Oral Presentations

Monday, 23 September 2013

Hall & Meeting Room, Kanazawa Bunka Hall

	Monday, 23 September				
Time		Hall		Meeting Room	
09:00-09:10	9:00	Arrangement for presentation			
09:10-09:20					
09:20-09:30					
09:30-09:40	9:30	Opening Ceremony			
09:40-09:50					
09:50-10:00					
10:00-10:10	10:00	**Hevesy Award Ceremony** R. S. Dybczyński			
10:10-10:20					
10:20-10:30					
10:30-10:40					
10:40-10:50					
10:50-11:00					
11:00-11:10	11:00	**Coffee Break**			
11:10-11:20	11:10	PL-01	**Plenary**		
11:20-11:30					
11:30-11:40			M. Yamamoto		
11:40-11:50	11:40	PL-02	**Plenary**		
11:50-12:00					
12:00-12:10			I. McKinley		
12:10-13:20	12:10	**Lunch Time**			
13:20-13:30	13:20	FKI-01	**Invited**	API-01	**Invited**
13:30-13:40					
13:40-13:50			H. Tsuruta		H. Harada
13:50-14:00	13:50	FKI-02	**Invited**	API-02	**Invited**
14:00-14:10					
14:10-14:20			Y. Takahashi		Y.L. Zhao
14:20-14:30	14:20	FKI-03	**Invited**	APO-01	General
14:30-14:40					T. M. Nakanishi
14:40-14:50			M. Aoyama	APO-02	General
14:50-15:00	14:50	FKI-04	**Invited**		S.H. Jung
15:00-15:10				APO-03	General
15:10-15:20			B. Grambow		M. Anvia
15:20-15:30	15:20	**Coffee Break**			
15:30-15:40					
15:40-15:50	15:40	FKO-01	General	NCO-01	General
15:50-16:00			A. Shimada		Z. Qin
16:00-16:10	16:00	FKO-02	General	NCO-02	General
16:10-16:20			Y. Miyake		W.M. Kerlin
16:20-16:30	16:20	FKO-03	General	NCO-03	General
16:30-16:40			T. Ohta		Y.K. Ha
16:40-16:50	16:40	FKO-04	General	NCO-04	General
16:50-17:00			Y. Muramatsu		I. Laszak
17:00-17:10	17:00	FKO-05	General	NCO-05	General
17:10-17:20			Y. Satou		Y. Xu
17:20-17:30	17:20	FKO-06	General	NFO-01	General
17:30-17:40			M. C. Honda		Y. Miyamoto
17:40-17:50	17:40	FKO-07	General	NFO-02	General
17:50-18:00			Z.J. Zhang		N. Gharibyan
18:00-18:10	18:00	FKO-08	General	NFO-03	General
18:10-18:20			D.R. Neville		R. Sudowe
18:20-18:30					
18:30-18:40					
18:40-18:50					
18:50-19:00	18:50	**Poster Session**			
19:00-19:20					
19:20-19:40					
19:40-20:00					
20:00-	20:00				

50 Years of Adventures with Neutron Activation Analysis with the Special Emphasis on Radiochemical Separations

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Radiochemical separations are the key element of analytical methods based on radiochemical neutron activation analysis (RNAA). At the same time, the work in this area is the best reference to the heritage of George Hevesy who received Nobel Prize in Chemistry 1943 *"for his work on the use of isotopes as tracers in the study of chemical processes"*. In this paper author's activities in devising new systems for the separation of inorganic ions, determination of trace elements by RNAA, but also purely instrumental NAA (INAA), are reviewed. In the early years of atomic era, only non-selective radiation detectors such as Geiger-Müller or proportional counters were available, so except of some special cases , the analysis had to rely on chemical separations. Radiochemical separation retained much of its significance even with the advent of scintillation spectrometry. After Ge(Li) and HPGe detectors became available, most of analyses were done by γ-ray spectrometry (INAA) but in several instances group separation was necessary. There were always two philosophies in radiochemical separations intended for RNAA. First, relied on addition of inactive carriers for the radionuclides to be quantified, isolation of a portion of an element in the state of sufficient radiochemical purity, followed by radioactivity measurement and determination of chemical yield. Second, assumed that sufficiently selective and practically quantitative separation of radionuclides into groups or individual species can be attained by properly designed and tested chromatographic procedures , thus obviating the need for the determination of chemical yield. This second approach was mostly used in author's laboratory. New anion exchange system for the separation of rare earth elements (REE) as complexes with EDTA was devised and used for the determination of traces of Lu, Ho and Dy in Er_2O_3 as well as La in Pr_6O_{11}. Fundamental study performed on the effect of temperature and resin cross-linking was helpful in optimization of the separation procedure. Ion exchange behavior of several elements in the system: Dowex50WX2[H^+] – HBr was studied and was the basis for selective separation and determination of La,Sc, Ga and Hf by NaI(Tl) spectrometry in refractory materials. Complex separation schemes involving some cation and anion exchange columns were devised for the determination of impurities in platinum and rhodium metals by RNAA. Traces of cesium in mineral salts (down to 8×10^{-9}%) were determined by pre-irradiation isolating cesium on phenolsulfonic resin followed by post-irradiation purification and measurement of short-lived ^{134m}Cs with very thin NaI(Tl) crystal. Pre-irradiation separation together with post-irradiation purification and γ-ray spectrometry was used for the determination of noble metals in geological materials as well as all lanthanides in biological materials. The uses of INAA included *inter alia* analysis of meteorites, human hair (for forensic, environmental and biomedical purposes), analysis of fly ashes (together with investigation of leaching of trace elements by water and acid rain), study on homogeneity of certified reference materials (CRMs), and contribution to the certification of new CRMs. The idea of "definitive methods" by RNAA was proposed, the essence of which is the combination of neutron activation with selective and quantitative post-irradiation separation of the desired radionuclide by column chromatography followed by γ-ray spectrometric measurement. A set of rules which should be observed when constructing definitive methods , as well as criteria which must be fulfilled to acknowledge the analytical result as obtained by definitive method, were formulated. The methods elaborated by us , e.g. those for the determination of Co, Se or Fe in biological materials , with their expanded uncertainties of 2.7-3.4% are comparable to those by ID-MS. Definitive methods by RNAA are the only methods of such class, possible for monoisotopic elements. In accordance with the ISO/IEC Guide 99:2007, definitive methods by RNAA may be termed: Ratio primary reference measurement procedures (RPRMPs). Such methods are intended for verification of accuracy of other methods of trace analysis and certification of the candidate reference materials.

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Overview of the Fukushima Dai-ichi nuclear power plant (FDNPP) accident, with amounts and nuclear compositions of the released radionuclides

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Since release of artificial radionuclide into the environment was first initiated in 1945 at Alamogordo, New Mexico, the emission developed through the World War II of Hiroshima and Nagasaki, and continued with nuclear weapons testings, which finished in 1980. Furthermore, accidental releases of radioactivities have occurred through the events such as the fall of nuclear-fueled satellites, and accident in nuclear power plants and the related facilities (Windscale (Sellafield), Three Mile Island, Chernobly, etc.). The Japanese also experienced tragedies of the Fifth Fukuryu-Maru accident at Bikini atoll (1954) and the JCO criticality accident at Tokai-mura (1999).

This time, as widely recognized, the *M 9.0* earthquake off the Pacific coast of Japan on 11 March 2011 and the subsequent tsunami induced an accident in the FDNPP. Total loss of electric power happed and the cooling systems of some of the reactor units 1-3 failed, resulting in hydrogen explosion in the reactor buildings and venting of gases, with significant releases of radionuclides into the atmosphere. In addition, highly contaminated water with large amounts of radionuclides was directly leaked or discharged into the North Pacific. Public health actions to reduce the negative consequence of this event were taken by government; a 20-km evacuation zone was put in place around the site, with a sheltering zone between 20 and 30 km. The Japanese Government and various prefectural governments started emergency monitoring of radioactivity to assess the environmental and human effects by the FDNPP accident. The details of the FDNPP accident have been already opened in a report by the Japanese Government to the IAEA (IAEA 2011, NISA, 2011, Japanese Government 2011). The Fukushima accident was classified on the INES (International Nuclear and Radiological Event Scale) scale at the maximum level of 7, being the same as that of the Chernobyl nuclear power plant (CNPP) accident (April 26, 1986). Compared to the CNPP accident, the FDNPP accident presents a much more difficult situation, since various reactor cores and spent fuel pools may have contributed to the emissions.

Several atmospheric radionuclide releases occurred mainly during the periods from March 12 through March 23, 2011. The air contaminated by the released radionuclides, especially noble gas (^{133}Xe, etc.) and volatile nuclides such as ^{131}I, ^{134}Cs and ^{137}Cs, eventually spread over large distances, and were observed at monitoring stations (IMS by CTBTO) throughout the world. In Japan, the radionuclide fallout resulted in a track of contaminated land that expanded approximately 50 km to the northwest of the FDNPP and later in a larger, lower level area of contamination mostly to the south and southwest. Total estimated atmospheric releases of ^{131}I and ^{137}Cs by government are around 160 and 15 PBq, respectively, although exact amount of radionuclides emitted are still being argued. These levels are lower for ^{131}I and ^{137}Cs by about a factor of 12 and 7, respectively, compared with those of the CNPP accident. More than 70% of the released radionuclides into the atmosphere were deposited over the North Pacific. Thus, by broad survey and early investigations, whole picture about levels and spreading areas of contaminants, especially ^{134}Cs and ^{137}Cs, has been becoming clear, together with the situation of the plant. For radioiodine released, this nuclide consists of gaseous and particulate forms, therefore, its behavior seems to be very difficult, resulting in large variation of ^{131}I/^{137}Cs ratios measured in air and soil. Since ^{131}1 is a short half-life (8 d), its reconstruction in the initial stage by ^{129}I is attempted to evaluate the impact of human health from radioiodine. For other possible released radionuclides, radiostrontium (^{89}Sr and ^{90}Sr) and transuranic nuclides, which have attracted much scientific and potential radiological concern, are poorly investigated, mainly because of the difficulties of analyzing and measuring these beta- and alpha-emitting radionuclides. These nuclides are much less volatile than other fission products such as cesium and iodine isotopes. TEPCO published a ^{90}Sr/^{137}Cs ratio in soils 10^{-3}. Actual environmental measurements showed variability in the ^{90}Sr/^{137}Cs ratios for different locations, ranging of 10^{-2}-10^{-4} in surface soils within the 50 km area from the FNPP. On the other hand, in addition to the limited data of Pu isotopes in soil and litter samples, ^{236}U, Pu isotopes (^{238}Pu, ^{239}Pu and ^{240}Pu), ^{241}Am and Cm isotopes (^{242}Cm and ^{243,244}Cm) have been measured by us for roadside dust collected at the Fukushima areas heavily contaminated. When the ratios among these nuclides measured are compared with those of fuel compositions in the FDNPP estimated by Nishihara et al (2012) of the JAEA group, fairly good agreement was found, indicating that traces of U and transuranic nuclides, probably with forms of fine particles, were released into the environment without their large fractionation. In any event, such measurements may allow us to give information (burn-up, conditions of fuel during the release phase, etc.) on the on-site situation, which may be difficult to receive otherwise.

In this presentation, I have two main objectives as follows: first, I will show the overview of the accident, second, I want to present the amounts and isotopic signatures of the released radionuclides, especially transuranic nuclides. We hope that this special session on Fukushima accident promotes further investigations about radiological impact of the accident and transport dynamics.

Fukushima Challenges in Perspective

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Keywords – Fukushima, decontamination, radioactive waste, knowledge transfer, communication

The accident at the Fukushima Dai-ichi nuclear power plant was undoubtedly a local industrial disaster that has had a global impact on the "nuclear renaissance", which was beginning to blossom in 2011. Nevertheless, from a purely radiochemical perspective, the environmental consequences of the core meltdowns were significantly less than a worst case scenario and much can be learnt from this. A key factor was containment of most of the radioactivity from the fuel melt within the reactor buildings, releases being limited to volatile elements, which were either vented to the atmosphere or picked up by cooling waters. This will make decommissioning of the heavily contaminated parts of units 1-4 tricky, but the overall situation is certainly less problematic than Chernobyl.

The most significant radionuclides off-site were isotopes of I and Cs, possibly the best understood of all environmental radionuclides due to the huge knowledge base built up since the middle of the last century [1]. Evacuation, issue of iodine tablets and limitation of consumption of contaminated foodstuffs has ensured that radiological risks to the general public have been negligible. Subsequent remediation actions will complement decay and "self-cleaning" to ensure that most of the evacuated populations can safely return home and resume normal lifestyles in the near future. Nevertheless, a huge volume of radioactive waste will result, which needs to be managed in a safe and efficient manner.

For the international community, there are two issues to be considered – how can experience from other locations be utilised to support recovery in Fukushima and how can the experience gained from this incident be taken over to reduce the risk of something similar happening elsewhere and also to increase the effectiveness of any similar large-scale clean-up operations, for example in military legacy sites? Here modern "knowledge management" technology can facilitate the process of capture and transfer of such experience.

Apart from such technical considerations, a special challenge after the accident was communicating information on extent of contamination and progress with cleanup to the general public. This is an international concern and is complicated by campaigns of disinformation by nuclear opponents and the tone of reporting by a generally critical mass media. The nuclear industry, government organisations and professional bodies have all performed poorly here - the response to public concerns being virtually non-existent. This indicates that, despite the pervasive nature of background radiation and the widespread use of radionuclides in medicine, industry and research, radiochemists need to take a more active role in public education, to help replace non-technical audiences' visceral fear of anything radioactive with a real understanding of the issues involved.

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FKI-01

Atmospheric transport of radioiodine and radiocesium released in the early phase by the Fukushima Daiichi Nuclear Power Plant accident from field measurements and a simulation model

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Abstracts – The continuous measurements of atmospheric concentration of ^{131}I and ^{137}Cs at ten stations in the Kanto area located 120km south from Fukushima, showed that $^{131}I/^{137}Cs$ and the ratio of particulate ^{131}I to the sum of particulate ^{131}I and gaseous ^{131}I significantly changed in the periods when the polluted air masses were transported, compared with those in the other periods. A numerical model well simulated the transport of the polluted air masses to the Kanto and Fukushima area, while any field data did not suggest the transport to Fukushima on March 20-21due to no precipitation.

Keywords – FD1NPP accident, gaseous and particulate ^{131}I, ^{137}Cs, $^{131}I/^{137}Cs$, atmospheric concentration

I. INTRODUCTION

A large amount of radioactive materials was released into the atmosphere after the accident of the Fukushima Daiichi Nuclear Power Plant (FD1NPP) caused by the Tohoku Earthquake and Tsunami on March 11, 2011, and was transported and deposited to the land surface in a regional scale. Many datasets have been opened such as the routine monitoring of radiation dose rate and fallout by MEXT, and the regional map of radionuclides deposited to the land surface by MEXT, and by aircraft monitoring by MEXT and DOE. In contrast, continuous monitoring of atmospheric radionuclides in an early phase after the accident, was made only in the Kanto area located more than 120km south from the Fukushima prefecture, although it is critical for evaluation of the internal exposure dose, reconstruction of time-dependent release rate of radionuclides, and for validation of numerical simulations by atmospheric transport models. The purpose of this paper is to summarize new findings on atmospheric ^{131}I and ^{137}Cs from the field measurements, and to discuss the results of transport pathways by a numerical model.

II. MATERIALS AND METHODS

In the Kanto area, ten research groups independently measured radionuclides in the atmosphere just after the accident, and their results and/or datasets were already reported, and most of them have been summarized elsewhere[1]. Furthermore, gaseous ^{131}Ig and particulate ^{131}Ia were separately measured at a few stations. The datasets were used for an analysis of time series of atmospheric concentration of ^{131}I and ^{137}Cs, ^{131}I/^{137}Cs (=R1), and ^{131}Ia/(^{131}Ia+^{131}Ig) (=R2). A numerical simulation of radioactive materials in the atmosphere was performed by using an atmospheric transport model for radionuclides based on a regional chemical transport model of WRF/Chem[2]. In the model, the radionuclide of ^{131}I and ^{137}Cs was taken into account, and their release rates were based on the estimate by Katata et al.[3].

III. RESULTS AND DISCUSSION

According to the field measurements in the Kanto area, high concentrations of ^{131}I and ^{137}Cs (>100 Bq m^{-3}) were measured during March 15-16 (the first period) and March 20-23 (the second period), and ^{131}I was much higher than ^{137}Cs. A numerical simulation by the atmospheric transport model showed that the polluted air masses with high ^{131}I and ^{137}Cs were directly transported to the Kanto area from the FD1NPP in the morning of both periods by northeasterly wind, in good agreement with the results of the field measurements. The model also simulated the transport of the polluted air masses to the Fukushima area in the afternoon to the midnight in both periods. The radiation dose rates and deposition rates in the Fukushima area increased only in the first period with precipitation, supporting the transport. On the contrary, they did not show any increase in the second period due to no precipitation. The recent analysis for stored filters on which atmospheric aerosols in the early phase were collected, revealed the high concentration of ^{137}Cs in both periods[4,5], validating the calculated transport of the polluted air masses by the model.

The time series of R1 at all the stations showed that R1 was around or less than 10 when the plume with high radionuclides from the FD1NPP was transported in the Kanto area, which was almost equal to the ratio in a calculated core inventory on March 11, 2011[6]. In contrast, R1 was around 100 in the other periods. On the morning of March 22 when the polluted air masses were also transported to the Kanto area, R1 increased to around 100, much higher than that in the previous day, suggesting the possible change in the release condition in the reactor units. The ratio of R2 was 0.4-0.8 when the plume was directly transported, while it was 0.1-0.3 in the other periods. Hence, the ratio of R1 and R2 at the time when the radionuclides were released into the atmosphere possibly suggests any change in conditions of the reactor units.

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Migration of Radiocesium and Radioiodine released by FDNPP accident in the terrestrial environment and its interpretation by their speciation analyses

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Abstract – Distribution of radiocesium and radioiodine such as vertical profile in soil layer, particulate matter-water distribution in river water, and size distributions in sediments were studied to understand their migration in the terrestrial environment in Fukushima area. In addition, speciation studies on cesium and iodine focusing on (i) the surface complex structure of cesium on clay minerals and (ii) formation of organoiodine in soil have been conducted, which can clearly explain the possible chemical processes that control the behavior of these radionuclides in the terrestrial environment.

Keywords – FDNPP accident, radiocesium, radioiodine, clay mineral, humic substances, X-ray absorption fine structure

I. INTRODUCTION

Radionuclides such as radiocesium and radioiodine were emitted from the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident caused by the Great East Japan Earthquake and Tsunami on March 11, 2011. Highly contaminated areas spread in the northwest direction from FDNNP in Fukushima Prefecture, which mainly resulted from the distribution of the wet deposition on March 15 [1]. After the deposition, they have migrated in the terrestrial environment depending on their chemical properties and interactions with various components in the soil, sediment, and water. In this presentation, we report our results on the distributions of radiocesium and radioiodine in soil, river water, and sediments in Fukushima coupled with speciation studies of cesium and iodine in the systems that should be important to understand their behaviors in the terrestrial environment.

II. EXPERIMENTAL

Distributions of radiocesium in the soil layer, river water, and river sediments mainly in Fukushima Prefecture were determined. Vertical profile in soil was also obtained for radioiodine. Sequential extraction studies have been also conducted for radiocesium and radioiodine to estimate main chemical species of the radionuclides. On the other hand, interactions of radiocesium with various clay minerals in the absence and presence of humic acid were examined by X-ray absorption fine structure (XAFS) to interpret the behavior of radiocesium in the soil-water and river water-sediment systems. Formation of organoiodine species were also examined using XAFS in laboratory and natural systems.

III. RESULTS AND DISCUSSION

After the deposition of radiocesium and radioiodine, their vertical profiles in soil in Fukushima showed that more than 90% of radiocesium and radioiodine have been retained within 5 cm from the surface [2]. Leaching experiment of the soil sample showed that radiocesium is strongly bound to soil particles. Size distribution analyses for particulate matters and sediment particles in rivers in the region showed that radiocesium is enriched in finer particle fractions. These results suggested that radiocesium has a high affinity for soil particles, in particular for clay minerals. Thus, XAFS spectroscopy has been used to characterize structure of surface complex of cesium to solid phase [3]. It was found that cesium forms inner-sphere complex to 2:1 phyllosilicate with medium interlayer distance such as vermiculite and weathered illite. In the presence of humic substances, however, formation of inner-sphere complex was inhibited because of the blocking effect of humic substances on the adsorption of cesium into the interlayer. This result also showed that direct complexation between radiocesium and humic substances is not important. These results are consistent with sequential extraction analysis of soil samples and clay mineral-humic substances hybrid containing cesium.

As for radioiodine, about 30% of radioiodine leached by NaOH solution (pH 10.5) from the soil collected one month after the accident [2]. When the extracted solution was acidified, more than 60% of radioiodine was precipitated possibly with humic materials that can bind iodine in the polyorganic structure. This leaching-precipitation behavior suggests that a part of iodine is in the organic form in the soil, which can be a reason for the retention of radioiodine in the soil surface. The formation of organic iodine in natural soil has been suggested by XAFS using X-ray microbeam [4], which can proceed in a relatively short period, such as within a week or a month. Thus, the formation of organoiodine is likely for radioiodine in the soil.

As seen above, speciation studies of cesium and iodine can explain the chemical processes controlling migration behaviors of radiocesium and radioiodine in Fukushima area.

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Oceanic and coastal dispersion of ^{134}Cs and ^{137}Cs released from the TEPCO Fukushima NPP1 accident: past, present and prediction

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Abstract: The bulk of the anthropogenic radionuclide ^{137}Cs present in the oceans today was injected about five decades ago from atmospheric nuclear weapons tests. In the North Pacific Ocean ^{137}Cs inventory was 290 ± 30 PBq in 1970 and it was 69 PBq just before the TEPCO Fukushima Dai-ichi Nuclear Power Plant (FNPP1) accident. An impact of FNPPP1 accident to the North Pacific Ocean in terms of inventory was estimated to be 10 – 13 PBq by atmospheric deposition and 3.5 ± 0.7 PBq by direct discharge, therefore the total ^{137}Cs inventory in the North Pacific Ocean increased by up to 20 – 23%.Fukushima released radiocaesium already subducted in 2011/2012 winter and formed subsurface maximum at a densities of Central Mode Water (CMW), and Subtropical Mode Water (STMW).

***Key words**: ^{137}Cs, Pacific Ocean, inventory, subduction, radioactive plume*

I. INTRODUCTION

On 11 March 2011, an extraordinary earthquake of magnitude 9.0 centered about 130 km off the Pacific coast of Japan's main island, at 38.3 ºN, 142.4 ºE, was followed by a huge tsunami with waves reaching up to 40 m height in Iwate region and about 10 m in Fukushima region. The station blackout developed into a disaster that left three of the six FNPP1 reactors heavily damaged, meltdown of core, and caused radionuclides to be discharged into the air and ocean[1, 2].

II. SAMPLING AND METHODS

We collected 2 litre surface seawater samples at more than 300 stations. The samples were treated by an improved ammonium phosphomolybdate, AMP, procedure [3, 4].

III.RESULTS

^{134}Cs and ^{137}Cs activities in surface water at Hasaki, a coastal station 180 km south of the Fukushima Dai-ichi Nuclear Power Plant (FNPP1) accident site, were observed in April to December 2011 [5]. The maximum in radiocaesium activity at Hasaki was observed in June 2011, representing a delay of two months from the corresponding maximum in April 2011 at FNPP1. Directly discharged ^{134}Cs and ^{137}Cs were transported dominantly southward along the coastline of north eastern Honshu, at least in May and June 2011.

Before the FNPP1 accident, ^{137}Cs was already exist which was originated from the nuclear weapon tests conducted in the late 1950s and in the early 1960s [4, 6]. In the western North Pacific Ocean, ^{90}Sr and ^{137}Cs activities in surface water was 10 – 100 Bq m^{-3} in the late 1950s and in the early 1960s, then it decreased gradually and the ^{137}Cs activity in surface water decreased to around a few Bq m^{-3} just before FNPP1 accident as shown in Figure 1[6, 7].

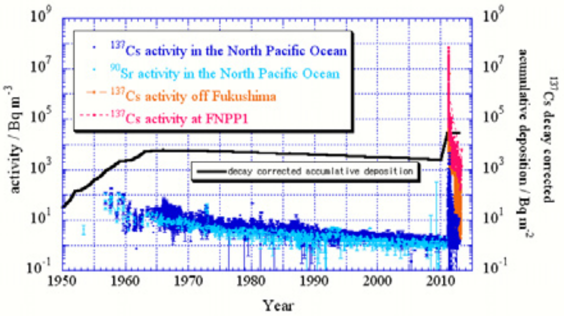

***Figure1**. 60 years trend of ^{90}Sr and ^{137}Cs in surface water in the North Pacific Ocean and decay corrected accumulative deposition in Tokyo/Tsukuba, Japan.*

The ^{137}Cs inventory in the North Pacific Ocean was 290 ± 30 PBq in January 1970 based on 10 º by 10 º mesh data of the ^{137}Cs deposition [7]. In 2003, ^{137}Cs inventory in the North Pacific Ocean was 86 PBq by the model study [8] and 85 PBq by the observation [9], then it decreased to 69 PBq in 2011 because due to decay [9].

The horizontal distribution of FNPP1 derived ^{134}Cs in the western North Pacific Ocean except just in front of the FNPP1 site showed that the high concentration area located close to the FNPP1 accident site which might have received both atmospheric deposition – showing good consistency with previous atmospheric transport model study [10] – and direct discharge [2] from the FNPP1 site. During the winter between 2011/2012, Fukushima derived radiocaesium subducted and formed subsurface maximum at a densities of Central Mode Water (CMW) of which depth is about 400 meters depths and Subtropical Mode Water (STMW) of which depth is about 150 meters depths due to cooling at sea surface. This implies that a speed of main body of Fukushima derived radiocaesium will be decreased much because of less wind driven force at subsurface layers rather than those at surface layers which was 8 cm s-1 as the average speed of radioactive plume at sea surface stated previously. [6]

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Interactions between nuclear fuel and water at the Fukushima Daiichi Reactors

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The rapid increase in temperature in the cores of the Fukushima reactors was caused by the loss of coolant in the aftermath of the damage from the tsunami. High temperatures caused partial melting of not only the UO_2 in the fuel but also the zircaloy cladding and steel, forming a quenched melt, termed corium. Substantial amounts of volatile fission products, such as Xe, Cs and I, were released during melting, but the less volatile fission products and the actinides (probably >99.9%) were incorporated into the corium as the melt cooled and was quenched. The corium still contains these radionuclides, which leads to a very large long-term radiotoxicity of the molten reactor core. Access by water to the core may constitute an important vector for transfer of radioactivity. The challenge for radiochemists is to assess the long-term interactions between water and the mixture of corium and potentially still-existing unmelted fuel, particularly if the molten reactor core is left in place and covered with a sarcophagus for hundreds of years. Part of the answer to this question can be found in the knowledge that has been gained from research into the disposal of spent nuclear fuel in a geologic repository.

Comparison of radionuclide release during the accident from the reactors with the radionuclide inventories remaining in the reactor and estimation of corium–water interaction from known spent fuel–water interaction provide important insight for developing assessment and management strategies for the molten fuel in the reactor cores. Furthermore, analyzing the radiochemical analyses of the temporal evolution of the radioactive elements in the cooling water of the accidental reactors provide valuable information on the chemical state of the corium and potential phase separations. Models for corium stability and for radionuclide release from corium upon contact with water will have to be developed based on (1) analyses of radionuclide activities in actual cooling waters, (2) chemical modeling of the analytical results in the context of the kinetics and thermodynamics of actinide and fission product release (solubility constraints, redox states, etc.), and (3) comparison with spent fuel behavior and experimental corium databases. Such models may be very useful in developing appropriate corium management strategies.

Determination of ^{129}I in the Accumulated radioactive water and processing water of Fukushima Daiichi Nuclear Power Plant

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Abstract – Accumulated radioactive water (AW) and processing water (PW) were sampled from some positions of the Accumulated Radioactive Water Processing Facility (ARWPF) at Fukushima Daiichi Nuclear Power Plant (FDNPP) to estimate the radioactivity of the secondary waste such as zeolite and sludge which adsorbed radioactive material. Separation method of I^- *from the radionuclides using solid phase extractant, Anion-SR, was developed. After the chemical separation, the concentration of* ^{129}I *in the sampled water was determined by Inductively Coupled Plasma Mass Spectrometry with dynamic reaction cell (DRC-ICP-MS).*

Keywords – ^{129}I*, Accumulated radioactive water, Fukushima Daiichi Nuclear Power Plant, Anion-SR*

I. INTRODUCTION

In the early stage of the handling to cool down the reactor core of FDNPP, seawater was poured in the severely damaged reactor buildings. Highly contaminated water was leaked and accumulated in the reactor and turbine buildings. The ARWPF were installed to decontaminate the radioactive materials and to desalinate. Highly contaminated sludge was generated from these apparatus as the secondary waste. To estimate the radioactivity of the waste, AW and PW were sampled from the inflow and outflow of the apparatus.

Because of the long half-life, ^{129}I is one of the important nuclide to assess the safety of radioactive waste disposal. The present study focuses the development of separation method of I^- and determination of ^{129}I in the sampled water. Separation method of I^- with Anion-SR was optimized to improve the detection limit of ^{129}I and to reduce radioactivity of the analyte. After separation, the ratio of ^{127}I and ^{129}I were determined by DRC-ICP-MS to reduce the influence of ^{129}Xe.

II. EXPERIMENTAL

Samples

The AW and PW were sampled at ①reactor/turbine building, ②, ③outflow of Cs adsorption apparatus, ④ outflow of decontamination instruments, ⑤outflow of Cs adsorption apparatus, ⑥outflow of desalination apparatus, ⑦concentrated sea water tank, ⑧processed water tank ⑨ outflow of evaporative concentration apparatus, as shown in Fig.1.

Separation of I with Anion-SR

Anion-SR disk was assembled suction filtration apparatus. The disk was conditioned by passing solutions as follows; 1. 10 ml acetone, 2. 10 ml methanol, 3. 5 ml ultrapure water, 4. 5 ml of 1 M HNO_3, 5. 10 ml ultrapure water, 6. 15 ml of 1 M NaOH (ultrapure), 7. 3 times of 15 ml ultrapure water. After then, sample solution was passed through the disk and the disk was washed with ultrapure water. The extracted I^- was recovered with 9.5 ml of 1 M HNO_3 in the 10 ml measuring flask, and 50 µl NaClO was added to oxidize I^- to IO_3^-. Finally, 1 ml of 1 M HNO_3 was added untill the total volume became 10 ml. The ratio of ^{127}I and ^{129}I was determined by DRC-ICP-MS.

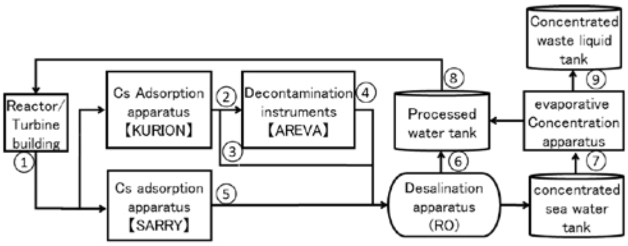

Fig.1 Sampling point of the AW and PW

III. RESULTS AND DISCUSSION

Because sample volume of the AW and PW was 0.1 ml, they were needed to be diluted by appropriate solution to carry out the separation of I^- with Anion-SR. Before analysis of the water samples, the dilutant was optimized. Five ml of 3 M NaOH (ultrpure), 3 M NaOH (97%), 2.7 M tetramethyl ammonium hydroxide (TMAH, ultrapure), and 3 M Na_2CO_3 (99.8%) solutions were examined as the diluent to obtain high recovery of I^- and low contamination for the DRC-ICP-MS measurement. Approximately 90% recovery was accomplished by all the examined dilutant, whereas the lowest back ground count from blank operation was obtained for ultrapure 3 M NaOH solution. Therefore, it was used for the analysis of AW and PW samples.

Iodide in AW and PW solution was analyzed with and without known amount of ^{127}I spike, and the concentration was calculated with the ratio of ^{127}I and ^{129}I. Table 1 shows the concentration of ^{129}I in the AW and PW samples. It was found that ^{129}I was decontaminated by desalination and evaporation apparatus. Results of periodically measurements and development of analysis of IO_3^- with I^- will be delivered on the presentation.

Table 1 Concentration of ^{129}I in the AW and PW samples

Concentration of ^{129}I /Bq· g^{-1}		
① 0.25±0.002	④ 0.085±0.001	⑦ 0.18±0.002
② 0.083±0.002	⑤ 0.13±0.001	⑧ <0.021
③ 0.27±0.003	⑥ <0.021	⑨ 1.3±0.03

Measurement of Iodine-129 in surface soil collected near the Fukushima Daiichi nuclear power plant accident site

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Abstract – Iodine-129 in soil around Fukushima Daiichi nuclear power plant were measured by Accelerator Mass Spectrometry and isotopic ratio of radioiodine was estimated. Surface deposition amount of Iodine-129 resulted in 6.7 to 5500mBq/m^2. The mean isotopic ratio between Iodine-129 and Iodine-131 at the accident was estimated that ^{129}I/^{131}I = 26 ± 6 as of March 11 2011. This result was compared to the calculation result of ORIGEN2 code to test the validity of this estimation.

Keywords – FDNPP accident, Iodine-129, Accelerator Mass Spectrometry, soil, isotopic ratio

I. INTRODUCTION

A lot of radioactive materials were released into the environment owing to the Fukushima Daiichi nuclear power plant (FDNPP) accident. Among them, Iodine-131 has already decayed out and cannot be detected now. On the other hand, Iodine-129, which is the isotope of Iodine-131, has long half-life and can be measured by Accelerator Mass Spectrometry. If isotopic ratio of radioactive iodine (^{129}I/^{131}I) at the initial stage at the accident is obtained, distribution of Iodine-131 at the accident can be reconstructed by measuring Iodine-129 in soil. In this study, Iodine-129 was measured in soils, which were collected within 60km distance from FDNPP on April 2011.

II. METHOD

50 soil samples were collected within 60km distance from FDNPP on April 20, 2011. Sampling strategy was shown in other paper [1]. Iodine-131 and other radionuclides have already been determined by gamma ray measurement [1]. In order to extract Iodine from soil, homogenization, combustion, solvent extraction, and back extraction were conducted [2]. After making AgI precipitation, samples were pressed into a cathode for AMS and ^{129}I was measured at MALT (Micro Analysis Laboratory, Tandem accelerator), The University of Tokyo. Iodine-127 in soil was measured by ICP-MS at the University of Tokyo.

III. RESULTS AND DISCUSSION

Surface deposition amount of Iodine-129 resulted in between 6.7 to 5500mBq/m^2 within the area 60km distant from FDNPP. These values were corresponding to Iodine-129 concentration between 7.8E7 to 5.9E10atoms/g. Iodine-127 concentration was distributed from 1 to 16ppm. The mean isotopic ratio of ^{129}I/^{131}I =26 ± 6 on March 11, 2011 was obtained.

In order to check the validity of analytical result, it was compared to the calculation result of ORIGEN2 code [3]. In Fig. 1, ^{134}Cs/^{137}C data were plotted against ^{129}I/^{131}I data. Each of nuclides was decay-corrected as of March 11, 2011. Not only observation results but also calculation data of isotopic ratio of Unit 1, Unit 2, and Unit 3 were shown here.

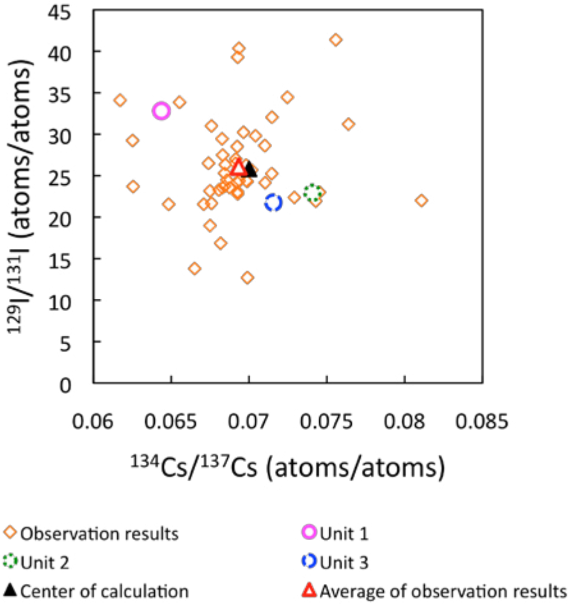

Fig. 1. Comparison of isotopic ratio of radioiodine and radio cesium between observation results and calculation result of ORIGEN2 code

In Fig. 1, average of observation results is located close to center of calculation and this average seems to be affected by Unit 1. This suggests contribution of Unit 1 might be larger than expected or there are other reasons. Problems are still under debate.

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Speciation of ^{137}Cs and ^{129}I in surface soil in Kanto loam layer after the Fukushima NPP accident

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Abstract

We measured chemical speciation of ^{137}Cs and ^{129}I in the surface soil of Kanto loam after Fukushima nuclear disaster. We observed the behavior of ^{137}Cs and ^{129}I in soil samples of the Kanto loam layer: more than 90% of ^{137}Cs was fixed by organically bound and residual fractions, while ^{129}I was mainly fixed by Fe-Mn oxidation and organically bound.

Keywords –Cs-137, I-129, Fukushima nuclear disaster, Kanto loam, Solid-phase extraction, leaching

Introduction

Sequential extraction has been proven to be a useful and practical technique for the speciation analysis of radionuclides in the soil and sediment samples (Desideri, et al., 2001; Desideri et al., 2002 ; Oughton et al., 1992; Riise et al.,1990; Tessier et al., 1979). We extracted ^{137}Cs and ^{129}I from surface soil samples from the Kanto-loam layer in eastern Tokyo metropolitan area.

Methods

The two soil samples of depths of 0−2.5cm were reduced by cone and quartering to approximately 10 g. Approximately 10 g of the samples were used in the sequential-extraction experiment. A solution/sample ratio of 5 (v/w) was used for extraction in each step (Fraction 1, 2, 3, 4, 5 and residue).
Fraction 1: Ultrapure water was added to the soil sample, and the sample was shaken for 24 h at room temperature. The sample was stored overnight. This fraction represents water-soluble species. The remaining solid on the filter paper was combined with the residue for the leaching in the next step.
Fraction 2: 1 M of NaAc was added to the residue from Fraction 1. The sample was shaken for 12 h at room temperature and stored overnight. This fraction represents exchangeable species.
Fraction 3: 1-M NaAc−HAc (pH 5) was added to the residue from Fraction 2, and the sample was shaken for 12 h at room temperature. This fraction represents carbonate-bound species.
Fraction 4: 0.04-M NH_2OH・HCl in 25% (v/v) HAc (pH 2) was added to the residue from the fraction and stirred in a hot-water bath at 80 °C for 4 h. This fraction represents species associated with solids via chemical-sorption mechanisms which can be released into the extraction solution with a weak reducing agent, and they mainly include species bound to Fe/Mn oxides.
Fraction 5: 30% H_2O_2 was added to the residue, in which HNO_3 had already been added to adjust the final pH to 2, and the sample was agitated for 2 h at 85 °C. After the sample solution was cooled to room temperature, 1.8-M NH_4Ac in 11% HNO_3 (v/v) was added, and the extraction continued for 30 mins at room temperature. This fraction is associated with organic matter.
After extraction, each solution was separated from the soil residue by centrifugation at 2000 rpm for 5 mins. The solution was filtered through a filter paper with a pore size of 0.45 μm. After each fraction was stored into the U-8 vessel, ^{137}Cs was measured by gamma-ray spectrometry (Hokkaido University). I-129 was measured by AMS (Tokyo University).

Result

The amount of ^{137}Cs leached into water (F1) from the Kanto-loam soil was below the detection limit. The rate of ^{137}Cs exchange from the two soil samples was less than 1%, with 50–60% of ^{137}Cs remaining in the residue. Approximately more than 90 % of ^{137}Cs was adsorbed on organic matter and the residue, while ^{129}I was mainly fixed by Fe-Mn oxidation and organically bound.

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Transfer of radiocesium and radioiodine in the environment following the Fukushima nuclear accident

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Abstract- Following the Fukushima accident, intensive studies have been carried out regarding the distribution and transfer of radionuclides that have been released into the environment. In this paper, the following two topics related to this theme are presented: (1) The importance of translocation pathways to understand the transfer of radiocesium into some crops such as tealeaves and citrus fruit. (2) The reconstruction of I-131 deposition in different places in Fukushima Prefecture through the analysis of long-lived I-129.

Keywords – Radiocesium transfer to plant, translocation pathway, I-129 analysis for the reconstruction of I-131 deposition

I. INTRODUCTION

Among radionuclides released from the accident of Fukushima Daiichi Nuclear Power Plant, radioiodine and radiocesium are very important from the viewpoint of environmental safety. Shortly after the accident, high I-131 concentrations were observed in leafy vegetables in Fukushima and in the surrounding Prefectures. The levels of I-131 in vegetables decreased markedly with time due to its short half-life (8 days), as a consequence more attention has been paid to the longer-lived radiocaesium (Cs-134 and Cs-137) deposited in soil. Results of the monitoring for agricultural crops harvested during spring to autumn in 2011 showed that most of crops had not exceeded the provisional guideline for radiocaesium of 500 Bq/kg for 2011. (After 2012 the guideline was changed to 100 Bq/kg.) However, values higher than the guideline were found in some crops such as bamboo shoots, some fruits (e.g. Japanese citron 'Yuzu') and new tealeaves. These high values could not be explained solely by root-uptake, which was previously assumed to be the primary pathway.

In this study we analyzed radiocesium concentrations in a variety of crops and studied the mechanisms of radiocesium transfer. Apart from radiocesium, we have studied the distribution of I-131 (half-life: 8 days) deposited in Fukushima Prefecture. Due to the short half-life of I-131, most of it decayed away after some months and there were not enough data to construct a deposition map for I-131. Since a long-lived I-129 (half-life: 15.7 million years) was also released from the accident, we have analyzed it for reconstructing I-131 deposition.

II. EXPERIMENTALS

Concentrations of radiocesium were determined with a Ge-detector in crop samples collected in Fukushima following the accident. For I-129 analysis, iodine fractions were separated from soil samples to make a AgI target for the determination of this nuclide by AMS.

III. RESULTS AND DISCUSSION

The distribution of radiocesium in an entire tea tree (old leaves, new leaves, bark, roots and soil) was studied and it was found that the new tealeaves that had not appeared until March 2011 also showed high values for this nuclide. It was found that translocation pathway from the contaminated old leaves and bark should be important to understand the high values observed in new leaves. Higher concentrations found in 'Yuzu' were also explained by the translocation pathway. The levels in tealeaves and 'Yuzu' harvested in the second year decreased significantly. High radiocesium concentrations found in bamboo shoots should be the effect of both translocation and root-uptake pathways.

Soil samples that had been determined for I-131 were analyzed for I-129 to estimate I-131/I-129 ratio. Amounts of I-131 deposition in different areas were reconstructed through the analysis of I-129 together with the obtained I-131/I-129 ratio.

FKO-05

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States of existence of the Cesium and Silver radionuclides at the sandy beach in Iwaki city, Fukushima

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Abstract

We have made an investigation that shows the states of existence of radionuclides from the Fukushima Dai-ichi nuclear power plant (FDNPP) accident on the sandy beach in Iwaki city, Fukushima Prefecture, Japan. The ^{137}*Cs and* ^{110m}*Ag were observed different behavior along the depth distribution of sand layer. As a result of the checking of the imaging plate photograph,* ^{137}*Cs from the FDNPP were attached to the granular spots. In addition, it is suggested that* ^{110m}*Ag and* ^{137}*Cs were independent for the same layer.*

Keywords
^{110m}*Ag,* ^{137}*Cs, Sandy beach, Depth distribution, Particle*

I. INTRODUCTION

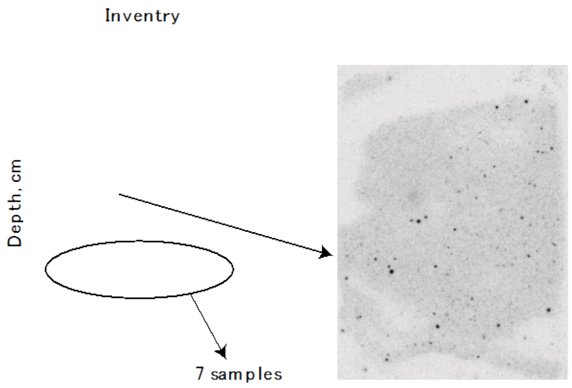
The Fukushima Daiichi nuclear power plant (FDNPP) disaster occurred in March 2011, various radionuclides were emitted from the FDNPP and deposited to a wide area of the northeastern Japan associated with precipitation. We already reported the fall out radionuclides were easily penetrated deeper layer in the sandy beach at the Iwaki city [1]. However, the cause of such a phenomenon is not yet understood clearly. For this reason, we have made a research that shows behavior and dynamics of months or longer half-life radionuclides such as ^{134}Cs, ^{137}Cs, and ^{110m}Ag in the sandy beach.

II. MATERIALS AND METHODS

Core soil sample (depth 30cm, D 5.0 cm) was collected at Yotsukura district, Iwaki city (E140.993, N37.1074) on 2 June 2011. Radionuclides in the sample were measured by a HPGe. More than one year has elapsed from the initial sample measurement, we have took the imaging plate photographs of the layer of more had accumulated ^{137}Cs in core sample. In addition, include soil sample of ^{110m}Ag was divided into 7 samples. Further were these samples measured radionuclides by using a HPGe detector.

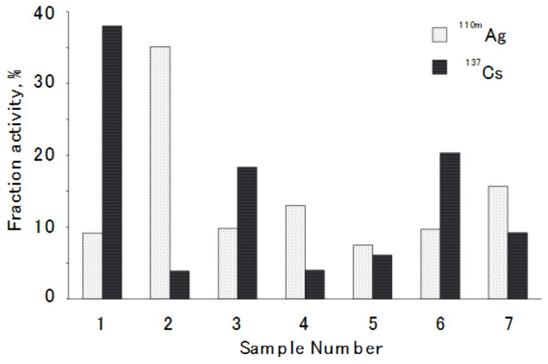
III. RESULTS AND DISCUSSION

Figure 1(a) shows the depth distribution of radionuclides from the FDNPP. ^{137}Cs, ^{129m}Te, and ^{131}I were distributed broadly. On the other hand, ^{110m}Ag are predominantly confined in the 5-6 cm layer from top. Figure 1(b) shows imaging plate (IP) photograph of the sample containing a relatively large amount of ^{137}Cs. The granular radioactive nuclides were observed, and it seems that granular spots were consist on ^{137}Cs from the FDNPP resulting gamma ray spectrometry. In Figure 1(c), shows the fraction activity of ^{110m}Ag and ^{137}Cs in each sample. From the above observational results can be shown that ^{137}Cs and ^{110m}Ag were independent. In order to make clear for relationship between ^{137}Cs and ^{110m}Ag, additional chemical experiments required.



(b) IP Photograph

(a) Depth distributions



(c) Fraction activity in divided soil

Figure 1 (a) Depth distribution of radioactivity inventories in the sandy beach core sample, (b) Imaging plate photograph in layer 4 from top level, (c) Fraction activity of 7 samples. Fraction activities are expressed as a percentage of the total activity (%)

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FKO-06

Vertical transport of FNPP1-derived radiocesium by settling particles in the Western North Pacific

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Keywords – FNPP1, radiocesium, Western North Pacific, settling particle, sediment trap

Introduction

On March 2011, the 2011 Tohoku-Oki Earthquake occurred. This earthquake and the tsunami seriously damaged the Fukushima Daiichi Nuclear Power Plant (FNPP1). As a result, large quantities of radionuclides were emitted. About one month after the FNPP1 accident, FNPP1-derived radiocesium was dispersed to broad area in the Western North Pacific (WNP). Based on mathematical simulation, it was suspected that radiocesium detected in the WNP originated from not only contaminated water directly discharged, but also eolian input (Honda et al., 2012). It is well known that biogenic and lithogenic materials in the surface ocean are quickly transported to the ocean interior by settling particles. At the time of the FNPP1 accident, settling particles' collectors (sediment traps) had already been deployed at time-series stations in the WNP. We measured radiocesium (^{134}Cs, ^{137}Cs) in settling particles collected by sediment traps and verified how FNPP1-derived radiocesium was transported to the ocean interior.

Methods

Sediment traps were deployed at 500 m and 4810 m of time-series stations K2 (47°N/160°E, ca. 2000 km from FNPP1) and S1 (30°N/145°N, ca. 1000 km from FNPP1) in July 2010 and successfully collected settling particles before and after the FNPP1 accident. In July 2011, 4 months after the accident, sediment traps were also deployed at 500 m and 1000 m of F1 (36-30°N/141-30°E, ca. 100 km from FNPP1) and started collection of settling particles. After recovery, collected samples < 1 mm were dried and pulverized. Specific activities (activities) of ^{134}Cs and ^{137}Cs were measured by gamma spectrometry with a Ge detector.

Results and discussion

At stations K2 and S1, radiocesium was detected at 4810 m by middle April 2011 (Fig. 1 a, b). The sinking velocity was estimated to be 8 – 36 m day^{-1} between surface and 500 m, and > 180 m day^{-1} between 500 m and 4810 m. At 4810 m of K2, maximum ^{134}Cs flux and activity were observed in June 2011 and, thereafter, ^{134}Cs flux and activity decreased gradually. At 4810 m of S1, the highest ^{134}Cs flux was observed in early May 2011. It was notable that the maximum ^{134}Cs activity and relatively higher flux was observed in late November and early December 2011. Total ^{137}Cs flux (^{137}Cs inventory) at 4810 m was about 3 Bq m^{-2} at K2 and 2 Bq m^{-2} at S1. These corresponded to about 0.7% and 0.3% of ^{137}Cs eolian input to respective stations by one month after FNPP1 accident. The ^{134}Cs was detected, at the earliest, by April 2012 at K2 and by February 2012 at S1. At 500 m of F1, the highest ^{134}Cs activity was observed in late August 2011 and ^{134}Cs activity decreased thereafter (Fig. 1 c). However ^{134}Cs activity temporary increased in March 2012 and ^{134}Cs flux was the maximum at that time during observation. ^{137}Cs inventory at 500 m of F1 during observation was about 60 Bq m^{-2} and 20 – 30 times higher than that at 4810 m of K2 and S1. It might be attributed to much higher ^{137}Cs inventory to surface around F1 (30000 – 40000 Bq m^{-2} by June 2011. Buesseler et al., 2011). In addition, lithogenic materials were pre-dominant in settling particle collected at F1 while biogenic materials such as biogenic opal and $CaCO_3$ were pre-dominant at K2 and S1. Station F1 was located on the continental shelf slope and the "nepheloid layer" was observed around 600 m depth and near seafloor. Lateral transport of radiologically contaminated clay minerals from/near the land might also contribute the higher ^{137}Cs inventory at sediment trap depth at F1.

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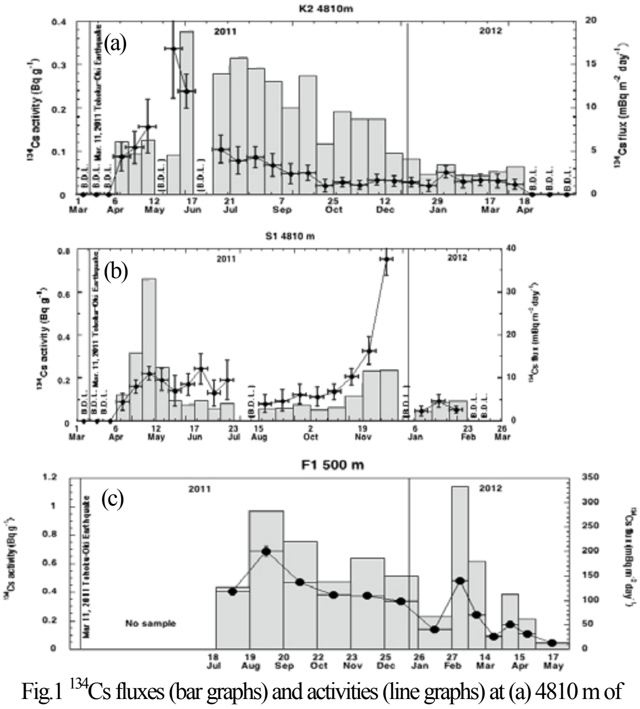

Fig.1 ^{134}Cs fluxes (bar graphs) and activities (line graphs) at (a) 4810 m of K2, (b) 4810 m of S1 and (c) 500 m of F1 (after Honda et al. submitted to Biogeosciences). Note that vertical scale is different between figures.

FKO-07

Strontium-90 determination in air dust filter using solid phase extraction after the accident of FD-NPS

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Abstract - Radioactivities of Sr-90 in air-dust filters collected in Hitachi, Kawasaki and Toyonaka were determined using solid state extraction method and low background beta-ray counting system. In Hitachi, though the Sr-90 activity concentration was decreased with time, the activity rates of Sr-90/Cs-137 kept about 10^{-3} order. This fact suggests that Sr-90 transportation behavior in the atmosphere is similar to that of Cs-137 during the time of sample collection.

Key word – Sr-90, solid-phase extraction, air dust

I. INTRODUCTION

On 12th March, 2011, a large amount of radioactive nuclides have been released into the environment by the nuclear accident at the Fukushima Daiichi Nuclear Power Station. Measurement about radioactive nuclides will give us much information about the accident circumstance. There are many measurement results of I-131, Cs-134, Cs-137 in natural samples. However, for other nuclides, such as the pure beta emitter nuclide Sr-90 has not been measurement sufficiently. Strontium-90 is considered one of the harmful radioactive nuclides. Therefore, measurement of Sr-90 in air dust is important for calculating exposure. We developed a new simple and quick strontium isolation technique using solid phase extraction and determined Sr-90 activities in air dust.

II. EXPERIMENTAL

In this study, we used the 3M Empore™ Strontium Rad Disk to extract strontium ion. This filter can collect mg order of Sr^{2+} ion efficiently. However, it is known that this filer also catches Pb^{2+}[1]. Natural radioactive nuclide Pb-210 seriously will be interferences for Sr identification in beta ray counting. In this study, cation exchange with EDTA solution was adopted for Sr purification after solid phase extraction. We made test experiments with radioactive Sr tracer and obtained high chemical yield as 90 %. The time for chemical operation of this method was 3-4 hours. The activity of Sr-90 was determined by the growth curve in sequential measurements of Cherenkov light from Y-90 by the low background liquid scintillation counter. Using Sr-90 standard solution, we determined that Cherenkov light detection efficiency for Y-90 68.7% and detection limit of Sr-90 is 0.004 Bq in this system.

III. RESULTS

We measured Sr-90 in air dust samples of Hitachi, Kawasaki and Toyonaka City. We analyzed some air dust samples for Sr-90 detection that had high Cs-137 activity, and strontium isolation with solid phase extraction was performed. The measurement result of Hitachi is shown in Table.1 and Fig.1. Without Pb separation, we can easily observe the Cherenkov light form Bi-210, that is daughter nuclide of Pb-210. However, there is a ND(not detectable) result and it indicates that the measurement sample was sufficiently Pb-210. In Hitachi, the Sr-90 activity concentration in air was decreased with time. All of the ratios of Sr-90/Cs-137 were about 10^{-3}. It is possible that after April, Sr-90 has been the same behavior of Cs-137. Strontium-90 was also determined in samples of Kawasaki and Osaka. In the presentation, we will discuss about the results of Sr-90 in air dust and compare with the results by other group about Sr-90 in soil and fallout.

Table.1 Sr-90 detection results of Hitachi

	Sampling Date	^{90}Sr Bq/m³	error%	^{90}Sr /^{137}Cs	error%
1	4/9	1.5×10^{-3}	3%	1.6×10^{-3}	10%
2	4/16	2.6×10^{-4}	3%	3.1×10^{-3}	11%
3	4/18	3.7×10^{-4}	3%	1.1×10^{-3}	10%
4	4/19	ND			
5	5/4	3.1×10^{-5}	15%	1.5×10^{-3}	18%
6	5/21	6.3×10^{-5}	12%	3.7×10^{-3}	16%

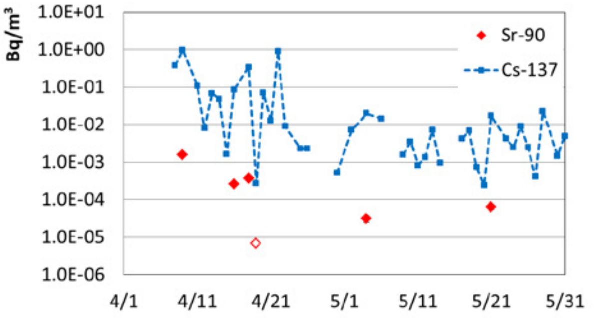

Fig.1 The time dependence change of Sr-90 and Cs-137 in Hitachi

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Dosimetric Implications of the Fukushima Release for Pacific albacore in the Northern California Current

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Abstract – Using activity concentrations in Pacific albacore at both pre-Fukushima and post-Fukushima levels, the average annual whole body internal dose for these nekton is estimated. MCNP & voxelized phantoms applied for determination of absorbed fraction. Analyzed tissues include both edible tissue, viscera and other non-edible tissues.

Keywords – Cs-137, Cs-134, Pacific albacore, radioecology, Fukushima

I. INTRODUCTION

An unfortunate result of the already devastating earthquake and tsunami on March 11, 2011 was a release of radionuclides from the Fukushima Daichi power generating station. It will be several years before this release into the North Pacific Gyre will be carried, at diluted and decayed activity concentrations, to the West Coast of North America[1]. During the interim, migratory species may be passing through the extent of this liquid plume, and feeding throughout that range. This work intends to address the dosimetric implications for migratory Pacific albacore, *Thunnus alalunga.*

A. State of existing body of knowledge

Historically, reported activity concentrations in the United States have almost exclusively sampled the edible tissues. In the case of albacore, this excludes not just skin, bone and viscera, but the fatty red muscle tissue along the belly. These were conducted at national labs, with the primary goal of ensuring Cold War-era radionuclides releases were not affecting food quality.

However, muscle tissue is one of the most radio-resistant tissues in the body. One goal of this work is to address the dosimetric impact to biota by determining concentrations for the whole body, rather than simply in edible tissue.

There is a large body of work reporting concentration ratios for nekton in the Pacific, which is the ratio of the activity concentration in the tissue over the activity concentration in the water, by mass. These concentration ratios vary wildly, as they depend on the assumption that the animal sampled is in equilibrium with activity in the surrounding environment, including the complicated food web transfer through other species. Nonetheless, they are still widely used for determinations of the expected concentrations after a release until a more thorough determination may be made. Another goal of this work is to relate edible muscle concentrations to concentrations elsewhere in the animal, to allow utilizing this existing body of work for animal dosimetric estimations

B. Whole Body Dosimetry

Absorbed fractions were calculated for activity in different body compartments using MCNP and a voxelized model developed from CT & MRI of a pelagic fish. Activity concentrations for Cs-134 and Cs-137 measured in Pacific albacore were then used to calculate annual internal dose to the animal for both those that exhibited trace concentrations of Fukushima effluents and those that remained at pre-Fukushima concentrations. The internal and external dose from naturally occurring K-40 is also provided for comparison. Additionally, dose estimates using the prior "edible-only" paradigm are presented.

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ANNRI at J-PARC

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The Accurate Neutron-Nucleus Reaction measurement Instrument (ANNRI) has been installed at the beam line no. 4 of the Material and Life science experimental Facility (MLF) in the Japan Proton Accelerator Research Complex (J-PARC). It was constructed in order to supply accurate neutron capture cross sections of minor actinides and fission products required for developing innovative nuclear systems [1].

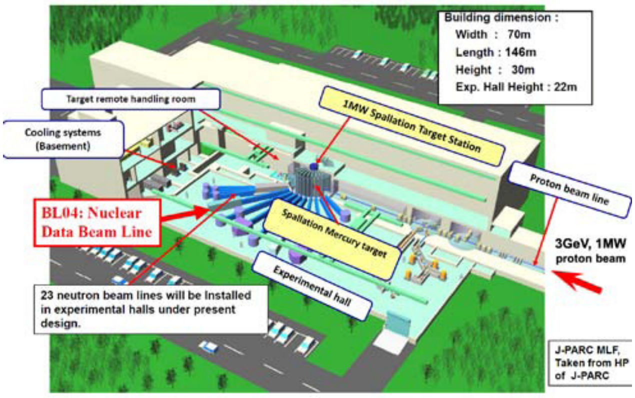

Fig. 1 A bird's-eye view of the layout of J-PARC/MLF

Fig. 2 Photo of ANNRI (outside) and Ge spectrometer

The ANNRI project team has developed the neutron beam line optimized for neutron time-of-flight experiments [2, 3], the advanced Ge [4] and NaI [5] spectrometers for detecting prompt γ rays, and the measurement method of neutron capture cross sections. The team has started the measurements of neutron capture cross sections of minor actinides and fission products since 2009, and successfully obtained the neutron capture cross sections of $^{244, 246}$Cm and ^{237}Np [6-8].

At the time of the Great East Japan Earthquake on March 11, 2011, the ANNRI suffered serious damages. However, the team members of BL04 immediately recovered from the situation. The recovered ANNRI has been used again for the user program since Feb. 2012. The project research using the ANNRI entitled as "Research on nuclear astrophysics, nuclear data, and trace-element analysis using pulsed neutrons" has also been started since April 2012.

The ANNRI is a unique instrument for high-resolution neutron-capture γ-ray spectroscopy by utilizing the world's strongest pulsed-neutron beam as shown in Fig. 3 and the high-efficiency Ge and NaI spectrometers. The ANNRI is expected to be usefully utilized not only for nuclear data measurements for the study of innovative nuclear systems, but also for the study of nuclear astrophysics [9-10] and for the analyses of trace elements [11-12].

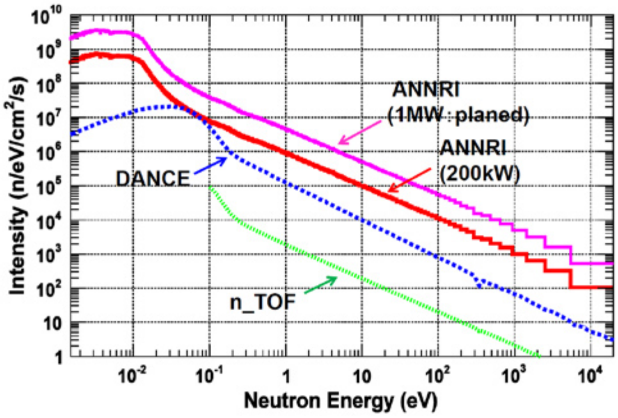

Fig. 3 Comparison of neutron flux of J-PARC /MLF/ANNRI with CERN/n_TOF and LANL/LANCE/DANCE

Current status and recent topics of the ANNRI will be reviewed in this symposium.

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Nanomaterial and nanotechnology in nuclear energy chemistry

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Keywords: Nanomaterial, Nanotechnology,
Nuclear energy chemistry

With the increasing human demands for energy, applications of newly emerging technology for safer and cheaper energy become new challenges and new front in energy sciences. Major nuclear countries in the world have initiated forward-looking researches toward future advanced nuclear energy systems, in which nanomaterials and nanotechnologies play important roles. Nanomaterials and nanotechnology show some exciting application potentials in future nuclear energy systems. In the talk, we will discuss the recent research progress in nanomaterials and nanotechnologies associated with advanced nuclear fuel fabrication, spent nuclear fuel reprocessing, nuclear waste disposal and nuclear environmental remediation, etc. We will focus mostly on chemical aspects of above processes. The talk will highlight research activities in our Laboratory and China, and future challenges and opportunities of nanomaterials and nanotechnologies in nuclear energy chemistry.

For example, graphene nanomaterials has been demonstrated to effectively loaded ions, molecules, and atomic clusters onto their basal plane through weak interactions such as van der Waal's forces, electrostatic interactions, and π-π stacking. Due to relatively strong noncovalent interactions, decorated graphene can be highly stable in both acidic and basic media. Carbon nanomaterials have great potentials in areas whose issues are difficultly solved by conventional methods or bulk materials. We may use nanoparticles-loading graphene layered materials (like a 3D network material) as fillers of separation columns for nuclear fuel cycling and radioactive wastes treatments. The enhanced performances make the graphene material be able to selectively adsorb heavy metals (e.g., lanthanides or actinide) with a super loadage and an in-situ rebirth capacity, which may bring revolutionary progress into the nuclear fuel cycling industries.

To integrate the advance of nanomaterials and the need of nuclear energy production is a challenge in nuclear energy chemistry. For example, a variety of tetradentate ligands, 6,6`-bis(5,6-dialkyl-1,2,4-triazin-3-yl)-2,2`-bipyridines (BTBPs), have been experimentally proved as effective ligands for selective extraction of Am(III) over Eu(III). Recently, in exploring the origin of their selectivity, we found that in 1:1 (metal:ligand) type complexes substitution of electron-donating groups to the BTBP molecule can enhance its coordination ability and thus the energetic stability of the formed Am(III) and Eu(III) complexes in the gas phase. Eu(III) can coordinate to the BTBPs with higher stability in energy than Am(III), no matter whether there are nitrate ions in the inner-sphere complexes. The presence of nitrate ions leads to formation of the probable Am(III) and Eu(III) complexes, $M(NO_3)_3(H_2O)_n$ (M = Am, Eu), in nitric acid solutions. It has been found that the changes of Gibbs free energy play an important role for Am(III)/Eu(III) separation. In fact, the weaker complexing ability of Am(III) with nitrate ions and water molecules makes the decomposition of $Am(NO_3)_3(H_2O)_4$ more favorable in energy, which may thus increase the possibility of formation of $Am(BTBPs)(NO_3)_3$. These findings may shed light on the design of novel extractants for Am(III)/Eu(III) separation. However, the single atom lay of the graphene nanomaterials can first use as novel substrate and then as novel designs of a complex-based the extractant-platform for Am(III)/Eu(III) separation, and for selective separations of other Ln and Ac ions, or selective separations of ions among Ac elements.

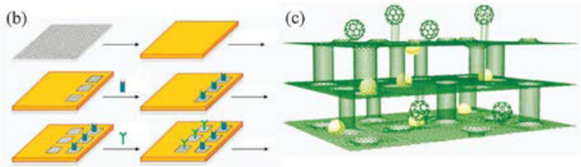

Figure 1, The superior performance of graphene-based materials. Basal plane functionalization could lead to graphene-based integrated function nanomaterials. Regiofunctionalization of graphene towards multifunctional and all-purpose devices. In the example, different functional groups for Am(III)/Eu(III) separation, or for separations of other Ln and Ac ions, or selective separations of ions among Ac elements, can be bonded in turn to the graphene substrate (Copyright @ RSC)[3].

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APO-01

APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
Kanazawa, Japan, 22-27 September 2013

Development of Real-Time Radioisotope Imaging System to Study Plant Nutrition

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Abstract – We have been developing two types of real-time radioisotope imaging systems, one for macroscopic imaging targeting the whole plant itself and the other for microscopic imaging under modified fulorescent microscope to get both fluorescent and radioisotope images (Hirose et al. 2012; Kanno et al. 2012; Kobayashi et al. 2012). Now we can visualize the real-time movement of C-14, Na-22, Mg-28, P-32, S-35, K-42, Ca-45, Rb-86 or Cs-137, from root kept in dark to up-ground part where light was irradiated. There are a wide range of application of this imaging , such as to measure the uptake manner in root, speed or distribution or translocation manner, as well as distribution, translocation or deposition of the nutrient element in upground part. Here we present some representative real-time images in plants.

Keywords – real-time radioisotope imaging system, plant nutrition, C-14, Na-22, Mg-28, P-32, S-35, K-42, Ca-45, Rb-86 or Cs-137

Plants Prepared for Imaging

Rice (*Oryza sativa*. L. cv. *Nipponbare*) seedlings and *Arabidopsis thaliana* seedlings were grown for about 12 days and 40days, respectively, in culture solution. Then the plant was placed in front of the fiber optic plate where CsI scintilator was deposited. Then the radioisotope (RI) was supplied to the water culture solution and the RI image from roots ro up-ground part was monitored by highly sensitive CCD camera (Fig.1).

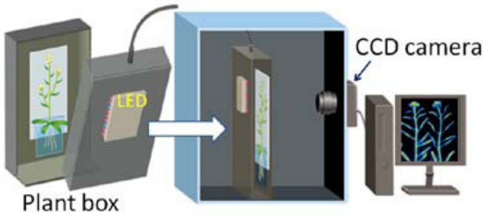


Fig.1a macoscopic real-time RI imaging system

The real-time images

The real-time images of absorption manner using varuious radioisotopes allows to calculate uptake amount and transfer rate both in macroscopic and microscopic images. As an example, Mg-28, P-32 and K-42 uptake manners were shown as successive images.

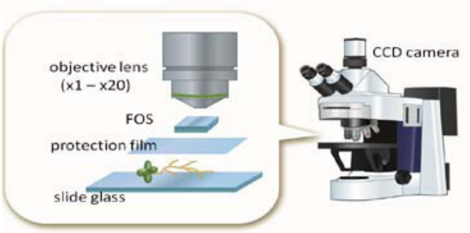
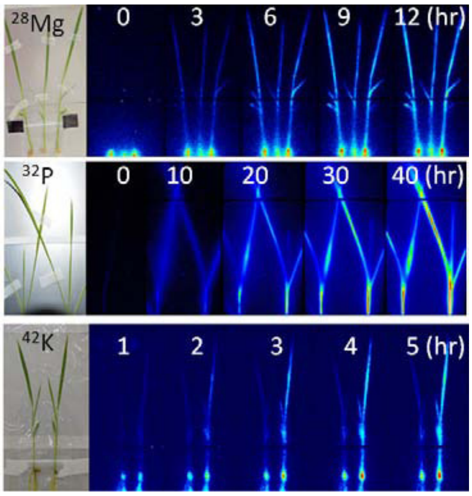


Fig.1b micoscopic real-time RI imaging system



Conclusion

The real-time imaging system we developed showed the uptake manner of the wide range of the nutrient elements. There are two great advantages of RI imaging, allows imaging under light and enables numerical treatment of the image, since the image is based on radiation count. The imaging system for C-14 labeled carbon dioxide gas is now developing to study real-time photosynthesis.

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APO-02

MCNP study on the development of industrial SPECT in terms of a radiation measurement design and void influence in multiphase media

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Abstract – There have been extensive studies on the development of SPECT (Single Photon Emission Computer Tomography) for industrial applications. Owing to its intrinsic limitation originated from the dimensions and density of objects in industrial process units, it has been a challenging issue to get a spatial resolution good enough to draw informative data from it. This study demonstrates the feasibility of a radiation measurement array proposed for a greater region of interest resulting in better spatial image resolution. Considering that the industrial process units are designed to mix up different materials in different phases, the influence of a void ratio into the image quality of the industrial SPECT was investigated with the Monte Carlo code for a Liquid/Vapor phase system.

Keywords –Industrial SPECT, Radioisotope tracer, Multiphase flow investigation, Gamma radiation collimation, MCNPX

I. INTRODUCTION

Industrial image diagnosis technology based on the medical SPECT principle has been studied at the Korea Atomic Energy Research Institute [1]. The technology visualizes the distribution of process media as a function of time at a certain cross-section of the object under investigation [2]. The system was redesigned in a diverging collimator configuration substituting the conventional parallel configuration.

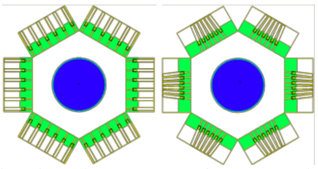

Fig. 1. Radiation detection geometry for MCNP simulation with conventional (left) and proposed (right) collimator arrays of industrial SPECT.

II. METHODS AND RESULTS

A. Redesign of radiation collimator configuration

The configurations in Fig. 1 show the conventional and newly proposed radiation measurement arrays for an MCNPX simulation. Besides the diverging orientation of collimation, the proposed array is identical to the conventional one. The cylindrical vessel is 40 cm in diameter and contains water. Radiation probes are NaI(Tl) with 1.3 cm in diameter and 2.5 cm in length. The radioisotope is ^{68}Ga with 511 keV of gamma radiation and the energy window for measurement was set to ±10% of it, 460-562 keV. The radioisotope was positioned at five different points, 0, 4, 8, 12, and 16 cm from the center to evaluate the precision of the reconstructed images at various locations.

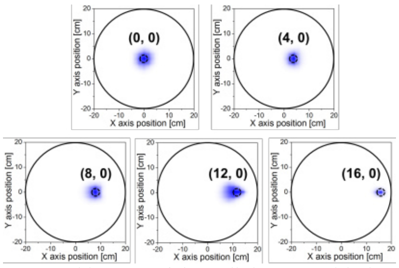

Fig. 2. Reconstructed images of the radioisotope with the geometry of diverging configuration.

B. Influence of void fraction to image quality

Homogeneous void formation at the same layer with the 6 detectors of industrial SPECT was modeled with MCNP code.

Table 1. NRMSE for quantitative comparison of image quality

Source	Counting Method	Void volume fraction		
		5%	10%	20%
^{68}Ga (511 keV)	Gross	1.93	2.33	3.67
	Peak	1.69	2.02	2.60
^{137}Cs (662 keV)	Gross	1.88	2.19	3.59
	Peak	1.42	1.99	2.52

III. CONCLUSION

The study showed that the diverging collimator demonstrates a better image quality because the collimators cover a wider angle being able to reconstruct the location of radioisotope more precisely compared to a parallel geometry.

Void formation in the vessel hardly affects the image quality in industrial SPECT. There are two reasons for these results: (1) the homogeneous void distribution in the vessel uniformly influences the signals of every detector, and (2) there are few gamma interactions in the void because the density of the void is as low as 0.001205 g/cm^3.

ACKNOWLEDGEMENT

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Tracking the Deportment of Uranium Chain Daughters during Alkaline Leaching of an Australian Monazite

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Monazite contains between 50–68% rare earths and is the second most abundant source of the rare earth elements after bastnasite [1, 2]. Monazite may contain up to 20% thorium and 0.3% uranium and so is an example of a naturally occurring radioactive material (NORM). The deportment of radionuclides from NORM is of particular concern during rare earth extraction [3]. Standard methods for measuring activity concentrations in order to track radionuclide deportment using techniques such as gamma, alpha and beta spectrometry have in general proved to be unsuccessful. In this work, we have developed an analytical method to track the deportment of ^{238}U and ^{235}U daughters during the alkaline leaching of an Australian monazite concentrate. During the alkaline leaching stage it was found that uranium isotopes (^{238}U and ^{235}U) and ^{210}Pb reported to both the trisodium phosphate liquor (leach liquor) and the rare earth hydroxide residue; while ^{230}Th, ^{226}Ra, ^{210}Po (^{238}U) and ^{231}Pa and ^{227}Ac (^{235}U) reported to the rare earth hydroxide. Following hydrochloric acid leaching of the rare earth hydroxide, the major contaminants found in the leach liquor included ^{210}Pb, ^{226}Ra and ^{210}Po. These contaminant radionuclides were later removed from the hydrochloric acid leach liquor by a 'deactivation' and 'lead elimination' step, which is commonly used in industry. The results indicated that removal for most radionuclides was greater than 90%.

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Nuclear chemistry and radiochemistry studies at IMP

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This paper will review the relative research of nuclear chemistry of IMP.

(1) Synthesis and chemical properties of the superheavy elements

The study of the chemistry of transactinide elements (Z $\geq$ 104) is a topic of great interest in current nuclear chemistry research. In IMP, two new transactinide isotopes of ^{259}Db and ^{265}Bh have been produced successfully via the reactions of ^{241}Am (^{22}Ne, 4n)^{259}Db and ^{243}Am (^{26}Mg, 4n)^{265}Bh, respectively[1,2]. In order to study the gas phase chemical behaviour of transactinide elements, an on-line isothermal chromatography apparatus has been established at IMP [3]. The isothermal gas chromatographic behaviour of the group 5 elements Nb, Ta and Db was investigated in a brominating atmosphere using the OLGA technique [4]. The nuclide ^{258}Db was synthesized successfully by the nuclear reaction ^{243}Am (^{20}Ne, 5n)^{258}Db registering ^{258}Db – ^{254}Lr α-decay chains. It was found that Db forms a very volatile compound, most likely the pentabromide, being more volatile than similar compounds formed under identical conditions with Nb and Ta, respectively. This observation is in disagreement with previous experimental investigations of the same compound [5] but in agreement with theoretical prediction [6].

At the same time, metal carbonyl complexes were used for studying the gas-phase chemical behavior of Mo and W isotopes with an on-line low temperature isothermal gas chromatography apparatus. The result showed that short-lived isotopes of Mo and W can form carbonyl complexes which are very volatile and interact most likely in physisorption processes. The first Sg(CO)6 experiment have been completed at RIKEN under a large scale international collaboration between GSI/Maunz, RIKEN, JAEA, LBNL and IMP.

The liquid-liquid extraction behavior of short-lived molybdenum and tungsten isotopes from HCl and HNO_3 as well as HF/HNO_3 acid media was also studied using the α-benzoinoxime/chloroform system [7].

(2) Synthesis of radiopharmaceutical

Positron emission tomography (PET) has become a powerful and widely used imaging technology. The most commonly used PET radiopharmaceutical is 2-[^{18}F] fluoro-2-deoxy-D-glucose ([^{18}F]-FDG). 10 MeV proton mini-medical cyclotron are under construction at IMP, [^{18}F]-FDG system will be developed by ourselves. The water target system was ready to test with proton beam.

(3) Extraction of uranium from the salt-lake

Many materials were developed and as the absorbent to remove uranium from salt lake. Adsorption of uranium from aqueous solution onto the yeast cells (*Rhodotorula glutinis*), magnetically modified yeast cells, magnetic Fe_3O_4@SiO_2 composite particles and magnesium silicate hollow spheres was investigated in a batch system [8,9]. The result showed that these absorbents exhibit much higher sorption capability for uranium.

At the present, the fabric containing amidoxime group as the absorbent for uranium has been synthesized by graft acryloonitrile (AN) onto polypropylene (PP) and amidoximation after electro-beam (EB) irradiation. The detail experiment is still underway.

(4) Transmutation chemistry

In order to transmutation of long-lived fission products and minor-actinides in ADS, the production of minor-actinide containing sphere-pac fuel is under development in collaboration with the international and domestic scientists.

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APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
Kanazawa, Japan, 22-27 September 2013

Preparation of Low Valent Technetium Metal-metal Bonded Species via Solvothermal Reduction of Pertechnetate Salts

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Abstract – A new one-step solvothermal synthesis route for reduction of pertechnetate salts to low valent technetium metal-metal bonded dimers will be presented. The reaction of potassium pertechnetate with glacial acetic acid plus either halo acids or halo salts under in-situ hydrogen production by sodium borohydride at various temperatures yields multiple products consisting of tetraacetate Tc-Tc (II,III) and Tc-Tc (III,III) paddle wheel dimers. Solid products isolated and analyzed via Single Crystal X-ray Diffraction (SC-XRD) in these reactions consist of polymeric chains Tc_2^{+5} *core:* $Tc_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)$, $Tc_2(\mu\text{-}O_2CCH_3)_4Cl$, $Tc_2(\mu\text{-}O_2CCH_3)_4Br$, $Tc_2(\mu\text{-}O_2CCH_3)_4I$, *molecular* Tc_2^{+5} *core:* $Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2{\cdot}H_2O$, $K[Tc_2(\mu\text{-}O_2CCH_3)_4Br_2]$, *and molecular* Tc_2^{+6} *core:* $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$, $Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$. *Of the compounds listed, four are newly discovered using the one-step technique and two more additions to crystal database. Additional spectroscopic (X-ray Absorbance Fine Structure, UV-Vis, and FT-IR) characterization of the new compounds will be shown and used to propose a mechanism. Analysis of the mother liquor of each reaction by UV-Vis and formation of crystals over time due to oxidation of solutions affords a possible insight into mechanism of the* Tc_2^{+5} *to* Tc_2^{+6} *core formation. The oxidation states of Tc-Tc dimers formed is also dependent on temperature and pH of the starting solutions and will be explained in extensive detail. These one step reactions of reducing Tc(VII) to low valent technetium provides high yield intermediates for potential waste forms, use in nuclear fuel cycle separations, and radiopharmaceuticals.*

Keywords – technetium carboxylates; metal-metal bonds; metal-halogen bond; hydro/solvo-thermal reactions; polymers

I. INTRODUCTION

Transition metals of groups six through nine exhibit unique direct multiple metal-metal bonding cores. The isotope ^{99}Tc ($\beta^- = 293$ keV) is a group seven radioactive element that is of concern in radioactive waste due to the long-lived half-life (2.13×10^5 years). Exploring and understanding the role of metal-metal bonding in Tc can provide routes for the development of novel and stable waste forms. The fundamental chemistry of low valent Tc is not well explored compared to the surrounding elements Mo, Re, and Ru. Currently over 200 compounds containing the Re_2^{+n} ($n = 4, 5, 6$) cores are known, whereas less than 30 compounds with Tc_2^{+n} ($n = 4, 5, 6$) core exist.[1] One example of a Tc_2^{+6} core is $Tc_2(O_2CCH_3)_4Cl_2$ and has been shown to be a stable starting compound for synthesis of technetium binary halides.[2,3] The reduction of pertechnate, a waste product of spent nuclear reprocessing, to lower valent intermediates provides potential waste forms and insight into radiopharmaceuticals cores.

II. EXPERIMENTAL

A. Synthesis of Tc_2^{+5} and Tc_2^{+6} cores

Addition of 6.0 mL of glacial acetic acid into a small glass vial containing 0.25 mmol potassium pertechnetate, and 4 molar equivalent of desired halogen salt (such as sodium iodide) or haloacid (such as hydrobromic acid) is placed into a 23 mL Teflon lined Parr 4749 autoclave vessel containing 320 mg of sodium borohydride and 200 uL of DI water. The autoclave system is sealed and placed in a oven at 210 °C for 72 hrs, Equations 1-3. Figure 1, shows single-crystals of the polymeric chain $Tc_2(\mu\text{-}O_2CCH_3)_4I$ and molecular view of $Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$.

$$2\,KTcO_4 + 4\,CH_3COOH + NaI + \text{ex. } NaBH_4 \rightarrow Tc_2(\mu\text{-}O_2CCH_3)_4I \quad (1)$$

$$2\,KTcO_4 + 4\,CH_3COOH + 2\,HBr + \text{ex. } NaBH_4 \rightarrow Tc_2(\mu\text{-}O_2CCH_3)_4Br_2 \quad (2)$$

$$2\,KTcO_4 + 5\,CH_3COOH + \text{ex. } NaBH_4 \rightarrow Tc_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3) \quad (3)$$

Bond lengths of Tc_2^{+5} cores are shorter than the Tc_2^{+6} cores and the effects of the bonding halogens will be discussed. These compounds are being considered potential waste forms sue to insolubility in all organic solvents and acidic solutions.

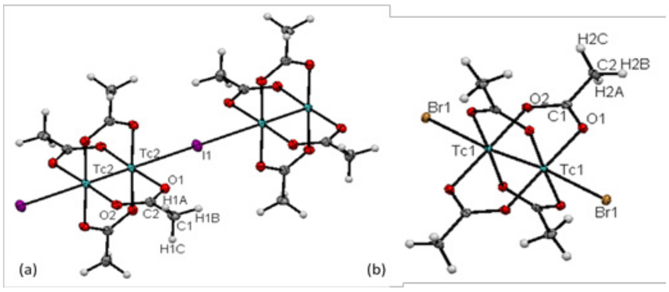

Figure 1. Ortep views of the (a) $Tc_2(\mu\text{-}O_2CCH_3)_4I$, (b) $Tc_2(\mu\text{-}O_2CCH_3)_4Br_2$

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The Statues of Chemical Characterization of a Spent Nuclear Fuel

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Abstract –The high burnup nuclear fuel requires an experimental data to support the fuel integrity, a safety analysis, and a shielding design. At high burnups, the composition of a nuclear fuel changes in a non-homogeneous manner throughout the radius. We present the R&D activities being performed in KAERI for spent fuels discharged from PWR in Korea; focused on the local chemical properties such as 'local burnup', 'structural changes' and 'the distribution of retained fission gas'.

Keywords – spent fuel, burnup, actinide, isotopic distribution, lattice parameter, fission gas

I. INTRODUCTION

To provide basic data about the local chemical properties of a spent fuel, 'radial distribution of isotopes', 'lattice changes along the radius' and 'the quantitative analysis of retained fission gas' were performed.

For the analysis of isotopic distribution and lattice changes, a shielded LA-ICP-MS and a micro-XRD were used, respectively. The generation yield, release fraction and retained fraction of fission gas of a fuel are important factors for determination of maximum burnup of commercial nuclear fuel. Thus, the gas analysis was performed along the axis and radius of a fuel rod.

II. EXPERIMENTAL

For the determination of average burnup of a PWR nuclear fuel, IDMS using ^{148}Nd-isotope as a burnup monitor was used. A shielded LA-ICP-MS system was used for the analysis of isotopic distribution of the spent fuel. A shielded micro-XRD system was used for the analysis of structural changes of a fuel pellet. The inert gas fusion method was used for the analysis of retained fission gas. A hydrogen analyzer equipped with electrode furnace was employed for complete fusion of a fuel to extract the retained gas, and a QMS was used as a gas analyzer.

III. RESULTS AND DISCUSSION

A. Isotopic Distribution and Structural Changes

By LA-ICP-MS system, radial distribution of actinides with respect to ^{235}U was measured successfully. The ^{236}U to ^{235}U ratio was almost constant, while the isotopic ratio of Pu and minor actinides were increased significantly at the pellet periphery. For a comparison, ORIGEN2 code was used to calculate the isotope ratios. The measured values agreed comparatively well with that of the calculated one.

The lattice parameters of the irradiated fuel revealed the larger values than that of non-irradiated UO_2 due to the radiation damage during the reactor operation and cooling after discharge.

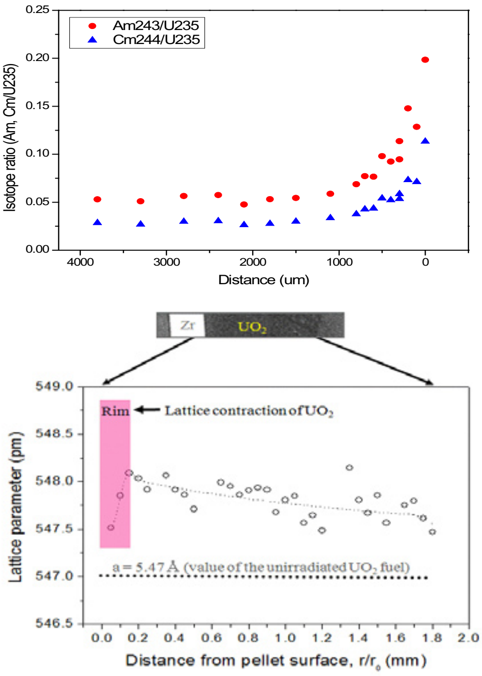

Fig. 1. The local chemical properties of a spent nuclear fuel; (top) actinides distribution, (bottom) changes in lattice parameters

B. Quantitative Analysis of Retained Fission Gas

A small fragment of spent fuel was fused with tin and nickel at a fussion current of 850A for 120 sec. The recovery of Kr and Xe was ca. 96~108 % during 2 min collection for reference materials in Al foil. The axial and radial distribution of RFG was investigated. The amount of retained Xe and Kr increased along the radius, and it decreased along the axis. The measured values were in the range of 75-84% of fission gas generation expected by code calculation. When combined with the released gas, the measured value was approached 95% of calculated one.

IV. CONCLUSION

The measured data can contribute to provide data needed for understanding an irradiation behavior of a high burnup fuel, and can contribute to study the advanced fuel such as ultra high burn-up fuel under developing.

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Determination of ^{93}Zr from intermediate level radioactive effluent

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The French Atomic Energy Commission (CEA) was asked by AREVA to develop a methodology in order to perform ^{93}Zr measurements on an intermediate level radioactive effluent. The difficulty encountered related to the solution containing high contents of fission products which is incompatible with the sample acceptance criteria of the CEA laboratory in charge of this development (Operator Support Analyses Laboratory - LASE). Indeed, the total radioactivity was about 400 GBq/L for the beta emitters and 4 GBq/L for the alpha emitters when the expected concentration of ^{93}Zr was roughly 2 MBq/L, thus implying a drastic decontamination step before acceptance and measurement.

This study is a joint work between the LASE and the LCC (Central Control Laboratory, AREVA NC La Hague) and required to establish a proper scientific and experimental coordination between these two laboratories.

The first experimental steps were performed at the LCC. Because zirconium was essentially contained in the solid phase within the sample solution, it was decided to separate the precipitate using centrifugation prior to mineralization. Once the Zr was perfectly and entirely solubilized, a simple 500 fold dilution was needed for the samples to be accepted at the LASE for further analysis. The main goal was then to perform additional decontamination on the samples and to eliminate the various interfering species, mostly ^{93m}Nb and ^{93}Mo, as the ^{93}Zr would be measured by ICP-MS because of the very low detection limit offered (0.05ng/g) and because it also allowed us to follow the ^{93}Zr decontamination completion. The main separating steps involve a co-precipitation of zirconium with $Ba_3[AlF_6]_{2(s)}$ followed by several solvent extraction steps. These are alternating stages of zirconium and of niobium / molybdenum extraction in the organic phase, using either N-benzoyl-N-phenylhydroxylamine or cupferron in $CHCl_3$ while tuning accordingly the aqueous phase in order to retrieve a maximum amount of zirconium (forming highly stable complexes). Ultimately, the aqueous phase contained all of the zirconium as an oxalate complex and ICP-MS measurement was performed to determine the ^{93}Zr concentration. The separation yield was then determined by measuring the total concentration of zirconium using ICP-AES. Care was taken throughout the whole procedure to circumvent any zirconium cross-contamination. The ^{93}Zr concentration was found to be of 15Bq/µg (Zr, total) with a separation yield above 90%. A 2g/L total concentration of zirconium was determined, leading to a 30 MBq/L ^{93}Zr concentration in the effluent, a result one order higher than the one expected.

Keywords – ^{93}Zr; zirconium; radiochemistry; ICP-MS; intermediate level radioactive effluent; AREVA; CEA.

Selective Separation of Cesium from Simulated High Level Liquid Waste using a Silica-based (Calix[4] + Dodecanol)/SiO_2-P Adsorbent

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Keywords – Cesium; Separation; (Calix[4] + Dodecanol)/SiO_2-P Adsorbent; High level liquid waste (HLLW); Macroporous silica-based supramolecular absorbent.

In order to separate Cs(I) from high level liquid waste (HLLW), a macroporous silica-based supramolecular recognition absorbent, (Calix[4] + Dodecanol)/SiO_2-P, was prepared by impregnating and fixing the 1,3-[(2,4-Diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene (Calix[4]arene-R14) extractant and its molecule modifier 1-dodecanol into a macroporous SiO_2 silica based polymer support (SiO_2-P). Adsorption and separation behavior of Cs(I) or other typical fission produces (FPs) onto adsorbent were investigated by batch and column methods, respectively. It was found that (Calix[4] + Dodecanol)/SiO_2-P adsorbent showed strong adsorption affinity to Cs(I). A relatively large K_d value of Cs(I) above 90 cm^3/g was obtained in the presence of 4 M HNO_3 solution and reach equilibrium state within 1hr at 298 K. From calculated thermodynamic parameters, this adsorption process for Cs(I) could occur spontaneously at the given temperature and was confirmed to be an exothermic reaction. Meanwhile, low value of TOC (total organic carbon) in separated liquid phase from batch experiment reflected that (Calix[4] + Dodecanol)/SiO_2-P adsorbent had excellent chemistry stability against concentrated HNO_3 solution. In addition, tested Cs(I) were eluted out with distilled water chromatographically and separated from simulated HLLW successfully using (Calix[4] + Dodecanol)/SiO_2-P packed column. All results showed that (Calix[4] + Dodecanol)/SiO_2-P adsorbent had excellent adsorption affinity and high selectivity for Cs(I) from HLLW.

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Age Determination of a single Pu and Pu/U mixed oxide particle

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Abstract – *Age-dating of a single Pu oxide particle and a Pu/U mixed oxide (MOX) particle ~1 μm in diameter was demonstrated. The particles were prepared from the U and Pu standard reference materials for this demonstration. They were separately dissolved, and Am, U, and Pu were chemically separated from the solution via anion-exchange chromatography. The isotope ratios of Am and Pu in the eluted fractions were measured using a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). The precision and accuracy of the Pu age were improved through the addition of* ^{243}*Am or* ^{243}*Am-*^{242}*Pu mixed spikes to the sample solutions and by the trace chemical separation of Pu and Am. The determined age in this work was in good agreement with the expected age with high accuracy and precision. These results indicate that a combination of measurement using a mass spectrometer and chemical separation of the spiked samples provides an effective tool for the analysis of environmental samples collected during nuclear safeguard inspections.*

Keywords – Age dating, MOX, Plutonium, Trace analysis, Ion-exchange separation, Safeguards

I. INTRODUCTION

Isotopic and quantitative analyses of U and Pu in environmental swipe samples collected during routine International Atomic Energy Agency (IAEA) safeguard inspections are important for detecting undeclared nuclear activities. Age determination of nuclear materials collected as environmental samples from nuclear facilities is also useful for detecting undeclared activities, as the age provides information regarding the origins and history of the nuclear material. Plutonium of less than nanograms (ng) purified within a few years may be contained in the environmental samples collected during IAEA safeguard inspections. We present a method for determining the purification age of a single Pu oxide and a Pu/U mixed oxide (MOX) particle. These oxide particles ~1 μm in diameter were prepared from U and Pu standard reference materials for this work, and accuracy and precision of the analytical results were evaluated.

II. EXPERIMENTAL

Some Pu oxide particles and five types of MOX particles which consist of different Pu/U atomic ratio were prepared from the standard reference materials, NBS-SRM 947 purified 3.9 years ago and NBL-CRM U010. Small portion of the mixture of these solutions was calcined, and the obtained oxides were ground[1]. The particles 0.5–2 μm in diameter were selected under SEM observation. Each particle was dissolved in a mixture of HF and HNO_3. Finally, an 8 M HNO_3 solution was prepared. The sample solution was spiked with an ^{243}Am or ^{243}Am-^{242}Pu mixed solution purified by anion-exchange chromatography. One-third of the sample solution was used for measurement of the Am/Pu atomic ratio via ICP-MS. The remaining portion was passed through a single anion-exchange column to chemically separate Pu, U, and Am. The isotope ratios in the collected each fraction were measured with a HR-ICP-MS (Element-1) equipped with an Apex-Q desolvating inlet system. All treatments, except for the particle preparation from the standard solution, were carried out in clean rooms (ISO Class 5 and 6) at the "CLEAR" clean laboratory at JAEA.

III. RESULT AND DISCUSSIONS

The Pu purification age was determined using the ^{241}Am/^{241}Pu ratio and the general age-dating equation. The addition of ^{243}Am and ^{242}Pu spikes to the samples gave a precise and accurate Pu age. The determined ages of both the Pu oxide and MOX particles were in good agreement with the expected age (3.9 years). The accuracy in the determined age in the Pu oxide particle was 7.1–105 days and the uncertainty was 0.16–0.5 years. Addition of purified spikes, including ^{243}Am and ^{242}Pu, to the samples led to more precise and accurate age determination, even for a young Pu particle purified only a few years ago[2].

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Kanazawa, Japan, 22-27 September 2013

Radiochemical measurement of 10-15 MeV proton induced fission yields for U-238

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[3]Air Force Technical Applications Center, Patrick Air Force Base, Florida

Abstract – The production of realistic nuclear forensics debris requires an accurate knowledge of cross sections and fission yields for large number of systems. Proton induced fission of U-238 was examined for incident energies in the range of 10-15 MeV. Fission yields were first measured directly from the irradiated materials. The valley and wing fission products were then isolated in various chemical fractions in order to increase the counting statistics leading to improvements in the fission yields. In addition to the total fission cross section and the fission mass yields for U-238, proton based reaction cross sections on U-238 and U-235 were also measured.

Keywords – Fission yields, protons, fission product separation, U-238

I. INTRODUCTION

The improvements in fidelity of nuclear forensic exercise samples require the development of analytical reference materials with the end goal of establishing a realistic exercise sample. This is designed to test the national laboratory analysis and data evaluation communities through a truly coupled, end-to-end "unknown sample" exercise. The fabrication of such a sample requires an accurate knowledge of cross sections and fission yields for numerous reactions that can be explored to obtain fission products and/or short-lived actinide isotopes. Due to the limited amount of nuclear data and the large uncertainties associated with the reported values of proton-induced fission for U-238, experiments were performed to measure the fission mass yields and the cross section. Radiochemical separations were established for fission products of interest in order to improve the fission yields in comparison to those obtained from the initially irradiated samples.

II. EXPERIMENTAL

A stacking foil technique was employed in the irradiation of nat. U foil with 10-15 MeV protons with Y as the beam intensity monitor. A series of irradiations were performed using the tandem Van De Graff accelerator located at the Center for Accelerated Mass Spectrometry at Lawrence Livermore National Laboratory (LLNL). Irradiated samples were transferred to the Nuclear Counting Facility on site at LLNL for the initial counting. After sufficient data were obtained, the uranium foils were dissolved and separated into three fractions: one as a standard and one each for the separation of wing and valley fission products. Various chemical separation methods were developed based on the sorption behavior of the fission products on ion exchange resins. Chemical fractions containing the fission products of interest were counted individually and the total fission yields were back calculated for each sample.

III. RESULTS

The measured fission yields are based on the results generated by the GAMANAL program [1] evaluation of the raw gamma spectra. Fission yields for short lived fission products, as low as $t_{1/2}$=14 minutes, were acquired. An example of a fission mass yield obtained from these experiments is provided in Figure 1. The measured values of the cross sections and fission yields are relatively close to those reported in literature [2-4].

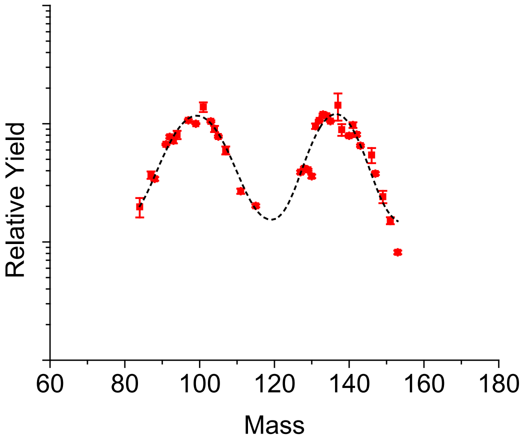

Figure 1. Fission mass yield from 11.9 MeV protons on U-238.

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Effect of Interferences on Actinide and Strontium Separations in Unusual Matrices

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Abstract – Insufficient information is currently available about the effects that the interferences present in complex matrices can have on radiochemical separations utilizing extraction chromatography. This poses a particular challenge for sample analysis in the aftermath of a nuclear incident involving an Improvised Nuclear Device or a Radiological Dispersion Device. This research aims at obtaining this information by examining the composition of common urban materials and by investigating the influence that their constituents have on radioanalytical separations. To address this issue the compositions of several different sample matrices of interest has been investigated. Subsequently the uptake of Sr, Pu, Am and Cm on different commercially available resins was studied in the presence of varying concentrations of potentially interfering elements such as Al, K, Ca, K, Cr, Fe, Ni, Zr and Nd.

Keywords – Extraction chromatography, Actinide, Strontium, Separations

I. INTRODUCTION

Most current radioanalytical methods have been developed for the analysis of air, water, soil and bioassay samples. While these protocols build the foundation of operational environmental monitoring, they are not necessarily suitable for the analysis of samples that will be encountered in the aftermath of a nuclear incident involving an improvised nuclear device or a dirty bomb. Of particular interest for emergency response and nuclear forensics are therefore methods that can be applied to the analysis of steel, concrete, melt glass, asphalt and bone samples. Extraction chromatographic resins have been used for radiochemical separations for many years now, and a large body of data has been published on the retention capabilities of many of these resins for a large variety of elements that can be found in environmental samples. Little can be found, however, on the effect that the matrix constituents found in debris samples can have on analyte uptake. Even though it is known that the elements of interested are retained on the respective resins to a high degree, the samples analyzed will have a much more complex composition than previously encountered. Their behavior might therefore potentially deviate from normal sorption characteristics. In particular the competition between the potential interference and the analyte of interest has to be studied in a systematic manner. The goal of this study is to obtain information about the major and minor constituents that are present in several sample matrices of interest for emergency response and to investigate the influence that they can have on the radiochemical determination of several actinide elements and radiostrontium.

II. EXPERIMENTAL

The composition of several different matrices of interest was determined by either obtaining information from reference materials or by performing elemental analysis on suitable samples. Batch studies were then used to determine the uptake of the analyte of interest on a particular resin in the presence of varying concentrations of different alkali, earth alkali and transition metals, as well as lanthanides. The uptake of Sr on SR resin [1] was investigated in addition to the uptake of Pu, Am and Cm on DGA and UTEVA resin [2, 3]. Single analyte solutions were contacted with small amounts of resin in the presence of varying concentrations of the potential interference. Aliquots were taken and the amount of analyte remaining in solution was determined using either LSC measurement or gamma spectroscopy. Simultaneously the concentration of the interfering element after contact with the resin was measured by ICP-AES.

III. RESULTS

The compositions of several different sample matrices of interest, such as bone ash, steel, concrete, asphalt and melt glass has been investigated. The uptake of Sr on Sr resin was studied in the presence of varying concentrations of Mg, Al, P, K, Ca, Cr, Fe, Ni, Cu and Zr. The adsorption of Pu, Am and Cm on DGA and UTEVA resin was studied in the presence of varying concentrations of Fe, Zr, Mo, Sr, Tc, Cs and Nd. The presence of several of the interferences studied led to a significant decrease in uptake of the element of interest on the resin. Others appeared to have no influence. In some cases the presence of the interference lead to an increased adsorption of the analyte on the resin, hinting at a synergistic effect that needs to be studied in greater detail.

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Poster Session 1

Monday, 23 September 2013

18:50 ~ 20:00

Scientific Topics (Abbrev.)

1. **Fukushima issues (FK)**
2. Education in nuclear and radiochemistry (ED)
3. Nuclear forensics (NF)
4. Nuclear energy chemistry (NE)
5. **Nuclear chemistry (NC)**
6. **Actinide chemistry (AC)**
7. **Environmental radiochemistry (EN)**
8. **Radiopharmaceutical chemistry and Nuclear medicine (RP)**
9. Nuclear probes for materials science (NP)
10. Activation analysis (AA)
11. **Application of nuclear and radiochemical techniques (AP)**

23-FKP-01

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^{137}Cs Accumulation Enhanced by Potassium Starvation in *Lotus japonicus*

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Abstract – Radionuclides released from Fukushima Dai-ich Nuclear Power Plant spread to the environment. The transfer of ^{137}Cs from soil to land plants is one of the most important steps for considering the influx of ^{137}Cs into ecosystem. To identify the responsible genes for ^{137}Cs uptake and translocation in plants, we focused on the K+ transport system in the model legume, Lotus japonicus. The dynamics of ^{137}Cs uptake and translocation was differed between two accessions, B-129 and MG-20, and K starvation drastically enhanced ^{137}Cs uptake in B-129. The expression levels of known K+ transporters were also investigated under several K conditions.

Keywords – cesium-137, potassium, accumulation, Lotus japonicus

I. INTRODUCTION

After the Fukushima Dai-Ichi Nuclear Power Plant accident, large amount of radioactive materials were released into the environment and the major radionuclides leaking was ^{137}Cs. Cesium is known as an analog of potassium in the plant nutrition and, therefore, one of the main route of ^{137}Cs into the ecosystem is an uptake process in land plant. Uptake and translocation of ^{137}Cs is thought to be carried out by the K^+ transport systems in plants [1]. However, because of the complexity of K^+ transport system, the responsible transporters, which transport ^{137}Cs, were not well identified. In this research, the identification of the K^+ transport system, which involved in the ^{137}Cs uptake and transport, in *Lotus japonicus* was attempted. *L.japonicus* has been proposed as a model legume for molecular biology, and the results obtained from *L.japonicus* are applicable to one of the major crops, soybean.

II. MATERIAL AND METHODS

Plant Materials and Growth Conditions

Two *L.japonicus* accessions, Gifu B-129 (B-129) and Miyakojima MG-20 (MG-20), were obtained from the Biological Resource Center in *Lotus* and *Glycine*, University of Miyazaki, Japan. Seedlings were grown with continuously aerated 1/10 strength Hoagland's solution in a 2 L plastic container under light- and temperature-controlled condition; light 16 h, darkness 8 h, 24°C. The solution was renewed every 3 days. At the last 3 days before ^{137}Cs uptake experiment, the solutions with and without K were prepared.

^{137}Cs Uptake

Plants grown for one month were transferred to 50 mL of 1/10 strength Hoagland's solution (without K) containing ^{137}CsCl and non-radioactive Cs (10 μM) for 12 h. After harvesting shoots and roots, distribution and radioactivity of ^{137}Cs was detected with an image analyzer (BAS) and gamma counter, respectively.

Real-time Radioisotope Imaging

RRIS (Real-time Radioisotope Imaging System) was used for obtaining the images of ^{137}Cs uptake and translocation in *L.japonicus*. RRIS is a non-destructive digital autoradiography system specialized for the use in living plant research [2]. The plants prepared as previous BAS experiment were placed in RRIS and the ^{137}Cs distribution images were obtained for 24 h.

III. RESULTS AND DISCSSION

As for the plants grown under normal K condition, ^{137}Cs in B-129 root was about twice the concentration of that in MG-20. However, ^{137}Cs concentration in shoot was not differed between two accessions. In the plants treated with -K solution for 3 days, drastic enhancement of ^{137}Cs uptake was observed in B-129 root. The increase of ^{137}Cs translocation from root to shoot was observed both in B-129 and MG-20. Because of the constant ^{137}Cs concentration in MG-20 root, the increase of ^{137}Cs concentration in MG-20 shoot suggested the high ^{137}Cs translocation activity in MG-20 under K starvation. Real-time ^{137}Cs images clearly indicated the ^{137}Cs uptake site in root and the rapid uptake and translocation of ^{137}Cs in B-129 (Figure 1).

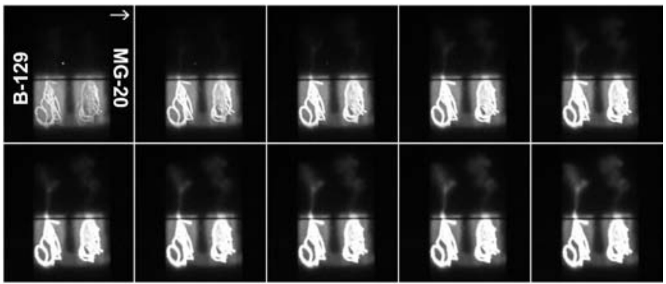

Figure 1 Real-time imaging of ^{137}Cs uptake and translocation in B-129 and MG-20 treated with -K solution for 3 days. Each panel indicates the radioactivity image obtained for every 2.4 h.

Potassium starvation promotes K uptake system, especially high affinity K^+ transporter, in root [3]. Therefore, the expression levels of known K^+ transporters in *L.japonicus* will be discussed.

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Decontamination of the Contaminated Water on Severe Nuclear Accidents by Titanium Oxide Adsorption

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Abstract – In order to establish a decontamination process for contaminated water that generated in a severe nuclear power plant accident such as the Fukushima accident, we proposed a new decontamination process. A new decontamination process is composed of co-decontamination of radioactive transition metals and Cs with hexacyanoferrate(II) ion, and decontamination of radioactive metals including Sr with titanium oxide adsorption. This study discussed the adsorptivity of a new titanium oxide and its applicability to the radioactive water after co-decontamination of transition metals and Cs.

Keywords – Sr decontamination, titanium oxide adsorption, contaminated water of Fukushima accident

The massive amount of radioactive contaminated water was generated in Fukushima Dai-ichi NPP. This water is unique compared to contaminated water generated in previous treated radioactive contaminated waters, concerning the amount of minerals due to the utilization of seawater during the emergency cooling of reactor cores. According to the analysis of the water, it contains fission products (^{90}Sr, ^{125}Sb and ^{134,137}Cs), corrosion products and large amount of non-radioactive metals. The special treatment system was applied to decontaminate it. If NPP accidents may be occur in the future, the experience on this accident is utilized effectively.

In order to minimize the amount of secondary waste from the water treatment system, we proposed a new decontamination process (figure 1) for radioactive contaminated water generated at NPP accidents. At first, this process decontaminates transition metals and Cs simultaneously by adding hexacyanoferrate(II) ion. This step was already discussed [1]. The next step is decontamination of Sr, Sb and remaining Co and Mn by titanium oxide adsorption. This study discusses the adsorptivity of a new titanium oxide and its applicability to the radioactive water after co-decontamination of transition metals and Cs.

Titanium oxide adsorption is commonly used to decontaminate Sr and Co. One of adsorbents is “READ-Sr”, which will be used for the treatment of low level liquid waste at the Tokai Reprocessing Plant in Japan. An investigation of its applicability to the decontamination of Sr from the contaminated water containing seawater suggested that titanium oxide adsorb other alkaline earth elements those are abundant in seawater[2]. Therefore, selectivity of Sr from other alkaline earth elements is necessary.

We synthesized a new titanium oxide with titanium sulfate and ammonium solution, and obtained distribution coefficient (K_d) of Sr, and separation factor (SF) between Sr and alkaline earth elements by batch method. And then the titanium oxide was added to the radioactive water after co-decontamination of transition metals and Cs. This mixture was stirred for 45 minutes and filtrated with 0.1 μm membrane, and then decontamination factor (*DF*) was calculated from concentration of each radioactive and non-radioactive elements.

On experiment of radioactive water, Sr, Mn, Co and Sb was successfully decontaminated, and their *DF*s were >16, 460, 260, 230, respectively. But Mg and Ca were adsorbed to titanium oxide; particularly Ca was adsorbed as much as Sr. Selectivity of Sr to alkaline earth elements is important to reduce secondary waste, so further improvement is necessary.

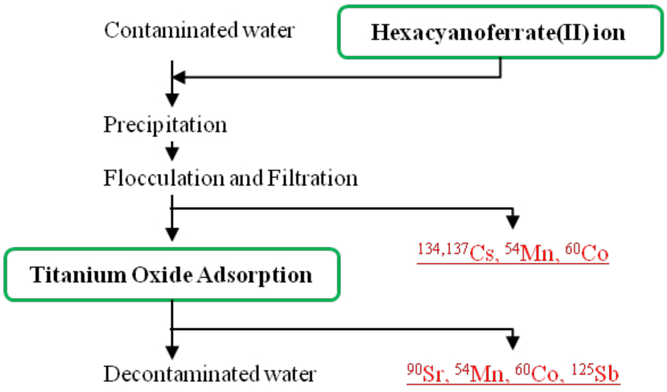

Figure 1. Schematic flow of a new decontamination process

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The authors would like to thank Masashi Kaneko, Kaname Kubo and Jun Hashimoto of Fuji Sangyo KK for synthesizing titanium oxide.

Iodine-129 in the aquatic environment adjacent to a spent nuclear fuel reprocessing plant, Rokkasho, Japan

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Abstract – The spent nuclear fuel reprocessing plant in Rokkasho, Aomori Prefecture, Japan, has been undergoing final testing since March 2006. Iodine-129 is one of radionuclides released into the atmosphere and the coastal water by the operation of the plant. We measured the concentrations of ^{129}I in various environmental samples such as water, sediment, and aquatic biota collected in the aquatic environment adjacent to the reprocessing plant from 2005 to 2012. The concentration of ^{129}I in the environmental samples increased during testing of the chemical separation of dissolved fuel. Since the end of that stage, the ^{129}I concentration in lake water and aquatic biota samples has been rapidly decreasing, whereas the concentration in sediment samples has remained steady.

Keywords – iodine-129, spent nuclear fuel reprocessing plant, water, sediment, aquatic biota

I. INTRODUCTION

Japan's first commercial spent nuclear fuel reprocessing plant, which is in Rokkasho, Aomori Prefecture (Fig. 1), is undergoing final testing. Since the cutting and chemical separation using actual spent nuclear fuel started in March 2006, small amounts of radionuclides (^{85}Kr, ^{3}H, ^{129}I, and ^{14}C) have been released into the atmosphere and the Pacific Ocean. Iodine-129 released from the plant into the atmosphere and the ocean enters Lake Obuchi, which is adjacent to the plant (Fig. 1), through various routes: from the ocean by tides, from river water, and from the atmosphere by deposition.

The aim of this study was to investigate the fluctuations of ^{129}I concentrations in water, sediment, and aquatic biota samples collected in the aquatic environment, mainly in Lake Obuchi, from 2005 to 2012.

II. MATERIALS AND METHODS

Water was sampled from five locations (Sts. 1–5), and sediment from two locations (Sts. 2, 3); samples from aquatic biota (fish, seagrass, shellfish, shrimp, and plankton) were collected from the lake in an area near the north shore (Fig. 1). The samples were analyzed for ^{129}I with an accelerator mass spectrometer (PRIME Lab, Purdue University, USA).

III. RESULTS AND DISCUSSION

The concentrations of ^{129}I in the water samples collected from Lake Obuchi during 2006 to 2008 were approximately an order of magnitude higher than the background level in 2005, whereas the concentrations in the seawater samples collected off the Rokkasho coast (St. 5) showed no increase over the background level during the study period. The ^{129}I concentrations in aquatic biota samples during 2006 to 2008 were also approximately one order of magnitude higher than the background level. Most of the chemical separation of fuel material was finished by 2008, and the rate of ^{129}I release from the plant markedly decreased thereafter. Corresponding with the decrease in the release rate, the ^{129}I concentrations in the lake water and aquatic biota samples rapidly decreased after 2008. In contrast, the ^{129}I concentrations in the sediment samples were stable even after the chemical separation was finished.

The committed effective dose due to annual ingestion of foods with the maximum ^{129}I concentration in the biota sample in Lake Obuchi was calculated as 6.7 nSv y^{-1}.

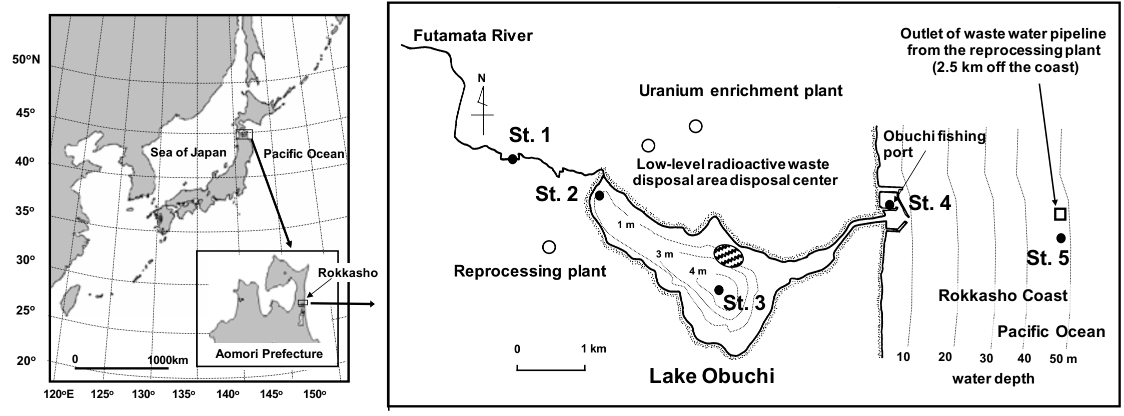

Fig. 1. Map of the sampling stations. Aquatic biota samples were collected in the hatched area.

This study was performed under a contract with the government of Aomori Prefecture, Japan.

Specific activity and time dependence of radionuclides in soils affected by the accident of the Fukushima Dai-ichi nuclear power plant (Part 2).

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Abstract – The purpose of this study is to clear the specific activity and the time dependence of the radionuclides in soils at Fukushima prefecture and neighborhood area. We performed soil sampling for six times at several points within 60km from FDNPP and at Tokyo to October 30, 2012 from March 23, 2011. The concentration of ^{131}*I,* ^{134}*Cs,* ^{136}*Cs,* ^{137}*Cs and* ^{129m}*Te were obtained, but only trace amounts of* ^{95}*Nb,* ^{110m}*Ag and* ^{140}*La were detected whitch were too low to provide accurate concentrations. The concentration of radioactivity on March 15, 2011 is 8234 kBq/m*^{2} *for* ^{131}*I and 882 kBq/m*^{2} *for* ^{137}*Cs at Fukaya, Iitate village. Some radionuclides, such as* ^{103}*Ru, and* ^{106}*Ru and* ^{140}*Ba, observed in the Chernobyl accident, were not measured in the soil samples. This is estimated that mainly noble gasses and volantile radionuclides were released from FDNPP. For the time dependence of* ^{137}*Cs concentration in soil, it was decreased approximately 30% in 19 months at Fukaya, Iitate village. However, at some sampling points, there was not a change at all.*

Keywords – Fukushima Dai-ichi N, ^{137}*Cs, specific activity, time dependence,* ^{134}*Cs*

I. INTRODUCTION

The Fukushima Dai-ichi Nuclear Power Plant (FDNPP) lost all electricity due to a huge tsunami after the Richter-scale magnitude 9 earthquake of March 11, 2011. The water circulation system was severely damaged, and the radionuclides were released to the environment, specially for days in the middle of March. The purpose of this study is to clear the specific activity and the time dependence of the radionuclides in soils at Fukushima prefecture and neighborhood area.

II. MATERIALS AND METHODS

We performed soil sampling for eight times at several points within 60km from FDNPP and at Tokyo from March 23, 2011 to October 30, 2012. Soil samples, at 0-2, 0-3, 3-6 and 6-10 cm depths, were taken using a scraper with a sampling area of 100cm^2 (10cm×10cm). The second and the subsequent sampling were carried out at 3 m intervals from the previous sampling points. The specific activity of samples were measured by Ge detectors (SEIKO EG&G) and decay corrected to March 15, 2011.

III. RESULTS AND DISCUSSION

Specific activity in soils

We were taken soil samples in Iitate village, Fukaya , on March 23, 2011. The concentration of ^{131}I, ^{134}Cs, ^{136}Cs, ^{137}Cs and ^{129m}Te were obtained, but only trace amounts of ^{95}Nb, ^{110m}Ag and ^{140}La were detected whitch were too low to provide accurate concentrations. Some radionuclides, such as ^{103}Ru, and ^{106}Ru and ^{140}Ba, observed in the Chernobyl accident, were not measured in the soil samples. This is estimated that mainly noble gasses and volantile radionuclides were released from FDNPP. The concentration of radioactivity on March 15, 2011 is 8234±1654 kBq/m^2 for ^{131}I and 882±182 kBq/m^2 for ^{137}Cs at Fukaya, Iitate village. The highest difference was more than 100 times in Fukusima. Only ^{137}Cs from global fallout was observed in the soil collected at kumamoto city. The ratio of the total amounts of ^{137}Cs in each section depth was shown in Fig.5. Approximatery 95% of deposited ^{137}Cs were found in the upper 3 cm of the soil. The ratio of the depth profiles did not change at all sampling points during the measurement period.

Time dependence of radionuclides in soils

Fig.1 shows the temporal changes of ^{137}Cs concentration in soil at several sampling points during from March 23, 2011 to October 30, 2012. For the time dependence of ^{137}Cs concentration in soil, it was decreased approximately 30% in 19 months at Iitate village, Fukaya district. It was decreased approximately 20% in 15 months at Minamisouma city. However, at some sampling points, there was not a change of the time dependence of ^{137}Cs concentration at all. For the environment half life of the cesium-137 in the comparatively land with a little vegetation, it was with the range for four years from two years except a physical half life.

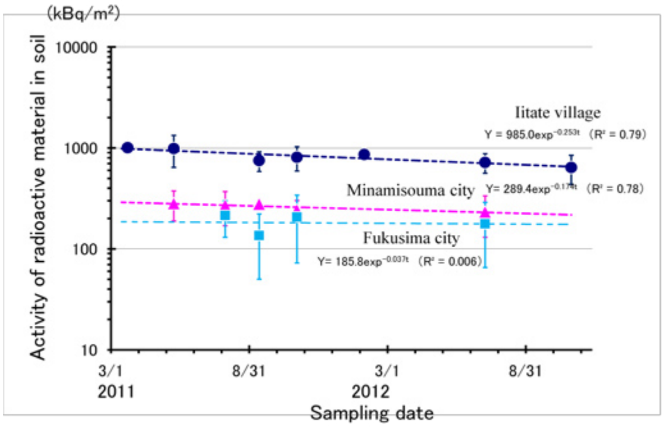

Fig. 1 The temporal changes of ^{137}Cs concentration in soil at several sampling points during from March 23, 2011 to October 30, 2012.

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Differences between year 2011 and 2012 in Cs-137 concentration in brown rice grown in Fukushima Prefecture

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Abstract – Brown rice was collected from ten paddy fields located in four sites in Fukushima Prefecture in year 2011 and 2012 to clear the year difference in radiocesium concentration in brown rice. Paddy fields with the same management including fertilization in both years were selected. Cs-137 concentration in brown rice was in the range of 2.8-290 Bq kg^{-1} in 2011 and 1.3-160 Bq kg^{-1} in 2012. The concentration of Cs-137 was decreased by 40 % in the average from year 2011 to year 2012.

Keywords – brown rice, Cs-137, paddy field, aging

I. INTRODUCTION

Radionuclides was released into the environment as a consequence of the accident at Fukushima Daiichi Nuclear Power Plant (FNPP) that was triggered by the earthquake and subsequent tsunami that occurred on 11 March 2011. Brown rice (unpolished rice) produced during the 2011 growing season was contaminated by radiocesium released from FNPP. Concentration of radiocesium in agricultural products is annually declined because radiocesium is fixed to sorption site for cesium of soil. In addition, potassium and/or zeolite was applied to farmland in Fukushima Prefecture to avoid the contamination of radiocesium to brown rice in the year 2012. In the results, concentrations of radiocesium in brown rice were much lower in the year 2012 than in the year 2011. The aim of this study is to clear the annually declined effect on the concentration of brown rice to evaluate the effects of potassium and zeolite application on uptake of radiocesium by crops.

II. MATERIALS AND METHODS

A. Brown rice sampled

Rice was grown in ten paddy fields in four sites (Aizu Bange, Inawashiro Koriyma and Nihonmatsu) located in Fukushima Prefecture during the year 2011 and 2012. Management including fertilizer followed the conventional practices in each site in both year except in Aizubange and Inawashiro. In these two sites, potassium had not been applied more than ten years in one paddy field and practical fertilizer had been applied in another one. Brown rice was sampled from the paddy fields in the year 2011 and 2012.

B. Measurement of Cs-137 concentration

The concentration of Cs-137 was determined using a germanium detector with a multichannel analyzer system. The actual decay date was determined as October 1, 2011, using the half-life (i.e., decay constant) of the Cs-137. Brown rice was dried for 48 h at 105 °C and dry weight was determined.

III. RESULTS AND DISCUSSION

Concentration of Cs-137 in brown rice investigated in this study was in the range of 2.8-290 Bq kg^{-1} in 2011 and 1.3-160 Bq kg^{-1} in 2012 (Table 1). There were differences in the concentration of Cs-137 between paddy fields in the same site in both years. The differences between paddy fields in the same sit would be due to the differences in exchangeable potassium content and/or the sorption sites for cesium in soil. The details will be published else where.

The concentration of Cs-137 in brown rice was 30-114 % in 2012 compared to those in 2011. It was increased in one of ten paddy fields. The concentration of Cs-137 in brown rice was decreased by 40 % in the average from year 2011 to year 2012. It was suggested that uptake of radiocesium by rice plant in the second year from the radiocesium contamination is a half of that in the first year without decontamination nor the application of potassium, zeolite and so on.

Table 1. Concentration of Cs-137 in brown rice.

Site	No.	Concentration of Cs-137 (Bq kg^{-1} dw)		2012 / 2011 (%)
		2011	2012	
Aizu Bange	1	22	10	48
	2	3.3	2.0	61
Inawashiro	1	17	19	114
	2	3.8	3.1	82
Koriyama	1	2.8	1.3	48
Nihonmatsu	1	200	160	80
	2	290	160	56
	3	130	50	41
	4	61	26	42
	5	74	22	30
Maximum		290	160	114
Minimum		2.8	1.3	30
Average		29	16	60

Geometric average is shown for the concentration of Cs-137.

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Size-distribution of airborne radioactive particles from the Fukushima Accident

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Abstract –The particle size distribution of radioactive aerosols has been observed using the Andersen-type classifier combined with a high volume air sampler. Estimated AMADs of ^{131}I-, ^{134}Cs- and ^{137}Cs-aerosols were ranging from 0.56 to 0.60 μm, which were larger than that of ^{7}Be-aerosols, about 0.2 μm.

Keywords – particle size distribution, radioactive aerosols, airborne radionuclide, nuclear power plant accident

INTRODUCTION

The release of radioactive materials from the Fukushima I nuclear power plant accident brought about seroius and wide contaminations in the area of northeastern Japan. Released radioacive materials from the reactors would migrate as radioactive aerosols, attaching to non-radioactive aerosols suspended in the surface air and being affected by a transport of air masses which is somewhat complex and strongly depends on the distribution of high and low atmospheric pressure regions around the Japanese Islands. In this report, we describe the results of radioactivity measurements in the region far from the site where the present nuclear accident had occurred. Especially, are shown the results obtained in the experiment done by using a high-volume cascade impactor to estimate the size distribution of aerosols attached by fission products.

EXPERIMENTAL

Air samplings were carried out at the sampling station on the roof of the building (height above ground level 12 m) located in our university campus (36°39′N, 138°12′E). Suspended particles attached by fission products were collected by using the Andersen-type classifier combined with the high volume air sampler (Model AH-600). The sampler is a jet cascade impactor consisting of five multi-jet stages (including a backup stage) and a filter, vertically stacked, designed for use at a flow rate of 566 L/min, and it can collect the particles classified into five sizes from 1.1 μm to 7.0 μm.

RESULTS AND DISCUSSION

The sampling was carried out at the sampling station from April 7 to April 24, during 17 days, with the flow rate of 566 L/min and the total volume of 138400 m^3. Aerosol particles were classified and collected on four glass fiber filters, and on a back-up filter for aerosols smaller than 1.1 μm in diameter. About 60% of collected activities were found on the back-up filter, which means that the majority of radioactivity would attached to aerosols with the diameters less than 1.1 μm. This tendency is much more remarkable for the case of ^{7}Be-aerosols, which is formed through attaching by the cosmogenic radionuclide of ^{7}Be and whose size distributions have been measured by using the same manner mentioned below during a couple of years.

In order to estimate a size distribution and a mean particle diameter, we used only three data, which the particle-size range is neatly known, that is, corresponding to particle-size ranges of 3.3-7.0, 2.0-3.3 and 1.1-2.0 μm. Under the assumption that the particle size distribution of radioactive aerosols in surface air is in a *lognormal* and *unimodal* distribution, the cumulative probability was plotted against the particle diameter, as is shown in Fig.1. Activity Median Aerodynamic Diameter (AMAD) was estimated by the value when the cumulative probability is 50%. Estimated AMADs of ^{131}I-, ^{134}Cs- and ^{137}Cs-aerosols were ranging from 0.56 to 0.60 μm, which were larger than that of ^{7}Be-aerosols, around 0.2 μm.

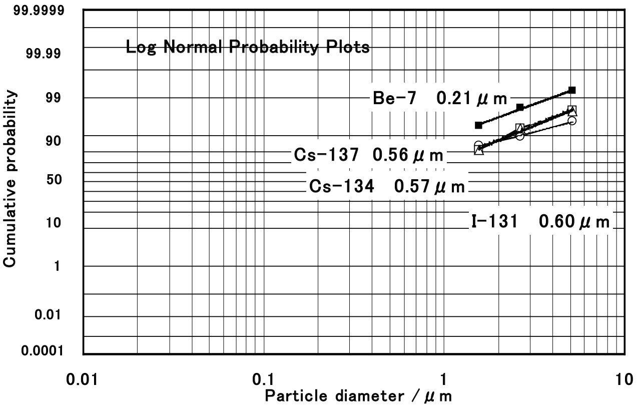

Fig.1 Probability plot for the cumulative percent as a function of aerosol particle diameter.

According to the physical characteristics reported by Whitby for sulfur aerosols [1], the geometric mean radii of 0.57, 0.60, and 0.56 μm for ^{131}I-, ^{134}Cs- and ^{137}Cs-aerosols, respectively, seem to belong to the *accumulation mode* whose mean value is (0.48 ± 0.1) μm. Beyond the difference in origin and chemistry between cosmogenic ^{7}Be and fission products of ^{131}I, ^{134}Cs and ^{137}Cs, what controls mean radius of radioactive aerosols is not clarified yet. It is surely considered that the difference in the formation and growth of both radioactive aerosols would be important.

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Long-term effects of radionuclides originating from the Fukushima nuclear power plant accident in airborne particulate matters in Kawasaki

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Abstract – This study is intended to elucidate the long-term effects of atmospheric radioactive cesium in Kawasaki City, Kanagawa. As a result, it became clear that the radioactive cesium activity concentration in December 2012 had decreased to about 1/10^5 of that observed immediately after the Fukushima Daiichi nuclear power plant (FDNP) accident in March 2011 and sulfate aerosols may act as a carrier and transport radioactive cesium.

Keywords – Fukushima Daiichi nuclear power plant accident, radioactive cesium, carrier, airborne particulate matters, Kawasaki

I. INTRODUCTION

The FDNP accident was caused by the Great East Japan Earthquake, which occurred on March 11, 2011. The artificial radionuclides ^{131}I, ^{134}Cs, and ^{137}Cs were detected in the Kanto region.

In this study, we focused on ^{131}I, ^{134}Cs, ^{137}Cs, and other radionuclides contained in airborne particulate matters (APM) sampled from filters in the Atomic Energy Research Laboratory of Tokyo City University located in the west of Kawasaki City, Kanagawa, which is about 250 km south-southwest from the FDNP.

The aim of this study was to determine the time series of the radioactive decay and the atmospheric dispersion of the artificial radionuclides by γ-ray spectrometry. Moreover, because we have been sampling the APM continuously from before the FDNP accident, we can compare the results before and after the FDNP accident.

II. METHODS

After sampling the APM from the filters, we compressed the filter into an acrylic case to measure the γ-rays. A high purity germanium semiconductor detector was used for the analysis. The measurements were carried out for 80,000 s. The Seiko EG&G spectrum navigator environmental analysis program was used for nuclide analysis.

III. RESULTS AND DISCUSSION

Immediately after the accident at the FDNP in March 2011, ^{95}Nb, ^{97}Nb, ^{110m}Ag, ^{129}Te, ^{129m}Te, ^{131}I, ^{134}Cs, and ^{137}Cs were detected. The activity concentrations of ^{131}I, ^{134}Cs, and ^{137}Cs immediately after the accident were 1.66, 0.61, and 0.60 Bq/m^3 respectively, and the ^{131}I/^{137}Cs activity concentration ratio was 2.78. The time series of the radioactive cesium activity concentration after the FDNP accident is shown in Fig. 1. The ^{134}Cs and ^{137}Cs activity concentration in December 2012 had decreased to about 1/10^5 of the activity concentration observed immediately after the FDNP accident. Sulfate aerosols can act as carriers of radioactive cesium. Because sulfates are formed from sulfur dioxide in the atmosphere, we indirectly examined the relationship between radioactive cesium and sulfate by comparing the activity concentration of radioactive cesium and the sulfur dioxide levels recorded by the Kawasaki pollution monitoring center. The fluctuations in the radioactive cesium concentration were similar to the fluctuation in the sulfur dioxide concentration. This finding suggests that sulfate acts as a carrier and transports radioactive cesium.

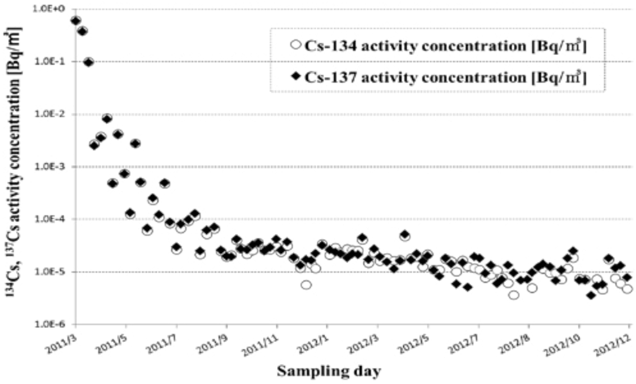

Fig.1 Time series of ^{134}Cs and ^{137}Cs activity concentration in Kawasaki

IV. CONCLUSION

(1) Immediately after the accident at the FDNP in March 2011, ^{95}Nb, ^{97}Nb, ^{110m}Ag, ^{129}Te, ^{129m}Te, ^{131}I, ^{134}Cs, and ^{137}Cs were detected.
(2) The activity concentrations of ^{131}I, ^{134}Cs, and ^{137}Cs immediately after the FDNP accident were 1.66, 0.61, and 0.60 Bq/m^3, respectively, and the ^{131}I/^{137}Cs activity concentration ratio was 2.78.
(3) The ^{134}Cs and ^{137}Cs activity concentration in December 2012 had decreased to about 1/10^5 of the activity concentration observed immediately after the FDNP accident (March 2011).
(4) The fluctuation in the radioactive cesium activity concentration was similar to the fluctuations in the sulfur dioxide concentration; therefore, sulfate aerosols may act as a carrier and transport radioactive cesium.

APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
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Measurement of Iodine-129 concentration in water samples in relation with Fukushima Daiichi Nuclear Power Plant accident

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Abstract – Iodine-129 (^{129}I) concentration in several water samples were measured by means of Accelerator Mass Spectrometry and discussed in relation with Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. ^{129}I concentration of river waters collected Iitate village and Minami-Soma city (North to North-west of FDNPP) showed as high as $1.0{\cdot}10^9$ atoms/L and had not vary significantly during period from March to October, 2012. The combination of ^{129}I/^{127}I ratio and ^{127}I concentration of these water samples can be explained as mixture of fossil rain water (ground water) and the rain radioactively contaminated by FDNPP accident.

Keywords – FDNPP accident, Iodine-129, Accelerator Mass Spectrometry, tap water, environmental water

I. INTRODUCTION

According to Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident, vast amount of radioactive nuclides including radioactive iodine were spilled out into the environment. A rare isotope Iodine-129 (^{129}I) was also widely distributed in a very short time by the FDNPP accident. ^{129}I directly landing on the soil surface had been trapped in the upper layer of the soil and the depth profile should indicate the migration and the interaction with the soil. If ^{129}I was trapped in the woods, it seems to take rather longer time for landing on the ground. Either way, a certain portion of the ^{129}I should be moving downward and finally washed out by the groundwater or river with a certain rate and transported into the sea. The concentration of ^{129}I in environmental water samples taken from rivers and ponds are considered to reflect the iodine transportation process by the fluvial system.

II. EXPERIMENTAL

River water samples and lake water samples were collected from the South-west region (Abukuma area) and North to North-west region (Minami-Soma city and Iitate village) during the period from April, 2011 to March, 2013. 500mL or 1 L of each water sample was served for analysis. 2mg of iodine carrier was added to water and mixed well in a little reduced condition. Iodine was extracted by the solvent extraction and the back extraction process and precipitated as a Silver Iodide (AgI). Collected AgI was mixed with Niobium powder and pressed into a cathode of Accelerator Mass Spectrometry (AMS). ^{129}I/^{127}I ratio was measured at MALT (Micro Analysis Laboratory, Tandem accelerator), The University of Tokyo. An aliquot taken from the water sample before adding carrier was analyzed for iodine concentration by ICP-MS.

III. RESULTS AND DISCUSSION

^{129}I concentration of river waters collected Iitate village and Minami-Soma city (North to North-west of FDNPP) showed as high as $1.0{\cdot}10^9$ atoms/L and had not vary significantly during period from March to October, 2012. This concentration is quite high compared to the pre-accident level ($1\text{-}2{\cdot}10^6$ atoms/L), which was determined from the result of measurement for tap water collected in 2006. The combination of ^{129}I/^{127}I ratio and ^{127}I concentration of these water samples can be explained as mixture of fossil rain water (ground water) and the rain radioactively contaminated by FDNPP accident (Fig. 1).

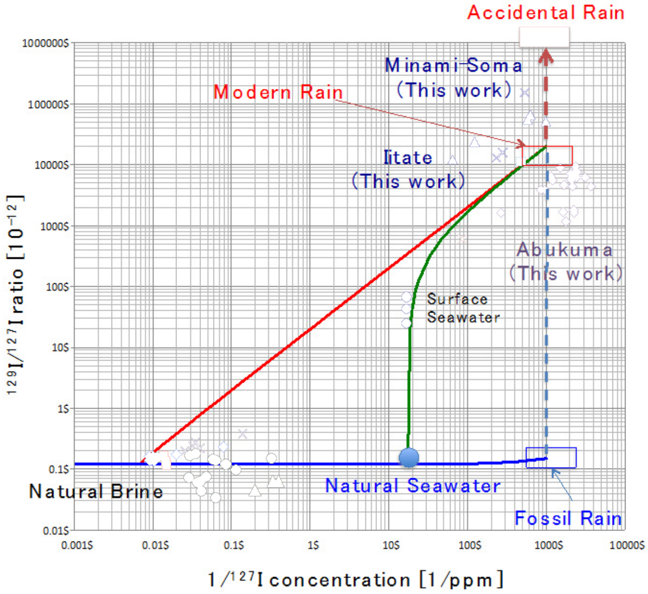

Fig. 1. ^{129}I/^{127}I – 1/^{127}I **plots of several water samples. Lines are the mixing lines between the end members.**

Considering the accidental ^{129}I deposition in Northwest of FDNPP (~$1.4{\cdot}10^{14}$ atoms/m^2) and annual precipitation rate (~1300 mm), it is figured out that no more than 1% of total inventory is transported by the river system annually.

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Observed radioactivities and activity ratios in aerosols from April 2011 at the Geological Survey of Japan, Tsukuba, Japan

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Abstract – The aerosol monitoring was started at the GSJ, Tsukuba, from the end of March 2011 for the assessment of environmental impact and residents' dose rate. This paper reviewed the obtained data and the geochemical behaviors of natural and artificial radionuclides were studied. Many artificial nuclides derived from the FDNPP accident as well as natural ^{7}Be and ^{210}Pb were observed in this study and the most of them with short half-lives became below the detection limit in June, 2011. Several high concentration peaks of ^{134}Cs and ^{137}Cs were observed after June, and around 10^{-4} Bq/m^{3} concentration was estimated as temporal background level. After middle April 2012, it became in half level. The observed ^{134}Cs/^{137}Cs, ^{136}Cs/^{137}Cs and ^{132}Te/^{137}Cs activity ratios showed relatively good attenuation corresponding to their half-lives. For ^{131}I and ^{129m}Te, the activity ratios showed a decreasing trend with fluctuations. ^{110m}Ag showed a bigger attenuation rate than its half-life and ^{95}Nb showed increasing trend. The variation of activity ratio with time observed at the GSJ was supposed to depend on particle size, their chemical species, the source, discharge amount, mixing and the transportation processes of nuclides.

Keywords – Radioactivity, Aerosol, the Geological Survey of Japan, Tsukuba, Activity ratio, Natural and artificial nuclides

I. INTRODUCTION

A big earthquake (M. 9.0) and the subsequent tsunami on 11 March 2011 resulted in severe damages to the Fukushima Daiichi Nuclear Power Plant (FDNPP). All the power supply was lost and the luck of cooling system caused the release of a large amount of radioactive nuclides such as ^{131}I and ^{137}Cs into the environment.

We started the monitoring of radionuclides in aerosols at the Geological Survey of Japan (GSJ) in Tsukuba from the end of March, about 20 days after the FDNPP accident, for the purpose of assessing their environmental impacts and the radiation dose for safety of the habitant. In this paper we summarize and focus on the geochemical behavior of artificial radionuclides as well as natural radionuclides using their activity ratios.

II. OBSERVED RADIOACTIVITIES IN AEROSOLS

Tsukuba is located about 170 km south-southwestward from the FDNPP. The radionuclide concentrations observed at the GSJ would be greatly dependent on those emitted from the FDNPP and the climate conditions, because the released radioactive nuclides would move as a plume. ^{95}Nb, ^{99}Mo/^{99m}Tc, ^{110m}Ag, ^{129m}Te/^{129}Te, ^{131}I, ^{132}Te/^{132}I, ^{134}Cs, ^{136}Cs, ^{137}Cs, ^{140}Ba/^{140}La, ^{141}Ce and ^{144}Ce were main artificial nuclides observed in this study and the most of them with short half-lives became below the detection limit in June, 2011. Several high concentration peaks of ^{134}Cs and ^{137}Cs were observed after June, and around 10^{-4} Bq/m^{3} concentration was estimated as temporal background level, which is about 2 orders of magnitude higher level than that before the accident. After middle April 2012, it became in a half level.

III. ACTIVITY RATIOS BETWEEN NUCLIDES

Supposing the nuclear reactions almost stopped at the time of accident, activity ratio of nuclide versus ^{137}Cs should decrease nearly with the half-life of nuclide because that of ^{137}Cs is by far larger. Variations of the activity ratio of ^{134}Cs, ^{136}Cs, ^{131}I, ^{129m}Te, ^{132}Te, ^{110m}Ag and ^{95}Nb versus ^{137}Cs were examined.

The observed macroscopic ^{134}Cs/^{137}Cs, ^{136}Cs/^{137}Cs and ^{132}Te/^{137}Cs activity ratios showed relatively good attenuation corresponding to their half-lives, although these nuclides might be released from the different three reactors that might have different activity ratios owing to the different burn-up. As ^{134}Cs, ^{136}Cs and ^{137}Cs are isotopes of the same element, the change and large fluctuation of activity ratio during transport would not occur. The small fluctuation after several months from the accident might suggest complex release and mixing of the source reactors at different situations. The ^{131}I/^{137}Cs activity ratio in aerosol showed a decreasing trend with a little fluctuation, and also the tendency of a little higher concentration after 60 d. The change of composition (gas/particle), the release rate and temperature at the reactors, transport processes and their mixing would contribute to the activity ratios. Although ^{129m}Te and ^{132}Te show the decreasing trend, the former showed rather large fluctuation with a high value. There may be complicated processes concerning the older and younger air masses whose ^{132}Te/^{129m}Te activity ratios differ from each other because of half-lives. On the other hand, ^{110m}Ag showed a bigger attenuation than that supposed from its half-life, probably owing to its chemistry and the discharge rate. Although ^{95}Nb was emitted in the atmosphere together with other radioactive nuclides in the accident, ^{95}Nb/^{137}Cs activity ratio showed increasing trend with time.

It was shown that the activity ratios of artificial nuclides observed at the GSJ might depend on their chemical species, particle size, diversity of the source, change of discharge and the transportation processes of nuclide. These facts would help the better understanding of the reactor conditions in and after the accident in addition to other information.

23-FKP-10

Chemical forms of radioactive Cs in soils originated from Fukushima Dai-ichi nuclear power plant accident, as studied by extraction experiments

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We conducted extraction experiments on soil samples contaminated with radioactive cesium originated from the Fukushima Dai-ichi nuclear power plant (FDNPP) accident in Japan in March 2011. The experimental results suggested that the majority of the radioactive cesium deposited on land surface was first adsorbed on exchangeable sites of clay minerals, and eventually it was strongly fixed in interlayer spaces of some 2:1 clay minerals. The experiment revealed that a very small amount of Cs-137 extractable with acetic acid solution existed in the surface soil layer.

Keywords: radioactive cesium, Fukushima Dai-ichi nuclear power plant accident, sequential extraction, soil contamination.

I. INTRODUCTION

The FDNPP accident in March 2011 resulted in radiological contamination mainly by radioactive Cs widely in Japan. It is highly probable that the behavior of radioactive Cs newly deposited on soils due to the accident is different from that of stable Cs that has existed in soils before the accident, because of the difference in chemical forms between them [1]. In this study, we discuss chemical forms of radioactive Cs in soils originated from the FNPP accident based on the results of extraction experiments conducted for Cs on soil samples.

II. EXPERIMENTAL

We first performed preliminary extraction experiments on some soil samples with various extracting solutions. The contents of Cs-133, the stable isotope of cesium, in the centrifuged/filtered extract solutions were determined.

Based on the results of preliminary experiments, we then performed two-step sequential extraction on a soil sample collected at Toride City, Ibaraki, Japan, which is located about 200 km southwest of the FDNPP and is one of the small radioactive hotspots near Tokyo found after the accident.

The soil core sample, collected with a core sampler (10 cm in diameter and 10 cm in length) in August 2011, was cut with 1 cm width layers. The contents of Cs in the surface layer of the sample were Cs-133, Cs-134, and Cs-137 in the 3.8 μg/g, 1.1 Bq/g, and 1.3 Bq/g , respectively. Five grams of the dried soil (upper three layers) samples were subjected to sequential extraction with 200 mL of 1 M ammonium acetate solution and then 0.11 M acetic acid for 24 hours each. The contents of Cs-133 and radioactive Cs (Cs-134 and Cs-137) in each extract solution were determined with spectrometry respectively.

III. RESULTS AND DISCUSSION

The preliminary experiments revealed that stable Cs in soil was hardly extracted with Milli-Q water and 0.11 M acetic acid, and that only the extractants prepared from ammonium salts could partially extract Cs from the soil samples. This indicates that stable Cs is predominantly extractable from clay minerals with the extractants including ammonium ion by ion exchange process.

Fig. 1 shows the results of the extraction experiments on the Toride soil layer sample. About 10 to 20% of radioactive Cs in the layer samples was extracted with 1 M ammonium acetate solution, while only about 3% of the stable Cs, Cs-133, was extracted. It is likely that the extracted radioactive Cs was incorporated in ion-exchangeable sites of clay minerals. Thus, radioactive Cs has apparently higher mobility than Cs commonly existing in soil. The portion of the radioactive Cs extracted with ammonium acetate solution is higher in deeper layers, which suggests that radioactive Cs has migrated into the deeper layer of the soil *via* ion-exchangeable sites of clay minerals. On the other hand, in the case of acetic acid as extractant, a small amount of Cs-137 was extracted from only the surface layer (0-1cm).

As a whole, more than 70% of radioactive Cs was not extracted by either ammonium acetate solution or acetic acid. A dominant part of radioactive Cs, which was not extracted from present extractants, is probably strongly fixed to interlayer spaces of 2:1 clay minerals.

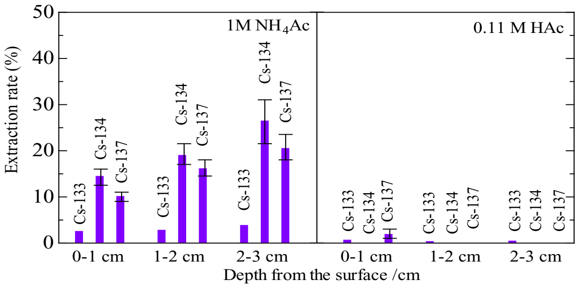

Fig.1 Extraction rates of Cs in the Toride soil sample with NH_4Ac-aq (left) and acetic acid (right).

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23-FKP-11

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Thermal Oxidation of Cesium Loaded Prussian Blue as a Precaution for Exothermic Phase Change in Extreme Conditions

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Abstract – Cesium adsorbed Prussian blue is studied for the thermal oxidation. The TG-DTA shows exothermic phase change of micro aggregates of nano-PB at above 270 ℃. For this reason, Cs loaded PB was heated between 180 to 260 ℃. Heating at 180 removed only the water. Neither the oxidation of Iron nor the removal of cyanide is observed at this temperature. Oxidation of cyanide is observed upon heating above 200 ℃ while loaded Cs is released after heating at >250 ℃ followed by washing with water. Thermal oxidation between 200 to 220 ℃ for more than 2 h showed control on exothermic phase change and loaded Cs is also not solubilized.

Keywords – Prussian blue, Cesium, Exothermic Phase Change

I. INTRODUCTION

Prussian blue (PB), ferric hexacyanoferrate (Fe-HCF), is an inorganic complex, mostly known in the history for its peculiar Cesium (Cs) selectivity.[1] In reference to the PB parent molecule, a number of transition metal hexacyanoferrate are synthesized and named as PB-analogues. The PB forms an open cage structure that possesses a typical zeolytic characteristic, an adjective typically given to any molecule capable of trapping other ions within its lattice cavities.[2] Interestingly, PB, different from the common zeolytic materials, possesses unique selectivity for the Cs-ion. Due to this structural coincidence, PB has become the ultimate Cs-trapper. From Ni-HCF for Cs in alkaline solutions to Cu-HCF for electrochemical removal of Cs or Fe-HCF for neutral to acidic solutions, no materials show high Cs selectivity, faster kinetics, and high capacity like PB-analogues. However, based on the Sax's Dangerous Properties of Industrial Materials some concerns were raised regarding the stability of used HCF analogues during long term storage.[3] Cash et. al. performed extensive study on ferrocyanide storage tanks in Hanford site (USA) for resolving such issues.[4] Their report ruled out all these postulations. Therefore, any speculations on the long-term storage of PB are unlikely. Even so, to ensure the post-use safety of the PB adsorbent for assured long-term storage, we propose the thermal oxidation of the Cs loaded adsorbent prior to the storage.

II. EXPERIMENTAL

As a parent molecule of number of analogues, PB itself is used for the thermal oxidation experiment. For this, PB is loaded with given amount of Cs from pure water or fly-ash extracted solution containing Cs along with high concentration other alkali metals, and other ions. Then it is heated at different temperature. The oxidized sample was washed with water and analyzed for the release of loaded Cs. ICP-MS, TG-DTA, IR, Mossbauer, etc. were used for different analyses.

III. RESULTS AND DISCUSSION

The phase change behavior of PB was studied by taking micro aggregates of PB nanoparticles. The TG-DTA taken with air, Figure 1, Shows the exothermic oxidation at about 272 ºC. Therefore, Cs loaded PB was heated at 180 ºC to 250 ºC. No oxidation of iron or cyanide but only water removal was observed at 180 ºC, while the loaded Cs is released upon washing the PB oxidized at 250 ºC. Heating above 200 ºC is necessary to induce the oxidation. But, the process may get vigorous when heated above 250 ºC. So, optimum oxidation temperature is above 200 ºC and below 250 ºC. Exothermic phase change was disappeared for a sample loaded with 0.2 wt% Cs when heated at 210 ºC for 3 h. Washing this sample after oxidation, Cs release was not observed.

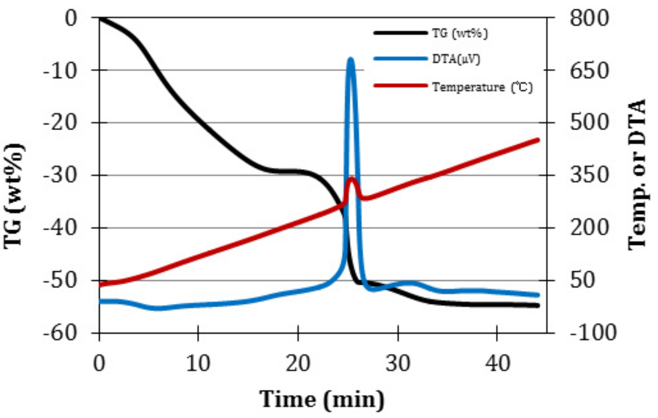

Figure 1. TG-DTA of Cs adsorbed PB taken in air. 10 mg, 10 ºC/min.

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23-FKP-12

Analysis of ^{134}Cs and ^{137}Cs distribution in soil of Fukushima prefecture and their specific adsorption on clay minerals

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Keywords – Radiocesium Interception Potential, Fukushima Daiichi Nuclear Power Plant accident

Various kinds of radionuclides were released from the Fukushima Daiichi Nuclear Power Plant (FDNPP) due to the accident that occurred in March of 2011. Of the radionuclides released from the FDNPP, ^{134}Cs and ^{137}Cs are the major radionuclides of concern in radiation dose because of large amounts in deposition on surface soil and their long half-lives. Cs is known to be adsorbed specifically on clay minerals in soil. The strong affinity of clay minerals for Cs is considered to be due to the presence of the frayed edge sites (FES). Cremers et al. (1988) proposed that the strength of the affinity can be explained by the radiocesium interception potential (RIP), which was defined by the product of the FES capacity and Cs-K selectivity coefficient on the FES [1]. The RIP would be usable as an index of the mobility of radiocesium in soil and expected to be used to predict the downward migration of radiocesium.

We collected surface soil samples within 60 km from the FDNPP and analyzed spatial and temporal radiocesium distributions with a Ge semiconductor detector. No large change in vertical distribution pattern of radiocesium has observed on the samples collected in April 2011 and April 2012 at the same location, suggesting strong adsorption of ^{134}Cs and ^{137}Cs on soil (Fig. 1). To confirm the specific adsorption of Cs on clay minerals, we divided the soil into different particle sizes by sieving and sedimentation method and measured the activity in each size fraction. The activity was highest in the clay fraction (< 2 μm) and it tended to decrease as the particle size increased. The RIP measurement was carried out based on the procedure adopted from Wauters et al. (1996) [2]. One g of soil was equilibrated with carrier free ^{137}Cs in a 100 cm^3 of 0.1 mol dm^{-3} $CaCl_2$ and 0.5 mmol dm^{-3} KCl solution. Under the above condition the amount of Cs adsorbed on the FES is negligibly small compared to that of K. A known amount of carrier-free ^{137}Cs was used for the equilibration experiment and the activity of ^{137}Cs in the solution was measured with a NaI scintillation detector for the determination of the solid-liquid distribution coefficient for Cs (K_d^{Cs}). The RIP can be calculated from the K_d^{Cs} and the K concentration in solution. The obtained RIP value ranged 200-1500 mmol kg^{-1} that seemed to be high enough to adsorb ^{134}Cs and ^{137}Cs derived from the accident. The relationship between the RIP and Cs soil depth profile will be discussed.

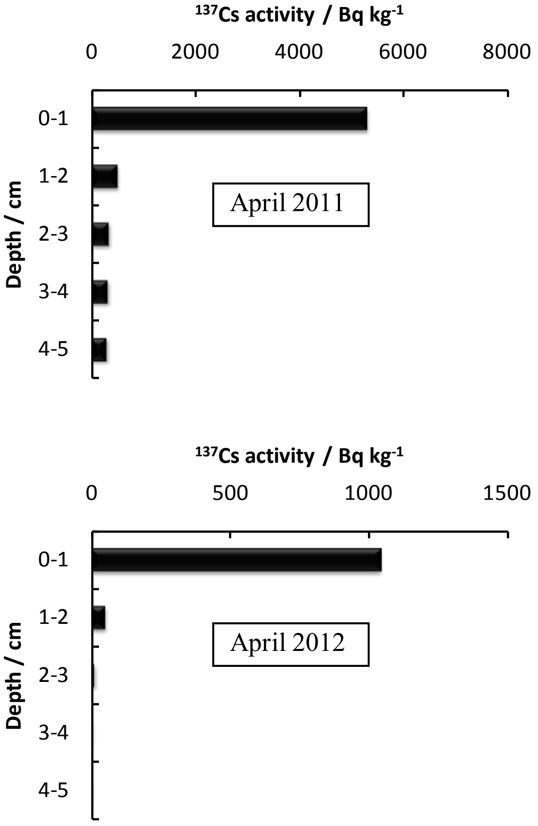

Fig. 1. Vertical distribution of ^{137}Cs in soil collected at the same location (30 km west of the FDNPP) in 2011 and 2012. The concentrations differ but the vertical distribution pattern was similar.

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Distribution of radionuclides in seabed sediments off Ibaraki coast after the Fukushima Daiichi Nuclear Power Plant accident

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Abstract – Various kinds of radionuclides were released into the atmosphere and the sea from the Fukushima Daiichi Nuclear Power Plant of Tokyo Electric Power Co. (TEPCO) by the accident and then reached to the neighboring prefectures. Therefore the accident influence in Ibaraki prefecture was investigated by measuring the concentrations of cesium-134, cesium-137, strontium-90 and plutonium isotopes in seabed sediments. The values for ^{137}*Cs ranged from 6.1 to 300 Bq/kg (dry wt) and the ratio of* ^{134}*Cs/*^{137}*Cs ranged from 0.48 to 0.77. The highest point of* ^{137}*Cs concentration was observed at the northernmost station and the concentration was similar to that reported by MEXT*[1].

Keywords – seabed sediments, Ibaraki coast, Fukushima Daiichi Nuclear Power Plant accident, cesium-134, cesium-137

I. INTRODUCTION

Various kinds of radionuclides were released into the atmosphere and the sea by the Fukushima accident, and then reached around the Tokai Reprocessing Plant (TRP) located about 120 km south of the Fukushima Daiichi Nuclear Power Plant. The influence of the radioactivity on the environment should be investigated because we have performed the routine environmental radiation monitoring around TRP. In this research, strontium-90, cesium-134 and cesium-137 concentrations in the additional special seabed sediments were measured with plutonium isotopes (^{238}Pu, $^{239+240}$Pu), to find out the accident influence on sea area. Moreover, strontium-90/cesium-137 radioactivity ratio was compared with the ratio before the accident. Finally, each radioactivity distribution in sea area was arranged to acquire the influence of the accident.

II. METHODS

From May to July in 2012, fifty-one Seabed sediments were collected by the Smith–McIntyre sampler set on a monitoring ship. The samples were dried at 105 °C for 3 days and then packed in measurement vessels. Cesium-134 and ^{137}Cs radioactivity concentrations were measured by high-purity germanium semiconductor detectors for 10,000 sec. On the other hand, Strontium-90 and plutonium isotopes were purified by chemical separation and were then measured by a beta gas-flow counter and a silicon semiconductor detector, respectively.

III. RESULTS AND DISCUSSION

Distributions of ^{137}Cs concentration in seabed sediments at each place are shown in Fig. 1(a), (b). Radioactivities of ^{137}Cs ranged from 6.1 to 300 Bq/kg (dry wt) and the ratio of ^{134}Cs/^{137}Cs ranged from 0.48 to 0.77. The concentration of ^{134}Cs and ^{137}Cs before the accident at the sea area in the past 10 years were < DL* and < DL* to 1.0 Bq/kg, respectively. The highest ^{137}Cs concentration was observed at the northernmost station near Kitaibaraki City and was similar to that reported by MEXT [1]. The higher ^{137}Cs concentrations were also observed along the coastal area of Tokai-mura including the mouth of the Kuji River. Therefore, the influence of the Kuji River on sea area should be investigated in detail. Radioactivity concentrations of ^{90}Sr and plutonium isotopes are under measurements.

* DL: detection limit (^{134}Cs:1 Bq/kg, ^{137}Cs:0.8Bq/kg)

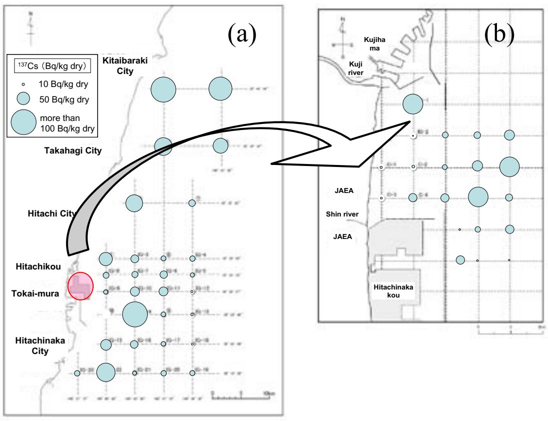

Fig.1 Distribution of ^{137}Cs concentration in seabed sediments of (a) Ibaraki coast and (b) Tokai coast

IV. CONCLUSION

In order to identify the accident influence, distribution of radionuclides in seabed sediments off Ibaraki coast was investigated. Cesium-137 concentrations had more than hundreds times higher than that before the Fukushima accident. Furthermore, the Fukushima accident influence was observed from the ratio of ^{134}Cs/^{137}Cs. The highest point of ^{137}Cs radioactivity was located at the northernmost station.

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Radiocesium Concentration Change in Tree Leaves Before and After Defoliation

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Abstract – Understanding the fate of radiocesium in a tree is of great important to estimate the removal rates of radiocesium. Defoliation is one of the important removal pathways, however, radiocesium might retranslocate from senesced leaves to other tree parts like potassium. In this study, several tree species were measured the cesium-137 concentrations in leaves before and after defoliation. It was found that a portion of radiocesium retranslocate from senesced leaves to other tree tissues; this mechanism will extend radiocesium retention time in trees.

Keywords – Cesium-137, Potassium-40, retranslocation, defoliation

I. INTRODUCTION

Two years after the TEPCO's Fukushima Daiichi Nuclear Power Plant (FDNPP) accident, radiocesium ($^{134+137}$Cs) is recognized as the only major contaminant in the terrestrial environment. Decontamination of houses, public places as well as some agricultural fields have been proceeded, however, forests are difficult to clean up because they occupies large areas in contaminated areas and countermeasures have not been established yet. Thus, radiocesium will be recycled in natural forest ecosystems.

Under these circumstances, it is important to know the reduction rate of radiocesium from a tree to understand the fate in forests after contamination. The most important removal pathway is defoliation; the old leaves fell off with some radiocesium in them so that radiocesium concentrations could decrease with time [1]. However, as it was found for potassium [2] retranslocate to developing tissues or internal stores before defoliation would occur for radiocesium because both elements are in the same group. The mechanism extends the radiocesium residence time in trees. However, there was no data on Cs retranslocation from senesced leaves to green leaves. In this study, therefore, we measured concentrations of radiocesium before and after defoliation to see whether the mechanism was found or not.

II. MATERIALS AND METHODS

Eight species of deciduous trees and evergreen trees were studied in October to November 2011, within the grounds of our institute (NIRS), Chiba Prefecture, Japan. Tree leaves both just after defoliated (senesced leaves) and the green leaves still remained on the tree branches were collected on the same sampling day. They were dried at 80˚C for 3 days at least to obtain constant weight. Each sample mass was 8-22 g on dry weight basis. After drying, each sample was mixed well and transferred into a plastic bottle to measure ^{137}Cs and ^{40}K concentrations with a Ge detecting system (Seiko EG&G). In order to check the stable Cs and K concentration change, a 0.1-g amount of selected leave sample was decomposed with mineral acids and the concentrations were measured by ICP-MS (Agilent 7500a) for Cs and ICP-OES for K (Seiko Vista-Pro).

III. RESULTS AND DISCUSSION

The retranslocate percentage (T_r) is defined as follows

$$T_r=(A_{green}-A_{senesced})/A_{green}x100$$

Where A_{green} is activity concentration of green leaves of a tree (Bq kg^{-1}-dry) and $A_{senesced}$ is activity concentration of fallen leaves of the tree (Bq kg^{-1}-dry). The T_r values of *Somei-yoshino* cherry trees (3 samples from different tree stands) showed 19-49% for ^{137}Cs while 16-40% for ^{40}K. Deciduous tree stands tended to show radiocesium translocation (Tr=0-81%) however, no clear result was found for evergreen tree stands because direct deposition effect on senesced leaves remained. The stable isotope determination results for K agreed well with ^{40}K data, however, the data for radiocesium and stable cesium did not agree due to the above mentioned reason. The T_r values of stable Cs for deciduous tree ranged 0-63%, while less Cs translocation was found for evergreen tree stands (0-17%).

The second year results will be added and discussed at the presentation.

Acknowledgement: This study was partially supported by the Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry (METI), Japan.

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Distributions and Concentrations of Radionuclides in Giant Butterbur after the Fukushima Nuclear Power Plant Accident

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Abstract – Distributions of radiocesium ^{137}*Cs) and radioiodine (*^{131}*I) in giant butterbur (Petasites japonicus) was studied to investigate translocation of these radionuclides. The concentration ratios (on dry weight basis) between petiole and leaf for the first samples (28 March 2011) showed about 0.2 for both isotopes, however, the ratio increased to ca 0.7 for* ^{131}*I while that for* ^{137}*Cs was ca. 0.4 by 5 May 2011. The newly emerged shoots showed the concentrations in between.*

Keywords – translocation, radioiodine, radiocesium, herbaceous plants

I. INTRODUCTION

Radioiodine and radiocesium released due to the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident were deposited around Kanto Plain, mainly on 20-22 March 2011 with rain [1]. Radionuclide behavior in herbaceous plants after deposition will provide information of radionuclide mobility and uptake from roots and through plant surfaces after emergency situation. Previously, newly emerged part concentrations were reported [2], however, the distribution patterns between old plant parts, which directly affected by deposition, and newly emerged plant part has not been reported yet.

In this study, we focused on giant butterbur (*Petasites japonicus*), which is a herbaceous plant and had already been grown at the time of FDNPP accident occurred. Distributions of radioiodine and radiocesium in this plant will provide us the fate differences between radioiodine and radiocesium after deposition.

II. MATERIALS AND METHOD

Plant samples were collected from 28 March 2011 at NIRS, about 210 km SSW from FDNPP. Newly emerged parts were collected from 13 April to 5 May 2011. The sampled plant parts are shown in figure 1. Immediately after the collection, each parts were cut and mixed well. The radioactivity concentrations were measured with a Ge detecting system (Seiko EG&G). Concentrations of iodine-131 (^{131}I) and cesium-137 (^{137}Cs) in the ground were 4500 and 8300 Bq m^{-2} at 25 April 2011. About 200 days after the first sampling, the concentrations of radiocesium in leaves and petiole samples were collected again, however, due to the low concentrations, the samples were dried to reduce volume.

The samples collected between 28 March to 5 May 2011 were measured in wet weight mass, thus, the concentration was estimated to dry weight mass using the following data.

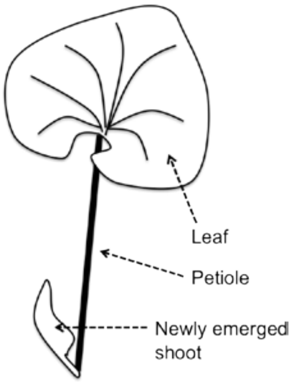

Figure 1. Schematic of giant butterbur sampling parts

III. RESULTS AND DISCUSSION

The average concentration ratios (on dry weight basis) between petiole/leaf for ^{137}Cs and ^{131}I showed 0.42 (0.34-0.51) and 0.59 (0.40-0.76), respectively, for the samples collected between 12 April to 5 May. The ratio for the first sampling date were the same (ca. 0.2), thus these radionuclide translocation showed different increments in the petiole part. The concentrations of ^{137}Cs and ^{131}I in newly emerged shoots were between those of leaves and petioles. Compared to other herbaceous plants, ^{137}Cs concentration in giant butterbur shoots was almost the same after 22 April, thus it was assumed that the root uptake pathway became major by that time. However, the concentration in shoots collected on 13 April was about 2.5 times higher than 22 April sample; probably, translocation from leaf surface to newly emerged shoots would partially affect.

Acknowledgement: This study was partially supported by the Agency for Natural Resources and Energy, Ministry of Economy, Trade and Industry (METI), Japan.

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The Behavior of Cs Adsorption of Microcapsule Beads Nano-Prussian Blue

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Abstract – A granular cesium adsorbent for column-type decontamination has been developed using Prussian blue nanoparticles with micro-capsule technique (MC-nPB). The MC-nPB shows the extraordinary Cs-adsorption capacity, over 120g(Cs)/Kg(Adsorbent). The lattice constant of MC-nPB was expanded after Cs adsorbed, indicating that Cs cations are adsorbed in the nano-PB crystalline frameworks.

Keywords – Cesium, Cesium adsorbent, Nano-Prussian blue, Microcapsule beads

I. INTRODUCTION

Prussian blue is known as an excellent cesium-ion adsorbent[1-3]. For the decontamination of the radioactive-Cs from the aqueous solution, a column of the adsorbent is quite effective. For the purpose, we have developed the granular adsorbent with Prussian blue nanoparticles by microcapsule technique (MC-nPB). Here we show its quite high adsorption capacity.

II. METHOD

The Cs adsorption properties of MC-nPB were evaluated in a batch adsorption experiment. 12.5 mg of the MC-nPBs were immersed in 10 mL of Cs solution and shaken at 25 °C for 24 h. (solid /liquid ratio = 800 mL/g). The Cs^+ concentration was determined using an inductively coupled plasma mass spectrometer (ICP-MS).

The crystal structure of MC-nPB before and after the Cs-adsorbed is examined by an X-ray diffract meter (XRD). The lattice constant a, b and c were estimated using XRD spectra or miller indices (200) (220) (400) (420) (422) and (440) assuming a cubic structure. The lattice constant a, b and c were refined with WPPF (Whole Powder Pattern Fitting); Pawley Method.

III. RESULTS

Figure 1 shows the Cs-adsorption isotherm of MC-nPB with the 1 mg/L Cs-solution. Over 6 hours, the Cs-adsorption is almost complete. The adsorption rates at 6, 12, and 24 hours are 96.0, 99.0 and 99.9 %, respectively. The adsorption speed is roughly proportional to the solid/liquid ratio.

With the solution with the high Cs-concentration until 500 mg/L, adsorption capacity is determined as the 120 g (Cs) /kg (adsorbent).

Figure 2 shows the XRD patterns of MC-nPB (a), that after 7% Cs-adsorbed (b) and that after 15% Cs-adsorbed (c). Accordingly to these results, a cubic structure shown in a stoichiometric PB was retained even after the Cs-adsorption. In addition, it was observed that the peaks for the Cs 15% adsorbed PB were sifted to be lower degrees compared to that of the MC-nPB. The lattice constants for the MC-nPB, 7% Cs adsorbed and 15% Cs adsorbed were determined as 10.167(4), 10.171(7) and 10.193(4) Å, respectively.

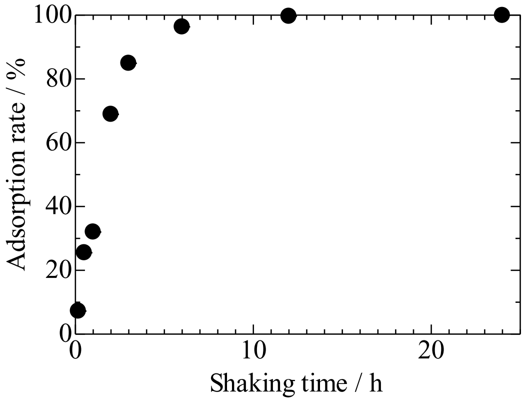

Figure 1 Relationship between Shaking time and Adsorption rate

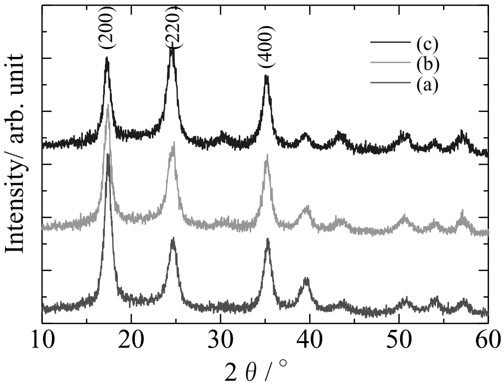

Figure 2 XRD pattern of microcapsule beads nano-PB (a), 7% Cs adsorbed PB (b), and 15% Cs adsorbed PB (c).

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Transfer of Radiocesium from Soil to Cut Flowers

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Abstract – Concentration and transfer factor of radiocesium, which was derived from the Fukushima Daiichi Nuclear Power Plant Accident, from soil to cut flowers was determined. Field experiment was performed in Gray Lowland soil located in Fukushima Prefecture from May to October of 2011 and seven species of plants, gypsophila paniculata, sunflower, chrysanthemum, gentian, lily, dahlia and eustoma, were cultivated. Concentration of radiocesium ($^{134+137}$*Cs) in the soil was 1800-4400 Bq kg*$^{-1}$ *and the range of the transfer factor in the plants was 0.008-0.066, which was within one order of magnitude.*

Keywords – cut flower, Fukushima Daiichi Nuclear Power Plant, radiocesium, transfer factor

I. INTRODUCTION

A huge amount of radionuclide was released into the environment at the Fukushima Dai-ichi Nuclear Power Plant accident. Radiocesium, which is major radionuclide, was deposited on the soil and agricultural products were contaminated. Radiocesium is an important radionuclide for the assessment of radiation exposure to the public and also need to know the contamination level of agricultural products for the public relief. Few data available on behavior in soil-cut flower interactions. This study was conducted to clarify the concentration and transfer factor of radiocesium in cut flowers.

II. MATERIALS AND METHODS

Field experiment was performed in Gray Lowland soil located in Fukushima Prefecture from May to October of 2011. The soils was sampling of 0–15 cm depth in five points and mixing. Seven species of cut flowers such as gypsophila paniculata (*Gypsophila paniculata*), sunflower (*Helianthus annuus*), chrysanthemum (*Dendranthema grandiflorum*), gentian (*Gentian triflora.*), lily (*Lilium* × *formolongo*), dahlia (*Dahlia pinnata.*) and eustoma (*Eustoma grandiflorum*) were cultivated in the field experiment. Cut flowers were harvested as when flowering.

After the plants maturing, they were collected from the fields. The samples were rinsed with water, and dried at 80°C for 3 d. The dried samples were pulverized with cutter blender and compressed into plastic vials (U-8). The soil samples were collected after harvesting the cutting flowers, air-dried at 25°C for 10 d, and passed through a 2-mm mesh sieve. The soil samples were also compressed into the plastic vials. The radioactivity of the samples was measured with a germanium semiconductor detector with a multichannel analyzer, over a period of 2,000-48,000 seconds for the plant and 1,200 seconds for the soil samples.

III. RESULTS AND DISCUSSION

The concentration of radiocesium in the soil was 1800-4400 Bq kg^{-1}. The concentration of radiocesium in cut flowers was from 33 to 120 Bq kg^{-1} dry wt, which was 4.0 times differences between the eustoma and gypsophila paniculata. The transfer factor of radiocesium in the seven plant was 0.008-0.066 which was 8.3 times differences between the eustoma and gypsophila paniculata. The transfer factor in cut flowers was a relatively similar order to the reported values in leafy vegetables.[1][2]

[1]http://www.maff.go.jp/j/press/syouan/nouan/pdf/110527-01.pdf (in Japanese)
[2]http://www-pub.iaea.org/MTCD/publications/PDF/trs472_web.pdf

Table 1 Concentration and transfer factor of radiocesium in cut flowers

Cut flower	Sampling day	Radiocesium concentration				Transfer factor
		soils	Plants			
		$^{134+137}$Cs	^{134}Cs	^{137}Cs	$^{134+137}$Cs	
		(Bq kg^{-1} dry wt)	(Bq kg^{-1} dry wt)			
Gypsophila paniculata	2011/8/18	1800 ± 260	60 ± 32	64 ± 34	120 ± 66	0.066 ± 0.028
Sunflower	2011/7/25	3500 ± 1100	39 ± 21	44 ± 30	84 ± 50	0.024 ± 0.013
Chrysanthemum	2011/8/17	2900 ± 310	20 ± 4.8	24 ± 5.9	44 ± 11	0.016 ± 0.005
Gentian	2011/10/5	3100 ± 170	19 ± 4.6	23 ± 3.9	42 ± 8.0	0.014 ± 0.003
Lily	2011/9/5	3000 ± 350	32 ± 3.3	33 ± 7.2	65 ± 11	0.022 ± 0.003
Dahlia	2011/8/5	4400 ± 880	42 ± 3.3	48 ± 6.4	90 ± 8.9	0.021 ± 0.006
Eustoma	2011/8/16	4400 ± 450	13 ± 4.0	19 ± 3.7	33 ± 7.7	0.008 ± 0.002

Decay correction was done from sampling day. Average ± SD (n = 3).

23-FKP-18

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CLEVASOL, a novel radiation hard cation exchanger suitable for treatment of liquid radioactive waste with high salinity

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Keywords – cation exchanger, ion selective, radiation resistant, radioactive waste treatment, water purification

I. INTRODUCTION

CLEVASOL is a novel strongly acidic inorganic cation exchanger designed for the purification of aqueous solutions from metal cations, and especially from caesium. This macroporous cation exchange resin has an ultra-high capacity, as well as a very high chemical stability and radiation hardness. The resin is absolutely not soluble in aqueous solutions at pH = 0÷14, and in common organic solvents. In general, the selectivity increases in the order $M^+ < M^{2+} < M^{3+} < M^{4+}$, but CLEVASOL has extremely high selectivity for heavy monovalent cations (caesium(I), silver(I), thallium(I) etc.) and for transition metal cations (e.g., Ni^{2+}, Co^{2+}, Mn^{2+}). High K_D values for cations of *d*-transition metals increase significantly by adding chelating ligands to solution. CLEVASOL has excellent kinetics resulting in high loading capacity and minimal ionic leakage. This product is ideal for use in radioactive waste treatment, water purification and nuclear medicine.

II. STRUCTURE OF CLEVASOL

CLEVASOL has an ionic structure – cations as counter ions are distributed inside of a resin grain. Solid crystal grains of a salt containing the dodecahydro-closo-dodecaborate anion $[B_{12}H_{12}]^{2-}$ are polymerized by cross linking monomeric anions $[B_{12}H_{12}]^{2-}$ to a polymeric anion $[B_{12}H_{(12-x)}L_x]_n^{2n-}$. Each polymeric anion is as big as a single crystal grain. The monomer unit is a regular boron icosahedron with a highly delocalized electron density. The icosahedron itself is a resonance hybrid involving both two-centre two-electron B-B and three-centre two-electron B-B-B bonds. Each boron atom contributes with two valence electrons to the B_{12} cage. The position and distances between monomers are given by the crystal structure of the initial salt.

III. PROPERTIES OF CLEVASOL

CLEVASOL is used usually as a solid cation exchanger loaded with H_3O^+ ions. The determined total ion-exchange capacity of the resin is 5.4±0.2 meq/g. We found that CLEVASOL has a high stability against ionizing radiation. Irradiating the resin with gamma-rays from ^{60}Co, an integral dose of ~$6\cdot10^6$ Gray did not cause any changes in the ion-exchange capacity. CLEVASOL is chemically stable and not soluble in concentrated acids, bases, and in common organic solvents. A change of CLEVASOL colour from dark grey to yellow occurs by loading the resin in H^+-form with metal cations (Fig. 1).

The distribution coefficients (K_D) for the following cations in nitric and/or hydrochloric acid media were determined in batch and column experiments: Na^+, Cs^+, Ag^+, Tl^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ra^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, UO_2^{2+}, Y^{3+}, Ac^{3+}, Eu^{3+}, Yb^{3+}, Lu^{3+}, Th^{4+} (see Fig. 2). The K_D values usually decrease with increasing the acid or salt concentration. For many cations K_D values obtained with CLEVASOL are significantly higher then values of the common used cation exchanger AG 50W-X8. By adding chelating ligands to solutions containing cations of transition metals, K_D value remains very high (~10^4) even at very high acid concentrations.

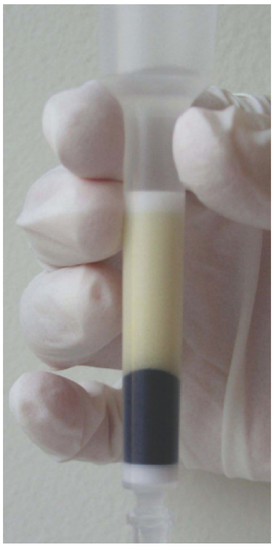

Fig. 1. Colour change from dark grey (H^+-form) to yellow (Na^+-form).

CLEVASOL can find application also in nuclear medicine, where ion exchangers are used to separate or purify medical radionuclides. It is especially suited for the separation of heavy monovalent cations (Cs, Tl, Ag) from various cation mixtures. CLEVASOL can be also employed for group separations of mono-, di-, and trivalent cations. Column experiments showed that the chromatographic separation of divalent and trivalent cations is feasible on CLEVASOL, even when one element is present in macro amounts.

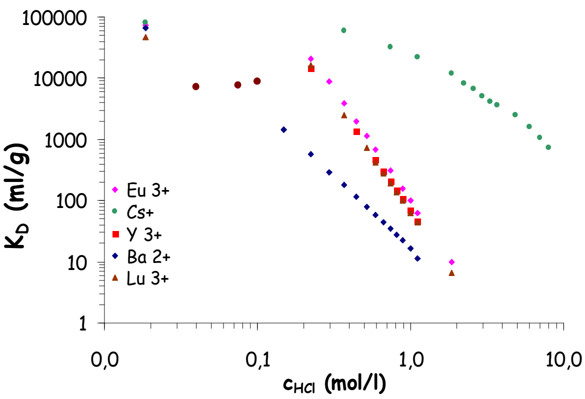

Fig. 2. Distribution coefficients of bi-, trivalent cations and Cs^+ in acid solutions.

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Estimation of I-131/I-129 ratios and vertical distribution of radioiodine in soil collected from Fukushima Prefecture

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I-131 was released by the accident of Fukushima Daiichi Nuclear Power Plant. However, due to its short half-life and there are not enough data for this nuclide to understand its dispersal. In this study we determined I-129 (half-life: 1.57×10^7 years) in soil samples by AMS for estimating I-131/I-129 ratios. We also studied vertical distribution of radioiodine in soil and compared it with the profile of radiocesium in soil.

Keywords – I-131, I-129, I-131/I-129 raitos, vertical distribution of radioiodine

I. INTRODUCTION

A severe nuclear accident occurred at Fukushima Daiichi nuclear power plant in March 2011, resulting in the release of enormous amounts of I-131 and Cs-137. Subsequently, soils in Fukushima Prefecture were contaminated. Because radioiodine accumulates in thyroid glands in human body, it is important to obtain data of I-131 in the environment at the time of the accident. However, I-131 was below the detection limit after a few months because its short half-life of 8.02 days. On the other hand, I-129 released simultaneously with I-131 still remained in soil in Fukushima Prefecture, due to its long half-life of 1.57 × 10^7 years. Therefore, we determined I-129 in Fukushima soil samples in which I-131 concentrations were known, and calculated I-131/I-129 ratios for radioiodine derived from the Fukushima accident.

II. EXPERIMENTALS

The soil sample collected in Fukushima Prefecture after the accident was measured for I-131 and Cs-137 by Ge-detector. Soil samples were dried and pulverized with ball mill. The powdered sample was placed in in a quartz tube and heated at 1000℃ to collect the evaporated iodine in alkaline trap solution (TMAH). Stable iodine (I-127) concentrations in the trap solution were measured by ICP-MS. Solvent extraction was performed using remaining solution, and iodine was separated and purified. Silver nitrate was added to precipitate AgI as a target for AMS and the I-129/I-127 ratios were measured for about 150 samples. For the estimation of I-129 concentrations the I-129/I-127 ratios and I-127 concentrations were used.

III. RESULTS AND DISCUSSION

The observed concentration of I-129 in soil samples showed a wide range, (4.1×10^{-5} to 6.3×10^{-2} Bq/kg). It is interested to note that a good correlation was found between the concentrations of I-131 and I-129. This finding suggests the possibility to estimate previous I-131 levels in soil samples through the analysis of I-129. We obtained an average I-131/I-129 ratio as (2.1 ± 0.7) × 10^7. However, due to the variations in the data, it is possible that the ratios are different according to the area.

We examined the depth distribution of I-129 and Cs-137 for investigating their behavior in soil. Most of the nuclides were found to be retained in surface soil. If we compare the distribution pattern for these two nuclides, we found that I-129 moved deeper than Cs-137. We also examined different soils such as wheat field, rice field and forest soils. It was found that I-129 did not migrate deeper in rice field (uncultivated) because of its dense nature, while in wheat field (uncultivated) I-129 penetrated deeper due to its high porosity. In case of forest soils, about 90% retained in the layer of leaf litters.

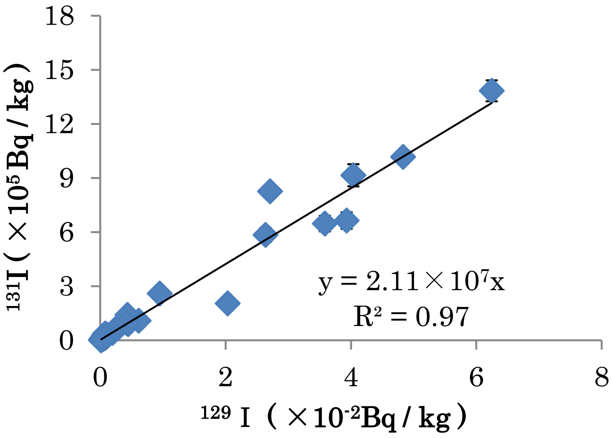

Fig.1 Relationship between the concentration of I-129 and that of I-131

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Effects of soil types on the transfer of radiocesium to plant

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Following the accident of Fukushima Daiichi Nuclear Power Plant, radiocesium was detected in agricultural crops cultivated in Fukushima Prefecture. Although the activity levels in crops significantly decreased in second year, some crops still exceeded the guideline (100 Bq/kg). In this study we cultivate agricultural crops using different types of soils contaminated by the accident and discuss the mechanisms of transfer.

Keywords – radiocesium, soil-plant transfer, agricultural crops

I. INTRODUCTION

Agricultural fields in Fukushima Prefecture were contaminated with radiocesium released from the accident of Fukushima Daiichi Nuclear Power Plant. From a perspective of agricultural safety, Cs-137 (half-life 30.1 y) and Cs-134 (half-life 2.06 y) are very important. Following the accident, radiocesium was detected in many agricultural crops. More than 2 years after the accident, however, some crops still show high concentrations. The mechanisms responsible for the transfer of radiocesium from soil to plants are poorly understood. Therefore, we investigated radiocesium and stable element concentrations in agricultural crops grown in different types of soils. For the purpose of our investigation, soils were collected from the contaminated fields in Fukushima Prefecture. We discuss mechanisms of radiocesium transfer with special reference to the soil characteristics in this study.

II. EXPERIMENTALS

Cultivation experiments using soil that was contaminated with radiocesium were carried out in Fukushima Agricultural Technology Centre and the radiocesium concentrations of both soil and plant samples were determined by a Ge-detector at Gakushuin University. Four different types of soil collected in Fukushima Prefecture were used in our experiments. The plant samples used in these experiments are: komatsuna (a leafy vegetable) and rice plants. The plants were cultivated in Wagner pots (3 L) in a greenhouse at Fukushima Agricultural Technology Centre. Some soils were mixed with contaminated fallen leaves or humus in order to examine whether there is a relationship between the transfer of radiocesium and the organic content of the soils. The soil and plant samples were decomposed with acid to determine concentrations of stable elements by ICP-MS. In addition, we operated extraction experiments with ammonium acetate to verify whether there is any correlation between the extractible radiocesium and the transfer factor to plants.

III. RESULTS AND DISCUSSION

Radiocesium concentrations in both the paddy rice and the komatsuna harvested in this study were found to be influenced by the soil types. The highest values for transfer coefficient were observed in agricultural crops grown in brown forest soils, while the plants cultivated in gray lowland soil showed the lowest values.

In order to compare soils with different radiocesium levels, we collected them from the top layer with high radiocesium concentrations (upper 5 cm) and from the underlying soil with lower concentrations (5–15 cm). We cultivated komatsuna and found that the transfer coefficients of plants grown in the underlying soils are greater than the transfer coefficients of komatsuna planted in the surface soils. This might be related to the speciation of radiocesium in the soils. Deeper layers may have more labile, plant-available radiocesium, while less labile particulate-bound radiocesium from the accident may be more common in the surface soils.

Additionally, we also noted that the transfer coefficients of komatsuna cultivated with the underlying soils mixed with contaminated fallen leaves or humus are higher than the transfer coefficients of komatsuna grown with underlying soils alone. Therefore, we speculate that the radiocesium that exists in organic materials is more mobile, and is subsequently more readily taken up by plants.

As a result of the analysis of stable cesium, we found that komatsuna absorbed more radiocesium than stable cesium. It would seem that stable cesium exists in a less labile form and is adsorbed tightly within the soils, particularly clay minerals.

The extraction experiments show that there is no clear relationship between transfer coefficients and the proportion of radiocesium that is extractable along with potassium using ammonium acetate. Further research should be done another methodologies for extracting plant-available radiocesium from soil.

23-FKP-21

Temporal distribution of plutonium isotopes in marine sediments off Fukushima and Ibaraki after the Fukushima Dai-ichi Nuclear Power Plant accident

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Large amounts of radionuclides were released into the atmosphere as well as discharged into the sea as a consequence of the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident caused by the earthquake and subsequent tsunami on March 11, 2011. The radionuclide contamination in the marine environment due to the FDNPP accident is of great public and scientific concern. Radiocesium (^{137}Cs and ^{134}Cs) were detected in the sediment traps in the deep sea in Pacific Ocean one month after the FDNPP accident, indicating the quick incorporating of radiocesium in seawater with the sediments.[1] In the coastal area of Fukushima and Ibaraki, spatial and temporal distributions of radiocesium in the marine sediments from June 2011 to February 2012 were determined.[2,3] Nevertheless, information about the temporal distribution of Pu in the sediments off Fukushima and Ibaraki after the FDNPP accident is limited.

Plutonium isotopes derived from the FDNPP accident have been detected in the soil and liter samples in the 20-30 km zone around the FDNPP, revealing the release of Pu from the accident.[4] In our previous works, we determined the distribution of Pu isotopes in the marine sediments off Fukushima and Ibaraki collected from April 2011 to July 2012, and observed no detectable Pu contamination from the FDNPP accident.[5,6] However, as no information about the Pu isotopes in the discharged liquids from the FDNPP accident is available to date and the release of radionuclides from the FDNPP site continued one year after the accident, Pu contamination in the marine sediments off Fukushima needs continuous investigation.[7]

In this work, we determined vertical distribution of Pu activities and Pu atom ratios (^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu) in a sediment core collected from the coastal areas off Fukushima in January 2013. For the analysis of Pu isotopes, ca. 2.0 g dried sediment sample was weighted out and spiked with 1 pg ^{242}Pu as yield monitor. The extraction of Pu was performed in a Teflon tube with 20 mL concentrated HNO_3 on a hot plate at 180-200ºC for at least 4 h. A two-stage anion-exchange chromatographic method was employed for the separation of Pu and for the further purification of Pu prior to the ICP-MS analysis. Combined with our previous results, the temporal distribution of Pu isotopes in marine sediments off Fukushima and Ibaraki will be discussed to understand the source and transport of Pu in the sediments after the FDNPP accident.

Acknowledgments This work was supported by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade and Industry (METI), Japan, and partly supported by the Ministry of Education, Culture, Sports, Sciences and Technology (MEXT) (24110004), Japan.

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Evaluation of Iodine-129 mobility and deposition amount in the soil contaminated by the Fukushima Daiichi nuclear power plant accident

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Abstract – Iodine-129 depth profiles of 13 soil cores were analyzed to evaluate the ^{129}I distribution and mobility in soil. The cores were sampled from various fields around the Fukushima Daiichi Nuclear Power Plant (FDNPP). Four cores out of the 13 were collected from almost the same position in Kawauchi village crop field 20 km apart from FDNPP at different times between May 2011 and June 2012 to observe the temporal variation of depth profile of ^{129}I in soil. Clear enhancement of the accidental origin ^{129}I was observed but no positive evidence of ^{129}I migration was found. Other 9 cores were collected from various fields including crop fields and man-made soils within 30 km from FDNPP on June 2012. These cores showed large variation of depth profile of FDNPP origin ^{129}I. The fraction of top 5 cm to the total inventory was varied from 56% to 100%.

Keywords – FDNPP accident, Iodine-129 concentration depth profile, crop field

I. INTRODUCTION

FDNPP accident (on 11 March, 2011) released a large amount of radionuclide into atmosphere such as ^{129}I ($T_{1/2}$= 1.57x10^{7} y), ^{131}I ($T_{1/2}$= 8.01d). Subsequently it caused extensive radioactive contamination. Among them, ^{131}I is absolutely essential radionuclide for the estimation of primary dose. However the data on deposition amount and distribution pattern of ^{131}I most contaminated area, is totally lacking because of its short half-life. Through the ^{129}I data, the ^{131}I levels at the time of accident can be estimated [2]. The accidental origin ^{129}I has also a great potential as a geographic and oceanographic tracer [3]. Predominant source of ^{129}I in global environment, including Japan, before FDNPP accident have been two large nuclear reprocessing facilities at Sellafield and La Hauge. They have released ^{129}I totally over 1.03 TBq (7.35x10^{26} atoms) [4] to atmosphere. To evaluate the distribution and the mobility of ^{129}I, it is essential to identify ^{129}I of FDNPP origin from that of previously existed. From this point, crop field is ideal because soil should have been tilled and well mixed by farmers to the depth of around 30cm until just before the FDNPP accident. Therefore it is speculated that the crop field soil had been made homogeneous, so that the direct accumulation from the accident should be clearly observed. This was confirmed by the observations that depth profiles of ^{127}I concentration, as well as carbon content, of these soil cores were roughly constant.

II. EXPERIMANTAL PROCEDURE

Collected column soil was cut into 1.5 or 3 cm layers. The soil sample were first dried by oven (80℃, 48h). Then homogenized well. An amount of about 0.2 or 0.5 g was mixed with V_2O_5 in a ceramic boat and placed in a quartz tube. The sample is then heated at 990℃ under a flow of oxygen gas and water vapor. The evaporated iodine is collected with a trap solution (2% TMAH solution). (Here, an aliquot was separated for ICP-MS for the determination of the stable iodine concentration.) Iodine in the aliquot of trap solution (2-9 mL) with 2-4 mg iodine carrier is purified by a sequential solvent extraction and back extraction and a finally extracted as AgI precipitation. Extracted AgI was dried well and pressed into a cathode of AMS system. ^{129}I was measured at MALT-AMS system, The University of Tokyo.

III. RESULTS AND DISCUSSION

The ^{129}I depth profiles of four cores from Kawauchi village commonly showed particularly high concentration at the top most layer, steep exponential decrease as a depth and constant blow 10 cm depth (Fig. 1). This enhancement in the top 10 cm layer can be considered as the direct accumulation from the FDNPP after the accident. However no positive evidence of ^{129}I migration was found because there was only a small difference among these profiles which can easily explained by the spatial variation of ^{129}I deposition amount suggested by other observation [1]. In any of the four cores, more than 89% of FDNPP origin ^{129}I was existed within top 5 cm and 98% within top 10 cm. Other 9 cores showed larger variation of depth profile of FDNPP origin ^{129}I. Especially the fraction of total inventory existed within top 5 cm were varied from 56% to 100%. This large profile variation for crop field and Man-made soil should be controlled by the soil properties such as porosity. Sampling site and/or should be carefully chosen not to underestimate the total deposition amount of ^{129}I originated from FDNPP.

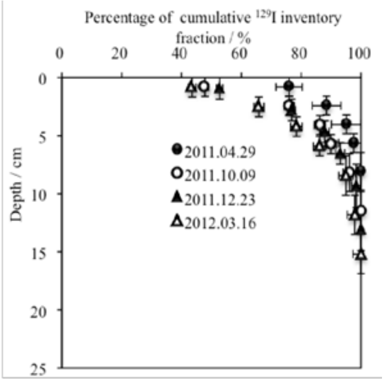

Fig. 1 Proportion of F1NPP generated ^{129}I per depth in Kawauchi village crop field

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Vertical distribution of the Fukushima-derived radiocesium in the western North Pacific in January and February 2011

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Abstract – The radiocesium in seawaters from surface to 800-m depth at stations more than hundreds km away from the Fukushima Dai-ichi nuclear power plants in the western North Pacific Ocean were measured in January and February 2012. Activity of the Fukushima-derived Cs-134 in the surface mixed layer (0 ~ 200-m depth approx.) was highest (~ 20 Bq m^{-3}) in the transition area between the subarctic (north of 40°N approx.) and subtropical regions (south of 35°N approx.), which was due to the direct discharge of radiocesium from the plants. In the subtropical region, we observed Cs-134 maxima just below the mixing layer (200 ~ 300-m depth approx.). The Cs-134 activities in the maxima corresponded to those in the surface mixed layers in the transition area, which implies that the Cs-134-rich waters in the transition area have been transported southwardly to the subtropical region across the Kuroshio Extension Current along isopycnal layers.

Keywords – Fukushima Dai-ichi nuclear power plants, radiocesium, North Pacific Ocean

I. INTRODUCTION

The massive Tohoku earthquake and consequent giant tsunami of March 11, 2011 resulted in global releases of radiocesium (Cs-134 and Cs-137) from the Fukushima Dai-ichi nuclear power plants (FDNPPs). In the North Pacific Ocean, a large portion of Fukushima-derived radiocesium has been settled in both through atmospheric deposition and direct discharge of contaminated waters. The total amount of the radiocesium derived from the direct discharge was estimated to be about 4 PBq for Cs-137 (Kawamura et al, 2011 [1]; Tsumune et al., 2012 [2]; Estournel et al., 2012[3]). On the other hand, evaluation of the radiocesium derived from the atmospheric deposition contains large uncertainty mostly due to the restriction of available data in the vast North Pacific Ocean. In particular, vertical distribution of the Fukushima-derived radiocesium in the open ocean is hardly known. We measured the radiocesium in seawaters from surface to 800-m depth at stations more than hundreds km away from FDNPPs in the western North Pacific Ocean in January and February 2012.

II. METHODS

We conducted water sampling during a cruise of R/V Mirai, Japan Agency of Marine-Earth Science and Technology (MR11-08) along the 149°E meridional line approximately. The seawater samples were collected into 20-L cubitainers using a bucket and a conductivity-temperature-depth rosette with Niskin water samplers. The sample were filtrated and acidified by nitric acid on board. Radiocesium in the seawater was concentrated onto ammonium molybdophosphate (AMP). The radiocesium in the AMP/Cs compound was measured using a gamma-spectrometry with well-type Ge detector. Detection limit of the radiocesium measurement was 0.2 ~ 0.3 Bq m^{-3}. Uncertainties for the measurement was about 8 %. The radiocesium decay were corrected to the sampling date.

III. RESULTS AND DISCUSSION

Before the FDNPPs accident, Cs-134 derived from the nuclear weapon tests and the Chernobyl accident was not detected in the environment because of its short half-life (about 2 years). Therefore Cs-134 observed in the North Pacific was derived from FDNPPs after the accident. Cs-134 was found in surface waters at all the stations from 20°N to 42°N about ten months after the disaster. Activity of Cs-134 in the surface mixed layer (0 ~ 200-m depth approx.) was highest (~ 20 Bq m^{-3}) in the transition area between the subarctic (north of 40°N approx.) and subtropical regions (south of 35°N approx.). Those in the subarctic and subtropical regions were less than 5 and 1 Bq m^{-3}, respectively. This meridional distribution was due to the direct discharge of radiocesium into the transition area from FDNPPs located at 37.4°N/ 141.0°E.

Below the surface mixed layer Cs-134 activity decreased sharply and was not detected in deeper layers than 400-m depth at stations in the subarctic region and transition area, which is explained by vertical one-dimensional penetration of radiocesium from the surface mixed layer to the deeper layers. However, at stations in the subtropical region, south of the Kuroshio Extension Current, we observed Cs-134 maxima just below the mixing layer (200 ~ 300-m depth approx.). The Cs-134 activities in the maxima corresponded to those in the surface mixed layers in the transition area, which implies that the Cs-134-rich waters in the transition area have been transported southwardly to the subtropical region across the Kuroshio Extension Current along isopycnal layers.

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Effect of Application Timing of Potassium Fertilizer on Root Uptake of ^{137}Cs in Brown Rice

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Abstract – We have already reported that potassium fertilizer is effective to reduce radiocesium in brown rice. In this study, we tried to find the most appropriate timing for potassium fertilizer application during the rice cultivation period in terms of ^{137}Cs concentrations in brown rice. The concentration of ^{137}Cs in brown rice cultivated without application of potassium fertilizer was 32 Bq kg^{-1}, while that with application of basal fertilizer including potassium was 5 Bq kg^{-1}. The concentration of ^{137}Cs in brown rice was increased with the late application timing. Therefore, application of potassium fertilizer in the early growing period reduced the uptake of ^{137}Cs by rice plant from contaminated soils effectively.

Keywords –^{137}Cs, Brown rice, Potassium fertilizer, Soil-to- brown rice transfer factor

I. INTRODUCTION

After the accident of Fukushima Daiichi Nuclear Power Plant, in 2011, the concentration of radiocesium in brown rice collected in some areas of Fukushima prefecture exceeded the provisional regulation value for brown rice (500Bq kg $^{-1}$). It is reported that the concentration of radiocesium in brown rice decreases with increasing exchangeable potassium concentrations in soil (Saito et al, 2012). In terms of more positive application method of potassium fertilizer for reducing radioactive concentration in rice, concentrations of ^{137}Cs in brown rice according to application timing of potassium fertilizer were investigated in the present study.

II. MATERIALS AND METHODS

A field test was carried out in the northern part of Fukushima Prefecture. Plowing, puddling and transplanting were performed on April 20, May 4 and May 10, 2012, respectively. The planting density was 17.1 hill m^{-2} (30× 19.5 cm). The nitrogen and phosphorus fertilizer (g m^{-2}) were applied to each plot of paddy field in the proportion 6.0:10 (N-P_2O_5) on April 17, 2012. The potassium fertilizer was applied to each plot of the field at a rate of 8.0 g m^{-2} before plowing, 50, 70 and 80 day after transplanting, respectively.

Rice straw had been applied to the test field every year. The soil in the rice paddy field was classified as Gray lowland soil. Soil samples (at the depth of 0-15cm) were collected from each plot of experimental rice paddy field after the cultivation of the rice plant on September 19, 2012. In order to determine the soil-to brown rice transfer factor, we collected soil from the vicinity of the rice plant. After the soil samples were air-dried for 21 days, the soil in each sample was properly mixed and sieved through a 2 mm sieve. Rice seeds were collected from the soil where the soil was sampled. After threshing rice samples were passed through a 1.80-mm sieve and grains remained on the sieve were used for the analysis. The dried soil was compressed into cylindrical polystyrene containers. The brown rice samples were compressed into 0.7 L Marinelli beakers. The concentration of ^{137}Cs in the soil and brown rice were measured using a Ge gamma- ray detector connected to a multichannnel analyzer system by counting for 3600-7200 s.

III. RESULTS AND DISCUSSIONS

The concentration range of ^{137}Cs in the soils of the experimental plot was 3262-3983 Bq kg^{-1}. The ^{137}Cs concentration in brown rice cultivated without potassium fertilizer was 32 Bq kg^{-1}, while that decreased to 5 Bq kg^{-1} with application of basal potassium fertilizer. On the other hand, the ^{137}Cs concentrations of brown rice to which potassium fertilizer was applied at 50, 70 and 80 d after transplanting were 15, 23 and 36 Bq kg^{-1}, respectively. As a result, the concentrations of radiocesium in brown rice increased with late application timing. These results show that application of potassium fertilizer in the early growing period decreases the uptake of ^{137}Cs by rice plants from contaminated soils effectively.

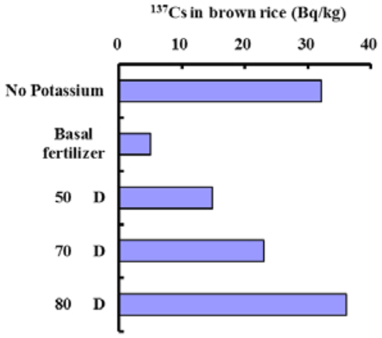

Fig.1 Concentrations of ^{137}Cs in brown rice by difference of application timing using potassium fertilizer

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Low levels of ^{134}Cs and ^{137}Cs in bottom sediments along the Japanese Archipelago side of the Sea of Japan after the Fukushima Dai-ichi NPP accident

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Abstract

We examined radiocesium concentrations in bottom sediment samples collected along the Japanese Archipelago side of the Sea of Japan before/after the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident. Low levels of ^{134}Cs were detected in an area located near estuaries. This was considered to be due to the riverine discharge rather than direct radioactive depositions to sea surface.

Key words- radiocesium; bottom sediment; riverine discharge; Fukushima Dai-ichi Nuclear Power Plant accident

I. INTRODUCTION

The FDNPP accident on March 11, 2011 resulted in the widespread release of large amounts of ^{134}Cs (half-life: 2.06 y) and ^{137}Cs (30.2 y) to the atmosphere and to land and sea surfaces over a wide region of eastern Japan. We analyzed the ^{134}Cs and ^{137}Cs concentrations in sediment samples collected in the Japanese Archipelago side of the Sea of Japan in May 2011, which indicated the slight contamination of the FDNPP-derived radiocesium in a sediment sample from site *D1* (Fig. 1) [1]. In the present study, we examined radiocesium concentrations of sediments in area *D* and clarify delivery process of radiocesium from the FDNPP.

II. SAMPLES and EXPERIMENTAL

We collected a total of 11 bottom sediment samples (0–3 cm depths) at four sites in Niigata offshore (*D*) area (230–530 m depths) during 2010–2012 (Fig. 1). Sediment samples were freeze-dried and crushed into a powder with an agate mortar after washing with distilled water (5–25 g-dry). γ-Spectrometry was performed on all samples using Ge-detectors designed for low-background counting and located at the Ogoya Underground Laboratory [2].

III. RESULTS and DISCUSSION

In area *D*, ^{134}Cs was detected in bottom sediments collected in 2011 and 2012 (*e.g.*, 7.7 mBq/g-dry at site *D2* in 2011) in contrary to the sediments at other coastal areas along the Japanese Archipelago side which were below the detectable limit [1]. In estuary areas, particle materials play important roles in the transportation of radiocesium. Due to the existence of the thermocline, the contamination of ^{134}Cs in sediment samples in area *D* could not be ascribed to the contribution of the soluble fraction accompanying downward water circulation, but to the transportation of the reactive fraction together with particle materials. Agano River and Shinano River meet around area *D*. Detection of ^{134}Cs in samples collected in May 2011 suggests that introduction of contaminated riverine particles from the estuary may lead to radiocesium contamination in the sediment samples, showing immediate transportation (within 1–2 months) of radioactive particle materials to the bottom of this area. Further clarification of the contamination levels and delivery patterns for ^{134}Cs and ^{137}Cs in this area can be achieved by obtaining additional sediment samples, including riverine sediments. This is an operation that we are currently engaged in.

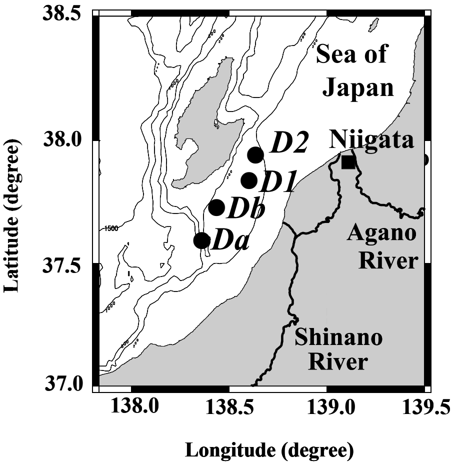

Fig. 1 sampling sites for sediment samples

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The heavy-ion reactions ^{238}U + ^{238}U and ^{238}U + ^{248}Cm and actinide production close to the barrier revisited

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Keywords – Quasi-elastic and damped collisions/Sequential fission/Total kinetic energy loss/Production of surviving heavy actinides/Excitation functions/Survival probabilities

Recent theoretical work [1,2] has renewed interest in radiochemically determined isotope distributions in reactions of ^{238}U projectiles with heavy targets that had previously been published only in parts [3,4]. These data are being revisited. The cross sections σ(*Z*) below the uranium target have been determined as a function of incident energy in thick-target bombardments. These are compared to predictions by a diffusion model [5] whereby consistency with the experimental data is found in the energy intervals 7.65 – 8.30 MeV/u and 6.06 – 7.50 MeV/u. In the energy interval 6.06 – 6.49 MeV/u, the experimental data are lower by a factor of 5 compared to the diffusion model prediction indicating a threshold behaviour for massive charge and mass transfer close to the barrier. For the intermediate energy interval, the missing mass between the primary fragment masses deduced from the generalised Q_{gg} systematics including neutron pair-breaking corrections and the centroid of the experimental isotope distributions as a function of *Z* have been used to determine the average excitation energy as a function of Z. From this, the *Z* dependence of the average total kinetic-energy loss $\overline{TKEL}$ has been determined. This is compared to that measured in a thin-target counter experiment at 7.42 MeV/u [6,7]. For small charge transfers, the values of $\overline{TKEL}$ of this work are typically about 30 MeV lower than in the thin-target experiment with the difference decreasing with increasing charge transfer developing into even slightly larger values in the thick-target experiment for the largest charge transfers. This is the expected behaviour which is also found in a comparison of the partial cross sections for quasi-elastic and deep-inelastic reactions in both experiments. The cross sections for surviving heavy actinides, e.g., $_{98}$Cf, $_{99}$Es, and $_{100}$Fm indicate that these are produced in the low-energy tails of the dissipated energy distributions, however, with a low-energy cutoff on the order of 35 MeV. Excitation functions show that identical isotope distributions are populated independent of the bombarding energy indicating that the same bins of excitation energy are responsible for the production of these fissile isotopes. A comparison of the survival probabilities of the residues of equal charge and neutron transfers in the reactions of ^{238}U projectiles with either ^{238}U or ^{248}Cm targets [4] is consistent with this cutoff as evaporation calculations assign the surviving heavy actinides to the 3n and/or 4n evaporation channels.

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Mechanism of Mo-99 Adsorption and Tc-99m Elution from Zirconium-Based Material in Mo-99/Tc-99m Generator Column Using Neutron-Irradiated Natural Molybdenum

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Keywords – adsorption mechanism/Mo-99/Tc-99m radionuclide generator/neutron-irradiated natural molybdenum

It is expected that the use of fission product Mo-99 for Tc-99m production can be replaced by neutron-irradiated natural molybdenum. The challenge in using neutron-irradiated molybdenum is that the Mo-99 has low specific radioactivity. Zirconium-based material has a great opportunity as an adsorbent in Mo-99/Tc-99m radionuclide generator using neutron-irradiated natural molybdenum since the material can adsorb molybdenum with high capacity. However, until now, there is still no data to explain the mechanism of Mo adsorption and Tc-99m elution process from the material. It is very important to investigate the mechanism for increasing the adsorption capacity, increasing the Tc-99m elution yield as well as reducing the Mo-99 breakthrough in Mo-99/Tc-99m generator using irradiated natural molybdenum. In this study, the Mo-99 adsorption and Tc-99m elution mechanism were investigated using Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDS) to analyze the elemental composition of the material surfaces before Mo adsorption, after Mo adsorption and after Tc-99m elution using saline solution. The results were compared with the value of adsorption capacity of the material to irradiated natural Mo and elution yield of Tc-99m. From the changes of elemental composition in the surface, it was found that molybdate ions were adsorbed into the adsorbent by ion exchange with Cl^- ions in the material. It was also revealed that Tc-99m can be eluted from the material column in high oxidation state ($^{99m}TcO_4^-$) since oxidizing agent was needed in the elution process. It was considered that in lower oxidation state the Tc-99m easily made coordination bonds with other elements in the adsorbent.

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Startup of a new gas-filled recoil separator GARIS-II

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Abstract – We developed a new gas-filled recoil separator GARIS-II, which consists of 5 magnets in a Q-D-Q-Q-D configuration, to study on actinide-based fusion reaction. The solid angle of the separator was determined to be 18.2 msr measured by a standard α-source of ^{241}*Am. Basic characteristics of the separator, such as a background suppression and transmission, was studied by using fusion products via well-known nuclear reactions of* $^{169}\mathrm{Tm}(^{40}\mathrm{Ar},4n)^{205}\mathrm{Fr}$ *and* $^{208}\mathrm{Pb}(^{40}\mathrm{Ar},3n)^{245}\mathrm{Fm}$*, respectively.*

Keywords – gas-filled recoil ion separator, GARIS, new element, superheavy element, SHE chemistry

We designed and constructed a new gas-filled recoil ion separator GARIS-II [1, 2] and installed it in an experimental hall at the RIKEN heavy-ion linear accelerator (RILAC) facility in March 2009. This separator has been developed for studying on actinide-based fusion reactions. The most interesting subjects studied by GARIS-II are a new element search with $Z \geqq 119$, chemical investigations of superheavy element, studies on nuclear reaction and nuclear structure of SHE nuclides, and understanding the operating principles of gas-filled typed recoil separators such as the equilibrium charge state with various filling gases.

This device consists of five magnets in a Q_v-D-Q_h-Q_v-D configuration as shown in **Fig. 1**, where Q and D denote quadrupole and dipole magnets, respectively. The Q1 magnet acts as a strong vertical focusing. This enables better matching to D1 acceptance. The D1 magnet has a large deflecting angle of 30 degree. This enables separation of evaporation residue ER from primary beam immediately. The Q2 and Q3 magnets have a large bore radius of 300 mm. These magnets act as a horizontal and vertical focusing to the focal point. The D2 magnet has a deflecting angle of 7 degree. This enables separation of ER from transfer products and light charged particles. The total path length is 5.06 m from the target position to the focal point. The solid angle of the separator was determined to be 18.2 msr measured by a standard α-source of ^{241}Am. This value well agrees with 18.5 msr estimated from ion optical characteristics.

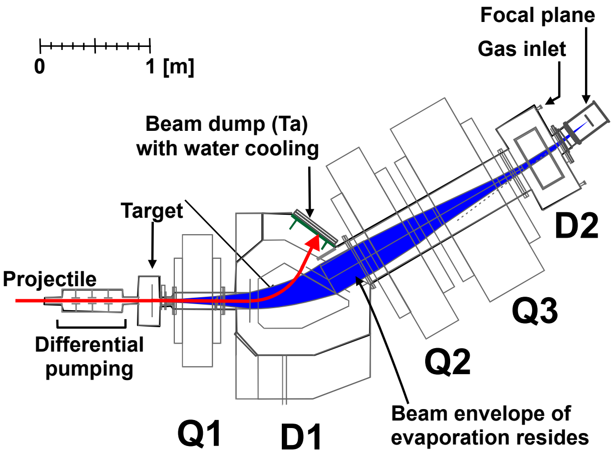

Fig. 1. Schematic of a new gas-filled recoil ion separator GARIS-II [2].

A gas-cooled rotating target system with differential pumping system was installed at an upstream of GARIS-II. Projectiles from accelerator is stopped at water-cooled Ta-beam dump. Filled gas is inlet from downstream of the separator. A pressure/ flow controller regulates continuous filling gas flow into the target chamber. The reaction products were separated in flight from projectiles and other by-products by GARIS-II, and guided into a focal plane detection system. The GARIS can be transported the ER with a magnetic rigidity $B\rho < 2.43$ T・m to focal plane. For the identification of ER and their successive radioactive decays, a system of a time-of-flight (TOF) detector, a double side silicon detector (DSSD) array, and a VETO silicon detector array were installed at the focal plane of GARIS-II.

In this symposium, we will talk about status of GARIS-II R&D and some operating tests by using 0 degree target recoils and reaction products, which were used as low energy ion-source, via the fusion reactions of $^{169}\mathrm{Tm}(^{40}\mathrm{Ar},4n)^{205}\mathrm{Fr}$ and $^{208}\mathrm{Pb}(^{40}\mathrm{Ar}, 3n)^{245}\mathrm{Fm}$.

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APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
Kanazawa, Japan, 22-27 September 2013

Purification of Scintillation Cocktails containing the alpha emitters americium and plutonium

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ABSTRACT

One efficient way of measuring alpha emitters is by the usage of liquid scintillation counting (LSC). A liquid sample is placed in a vial containing a scintillation cocktail. The alpha particles excite electrons in the surrounding liquid, and when they are de-excited photons are emitted. The photons are detected and the activity can be quantified. LSC has a high efficiency for alpha radiation and is therefore a fast and easy way for measuring alpha emitting samples. One drawback is that it does not differentiate very well between alpha energies; measurements of for example curium and plutonium simultaneously are impossible and demand other techniques. Another drawback is the production of a liquid alpha active waste.

In Sweden alpha radioactive waste liquids with an activity over some kBq per waste container cannot be sent for final storage. If, however, the activity of the liquids could be reduced by precipitation of the actinides, it would be possible to send away the liquid samples to municipal incineration. In this work a method for a purification of alpha active scintillation cocktails was developed. The method was first tried on a lab scale, and then scaled up. Until today (March, 2013) more than 20 liters of scintillation liquids have successfully been purified from americium and plutonium at Chalmers University of Technology in Sweden.

The four scintillation cocktails used were Emulsifier Safe®, Hionic-Fluor®, Ultima Gold AB® and Ultima Gold XR®. The scintillation cocktails could all be purified from americium with higher yield than 95 %. The yield was kept when the liquids were mixed. Also plutonium could be precipitated with a yield over 95 % in all cocktails except in Hionic-Fluor® (>55 %). However, that liquid in particular could be purified (>95 %) by mixing it with the three other cocktails. Up-scaling was performed to a batch size of 6-8 L of scintillation cocktail. In neither the americium nor the plutonium system, adverse effects of increasing the volume were detected. The products of the process are a solid fraction that can be sent to final storage and a practically non-radioactive liquid fraction that can be sent to municipal incineration.

Liquid scintillation counting, Alpha emitting waste, Co-precipitation

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Formation and stability of sulfides of the superheavy elements Cn and Fl

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First chemistry experiments with Cn and Fl revealed a relativistic stabilization of their elemental state leading to a much weaker metallic interaction with gold compared to their lighter homologues in the groups 12 and 14 of the periodic table [1,2]. Extrapolative predictions, in which thermochemical state functions were correlated mutually, showed that Cn and Fl may form stable sulfides. However, the stability trends in group 12 and 14 are predicted to be opposite. Hence, FlS is expected to be more stable compared to CnS. An experimentally exceptionally favourable case for comparative studies of Cn and Fl is the possibility of a simultaneous production of both elements in Ca-48 induced nuclear fusion reactions with Pu-242/Pu-244 [3]. The affinity of mercury towards sulfur is well known, and the formation of HgS is thermodynamically favored [4]. Hence, this chemical system is an ideal model system to investigate the kinetics and thermodynamics of the adsorption and reaction of a volatile noble metal with sulfur surfaces. For this purpose the method of isothermal reaction chromatography is used. Here, first results from these investigations will be presented. Some conclusions will be drawn, which are important for the preparation of further chemical investigations of Cn and Fl.

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23-NCP-06

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Development of a Batch-Type Solid-Liquid Extraction Apparatus for Repetitive Extraction Experiment of Element 104, Rf

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Abstract – For the extraction of element 104, Rf, an automatic and rapid solid-liquid extraction apparatus by batch method was newly developed. On-line solid-liquid extraction experiments using an accelerator were performed in the TIOA/HCl system with ^{89m,g}*Zr and* ^{175}*Hf produced in the nuclear reactions. As a result, the distribution coefficients in equilibrium were obtained within 10 s in 7–11 M HCl. This indicates the applicability of the present apparatus to Rf experiment.*

Keywords – Solid-liquid extraction, Triisooctylamine (TIOA), Zr, Hf, Superheavy element

Chemical properties of transactinide elements ($Z \geq 104$) are expected to be characteristic due to strong relativistic effects on their electronic shells. Therefore, transactinide chemistry is very fascinating. It is, however, very difficult to perform chemical experiments of these elements because of their short half-lives and low production rates in the nuclear reactions. On-line chemical experiments on a "one-atom-at-a-time" basis are required. In recent years, the fluoride complex formation of Rf was successfully investigated under the condition that chemical equilibrium is attained for its homologues. To systematically study the complex formation of Rf, we are interested in the chloride complexation of Rf.

Purpose of the present study is to clarify the chloride complex formation of Rf based on the extraction data in equilibrium and further to investigate time dependence of the chemical behavior of Rf for the first time. In our previous work [1], solid-liquid extraction of Zr and Hf, the homologues of Rf, using triisooctylamine (TIOA) from HCl was performed by batch method. In this work, we newly developed the automatic apparatus to perform batch-wise solid-liquid extraction of transactinide elements rapidly and repeatedly. On-line experiments using this apparatus were conducted with ^{89m,g}Zr and ^{175}Hf tracers produced at the AVF cyclotron in RIKEN. We investigated the equilibrium time in extraction in several HCl concentrations by determining time dependences of the K_d values.

Schematic view of the solid-liquid extraction apparatus is shown in Fig. 1. Nuclear reaction products transported by the gas-jet system are deposited on the collection site of the dissolution section and then dissolved with an aqueous solution. The solution sample passes through two valves and a slider which moves horizontally to three positions, and then enters a Teflon reactor containing TIOA resin, reactor 1 in Fig. 1. After shaking the reactor using a vortex mixer, only the liquid phase is pneumatically pushed out of the reactor, and is subjected to the radiation measurement. To measure the radioactivity on the resin, the control experiment without the resin is performed using reactor 2. The present apparatus is controlled by a computer through a LabVIEW system.

In the on-line experiment, ^{89g,m}Zr ($T_{1/2}$ = 3.27 d, 4.18 min) and ^{175}Hf ($T_{1/2}$ = 70 d) were produced in the ^{89}Y(p,n)^{89g,m}Zr and ^{175}Lu(p,n)^{175}Hf reactions, respectively. Extraction experiments were performed by the above operations with the 25–57 wt. % TIOA resin (2.6–3.8 mg) and 6–11 M HCl (160–230 μL). Shaken time was varied to be from 10 s to 120 s. Remained Zr and Hf on the resin were eluted by washing the resin with ca. 220 μL of the mixture of 5.1 M HNO_3 and 0.01 M HF three times. The TIOA resin was reused 3–6 times. Each solution sample was assayed by γ-ray spectrometry using a Ge detector to obtain the K_d values by the equation K_d (mL/g) = $[M]_{resin}/[M]_{soln}$ (M = Zr or Hf).

It was found that the K_d values are basically constant in the studied time range, and are consistent with those obtained in our previous batch experiment [1] in 7–11 M of HCl. This result suggests that chemical reactions in the extraction reach the equilibrium within 10 s for ^{89m}Zr and ^{175}Hf under the present experimental conditions. It took about 35 s until the end of elution of the HCl solutions. These results suggest the applicability of the present apparatus to Rf experiment.

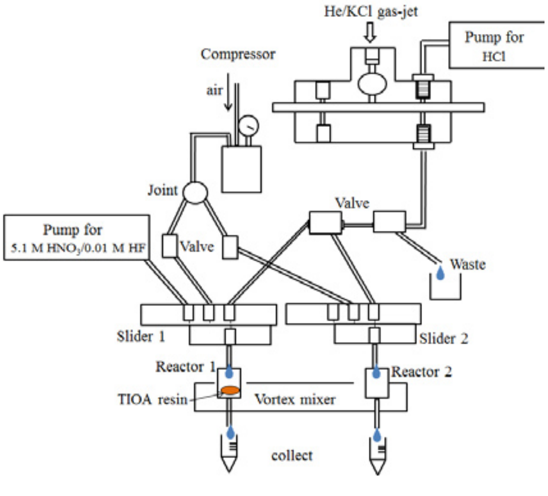

Fig. 1 Schematic view of the solid-liquid extraction apparatus

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Coprecipitation of Zr, Hf, and Th with Sm Hydroxide for Chemical Study of Rf

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Abstract – The purpose of our study is to perform hydroxide coprecipitation experiments of element 104, rutherfordium (Rf), to investigate its complex formation with hydroxide ions. In this work, we investigated the hydroxide coprecipitation behaviors of the group-4 homologues Zr and Hf, and the pseudo homologue Th in aqueous NH_3 and NaOH solutions by coprecipitation method with Samarium (Sm) hydroxide. In addition, we developed the semiautomatic and rapid suction filtration apparatus for repetitive experiment of Rf, and tested its performance by on-line experiments of Zr and Hf using an accelerator.

Keywords – Superheavy elements, Rutherfordium, Coprecipitation

I. INTRODUCTION

Elements with the atomic numbers $Z \geq 104$ are called superheavy elements (SHEs). They have short half-lives and are produced only by nuclear reaction with an accelerator. Therefore, much repetition of rapid experiments targeting one atom is required. This is why it is difficult to perform experiments of SHEs, and their chemical properties are hardly elucidated. So far, chemical properties of SHEs have been studied mainly by chromatographic methods. Experiments of SHEs in more various chemical systems should be performed to study their chemical properties in more detail. We have been developing a new method to investigate chemical properties of SHEs.

The purpose of our study is to perform coprecipitation experiments of element 104, rutherfordium (Rf), to investigate its complex formation with hydroxide ions by the coprecipitation method with samarium (Sm) hydroxide. By this method [1], we can prepare a precipitate sample which has good energy resolution in α spectroscopy in a few min. Therefore, this method is expected to be applicable to SHE chemistry that requires rapid operations. In this work, we investigated the hydroxide coprecipitation behaviors of the group-4 homologues Zr and Hf, and the pseudo homologue Th with Sm in aqueous NH_3 and NaOH solutions with various concentrations. In addition, we developed a semiautomatic and rapid suction filtration apparatus for repetitive experiments of Rf and tested its performance by on-line experiments of Zr and Hf using an accelerator.

II. EXPERIMENTS AND RESULTS

The Sm standard solution (1 M HNO_3) with the volume of 20 μL containing 20 μg of Sm was added into the HCl solution containing ^{88}Zr, ^{175}Hf, and ^{228}Th radiotracers. The solution was stirred and then the basic solution (dilute and concentrated aqueous NH_3, and 0.1–12 M NaOH solutions) was added. The solution was stirred for 10 s or 10 min. The solution containing the precipitate was filtrated by suction with a polypropylene membrane filter. The filtrate was collected in a vial. Both the precipitate and filtrate were dried on the heater at 100°C. The precipitate, filtrate, and beaker used were subjected to α and γ spectrometry. The precipitation yields of Zr, Hf, and Th were determined from each radioactivity. Above experiments were performed changing conditions such as solution volume and filter stick size to determine suitable conditions for Rf experiment. The precipitation behaviors of Zr, Hf, and Th without Sm were investigated using macro amounts of Zr, Hf, and Th samples in the same conditions to coprecipitation experiments with radioactive tracers.

As a result, the coprecipitation yields of Zr and Hf were lower as concentration of the hydroxide ions increases. On the other hand, the precipitation yields of Th were approximately 100% under all conditions. We observed clear differences in precipitation yields among these elements, suggesting that it is possible to investigate the stability of complex formation with hydroxide ions by this method. Because precipitation yields of the samples stirred for 10 s and 10 min were almost the same, it was found that precipitate is rapidly formed within 10 s. We were able to prepare a precipitate sample of Th with good energy resolution in α spectrometry. These results are preferred in Rf experiment. In the presentation, we will also report the development of the semiautomatic apparatus and results of the on-line experiments using an accelerator, and propose suitable conditions for Rf experiment.

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23-NCP-08

Development of modified epoxy paint films to reduce the volatile iodine source term in the containments of LWRs during severe nuclear accidents

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During a severe nuclear accident in a light water reactor (LWR) significant amounts of iodine will be released from damaged UO_2 fuel into the containment. Primarily released cesium iodide aerosols and elemental iodine will partly dissolve in steam or the containment water pools. The remaining gaseous species can undergo complex reactions with released radiolysis- (e.g. ozone) and pyrolysis products such as volatile short chained organics released from e.g. cable plastics to form under the conditions of a severe nuclear accident (high temperatures, high radiation field) a series of different volatile iodine species. While inorganic iodine oxide aerosols (IOx) are rather water soluble and are likely to deposit on metal surfaces, organic iodides such as methyl- and ethyl iodide are less reactive with metal surfaces and more hydrophobic and thus are more likely to remain in gaseous phase. While gaseous elemental iodine can be sufficiently trapped with the currently used charcoal-, spray- and wet-scrubber filter systems, the used filter materials are less selective for organic iodides. Thus, both in case of a venting of the containment and in case of a failure of the containment these highly volatile species are more likely to be released into the environment and cause harm to the public. In case of a Fukushima like containment pressure increase in a nuclear power plant which is not equipped with an external wet-scrubber filter system through which the vented air can be filtered, significant amounts of both volatile inorganic and organic iodine species will be released into the environment.

In modern nuclear power plants bisphenol-A based epoxy paints are commonly used as coatings within the containment. These aromatic rich paints withstand higher radiation doses and thus they are expected to contribute less to the formation of highly volatile organic iodides such as methyl iodide than formerly used (partly) oil based paint films.

Experimental studies at Chalmers University of Technology on Teknopox Aqua VA epoxy paint, which is recently used in Swedish and Finish nuclear power plants, have shown that the paint can chemisorb significant amounts of both inorganic- and organic iodine species. The chemisorbed iodine will be partly washed out in steam or can be revapourised under the increased temperature and gamma irradiation field during a severe nuclear accident.

Attempts are made at Chalmers University of Technology to develop a modified epoxy paint to increase the retention of gaseous iodine species already inside the containment. For this purpose different organic and inorganic, irradiation stable, water insoluble and for different iodine species reactive additives are tested using e.g. a Co-60 gamma irradiator with a dose rate of 14 kGy/h.

New insights into the formation and stability of Molybdenum carbonyl compounds

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The "Ms. Piggy" ^{252}Cf spontaneous fission (SF) source installed at the University of Bern allows for production of different transition metal fission products with a wide variety of half-lives. Volatile metal carbonyl compounds were formed in situ and transported by flushing pure CO or CO mixed with inert gas (N_2, Ar, He) through the recoil chamber of this source at a flow rate of 1 l/min [1]. Thus, these compounds are available outside of the source for radiochemical experiments. Our work focuses on the decomposition or thermal stability of the formed complexes. Therefore, the carbonyl complexes are transported trough a decomposition column held at variable temperatures between 25°C and 800°C. The surviving complexes are trapped in a charcoal filter, which was monitored by a HPGe gamma-ray detector. The fused silica decomposition column (1 m, 4 mm i.d.) covered by selected stationary surface materials was heated up within a steel cladding tube by means of a resistance furnace. By performing a gamma spectrometric measurement of the charcoal trap decomposition curves for carbonyl complexes were obtained. We will discuss here the results obtained for ^{104}Mo. Several different surface materials were examined: quartz, silver, gold, palladium, and PFA-Teflon®. Formation and decomposition of the complexes has been studied also in dependence on the CO concentration and on the inert gas used to dilute the CO. Thus, decomposition curves were obtained for different isotopes and different carrier gas mixtures, which allowed for determination of a pseudo-reaction order on carbon monoxide in the metal carbonyl formation. For the first time formation of nitrogen containing carbonyl complexes with the neutral transition metal atom Mo was observed. It was also shown that the beta decay of the Mo central atom in the carbonyl complex does not lead to the formation of volatile compounds of the daughter nuclide Tc. Obtained results are discussed in the light of upcoming decomposition studies of transactinide carbonyl complexes.

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23-NCP-10

Adsorption behavior of super-heavy elements ($Z \geq 112$) on metal and inert surfaces

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Investigation of chemical and physical properties of the heaviest elements (those beyond Lr) is a hot topic since several decades. In this time period, many new elements were discovered and after a proper characterization were added to the Periodic Table of the elements. The main problem of such investigations, however, is the rather short half-life of these elements, which requires the development of innovative experimental techniques. Nowadays the research focusses on the chemical properties of the element 114. So far, two gas chromatography experiments to study the interaction strength of element 114 with a gold surface have been performed with conflicting results. One experiment [1] reported a weak interaction of element 114 with a gold surface, leading to adsorption only at very low temperatures of approximately -90°C, while in the second experiment [2] adsorption on gold has been observed at the room temperature, indicating a much stronger bond between element 114 and gold. To resolve this conflict, further experiments on chemical properties of the element 114 will be performed at GSI and PSI/JINR in the next two years. For theoretical studies, standard quantum-mechanical packages that treat a system mostly non- or only scalar-relativistically are not satisfactory: Due to rather significant relativistic effects on the electron shells of the heaviest elements a fully-relativistic four-component description is required.

Recently, we have studied the adsorption behavior of elements 112, Cn, and 114 and their lighter homologues Hg and Pb, respectively, on gold surfaces [3] by using a cluster-approach [4]. We found that Hg/Cn and Pb/114 prefer different adsorption sites. Also, the adsorption energies of elements 112 and 114 are related to those of their lighter homologues in a different way. Thus, E_b(Cn) is only slightly (0.1-0.2 eV) lower than E_b(Hg), while E_b(114) is much lower (1.4 eV) than E_b(Pb). This is due to the fact, that in element 112 both the relativistically stabilized 7s and destabilized 6d AOs take part in the binding, while for element 114 binding is mostly determined by the relativistically stabilized $7p_{1/2}$ orbital. In contrast to Pb, where $6p_{3/2}$ strongly contributes to the surface bond, the $7p_{3/2}$ participate much less due to its large relativistic destabilization (the spin-orbit splitting between $7p_{1/2}$ and $7p_{372}$ is about 3.5 eV). Furthermore, binding of element 114 to gold is similar to that of Cn, however, about 0.2 eV stronger. Our predicted sequence in the E_b values is Cn < Hg < E114 << Pb. Thus, we predicted that in the thermochromatography experiments, element 114 will adsorb right at the beginning of the chromatography column with the hot end of 35°C, at the position of Hg. This prediction was recently confirmed experimentally [2].

In this talk we will present theoretical results on adsorption energies and distances of the elements from 112 to 114 and their homologues on metal (gold) and inert (SiO_2) surfaces.

Acknowledgment – J.A. gratefully acknowledges the support by the Deutsche Forschungsgemeinschaft (DFG) and BMBF

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Structural studies of the Eu(III) and U(VI) interactions with pentapeptides

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It is of great importance to assess the mechanisms governing radionuclide impact on the environment (particularly the biosphere) and to unravel the molecular processes underlying actinide transport and deposition in tissues. But most data available on the interaction of actinides with biological systems are based on physiological or biokinetic measurements, with scarce information on the microscopic factors such as structure of the actinide coordination site within biological molecules (proteins, peptides...). These structural data are essential to understand structure, function and affinity interdependence, which governs the organ deposition of such elements. In this paper, we will present first results on the complexation of trivalent and hexavalent metals (in a first step, Eu^{3+} was used as a surrogate to Am^{3+} and UO_2^{2+} represented the VI oxydation state) with peptides containing various, biologically relevant, geometrical constraints. The pentapeptide sequences contain sequential differences that induce conformational change, but relatively close enough so one parameter was varied at a time. We used the three DGDGD, ADPDA and DPDPD peptides, since they are differentiated by the number of proline (P) residues, that induce different angular strains. Both experimental (EXAFS, micro-calorimetry, laser fluorescence, ATR-FTIR) and theoretical (DFT methodology) approaches have been performed in order to determine the structure of the obtained complexes and the consequences on their stability.

23-ACP-02

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Solubility of Amorphous UO_2 and NpO_2 in Nitrate Media Containing Platinum Catalyst

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Significant amount of nitrate salts are contained in a group of TRU wastes which may be disposed under deep underground together with high-level radioactive waste. Nitrate may oxidize redox-sensitive elements, e.g., uranium and neptunium. Although it was found that no effects of nitrate on solubility of amorphous neptunium(IV) dioxide (NpO_2(am)) was observed under anoxic conditions [1], it is still concerned that some catalysts may promote redox reactions between nitrate and elements reduced. Therefore, solubility of NpO_2(am) was investigated under nitrate media containing platinum catalyst. Similar experimental study was applied to amorphous uranium(IV) dioxide (UO_2(am)) to compare results with those for NpO_2(am).

An oversaturation method was applied to prepare the UO_2(am) and NpO_2(am) using stock solutions of uranium(VI) and neptunium(V), respectively, with addition of the reducing agent sodium dithionite ($Na_2S_2O_4$). After removing the solution containing $Na_2S_2O_4$ and washing several times, various concentration of sodium nitrate ($NaNO_3$) solution was added to UO_2(am) and NpO_2(am). A porous platinum black powder was added to some samples as a catalyst. The pH of solution was adjusted around 9, and no adjustment of redox potential was carried out. After contacting from 2 weeks to 5 months, an aliquot of sample solution was picked up, centrifuged (CF), filtered with 0.45 μm membrane, and filtered with molecular weight cut-off of 10^4. All the experimental procedures were performed in an argon-filled glove box to avoid contamination of oxygen gas.

The obtained solubility values of UO_2(am) and NpO_2(am) as a function of $NaNO_3$ concentration are shown in Figs. 1 and 2, respectively. Due to no dependences of nitrate concentrations on solubility of UO_2(am) and NpO_2(am) containing platinum black powder, no redox effects of $NaNO_3$ on their solubility were found. On the other hand, it was found that the obtained solubility values of UO_2(am) and NpO_2(am) containing porous platinum black powder were larger than those without porous platinum black powder. Considering with large difference of solubility by filtration types, aqueous uranium and neptunium species may form colloidal species in lower $NaNO_3$ concentrations and be physically absorbed into porous platinum black powder in higher $NaNO_3$ concentrations.

It was found that the oxidation state of uranium solid was 4 even after the solubility experiment using X-ray diffractometry. According to thermodynamic calculations, the oxidation state of neptunium solid can also be 4.

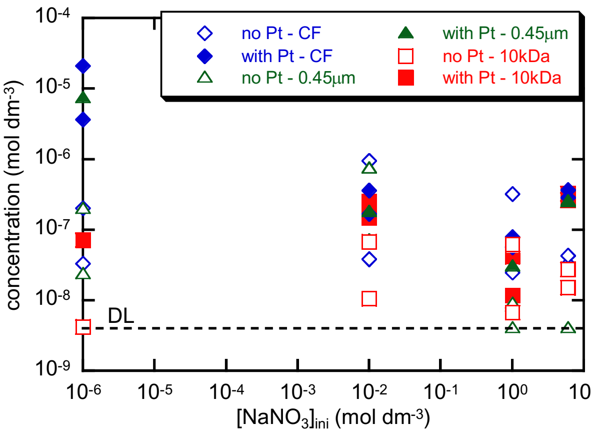

Fig. 1 – Solubility of UO_2(am) as a function of $NaNO_3$ concentration with/without platinum black

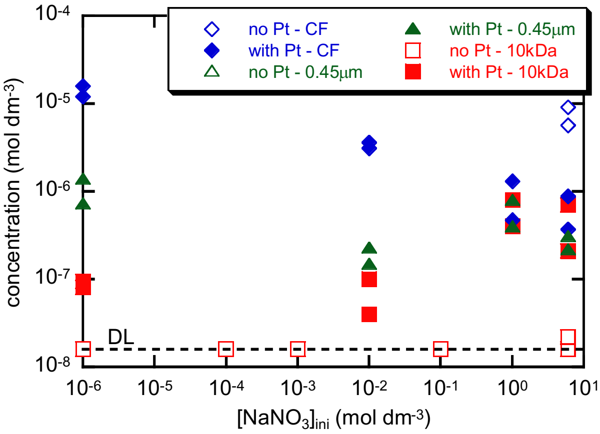

Fig. 2 – Solubility of NpO_2(am) as a function of $NaNO_3$ concentration with/without platinum black

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23-ACP-03

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Apparent formation constants of actinide complexes with humic substances determined by solvent extraction

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Abstract – Apparent formation constants of Pu(IV) with two kinds of humic substances (HSs) were determined in 0.1M NaClO$_4$ at 25 ◦C using a back-solvent extraction method. The effect of solution conditions, such as the pH, the initial metal and HS concentrations, and the ionic strength, on the formation constants was investigated. The obtained data were compared with the other actinide series.

Keywords – Humic substances / Actinides / Apparent formation constant / Solvent extraction

Organic substances may greatly affect the speciation and solubility of tetravalent actinides in groundwater, depending on the complex formation constants, pH, the ionic strength, the organic ligand-to-metal concentration ratio, and so on. In order to estimate how these parameters influence the apparent solubility, reliable thermodynamic data on the interaction of tetravalent actinide ions with counter anions in aqueous solutions are required in the safety assessment of geological disposal. In the present study, we investigate the formation constants of Pu(IV) with typical HSs in groundwater.

The formation constants were determined using the solvent extraction method which was conducted in a similar manner as described in a previous study [1,2]. The organic phase of xylene containing thenoyltrifluoroacetone (HTTA) without further purification and the aqueous phase containing Pu at a pH$_c$ ~3 were placed in a polypropylene tube and shaken by hand for several minutes. The concentration of Pu^{IV}(TTA)$_4$ complexes extracted into the organic phase was ca. $10^{-6\sim-9}$ M, while the hydrophilic polymer/colloidal species and species with other oxidation states such as Pu^{III,V}(TTA)$_x$ could not be co-extracted under the present condition. Soon after, the organic phase was isolated and brought into contact with fresh aqueous phases containing HS of pH$_c$ 4 to 8, and ionic strength I = 0.1 M (NaClO$_4$). In this back-extraction, two kinds of humic acids were used. One is the purified Aldrich humic acid (ALHA). The other is the Elliott soil humic acid (1S102H, the International Humic Substance Society) abbreviated to SHA. Back-extraction was performed using a mechanical shaker at 25 ± 1 °C, and the pH$_c$ and E_h values were measured.

The E_h values were stable at around +0.5–+0.6V (*vs*.SHE) throughout the measurement period at the examined pH values. The predominant species of plutonium was tetravalent state as discussed in ref. [1]. The concentration in both phases was determined by alpha spectrometry (5.16MeV). Though the recovery ratio for Pu was approximately 50% due to strong adsorption of Pu on the polypropylene vessel wall, the ratio was not dependent on the shaking time. Hence, the presence of the adsorbed Pu was ignored in the analysis.

The apparent formation constant is expressed by the binary or ternary complex, depending on the definition of the species.

$$\beta_{\mathrm{app},q} = \frac{[\mathrm{M(OH)}_q\mathrm{L}]}{[\mathrm{M}^{4+}][\mathrm{OH}]^q[\mathrm{R}^-]},$$

where q=0 or 1 is assumed in the present study. From the difference of the distribution ratio between the presence (D) and absence (D_0) of HSs,

$$\log\left(D_0/D\right) = \log\left(\frac{1+\sum\beta_{\mathrm{OH},p}[\mathrm{OH}^-]^p + \beta_{\mathrm{app},q}[\mathrm{OH}^-]^q[\mathrm{R}^-]}{1+\sum\beta_{\mathrm{OH},p}[\mathrm{OH}^-]^p}\right)$$

For $A = 1 + \sum\beta_{\mathrm{OH},p}[\mathrm{OH}]^p$,

$$\log D = \log D_0 - \log(A + \beta_{\mathrm{app},q}[\mathrm{OH}^-]^q[\mathrm{R}^-]) + \log A$$

where the $\beta_{\mathrm{OH},p}$ values at a given ionic strength calculated from specific ion interaction theory (SIT). In Figure, the $\log\beta_{\mathrm{app}}$ values for tetravalent Pu are higher than those for Th due to an effect of actinide contraction.

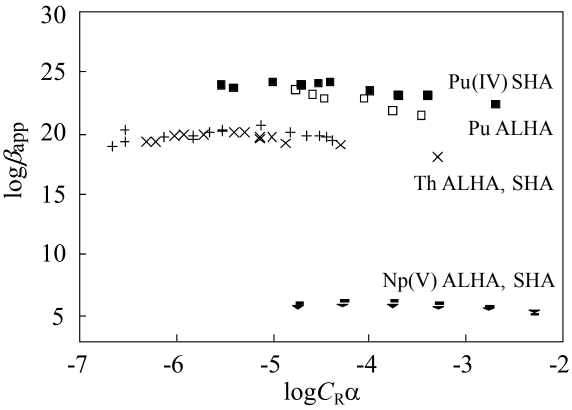

Fig. Comparison of the $\log\beta_{\mathrm{app}}$ (I=0.1 (NaClO$_4$) and 25°C) values for Pu– and Th–OH–HS (as q=1) ternary complexes at pH 4 [1] and Np-HS binary complexes at pH 6 [2] as a function of C_{R}.

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The solubility of Np(IV) under alkaline and anoxic conditions

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The solubility of Np(IV) has been studied under alkaline ($10 < pH < 14$) and reducing conditions. Previously the solubility of Np(IV) has been studied under acidic and near neutral conditions, with just a few studies in the range of $11 < pH < 13$. In these studies the analysis technique used was liquid scintillation counting on ^{237}Np, resulting in a detection limit of about 10^{-8} M. The results from these studies have indicated solubility around or below this limit resulting in a high degree of uncertainty. Another problem with the previous studies is that they have been made on the amorphous hydrous hydroxide which may not be a uniquely defined phase. This study was initiated to test if the alkaline solubility of $NpO_2(c)$ would be within the detection limit using ICP-MS technique.

Experiments on Np(IV) in the form of $NpO_2(c)$ were performed in (Na^+, OH^-, ClO_4^-) media at 8 different pH values in the range of 10 to 14 and an ionic strength of 2 M. In trying to achieve reducing conditions hydrogen atmosphere was used, and Pt(s) catalyst added to the solutions. The neptunium concentration was determined using ICP-MS technique thereby lowering the detection limit to between 10^{-12} and 10^{-11} M. In most of the studied pH region the solubility of Np(IV) was found to be below the detection limit. However, at two pH values, 10.4 and 13.5 the Np(IV) concentration was found to be at least $3 \cdot 10^{-10}$ and $3 \cdot 10^{-11}$ M respectively.

Np(IV), solubility, LSC, ICP-MS, detection limit

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Separation of Am and Cm by Using TODGA and DOODA(C8) Adsorbents with Hydrophilic Ligand-Nitric Acid Solution

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Abstract – Extraction chromatographic separation of Am and Cm was studied by using TODGA and DOODA(8) adsorbents and nitric acid eluents containing hydrophilic ligands, DOODA(C2) and TEDGA, respectively, in order to produce a synergistic effect in mutual separation properties.

Keywords – Chromatographic Separation of Am and Cm, TODGA and DOODA(C8) Adsorbents, Hydrophilic Ligands

For an improved partitioning of high level radioactive waste containing trivalent minor actinides (MA: Am, Cm) [1,2], extraction chromatographic separation of Am and Cm was studied by using porous silica/polymer support (SiO_2-P particles), into which two lipophilic diamide-type extractants, tridentate ligands TODGA (*N,N,N',N'*-tetraoctyl-1,3-oxapentane-1,5-diamide) and tetradentate ligands DOODA(8) (*N,N,N',N'*-tetraoctyl-3,6-dioxaoctane-1,8-diamide) were impregnated (TODGA and DOODA(C8) adsorbents, respectively). For the TODGA and DOODA(C8) adsorbents, nitric acid eluents containing hydrophilic ligands, DOODA(C2) (*N,N,N',N'*-tetraethyl-3,6-dioxaoctanediamide) and TEDGA (*N,N,N',N'*-tetraethyl-diglycolamide), respectively, were selected as masking agents in order to produce a synergistic effect in mutual separation of trivalent lanthanides (Ln) and/or MA.

Mutual separation properties of Ln were preliminarily investigated in both separation systems by batch and column methods, especially paying attention of separation between Nd and Sm. In nitric acid solution, the uptake of Ln onto the TODGA and DOODA(C8) adsorbents increased with nitric acid concentration. While the distribution coefficient (K_d) values of Ln for the TODGA adsorbent increased with atomic number of Ln, those for the DOODA(C8) adsorbent decreased with atomic number of Ln [3]. In nitric acid solution containing hydrophilic ligands, the K_d (Ln) values onto the TODGA and DOODA(C8) adsorbents decreased with concentration of DOODA(C2) and TEDGA ligands [4]. Relative separation factors (*SF*) of Ln (Nd~Tb) for the TODGA/DOODA(C2) system were almost the same degree irrespective of DOODA(C2) concentration, but those for the DOODA(C8)/TEDGA system were enlarged in lower TEDGA concentration. Consequently satisfactory eluent concentration of hydrophilic extractant and nitric acid concentration for each adsorbent was determined to be 0.05 M DOODA(C2)-0.1 M nitric acid eluent for TODGA adsorbent and 0.005 M TEDGA-3 M nitric acid eluent for DOODA(C8) adsorbent. Chromatographic separations of Ln (Nd~Tb) by both systems were effectively performed (*SF* (Nd/Sm): 4.2 for the TODGA system and 2.7 for the DOODA(C8) system and peak resolution (*R*) of Nd/Sm: 2.5 for the TODGA system and 2 for the DOODA(C8) system).

In this presentation, separation of MA(III) in both systems was demonstrated using not only Am-241 and Cm-243 but also Eu-152 for comparison between MA and Ln adsorbabilities. In the TODGA system, *SF* (Am/Cm) was considerably large (4.2), but chromatographic development was not sufficient and *R* (Am/Cm) was *ca.* 0.9 since the K_d (Am) value was unexpectedly small (0.7~0.8). In the DOODA(C8) system, *SF* (Am/Cm) was not so large (2.3) and *R* (Am/Cm) was *ca.* 1.2 because of adequate developed elution. It seems that the DOODA(C8) system is better than the TODGA system for practical use from a viewpoint of 3 M nitric acid eluent. On the other hand, the latter was superior to the former from an angle of mutual separation of Ln (Nd~Gd). In near future, the optimum elution condition will be searched for more effective separation of MA in pursuit of higher peak resolution between Am and Cm ($R \geq 1.5$).

A part of this study is the result of "Development of mutual separation technology of minor actinides by the novel hydrophilic and lipophilic diamide compounds" entrusted to "Japan Atomic Energy Agency" by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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23-ACP-06

Growth of uranyl hydroxide nanowires and nanotubes with electrodeposition method

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Abstract –Actinides nanomaterials have great potential applications in fabrication of novel nuclear fuel and spent fuel reprocessing in advanced nuclear energy system. [1-2] *However, the relative research so far still lacks systematic investigation on the synthetic methods for actinides nanomaterials. In this work, we use track-etched membranes as hard templates to synthesize uranium based nanomaterials with novel structures by electrodeposition method. Through electrochemical behavior investigations and subsequent product characterizations such as energy dispersive spectrometer (EDS), fourier transform infrared spectroscopy (FTIR), the chemical composition of deposition products have been confirmed as the uranyl hydroxide. More importantly, accurate control of morphology and structures (nanowires and nanotubes) could be achieved by carefully adjusting the growth parameters such as deposition time and deposition current density. It was found that the preferred morphology of electrodeposition products is nanowire when a low current density was applied, whereas nanotubes could be formed only under conditions of high current density and the short deposition time. The mechanism for the formation of nanowires in track-etched membranes is based on the precipitation of uranyl hydroxide from uranyl nitrate solution, according to the previous researches about obtaining nanostructures of hydroxides from nitrate salt solutions.* [3-4] *And we have concluded that the formation of nanotubes is attributed to the hydrogen bubbles generated by water electrolysis under the condition of over-potential electro-reduction. The conveying of hydrogen bubbles plays the role of dynamic template which can prevent the complete filling of uranyl hydroxide in the channels. Additionally, we transform the chemical composition of deposition products from uranyl hydroxide to triuranium octoxide by calcining them at 500 and 800 degree centigrade, respectively, and SEM results show the morphologies of nanowires and nanotubes are maintained very well. Our work provides new idea for synthesizing one-dimension uranium based nanomaterials. Further investigations are needed to unveil the size and shape effect on the physical and chemical properties of these nanowires and nanotubes, and to demonstrate their potential applications.*

Keywords – uranium based nanomaterials, uranyl hydroxide, electrodeposition, track-etched membranes, template method, nanowires, nanotubes.

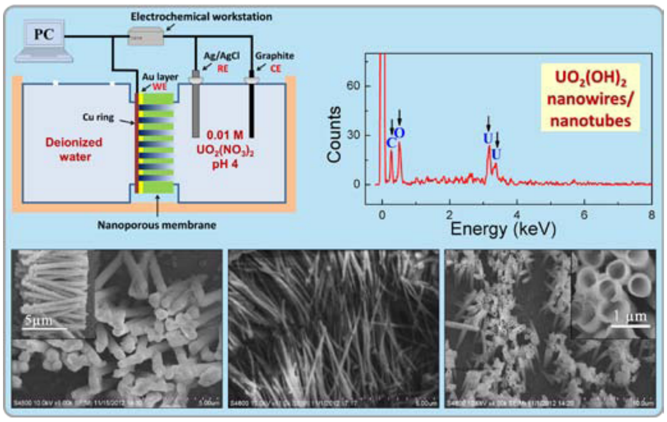

Figure 1. Growth of uranyl hydroxide nanowires/nanotubes with electrodeposition method. Top left, scheme of electrodeposition system; top right, result of elemental analysis for nano-structured products; down left, SEM images of uranyl hydroxide nanowires with diameters of 400 nm; down middle, SEM image of uranyl hydroxide nanowires with diameters of 50 nm; down right, SEM images of uranyl hydroxide nanotubes.

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23-ACP-07

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Adsorption Behavior of Neptunium Ions on Pyridine Resin in Hydrochloric Acid Solutions

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Abstract - The adsorption behavior of neptunium ions on pyridine resin in hydrochloric acid solutions has been studied at room temperature. Neptunium has many kinds of valence states of ions; mainly tetravalent, pentavalent, and heptavalent ions. We controlled the neptunium valence states and confirmed the valence states in hydrochloric acid solution by a UV-vis. spectrometry. The adsorption study on the neptunium ions which has the confirmed valence states, using pyridine resin was studied by batch-wise experiments. The distribution coefficients of neptunium on pyridine resin in hydrochloric acid solution were obtained.

Keywords – neptunium, pyridine resin, nuclear fuel reprocessing

I. INTRODUCTION

The noble nuclear reprocessing process based on chromatography in hydrochloric acid solutions has been developed [1]. This pyridine resin is used as the adsorption medium. In our previous works, the adsorption behavior of many elements was investigated, and the reprocessing process with nuclide separation system has been proposed from these results [2]. However we have not obtained the adsorption behavior of neptunium ions on pyridine resin in hydrochloric acid solution. It is well known that the neptunium has many valance states in solution. Thus, we controlled the valence states of neptunium, and obtained the adsorption behavior of each valence state of neptunium.

II. EXPERIMENTAL

1. Confirmation of valance states of neptunium

An ultraviolet-visible absorption photospectrometry (Lambda750, Perkin Elmer) was used for confirmation of valence states of neptunium. The wavelength of absorption peaks used for confirmation of Np(IV), Np(V), and Np(VI) species are about 750 and 960 nm, 980 nm, and 1230 nm, respectively.

Neptunium we used was confirmed to consist of pentavalent and heptavalent ions in original solution. In addition, we also confirmed that the neptunium can be controlled to be heptavalent by twice treatments of evaporation to dryness with the concentrated nitric acid solution and the perchloric acid solution. Tetravalent condition was confirmed to be able to be obtained by adding 0.5 M of hydroxylamine hydrochloride to the original solution. It was confirmed that Np(V) species are able to be obtained by adding peroxide to Np(VI) solution.

2. Adsorption experiments

Adsorption behavior was investigated by batch-wise experiments at room temperature. The neptunium with the controlled valences in a hydrochloric solution was added to the hydrochloric acid solution of adjusted concentrations. 0.1 g of pyridine resin was added to 1.0 mL of a neptunium solution. Adsorptions of neptunium ions on pyridine resin were evaluated by comparison of activity of neptunium before and after adding the pyridine resin.

III. RESULTS

We confirmed the methods of neptunium valence control. Distribution coefficients of neptunium with each controlled valence in hydrochloric acid solutions were obtained. Distribution coefficients of heptavalent neptunium are shown in Fig. 1. In this experiment, the neptunium-239 obtained by milking of americium-244 decay was used. The gamma-ray spectrometry was used for measurement of neptunium activity. We found that the heptavalent neptunium is strongly adsorbed on pyridine resin in higher concentrated hydrochloric acid solution, and this behavior is similar to heptavalent uranium.

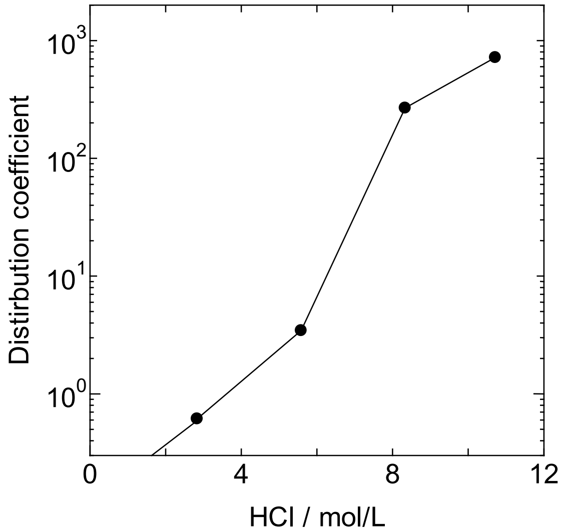

Fig. 1 Distribution coefficients of heptavalent neptunium on pyridine resin in hydrochloric acid solution.

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23-ACP-08

A method for ^{237}Np determination with liquid scintillation counting in the experiment of neptunium sorption onto bentonite

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Among various analytical methods developed and used for the determination of neptunium (alpha spectroscopy, Neutron Activation Analysis (NAA), High Resolution γ-Spectroscopy (HRGS), Inductively Coupled Plasma Mass Spectrometry (ICP–MS), luminescence method and Liquid Scintillation Counting (LSC) etc.), The Liquid Scintillation Counting (LSC) method does not require extensive sample preparation and is very sensitive for alpha-decaying radionuclides such as ^{237}Np[1]. However, direct determination of ^{237}Np from its β-active daughter ^{233}Pa is difficult.

In this study, a new method was developed for the determination of ^{237}Np with liquid scintillation counting (LSC), the α/β discrimination is carried out with the function of pulse shape analysis (PSA) without a pure α emitter or a pure β emitter. Before we use the PSA technique to discriminate α/β, an approach was developed to set the optimum PSA by measuring a mixed α/β emitters sample and a background sample. The mathematic treatment of neptunium peak indicated that at the selected PSA-level (38), we detected ~86% of the total α emission[2]. It is suitable for the sample determination in the sorption experiments at this PSA-level with LSC. Moreover, we confirmed that, at m/V(bentonite) = 0~10g/L the suspension in sample did not influence LSC determination obviously. Thus, we could detect ^{237}Np samples containing bentonite suspension directly with LSC by setting PSA-level=38.

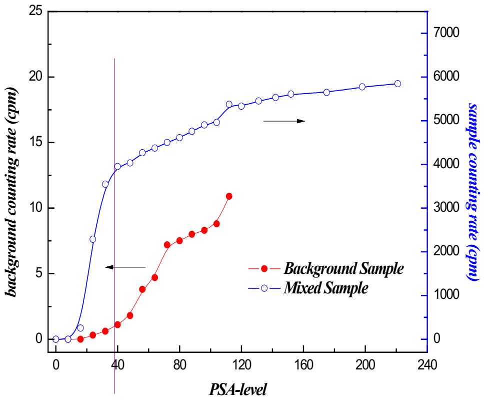

Fig.1 Count rate of a mixed sample and a background sample as a function of the PSA-level used.

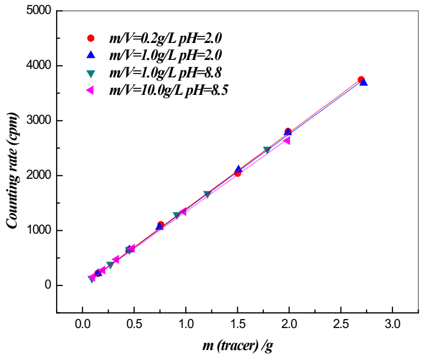

Fig. 2 Influence of bentonite on LSC measurement at a PSA-level=38.

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Determination of Stability Constants for the Thorium Iminodiacetic acid Complexes

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Abstract: *Potentiometric method of determining the stability constants was employed to study the complexation of thorium with iminodiacetic acid. All the stability constant values have been determined at temperature of 298 K and in 1 M $NaClO_4$ medium. The formation and determination of log β was not reported in the literature for ML_2 complex. Under our experimental conditions 1:1 and 1:2 complexes are found to be formed and no partially protonated ligand metal complexes such as MLH, ML_2H were observed. The determined log β values for ML and ML_2 complexes are 10.78 ± 0.03 and 19.81 ± 0.07 respectively.*

Keywords:*Thorium, Iminaodiacetic acid, stability constants*

INTRODUCTION

The complexation of actinides with various naturally present and anthropogenic organic ligands plays a vital role in understanding their speciation and migration in the environment. Thermodynamics of complexation of actinides with various organic and inorganic ligands have been reported in the literature. To know the binding nature and the effect of hetero atom present in the ligand on complexation with actinides, we initiated the study to determine the thermodynamic parameters for complexation of actinide ions with carboxylates containing hetero atom like nitrogen, sulphur, etc. As a part of this study, in the present paper the stability constants for the complexation of thorium with iminodiacetic acid have been reported. The complexation of thorium with iminodiacetic acid have also been reported in the literature [1] which show the formation of MLH and ML complexes whereas in our study we determined for the completely deprotonated ligand metal complexes ML and ML_2.

EXPERIMENTAL

The details on the preparation and standardization of Th(IV) solution was given elsewhere [2]. The iminodiacetic acid (IDA) was procured from sigma Aldrich and was used as such. Carbonate free NaOH was used for the electrode calibration. Potassium hydrogen phthalate as a primary standard has been used to standardize the NaOH. The ligand solution was prepared by adding known amount of standardized NaOH to iminodiacetic acid solution. The acidic metal ion solution was titrated with the ligand solution to determine the stability constants of the Th(IV) – Iminodiacetate complexes. The data collection was stopped before the appearance of turbidity and the collected data was analyzed by Hyperquad software.

RESULTS AND DISCUSSION

There is always a competition from H^+ during the complexation of metal with a ligand containing dissociable proton. Therefore, in order to determine the stability constants of the metal ligand complexes, knowledge of the protonation constants is essential. The protonation constants of iminodiacetate ion were taken from our previous experiment results [3]. During the titration of acidic metal ion solution with the buffered ligand solution, following reaction can occur in the reaction vessel.

$$H^+ + L^{2-} \rightarrow HL^-$$

$$H^+ + HL^- \rightarrow H_2L$$

$$Th^{4+} + nL^{2-} \rightarrow ThL_n^{(4-2n)+}$$

The overall stability constant for the complex formed by thorium can be given by

$$\beta_{ML_n} = \frac{[ThL^{(4-n)+}]}{[Th^{4+}][L^{2-}]^n}$$

Figure:1 shows the speciation diagram for the complexation of thorium with iminodiacetic acid along with the fitted data of pH. Under the experimental conditions, ML and ML_2 complexes are observed predominantly and the log β values for these complexes are shown in the table 1. The log β for the complex ML was comparable with literature value (log β =9.69) [1]. The higher values of log β indicate the role of chelation in these complexes. Studies on the coordination structure in these complexes are in progress.

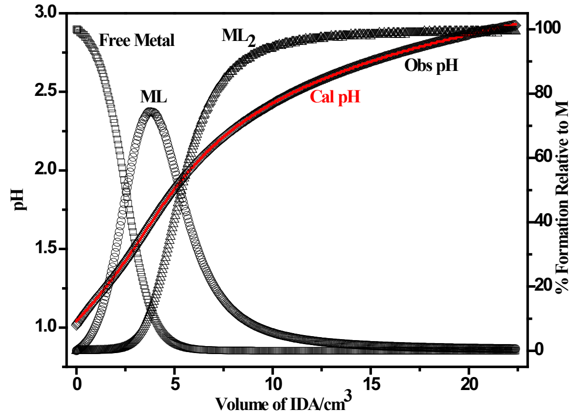

Figure:1 Speciation diagram of complexation of thorium with iminodiacetic acid along with the fitted data of both calculated and observed pH. ([Th] = $3*10^{-3}$ M, [H] = 0.0890 M and [IDA] = 0.2997 M, [H] = 0.2987 M, initial volume = 25 cm^3, I = 1 M $NaClO_4$, T = 298 K).

Table: 1 stability constants of thorium complexes with IDA ([Th] = $3*10^{-3}$ M, [H] = 0.0890 M and [IDA] = 0.2997 M, [H] = 0.2987 M, initial volume = 25 cm^3, I = 1 M $NaClO_4$, T = 298 K)

S.No.	Reaction	log β
2	Th + IDA → [Th(IDA)]	10.78 ± 0.03
3	Th + 2 IDA → [Th(IDA)$_2$]	19.81 ± 0.07

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Time-resolved laser fluorescence spectroscopy combined with parallel factor analysis: a robust speciation technique for UO_2^{2+}

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Speciation is a key issue for the fate of actinides and fission products in natural environments. Time-resolved laser fluorescence spectroscopy (TRLFS) is a popular speciation technique for fluorescent metal ions and can be further extended by combining multivariate data reduction methods such as parallel factor analysis (PARAFAC). This study demonstrates the applicability of TRLFS combined with PARAFAC for the speciation of UO_2^{2+} *in solution as well as on mineral surface.*

Uranium, time-resolved laser spectroscopy, PARAFAC, speciation, adsorption, complexation

I. INTRODUCTION

Chemical speciation governs the reactivity and migration of radionuclides released from nuclear waste disposal or an accident of a nuclear power plant in environments. Various analytical techniques are used for this purpose. Preferably, such speciation techniques shall possess all of the following capabilities: (i) discrimination of species by their different chemical and/or physical properties, (ii) quantification, and (iiii) structural determination of the species. Time-resolved laser fluorescence spectroscopy (TRLFS) is a particular speciation technique for fluorescent actinide ions such as UO_2^{2+} and Cm^{3+}. The above three characteristics are well-balanced in TRLFS; the discrimination and quantification of species can be achieved, based on their excitation/emission spectra and decay lifetimes; the concentrations of the species are proportional to their fluorescence intensities. The favorable characteristics of TRLFS as a speciation technique largely rely on the inherent multi-dimensional nature of its data, which makes the combination of multivariate statistics method suitable for the data reduction. Parallel factor analysis (PARAFAC) is a multi-model factor analytic method, which can only be applied for data having more than three dimensions. It has been shown that combining TLRFS with PARAFAC provides robust speciation capability for the speciation of Eu^{3+}, a chemical homologues of the trivalent actinide ions [1-3]. In this study, the applicability of TRLFS-PARAFAC for the speciation of UO_2^{2+} is firstly demonstrated.

II. EXPERIMENTAL

A set of the time-resolved fluorescence spectra of UO_2^{2+} complexed with orthosilicate (H_2SiO_4) or adsorbed on gibbsite (α-$Al(OH)_3$) surface were obtained with a TRLFS system equipped with the forth harmonics of Nd:YAG laser. The complexation of UO_2^{2+} with H_2SiO_4 was studied as a function of the H_2SiO_4 concentration at different pH; the adsorption of UO_2^{2+} on gibbsite as a function of pH at the different concentrations of UO_2^{2+}. The entire data set in each series was processed by PARAFAC, using the N-way toolbox for MATLAB®[4].

III. RESULTS AND DISCUSSION

Three species were found for the complexation of UO_2^{2+} with H_2SiO_4 at pH 4, exhibiting the characteristic fluorescence spectra (Figure 1) and decay curves. The fluorescence intensity profiles, which approximated the concentration profiles of the species as a function of the H_2SiO_4 concentration, were used to determine the stability constants of the complexation.

Three surface species of UO_2^{2+} on gibbsite were obtained from the TRLFS data set by applying PARAFAC. Based on the fluorescence spectra, decay lifetimes, and the dependence of the intensity profiles on pH and the UO_2^{2+} concentration, these species likely corresponded to mono-nuclear surface complexes with and without hydrolysis and a multi-nuclear surface complex.

IV. CONCLUSION

It was shown that the combination of TRLFS with PARAFAC was capable of discriminating the contribution of multiple species of UO_2^{2+}. The obtained spectra, decay curves, and intensity profiles were invaluable to understand and model the underlying speciation both in solution and on mineral surface.

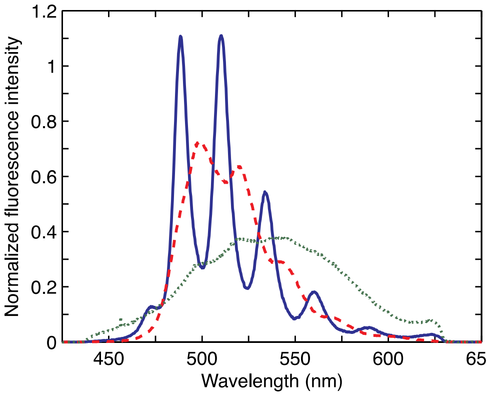

Figure 1. Fluorescence spectra of the three UO_2^{2+} species with H_4SiO_4 obtained from a series of TRLFS spectra by PARARAC.

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Determination of ^{55}Fe and ^{89,90}Sr in liquid samples using Sr and/or Pb resins for the mutual separation of Fe and Sr

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Abstract. The determination of ^{55}Fe and strontium isotopes is complicated and time-consuming, especially the determination of ^{89,90}Sr. In the last decade, a number of methods have been developed for radioactive strontium isolation and determination in various types of samples. On the other hand, only few methods for ^{55}Fe determination are developed, mainly in liquid radioactive waste samples. Since strontium isotopes are highly radiotoxic fission products (especially ^{90}Sr with long half-life), they are an interesting subject for various investigations, from their distribution and behavior in natural systems to the influences on the human health. In distinction from strontium isotopes, ^{55}Fe is an activation product, low energetic emitter with approximately 2.74 year half-life. As such, it is not as interesting as strontium, but environmental concerns prompted the responsible institutions in the radiological monitoring program to include ^{55}Fe determinations in their procedures. In almost all published methods, isolation and determination of ^{89,90}Sr and ^{55}Fe are separated. Therefore, the aim of the paper is to present a method for the isolation of ^{55}Fe and ^{89,90}Sr from liquid sample in one step by using Sr and/or Pb resin and mixture of nitric and hydrochloric acid, because Fe and Sr can be bound on Sr resin from mixture of HNO_3+HCl as shown earlier.[1] Namely, Sr and Pb resins were primarily developed as Sr, Pb specific resins which enable very efficient separation of Sr and Pb from other elements as well as for their mutual separation. The main focus in the literature was directed on their application in the determination of ^{89,90}Sr and ^{210}Pb in different kinds of samples,[2,3] while determination of ^{55}Fe was not in focus from above mentioned reason. Therefore, it will be shown how Fe and Sr can be bound and mutually separated (and from many other elements) on Sr and Pb resin column. It will be shown that binding strength and selectivity on both resins depend on concentration of HCl and HNO_3. By changing the eluent composition, separation of Fe from Sr, as well as Pb from Fe and Sr ions, can be achieved on both resins. Based on these results, methodology for rapid determination which involves, binding of Fe and Sr on the column from the mixture of HNO_3+HCl, elution of Sr with HCl, Fe with H_2O and detection on LSC is created. It will be shown that ^{55}Fe and ^{89,90}Sr can be easily separated on both resins from different types of samples with almost same efficiency. Methodology is tested by determination of ^{55}Fe and ^{89,90}Sr in proficiency testing samples and radioactive waste samples and obtained results will be presented and discussed in detail.

Keywords: Sr and Pb resin, Iron-55, Strontium-89, 90, separation

Table 1. Distribution coefficients of elements on Pb resin

K_d [mLg^{-1}]	Pb resin				
	Sr	Mn	Fe	Ni	Pb
0,5 M HCl	-	-	-	-	322
2 M HCl	-	-	-	-	218
4 M HCl	-	-	220	-	68,7
6 M HCl	-	-	442	-	8,94
6 M HCl + 1 M HNO_3	58,91	-	796	-	3,54
6 M HCl + 3 M HNO_3	101,12	-	210	-	-
6 M HCl + 5 M HNO_3	105,66	-	102,5	-	-
5 M HNO_3	108,42	-	-	-	>399

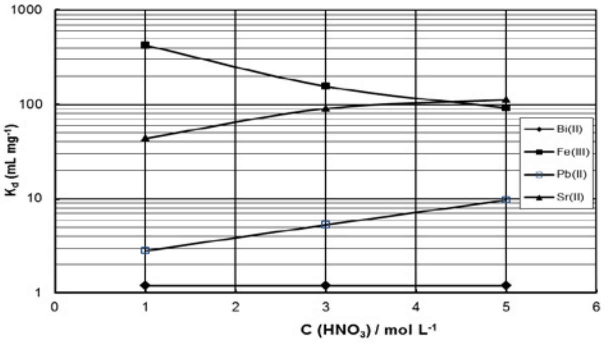

Figure 1. Distribution coefficients of elements in mixture of 6M HCl and HNO_3 on Sr resin

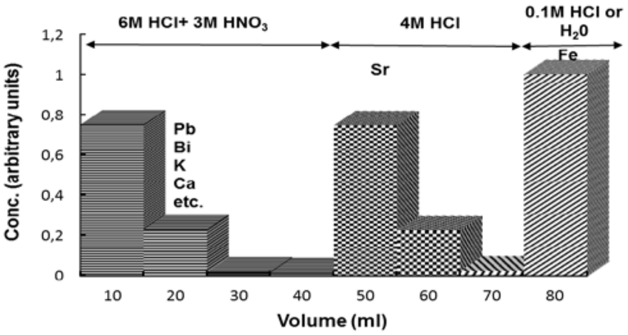

Figure 2. Separation of Sr and Fe from other elements on Pb resin column

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APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
Kanazawa, Japan, 22-27 September 2013

Implementation of Dry Cow Dung Powder for Biosorption of ^{90}Sr(II) from Simulated Radioactive Waste

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Abstract – ^{90}Sr is one of the major fission product found in the radioactive waste. The anthropogenic activities such as nuclear weapon testing, reprocessing of liquid spent fuel etc. are major sources of ^{90}Sr in our environment. Some of the well-established processes such as chemical precipitation, membrane process, liquid extraction and ion exchange have been applied as a tool for the removal of this metal ion. All the above methods are not considered to be greener due to some of their shortcomings such as incomplete metal ion removal, high requirement of energy and reagents, generation of toxic sludge or other waste materials which in turn require further treatments for their cautious disposal. The present investigation entails the biosorption studies of ^{90}Sr(II) from simulated radioactive waste employing dry cow dung powder (DCP) as an indigenous, inexpensive and, eco-friendly material without any pre or post treatments. As DCP is easily available, it is superior to other processed natural adsorbent considering their cost, time and energy efficiency. The Batch experiments were conducted employing ^{90}Sr as a radiotracer and the effect of process parameters such as pH, temperature, amount of resin, time of equilibration, agitation speed and distribution co-efficient have been studied for simulated reactor and reprocessing waste with and without carrier. The efficiency of adsorption was found to be more than 70%. The prime amenity of using DCP over other biosorbents is that it doesnot require any degree of physical and chemical enhacement for optimization of the method and inturn adds to the economy of entire adsorption process. Thus use of DCP manifests the principles of Green Chemistry and proves to be an eco-friendly alternative for the remediation of radiotoxic ^{90}Sr(II).

Keywords – Biosorption, Strontium, Dry cow dung powder, Simulated radioactive waste

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Application of Simplified Desorption Method to Sorption Study: (1) Sorption of Americium (III) on Bentonite and Its Major Components

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Abstract – To elucidate the sorption behavior of americium on bentonite, which is a mixture of montmorillonite clay, quartz and so on, simplified desorption experiments were applied to the solid phases collected after the sorption experiments. Almost 100% of Am was sorbed on bentonite and montmorillonite at pH from 2 to 8. A fraction of the Am sorbed on the solid phases was desorbed by twice treatment with a 1M KCl aqueous solution, and the residual Am was completely desorbed by twice treatment with a 1M HCl aqueous solution. The desorption behaviors of Am from bentonite and montmorillonite were very similar to each other and symmetrical at pH 7. Most of the Am sorbed below pH 7 was desorbed with 1M KCl solutions and that above pH 7 was not desorbed with 1M KCl but with 1M HCl solutions. The trend in the KCl-desorbable fraction vs. pH is very similar to the abundance ratio of cationic Am species (Am^{3+}) and so is the trend in the KCl-nondesorbable fraction to that of the hydrolyzed species of Am.

Keywords – Americium, sorption, desorption, pH, montmorillonite, bentonite, quartz

I. INTRODUCTION

Sorption is one of the key mechanisms to control the subsurface environmental behavior of the radionuclides. It is known that sorption behavior of elements on solid phases may vary depending on the concentration of the element [1]. Thus, for the environmental study, it is desirable to examine sorption behaviors at tracer concentrations (nanomolar or less). To date it is however impossible to apply any instrument analysis except radiation measurements to the analysis of the tracer level radionuclides on solid phases.

To analyze the tracer level neptunium sorbed on clays, a simplified desorption method sequentially using two kinds of desorption agent solutions was effective [2]. This paper applies the desorption method to the sorption study of Am on bentonite and discuss the sorption and Am species. Bentonite is a clay found ubiquitously in soil environment. Its main component is montmorillonite, and minor components are calcite, dolomite, quartz, pyrite, cristobalite, zeolite, etc. Owing to high cation exchange capacity of montmorillonite, bentonite clay plays a very important role for migration of radionuclides in the subsurface environment.

II. EXPERIMENTAL

Tsukinuno montmorillonite (Kunipia F®, Kunimine Industries Co. Ltd.) was used after the montmorillonite was converted to homoionic Na^+ forms (Na-montmorillonite). Tsukinuno bentonite (Kunigel V1®, Kunimine Industries Co. Ltd.) was used with no pretreatment. Kunipia F is a purified product from this bentonite. An Am (III) nitrate stock solution was diluted with 0.01 M $NaClO_4$ to yield a working solution having an Am concentration of about $5x10^{-10}$ M.

For the sorption experiments, the initial pH of the Am solution was adjusted over a range of 1.8 to 10. A weighed amount (0.06 g) of sold phases was soaked in 6 cm^3 aliquots of the Am solution and stored at 20^oC. This solid-solution mixture was agitated once a day. After 10 days, a supernatant was collected by centrifugation.

Desorption experiments were conducted in two steps. First, 6 cm^3 of 1 M KCl solution was added to the solid phases collected after the sorption experiments. After 2 days, the KCl solution was separated by centrifugation. Second, desorption with a 1 M HCl solution was undertaken in the same way as the desorption with a 1 M KCl solution. The desorption with each solution was carried out twice to confirm complete desorption of Am.

III. RESULTS AND DISCUSSION

In the examined final pH range (2 – 8), almost 100% of Am was sorbed on bentonite and montmorillonite. All of the Am sorbed on bentonite and montmorillonite were desorbed by the two step desorption procedures. The desorption behaviors of Am from bentonite and montmorillonite were very similar to each other. Most of the Am sorbed below pH 5 was desorbed by the twice treatment with 1M KCl solutions. The KCl-desorbable fraction of Am sharply decreased with increasing pH above pH 5 and most of the Am sorbed above pH 7 was not desorbed with 1M KCl solution but with 1M HCl solution. The trend in the KCl-desorbable fraction vs. pH is very similar to the abundance ratio of cationic Am species (Am^{3+}) and so is the trend in the KCl-undesorbable fraction to that of the hydrolyzed species of Am. It is intuitively understand that the Am desorbable from the bentonite with KCl solution is the Am sorbed on the montmorillonite fraction in the bentonite.

This paper further discuss the sorption behavior of Am on bentonite with the result of blank experiments to examine the sorption on the reaction vessels and with that of sorption and desorption experiments on quartz, which is the second major mineral in the bentonite.

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Effect of aging on availability of iodine in grassland soil collected in Rokkasho, Japan

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Abstract – In the laboratory, we investigated the time-dependent changes in the availability of I in soil over the course of 23 months. Stable I was added as iodide or iodate to a soil sample collected from a grassland area in Rokkasho, Japan. Whether I was added as iodide or iodate, its water solubility, and soil-to-grass transfer factor decreased drastically over the course of 4 months after addition and then slightly decreased thereafter.

Keywords – iodate, iodide, radioiodine, soil-to-plant transfer

I. INTRODUCTION

The first commercial nuclear fuel reprocessing facility in Japan, located in Rokkasho, Aomori Prefecture, is undergoing its final testing using actual spent nuclear fuel. Iodine-129 (half-life, 1.6 × 10^7 y) is discharged from the facility, and the radiation dose to the public resulting from discharge of this radionuclide must be assessed. Some of the ^{129}I discharged to the atmosphere is deposited on the land surface and retained in surface soil. The mobility of I in soil is expected to decrease with time after its deposition, and investigation of the time-dependent changes in I mobility in soil is necessary for the better prediction of long-term I behavior in the surface soil environment. We conducted a laboratory study of the changes in the water solubility and phytoavailability of trace I added to soil collected from Rokkasho.

II. MATERIALS AND METHODS

A soil sample was collected from the surface of a pasture field in Rokkasho, Japan. Aliquots (200 g) of the dried soil sample were placed in plastic pots, and a solution of NaI or $NaIO_3$ was added to the soil in each pot at a concentration of 20 mg-I kg^{-1}-soil. The pots were stored in an artificial climate chamber for about 23 months. The water content of the soil was adjusted to 60% of its maximum water-holding capacity every 2 weeks. The soil in the pots was stirred every 4 weeks. As controls, pots of soil without added I were treated the same way.

Soil samples were collected from the pots at 0, 2, 9, 29, 64, 113, 204, 372, and 687 d after addition of the I solution. The soil samples were extracted with deionized water, at a 1:10 w/v ratio of soil to water, for 1 h at 20°C. The supernatants were separated from the soil by means of high-speed centrifugation and then filtered through a 0.22-µm-pore membrane filter.

Orchardgrass (*Dactylis glomerata*) was cultivated in the pots 2–29 d, 37–64 d, 86–113 d, 117–204 d, 345–372 d, and 660–687 d after the addition of I. The cultivation experiments were carried out in triplicate for each time period. Twenty germinated seeds were sown in each pot. The water content of the soil was adjusted with deionized water to 60% of maximum water-holding capacity of the soil three times a week during the cultivation period. The aboveground parts of the plants were sampled at 28 d after sowing. The plant samples were freeze-dried and finely ground. Iodine in the plant samples was extracted with tetramethyl ammonium hydroxide at 60ºC overnight. The concentrations of I in the soil and plant extracts were determined by inductively coupled plasma mass spectrometry. Concentrations of added I in the soil extract and plant were calculated by subtracting the I concentrations in the control samples, to which I had not been added.

III. RESULTS AND DISCUSSION

The water-solubility of I in the soil decreased with time after its addition. Soon after addition, 98% of the I added as iodide and 54% of the I added as iodate were extracted with water. In contrast, the extraction yield of the added I at 113 d after addition was 2%, and no difference was observed between the chemical forms of the added I. The extraction yield of the added I was nearly constant thereafter, and was 1.5% at 687 d after the addition.

The concentration of added I in the orchardgrass plants was relatively lower in the later stage compared to soon after addition of I to the soil. The soil-to-plant transfer factor, which is defined as (concentration of added I in the aboveground part of the plant)/(concentration of added I in the soil) (mg kg^{-1} dry plant)/(mg kg^{-1} dry soil), decreased with time after the addition: from 0.80 to 0.042 for the soil with added iodide, and 1.3 to 0.041 for the soil with added iodate over the course of the experiment (Fig. 1). The decreasing trend was similar to that for the water extractability from the soil.

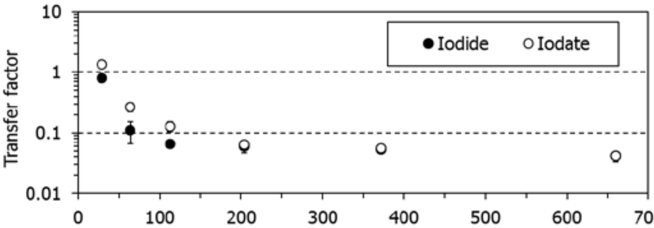

Fig. 1 Time-dependence of soil-to-plant transfer factor of I after its addition to the soil. Error bars indicate standard deviations (n = 3). Orchardgrass was cultivated for 28 d in each pot experiment. The plotted transfer factors are values for the end of each cultivation period.

This study was performed under a contract with the government of Aomori Prefecture, Japan.

Study on ^{14}C spatial distribution around Qinshan nuclear power plant in China

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Abstract –To understand the spatial distribution of ^{14}C discharged by Qinshan nuclear power plant (NPP), where two heavy water reactors (Plant III) are on commercial operation, both experimental investigation and model prediction (Gaussian plume model) were carried out by this work. Twenty one moss samples were collected in five different wind directions near Qinshan NPP, and analyzed by accelerator mass spectrometry (AMS). The ^{14}C specific activities in moss samples ranged from 265.6 to 233.0 Bq/kg C (the background is 233.8 ±1.1 Bq/kg C), decreasing with increased distance from the stacks of Plant III. Simulation of ^{14}C spatial distribution in air was calculated by using a Gaussian plume model, which was based on monthly meteorological data, ^{14}C discharge record, local dispersion parameter and other parameters. A good fit was found between the predicted and measured values, indicating that the spatial distribution of ^{14}C follows a Gaussian model. It can be concluded furthermore, that the influence of the Hill Qinshan (located at W of Plant III, 170 meters high) on ^{14}C's distribution is quite limited at this site - compared to meteorological influences.

Key words: Qinshan NPP; ^{14}C; Gaussian plume model

Atmospheric deposition of radionuclides (^{7}Be, ^{210}Pb, ^{134}Cs, ^{137}Cs, and ^{40}K) during 2000–2012 at Rokkasho, Japan, and impact of the Fukushima Dai-ichi Nuclear Power Plant accident

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Abstract – Radionuclides, including radiocesium (^{134}Cs and ^{137}Cs), were measured in atmospheric deposition samples collected in Rokkasho, Aomori, Japan, from 2000 to 2012. After the accident at the Fukushima Dai-ichi Nuclear Power Plant, radiocesium deposition rapidly increased and reached a maximum in April 2011. Since then, monthly radiocesium deposition has gradually decreased. Monthly ^{137}Cs deposition has almost reached pre-accident levels, although ^{134}Cs is still being detected.

Keywords – atmospheric deposition, Rokkasho Village, Fukushima Dai-ichi Nuclear Power Plant accident

I. INTRODUCTION

Natural and anthropogenic radionuclides are useful tracers for studying processes in the atmospheric environment. Atmospheric deposition of radionuclides has been measured at many sites for geochemical studies and radiation protection. We have been measuring atmospheric deposition of radionuclides in the village of Rokkasho, Aomori Prefecture, Japan, since 2000 [1, 2]. In this study, we report the impact of the accident at the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) on the atmospheric deposition of radiocesium (^{134}Cs and ^{137}Cs) in Rokkasho.

II. EXPERIMENTAL

Atmospheric deposition samples were collected on the roof of a building at the Institute for Environmental Sciences in Rokkasho (40° 57′ N, 141° 21′ E), approximately 13 m above ground level. Bulk atmospheric deposition samples were collected biweekly in a polyethylene basin from March 2000 until March 2006, and samples were collected monthly after April 2006. Each sample was passed through a Powdex resin (Ecodyne Co., USA) column to separate ionic radioactive species and particulates from the sample. The homogenized resin was dried and packed into a plastic case for γ-ray spectrometry. The concentrations of γ-ray-emitting radionuclides, including ^{7}Be, ^{210}Pb, ^{137}Cs, and ^{40}K, in the sample were measured with a low-energy photon spectrometer with a Ge detector. After the accident at the FDNPP, ^{134}Cs concentrations were also measured.

III. RESULTS AND DISCUSSION

Annual deposition of ^{137}Cs from 2001 to 2010 ranged from 0.04 to 0.69 Bq m^{-2} with a mean value of 0.21 Bq m^{-2}. We have already reported that recent background ^{137}Cs deposition was affected by Asian dust [1]. On 11 March 2011, large amounts of radiocesium were released into the atmosphere from the accident at the FDNPP. After the accident, monthly radiocesium deposition increased, reaching a maximum in April 2011. Thereafter, monthly ^{137}Cs deposition decreased rapidly until September 2011 (apparent half-time ~0.8 month) and more gradually (half-time ~0.7 y) from September 2011 until December 2012. Annual deposition of ^{137}Cs was 86.9 Bq m^{-2} in 2011 and 1.89 Bq m^{-2} in 2012. Monthly ^{137}Cs deposition has dropped almost to the pre-accident level, although ^{134}Cs is still detectable.

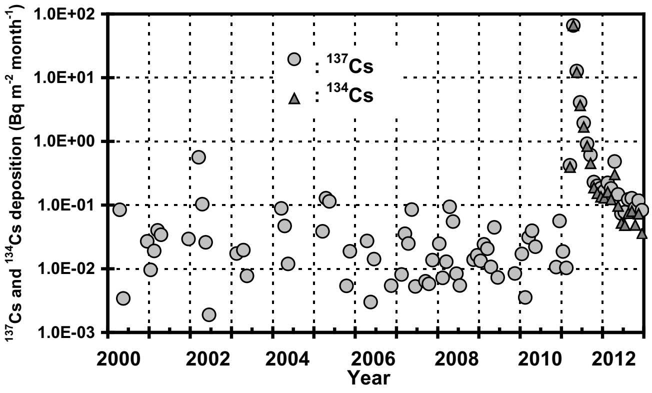

Fig. 1 Monthly atmospheric deposition of ^{137}Cs and ^{134}Cs in Rokkasho

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This study was performed under a contract with the government of Aomori Prefecture, Japan.

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Effect of Aging on Water Extractability of Radioactive Iodine and Cesium from Soil

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Abstract – Water extractabilities of radioactive ^{125}I and ^{137}Cs from soil were determined by tracer experiments. Career free ^{125}I (iodide or iodate) or ^{137}Cs was spiked to soil samples, which were then stored in an artificial climate chamber where a wetting-and-drying treatment was repeated. Extraction yield of ^{125}I at 4 h after spiking with iodide was higher than that with iodate, and then both yields decreased with aging independent of the chemical forms. Chemical form of ^{125}I in the water extracts at 29 d was predominantly iodide, regardless of whether the spiked form was iodide or iodate. Water extraction yield of ^{137}Cs immediately decreased after spiking in the soil, which was 0.015 at 4 h, and then less than 0.001 at 320 d after spiking.

Keywords – radioactive ^{125}I, iodide, iodate, ^{137}Cs, water extractability, aging

I. INTRODUCTION

Aging of radionuclides in soils after deposition can play an important role in the change of the physicochemical form, which is an important factor in determining the fate of radionuclides in the environment. Radioactive iodine and cesium were the major radionuclides released from the Fukushima Daiichi Nuclear Power Plants after the accident in March 2011. Water extractable forms in soil make up the most mobile fraction, which can migrate and be taken up by plants. In the present study, water extractabilities of radioactive ^{125}I (iodide and iodate) and ^{137}Cs were determined at different elapsed time intervals.

II. MATERIALS AND METHODS

Volcanic ash soil (Andosol), which is a typical upland soil in Japan, was collected from the surface of a grassland in Aomori Prefecture (40°52'23"N, 141°16'57"E). The soil was dried at 50°C and passed through a 2 mm sieve. Career free ^{125}I (iodide or iodate) or ^{137}Cs of 10 kBq was spiked to 1 g of soil sample. Iodate solution was prepared by the oxidation of iodide solution by adding bromine water. The samples were stored in an artificial climate chamber (17°C, 60% relative humidity, 30 klx, 12 h of daylight), and wetting-and-drying treatments were repeated by adding 1 ml of deionized water every 2 weeks. The soil samples were extracted with deionized water for 1 h at room temperature with a 1:10 ratio of soil weight to extract. The samples were extracted from 4 h to 320 d after spiking for ^{125}I, and 4 h to 1110 d for ^{137}Cs. The extracts were filtered through a 0.22 μm pore membrane filter (Millipore, Steriflip®) after centrifugation at 10,000 rpm for 5 min. Chemical forms of ^{125}I in the water extracts were also determined at 2 and 29 d after spiking by using an anion exchange disk (3M, Empore Anion-SR®). Radioactivity of the extract and disk samples were measured with NaI(Tl) detectors.

III. RESULTS AND DISCUSSION

Water extraction yield of ^{125}I at 4 h after spiking with iodide was 0.87, which was higher than that with iodate (0.33), and both yields after spiking decreased to 0.033-0.034 at 320 d independent of the spiking chemical forms (Fig. 1). Content of $^{125}IO_3^-$ in the water extract at 2 d after spiking with iodate was 28%, and that it decreased to 1% at 29 d. Iodine-125 in the water extract at 2 and 29 d after spiking with iodide existed as $^{125}I^-$. This suggests that the chemical form of ^{125}I in the water extracts was predominantly iodide excluding the time just after spiking, regardless of whether the spiking form was iodide or iodate.

Water extraction yield of ^{137}Cs in the soil immediately decreased after spiking, from 0.015 at 4 h to 0.0075 at 30 d. After that, the yield was gradually decreased from 0.0012 at 120 d to less than 0.001 at 320 d, and was 0.00050 at 1110 d after spiking. It is well known that radioactive Cs is strongly fixed in clays, and that its mobility is limited.

The results show that transferability of radioactive iodine and cesium in soil immediately decreases in early stage after deposition.

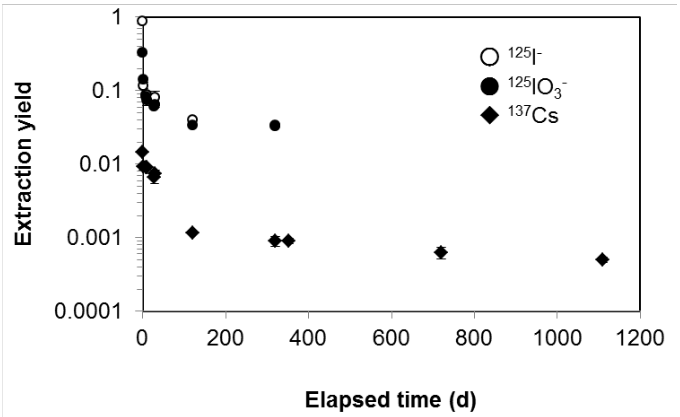

Fig. 1 Time dependecy of water extractabilities of ^{125}I (iodide and iodate) and ^{137}Cs from soil. Error bars indicate one standard deviation (n=3).

This study was performed under a contract with the government of Aomori Prefecture, Japan.

Background internal dose rates of earthworm and arthropod species in the forests of Aomori, Japan

Yoshihito Ohtsuka, Yuichi Takaku, Shun'ichi Hisamatsu
Department of Radioecology, Institute for Environmental Sciences

Abstract – We measured naturally occurring radionuclides in samples from an earthworm species and 11 arthropod species collected in coniferous forests in Rokkasho, Aomori, Japan, to assess background internal radiation dose rates. The rates were calculated from the measured concentrations of the radionuclides and dose coefficients from the literature. The mean internal dose rate of composite earthworm samples was 0.35 μGy h^{-1}, whereas the mean dose rates of the arthropod samples ranged from 36 nGy h^{-1} to 0.79 μGy h^{-1}. Polonium-210 was the radionuclide with the highest contribution to the internal dose rate for all the species, except the longhorn beetle.

Keywords – non-human species, background radiation, naturally occurring radionuclides, forest ecosystem

I. INTRODUCTION

Protection of the environment from radiation and assessing effects of radiation on nonhuman species have been discussed by international organizations such as the International Commission on Radiological Protection [1]. Many researchers have reported concentrations of artificial radionuclides in animals living in terrestrial environments contaminated by the nuclear accidents at Chernobyl and Fukushima [e.g., 2, 3]. However, few studies have compared background radiation doses with artificial radionuclide doses.

In this study, samples of an earthworm species and 11 arthropod species were collected in coniferous forests around the nuclear fuel reprocessing plant currently under construction in Rokkasho, Aomori, Japan, and the internal background dose rates of natural radionuclides were determined.

II. MATERIALS AND METHODS

One species of earthworm and 11 species of arthropods were collected monthly in coniferous forests in Rokkasho from June to October 2008; the animals were collected with falling traps buried in the ground in four areas (Fig. 1). After being washed with pure water, the animals were freeze-dried. For each animal species, a composite sample was prepared from the dried animals for each sampling site and each collection month. The composite samples were analyzed for ^{210}Po, ^{210}Pb, ^{238}U, ^{232}Th, ^{40}K, and ^{87}Rb by γ-ray and α-ray spectrometry, and ICP-AES and ICP-MS.

III. RESULTS AND DISCUSSION

Polonium-210 was the natural radionuclide with the highest concentration in the earthworm samples, whereas ^{40}K was the radionuclide present at the highest concentration in the samples of all the arthropods, except for a millipede and a Japanese ground beetle. The mean ^{210}Po concentration in the earthworm samples was 0.10 Bq g^{-1}-wet, and the mean ^{210}Po concentrations in the arthropods varied widely, from 0.0042 Bq g^{-1}-wet in a longhorn beetle to 0.24 Bq g^{-1}-wet in a millipede.

The internal dose rates were calculated by using the measured concentrations of ^{210}Pb, ^{210}Po, ^{232}Th, ^{238}U, and ^{40}K, and the dose coefficients for the earthworm and the woodlouse reported by the Framework for Assessment of Environmental Impact [4]; the dose coefficients for the woodlouse were applied to all the arthropods. The mean internal dose rate for the earthworm was calculated to be 0.35 μGy h^{-1}, approximately 90% of which was due to ^{210}Po. The dose rates for the arthropods ranged from 36 nGy h^{-1} to 0.79 μGy h^{-1}, with the actual value depending mainly on the ^{210}Po concentration. The contribution of ^{210}Po to the dose rate of the arthropods varied from 36% to 95%.

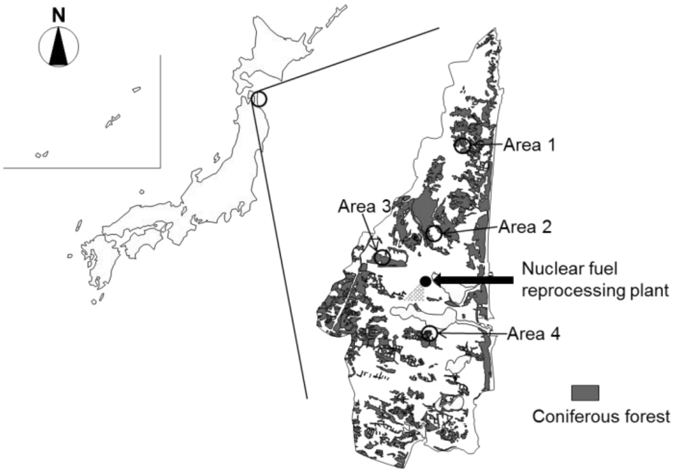

Fig. 1 Sampling areas for earthworms and arthropods, along with the distribution of coniferous forests in Rokkasho, Aomori, Japan.

This study was performed under a contact with the government of Aomori Prefecture, Japan.

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An EXAFS Study on the Effect of Natural Organic Matter and Mineralogy Composition on Cesium Mobility in Environment

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Abstract: The sorption of Cs was clearly inhibited in the ternary clay+HA+Cs system (the addition sequence of reagent) with respect to the blocking to the access of frayed edge sites (FESs) and interlayer sites by HA for both illite and vermiculite. Both inner-sphere complexes (ISCs) and outer-sphere complexes (OSCs) of Cs^+ have attribution to its adsorption on illite (non-expansion). However, on vermiculite (intermediate expansion), the partially dehydrated Cs^+ was liable to be present as ISCs associated with the siloxane group of the ditrigonal cavity in the SiO_4 sheet. However, nearly complete OSCs were observed at the planar sites of montmorillonite (high expansion).

Keywords: Cesium, EXAFS, Clay mineral, Mobility, Natural organic matter

Introduction

There is a consensus that radiocesium (RCs) strongly and selectively interacts with the phyllosilicate fraction of soil, sediment, and suspended particles such as illite, vermiculite, and montmorillonite. Natural organic matters (NOMs) normally play various important roles in the environment because of its correlations with soil properties and Cs bioavailability. Herein, the speciation of Cs on clay minerals in presence of humic acid (HA) were investigated by batch experiment, modified sequential extraction [1] and Cs L_{III}-edge EXAFS approaches.

Experimental

IMt-1 illite (Cambrian shale, Silver Hill, Montana) and SWy-2 montmorillonite (Mont) from the University of Missouri were purchased from The Clay Minerals Society. Vermiculite (Verm) from Kent, Connecticut was supplied by Ward's Natural Science Establishment, Rochester, NY, USA.

Cs L_{III}-edge extended X-ray absorption fine structure (EXAFS) spectra were collected at BL-12C and BL-9A stations at KEK Photon Factory (Tsukuba, Japan). EXAFS analysis was performed using REX 2000 (Rigaku Co. Ltd) and FEFF 7.0 [2].

Results and Discussion

Cesium sorption on vermiculite increased significantly over the pH range of 3.0 to 7.0, whereas weak pH dependence was observed for Cs sorption on illite. The pH dependence can be ascribed to the competitive sorption with proton, wherein the available exchange site for Cs increases with pH increasing. In Verm+HA+Cs system, Cs sorption is clearly depressed, but this inhibition becomes weaker with increasing pH. A similar phenomenon could also be found in the illite+HA+Cs system.

EXAFS analysis demonstrated that Cs speciation strongly depends on mineralogy and NOMs. The increase in pH from 3.0 to 7.0 increases ISCs from 42% to 80% for illite. However, in vermiculite system, ISCs mostly dominate Cs fixation and weakly depend on pH. Vermiculite with a 1.4 nm layer distance is enough to the entrance of Cs^+ and to form the ISCs associated with the siloxane groups of ditrigonal cavities even at low pH. XRD patterns showed that the characteristic peak of vermiculite (6.1°) shifted to a large angle after Cs adsorption at low Cs concentration even in the presence of HA and disappears at high Cs concentration. The dehydrated Cs^+ replacement of Mg^{2+} or K^+ causes the partial collapse of vermiculite layers at low Cs coverage and complete collapse at high Cs coverage, which is a more stable state to Cs [2]. However, no such change was observed in the illite systems. The negative charge of montmorillonite with a 2.0 nm layer distance (high expansibility) is mainly derived from the isomorphic substitution of Mg^{2+} for Al^{3+} in the octahedral AlO_6 sheet, which drives hydrated Cs^+ to form OSCs in the interlayer sites.

EXAFS analysis indicates that HA molecules could efficiently block the accesses to FESs and interlayer even at relative large layer distance such as vermiculite (1.4 nm) to reduce Cs sorption to a large extent. Obviously, the OSCs proportion increase in the illite+HA+Cs system, because the coated HA molecules make Cs form OSCs through electrostatic attractive force, which was also consistent with the sequential extraction results.

Conclusion

The strong retard Cs in soil or sediment could attribute to the ISCs related to the FESs and interlayer of illitic clay minerals. However, the presence of NOMs could provoke Cs mobility largely by the indirect effect, i.e., the blocking effect.

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Using Factorial Design to the Robustness Analysis of the Classic Sample Preparation Method for ^{90}Sr Determination in Tea Leaf

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Abstract

The classic sample pretreatment method for ^{90}Sr determination based on a series of precipitations including the separation of Sr from Ca by fuming nitric acid is the standard and popular method around world. To select a best set of operational conditions for such an analytical method with numerous of experimental steps is a difficult task. Even when the optimum values of these factors are found, practically it is difficult in accurately controlling them and sometimes leads to wide variations of results. Procedures for optimization of factors by multivariate techniques have been encouraged, as they are faster, more economical and effective, and allow more than one variable to be optimized simultaneously for sample preparation. However, the application of these techniques for the robustness analysis in the method for radiochemical analysis has been limited. In this study, a robustness test was performed to provide a better insight into which critical process affect ^{90}Sr determination in the sample preparation method. To assess method robustness, the empirical optimum procedures set for this method have been test by slightly modified and were evaluated using the factorial design approach at two levels. The evaluated sensitivity of parameters includes pHs in precipitation procedures, concentration of fuming nitric acid, and times for reactions. The result allows us to analyze the influence of significant factors upon the ^{90}Sr radioactivity and the recovery of carrier and to establish intervals that ensure the robustness of our method.

Keywords *^{90}Sr, robustness, factorial design, fuming nitric acid method*

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A simple method for dehydrogenase assay of soil microorganisms to evaluate the biospheric behavior of C-14 originated in transuranic waste

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Abstract – When carbon-14 (^{14}C) that originated in transuranic (TRU) waste reaches the ground surface in low molecular weight organic forms, it is reported that soil microbial activity has influence on $^{14}CO_2$ gas production. This study aims to develop a simple method to determine soil microbial respiratory activity, which results can be applied to evaluate their correlations with ^{14}C gasification ratios. Respiratory activity was measured using 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetraxolium chloride (INT). Agricultural soil samples were incubated at a solid: liquid ratio of 1 to 10, often used in the gasification ratio experiments. Primarily, INT incubation time, INT-formazan extraction method, and storage time for the extracted INT-formazan were examined.

Keywords – C-14, Soil microbial activity, CO_2 production

I. INTRODUCTION

Carbon-14 (^{14}C) is one of the important radionuclides in transuranic (TRU) waste, which are concerns to human dose assessment due to its relatively long half-life (5730 y) and potential for migration to the biosphere. It was reported that ^{14}C released from TRU waste is partially released as low molecular weight organic forms, such as acetic acid, formic acid, and methanol. These forms have low adsorption properties and are expected to pass through barrier materials. However, there is little information available on the fate of organic ^{14}C after reaching the ground surface. Although it has been showed that soil microbial activity influences CO_2 gas production [1], few studies have been conducted to estimate the gasification ratio using soil microbial activity as an indicator. Understanding the relationship between soil microbial activity and CO_2 gas production may enable to estimate gasification ratio of ^{14}C in different soil in the future.

Since CO_2 gas production is influenced by microbial decomposition of organic ^{14}C, microbial respiratory activity is involved. However, the microbial respiratory activity determination method corresponding to the $^{14}CO_2$ gas production study has not been developed yet. Therefore, this study was conducted to develop a suitable and easily replicable method to determine soil microbial respiratory activities, which results can be applied to evaluate the correlation with ^{14}C gasification ratio. For the microbial activity determination, electron transport system (ETS) was measured by dehydrogenase assay using the redox dye 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetraxolium chloride (INT) as the substrate, which is reduced to INT-formazan by the dehydrogenase enzyme. In the method development, primarily three points were examined—INT incubation time, extraction method, and storage time for the extracted INT-formazan.

II. MATERIALS AND METHODS

Agricultural soil samples that were air-dried and sieved through a 2-mm mesh were incubated beforehand at a solid: liquid ratio of 1 to 10 (0.5 g to 5 mL), which is commonly used in the experiments to determine $^{14}CO_2$ gasification ratio, so as to share the method [2]. After the incubation, 4mL of supernatant was discarded, and INT aqueous solution (0.05%) was added to the sample. INT incubation time was evaluated up to four hours by comparing the amount of extracted INT-formazan detected with a spectrophotometer at 480 nm. INT-formazan extraction methods using methanol as the extractant were also evaluated, regarding the volume of methanol and extracting time. Storage time of extracted INT-formazan before absorbance reading was assessed by keeping samples in the dark at 4℃ or room temperature (approx. 20℃).

III. RESULTS AND DISCUSSION

Based on the experiments, three hours was chosen for INT incubation time because resultant INT-formazan increased over time for the first three hours and then started to be stabilized. As regards INT-formazan extracting method, our experiment showed that mixing samples with 8mL of methanol vigorously for one minute was sufficient. Extracted INT-formazan was stable in both conditions at least for 24 hours. Because our method considered the method of gasification ratio experiments, it enables the evaluation of correlation between soil microbial activity and gasification ratio.

This work was partially supported by the Agency for Natural Resources and Energy, the Ministry of Economy, Trade and Industry (METI), Japan.

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Effect of humic acid on the sorption of selenium (VI) on ferric oxide hydrate

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Abstract – Selenium-79 ($T_{1/2}$= 6.5×10^5 a) is one of the long-lived fission products, which is chemically and radiologically toxic, and one of the main radionuclides of special concerned in the disposal of high level nuclear waste. In this paper we studied the effect of humic acid (HA) on the sorption of selenium (VI) on ferric oxide hydrate (HFO) via *batch-type experiments. We researched the effects of contact time, pH, ion strength, concentration of Se (VI) and HA on the sorption of Se (VI) and found that the equilibrium time of the Se (VI) sorption on HFO was around 3 h, the sorption decreased with the increasing pH and increased with the decreasing ion strength. The sorbed amount decreased with equilibrium concentration in aqueous phase, and the sorption isotherms were fitted to Langmuir equation to figure out the max sorbed amount which was 3.82×10^{-4} mol/g. HA significantly suppressed the sorption of Se (VI).*

Keywords – selenium, sorption, ferric oxide hydrate, humic acid

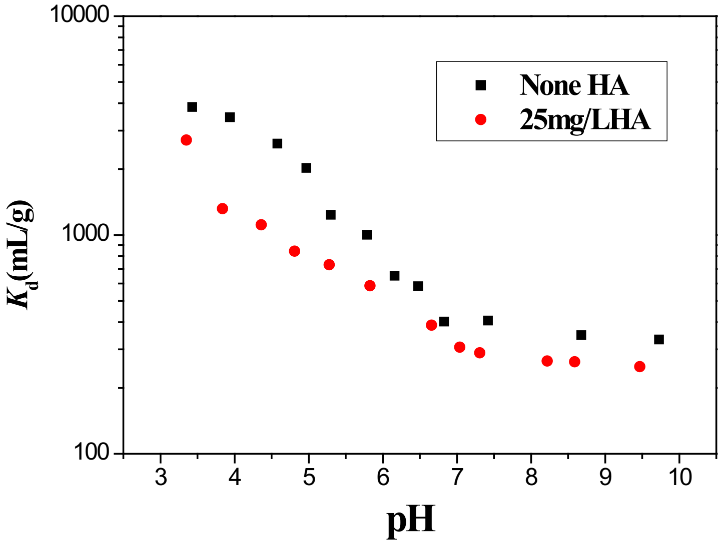

Fig 1. Effect of HA on the sorption of Se (VI) on HFO: C_{Se} = 1.5×10^{-4} mol/L, I = 0.1 mol/L (NaCl), T = 25±1 ℃

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Uranyl ions Adsorption to Na-GMZ and Interactions with FA Adsorption: experiments and modeling

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Abstract –In this work, data for the interactions betwee fulvic acid (FA) with uranyl ions at the surface of Na-GMZ are presented. U adsorption to Na-GMZ in the presence of FA can be well predicted with the SCD model (surface and complex distribution). According to the model calculations, the nature of the interactions between FA and U at Na-GMZ surface is mainly surface complex.

Keywords –Uranyl ions, Na-GMZ, FA, Surface Complex Model

I. INTRODUCTION

In the environment, an important factor of radionuclide mobility is their interaction with mineral–water interfaces. To predict radionuclide mobility, it is necessary to understand fundamental processes such as surface precipitation and surface complexation. Studies of uranium sorption onto mineral surfaces have great practical importance for risk assessment.what’s more, in recent years it has been revealed that many groundwaters in granitoidic environments contain excessive amounts of dissolved U[1].In addition to the effects for sorption, NOM may influence U(VI) distribution via some other mechanisms. In addition, some studies also postulated that U(VI) can form organic complexes with NOM possibly via metal ion bridging The formation of organic U(VI) complexes at the mineral surface or in the solution may decrease or increase U(VI) solubility in groundwater[1-2].

A. Uranyl ions Adsorption to Na-GMZ and Interactions with FA Adsorption

Figures 1 and 2 show the two relatively gentle sorption edges from pH 2 to 8. It is also seen that FA causes a relative enhancement in the U(VI) sorption at pH<6. U adsorption to Na-GMZ in the presence of adsorbed FA can be well predicted with the SCD model (surface and complex distribution) U adsorption to Na-GMZ in the presence of adsorbed FA can be well predicted with the SCD model (surface and complex distribution).

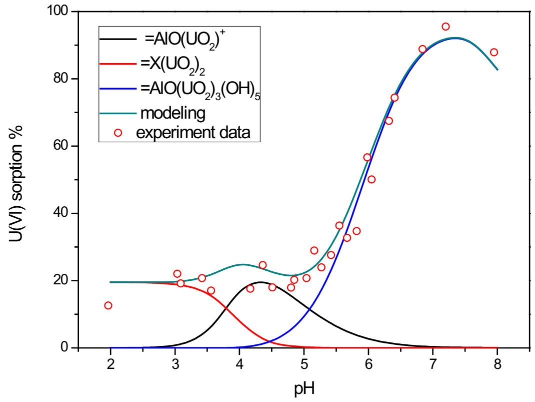

Figure 1 Adsorption curves of U(VI) vs. pH on Na-GMZ , C[U(VI)] =1.003E-4 mol/ L, m/ V = 20 g/ L , T = 22±1 ℃, I =0.1 mol/ L (NaCl).

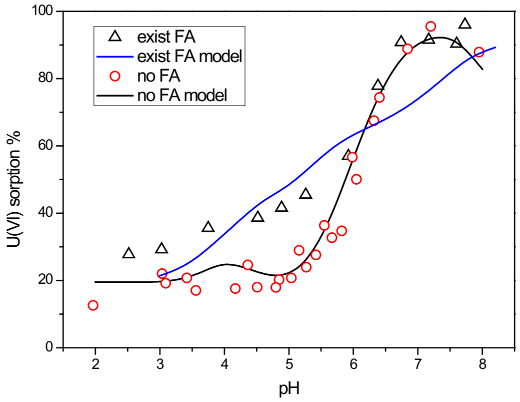

Figure. 2 Adsorption curves of U(VI) vs. pH on Na-GMZ in the absence and presence of FA, C[U(VI)] =1.012E-4 mol/ L, C[FA] =10 mg/L, m/ V = 20 g/ L , T = 22±1 ℃, I =0.1 mol/ L (NaCl).

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Foliar uptake and translocation of stable cesium and iodine by radish

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Abstract – We studied foliar uptake of Cs and I by radish (Raphanus sativus L. cv. Redchim) by applying droplets of a solution of Cs (as CsCl or $CsNO_3$) or I (as NaI or $NaIO_3$) on an upper leaf surface. The uptake of Cs decreased with increasing $CsNO_3$ concentration in the applied solution. Approximately 80% of applied Cs was absorbed no matter what the initial concentration of the applied solution. The uptake of I in either form was independent of the concentration of the applied solution. Approximately 80% of applied I^- was absorbed, whereas 90% of IO_3^- remained on the surface.

Keywords – foliar uptake, translocation, cesium, iodide, iodate

I. INTRODUCTION

Direct deposition of radioactive materials onto crops is an important pathway for radiation dose assessment of radionuclides released from nuclear facilities. Cesium and iodine radioisotopes are transferred into agricultural products both by direct deposition from the atmosphere onto the plants and by absorption from the soil via the roots. We have already reported that foliar uptake of stable Cs is higher from droplets of a CsCl solution than from droplets of a $CsNO_3$ solution. In this study, we investigated the concentration dependence of the foliar uptake of Cs from a CsCl or $CsNO_3$ solution applied as droplets onto the leaf surface of radish plants (*Raphanus sativus L.* cv. Redchim). A similar experiment was carried out with NaI and $NaIO_3$ solutions.

II. MATERIALS AND METHODS

Details of radish plant cultivation and the method for applying the solutions to leaf surfaces are described elsewhere [1]. A solution of CsCl or $CsNO_3$ at a concentration of 0.001, 0.01, 0.1, or 1 g Cs L^{-1} was applied to the upper surface of radish leaves (*Raphanus sativus L.* cv. Redchim) 28 d after germination. A solution of NaI or $NaIO_3$ at a concentration of 0.2, 0.5, or 1 g I L^{-1} was also applied in a similar manner. The plants were harvested 4 d after the application of test solutions and were divided into leaves, root tubers, and lateral roots. The leaves were washed with a solution containing detergent. The washing solution, leaves, and root tubers were analyzed for Cs and I by means of inductively coupled plasma mass spectrometry.

III. RESULTS AND DISCUSSION

We determined the absorption ratios of Cs and I, calculated as (amount of Cs or I detected in the inner leaf or root tuber)/(applied amount of Cs or I), and we plotted the ratios against the Cs or I concentration of the applied solution (Fig. 1). When Cs was applied as a $CsNO_3$ solution, the Cs absorption ratio decreased with increasing Cs concentration in the applied solution. In contrast, when Cs was applied as a CsCl solution, the absorption ratio was nearly constant. There was a clear difference in I absorption ratio between NaI and $NaIO_3$. This result suggests that the chemical form of I strongly affected the absorption ratio of I.

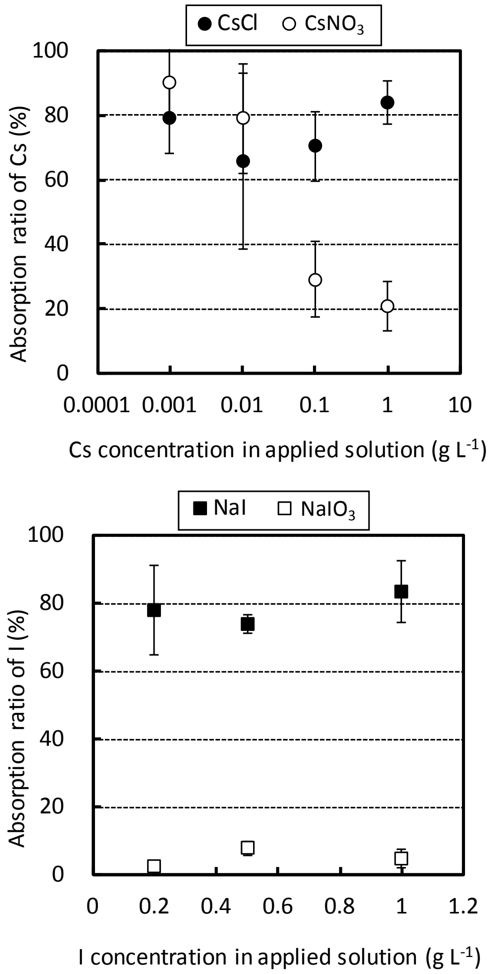

Fig. 1 Absorption ratios of Cs and I into radish plants from upper leaf surfaces

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The rapid determination of radiostrontium from a large amount of seawater (within 72hrs) for an emergency situation

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Abstract – This paper describes the results of the development of an automated radionuclide separator from a large seawater sample. It consists of two parts, which are a concentration part with a cation exchange resin (Dowex50Wx8, Sigma-Aldrich) and a purification part with Sr resin (Eichrom Technology). The volume of raw seawater sample was reduced by about 25% at the concentration part, and radiostrontium was purified at the Sr-resin part. The chemical yield ranged from 92% to 96%. This automated system can simultaneously execute four samples. Using liquid scintillation counting (LSC) and Cherenkov counting, the analysis of Sr-89/90 from seawater could be completed within 3 days.

Keywords – radiostrontium, seawater, automated system, rapid determination

Radiostrontium is one of the main fission products and can be released into the environment through nuclear test or NPP accidents. During emergency situations such as FDNPP, a radionuclide analysis should be completed in a short time to support rapid decision making and maintain public safety. The determination of radiostrontium following traditional methods involves a significant number of separation steps such as precipitation which are time-consuming and labor intensive. This paper describes Modular Automated Radionuclides Separator Sr-seawater (MARS Sr-sw) which allows the purification of radiostrontium from four seawater samples at the same time within 3 days. MARS Sr-sw can reduce the analytical time and labor intensity.

MARS Sr-sw was based on column chromatography. It consists of a concentration part and purification part, which contain a control module, a pump module, a valve module, and four column modules. We developed the control software using LabVIEW (National Instrument). The operational procedure is shown in figure 1.

In the concentration part, Dowex50Wx8(100~150um) was used to concentrate a large seawater sample, the volume of which was reduced from 20% to 30%. Seawater consists of many cations, such as Ca^{2+}, Mg^{2+} and Sr^{2+}. However, the selectivity of Sr for Dowex50Wx8 is relatively higher than that of Ca or Mg, which are dominant ions in seawater. It enables Sr concentration from seawater without significant loss of Sr. In a Sr breakthrough test, 500g of Dowex50Wx8 can isolate 99% of Sr from 10L seawater (0.16mg Sr/g of Dowex50Wx8). The low level of Ca was found in the elution sample, which did not affect the Sr recovery by Sr resin. The Sr recovery was quantitative for Ca levels of up to 320mg, which was higher than that of Ca in the elution sample. About 99% of Sr in seawater from 1L to 10L was collected by the concentration part. A pre-concentration of Sr from 10L seawater was completed within 5hrs.

We prepared a Sr resin column using a benchmark glass column (Omnifit Ltd.) in the purification part. The amount of Sr resin depends on the sample size because the level of Sr in seawater is around 8ppm. All procedures were automatically completed by MARS Sr-sw. It took 4hrs to complete the purification of Sr from 10L of seawater The Sr recovery was about 93%.

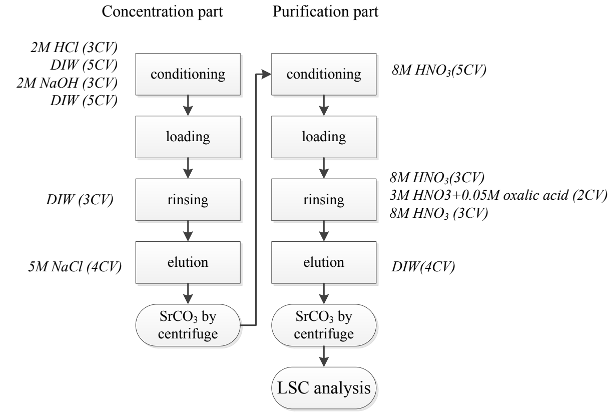

Figure 1 Procedure of MARS Sr-sw (CV: column volume)

This study suggests that MARS Sr-sw can complete the determination of radiostrontium from a large amount of seawater within 3 days using LSC and Cherenkov counting which provide spectral information. It allows the identification of Sr-89/90. The remarkable aspects of MARS Sr-sw are the automation and capability to handle multiple samples at the same time.

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Peak Tailing Correction in Measurement of ^{222}Rn/^{220}Rn Activity Concentration with α Spectrum Method

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Abstract – α spectrum method is one of the most important methods for ^{222}*Rn/*^{220}*Rn concentration measurement. The peak tailing from high energy α particle to low energy region influences the measurement accurateness. To improve α spectrum method, the theory of peak tailing was analyzed and a series of calibrating experiments was carried out. For a commercial radon monitor ERS-2, the experiment values of peak tailing correction factors* C_5 *and* K_4 *is 15.25%±0.24% and 36.23%±0.68%, the calibration factors of* ^{222}*Rn and* ^{220}*Rn(*KF_{Rn} *and* KF_{Tn}*) is 2.08±0.02 Bq•m*$^{-3}$*/cph and 5.23±0.28 Bq•m*$^{-3}$*/cph. After peak tailing correction, the measurement results agree with reference value very well.*

Keywords – ^{222}Rn/^{220}Rn; α spectrum method; peak tailing correction factor; calibration factors

23-ENP-17

Underwater Analysis of Sediment Chemistry using an Autonomous Platform

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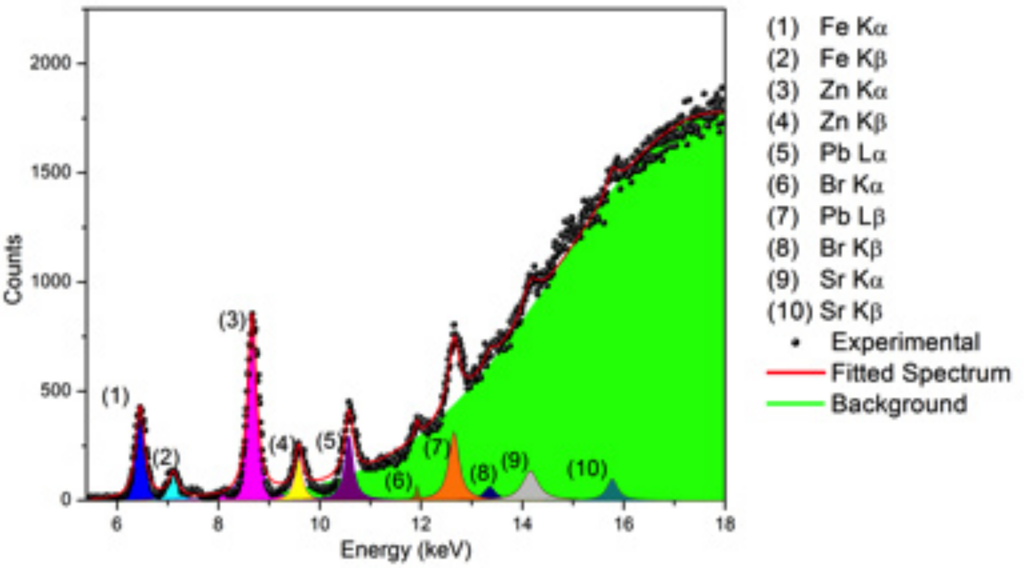
Abstract – The increasing number and size of marine reserves comes with additional challenges and responsibilities concerning environmental monitoring, including sediment chemistry. The characterisation of sediments can shed light on past events like anthropogenic contamination and natural events as well as provide information to guide mineral exploration. However, the costs associated with the monitoring of sediment chemistry are high and traditional methods can disturb the sediment and influence the results. Here we present original results of X-ray fluorescence measurements performed underwater, in-situ, using an autonomous underwater vehicle in the Derwent Estuary, which is located in South East Tasmania Australia and has a long history of contamination from heavy metals. To demonstrate the capability of performing in situ, underwater analysis of sediments we analysed three distinctive sites on the Derwent estuary floor. XRF spectra with good signal-to-noise ratios have been recorded. The results show spatial variation of zinc, lead and iron concentration. The contamination of heavy metals we found reflects proximity to potential sources and patterns of the hydrodynamics of the estuary. We suggest that XRF in submersible autonomous platforms could be used to perform an initial, cost effective, assessment of heavy metals contamination of sediments to guide comprehensive surveys.

Keywords – XRF, Sediments, AUV



XRF spectra recorded underwater. Typical least-squares fitted XRF spectrum record at site D (Ralphs Bay) at 10m-depth. The broader line between 10 keV and 30 keV overlaps Lead, Bromine and Strontium signals and are caused by bremsstrahlung from the XRF housing (high density polypropylene).

Development of the in-line, multiple elution cartridge-based radioisotope concentrator device for increasing ^{99m}Tc and ^{188}Re concentration of commercial radionuclide generator eluates

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I. INTRODUCTION

^{99m}Tc is used in approximately 85% of diagnostic imaging procedures in nuclear medicine world-wide. ^{188}Re is important radio-therapeutic radionuclide. The expansion of ^{99m}Tc and ^{188}Re application depends on the generator availability. However, the cost-effective utilisation of ^{99m}Tc and ^{188}Re generators and the quality of SPECT imaging diagnosis and radiotherapy are controlled by the ^{99m}Tc and ^{188}Re generator operation/elution management, which is determined by the ^{99m}Tc and ^{188}Re concentration in the generator eluate. Generally ^{99m}Tc and ^{188}Re eluates are produced from the generators in fixed volume and the ^{99m}Tc and ^{188}Re concentration of the eluates decreases with the life time of the generators due to radioactive decay of parent nuclides ^{99}Mo and ^{188}W, respectively. Consequently, the useful life time of the generator is also a function of available ^{99m}Tc and ^{188}Re concentration of the eluate. The injection dose activity of ^{99m}Tc- and ^{188}Re-based radiopharmaceuticals delivered in 1 mL solution (^{99m}Tc- or ^{188}Re- concentration, mCi/mL) is an important factor in determining the useful life time of the ^{99m}Tc and ^{188}Re generators and the quality of ^{99m}Tc based SPECT imaging diagnosis or ^{188}Re –based radiotherapy, respectively. So, the radioisotope concentrator device should be developed to increase the concentration and quality of injectable ^{99m}Tc and ^{188}Re eluates and the life time of the generators.

II. METHODS

A multi-elution, radioisotope concentrator device [1], in-line eluted via evacuated-vial and through disposable sterile filters was developed to increase the concentration of ^{99m}Tc or ^{188}Re in the elution of aged commercial ^{99m}Tc or ^{188}Re generators. The increase in ^{99m}Tc concentration in the eluate enhances the utilisation of technetium in Technegas generator-based lung perfusion (100-250 mCi/mL) and other SPECT (20-30 mCi/mL) imaging studies. A self-shielded radioisotope concentrator device (Fig. 1a) was created based on a newly developed sorbent/concentrator column which selectively retains $^{99m}TcO_4^-$ ions from downstream of 10 mL ^{99m}Tc solution eluted from the generator. The eluate is freed from Cl^- and MoO_4^- ions by passing through a competitive ion-selective column. ^{99m}Tc is then eluted from the concentrator column with 1.0 mL saline into an evacuated vial through a millipore filter and ready for injection. The design of the device in form of a disposable cartridge was optimised to make elution process effective, simple, sterile and radiation safe. Gentech ^{99m}Tc generator of 110 GBq activity eluted with 10 mL saline was chosen to test our radioisotope concentrator device.

III. RESULTS

As a result obtained from our project, the ^{99m}Tc eluate was concentrated more than 10-fold with a ^{99m}Tc recovery yield of > 85% using this radioisotope concentrator device. 5 or 10 repeated elutions were successfully performed with each cartridge coupled to the 10 mL or 5 mL saline solution eluted generators, respectively. So, each cartridge can be effectively used for one week in the hospital environment for radiopharmaceutical formulation. The useful lifetime of the ^{99m}Tc generator was significantly extended from 10-20 days for the generators of 300-3000 mCi activity, respectively. The ^{99}Mo impurity in the ^{99m}Tc solution eluted from the Gentech generator was totally eliminated by this radioisotope concentrator device (Fig. 1c).

IV. CONCLUSION

We conclude that the radioisotope concentrator device functioned well and is robust in operation. This device will, to some extent, mitigate the global ^{99m}Tc crisis. This concentrator device is under patent-pending.

Fig. 1. Radioisotope concentrator device with standard accessories (a) and the radioisotope concentrator device coupled with ^{99m}Tc generator for in-line elution/concentration of ^{99m}Tc eluate (b).

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Production and Preclinical Evaluation of Diagnostic and Therapeutic Radionuclides in Tumor-Bearing Mice: Recent Developments at Paul Scherrer Institute

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Abstract – At PSI we have initiated a close collaboration of the Laboratory of Radiochemistry and Environmental Chemistry and the Center for Radiopharmaceutical Sciences to bring novel diagnostic and therapeutic radiopharmaceuticals to the point of clinical trials. Pre-clinical studies using tumor-bearing mice were conducted at PSI and ETH Zürich. At the university hospital in Bern the required infrastructure for clinical trials was established.

Keywords – theranostics, diagnostic radionuclides, ^{44}Sc, ^{152}Tb, ^{155}Tc, therapeutic radionuclides, ^{149}Tb, ^{161}Tb, DOTA-folate conjugate, targeted radionuclide therapy,

I. INTRODUCTION

Radiopharmaceuticals which comprise metallic radionuclides are valuable diagnostic and therapeutic tools in nuclear oncology. Several clinics worldwide have started targeted radionuclide therapies based on ^{177}Lu- or ^{90}Y-DOTA-TOC, a somatostatin receptor targeting peptide to treat metastatic gastro-entero-pancreatic neuroendocrine tumors. For diagnostic purposes ^{177}Lu can be replaced with the short-lived positron emitter ^{68}Ga available from a ^{68}Ge/^{68}Ga generator system.

Further development and implementation of such innovative radiometallated drugs depend, however, directly on the availability of radiometals. Compared to other lanthanides, the element Tb comprises a quadruplet of clinically attractive radionuclides, such as ^{152}Tb and ^{155}Tb, with suitable decay properties for PET and SPECT imaging, and, ^{149}Tb and ^{161}Tb, suitable for targeted alpha- and beta-radionuclide therapy. To assess the diagnostic and therapeutic features of these four radioisotopes we employed the folic acid/folate receptor (FR)-targeting strategy.

In addition, we investigated the use of ^{44}Sc ($t_{1/2}$ = 3.97 h, E+av = 632 keV) as a valuable alternative to short-lived ^{68}Ga ($t_{1/2}$ = 68 min, $E\beta^{+}_{av}$ = 830 keV) for imaging of cancer prior to ^{177}Lu-based radionuclide therapy. The aim of the study was the preclinical evaluation of a folate conjugate labeled with cyclotron-produced ^{44}Sc and to compare these data with those of the ^{177}Lu-labeled match.

A. Production of Radionuclides

The neutron deficient ^{149}Tb, ^{152}Tb, and ^{155}Tb were obtained in several beam times at CERN-ISOLDE by spallation of a Ta target with 1 GeV protons followed by mass separation. The low energy isobaric ion beams were implanted in Zn covered Au foils.

A production facility for up to 20 GBq of n.c.a. ^{161}Tb was established at PSI. Samples of enriched ^{160}Gd were irradiated at PSI-SINQ, FRM-II Munich, or ILL Grenoble. It was possible to routinely produce ^{161}Tb of excellent radionuclidic purity and highest specific activity (i.e. >3700 GBq/mg), so that labeling of i.e. DOTATATE was possible with a molar ^{161}Tb:DOTATATE – ratio of 1:3.5 with 99.41 % yield.

^{44}Sc was produced via the ^{44}Ca(p,n)^{44}Sc-nuclear reaction at the PSI Injector 2 cyclotron using highly enriched ^{44}Ca-targets. Separation from the target material was carried out by a semi-automated process using extraction- and cation exchange chromatography.

B. Preclinical Evaluation

A summary of results obtained in *in-vivo* experiments with all four Tb-isotopes is shown in Figure 1.

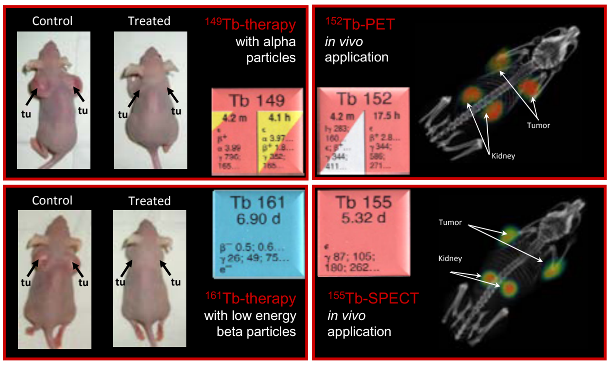

Figure 1: Left-hand side: treatment of tumor bearing mice with ^{149}Tb (α-particle therapy) and ^{161}Tb (β-particle therapy) DOTA-FOLATE. Right-hand side: PET and SPECT images of tumor bearing mice with ^{152}Tb and ^{155}Tb DOTA-FOLATE, respectively.

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^{99}Mo production by ^{100}Mo(n,2n)^{99}Mo using accelerator neutrons

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Abstract – We proposed a new route to produce a medical radioisotope ^{99}Mo by the ^{100}Mo(n,2n)^{99}Mo reaction using accelerator neutrons. A high-quality ^{99}Mo with a minimum level of radioactive waste can be obtained by the proposed reaction. The decay product of ^{99}Mo, ^{99m}Tc, is separated from ^{99}Mo by the sublimation method. The proposed route could bring a major breakthrough in the solution of ensuring a constant and reliable supply of ^{99}Mo.

Keywords – ^{99}Mo radioisotopes, diagnosis, accelerator neutrons, neutron induced reaction, SPECT

I. INTRODUCTION

^{99m}Tc (half-life, $T_{1/2}$ = 6.0 h), the daughter nuclide of ^{99}Mo ($T_{1/2}$ = 66 h), is the most common radioisotope used in diagnosis, and its use accounts for 80% of all nuclear medicine procedures worldwide.1) ^{99m}Tc has a versatile chemistry that allows it to be incorporated into all sorts of molecules, and because of the short half-life of ^{99m}Tc, ^{99m}Tc is routinely produced in ^{99}Mo/^{99m}Tc generators. ^{99}Mo has been mostly produced by the fission reaction of highly enriched ^{235}U in research reactors. However, an unscheduled shutdown of some of these reactors has recently caused a crisis shortage of ^{99}Mo worldwide, which triggered widespread discussions on the ^{99}Mo supply.2) The ^{99}Mo production using a charged-particle induced nuclear reaction, such as the ^{100}Mo(*p*,*pn*)^{99}Mo, ^{100}Mo(*d*,*p2n*)^{99}Mo, and ^{100}Mo(*p*,*2n*)^{99m}Tc reactions, has been investigated.3) We proposed a new route to produce ^{99}Mo using fast neutrons from an accelerator,4) and we have been carrying out important steps necessary to obtain high-quality ^{99m}Tc.

II. ^{99}MO PRODUCTION BY ACCERELATOR NEUTRONS

Intense neutrons with an average energy of 14 MeV are necessary to produce a large amount of ^{99}Mo by the ^{100}Mo(*n*,2*n*)^{99}Mo reaction. Neutrons can be produced from the ^{nat}C(*d*,*n*) or ^{9}Be(*d*,*n*) reactions at deuteron energy of 40 MeV. The production yield of ^{99}Mo was estimated using the evaluated cross section of ^{100}Mo(*n*,2*n*)^{99}Mo,5) and the neutron intensity. Typically, we assumed a metallic ^{100}Mo sample (251 g, 100% enriched) with a radius of 2 cm and a thickness of 2 cm was irradiated by neutrons. The sample was placed 2 cm downward from the ^{nat}C or ^{9}Be target.

The ^{99}Mo harvest frequency, determined by the ratio, $R = N(^{99}\mathrm{Tc})/N(^{99m}\mathrm{Tc})$, is also important. Here, $N(^{99}\mathrm{Tc})$ and $N(^{99m}\mathrm{Tc})$ are the numbers of ^{99}Tc ($T_{1/2} = 2.1 \times 10^{5}$ y, useless in diagnostic use), and ^{99m}Tc. The calculated *R* values were 1.2, 3.0, and 11 for one, two and six-days of irradiation. The harvest frequency will be every two or three days by considering the available amounts of ^{100}Mo and the ^{99}Mo decay during the ^{100}Mo sample irradiation.

III. EXPERIMENT AND RESULT

^{99}Mo was produced by irradiating an enriched ^{100}MoO$_3$ sample with ~14 MeV neutrons from the ^{3}H(*d*,*n*)^{4}He reaction at the Fusion Neutronics Source (FNS) facility of Japan Atomic Energy Agency (JAEA). Gamma-rays from the decay of ^{99m}Tc and ^{99}Mo were clearly observed. Yields of impurity isotopes, such as ^{97}Zr and ^{97}Nb, were much smaller than that of ^{99}Mo.

To separate high-quality ^{99m}Tc from the produced ^{99}Mo, we used the sublimation method, which is based on a different volatility of Tc$_2$O$_7$ and MoO$_3$.6) The irradiated ^{100}MoO$_3$ sample was placed in a furnace, and heated so as to form gaseous materials containing vaporized ^{99m}Tc$_2$O$_7$ in a stream of oxygen carrier gas. ^{99m}Tc was condensed at the exit of the furnace, and was eluted with a saline solution. As a result of the γ-ray measurement of the separated ^{99m}Tc, the upper limits of γ-rays from any impurity isotopes were found to be very small. A sublimation method allows us to recycle any irradiated enriched ^{100}Mo. Labeling efficiency, an important factor in the compounding and dispensing of radiopharmaceuticals, was shown to be higher than 90% by formulating a radiopharmaceutical.

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23-RPP-04

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Production and Separation of ^{64}Cu and ^{67}Cu using 14 MeV Neutrons

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Abstract –^{64}Cu and ^{67}Cu were produced from 14 MeV neutron irradiated natural ZnO and enriched ^{64}ZnO targets via ^{64}Zn(n, p)^{64}Cu and ^{67}Zn(n,p)^{67}Cu reactions. The ZnO disc targets were irradiated for 6 hours by 14 MeV neutrons, which are generated by bombarding a tritiated titanium target with deuteron beam at the Fusion Neutronics Source (FNS) at Japan Atomic Energy Agency (JAEA). After irradiation, ion chromatographic separations were carried out to obtain purified no-carrier-added Cu radionuclides. Elution pattern clearly showed separation of ^{64}Cu and ^{67}Cu giving a yield of > 90%, and a very low radionuclide impurity ratio of ^{65}Zn within the purified ^{64}Cu.

Keywords – ^{64}Cu, ^{67}Cu, radioisotope production, 14 MeV neutrons, nuclear medicine,

I. INTRODUCTION

^{64}Cu ($T_{1/2}$ 12 h, E.C.= 43%, β^+ = 18%, β^- = 40%) and ^{67}Cu ($T_{1/2}$ 62 h, β^- = 100%) [1] have attracted attention in radiopharmaceutical applications for their unique decay properties and chemical characteristics [2]. Being a positron and a beta emitter, ^{64}Cu is a strong candidate for the agents of both positron emission tomography imaging and targeted radiotherapy. ^{67}Cu, a longer-lived beta emitter can be used for radiotherapy to treat small tumors with a diameter of 2-3 mm [3]. Cu radionuclides can be produced either with cyclotrons by bombarding Ni or Zn targets with proton beams, *e.g.* ^{64}Ni(p,n)^{64}Cu, ^{68}Zn(p,αn)^{64}Cu, ^{68}Zn(p,2p)^{67}Cu, or in a nuclear reactor by bombarding a target with thermal neutrons [4,5]. The studied methods using cyclotron generated proton beams, however, include relatively expensive targets, unwanted radionuclides or complex chemical separation [5-8]. The current study investigates a production route of ^{64}Cu and ^{67}Cu from ^{64}Zn(n,p)^{64}Cu and ^{67}Zn(n,p)^{67}Cu reactions, by irradiating ^{nat}ZnO or ^{64}ZnO with 14 MeV neutrons [9], and a subsequent chemical separation.

II. EXPERIMENTAL

^{nat}ZnO and ^{64}ZnO (99.935% enriched ^{64}Zn) disc targets ($20\phi \times 5$ mm, 5 g) were individually irradiated by 14 MeV neutrons at FNS in JAEA for 6 hours. The average neutron flux was *ca.* 1.0×10^{11} n/s generated via ^{3}H(d,n)^{4}He reaction. The irradiated target was dissolved in 20 ml of 36 wt% HCl after which the pH was adjusted to 3.5-4.0 with 10 M NaOH. The sample was passed through a Chelex-100 exchange column ($1.1\phi \times 11.5$ cm) followed by washing with 100 ml of 0.001 M HCl to remove Zn [10]. The ^{64,67}Cu was then eluted with 20 ml of 2 M HCl and passed through an AG1-X8 column ($0.8\phi \times 12.0$ cm) to remove traces of Zn followed by a washing with 10 ml 2 M HCl [10]. The drop rate was regulated to be 1 ml/min throughout the separation. The purified ^{64,67}Cu solution was evaporated and dissolved in 1 ml 0.4 M ammonium acetate (pH5.5), filtered, and then reacted with TETA (1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetraacetic acid) solution for 2 hours [11]. The labeling yield was determined by silica gel TLC / 1:1 methanol-10 % ammonium acetate.

III. RESULTS & DISCUSSION

The production of $^{64,\,67}$Cu by irradiating $^{nat,\,64}$ZnO with 14 MeV neutrons reduced the consequent chemical separation process because of fewer side products (*e.g.* only ^{65}Zn if enriched ^{64}ZnO is used), which saves considerable time in comparison with $^{64,\,67}$Cu production by proton-irradiation [8, 10]. The time required for the column separation process was 3 hours and could be shortened further if the system was fully automated. Over 95% of the $^{65,\,69}$Zn side products were separated by the ion exchange Chelex-100 column, which can be recovered as $Zn(OH)_2$ by alkaline precipitation and decomposed to ZnO upon heating [8]. Radioactivity of 0.79 MBq/g ^{64}Cu, 6.3 kBq/g ^{67}Cu from ^{nat}ZnO and 2.5 MBq/g ^{64}Cu were obtained from ^{64}ZnO at the end of bombardment. A high separation efficiency was observed from the Chelex-100 (98%) and the AG1-X8 (95%) based on the ^{64}Cu yield of two experiments, with the final product having a ^{65}Zn radionuclide impurity below the detection limit of gamma-ray spectrometry. The labeling efficiency of Cu-TETA for clinical radiotherapy applications was found to be good at 94.4%.

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Novel radiochemical separation of arsenic from selenium for ^{72}Se/^{72}As generator.

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Keywords – selenium-arsenic separation, extraction chromatography, PET, ^{72}Se/^{72}As generator

The potential usage of arsenic isotopes for nuclear medicine has been reported recently. One of the way for obtaining appropriate radioarsenic species is using radionuclide generator, where As is formed by the radioactive decay, eg. $^{72}\text{Se} \rightarrow {}^{72}\text{As}$. A new radiochemical separation scheme based on extraction chromatography for isolation As from Se is presented. The distribution coefficients of As and Se on prepared sorbents were determined in order to find the best condition for separation of both elements. Batch experiments were verified by column studies. Elaborated radiochemical separation scheme insures high selectivity and radionuclide purity of separated arsenic fraction, whereas examined sorbents have been found to have a very high selectivity with reference to selenium (IV). Arsenic is easily eluted by diluted HCl and NaCl solutions. Proposed approach insures high selectivity and radionuclide purity of separated arsenic fraction; it is also characterized by high elution efficiency (>95 %) using small volume (2 mL) of 0.9 % NaCl with very low breakthrough (<0.01 %) of selenium.

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Training Program of Synthesizing a Radiopharmaceutical in KAERI

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Radiopharmaceuticals have widely been used in diagnoses of various medical conditions. Medical facilities using radiopharmaceuticals such as 2-deoxy-2-[^{18}F]fluoroglucose (^{18}F-FDG) have increased in number in Korea. ^{18}F-FDG is absorbed into cells such as brain and kidney along with cancer cells. Without the hydroxyl group replaced to ^{18}F it fails to undergo glycolysis in the cell and cannot leave it before its radioactive decay, which provides a quantitative distribution of glucose uptake and phosphorylation in cells. As ^{18}F-FDG is used in many medical facilities, a reliable quality control system is needed in its synthesis in addition to technical staff who can handle the process. KAERI recently started to operate its own 30-MeV cyclotron at Jeongeup, where ^{18}F-FDG is to be produced. A month-long training program is planned for college undergraduates and graduates to learn synthesis of ^{18}F-FDG and its handling, which would fill national future demand of skilled technical personnel.

23-RPP-07

Synthesis of ^{64}Cu-Labeled MARSGL Peptide as an Imaging Probe for HER2/neu Overexpressing Tumors

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Abstract – ^{64}Cu was produced by the cyclotron using ^{64}Ni(p,n)^{64}Cu nuclear reaction. MARSGL peptide has high affinity to HER2/neu overexpressing in various cancer cells. In this study, ^{64}Cu-DOTA-MARSGL was designed and synthesized as a novel PET imaging probe for HER2/neu overexpressing tumors.

Keywords – ^{64}Cu, Positron, DOTA, Peptide, HER2/neu

Copper-64 is an attractive radionuclide for positron emission tomography (PET) imaging as well as radiotherapy due to its half-life ($T_{1/2}$=12.7 h) and decay characteristics (β^+ 17.4%, β^- 39%). MARSGL (H-Met-Ala-Arg-Ser-Gly-Leu-OH) is a linear peptide having high affinity to HER2/neu overexpressing in various cancer cells [1]. 1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) is a macrocyclic ligand for various metal ions.

In this study, we designed ^{64}Cu-labeled MARSGL peptide conjugated with DOTA as an imaging probe for HER2/neu overexpressing tumors.

^{64}Cu was produced by the AVF cyclotron of Takasaki Ion Accelerators for Advanced Radiation Application facility at Japan Atomic Energy Agency using the nuclear reaction of ^{64}Ni(*p,n*)^{64}Cu. Radiochemical separation of ^{64}Cu was carried out by chelating ion-exchange method [2].

Protected MAR(Pbf)S(^{t}Bu)GL-Trt(2-Cl) resin was prepared by solid-phase peptide synthesis using automatic peptide synthesizer (Aapptec, Titan 357). As shown in Fig.1, tri-*tert*-butyl 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate was allowed to react with the peptide resin by 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl) and 1-hydroxy-1H-benzotriazole (HOBt) in dimethylformamide. And then the cleavage and the deprotection were performed at the same time using trifluoroacetic acid (TFA), 1,2-ethanedithiol (EDT), and triisopropylsilane (TIS).

^{64}Cu-labeling of DOTA-MARSGL was carried out in acetate buffer. The formation of ^{64}Cu-DOTA-MARSGL was determined by reversed-phase TLC and HPLC.

In order to evaluate the usefulness of ^{64}Cu-DOTA-MARSGL peptide as a PET imaging probe, *in vitro* stability and affinity to HER2 are under investigation.

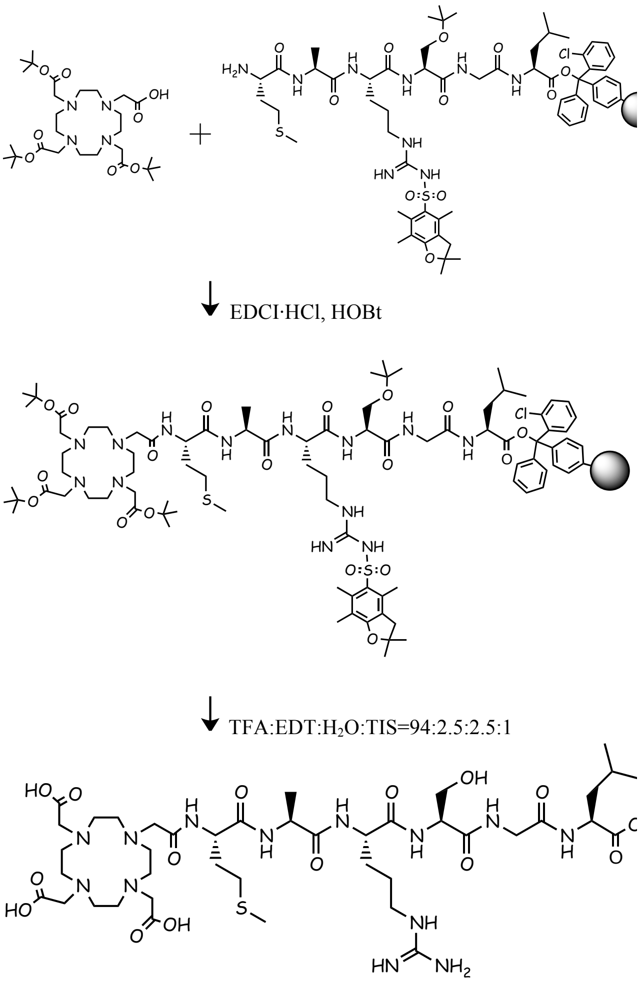

Fig. 1 Synthesis of DOTA-MARSGL by solid-phase conjugation.

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Molybdenum Isotope Fractionation in Ion Exchange Reaction by using Anion Exchange Chromatography

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Abstract – The molybdenum isotope fraction in ion exchange reaction in hydrochloric acid solution was investigated by using the anion exchange chromatography. We confirmed that the heavier isotopes are enriched in solution phase.

Keywords – technetium-99m, molybdenum-99, molybdenum isotope, isotope enrichment

I. INTRODUCTION

Technetium-99m (^{99m}Tc) is one of the most important radioisotopes in nuclear medicine. ^{99m}Tc is generated from molybdenum-99 (^{99}Mo). Now, ^{99}Mo is mainly produced by fission of highly enriched uranium-235 (HEU). However, the supply of 99Mo becomes unsteady, since the reactors for the generation of ^{99}Mo become older. In addition, the use of HEU causes the problem of nuclear proliferation. Thus, new production technologies for ^{99}Mo and ^{99}mTc by non-use of HEU are required and investigated [1,2]. The typical technologies use the molybdenum targets, such as ^{100}Mo(n, 2n)^{99}Mo [3], ^{100}Mo(p,x)^{99}Mo or ^{99m}Tc [4], ^{98}Mo(n,γ)^{99}Mo [5]. These methods are required the enriched molybdenum isotopes. We are investigating the molybdenum isotope separation by chemical exchange. In the present work, the molybdenum isotope fractionation by ion exchange is studied. The geochemists have also much interest in the molybdenum isotope fraction in chemical reaction, recently [6,7]. Our study may help the understanding of molybdenum fraction in nature.

II. EXPERIMENTAL

1. Materials

$Na_2MoO_4 \cdot 2H_2O$ supplied by Junsei Chemical Co., Ltd. was used. The purity of Mo(VI) was more than 99.0 %. The acidic concentrations of the solutions dissolved Mo species of 0.1 M(M = mol/L) were adjusted to 0.1, 0.5, 1.0, 2.0, 4.0, 6.0, 9.0, and 11.2 M using HCl. The high-porous benzimidazole-type anion-exchange resin embedded in high-porous silica beads which has two functional groups consisted of 4-(1-methylbenzoimidazole-2-yl)phenyl and 4-(1,3-dimethyl-benzoimidazole-2-yl)phenyl was used for Mo isotope fractionation.

2. Chromatography Experiments

Five columns connected in series were used for the isotope fractionation chromatography. Each column has the diameter of 0.8 cm and the length of 100 cm. Total volume of the resin packed into these columns was 84.8 mL. The temperature of columns was kept at 308 K. The breakthrough experiments using 0.1 M of Mo species dissolved in 0.10 - 11.2 M HCl were performed. The flow rate was controlled at 0.35 mL/min by using the high pressure pump made of Nihon Seimitsu Kagaku Co., Ltd. The Mo isotope ratios were measured using ICP-MS(7700x, Agilent). Mo concentrations in samples for isotope ratio measurements were adjusted at *ca.* 1.0 ppb (ppb = ng/g), and all sample solutions was used as 2.0 % HNO_3.

III. RESULTS AND DISCUSSION

The breakthrough experiments for Mo isotope fractionation were carried out under conditions, $[Mo]_T$ = 0.1 M(subscript T means total concentration), $[HCl]_T$ = 0.1 - 11.2 M, and Temp. = 308 K. The typical result of Mo isotope fractionation was shown in Figure 1. As shown in the figure, it was found that heavier isotopes are disproportionately distributed into a solution phase. The hexavalent molybdenum in solution is known to have many type of chemical species, such as oxoacid ions, complexes, and their combines. Mo isotope fractionations are attributed to the chemical exchange among their species.

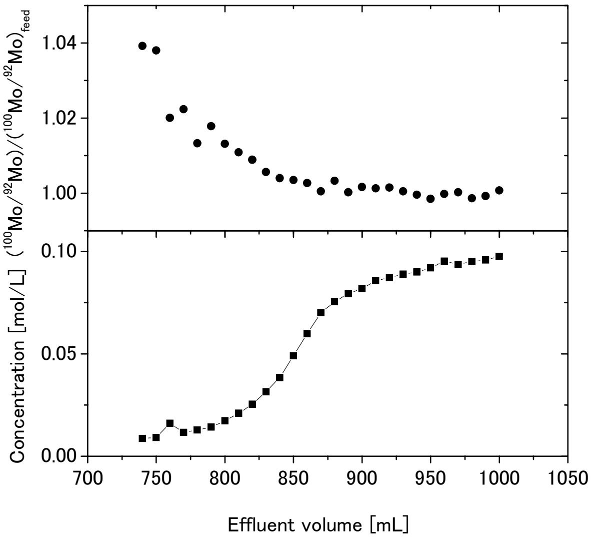

Figure 1. Molybdenum breakthrough curve and molybdenum isotope fractionation by anion exchange chromatography using 2 M HCl solution.

ACKNOWLEDGEMENT

This work was partially supported by the Grant-in-Aid for Challenging Exploratory Research (KAKENHI No. 24656567).

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The Mechanism of Oxidized Multi-walled Carbon Nanotubes across Placental Barrier and Its Effects on Pregnany

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Abstract

The mechanism of nanoparticles across placental barrier was studied post injected intravenously with solution of oxidized multi-walled carbon nanotubes (oMWCNTs) labeled by technetium-99m into pregnant mice, the rate and mechanisms of abortion were also investigated via measuring content of progesterone and estradiol in maternal serum. The results indicated that oMWCNTs could across placental barrier and enter into fetus body, and caused high distribution of fetal lung, and then eliminated gradually; oMWCNTs could decrease level of progesterone and increase level of estradiol in serum, that depended on exposure dosage and time, but weakened with the extension of gestational ages; the abortion rate of primiparous, second-parous and fourth-parous pregnant mice caused by oMWCNTs was 70%, 40% and 50%, respectively, and also the maternal body weight growth were inhibited until gestational age of 13, 10 and 11 days, respectively. Therefore, oMWCNTs can damaged normal pregnancy, and that was more serious for primiparous.

Keywords: oMWCNTs; placenta; biodistribution; abortion rate; progestational hormone.

Table 1.The statistics of abortion rates after exposure oMWCNTs (n=10).

Group	Ectroma (colpo-bleeding)	Normal parturition	Average weight change before and after production /g	Total abortion rate
First-oMWCNTs	7	3	8.57±8.95*	70%
First-control	1	9	20.73±9.00	10%
Second-oMWCNTs	4	6	13.99±9.44	40%
Second-control	0	10	15.83±4.24	0
Fourth-oMWCNTs	5	5	11.18±5.82	50%
Fourth-control	3	7	12.72±5.78	30%

*$p<0.05$, group *vs*. normal.

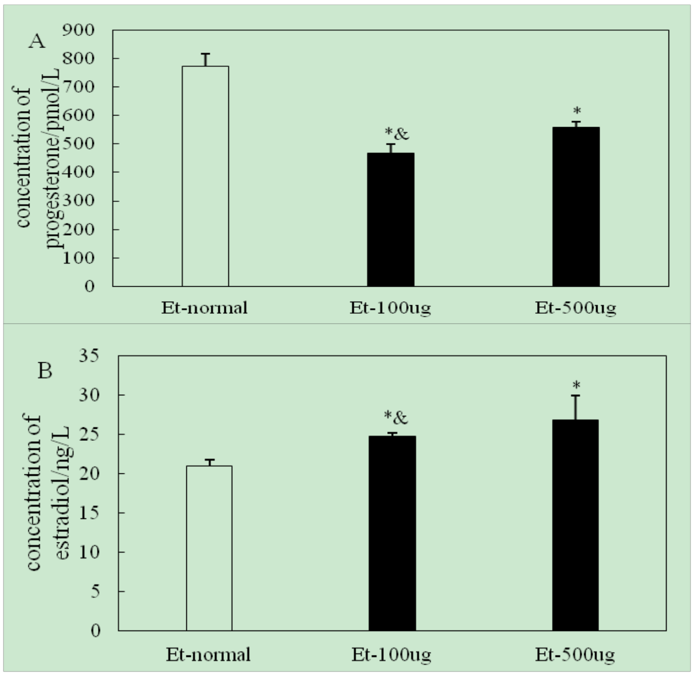

Figure. The exposure time of oMWCNTs effects on the progesterone in the mice at gestational age of 18 days (n=4-5, *$p<0.05$, group.*vs* normal, &$p<0.05$,group *vs*. Et-500ug).

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Prompt Gamma Test of a Large Volume Lanthanum Bromide Detector

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Abstract – Response of a large $LaBr_3$:Ce detector has been tested over broad range of gamma rays using prompt gamma ray neutron activation analysis technique,. Due to its larger size, the detector has poorer energy resolution a 76 mm x 76 mm (diameter x height) cylindrical $LaBr_3$:Ce detector

Keywords – Large $LaBr_3$:Ce detector, performance tests using prompt gamma rays, portable neutron generator, chlorine, mercury and cadmium contaminated bulk water samples

I. INTRODUCTION

The application of Prompt Gamma-ray Neutron Activation Analysis (PGNAA) technique is growing further due to the fabrication of radiation hardened lanthanum-halide ($LaBr_3$:Ce and $LaCl_3$:Ce) gamma ray detectors. Although $LaCl_3$:Ce detectors and $LaBr_3$:Ce detectors have a fast rise time, excellent light output and energy resolution but they have intrinsic activity, which increases with detector volume. This may limit their utilization in PGNAA application. King Fahd University of Petroleum and Minerals , Dhahran, Saudi Arabia has acquired a cylindrical 100 mm x 100 (diameter x height) $LaBr_3$:Ce detector for its prompt gamma ray program. Performance test of the large volume detector were carried **out** over broad range of gamma ray energies emitted in thermal neutron capture in bulk samples.

A prompt gamma ray neutron activation analysis setup has been developed using a MP320 D-D reaction-based portable neutron generator to analyze elemental concentration of bulk samples. Response of the cylindrical 100 mm x 100 mm (diameter x height) $LaBr_3$:Ce detector has been measured for detection of chlorine, mercury and cadmium contaminated bulk water samples, Compared with performance of a smaller 76 mm x 76 mm $LaBr_3$:Ce detector reported earlier [1], the larger volume $LaBr_3$:Ce detector has higher intrinsic activity and poorer energy resolution. Results of the study will be presented.

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Radiation-Induced Reactions in D, L-α-Alanine Adsorbed in Solid Surfaces

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Abstract
The aim of this work is to study the behavior under irradiation of D, L and D-L α-alanine adsorbed in solid surfaces, as possible phase in the chemical evolution that may have occurred on the primitive Earth or in extraterrestrial environments and to evaluate the contribution of solids (a clay mineral) as shields for the adsorbed amino acids against a external energy source. The results show that α-alanine is adsorbed in the surfaces as function of pH and its yield of decomposition in mineral suspension is lower than the system without the solid surface. These results show the importance of nuclear techniques in these types of studies.

Keywords – α-Alanine, chemical evolution, gamma radiation, clay mineral

I. INTRODUCTION

The emergence of life on Earth needed a physical and chemical preamble. There is a large variety of experimental data to support the hypothesis for the abiotic formation of organic compounds [1, 2]. Although much knowledge has been obtained, many questions remain. One important factor in chemical evolution is related to the importance of random chemical synthesis/decomposition *versus* more selective pathways forming compounds of biological relevance. It is important then to explore chemical mechanisms able to narrow the variety of prebiotic chemical compounds liable to be used in the construction of primitive living systems. We study a simple chemical system: an amino acid adsorbed in a clay mineral and exposed to ionizing radiation.

Our interest is twofold: (1) to evaluate the role that a solid surface plays to protect the compound adsorbed in the solid. (2) To show experimentally that biased reactions might have occurred in geologically relevant conditions on the primitive Earth, for example to study if there is a preferential destruction by ionizing radiation of one of the optical isomers of α-alanine.

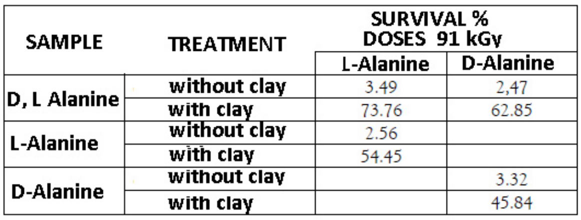
II. EXPERIMENTAL PROCEDURES

The solid surface was sodium montmorillonite of Wyoming bentonite. Aqueous solutions of α-alanine were tested (racemic and pure enantiomeric forms) at concentrations of 0, 01 M and different pH values (2, 4, and 6). The oxygen was removed by passing argon through the solutions. The irradiations were carried out in a ^{60}Co- gamma source. The radiation doses were from 0 to 91 kGy. The analyses were made by high pressure liquid chromatography with a Chiral column (ChirobioticT®), coupled to light scattered detector (ELSD). The solid phase was analyzed by X-ray, IR and electron spin resonance. The experiment was carried out 15 times to check the repeatability of the results.

III. RESULTS

The adsorption data shows that the α-alanine (D and L or D; L) is absorbed readily in the clay. The adsorption occurs to a maximum degree at low pH. At basic pH the adsorption was very low. The gamma irradiation of samples show low yield of recovery of the amino acid without clay. The summary of the recovery percent is in Table I.

Table I Survival Percent of α-Alanine after irradiation



SAMPLE	TREATMENT	SURVIVAL % DOSES 91 kGy	
		L-Alanine	D-Alanine
D, L Alanine	without clay	3.49	2,47
	with clay	73.76	62.85
L-Alanine	without clay	2.56	
	with clay	54.45	
D-Alanine	without clay		3.32
	with clay		45.84

IV. REMARKS

It was observed that the presence of mineral drastically decreases the damage to that amino acid by action of the gamma radiation. The observed general tendency shows the L-α-alanine as the most resistant to ionizing radiation, especially when is radiated in enantiomerically pure solutions, the difference is very slight, but this small difference may be amplified with time and by other mechanism. This result shows the important role of minerals in chemical evolution processes.

ACKNOLEDGEMENTS

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APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
Kanazawa, Japan, 22-27 September 2013

^{36}Cl determination in steel radioactive waste

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Abstract – APSORC'13 Abstract

Within the framework of the nuclear power plants dismantling, approximately 3600 tons of metallic radioactive wastes will be generated. Located near the reactor core, some of them are highly activated and ^{36}Cl produced from the natural stable isotope ^{35}Cl, due to high mobility and long half life, becomes one of the radionuclides that significantly control the ultimate disposal. In steel materials, concentrations between 0.15 and 12.9ppm have been reported [1, 2]. Depending on neutron flux intensity, ^{36}Cl activity calculated for a stable chlorine concentration of 1ppm varies from 0.03 to 91 Bq/g, while the upper acceptance limit for medium activity waste is 5 Bq/g. 200 steel samples have already been collected in nuclear plants under dismantling. Without further available data on stable chlorine content, ^{36}Cl has to be measured.

French standard methods [3] dedicated to ^{36}Cl measurement in wastes does not describe this first step in details and the radiochemical method includes no more than 3mmole of stable chlorine used as carrier and chemical yield tracer. ^{36}Cl is measured by liquid scintillation. A radiochemical process dedicated to ^{36}Cl measurement in steel radioactive waste, has been developed in order to

- *ensure a detection limit far below 5Bq/g,*
- *treat a great flow of samples.*

Furthermore, it must be adapted to as well as carbon than stainless steel samples. And, as ^{36}Cl is an activated product, a total dissolution must be guaranteed.

A dissolution mixture of nitric and chlorhydric acid needed to assure a complete dissolution specially for stainless steel samples has been optimized in order to minimize the quantity of chlorine added. Nevertheless, 25mmole of chlorine are required to dissolve 0.2g of stainless steel, while 15mmole are necessary for 1g of carbon steel. As a result, the following separation steps have to be adapted. The experimental set-up for the dissolution step is a three-neck flask, containing the sample and KCl as chloride source. After gently added nitric acid, nitrogen is bubbled in the solution in order to carry on the gas Cl_2, in a trapped bottle. With this process, only volatile radionuclides such as ^{14}C, ^{129}I... are trapped.

In order to sort the samples, an aliquot of the bubbler solution is directly analyzed. For sample with an activity higher than 3Bq/g, the radiochemistry is carried on to isolate ^{36}Cl in a pure fraction in only two days. The recovery yield is determined at the different stages of the radiochemical procedure, measuring stable chlorine by ionic chromatography.

The method has been evaluated in terms of recovery yield and limit of detection according to the French AFNOR NFT90-210 standard [4]. Thus, a limit of quantification of 0,15Bq has been experimentally verified. Considering the mass analyzed and the limit of quantification the limit of detection is 3 times lower than this limit of quantification, leading to a limit of detection at 0,3Bq/g and 0,15 Bq/g for stainless steel and carbon steel samples respectively.

Results on activated steel will be presented.

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Kanazawa, Japan, 22-27 September 2013

Naturally Occurring Radioactive Materials(NORM) in Malaysian Oil Sludge Samples

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It was in the early 70's, when concern was started regarding the presence of NORM associated with the oil & gas production. During 1980's a lot of work has been devoted to the hazards arising from the measured elevated concentration of NORM in this field. Recently, most publications concern about the effect of NORM on personnel and environment. It was the scope of this paper to analyze the sludge waste resulted from the Malaysian oil fields for the presence of Naturally Occurring Radioactive Materials (NORM) and investigated the hazardous risk associated. This can be also used in future as a reference data to monitor any level changes. About 30 dried sludge samples were characterized using gamma-ray spectroscopy based on a well shielded HPGe detector for the determination of the activity concentrations of ^{238}U, ^{232}Th, their important progenies and ^{40}K. The range of activity concentrations were (10.1 – 51.0) Bq/Kg for ^{226}Ra (186 keV), (6.2 – 34.8) Bq/Kg for ^{214}Pb (352keV), (4.7 – 17.7) Bq/Kg for ^{208}Tl (583 keV), (5.8 – 40) Bq/Kg for ^{214}Bi (609keV), (5.45 – 15.7) Bq/Kg for ^{228}Ac (911keV) and (9.2 – 46) Bq/Kg for ^{40}K (1460keV). The radiation doses resulted from the sample total activities were measured and compared with standard dose limits which would be investigated in the full manuscript.

APSORC'13 - 5th Asia-Pacific Symposium on Radiochemistry
Kanazawa, Japan, 22-27 September 2013

On the Use of ^{233}U and ^{237}Np as Radiotracers for Redox Potential Measurements

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Abstract

Reduction/oxidation (redox) potential measurements in environmental samples are usually made with electrodes. However, these have certain weaknesses in terms of stability and memory effects. Alternative methods for determination of redox are therefore of interest and the use of radioactive tracer elements may be one such method, which is the subject of this investigation. It is suggested that the actinides are particularly appropriate for use as indicators of redox, provided that their different redox states can be separated in a fast and reliable way. A literature survey show that solvent extraction is an established method for separation of tracer amounts of actinides into their redox states and three of the most commonly used extraction reagents of the beta-diketone type were investigated: thenoyltrifluoroacetone (TTA), dibenzoylmethane (DBM) and 4-benzoyl -3-methyl-1-phenyl pyrazol-5-one (PMBP). U and Np were reduced to tetravalent state, which was confirmed with spectropscopic measurements. Extraction curves in the pH range 0.6-7 were then measured for An(IV),(V) and (VI) . It was found that 0.5M DBM in chloroform and 0.05M PMBP in xylene gave the best separation factor (SF=1700 resp. 1100) for actinide (IV)/(VI) and (IV)/(V) oxidation state separation, respectively, when pH of aqueous phase was in the region 1-2. Actinide tracer was used for redox determinations of prepared samples with an artificial groundwater, with or without addition of grains of rock and pyrite and also a Fe(II)/Fe(III) redox-buffer. Comparison with electrode (Pt/Ag/AgCl) measurements gave values that were considerable lower: for example 30mV for a non-redox-buffered synthetic groundwater measured with actinide speciation, compared with about 300mV with electrode. The actinide speciation reflects a slower response to redox changes and a preservation of an earlier redox state of the groundwater, while the electrode responds seems to respond fasterto changes but is thereby also more sensitive to undesirable Eh drift. It was also found that U and Np redox speciation method also have a limited working range of about -100>Eh<100 mV so an absolute correspondence between the methods may therefore be impossible to attain if Eh is outside this range.

Keywords – Redox potential measurements, Groundwater, Uranium, Neptunium, Solvent extraction

23-APP-07

Analysis of ^{129}I/^{127}I ratios from underground fluids collected in Japan

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Keywords – I-129, dating, underground fluids

1. INTRODUCTION

There are many isotopes of iodine. Specialty, the long-lived iodine isotope, ^{129}I is produced by the spallation of atmospheric and by spontaneous fission ^{238}U. ^{129}I and the stable isotope ^{127}I are in steady state before being released and mixed with anthropogenic ^{129}I. So this ratio was measured in order to provide an estimation of the age of iodine.

The purpose of this study is to understand the origin of high salinity groundwaters related to the geological settings of the area. In this study we analyzed ^{129}I (half-life 15.7 m.y.) in the fluids in older to estimate the age of the dissolved iodine in hot spring waters collected from various places in Hokkaido. It is known that several hot springs in Hokkaido, the northern Japanese island, contain high concentrations of halogens including iodine. However, the origin of the salts in these springs is not well known. We analyzed I, Br and Cl concentrations.

2. Samples and Analytical method

Hot springs and groundwaters were collected in Hokkaido. In the sampling interpretation of sample types we considered the classification based on Matsunami et al (1999).

Concentrations of Cl in the hot spring samples were determined by an ion chromatography. Concentrations of I and Br were determined by ICP-MS.

The ^{129}I/^{127}I ratios were determined by accelerator mass spectrometry (AMS). Samples were precipitated as AgI (target cell) after separated iodine, and analyzed by AMS at MALT (Micro Analysis Laboratory, Tandem accelerator, University of Tokyo).

3. Results and discussion

In the Hokkaido hot spring samples, the relationship between iodine concentration and ^{129}I/^{127}I ratios is classified in 2 types. In general, if iodine concentrations increase, ^{129}I/^{127}I ratios are higher. But, a part of sample didn't show this trend.

^{129}I/^{127}I ratios ranged between 0.05×10^{-12} and 0.38×10^{-12} in Hokkaido hot springs samples. Samples collected from north-western area showed very low ^{129}I/^{127}I ratios of 0.05×10^{-12} to 0.1×10^{-12}. Low values are also observed along the longitude 141-142. These values are markedly lower than the ^{129}I/^{127}I ratios observed in iodine-rich fluids in other areas in Japan, such as Chiba (0.18×10^{-12}), Niigata (0.3-0.4×10^{-12}, Tomaru et al. 2009) and Satsuma-Iwojima (0.78×10^{-12}, Snyder et al. 2002). Considering the ^{129}I systematics (Fehn et al. 2004), iodine age in Hokkaido samples of the lowest ^{129}I/^{127}I ratios is estimated to be 60-70 Ma. This indicates that the iodine-rich fluids are likely be derived from old marine sediment, which was later uplifted to form older rock formations in the present day coastal region of Hokkaido.

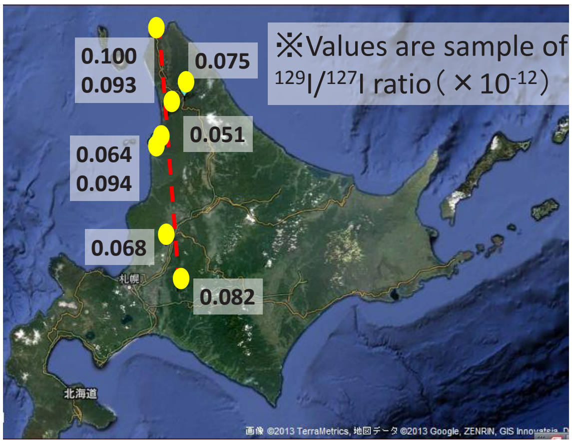

Fig. 1 Mapping of location of low ^{129}I/^{127}I ratio samples in Hokkaido

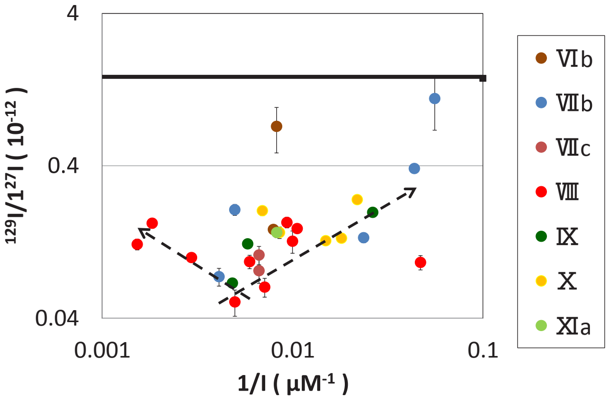

Fig. 2 Iodine concentrations vs. ^{129}I/^{127}I ratios

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Radiocarbon Dating of Ancient Japanese Calligraphy Sheets: Checks with Ancient Documents of Known Age and Its Application to Kohitsugire Calligraphies

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[2]Faculty of Letters, Chuo University
[3]Taga High School
[4]Degital Archives Research Center, Ryukoku University

Abstract – Radiocarbon ages of ancient documents, sutras and books of known age were measured by AMS. The calibrated radiocarbon ages corresponded to the years in which they were written. The result shows that Japanese paper is suitable for radiocarbon dating. Radiocarbon dating on ancient calligraphies of unknown age clarified their historical ages and academic value.

Keywords – AMS, Radiocarbon dating, Ancient calligraphy.

I. INTRODUCTION

Kohitsugire are ancient paper sheets or fragments containing elegant calligraphy. They were originally pages of ancient manuscripts. The old manuscripts written before the 14th century hardly remain as complete books; therefore, kohitsugire potentially has high academic value. However, among kohitsugire attributed to famous calligraphists, many copies and counterfeits written several centuries later are in circulation. Therefore, in this study, we measured radiocarbon ages of kohitsugire by accelerator mass spectrometry (AMS). In the first, we measured ancient documents, sutras and books of known age for check of the method. Then, we applied to kohitsugire calligraphies of unknown age to determine their historical ages and academic value.

II. EXPERIMENTAL

Paper samples were cut from the margins of kohitsugire. A kohitsugire is commonly mounted on other paper sheets that form a lining. The samples were soaked in distilled water to peel the surface sheet of the calligraphy from the mounts. The surface sheets were first washed in distilled water with an ultrasonic cleaner and then treated with 1.2N HCl and 1.2N NaOH solutions (60-70°C). After re-treating with 1.2N HCl and rinsing with distilled water, they were combusted using CuO (850°C, 3h) to form CO_2. The CO_2 was reduced to graphite by H_2 (650°C, cat-Fe, 6h). The radiocarbon ages were measured by AMS.

III. RESULTS AND DISCUSSION: THE KNOWN-AGE DOCUMENTS

The results of the known-age documents, sutras and books were plotted on the calibration curve (Fig. 1). The obtained radiocarbon ages of the documents correspond to the paleographical ages. Although ancient Japanese paper can be considered as a wooden sample, it was made from short-lived branches of trees. In addition, old paper is not used for calligraphy because it repels India ink and is unsuitable for elegant handwriting. The result indicates that ancient Japanese paper is suitable for radiocarbon dating.

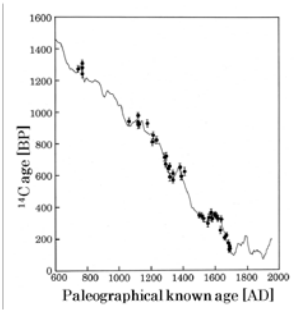

Fig. 1. Result on the known-age documents

IV. RESULTS AND DISCUSSION: KOHITSUGIRE CALLIGRAPHIES

We applied to kohitsugire of unknown age to clarify their historical ages and academic value. For example, Fig. 2 is kohitsugire attributed to Nakatomi no Kamatari (614-669). However, radiocarbon dating indicated that it was written in the 14th century and is not his genuine handwriting. According to legend, calligraphy of Fig. 3 is Shibunritsu sutra brought from China by the priest Ganjin (688-763). Although radiocarbon dating cannot show that the legend is true or not, it indicated that it is old sutra written in the 7-8th centuries as the legend.

皆於身中現　諸佛及聲聞　佛子菩薩等
若獨若在衆　說法悉皆現　雖未得無漏
法性之妙身　以清淨常體　一切於中現

Fig. 2. Kohitsugire attributed to Nakatomi no Kamatari

Fig.3 Shibunritsu sutra

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μ-XRF study on Wiangkalong pottery

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Abstract- It was proved that non-destructive and non-sampling methods were used to analyze the composition of the archaeological objects. It was well-known that differences of them found in Thailand such as glasses, potteries and metal wares. Due to the complex nature of materials and objects, extremely sensitive, spatially resolved, multi-elemental and versatile analytical instruments are needed. In this work, micro-beam X-ray fluorescence spectroscopy (μ-XRF) based on synchrotron radiation was firstly used to characterize the elemental composition of ancient Wiangkalong pottery. Wiangkalong was one of major ceramic production cities in northern of Thailand, once colonized by the ancient Lanna Kingdom (1290 A.D.). Potteries were produced with shapes and designs as similar as those of the Chinese Yuan and Ming Dynasties. The results showed the variations in elemental composition of the body matrix, the glaze and the painting. μ-XRF was successfully to characterize the elemental composition of this ancient pottery.

Keywords – Wiangkalong pottery, μ-XRF

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