

Modelling of nitric acid production in the Advanced Cold Process Canister due to irradiation of moist air

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AEA Technology, Decommissioning & Waste Management/Reactor Services, Harwell, UK

January 1994

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author(s) and do not necessarily coincide with those of the client.

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ABSTRACT

This report summarises the work performed for SKB of Sweden on the modelling of nitric acid production in the gaseous environment of the Advanced Cold Process Canister (ACPC). The model solves the simultaneous chemical rate equations describing the radiation chemistry of a $He/Ar/N_2/O_2/H_2O$ gas mixture, involving over 200 chemical reactions. The amount of nitric acid produced as a function of time for typical ACPC conditions has been calculated using the model and the results reported.

AEA Technology Decomissioning & Waste Management/ Reactor Services

540.1, Harwell, Didcot Oxfordshire OX11 ORA United Kingdom Telephone 0235 435804 Facsimile 0235 436314 Abstract (Swedish)

Denna rapport sammafattar det arbete som utförts för SKB, Sverige, vad avser modellering av produktionen av salpetersyra i gasmiljön inuti Advanced Cold Process Canister (ACPC). Modellen löser de simultana kemiska ekvationer som beskriver strålningskemin i en gasblandning av $He/Ar/N_2/O_2/H_2O$ med mer än 200 kemiska reaktioner. Mängden producerad salpetersyra som funktion av tiden för typiska ACPC förhållanden har beräknats med modellen och resultaten har redovisats.

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1. Introduction.

SKB of Sweden and TVO of Finland are both assessing the use of the Advanced Cold Process Canister (ACPC) for the encapsulation and geological storage of light water reactor fuel. The design of the ACPC canister has been discussed^{1,2} and is therefore not discussed here. These canisters will be filled and then 'leak tight' sealed to prevent air ingress and release of volatile fission product material. Once sealed the gaseous atmospheres within these canisters will contain air and water vapour and it is known that irradiation of moist air mixtures produces nitric acid which is a potential corrodent of waste canister material. It is important therefore to know how much nitric acid may be produced and in what time period, given certain initial conditions of the gaseous material in the canister. In reference 1 a very approximate estimate of the amount of nitric acid that might be expected to be produced and in what time scales was estimated. This assessment was later refined by Henshaw et al^3 by modelling the detailed gaseous radiation chemistry for typical gas mixtures prevailing in the canister. The initial gaseous atmosphere modelled in reference 3 consisted of simply H₂O/O₂/N₂, however, it is now being considered that before the canisters are sealed that they will be filled with an inert gas (He, Ar etc.) to minimise the initial air content. The prevailing atmosphere inside the canister will therefore consist of inert gas/H2O/O2/N2, the most probable inert gas being He. This report describes extensions to the radiation chemistry model outlined in reference 3, in particular what additional chemistry is required to describe the behaviour of the inert gas.

In order to model the gas phase chemistry of the $H_2O/O_2/N_2$ system, which leads to the production of nitric acid, an appropriate set of chemical reactions and corresponding rate constants are required. G-values (molecules produced per 100eV of energy absorbed) are also needed to describe the primary interaction of the radiation with the gas phase species. The chemical rate equations can then be integrated numerically, starting with an initial set of concentrations, for a given temperature, pressure and dose rate to give the species concentrations as a function of time. The chemistry, rate constants, G-values, method of integration and comparisons with experimental data for the $H_2O/O_2/N_2$ gas phase system have been described in reference 3. The temperature and pressure dependencies of the chemical rate constants in the model have been updated and the chemistry expanded to include the effects of helium and argon. Also included in the new version of the model are equations for the evaporation and condensation of water.

The following sections give a brief outline of the radiation chemistry of $H_2O/O_2/N_2$ gas mixtures, how the chemical rate constants in the model have been updated and a brief review of the He and Ar radiation chemistry that has been included. The results of calculations for particular conditions of relevance to the ACPC canister are then reported. The final section briefly discusses the results of the calculations.

2. Air/Water Radiation Chemistry.

The radiation chemistry of moist air can be categorised into three phases:-

Primary Interactions: Here the radiation interacts directly with the molecular species, so that reactions of the following type occur,

$$\begin{array}{ccc} \text{Radiation} \\ \text{N}_2 & \rightarrow & \text{N}_2^+ + e^- \end{array} & 1 \end{array}$$

These reactions produce ions, electrons and excited radical species.

Ion-molecule and Ion-Ion Reactions: These are very fast reactions whose rate constants are largely temperature independent. They include charge transfer reactions, neutralisation reactions, etc. For example:

$$N_{2}^{+} + O_{2} \rightarrow N_{2} + O_{2}^{+} \qquad 2$$
$$N_{2}^{+} + e^{-} \rightarrow N + N \qquad 3$$

Thermal free radical chemistry: Here the rate constants may have a large temperature dependence and in the case of third body reactions a pressure dependence, for example:

$$OH + NO_2 + M \rightarrow HNO_3 + M$$
 4

which is the main reaction leading to nitric acid production (M is an arbitrary third body).

In the presence of a radiation field all three stages of the radiation chemistry outlined above will be taking place simultaneously. In the current reaction scheme describing the radiation chemistry of $H_2O/O_2/N_2$ there are over 200 reactions. Associated with each reaction is a chemical rate expression describing how the species concentrations change with time. Thus, for equation 2 above

$$\frac{d[O_2]}{dt} = -k[O_2][N_2^+]$$
 5

where the square brackets denote concentrations and k is a chemical rate constant. In order to describe the primary interactions, such as equation (1), equations of the form

$$\frac{d[N_2^+]}{dt} = G(N_2^+)D\rho F$$
 6

are integrated, where $G(N_2^+)$ is the G-value for N_2^+ production, ions produced per 100eV of energy absorbed, D is the dose rate, ρ is the gas density and F is that fraction of the total dose rate absorbed by the parent species, in this case N_2 .

In the current model the expressions for the chemical rate constants have been updated from the constant temperature terms used in reference 3 and these forms are outlined below.

3. Temperature and Pressure Dependence of the Chemical Rate Constants.

In the case of reactions involving ions, the temperature dependence of the rate constants is small so that it can be ignored. However, the temperature dependence of the rate constants for radical-radical, radical-molecule and molecule-molecule reactions can be large. The temperature dependence of these rate constants is given by the familiar Arhenius equation

$$\mathbf{k} = \mathbf{A} \, \mathbf{T}^{\mathbf{n}} \exp\left(-\mathbf{E}/\mathbf{T}\right) \tag{7}$$

where T is the temperature and the activation energy E is in K. This expression is adequate for second order reactions but in the case of third order reactions such as

$$H + O_2 + M \rightarrow HO_2 + M$$
 8

where M is an arbitrary third body, it does not take into account the pressure dependence of the rate constant. For third order reactions the following expression is used for the rate constant⁴

$$\mathbf{k} = \begin{bmatrix} \frac{\mathbf{k}_{o} \mathbf{k}_{\infty} \mathbf{M}}{\mathbf{k}_{o} \mathbf{M} + \mathbf{k}_{\infty}} \end{bmatrix} \mathbf{F}$$
 9

where

$$\log F = \log F_{e} / (1 + (\log(k_{o} \times M / k_{o}))^{2})$$
 10

Both k_0 (the rate constant at low pressures) and k_* (the rate constant at high pressures) are expressed as Arhenius expressions and F_c is a constant.

The main sources of data for the temperature dependent rate constants are references 4, 5 and 6.

4. Helium/Argon Radiation Chemistry

The inclusion of an inert gas species in the free gas space of the ACPC canister will lower the direct interaction of the radiation with the N₂, O₂ and H₂O species and therefore, simplistically, prevent nitric acid production. However, energy absorption by the inert gas species leads to ionised or excited inert gas species and these will interact with N₂, O₂ and H₂O as described below leading eventually to nitric acid production. Some work⁷ has suggested that the presence of Ar may enhance the rate of production of nitric acid in moist air; however this is discussed later. In the experimental work of Wood et. al.⁸ nitrogen exchange between ¹⁴N₂ and ¹⁵N₂ was measured in the presence of an inert gas during irradiation of these gas mixtures using a ⁶⁰Co gamma source. This work suggested that the chemical mechanism describing the interaction of helium with nitrogen is

$$\begin{array}{c} \text{Radiation} \\ \text{He} \rightarrow \text{He}^+ \end{array} \qquad 11 \end{array}$$

$$\begin{array}{ccc} \text{Radiation} \\ \text{He} & \rightarrow & \text{He}^* \end{array} \qquad 12$$

$$He^+ + N_2 \rightarrow N_2^{+*} + He \qquad 13$$

$$He^+ + N_2 \rightarrow N^+ + N + He$$
 14

$$He^* + N_2 \rightarrow N_2^+ + e^- + He \qquad 15$$

Subsequent reactions of the above product species are present in the model and the rate constants and G-values for the above equations are given in references 8 and 9. Also included in the model are the equivalent reactions with O_2 and H_2O , e.g.

$$He^+ + O_2 \rightarrow O_2^+ + He$$
 16

along with all the appropriate neutralisation chemistry, e.g.

$$He^+ + e^- \rightarrow He$$
 17

$$He^+ + O_2^- \rightarrow He + O_2$$
 18

The radiation chemistry of argon is very similar to helium

Radiation
Ar
$$\rightarrow$$
 Ar⁺ + e⁻ 19

$$Ar^+ + N_2 \rightarrow Ar + N_2^+$$
 20

In the presence of O_2 and H_2O the following reactions will also take place

$$Ar^+ + O_2 \rightarrow Ar + O_2^+$$
 21

$$Ar^+ + H_2O \rightarrow Ar + H_2O^+$$
 22

$$Ar^+ + H_2O \rightarrow ArH^+ + OH$$
 23

All the charge exchange reactions are energetically favourable since the ionisation potentials for He and Ar are 24.6 and 15.8eV respectively, while those of N₂, O₂ and H₂O are 15.6, 12.1 and 12.6 eV respectively. The Ar⁺ neutralisation reactions have also been included in the model, such as

$$Ar^+ + e^- \rightarrow Ar$$
 24

$$ArH^+ + O_2^- \rightarrow Ar + H + O_2$$
 25

etc. The rate constants and G-values for all the above reactions were obtained from references 8 and 9.

5. Helium and Argon Radiation Chemistry Effects on Nitric Acid Production.

The experimental work of Wood et al^8 indicated that for a mixture of $14N_2$ and 15_{N_2} , isotope exchange was increased in the presence of helium and argon. This was due to the increase in the production of N_2^+ in the presence of inert gas species leading to N atoms on neutralisation. In the work of Linacre et al¹⁰, irradiating moist air mixtures using a test reactor radiation source (neutrons+gammas) in the presence of helium, indicated that the inert gas lowered the G-value for nitric acid production. The work of May et al^7 suggested that there was an enhanced production of nitric acid in the presence of argon when moist air mixtures were irradiated. It was suggested that the mechanism for this enhancement was the same as in the isotope exchange work of reference 8. We have carried out a number of calculations with the model to examine the results of reference 7 to see if there is a significant enhancement of the rate of nitric acid production in the presence of argon. In general the model indicates that the argon chemistry has little effect on the rate of production of nitric acid. The reason for this is clear if the chemistry of the system is considered. In the absence of argon under typical conditions used in the experiments of reference 7, (gas volume 170cm³, dose rate 1.1 Mrads/hour, 700mmHg gas pressure and temperature 300K), the main mechanism leading to nitric acid production is

$$N_2 \rightarrow N + N$$
 26

$$N_2 \rightarrow N_2^+ + e^-$$
 27

$$N_2^+ + e^- \rightarrow N + N$$
 28

$$N + O_2 \rightarrow NO + O$$
 29

$$NO + HO_2 \rightarrow NO_2 + OH$$
 30

$$OH + NO_2 + M \rightarrow HNO_3 + M$$
 31

while the following reactions form a major nitric acid destruction pathway

$$NO_2 + e^- \rightarrow NO_2^-$$
 32

$$NO_2^- + HNO_3 \rightarrow HNO_2 + NO_3^-$$
 33

The net effect of the N₂⁺-N-NO-NO₂-HNO₃ pathway to nitric acid production is small. Although the production of N₂⁺ produces more nitrogen atoms and therefore increases the rate of nitric acid production, the creation of N₂⁺ also results in a larger concentration of electrons which are produced simultaneously (reaction 27). This, via reactions 32 and 33, reduces the rate of production of nitric acid. The creation of Ar⁺ also leads to a subsequent higher electron concentration which cancels the enhancement effects of the argon ion. Calculations indicate that in fact the argon chemistry reduces the rate of nitric acid production. Thus for a gas volume consisting of Ar/10%Air/10%Relative Humidity Water at the conditions described above for the experiments in reference 7 the model predicts, for a dose of 19Mrads, that approximately 7.2x10⁻¹⁴g of nitric acid is produced. If the G-value for Ar⁺ production is set to zero and the calculation repeated (so there is no Ar⁺ chemistry) then the amount of nitric acid produced is $1.1x10^{-13}g$.

Therefore it is not clear why reference 7 reports an apparent enhancement of nitric acid formation due to argon. This conclusion is largely based on figure 3 of reference 7 in which two curves are plotted of the amount of nitric acid produced after a dose of 19 Mrads. One curve is a function of the percentage of air in an Ar/Air mixture at 700 mmHg but the other (pure air) is a function of the pressure of air as a fraction of the maximum pressure, 700 mmHg. The curve is reproduced here in figure 1. For a given point on the x-axis the amount of air considered is the same, and the y-axis points indicate the amounts of nitrate measured with and without argon. However, there is an important difference between a point on one curve and a corresponding point on the second curve, which is not stated explicitly in reference 7. That is, for a given x-value, the experiments to determine the y-axis values (amounts of nitrate) were carried out at different pressures. From the previous discussions it is clear that a number of rate constants for key chemical reactions leading to the production of nitric acid are pressure dependent. Therefore this difference in pressures between the experiments carried out on pure air and experiments carried out on air/argon mixtures may account for the difference in the relative amounts of nitrate produced.

To test this hypothesis calculations of the amount of nitric acid after a dose of 19Mrads were performed with the new model on an argon/air/water mixture at 700 mmHg, varying the air/argon ratio to match the conditions used in reference 7. For these calculations the production rate of Ar^+ was set to zero so that no argon ion chemical reactions took place. Calculations were also performed on an air/water mixture at the same temperature, dose rate, relative humidity and gas volume. For this second set of calculations the pressure of air was varied from 10 to 700mmHg. The results of both these sets of calculations are plotted in figure 2, where, as in reference 7, the x-axis for the air/water/no argon system is plotted as a fraction of the pressure of 700 mmHg (e.g. 350 mmHg Air/700 mmHg = 0.5). This plot is the theoretical equivalent to figure 1 from reference 7, although the absolute magnitude of the nitrate products cannot be compared. From figure 2 it is clear that for a given amount of air (x-value) the amount of nitric acid produced is largest when argon is present. Since the model including argon had <u>no argon chemistry</u> this indicates that the enhancement in nitric acid production due to argon is simply the result of pressure

differences between the calculations carried out on air/argon/water mixtures and those carried out on air/water mixtures with no argon.

In general then, the experimental evidence on the effects of inert gas species on nitric acid production are inconclusive. Calculations indicate that the effect of the ion chemistry will be small. However, the presence of the inert gas will lower the direct interaction of the radiation with N_2 , O_2 and H_2O therefore reducing the rate of nitric acid production.

6. Calculation of Nitric Acid Production in the ACPC.

Having extended the chemistry in the model, as discussed above, calculations were performed for typical conditions prevailing in the ACPC. After the canister has been sealed the internal gas atmosphere will consist primarily of inert gas with trace amounts of air. Trapped liquid water will maintain a constant water vapour pressure in the gas phase and this gaseous water will be replenished from the liquid phase as it is consumed in gas phase chemical reactions. The conditions for the present calculations are given in Table 1.

Table 1. ACPC Conditions Used For The Present Calculations.

Gas Volume/m ³	0.7 (50% of total void volume)
Initial Dose Rate/Gy h ⁻¹	310
Half Life For Dose Rate/Years	30
Volume of Liquid Water/cm ³	50
Total Pressure/atm	1
Water Vapour Pressure/atm	3.262×10^{-2}
He Vapour Pressures/atm	0.95, 0.96, 0.966, 0.967, 0.96728
Air Vapour Pressures/atm	$0.017, 0.00738, 0.00138, 3.8 \times 10^{-4}, 1 \times 10^{-4}$

Given the helium pressure and water vapour pressure, the air vapour pressure was chosen such that the total vapour pressure was one atmosphere. This gave a percent air range of 1.7 to 0.01%. Five calculations were performed for each of the helium vapour pressures in Table 1. In figures 3 to 8 the total mass (in grams) is plotted against time, for the various nitrogen species in the container at each of the helium pressures. If the relative amount of a particular species is small then this is not plotted but the order of magnitude of the amount of that species is given in the figure heading.

With 95% He (1.7% Air) in the gas phase (figure 3) the nitric acid content in the container increases to approximately 3 to 3.5g over a period of twelve years and in the following two years decomposes to primarily NO₂. This formation and subsequent decomposition of HNO₃ upon irradiating moist air has been noted

experimentally by Jones¹¹. In figure 8, the concentrations of the other initial species in the system, H₂O, O₂, N₂ and He are plotted against time for the 95% He case. It is apparent from figure 8 that consumption of O_2 limits the amount of nitric acid produced. The results for 96% (figure 4) and 96.6% He (figure 5) are similar to those for 95% He except that the amounts of the maximum nitric yields are smaller, due to the smaller amounts of O_2 initially present in the system. For 96.7% He (~0.04%) Air), after twelve years, figure 6 indicates the decomposition of nitric acid starts to take place but stops after a further 2 to 3 years, leaving a residual amount of 0.05g of nitric acid. This behaviour is also seen for the case when 96.728% of He (0.01% Air) is present (figure 7); the residual amount of nitric acid being approximately 0.016g. Figure 9 is a plot of the other initial species in the system, H₂O, O₂, N₂ and He against time for the 96.726% He case and it is clear again that the O_2 present is limiting the amount of nitric acid produced. In figure 10 the masses of the oxidised nitrogen species are plotted against time for the equivalent calculation to the 96.728% He (0.01%Air) scenario, except He was replaced by Ar for these calculations. When Ar is present the system takes longer to reach its steady state (20 to 25 years) than for helium (15-20 years) and the final amount of nitric acid produced, 0.019g, is higher then in the helium case, 0.016g. The equivalent calculation was then performed using N_2 instead of Ar and the results of this calculation are given in figure 11. The system reaches its steady state in approximately 0.005 years, producing 0.017g of nitric acid.

7. Discussion and Summary.

There are a number of uncertainties in the current model and previous experimental results describing the radiolysis of air/inert gas/water mixtures. Previous experimental work looking at the effects of helium indicated that the presence of helium reduces the G-value for nitric acid production in moist air mixtures. However, experimental work using argon indicated an enhanced production of nitric acid when irradiating moist air/argon mixtures. The model calculations presented here indicate that these observed enhancement effects of argon on the rate of nitric acid production may, at least partly, be due to the effect of pressure on some of the reaction rate constants. Theoretically it is expected that argon ion chemistry has little effect as a result of subtleties in the chemical mechanism discussed above. The presence of helium or argon therefore primarily reduces the fraction of the radiation absorbed directly by N₂, O₂ or H₂O, thereby slowing down their conversion to nitric acid, but does not prevent nitric acid production.

For the expected conditions in the ACPC (0.01% air) the amount of nitric acid produced would be of the order of 0.02g and should take in the region of 10 to 20 years to form. Higher levels of air in the canister (of the order of 0.1-1%) lead to greater production of nitric acid. However, this nitric acid is, in time, decomposed by the radiation present. In reality any nitric acid formed may attack surfaces present and therefore would not undergo this decomposition process, but this phenomenon is not modelled here. If the inert gas is replaced with nitrogen in these gas mixtures then the rate of production of nitric acid increases. This behaviour is expected since the production of N atoms will be faster due to the greater extent of primary interactions of the radiation with nitrogen molecules. In general the calculated amounts of nitric acid reported here are much smaller than those reported in our previous study³ (of the order of tens of grams). This is because of the limited supply of oxygen for the calculations reported here, due to the presence of the inert gas species. In the present calculations nitric acid is formed faster then in reference 3, and this is largely due to the increased initial dose rate used here, 310 Gy/h, compared to 10 Gy/h used previously.

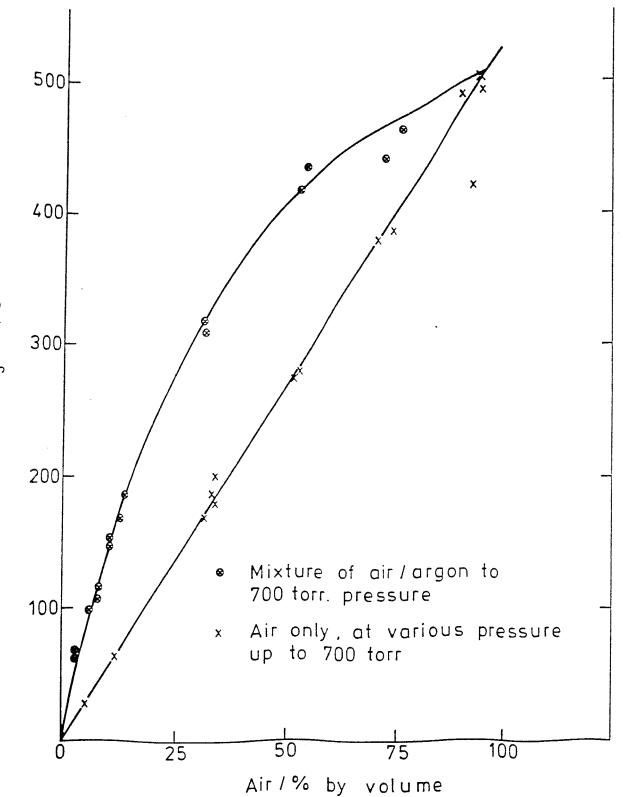
Acknowledgements

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Figure 1. This is figure 3 from reference 7, experimental results of May et al. Dose 19Mrads, dose rate 1.1 Mrads/hour, temperature 300K, gas volume 170cc. Pressure of Air/Argon/Water mixture 700 mmHg.



[N0²] / µg

Figure 2. Plot of Nitric acid produced after a dose of 19Mrads. Dose rate 1.1 Mrads/hour, temperature 300K, gas volume 170cc. Pressure for Air/Argon/Water mixture 700mmHg.

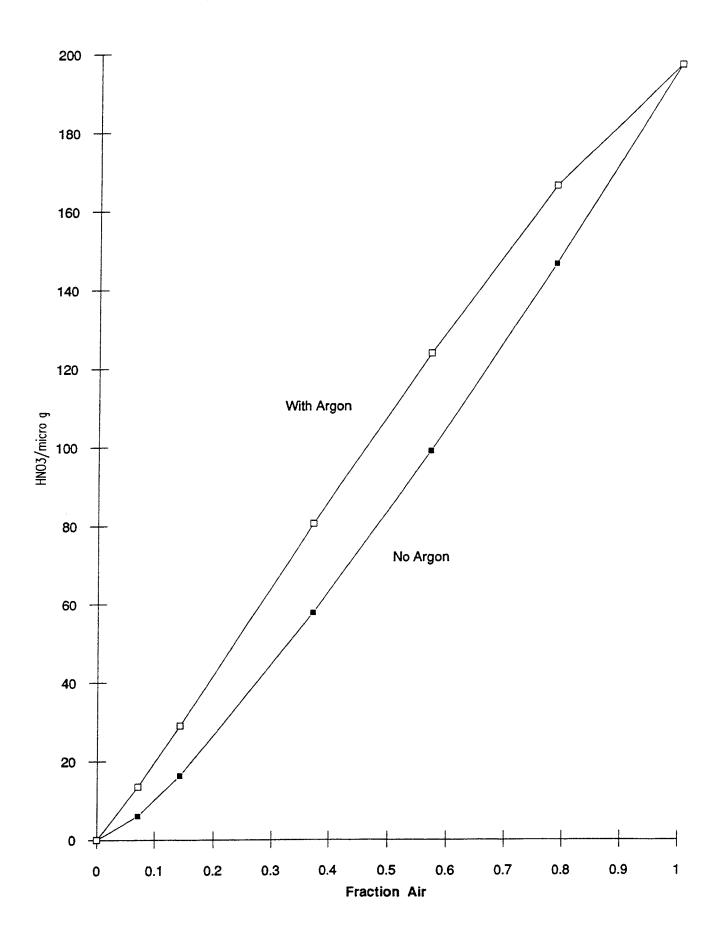


Figure 3. Nitrogen Species against time for a gas mixture containing 95% He (HNO2 of the order of 1e-6g, and NO3 and N2O5 of the order of 1e-4g)

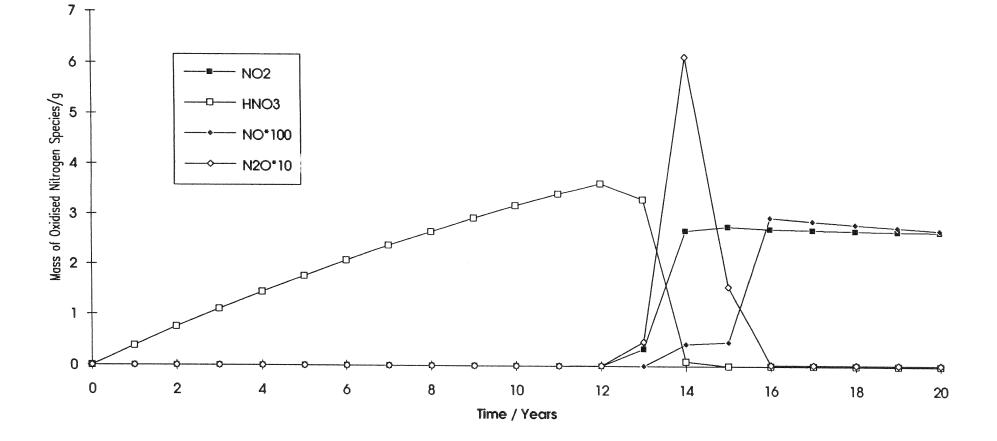


Figure 4. Nitrogen Species against time for a gas mixture containing 96% He (HNO2 of the order of 1e-6g, NO3 of the order of 1e-5g, and N2O5 of the order of 1e-4g)

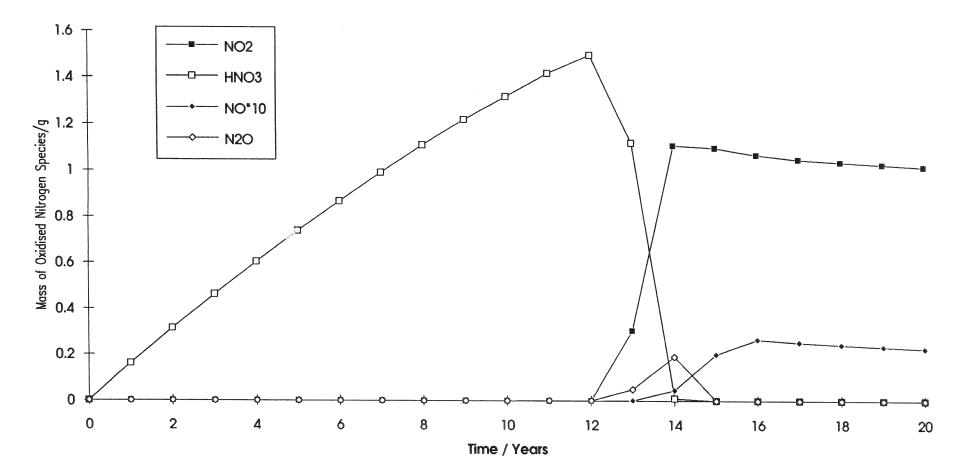
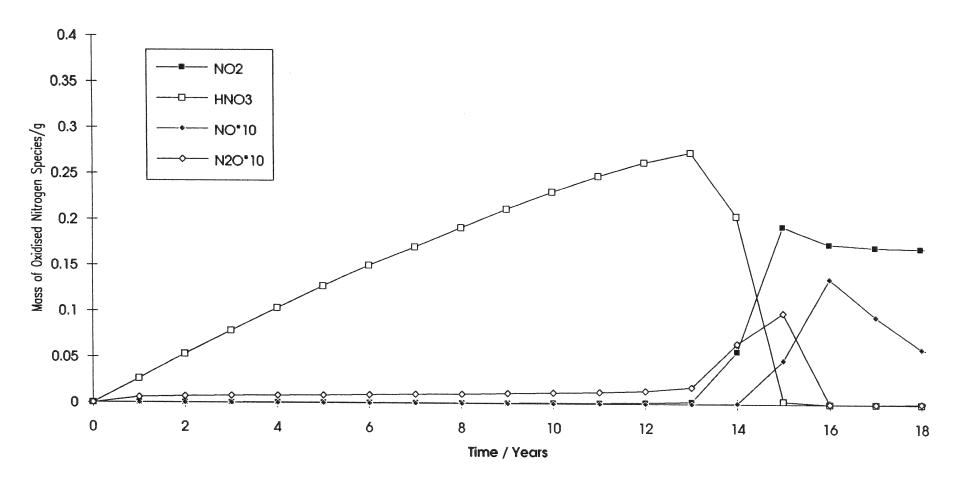


Figure 5. Nitrogen Species against time for a gas mixture containing 96.6% He (HNO2 of the order of 1e-6g, NO3 of the order of 1e-5g, and N2O5 of the order of 1e-4g)



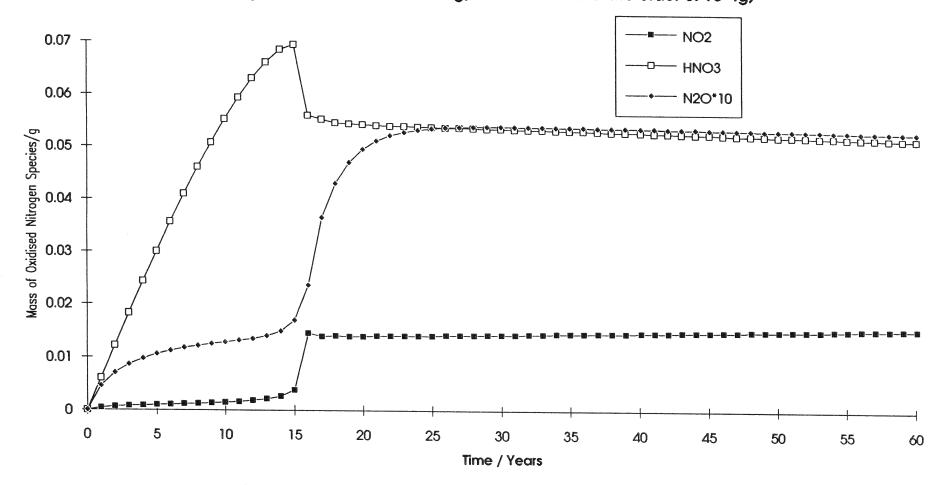


Figure 6. Nitrogen Species against time for a gas mixture containing 96.7% He (HNO2 of the order of 1e-6g, NO3 of the order of 1e-5g, N2O5 and NO of the order of 1e-4g)

0.016 0.014 Mass of Oxidised Nitrogen Species/g 800.0 800.0 90000 800.0 - HNO3 - NO2 - N2O*10 0.002 Time / Years

Figure 7. Nitrogen Species against time for a gas mixture containing 96.728% He (NO and NO3 of the order of 1e-5g, HNO2 of the order of 1e-6g, N2O5 of the order of 1e-4g)

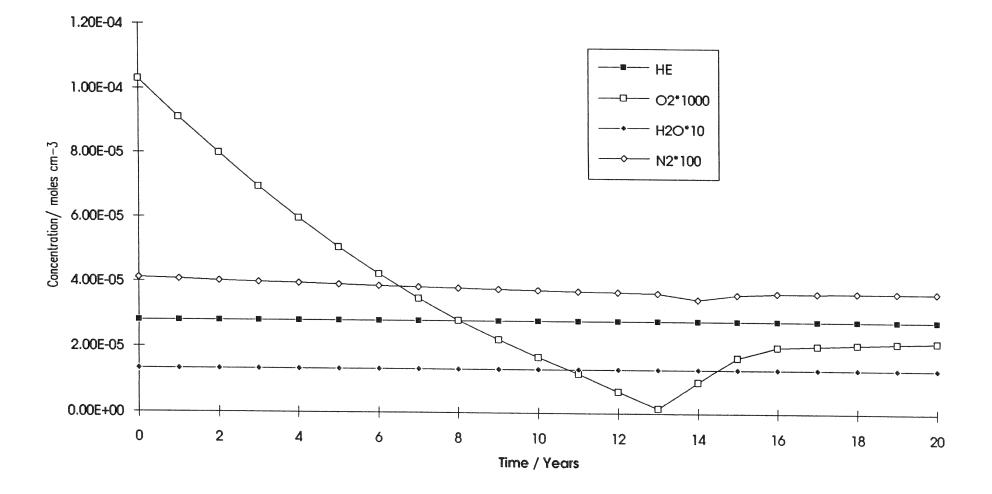


Figure 8. Gas phase species concentrations against time for a mixture containing 95% He.

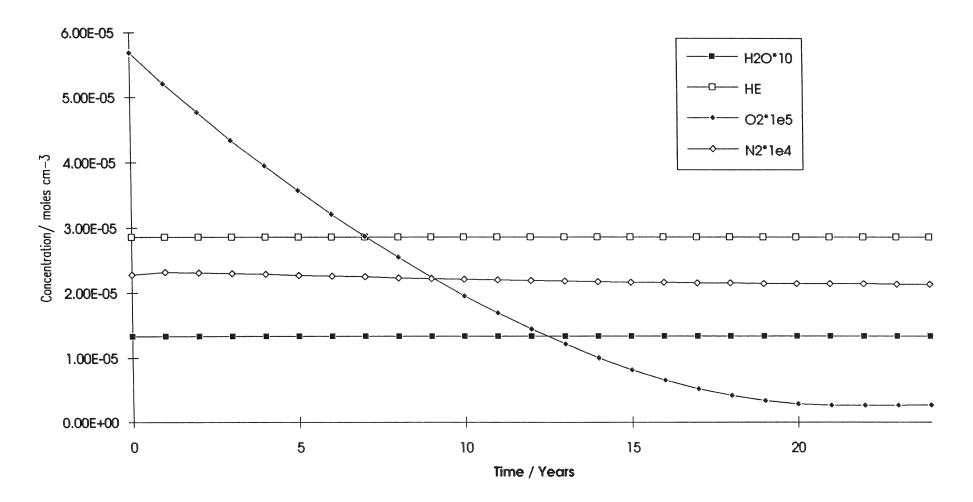


Figure 9. Gas phase species concentrations against time for a mixture containing 96.728% He.

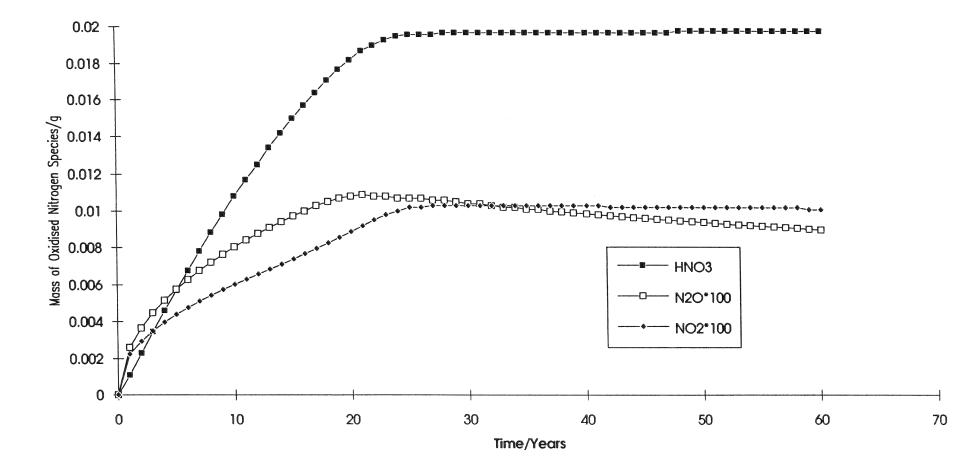


Figure 10. Nitrogen species against time for a gas mixture containing 96.728% Ar (NO of the order of 1e-8g, NO3 and N2O5 of the order of 1e-5g and HNO2 of the order of 1e-6g).

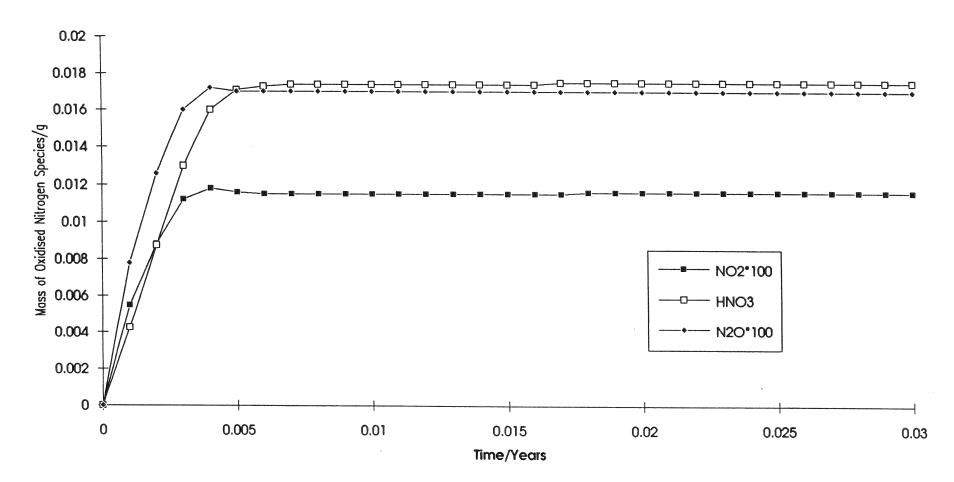


Figure 11. Nitrogen species against time for a gas mixture with 96.728% N2 (+Air) (NO, HNO2, N2O5 and NO3 of the order of 1e-6g)

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Calin Cosma¹, Christopher Juhlin², Olle Olsson³

- ¹ Vibrometric Oy, Helsinki, Finland
- ² Section for Solid Earth Physics, Department of Geophysics, Uppsala University, Sweden
- ³ Conterra AB, Uppsala, Sweden
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Jan Cramer (ed.)¹, John Smellie (ed.)² ¹ AECL, Canada

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Sven Åke Larsson^{1,2}, Eva-Lena Tullborg² ¹ Department of Geology, Chalmers University of Tabbada m/O to be an University

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Olle Olsson¹, Göran Bäckblom², Gunnar Gustafson³, Ingvar Rhén⁴, Roy Stanfors⁵, Peter Wikberg²

- 1 Conterra AB
- 2 SKB
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- 4 VBB/VIAK

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- ¹ MBT Umwelttechnik AG, Zürich, Switzerland
- ² Chalmers University of Technology, Gothenburg, Sweden

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Hans Widén¹, Patrik Sellin²

- ¹ Kemakta Konsult AB, Stockholm, Sweden
- ² Svensk Kärnbränslehantering AB,
- Stockholm, Sweden

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