RESEARCH REPORT

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Formation of nitric acid during high gamma dose radiation

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Confidentiality: Public

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Formation of nitric acid during high gamma dose radiation	
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Summary

The formation of nitric acid in water/air system was measured by irradiating the known mixture with a gamma source and determining the amount of nitric ions formed in the irradiation after chemical treatment by spectrophotometry. The formation of radiolytic products can be commonly characterized by the so-called G-values, i.e., the number of molecules formed per 100 eV of radiation energy absorbed.

First series of tests were done with a small amount of distilled water and air irradiated in a closed vessel, so called moist air test. In addition some tests only with pure water phase were done. The last preliminary tests were done using moisture air and painted concrete block to see what effect painted surfaces is.

The G-value calculated of these moist air results is 2.42 parallel experiments gave the G-value 2.32. The G values found in literature for nitric acid formation from air range $G_{(HNO3)}$ = 2.3 - 2.7 molecules/100 eV [1,2]. Compared to literature values measurements yield was the same. The determination of the G-value for NO_3 formation of water in radiation gave the G-value 0.024. This is three times that given in literature. The G values found in literature for nitric acid formation from water is $G_{(HNO3)}$ = 0.007 molecules/100 eV [3]. Our experiment was made in room temperature. Increasing the temperature decreases the amount of nitrogen dissolved in water and decreases the G-value for nitric acid formation in water.

A preliminary experiment to study the influence of painted surface in the nitrate concentration was made by irradiating water with and without painted concrete block. These are very preliminary results with one dose value and before any conclusions more tests is needed. Anyway it seems that painted surfaces could have some influence also nitric acid productions.

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Contents

1 Introduction

Nitric acid is a principal radiolytic compound produced in large quantities and its production is another important problem concerning pH of solutions, owing its chemical properties of being a strong acid and a strong oxidizing agent.

The studied issue is the additional acid formation in steam-rich air or N_2 atmosphere in nuclear containment where radiation source is the airborne fission product activity or in sump water with N_2 dissolved in the water pools and radiation source coming from fission products trapped in sump water. Nitric acid formation with irradiation has previously been studied in ORNL by Beahm et al, (1992) NUREG/CR-5950. However, very little further studies have been performed although NUREG/CR-5950 formulas are applied in plant evaluation and pool pH estimation e.g. in USA. Consideration of additional HNO_3 formation contributes to estimation of pool pH and thus should be evaluated in connection with iodine source term.

The potential end users are nuclear authorities and utilities who are evaluating severe accident source terms. The results can be applied to calculation of HNO_3 production in air and in water pools for pool pH evaluation or design of pH control. The results can also be used to evaluate iodine pool model in MELCOR code (MELCOR calculated HNO_3 formation with ORNL formula).

2 Goal

The formation of nitric acid during high dose rates was tested. It is known that gamma irradiation of air/water will lower the pH. The high dose is achievable using Gammacell 220 ^{60}Co gamma source in Otaniemi.

The formation of radiolytic products can be commonly characterized by the so-called G-values, i.e., the number of molecules formed per 100 eV of radiation energy absorbed. The measured results will be used to double-check the coefficient proposed by ORNL twenty years ago for linear dependency of HNO_3 production on radiation dose for pure water.

The radiation dose rate of the source was measured by using Fricke dosimetry, where dose rate is determined by measuring the rate of formation of Fe^{3+} in the oxidation reaction $Fe^{2+} \rightarrow Fe^{3+}$. The concentration of Fe^{3+} is measured after irradiation of $FeSO_4$ solution and the dose rate can be calculated.

3 Experimental

In this work, the G-value for nitric acid production was measured by irradiating air and/or water phase with a ^{60}Co gamma source.

The radiolytic-yield value, the G-value, is defined as the number of reaction products per 100 eV of ionizing radiation absorbed by the system. Accordingly, the G-value for nitric acid production is expressed by

$$G=N/(E/100),$$

where N is the number of nitric acid molecules produced, G the G-value for nitric acid production (number of molecules/100 eV), and E the deposited energy (eV). In this study, the number of nitric acid molecules produced was experimentally obtained.

3.1 Fricke dosimetry

The Fricke dosimeter, also called the ferrous sulfate dosimeter, is one of the most useful chemical dosimeters. It depends on the oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) by ionizing radiation. The increase in concentration of the ferric ions is measured spectrophotometrically at the optical absorption maxima at 304 nm. The Fricke dosimeter is 96% water (by weight), hence its attenuation of radiation closely resembles that of water. It is usable in the dose range of 5-400 Gy and at dose rates up to 10^6 Gy/s. Its disadvantages include a very high sensitivity to organic impurities that act as scavengers of hydroxyl radicals, ultimately resulting in over-response and the fact that the sensitivity of the system decreases when the oxygen present in the solution is depleted.

For precise measurements, the doses delivered to the dosimeters do not exceed 100 Gy and typically range between 5 and 25 Gy. Ultimately, a plot of the net absorbance versus irradiation time (for ^{60}Co) is obtained and the slope of the line is used to calculate the average dose rate to the Fricke solution in a given volume. In the case of irradiations with high energy electrons or x-rays, the dose per monitor unit is determined using the slope of the line of the optical density versus monitor units. With proper care and a state-of-the-art spectrophotometer, the Fricke dosimetry system at NRC is capable of determining the absorbed dose with a typical precision of 0.1% (1σ) [1,2].

$$E = \frac{279 * A}{1 - 0.007(25 - T)}$$

E = absorbed dose (Gy)
A = absorbance
T = temperature (°C)

3.2 Measurement of nitric acid

The formation of nitric acid in water/air system was measured by irradiating the known mixture with a gamma source and determining the amount of nitric ions formed in the irradiation after chemical treatment by spectrophotometry. When nitric acid is formed during the irradiation in a closed system with water present it is totally absorbed into the water phase. The sample of this water is treated with sodium hydroxide, heated to dryness and the residue is dissolved to a dilute perchloric acid. The amount of nitrate is measured quantitatively by spectrophotometry (λ = 210 nm). When experiments are performed using various gamma doses, the G-value for the formation of nitric acid can be calculated by using the slope of the absorbance/ dose graph [1,2].

$$G = \frac{n}{100eV} = \frac{A * V1 * NA}{\dfrac{a * b}{6.24 * 10^{15} eV / g * V2 * \sigma}}$$

A= X coefficient (slope angle)
V1= water volume
NA= Avogadro number
a= 7850 l/mol*cm
b= 1 cm
V2= air volume
σ= 1.176 g/l

3.3 Test matrix

First series of tests were done with a small amount of distilled water and air irradiated in a closed vessel, so called moist air test. In addition some tests only with pure water phase were done. These test give more information on the formation of nitric acid in the water phase where the concentration of nitrogen is very low compared to the gas phase (air/nitrogen), figure 1. When temperature raise the nitrogen solubility to water reduce. The last preliminary tests were done using moisture air and painted concrete block to see the effect of painted surfaces. All tests were done in temperature (c.a. 25 C°, 1 atm), table 1.

Table 1. Test matrix.

Test	water phase	gas phase	matrix	system
1	distilled water	air	moist air	closed
2	distilled water	air	moist air	closed
3	distilled water	no gas phase	water	closed
4	distilled water	air	moist air + painted concrete block	closed

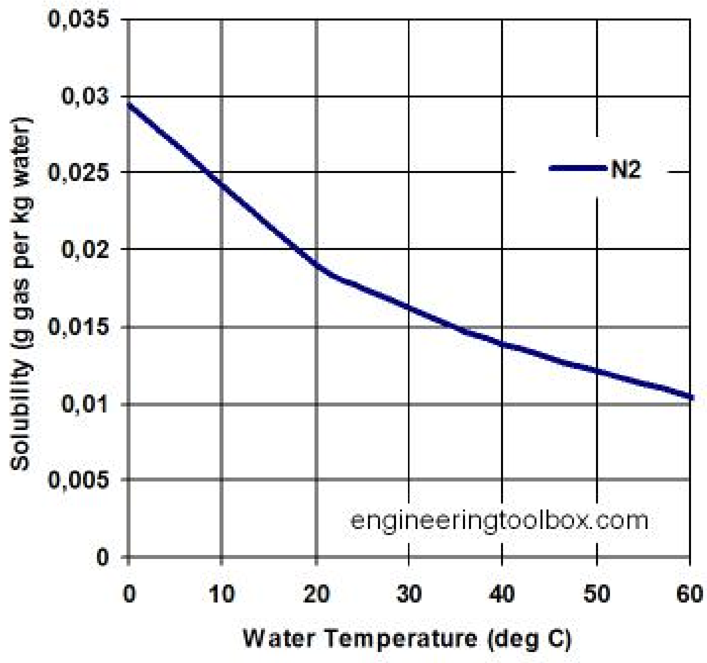

Figure 1. Solubility of Nitrogen - N_2 - in Water

Used vessel was normally 500 ml with 25 ml of distilled water in moist air tests. In the pure water irradiation test the gas phase was less than 100 ul. The amount of air in the painted concrete block experiment was 200 ml and water 20 ml, figure 2. The block size was 3 cm x 3 cm x 3 cm. The blocks were painted by TEKNOS using concrete blocks manufactured by VTT. Painting was performed as in the real reactor building using four layers of TEKNOPOX paint.

Figure 2. The position of painted concrete block sample in Gammacell 220 ready for irradiation.

4 Results

The sample was irradiated in a ^{60}Co source (Gamma Cell 220, manufactured by Atomic energy of Canada), with a dose rate of 135 Gy/h at 25 ºC. Dose rates were estimated from Fricke dosimetry performed in similar geometries than real experiments. Results of at least three different irradiations with different doses were used to analyse in each case to calculate x coefficient in the linear plot. The figure 3 shows results of one experiment with moist air in closed system.

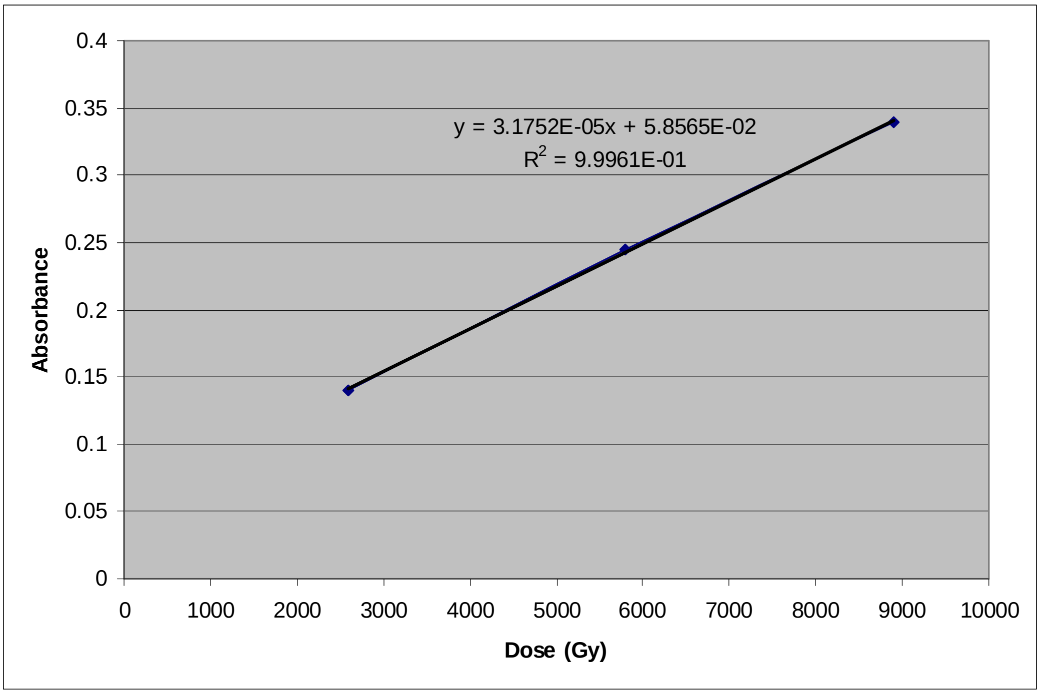

Figure 3. Typical absorbance versus dose results in experiments with moist air in closed system.

The absorbance versus gamma dose should be linear. Using the slope G-value of nitric acid was calculated. The results of VTT experiments can be seen in table 2.

Table 2. The G-values of different cases, in moist air cases two parallel test were done.

Test	matrix	G-value	G-value form published literature [1,2,3]
1	moist air	2.42	2.3 -2.7
2	moist air	2.32	2.3 – 2.7
3	water	0.024	0.007
4	moist air + painted concrete block	preliminary results only	Not available

5 Discussions and conclusions

In this project, the G value was determined for nitric acid formed from air and for the nitric acid formed from the water. The G-value calculated of these moist air results is 2.42 parallel experiments gave the G-value 2.32. The G values found in literature for nitric acid formation from air range $G_{(HNO3)}$ = 2.3 -2.7 molecules/100 eV [1,2]. The results were in good agreement with those found in the literature.

The determination of the G-value for NO_3 formation of water in radiation gave the G-value 0.024. This is three times that given in literature. The G values found in literature for nitric acid formation from water is $G_{(HNO3)}$ = 0.007 molecules/100 eV [3]. Our experiment was made in room temperature. Increasing the temperature decreases the amount of nitrogen dissolved in water and decreases the G-value for nitric acid formation in water.

A preliminary experiment to study the influence of painted surface in the nitrate concentration was made by irradiating water with and without painted concrete block. The results with one 2.6 kGy dose gave 4 times more nitrate into the water than the blank case without paint. These are very preliminary results with one dose value and before any conclusions more tests are needed. Anyway it seems that painted surfaces could have some influence also in the nitric acid production.

This work will continue the following SAFIR2014 research programme [4].

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