



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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.



	Experiment title: Investigation of uranium sorption in synthetic zeolites by HERFD-XANES and EXAFS	Experiment number: A20-01-838
Beamline:	Date of experiment: from: 24/05/2022 to: 30/05/2022	Date of report: 25/09/2022
Shifts:	Local contact(s): Prof. Kristina Kvashnina PhD Elena Bazarkina	<i>Received at ESRF:</i> 25/09/2022
Names and affiliations of applicants (* indicates experimentalists): Sobczyk M., ^{(1)*} Bajda T., ^{(1)*} Bazarkina E., ^{(2)*} Kvashnina K. ^{(2)*} <i>(¹)AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, al. Mickiewicza 30, 30-059 Cracow, Poland</i> <i>(²)The Rossendorf Beamline (BM20), European Synchrotron Radiation Facility, 71 Anenue de Martyrs, 38043 Grenoble, France</i>		

Report:

The spectroscopic experiments were carried out at the Rossendorf Beamline - ROBL20 of the ESRF between 24th of May 2022 until 30th of May 2022. The investigation accounts for removal of U by synthetic zeolites as prospective sorbents possible to be hydrothermally synthesized out of industrial by-products (fly-ashes) and applied as water purification agents from highly valent radionuclides. Zeolites of both the natural origin (Chmielewska et al., 2022; Jiménez-Reyes et al., 2021; Khan et al., 2021) as well as synthesized out of raw materials, such as kaolinite and fly-ash (Boycheva et al., 2020) were previously widely used in water purification from uranium.

In the present study, we have investigated the U removed from water solutions by synthetic zeolites resembling naturally occurring structures of the sodium faujasite (FAU), gismondite (GIS) and (LTA) zeolites. We have investigated how different speciation of U present in water solution once varying pH conditions are applied, affects both sorption properties of studied materials as well as their removal efficiency. In total, during the six days of the allocated beamtime, we were able to measure 16 samples (15 zeolites = 5 structures on 3 equilibrium pH levels - 4, 7 and 10 + one reference, pure U salt - $\text{UO}_2(\text{NO}_3)_2$) at both U-M₄ and U-L₃ edges together with long scans on U-L₃ edge to measure the EXAFS spectroscopy region.

The spectrometer was aligned using the reference compound $\text{UO}_2(\text{NO}_3)_2$, the geometry was optimized for recording M_β or L_α emission line for U M₄ and U L₃ edges.

Obtained U-M₄ spectra revealed U removed onto assessed synthetic zeolites at various pH keeps the hexavalent oxidation state after sorption. Small energy shifts ~0.6eV (Table.1) are visible on the M₄ spectrum for LTA zeolite. Such energy shift can be associated with shortening the axial O=U=O bond length of around 0.035Å in the hexagonal bipyramid (Boulanger et al., 2020). This further showcases the partially-hydroxylated uranyl cation's free diffusion inside the zeolite's channels caused by distorted structure of LTA zeolite crystallites where the diffusion process itself might be deteriorated. In the case when zeolite crystallites are well developed after the hydrothermal synthesis (based on the SEM microimages with EDS chemical analysis in the microspot), the energy shift in the region of 3732.4eV ± 0.4eV does not appear as clearly visible for both, NaP1-FA (GIS) zeolite as well as NaX-FA (FAU) zeolite, independently of the reaction's pH. Furthermore it can be concluded, that the peaks with highest intensities around 3726.6eV, are present for zeolites reacted under the neutral pH region, where sorption of U has the highest values, equals to 918.41ppm U and 892.71ppm U, for FAU and GIS zeolites, respectively (Figure 1.). For acidic pH (pH_{eq} ~ 4) and basic pH (pH_{eq} ~ 10) the peaks intensities lower down, hence U sorption efficiency lowers as well which is observable onto U-M₄ spectrums unanimously for all three studied synthetic zeolites.

The spectra obtained at U L₃-edge reveal the similar pattern and confirms observations from the U M₄-edge measurements. At basic pH, uranyl dication (UO₂²⁺) forms neutral or negatively charged polyhydroxo-uranyl species (UO₂(OH)₂, UO₂(OH)₃⁻ (Maher et al., 2013) that perturbs zeolites sorption efficiency due to the electrostatic interactions between sorbent and the sorbate along with free diffusion where large uranyl hydroxy complexes are unable to penetrate the channels and cavities in the zeolite structure due to size-selective repulsion of too large ionic species.

To conclude, all U removed by investigated zeolitic sorbents is present at the hexavalent oxidation state, independently of the reaction's pH and structure of the zeolite. An ion-exchange with extraframework Na⁺ cations along with U precipitation in the form of Na-metaschoepite are elucidated as the predominant sorption mechanisms responsible for the U removal on studied zeolites (complementarily to U-M₄ and U-L₃ edges HERFD-XANES spectrums, based on the XPS peak of U 4f_{7/2} equals to 382.2eV of the binding energy) (Ilton & Bagus, 2011). Therefore, at neutral pH range, uranium is also immobilized on the studied materials, in the form of three-dimensional solid mineral precipitate. Moreover, the micromorphology of the zeolite crystals affects the sorption of U, which is visible as energy shifts in the region close to 3732eV on U-M₄ spectrum for LTA zeolite, which crystals are insufficiently crystallized, probably due to limitations originating from the applied hydrothermal synthesis procedure and complex raw material use as a hydrothermal reaction substrate (coal fly-ash).

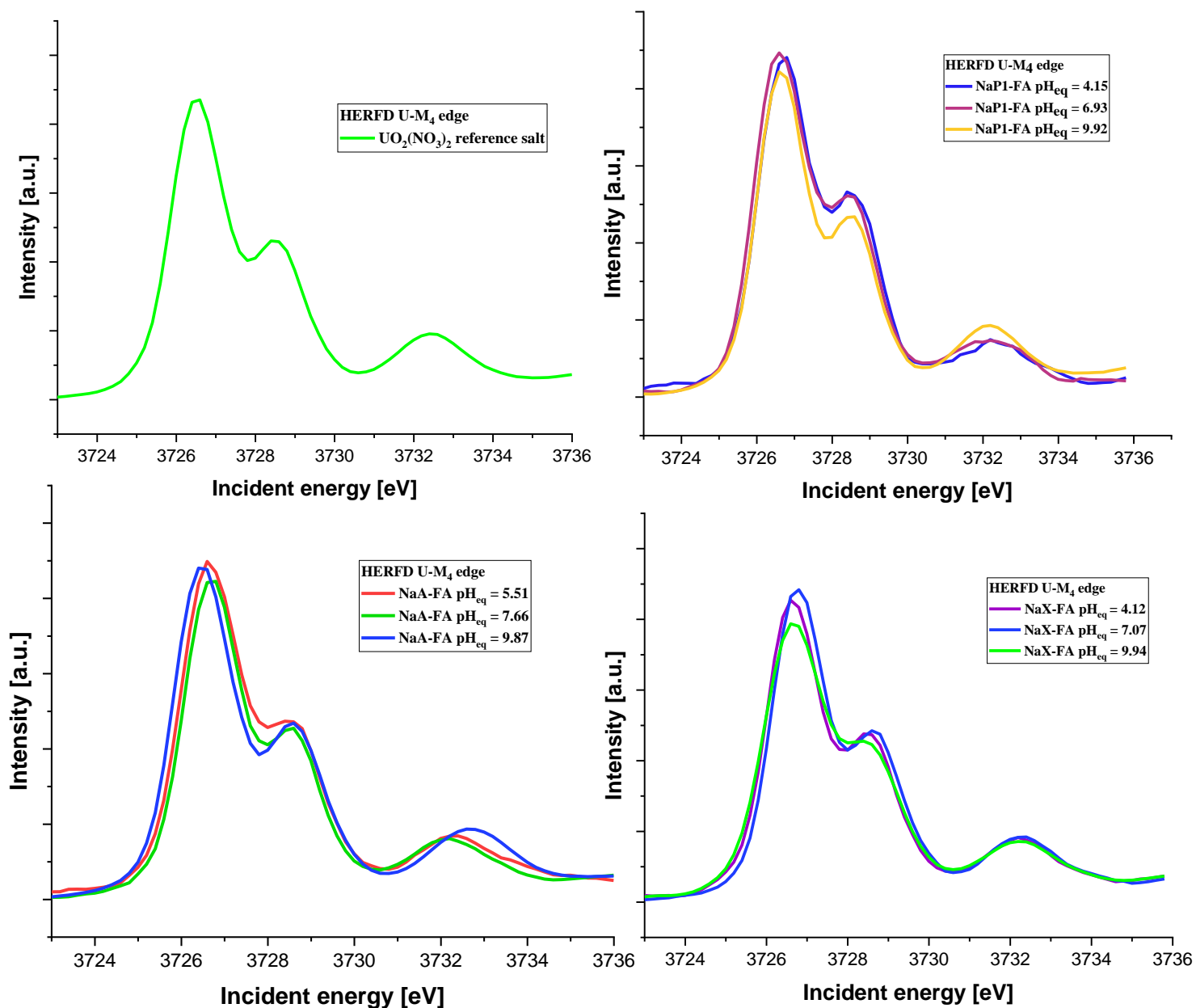


Figure 1. U-M₄ spectras for all assessed zeolite samples at varying pH conditions (NaP1-FA - GIS structure, NaA-FA- LTA structure, NaX-FA - FAU structure) along with the reference salt spectrum - UO₂(NO₃)

Table 1. U-M₄ peak positions for all assessed synthetic zeolites with energy shifts at varying pH and maximum U sorption capacity marked in bold

Material	Position of the 1 st shoulder on U M ₄ edge spectrum [eV]	Position of the 2 nd shoulder on U M ₄ edge spectrum [eV]	Position of the 3 rd shoulder on U M ₄ edge spectrum [eV]	U sorption capacity [ppm U]
Reference salt - UO ₂ (NO ₃) ₂	3726.4	3728.6	3732.4	-
GIS, pH _{eq} = 4.15	3726.8	3728.4	3732.2	176.66
GIS, pH _{eq} = 6.93	3726.6	3728.4	3732.2	918.41
GIS, pH _{eq} = 9.92	3726.6	3728.4	3732.2	412.99
FAU, pH _{eq} = 4.12	3726.6	3728.4	3732.2	254.61
FAU, pH _{eq} = 7.07	3726.8	3728.5	3732.2	892.71
FAU, pH _{eq} = 9.94	3726.8	3728.4	3732.2	212.24
LTA, pH _{eq} = 5.52	3726.6	3728.4	3732.2	505.25
LTA, pH _{eq} = 7.66	3726.8	3728.6	3732.2	829.66
LTA, pH _{eq} = 9.87	3726.5	3728.6	3732.8	153.84

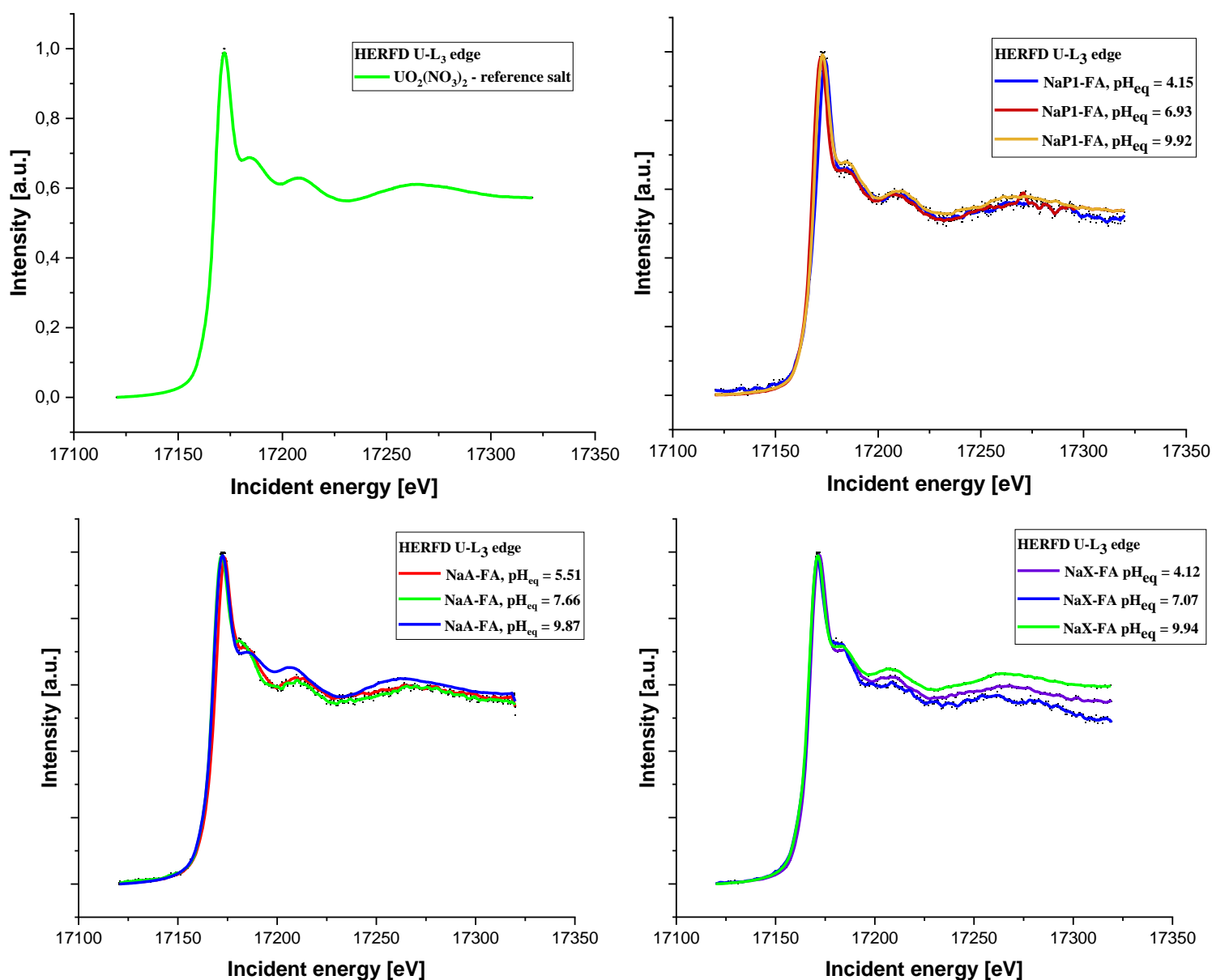


Figure 2. U-L₃ spectras for all assessed zeolite samples at varying pH conditions (NaP1-FA - GIS structure, NaA-FA- LTA structure, NaX-FA - FAU structure) along with the reference salt spectrum - UO₂(NO₃)

References

1. Boulanger, N., Kuzenkova, A. S., Iakunkov, A., Romanchuk, A. Y., Trigub, A. L., Egorov, A. v., Bauters, S., Amidani, L., Retegan, M., Kvashnina, K. O., Kalmykov, S. N., & Talyzin, A. v. (2020). Enhanced Sorption of Radionuclides by Defect-Rich Graphene Oxide. *ACS Applied Materials and Interfaces*, 12(40), 45122–45135. <https://doi.org/10.1021/acsami.0c11122>
2. Boycheva, S., Zgureva, D., Lazarova, K., Babeva, T., Popov, C., Lazarova, H., & Popova, M. (2020). Progress in the utilization of coal fly ash by conversion to zeolites with green energy applications. *Materials*, 13(9). <https://doi.org/10.3390/MA13092014>
3. Chmielewská, E., Majzlan, J., & Bujdoš, M. (2022). Clinoptilolite with surface-enhanced functionality for radionuclide and inorganic pollutants removal . *Journal of Radioanalytical and Nuclear Chemistry*. <https://doi.org/10.1007/s10967-022-08375-1>
4. Ilton, E. S., & Bagus, P. S. (2011). XPS determination of uranium oxidation states. *Surface and Interface Analysis*, 43(13), 1549-1560. <https://doi.org/10.1002/sia.3836>
5. Jiménez-Reyes, M., Almazán-Sánchez, P. T., & Solache-Ríos, M. (2021). Radioactive waste treatments by using zeolites. A short review. *Journal of Environmental Radioactivity*, 233. <https://doi.org/10.1016/J.JENVRAD.2021.106610>
6. Khan, S., Anjum, R., & Bilal, M. (2021). Revealing chemical speciation behaviors in aqueous solutions for uranium (VI) and europium (III) adsorption on zeolite. *Environmental Technology and Innovation*, 22. <https://doi.org/10.1016/j.eti.2021.101503>
7. Maher, K., Bargar, J. R., & Brown, G. E. (2013). Environmental speciation of actinides. In *Inorganic Chemistry* (Vol. 52, Issue 7, pp. 3510-3532). <https://doi.org/10.1021/ic301686d>
8. Scheinost, A. C., Claussner, J., Exner, J., Feig, M., Findeisen, S., Hennig, C., Kvashnina, K. O., Naudet, D., Prieur, D., Rossberg, A., Schmidt, M., Qiu, C., Colomp, P., Cohen, C., Dettona, E., Dyadkin, V., & Stumpf, T. (2021). ROBL-II at ESRF: a synchrotron toolbox for actinide research. *J. Synchrotron Rad*, 28, 333–349. <https://doi.org/10.1107/S1600577520014265>