

# Transactions on GIGAKU



GIGAKU Press Nagaoka University of Technology

# **Transactions on GIGAKU: Scope and Policy**

Nagaoka University of Technology publishes an online, open access journal titled "Transactions on GIGAKU", which is focused on the science and technology related to GIGAKU<sup>\*</sup>. The mission of this journal is to spread out the concept of GIGAKU and the fruits of GIGAKU to the global world and to be a strong network for innovations in science and technology and for development of next generations of high-level human resources. This journal, therefore, covers research and education activities related to GIGAKU in broad areas.

\* See 'What is GIGAKU?' below.

# 'What is GIGAKU?'

GIGAKU is a term composed of two Japanese word-roots; GI and GAKU. The word GI [技] literally stands for all kinds of arts and technology, and GAKU[学] stands for scientific disciplines in general when used as a suffix.

The term was originally coined to describe the fundamental philosophy of education and research of Nagaoka University of Technology (NUT) when it was established in 1976. Through this term the founders of NUT intended to express their recognition that all technical challenges in the real world require a scientific approach. And NUT has a relentlessly pursued GIGAKU since then.

Fourty-one years have passed and all surrounding conditions have changed dramatically during those years. We are witnessing rapidly globalizing economics and huge scale changes in demographic, industrial and employment structures. All those changes seem to necessitate the further evolution of GIGAKU. In response to this, NUT recently announced its new "Growth Plan" and a renewed definition of the term is given;

GIGAKU is a science of technologies, which gives us an angle to analyze and reinterpret diverse technical processes and objects and thus helps us to advance technologies forward. By employing a broad range of knowledge about science and engineering, management, safety, information technology and life sciences, GIGAKU provides us with workable solution and induces future innovations.

October 2017 Nobuhiko Azuma, President of Nagaoka University of Technology Editors (2017 to 2018):

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# The 6th International GIGAKU Conference in Nagaoka (IGCN) (October 5-6, 2017, Nagaoka University of Technology, Nagaoka, Japan)

The IGCN is designed and organized to provide a cross-border, cross-sector, cross-disciplinary forum for those researchers, educators, and industrial leaders who are creating and practicing GIGAKU in various technology domains in various countries. Some papers presented in the IGCN are published in this first volume of Transactions on GIGAKU.

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# Operation of Engineering Design Educational Program Covering Environmental Problems in Local Community

### Tsukasa Sato\*, Michiaki Shishido, Takeshi Houga, Ryoji Onodera

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In order to train engineering design ability for the students in advanced course in Tsuruoka college, the unique program has been developed and operated. This program includes three policies; 1) cooperation with the local community type education, 2) grouping by mixing different subject-of-study, 3) training camp activities at off-campus area. Themes were proposed by teachers. For example "development of beach cleaning equipment", "producing naturel salt from sea water and its application", and so on. According to the student's self-evaluation, the student was aware of improvement by lesson. However, the difference of the results arose by the group. We felt the necessity for suitable theme which raises a student's motivation.

### 1. Introduction

The industrial technical society has been highly developed and complicated in recent years. In order to correspond to such trends, the educational curriculum "engineering design" has been extended in technical college rapidly. In the engineering design the students learn how to make the objects or propose systems fulfilling social needs by combining various knowledges and technologies [1]. The social needs or problems do not necessarily have a correct one answer, and they must find out the practical solutions. The engineering design program educates the students to have creativity, integration of various knowledge, communication skills, and teamwork ability, and so on. From 2012 in Tsuruoka college, the new subject named "practical design engineering exercise" has been operated for the students in 1st year of advanced course. This paper reports practice of the engineering design education on the theme of the environmental problem of remote island "Tobishima" of Yamagata Prefecture. This paper also discusses the some problems found in the program operated. The program includes unique three policies; 1) Cooperation with local community, 2) Grouping by mixing different subject-of-study, 3) Training camp activities at Tobishima [2, 3].

### 2. Proposed Program

In order to carry out the engineering design education program effectively, unique three policies are introduced in the program, which are described as follows:

1) **Cooperation with local community**; Students recognizes clearly the problems peculiar to the local area, and make effort to draw solutions from various view of points. In the program we tackled the subject in connection with the environmental problems in Tobishima island. The meeting was held between the staffs of the college and local government before the program. And the suitable plan was constructed.

**2) Grouping by mixing different subject-of-study**; The group comprised of students was composed by mixing of different subject-of-study, i. e., departments of mechanical engineering, electrical and electronic engineering, control and information systems engineering, and chemical and biological engineering(Fig. 2). The purpose of such grouping is that the students tackle the problems from various aspects. Members of groups were decided by the teachers.



**Figure 1** Scenes of cooperation with local community; (a) meeting with local resident, (b) lecture about problems in local community.



Figure 2 Concept of grouping by mixing different subject, and setting theme.

**3)** Training camp activities at off-campus area; Training camp at Tobishima was carried out for the students to understand the importance of collaboration and the responsibility of the individual in groups. As other purpose, the students can concentrate on activity all day. During training camp, lecture meeting by invited visiting lecturer were also held, in order to gain useful knowledge to the students.



**Figure 3** Scenes of training camp activities at Tobishima island; (a) group working in the school gym, (b) cooking at kitchen.

The operation time of this program consists of 90hours (school hours) and is equivalent to two credits. The time arrangement for this program is shown in Table I [4, 5]. The group division and theme setting were at the 1st time of the term, which were carried out in 1) preliminary investigation in Table I. The training camp was held twice in that turn. The 1st camp was performed for the purpose of inspection and of understanding of Tobishima Island, which was held for two days at from

Fri., May 27 to Sat., May 28 in 2016. It should be noted that the 1<sup>st</sup> camp should be carried out early time as well as possible for the purpose of the camp. However, on account of the schedule of a school events and teaching staffs, the camp time was carried out as above. In the 2<sup>nd</sup> camp, the field trial of the products of manufacturing was conducted. It carried out for 4days at from July 22 (Fri.) to February 25 (Mon.) in 2016.

The scholastic evaluation for students was judged by the following aspects and score distribution:

1. Evaluation from auditor in presentation	40%
2. Evaluation from the teacher in charge in presentation	
3. The resulting report after practice	25%
4. Activity in this practice	10%
	total 100%

Contents	Description	Operation turn
1) preliminary investigation	investigation about Tobishima	8hrs
	island and suitable engineering	
2) camp activity at off-campus	field study, lecture, meeting, etc.	32 ~ 48hrs (4 ~ 6days)
3) group work in campus	continuing manufacturing	26hrs
		(2h/weeks×13weeks)
4) presentation	proposal about their design or products	8hours
5) others	additional activity time	0 ~ 6 hrs
total		90hrs

**Table I**Time arrangement for the program.

### **3. Practice of Program**

Tobishima is only one of remote manned island in Yamagata Prefecture. The area of an island measures 2.7km<sup>2</sup>. Population is about 200 persons. An elderly ratio is about 67%. Although the industries are fishing and sightseeing, the industries should be more activated for sustaining the living in the island. From the meeting between the teaching staff and the local government decided as main theme relevant to problems of environmental issues. Beach waste is washed up on the seaside, generating of the horse fly which troubles a tourist, needs sightseeing guidance tool for tourist, and so on. Then, the teachers decided to carry out about four themes as listed in Table II. The number of students was twenty persons in all. Since the student was divided into four groups, the number of students of each group was five persons.

group	theme
group 1	Development of beach cleaning equipment
group 2	Producing naturel salt from sea water and its application
group 3	Making the three-dimensional model of Tobishima island with 3D printer
group 4	Collecting equipment of a noxious insect (horse fly)

**Table II**Themes of activity for each groups.

The site of training camp was kindly offered from city staff to use the gymnasium of elementary and junior high schools in island. Since public transport in the island was poor, the school car was

brought and used for convenience. Meal was prepared by themselves borrowing the kitchen in the school.

For example, details of activities of groups 1 and 2 are as follows:

**group1** At beginning of making the equipment, students researched the commercial one and recognized that is expensive and large weight. Therefore they turned out that low cost and lightweight equipment would be useful. The students tried to make the equipment by using familiar materials such as plastic nets and the frame made from aluminum. This equipment consists of eight rotors. Wings are plastic nets. If equipment is pulled, a rotor will move on sand, and sand and garbage will be picked up together. Sand falls from through a net and the garbage remains. At last the garbage is brought together in the cave inside the axis of rotation. However, since the sand was tend to condense, separation of garbage and sand was not fully completed. In addition, the rooters left garbage on sand in many cases. In order for a rotor to collect garbage efficiently, it need to be improved on structure of the rotor.



Figure 4 Test run of the beach cleaning equipment.

**group 2** On the producing naturel salt from sea water, it was found out that the concentration of magnesium of the sea water around Tobishima was high compared with other ocean space as a result of quantitative analysis of minerals. Taking advantage of this characteristic, they thought of the application as bittern. Bittern is an additive used when making tofu. The students studied making tofu by themselves, and completed. In the beginning stage, tofu did not become hard and their failure continued. At last, using the condensed sea water, they completed by carrying out with the optimal temperature of soy milk.



Figure 5 Excerpt a part from student's (group 2) presentation data.

The proposal for the citizens about results obtained from this activity was held at "Environmental fair in Tsuruoka 2016" as large environmental event in the city held on September 25, 2016 in the city gymnasium. Students presented using the poster and exhibiting the manufacture products.

After the practice of the program in Tobishima island, the questionnaires to the students were conducted in order to investigate the improvement of a student's consciousness. The self-evaluation, how are the degree of achievement for students in his own consciousness and capability at before and after the program were conducted.



Figure 7 Proposal towards citizens in "Environmental fair in Tsuruoka 2016"

Question items were 1 team work, 2 sence of ethics, 3 problem solving systematically, 4 communication, 5 sincerity, 6 cooperativeness, 7 leadership, 8 special capability, 9 activity and 10 creativity. Each of items were evaluated by marking numbers from 1(weak) to 5(strong), and all scores were averaged (Fig. 8). The questionnaire survey was conducted to all the students, after that the data was divided into each group and was averaged by the group number (five persons).



Figure 8 Results of self-analysis by students before and after the program

As shown in the figure, it seems that the students themselves realized the progress in the all items, especially in motivation to the activity, contribution to local community, and cooperation and communication in group. However, the difference in a result became clear between groups. The improvement has been weaken in the group 1. Typical students' comments are listed Tab. III.

group	student's comments
Group1	I was not unsatisfactory with the theme
	There was an uncooperative student.
	I felt inconvenience at training camp activities at Tobishima island.
Group2	Everybody was cooperative.
	The theme was attractive.

**Table III** Students' comments (group 1 and 2) after the program

The final report of the students in group 1 told that there was an uncooperative student in their group. The student was unsatisfactory with the theme because the theme does not meet a special field of study. Since the students in this case have been familiar with convenient social life, probably they want to avoid inconvenience and difficulties. On the other hand, the group 2 had the highest result of self-valuation of all the groups. The reasons were the theme was attractive and the member were cooperative. Thus, for group activity the cooperativeness of students and attractiveness of a theme is important. Moreover, an understanding for students of the importance of combining of a subject-of-study is also crucial. In these activities, teachers at first construct four groups arbitrarily. And then themes and detailed directions were given to the each group from the teachers. However, the suitable theme might not be given for some students. It would become unsatisfactory for the students. The following improvements should be planned from now on. For example, at first teachers show some themes toward students, and then the students can choose the subject which got interested. However, combination of a subject-of-study must be maintained. Such improvements have been introduced in activity in 2017. The students are working very enthusiastically till the present, and the completeness of a products are high. The results will be reported next time.

### 4. Conclusion

The engineering design education based on the environmental problem at remote island "Tobishima" of Yamagata Prefecture was carried out in 2016. The working group was composed by the students who consists of different subject-of-study combination. The theme made by the teacher presented to the groups. Throughout training camp activities in Tobishima, the students learned importance of engineering design activity. According to the student's self-evaluation, the student was aware of improvement by lesson. However, the difference of the results arose by the group. We felt the necessity for suitable theme which raises a student's motivation.

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# Training of Practical and Creative Nuclear Engineers Using Unsealed Radioisotopes

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We have successfully developed one of the novel curriculum to train practical and creative nuclear engineers, combined systematically with the Act on Prevention of Radiation Hazards due to Radioisotopes, etc. which is one of the law in Japan and the handling of unsealed radioisotopes. These key points updated for our department's laboratory experiment have been introduced. We have also conducted the laboratory experiment to confirm whether the revised contents work well or not. Concretly, we have practically tested the wellknown methods for surface contamination inspection in the controlled area before and after laboratory experiment. The two types of inspections classified as survey and smear methods were used in the experiment. It was evident that the experiment rooms and appatatuses had no traces of contamination. In addition, the experiments for nuclide separation and identification of nuclides were also carried out in the methanolic nitric acid solution. We also confirmed to separate mutually many metal ions by using anion-exchange chromatographic technique because a little difference among the individual peak positions in the chromatograms has been observed clearly. Also, the yield and distribution coefficients obtained from ICP-MS measurements of Europium (Eu) element were identical to those of Germanium (Ge)-detector measurements. Based on these results, we have finally confirmed that our proposing contents are suitable for the prospective students to be practical and creative nuclear engineers.

### 1. Introduction

National Institute of Technology (NIT) has produced a large number of practical and creative engineers to support Japanese industries. As well as engineers graduated from universities, engineers graduated from NIT are actively involved at the forefront of various sections such as research and development, production management, manufacturing technology, etc.. In the industrial world, they are highly regarded as an engineer. Recently, they have tried to learn advanced technology and more profound knowledge. Hence, it has become natural for them to go to university. The nuclear industry has also been dramatically developed by their great efforts. Although the education in nuclear technology has been already carried out there, NIT does not have the department related to nuclear technology. In addition, there are few controlled laboratories which can handle radioisotopes in NIT.

Nagaoka University of Technology has performed the original education and research activities in cooperation with NIT. The department of Nuclear System Safety Engineering has also educated many students graduated from NIT, by conducting many lectures for them. However, the knowledge and experience for handling unsealed radioisotopes have been still insufficient. We must surely train engineers with more practical and creative nuclear abilities. It is important for them to learn the unsealed radioisotope handling technologies and radiation measurement technologies. Therefore, we have been carrying out the chemical separation experiments using unsealed radioisotope as a part of the laboratory experiment in our department since 2015. However, our previous curriculum did not refer to much practical knowledge and methods to keep the radiation controlled area safe, i.e., this curriculum does not mention clearly how to do the surface contamination inspection before and after

laboratory experiment, how to take out unsealed radioisotopes from storehouses for radioisotopes, and how to keep them temporarily in storehouses for spent radioisotopes as typical examples. Especially, how to fill out a special document to use radioisotopes, following the Act on Prevention of Radiation Hazards due to Radioisotopes, etc. should be understood surely. Unfortunately, for overseas student studying in Japan, our previous textbook was written in Japanese. As a result, it should be modified with "novel curriculum to train practical and creative nuclear engineers". In this curriculum, all students act a role of first-class Radiation Protection Supervisor at Radioisotope Center, Nagaoka University of Technology and can systematically learn basic manners and typical operation procedures using unsealed radioactive sources in the radiation controlled areas, based on the Act on Prevention of Radiation Hazards due to Radioisotopes, etc. [1]. The recommendation from International Commission on Radiological Protection, supported by International Atomic Energy Agency, Organization for Economic Co-operation and Development, Nuclear Energy Agency, International Radiation Protection Association, etc. is also adopted into the act and the contents are revised one after another. In addition, they can learn how to separate a simple element from aqueous solutions containing fission products and how to use leading-edge analyzers for its ultramicroanalysis. There are no educational institutes which works on our suggested method of guidance. It has been expected that most of students including students with a full-time job are satisfied with our very well versed latest curriculum.

On the basis of these backgrounds, we have developed the novel curriculum to train practical and creative nuclear engineers, combined systematically with Act on Prevention of Radiation Hazards due to Radioisotopes, etc. and the handling of unsealed radioisotopes. These key points updated for our department's laboratory experiment have been introduced and we have also conducted the novel laboratory experiment to confirm whether the revised contents work well or not.

### 2. Concept of Laboratory Experiment

### 2.1. Importance of Surface Contamination Inspection

When students do some experiments using unsealed radioactive sources in radiation controlled areas, students must definitely carry out surface contamination inspection before and after our department's laboratory experiment. If students do not carry out the inspection before their experiments, students may be exposed to radiation due to the contaminated surroundings. Hence, students certainly have to perform the inspection and try to minimize their radiation exposure. In addition, it is necessary for the following handler to carry out the inspections after the completion of their experiments because they can devote themselves to do their works using unsealed radioactive sources without any decontamination procedures. The two types of inspections classified as survey and smear methods are reliable generally. For example, a survey method is to examine some areas with the possibility of contamination using a handy-type survey meter such as ref. [1]. However, students are not able to utilize a survey meter in surroundings at a high dose rate. For radioactive nuclides emitting  $\gamma$ -ray and  $\beta$ -ray, students can make use of a Geiger Muller survey meter and a gas flow proportional counter is useful for the detection of radioisotopes emitting  $\beta$ -ray with comparatively low energy. Moreover, a survey meter with a scintillation counter or a semiconductor counter is capable of the detection of  $\alpha$ -emitters. On the other hand, the smear method is to wipe some areas with the possibility of contamination using a smear filter paper and measure the wiped samples using an automatic measuring apparatus equipped with  $\alpha$ -ray and  $\beta$ -ray detectors such as ref. [1]. In case of a smear method, it is generally difficult to completely wipe with radioactive nuclides impregnated onto the floor. Therefore, students must always carry out both the types of surface contamination inspection to complement the individual defects before and after the laboratory experiments.

# 2.2. Summary of Nuclide Separation Experiment Using Anion-Exchange Chromatography and Nuclide Analyses Using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Gamma-ray Spectroscopy with Germanium Detector (Ge-Detector)

# 2.2.1. Nuclide Separation Using Anion-Exchange Chromatography

In the laboratory experiment, students perform radioactive nuclide separation experiment using typical anion-exchange reactions. Ion exchange process is classified as cation-exchange and anion exchange processes indicating an exchange of ions between two electrolytes or between an electrolyte

and a complex in a solution. When metal cations try to adsorb chemically with anion-exchanger, metal anions must be formed via complexation reactions such as the following equilibrium reaction (1). The existence of a number of ligands for a metal ion depends on its electronic state in solvents. In brief, many chemical surroundings of anions and complexes are strongly dependent on kinds of elements in solvents. As a result, different adsorption abilities of metal anions for anion-exchangers are expressed spontaneously. In addition, even if the difference of distribution coefficients per plate is small, it is comparatively easy to prepare a multistage chromatographic apparatus, i.e., it is possible to separate mutually many metal ions using anion-exchange chromatographic technique.

$$\operatorname{Eu}^{3+} + n\operatorname{NO}_{3^{-}} \rightleftarrows [\operatorname{Eu}(\operatorname{NO}_{3})_{n}]^{3-n} \quad (n \ge 4)$$
<sup>(1)</sup>

In a nuclide separation experiment, students use a benzimidazole-type anion-exchange resin embedded in high-porous silica beads (AR-01 resin). The AR-01 resin which has two types of functional groups consisted of 1-methylbenzimidazole and 1,3-dimethylbenzimidazole was chosen for the nuclide separation experiments because the AR-01 resin has much higher resistance to redox reactions, radiation, and heat, compared with those of other resins [2]. The chemical formula and the SEM images of AR-01 resin (VE-8800, Keyence) are shown in Fig. 1 and 2, respectively. The quaternization ratio of AR-01 resin is 58.8 % and the diameter of the silica beads is 40-60  $\mu$ m [3]. The AR-01 (Cl form) resin was synthesized and supplied from Laboratory for Advanced Nuclear Energy, Tokyo Institute of Technology, Tokyo, Japan [4]. The equilibrium reaction (2) is available in the experiment [5].

$$AR-01^{+} \cdot Cl^{-} + [Eu(NO_{3})_{n}]^{3-n} \rightleftarrows AR-01^{+} \cdot [Eu(NO_{3})_{n}]^{3-n} + Cl^{-} \qquad (n \ge 4)$$
(2)



- AR-01 -

Fig. 1 Structural formula of AR-01 resin



Fig. 2 SEM images of AR-01 resin

Students use Eu-152 as a radioactive tracer in the experiment. Stable isotopes consisting of Cs, Sr, Y, Ru, Rh, Sb, Te, Ba, Mn, Co, Eu-151, -153, and Na elements are also used in the experiment. Eu element is classified as lanthanide series which composes the f-block of period 6 in the periodic table and is also one of typical fission products contained in high-level radioactive wastes [6]. Cs, Sr, Ru, Rh, Sb, Te, Ba, Mn, and Co elements are mainly contained in the contaminated water from Fukushima Daiichi Nuclear Power Plant Accident [7]. We use Na species to measure the dead volume of the flow path of separation apparatus [8]. It has been known that Cs<sup>+</sup>, Sr<sup>2+</sup>, Y(III), Ru(IV, VI, VII), Rh(III), Sb(III, V), Te(II, IV, VI, etc.), Ba<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Eu(III), Na<sup>+</sup> exist in aqueous solutions, respectively. It can be estimated that some metal cations in these species coordinate with one and more nitrate ion in nitric acid solutions. We have considered that the favorable tendency for the nitrate coordination will be in order of Na  $\leq$  Mn = Co  $\leq$  Cs  $\leq$  Sr = Ba  $\leq$  Y < Eu. Until now, the reasonable chemical structures of Y, Ru, Rh, Sb, and Te elements have not been determined in the experimental conditions which is expected to be clear soon [9]. The permittivity ( $\varepsilon$ ) of water ( $\varepsilon_{water} = 80.1$  at 20°C) is higher than that of alcohols such as methanol (MeOH) ( $\varepsilon_{Methanol} = 33.4$  at 20°C) [10], i.e., an addition of sufficient volume of methanol into nitric acid solutions trigger the increase of the coordination number of metal ions [11]. Therefore, a nitric acid solution containing methanol has been decided to use as a mobile phase in the experiment.

### 2.2.2. Nuclide Analyses Using ICP-MS and Ge-Detector

The qualitative and quantitative analyses of the examined metal ions in the collected samples is performed by using a ICP-MS analyzer (7700x, Agilent). On the other hand, it has been known that Eu-152 emits mainly gamma-ray with an energy range between 0.122 and 1.408 MeV [12]. Hence, it is also possible to identify Eu-152 by using a Ge-Detector (DSPEC jr 2.0, Seiko EG&G). In this experiment, students use ICP-MS and Ge-Detector to calculate the concentration of samples collected from chromatographic experiments.

### 2.2.3. Individual Role

When students carry out some experiments using unsealed radioactive sources in the radiation controlled area, it is very important for students to decide the individual role in the group. This decision could decrease many chances of unprecedented radiation exposure. For example, we have suggested that students should decide the individual role on one as the handler of radioisotopes, two assistants for the radioisotope handler, two operators of ICP-MS and Ge-Detector, and one person to record the data.

### 3. Validity of Contents

### 3.1. Surface Contamination Inspection before and after Laboratory Experiment

Before and after the laboratory experiment, we carried out the surface contamination inspection to keep controlled rooms clean at Radioisotope Center. This inspection was performed by using a handheld Geiger Muller survey meter with a wide mica window (GM) (TGS-146B, Hitachi-Aloka Medical), a handy-type survey meter with a scintillation counter (Scintillation) (TCS-362B, Hitachi-Aloka Medical), and additionally we inspected the controlled rooms by using a smear method. We used an automatic measuring apparatus equipped with detectors of  $\alpha$ -ray and  $\beta$ -ray (Hitachi-Aloka Medical, JDC-5300) for samples from the method using a smear filter paper provided from Chiyoda Technol. Compared with values calculated from blank samples, we confirmed whether the collected samples were contaminated or not. Each sample had a measurement time of 1.5 minutes. The obtained values were strictly confirmed to be within 4 Bq/cm<sup>2</sup> for  $\alpha$ -ray and 40 Bq/cm<sup>2</sup> for  $\beta$ -ray [1], following the law. When they exceed the maximum values regulated under law, we wiped the entire contaminated area with special cleaners as soon as possible.

Table 1 shows the result of surface contamination inspection before and after laboratory experiment. From the results of GM and Scintillation before laboratory experiment, we found that all values are similar to the background value. It was also found that all values before the experiment are almost the same as those after the experiment. The background value was also not excluded from these values in case of the survey method. Based on the results of the survey method, the results indicated that the experiment rooms and apparatuses accompanying them, are not contaminated. On the other

hand, it was impossible to calculate the radioactivity of  $\alpha$ -ray and  $\beta$ -ray using an automatic measuring apparatus equipped with detectors of both radiation because of much lower radioactivity of all samples. Therefore, those results were attributing to no contamination.

 Table 1 Evaluation sheet for the result of surface contamination inspection before and after laboratory experiment

	Survey method (GM-type / Scintillation-type)			Smear method (Scintillation-type)				
Measurement points	Before (cpm)	After (cpm)	Ве	Before (Bq)		A	After (Bq)	
1 Disub seconds	$(75 \pm 17) / (GM)$ $\alpha (0)$	$(81 \pm 18) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
1. Blank sample	$\beta$ (183 ± 27) / (Scintillation)	$\beta$ (189 ± 28) / (Scintillation)	β(	ND	)	β(	ND	)
2. Thermostat apparatus,	$(77 \pm 18) / (GM)$ $\alpha (0)$	$(70 \pm 17) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
column stand, fraction collector	$\beta$ (136 ± 23) / (Scintillation)	$\beta$ (141 ± 24) / (Scintillation)	β(	ND	)	β(	ND	)
	$(69 \pm 17) / (GM)$ $\alpha (0)$	$(64 \pm 16) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
5. plastic vat	$\beta$ (148 ± 24) / (Scintillation)	$\beta$ (164 ± 26) / (Scintillation)	β(	ND	)	β(	ND	)
4. Laboratory	$(77 \pm 18) / (GM)$ $\alpha (0)$	$(72 \pm 17) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
benches	$\beta$ (187 ± 27) / (Scintillation)	$\beta$ (159 ± 25) / (Scintillation)	β(	ND	)	β(	ND	)
5. Floor around a	$(60 \pm 15) / (GM)$ $\alpha (0)$	$(67 \pm 16) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
laboratory bench	$\beta$ (152 ± 25) / (Scintillation)	$\beta$ (167 ± 26) / (Scintillation)	β(	ND	)	β(	ND	)
6. Laboratory	$(77 \pm 17) / (GM)$ $\alpha (0)$	$(74 \pm 17) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
hood	$\beta$ (166 ± 26) / (Scintillation)	$\beta$ (173 ± 26) / (Scintillation)	β(	ND	)	β(	ND	)
7. Floor in front	$(71 \pm 17) / (GM)$ $\alpha (0)$	$(68 \pm 16) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
of a fume hood	$\beta$ (169 ± 26) / (Scintillation)	$\beta$ (168 ± 26) / (Scintillation)	β(	ND	)	β(	ND	)
8. Floor and	$(66 \pm 16) / (GM)$	$(67 \pm 16) / (GM)$	α(	ND	)	α(	ND	)
Ge-detector	$\beta (181 \pm 27)$	$\beta$ (179 ± 27)	β(	ND	)	β(	ND	)

	/ (Scintillation)	/ (Scintillation)						
9. Floor and	$(72 \pm 17) / (GM)$ $\alpha (0)$	$(72 \pm 17) / (GM)$ $\alpha (0)$	α(	ND	)	α(	ND	)
ICP-MS analyzer	$\beta$ (191 ± 28) / (Scintillation)	$\beta$ (143 ± 24) / (Scintillation)	β(	ND	)	β(	ND	)
10. Floor and pipes around general reservoir and reservoir for dilution process	$(70 \pm 17) / (GM)$ $\alpha (0)$ $\beta (176 \pm 27)$ / (Scintillation)	$(61 \pm 16) / (GM)$ $\alpha (0)$ $\beta (165 \pm 26)$ / (Scintillation)	α( β(	ND ND	) )	α( β(	ND ND	) )
<judgment> (Please mark</judgment>	Contamination	Contamination	Co	ntaminatio	on	Co	ntaminatio	on
your decision with a circle)	No Contamination	No Contamination	No C	Contamina	tion	No C	Contaminat	tion

ND = not detected.

### 3.2. Experiments for Nuclide Separation and Identification of Nuclides

Following the flowchart, the experiments for nuclide separation and identification of nuclides were carried out in two kinds of aqueous solutions at our Radioisotope Center.

1) We turned on power to a SJ-1211-type peristaltic pump, a LTCi-150HP-type water circulating pump, a CHF100AA-type fraction collector. Although their default values ought to be established before, we checked their condition again. If not, we must manage to set up. The temperature was kept constant at 60°C. Each effluent volume was collected every 1.0 mL.

2) The radioactive nuclide separation apparatus is illustrated in Fig. 3. The above-mentioned AR-01 resin ( $V_R = 1.15 \text{ mL}$  (without a volume of high-porous silica beads)) was packed into the column in advance. For conditioning of this column, we washed a series of flow path by using the ca. 30 mL methanolic nitric acid solution (1.0 M HNO<sub>3</sub> / MeOH = 2 : 8 (vol%) as a mobile phase. Both chemicals were provided from Nacalai Tesque, Inc.. 1.0 M HNO<sub>3</sub> solution was prepared carefully without any contamination using ultrapure water (Specific electrical resistance:  $\geq 18.2 \text{ M}$  cm, total organic carbon:  $\leq 3 \text{ ppb}$  (ppb = ng/g)) produced using a Merck Millipore apparatus (Milli-Q Integral 3 Water Purification System). We used the previously prepared mobile phase on the plastic vat. "M" and "L" represent "mol / dm<sup>3</sup>" and "dm<sup>3</sup>". Through this process, the initial form of AR-01 resin was converted into Cl form. By way of caution, we checked to be adjusted to the 4th dial number on the peristaltic pump again. This 4th dial number means that the flow velocity is adjusted to 0.50 mL / min.

**3)** We filled out the form to handle unsealed Eu-152 (Japan Radioisotope Association) and took carefully the reagent bottle containing unsealed Eu-152 from the storehouse for radioisotopes. We added Eu-152 adjusted to 50 kBq into 10 mL beaker. 60 wt% HNO<sub>3</sub> solution of 1.0 mL with Cs, Sr, Y, Ru, Rh, Sb, Te, Ba, Mn, Co, Eu, and Na elements (Wako Pure Chemical Industries) were also added into the same beaker. This initial sample of 1.0 mL contains 50 kBq Eu-152 on June 1, 2017 and twelve kinds of elements with an approximate concentration of 1.0 mM. By handling an infrared heating and drying lamp and a digital hotplate kept constant at about 100°C in the fume hood, the foregoing sample solution was evaporated slowly until completion. Then, we added the dry samples in the fume hood into the 1.0 mL mixture solution of HNO<sub>3</sub> and MeOH (HNO<sub>3</sub> : MeOH = 2 : 8 (volume ratio)). The VS-25-type ultrasonic cleaning machine was used to dissolve the mixture as soon as possible. The person handling Eu-152 compulsorily wore safety glasses during the experiment.

**4**) We measured the aforesaid samples using the Ge-Detector. The measurement duration was 3 minutes. The obtained value was used as one of the initial samples.

**5**) After we numbered sample tubes made of polypropylene with a black marker from 1 to 50, we kept them carefully in the fraction collector. Parallel to the experimental section from II to IV, this

preparation was separately carried out to minimize their unnecessary radiation exposure. 6) We turned off the SJ-1211-type peristaltic pump, confirmed that the pressure in the glass column returns to atmospheric pressure, and carefully opened the top cap of the glass column. Subsequently, we carefully added the initial sample into the glass column not to overflow the initial sample. 7) Before flowing the mobile phase of 30 mL (HNO<sub>3</sub> : MeOH = 2 : 8 (volume ratio)) into the glass column, we turned on the fraction collector. The nuclide separation experiment was started.



Fig. 3 Chromatographic apparatus for nuclide separation experiment.

**8**) Following the flow of methanolic nitric acid solution, we ensured the flow of 30 mL or above 1.0 M HNO<sub>3</sub> and ultrapure water of 30 mL through the glass column. Because the collected mobile phase may be contaminated by Eu-152. We collected the eluted mobile phase in a special glass beaker after collecting 50 samples.

**9)** We fixed tightly the sample tubes using a handmade holder in Ge-Detector before measuring Eu-152. The measurement time was 3 minutes per sample. We chose one value of energy of  $\gamma$ -ray from Eu-152 (see Table 2).

Energy of γ-ray / MeV	Emission ratio / %
0.122	28.6
1.408	21.0
0.964	14.6

**Table 2** Main energy of  $\gamma$ -ray of Eu-152 and their emission ratios [12]

**10**) We diluted the collected samples about 100 times with a 1.0 wt% HNO<sub>3</sub> solution. Firstly, we prepared 50 sample tubes containing each 1.0 wt% HNO<sub>3</sub> solution of 10 mL. Then, the collected samples of 0.1 mL were added into them.

**11**) We conducted the qualitative and quantitative analyses of the examined metal ions for all collected samples with the ICP-MS analyzer.

**12)** After measurements, we wasted all the spent solutions into a 500 mL glass beaker in the fume hood while taking care of handling an infrared heating and drying lamp and a digital hotplate. In case of washing all sample tubes, we used deionized water. We separated and sorted laboratory waste into burnable, flame retardant, nonburnable, inorganic, and organic and the wastes were temporarily kept in the storehouse for spent radioisotopes. Finally, we filled out the form to ensure the storage of Eu-

152 in the storehouse.

Based on these results, it is important to examine practically the validity of our proposed contents to understand the Act on Prevention of Radiation Hazards due to Radioisotopes, etc. and the handling of unsealed radioisotopes. Hence, we have described the graph showing the plots of I / I<sub>0</sub> (I = concentration of metal ions, I<sub>0</sub> = initial concentration of metal ions) against every elution volume and the dead volume was calculated using Na ion (see Fig. 4). As mentioned above, the concentration of metal ions was determined by using the ICP-MS analyzer and the Eu concentration was obtained using both of ICP-MS and Ge-detector. The distribution coefficients,  $K_d$  and yields of metal ions were also calculated [5]. The yield and  $K_d$  obtained from ICP-MS measurements of Eu element were identical to those of Ge-detector measurements. As a result, it was found that the effluent volume of Eu element increased, compared with other elements. In brief, this phenomenon means that Eu element strongly adsorbed with AR-01 resin in 1.0 M HNO<sub>3</sub>/ MeOH solutions. Particularly, Sb element cannot be detected up to effluent volume of 50 mL because of its strong adsorption ability for AR-01 resin. Some techniques could be required to elute Sb element into mobile phase.



Fig. 4 Chromatograms of metal ions adsorbed on AR-01 in 1.0 M HNO<sub>3</sub>/ MeOH and 1.0 M HNO<sub>3</sub> solutions

### 4. Conclusion

We have successfully prepared one of the novel curriculum to train practical and creative nuclear engineers, combined systematically with the Act on Prevention of Radiation Hazards due to Radioisotopes, etc. and the handling of unsealed radioisotopes. These key points updated for our department's laboratory experiment have been introduced. We have also conducted the laboratory experiment to confirm whether the revised contents work well or not. Specifically, we have practically tested the well-known methods for surface contamination inspection in the controlled area before and after laboratory experiment. The two types of inspections classified as survey and smear methods were performed. As a result, it was found that the experiment rooms and apparatuses accompanying them, which were examined for laboratory experiment were not contaminated. Moreover, the experiments for nuclide separation and identification of nuclides were also carried out in the methanolic nitric acid solution. By considering a little difference of the calculated individual peak positions, we confirmed to separate mutually many metal ions by using anion-exchange chromatographic technique. The yield and  $K_d$  values obtained from ICP-MS measurements of Eu element were identical to those of Gedetector measurements.

Based on these results, it can be regarded that our proposing contents are useful for students to be practical and creative nuclear engineers. On the other hand, we should lend an ear to the students' and advisers' impressions and opinions before and after experiments and have to provide an education to

meet the needs of the times. After sufficient consideration, as necessary, it is very important to improve and update the present curriculum every year.

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### Folding Characteristics of Multiple-Scored Portion of Corrugated Fiberboard

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This paper describes the bending moment resistance of scored portion of corrugated fiberboard (Cfb) and the corresponded bulging behavior of scored portion. In order to reveal the folding mechanism of scored Cfb using one-point type and three-point type die-set when varying the indentation depth of attacker bite, two kinds of prototype die-set were developed and the folding process was investigated using the folding test apparatus. The difference of one-point type and three-point type scoring was revealed as the characteristics of bending moment resistance of scored Cfb and the occurrence limit of failure modes of folding with respect to the folding direction.

### 1. Introduction

A corrugated fiberboard (Cfb) consists of outer/inner liners and corrugated mediums, and its layered configuration is produced as several combinations, such as single face, double face (single wall), double wall (twin cushion) and triple wall<sup>[1][2]</sup>. The Cfb is superior for the high strength-toweight ratio and provides a good shock absorption for transport products. It is one of the most important materials for making packaging containers. Generally, a packaging container box made of Cfb is composed of vertical wall panels and slotted flaps. When making the flaps and wall panels, a sheet of Cfb is usually scored for making a folding line by a rotary type or platen type scorer machine using the three point type bites <sup>[3]</sup>. Regarding the scoring process (across to the corrugated medium) and creasing process (parallel to the corrugated medium), there are known several types of bite combination. The three point type, which is well used for making a score line, consists of one point (a convex bite) and two edge points (a concave-grooved anvil), while the one point type is used normally for making a crease line<sup>[4]</sup>. In those cases, since the scored side is located at the inside of formed box, the bending moment resistance of scored line tends to be small for closing a flap, while the bending moment resistance is fairly large for opening the flap. Namely, the open wise bending resistance of scored line is usually larger than the close wise bending resistance. Recently, the difference of flap opening/closing resistance of container boxes becomes one of severe problems for workers in various packaging industries. This kind of opening/closing resistance is desired to be even or at least similar in the both moving directions. In this recent situation, a new processing method is desired for performing the evenness of closing/opening resistance of the scored lines of container boxes. Regarding the pattern of scoring bite, the five point type is known for making a sort of multiple scored lines. Principally, it is possible to make arbitrary-multiple scored lines for folding an open-purpose line and a closepurpose line, respectively. However, the performance of folding resistance <sup>[5][6]</sup> and the buckling behavior of wall panel structure under a compressive test were not investigated sufficiently in the past <sup>[7]</sup>. Also, the multiple point type bites of the scorer are used empirically depending on the application. There seemed to be no reports about the performing difference among the one-point type, three-point type and five-point type scoring <sup>[3]</sup>.

In this work, in order to reveal the relationship between the pitch pattern of multiple point type bites and the open/close wise folding resistance, two kinds of score line processing die-set (one-point type and three-point type) were developed and used for making a scored portion on the specimen of A-flute <sup>[8]</sup> Cfb. A folding test <sup>[9]</sup> of the scored portion was experimentally carried out for investigating the bending moment resistance and the crushing profile of the scored portion.

### 2. Experimental condition and method

The layered configuration of A-flute (single-wall, double-face) sheet was shown in **Fig.1**. The three layers are composed of (1) a jute liner of basis weight 150 g·m<sup>-2</sup>, thickness of 0.15mm (2) a corrugated medium sheet of basis weight 120 g·m<sup>-2</sup>, thickness of 0.16mm and (3) a jute liner of basis weight 150 g·m<sup>-2</sup>, thickness of 0.15mm. The wave length of A-flute was  $\lambda_A \approx 8.5$ mm, and the stacked height of A-flute plus upper/lower liners was  $t_A = 4.9$ mm (4.81~4.99mm).

The specimen size of Cfb was prepared as a rectangle which has a width of 20mm and a length of 120mm, as shown in Fig. 1. Here, the effective wave number was chosen as 2 and the longitudinal direction of 120mm was assigned to the cross machine direction (CD) of Cfb.



Fig.1 Layout of single wall corrugated, double face sheet.

One-point type scoring and three-point type scoring were processed by the use of the score line processing die-set as illustrated in **Fig.2**. Here, the upper-attacker bite of apex angle 120° and the lower-receiver bites of apex angle 120° had a length of 50 mm and were made of ABSplusP430 thermoplastics <sup>[10]</sup>, which had the hardness of 109.5 HRC, the tensile strength of 33 MPa, the yield stress of 31 MPa, the tensile elastic modulus of 2.2 GPa. The counter face plate (flat anvil) was made of SUS630, the hardness of which was 510HV. An indentation of the upper-attacker bite *d* was chosen from 0.5 up to 4.5 mm with 0.5mm interval.



(a) One-point type Top (out-of-plane) view and layout of specimen for s

120mm

Fig.3 Top (out-of-plane) view and layout of specimen for scoring and clamping on folding test apparatus

120mm

(b) Three-point type

**Figure 3** shows the dimensions of rectangle specimen (worksheet) of A-flute Cfb for scoring at the processing die-set and clamping on a folding apparatus. The specimen of A-flute Cfb was scored with the indentation d and the pushing velocity of 0.05 mm·s<sup>-1</sup>, using the score line processing die-set in a compressive testing apparatus.



Fig.5 Schematic diagrams of folding test and upper in-plane view of folded Cfb specimen

After that scoring, the bending line moment resistance *M* of the scored specimen was measured with the folding angle  $\theta$  by using the folding test apparatus (Crease Stress Tester) CST-J-1<sup>[9]</sup>. **Figure 4** showed a general view of a specimen mounted on CST-J-1, while **Fig.5** (a) illustrated the one-point type folding and Fig.5 (b) illustrated the three-point type folding when carrying out the normal wise direction. Here, the end position of fixture was 10mm apart from the scored zone of the specimen as shown in Fig.3 and Fig.5. The distance between the fixture end and the load cell was 60 mm when  $\theta$ = 0°. Namely, the arm length between the load cell and the scored position was 50mm. In the duration of folding test, the folding angle  $\theta$  was varied from 0 up to 90°, while keeping the average rotational velocity as  $\omega$ = 0.2 rps. In Fig.5, when turning over the scored specimen, the folding angle  $\theta$  was also varied from 0 up to 90° for the reverse bending mode. The experiment was carried out under the following conditions: room temperature of 297K and room humidity of 50%RH. Number of samples was three pieces for each case.

### 3. Results and Discussion

Table.1 (a) and (b) indicate the success rate of expected folding. The success rate was counted when the scored line matched the folding position. In case of failure state, the folding position was at the end position of fixture. **Figure 6** shows the initial set-up states of the Cfb specimen scored with the indentation d=1.0mm and 4.0mm. In the case of Fig.6, the folding direction of fixture was chosen as the normal wise as illustrated in Fig.5. Since the reverse wise was simply processed using the upset specimen with respect to the scored surface, its corresponded photographs were similar to Fig.6, except for the opposite scored side. **Figure 7** shows the normal wise 90° folded state of the Cfb specimen scored with the indentation d=1.0mm and 4.0mm, while **Fig.8** shows the reverse wise 90° folded state of that. Seeing Table 1 and Fig.7~8, several features were detected. (1) The three-point type stably tends to be folded at a scored position (one of three scored positions) for both the normal and reverse wise folding when choosing  $d/t_A=0.1~0.92$ . (2) The one-point type was limited in  $d/t_A>0.7$  to make an expected folding at the scored position for the reverse wise folding, although there was no limitation to make the expected folding at the scored position for the normal wise folding when choosing  $d/t_A=0.1~0.92$ . These difference of folding behavior seems to be caused from the difference of scored portion.

**Table 1** Folding state of scored portion (success rate % of 3 samples)

(a) One-point type scoring									
Indentation d /mm	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Normal bending	0	100	100	100	100	100	100	100	100
Reverse bending	0	0	0	0	0	0	100	100	100
(b) Three-point type scoring									
	(b	) Three	e-poin	t type s	scoring	5			
Indentation <i>d</i> /mm	(b 0.5	) Three 1.0	e-poin 1.5	t type s 2.0	scoring 2.5	3.0	3.5	4.0	4.5
Indentation <i>d</i> /mm Normal bending	(b 0.5 0	) Three 1.0 100	e-poin 1.5 100	t type s 2.0 100	scoring 2.5 100	g 3.0 100	3.5 100	4.0 100	4.5 100



(a) One point normal d = 1.0mm, initial set-up



(b)One point normal d = 4.0mm, initial set-up

5.0mm (c)Three point normal d = 1.0mm, initial set-up



(d)Three point normal d = 4.0mm, initial set-up

**Fig.6** Side views of scored Cfb mounted on the folding tester in case of normal set-up at  $\theta = 0^{\circ}$ 





(a) Initial score (b) Normal folding (c) Reverse folding **Fig. 9** Conceptual folding modes of three point type scored portion

**Figure 9** illustrates the folding modes of three-point type scored portion. In the reverse wise folding, one of scored positions which were processed by the receiver blades can be easily buckled as shown in Fig.9 (c). However, in the case of the one point type, since there is not any scored positions on the inside (lower) surface for the reverse wise folding, the occurrence of buckling on the inside surface becomes unstable against the opposite side scored position. Only when  $d/t_A > 0.7$ , namely in case of bending stiffness is sufficiently reduced at the scored position, the bent-buckling position

settles down at the scored position. Regarding the normal wise folding, both the one point type and the three point type scored portions have almost the same structure with each other.

**Figure 10** shows the bending moment resistance M per unit width of Cfb specimen (as the representative examples) when varying the folding angle  $\theta = 0^{\circ} \sim 90^{\circ}$  under keeping the angular velocity of  $\omega = 0.2$  rps. Here, two cases (c), (d) of reverse wise folding with d=1.0mm were failed in forming of expected folding at the scored position. As the result, the peak maximum bending moment reached about 9 Nm·m<sup>-1</sup> when the span length was assumed to be L= 60mm due to the failure of deformation of scored position. When the folding occurred successfully at the scored position, the span length was considered as L=50mm for calculating the bending moment M. When the folding angle  $\theta$  is larger than  $60^{\circ}$  with d=1mm in the graphs of (a),(b),(d), M tends to be increased, compared to the middle zone of  $\theta = 20-60^{\circ}$ . This resistance increasing appeared to be caused by the interference of bulged inside surface. When d=4.0mm, since the scoring was sufficient for avoiding that interference, the response of M was simply decreased with  $\theta$ . Generally, the peak maximum bending moment resistance is large and unstable for making the inside bent-buckling in the reverse wise folding due to a lack or weak-existence of scored portion on the inside surface. However, it was found that the three-point type scoring by a deep indentation (e.g., d= 4.0mm) made the folding deformation stable as shown in Fig.6 (d). This mechanism was already discussed above using Fig.9 (c).





(d) Reverse wise, three-point type

**Fig.10** Relationship between bending moment and folding angle (representative examples), (a) Normal wise folding by one-point type score, (b) Normal wise folding by three-point type score, (c) Reverse wise folding by one-point type score and (d) Reverse wise folding by three-point type score.

The relationship between the peak maximum bending moment  $M_{\text{peak}}$  and the indentation depth d was shown in **Fig.11** (a)(b), while the corresponded peak folding angle  $\theta_{\text{peak}}$  was shown in Fig.11 (c)(d). Here, the normal wise and the reverse wise folding were arranged for the one-point and three-point type scoring, respectively.



Fig.11 Peak maximum bending moment and its folding angle for indentation depth of d=0.5~4.5mm

$M_{\rm peak} = -6.96(d/t_{\rm A}) + 6.95$	for $0.2 < d/t_{\rm A} < 0.92$	(1)
$M_{\text{peak}} = -13.9(d/t_{\text{A}}) + 17.4$	for $0.6 < d/t_{\rm A} < 0.92$	(2)
$M_{\rm peak} = -8.19(d/t_{\rm A}) + 8.53$	for $0.2 < d/t_{\rm A} < 0.92$	(3)
$M_{\rm peak} = -8.93(d/t_{\rm A}) + 10.1$	for $0.2 < d/t_{\rm A} < 0.92$	(4)

Detected features were as follows. (1)  $M_{\text{peak}}$  tends to decrease with d for both the normal and reverse wise folding. Except for the failure mode of folding,  $M_{\text{peak}}$  was estimated using a linear approximation for each case. Four equations were derived as Eq. (1)~(4). (2) The difference of  $M_{\text{peak}}$ between the normal and reverse wise folding was remarkably large (4~7 Nm·m<sup>-1</sup>) in case of one-point type when d > 2mm, while the difference of them was relatively small (about 1.5 Nm·m<sup>-1</sup>) in case of three-point type. In other words, seeing the gradient  $-\partial M_{\text{peak}}/\partial (d/t_{\text{A}})$ , that of normal wise in onepoint type was about a half of that of reverse wise and that of normal wise in three-point type was almost equal to that of reverse wise. (3) Seeing the failure states of folding position, the upper-bound bending moment resistance appeared to be 9 or 10 Nm·m<sup>-1</sup>. This value was the nominal bending strength of A-flute Cfb without any scoring. (4) Comparing  $M_{\text{peak}}$  of the normal wise in (a) and that of the normal wise in (b), the latter was a little larger than the former, and also the gradient  $-\partial M_{\text{peak}}/\partial (d/t_{\text{A}})$  of the latter 8.19 was larger than that of the former 6.96. This difference seems to be caused from the fixing structure of the attacker bite and the receiver. Since three-point type (latter) had two wedge bites on the receiver, the receiver bites were easily indented against the specimen, while the counter plate support the specimen without any damages. As the result, the attacker bite of onepoint type (former) tended to be strongly indented to the specimen. This effect seems to generate the difference of bending moment and its gradient. (5) The peak position  $\theta_{\text{peak}}$  of three-point type was stably  $6\sim12^{\circ}$  for both the normal and reverse wise folding, while that of one-point type was  $6\sim16^{\circ}$  for the normal wise, but that was restricted in a narrow range of 4~8° in the case of reverse wise folding. From the aspect of application works (e.g., when opening a flap of box), the peak position of  $\theta_{peak}$ 

ought to be stable and similar with the normal and the reverse wise folding. Synthetically, the threepoint type seems to be superior for opening/closing performance of scored portion of Cfb.

### 4. Conclusions

Two scoring methods, one-point type and three-point type scoring of A-flute corrugated fibreboard (Cfb) have been experimentally investigated using a prototype flatbed die-set made of 3D printing thermoplastics. Seeing the in-process deformation and bending moment resistance of folded portion at scored position, the following results were obtained.

(1) In the normal wise folding (scored surface is located on the inside of folding), 10% indentation depth of attacker bite is at least required for performing the successful folding at the scored position in both the one-point and three-point type scoring. In the reverse wise folding (scored surface by the attacker bite is opposite against the inside of folding), the failure state of expected folding occurred when the indentation depth of attacker bite was less than 60% of the height of Cfb in the case of one-point type scoring, while the failure state occurred for the indentation depth was less than 20% of the height of Cfb in the case of three-point type scoring.

(2) The bending moment resistance of scored portion is decreased with the indentation depth of attacker bite. The effect of the bite indentation depth on the bending moment response was experimentally characterized using a linear approximation method.

(3) For both one point type and three point type, the peak maximum bending moment of reverse folding was apt to be larger than that of the normal folding. In the case of one-point type, the difference of peak maximum bending moment between the normal and reverse wise folding was remarkably large. In the case of proposed three-point type, the difference of peak maximum bending moment between the normal and the reverse wise folding was negligible. This mechanism was revealed and explained using a conceptual deformation model.

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# Preparation and Characterization of Cellulose Hydrogel Films from Myanmar Thanaka Heartwood

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Waste thanaka heartwood was used as a starting material which was chemically pretreated using sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide (NaOH). When this sample was bleached by sodium hypochlorite (NaOCl), treated thanaka fibers were obtained. FTIR and SEM measurements were utilized to characterize the properties of pretreated samples. Following this, solvent exchange processes were performed making use of water, ethanol and DMAc respectively. Using a dimethylacetamide/lithium chloride (DMAc/ LiCl) system, it became possible to obtain cellulose hydrogel solutions. The cellulose hydrogel films were prepared by phase inverse method without cross-linker. The resultant hydrogel films were transparent and flexible. Then, the effect on the properties of three types of hydrogel films (TW-RT, TW-40,TW-50) depending on the bleaching process at different temperatures (room temperature RT,  $40^{\circ}$ C,  $50^{\circ}$ C)of thanaka fiber was comparatively studied. It was found that water contents were in the range of 162.50 -185.71 % and the poly dispersity index (PDI) in the range of 4.02 - 5.54. Viscoelastic data showed the deformation of hydrogel films-TW-50 being lower than that of films TW-40 and TW-RT. From our observations, thanaka cellulose hydrogel could transform to hydrogel films by phase inversion method and these films had the potential to be used in environmental friendly and biocompatible products for tissue regeneration.

### **1. Introduction**

Recently, regeneration of agro biomass cellulose hydrogel has become especially attractive as it can be easily transformed into advanced materials. Among them, hydrogels prepared from collagen, chitosan and other biomass polymers are capable of yielding material including matrices for repairing and regenerating a wide variety of tissue and organs used in "tissue engineering"[1-3]. Hydrogels consisting of hydrophilic polymer networks can retain high water contents; meaning that it can absorb water from 10-20% up to thousands of times their dry weight in water. Various hydrogels originated from natural polymers have been used in hyaluronate [4,5] alginate [6], starch [7], chitosan, cellulose[10-14] and their derivatives. They have shown potential applications in biomaterial field because of their ability to be used safely, along with their hydrophilicity, biocompatibility and biodegradability. In the aforementioned polymers, cellulose is the most abundant renewable resource on earth [15,16]. Moreover, it is numerous new functional materials that have been using a broad range of applications because they are environmentally friendly and biocompatible products [17,18]. Extremely limited work, however, has been performed by using cellulose fibers in order to prepare hydrogel films. Cellulose hydrogel films prepared from bamboo [19], agave fiber[20], sugarcane bagasse [21] and corn cobs[22] have been reported by researchers. They portrayed that these films have good bio and cytocompatibilities [19-22]. Moreover, Tovar-Carrillo et. al purified cellulose with Agave bagasse, studied the effect of lithium chloride and sodium hypochloride treatment on agave cellulose and used this to elaborate cyto and biocompatibility of hydrogel films[23,24]. In these cases, agave tequilana bagasse was used as the regeneration source for cellulose hydrogel. Nakasone et.al examined sugarcane bagasse for hydrogel preparation [21]. In the present work, the effect of temperature on the properties of obtained cellulose hydrogel films prepared from thanaka is focused, because each plant has its own unique type of cellulose. In addition, thanaka is one of the valuable and precious natural resources in Myanmar since it has been using for many years as a natural cosmetic in daily lives. Both female and male apply grounded thanaka paste on their faces as well as bodies for the purposes of protection against ultraviolet (UV) rays, also for its cooling sensations and feeling of freshness. Thanaka trees usually grow in the upper portions of Myanmar especially in Shwe Bo, Pakokku, ShinmaTaung and Monywa. It is worthy to note that thanaka has strong anti-inflammatory, significant antioxidation, mild tyrosinase inhibition and antibacterial activities [25]. Commercial products of thanaka can be available in various forms such as powder, liquid, paste and bark in Myanmar. Generally only the outer part, the bark of thanaka, is used for these products. Thus, the heartwood usually becomes a waste material after the powder and essence are extracted.

Since biomass-based cellulose has an important role these days, they are an attractive strategy for reproducing advanced materials. Such approach in cellulose hydrogel films produced from various

biomasses is interesting, but no one has published the preparation of hydrogel films from Myanmar's thanaka. Therefore, the aim of this work is to fabricate the thanaka cellulose hydrogel films in effective cosmetic materials like facial masks and medical plaster.

### 2. Experimental Methods

### 2.1. Materials

2. Experimental Methods

Thanaka samples were obtained from Pakokku, Myanmar. As solvent, N,N, Dimethylethylenediamine(DMAc) was purchased from TCI, Tokyo, Japan, and stored for more than 5 days over potassium hydroxide before being used. Lithium chloride was dried in a vacuum oven at 80°C for 12 hours before use. Ethanol, sodium hydroxide, sodium hypochlorite and sulfuric acid were purchased from NacalaiTesque, Inc. Tokyo, Japan.

### 2.2. Thanaka Treatment

Thanaka trunk was crushed and tipped (Figure 1). The samples were then washed three times with distillated water and then dried in an oven at 50°C. The thanaka fibers were treated with acid. 10g of the sample was immersed in 500mL of 4%H<sub>2</sub>SO<sub>4</sub> and stirred for 2hours at 90°C. Following the acid treatment, the sample was washed with abundant distilled water five times to remove any residue of the sulfuric acid solution.

After filtering the sample, 500mL of 10 vol% of sodium hydroxide solution was added. Then the solution and the tipped samples were stirred for 24 hours at 90°C until a black liquor solution was obtained. Afterwards, the tipped sample was washed five times with abundant distilled water to eliminate all traces of the sodium hydroxide solution. The remaining fiber was then immersed in distilled water while stirring at room temperature until pH is neutral. The sample is filtered once more, bleached by sodium hypochloride to obtain the light colored fibers for preparation of cellulose solution. In the bleaching process, the sample was immersed in 500mL of 10 vol% sodium hypochloride solution and stirred for 2 hours at room temperature, 40°C and 50°C. After the fibers were obtained, they were washed five times with abundant distilled water and dried under vacuum for 2 days.



### 2.3. Preparation of Cellulose Solution

The treated fibers were used for the following process in the preparation of the thanaka cellulose in DMAc/LiCl solution [28]. The treated fiber (1g) was suspended in 300mL of distilled water and stirred overnight to allow thorough swelling of the fiber. After water was removed from the suspension by use of

an adapter glass filter under vacuum, ethanol (300 mL) was added to the swelled fiber and the mixture was stirred for 24 hours. The 300 mL of ethanol was removed, and the treated fiber was added to 300 mL of DMAc. This fiber was then left overnight under the stirred condition. Dried lithium chloride and DMAc were added to the swelled thanaka fiber to obtain a 1wt% concentration of the treated thanaka solution. Following this, the mixture was stirred at room temperature for 3 days until a viscous cellulose solution was obtained. Three types of cellulose solutions (TW-RT, TW-40 and TW-50) were obtained under the same procedure.

### 2.4. Preparation of Cellulose Hydrogel Films

For the preparation of hydrogel films, 10g of the cellulose solution was poured into a glass tray (10 cm diameter), and kept again for 24 hours in a container filled with ethanol by using phase inverse method [28]. With time, gradual coagulation of cellulose was observed because of phase inversion of the cellulose from liquid to solid gel in ethanolic vapor [29] and cellulose hydrogel film was obtained in the petri dish. The resultant hydrogel film, as shown in Figure 3, was washed with excess water and then placed in distilled water for 24 hours to remove DMAc and lithium chloride. Then, the obtained hydrogel films were kept in a plastic container filled with distilled water for further experiments. Three types of cellulose hydrogel films (TW-RT, TW-40, TW-50) are prepared by similar procedures.



Fig.3 (a) Transparent Cellulose Hydrogel Film(b) and (c) Cellulose Hydrogel Film Showing Flexibility and Strength for TW-50 Film

### 2.5. Characterization of Hydrogel Films

The formation of prepared samples was monitored by FTIR spectrometer and scanning electron micrograph (SEM). The structural changes of the samples were analyzed by FTIR 4100 series (Jasco Corp. Japan) using KBr pallet method in the Mid IR radiation with the wave number from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> range, using a resolution of 4.0 cm<sup>-1</sup>. Surface morphology of the samples was investigated by SEM (JSM 5300LV Scanning Microscope, JEOL, Japan). The X-ray diffraction (XRD) patterns of Thanaka raw sample and pretreated cellulose fibers were recorded with CuK $\alpha$  radiation ( $\lambda = 1.5418$ ) at 40 kV and 30mA in the range of  $2\theta = 10^{\circ}$ -  $40^{\circ}$  by X-ray diffractometer (Smart Lab, Rigaku, Japan). The samples were dried in vacuum at room temperature before measurements. The crystalinity index (CI) was calculated according to reported method using the following equation:

CI (%) = 
$$(I_{002}-I_{am})/I_{002}) \times 100$$

where  $I_{002}$  is the maximum intensity of the peak (002) lattice diffraction and  $I_{am}$  is the intensity of diffraction attributed to amorphous cellulose [30].

The relative molecular weight and the distribution for resulting celluloses were determined by gel permeation chromatography (GPC)[31]. From the calibration curve of polystyrene standard, the values of  $M_n$ ,  $M_w$  and polydispersity index could be calculated. Here, the abbreviation is as follows:  $M_i$ =molecular weight,  $N_i$ =number of molecule,  $H_i$ =peak height,  $M_n$ =number average molecular weight,  $M_w$ =weight average molecular weight and PDI=polydispersityindex.

Water content of the hydrogel films were determined by weighing dry and wet samples by the procedure that follows. Disk samples with 5 mm diameter were cut from cast films and dried in vacuum oven for 24 hours and weighed ( $W_0$ ). Then, samples were immersed in distilled water for 36 hours. After this process, films were removed from water and wrapped with filter paper in order to remove excess water and weighed again ( $W_1$ ). Finally, the equilibrium water content was calculated from the wet ( $W_1$ ) and dried ( $W_0$ ) hydrogel films. For each sample, four independent measurements were made and the average calculated.

### Water content (%) = $(W_1-W_0)/W_0x \ 100$

Viscoelasticity of the hydrogel film, 2 cm in diameter and 5 mm in thickness, was determined by Auto Paar-Reoplus equipment(AutonPaar Japan, Tokyo) in wet conditions at 37 °C.

### 3. Results and Discussion

### 3.1. Properties of Thanaka Celluloses



Fig. 4 FTIR Spectra of (a) Thanaka Raw Sample (b) Thanaka Wood (c) Acid Treated Sample (d) Alkali Treated Sample and (e) Cellulose Fiber

In Figure 4, FTIR spectra showed remarkable differences between the raw sample and obtained treated samples. All samples presented the strong broad band in 3354 cm<sup>-1</sup> due to the O-H stretching vibration, giving considerable information concerning the hydrogen bonds. The strong bands at 2915cm<sup>-1</sup> and 2850 cm<sup>-1</sup> were due to C-H stretching vibration referring to CH<sub>2</sub>group [32]. The absorption band at 1730 cm<sup>-1</sup> indicated the C=O stretching in carbonyl group of pyrone [33]. Appearance of the band 1640-1618 cm<sup>-1</sup> was owing to relative pure ring stretching mode similar to the aromatic ring C=C stretching in benzene as well as in pyrone ring. This might be due to presence of coumarin and its derivatives which are active compounds of thanaka [34]. From the comparison of the presented FTIR spectra, the peaks around 1510 and 1520 cm<sup>-1</sup> showed the presence of lignin and lignocellulose in the initial raw sample [35,36]. Moreover, the band at around 1200 cm<sup>-1</sup> disappeared in treated fiber assigning to the removal of hemicelluloses. The changes of the bands in the region from 1423 cm<sup>-1</sup> to 1080 cm<sup>-1</sup>were due to the removal of lignin and hemicelluloses [37,38]. This clearly indicated that the amount of lignin from the thanaka raw sample was successfully reduced by the chemical and temperature treatments.

SEM microphotographs of treated samples are shown in Figure 5. The SEM micrograph of thanaka wood sample showed the major constituents of natural fibers in Figure 5(a). The SEM images of treated samples in Figures 5(b) and (c) have changed in their morphologies due to the removal of lignin and hemicelluloses. From Figure 5(d) (e) and (f), it can be seen that the main structural units of cellulose in the plant wall which consists of cellulose microfibrils bonded together in a polymeric matrix. The cellulose fibrils had average diameters of approximately 0.15  $\mu$ m and up to 20cm or more in length [39].

According to the investigation of Adap *et al*, 2011, the cellulose, hemicellulose and lignin percentages were 37%, 21% and 24% in the wood sample. However, they were changed to 49%, 15% and 18% respectively after being pretreated with acid and sodium hydroxide solution caused by dissolution of amorphous materials from the initial wood sample [40]. Xue *et al*, 2007 also mentioned that pretreatment of sodium hydroxide tended to decrease the lignin and hemicellulose which in turn increased the content of cellulose [41]. The result was that the individual cellulose fibrils became clear due to bleaching processes as shown in Figures 5(d)(e) and (f).

Thanaka

Treated

Treated

(a)

Acid

Alkali



Fig. 5SEM Images of Wood (b) Sample (c)

Sample (d) TW-RT (e) TW-40 (f) TW-50

In order to evaluate the effect of the pre-treatment condition on the crystalline structure of the cellulose fibers, XRD measurement was carried out. Figure (6) shows the XRD patterns of raw thanaka and the treated fibers. The patterns (a) to (d) exhibited typical crystalline lattice of cellulose with peaks at 22.6° and 16.1° [42]. This cellulose crystalline can be found in natural plant cellulose. In the crystalinity of thanaka and cellulose fibers, the peak ratio showed that raw thanaka and pre-treated fibers were for 68.5%, 82.1%, 84.2%, and 85.4%, respectively. The increment of the crystalinity in the pre-treated fibers was attributed to the removal of hemicelluloses and lignin by sodium hydroxide and sodium hypochloride treatment, indicating especially higher purity of alkali treated fibers.



Fig.6 XRD X-ray Diffraction Patterns of (a) Raw Thanaka (b) Acid Treated (c) Alkali Treated Sample and (d) Cellulose Fiber

In Table (1), the values of number average molecular weight, weight average molecular weight and poly dispersity index for thanaka cellulose solution samples can be seen. The polydispersity index is used as a measure of the broadness of a molecular weight distribution of a polymer, and is defined by: Polydispersity index = Mw/Mn.

The larger the polydispersity index, the broader the molecular weight [31]. It was found that the sample prepared at 50°C (TW-50) had better distribution of molecular weight and more polydispersity index than the other samples. Therefore, it is meaningful to relate between the nature and physical properties of the cellulose samples and their treated temperatures. In other words, the bleaching temperature affected the properties of the resulting cellulose samples.

Table1. Properties of the Chemically Treated Thanaka Celluloses	

Sample	NaOCl	Yield(%)	Mn	Mw	Mw/Mn=PDI	Water
	Treatment (°C)					Content(%)
TW-RT	25	21.5	149000	599000	4.02	185.71
TW-40	40	15.0	155000	764000	4.93	175.00
TW-50	50	12.5	170000	943000	5.55	162.50

### 3.2. Properties of Thanaka Hydrogels

As shown in Table (1), the values of water content significantly decreased with increasing temperature. These differences significant to TW-RT film was compared with TW-40and TW-50. All of the samples reached equilibrium after 36 hours in the swelling process. The values of water content were found to be

185.71%, 175.00 % and 162.50%, as the temperatures of hydrogel film were at RT,40 °C and 50 °C respectively. Thus at room temperature, the treated sample was able to retain water hence softening the sample more than the others.



Fig. 7(a) Relationship between storage elastic modulus(G'),loss elastic modulus(G''),and strain for the Thanaka cellulose hydrogel films prepared at different temperatures

(b)Relationship between tangent  $\delta$  and strain for the cellulose hydrogel films

Regarding viscoelasticity measurements, it was known that the viscoelastic response to the deformation of cellulose hydrogel films only occurred under momentary deformation. Figure 7(a) shows the viscoelastic data for the thanaka hydrogel films prepared at different bleaching temperatures. It was noticed that the deformation of hydrogel films had  $G' = 8x10^4$  and  $G'' = 7x10^3$  Pa, 5 x10<sup>3</sup> and 3x10<sup>3</sup> Pa for TW-50, TW-40 and TW-RT respectively at 1x10<sup>-2</sup> to 3% strain [43]. The loss elastic modulus (G") of TW-RT was lower than that of the others. This meant that the elastic nature was low and deformation was high in TW-RT sample. It appeared that the hydrogel film TW-RT showed soft nature in the deformation during the strain sweep measurements. Under the prolonged deformed condition, the hydrogel film was observed to recover into its original shape. Figure 7(b) shows the relationship between strain sweep and tan $\delta$ , which was defined as G"/G'. If the value of tan $\delta$  was between 0 and 1, the sample would be a viscoelastic solid. If the value of  $\tan \delta$  was 1, the sample would be at gel point. For values above 1, the sample behaved like a viscoelastic liquid [43]. In the case of strongly cross-linked gel materials,  $\tan \delta > 1$  meant fracture of material or inability to follow deformation, because rigid polymer networks might not flow. In the prepared cellulose hydrogel, cross points of G' and G'' (tan  $\delta = 1$ ) shifted towards low strain range in order of strength of fiber treatment. It was regarded that these viscoelastic changes were caused by the change in the interaction of polymer chains. As a result, pretreatment at 50°C during the sodium hypochloride treatment strengthened the cellulose hydrogel film. Therefore, the fiber structure of the hydrogels was influenced by the pretreatment condition.

### 4. Conclusions

Thanaka cellulose hydrogel films were successfully prepared by phase inversion of the DMAc solution with LiCl. The effect of the sodium hypochloride bleaching on the resultant celluloses was investigated in the fabrication hydrogels. These prepared samples were characterized by FTIR, SEM and XRD which showed that the amount of lignin and hemicelluloses from the thanaka wood sample was successfully reduced by chemical and temperature treatments. Based on the viscoelasticity data, it was found that the temperature affected the properties of cellulose hydrogel films, especially for loss elastic modulus(G"). When the temperature was increased, deformation of the films decreased and thus elasticity increased.

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## **Palladium Ion Adsorbent of Fibrous Silk Fibroin Prepared from**

# Silkworm, Bombyx Mori

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Silk fibroin (SF) fiber in Tsuruoka, Japan was treated for palladium ion adsorbent. The ability of adsorption of  $Pd^{2+}$  was highest among the ions of  $Cu^{2+}$  and  $Cs^+$  used regardless pH condition. The addition of buffer salts decreased  $Cs^+$  adsorption, while  $Pd^{2+}$  was independent of the salt addition. The absorbency of  $Cu^{2+}$  was changed by pH condition, while the  $Cs^+$  adsorption was effectively disturbed by Na<sup>+</sup> added from the buffer salts. Fiber-type protein like SF fiber is promising as effective adsorbent for  $Pd^{2+}$ .

### 1. Introduction

The silk fibroin obtained from the silkworm, Bombyx mori, has been used as a textile fabric for a long time. Recently, many kinds of investigations for their applications in various fields, such as surgical sutures [1], food additives [2], cosmetics [3], drug-release materials [4, 5], and so on, have been extensively carried out. When such silk worm textile is applied for adsorption of metal ions from aqueous solutions, a special interest is attractive for recovering metals and contributes on environmental problems. In commercial uses, zeolite and activated carbon have been used as such adsorbent [6, 7]. However, because of their particle shape the handling and treatment are not easy to condense and precipitate in solutions. The fiber shape like as silk makes easy to suspend them and therefore becomes possible to adsorption more effectively in the solution. The natural silk fiber is constituted of silk fibroin (SF) and a water-soluble protein glue, silk sericin (SS) (Fig. 1). It has been reported that the silk protein has the capability to adsorb some metal ions on its specific chemical structures [8-10]. The amino acid structure of the silk protein provides the ability to adsorb metal ions at the amino (NH<sub>2</sub>) and carboxyl groups (COOH), since the terminals are present in the protein macromolecule. Silk protein has in water isoelectric point (pH =3.7) and at over the pH region the NH<sub>2</sub> forms positively charged ammonium (NH3+). They can be thought that the carboxylate ions electrostatically attract the metal ions in the acidic region. At higher the pH, the amino groups can be coordinated to metal ion(Fig. 1).

(a)  
(b)  

$$NH_2 - (SF) - COOH$$
  
Silk fibroin (SF)  
 $F \rightarrow COO^{-} - M^{n+}$   
 $PH > 5$   $M^{n+} - NH_2 - (SF) - COO^{-} M^{n+}$ 

**Figure 1.** The image of sectional view of raw silk (a), and adsorption mechanism of metal ions to terminals of the SF(b)

It was known for SF fibers that the thermodynamic study about adsorption of  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Mn^{2+}$  was reported [6-8]. But, there is no report palladium (Pd), which is known as the precious metal and used as a material for fuel cells, catalysts and electrodes. This has been emphasizing the importance of research of the process of recovering the precious metals from industrial waste. Although in the some methods for Pd recovery, the sedimentation and the adsorption using activated carbon have been proposed, high selectivity and simple operatively are still required [11]. Therefore, this paper describes adsorption of metal ions including Pd<sup>2+</sup> on SF fiber shape, is expected that SF has large adsorption surface area and the solid-liquid separation after adsorption proceeds rapidly. In this study, we investigated adsorption tendency in some metal ions, Pd<sup>2+</sup>, Cu<sup>2+</sup>, and cesium (Cs<sup>+</sup>) in the aqueous solutions.

### 2. Experiment

### 2.1 Preparation of silk fibroin

The raw silk cocoons kindly supplied by MATUOKA Co., Inc. Japan were boiled with an aqueous solution of 5 % Na<sub>2</sub>CO<sub>3</sub> for 1 hour to remove SS, and then was in suction filtration to obtain SF (Fig. 2). The SF obtained was washed by distilled water and dried at 45 °C for more than 24 hrs under the atmosphere. The SF was immersed to the saturated CaCl<sub>2</sub> aqueous solution. The solution of CaCl<sub>2</sub> destroy aggregation of the SF fibers and increase surface areas. Then the SFs were rinsed by distilled water to remove Ca<sup>2+</sup> and Cl<sup>-</sup>, and then were dried. Thus, the fibrous SF was obtained. Analysis of SF was operated by FTIR obtained using a Shimadzu IRAffinity-1 in the spectral region of 4000-400cm<sup>-1</sup>. Sample of SF film was made by solution casting[12]. For the SF, the observed band at 3200cm<sup>-1</sup> was due to N-H stretching vibration, and the bands appeared at 1650cm<sup>-1</sup>, 1540cm<sup>-1</sup>, 1235cm<sup>-1</sup>, and 650cm<sup>-1</sup> are assigned, respectively, to amide I, amide II, amide III, and amide V for random coil or silk I-form[13]. O-H stretching vibration was overwrapped with N-H stretching at 3100-3400cm<sup>-1</sup>.



Figure 2 Appearance of silk cocoons (a) and SF fibers (b)

### 2.2 Adsorption of each metal ion

The aqueous solutions of metal ion of 5-100 mg/L were prepared by diluting the original solutions of PdCl<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and CsCl with a concentration of 1000 mg/L. These solutions as an AAS (Atomic Absorption Spectrometry) grade were purchased from Kanto Chemicals Co., Inc. The 0.5 g of the SF prepared was added into 50 ml of the solution and then added 30 mL of the buffer solution to adjust the pH. The buffer solution was prepared by mixing the 5 g of 0.1 M solution of acetic acid and 40.8 g of 0.6 M solution of sodium acetic acid(CH<sub>3</sub>COOH/CH<sub>3</sub>COONa). The value of pH was controlled at 6.9. The adsorption experiments were carried out under shaking for 3-480min in the water bath controlled at 40 °C [8-10]. After that, SF was removed from the solution by filtration. The concentrations of the ions of Pd<sup>2+</sup> and Cu<sup>2+</sup> in the aqueous solutions were measured by ICP analysis (Inductively Coupled Plasma, Hitachi High-technologies SPS3500DD) and the Cs<sup>+</sup> was AAS analysis (Hitachi High-technologies Z-5010).

three times and the average values of the concentrations were determined. The removal efficiency can be calculated according to the following equation:

$$RE\left[\%\right] = \frac{c_i - c_f}{c_i} \tag{1}$$

where RE is the removal efficiency of metal ions,  $C_i$  and  $C_f$  are the initial and the final concentrations of metal ions (mg/L), respectively. In order to confirm existence of some kinds of elements on SF surface, measurements using SEM-EDX (Hitachi FE-SEM S-4800 EDX) was employed.

### 3. Results and Discussion

3.1 Effects of contact time and initial concentration

First, effect of contact time on the adsorption efficiency was discussed for the SF fiber. Figure 3 shows effect of adsorption time on the removal efficiency for  $Pd^{2+}$ ,  $Cu^{2+}$  and  $Cs^+$ . The initial concentration was 50mg/L, for the buffer solution (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) added. As shown in the figure, the value of RE for Cs<sup>+</sup> and Cu<sup>2+</sup> reached maximum at an early stage 3min. After that the RE value somewhat decreased, implying the occurrence of desorption. From above result, we assumed that the equilibrium was realized explained by two features of rate of adsorption and adsorption capacity, meaning that the capacity is determined by total amount of adsorption sites. On the while the capacity is determined by total amount of adsorption[9, 10]. This is a reason of less adsorption capacity of Cu<sup>2+</sup> and Cs<sup>+</sup>. It was noted that Pd<sup>2+</sup> was highly adsorbed to the SF fiber. The high absorbency for Pd<sup>2+</sup> considered by formation of complex peculiar to metal-protein structure at pH6.9[14].



**Figure 3.** Effect of adsorption time on the removal efficiency for metal ions. The initial concentration was 50 mg/L, and buffer solution was added.

### 3.2 Removal efficiency for each metal ion

The results of RE for each metal ion were shown at 120min (Figure 4). The figures (a) and (b) were compared with and without the buffer (CH<sub>3</sub>COOH/CH<sub>3</sub>COONa) added. The value for Pd<sup>2+</sup> was the highest among the ions employed, while the RE of the Cs<sup>+</sup> was 4 %, with the buffer at pH7.2, *i. e.*, the ion hardly adsorbs on the silk fibroin, but the value increased without the buffer. This meant that that electrostatic force was acted in the adsorption. The tendency of removal efficiency was in the order of Pd<sup>2+</sup> Cu<sup>2+</sup> > Cs<sup>+</sup>. For Cu<sup>2+</sup>, the presence of the buffer was effective for the adsorption at pH 6.9 although the absence at pH 3.8 was significantly decreased. However, the

independence of the buffer addition was observed in the  $Pd^{2+}$  systems. It was interesting that the high adsorption was obtained at acidic region of pH 1.4. This meant that the coordination was stable when the salt concentration was changed in the solution.



**Figure 4.** Results of removal efficiency of each metal ion with and without the buffer solution (a and b, respectively).

### 3.3 Effect of adsorption disturbance by Na<sup>+</sup>

In order to compare their adsorption behavior, the influence on RE for  $Pd^{2+}$  and  $Cs^+$  was measured at different concentration of the sodium ion (Na<sup>+</sup>) which coexisted in the solution (Figure 5). The value of the RE of the  $Pd^{2+}$  system was almost high value regardless change in the Na<sup>+</sup> concentration, while that of the  $Cs^+$  one decreased as the concentration of Na<sup>+</sup> increased. This result suggests that Na<sup>+</sup> may disturb the adsorption of  $Cs^+$  on the SF adsorbent by electrostatic shielding effect. However, the  $Pd^{2+}$  ion could coordinate to the NH<sub>2</sub> groups of the SF fiber without the disturbance with the salt effect.



**Figure 5.** Effect of concentration for Na<sup>+</sup> on the adsorption for cesium ions (initial concentration of cesium ions: 50mg/L, without the buffer solution, time:120minutes)

SEM-EDX analysis was conducted in order to check the trace of the sodium which remains on SF surface. The images obtained by SEM-EDX for SF after Cs<sup>+</sup> adsorption are shown in Fig. 6.



**Figure 6**. Results for SEM.EDX observations for SF after adsorption experiments of  $Cs^+$ ; (A) without the buffer solution, (B) with the buffer solution; (a) normal SEM image, (b) EDX image of all detected atoms, and respective image for (c) carbon, (d) oxygen, (e)nitrogen, (f) sodium, (g) calcium.

In SEM image (a) of (A) and (B), smooth surface peculiar to SF fiber was confirmed. This was due

to result of eliminating sericin from the surface of raw silk. The diameter of the fiber was about 10 micrometers in general. The difference in the surface with or without of buffer solution system was not observed. The detection result of carbon, calcium, nitrogen, and oxygen were also exhibited for comparison. Existence of carbon, nitrogen, and oxygen is ordinary and is originated in silk protein. The trace of the calcium used at the preparation of SF was not detected. The results of sodium showed the distinctive situation by the existence of use of buffer solution. The peak which corresponds to Na in the sample exhibited without buffer solution was almost nothing. On the other hand, the result of the silk using buffer solution showed large peak originating in the Na, suggesting disturbing adsorption instead of Cs<sup>+</sup>. Although the EDX analysis by a SEM photograph was served as observation on only surface of the sample, this was evidence that Na<sup>+</sup> disturbed the adsorption of Cs<sup>+</sup> by ion exchange like a electrostatic shielding to the ionized protein groups.

### 4. Conclusion

The RE of  $Pd^{2+}$  was the highest among the ions used, because of suitable conditions of the coordination adsorption. For  $Cu^{2+}$  adsorption, the buffer solution was effective to obtain suitable pH condition and  $Na^+$  was adsorbed more preferentially than  $Cs^+$  by ion exchange. For  $Pd^{2+}$  recovery, the SF fiber was promising as effective adsorbent.

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# Numerical Study on Controlling Factors of Convection Behavior of Hydrogen Generated in Radioactive Waste Long-term Storage Containers

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> Fuel debris which is removed from the Fukushima Dai-ichi Nuclear Power Plant is packed to the inside of a radioactive waste long-term storage container. When the fuel debris includes water, hydrogen and oxygen are generated by decomposition of water by radiation from the fuel debris. Since hydrogen is flammable gas, it has a risk of combustion or explosion. Therefore, it is important to clarify the hydrogen behavior in the radioactive waste long-term storage container. As for previous studies on hydrogen behavior in the sealed container, experimental studies and analyses have been performed by several researchers. However, those studies on hydrogen behavior to various packing conditions of the fuel debris have not been found. Then, controlling factors which define the convection behavior of hydrogen were investigated numerically for various packed conditions. The present study shows the predicted results on convection behavior of hydrogen in a simply simulated radioactive waste long-term storage container. The influence of the bulk density, inflow velocity, temperature, etc. upon the convection behavior of hydrogen was clarified quantitatively.

### 1. Introduction

Fuel debris which is removed from the Fukushima Dai-ichi Nuclear Power Plant (1F) is packed to the inside of a radioactive waste long-term storage container. When the fuel debris includes water, hydrogen and oxygen are generated by decomposition of water by radiation from the fuel debris. Since hydrogen is flammable gas, it has a risk of combustion or explosion. Therefore, it is important to clarify the hydrogen behavior in the radioactive waste long-term storage container under the conditions that the fuel debris containing water is accumulated. Moreover, the bulk density of the fuel debris is not constant and the arrangement of that in the container is not uniform. That is, it is considered that the fuel debris accumulated in the container has arbitrary distributions in the vertical and horizontal directions on the bulk density and the arrangement depending on the packing condition of the fuel debris into the container. However, it is not easy to clarify hydrogen behavior in the storage container experimentally in terms of time and cost. Therefore, we conducted a study by numerical analysis.

As for studies of hydrogen behavior in the sealed container, Inoue, et al. [1] evaluated experimentally evaluating hydrogen diffusion using the Hallway model. On the other hand, Hoyes and Ivings [2] performed CFD modelling of hydrogen stratification in enclosures and Visser, et al. [3] predicted numerically hydrogen distributions in a containment vessel. However, experimental and analytical studies on hydrogen behavior to various packing conditions of the fuel debris have not been found. Then, the influence of the bulk density, inflow velocity, temperature, etc. upon the convection behavior of hydrogen was analyzed numerically.

The present study shows the predicted results on convection behavior of hydrogen in a simply simulated radioactive waste long-term storage container. Controlling factors which define the convection behavior of hydrogen are described in detail.

### 2. Numerical Analysis

### 2.1 Basic equations

For the analysis, The ANSYS FLUENT [4-5] was used. The basic equations on thermal-hydraulics of the multi-component gases considering compressibility are as follows.

- Mass conservation equation

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j) = 0 \qquad (1)$$

- Momentum conservation equation

$$\frac{\partial}{\partial t}(\rho u_i) + \frac{\partial}{\partial x_j}(\rho u_i u_j) = -\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}\left[\mu\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)\right] + \rho g_i \quad (2)$$

- Energy equation

$$\frac{\partial}{\partial t}(\rho h) + \frac{\partial}{\partial x_j}(\rho h u_j) = \frac{\partial p}{\partial t} + u_j \frac{\partial p}{\partial x_j} + \frac{\partial}{\partial x_j} \left(\lambda \frac{\partial T}{\partial x_j}\right) + \frac{\partial}{\partial x_j} \left(\rho \sum_s h_s D_s \frac{\partial Y_s}{\partial x_j}\right) + Q \quad (3)$$

- Mass conservation equation of species

$$\frac{\partial}{\partial t}(\rho Y_s) + \frac{\partial}{\partial x_j}(\rho Y_s u_j) = \frac{\partial}{\partial x_j}\left(\rho D_s \frac{\partial Y_s}{\partial x_j}\right) \quad (4)$$

- Equation of state

$$p_s = \rho_s \frac{R_0}{M_s} T \qquad (5)$$

The density r, pressure p, enthalpy h and mass fraction  $Y_s$  and in the above basic equations are defined as follows.

$$p = \sum_{s} p_{s} \quad (6)$$
$$h = \sum_{s}^{s} Y_{s} h_{s} \quad (7)$$
$$Y_{s} = \frac{\rho_{s}}{\rho} \quad (8)$$

### 2.2 Porous model

In the porous media model, an empirically determined flow resistance is used to the region defined as "porous" [5]. Porous media are modeled by the addition of a momentum source term to the standard fluid flow equations. The source term is composed of two parts; a viscous loss term and an inertial loss term.

$$s_i = -\left(\sum_{j=1}^3 D_{ij} \,\mu \nu_j + \sum_{j=1}^3 C_{ij} \frac{1}{2} \rho |\nu| \nu_j\right) \tag{9}$$

where  $S_i$  is the source term for the *i*-th (x, y, or z) momentum equation, |v| is the magnitude of the velocity and D and C are prescribed matrices.

In the present study the porous media is assumed as homogeneous and the following equation is derived.

$$S_{i} = -\left(\frac{\mu}{\alpha}\nu_{i} + \sum_{j=1}^{3}C_{2}\frac{1}{2}\rho|\nu|\nu_{j}\right)$$
(10)

where  $\alpha$  is the permeability and  $C_2$  is the inertial resistance factor. From the assumption of packed beds, those values are shown as

$$\alpha = \frac{D_p^2}{150} \frac{\varepsilon^3}{(1-\varepsilon)^2} \qquad (11)$$
$$C_2 = \frac{3.5}{D_p} \frac{(1-\varepsilon)}{\varepsilon^3} \qquad (12)$$

The scheme of solution method uses the SIMPLE (Semi-Implicit Method for Pressure-Linked Equation) method. In order to analyze transport behavior of two component gases between air and

hydrogen, the mixture model was chosen. The fluid in the container is set to be mixture of air and hydrogen. At the initial condition, the inside of the container is filled air completely and hydrogen is nothing.

### 3. Analytical Conditions 3.1 Computational grid

Figure 1 shows the computational grid used in this calculation. The radioactive waste storage container is simulated with a sealed two-dimensional rectangular container. Here, fuel debris is simulated by 'Porous model'. In this calculation, a packed bed model which is one of the 'Porous model' is used. In the packed bed model, it is expressed by inertial resistance and viscous resistance which can be obtained by Eq. (11) and (12). The resistances of Eq. (11) and (12) are determined by the porosity and the particle diameter. The heat of decay is simulated by giving heat to the porous zone. The generation of hydrogen is simulated by flowing from the nozzle which is positioned at the bottom of the container. The dimensions of the container are the same as the experimental setup which is shown Fig.2. The computational grid is set to  $45 \times 90$  cells, and adopted a non-uniform mesh division which makes a finer mesh at the vicinity of the wall.

As an outline of this calculation, the container is filled with air initially, the lower half of the container is set to the porous, and hydrogen is flowed from one of the three nozzles at the bottom of the container. The heat transfer rate is given to the porous media. In this calculation, only one positioned nozzles at the center are used.



### **3.2 Calculation Parameters**

Table 1 shows the controlling factors which specify to influence the hydrogen behavior. On the controlling factors, the hydrogen generation amount, the decay heat amount, and the bulk density of fuel debris are considered. In order to investigate numerically the effect of these controlling factor, parameters of the initial flow rate of hydrogen, the heating amount, and the porous packing density are used.

As for a method of estimating hydrogen generation amount and decay heat amount, the decay heat amount was calculated using the TODRES equation [6-8]. The equation of TODRES is shown in equation (13).

$$\frac{P(t)}{P_0} = 0.066[t^{-0.2} - (t_s + t)^{-0.2}] \quad (13)$$

Where P is the decay heat,  $P_0$  is the thermal output during normal operation of the reactor, t is the elapsed time since reactor shutdown,  $t_s$  is the time of fuel rod use,  $P_0$  is given 1380 MW from the data of 1F [8-9], and  $t_s$  is given 1.74 years from reference [8-10]. The calculation results are shown in Fig. 3. The horizontal axis in Fig. 3 is the elapsed time after reactor shutdown, and the vertical axis is the ratio of decay heat to normal output. Subsequently, on the assumption that debris is packed in the inside of the container entirely, the decay heat quantity is obtained using the volume of the

container, which is calculation by Eq. (14).

$$P = \frac{P \times V}{9.924} \qquad (14)$$

Where P is the decay heat in the container and V is the volume of the container, and the value of 9.924 is the volume of all the fuel rods in 1F. The calculation result is shown in Fig.4. The horizontal axis of Fig. 4 shows the elapsed time from the reactor shutdown, and the vertical axis shows the decay heat amount.

In addition, the hydrogen generation amount was estimated from the decay heat amount and the hydrogen generation value (G value). The G value was  $4.7 \times 10^{-8}$  mol/J from the reference of [11] and [12]. The calculation result is shown in Fig.5. The horizontal axis of Fig. 5 is the heating transfer rate, and the vertical axis is the initial flow velocity calculated in consideration of the hydrogen generation amount and the cross-sectional area of the nozzle from the hydrogen generation amount.

Calculation matrix was prepared from calculation of hydrogen generation amount and decay heat amount. The calculation matrix is shown in Table 2. Here, the inlet velocity of 0.4 m/s means the hydrogen flow rate which is generation in a container after one month from the shutdown of the reactor core. Similarly, the inlet velocity of 0.1 and 0.4 m/s mean average hydrogen flow rate in a container after 1 year and 10 years from the shutdown of the reactor core. For setting of porosity and particle diameter. In the calculation, the particle diameter was fixed to 10 mm, porosity was set to 0.2 (state with many substance), 0.5 (middle), and 0.8 (state with many space).

Table.1 Estimated controlling factors						
Controlling factors	Analysis time conditions	Estimated parameters				
Hydrogan gaparation amount	Inlet velocity	U2 male concentration				
Hydrogen generation amount	& Inflow time	H2 mole concentration				
Decey heat	Heating transfer rate	Tomporatura				
Decay heat	(Source term)	Temperature				
Dangity of the fuel debris	Packed bed model	Eviction loss				
Density of the fuel debris	(Porosity and particle diameter)	FIICHOIL IOSS				



Table.2 Calculation matrix			
	Inlet velocity [m/s]		
Heating amount (W)	0.01	0.1	0.4
830			
7600			
31000			

### Fig.5 Hydrogen generation rate estimation

### 4. Preliminary calculation result 4.1 Velocity

Preliminary analysis was carried out based on the calculation conditions shown in Table 2. First, the results on the difference in inlet velocity are shown. The analysis was performed by the non-steady state, the calculation time was 10 seconds. The inlet flow velocity of hydrogen is changed, heating amount and porosity are constant, which are 7600W and 0.5, respectively. Figure 6 shows the  $H_2$  molar concentration distribution at inlet velocities of 0.1 m/s and 0.4 m/s. As compared with 0.1 m/s, 0.4 m/s shows that diffusion of hydrogen is observed in the upper region of the container, and the concentration is higher. Next, the relationship between the inlet velocity and molar concentration is shown in Fig. 7 is the inlet velocity, and the vertical axis is the maximum molar concentration in the porous region and the non-porous region. At 0.01 m/s it was confirmed that the concentration is low even in the porous region, and at 1 m/s, it has high concentration even in the non-porous region.



### 4.2 Heating amount rate

The calculation was performed up to 300 s to investigate the effect on heating amount. The heating amount is changed, inlet flow velocity of hydrogen and porosity are constant, which are 0.1m/s and 0.5, respectively. The temperature distribution of 7600 W and 31000 W is shown in Fig.8. The change in temperature was 4 K for 7600 W and 8 K for 31000 W. Next, the relationship between heating amount and temperature is shown in Fig.9. The horizontal axis in Fig.9 is the heating amount, and the vertical axis is the temperature difference  $\Delta T$  at the center positions between the porous region and the non-porous region. From Fig.9, it was confirmed that the temperature of both the porous region and the nonporous region rises logarithmically.



### 4.3 Porosity

The calculation was performed up to 10 s to investigate the effect on porosity. The porosity changed, inlet flow velocity of hydrogen and heating amount are constant, which are 0.1m/s and 0.5, respectively. The difference in Porosity in the packed bed model is represented by the difference between inertial resistance and viscous resistance. In this calculation, the particle size was fixed at 10 mm in order to investigate the effect of Porosity. The flow velocity distributions with the Porosity of 0.4 and 0.8 are shown in Fig.10. When the porosity is 0.4, it flows straight ahead, and when the porosity is 0.8, we see that the diffusion has started. Next, the relationship between Inertial resistance (C<sub>2</sub>) derived by Eq. (12) and porosity is shown in Fig.11. The horizontal axis is porosity, and the vertical axis is inertial resistance. The higher the porosity, the higher the inertia resistance and the smaller the particle diameter, the higher the inertia resistance. The difference in resistance between the particle diameter of 10 and 100 mm is around  $10^2$  for a unit length.



### 5. Conclusions

In this research, preliminary analysis was conducted on the hydrogen behavior in the radioactive waste storage container associated with the decommissioning reactor of 1F. The influence of the controlling factors were analyzed by numerical analysis. As the present results, the following conclusion was derived.

- 1) As for the influence of the inlet velocity of hydrogen, the molar concentration distribution of hydrogen changes and the time required to pass through the porous region varies.
- 2) In the influence of heating amount, there is little influence on hydrogen behavior without heat or time above a certain level. In both the non-porous region and the porous region, the temperature increases logarithmically.
- In the influence by porosity, porosity has changed its resistance to flow, and the velocity distribution in the porous region changes greatly and the time required to pass through the porous region varies.

In the future, we will analyze for a long time, and we will clarify the influence due to particle diameter,

and buoyancy effect due to the heat transfer rate by the decay heat.

### Nomenclature

- $C_2$  the inertial resistance factor [1/m]
- $D_p$  mean particle diameter [m]
- $D_s$  effective diffusion coefficient of chemical species s [m<sup>2</sup>/s]
- g gravity  $[m/s^2]$
- h enthalpy [J/kg]
- $h_s$  enthalpy of chemical species s [J/kg]
- $M_s$  Molecular weight  $\cdot$  atomic weight of chemical species s [kg/mol]
- P decay heat [W]
- $P_0$  thermal output during normal operation of the reactor [W]
- *P* decay heat amount in the volume of the container [W]
- *p* pressure [Pa]
- *p<sub>s</sub>* partial pressure of chemical species s [Pa]
- Q calorific value [W/m<sup>3</sup>]
- $R_0$  universal gas constant (= 8.314) [J/mol/K]
- T temperature [K]
- t elapsed time from reactor shutdown [s]
- $t_s$  fuel rod use time [s]
- *u* velocity [m/s]
- V volume [m<sup>3</sup>]
- x descartes coordinates [m]
- $Y_s$  mass fraction of chemical species s [-]
- $\alpha$  permeability [m<sup>2</sup>]
- $\epsilon$  porosity [-]
- $\lambda$  heat conduction coefficient [W/m/K]
- $\mu$  viscosity [Pa·s]
- v kinetic viscosity [m<sup>2</sup>/s]
- $\rho$  density [kg/m<sup>3</sup>]
- $\rho_s$  density of chemical species s [kg/m<sup>3</sup>]
- Subscripts
- *i* x direction lattice index
- j y direction lattice index

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