Developing an in situ EXAFS experiment of microwave-induced gelation

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Abstract Internal gelation is an advanced route to produce small spheres of metal from a nitrate solution. In this work, microwave heating is used to trigger the gelation of the solution. X-ray absorption spectroscopy is a powerful tool to follow the gelation advancement and verify the completeness of a reaction, but in order to use it on falling nitrate droplets, the study is split into two experiments. First, a fluorescence measurement has been carried out on a trickle of small falling cerium nitrate droplets generated at high frequency to verify that capturing a discontinuous signal would not generate too much noise. Then, a measurement of silver nitrate undergoing gelation in a microwave cavity has been performed in transmission mode, which proved that a fast recording method is suitable for following the evolution of chemicals during such a reaction. The combination of both analyses confirms that it is possible to study microwave gelation of falling droplets using X-ray absorption spectroscopy at the SuperXAS beamline.

Graphical Abstract

Keywords EXAFS · Internal gelation · Microwave · Reaction advancement

1 Introduction

In order to produce metal particles in small size and spherical shape for nuclear fuel, the gelation route has been used for more than 40 years [16, 25]. The sphere particles are obtained by precipitation of a metal nitrate solution in the form of droplets. Unlike in the classical (external) gelation, internal gelation is an advanced process where the precipitation of the metal nitrate is triggered by thermal

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decomposition of a reactant (hexamethylenetetramine also called HMTA) [18]. This leads to a pH shift activating the metal hydroxide precipitation, leading to the formation of colloids in the solution. An introduction to internal gelation has already been presented by Ganguly in [10].

In the PINE project [17], which aims to reduce the amount of nuclear waste, microspheres of nuclear fuels are obtained by a microwave internal gelation (MIG) process [5]. The heat is usually brought to the mixture through conduction by contact with hot silicon oil; however, MIG significantly simplifies the process since it suppresses the recycling step of the oil and washing phases of the microspheres [7]. The microspheres, generated at high frequency (several kHz), pass in a microwave resonance cavity, where their heating occurs. The residence time of a droplet in the cavity is about 50 ms.

Because of the necessary addition of reactants, the number of species present in the MIG solution is therefore higher than for the external gelation process, and the possible interactions are much more numerous. In order to understand and improve the process, the degree of advancement of the gelation inside the falling droplet needs to be determined. This can be done thanks to a X-ray absorption spectroscopy (XAS) measurement of droplets at different heights in the cavity. The metal nitrates used in this study are Ce(III) and Ag(I) so that no radioprotection from active material is required at the beamline. The extended X-ray absorption fine spectrum (EXAFS) analysis provides information on the chemical environment of the atoms inside the solution, thus enabling the identification of the species inside the sample, and is commonly used to study actinides in nuclear fuel [4, 6, 8, 9].

Since the XAS measurements have to be performed on drops during their precipitation happening in the microwave cavity, the drop generation and microwave heating device need to be set up in the hutch. The main aim of these experiments is therefore to verify the applicability of the setup in the superXAS beamline, tackling two challenges: the mobility of the drops and the swiftness of the chemical reaction.

The present work is a preparation study to a future XAS experiment in which the evolution of the chemistry will be measured during internal gelation inside the droplets of heavy metal generated with the final production unit.

2 Experimental

In the XAS measurement, the sample is positioned and fixed in front of the synchrotron light beam. As the energy of the synchrotron photons varies, the detector counts photons from the sample (in transmission, reflection or fluorescence mode) over an integration time.

Although XAS is a widely used method [3], the experiment described in this work is challenging for two reasons. In order to collect a spectrum, a few minutes are usually needed. In our application, the sample is (a) moving (in a free fall movement) and (b) evolving, i.e., the complete chemical change of the sample between initial and final phases due to the reaction occurs in the order of the minutes (much below the usual spectrum recording time) and a sufficient number of spectra have to be recorded in that time frame. Given the differences between a classical setup and our experiment, the experiment was an opportunity to reproduce the real conditions of the MIG process and check the feasibility of EXAFS measurements on our samples, treating separately these two aspects. Therefore, on one hand, one static sample was measured at high speed during its gelation, and on the other hand, a stream of droplets was recorded by fluorescence at a given position inside the cavity (see Fig. 1).

Experiments have been carried out in the SLS at the SuperXAS beamline [1]. The beam energy range of the SuperXAS beamline and its specific equipment (such as the Quick EXAFS monochromator) made that beamline a perfect candidate for the study. Two types of samples have been studied, depending on the task:

1. Falling droplets of a cerium solution composed of:
 - metal solution made with cerous nitrate $\text{Ce}(\text{NO}_3)_3$ and water (0.8 M). This is the surrogate part of the experiment (the radioactive uranium being replaced by a non-radioactive element cerium). Cerium was selected because its chemical properties and therefore synthesis behaviour are similar to

Fig. 1 The goal of the present study is to demonstrate the feasibility of measuring gelation advancement in small drops falling through a microwave cavity

Fig. 2 Equipment used for the cerium experiment. *Left* View of the vibrator. *Center* Droplet trickle and stroboscope. *Right* Droplets under stroboscope light

those of plutonium [27], and uranium to a lesser extent [13].

- hexa-solution made with urea $\text{CH}_4\text{N}_2\text{O}$, hexamethylenetetramine (HMTA) $(\text{CH}_2)_6\text{N}_4$ and water. This solution contains the HMTA which decomposes with temperature rise and triggers the gelation reaction. The composition of this solution is similar to that of the internal gelation of radioactive elements [22].
2. Precipitating metal: silver nitrate (AgNO_3) was mixed to water or ammonia. During this experiment, the precipitation of the silver is triggered by microwave heating.

2.1 Falling droplets

The droplets were created by an oscillatory system (see Fig. 2, left). The size of the ejected spheres is chosen by selecting a diameter for the capillary placed at the edge of the feeding pipe. At this high drop generation frequency (several kHz), the eye cannot distinguish discrete falling droplets from a constant flow (Fig. 2, center), and a stroboscope is used to visualize the shape and spacing of the droplets (Fig. 2, right).

In the case of a discrete flow (sometimes a droplet is being measured, sometimes nothing), due to a too high noise/signal ratio, a measurement in transmission is not possible without a well-tuned chopper. For this reason, a transmission measurement could be performed only with the use of a chopper that would hide the measurement window when no drop is in it: this requires that the chopper is synchronized (in phase) with the drop generator. However, a fluorescence mode does not cause this problem, and focus was brought on the fluorescence measurements of the solution.

2.2 Silver precipitation

The reaction(s) occurring during internal gelation of heavy metal nitrates is of the order of the second (similar to the precipitation of silver studied in this work), and the time resolution of the measurements has to be of the same order of magnitude in order to obtain information on the sample at different degrees of reaction advancement.

The precipitation of the silver solution occurs within a few seconds, and the QEXAFS is chosen for its high sampling frequency: the concentration variations of the species can be retrieved. Thus, the measured signal provides information on the evolution of the sample.

Fig. 3 Setup to hold and heat the sample in the hutch.

- a** Photograph of the setup.
b Scheme of the setup

For this experiment, the silver-based solution was used because the experimental conditions of silver particle formation by photoreduction are well detailed in the literature [11, 12, 21, 26] and easy to reproduce. The gelation corresponds to the synthesis of colloidal dispersions of Ag particles [23]. A small amount of solution is placed in a capillary (see Fig. 3). The precipitation of silver is thermally driven, and the heating is provided thanks to a microwave setup where a microwave resonating cavity is placed around the X-ray target. Different amounts of heating time were used to simulate corresponding time spent by a falling drop inside the cavity. The spectra were recorded in transmission.

During its free fall, a droplet goes through a microwave resonance cavity. There, it absorbs the microwave energy. The time spent by the droplet inside the cavity is directly correlated with its vertical position during its fall and to the total energy absorbed by the droplet, or its temperature. Therefore, in order to simulate the droplet at different vertical positions in the cavity, measurements on a sample inside a capillary placed in a special cavity (containing an aperture for measurements) could be carried out for different microwave irradiation durations. However, the reaction time is very fast and the measurement time should be of the same order of magnitude (in the range of a second). The aim of this study is to ensure that the evolution of such a chemical reaction can be measured with the Quick EXAFS Monochromator of the SuperXAS (SLS). In order to gain time between two scans, the system scans with an increasing energy, and then decreasing, without interruption. The scan function is sinusoidal with a minimum and maximum energies at 25,480 and 27,480 eV, respectively, chosen around the absorption K-edge of silver at 25,514 eV. The period is 1/2 s, meaning that 2 full spectra are recorded every second (1 spectrum is recorded with increasing energy in the first half second, and another with

decreasing energy in the following half). The duration of the microwave irradiation was not used as a parameter (the microwave irradiation was turned on at $t = 0$ s).

3 Results and interpretation

For both experiments, the EXAFS spectra have been recorded. They have been analyzed with the IFFEFIT package [15, 20].

3.1 EXAFS of droplets

In parallel, a model was developed in order to simulate the studied sample in the case of a pure salt. The crystal structure simulations have been performed for $\text{Ce}(\text{H}_2\text{O})_5(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ with the FEFF code [2, 19], with the cerium atom as absorber. The crystallographic data from Milinski [14] were used for the modeling of the pentaaquatri nitrate cerium(III) monohydrate. The FEFF code cannot be used to calculate the pre-edge and white line regions of the spectra, making it impossible to compare directly the calculated values to the measured ones in the X-ray absorption near-edge structure (XANES) region. Therefore, the calculated spectrum is not represented Fig. 4a. However, this feature is not relevant in the Fourier transform.

The range $k = [1-8 \text{ \AA}^{-1}]$ was chosen for the Fourier transform analysis of the spectra, which is the maximum available window given the recorded energy range. k values below $1 \text{ \AA}^{-1}$ are not considered because they account mostly for multiple scattering effects. Thanks to the FT of the spectra (plotted in Fig. 4b), the distance to the next neighbors of the absorber [the Ce(III) atom] is calculated.

Fig. 4 Ce(III) fluorescence EXAFS spectrum recorded on solution droplets at the (L_{III} -edge = 5723 eV) compared to the literature and modeling. **a** EXAFS normalized spectrum. **b** FFT of k^3 weighted normalized absorption

The FFT analysis of the experimental spectrum shows a surrounding of the Ce(III) similar to that of the FEFF calculation. Because of the rather small k -window used, little can be said about the further shells of neighbors. For the modeled sample, the well-defined position of the next neighbor induces a high order in the sample; therefore, the maximum of the peak is higher for the modeled sample than for the experimental one. For both cases, most of the first neighbors are located at ca. 2.3 Å, corresponding to cerium in a $\text{Ce}(\text{H}_2\text{O})_5(\text{NO}_3)_3$ molecule. With this experiment, the chemical analysis of cerium microdroplets at high frequency by X-ray fluorescence was demonstrated.

3.2 QEXAFS

In this experiment, the machine had to be tuned in order to read correctly the signal at the K-edge of silver (25,514 eV). As a test, a mixture of silver nitrate in water was used ($m(\text{AgNO}_3) = 0.195 \text{ g}$ and $V(\text{H}_2\text{O}) = 100 \text{ mL}$). Once the measurement settings optimized, a new solution consisting of the highest possible concentration of silver nitrate in ammonia ($m(\text{AgNO}_3) = 0.170 \text{ g}$ for $V(\text{NH}_3) = 300 \text{ mL}$) was investigated, and the sample was heated with 100 W of microwave during the recording of the EXAFS spectra. The microwave heating triggers a reduction in Ag(I) toward Ag(0) which precipitates and forms clusters.

For this experiment, 230 spectra were recorded as shown in Fig. 5. In order to reduce the noise, it is typical in EXAFS to record several spectra and average them. This was also done in the study for five packs of eight spectra: 1–8, 50–57, 90–97, 150–157 and 200–207. Although each spectra is different due to the occurring reaction, it is acceptable to consider that the change is minimal for eight spectra, i.e., 16 ms. The first spectra (1–8) correspond then to the solution at the beginning of reaction, whereas the last ones (200–207) refer to an advanced reaction stage.

Fig. 5 Spectra obtained from the normalization, merging and smoothing of the packs of recorded spectra. *Left* Evolution of the spectra. *Right* 3D representation

Fig. 6 FT magnitude of EXAFS spectra during silver precipitation

A Fourier transform calculation of the measured spectra is plotted in Fig. 6. The chosen k -range [$1-8 \text{ Å}^{-1}$] is large enough to analyze the radial distance between the X-ray absorbing (Ag) atom and its next neighbor. In this analysis too, the results are in agreement with those of Harada [12]. When the silver is in its ionic form, the signal is flattened; indeed, in a liquid solution the particles have a high mobility and no specific interionic distance can be read. However, in precipitated silver two atoms are 288.9 pm distant [24]. The main peak growing with the advancement of the precipitation reaction is located at this distance and corresponds to the formation of metallic silver in the solution. The magnitude of the peak I_{sample} , when compared against that of the reference sample I_{ref} , can be used to evaluate the $[\text{Ag}^+]/[\text{Ag}]$ ratio at any time during the experiment: $[\text{Ag}^+]/[\text{Ag}] = I_{\text{ref}}/I_{\text{sample}} - 1$. Its constantly raising value indicates an increasing quantity of metal silver in the sample. This peak magnitude will reach its maximum I_{ref} , only when all the silver present in the solution is precipitated. The comparison with the reference

metal foil shows that at the end of the reaction all the silver is the solution has precipitated. This experiment has demonstrated that of the QEXAFS equipment is suitable for the study of gelation advancement in the time range of seconds.

4 Conclusions

In order to check the feasibility of recording EXAFS spectra on falling microspheres undergoing gelation in a microwave cavity, the study was divided into two approaches corresponding to the two challenges to overcome.

Firstly, spectra had to be recorded on falling microspheres in fluorescent mode. The result could be validated with a FEFF calculation of the spectra for the same salt (cerium nitrate). The Fourier transform would provide better results if the spectra could be recorded over a larger energy range, yet the experimental and modeling results are in good agreement. Secondly, using the well-known silver mirror reaction (with a reaction kinetics similar to that of cerium nitrate), fast spectra could be recorded in transmission mode during microwave heating of a silver nitrate solution. The results have shown that it is possible to follow silver precipitation with the equipment of the SuperXAS beamline. In addition, since a reference measurement was also taken with a silver foil, it is possible to determine the ratio of precipitated silver from the FFT spectra and therefore assess the advancement of the precipitation reaction.

The combined results of the two experiments demonstrate the suitability of the SuperXAS beamline for the investigation of the microwave internal gelation. In order to complete the feasibility study, the chemical evolution of the cerium solution during its precipitation remains to be investigated with the same technique. Achieving this step will make it possible to consider the final phase of the investigation: a gelation of uranyl nitrate. The control of the microwave-triggered gelation of nuclear microspheres will open the way to a safer and cleaner fuel production route which will be used to reduce the amount of nuclear waste.

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