

Waste Management in a Hot Laboratory of Japan Atomic Energy Agency – 2: Condensation and Solidification Experiments on Liquid Waste

Sou Watanabe, Hiromichi Ogi, Atsuhiko Shibata, Kazunori Nomura

Abstract—As a part of STRAD project conducted by JAEA, condensation of radioactive liquid waste containing various chemical compounds using reverse osmosis (RO) membrane filter was examined for efficient and safety treatment of the liquid wastes accumulated inside hot laboratories. NH_4^+ ion in the feed solution was successfully concentrated, and NH_4^+ ion involved in the effluents became lower than target value; 100 ppm. Solidification of simulated aqueous and organic liquid wastes was also tested. Those liquids were successfully solidified by adding cement or coagulants. Nevertheless, optimization in materials for confinement of chemicals is required for long time storage of the final solidified wastes.

Keywords—Radioactive liquid waste, condensation, solidification, STRAD project.

I. INTRODUCTION

RADIOACTIVE liquid waste generated in hot laboratories involves not only radioactive elements but also various chemicals which have been used or added for experimental or analytical purposes. Some of those liquid wastes have not been processed but stored inside the facilities due to reactivity of the chemicals. In some cases, even mixing of the liquids is not appropriate, and the liquids should be stored separately. Treatment of the various kind accumulated liquid wastes would be one of the most difficult challenges in the step of decommissioning or dismantling of the facilities.

Japan Atomic Energy Agency started fundamental studies to develop new technologies for processing the accumulated liquid waste considering treatments inside shielded environments with remote handling devices. The study is conducted as a collaborative research project with universities, institutes and private companies, and the project was named as Systematic Treatment of Radioactive liquid waste for Decommissioning (STRAD) [1], [2]. Liquid wastes generated by analyses on experimental samples contain many kinds of chemicals, and they are one of the most difficult targets in this project.

Separation and decomposition of NH_4^+ in order to prevent explosive NH_4NO_3 formation are primal treatments of the analytical liquid wastes since this specie is commonly involved in them. We have shown that separation of NH_4^+ by ion

exchange or vaporization and decomposition of NH_4^+ by ozone oxidation under existence of Co^{2+} homogeneous catalyst are one of the most promising procedures [3]-[5]. In order to achieve efficient treatment, condensation of the waste solution in advance with the separation process is desirable. However, some chemicals involved in the analytical liquid waste should not be heated due to safety reasons. Condensation technologies without heating are required to be developed. In this study, condensation of analytical waste solutions using RO membrane was examined and enrichment performance of NH_4^+ ion was evaluated.

Even after the removal of NH_4^+ ion from the aqueous wastes, some chemicals still remain in the solution. Those chemicals are also desirable to be treated if they have chemical reactivity. One of the easiest treatments must be confinement of those chemicals into chemically and physically stable solids. Solidification of the liquid wastes might be promising not only for aqueous wastes but also for organic wastes. In this study, solidification experiments on simulated aqueous and organic wastes were also carried out. Cementation and solidification by adding coagulants were tested for aqueous and organic liquids, respectively.

II. EXPERIMENTAL

A. Condensation by RO Membrane

Waste solution generated by titration analysis on Pu containing solution was supplied to condensation experiments. The waste solution contains HNO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaOH and Pu. Fig. 1 shows an experimental apparatus, where the system consisted of a RO membrane filter (SW301-251, The Dow Chemical Company), a double plunger pump and a pressure gauge. The system was set inside a glove box of Chemical Processing Facility (CPF) of Japan Atomic Energy Agency. Feed solution was supplied into the filter through the pump and the pressure gage, and then condensed product solution and effluent was obtained. Pressure of the feed solution at inlet of the filter was controlled not to exceed an upper pressure limit of the filter; 5.5 MPa. Concentration of NH_4^+ in each solution was analyzed by an ammonia electrode (5002S-10C, HORIBA, Ltd.). Temporal target of NH_4^+ concentration in the effluent was set to be 100 ppm which was evaluated under liquid waste management of CPF.

Sou Watanabe, Atsuhiko Shibata, and Kazunori Nomura are with Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki 319-1194 Japan (corresponding author, phone: +81-29-282-1111; fax: +81-29-282-9290; e-mail: watanabe.sou@jaea.go.jp).

Hiromichi Ogi is with Inspection Development Company Ltd., 4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki 319-1112 Japan.

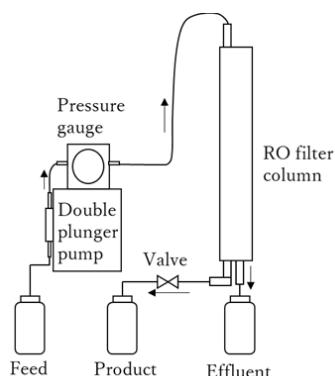


Fig. 1 Condensation experimental apparatus

B. Solidification of Aqueous Solution

Simulated aqueous waste shown in Table I was supplied to the cementation experiments, where those compositions were estimated from typical analyses for radioactive solutions employed in CPF. pH of the solutions were adjusted to 7 by adding 1 mol/L Na_2CO_3 solution, and then twice weight of Portland cement powder was added into the solutions. The slurries were stirred 10 min, and were placed in atmosphere during 10 months.

The solidified cements were smashed into powders and large fractions were removed through 500 μm mesh. 1 g of the mesh controlled powders was immersed into 10 mL of water for 24 hours, and leached chemical species in the supernatant solutions were analyzed by ion chromatography.

TABLE I
CHEMICAL REAGENTS INVOLVED IN THE SIMULATED AQUEOUS LIQUIDS FOR CEMENTATION

ID	Chemicals involved	Source
A	Ammonium peroxodisulfate, AgNO_3 , H_3NSO_3 (sulfamic acid), HNO_3 , $(\text{NH}_4)_2\text{SO}_4$, NaOH , $\text{C}_6\text{H}_8\text{O}_6$ (ascorbic acid)	Mixture of Pu analysis and acidity analysis
B	HAN , NaNO_2 , FeSO_4 , H_3NSO_3 (sulfamic acid)	Pu analysis
C	$(\text{NH}_4)_2\text{SO}_4$, HNO_3 , Hydroxylamine sulfate, Hydroxyl amine nitrate, Hydrazine, Ammonium peroxodisulfate, AgNO_3 , H_3NSO_3 (sulfamic acid), Sulfamic acid iron(II) salt, HNO_3 , TOPO, Ethyl acetate, Dibenzoylmethane, Pyridine, $\text{C}_2\text{H}_5\text{OH}$, $\text{Mg}(\text{NO}_3)_2$, EDTA	Mixture of several analyses
D	FeSO_4 , Hydrazine, HNO_3	Np analysis
E	$\text{Fe}_2(\text{SO}_4)_3$, NaN_3 , HNO_3	HN_3 analysis
F	$(\text{NH}_4)_2\text{SO}_4$, NaOH , FeSO_4 , H_3NSO_3 (sulfamic acid), $\text{Na}(\text{NO}_2)$, $\text{C}_6\text{H}_8\text{O}_6$ (ascorbic acid)	Mixture of MS analysis and acidity analysis

C. Solidification of Organic Liquid

Simulated liquid waste containing organic compounds was solidified by adding coagulant which is commercially available. Simulated organic liquid waste containing sulfamic acid, Fe^{2+} , silver nitrate, tolyltriazole (TTA) and xylene which is typically generated by Np analysis was supplied to the solidification experiment. The coagulants shown in Table II were added into 10 mL of the waste solution until the liquid became viscous. Resultant solids were placed in glass vials during 10 months, and change in appearances was observed.

1 g of the solids just after the solidification were sealed in

glass vials with 100 mL volume, and were irradiated by gamma-ray at the irradiation room No. 1 in Co-60 Gamma-ray Irradiation Facility in Takasaki Advanced Radiation Research Institute, QST, Japan. Dose rate and integrated irradiation dose of the irradiation were 3 kGy/h and 2 MGy, respectively. Changes in their appearance were observed and amount of H_2 gas generated by the irradiation was measured by gas chromatography in order to evaluate durability of the solids against irradiation.

TABLE II
COAGULANTS USED FOR SOLIDIFICATION EXPERIMENTS

ID	Name of coagulant	Producer	Type
1	NIP GEL (AZ200)	TOSOH SILICA Co.	Silica gel
2	OIL SOLUTIONS POWDER	Oil Solutions International, Inc.	Microcapsule
3	Fyugel A	Eco Field Co., Ltd.	Polymer
4	$\alpha\text{Gel-1650}$	ALPHA JAPAN Inc.	Polymer
5	LONGCRIN S-101	Kurita Water Industries Ltd.	Polymer
6	M.S.GEL D-120A	AGC Si-Tech Co., Ltd.	Silica gel

III. RESULTS AND DISCUSSION

A. Condensation by RO Membrane

RO membrane filtering system set in a glove box is shown in Fig. 2, where operation for pressure control was performed by hands through gloves. Currently improvement of the system for operation with MS manipulators is progressing.

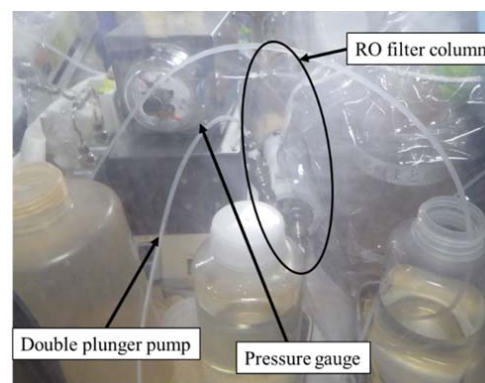


Fig. 2 RO membrane filter system set in a glove box

4000 mL of the feed solution was processed with 400 mL/h and 5 MPa, and 800 mL of effluent and 3200 mL of NH_4^+ enriched product solution were obtained. Concentrations of NH_4^+ in the feed solution, the effluent and the product were 2934, 10, 2807 ppm, respectively. NH_4^+ in the product solution was diluted by water which was initially filled in the filter column, thus it resulted in smaller value than the initial one. The target NH_4^+ concentration in the effluent was achieved by the operation. Material balance of NH_4^+ resulted in about 75%. The poor material balance must be caused by accuracy of the measurements (error bar is about 20%) and liquid retained in the system. More precise NH_4^+ analysis for solutions with complicated composition is under consideration.

The product solution was supplied into the filter again to

obtain more concentrated product and more volume of effluent satisfying target NH_4^+ concentration. Totally 4 times repeated operations were carried out, and 1550 mL of the final product and 2450 mL of effluent were obtained. Concentrations of NH_4^+ in the product and effluent were 2124 and 73 ppm, respectively. The final effluent also satisfied the target NH_4^+ concentration. Through those experiments, the RO filter technology was shown to be promising for condensation of radioactive liquids containing various chemicals without heating. Condensation performance on other chemical species is currently underway.

B. Solidification of Aqueous Solution

Appearances of the slurry after mixing are shown in Fig. 3. 10 mL of Na_2CO_3 solution and 62 g of the cement was added in ID = A. During the pH adjustment procedure, the liquid became milky color and bubbles were released from the liquid. Decomposition of some chemicals is suspected to lead the behavior. Chemical form of the gas has to be identified for safety treatment, and some chemicals should be treated in advance with the solidification process if necessary. Remaining solution was successfully solidified and resultant volume was 45 mL.

Solidification of liquid with ID = B was also successfully done. However, about 39 mL of Na_2CO_3 solution was required for pH adjustment, and consequently volume of the product became 100 mL. Some chemicals involved in the solution can behave as buffer, and it may cause moderate pH increase. Thus, more concentrated alkaline solution might be appropriate for the pH adjustment in order to reduce volume of the final waste.

For ID = C and D, cementation was done without any difference from previous one except for the volume of the alkaline solution used for pH adjustment, i.e. 9 and 20 mL of the alkaline solution were required for ID = C and D, respectively, and volumes of the final form were 45 and 65 mL, respectively.

Precipitation and bubbles were generated during the pH adjustment for ID = E. The precipitation and the gas might be attributed to $\text{Fe}(\text{OH})_3$ and HN_3 gas, respectively. Azide ion should be treated in advance with cementation process in the respect of safety because HN_3 is easily vaporized at low temperature (b.p. = 310 K) and it has chemical toxicity.

Solidification of the liquid with ID = F was not immediately done and the slurry was separated into 2 phases. Extra addition of the cement powder prevented the phase separation; consequently the liquid was solidified by adding totally two times of the initial amount of the cement powder.

Solutions with ID = A, E and F should be carefully treated for the cementation due to stability of involved chemicals. Since ascorbic acid is involved commonly in solutions with ID = A and F, it might cause the different cementation behavior. Behavior of ascorbic acid during cementation should be precisely investigated in order to establish a stable solidification process. As discussed above, sodium azide should be also treated before the solidification.

The product solids were stable during 10 month in the respect of their appearances, and those were supplied to the

leaching test.

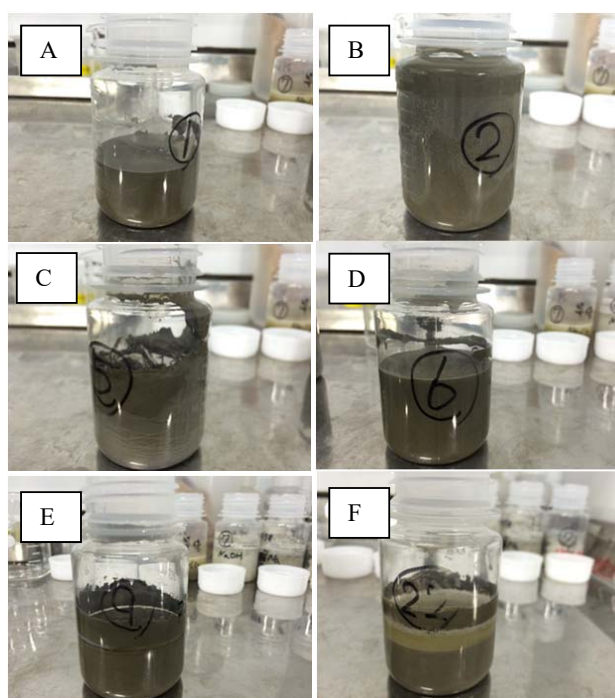


Fig. 3 Slurries of the simulated aqueous wastes with cement

Chemical species found in the supernatant solutions after the leaching tests are shown in Table III. Most part of the observed species was metallic cations which compose the cement. However, small amount of chemicals involved in the simulated waste solutions were also detected. Those species were considered to be dissolved from the cement into water. NH_4^+ was not observed by the ion chromatography. It must be vaporized during pH adjustment because most part of NH_4^+ became NH_3 molecule at middle pH region [6]. Analysis on organic compounds in the solutions is also required to evaluate more precise dissolution behavior.

TABLE III
CONCENTRATION OF THE DETECTED CHEMICALS IN THE SUPERNATANT SOLUTION (ppm)

ID	Na^+	K^+	Ca^{2+}	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}
A	610	199	345	5.8	-	0.5	0.04
B	914	203	356	5.8	6.8	1.2	0.03
C	599	231	363	-	-	0.4	0.03
D	822	223	333	6.0	28	0.9	0.02
E	449	186	344	5.3	-	0.3	0.03
F	574	202	258	5.3	-	0.3	0.06

According to the experimental results, cementation of the liquid waste containing various chemicals is effective to confine several kinds of chemical compounds in the solid waste. However, dissolution of the solidified chemicals is not negligible. If cementation is employed for the liquid waste treatment, the final wastes should be stored in dried atmosphere.

C. Solidification of Organic Liquid

Solidified organic liquid by mixing with the coagulants are shown in Fig. 4. 2 g of NIP gel (ID = 1) made the liquid viscous, and they became rubber-like elastic solid after mixing. 4 g of oil solutions powder (ID = 2) was required to make solid. The resultant was not viscous but crumbly. Solid with Fyugel A (ID = 3) was also crumbly, and it took 3 g of the coagulant. 6 g of α Gel-1650 (ID = 4) and 3 g of Longcrin S-101 (ID = 5) also made viscous solids as seen in the first case. 4 g of M.S.Gel D-120A (ID = 6) was required for solidification, and product was crumbly. Form of the resultant solids did not depend on the type of the coagulant, and required amounts of the coagulants for the solidification were also different. Those different behaviors should be caused by difference in chemical characteristics of the coagulants, and improvements in the performance might be possible if suitable chemical structure of the coagulant can be designed for solidification of the target organic compounds. Solidification mechanism by those coagulants is now in investigation.

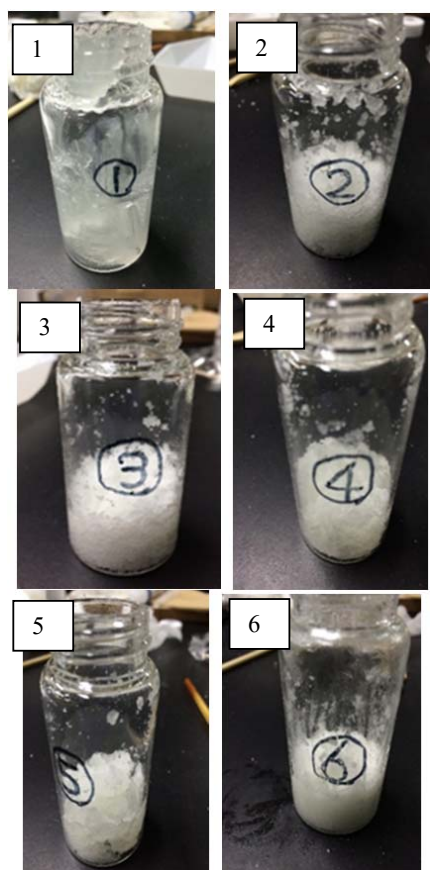


Fig. 4 Solidified organic liquid by mixing with coagulants

Appearances of the solids 10 months after the operation are shown in Fig. 5. Some parts of solids with ID = 2, 4 became liquids, and the colors of the solids were changed from white to yellow or brown. Color of solid with ID = 6 also changed into brown. States of ID = 1 and 6 were still solids after 10 months,

but forms of them changed into powder-like materials. Solid with ID = 3 kept its appearance even after 10 months. Coagulants with ID = 2, 4, 5 might not be appropriate for solidification of some chemical compounds involved in the test liquid, and they seem to chemically reacted after solidification. Since those coagulants were developed for solidification of organic compounds, reaction with coexisting inorganic compounds such as sulfamic acid is suspected. Influence of each chemical compound on the solidification performance should be precisely investigated for the practical use. For ID = 1 and 6, some chemical compounds possibly escaped from the solid. Silica gel, which is a type of those two coagulants, might not be suitable for keeping organic compounds inside for long time. Modification in surface or pore structure of the particle would improve the performance. In the respect of stability during 10 month, coagulant with ID = 3 is the most suitable for solidification of organic compounds. For further discussion, longer time storage performance, gas generation during storage and leaching behavior of the organic compounds should also be investigated.

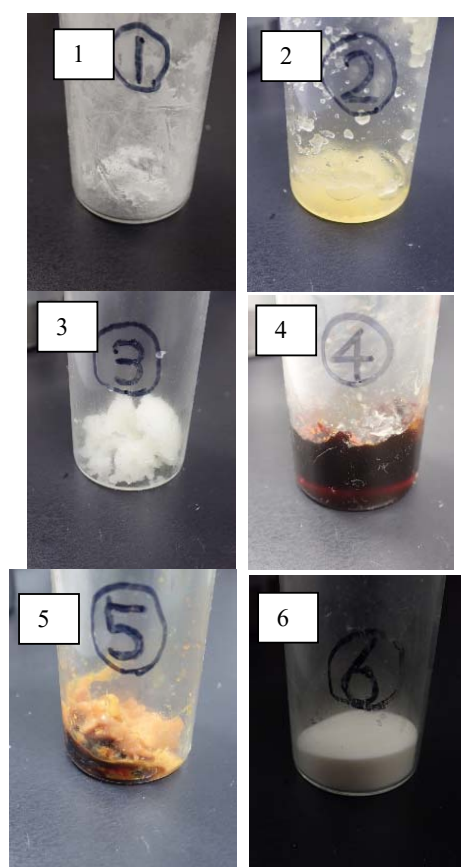


Fig. 5 Appearances of the solids after 10 months

Solidified organic liquids sealed in vials were set in front of ^{60}Co gamma-ray source as shown in Fig. 6. Distance from the source to the samples was determined according to dose rate measurement with alanine-ESR method [7], [8] to give 3 kGy/h. The samples were irradiated continuously for 666 h, and

significant damages on the vials and caps were not confirmed after the irradiation.



Fig. 6 Gamma-ray irradiation experiment

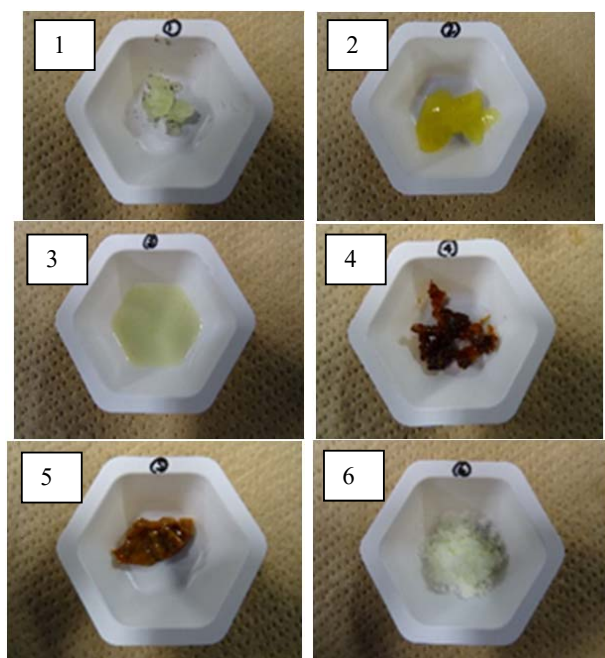


Fig. 7 Appearances of the solids after gamma-ray irradiation

Appearance of the solids after the gamma-ray irradiation is shown in Fig. 7. 2 MGy irradiation changed appearances of solids with ID = 2, 3, 4 and 5. The coagulants for those solids are considered to consist of organic compounds such as polymers. On the other hand, solids made with silica gel (ID = 1 and 6) seemed to be stable even after the irradiation. On general, organic compounds tend to be damaged by irradiations. Therefore, radioactive waste should not be confined in inorganic compounds in order to prevent degradation during storage. As discussed above, improvements in structure of silica gel particle might be required.

Amount of H_2 gas generated by the irradiation was almost the same for all solids. H_2 gas should be generated by

decomposition of organic compounds involved in the feed solution or in the coagulants. Thus, degradation of chemicals in the feed solution might be more significant than that of polymer contained in the coagulants.

The G value for H_2 generation was about two times larger than that of water but smaller than that of adsorbent used for extraction chromatography technology for trivalent minor actinides recovery [9]. According to our study on safety management of the extraction chromatography system, accumulated hydrogen gas and heat inside beds can be removed with continuous flow of mobile phase inside the packed column [10]. In a similar way, supplying gas or water into waste vessel is expected to remove generated gas from the wastes. However, precise chemical composition of the generated gas and leaching behavior of chemical compounds from the solids to the mobile phase have to be investigated to discuss safety longtime storage of the solid wastes.

IV. SUMMARY

Condensation of radioactive aqueous waste by RO filtering technique and solidification of aqueous and organic liquid wastes were examined as a part of STRAD project for systematic treatment of radioactive liquid waste containing various chemicals. Several times filtering operation successfully enriched NH_4^+ , and the effluent could be safely disposed. Cementation of aqueous waste was shown to be a promising method to confine chemical species inside solids. The product cements should be stored in dry atmosphere in order to prevent leakage of chemical compounds. Silica gel would be a promising coagulant to solidify organic waste liquids in the respect of stability of the product solid for long time storage and irradiation. Modification in structure of the particles is expected to improve confinement performance for organic compounds.

REFERENCES

- [1] Sou Watanabe et al., "Overview of STRAD project for systematic treatments of radioactive liquid wastes generated in nuclear facilities", Proc. DEM2018, France, Avignon, October22-24, 2018.
- [2] Sou Watanabe et al., "Treatments of Radioactive Waste Solutions Generated in a Laboratory of Japan Atomic Energy Agency", Book of Abstract of 55th Annual Meeting on Hot Laboratories and Remote Handling -HOTLAB2018, Finland, Helsinki, Sep.17-19, 2018
- [3] Haruka Aihara et al., "Development of treatment method for analytical waste solutions in STRAD project (1) Oxidative decomposition of ammonium ion with catalyst", Proc. DEM2018, France, Avignon, October22-24, 2018.
- [4] Noriko Asanuma et al., "Development of treatment method for analytical waste solutions in STRAD project (2) Ammonium ion adsorption onto zeolites", Proc. DEM2018, France, Avignon, Oct.22-24, 2018.
- [5] Haruaki Matsuura et al., "Development of treatment method for analytical waste solutions in STRAD project (3) Separation of ammonia by vaporization", Proc. DEM2018, France, Avignon, Oct.22-24, 2018.
- [6] N. Nakazawa, M. Akeo, M. Sato and T. Okubo, "Vapor-Liquid Equilibrium of Dilute Ammonia-Saline Water System", Bulletin of the Society of Sea Water Science, Japan, 38, 6, 348-352 (1984) in Japanese.
- [7] Kojima, T., "Alanine Dosimeters using polymers as binders", International Journal of Radiation Applications and Instrumentation. Part A. Applied Radiation and Isotopes, Vol. 37, Iss.6, 1986, pp.517-520
- [8] Kojima, T., "Orientation Effects on ESR Analysis of Alanine-polymer Dosimeters", Applied Radiation and Isotopes, Vol. 46, Iss.12, 1986, pp.1407-1411
- [9] Y. Koma et al, "Extraction chromatography for Am and Cm recovery in

engineering scale”, Proc. ATALANTE2008, France, Montpellier, May 19-23, 2008.

- [10] S. Watanabe et al, “Safety operation of chromatography column system with discharging hydrogen radiolytically generated”, EPJ Nuclear Sci. Technol. 1, 9, 1-8 (2015).