon_{O_2} \cdot C_{Kr} \left[Mol \cdot l^{-1} \cdot s^{-1}\right]$$

<u>FIGURE 5</u>

Ozone formation rate in cryogenic rare gas mixtures

shows that ozone formation is not a serious problem in cryogenic Kr
separation, since it can be controlled by proper design of the pro-
cess. It must be kept in mind, however, that further build-up of the
ozone level may take place in the second column, especially in the Xe
product, if an ozone and oxygen reduction step between the columns is
not considered (4, 17, 19).

Table I indicates another inherent safety aspect: the inventory
of Kr and thus of the activity. It varies by almost three orders of
magnitude and is lowest in the O_2 operation mode and highest in the
Kr recycle mode.

3. Points of Krypton Leakage Inherent to the Process

The head of the first column is the most important, but not the
only point, where Kr is released to the atmosphere. Two additional
points are discussed in the following sections.

3.1 Adsorption Unit

A conventional adsorber unit is provided in our pilot plant to
dry the feed gas and, lateron, to retain all offgas components which,
if present, would freeze out in the cryogenic part, i.e. CO_2, NO_x
and NH_3. Some Kr is also adsorbed during this step. Although this
coadsorption of Kr is weak at room temperature (20), it would be
sufficient to spoil the good column decontamination factor, if it
would be released to the atmosphere on regeneration of the adsorber.
Therefore a purging step is included in the operation mode of the ad-
sorber bed, where the coadsorbed Kr is selectively desorbed and re-
cycled. This concept led to the design of three adsorber lines each
consisting of two beds. The first one is presently filled with 70 kg
of silicagel, the second one with 100 kg of molecular sieve type 10A.

Breakthrough (at c/c_E = 0,5) of Kr (160 ppm by vol.) and Xe
(1600 ppm) in 31 m^3/h (S.T.P.) at 5 bar and room temperature takes
place after 4.2 and 26.0 minutes, respectively, through the two beds
of a line. Desorption curves for Kr labelled with Kr-85 , and Xe
using a purge gas stream of 5 m^3/h (S.T.P.) at 1 bar and room tempe-
rature are shown in fig. 6. The bulk amount of Kr has been desorbed
already after 30 minutes, after 2 hours only 1 %o of the Kr original-
ly adsorbed remains on the beds. If one would stop the purging step
at this point, this residual Kr would be released on heating the bed
in the regenerating step. It can be shown that a release of 14 %o in-
stead of 1 %o residual Kr would still limit the release to the same
amount which is released at the head of the first column at a column
decontamination factor of 10^3.

3.2 Xenon Product

The bottom product of the first column after transfer to the
second column (packed bed) is separated by distillation into Kr (head
product) and Xe (bottom product). This process step is only sensible,
if storage volume of radioactive product can be saved. This is pos-
sible only, if the inactive Xe can be purified from Kr-85 to such an
extent that it can be released to the atmosphere (or utilized com-
mercially). If we postulate again that the amount of Kr-85 released
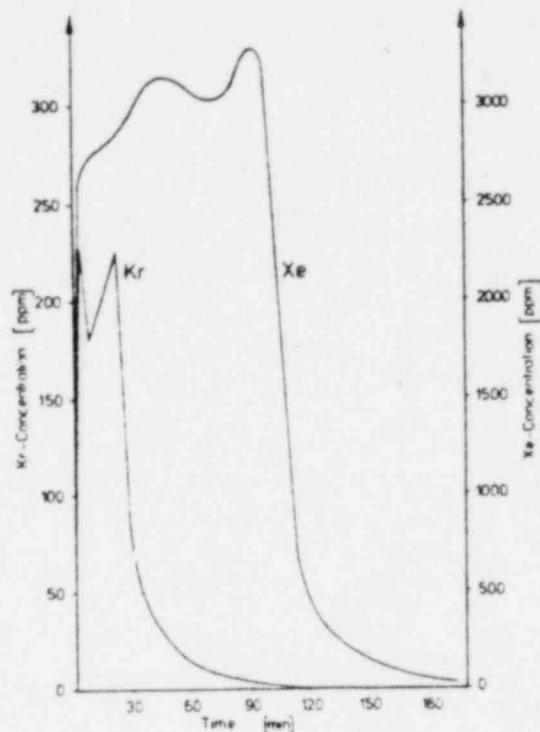with the Xe product should not exceed the amount released at the head

FIGURE 6

Desorption of Kr and Xe from the silica and molecular sieve
beds in the pilot plant ADAMO with 5 Nm³/h N₂ at 1 bar and 25°C

head of the first column at a DF = 10^3, then the Kr content of the
Xe must be limited to 100 ppm by vol.

This postulate could be fulfilled almost routinely. At the
moment, the Kr and Xe products are both collected in steel cylinders
by means of a membrane compressor. Lateron, transfer of the products
into the cylinders by way of cryogenic pumping will be applied.

4.   Catalytic Reduction of O_2 and NO_x

4.1 Poisoning of Noble Metal Catalysts

On the basis of laboratory experiments a Ru catalyst on Al_2O_3
carrier of relatively low specific surface area (9 m²/g) has been
selected as catalyst for the reduction of O_2 and residual NO_x with H_2.
From all nobel metals investigated, this catalyst is most resistant
to poisoning by iodine and organic phosphorus compounds which are
both trace components of reprocessing offgases. The poisoning effect
of I_2 was studied with respect to activity and selectivity on a
series of Pt, Pd and Ru catalysts. Some of the results are shown in
Fig. 7 and 8. The activity of Pt and Pd is definitely reduced by
increased loading with I_2. As can be expected, the activity of cata-
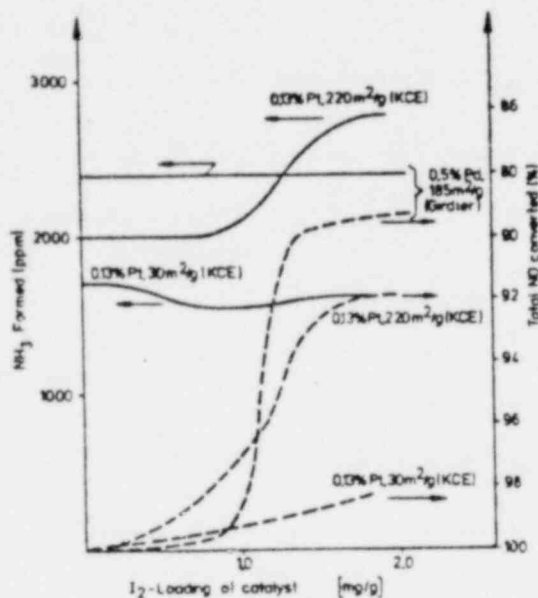lysts of high specific surface is more strongly affected than of

FIGURE 7

Poisoning effect of I_2 on Pt-and Pd-catalysts with respect
to activity and selectivity of NO-reduction.
Inlet concentration: 0,75vol-%O_2, 0,5vol-%NO, 2,75vol-%H_2.
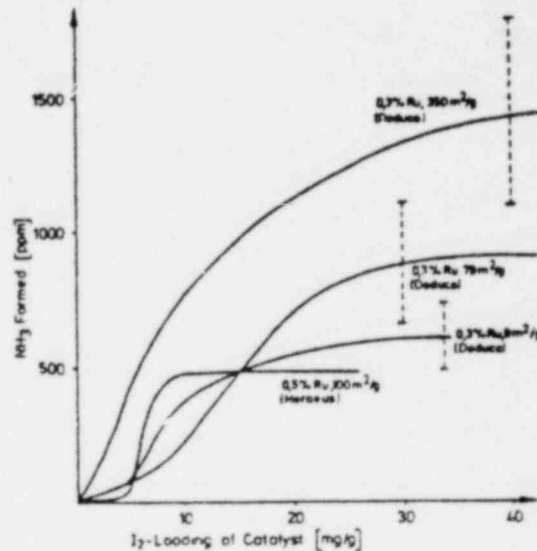Space velocity : 5000h⁻¹, 400 °C.

FIGURE 8

Poisoning effect of I_2 on Ru-catalysts with respect to
selectivity of NO-reduction.
Inlet concentrations: 0,75Vol-% O_2, 0,5 Vol-% NO, 2,75Vol-%H_2;
space velocity: 5000h⁻¹, 400°C.

types of lower specific surface area. The selectivity which is not
good at the beginning (about 40 - 50 % NH_3 formed, the rest N_2), is
not affected significantly, however [21].

On the contrary, the activity of Ru catalysts is not influenced
even by very high I_2 loadings: under the experimental conditions, NO
is reduced throughout to a residual level of $\leq$ 1 ppm. A poisoning
effect can only be observed in the selectivity: formation of NH_3 which
is very low in the unpoisoned state (22), increases more or less
strongly on increasing I_2 loading (fig. 8). Again, the influence of
the specific surface area is obvious. The NH_3 formation never reaches
the amount produced at Pt and Pd.

Thus, on the basis of these data, further work will be carried
out with the Ru catalyst of low specific surface area. It can be shown
that in a real offgas the time of operation of such a catalyst bed
should not be limited below about one year by iodine poisoning, if an
iodine filter with a DF of 10^3 or better is installed before the cata-
lyst.

4.2   Formation of Methane

- It is well known that Ru is an active catalyst for the reduc-
tion of CO_2 to CO and CH_4 (23). CO_2 is an essential component of the

offgas if air is the carrier gas. In addition, CO_2 is formed, if organic substances are burned on an oxidation catalyst, which is conventional practice in air liquefaction plants. Also, C-14 is set free from the fuel elements predominantly as $^{14}CO_2$. CO and CH_4, if formed at the reduction catalyst, will not be retained at the adsorption bed and will reach the cryogenic column. According to their boiling points (81.7 K and 111.6 K at 1 bar, respectively) they will attain a certain equilibrium concentration there. For two reasons CH_4 formation must be avoided:

- it is a safety hazard in the presence of O_2 (or O_3);

- retention of C-14 will be inhibited.

The reduction of CO_2 by H_2 is governed thermodynamically by the equilibria given in table II (23). Whereas CO is formed preferably at higher temperatures ("water gas" reaction), CH_4 is formed preferably at lower temperatures ("Fischer-Tropsch" reaction).

Table II: Reduction of CO_2 by H_2

I. $\quad CO_2 + H_2 \rightleftharpoons CO + H_2O$

$$Kp^I = \begin{cases} 0.067 \text{ at } 350\,°C \\ 0.017 \text{ at } 250\,°C \end{cases}$$

II. $\quad CO + 3H_2 \rightleftharpoons CH_4 + H_2O$

$$Kp^{II} = \begin{cases} 2.62 \text{ at } 350\,°C \\ 3.04 \text{ at } 250\,°C \end{cases}$$

III. $\quad CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$

$$Kp^{III} = Kp^I Kp^{II} = \begin{cases} 0.18 \text{ at } 350\,°C \\ 0.05 \text{ at } 250\,°C \end{cases}$$

The overall equilibrium constant is the product of both Kp^I and Kp^{II} shifting reaction III to the right with increasing temperature. The experimental results show that at temperatures above $400\,°C$ substantial amounts of CO, but little CH_4 is formed, whereas at lower temperatures high yields of CH_4 are obtained depending strongly on the H_2-concentration. Thus one requirement for the minimization of CO_2-reduction is to keep the overstoichiometric H_2 amount with respect to

the reduction of O_2 and NO_x as low as possible.

As a matter of fact, the presence of O_2 suppresses the formation of CH_4 drastically, the overall atmosphere still being reducing. If O_2 is added to a gas mixture containing only CO_2 and H_2 in N_2, the formation of CH_4 immediately drops down below the level of detection (20 ppm by gaschromatography). Equilibrium III (table II) is shifted to the left by a decrease of the H_2- and an increase of the H_2O-concentration.

It can be concluded from these results that in a realistic offgas formation of CH_4 at the reduction catalyst can be controlled to such an extent that it poses no serious problems from a safety standpoint.

Acknowledgements

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