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THE RADIOLYTIC AND RADIOLYTICALLY INDUCED GAS GENERATION IN HANFORD WASTE TANKS

C. D. Jonah, D. Meisel, and M. C. Sauer, Jr.

Chemistry Division, Argonne National Laboratory

A task force operating in ANL/CHM has been developing a mechanistic understanding of the radiolytic processes that lead to the generation and retention of gases within tanks of radioactive waste at the Hanford site. This chemistry is one of the important factors that must be considered in devising remediation procedures to eliminate the great potential hazard of these tanks. A quantitative description of much of the chemistry involved in the production of H_2 and, to a lesser extent, in the production of N_2O has been achieved. Direct radiolytic generation was experimentally quantified and this new information was utilized in computer modeling to provide predictive capabilities so that changes of chemical composition of various waste tanks under different remediation procedures could be assessed. Oxygen in the waste solutions is effectively consumed upon irradiation and thus is of no concern. The mechanism of the radiolytic degradation of the chelators was established. The end products are simple organic molecules, in particular, formaldehyde and glyoxylate, that are very efficient in the thermal generation of H_2 .

These studies were supported by Westinghouse Hanford Corp., but the expertise and knowledge of the radiation chemistry involved were developed during years of support by the Division of Chemical Sciences of DOE.

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Several radioactive and mixed waste storage tanks at the Hanford reservation present a potential hazard of vital national concern. Some of them (exemplified by the one million gallon tank labeled 101-SY) generate gases, primarily hydrogen (H_2) and nitrous oxide (N_2O), that are trapped within the waste slurry for weeks. Periodically, however, the accumulated gases are released within minutes, creating a potentially explosive mixture in the head space of the tank. Understanding the chemical and physical processes involved in the production and retention of these gases is vital to the design of a safe remediation strategy for the problem.

A task force, which included Drs. Dan Meisel, Myran Sauer, and Charles Jonah, was established at ANL/CHM to investigate the radiolytic contribution to the gas generation and retention. Technical support and contributions from other scientists in the Division were also utilized as the needs emerged. Operations of the task force were fully supported by Westinghouse Hanford Corp., but were made possible only by the expertise in radiation chemistry and reaction kinetics acquired during many years of support by the Division of Chemical Sciences of DOE. Instrumentation required for these studies, including the high-current picosecond linac facility, was also acquired through the long-term commitment of Chemical Sciences to support radiation chemistry at CHM.

A standard waste simulant that included high (≥ 1 M) concentrations of NaOH, NaAlO₂, NaNO₃, and NaNO₂ and medium (≤ 0.2 M) concentrations of organic chelators and their degradation products was used to mimic the contents of the tank. Two sources of radiolytic H_2 were identified; some H_2 is generated from the direct deposition of the energy in water and the reactions of the water fragmentation species among themselves within localized areas of high concentration of these radicals ("spurs"). The second source for radiolytically generated H_2 is the abstraction of H atom from the

organic compounds by H atoms fragmented from the water. The latter contribution depends on the rate constants for this reaction, and relevant rate constants under conditions similar to those in the tank were measured.

A previously developed computer model was modified to encompass the high-solute concentrations typical for the waste solutions. The calculated dependence of the yield of H_2 on the rate of the hydrogen abstraction reaction is shown in figure 1. This model can be used to predict the yields of H_2 in various waste compositions; to within a factor of two, the model calculations agree with experimental observations. It was concluded from these studies that it is very important to maintain high (>1 M) concentrations of NO_3^- and NO_2^- in order to minimize the radiolytic formation of hydrogen. Under these conditions, the yield of H_2 will depend on NO_2^- concentration but not on NO_3^- concentration. On the other hand, as long as the concentration of these two components is high, it is unlikely that other additives will efficiently reduce the yield of the radiolytically generated H_2 .

Figure 1. Calculated yield of H_2 as a function of the rate for the H-atom abstraction reaction from the organic solute. All concentrations of the inorganic solute are the same as in the standard simulant.

A major effect of the irradiation was found to be the degradation of the original organic chelators that were added to the tank solutions. Some of these degradation products thermally generate H_2 and N_2O more efficiently than the original compounds. The dependence of the rate of the thermal generation of the two gases on the dose of preirradiation is shown in figure 2. This figure suggests that the rate of thermal generation in the tank is presently declining because the effective degradation products are themselves degraded by the radiolysis. This dependence on radiation dose is also proposed as an optional remediation strategy. Nitritotriacetate, iminodiacetate, aminoacetate, glycolate, glyoxylate, and formaldehyde are known degradation products that we determined will yield H_2 thermally. It was found that the rate of thermal generation of H_2 by the latter two is much greater than by any of the other degradation products or the original chelators. The activation energies for the thermal generation of H_2 by both were determined.

Figure 2. Rate of thermal generation of H_2 (circles) and N_2O (triangles) at 60 °C as a function of dose of preirradiation. The dashed line indicates the rate in the tank. Standard waste simulant containing 0.065 M HEDTA, EDTA and 0.1 M citrate.

The presence of organic compounds was found to lead to highly efficient radiolytic destruction of O_2 . Thus, it was concluded that the solution in the tank is essentially deoxygenated, an important consideration in the construction of flammability diagrams. Whereas the organic compounds were found to be necessary for the generation of N_2O , isotopic labeling (^{15}N) of an organic chelator, and the fact that organic compounds that do not contain nitrogen still generate N_2O , show that the source of N_2O is the inorganic nitrite and nitrate components. The radiolytic kinetics of NO_3^- and NO_2^- reactions have been extensively studied and these might generate N_2O . However, computer modeling showed that in our experiments, and in the tank, the generation of N_2O cannot result from known radiolytic mechanisms. The present knowledge of the reactions of nitrogenous radicals (e.g. NO_2 , NO_3) with organic compound does not allow quantitative modeling of the chemistry of N_2O generation.

In spite of the hydrogen generation, there would be little reason for concern if the gases were not retained within the waste volume in the tank, because only during the episodic releases does the composition reach flammability levels. To prevent the retention and subsequent venting, it is necessary to understand the retention mechanisms. Two surrogate systems for measuring hydrogen retention were studied - bubbling and pressurization - however, the retention was found to be strongly dependent on the method of gas introduction to the system. It was, therefore, concluded that the most realistic surrogate to the tank conditions would be to study the retention of radiolytically generated gases. Retention studies of the radiolytically produced gases showed two forms of retention of the gases; one that is tightly retained and therefore will not be released during venting episodes and the second that is easily released. The amount of the easily released gas that is retained depends strongly on the morphology of the slurry mixture. The ratios of the retained H_2 to retained N_2O determined for different conditions suggest that nonspecific interactions at the gas-liquid-solid interfaces dominate.

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