Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the HZDR. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the reference number of the proposal / experiment to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF ROBL-CRG	**Experiment title:** Effect of the preparation method on the properties of Pu(IV) intrinsic colloids	**Experiment number**: 20-01-759
Beamline: BM 20	**Date of experiment**: from: 13.11.2015 to: 17.11.2015	**Date of report**: 26.01.2017
Shifts: 12	**Local contact(s)**: Christoph Hennig	*Received at ROBL:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Fundamental knowledge on intrinsic plutonium colloids is important for the prediction of plutonium behaviour in the geosphere and in engineered systems. The first synthetic route to obtain salt-free intrinsic plutonium colloids by ultrasonic treatment of PuO_2 suspensions in pure water is reported. Kinetics showed that both chemical and mechanical effects of ultrasound contribute to the mechanism of Pu colloid formation. In the first stage, fragmentation of initial PuO_2 particles provides larger surface contact between cavitation bubbles and solids. Furthermore, hydrogen formed during sonochemical water splitting enables reduction of Pu(IV) to more soluble Pu(III), which then re-oxidizes yielding Pu(IV) colloid. This mechanism is shown in Figure 1. A comparative study of nanostructured PuO_2 and Pu colloids produced by sonochemical and hydrolytic methods, has been conducted using HRTEM, Pu L_{III}-edge XAS (Figure

2), and O K-edge NEXAFS/STXM. Characterization of Pu colloids revealed a correlation between the number of Pu-O and Pu-Pu contacts and the atomic surface-to-volume ratio of the PuO_2 nanoparticles. NEXAFS indicated that oxygen state in hydrolytic Pu colloid is influenced by hydrolysed Pu(IV) species to a greater extent than in sonochemical PuO_2 nanoparticles. In general, hydrolytic and sonochemical Pu colloids can be described as core-shell nanoparticles composed of quasi-stoichiometric PuO_2 cores and hydrolyzed Pu(IV) moieties at the surface shell. Figure 3 demonstrates HRTEM image of the sonochemical and hydrolytic plutonium nanocolloid. The results have been submitted as a full paper to Scientific Reports and is currently under review:
Dalodière E., Virot M., Morosini V., Chave T., Dumas T., Hennig C., Wiss T., Dieste Blanco O., Shuh D.K., Tyliszcak T., Venault L., Moisy P., Nikitenko S.I. " Insights into the sonochemical synthesis and properties of salt-free intrinsic plutonium colloids" *Scientific Reports* 2016, submitted.

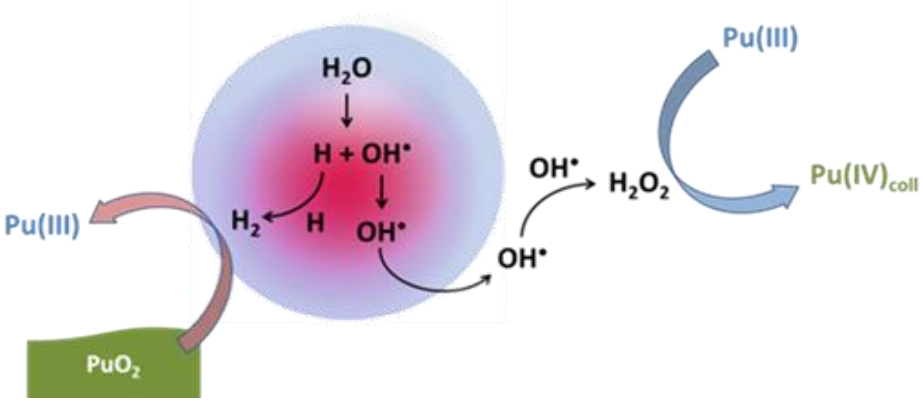

Figure 1. Suggested mechanism of the sonochemical plutonium colloids formation.

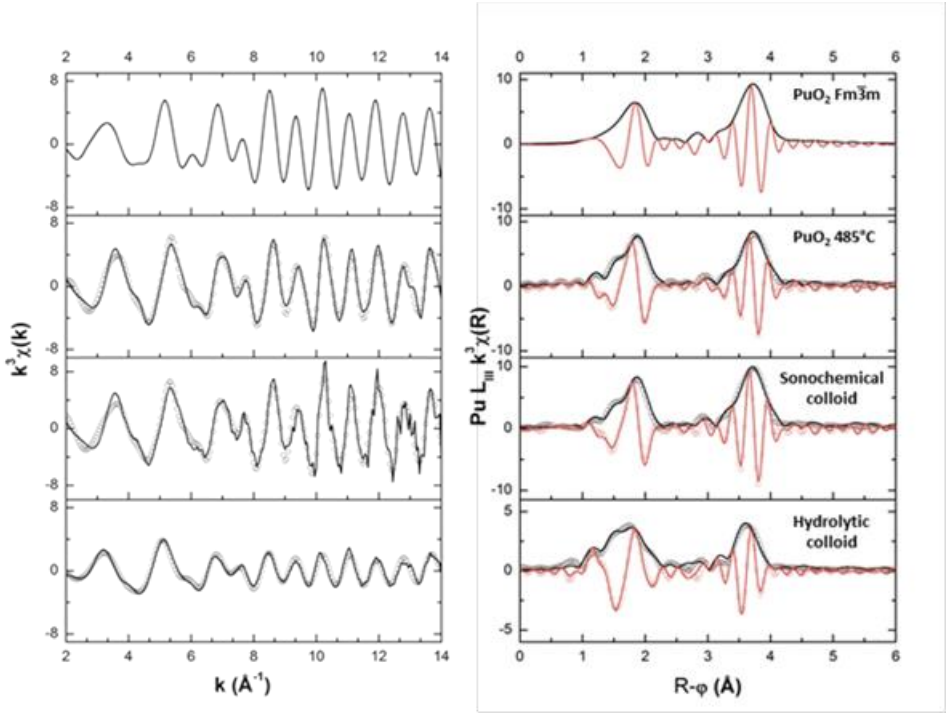

Figure 2. Experimental k^3-weighted EXAFS spectra (left column) and corresponding real parts obtained for Fourier Transform magnitudes. Data are obtained in the $2Å^{-1}<k<14Å^{-1}$ range.

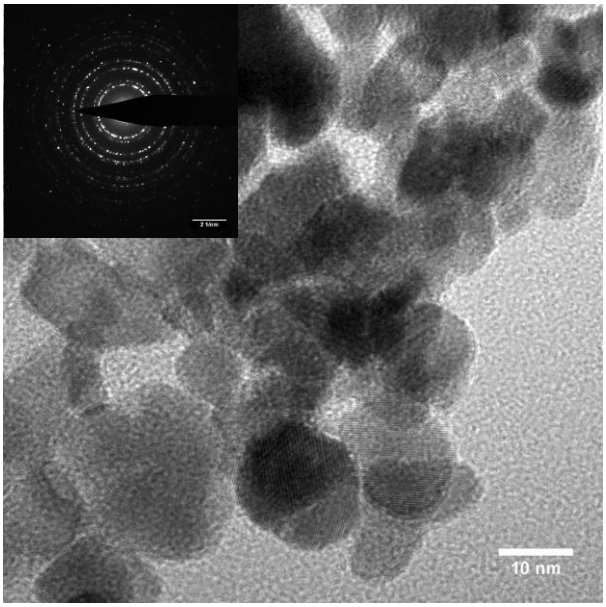

Figure 3. HRTEM images and electron diffraction patterns of PuO_2 nanoparticles from sonochemical colloid.