Aqueous hydroxylation mediated synthesis of crystalline calcium uranate particles

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ABSTRACT

Metal uranates(VI) are solubility limiting U(VI) phases under high pH conditions and may act as suitable long-term wasteforms. The precipitation and thermal phase development mechanisms of calcium uranate particles formed via aqueous hydroxylation reactions are studied in order to address the lack of aqueous synthesis methods currently available. Hydrous Ca-deficient uranate particles formed from aqueous solutions saturated in U(VI) oligomers were found to thermally decompose via several weight-loss steps between 100 and 800 °C. Crystalline calcium uranate ($Ca_2U_3O_{11}$) is initially formed at 700 °C via dehydration and dehydroxylation-olation reactions under redox-neutral conditions. This initial phase decomposes to biphasic $CaUO_4$-UO_2 particles at 800 °C via a reductive pathway.

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1. Introduction

Global legacy civil and military nuclear activities have accumulated ~1200 kt [1] of depleted uranium (dU at ~0.3% U-235). The low market cost of natural uranium and a lack in fast reactor technology until at least 2030 [2] reduces the economic case for using dU in civil power generation. Whilst down-blending of highly enriched U stocks (1.44 kt, ~90% U-235 [3]) with dU towards thermal fission fuel (~4% U-235 equivalent) is possible, this would consume only ~55 kt dU. The dU is therefore regarded as being a zero value asset [4] and may require long-term storage or disposal. In most nuclear states, some 80% of legacy dU is stored as uranium hexafluoride (UF_6) [1]; a hygroscopic crystalline solid that reacts violently with moisture to release highly chemo-toxic uranyl and hydrogen fluoride.
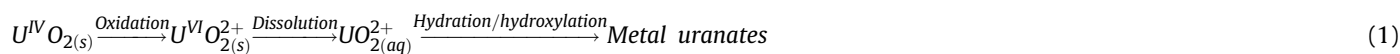
Currently, dU disposal is envisioned to be within deep cementitious geological disposal facilities (dGDF) [5]. The majority of dGDF post closure safety cases predict infiltration of groundwater, resulting in dissolution/re-precipitation of radionuclides present in the waste packages. This precludes direct dGDF disposal as a viable option for UF_6, instead deconversion to U_3O_8 may be achieved through steam quench-calcination processes [6].

The majority of ILW will be encapsulated in Portland grouts and contained in stainless steel drums. When a dGDF is re-saturated with groundwater, Na, K and Ca ions will be released into pore-water and near-field groundwater. Dissolution of K/Na hydroxide will initially alkalise groundwater towards pH 13.5, which is then buffered towards pH ~12.5 by Portlandite present in grouts. This hyperalkaline plume will be enriched with radionuclides such as Cs, Sr and more so uranium as the largest radionuclide faction by mass. Although U(VI) exhibits low solubility under these pH 12.5—13.5 conditions, its ubiquity in the dGDF will increase U(VI) concentrations. U(VI) is present in almost all aqueous solutions as the uranyl ion (UO_2^{2+}) which forms uranyl hydroxide clusters in the presence of hydroxyl ions [7—9]. Subsequent inorganic polymerisation will result in nucleation of uranyl hydroxide precipitates that crystallise with aging towards uranyl oxide hydrates (Schoepite, meta-Schoepite [10]:

$$U^{IV}O_{2(s)} \xrightarrow{Oxidation} U^{VI}O_{2(s)}^{2+} \xrightarrow{Dissolution} UO_{2(aq)}^{2+} \xrightarrow{Hydration/hydroxylation} Metal\ uranates \qquad (1)$$

Incorporation of background cations will cause phase alteration [11,12] towards Ca/Sr-Becquerelite [13] or solubility-controlling uranates (CaUO$_4$, CaU$_2$O$_7$) [14,15]. These geologically persistent U(VI)-phases could further sequester key radionuclides (e.g. Cs, Sr, Np), affecting the long-term safety case of a dGDF [16–19].

Whilst crystalline metal uranates may become a suitable wasteform for permanent disposal or interim storage of uranic wastes, their synthesis pathways are often limited in the literature to ceramic methods involving direct calcination. Poor mixing between uranium and alkali metal salt particles will result in repeated grinding and prolonged calcination at high temperatures being required; reducing the overall process efficiency. Despite this, the ease of tuning Ca/U stoichiometry has resulted in the successful synthesis of Ca-uranates with Ca/U ratios of 0.25 [20], 0.5 [21], 0.337 [20], 1 [22], 2 [23], 3 [24]; in addition to other alkali uranates [25–27].

Sol-gel or co-precipitation chemistry is an attractive solution based route to synthetic metal oxides [28,29] that are low cost and typically require low temperatures, making processing convenient whilst also permitting control of particle morphology via frameworking agents [30]. Traditionally, metal alkoxides are used as solution phase precursors that readily undergo condensation [31] which may be expensive or complex to prepare as well as being heat, moisture and photo- sensitive. With the exception of titanium and zirconium alkoxides, most transition and actinide metal alkoxides are commercially unavailable.

Inorganic uranyl salts have been used during the synthesis of UO$_2$, U$_3$O$_8$ and UO$_3$ via direct [32] or indirect [33] alkalisation of uranyl nitrate solution. Precipitates are often amorphous, requiring calcination at 600 °C to crystallise the anhydrous uranium oxides [34,35].

Thus far, sol-gel syntheses have only been used to explore pure uranium oxides, whilst uranates have been formally explored only via the aforementioned anhydrous processes [36]. This study explores a simple and rapid aqueous based route towards calcium uranate particles, with potential for integration with current uranic waste stabilisation or dUF$_6$ deconversion processes [37]. It forms part of an effort to understand the underlying mechanisms leading to aqueous nucleation of hydrous metal uranates, whilst defining changes in their chemo-physical properties during anhydrous crystallisation.

2. Experimental

2.1. Materials and preparation

All reagents were of Analar grade and used as supplied without further purification.

Uranyl nitrate stock solution A 1.04 M uranyl nitrate solution was prepared by dissolving 1.51 g of uranyl nitrate hexahydrate (UO$_2$(NO$_3$)$_2$·6H$_2$O, BDH Laboratory supplies) in 2.89 ml of deaerated deionised water (18 MΩ) to form a clear bright yellow solution.

Calcium nitrate stock solution: 0.28 g of calcium nitrate tetrahydrate (Ca(NO$_3$)$_2$.4H$_2$O, BDH Laboratory supplies) was added to 1.145 ml of deionised water to give a 1.04 M solution.

Calcium hydroxide stock solution: 0.7 g of calcium oxide (CaO, Sigma Aldrich) was added to 1 l of deaerated water (20 min N$_2$ sparged) in a stirred borosilicate Duran bottle. After solution becomes clear, a sealed cellulose semi-permeable tube containing 3 g/ml calcium hydroxide slurry was added to the solution and allowed to equilibrate to ~ pH 12.5 over 14 days at 20 °C.

Experimental procedure: In a typical synthesis, a 2.29 ml calcium enriched uranyl solution was prepared from mixing 1.145 ml of calcium and 1.145 ml of uranyl stock solutions to give 2.29 ml of preliminary reaction solution (pH 1.5) at 0.52 M: 0.52 M U(VI):Ca(II) concentrations respectively. To this initial solution, saturated calcium hydroxide solution was added slowly dropwise under vigorous stirring until pH 12 was reached. The reaction mixture was centrifuged at 14400 *g* for 3 min to collect and pelletize the bright orange precipitate. The remaining colourless clear supernatant was removed with pipette. The precipitated particles were rinsed with DI water and pelletised. The rinsed solids were re-suspended in 40 ml of propan-2-ol and centrifuged to prevent further ripening/hydrolysis reactions via displacement of surface water with alcohol groups. This was repeated twice and the solids were concentrated into 5 ml of propan-2-ol for storage, allowing rapid drying prior to analysis using the methods described below.

2.2. Sample analyses

Quartz crystal microbalance (QCM) A chrome-gold quartz crystal (d = 25.4 mm) (Stanford Research Systems, Sunnyvale, California) was rinsed using Millipore water followed by isopropanol then air dried. The crystal was mounted onto a 5 MHz Stanford Research Systems QCM200 probe and the sensor was left to reach a stable frequency and resistance reading in air, then repeated upon submersion in the stirring reaction solution. A shift of at least 0.75 Hz h^{-1} and 0.34 Ohm hr^{-1} in air and 3 Hz h^{-1} and 1.65 Ohm hr^{-1} in solution was considered stable. Calcium hydroxide solution was added to the reaction solution until pH 12 and the frequency and resistance data was recorded throughout the process.

Zeta potential measurements Precipitates were disaggregated using pestle and mortar then suspended in deionised water (18 MΩ). Remaining aggregates were allowed to settle and aliquots of the suspended fraction were added to prepared pH solutions buffered using 0.1 M HNO$_3$ and (CH$_3$)$_4$NOH solutions to a final concentration of ~1000 ppm immediately prior to measurement. Triplicate samples were loaded into folded capillary zeta cells then analysed using a Malvern Instruments Zetasizer Nano. The refractive index was taken to be 1.63 (see Dynamic light scattering measurements below).

UV–Vis analyses Aliquots of reaction solution were removed at selected solution pH values followed by centrifugation to pelletize solids. The supernatant was removed and their single wavelength optical absorbance measured using a Jenway 6715 spectrophotometer to follow changing solution absorption throughout the reaction. 414 nm was found to be the maximum absorbance peak (A414) in a UV–Vis spectrum of stock uranyl nitrate solution at ~ pH 2.

The raw total spectrophotometric absorbance at 414 nm (A414) of the pelletised reaction aliquots was treated by subtracting the A414 of UO$_2$(NO$_3$)$_2$ solution of equivalent dilution to isolate ΔA414 due to variation of U(VI) speciation. This treated data was then fitted using a Gaussian function to guide the eye (Fig. 4a black square, Gaussian fit in dashed black). Fresh solutions were prepared