UCRL-JC-122573
PREPRINT
CONF-960421--11

Uranium Dioxide Dissolution Under Acidic Aqueous Conditions

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This paper was prepared for submittal to the
1996 International High Level Radioactive Waste Management Conference
Las Vegas, NV
April 29 - May 3, 1996

November 20, 1995

Lawrence Livermore National Laboratory

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I. INTRODUCTION

Understanding of the long-term dissolution of waste forms in groundwater is required for the safe disposal of high level nuclear waste in a geologic repository, because waste-form radionuclides could be released by dissolution and transported in groundwater. The dissolution of the uranium dioxide (UO_2) matrix in spent nuclear fuel is considered the rate-limiting step for release of radioactive fission products. The intrinsic UO_2 dissolution rate sets an upper limit on the aqueous radionuclide release rate.

Unsaturated spent fuel tests (1) have shown that pH's of leachates have decreased to a range of 4 to 6, presumably due to air radiolysis that oxidizes nitrogen, producing nitric acid. Dissolution rates under such acidic conditions may be different than those previously reported for alkaline groundwater conditions. No dissolution rate measurements of UO_2 or spent fuel have been reported for acidic conditions possibly relevant to a geologic repository.

The purpose of our work has been to measure the intrinsic dissolution rates of uranium dioxide under acidic conditions that are relevant to a repository and allow for modeling. Experiments have been completed at room-temperature and 75 C, pH's of 4 and 6, and air and oxygen saturated aqueous solutions. These are compared with earlier work on spent fuel and UO_2 using alkaline solutions.(2)

II. DESCRIPTION

A planned set of 27 UO_2 dissolution experiments was developed using statistical experimental design methodology. These experiments would allow a systematic evaluation of the effects of temperature (25-75°C), pH (4-6) and dissolved oxygen (80-8000 ppb) concentrations on the uranium dissolution rate. The initial results reported here include dissolution rates for two UO_2 polycrystalline samples at 25 and 75°C, and pH's 4 and 6, all at atmospheric oxygen conditions, 8 ppm dissolved oxygen.

The experiments use single-pass flowthrough conditions to prevent precipitation and other competing reactions from distorting dissolved uranium concentration measurements. The samples were from the same batch of polycrystalline UO_2 used in previous experiments.(2) Nitric acid was used to adjust pH.

III. RESULTS AND CONCLUSIONS

Figure 1 shows a time history of the dissolution results. The sample 1 (S1) leaching solution was initially at a pH of 3.8 (4), while the sample 2 (S2) leaching solution initially had a pH of 5.9 (6). Both samples were initially at room temperature (~20°C). The dissolution rates (DR) appear similar in the range of 2 to 6 mg/(m^2·day). After day 11 the buffer solutions were switched. Sample 2, now at pH=4, initially increased its dissolution rate and sample 2, switched to pH=6, decreased. They both returned closer to their earlier value, although the ratio of dissolution rates [DR(pH=4)/DR(pH=6)] seems to have increased. After day 20 the leaching solutions were switched back to their original samples and the temperature increased to 75°C. The dissolution rate of sample 1, again at pH=4, increased about ten-fold while sample 2 at pH=6 unexpectedly remained about the same. After four more sampling days the sparge gas was switched to air, with its small fraction of CO_2. This did not have any readily apparent affect on the dissolution rates. The samples were returned to room temperature after day 30. The pH= 4 dissolution rate returned to near its original room-temperature value. The pH=6 sample rate dropped below its previous room-temperature amount to a barely detectable level.

Previously measured room-temperature UO_2 dissolution rates in alkaline, low-carbonate waters yield a uranium dissolution rate of 3.9 mg/(m^2·day) at a leaching solution pH of 8 and 2.6 mg/(m^2·day) at a pH of 10. For the pH ranges of 4 to 6 and 8 to 10, these early results indicate that there is no significant effect of acidity versus alkalinity on room-temperature UO_2 dissolutions rates. The ten-fold effect on dissolution rate of increasing temperature of the pH=4 sample seems closer to the outcome from the high-carbonate alkaline conditions reported earlier.[2]

ACKNOWLEDGMENTS

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48. This work was supported under activities D-20-53 of the Yucca Mountain Project Spent Fuel Waste Form Task (YMP WBS element 1.2.2.4.1) and the AECL/USDOE Cooperative Project sponsored by the DOE Office of Civilian Radioactive Waste Management.

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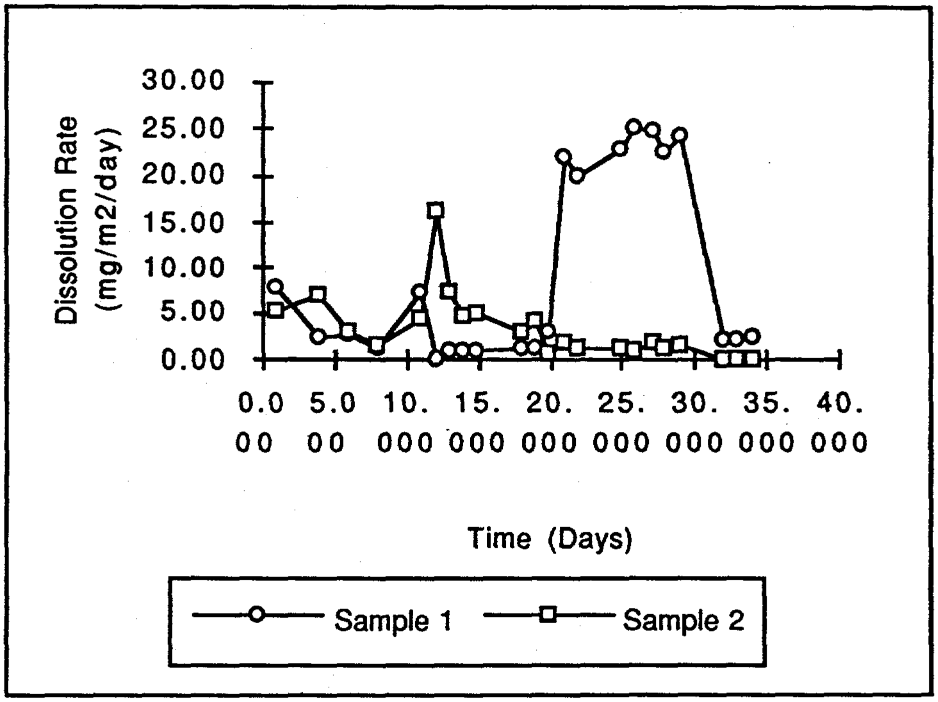
Figure 1. Acidic Dissolution Rates of Uranium Dioxide



Work performed under the auspices of the U.S. Department of Energy and the AECL/USDOE Cooperative Project by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.