

# Alterations of thorium oxalate morphology by changing elementary precipitation conditions



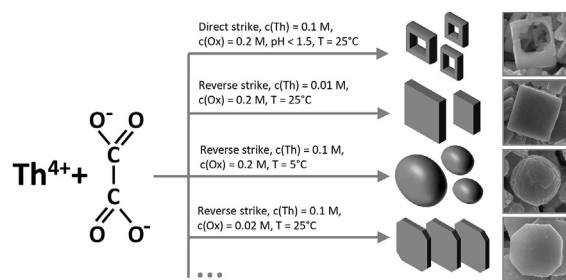
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## GRAPHICAL ABSTRACT



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## ABSTRACT

Oxalates of actinide elements are widely used in research and industry mainly due to their low solubility in aqueous solution and easy conversion to oxide. Although thorium oxide is worldwide mostly produced by the oxalate precipitation and conversion route, the powder morphology obtained through this process is known to inhibit the packing and sintering step of the pellet production. The presented work investigates the effects of oxalate precipitation conditions on the final powder morphology. Among the precipitation conditions considered are: pH of the thorium feed solution, concentration, temperature and the order of addition (thorium solution in oxalic acid solution and vice versa) known as reverse/direct strike. Herein, we show that the morphology of the final oxalate depends significantly on the above mentioned precipitation parameters.

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## 1. Introduction

Thorium has been considered for many decades as a “fertile” element for several types of nuclear fuel, which instigated sizeable research and demonstration programs both in USA and in Europe from the early 1960’s. Resource concerns remain the primary

interest for countries, such as India, which have vast thorium reserves and limited uranium reserves [1–7]. More recently, thorium based fuels regained interest in Europe in the context of actinide management, in particular for burning excess Pu stockpiles [8]. Furthermore, reserves of thorium have become readily available as a side product of increased rare earth metal mining [9]. Most of this is used as ThO<sub>2</sub> (thoria), which worldwide is produced mainly by oxalate precipitation and conversion to oxide [2–5]. The low solubility of actinide oxalate salts makes them scientifically and

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commercially interesting [10].

Thorium oxalate is known as hexa- and di-hydrate, but the ICSD database contains only a structure file of the dihydrate [11,12]. Since  $U^{4+}$  is analogous with  $Th^{4+}$ , it is apparent that the thorium oxalate hexahydrate is isostructural with uranium (IV) oxalate hexahydrate [13]. This structure is depicted in Fig. 1. The crystal structure of  $U^{4+}$  and  $Th^{4+}$  oxalates is usually well reflected in the powder morphology. The a and b lattice directions, see the view in the (001) direction, confine the square shape of the platelets, while the weaker hydrogen bonding of the crystalline water in the c lattice direction, see view in the (100) direction, keeps the platelets thin.

During the 1940–1960's, several authors [14–16] pioneered the studies of thorium precipitation by oxalic acid yielding crystals with specific platelet morphology, that are easily convertible to oxide. Allred et al. [16] showed that the precipitation temperature has an impact on the size and morphology of the oxalate crystals. At low temperatures (10 °C), the crystals are smaller (~1 μm) and thicker (3:2 ratio edge length:thickness), while they are larger and thinner at high temperature (~4–7 μm with aspect ratio 6:1 at 100 °C). At that time, it was concluded that none of the reaction conditions (pH and concentrations of starting solutions or temperature) had a crucial effect on the surface area of the oxide, obtained after calcination. The critical factor affecting the surface area was identified to be the calcination temperature. Shortly thereafter, Kantan et al. [17] published a study of the effect of the thorium oxalic precipitation temperature on the density of sintered pellets. The highest sintered pellet density (~95%) was obtained for powders precipitated at 20 °C, calcined at 900 °C and sintered for 1 h at 1500 °C. These early attempts were enriched in the 1980s by the study of White et al. [18], in which the authors studied the effect of precipitation temperature, stirring and digestion time on the powder morphology and sinterability. The work confirmed previous findings considering the temperature effect on the powder morphology. The oxide powder derived from oxalate precipitated at 10 °C packed into green bodies with about 5% less theoretical density (TD) than powder from oxalate precipitated at 70 °C. However, the powder obtained at low temperature showed the highest sinterability yielding pellets systematically over 90% of TD. Some other reports related to powder morphology of single actinide oxalates cover U, Th [19], Np [20–22], Pu [23,24], Am [25,26] and some multiple actinide oxalates [27,28], but a systematic study on how the synthesis conditions affect the powder morphology has not been published yet.

The reluctance of  $ThO_2$  to sinter to near-complete density could be eliminated by powder milling or dopant addition [29–31]. However, from an industrial point of view the milling step might be undesirable due to dust formation, while dopant addition might lead to property changes. Therefore, we intended to avoid these steps. In the present paper, we report on a systematic study of the effect of the precipitation conditions on the shape of the thorium oxalate polymorphs.

## 2. Experimental part

### 2.1. Preparation procedures

A set of experiments was defined in order to map the conditions affecting the precipitation of thorium oxalate. The initial thorium feed solution has been provided by Solvay, specifically 1.9 M  $Th(NO_3)_4$  with 1.6 M free  $HNO_3$ . Oxalic acid dihydrate (Sigma Aldrich, p. a.) was used to prepare oxalic acid solutions. The chemicals were diluted with demineralized water and used without further purification. All tests were performed on a small scale, leading to thorium oxalate yields of about 100 mg.

Systematic variations of the following base experimental conditions were explored:  $Th^{4+}$  feed solution diluted to 0.1 M, oxalic acid to 0.2 M, at room temperature, with the pH of the  $Th^{4+}$  solution unadjusted (value of 1.3). Both versions of precipitation were always performed - “direct strike” (oxalic acid solution dropped into thorium solution, “DS”) and “reverse strike” (thorium solution dropped into oxalic acid solution, “RS”). All the experiments are summarized in Table 1 and can be split into four groups:

- *Experiments with adjusted pH:* The thorium feed solution was diluted to 0.1 M concentration, while adjusting the pH using ammonia or nitric acid to the desired value. The pH was adjusted using diluted solutions of ammonia (28% Sigma Aldrich) or nitric acid (70% Sigma Aldrich). The concentration feed oxalic acid solution was kept to 0.2 M and pH was not adjusted. All precipitations were performed at room temperature. #1-10
- *Experiments with adjusted concentrations:* The concentrations of either thorium or oxalic acid in the solutions were changed logarithmically. The upper concentration of oxalic acid was limited to 1 M due to solubility limits at room temperature. pH was not adjusted and all experiments were done at room temperature. #11-20

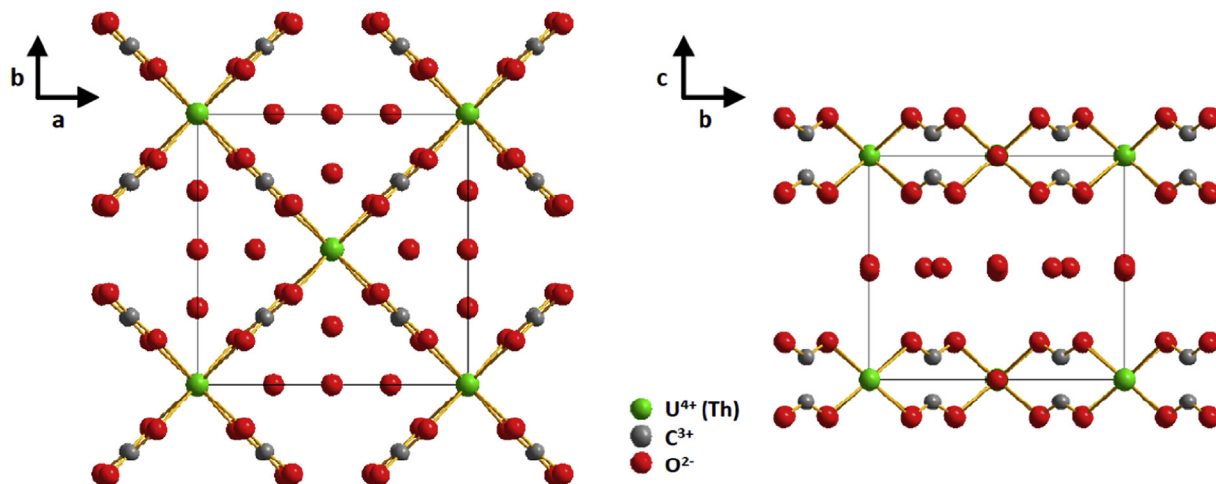


Fig. 1. Crystal structure of  $U(C_2O_4) \cdot 6H_2O$  [9] that is isostructural with the thorium analog. The left picture presents a view in the direction (001) and the right picture in the direction (100). Unbound oxygen atoms represent crystalline water; hydrogen atoms are not represented.

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