

Review

A review of plutonium oxalate decomposition reactions and effects of decomposition temperature on the surface area of the plutonium dioxide product



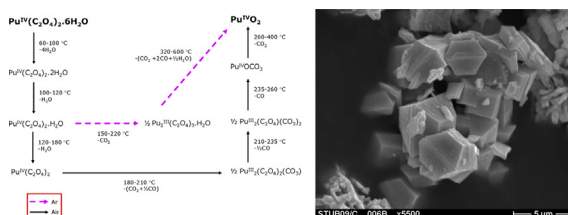
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HIGHLIGHTS

- Critical review of plutonium oxalate decomposition reactions.
- New analysis of relationship between SSA and calcination temperature.
- New SEM images of plutonium oxide product powders.
- Focus on oxalate decomposition mechanism (Pu, Ce, Th, Nd oxalates compared).

GRAPHICAL ABSTRACT



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ABSTRACT

Plutonium (IV) and (III) ions in nitric acid solution readily form insoluble precipitates with oxalic acid. The plutonium oxalates are then easily thermally decomposed to form plutonium dioxide powder. This simple process forms the basis of current industrial conversion or ‘finishing’ processes that are used in commercial scale reprocessing plants. It is also widely used in analytical or laboratory scale operations and for waste residues treatment. However, the mechanisms of the thermal decompositions in both air and inert atmospheres have been the subject of various studies over several decades. The nature of intermediate phases is of fundamental interest whilst understanding the evolution of gases at different temperatures is relevant to process control. The thermal decomposition is also used to control a number of powder properties of the PuO₂ product that are important to either long term storage or mixed oxide fuel manufacturing. These properties are the surface area, residual carbon impurities and adsorbed volatile species whereas the morphology and particle size distribution are functions of the precipitation process. Available data and experience regarding the thermal and radiation-induced decompositions of plutonium oxalate to oxide are reviewed. The mechanisms of the thermal decompositions are considered with a particular focus on the likely redox chemistry involved. Also, whilst it is well known that the surface area is dependent on calcination temperature, there is a wide variation in the published data and so new correlations have been derived. Better understanding of plutonium (III) and (IV) oxalate decompositions will assist the development of more proliferation resistant actinide co-conversion processes that are needed for advanced reprocessing in future closed nuclear fuel cycles.

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1. Introduction

The conversion of plutonium (III/IV) nitrate solutions to plutonium dioxide (PuO₂) solid products via the oxalate precipitation route dates back to the 1940s [1–3] and (the Pu(IV) route)

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List of acronyms

AIT	auto-ignition temperature
BET	Brunauer–Emmett–Teller
CEA	Commissariat à l'énergie atomique et aux énergies alternatives
CFD	computational fluid dynamics
Cp	cyclopentadienyl (C ₅ H ₅)
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EAS	electronic absorption spectroscopy
IR or FTIR	infra red or Fourier-transform IR
LFL	lower flammability limit
MOX	mixed oxide
MS	mass spectrometer
OECD-NEA	Organisation for Economic Co-operation and Development–Nuclear Energy Agency
PSD	particle size distribution
R&D	research and development
SEM	scanning electron microscope
SSA	specific surface area
TGA	thermogravimetric analysis
XRD	X-ray diffraction

is now the standard production method used at industrial scales in nuclear fuel reprocessing plants [4]. It is also widely used to recover plutonium from waste solutions and residues, to produce PuO₂ for laboratory use and in the purification of ²³⁸PuO₂ for power applications (usually *via* the Pu(III) route) [5–7]. After the plutonium oxalate precipitate is prepared (including filtration and washing), it is thermally decomposed to the oxide. Industrially, this involves discrete stages of drying and calcining at elevated temperatures during which the oxalate decomposes through a series of intermediate plutonium compounds to PuO₂ with gaseous products liberated [8–20]. Decomposition of the oxalate by auto-radiolysis can also occur during prolonged room temperature storage and this process follows similar routes [1,17,21,22]. The decomposition of plutonium oxalate has been a subject of study for ~50 years as it exhibits a complex mechanism with potential safety implications for laboratory scale and industrial scale operations [23–27]. Also, depending on the calcination conditions, some important features of the plutonium dioxide product quality [28] can be affected, most importantly the specific surface area (SSA) [29,30], adsorbed volatiles (moisture, nitrogen oxides, carbon oxides) [31–34] and residual carbon content [12,16,24,35,36]. These properties can affect the suitability of the PuO₂ for either long term storage [34,37–39] or mixed oxide fuel manufacturing [40–44]. Latterly, the co-conversion of mixed actinide oxalates to form solid-solution mixed actinide oxides has become a subject of interest in the promotion of more proliferation resistant nuclear fuel reprocessing [43,45–59], so it is timely to review historic experience in plutonium oxalate decomposition. This paper thus reviews available data on plutonium oxalate decomposition reactions that are of significance in oxide production, *viz*:

- The mechanism of decomposition
- Exothermic heating during decomposition and CO flammability
- Effects on the oxide product (morphology, carbon content)
- Evaluation of the effects on surface area of the oxide product

2. Mechanism of plutonium oxalate decomposition**2.1. Introduction**

The mechanism by which PuO₂ is formed from Pu(III,IV) oxalates is of primary importance in understanding what products (solid and gaseous) are formed at specific temperatures under varying atmospheric conditions. The mechanism follows different paths in inert atmospheres compared to air (oxidising) atmospheres and all these processes have been studied a number of times with conflicting results. Such studies have primarily used thermal methods (such as TGA, DTA), with some associated characterisation of intermediate compounds using other analytical methods. The main steps in the decomposition are generally agreed to be endothermic dehydration with loss of water molecules followed by decompositions of the oxalate ligands, which may be endothermic or exothermic depending on the atmosphere; however, the exact sequence of reactions has been re-interpreted several times by different authors based on their data. This has generated some uncertainty as to the solid intermediate products and the temperatures at which the gaseous products (H₂O, CO, CO₂) are formed. Whilst the main focus in this paper is on the industrially relevant plutonium (IV) oxalate [Pu^{IV}(C₂O₄)₂·6H₂O] reactions, comparisons are made with the decomposition of plutonium (III) oxalate [Pu^{III}₂(C₂O₄)₃·9H₂O] which may be more relevant to future co-conversions of mixed actinide solutions [52] and other related compounds.

2.2. Thermal decomposition**2.2.1. Early studies**

Early studies of the decomposition reactions gave conflicting results. Myers [8] presented a scheme in an inert atmosphere involving dehydrations at 80 °C and 80–150 °C to remove five and one water molecules respectively; then at 160–250 °C conversion to Pu₂(C₂O₄)₃ occurs with evolution of CO₂. “Intermediate compounds” were formed up to 275 °C followed by conversion to the oxide at 300–500 °C with evolution of CO₂+2CO. Kartushova [9], in the case of Pu(IV)-oxalate, found endothermic effects at 110, 170–200 and 350 °C and a small exothermic effect at 485 °C. A blue Pu(III) oxalate intermediate was observed at 170–190 °C. Complete oxidation to oxide occurred at 350–380 °C. In the decomposition of Pu(III) oxalate endothermic effects were found at 120 and 300 °C and an exothermic effect at 460 °C. The paper implies that this is under flowing nitrogen; in which case an exothermic decomposition is not expected. Analysis of the product formed at 330 °C gave Pu(C₂O₄)(CO₃)_{0.59}. The peak on the heating curve at 460 °C was thus attributed to the decomposition of the oxalate-carbonate to PuO₂ with oxidation of Pu(III) to Pu(IV). In air, Pu(III) oxalate had an endothermic effect at 170 °C (dehydration) and an exothermic effect at 270 °C (formation of PuO₂). In a report by Waterbury [10] the hydration of the initial oxalate was uncertain but no stable intermediates were found with greenish-brown PuO₂ formed. By chemical analysis, Rao [11] identified the intermediate of Pu(IV) oxalate decomposition in air to be Pu₂(C₂O₄)₂(CO₃). Pu(III) oxalate was found to lose waters of hydration but no intermediate decomposition products were observed either in air or an inert atmosphere. Jenkins and Waterman [12] noted that formation of PuO₂ from Pu(IV) oxalate at temperatures below 310 °C, the onset of oxidation in nitrogen, may be due to rapid local heating due to exothermic oxidation of CO in air. No evidence for a Pu(III) intermediate was found and they suggested that the oxalate decomposes *via* the carbonate Pu(CO₃)₂, perhaps with simultaneous decomposition directly to the oxide. Mass changes during decomposition in nitrogen could be attributed to intermediate production

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