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RADIOLYSIS EFFECTS ON THE COMPOSITION AND RATE OF GAS GENERATION IN AN AQUEOUS HOMOGENEOUS REACTOR

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Abstract

We will present our program plans and results-to-date on the composition and rate of radiolytic-gas generation under the conditions similar to those present in an aqueous homogeneous reactor. Under a high radiation field, nitrogen will be removed from a uranyl-nitrate solution in the form of gaseous N_2 and NO_x. Loss of the nitrogen will increase the pH value of the solution, which can lead to the formation of precipitates. Another concern is the gas generation rate, which needs to be accounted for in design of the reactor off-gas system. This experimental study will be performed using simulated fuel solutions, a Van de Graaff accelerator as a radiation source, and a gas chromatograph for detection of the gasses. The Van de Graaff can deliver doses up to 1 kGy/sec (1 kW/kg β, γ) to successfully simulate the dose rates in the reactor. Samples can be collected for analysis following irradiation, or measurements can be made on-line during the irradiation. Evaluation of radiolytically induced generation of gases will be used to develop recommendations for (1) pH adjustments during or between reactor cycles and (2) for design of the off-gas system.

1. Introduction

The use of Aqueous Homogeneous Reactors (AHRs) or solution reactors presents an attractive alternative to the conventional target irradiation method of producing ^{99}Mo in that solutions eliminate the need for targets and can operate at much lower power than required for a reactor irradiating targets to produce the same amount of ^{99}Mo. As the name implies, solution reactors consist of an enriched uranium salt dissolved in water and acid and contained in shielded tank or vessel. The first solution reactors earned the name "water-boilers" because of the observed bubbling or frothing that result from the radiolytic decomposition of water by fission fragments and subsequent evolution of radiolytic gases

(hydrogen and oxygen). Because nitrate ion also undergoes radiolytic decomposition, uranyl-nitrate-based AHRs will also generate N_2 and NO_x in the off gas. The radiolytic decomposition of nitrate ion will also have the effect of increasing the pH of the fuel solution.[1] The rate and composition of the radiolytic gas generation is of practical importance for the design and operation of AHR for two reasons. First, the design of the reactor off-gas system depends on the generation rate and the composition of the gas stream. Second, an increase of the fuel-solution pH can lead to the formation of the precipitates.[2]

While radiation chemistry of the nitrate solutions has been investigated over the past fifty years, less attention was given to the analysis of total gas evolution. Observations of the formation of nitrogen-containing gases under radiation are numerous, but N_2 and NO_x formation was not studied systematically. Sowden reported formation of the N_2 in addition to the H_2 and O_2 in neutron and gamma irradiated $Ca(NO_3)_2$ solutions.[3] Byakov and Nichiporov have found that N_2O is generated under gamma radiation of nitrate solutions in addition to the above-mentioned gases.[4] Irradiation of the thorium-nitrate solutions[5] and plutonium solutions in nitric acid[6] also yields N_2. Despite numerous evidences for radiolytic N_2 and NO_x gas formation, no mechanism for formation of those gases was proposed; the reported values of the radiolytic yields for these gases also vary by an order of magnitude. The aim of this project is to obtain reliable data for radiolytic gas formation in model nitrate solution, and subsequently to expend experiments to the uranyl-nitrate solution that is of practical interest to the AHR.

Radiation Induced Chemistry of the Concentrated Nitric Solutions

Comprehensive overview of the radiation chemistry of the nitrate solution for pH >6 can be found in reference.[7]

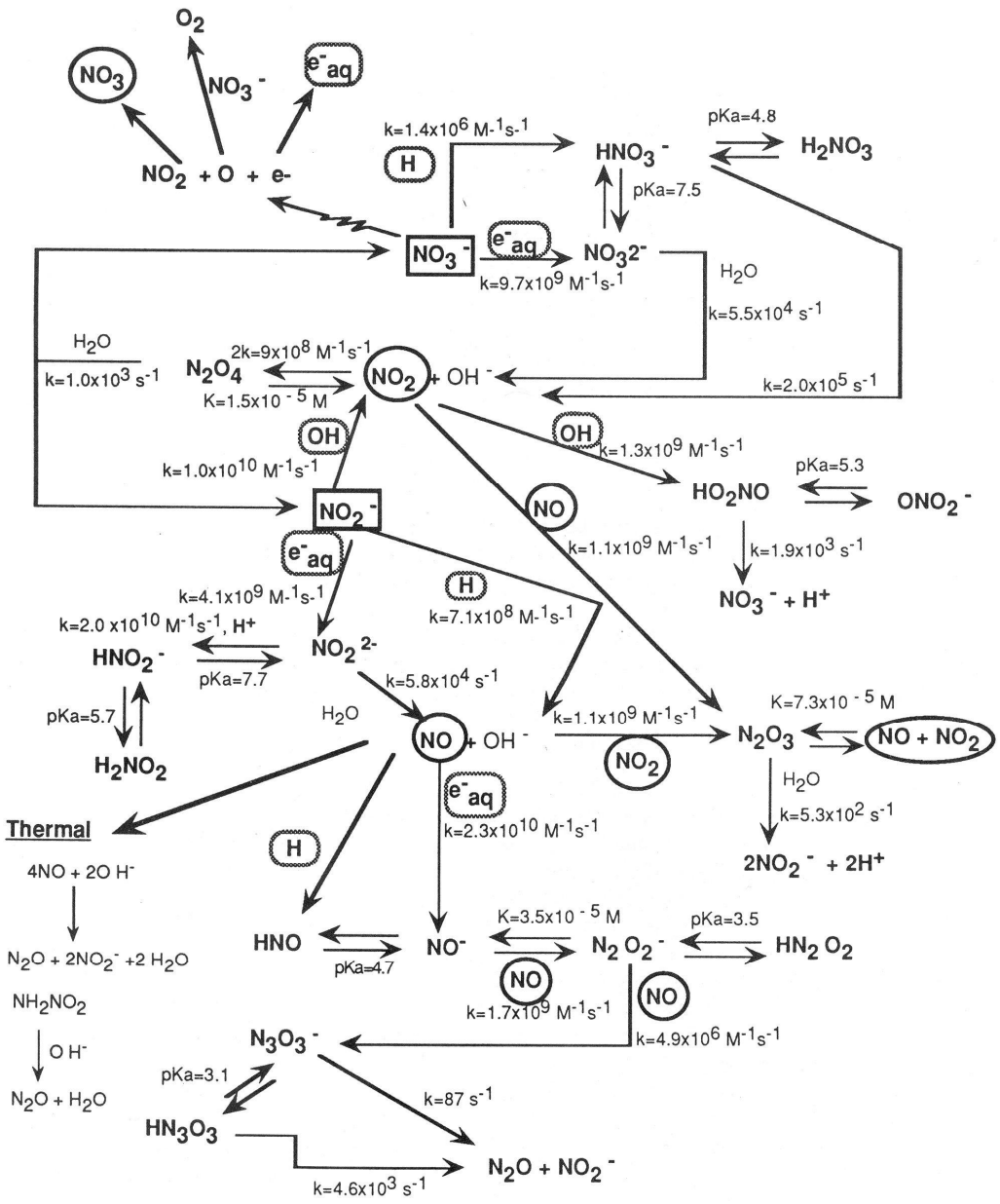

Figure 1. Radiation chemistry of nitrate solution scheme developed in reference [7]

While the above scheme was developed for conditions present in waste solutions at high pH, the same equations will likely be valid for acidic nitrate solutions. According to this scheme, nitrogen will escape the solution in the form of N_2O. Consequenty, N_2O will react with solvated electron and form N_2

$$N_2O + e^- \rightarrow N_2 + O^-$$

Other reaction also can lead to the formation of the gaseous NO_x, but they were not evaluated due to the low steady-state concentrations of the intermediates (for example NO) under low radiation fields present in waste storage tanks.

Boyle and Mahlman [3] have noted that stoichiometry for the gas evolution from nitrate solution can be reasonably described by following over-all decomposition equations:

$H_2O \rightarrow H_2+1/2O_2$
$2NO_3^- + H_2O \rightarrow N_2 + 5/2O_2 + 2OH^-$
$2NO_3^- + H_2O \rightarrow N_2O + 2O_2 + 2OH^-$

They also proposed that nitrogen yield increases as nitrate concentration increases, and nitrogen production is due to the direct action of the radiation on the nitrate ion.

2. Experimental Setup

We are using 3-Mev electron Van de Graaff to irradiate the test solution. The electron accelerator has an advantage over a gamma source because it can deliver much higher dose rates and successfully simulate the radiation field inside the reactor. To evaluate radiation-induced gas formation in acidic solution of nitrates we designed an experimental setup that can accommodate this high dose rate. The irradiation-apparatus design is optimized for dose rate in irradiated solutions. Penetration depth for 3-MeV electrons in water is 15 mm, which limits the thickness of the irradiated solution to 10 mm because the irradiation vessel must have a metal window and a minimal wall thickness of the glass ampoule of 0.5 mm. Also, we need to allow some space between the aluminum window and glass tube for a significant flow of cooling water. The design of the apparatus is shown on Figure 2.

The gaseous products of radiolysis will be analyzed using a SRI 8610 gas chromatograph with a high-sensitivity thermal conductivity detector (TCD). For O_2, N_2 and NO_x, helium is used as a carrier gas, while Ar is used for the detection of the H_2. Total gas evolution will be measured via a monometer directly attached to the glass tube during the radiation. The absorbed dose is measured using an oxalic-acid dosimeter [8]. Our preliminary experiments show that we can achieve the dose rate of 30 kGy/sec while keeping the temperature of the irradiated solution below 65^oC.

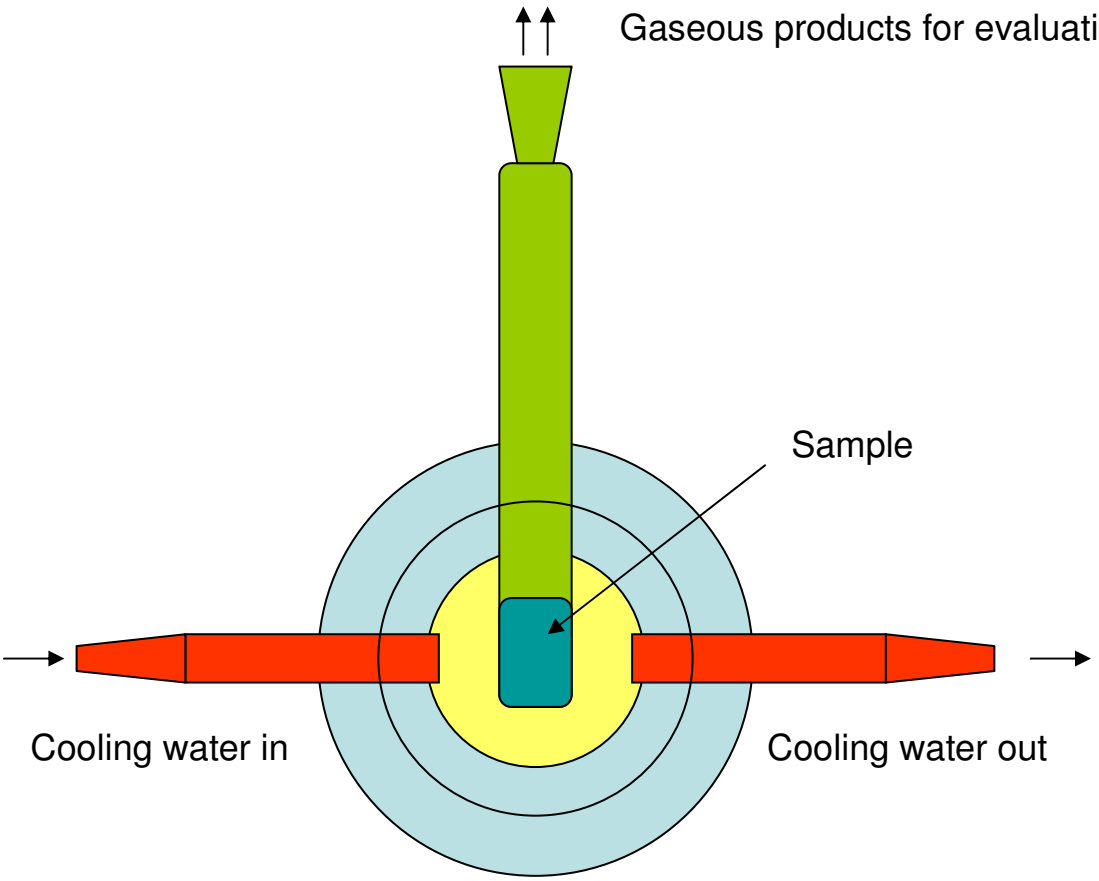

Figure 2. Experimental apparatus for nitrate solution irradiation

3. Research Direction

Using the experimental setup described above, we will initially evaluate radiolytic gas formation in a $NaNO_3$ solution containing HNO_3, measuring the dependence of the composition and rate of gas formation on the concentration of the nitrate and pH of the solution. Once we are confident in our methods and apparatus, we plan to repeat similar experiments for uranyl-nitrate solutions. The end result of this research will be recommendations for pH control measures and design off-gas system for a nitrate-based aqueous homogeneous reactor. However, before final design is initiated, the results of this study will need to be validated by irradiation of actual LEU nitrate solution in a neutron flux, where fission particles will have a strong influence on the radiolysis of water and nitrate.

4. Acknowledgements

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