



# LEACHING TESTS OF SIMULATED COGEMA BITUMINIZED WASTE FORM

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91

The leaching behavior of COGEMA-type bituminized radioactive waste was studied for the atmospheric and anaerobic conditions. Active and inactive laboratory-scale bitumen samples, including two major salts of  $\text{NaNO}_3$  and  $\text{BaSO}_4$ , were contacted with deionized water, an alkaline solution (0.01 mol/L  $\text{Ca}(\text{OH})_2$  or 0.03 mol/L  $\text{KOH}$ ), or a saline solution (0.5 mol/L  $\text{KCl}$ ). It was found that the release of salt was reduced in the  $\text{Ca}(\text{OH})_2$  solution compared with deionized water under the atmospheric conditions. No significant difference in the concentrations of  $^{237}\text{Np}$  in leachants contacted with the samples for 7 days was observed between the atmospheric and the anaerobic conditions.

## INTRODUCTION

Bituminized radioactive waste will be returned to Japan from COGEMA reprocessing plants of spent nuclear fuel. This waste is categorized into "TRU waste" in Japan and will possibly be buried in the deep underground repository(1). The leaching behavior of and the release of radionuclides from buried bituminized waste form are needed to be quantitatively evaluated for the radiological safety assessment of the disposal. The leaching behavior depends on the physical property and the chemical composition of the waste form, and the chemical environment of the repository. Leaching behavior of the COGEMA bituminized waste has not studied much(2,3) and the release of transuranium elements and radionuclides for deep underground conditions has been scarcely reported.

The COGEMA bituminized waste is dual-salt system, containing two major salts: an insoluble salt, barium sulfate ( $\text{BaSO}_4$ ), and a soluble salt, sodium nitrate ( $\text{NaNO}_3$ ). Waste elements are incorporated in either or both of these salts in bitumen matrix. We have performed laboratory-scale leaching tests for the active and inactive dual-salt bituminized waste under the atmospheric and anaerobic conditions. Deionized water, an alkaline solution and a saline water were employed as the leachant: The alkaline water represents the cement-contacting groundwater, and the saline water the sea water environment. The part of the results including the release of total organic carbon, Na as a salt element and  $^{237}\text{Np}$  and  $^{239}\text{Pu}$  as waste elements are presented.

## EXPERIMENTAL

### Preparation of Simulated Bituminized Waste Samples

Simulated bituminized waste was fabricated in a 1L-stainless steel beaker. Salts ( $\text{NaNO}_3$ ,  $\text{BaSO}_4$ ) and waste elements (Sr, Cs and I) were mixed with molten straight bitumen 60/80 at 140 – 160°C. Cesium, I and the soluble salt,  $\text{NaNO}_3$ , were added as aqueous mixture solution of  $\text{CsI}$  and  $\text{NaNO}_3$ . Strontium was added as a preconditioned powder of a solid solution,  $(\text{Sr}_x, \text{Ba}_{1-x})\text{SO}_4$ . The composition of the fabricated inactive bitumen samples was: 60 wt% of straight bitumen, 2.5 wt% of  $\text{CsI}$ , 17.5 wt% of  $\text{NaNO}_3$  and 20 wt% of  $(\text{Sr}_x, \text{Ba}_{1-x})\text{SO}_4$ . Active samples were prepared in a similar manner, and divided into two fractions depending on the determination method: Samples of the first fraction were doped with only  $^{90}\text{Sr}$ , where part of the Sr of  $(\text{Sr}_x, \text{Ba}_{1-x})\text{SO}_4$  was replaced by  $^{90}\text{Sr}$ , and the other samples contained  $^{134}\text{Cs}$ ,  $^{237}\text{Np}$  and  $^{239}\text{Pu}$ . Cesium iodide was doped with  $^{134}\text{Cs}$ . Both of  $^{237}\text{Np}$  and  $^{239}\text{Pu}$  were added as nitric acid solution.

The bituminized mixture was poured into 49mm $\phi$  x 15mm<sup>H</sup> stainless dish, and cooled down at room tem-

perature. A care was taken in mixing molten bitumen and chemicals in a heated beaker to avoid precipitation of heavy salt,  $(\text{Sr}_x, \text{Ba}_{1-x})\text{SO}_4$ . The precipitation results in heterogeneous waste form and makes a proper interpretation of leaching data impossible.

### Leaching Tests

The bituminized waste samples were contacted with 190mL of leachant in a sealed polypropylene container. The initial surface-area-to-volume ratio was 0.1m. The leachant was deionized water, an alkaline solution (0.01 mol/L  $\text{Ca}(\text{OH})_2$  or 0.03 mol/L KOH), or a saline water (0.5 mol/L NaCl or KCl). The samples were kept at 25°C or 45°C. Leaching tests under anaerobic conditions were performed in a controlled atmosphere glove box under argon ( $\text{O}_2 < 1\text{ppm}$ ), and the reducing conditions of the leachant were kept by hydrazine monohydrate. Only the top surface of the samples was brought in contact with the leachant.

At fixed intervals of time, the pH and the redox potential (Eh) of the leachants were measured, and the leachants were removed for analysis. The concentrations of stable isotopes (Na, Sr, Ba, Cs and I),  $^{239}\text{Np}$  and  $^{239}\text{Pu}$  in the leachants were determined with inductively coupled plasma mass spectroscopy, ICP-MS. The concentrations of  $^{90}\text{Sr}$  and  $^{134}\text{Cs}$  were determined radiometrically through  $\beta$ -counting with liquid scintillation counter and  $\gamma$ -counting with Ge(Li) detector, respectively. The total organic carbon (TOC) was also determined as an indicator of degradation of bitumen matrix.

## RESULTS AND DISCUSSION

### Leaching Behavior of Bituminized Waste

A typical physical evolution of bituminized waste form in contact with aqueous solution is swelling. Channeling and cracks are formed in the course of swelling, which lead to the expansion of the surface area of the bitumen-salt mixture exposed to the surrounding media, and results in the enhanced release of embedded salts and radionuclides. In the present test, an abrupt increase in the amount

of a salt element, Na, was observed as shown in Fig. 1(a). A bituminized waste sample leached with deionized water at 25°C under the atmospheric condition began swelling at around the 100-th day of leaching and remarkably swelled after the 150-th day. The release of Na increased accordingly, and that of other elements of Ba, Sr, Cs and I also increased although not shown here.

The degradation of bitumen matrix is not affected by swelling, as shown in Fig. 1(b) where the amount of TOC was plotted as a function of time. The TOC concentrations increased gradually with time with no appreciable effect of the swelling. The amount of TOC released is larger at a higher temperature like as seen for Na. However, unlike Na, the release of TOC was larger in  $\text{Ca}(\text{OH})_2$  solution than in deionized water. The release of salt

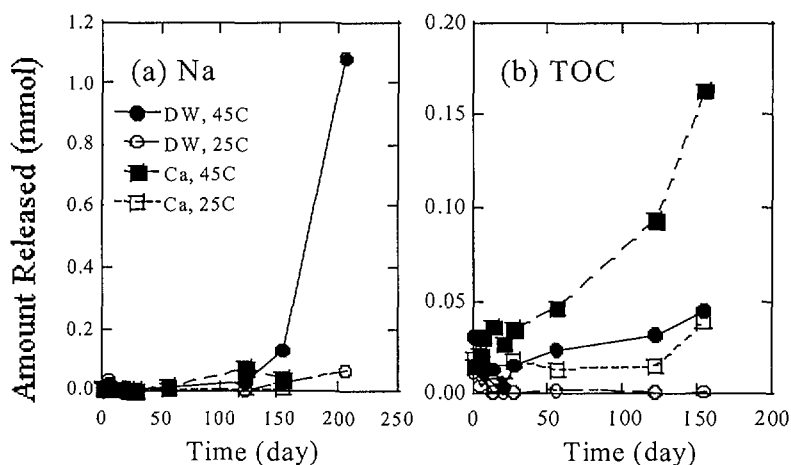


Fig.1 The release of (a) Na and (b) TOC from a COGEMA-type bituminized waste leached under the atmospheric conditions: DW: Deionized water, Ca: 0.01 mol/L calcium hydroxide solution.

elements under the atmospheric condition is suppressed in  $\text{Ca(OH)}_2$  solution as reported by Brodersen(4) and Sazarashi *et al.*(5). It may be because the surface of the bituminized waste sample was covered by precipitate of  $\text{CaCO}_3(\text{s})$  formed using  $\text{CO}_3^{2-}$  dissolved in the leachants. Such suppression was not observed in the samples leached under the an-

aerobic Ar-gas atmosphere where  $\text{CO}_2$  gas is not introduced in the leachants. The comparison between the release of Na and TOC indicates that the release of salts from the COGEMA-type bituminized waste is dependent on swelling rather than degradation of the bitumen matrix, and degradation of bitumen matrix is thought to be less responsible for the performance of bituminized waste regarding confinement of salts.

The similar leaching behavior was observed for the anaerobic conditions except the effect of  $\text{Ca(OH)}_2$  solution. The amount of release of salts and waste elements was similar between the atmospheric and anaerobic conditions. Swelling and the associated increase in release were observed also under the anaerobic conditions.

The mass transport in the waste form has been assumed to be diffusion-controlled(7), and approximated by the Fick's law. No physical transformation of diffusion medium is permitted in applying the Fick's law. This is not always the case for bituminized waste due to swelling. The Fick's law was applied, however, to the present results on the release of Na for approximate estimates of the diffusion coefficient,  $D$ . The  $D$  was calculated for the release before (< 120 days) and after (120-260 days) swelling for the leach test at 45°C. Two different values of  $D$  were obtained as listed in Table I. The  $D$  value for swollen sample (120-260 days) is obviously larger than that for the intact sample (<120 days), which indicates the transport of Na through preferential channels or cracks in the sample formed in response to the internal swelling pressure.

The values of  $D$  obtained in this study are smaller than those estimated for other types of bituminized waste as seen in Table I. This indicates slower diffusion of Na ion in COGEMA-type bituminized waste form. The diffusion behavior of bituminized waste depends on the swelling, and hence reflects both the physical and chemical property of the waste form. The affecting physical property may include hardness and the size of salt particles, and the chemical property is the composition of the embedded salts. A chemical feature of COGEMA-type bituminized waste is the dual-salt composition: soluble  $\text{NaNO}_3$  and insoluble  $\text{BaSO}_4$ , as two major salts. The difference in diffusion coefficient shown in Table I may reflect the effects of these factors. The presence of the insoluble salt particles is considered to partly function to reduce the release from bituminized waste, and a study on this function is underway.

Table I Diffusion coefficient,  $D$ , of Na in bituminized waste

Type	Leachant	Temp.	$D$ ( $\text{m}^2/\text{sec}$ )	Ref.
CEA	deionized water	25°C	$3 \times 10^{-18}$ (206 d)	This study
		45°C	$8 \times 10^{-18}$ (<120 d)	
			$5 \times 10^{-15}$ (120-206 d)	
"Kansai Electric"	deionized water, mortar water	RT, 60°C, 90°C	$(3-4) \times 10^{-14} *$ (15 months)	(6)
Eurobitum R85/40	clay water	23°C	$1.4 \times 10^{-13}$ (720 d)	(3)
	clay-cement water		$1.5 \times 10^{-13}$ (720 d)	

\* The value of  $D$  is not shown in ref. (6). Calculated from the data given.

### Concentrations of $^{237}\text{Np}$ and $^{239}\text{Pu}$ in leachants

Neptunium, added as Np(V) to heated bitumen in preparing the mixture of bitumen and chemicals, is expected to be present as Np(V) in the samples during the equilibration of the leach tests. The released Np was not probably reduced in the leachants for the 7-day equilibration under both the atmospheric and anaerobic conditions, and kept the pentavalent state. The almost the same concentrations in the same leachants under atmospheric and anaerobic conditions, as shown in Table II, consequently implies the formation of the same Np(V) compound in the leachants. A clear difference is observed in the concentration of Np between different leachants. The concentration was lower in 0.5 mol/L KCl solution than in other two leachants. Although a quantitative explanation is difficult for the difference, the lower concentrations of Np in the 0.5 mol/L KCl solution is likely due to the high ionic strength. The release of  $^{239}\text{Pu}$  was so small under the detection limit that thermodynamic consideration is unable to apply to understand the result.

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Table II The concentrations of  $^{237}\text{Np}$  and  $^{239}\text{Pu}$  in leachants contacting with COGEMA-type bituminized waste at 45°C for 7 days (mol/L)

condition	leachant	$^{237}\text{Np}$	$^{239}\text{Pu}$
atmos- pheric	deionized water	$5.5 \times 10^{-7}$	$<1.3 \times 10^{-10}$
	0.5 mol/L KCl	$2.2 \times 10^{-9}$	$<1.3 \times 10^{-10}$
	0.03 mol/L KOH	$4.0 \times 10^{-8}$	$<1.3 \times 10^{-10}$
anaerobic	deionized water	$1.4 \times 10^{-7}$	$<1.3 \times 10^{-10}$
	0.5 mol/L KCl	$7.6 \times 10^{-10}$	$<1.3 \times 10^{-10}$
	0.03 mol/L KOH	$2.8 \times 10^{-8}$	$<1.3 \times 10^{-10}$

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