

UO₂ as a New Filling Material for Cesium Retention in a High-Level Nuclear Waste Repository

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Abstract

Depleted uranium dioxide has been proposed as an inert material to fill out spent nuclear fuel canisters in geological repositories and the sorption capacity of this material to retain radionuclides released from the fuel needs to be determined. Radiocesium is one of the radionuclides of concern in case of a nuclear accident or in a high-level nuclear waste repository and is highly mobile in aquatic systems. The results obtained in this work show that sorption of cesium on UO₂ is a fast process (the equilibrium is reached in less than 1 h at pH 9).

Key words: depleted UO₂, Langmuir isotherm, radiocesium, spent fuel canister, UO₂ sorption.

Introduction

DEPLETED UO₂ WAS proposed as a filling material in the geological disposal of spent nuclear fuel, placed in the voids of spent nuclear fuel waste containers for storage, transport, or disposal (Forsberg, 1997; Puig *et al.*, 2008). Depleted UO₂ seems to be very beneficial in the spent nuclear fuel repository because it provides shielding due to its relatively high capacity for neutron absorption, reduces the potential for repository nuclear criticality events, and could reduce the long-term release of radionuclides from spent nuclear fuel at the repository, depending on the sorption capacity of the UO₂ (Brown *et al.*, 1997), which is unknown for most radionuclides. Only after the start of a USA–Russia program on the beneficial use of the depleted uranium (Haire and Shapovalov, 2005), a couple of studies were carried out on the UO₂ retention capacity for some radionuclides and it was demonstrated that UO₂ was able to retain ²³⁷Np(IV), ²³⁷Np(V), and ⁹⁹Tc(IV) (Kazakovskaya *et al.*, 2006; Kazakovskaya *et al.*, 2010). However, there are no data on the sorption capacity of other highly mobile radionuclides, yet.

Cesium, a fission product present in radioactive wastes, is a radionuclide of concern because of different reasons. On one hand, it has two harmful isotopes that contribute to the radiation hazard of nuclear waste: ¹³⁵Cs (half-life: 3 × 10⁶ years) and ¹³⁷Cs (half-life: 30 years). On the other hand, most cesium-containing solid phases have a very high solubility product and the cesium-predominant species in solution is the Cs⁺ ion, which is highly mobile in aqueous media (Comans *et al.*, 1989; Avery, 1996; Flury *et al.*, 2002), facilitating its involvement in the hydrological cycle (Carlton *et al.*, 1992; Steefel *et al.*, 2003).

For these reasons, in the safety analysis of a high-level nuclear waste repository or in the case of a nuclear accident, as it happened in Fukushima Daiichi nuclear power plant on March 11, 2011, where large amounts of seawater got in contact with irradiated fuel, cesium is one of the main radionuclides considered from the standpoint of long-term external and internal radiation exposure (Funaki *et al.*, 2014).

In this work, the kinetics of sorption of cesium on uranium dioxide as well as the variation of the sorption capacity with cesium concentration in solution (sorption isotherms) and with ionic strength were studied through batch experiments. The main objective was the knowledge of the sorption mechanism as well as the maximum sorption capacity of the UO₂ for cesium. From the sorption data obtained, a calculation of the weight of depleted UO₂ needed as filling material was made.

Experimental Protocols

Solid phase

Crystalline uranium dioxide with a particle size between 50 and 100 μm was obtained from a UO₂ pellet supplied by ENUSA (Empresa Nacional del Uranio S.A.). The composition of the bulk of the solid was UO_{2.01}, determined by X-ray diffraction analysis. The surface area of the solid was determined by the BET method, the result obtained was 0.019 ± 0.002 m²/g.

Before the experiments and to dissolve fines and oxidized fractions, UO₂ was submerged in a 1 × 10⁻³ mol/dm³ HCO₃⁻ solution. After this step, the solid was filtered and dried under N₂ atmosphere.

Methodology

Sorption experiments were carried out inside a glovebox filled with N₂ (g), avoiding the presence of O₂ (g) and CO₂

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(g), which could either oxidize UO_2 or modify the UO_2 solubility by the formation of carbonate complexes in solution, respectively. Temperature was $25^\circ\text{C} \pm 1^\circ\text{C}$.

A known amount of UO_2 (~ 0.05 g) was added to a known volume (20 cm^3) of cesium solution in stoppered polystyrene tubes. The initial cesium concentration ranged from 7.0×10^{-4} to 1.4×10^{-8} mol/dm³. Considering that the maximum sorption of cesium on other uranium solids occurred at $\text{pH} > \text{pH}_{zpc}$, and that the pH_{zpc} of the UO_2 was determined to be 7.7 ± 0.4 (Clarens *et al.*, 2003), in this work the pH was kept at 9.2 ± 0.3 by adding HClO_4 or NaOH when necessary. This pH is considered high enough to neglect the effect of pH in the sorption, but still a pH that could be found in the groundwater of a deep geologic repository [for example: Grimsel groundwater $\text{pH} = 9.7$ (Missana *et al.*, 2003)].

The tubes were continuously stirred by using an end-over-end stirrer. At the end of the experiment, aqueous samples were filtered through $0.20\text{-}\mu\text{m}$ MICROPORE pore size filters and acidified with concentrated HNO_3 . Cesium and Uranium concentrations were determined using ICP-MS (Agilent 7,500 cx). Uranium concentration was analyzed only to detect an unexpected dissolution of UO_2 . The average concentration of uranium in all the samples was $(2.73 \pm 2.87) \times 10^{-7}$ mol/dm³, meaning that only 0.003% of the UO_2 was dissolved. The pH of the solutions was monitored with a CRISON pH Meter GLP22 before the addition of the UO_2 solid to the solutions and at the end of the experiments, when the equilibrium was reached.

The concentration of cesium sorbed onto the solid in moles of Cs per m² of dry solid, $\{Cs\}_s$, was calculated by subtracting the final concentration, $[Cs]_{eq}$ in mol/dm³, to the initial concentration of cesium added to the solution, $[Cs]_0$ in mol/dm³, and normalizing with the volume (V) to the surface area (SA) ratio:

$$\{Cs\}_s = ([Cs]_0 - [Cs]_{eq}) \cdot \frac{V}{SA} \quad (1)$$

The main objectives of this work were to determine the UO_2 sorption capacity for Cs as well as to improve the knowledge of the mechanism of the sorption process to evaluate its suitability for cesium retention in a high-level nuclear waste repository.

To reach these objectives, three different sets of experiments were carried out: (1) sorption kinetics (with a constant cesium concentration, 10^{-5} mol/dm³); (2) sorption isotherms (with $[Cs]_0$ ranging from 1.5×10^{-7} to 7.7×10^{-4} mol/dm³); and (3) the effect of ionic strength (in the same range of cesium concentrations in the sorption isotherm experiments).

Results and Discussion

Cesium sorption as a function of time

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The variation of Cs sorption as a function of time is shown in Figure 1. As it can be seen, sorption is very fast under the experimental conditions with equilibrium values reached in 2 h. The percentage of sorption at equilibrium calculated as $100\{Cs\}_s/[Cs]_0$ is 21%.

Since the kinetics of the sorption is very fast, modelization of the experimental data cannot provide any additional information, and therefore, no models were used.

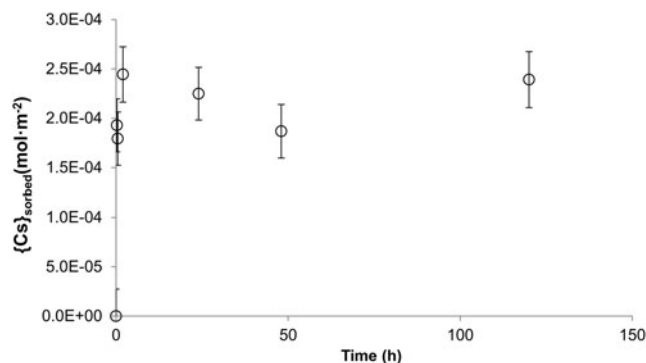


FIG. 1. Variation of cesium sorbed onto uranium dioxide as a function of contact time. Experiments carried out with 0.05 g of UO_2 , $[Cs]_0 = 6.1 \times 10^{-5}$ mol/dm³ in the presence of 0.1 mol/dm³ NaClO_4 at $\text{pH} = 9$. Very fast sorption can be observed.

Isotherms of cesium sorption: influence of ionic strength

The concentration of cesium sorbed on $\text{UO}_2(s)$ as a function of cesium remaining in solution at equilibrium is shown in Figure 2, at the two ionic media studied in this work: 0.01 and 0.1 mol/dm³ fixed by using NaClO_4 . In the case of ionic strength 0.01 mol/dm³, the shape looks linear, but in the case of ionic strength 0.1 mol/dm³, the shape tends to a maximum of cesium sorbed into the solid, which is the typical trend of a monolayer sorption. In the case of ionic strength 0.01 mol/dm³, only the linear model was fitted.

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$$\Gamma = K_d [Cs] \quad (2)$$

The parameter gamma, Γ , is defined as the cesium concentration sorbed on the UO_2 at equilibrium (mol/m²), and the K_d is the linear constant of sorption (dm³/m²). The K_d has a value of 6.61 ± 0.08 dm³/m² and the fitting has a correlation coefficient of 0.999.

Regarding the samples with 0.1 mol/dm³ ionic strength, the experimental data were fitted to three different models: Lineal, Langmuir, and Freundlich.

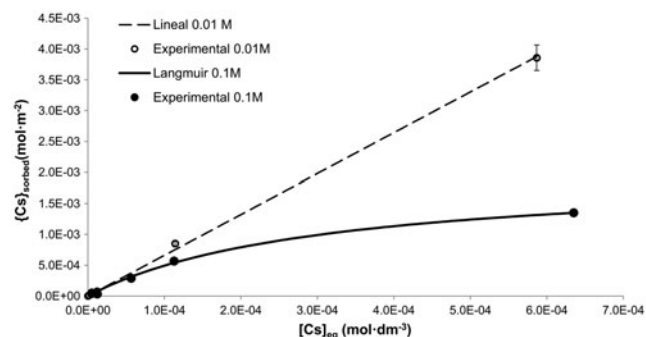


FIG. 2. Sorption isotherm of cesium sorbed onto UO_2 . Experiments carried out with 0.05 g of uranium dioxide, at 0.1 and 0.01 mol/dm³ NaClO_4 . See the difference between the ionic strengths.

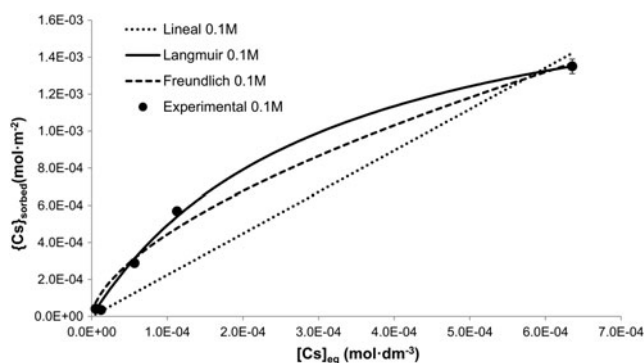


FIG. 3. Sorption isotherm of cesium sorbed onto UO₂. Experiments carried out with 0.05 g of uranium dioxide, at 0.1 mol/dm³ NaClO₄. Fitting of the Linear, Langmuir, and Freundlich models. Note that the Langmuir model is the one that best fits.

F3 ▶ Since the isotherm is not linear, the linear model is the one with the worst fitting (Fig. 3). The K_d value is 2.24 ± 0.28 and the correlation factor is 0.926.

The noncompetitive Langmuir isotherm model has the following expression:

$$\Gamma = \Gamma_{\max} \frac{K_L \cdot [Cs]}{1 + K_L \cdot [Cs]} \quad (3)$$

K_L is the Langmuir constant (dm³/mol), Γ_{\max} is the maximum cesium sorption (mol/m²), and $[Cs]$ is the concentration (mol/dm³) of cesium at equilibrium.

The Langmuir isotherm is the one that best fits the experimental data (Fig. 3), which corroborates monolayer coverage on the UO₂ surface. The Γ_{\max} has a value of $(2.00 \pm 0.12) \times 10^{-3}$ mol/m² and the K_L is $(3.27 \pm 0.44) \times 10^3$ dm³/mol. The correlation factor is 0.996.

The characteristics of the Langmuir isotherm may be expressed by the separation factor, R_L , defined as:

$$R_L = \frac{1}{1 + K_L \{Cs\}_0} \quad (4)$$

If the value of R_L is 0, the sorption is irreversible; a value between 0 and 1 indicates that the sorption is favorable; $R_L = 1$ indicates that the sorption is linear and, finally, if the value is higher than 1, the sorption is unfavorable. The R_L values were between 1.00 and 0.23. For cesium concentrations above 5×10^{-6} mol/dm³, the isotherm loses its linearity and R_L values are lower than 1.

The Freundlich isotherm takes into account the interactions between the adsorbed molecules and the exponential decrease in the sorption energy with the increase in occupied sorption sites.

The Freundlich isotherm is an empirical model that has the following form:

$$\Gamma = K_f \cdot [Cs]^{1/n} \quad (5)$$

The Freundlich constant K_f (mol sorbed/mol in equilibrium) is considered the adsorption coefficient, the quantity of sorbate sorbed per unit of sorbate concentration in equilib-

rium. The heterogeneity factor $1/n$ can be used to measure the deviation from linearity of the sorption isotherm. The linear model would have an n of 1. If the sorption process occurs due to chemical factors, then, the n is lower than 1. If the adsorption is produced by a favorable physical process, then, the n is higher than 1.

The fitting of the Freundlich isotherm can be seen in Figure 3. The correlation factor is 0.979. K_f has a value of $(1.20 \pm 0.62) \times 10^{-1}$ mol_s/mol_{eq} and n is 1.64 ± 0.18 . With this heterogeneity factor, the Freundlich model suggests that the sorption of cesium onto UO₂ is due to a favorable physical process.

A decrease in the sorption of Cs into UO₂ is observed when the ionic strength increases (Fig. 2). This dependence is common of the outer-sphere complexes based in electrostatic bonds, which corroborates a cesium sorption on UO₂ governed by electrostatic interactions between cesium and the surface of the solid.

Retention of cesium by UO₂(s) used as inert material in spent nuclear fuel canister

The data obtained allow the calculation of the weight of depleted UO₂ that would be necessary to sorb cesium released from the spent nuclear fuel. In the calculations shown below, only cesium is considered. In future calculations, with more information on other radionuclides sorption on UO₂, competition processes must not be discarded, producing a decrease in the surface sites available for cesium sorption. In these calculations, a continuous flow of water was supposed as a transport system for the Cs released, therefore, the Cs that has escaped the fuel matrix does not contact the fuel matrix again and the mass of UO₂ of the fuel itself cannot be subtracted from the mass of depleted UO₂ necessary to adsorb the Cs.

The total cesium released from the spent nuclear fuel might be calculated considering the cesium inventory in the fuel. Cesium inventory in a pressurized water reactor (PWR) and UO₂ spent nuclear fuel with a burn-up of 50 MWd/kgU were calculated by using KORIGEN code (Wiese and Schwenk-Ferrero, 2007). The total cesium release obtained from the total fuel matrix was 0.15% for both ¹³³Cs and ¹³⁷Cs, which corresponds to 1.52 g of ¹³³Cs plus 1.48 g of ¹³⁷Cs per kg of UO₂.

For final disposal of spent fuel, a canister with four PWR assemblies is being designed (Puig *et al.*, 2008), each assembly containing 523.4 kg of UO₂. The total quantity of cesium released from the resulting 2093.6 kg of UO₂ fuel will be 3.18 kg (23.9 mol) of ¹³³Cs and 3.10 kg (22.6 mol) of ¹³⁷Cs.

The mass of depleted UO₂ necessary to adsorb all the cesium released from the fuel, w_{D-UO_2} (kg), can be calculated by:

$$w_{D-UO_2} = \frac{mol_{Cs}}{Q_{\max} \cdot S} \quad (6)$$

Where mol_{Cs} are the total moles of cesium released from the fuel (46.1 mol); Q_{\max} is the maximum sorption capacity, obtained from the sorption isotherms (2×10^{-3} mol/m² at 0.1 mol/dm³ ionic strength was chosen to be conservative. At 0.01, the sorption capacity was much higher.); and S is the

surface area of the depleted UO_2 ($0.0019 \text{ m}^2/\text{g}$ if a UO_2 with the same surface area is considered).

The value obtained is $w_{D-\text{UO}_2} = 1223.7 \text{ kg}$. Considering the void space in a PWR canister, 1.343 m^3 (1), and the UO_2 density, $10,970 \text{ kg/m}^3$, the weight calculated could be easily introduced in the void space of the canister, which indicates that the canister could contain enough weight of depleted UO_2 to incorporate the cesium released from the fuel. It was proved that depleted UO_2 would be a good filling material to retain Cs released from the spent nuclear fuel.

Conclusions

From the sorption data obtained, it was concluded that the sorption of cesium on UO_2 is a relatively fast process.

At 0.01 mol/dm^3 ionic strength, the sorption isotherm was linear. The sorption at 0.1 mol/dm^3 ionic strength was based on electrostatic interactions and followed a monolayer coverage, which could be modeled considering a Langmuir isotherm. The maximum sorption capacity determined was $2.00 \times 10^{-3} \text{ mol/m}^2$.

From the maximum sorption capacity of the UO_2 at 0.1 mol/dm^3 ionic strength and the total inventory of cesium in the spent nuclear fuel, it was determined that the total amount of depleted UO_2 contained in the canister would be able to retain the cesium released from the fuel.

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Author Disclosure Statement

No competing financial interests exists.

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