

Thesis Summary

Cationic Surfactant for Remediation of ^{137}Cs -contaminated Soil and the Influence of Its Head Group Structure on the Cs Desorption from Clays and Clay Minerals

(^{137}Cs で汚染した土壌修復のためのカチオン界面活性剤とそのヘッドグループ構造の粘土と粘土鉱物からの Cs 除去への影響)

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Substantial amounts of radionuclides released following the 2011 Fukushima Daiichi Nuclear Power Plant accident have contaminated lands in the Fukushima area of Japan. Of the radionuclides found in Fukushima soil, radioactive cesium (^{137}Cs) is still of major concern because of its long half-life ($t_{1/2} = 30.1$ years), consequently, being major contributor to public health impact of long-term effect. Particularly, deposited ^{137}Cs in the soil takes part in the internal exposure when crops cultivated from contaminated land are consumed. It has been

observed that Cs ions are strongly bonded to clay minerals of the Fukushima soil, causing their retention in the upper 5-cm soil layer.¹ Cs was mainly adsorbed to micaceous clay minerals¹ and probably also presented in kaolinite-, and smectite-like clay minerals.² In order to overcome the issues, soil remediation strategy is necessary both to reduce radiation effect on public health and to recover the land. The soil washing method by cationic surfactants ($\text{R-N}(\text{CH}_3)_3^+$; R=long hydrocarbon chain group; $\text{N}(\text{CH}_3)_3^+$ = head group) has been widely used as desorption agent (desorbent) to effectively desorb Cs from clay minerals via ion exchange between positively charged amine groups with Cs ions. Moreover, the length of their hydrocarbon chain group plays essential role in enhancing Cs desorption. The longer the surfactant chain length, the more Cs were released from kaolinite due to the stronger affinity of longer chain with kaolinite surfaces.³ In the case of montmorillonite, a longer hydrocarbon chain increased its interlayer distance, therefore enhancing Cs desorption efficiency.⁴ Although the influence of different surfactant chain lengths on the Cs desorption from clay minerals has been studied extensively, the contribution of their head group to such desorption mechanism has not been well understood. The present PhD thesis aims to examine the effectiveness of cationic surfactant of benzyldodecyldimethylammonium bromide (BDAB) to desorb Cs from actual ^{137}Cs -contaminated soil from Fukushima Prefecture and to investigate the influence of cationic surfactant head group on the desorption of Cs from specific clays and clay minerals by comparing two kinds of surfactants having the same 12 hydrocarbon chain lengths but different head group types. In this case, BDAB which has bulky head group was compared to dodecyltrimethylammonium bromide

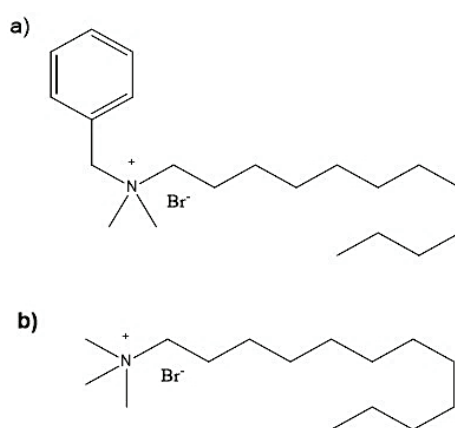


Fig. 1. Structure of (a) BDAB and (b) DTAB

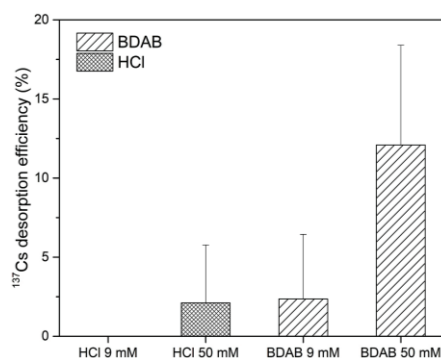


Fig. 2. ^{137}Cs desorption from Fukushima soil

BDAB which has bulky head group was compared to dodecyltrimethylammonium bromide

(DTAB) with linear structure (Fig. 1). The clays used in this study included Na- and Ca-bentonite, which are dominantly composed of montmorillonite. Clay minerals such as kaolinite and illite were also used. Chapter 1 shows general introduction.

Chapter 2 shows comparison of cationic surfactant and acid solution for remediation of actual ^{137}Cs -contaminated soil taken Fukushima Prefecture. The experimental results indicated that cationic surfactant of benzyldimethyldodecylammonium bromide (BDAB) was more effective in desorbing ^{137}Cs from contaminated soil of Fukushima even by using a low concentration in comparison to the commonly used desorbent, HCl (Fig. 2).⁵

Chapter 3 shows the influence of cationic surfactant head group structures on the Cs desorption from clays and clay minerals. Samples were first contaminated by Cs solution with maximum adsorption capacity, followed by desorption experiment using desorbents. Batch desorption experiment indicated that, in general, desorption efficiency for all studied samples increased by increasing surfactants concentration.⁶ In swelling bentonites that highly contain montmorillonite, Cs desorption was accompanied by interlayers' expansion. In the case of Na-bentonite, BDAB showed higher Cs desorption efficiency than DTAB due to larger Na-bentonite interlayers expansion after intercalation of BDAB (bulkier ammonium head group structure). In contrast, Cs desorption efficiency from Ca-bentonite was relatively similar, which corresponded to the identical interlayers' expansion after intercalation of both surfactants. It was because divalent cation of Ca^{2+} must associate with two negatively charged interlayers, limiting interlayer expansion of Ca-bentonite. Cs desorption from kaolinite was more governed by surfactant micelles. In comparison to surfactant ions, surfactant micelles had a stronger affinity to the clay surface, enhancing Cs desorption efficiency. Fig. 3. shows that as the surfactant micelle formed earlier for BDAB, a faster Cs desorption was achieved. Thus, BDAB desorbed Cs efficiently than DTAB due to formation of surfactant micelle at low concentration in BDAB solution. For Cs desorption from illite, both surfactants even showed relatively similar performance with HCl used as a desorbent control. This was due to the existence of frayed edge sites in illite, which provokes strong Cs retention. Desorption kinetic model of pseudo-second order fitted well to all studied samples by BDAB and DTAB suggested that desorption process was ion-exchange process.

Chapter 4 shows the general conclusions.

References

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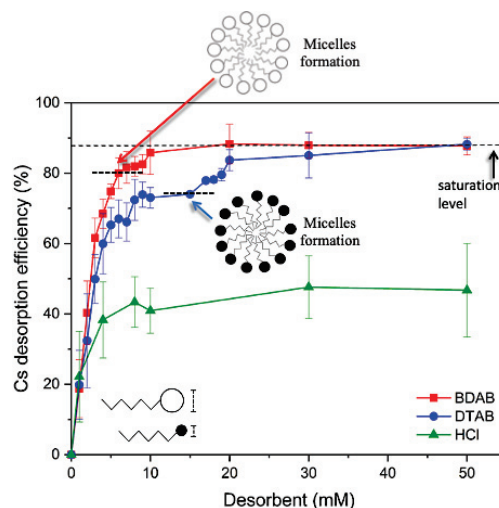


Fig. 3. Cs desorption from kaolinite