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Formation of nitric and organic acids by the irradiation of ground water in a spent fuel repository

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Studsvik Energiteknik AB
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STUDSVIK/NW–84/768

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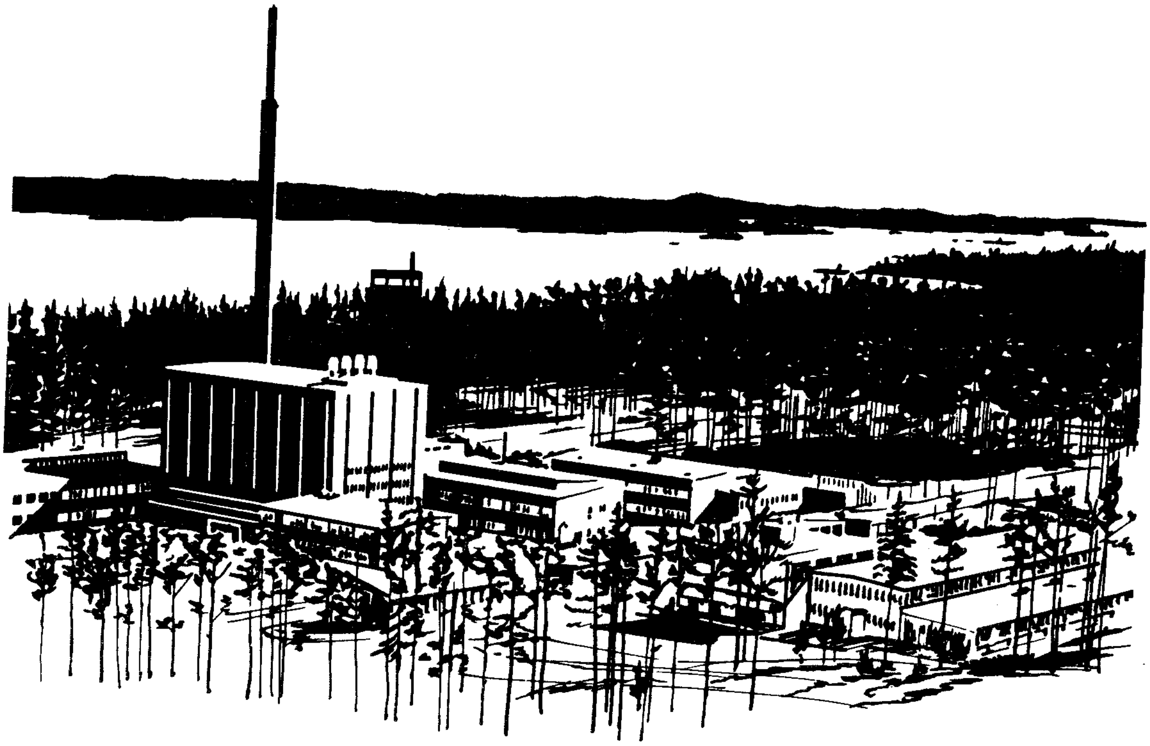

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ABSTRACT

The formation of nitric acid has been reported in the literature, e g in connection with studies of glass leaching during irradiation. These experiments were carried out in order to evaluate the behaviour of glass as a matrix for highly radioactive waste. The presence of a nitrogen containing gas phase has been found to be important for the yield of the reaction.

The formation of organic acids by radiolysis of carbonate solutions has been reported. The literature on the formation of organic and nitric acids have been surveyed and discussed. A conservative estimate of the formation of nitric and organic acids has been made based on dissolved nitrogen and carbonate in groundwater in a spent fuel repository.

Outside a 10 cm thick copper canister containing spent fuel (the Swedish KBS-3 concept) the conservatively estimated total production of nitric, formic and oxalic acids after 1 million years is 0.08 mol HNO_3, 0.06 mol HCOOH and 0.04 mol $(COOH)_2$

For a thinner version of this canister with a wall thickness of only 1 cm , the conservatively estimated total production after 1 million years is 5 mol HNO_3, 4 mol HCOOH and 3 mol $(COOH)_2$.

Approved by

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1 INTRODUCTION

It is well-known that nitric and nitrous acids are formed when water is irradiated in the presence of air (1-3). Severe corrosion of high pressure loop instrumentation due to radiolytically produced nitric acid has been reported (4). Nitric acid has also been formed as a product when glass is leached under irradiation (5-14).

Recently Barkatt et al (13, 14) have shown that oxalic and other acids may be formed when CO_2-containing water is irradiated.

In the present report the production of nitric, oxalic and other acids in ground water irradiated from high level waste (HLW) is evaluated.

2 FORMATION OF NITROUS AND NITRIC ACIDS

A number of studies on the fixation of nitrogen by irradiation of nitrogen mixtures have been carried out (2). According to the literature, the fixation takes place predominantly, if not exclusively, in the gas phase. G-values from 10^{-4}, or less, and up to above 1 have been reported, calculations of G-values having been based on the energy absorbed in the water phase. According to Linacre and Marsh (4) the concentration of nitrate in solutions is proportional to the ratio of gas to liquid volumes, see Figure 1. In Linacre and Marsh's experiments the total irradiated volume was constant. All their results could be reproduced on one line, see Figure 2, corresponding to the equation

$$[NO_3^-] = 1.2 \times 10^{-15} \times \frac{G}{L} \times D \qquad \text{(Eq 1)}$$

where

$[\ ]$ = concentration in μM

$\frac{G}{L}$ = the ratio of gas to liquid volume

D = is the thermal neutron dose in $n \cdot cm^{-2}$

The equation is applicable for an air-water system. For a nitrogen-water system the proportional constant is 1.3×10^{-15} $\mu M \cdot cm^2 \cdot n^{-1}$. At high ratios of gas to liquid volumes NH_3 is also formed, see Figure 3.

Linacre and Marsh conclude that the fixation of nitrogen is initiated in the gas phase.

As can be seen from Table 1, the amount of nitrate produced (as HNO_3) is proportional to the gas phase volume, i.e. to the dose in the gas phase.

Furthermore the line in Figure 1 passes through the origo. These two facts demonstrate that the formation of HNO_3 only takes place in the gas phase, and that the production takes place at a rate which is proportional to the energy absorbed in the gas phase.

According to Table 3V in ref 3, the energy absorbed by N_2 in 1 ml of gas (air) at 0.1MPa is 44 eV per $n \cdot cm^{-2}$, i.e. equation 1 can be rewritten

$$[NO_3^-] = 2.7 \times 10^{-17} \times \frac{G}{L} \times D \qquad \text{(Eq 2)}$$

where D is the dose absorbed by N_2 in eV/ml gas (air).

In a pure nitrogen-water system the corresponding equation would be

$$[NO_3] = \frac{1.3 \times 10^{-15} \times 78}{44 \times 100} \times \frac{G}{L} \times D$$

$$[NO_3^-] = 2.3 \times 10^{-17} \times \frac{G}{L} \times D \qquad \text{(Eq 3)}$$

where D is the dose absorbed by N_2 in eV/ml gas (N_2) (In pure nitrogen 1 n cm^{-2} corresponds to $44 \times \frac{100}{78}$ eV, air contains ∿78 % N_2)

The formation of nitric acid has also been studied in connection with studies of the effect of irradiation during the leaching of glass (5-14). McVay et al (5-7) have found that leaching glass samples in a γ-radiation field under aerated conditions increases the leach rate, mainly due to the production of nitric acid. The solution pH was 3.3 after 5 days irradiation at 50°C and a dose rate of 2.4 Mrad/h. Leaching in the absence of air (no formation of nitric acid) also increased the leach rate of certain elements.

Burns et al have also studied the effect of radiolysis on leaching (8-10). They have further developed the equation of Linacre and Marsh for the production of nitric acid into the following equation:

$$N = 2\ C_o\ R\ [1 - \exp\ (1.45 \times \times 10^{-5}\ GDt)] \qquad \text{(Eq 4)}$$

where

N = concentration of nitric acid in water, $\mathrm{mol \cdot dm^{-3}}$

C_o = concentration of N_2 in air, $\mathrm{mol \cdot dm^{-3}}$

R = ratio of the volume of air to the volume of liquid

G = G-value for the formation of nitric acid in air (=1.9)

D = dose rate in the gas phase, $\mathrm{Mrad \cdot h^{-1}}$

t = time, h.

They were able to correlate their experiments with Eq 4.

Burns et al claimed that the formation of nitric acid was negligible in the absence of a gas phase.

Barkatt's production of nitric acid does not correspond to equation 4.

$$N = 2 \cdot \frac{1 \times 273 \times 0.78}{22.4 \times 293} \cdot 0.2\ (1-e^{-1.45 \times 10^{-5}} \times$$

$$\times 1.9 \times 8.6 \times 10^{-2} \times 24 \times 3) = 2.2 \times 10^{-6}\ \mathrm{M}$$

(3 days production at a dose rate of 8.6×10^{-2} Mrad/h and a gas to liquid volume ratio of 0.2; C_o at 273 K, 1 atm of air, i e 78% N_2 = $= \frac{0.78}{22.4} \times \frac{273}{294}\ \mathrm{mol\ dm^{-3}}$)

Under these conditions Barkatt et al have found a production of 7.8×10^{-5} M. This means that equation 4 is not generally applicable and probably less applicable the smaller the gas to liquid volume ratio is.

If instead the production of nitric acid is calculated as taking place in the liquid phase the following yield is obtained

$$G = \frac{\text{Concentration (M)} \times 0.963 \times 10^{9}}{\text{Dose rate (rad/h)} \times t\ \text{(h)}} \qquad \text{(Eq 5)}$$

$$G(HNO_3) = \frac{7.8 \times 10^{-5} \times 0.963 \times 10^{9}}{8.6 \times 10^{4} \times 72} =$$

$$= 1.2 \times 10^{-2}$$

which, in comparison with other results (2) may be regarded as a high value.

Nitric acid is also formed by alpha radiation during the dissolution of Pu compounds (12)

3 FORMATION OF ORGANIC ACIDS

Barkatt et al (13, 14) have shown that in addition to nitric acids organic acids may be formed when glass is leached in a radiation field in the presence of CO_2. Barkatt et al showed that OH radicals are responsible for the production of formic and oxalic acids. HCOOH and $(COOH)_2$ were formed in yields of 46 and 30 μM respectively, after the irradiation of 25 ml deionized water for 3 days at a dose rate of $8.6 x 10^4$rad/h. According to Eq 5:

$$G(HCOOH) = \frac{46 \text{ x } 10^{-6} \text{ x } 0.963 \text{ x } 10^{9}}{8.6 \text{ x } 10^{4} \text{ x } 72} =$$

$$= 7.2 \text{ x } 10^{-3}$$

$$G((COOH)_2) = 4.7 \text{ x } 10^{-3}$$

assuming that the production takes place in the liquid phase.

The formation of small yields of formic acid, formaldehyde and oxalic acid by the irradiation of CO_2 has been reported previously (15, 16). Formation of oxalic acid by the irradiation of solutions of HCO_3^- has also been reported (17) More complex acids, such as glyoxylic and dihydroxytartaric acids, may have been formed by the radiolysis of formic and oxalic acids (18).

4 FORMATION OF NITRIC, FORMIC AND OXALIC ACIDS IN A REPOSITORY

The occurence of aerated bubbles in which the conditions for the formation of nitric acid is largest - is not very likely in a waste repository, at least not in a later stage when the buffer material surrounding the nuclear waste canisters has become completely saturated with ground water. Instead, an estimate of the formation of acids in ground water may be based on G-values in the liquid phase. The following equations can be used:

$$\frac{dc(\text{acid})}{dt} \cong G(\text{acid}) \times DR \times 10^{-9} \qquad \text{(Eq 6)}$$

where

C = concentration, M(=mol/l)

G = G-values

DR = dose rate, rad per time unit

In connection with the storage of high level waste the integrated energy deposition, E, outside the canisters has been calculated (20). In this case the following equation can be used for the calculation:

$$\text{mol(acid)} = \frac{E(\text{in eV}) \times G(\text{acid})}{100 \times 6.02 \times 10^{23}} = G \cdot E(\text{ev}) \times$$
$$\times 1.66 \times 10^{-26} \qquad \text{(Eq 7)}$$

The following G-values can be used: (the G-value for nitric acid formation can be regarded as conservative)

Acid	HNO_3	HCOOH	$(COOH)_2$
G-value	0.01	0.007	0.005

4.1 Examples of calculation using G-values

Based on equations 6 and 7 estimates on acid concentrations and integrated acid productions can be made. Two reference cases have been selected here

A. a 10 cm thick copper canister according to the Swedish KBS-3 concept (19): BWR fuel with a burnup of 33 MWd/kgU.

B. a 1 cm thick version of the original canister. BWR fuel with a burnup of 33 MWd/kgU.

Total doses and integrated energies have been taken from ref 20 a, Tables 9 and 10 (total doses) and 20 b (integrated energies).

Accumulated acid concentrations at the surface of a case A canister (10 cm) assuming no diffusion away from the canister.

Storage time, y	10^2	10^3	10^4	10^5	10^6
Total dose Mrad	1.0	1.2	1.3	3.2	27
HNO_3mol/l	1.0E-5	1.2E-5	1.3E-5	3.2E-5	2.7E-4
HCOOH, mol/l	7E-6	8E-6	9E-6	2.2E-5	1.9E-4
$(COOH)_2$, mol/l	5E-6	6E-6	7E-6	1.6E-5	1.4E-4

Accumulated acid concentrations at the surface of a case B canister (1 cm) assuming no diffusion away from the canister.

Storage time, y	10^2	10^3	10^4	10^5	10^6
Total dose, Mrad	560	740	780	890	2980
HNO_3, mmol/l	5.6	7.4	7.8	8.9	30
HCOOH, mmol/l	3.9	5.2	5.5	6.2	21
$(COOH)_2$, mmol/l	2.8	3.7	3.9	4.5	15

The concentrations calculated above will not be attained in the repository - because the acids will diffuse away from the canister. Also the G-values used for calculation of HNO_3 production is chosen conservatively. The total integrated acid production in the whole volume outside the canister calculated according to Eq 7 may therefore give a better view of the situation. The total energy deposited at varous times has been calculated based on references 20 and 21.

Total integrated acid production outside a case A canister (10 cm).

Storage time, y	10^2	10^4	10^6
Total energy, MeV	2.6E19	3.2E19	4.8E20
HNO_3, mmol	4	5	80
HCOOH, mmol	3	4	60
CCOOH, mmol	2	3	40

Total integrated acid production outside a case B canister (1 cm)

Storage time, y	10^2	10^4	10^6
Total energy, MeV	8E20	1.0E21	2.7E22
HNO_3, mol	0.13	0.17	4.5
HCOOH, mol	0.09	0.12	3.2
$(COOH)_2$, mol	0.07	0.08	2.2

5. CONCLUSIONS

The formation of nitric acid has been reported in the literature, eg in connection with leaching of glass during irradiation. The experiments were carried out in order to evaluate the behaviour of glass as a matrix for highly radioactive waste. The formation of nitric acid has been found to take place predominantly in the gas phase.

The formation of organic acids by radiolysis of carbonate solutions has also been reported. Natural granitic ground water contains typically about 0.5 mM nitrogen (corresponding to air saturation at 1 atm) and about 2 mM carbonate ions. Irradiation from high level nuclear waste may thus produce nitric and organic acids in the surroundings of a canister.

A conservative estimate of the production of acids outside a 10 cm thick copper canister containing spent fuel has been made. This canister corresponds to the concept proposed in the KBS-3 report (19). For comparison calculations have also been made on a 1 cm thick canister.

For a 10 cm canister the calculated total production of acids after 1 million years is 0.08 mol nitric, 0.06 mol formic, and 0.04 mol oxalic acids.

Corresponding values for a 1 cm thick canister are 5 mol nitric, 4 mol formic, and 3 mol oxalic acids.

The estimates were based on G-values of 0.01 (uncertain but conservative value), 0.007 and 0.005 for formation of nitric, formic and oxalic acids, respectively.

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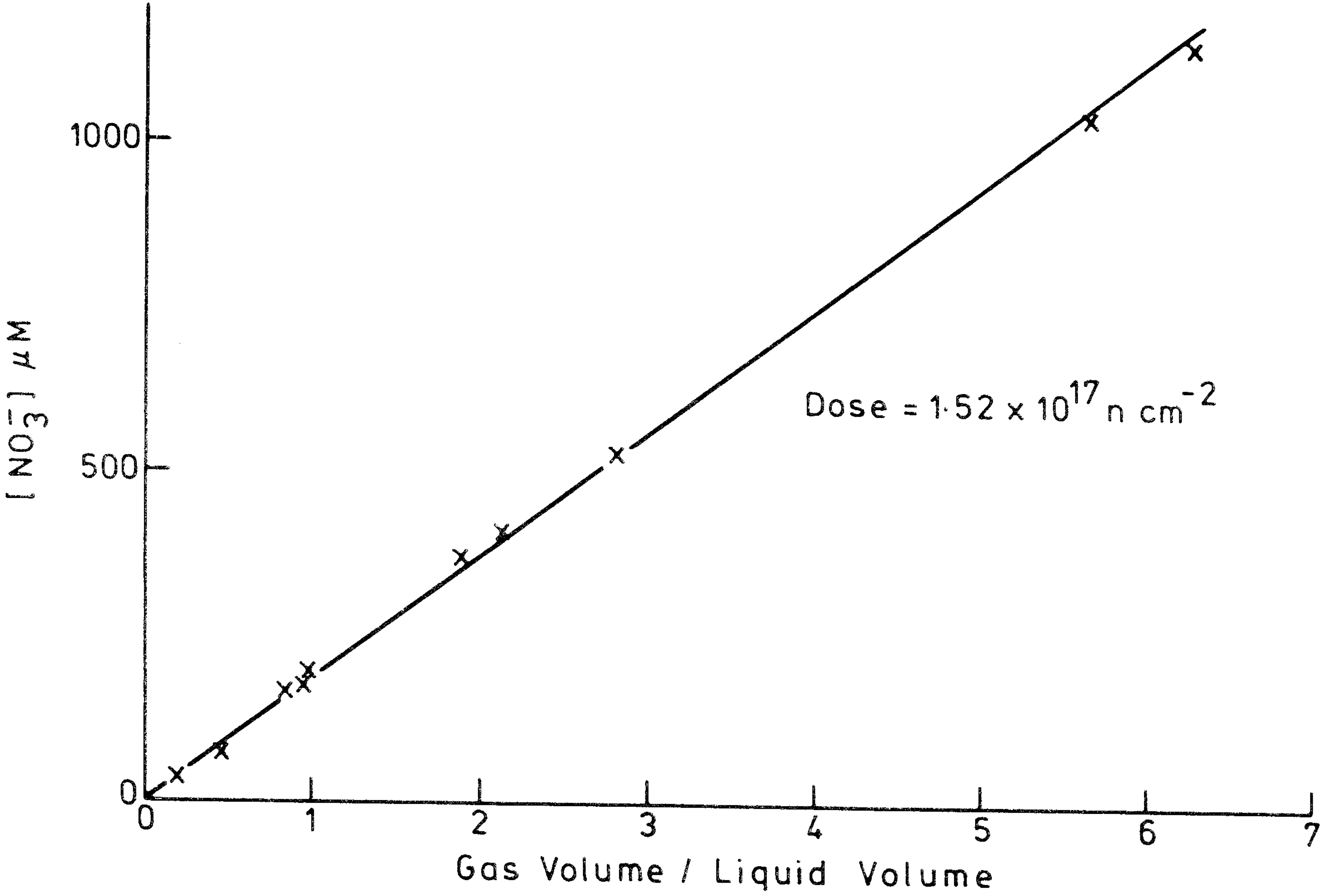

Figure 1

Irradiation of air-water system, variation of nitrate concentration with gas volume to liquid volume ratio. From AERE-R10027. (Copyright UKAEA)

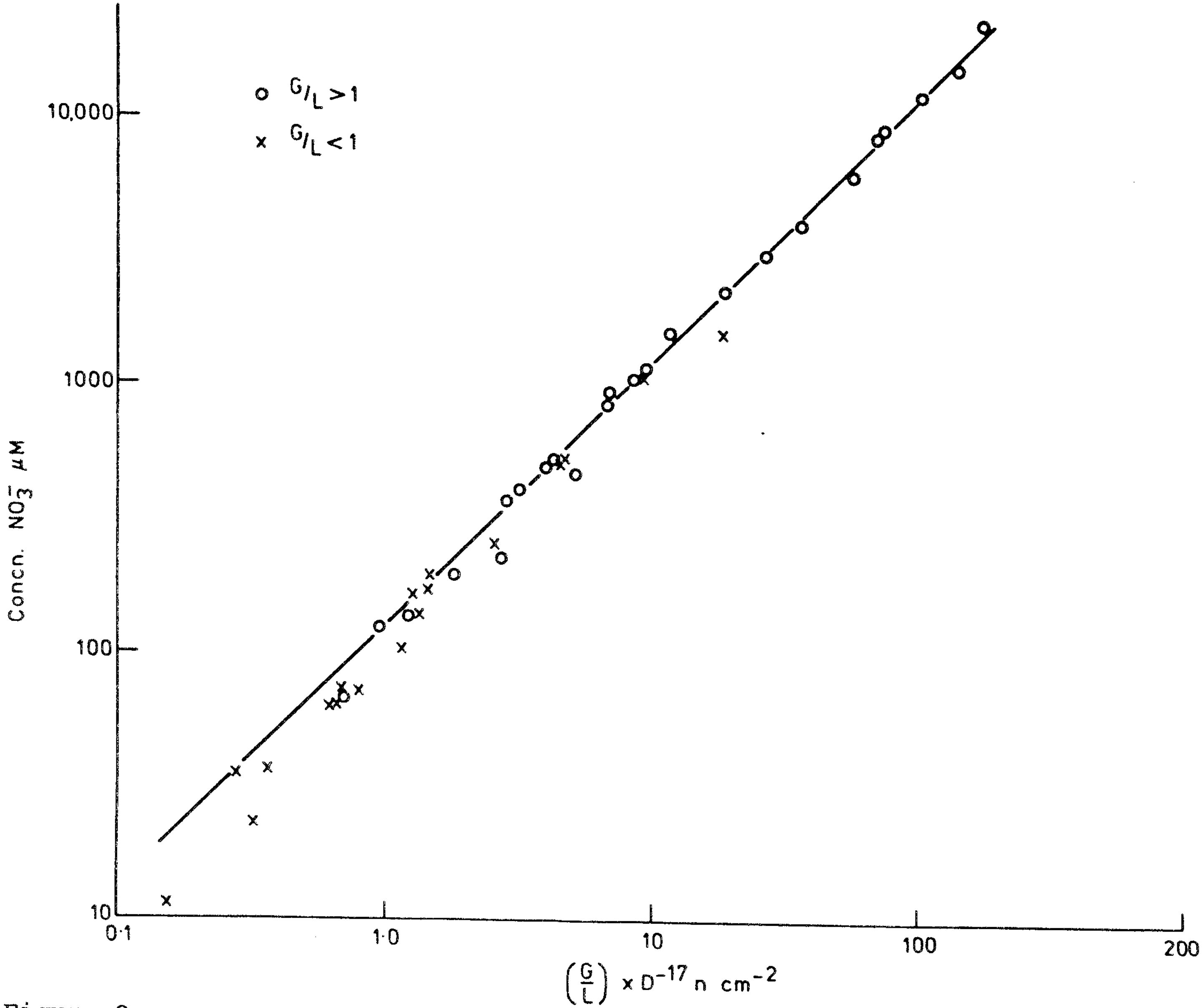

Figure 2

Irradiation of air-water system. From AERE-R10027. (Copyright UKAEA)

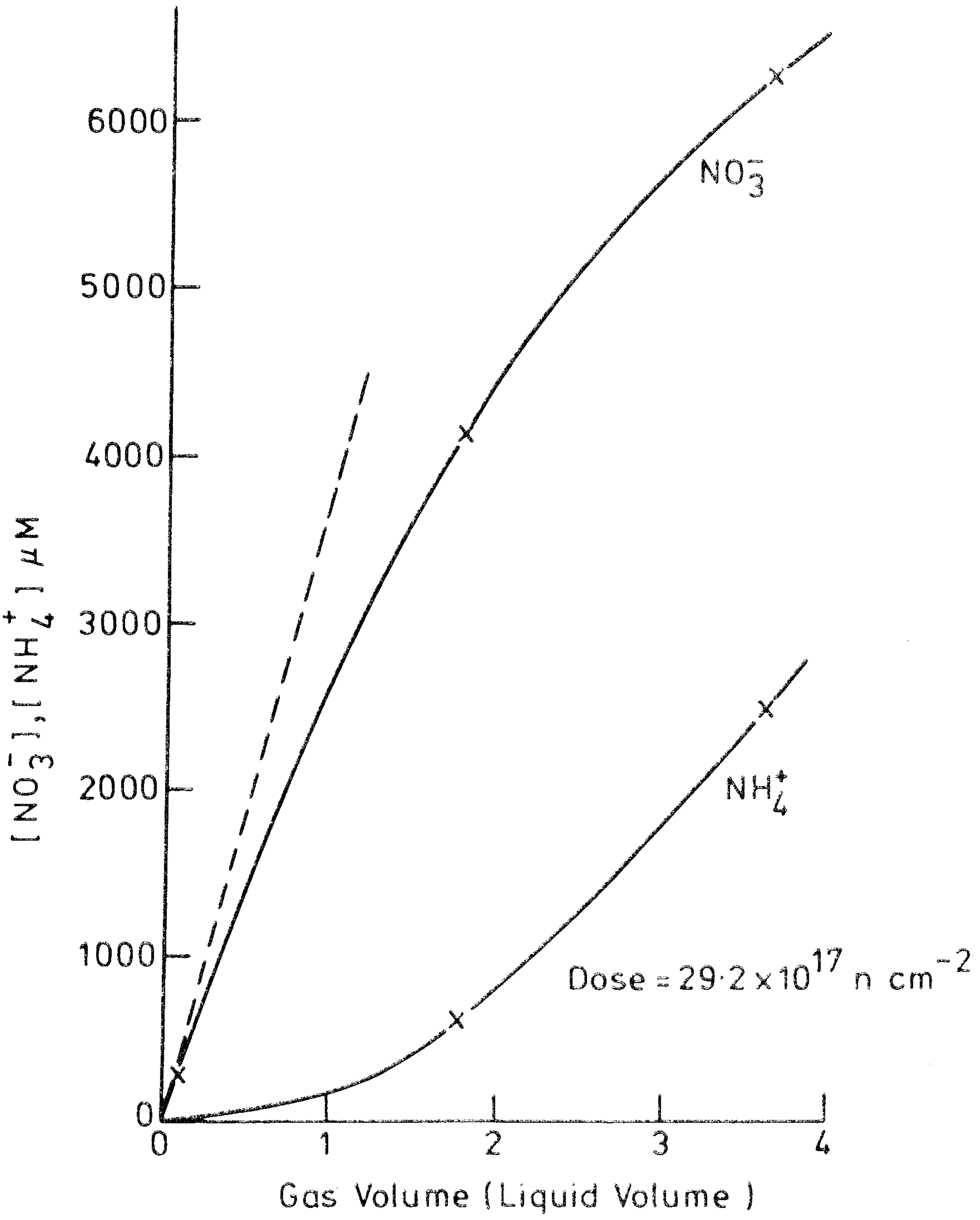

Figure 3

Irradiation of nitrogen-water system to high dose, formation of ammonium ion. From AERE-R10027. (Copyright UKAEA)

Table 1

Production of NO_3^- in Linacre and Marsh's experiment for various ratios of gas to liquid volume (G/L). The total volume is constant (about 60 ml).

G/L	V(gas) ml	V(liq) ml	$C_l(NO_3^-)$ M	Amount NO_3^- mmol
½	20	40	0.5a	20a
1	30	30	a	30a
2	40	20	2a	40a
3	45	15	3a	45a
4	48	12	4a	48a
5	50	10	5a	50a

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Kurt-Åke Magnusson
Oscar Duran
Swedish Geological Company
Uppsala September 1984

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Bertrand Fritz
Marie Kam
Yves Tardy
Université Louis Pasteur de Strasbourg
Institut de Géologie
Strasbourg, France July 1984

TR 84-11

Smectite alteration

Proceedings of a Workshop Convened at The Shoreham Hotel, Washington, D.C., December 8—9, 1983
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November 1984