



Desorption kinetics of cesium from Fukushima soils



Kento Murota ^a, Takumi Saito ^{b,*}, Satoru Tanaka ^{a,1}

^a Department of Nuclear Engineering and Management, School of Engineering, The University of Tokyo, 7-3-1 Bunkyo-ku, Tokyo, 113-8656, Japan

^b Nuclear Professional School, School of Engineering, The University of Tokyo, 2-22 Shirakata Shirane, Tokai-mura, Ibaraki, 319-1188, Japan

ARTICLE INFO

Article history:

Received 3 September 2015

Received in revised form

27 November 2015

Accepted 15 December 2015

Available online 7 January 2016

Keywords:

¹³⁷Cs

¹³³Cs

Fukushima

Desorption rate

Soil

Sorbent

ABSTRACT

Understanding the behaviors of Cs⁺ in soils is crucial for evaluation of the impacts of disposal of soils contaminated by radiocesium, ¹³⁷Cs. The desorption rate of Cs⁺ evaluated in relatively short periods of time may not be adequate for such a purpose. In this study, we investigated long-term desorption kinetics of ¹³⁷Cs and ¹³³Cs from soils collected in Fukushima Prefecture by batch desorption experiments in the presence of cation exchange resin as a sorbent. The sorbent can keep the concentration of Cs⁺ in the aqueous phase low and prevent re-sorption of desorbed Cs⁺. Up to 60% of ¹³⁷Cs was desorbed after 139 d in dilute KCl media, which was larger than the desorption by conventional short-term extraction with 1 M ammonium acetate. Desorption of ¹³⁷Cs continued even after this period. It was also found that high concentration of K⁺ prevented desorption of Cs⁺ in the initial stage of desorption, but the effect was alleviated with time. The desorbed fraction of stable Cs was smaller than that of ¹³⁷Cs. This indicated that ¹³⁷Cs may gradually move to more stable states in soils. The half-life of ¹³⁷Cs desorption from the slowest sorption site was estimated to be at least two years by a three-site desorption model.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

An off-shore earthquake with an intensity of 9.0 on the Richter scale and tsunamis hit the eastern part of Japan on March 11th, 2011, which caused the accident of the Fukushima Dai-ichi Nuclear Power Plant (FDNPP). Many radionuclides were released to the environment from the damaged plants (Thakur et al., 2013). Vast areas of Fukushima and surrounding prefectures were thus contaminated by radionuclides such as ¹³⁴Cs, ¹³⁷Cs, and ¹³¹I (Yoshida and Takahashi, 2012). The area of highly contaminated region (≥ 1000 kBq m⁻² as the sum of ¹³⁷Cs and ¹³⁴Cs) was reported to be 646 km² only in Fukushima Prefecture (Hashimoto et al., 2012). Among the radionuclides ¹³⁷Cs is most considerable for its long-term environmental effects because of its relatively long half-life (30.1 y), compared with the other radionuclides (2.1 y for ¹³⁴Cs and 8 d for ¹³¹I). Cesium is known to be strongly fixed in a surface layer of soil (Fujii et al., 2014; Kato et al., 2012; Takahashi et al., 2015); thus topsoil stripping is an effective way for reduction of dose from contaminated soils and has been conducted in the contaminated areas.

A tremendous mass of contaminated soils is being generated by such decontamination, and the preparation of interim storage and disposal sites for excavated soils are important. To construct these facilities knowledge on chemical speciation and migration of ¹³⁷Cs in soils is needed. The volume of contaminated soils from Fukushima Prefecture is estimated to be about 2×10^7 m³ after the incineration (Ministry of the Environment, 2015), which is equivalent to about 20% of the rest of total capacity of all the final disposal sites of non-radioactive wastes in Japan. Knowledge on desorption processes or chemical and mineralogical distribution of ¹³⁷Cs in soils is useful for some volume reduction methods, where ¹³⁷Cs is extracted from contaminated soil to a liquid phase and captured by sorbents or relatively small-sized grains with greater ¹³⁷Cs concentrations are collected by for instance elutriation. The radiological and environmental impact of the disposal will be assessed by considering a type of a waste form used to stabilize ¹³⁷Cs, if any, and a specific design of the disposal site. If raw contaminated soils are directly disposed, this also includes the long-term estimation of the release of ¹³⁷Cs from soils and its migration through engineered barriers and surrounding soils in a similar way to the performance assessment of the disposal of high-level radioactive wastes, which contain a long-lived radioisotope of cesium, ¹³⁵Cs. Investigation on the desorption characteristics according to chemical and mineralogical properties of disposed soils could decrease uncertainty of the assessment.

* Corresponding author.

E-mail address: saito@n.t.u-tokyo.ac.jp (T. Saito).

¹ Present address: Nuclear Regulation Authority, Japan, 1-9-9, Roppongi, Minato-ku, Tokyo 106–8450, Japan.

Cesium is known to be sorbed to clay minerals, particularly micaceous minerals, in soils (Absalom et al., 1995; McKinley et al., 2001; Nakao et al., 2008). When Cs^+ is sorbed to so-called frayed edges of micaceous minerals located in peripheral wedged regions of the minerals, where the interlayer spaces are partly expanded due to weathering, the sorption causes partial collapse of the interlayer and induces strong fixation of Cs^+ (Sawhney, 1972). This collapse of interlayer is due to the small hydration energy of Cs^+ (287.3 kJ/mol), compared with those of other alkaline metal ions such as K^+ (337.1 kJ/mol) and Na^+ (420.8 kJ/mol) (Brouwer et al., 1983). This specific sorption occurs only at a limited part of the total sorption sites of micaceous minerals; it becomes dominant only when the concentration of Cs^+ in solution is low (Benedicto et al., 2014).

Although many researchers have studied desorption of Cs^+ from sites with various selectivity for Cs^+ in soils or in pure minerals, they might underestimate the desorption amount and rate due to relatively short periods of the experiments and the presence of re-sorption. The reversibility of sorption of Cs^+ on soils or pure minerals has been studied by batch-wise desorption experiments with soil or minerals spiked with a small amount of $^{137/134}\text{Cs}$, and the irreversible sorption of Cs^+ has been reported. However, most of the desorption experiments were carried out for relatively short desorption periods like one day to two weeks (Comans et al., 1991; Rigol et al., 1999; Wang and Staunton, 2010; Wauters and Cremers, 1996). A few studies have shown slow desorption of Cs from sediments or micaceous minerals, based on desorption experiments over two weeks (De Koning and Comans, 2004; Liu et al., 2003). Moreover, it is reported that an increase of sorption time slows down subsequent Cs^+ desorption and leads to the irreversibility of the sorption (Absalom et al., 1995; Shenber and Eriksson, 1993; Takeda et al., 2013). This means that the distribution of Cs^+ in soils may change to more stable forms with time and that Cs^+ desorption evaluated in a relatively short period of time can be underestimated. This is especially the case for actual contaminated soils after some time since the deposition. The other problem is the effect of re-sorption of Cs^+ on soils. It has been well known that Cs^+ sorption onto illite, vermiculite, or similar micaceous minerals are relatively fast at least in their initial stages (De Koning and Comans, 2004). It was reported that Cs^+ desorbed once from micaceous minerals was sorbed again to them (Comans et al., 1991; Wahlberg and Fishman, 1962). This re-sorption constrains apparent exchangeability and prevents evaluation of intrinsic desorption kinetics.

The objective of this research is to evaluate the long-term desorption kinetics of Cs^+ from contaminated soils collected near the FDNPP after the accident. Long-term desorption experiments up to 139 d have been conducted in the presence of cation exchange resin so that released Cs^+ is immediately captured by the resin. In this setting re-sorption of Cs^+ to soils and an increase of its aqueous concentration, both of which result in a decrease of the apparent desorption rate, are diminished. A pseudo first-order desorption model with multiple Cs-sorption sites in soils was applied to the obtained desorption curves to estimate the desorption rate constants. The ^{137}Cs desorption from one of contaminated soils by the different concentrations of K^+ was studied to evaluate the effects of competing K^+ . Furthermore, the desorption of ^{137}Cs was compared with that of ^{133}Cs , which had existed in soils before the accident and whose distribution is likely in the steady state, to infer the impact of the contact time of Cs^+ with soils on its desorption.

2. Materials and methods

2.1. Materials

For the entire experiments, Milli-Q grade pure water and

analytical-grade chemicals purchased from Wako Pure Chemical Industries were used, unless otherwise noted.

Four soil samples collected near the FDNPP in Fukushima Prefecture on April 20th, 2011, were used in this study. The soil collection and the determination of the inventories of γ -emitting radionuclides including ^{137}Cs were reported elsewhere (Fujiwara et al., 2012). The geochemical and grain-size distribution of ^{137}Cs in the soils as well as their physicochemical properties such as the size distribution, CEC, and mineralogical composition were also previously determined by Saito et al. (2014) and are summarized in Table 1. The amounts of ^{133}Cs in these soils were determined by ICP-MS (7500cx, Agilent Technologies) after total dissolution of the soils and presented in Table 1. For this, aliquots (0.1 g) of a soil sample were added to the mixture of nitric, perchloric, and hydrofluoric acids in a Teflon® beaker, and the suspension was heated to 200 °C and evaporated to dryness. After cooling the acids were added and the treatment was repeated twice. Finally, nitric acid was added and the sample was heated to 200 °C for 4 h with a watch glass as a lid to completely dissolve the remaining solids. The contents of micaceous minerals in these soils are similar and around 4% except for the soil No. 32, which exhibits a somewhat larger content (12.1%) (Saito et al., 2014).

2.2. Desorption experiments with a sorbent

The desorption of Cs^+ from the soils was conducted according to the so-called “infinite bath” technique (Wauters et al., 1994). In this technique Cs^+ extracted to the aqueous phase is captured by a sorbent. By this way the concentration of Cs^+ in the solution is kept low and re-sorption of Cs^+ to soils is diminished. Different sorbents have been used for this purpose, including ammonium–copper–hexacyanoferrate called Giese granulate (De Koning and Comans, 2004; Madruga and Cremers, 1997; Vidal et al., 1995; Wauters et al., 1994) and cation exchange resins (Maes et al., 1999; Valcke and Cremers, 1994; Wauters et al., 1994). Although the former exhibits higher selectivity for Cs^+ , it is difficult to extract ^{133}Cs for quantification in our case. Therefore, this study adopted cation exchange resin, Dowex 50Wx8 (mesh size: 50–100, The Dow Chemical Company), as a sorbent. The resin was used after saturation with K^+ by 2 M KCl solution twice. We confirmed the overall rate of the transport of Cs^+ through the dialysis membrane and the sorption to the resin by adding 5 ml of the resin in a dialysis bag to 0.1 mM NH_4Cl solution containing 0.1 μM CsCl . As a result, almost all Cs^+ were adsorbed to the resin within 12 h.

To compare the desorption behaviors among different soils, 5 g of each soil (soil no. 15, 32, 37, and 48) was dispersed in 10^{-3} M KCl solution. Similarly, to investigate the effect of the competing cation, 1 g of the soil no. 37 was dispersed in 10^{-1} , 10^{-3} , and 10^{-5} M KCl solutions. The mass of soils used in the desorption experiments was decided, based on the radioactivity of ^{137}Cs in a given soil sample and the detection limit of the detector. During extraction, pH of the suspensions was periodically measured. Each soil was agitated in 400 ml of KCl solution in the presence of 10 ml of the resin in a dialysis bag. The capacity of 10 ml of the resins corresponds to more than twenty times larger than total exchangeable cations in the soils. The desorption experiments were continued for 139 d, during which the resins was replaced with new ones ten times. Considering the selectivity between Cs^+ and other mono- and di-valent cations (Patnaik, 2004), we assume that the competition of cations released from the soils against Cs^+ sorption by the resin is negligible. The removed resin samples were weighed, and half of them were dried and used for the activity measurements of ^{137}Cs . The ^{137}Cs concentrations of the dried resin samples in plastic containers (U8, AS ONE corporation) were determined by γ -ray spectrometry with a Ge detector (GCW1521, CANBERRA Industries). The

Download English Version:

<https://daneshyari.com/en/article/8082027>

Download Persian Version:

<https://daneshyari.com/article/8082027>

[Daneshyari.com](https://daneshyari.com)