CHARACTERISTICS OF AQUEOUS COLLOIDS GENERATED BY CORRION OF METALLIC URANIUM FUEL

Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, IL 60439

by

Jeffrey A. Fortner, Carol J. Mertz, and S. Seifert

To be presented at the BESSRCAT Users' Meeting, May 3, 2002, and also at the Synchrotron Environmental Science-II Meeting, May 6-8, 2002

This work is supported by the by the Department of Energy, Basic Energy Sciences, Office of Science, under Contract W-31-109-ENG-38.

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Jeffrey A. Fortner and Carol J. Mertz
Chemical Technology Division,
Soenke Seifert
Chemistry Division
Argonne National Laboratory

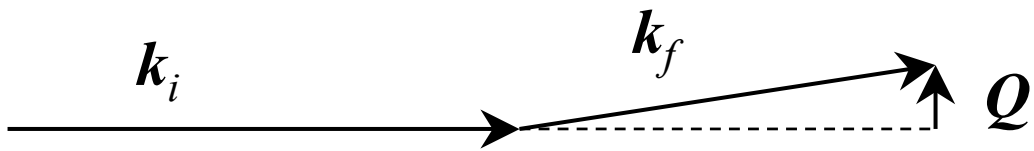
- INTRODUCTION

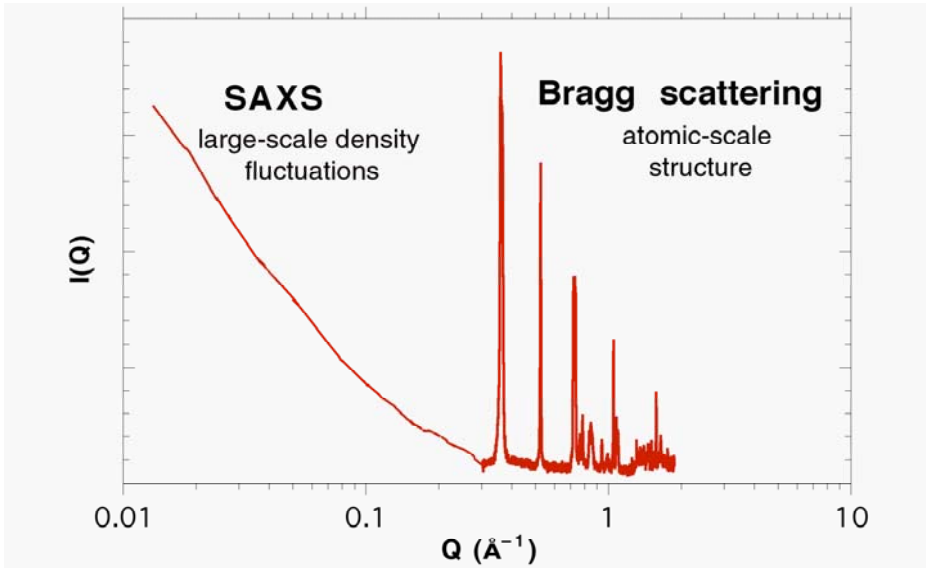
  Metallic uranium fuel from the Hanford N-Reactor has been corroded by contact with solution chemistry conditions ranging from deionized water to simulated repository groundwater (silicate/carbonate saturated). The metallic uranium fuel represents a substantial portion of the DOE-owned spent fuel inventory. While it is widely observed that the aqueous corrosion of metallic uranium fuels is generally rapid, little attention has been paid to the generation of uranium-containing colloids arising from this corrosion. These colloids may be of concern in the environment of a geologic repository, such as the proposed Yucca Mountain site. Waste-generated colloids may provide a transport mechanism for radioisotopes that is independent of solubility and sorption limitations.

Analyses of solution (including colloids) and altered solids were done by inductively coupled plasma mass spectrometry, x-ray diffraction, transmission electron microscopy (TEM), photon correlation spectrometry (PCS), and synchrotron small-angle x-ray scattering (SAXS). The SAXS was done using the pinhole camera with a 3 m flight path at the BESSRCAT beamline, with a high-energy incident beam (17.1 keV), approximately 50 eV below the U-L_{III} edge. The resulting small-angle scattering was due *only to the uranium*, as confirmed by running blank solutions of the silicate and carbonate solutions. Most corrosion conditions yield nanophase UO_2 colloids, except the high-carbonate solutions, where distinct $(Ca,U)CO_3$ plate-like colloids are observed. Excellent quantitative agreement among the complementary TEM, PCS, and SAXS data are found.

Small Angle X-ray Scattering

- SAXS: $Q\,\lambda << 1$, where $Q = |\boldsymbol{k}_f - \boldsymbol{k}_i|$ and $k = 2\pi/\lambda$





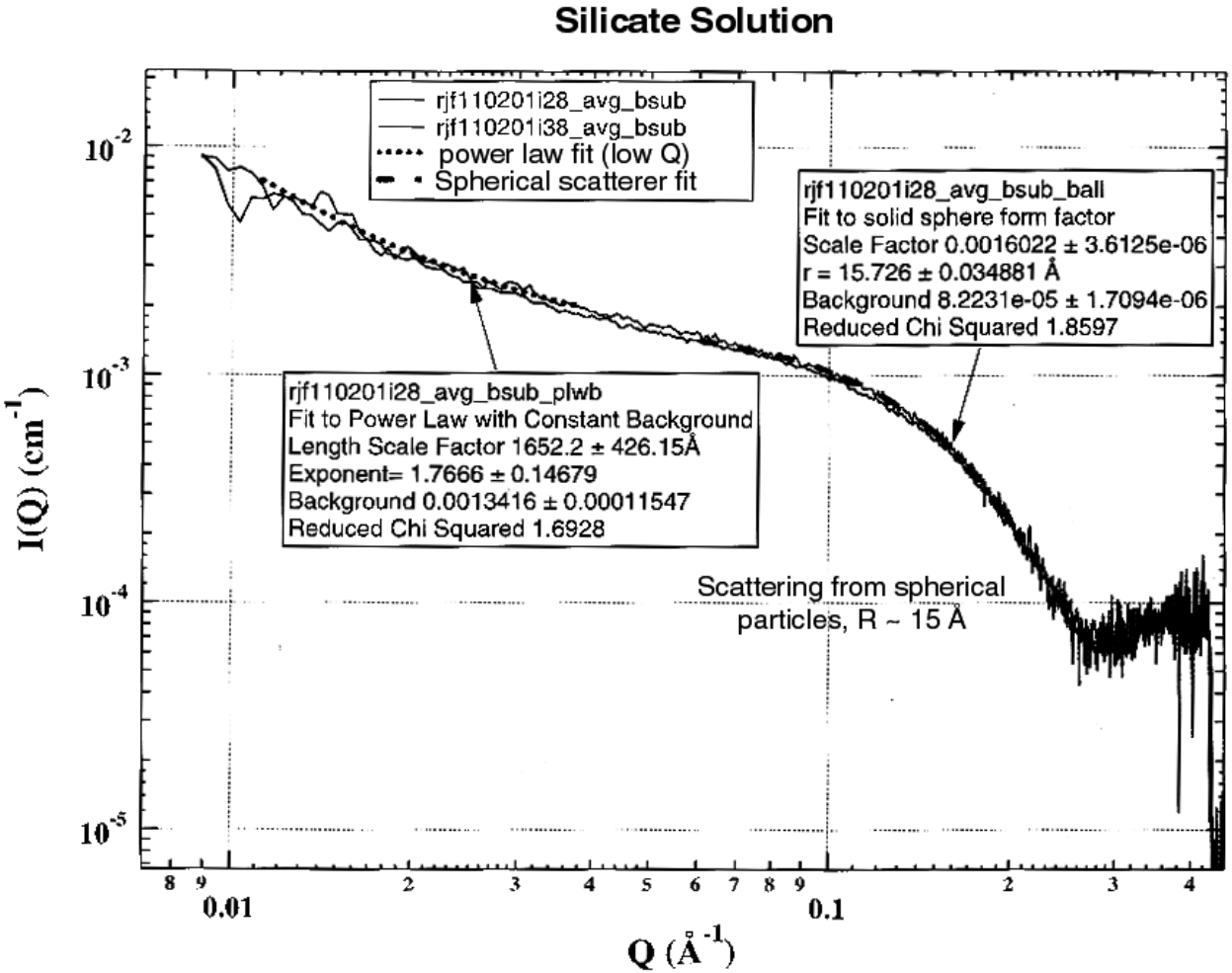
Experimental conditions

- Pinhole camera, 3m flight path at BESSRCAT beamline.
- High-energy incident beam, 50 eV below U-L_{III} edge (17.1 keV).
- Observed scattering only from uranium-bearing colloids. The blank solutions (no uranium colloids) of silicate and carbonate were indistinguishable from DIW.

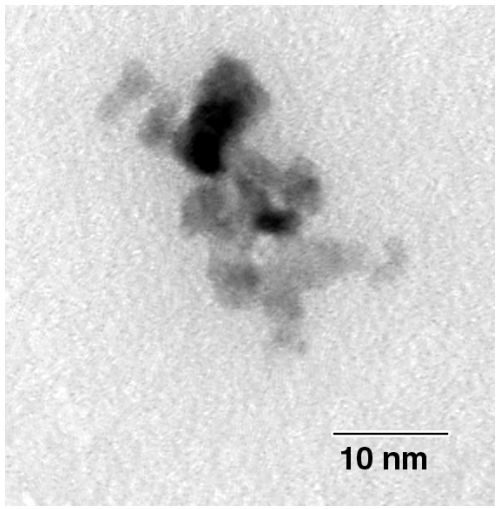
Generation of Colloids

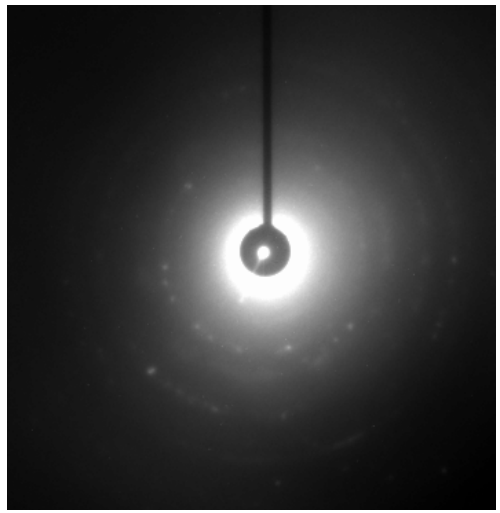
- Static corrosion tests reacted unirradiated Hanford N-reactor metallic uranium fuel coupons at 30ºC for 200 days.
- Leachate solutions included deionized water (DIW), silicate (1 mM), carbonate (1 mM), and Nevada Test site well water (USGS J-13 well).
- Rapid corrosion of metallic uranium generates nanophase UO_2 and other uranium-bearing colloids

SAXS from uranium oxide colloids in silicate water



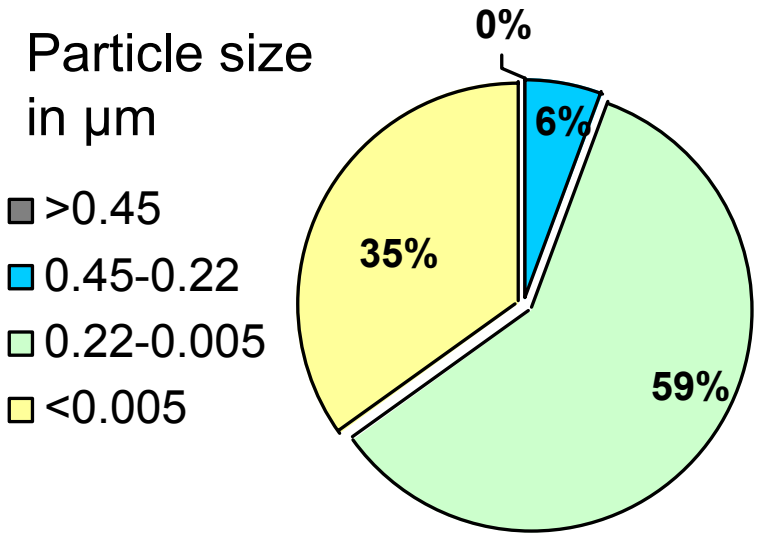
UO_2 Colloids-TEM



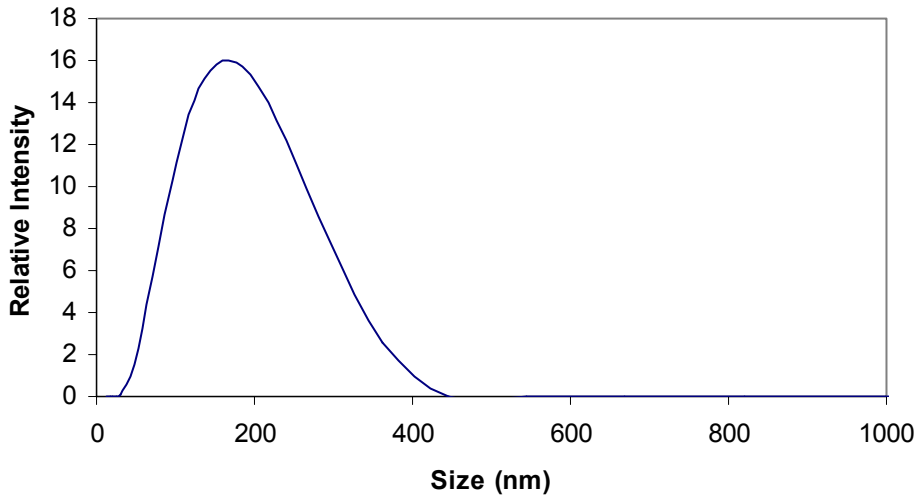


Colloids formed in silicate solution

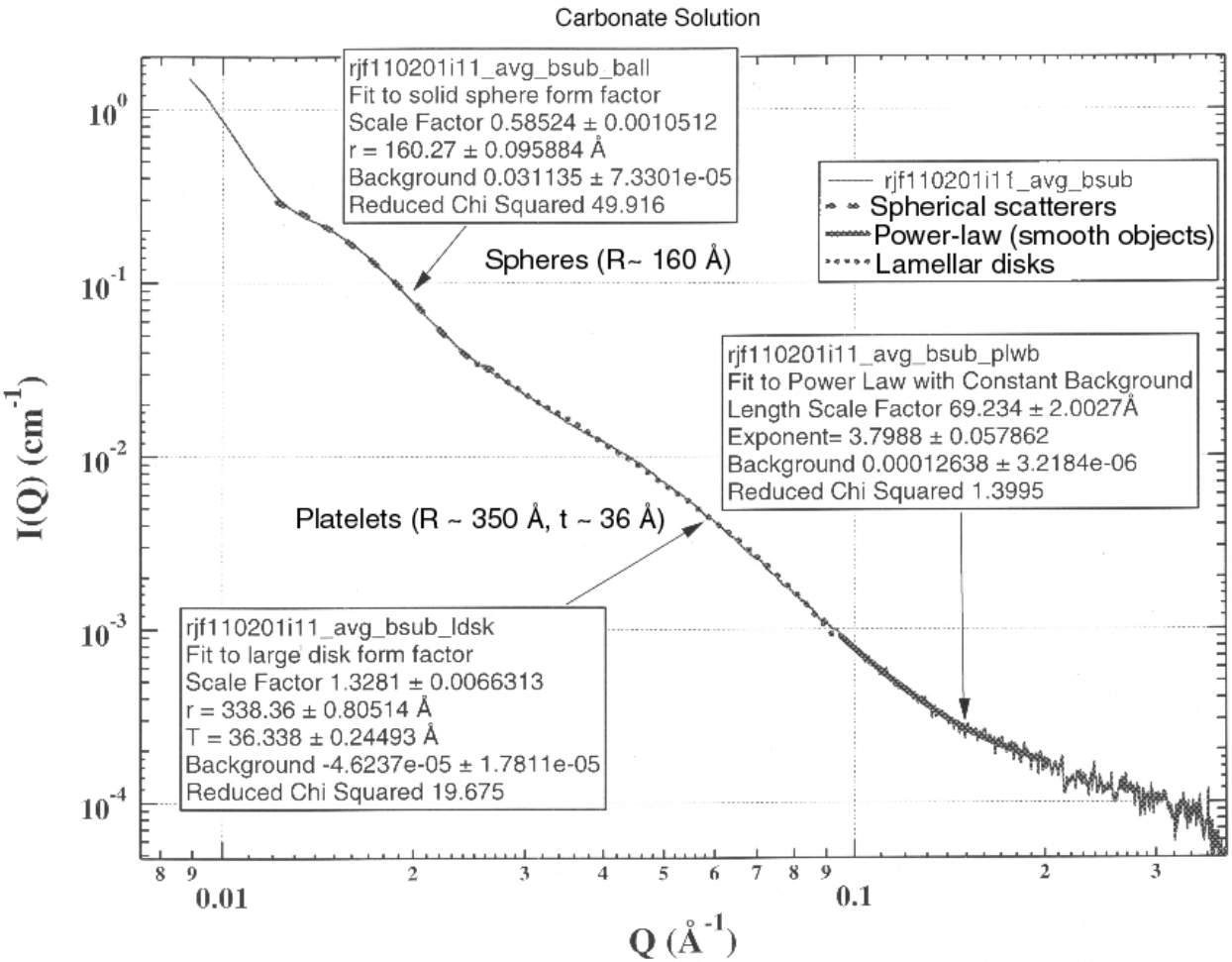
ICP-MS: predominantly uranium-bearing colloids



PCS: mean diameter ~140 nm, low colloid concentration (ppm range)



SAXS from uranium oxide colloids in carbonate water



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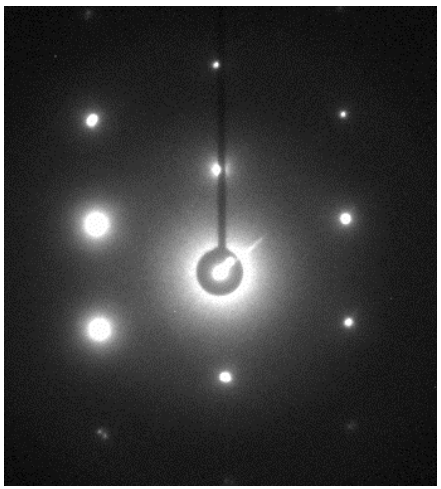
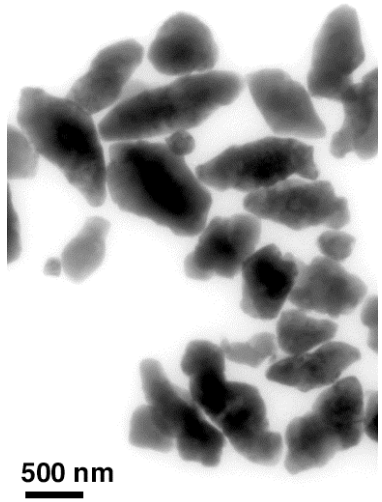
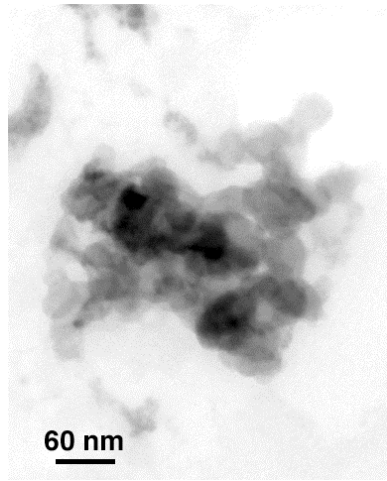
Carbonate colloids-TEM





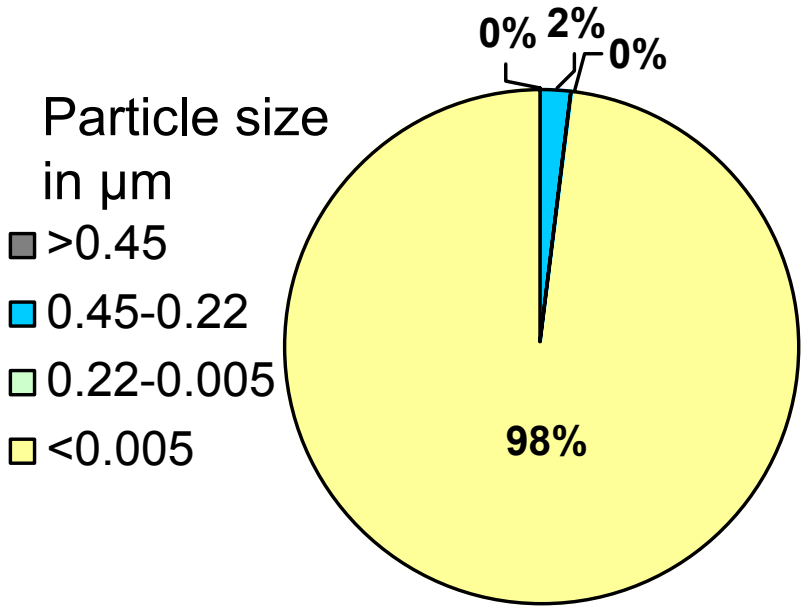
Ca-carbonate with U



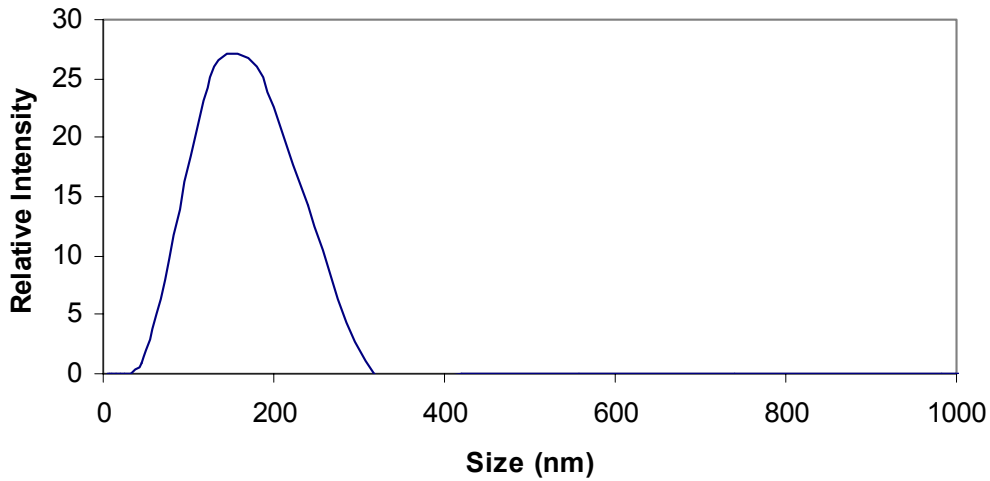
U carbonate

Colloids formed in carbonate solution

ICP-MS: predominantly dissolved uranium



PCS: mean diameter ~160 nm, very low colloid concentration (sub-ppm range)



[Ca] ~4-5 times above $CaCO_3$ solubility limit