SKBF TECHNICAL
KBS REPORT

84-02

Radiolysis of concrete

Hilbert Christensen
Studsvik Energiteknik AB,
Nyköping, Sweden

Erling Bjergbakke
Risö National Laboratory,
Roskilde, Denmark 1984-03-16

RADIOLYSIS OF CONCRETE

Hilbert Christensen
Studsvik Energiteknik AB
Nyköping, Sweden

Erling Bjergbakke
Risö National Laboratory
Roskilde, Denmark

1984-03-16

Hilbert Christensen*
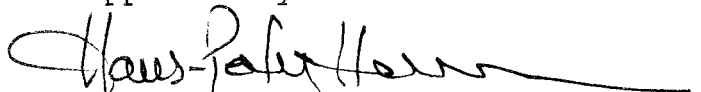Erling Bjergbakke*

SKBF/KBS

RADIOLYSIS OF CONCRETE

A computer based radiation chemical program has been used to simulate experiments with gamma and alpha radiolysis in concrete. The experiments have been performed at Savannah River by Ned Bibler and co-workers. The calculations showed that the gas yields were very sensitive to the pH of the water phase. At a pH of 12.3 fairly good agreement was obtained between measured and calculated gas yields, assuming that the gas production only took place in the free water phase of the concrete. The following main conclusions could be made from both measurements and calculations:

1)   A steady state is obtained by gamma radiolysis of a NO_3^- free concrete.

2)   The yields are higher and a steady state is not obtained if NO_3^- is present.

3)   The yields are higher and a steady state is not obtained by alpha radiolysis.

Calculations were also carried out on radiolysis from cladding hull waste stored in a cement matrix assuming both alpha and beta radiation. In the presence of an aerated gas phase a steady state pressure of more than 0.21 MPa was obtained.

*Risö National Laboratory, Risö,
DK-4000 Roskilde, Denmark

Approved by

CONTENTS

1.   INTRODUCTION

One of the waste products from reprocessing is fuel cladding hulls which is planned to be encapsulated in cement. Radiolysis is an important aspect for the safety of the storage of this product. Concrete has been considered as the storage form for defense waste in USA, and an experimental programme, including radiolysis studies, has been carried out, primarily at the Savannah River Laboratory, SRL (1, 2).

Bibler at SRL has studied the gas production from the radiolysis of concrete, by external and internal gamma or alpha irradiation for different types of waste. The conclusions from Bibler's studies are that hydrogen is produced from both gamma and alpha radiolysis. Oxygen is produced in alpha radiolysis but it is normally consumed in gamma radiolysis. A steady state is obtained from gamma radiolysis. The steady state concentration is proportional to the square root of the dose rate. Gas production by alpha radiolysis continues with a constant G-value. Pressures of up to 1.4 MPa have been measured, and based on this a pressure exceeding 14 MPa has been calculated to exist after a storage time of 10^5 year (2). Steady state concentrations were not achieved by gamma irradiation at higher dose rates (2.8×10^7 rad/h) in the presence of NO_3^- or NO_2^-.

We have made calculations simulating the conditions in Bibler's experiments in order to check whether the radiolysis in concrete can be described by radiolysis of the water phase in the concrete.

In addition we have made calculations of radio-
lysis in concrete under storing conditions
anticipated for Swedish waste.

Radiolysis in water of crystallization has not
been considered here, but has been described in
a separate report by Z P Zagorski (3). Zagorski's
report has been included as Appendix 1 of the
present report.

Radiolysis of concrete containing organic waste
has not been considered here.

2.   COMPUTER MODEL

2.1   Computer program

We have used a computer program based on DIFSUB
(7) and developed by Lang-Rasmussen, Risö,
Denmark. In principle the program translates the
chemical equations of the complete reaction
system into a set of differential equations,
which is solved by numerical integration after
specifying of rate constants, initial concen-
trations, G-values, irradiation dose and duration.
The results are presented in tables giving the
concentrations of the various species at various
times during, and even after, the irradiation
(if wanted). As an option, the results can also
be presented as curves showing the concentrations
as a function of time.

As input data the program requires
a)   a list of all the chemical reactions
     involved,
b)   rate constants for these reactions,
c)   G-values for all the primary products,
d)   initial concentrations of all species at
     the start of irradiation,

e)   dose and duration of the irradiation.

a) and b) are shown in Table 3.

The predictive capacity of the program has been
tested by comparing calculations with results of
measurements by T Eriksen and J Lind (8).
Eriksen and Lind irradiated bentonite/water
mixtures to various doses and measured the
hydrogen production in the gas phase. The
hydrogen was analysed by gas chromatography. O_2
and H_2O_2 were not determined in the experiments.
The correlation between measured and calculated
results was very good (4). Calculated results
have also been compared with literature data. In
this case the correlation was also very good
(9).

In the presence of iron, NO_2^-, and NO_3^- ions the
reactions listed in Table 4 have been included
in the mechanism.

2.2   Presence of gas phase

The program is designed for a homogeneous liquid
phase. However a gaseous phase can be simulated
by using two elements: Dummy I and II, which
represent H_2 and O_2 in the gaseous phase,
but which the program treats as components in
the liquid phase. Equations 37-41 describe the
partition between the liquid and gaseous phases:
equations 37 and 40 apply to H_2 and 39 and 41
to O_2. The relationship between the volumes of
gas and liquid have been taken in account. The
ratios K_{37}/K_{40}, and K_{39}/K_{41} are determined by
the solubility of hydrogen and oxygen respecti-
vely. The absolute values have been taken to be
large so that the equilibrium between the liquid
and gaseous phases will be established quickly.

From equations 37 and 40 it can be seen that at equilibrium

$$K_{37}/K_{40} = \frac{(Dummy\ I)}{(H_2)_{liq}} = K$$

$$(Dummy\ I) = (H_2)_{gas} \times \frac{V_{gas}}{V_{liq}}$$

$$K_{37} = K_{40} \times K_D \times \frac{V_{gas}}{V_{liq}}$$

2.3   Primary yields of radiolysis products

The primary yields of radiolysis products discussed and applied previously (4) have been used and are summarized in Table 1.

3.   COMPARISON WITH MEASUREMENTS

3.1   Introduction

Bibler has presented results from radiolysis experiments under different conditions (1, 2). In the following results from calculations are compared with the experimental values for 12 cases. They include experiments with pure gamma-irradiation, pure alpha-irradiation and combinations of alpha and gamma-irradiation. The effect of NO_3^--ions is also included.

As far as possible the data given by Bibler have been used. In some cases the initial conditions were not specified directly in Bibler's reports, but could be inferred.

All the experiments were carried out in closed containers assuming an initial air pressure of 1 atm.

3.2   Effect of pH

The pH of concrete is normally in the range of
12.5 - 13.5. In the beginning pH is about 13 and
is determined by NaOH and KOH. Later on the pH
is determined by CaOH and is then 12.6. However,
contents of SiO_2 and other oxides may decrease
the pH. In the first calculations a pH of 13 was
assumed . However, the calculated results were
not in good agreement with the experiments (case
1 below). Therefore the results of calculations
carried out at various values of pH (7, 12.0,
12.3, 12.7 and 13) were compared. It can be seen
from Figs 1-2 that the pH is an important
parameter. This is because of the changes in the
rate constants with pH, mainly K3, K8, K14 and
K15. The species OH and H_2O_2, which exist in
neutral and acid solutions, are substituted by
O^- and HO_2^- in alkaline solutions, the pK being
about 11.9 for both species (10). The species O^-
and HO_2^- react with other rate constants than
the species OH and H_2O_2.
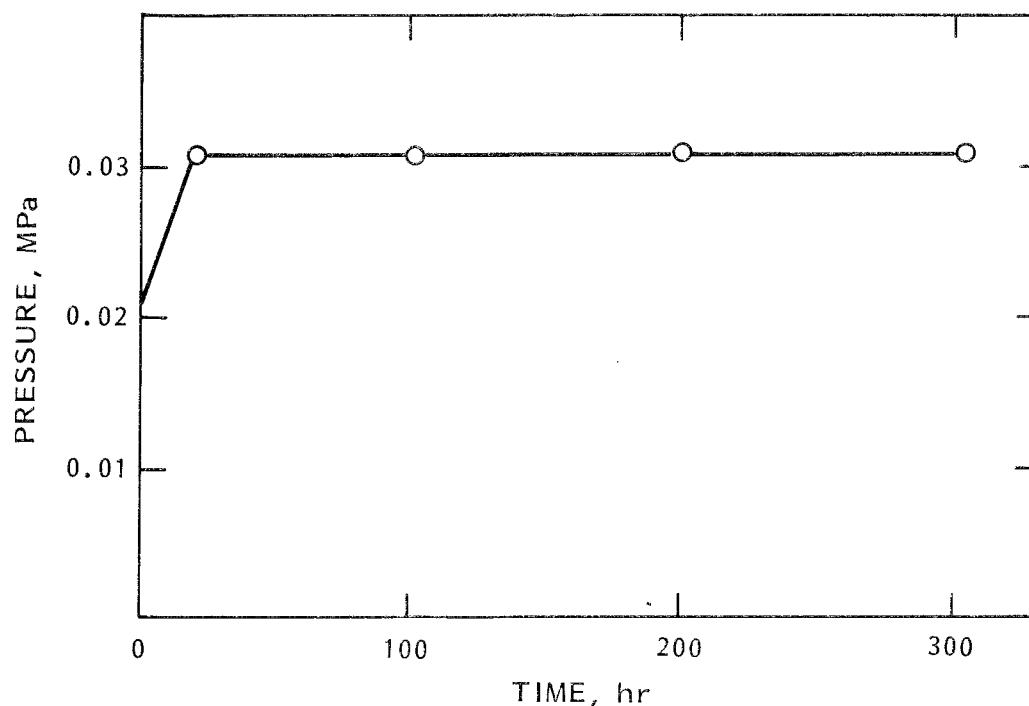
Figure 1. Calculated results for case 1 at a pH
of 7.0

MPa   psig
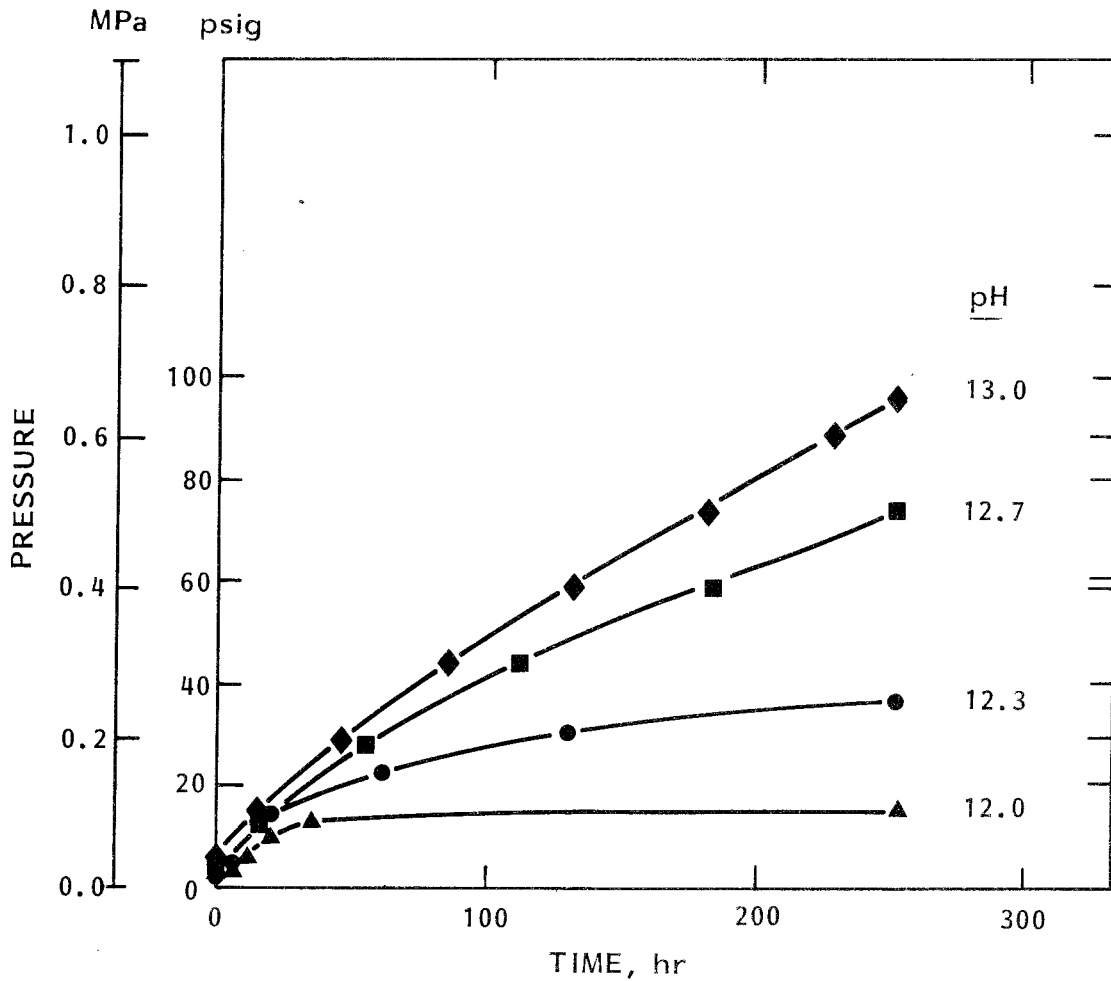

Figure 2. Calculated results for case 1 as a
function of pH.

The best agreement was obtained using a pH of
12.3. Therefore, we have assumed this pH to
be relevant for the experiments and used it in
all subsequent calculations.

3.3   Test cases

3.3.1   Gamma irradiation

Case 1 and 2
Portland cement and gypsum perlite based
concrete.Experiments described in Ref 1, Fig 1.

Conditions and results

	Case 1	Case 2
Water volume, ml	65*	61*
Gas volume, ml	168	112
Dose rate (gamma), rad/h	1.4E7	2.6E7
Irradiation time(expt), h	400	400
" " (calc), h	800	800
Pressure after 400h(expt),MPa	0.23	0.31
" " (calc),"	0.25	0.25

* This is a reduced water volume used in the
calculations. The reduction is 25% which is
motivated by reactions and water of crystalli-
zation, which is assumed not to take part in the
radiolysis.

Measurements and calculations can also be seen
in Figure 3.
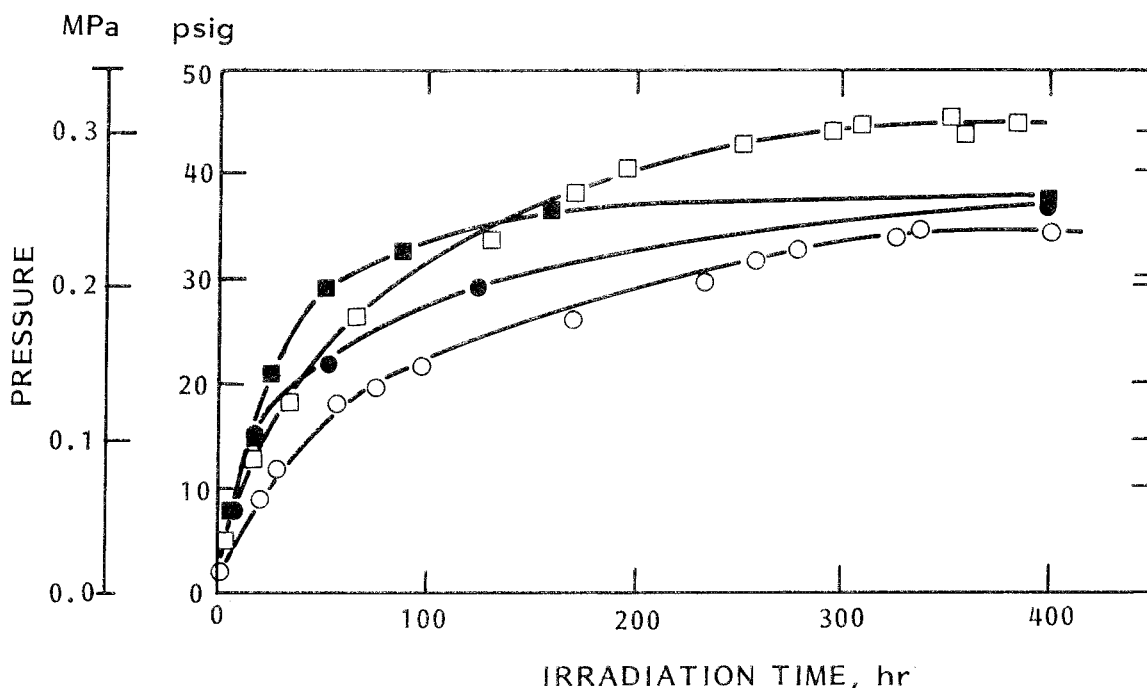

Figure 3. Gamma radiolysis.

Pressurization from gamma radiolysis of concrete at
47°C.

Experimental results (From DP-1459, Fig. 1):
O =:1.4x10^7 rad/h,☐:2.6x10^7 rad/h.

Calculated results: ●:1.4x10^7 rad/h (case 1);
■ :2.6x10^7 rad/h (case 2).

In the calculations, stoichiometric amounts of hydrogen and oxygen are formed. In the experiments oxygen in the air trapped in the container was partially consumed and N_2 was unaffected.

The calculated curves agree fairly well with the experimental curves, however the difference in the calculated final pressures is small in the two cases.

We have also made calculations in order to determine the effect of dose rate: Case 1 was repeated but with 10 and 100 times lower dose rates (389 and 39 rad/s, respectively). As can be seen from Table 8, the equilibrium pressure appears to be independent of dose rate, contrary to the experimental findings.

Case 3-6
Experiments described in Ref 2, Table 2 and Fig 3.

Conditions and results

	Case 3	Case 5	Case 4	Case 6
Water volume,ml	55	55	55	55
Gas " ,ml	167	167	167	167
Gamma dose rate, rad/h	2.8E7	2.8E7	2.5E7	2.5E7
Irradiation time,h				
- experiment				260
- calculations	560	560	560	560
Iron conc(Fe^{3+}), µM	0	1	0	1
Measured equil pressure, MPa		0.72		0.83
Calculated equil pressure, MPa	0.26	0.25	0.26	0.24

Measured and calculated results are shown in
Figure 4. The yields are a little lower in the
presence of iron.
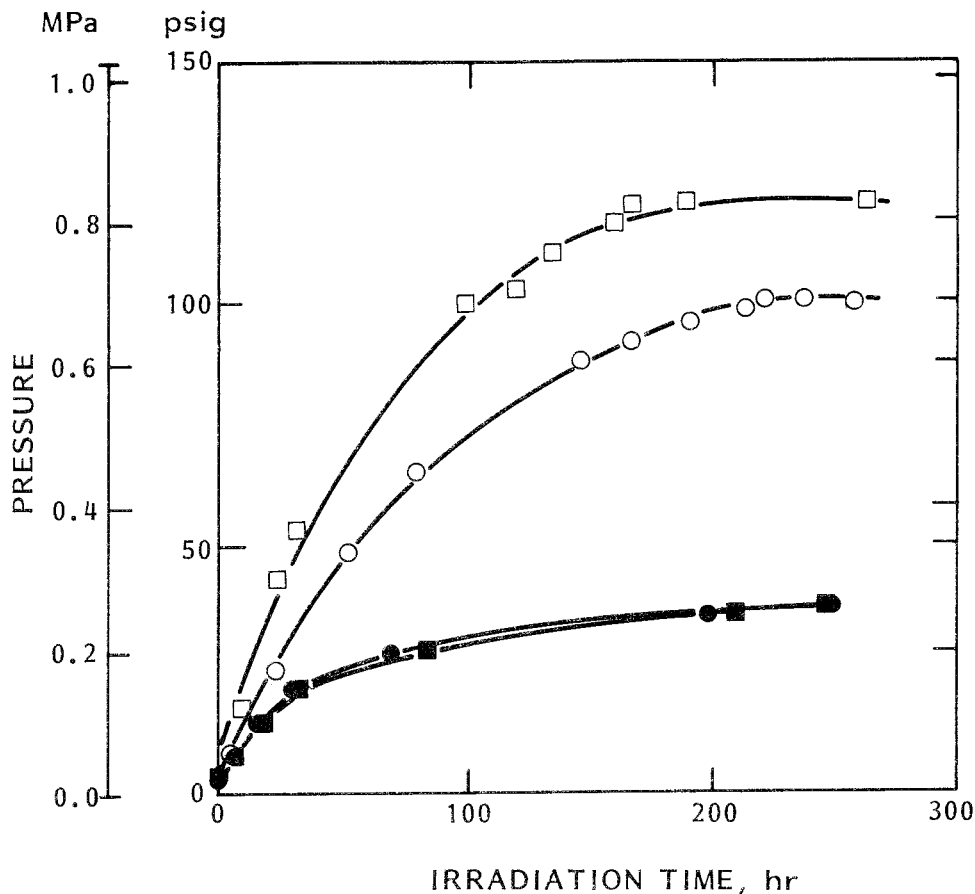
Figure 4. Gamma radiolysis

Pressure from gamma radiolysis at two dose rates of
concrete containing Fe_2O_3.
Experimental results (From DP-1464, Fig.3)
$O:1.4x10^7$ rad/h; $\square:2.5x10^7$ rad/h.
Calculated results: $\bullet:2.8x10^7$ rad/h (case 3);
$\blacksquare:2.5x10^7$ rad/h (case 4).

In the calculations stoichiometric amounts of
hydrogen and oxygen are formed. This was not
always the case in Bibler's experiments, indi-
cating that some unknown (oxygen consuming)
reactions were taking place.

3.3.2   Alpha irradiation of concrete

^{244}Cm is used as an internal alpha-source.

Case 7
Experiment described in Ref 1, Figure 4.

Conditions and results

Water volume, ml	3.5
Gas volume, ml	11.6
Alpha dose rate, rad/h	2.8xE6
Irradiation time, h	
- experiment	330
- calculations	700
Measured pressure after 330 h, MPa	1.39
Calculated " " " , MPa	1.13
Calculated pressure after 330 h including decomposition of H_2O_2 to O_2, MPa	1.39

In both the measurements and the calculations
the pressure increased at a constant rate, see
Figure 5.

The calculated hydrogen peroxide concentration
after 330 h was 0.725 M, which is probably an
unrealisticly high concentration. H_2O_2 is
probably decomposed to oxygen through catalytic
reactions.

NW76 EG
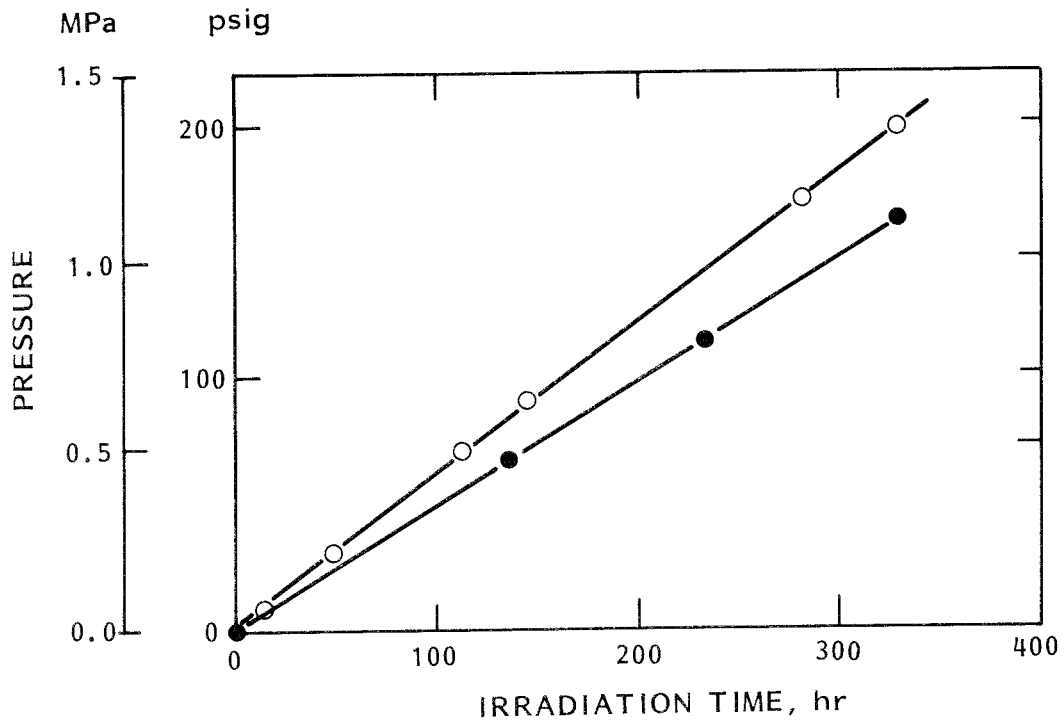
Figure 5. Alpha radiolysis.

High pressure generated from alpha radiolysis of
concrete at $23^{\circ}C$.
Experimental results (From DP-1459): O
Calculated results (case 7): ●

Case 8

Experiment described in Ref 2, Figure 13.

Conditions and results
Water volume, ml	3.4
Gas " , ml	9
Alpha dose rate, rad/h	2.7xE5
Irradiation time, h	
- experiment	3670
- calculations	8000
Measured pressure after 3670 h,MPa	1.33
Calculated " " ,MPa	1.47
Calculated pressure after 3670 h including O_2 from decomposition of H_2O_2, MPa	1.83

Measured and calculated results can be compared in Figure 6.
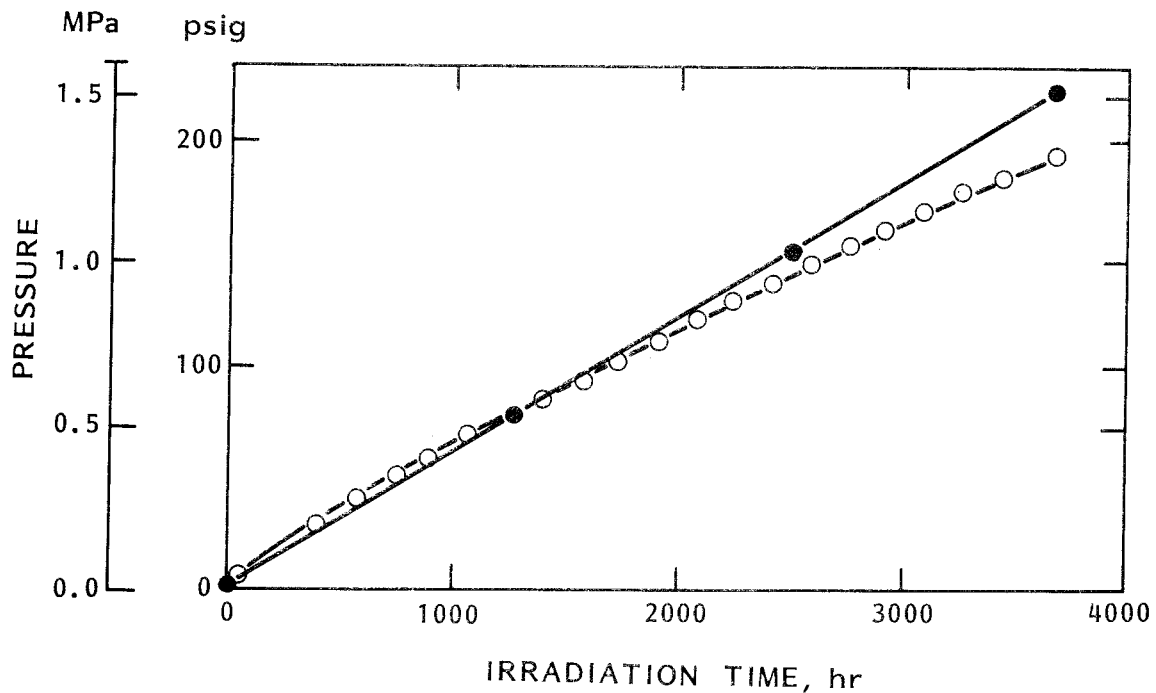

Figure 6. Alpha radiolysis.

Pressure from Long-Term Alpha Radiolysis of Concrete Container Fe-Mn Simulated SRP Waste.
Experimental results (From DP-1464): O
Calculated results (case 8): ●

Stoichiometric formation of oxygen and hydrogen
was found both in experiments and in calculations.
In both cases 7 and 8 the pH decreased from 12.3
to 10.2. In both cases 7 and 8 the G-value for
the hydrogen production was 1.29, if the calcu-
lation is based only on the radiation absorbed
in the water phase.

3.3.3   Combined alpha and gamma irradiation

Case 9

Experiment described in ref 2, p 28-29. 165 g
concrete containing actual SRP waste (SRP:
Savannah River Plant) was used.

Conditions and results	
Water volume, ml	82
Gas volume, ml, aerated	167
Dose rate, rad/h	gamma: 3×10^{4}
" " "	alpha: 4×10^{2}
Irradiation time:	
− experiment, y	1
− calculations, y	2

Bibler's results and the corresponding calculated
results are presented in Figure 7. After one
year both containers leaked. The calculated
pressure after 1 y was 0.11 MPa and the measured
pressure was 0.05 MPa. After 250 d the calculated
pressure was 0.09 MPa and the measured pressure
was 0.05 MPa. A possible explanation for the
differences may be the uncertainty in pH or
water volume.
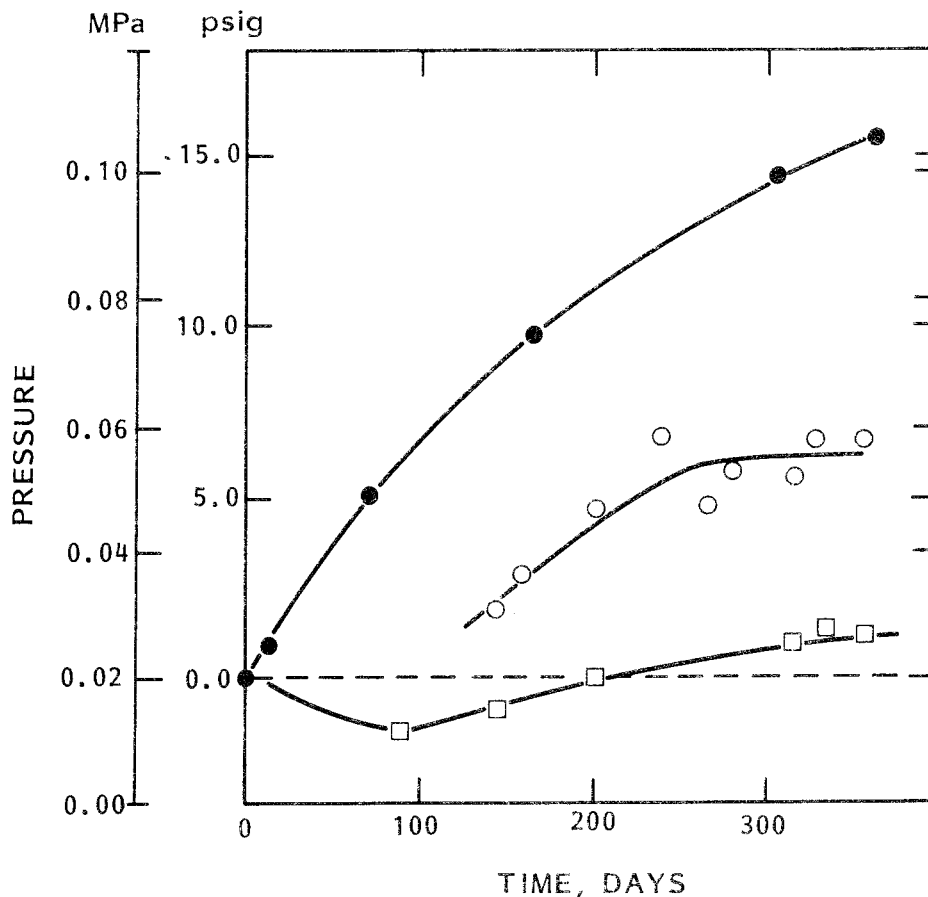
Figure 7. Radiolysis in waste containers.

Pressure from Concrete Containing Radioactive SRP
Waste.
Experimental results from two containers (From
DP-1464): O, $\square$
Calculated results (case 9): $\bullet$

The contribution of alpha radiation is only
about 1% in this case.

The composition of the gas in the experiments is
not given. In the calculations stoichiometric
amounts of oxygen and hydrogen are formed.

3.3.4   Gamma irradiation of concrete containing
         NO_3^- and/or NO_2^-

Case 10-12
Experiments described in Ref 2, Figure 7.

Conditions and results

	Case 10	Case 11	Case 12	Case 5
Water volume (assumed),ml	55	55	55	55
Gas volume (assumed),ml	167	167	167	167
Gamma dose rate, rad/s	2.8E7	2.8E7	2.8E7	2.8E7
Iron conc, μM in water	1	1	1	1
NO_3^- , wt% of concrete	1	5	5	0
NO_2^- , " " "	0	0	2.5	0
Irradiation time, h	143	143	143	143
Measured pressure, MPa	1.28			
Calculated " , MPa	2.34	2.54	2.28	0.22

The results are shown in Figure 8.
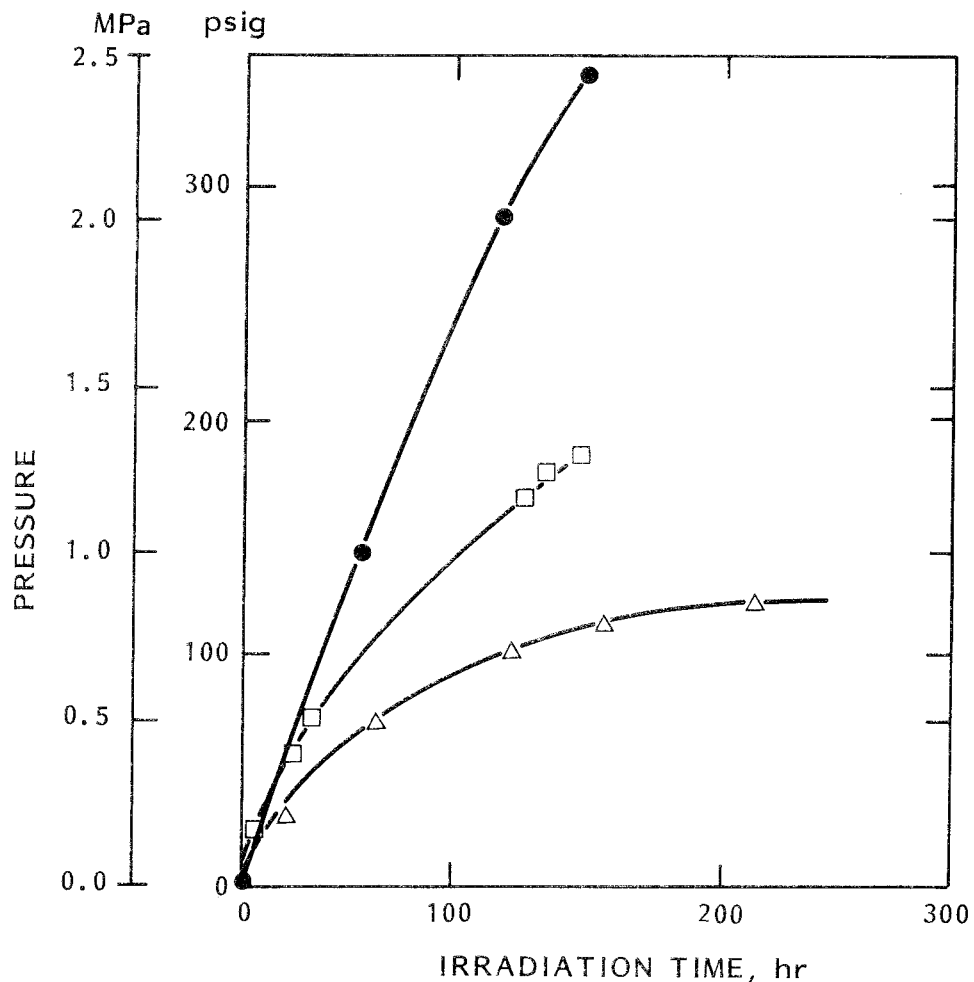

Figure 8. Effect of NO_3^-. .

Pressure from gamma radiolysis at 2.8×10^7 rads/hr
of concrete containing Fe_2O_3 with sorbed NO_3^- ions.
Experimental results (From DP-1464): □ : 1% NO_3^-;
△ : 0% NO_3^-.
Calculated results (case 10): ● : 1% NO_3^-

Both experiments and calculations show a considerable effect of NO_3^- on the gas production, which is much higher in the presence of NO_3^-. It should be noted that a steady state is not obtained in the presence of NO_3^-.

Almost stoichiometric amounts of hydrogen and oxygen are formed in addition to small yields of nitrogen oxides.

The calculated pressure (case 10) is higher than the measured pressure. The difference could be caused by a lower pH in the experiment than is to be expected (if acid nitrates are added to the concrete). We have interpreted Bibler's description of the experiment to mean NO_3^- contents of 1 and 5 wt% of the concrete, and have then assumed the concentrations in the water phase to be 3 times higher.

3.4   Conclusions

The comparisons between Bibler's measurements and our calculations show that the latter can describe the principles derived in the measurements:

1)   A steady state is obtained by gamma
        radiolysis of a NO_3^- -free concrete

2)   The yields are higher and a steady
        state is not obtained if NO_3^- is
        present

3)   The yields are higher and a steady
        state is not obtained by alpha radio-
        lysis.

In some cases we have calculated lower and in other cases higher yields than found in the experiments. It has been shown that the gas

yields are very sensitive to the pH in the water
phase of the concrete, which must consequently
be known accurately. Other important parameters
are type of radiation, dose, initial concentra-
tions of NO_3^-, O_2, and organics, type of organics,
and - especially for alpha irradiation - the
gas/liquid ratio.

Obviously, in the experiments there is an
unknown oxygen consuming process. Radiolysis of
pure water yields stoichiometric quantities of
oxidizing and reducing species. An oxygen
consumption may be caused by organics or Fe^{2+}
ions. Despite the excess of hydrogen found in
the experiment we obtain roughly the same
pressure in experiments and calculations. It
might be possible to include oxygen consuming
reactions and at the same time change the pH in
the calculations and thus obtain another fit to
the experiments.

As can be seen from Table 1 the radical yields
(e_{aq}^-, H and OH) are much larger and the molecular
yields (H_2 and H_2O_2) much lower for gamma
radiation, in comparison with alpha radiation.
Therefore, the recombination reactions 8, 14 and
16 are important for gamma irradiation. The
result of these reactions is that a steady state
is obtained. Scavengers, which react with the
radicals and thus impede the recombination, may
change the situation drastically. This can be
seen in the cases where NO_3^- is added. If the
recombination is blocked totally a $G(H_2)$ value
of 0.5 vould be expected. Due to the low yields
of radicals in alpha irradiation, scavengers are
not expected to have a great effect in this
case.

Stoichiometric amounts of hydrogen and oxygen
are formed according to the calculations, but
only hydrogen was found in the gamma-experi-
ments in the absence of NO_3^-.

4.   RADIOLYSIS IN CEMENTED CLADDING HULLS

4.1   Activity content and dose rates

Dose rates in the cemented cladding hulls were
calculated using the following information, (5):

1 ton U gives 300 kg cladding hull waste con-
taining: 6000 Ci activation products, mainly
^{60}Co and ^{55}Fe, 10000 Ci fission products,
mainly ^{106}Ru and 0.1% of the fuel, i e about
1000 Ci, including alpha activities. These
activities give a gamma and beta dose rate of
8.5 rad/s (in 3 year old waste) if the radiation
is absorbed homogeneously in the concrete.

1 ton U was contained in 354 fuel pins. If the
0.1% fuel is assumed to cover the inside of the
fuel cladding uniformly, a $2x10^{-4}$ cm thick
layer is obtained over an area of $4x10^5$ cm^2.
Further the alpha irradiation is assumed to be
absorbed in a 0.03 mm thick water layer, corre-
sponding to 1.3 l. The 0.1% fuel develops a
power of 0.18 W after 40 y, 50% of which is
assumed to be absorbed in the water layer,
corresponding to an alpha dose rate of 7 rad/s.
The corresponding beta dose rate is assumed to
be 2.5 rad/s, in accordance with the calculations
of Klas Lundgren (6). The dose rates after
various storage times are given in Table 2; they
have been calculated based on data from Lundgren
(6).

4.2   Results of calculations

We have calculated the results of alpha radiolysis
(including a contribution of beta radiolysis),
in a thin water layer on the inside of the fuel
cladding (1.3 1) for various times up to 10^5y,
see Table 5. It was assumed that hydrogen and
oxygen could diffuse out of the system. The
diffusion rate constants used are those valid
for water (1.34×10^{-4} s^{-1} and 4.78×10^{-5} s^{-1} for
H_2 and O_2 respectively (11)).

Initially the water was assumed to be deaerated
and to have a pH of 12.3. At each storage time
(Table 5) calculations were carried out to
simulate irradiation for at least 4 months,
during which production rates were constant. The
results from fuel irradiation are given in
Table 5. If the yields are integrated, substantial
amounts of gas are obtained (60 m^3 after 10^5 y).

However, it is most likely that the hydrogen and
oxygen produced in the thin alpha irradiated
water layer (1.3 1) diffuse into the bulk water
(190 1 for concrete waste from 1 ton UO_2).
Therefore we have carried out calculations on
beta irradiation of the bulk water, including a
continuous supply of hydrogen and oxygen produced
in the thin water layer. The effect of the beta
irradiation in the bulk water phase is to
recombine the hydrogen and oxygen produced in
the thin layer. The resultant total gas produc-
tion is therefore decreased due to the effect of
beta irradiation, see Table 6a, which shows that
the yield of hydrogen is very low. In this
calculation we have neglected the gaseous phase,
and instead assumed that oxygen and hydrogen
diffuse out of the system through a surrounding

bentonite layer, where the diffusion coefficients
are very low, approximately 700 times lower than
in water (12). The production values given in
Table 6a would therefore be approximately 700
times higher if hydrogen disappeared by diffusion
in water instead of in bentonite.

In the calculations shown in Table 6a it was
assumed that the water was oxygen free initially.
If it is assumed that the water is aerated at a
pressure of 0.1 MPa the results shown in Table
6b and 6c, corresponding to diffusion through
bentonite and water respectively, are obtained.
In these cases (6b and 6c) it is also assumed
that the system is surrounded by aerated water.

As can be seen from Tables 6a-c the initial
oxygen concentration in the irradiated water
phase is a very important parameter.

We have also carried out a calculation, in which
we have assumed that the 190 l free water is in
equilibrium with a gaseous phase of 100 l inside
the concrete. Even in this case hydrogen and
oxygen are supplied to the system from the thin
alpha irradiated water layer. The results of
this calculation are shown in Table 7. The
steady state pressure is surprisingly low, when
compared with Bibler's measurements and corre-
sponding calculations, see for example Case 1.

The main differences from Case 1 are a different
dose rate (Case 1: 3.890 rad/s; cladding hull
waste, 3-4 y; 5.5 rad/s) and a different initial
oxygen concentration (Case 1: air-saturation
assumed; cladding hull waste, deaerated conditions
assumed). Therefore further calculations have
been made in order to explain the low equilibrium
pressure obtained at steady state.

The water phase (190 1) was irradiated in the presence of an air-saturated gas phase (100 1). After 3.7 y irradiation $/H_2/_{gas}$ was 5.51×10^{-2} M, corresponding to a pressure of 1.3 atm (19 psig). The total pressure increase was 2.0 atm (28 psig), see Table 7; the gas pressure was still not at its equilibrium value. It is obvious from this calculation that an initial presence of oxygen is very important for the formation of gases from the radiolysis of water.

5.   CONCLUSIONS

The gas yields are very sensitive to the pH of the water phase. At a pH of 12.3 a fairly good agreement was obtained between measured and calculated yields, assuming radiolysis of the free water phase only.

The gas yields are very sensitive to the initial oxygen concentration. The yields are approximately 10^3 times higher in aerated conditions compared with deaerated conditions.

The following main principles were found in both measurements and calculations:

1)   A steady state is obtained by gamma radiolysis of a NO_3^--free concrete.

2)   The yields are higher and a steady state is not obtained if NO_3^- is present.

3)   The yields are higher and a steady state is not obtained by alpha radiolysis.

In the measurements it was found that during gamma radiolysis the steady state pressure was proportional to the square root of the radiation intensity.

In the calculations it was found that during
gamma radiolysis the steady state pressure was
independent of dose rate in the range
39-3890 rad/s.

It is possible that some reactions take place in
the experiments which have been disregarded in
the calculations. The square root law was
obtained partly by pressurization with hydrogen,
which, however, may change the result of the
irradiation.

Studies carried out by Zagorski, pages 9 and 20
of ref (3) indicate that radiolysis in water of
crystallization is unimportant for the production
of the gases.

Experiments of Möckel and Köster (13) also
indicate that chemically bonded hydrate-water is
less susceptible to radiolysis than the bulk
water.

Möckel and Köster have found that hydrogen alone
is formed by gamma-radiolysis of NO_3^- free
cement. In the presence of 10% $NaNO_3$ the hydrogen
production is reduced by a factor of 10 and the
gas produced consists to more than 60% of
oxygen. No nitrogen oxides are formed. Möckel
and Köster added fluidizer to the concrete.
M & K also remark that the yield of H_2 increases
linearly with dose, i e saturation is not
observed, dose rate $(2.5-4.9) \times 10^5$ rad/h, dose
$(0.7-9) \times 10^{22}$ eV.

The gas production in Bibler's experiment seems
to be independent of the w/c ratio (at ratios of
3-4). The calculated steady state pressure is
also independent of the w/c ratio. However, the
initial rate of production found in the calculations
is dependent on this ratio.

Möckel and Köster (13) have found an increasing
hydrogen yield with increasing w/c ratio (in the
range w/c 0.2-0.6).

A possible presence of organic material in the
waste product might explain the preferential
formation of hydrogen found in Bibler's gamma-
irradiation experiments. The presence of Fe^{2+}
ions may have the same effect.

REFERENCES

1.   BIBLER N E and OREBAUGH E G,
        Radiolytic gas production from tritiated
        waste forms.
        Report DP-1459, Savannah River Labora-
        tory, Aiken, SC, 1977.

2.   BIBLER N E,
        Radiolytic gas production from concrete
        containing Savannah River Plant waste.
        Report DP-1464, Savannah River Labora-
        tory, Aiken, SC, 1978.

3.   ZAGORSKI Z P,
        Electrons trapped in crystalline
        systems containing water.
        Studsvik Technical Report NW-83/416,
        (1983-01-25).

4.   CHRISTENSEN H and BJERGBAKKE E,
        Radiolysis of ground water from spent
        fuel.
        Studsvik Report NW-82/364.

5.   FORSSTRÖM H,
        Personal communication, Dec 1982.

6.   LUNDGREN K,
        Strålningsnivå och till vatten deponerad
        strålningsenergi utanför kapslar i
        slutförvaret. (In Swedish)
        KBS TR 106(1978).

7.   GEAR C W,
        Algorithm 407, DIFSUB, Commun. ACM,
        1971, 14, 185.

8.   ERIKSEN T and LIND J,
        Mätning av radiolytiskt bildat vätgas i
        bentonit. (In Swedish)
        KBS TR 79-13 (1979).

9.   BJERGBAKKE E,
        Computer simulations control.
        Private communication, 1981-08-28.

10.   CHRISTENSEN H, SEHESTED K and CORFITZEN H,
        Reactions of hydroxyl radicals with
        hydrogen peroxide at ambient and
        elevated temperatures, J Phys Chem
        1982, 86, 1588.

11.   CHRISTENSEN H and BJERGBAKKE E,
        Radiolysis of ground water from HLW
        stored in copper canister.
        KBS TR 82-02 (1982).

NW76 EG

NW76

12.   NERETNIEKS I and SKAGIUS E,
             Diffusioismätningar av metan och väte i
             våt lera. (In Swedish)
             KBS TR 86 (1978).

13.   MÖCKEL H J and KÖSTER R H,
             Gas formation during the gamma-radio-
             lysis of cemented low- and inter-
             mediate-level waste products.
             Nucl Techn 59, 494-97 (1982).

TABLE 1. Primary G-values by irradiation of water

	α	γ and β	$\alpha + \beta$ (thin water layer)
H_2	1.3	0.49	1.08
H	0.21	0.44	0.27
e^-	0.06	2.68	0.75
HO_2^-	0.985	0.74	0.92
O^-	0.24	2.59	0.86
O_2^-	0.22	0.01	0.16
H^+	1.505	6.11	2.71
OH^-		0.09	0.02
$-H_2O$	2.71	6.86	3.79

TABLE 2. Dose rates in the water phases of the cemented cladding hull waste

Storage time	Thin water layer (1.3 l) irradiated from fuel Dose rates in rad/s		Free water in the concrete Dose rates in rad/s
y	α	β	β
3	7	2.5	8.5
40	7	2.5	2.5
100	5.75	1.73	1.73
10^3	1.75	5.3E-1	0.53
10^4	0.38	1.1E-1	0.11
10^5	1.88E-2	4.3E-3	4.3E-3

TABLE 3. Reaction scheme

	Rate constant $M^{-1} s^{-1}$
RE1: $2E^- = 2OH^- + H_2$	5E9
RF2: $E^- + OH = OH^- + H_2O$	3E10
RE3: $2OH = H_2O_2$	4.5E9
RE4: $OH + O_2^- = O_2 + OH^-$	1.2E10
RE5: $OH^- + H = E^-$	2E7
RE6: $E^- + H^+ = H + H_2O$	2.4E10
RE7: $E^- + H = OH^- + H_2$	2.5E10
RE8: $E^- + H_2O_2 = OH + OH^- + H_2O$	1.3E10
RE9: $E^- + H_2O = H + OH^- + H_2O$	1.6E1
RE10: $H^+ + OH^- = H_2O$	1.43E11
RE11: $H_2O = OH^- + H^+$	2.599E-5
RE12: $2H = H_2$	8E9
RE13: $H + OH = H_2O$	2E10
RE14: $OH + H_2 = H + H_2O$	4.5E7
RE15: $OH + H_2O_2 = H_2O + HO_2$	2.3E7
RE16: $H + H_2O_2 = OH + H_2O$	9E7
RE17: $E^- + O_2 = O_2^- + H_2O$	1.9E10
RE18: $H + O_2 = HO_2$	1.9E10
RE19: $HO_2 = O_2^- + H^+$	8E5
RE20: $H^+ + O_2^- = HO_2$	5E10
RE21: $HO_2 \ O_2^- = O_2 + HO_2^-$	7.9E7
RE22: $H + HO_2 = H_2O_2$	2.2E10
RE23: $H + O_2^- = HO_2^-$	2E10
RE24: $E^- + HO_2 = HO_2^- + H_2O$	2E10
RE25: $E^- + O_2 = HO_2^- + OH^-$	1E10
RE26: $OH^- + H_2O_2 = HO_2^- + H_2O$	5E3
RE27: $H_2O + HO_2^- = H_2O_2 + OH^-$	5.735E-1
RE28: $O^- + O^- = O_2^{--}$	E9
RE29: $O^- + HO_2^- = OH^- + O_2^-$	4E8
RE30: $O_2^{--} + H_2O = HO_2^- + OH^-$	1
RE31: $O^- + H_2O = OH + OH^-$	2
RE32: $O^- + H_2 = OH^- + H$	8E7
RE33: $OH + OH^- = O^- + H_2O$	1.4E4
RE34: $O^- + E^- = 2OH^-$	2E10
RE35: $E^- + HO_2^- = O^- + OH^- + H_2O$	3.5E9

Table 3 continued

	Rate constant $M^{-1} s^{-1}$
RE37: H_2 = Dummy 1	E4
RE39: O_2 = Dummy 2	E4
RE40: Dummy 1 = H_2	62.9
RE41: Dummy 2 = O_2	104
RE42: O_2^- + $O2^-$ = O_2 + O_2^{--}	E6
RE43: OH + O^- = HO_2^-	1.8E10
RE44: OH + HO_2^- = H_2O + O_2^-	7.5E9
RE45: O^- + O_2^- = O_3^{--}	6E8
RE46: O^- + H_2O_2 = O_2^- + H_2O	5E7
RE47: O_3^{--} + H_2O = O_2 + $2OH^-$	1

TABLE 4. Additional reactions in the presence of iron ions, NO_2^- and NO_3^-

	Rate constant $M^{-1} s^{-1}$
RE48: $FE^{++} + O^- = FE^{+++} + O^{--}$	3.4E8
RE49: $FE^{++} + OH = FE^{+++} + OH^-$	3.4E8
RE50: $FE^{++} + E^- = FE^{+++} + OH^- + H^-$	1.2E8
RE51: $H^- + H_2O = H_2 + OH^-$	E-2
RE52: $FE^{++} + HO_2^- = FE^{+++} + OH^- + O^-$	60
RE53: $FE^{++} + H_2O_2 = FE^{+++} + OH^- + OH$	60
RE54: $FE^{++} + H = FE^{+++} + H^-$	1.3E7
RE55: $FE^{++} + O_2^- \quad FE^{+++} + O_2^{--}$	4E8
RE56: $FE^{+++} + E^- = FE^{++} + H_2O$	2E10
RE57: $FE^{+++} + O_2^- = FE^{++} + O_2$	4E8
RE58: $FE^{+++} + H = FE^{++} + H^+$	E8
RE59: $O^{--} + H_2O = 2OH^-$	E-2
RE60: $O^- + NO_2^- = NO_2 + O^{--}$	2.4E8
RE61: $OH + NO_2^- = NO_2 + OH^-$	2.4E8
RE62: $E^- + NO_3^- = NO_2 + 2OH^-$	9.5E9
RE63: $H + NO_3^- = NO_2 + OH^-$	E7
RE64: $H + NO_2^- = NO + OH^-$	E9
RE65: $NO + NO_2 = N_2O_3$	E2
RE66: $N_2O_3 + H_2O = 2H^+ + 2NO_2^-$	E-2
RE67: $NO_2 + NO_2 = N_2O_4$	E2
RE68: $N_2O_4 + H_2O = 2H^+ + NO_3^- + NO_2^-$	E-2

TABLE 5. Production of hydrogen and oxygen in cemented
cladding hull waste in a thin alpha irradiated water layer

Time period Y	H_2 mol/y	G-value	O_2 mol/y	G-value	Integrated gas product. 1 at $0°C$, 0.1MPa
3-40	0.427	1.05	0.213	0.52	530
40-100	0.376	1.05	0.188	0.52	1290
$100-10^3$	0.212	1.04	0.106	0.52	7700
10^3-10^4	0.0611	1.04	0.03055	0.52	26000
10^4-10^5	0.0113	0.91	0.00565	0.45	60000

TABLE 6a. Production of hydrogen in the free water phase of cemented
cladding hull waste. Hydrogen is assumed to disappear by diffusion
through a bentonite layer. The water is assumed to be initially deaerated.

Storage period, y	Mean dose rate rad/s	Equilibrium concentr in liquid phase µM H_2	O_2	$G(H_2)$	$Prod(H_2)$ mol/y	Integrated hydrogen production 1 (STP)
3-40	5.5	0.44	0.13	1.09E-7	4.4E-6	2.6E-3
40-100	2.1	0.46	0.18	3.2E-7	4.0E-6	8E-3
100-1000	1.13	0.51	0.25	5.7E-7	4.0E-6	8.9E-2
10^3-10^4	0.32	0.43	0.21	1.68E-6	3.4E-6	0.77
10^4-10^5	0.77	0.35	0.17	5.7E-6	2.7E-6	6.2

TABLE 6b.Production of hydrogen in the free water phase of cemented
cladding hull waste. Hydrogen is assumed to disappear by diffusion
through a bentonite layer. The water is assumed to be initially aerated
at 0.1 MPa

Storage period, y	Mean dose rate rad/s	Equil.conc. mM, H_2^-	$G(H_2)$	Prod(H_2) mol/y	Integrated H_2 prod. 1 (STP)
3-40	5.5	0.235	8.9E-5	3.04E-3	2.5
40-100	2.1	0.248	1.53E-4	2.01E-3	5.2
$100-10^3$	1.13	0.248	2.78E-4	1.94E-3	44.7
10^3-10^4	0.32	0.250	9.81E-4	1.96E-3	4.38
10^4-10^5	0.077	0.244	4.00E-3	1.90E-3	4265

TABLE 6c. Production of hydrogen in the free water phase of cemented
cladding hull waste. Hydrogen is assumed to disappear by diffusion
through a water layer. The water is assumed to be initially aerated
at 0.1 MPa.

Storage period, y	Mean dose rate rad/s	Equil. conc. mM, H_2	$G(H_2)$	Prod(H_2) mol/y	Integrated H_2 prod m^3 (STP)
3-40	5.5	0.234	3.58E-2	1.22	1.0
40-100	2.1	0.218	8.59E-2	1.13	2.5
$100-10^3$	1.13	0.191	1.38E-1	0.970	22
10^3-10^4	0.32	0.099	2.65E-1	0.527	128
10^4-10^5	0.077	0.035	4.00E-1	0.190	510

TABLE 7. Production of hydrogen in cemented cladding hull waste.
Assumption: 190 l free water in contact with 100 l gas phase

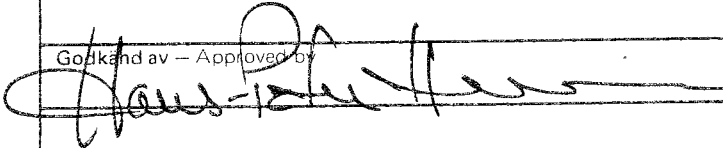| Storage period, y	Mean dose rate rad/s	Equilibrium concentration in liquid phase µM		Equilibrium pressure, MPa		Total pressure MPa
		H_2	O_2	H_2	O_2	
3-40	5.5	1.02	0.80	1.3E-4	6E-5	Deaerated
40-100	2.1	0.94	0.74	1.2E-4	6E-5	conditions
3-40	5.5	1070	1090	0.14	0.07	0.2 Aerated*
40-100	2.1	1370	1340	0.18	0.09	0.26 conditions

* The given values are a little below equilibrium values

TABLE 8. Gamma-radiolysis of concrete at a pH of 12.3
using varying dose rates (see text, case 1)

Dose rate rad/s	Final gas Pressure MPa	psig	Irradiation time s	
3.890	0.25	37	2xE6	Steady state obtained
389	0.24	34	1.3E7	Steady state, not yet
39	0.24	34	1.1E8	obtained

APPENDIX 1

Studsvik **Arbetsrapport** - Technical Report

Projektidentifikation — Project identification	Datum — Date	Org enh och nr — Report No.
	830125	NW-83/416

Titel och författare — Title and author

ELECTRONS TRAPPED IN CRYSTALLINE SYSTEMS CONTAINING WATER

Z P Zagórski
Department of Radiation Chemistry
Institute of Nuclear Research
Warsaw, Polen

Distribution

Godkänd av — Approved by	Kontonr — Internal notes	Rapporten skall
	PN4956A	förhandsaviseras

INTRODUCTION

The majority of work on electrons at low
temperatures has been done on glass systems.
One of the reasons for this is without any
doubt the simplicity of experimental approach.
The easiest method of studying trapped
electron is to deal with its characteristic
and intense absorption spectrum. The glass
matrix makes the task comparatively easy.
There is, of course the deeper motivation for
the glass system. Such a matrix is well
motivated as the object of study by its
direct relation to the liquid systems. Like
in liquids, one can add a diversity of
additives, and have a homogenous and trans-
parent but rigid system of high viscosity
with elements of the structure practically
immobilized.

However, the fact of life is, that the
majority of solid aqueous systems, at any
temperature, is of crystalline structure,
usually more stable than the glassy one.
Electrons are easily stabilized in crystalline
material; in a variety of ways the e_t^-
chemistry seems to be even richer and more
interesting than it is in glass systems.

The experimental approach is much more difficult
and the present paper gives only a few facts in
the. hope that the radiation chemistry of electrons
in crystalline material will eventually reach
the level corresponding to e_t^- in glass materials.

General survey of the irradiated matrix

The matrix treated in the present paper is
limited to alkaline-aqueous systems. It comprises
not only Na and K hydroxides but takes into
account tetralkylammonium hydroxides which
behave in many respects similar, thus helping to
eliminate the role of cations.

Figure 1 shows the field of research: the
variety of systems at different temperatures. It
is obvious that the glassy state is rather an
exceptional, rigid state of undercooled liquid,
thus thermodynamically unstable. It changes
easily into polycrystalline state. Limits of
concentration of hydroxides in which glass is
formed are well defined: there is no possibility
to obtain a glassy state below 6 mole KOH (NaOH)
per liter. The limited solubility of R_4NOH in
water probably prevents the preparation of glass
at all. There is no possibility to obtain mixed,
Na^+, K^+, R_4N^+ hydroxides in the glassy
state, because of salting-out effect.

Glassy versus crystalline state

A popular criterion of the glassy state is the
transparency of the frozen sample. In the case
of sodium and potassium hydroxides that criterion
is true but it fails in the case of tetrabutyl-
ammonium hydroxide - clathrate, not to mention
solid ammonia and other systems.

Looking for a deeper understanding of the
differences between crystalline and glassy
states, we have determined systematically the
density of KOH and NaOH solution at 77 K.
Results show a marked difference between the two
states (Fig 2). The glassy state is substantially
more dense, i e more tightly packed than the
crystalline or polycrystalline preparation. The
average distance between molecules and ions is
significantly shorter in glasses. The difference
is substantial indeed: Taking the NaOH solution
of starting concentration of 6.2 mole/l at room
temperature, the crystalline material has a
density of 1.19 g/ml (77 K) whereas the corre-
sponding glassy material has 1.28 g/ml (77 K).
Or, if we consider the density 1.19 g/ml, it
corresponds to 3.8 mole/l (hypothetical) glassy
material, or 6.2 mole/l - polycrystalline
material.

Still more examples may be found in the high
concentration zone.

In view of the drastic differences in density,
it would be reasonable to refer to the real
volume when describing the concentration. E g
the glass obtained from 12 mole/l NaOH solution,
att 77 K is really 12.3 mole/l. Correspondingly,
the solid $NaOH.1H_2O$ has the molarity of 29.8 mole/l
at room temperature or 29.6 at 77 K.

The differences of densities have a practical
aspect in the experimental technique. Glass is
prepared easily because substantial contraction
does not introduce any mechanical forces.
However, the freezing of 0-5 M solutions or slow
freezing of a concentrated solution (e g 12 M at
-138 K) invariably destroys all vessels by

forceful expansion. Also the slow rewarming of
glass systems, connected with the formation of
an .expanded crystalline phase, destroys the
vessel.

The determination of density also learns that a
rapidly cooled polycrystalline material has a
pretty regular composition. The glassy material
obtained by rapid cooling of concentrated
solutions (at the same rate of cooling), is no
longer as regular. We can conclude that poly-
crystalline material does not contain a heavy
packed glassy fraction, but in glassy material
some crystalline, light fraction may be present.
That applies specially to KOH solutions (cf
Fig 2b). Figures 2a and 2b were originally
published in 1979 /1/, but since that time
enriched with more points, expecially describing
crystalline preparations of high sodium hydroxide
concentration.

Methods of polycrystalline matrix investigations

Before describing experiments on electrons
trapped in a polycrystalline matrix, one has to
do as much as possible about the recognition of
the matrix itself.

The knowledge of this sort of matrix is rather
poor and the solid state chemistry does not
contribute very much in this respect. Our
systems are outside the traditional interests of
solid state chemistry, which is, still traditio-
nally limited to silicates as concern glassy
material and to cases of crystalline materials
of applied interest, like semiconductors. Very
seldom hydroxides, nitrates, hydrates etc are
investigated.

Especially solid hydrates, which are the main
object of our investigation, a favourable matrix
for electron traps, are poorly known. Except for
a few celebrated cases like $LiClO_4.3H_2O$. $BeSO_4.4H_2O$,
$CuSO_4.5H_2O$ and others, the knowledge is not
deep. The knowledge is specially insufficient in
the case of hydrates which trap electrons with
special efficiency.

For instance, there is only one paper written in
the recent two decades on the system water-sodium
hydroxide /2/ describing the existence of
several hydrates and one study on $NaOH.4H_2O$
structure. There is no information on KOH.

The most important is X-ray analysis but the
majority of equipment does not accept hygroscopic
and caustic samples and low temperature work.
Only few measurements were performed in the
Institute of Physical Chemistry in Warsaw, were
X-ray diffraction patterns confirmed our conclusions
(see the paragraph about density) that the
glassy material contains varying amounts of
crystalline centers.

There are other simple experimental approaches
possible, which contribute to the knowledge of
the matrix. We have applied thermogravimetric
and differential thermoanalysis which earlier
proved its value in the investigation of hydrates.
Indeed, that method helped us to formulate the
composition of $KOH.1/2H_2O$, to decide if all the
water in a hydrate containing more than one
molecule of water, is equally coordinated.

Looking for a specific behaviour of some hydrates,
we have also applied IR spectrophotometry. The
reason was the distinct behaviour of hydrates
obtained from alkaline solutions:

$NaOH.H_2O$, $K_3PO_4.3H_2O$, $Na_2HPO_4.2H_2O$ (but not
$NaH_2PO_4.H_2O$), $Na_2CO_3.H_2O$, $Na_2SO_3.7H_2O$,
$2K_2CO_3.3H_2O$, $LiOH.H_2O$, $Ba(OH)_2.8H_2O$,
$(CH_3)_4NOH.5H_2O$, $BaCl_2.2H_2O$.

Finally some methods had to be applied, which
say something about the homogeneity and texture
of polycrystalline materials. These methods are
not necessary in the case of glassy systems,
where one believes, probably with justification,
that the sysem is ideally disordered and that
every additive is distributed with a perfect
homogeneity.

It may not be the case with polycrystalline
material. During the crystallization the process
of fractionation takes place. However, a rapid
cooling secures at least a macro-homogeneous
composition.

Experimental investigation of electrons trapped
in polycrystalline material at low temperatures.

Polycrystalline material is usually opaque, from
semitransparent, slowly frozen <6 mole/l solutions,
to more opaque, cooled melts of hydrates, to
practically white pigmentlike 10 mole/l NaOH
solutions frozen first under mixing at 135 K and
later cooled to 77 K. Even semitransparent
preparations can not be investigated spectrophoto-
metrically because the extinction at 1 mm
thickness, already without trapped electrons,
exceedes 3. The reflective spectrometry is
vaguely mentioned, but no results has been
published yet.

The pulse radiolysis method using the Cherenkov
light selfabsorption brought the solution to the
problem of detection of intermediates in opaque
media. The method helped to investigate the
phenomenon of trapped electrons in a matrix of
very low water content (e g $KOH.1/4H_2O$) and to
formulate the thesis of "one water molecule-one
electron" responsible for the electronic spectrum
/3/.

Our Cherenkow Light Selfabsorption Method is
useful in measurements also at low temperatures.
It is a little more complicated than at room
temperature but a proper vessel makes the task
comparatively easy. The opaqueness of the sample
slows down the process of bleaching, if such is
needed. For that purpose we are using light with
the maximum of intensity shifted to IR. The
increase of the local temperature and higher
penetration of IR in the matrix of many internal
reflections speeds up the bleaching. Such a
procedure would not have been acceptable in the
case of glass, where local warming could produce
annealing phenomena. With the polycrystalline
material no structural changes are expected, and
only desired ones, i e the emptying of traps, is
achieved.

The second method used in the investigation of
electrons at low temperatures in polycrystalline
material consists in collection of the charge,
released later during the illumination of
previously irradiated samples /4/.

RESULTS

The unconventional method of pulse radiolysis
using the Cherenkov Light Selfabsorption may
rise doubts concerning its veracity. Therefore
we have applied it to the transparent system
which may be investigated by both spectrophoto-
metric methods, using external or internal
analyzing light. The system chosen was electrons
trapped in glassy NaOH solution, 10 mole/l.
Figure 3 shows that the maximum of absorption
measured by both methods is the same. The
Cherenkov Method gives more information i e the
spectra at the beginning of the pulse is the
same. The slight difference at the red part of
the spectrum cannot be explained until IR
measurements will be done. They are very diffi-
cult due to the low level of Cherenkov light in
the red region. Experiments on monocrystals by
conventional pulse radiolysis are also planned.

The polycrystalline systems investigated by
pulse radiolysis at low temperatures were
hydroxides of sodium, potassium and tetraalkyl-
ammonium cations. Spectra are very similar and
small shifts of maxima can hardly be attributed
to the cation, but there are blue shifts of the
spectrum with diminishing contents of water
/5, 6/.

At a very low content of water (e g $KOH.1/4H_2O$)
in the matrix only the blue shift is observed,
but the difference between room temperature and
77 K is not a marked one. The interaction of
electron with one molecule of water is decisive
and the influence of the matrix is slightly more
pronounced in comparison with the mainly aqueous
system (Fig 4).

Figure 5 shows the estimated kinetics of the e_t^-
decay, extrapolated from calculations of the
build-up curve. That curve results from the
linear formation and exponential decay of e_t^-.
The algorythm is similar to the case of activation
by the neutron beam of a nuclide which decays
rapidly.

The question is very often asked about the
e_t^- spectrum in KOH or NaOH free from water.
With the disappearance of the last traces of
water also the characteristic spectrum
disappears. One observes a very faint spectrum
(Fig 6) with the maximum at ca 400 nm which does
not disappear in microseconds at room
temperature, but is permanent like F centers in
irradiated halogenides (e g KCl).

Final conclusions are hoped to be reached after
the completion of esr investigations, which have
just started, of the X-ray and neutronographic
ones due to begin, and analysis of products,
expecially important in the case of $R_4NOH \cdot nH_2O$.

Another question asked is that of the final
stable products. Already the pulse radiolysis
work shows that the production of stable new
compounds is rather low. Subsequent pulses
applied to the same sample after the time needed
for recording of the kinetic curve give the same
result. That indicates either the formation of
products of radiolysis which do not take part in
the stabilization of electrons or the yield of
radiolysis calculated as permanent radiation
damage is negligible. We were looking for the
presence of hydrogen by gas chromatography and
for hydrogen peroxide by polarography, after the
dose of 10 Mrads applied carefully without an

increase of temperature higher than is the case
during pulse radiolysis work. No products of
radiolysis could be found.

As experiments performed at extreme temperatures
(room temperature and liquid nitrogen) give
different results as concerns the stability of
the trapped electron, we have made an attempt to
look into phenomena at intermediate temperatures.
Such an approach was necessary also because of
the necessity to compare results with only two
papers dealing with radiation chemistry of
sodium hydroxide hydrates, low water, crystalline,
but at liquid nitrogen temperature. Our experiment
was difficult, because of the slow adjustment of
a precise intermediate temperature. One can make
a vague statement that around $-50^{\circ}C$ a rather
stable trapping occurs, but if that temperature
has the character of a threshold remains an open
question. However, already at that temperature a
distinct difference between the first and
subsequent pulses is observed. The first pulse
produces the familiar kinetic curve of build-up
of the trapped electron spectrum. Next pulses
applied to the same sample produce only constant
Cherenkov emission without the usual selfabsorption.
That indicates a saturation of existing traps.

Irradiation of concrete

After 10 years of operation of our linear
electron accelerator, we have realized, that
below the processing window, the concrete
received the dose of ca 1 Trad (10GGy) of
electrons (10-13 MeV). The place was always
covered with a thin sheet of aluminium, thus
being not spoiled by dirt and graphite etc from
the conveyor. The temperature at that place
reached sometimes up to $100^{\circ}C$ (empty
conveyor).

Except of a light reddish colour, the concrete
did not show a dramatically diminished resistance,
indicating dissipation of ionizing energy into
heat with negligible chemical effect.

To examine the phenomenon more closely, samples
of Portland cement SP 550 of Polish production
(Cement Works Gorażdże - Danish Licence)
were hydrated for 30 days at room temperature,
and later, after drying, were irradiated under
controlled conditions with the same machine, but
this time using the polyenergetic straight beam
of electrons. The sample was placed 17 cm from
the window. The diameter of the beam (half-gaussian)
was 18 mm. At the centre of the sample, a
thermoelement was placed (Sodern Thermocoax,
Chromel Alumel 2AB Ac o5, Gaine Inox diam 0.5
mm) of the sort used in reactor technique,
extremely resistant to ionizing radiation. The
sample was intensively cooled by air. The flux
of energy was adjusted at such a level that the
temperature did not reach a zone higher than
$108-116^{\circ}$C. These were the limits in which the
equilibrium oscillated, between the supplied
energy and the heat taken by air. Thus the
maximum dose rate was reached, ca 2000 Mrad/h.
The sample looked unchanged, except small cracks
(the cement was hydrated without sand). It did
not change colour like our old sample. The last
one probably contained much iron.

More experiments are planned on irradiated
samples, expecially thermogravimetric and
thermoanalytical ones.

DISCUSSION

Several aspects of the investigated system have
to be considered if a reasonable understanding
of the phenomena is the aim of our research. The
first thing is a clear differentiation between
the liquid, solid-glassy and the solid-poly-
crystalline states from the point of view of
radiation chemistry. Early phenomena are slightly
influenced by the state of the system, but if we
move deeper in the time scale, the influence of
the structure, and later even of the texture of
the system is more and more pronounced.

Figure 7 shows the space-time development of
small isolated energy deposit (spur) in a
diluted aqueous system, slightly modified, or
rather edited from the recent paper by Magee and
Chatterjee (7). Although some points in that
scheme are still controversial, the picture is
generally accepted. The next Figure 8 shows in
the same ordinates phenomena in a chemically
similar but rigid system. The impossibility for
intermediates to diffuse as quickly as in the
solution is obvious. Less obvious is the difference
in the dielectric relaxation. Here we are
touching an old question, raised already in the
fifties, before the discovery of the hydrated
electron: How far may an electron travel from
the parent positive ion. The critical radius,
called the Onsagers radius, depends on the
dielectric constant of the medium. The classical
textbook calculations says, that in polar
liquids like water ($\epsilon \sim 80$) the critical distance
is only 0.7 nm at 300 K, whereas in nonpolar
liquids (e g liquid hydrocarbons) the distance
is ca 28 nm. Looking into rigid systems containing
water, are we allowed to draw the same conclusions?

If so, the travelling distance of the electron
here is always rather long because the
dielectric cosntant (the high frequency one, the
same as accepted for liquid water) is low both
in solid hydrates and in ice. The dielectric
constants for the hydrates we are mainly
investigating are not available, but similar
ones have low values: $Na_2CO_3.10H_2O$ - 5.3
(anhydrous has even 8.4!), $BaCl_2.2H_2O$ has 9.4
(anhydrous has even 11.4), all values for
frequency $6x10^7$ Hz, etc, etc (according to /8/).
The same source does not quote values for ice,
but in monographs on water /9,10,11/ we can find
low values. In one of the handbooks /12/ we
found ε = 69.4 at $-10^{O}C$ falling sharply down to
3.8 at $-50^{O}C$. In spite of the enormous work done
on frozen glassy systems, we were not able to
find date on dielectric constants of alkaline
glasses.

Nevertheless, a low dielectric constant in
frozen aqueous systems and of hydrates at all
temperatures, seems to be a general fact and may
be used in the discussion.

What really matters is not the dielectric
constant itself, but a proper estimate of the
kinetics of relaxation of water molecules.
Looking for that, Kevan /13/ has calculated,
that if the temperature is decreased from 260 K
to 77 K the duration of the dielectric relaxation
in water ice, is increased from 6.4×10^{-5} to
10^{22}s. It means that in the range of 130-110 K
water dipoles are already practically motionless
and fixed. The obvious next conclusion is that
the electron is trapped in existing defects of
the lattice. The presence of ready electron
traps is suggested also by Taub and Eiben /14/.

The very large differences in density between
systems in the glassy an polycrystalline states
drew our attention to interprete them in terms
of internal energy. Sodium (or potassium)
hydroxide solutions of concentrations higher
than 6 M mentioned in "Results" are well suited
for this sort of consideration, because their
chemical summary composition is the same, but
structural differences are reflected in a
different density of packing. The glassy variety
is meta-stable and is relaxing to the polycrystalline
form of more loose structure and higher volume.
Lower density manifests itself sometimes in a
very dramatic mode, causing a violent destruction
of the vessel with frozen glass, if the heating
is slow, and the system has time to rearrange
into crystals before melting.

The investigation of the glassy vs. the polycry-
stalline system from the point of view of
thermodynamics has just started. We are trying
to make as much use from the rather precisely
measured difference in density. Other measurements
would be necessary to have a full picture: the
heat of change from glassy into crystalline
form, the temperature coefficient of density
around 77 K, $\alpha_p = \left(\dfrac{\partial \ln V}{\partial T} \right)_p$ as well as the influence
of pressure on the density at constant temperature.
The first characteristics seems simple enough to
realize from the Hess cycle: what is needed is
only the dissolution of glassy and in the next
experiment the crystalline sample in the water
calorimeter, both samples of the same weight and
frozen to the same temperature of 77 K. We did
not succeed yet in making that experiment with a
satisfactory precision. The same applies to the
measurement of the temperature coefficient of
density. There is little choice of liquefied
gases with boiling temperature close to that of

liquid nitrogen. The third value (that of the
dependence of the density on pressure, practically
impossible to measure, may be neglected, because
it is of little influence on the result.

We may safely accept, that the transformation
from glassy state into crystalline ($\alpha \rightarrow \beta$) is not
connected with any chemical changes, with any
changes of the hydration of ions involved
(sodium and hydroxide) and of their interaction
with the medium. If so, we may consider a change
from a densely packed system of randomly arranged
molecules of hydration into a more loosely
packed system of similar molecules of hydration,
this time rearranged and regularly filling the
space. Both systems may be characterized by
distinctly different potential energy curves.
Now the difference of internal energy may be
described as

$$\beta_\Delta^\alpha H = \int_{\rho\alpha}^{\rho\beta} \left(V - T \left(\frac{\partial V}{\partial T} \right)_p \right) \left(\frac{\partial p}{\partial \rho} \right)_T d\rho$$

$$\beta_\Delta^\alpha H = \int \left(T \left(\frac{\partial \ln V}{\partial T} \right)_p - 1 \right) \frac{1 \text{ kg}}{\rho} \left(\frac{\partial p}{\partial \ln V} \right)_T \frac{d\rho}{\rho}$$

After several simplifications substituting the
lack of experimental data one obtains for $\beta_\Delta^\alpha H$
value -560 kJ/kg, or -135 kcal/kg. At this stage
of research it would not be reasonable to make
further conclusions. However, operating with
order of magnitudes one can state that the
indicated energy recalculated on 1 mole of water
is equivalent to the energy of 1 mole of hydrogen
bonding. Even another comparison is possible:
The enthalpy of transformation $\alpha \rightarrow \beta$ recalculated
into 1 mole of water equals approximately one
third of the enthalpy of evaporation at $100^\circ C$.

What consequences may be expected from the
differences in internal energy of glassy and
crystalline systems? It may be certainly noted
that the radiation chemistry of glassy systems
may be closer to liquid water than to ice.

Many interesting questions appear: May the local
heating by the deposition of radiation energy
cause local crystallization and release of new
amounts of energy? Has the extra amount of
energy in the shape of compressed matter something
to do with the phenomenon of tunneling?

It is time now to arrive at some proposals of
models on what is going on in crystalline, low
water content systems, irradiated with almost
any dose rate and total dose at room temperature.
Proposing a mechanism we are in a much more
difficult position in comparison to our collegues
working with systems more rich in water. Without
any doubt the chief obstacle in the application
of one of the models developed for the last
mentioned systems is the most meager presence of
water, not sufficient to secure the minimum of 4
water molecules around the electron to produce
something like e_{aq}^-. We are able to eliminate
some concepts from further consideration. For
instance we may reject the concept of cation-
electron pair, because of our most convincing
experiment: introduction of tetraalkylammonium
cation for sodium or potassium the picture of
phenomena is the same - the electron does not
"see" the cation at all. It would have been most
difficult to imagine identity of the Na^+e^- pair
and the $NR_4^+e^-$ pair - of completely different
size and mode of hydration. The idea of electron-
cation pairs has been rejected also by Kevan in
1981 /15/: "Even though there is a very large

concentration of sodium ions (10 M), the electron
spin-echo results show that the solvated electron
has only water molecules in its first solvation
shell". In spite of that the idea of ion pairs
is very persistent, expecially in Russian
papers.

CONCLUSIONS

As it is a normal case in radiation chemistry
and chemistry in general, the facts are clear
reproduceable observed with reasonable precision
and satisfaction, but their explanation is very
obscure. I have spent quite a time looking for
inspiration in cold glass radiation chemistry,
which in two cases (Report by Wieczorek, /16/
and a paper by Puntezhis, Ershov and Pikaev
/17/) was trying to investigate well defined
sodium hydroxide hydrates, unfortunately not
going below 2 molecules of water per 1 of NaOH.

However, even the aqueous glass radiation
chemistry is in confusion, concerning the origin
of traps, their depth, kinetics of trapping and
of the release, reactions of holes, bleaching
etc. Considerations of phenomena described by
the dielectric constant at different frequencies,
which were giving rather good results, being a
right guide in the liquid state of different
polarity, here, i e in the solid state, seem to
be meaningsless. Kieffer /18/ writes in his
recent (1981) NATO lecture: "The case of electron
solvation in ice is particularly interesting in
that it occurs on a time-scale which is completely
incompatible with the dielectric relaxation time
of the medium". I did not even touch the question
of tunneling, popular in low temperature glasses

but not clear as concerns the mechanism. In
crystalline hydrates research no tunneling was
observed yet.

Let us make some speculations on the radiation
chemistry of crystalline hydrates irradiated at
room temperature. A look at Magees scheme
(Fig 7) will help to find out some real differ-
ences. The first energy deposit is probably not
affected by the particular state of the condensed
phase, the high energy radiation does not see
the movement of molecules. Consequently, the
spurs are of the same structure as in any
condensed phase. As usual, the degradation of
energy results in closer and closer ionization
sites and in the inevitable occurence of several
ionizations very close to themselves in a small
volume located in the unchanged bulk of the
medium. Therefore, also in the solid state, the
classical diagram by Mozumder and Magee /19/ is
valid here describing the percentage constribu-
tion of spurs, short tracks and blobs, according
to the energy of primary electrons. Quantum
mechanical treatment of low energy electrons is
also valid here. The length of the De Broglie
wave (λ = h/mv) is for a 100 eV electron 0.1 nm,
for 1 eV 1.2 nm, for 0.1 eV ca 4 nm and for
thermal energies a 7 nm. Unfortunately there is
nothing known yet about infrared electrons in
crystalline hydrates (the experiment is still in
preparation due to many difficulties).

If there is no doubt about the same spur distri-
bution in liquid and glassy solid states, so
there may be some questions whether the cry-
stalline state may influence the early deposition
of energy. There are some indications that the
reactive intermediates may migrate in the

crystal to its surface. Another question is the
role of defects more or less specific to hydrates.
Practically nothing is known, and there may be
only our guess about that. Another justified
guess is the presence of phonons, without any
doubt very active at room temperature in the
annealing of radiation induced changes.

At present I am trying to formulate the following
picture of events in hydrates of low water
content: Electrons released in the ionization
process and almost thermalized are trapped by
one molecule of water. It is practically only
Hamill who postulated the formation of H_2O^-
/20/. My argument for that species is purely a
geometrical one: I cannot imagine the formation
of the usual e_{aq}^- with four or six water molecules
in $KOH.1/4H_2O$. Indeed, moving to higher hydrates
the spectrum comes more and more close to
classical e_{aq}^-. Nevertheless the majority of
radiation chemists rejects the H_2O^- idea. If
really that idea is theoretically indigestible,
I can propose as an alternative the trapping of
the electron in the OH^- vacancy close to the
water molecule. That concept may be supported by
the higher oscillator strength of the spectrum
in hydrated hydroxides or hydrates in which OH^-
ions may be present and by the effect of saturation
of traps occuring already at ca $-50^{\circ}C$.

The positive hole has to be identified as H_2O^+,
but its fate is as mysterious as the electron
trap. There are all indications that H_2O^+ does
not react with the neighbouring water molecule,
or the participation of that reaction, called by
Magee in the case of liquid aqueous solutions as
the fastest reaction in radiation chemistry, is

negligible. Otherwise the total degree of radio-
lysis would have been larger. We have to accept,
that H_2O^+ is waiting for an electron, released
after a short sojourn from the trap. The e_m^-
is of lower than initially energy so that the
excited water formed in the reaction with
H_2O^+ does not produce an overexcited water
molecule, able to dissociate into radicals;
instead, it becomes thermalized without any
chemical effect.

In low water hydrates, H_2O constitutes only as a
part of the system and the rest, usually the
main constitutents, is of a quite different
composition. Some sort of radiolysis goes on
parallel to radiolysis in the aqueous part of
the system and also with no chemical result. The
intermediates in the nonaqueous part do not
manifest themselves in pulse radiolysis because
of lack of optical absorption or a low ε. The
situation may change in the case of organic
cations or a neutral compound in the case of
organic hydrates. Literature data show /21/ that
penicillin trihydrate undergoes very low decomposi-
tion during radiation sterilization. The phenomena
are similar to that described above, but one can
assume vaguely that a part of the energy is
taken by the aqueous part of the system thus
acting as some sort of energy sink.

The continuing research is hoped to bring new
facts which may confirm or totally change the
presented picture.

REFERENCES

/1/   ZAGÓRSKI Z P, GRODKOWSKI J
        Nukleonika 24, 965 (1979).

/2/   COHEN-ADAD R, TRANQUARD A, PÉRONNE R,
        NEGRI P AND ROLLET A P
        C. Rendus 1960, 2035.

/3/   ZAGÓRSKI Z P
        Nukleonika 22, 725 (1977).

/4/   GRODKOWSKI J, ZAGÓRSKI Z P
        Nukleonika 24, 867 (1979).

/5/   ZAGÓRSKI Z P, BOBROWSKI K, GRODKOWSKI J
        Chem. Phys. Letters 59, 533 (1978).

/6/   ZAGÓRSKI Z P, GRODKOWSKI J, BOBROWSKI K
        Radiat. Phys. Chem. 15, 343 (1980).

/7/   MAGEE J L AND CHATTERJEE A
        LBL-9078, Berkeley 1979.

/8/   Handbook of Chemistry and Physics,
        56th Ed., CRC Press, Cleveland, Ohio
        1976.

/9/   EISENBERG D AND KAUZMANN W
        "The Structure and Properties of
        Water", Oxford at the Clarendon Press,
        1969.

/10/   HORNE R A (editor)
        "Water and Aqueous Solutions", John
        Wiley, New York, 1972.

/11/   FRANKS F (editor)
        "Water a Comprehensive Treatise",
        Plenum Press, New York, London 1973-1979,
        6 Volumes.

/12/   "Spravochnik Khimika", 7 Volumes, Izd.
        "Khimiya", Leningrade 1968.

/13/   KEVAN L
        Radiation Chemistry of Aqueous Systems,
        G. Stein (editor), Interscience Publishers,
        London 1968, 21 and in Action Chimiques
        et Biologiques des Radiations, M.
        Haissinsky (editor), Masson, Paris
        1969, Vol 13, 57.

/14/   TAUB I A, EIBEN K
        J. Chem. Phys. 49, 2499 (1968).

/15/   KEVAN L
         Accounts of Chemical Research $\underline{14}$, 138
         (1981).

/16/   WIECZOREK H
         KFK 1717, Karlsruhe 1972.

/17/   PUNTEZHIS S A, ERSHOV B G, PIKAEV A K
         Khim. Vys. Energ. $\underline{6}$, 153 (1972).

/18/   KIEFFER F
         "The study of fast processes and
         transient species by electron pulse
         radiolysis" (Proc NATO Adv. Study
         Institute, Capri 1981), D. Reidel,
         Dordrecht 1982, p. 363-397.

/19/   MOZUMDER A AND MAGEE J L
         Radiat. Res. $\underline{28}$, 203 (1966).

/20/   RAŽEM D, HAMILL W H
         J. Phys. Chem. $\underline{81}$, 1625 (1977).

/21/   JACOBS G P
         Int. J. Appl. Radiat. Isotopes $\underline{30}$, 417
         (1979).

Figure 1

CATION$^+$ OH$^-$ - H$_2$O MATRIX

LIQUID

0 → 20M (Na, KOH)
→ 1,7 R$_4$NOH
HYDRATES e$^-$aq
1 μs life
λ 720 - 65?

GLASS
pure or with
scavenger

6-18M Na, KOH
STABILIZED e$^-$t

(r.) λ ≈ 600

P.R.   P.R. ?

There is no R$_4$NOH glass

rapid cooling

rapid warming

slow warming

CRYSTALS
poly -
diff. texture-
large -
mono -
doped -

0,001M (mixed l.t.) up to NaOH·1H$_2$O, KOH·¼ H$_2$O   all
also (C$_4$H$_9$)$_4$NOH·nH$_2$O clathrate, (CH$_3$)$_4$NOH·5H$_2$O   temp.

O.D.   STABILIZED e$^-$t

λ = 515 (3.5!)
= 550 (7.4?)

P.R. ?   7.R. ?

P.R. CHER.
ROOM TEMP.
μs - ms life
λ ≈ 550 - 700
(¼H$_2$O - cla.)

.4   77K   ROOM

TEMPERATURE ⟶

Figure 1. Types of motions in the cation $^+$OH=
H$_2$O system and behaviour of trapped electron.
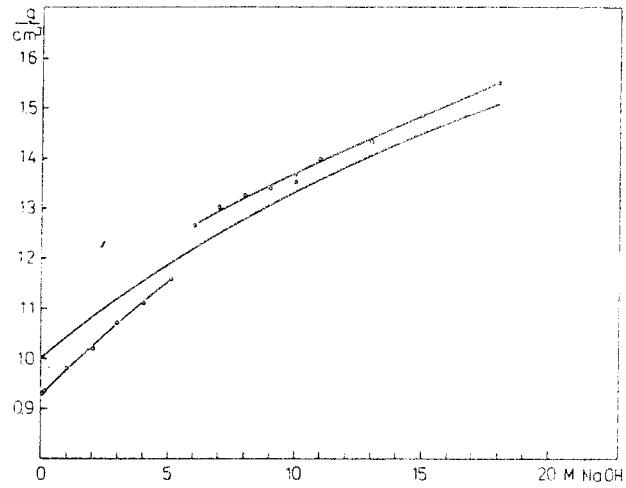
Fig. 2a Density of frozen NaOH solutions at 77 K vs the concentration (upper and lower curves). The continuous line without experimental points denotes the density of liquid solution at the room temperature (literature values).
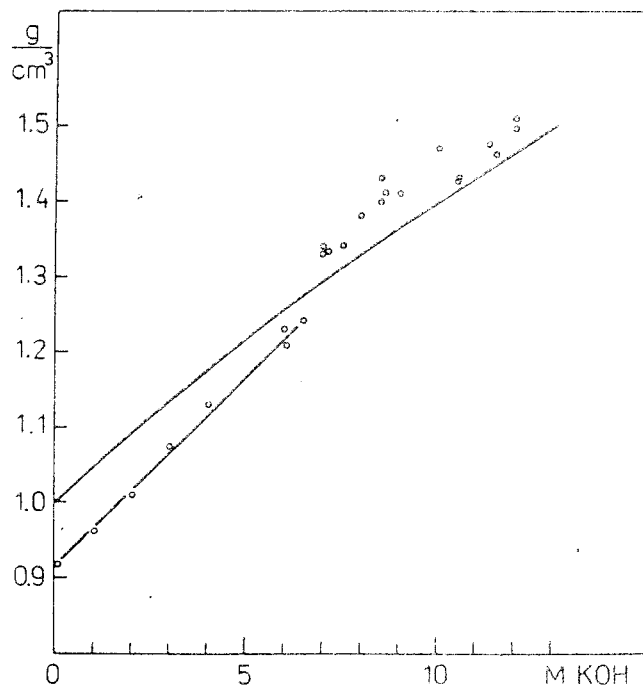
Fig. 2b Density of frozen KOH solutions vs the concentration. The continuous line without experimental points denotes the density of liquid solution at the room temperature.
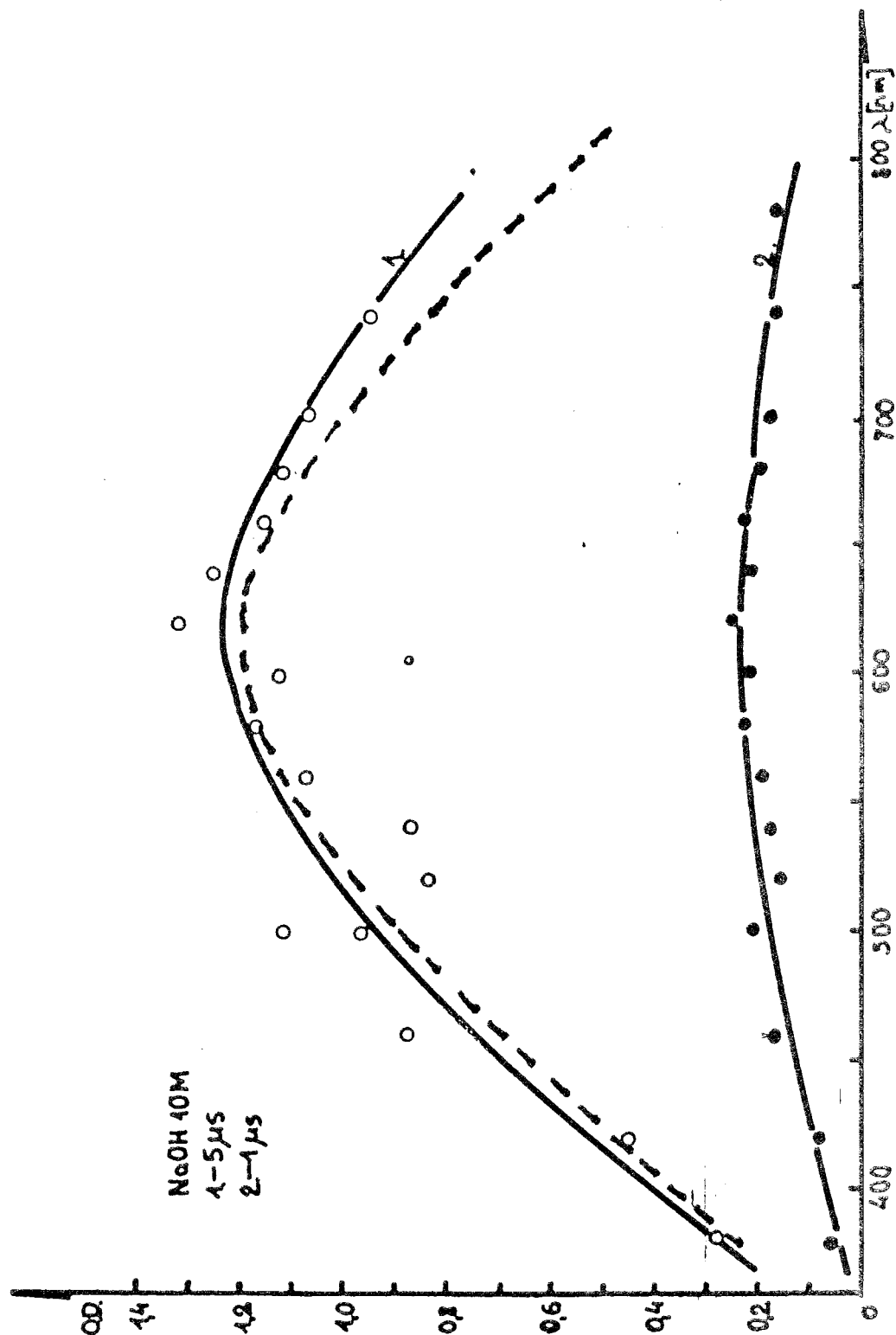
Figure 3

Figure 3. Comparison of e_t^- (glassy) spectra
obtained by Cherenkov Method (continous lines)
and the conventional pulse radiolysis method
(dotted line).

Figure 4
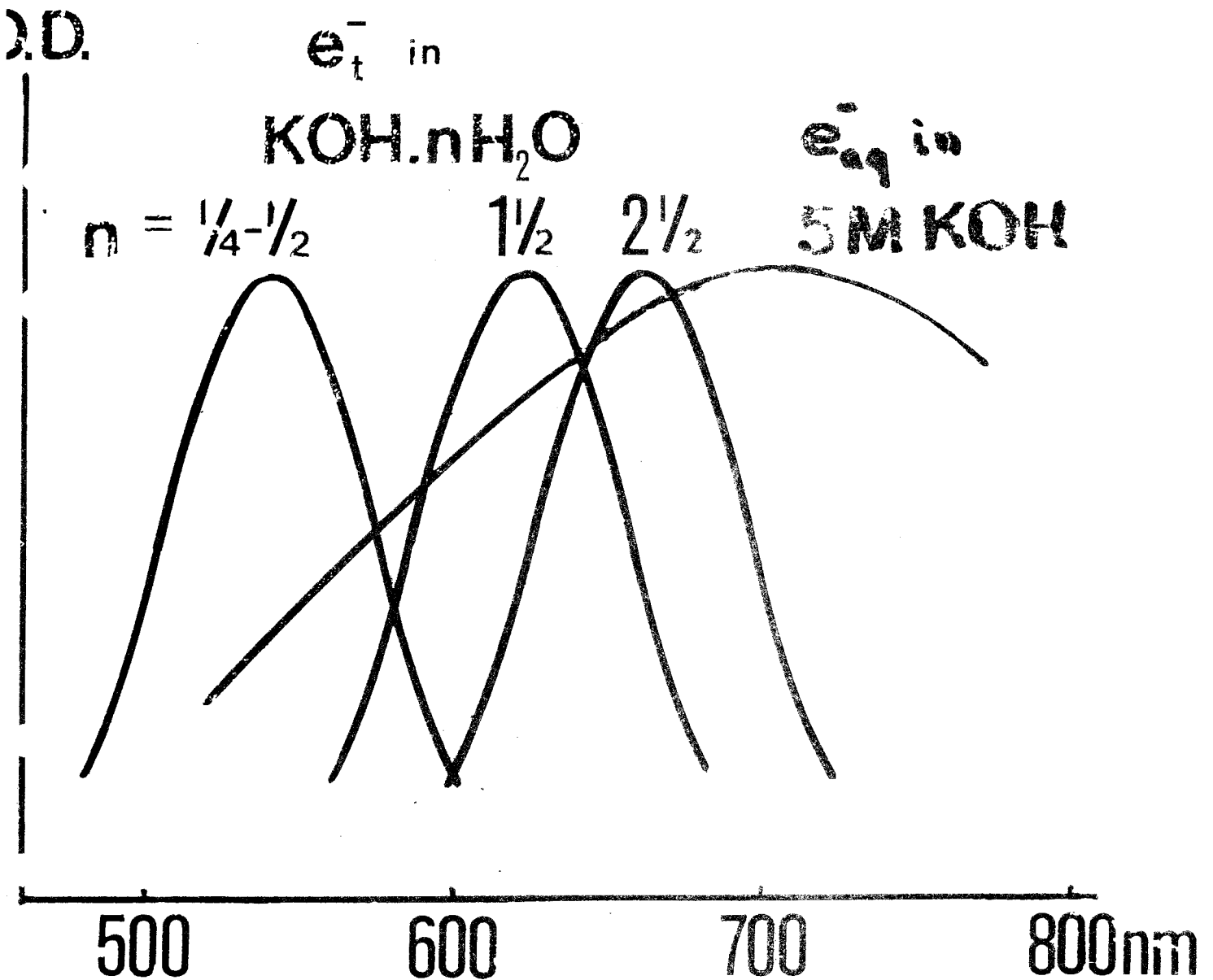
Figure 4. Comparison of normalized spectra of
electron trapped in KOH.nH$_2$O crystal hydrates
with the spectrum of e$_{aq}^-$ in 5MKOH (liquid. All
spectra at ambient temperature.

Figure 5

Figure 5. Rough estimate of e_t^- decay in
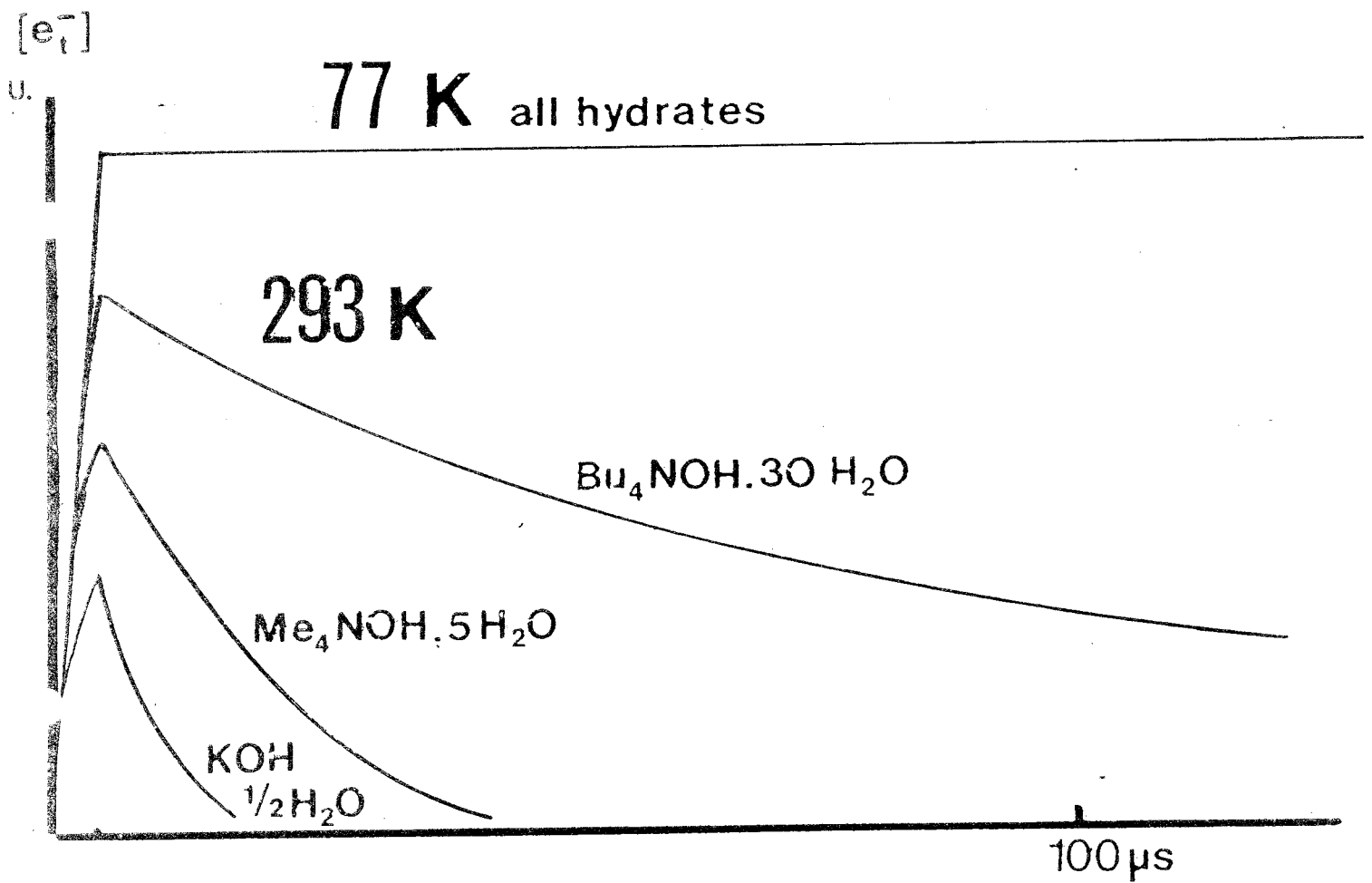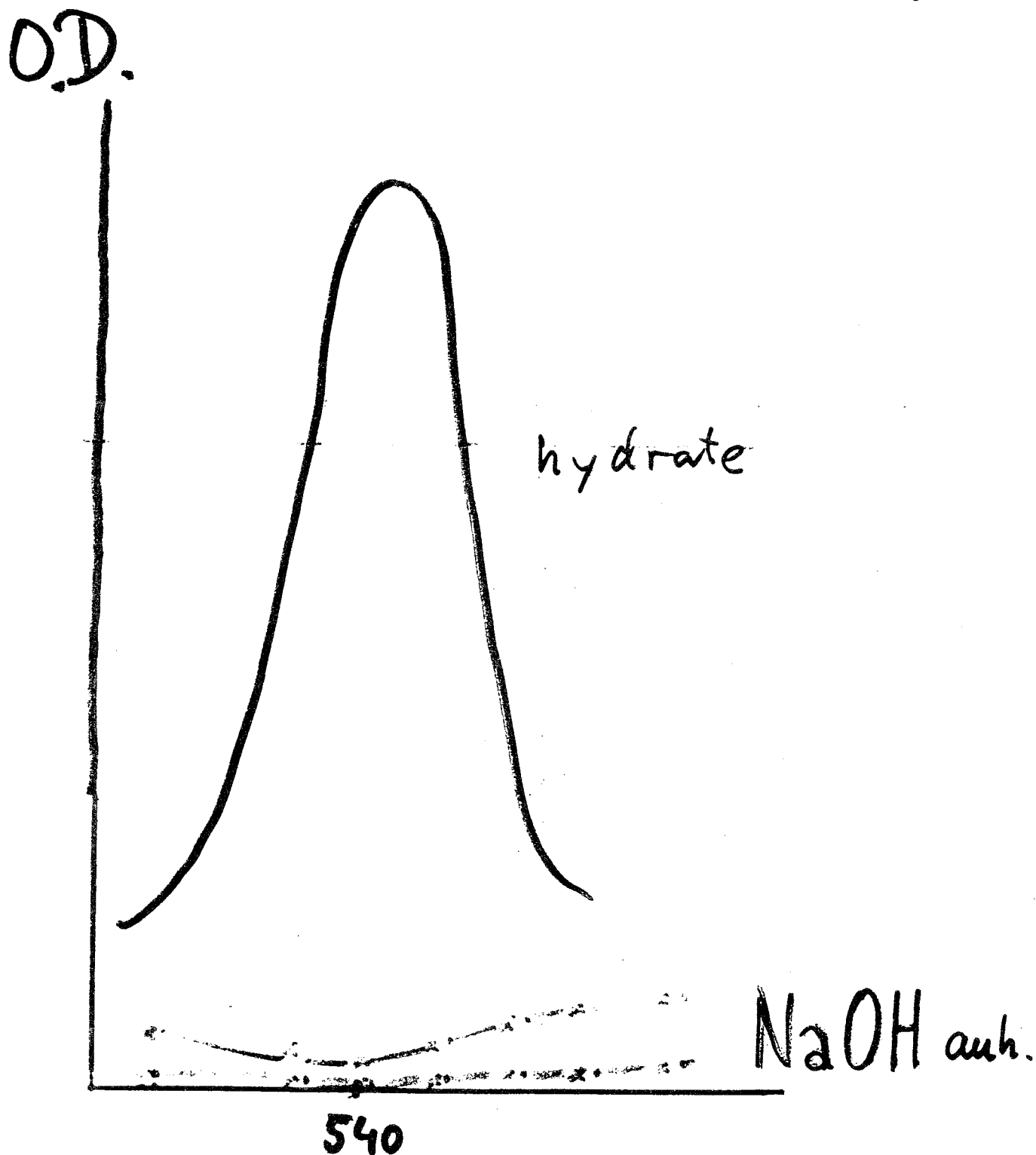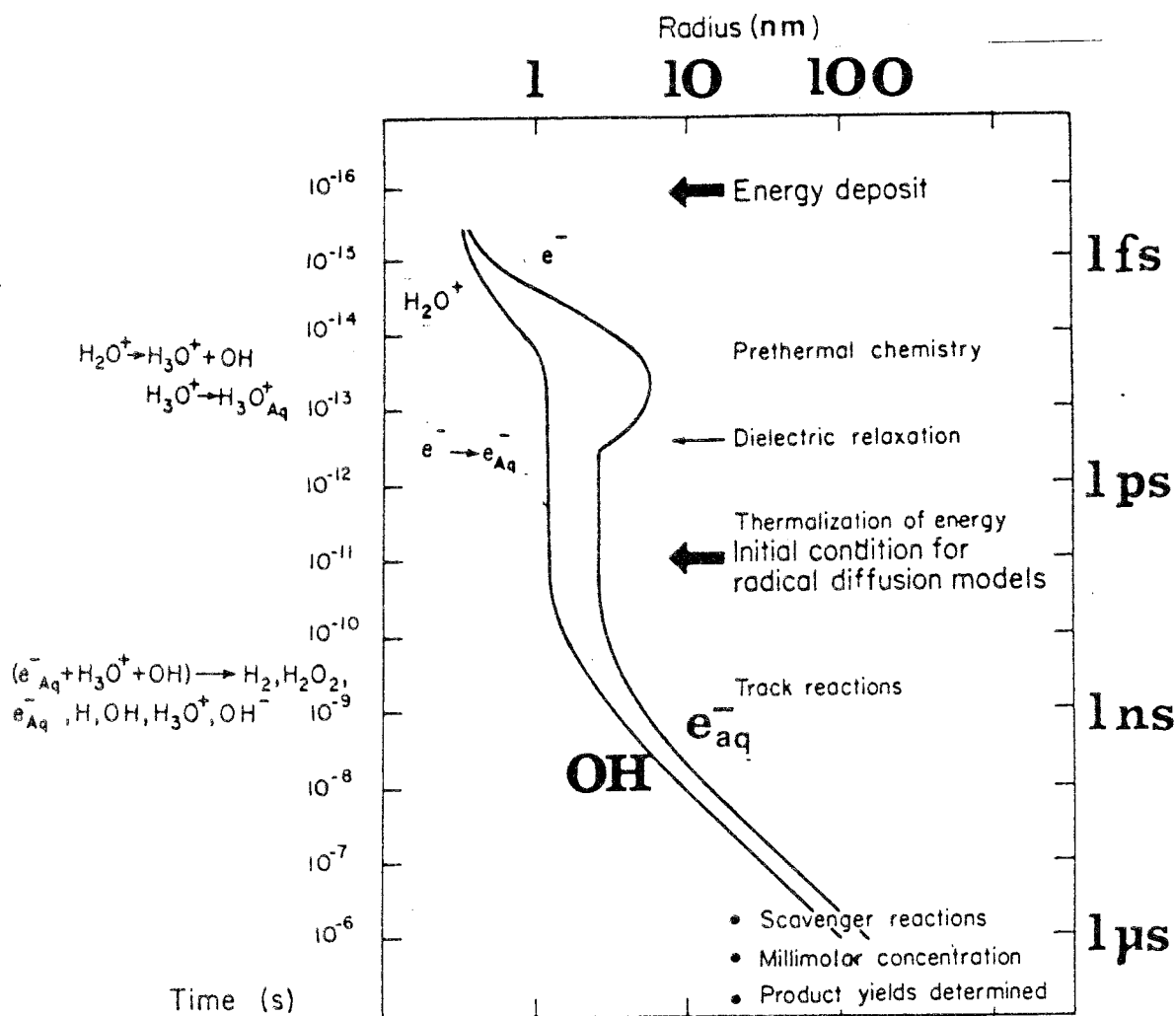different matrices.

Figure 6

O.D.

hydrate

NaOH anh.

540

Figure 6. Spectrum of e_t^- in NaOH-1H$_2$O (decaying
fast) and of e_t^- as F-center (permanent) in
anhydrous NaOH (lower dotted curves). Ambient
temperatures.

Figure 7

Space-time development of small isolated energy deposit (spur) in a dilute aqueous system

Figure 7. Spare time development of small isolated energy deposit (spur) in a dilute aqueous system.
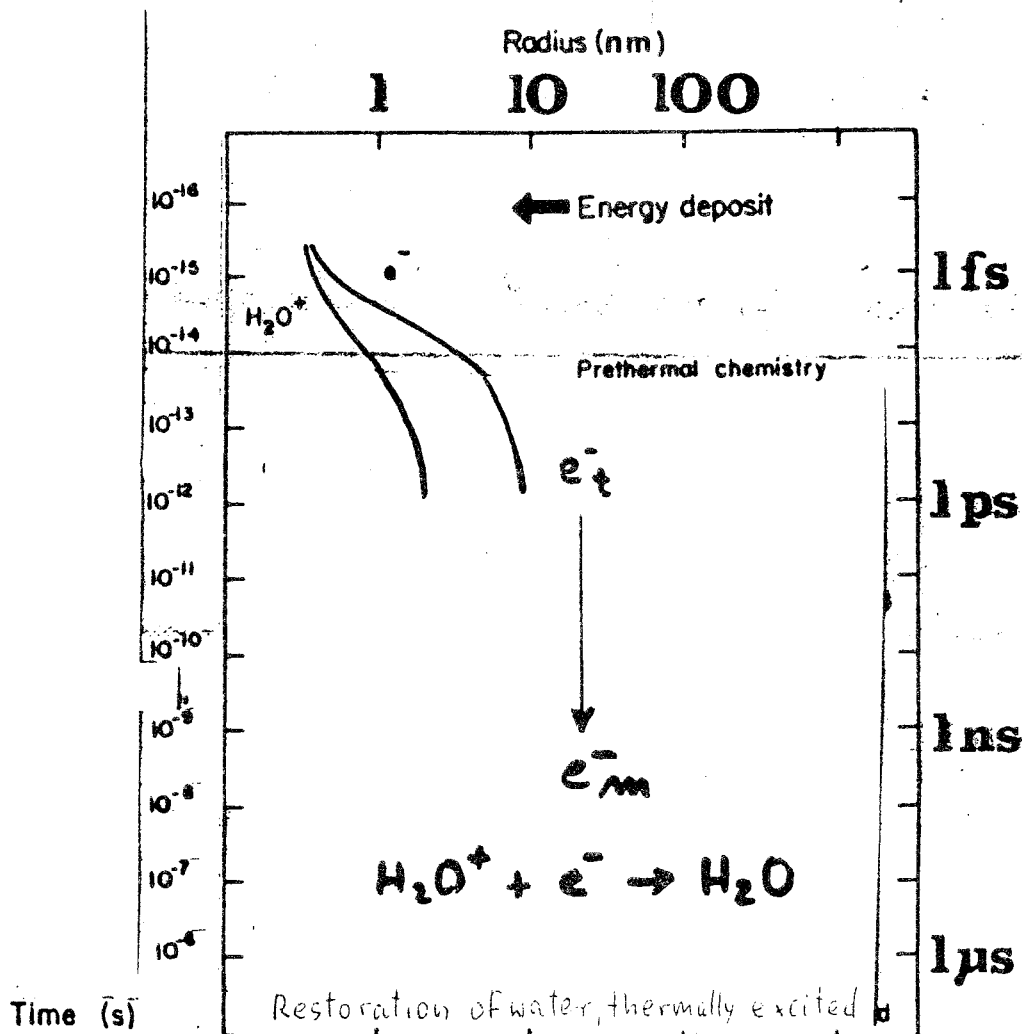
Figure 8

Figure 8. Proposed restoration of water at an early stage in solid crystalline phase.

List of KBS's Technical Reports

1977-78
TR 121
KBS Technical Reports 1 – 120.
Summaries. Stockholm, May 1979.

1979
TR 79–28
The KBS Annual Report 1979.
KBS Technical Reports 79-01 – 79-27.
Summaries. Stockholm, March 1980.

1980
TR 80–26
The KBS Annual Report 1980.
KBS Technical Reports 80-01 – 80-25.
Summaries. Stockholm, March 1981.

1981
TR 81–17
The KBS Annual Report 1981.
KBS Technical Reports 81-01 – 81-16.
Summaries. Stockholm, April 1982.

1982
TR 82–28
The KBS Annual Report 1982.
KBS Technical Reports 82-01 – 82-27.

1983
TR 83–77
The KBS Annual Report 1983.
KBS Technical Reports 83-01–83-76
Summaries. Stockholm, June 1984.

1984
TR 84–01
Radionuclide transport in a single fissure
A laboratory study of Am, Np and Tc
Trygve E Eriksen
Royal Institute of Technology
Stockholm, Sweden 1984-01-20

TR 84-02
Radiolysis of concrete
Hilbert Christensen
Studsvik Energiteknik AB,
Nyköping, Sweden
Erling Bjergbakke
Risö National Laboratory,
Roskilde, Denmark 1984-03-16