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View Abstract

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ABSTRACT

TITLE: Surface sites characterization of UO_2: A comparison between caesium sorption and potentiometric titration.

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ABSTRACT BODY:

Abstract Body: The back-end of the nuclear fuel cycle includes, at least, 1) on-site pool storage, 2) either on-site or off-site dry or wet interim storage, and 3) long-term waste disposal. The purpose is that both the temperature and radioactivity of radioactive wastes gradually decrease, while containing and isolating from human's environment, and for future generations, until their radiotoxicity has decayed to non-hazardous levels for hundreds of thousands to millions of years. To demonstrate the safety of disposal in a deep underground repository, the selected location should be justified through the use of predictive modeling calculations and experimental evidences, to confirm that the potential release rate of radionuclides will be slower than their rate of radioactive decay. An important component of a safety case is the long-term predictive modeling of Spent Nuclear Fuel (SNF) based on theoretical and semiempirical models, and based on dissolution rate data as function of environmental variables [1]. Alteration rates for reactions between groundwater and the solid surface of SNF (mainly UO_2 or pre-oxidized layer) are typically based on the surface area of the solid material, in most cases determined by the BET isotherm, and/or based on site density. The specific surface area, the density of reactive surface sites (NS) or sorption sites and other geometric parameters are directly involved in the dissolution of the SNF [2] and are a key input parameters that are still not well defined by means of systematic studies. Most models neglect the solubility of the non-oxidized matrix while reducing conditions are expected. The improvement of these input data and methods for determining sorption and site densities would significantly enhance the knowledge for predictive models by providing the reactive surface area of solids.
In this work, we have experimentally studied the characteristics of UO_2(c) surface sites by two approaches: potentiometric titration and ^{137}Cs sorption isotherm, varying Cs concentration. The sorption of Cs^+ ions from aqueous solutions at 0.1 M ionic strength by powdered UO_2(c) surface, as the main component of the SNF, was evaluated in order to simulate the removal of radioactive Cs released from irradiated fuel. It is known that the fission product caesium is representative element of the instant release fraction.
The maximum sorption capacity of Cs^+ onto the UO_2 surface (particle size: 20-32 μm, BET surface area: 0.357±0.007 $m^2 \bullet g^{-1}$) obtained from the sorption isotherm (0.1 mol L^{-1} $NaClO_4$ at 25°C and pH=6.3) was $6.3 \bullet 10^{-5}$ $mol \bullet g^{-1}$, value that can be considered as an estimate of UO_2(c) surface site density. The surface acidity constants and site density were also determined by potentiometric titrations. Modelling the titrations data collected in 0.1 $mol \bullet L^{-1}$ $NaClO_4$ with the double diffuse layer model, using Chess code [3], led to acidity constants of pKa1= 3.2 and pKa2=-10.8. The experimental solubility of the UO_2 in 0.1 $mol \bullet L^{-1}$ $NaClO_4$ system (m/v ratio of $40g \bullet dm^{-3}$) at different pHs was previously determined as $pK_{s,0} = -(3.2 \pm 0.2)$, in agreement with UO_2(am, hydr.) [4]. From our experiments, it can be concluded that there is a large effect of dissolution on surface charge determination for pH<4 and pH > 12.

REFERENCES

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KEYWORDS: Synthesis & Processing/Chemical Reaction/chemical reaction, Composition & Microstructure/Material Type/oxide.
