



Review

Uranium minerals and their relevance to long term storage of nuclear fuels



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ABSTRACT

The storage of spent nuclear fuels for long periods of time in geological repositories is one proposed solution to the stewardship of legacy, current and future nuclear waste. Recent studies have shown that UO_2 , the major component of spent nuclear fuel, can oxidise under repository conditions to a number of secondary phases. The weathering of naturally occurring uranium minerals can give an insight into the behaviour of SNF and this review highlights the structural and spectroscopic characterisation of a number of relevant minerals. Conversely, reducing conditions could also be possible and these phase alterations are also discussed. Furthermore, the interaction of these minerals with the common fission products caesium, strontium, technetium, iodine, selenium and the transuranic elements (Np, Pu, Am, Cm) is reviewed, as these minerals may provide a mechanism for the retardation of the mobility of these radioisotopes.

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1. Introduction

The safe stewardship of nuclear waste is a large societal challenge, where chemists can make a substantial input into delivering technologies that address the fundamental issues of long term storage of highly radioactive waste. European policy is to store spent nuclear fuels (SNFs) in underground repositories, and a number of countries are planning or in the process of building these [1]. The US has recently decided against the opening of a repository in the Yucca Mountains in Nevada [2]. However, there is obvious concern about the long term environmental consequences of long term storage. For instance, the steel drums used as containment will eventually corrode and actinides will leach into the near-field. As SNF is principally made up of UO_2 , in an oxygen rich environment corrosion (oxidation) to uranyl species would be expected [3]. Reducing, anoxic conditions may also be present [4] and the role of the iron in the containers may be relevant [5]. This poses further problems as U(IV) species are generally insoluble whilst the U(VI) compounds can have appreciable solubility in water, and the speciation is sometimes complex [6]. The interactions of radioactive ions with mineral surfaces can act as a mechanism to retard the mobility of the metal or even participate in redox chemistry. Moreover, if power generated by nuclear fission is to be included in national energy policies then the demand for uranium will also increase; this could pose a threat to the environment. Finally, historic and current uranium mining, processing and disposal operations has resulted in contamination of local environment, which have been particularly well studied in US Department of Energy sites and the remediation efforts have enhanced the understanding of uranium and plutonium speciation and biogeochemistry [7] and particle transport mechanisms in the environment [8] under different conditions. In particular, it has been noted that phosphate and silicate ion in the groundwater can react with uranyl compounds to form uranyl silicate or phosphate minerals. The phosphates have very low solubility so could act as important sinks for the mobility of uranium in the environment, however microbial and bacterial activity can change this [9].

In long term storage, oxidative weathering of natural ores and environmental speciation studies, the importance of uranium mineral phases has come to the fore. For example, under laboratory based studies, both surrogate and real spent nuclear fuels have been observed to undergo phase changes when immersed in water for ~2 years. These phase changes are principally from UO_2 to uranyl bearing minerals. Reactions with H_2O_2 , generated by α -radiolysis of water, causes further phase changes. Therefore it is obvious that the speciation is complex and will influence the further chemical transformations. In particular, how other radionuclides with long half-lives can interact with these phase changed uranyl compounds is important as it may offer further retardation or redox reactions to occur that further influences the near-field impact on storage of SNF.

The purpose of this review is to highlight the spectroscopic and structural chemistry associated with these mineral phases that give molecular information rather than measuring low concentrations of uranium in environmental conditions [10]. Furthermore, it will collate the reactivity studies of these minerals towards the trans-uranic elements and other fission products such as strontium, barium, iodine etc. Explicitly excluded from this review is a discussion of how uranium compounds react with other minerals such as the iron bearing goethite, as these issues have been covered in a recent review [11]. An important determining factor in the stability of uranyl phases is the thermodynamics of formation and solubility measurements; these have been the subject to recent reviews so are also excluded [12]. The structural formulae for all minerals mentioned in the text can be found in Section 6.

2. Phase transitions of uranium bearing minerals

2.1. Transitions on natural ores

The study of weathering of naturally occurring mineral deposits has been used as a model for SNF corrosion, as uraninite (UO_2 or pitchblende) is a major composition of uranium ore. There are a number of well-studied deposits and their geochemistry has been reviewed [13]. The Shinkolobwe mine in the Democratic Republic of Congo has been studied extensively for weathering and the uranyl oxy(hydroxides) becquerelite, compregnacite, vanderiesscheite, fourmarierite, billietite and schoepite are first formed, but these react with the silica rich ground water to form the uranyl silicates uranophane and cuprosklodowskite [14]. The Nopal I deposit of the Sierra de Peña Blanca District in Mexico has been used as a model for the geochemistry for the Yucca Mountain, where the US initially proposed as the site for their geological disposal. A series of secondary minerals have been observed (Scheme 1), beginning with the uranyl (oxy)hydroxides ianthinite, schoepite and dehydrated schoepite, but the majority of the uranium (95%) exists as the uranyl silicate uranophane [15]. At the Koongarra uranium deposit in Australia uraninite has been altered to curite and sklodowskite but upstream from the deposit, saleeite has replaced sklodowskite [16]. The natural fission reactors at Oklo in Gabon have proven to be useful models [17] and the primary minerals are uraninite and coffinite but fourmarierite, bassetite, chernikovite, torbernite, Ce-rich françoisite, uranopilite and autunite have been reported [18]. A unique alteration sequence has been reported from the weathering of uraninite at Marshall Pass, Colorado. This is significant as there are a number of trace elements that are also fission products and the formation of uranyl molybdates may also be important to understand the stability of secondary phases in SNF corruptions [19].

As uranium eventually decays to lead, the study of lead containing minerals may be important for long term storage, as many Pb–uranyl minerals are formed though the accumulation of radiogenic lead. For example, clarkeite has been shown to transform to wölsendorfite or curite [14], with the latter predicted to be the end product of lead incorporation. The common sheet topology can also incorporate lead, as shown in the crystal structure of clarkeite [20] or vanderiesscheite [21]. Moreover, when the crystal structures of lead containing uranyl (oxy)hydroxides are compared to those uranyl (oxy)hydroxides there is a clear topological relationship [21]. The alteration of curite to uranyl phosphates such as chernikovite and autunite has been noted in old uraninite ores [14]. α -Radiolysis of water to produce H_2O_2 can react with uranyl minerals to form studtite [22].

2.2. Transitions on the surface of SNF and UO_2

Studies on commercial nuclear fuels are, as might be expected, rare. However the reported ones are of vast importance to the current knowledge of how UO_2 corrodes. The first attempt at observing corrosion products on the surface of UO_2 disks was conducted as a 10 year drip test at 90°C using simulated ground water from the Nevada region [23]. The results clearly indicated corrosion of the surface of UO_2 and a number of secondary phases were observed (Scheme 1), which are very similar to those seen in the natural ores. Additional studies on unirradiated UO_2 show silicates [24] and phosphates [25] are also present, depending upon the chemical composition of the water. When H_2O_2 is introduced to the surface of UO_2 , studtite is quickly formed as the only identifiable phase [26]. Uranyl (oxy)hydroxides and group 1 and group 2 uranyl silicates have been identified as corrosion products on the surface of SNF [27], but significantly more complex sequence is also observed as alteration phases were found to include fission products [28] and a new uranyl oxyhydroxide phase

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