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MEASUREMENTS OF COMPOSITION AND RATES OF GAS GENERATED IN AN AQUEOUS HOMOGENEOUS REACTOR.

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ABSTRACT

Under the high radiation field of an Aqueous Homogeneous Reactor, the main gaseous products from an acidic uranyl-nitrate fuel solution are H_2 and O_2. The generation rate for N_2O is ten times less and N_2, NO and N_2O is 100 times less than for hydrogen. Loss of the nitrogen compounds from a uranyl-nitrate solution will increase its pH, which can lead to the formation of precipitates. The composition and generation rate of the off-gas will also be critical engineering data for the design of the off-gas system. Experimental studies were 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 simulate the dose rates in the reactor. Also presented are our plans for experiments at the Armed Force Radiobiology Research Institute (AFRRI) reactor. These experiments will be done using small volumes of low-enriched uranyl-nitrate solution in conditions representative of an aqueous homogeneous reactor. Evaluation of radiolytically-induced generation of gases, as well as changes of pH and peroxide concentration, will be used to develop recommendations for (1) pH adjustments during or between reactor cycles and (2) 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 for producing ^{99}Mo in that they 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 nitrate-based AHRs will also generate N_2 and NO_x in the off gas. The radiolytic decomposition of nitrate ion will have the effect of increasing the pH of the fuel solution. 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.

While radiation chemistry of nitrate solutions has been investigated over the past fifty years, less attention was given to the analysis of gas evolution especially at high radiation doses. Observations of the formation of nitrogen-containing gases under radiation are numerous [1-5], but N_2 and NO_x formation was not studied systematically; no mechanism for formation of those gases was proposed. Also, the reported values of the radiolytic yields for these gases 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.

2. Development of the radiolytic off-gas detection method.

2.1. Sample preparation

We have used 1M solution of $NaNO_3$ in 0.1M HNO_3. A 1-mL volume was placed into Pyrex tube with valve (see Figure 1). The tube with closed, the valve was connected to the vacuum manifold, and the sample was equilibrated with a water/ice slurry for 15 minutes. The sample was then evacuated for one minute and filled with helium gas to 1.2 atm. The fill/evacuation cycle was repeated five times to ensure complete exchange of air to helium in the solution. Before the closed samples were transferred to the Van de Graaff facility for irradiation, they were filled with 1.2 atm of He gas.

Figure1. Sample tube for off-gas analysis

2.2. Irradiation

We are using a 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 an acidic nitrate solution, we designed an experimental setup that can accommodate this high dose rate. 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. Samples were irradiated to 20-200 MGy at 8 μA average electron beam current.

2.3 Gas analysis

The gaseous products of radiolysis have been analyzed using a SRI 8610 gas chromatograph (GC) with a high-sensitivity Thermal Conductivity Detector (TCD) and Helium Ionization Detector (HID). We used He as the carrier gas for all experiments. A diagram of the setup is presented on Figure 3. A vacuum system is directly connected to the injector valve of the GC.

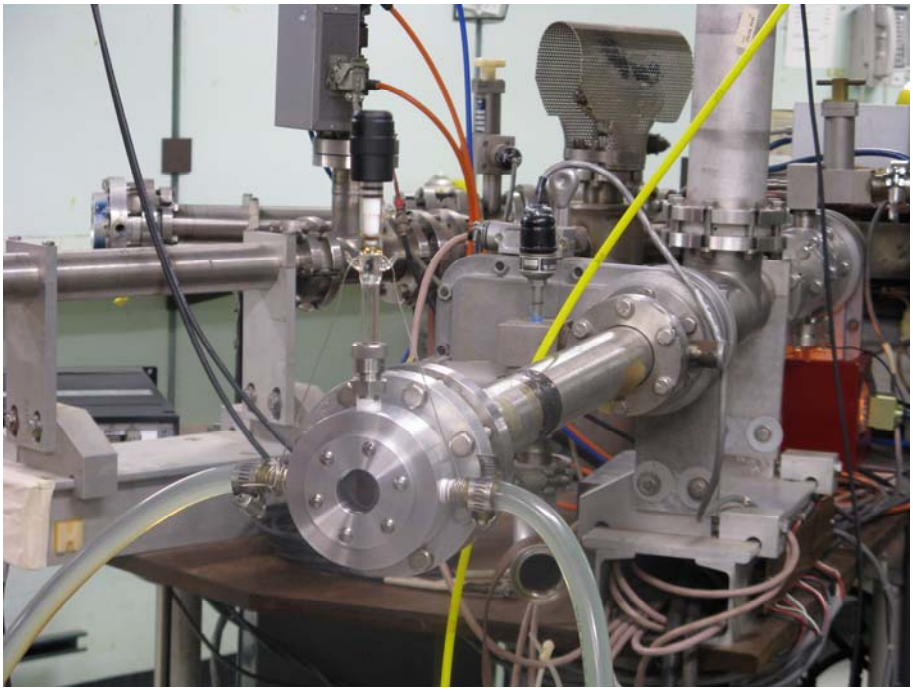

Figure 2. Experimental apparatus for nitrate solution irradiation

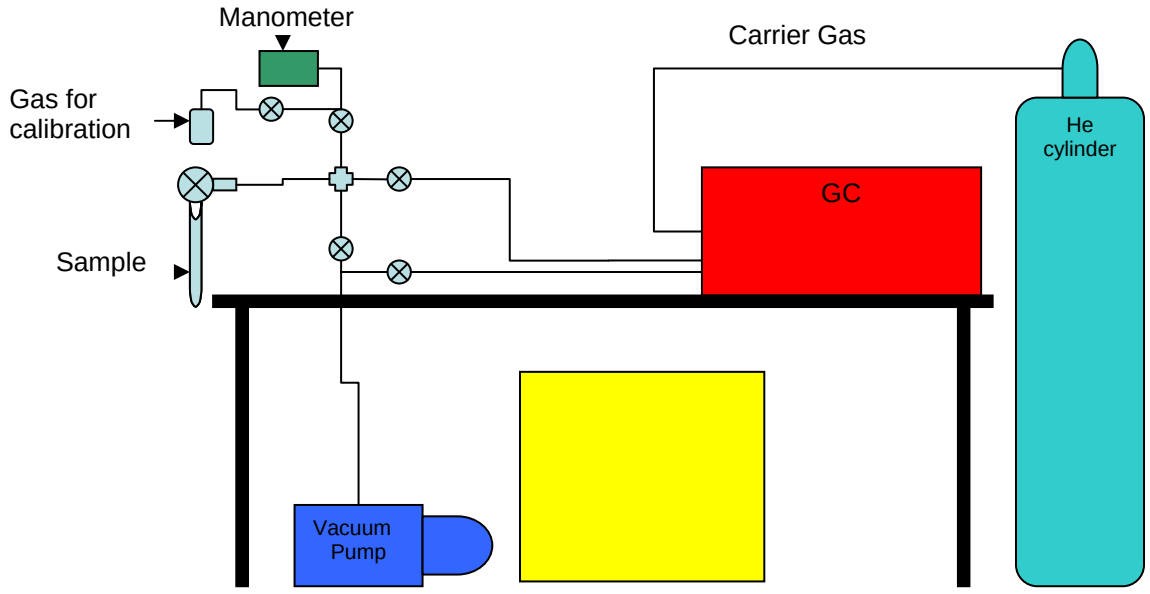

Figure 3. Off-gas analysis setup.

To analyze gas composition, we have used the following procedure. The sample tube is connected to the vacuum manifold. The whole manifold, including sample loops, is evacuated to 10^{-3} Torr. Then the manifold is isolated from the vacuum pump, and the valve on the sample tube is opened to allow gas from the sample head space to expend into the sample loops (two 1-mL sample loops, one to feed to each of the two columns). Gas in one sample loop is injected into the first, and that in the second sample loop is injected into second column. The mass of

gasses injected into GC was calculated using pressure (monometer reading) and volume of the sample loops. The GC is equipped with two columns Molecular sieve 13X and HyesepD that are configured in parallel. The gas stream from the column is analyzed by TCD and HID detectors configured in series. Optimal conditions for NO_2 and NO detection are different then for other permanent gasses, and optimal temperature for two different columns for optimal gas separation is also different. Ideally one would like to conduct runs for NO_2 and other gasses separately, but we have found a temperature regime for the columns that allows us to separate different gasses in the single run.

2.4. Radiolysis of sodium nitrate solutions.

The main products of radiolysis of concentrated solution of $NaNO_3$ in 0.1M HNO_3 are hydrogen and oxygen. Nitrogen, NO_2, N_2O, and NO are also present (see Figure 4).

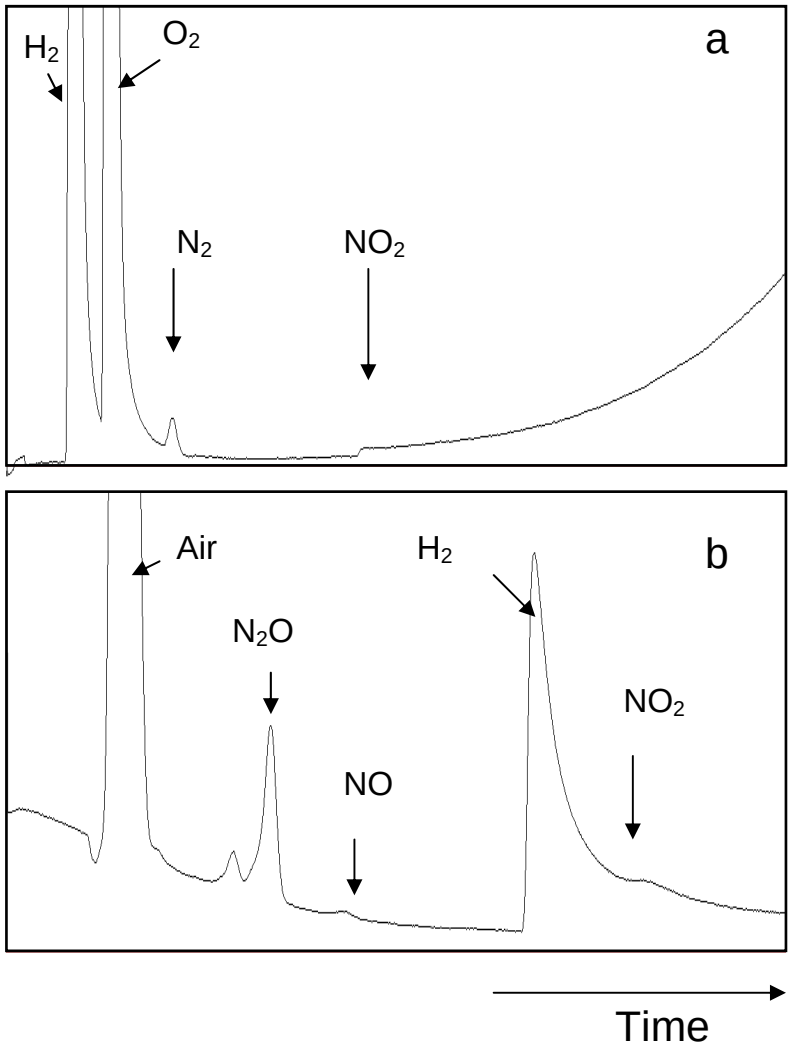

Figure 4. Chromatogram of radiolytically generated gases from irradiated 1M $NaNO_3$ solution in 0.1 HNO3. (a) Separation on Molecular sieve 13X column and (b) Hyesep D column.

The dose dependence of the yield of those gasses is shown on Figure 5. While NO gas was detected, yield for this gas was not calculated because it depends on the concentration of the oxygen due to the reaction

$2NO + O_2 \rightarrow NO_2$

and condition of the separation column (level of saturation with NO_2)

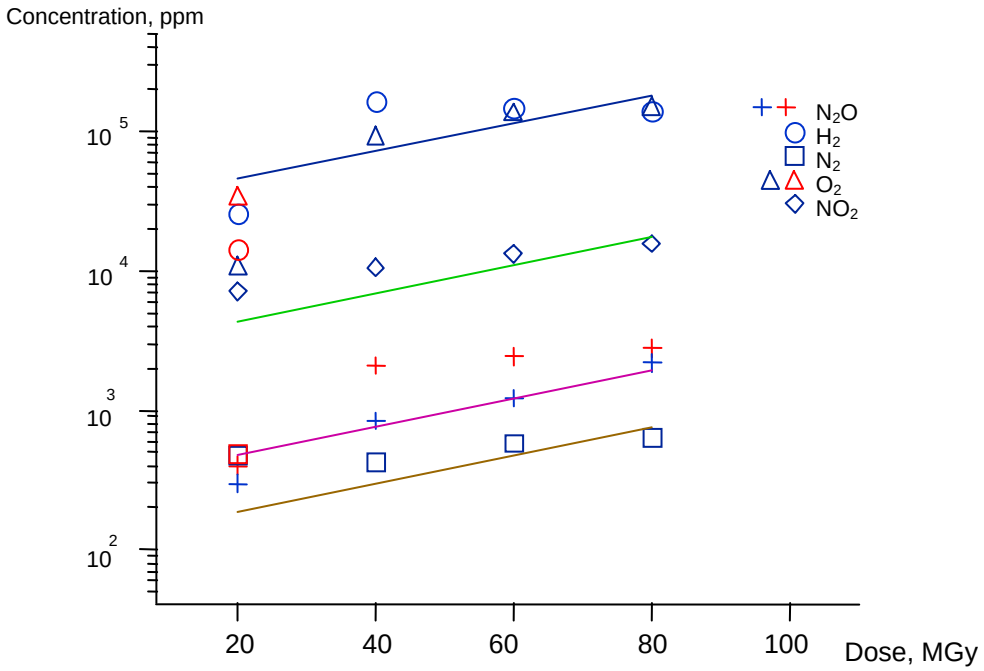

Figure 5. Relative radiolytic-gas formation vs. dose for irradiation of 1M $NaNO_3$/0.1M HNO_3

As one can see, radiolytic-gas formation is dominated by hydrogen and oxygen, while NO_2 is generated ten-fold less and N_2O and N_2 hundred-times less. Nevertheless, these preliminary results show decomposition of the nitrate in the solution that have to be taken into account when designing off-gas-handling system and control of the pH of the solution during irradiation. Our measurements of the pH of the solutions before and after irradiation show that indeed pH increases in irradiated samples. This is still an ongoing project and final results will be reported later.

3. Plans for Experiments at Armed Force Radiobiology Research Institute Reactor

While electron irradiations of nitrate solutions at 3-MeV Van de Graaff accelerator show NOx formation and changes in pH of the solution, to quantitatively assess radiolytic off-gas formation in the condition of the AHR, one would need to conduct experiments in the neutron flux similar to that expected inside the reactor. For this purpose, we are planning to conduct experiments at AFRRI TRIGA reactor. Those experiments will allow the direct comparison of the results obtained at the Van de Graaff facility using 3-MeV electrons for the rate and composition of the radiolytic gases and changes in pH with radiolysis by neutrons and fission fragments.

We will use 3-5 ml of solution in a glass container with an in-line valve. The solutions to be irradiated will low-enriched uranium nitrate solutions containing 90-235 g-U/L and 0.1 M HNO_3. Irradiation in the reactor pool will generate the same power density in the solutions as is expected in AHR. The latest version of the container design is shown on Figure 6. The plastic parts of the valve are of radiation-resistant materials because whole container will be irradiated. The mechanical integrity of the container is an important condition for in-core irradiation of the samples.

Figure 6. Glass container for small volume irradiations at AFRRI.

To mimic the MIPS-reactor conditions the power density, with 10^{12} neutron/sec in the exposure tube near the reactor in the pool will provide in the neighborhood of 1 watt/ml energy deposition rate. This is a significant thermal load, so the glass capsule will be placed in an aluminum container with the interstitial space filled with water for heat transfer to the bulk pool.

4. Acknowledgement

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5. References

[1] R. G. Sowden, J. Amer. Chem. Soc, 1957, vol. 79, 5, p1263.
[2] V. M. Byakov, and F. G. Nichiporov, Radioliz vody v yadernykh reaktorach (Radiolysis of Water in Nuclear Rectors), Moscow: Energoatomizdat, 1990.
[3] J. W. Boyle and H. A. Mahlman, Nuclear Science and Engineering, 1957, 2, p 492.
[4] J. C. Sheppard, Alpha radiolysis of plutonium (IV) – nitric acid solutions. Report BNWL-751.

[5] D. Meisel, C. D. Jonah, S. Kapoor, M. S. Matheson, and M. C. Sauer, Jr., Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes., Report ANL-93/43.