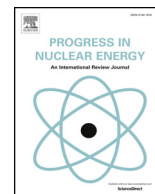


STRAD project for systematic treatments of radioactive liquid wastes generated in nuclear facilities

著者	Watanabe Sou, Ogi Hiromichi, Arai Yoichi, Aihara Haruka, Takahatake Yoko, Shibata Atsuhiro, Nomura Kazunori, Kamiya Yuichi, Asanuma Noriko, Matsuura Haruaki, Kubota Toshio, Seko Noriaki, Arai Tsuyoshi, Moriguchi Tetsuji
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STRAD project for systematic treatments of radioactive liquid wastes generated in nuclear facilities



Sou Watanabe^{a,*}, Hiromichi Ogi^a, Yoichi Arai^{a,e}, Haruka Aihara^{a,b}, Yoko Takahatake^a, Atsuhiko Shibata^a, Kazunori Nomura^a, Yuichi Kamiya^b, Noriko Asanuma^c, Haruaki Matsuura^d, Toshio Kubota^e, Noriaki Seko^f, Tsuyoshi Arai^g, Tetsuji Moriguchi^h

^a Japan Atomic Energy Agency, 4-33, Muramatsu, Tokai-mura, Ibaraki, 319-1194, Japan

^b Hokkaido University, Kita-10, Nishi-5, Kita-ku, Sapporo 060-0810, Japan

^c Tokai University, 4-1-1, Kitakaname, Hiratsuka-shi, Kanagawa 259-1292, Japan

^d Tokyo City University, 1-28-1, Tamazutsumi, Setagaya-ku, Tokyo 158-8557, Japan

^e Ibaraki University, 4-12-1, Nakanarusawa, Hitachi-shi, Ibaraki, 316-8511, Japan

^f National Institute for Quantum and Radiological Science and Technology, 1233, Watanukicho, Takasaki, Gunma 370-1292, Japan

^g Shibaura Institute of Technology, 3-7-5, Toyosu, Koutouku, Tokyo 135-8548, Japan

^h Kyushu Institute of Technology, 1-1, Sensui-cho, Tobata-ku, Kitakyushu-shi, Fukuoka, 804-8550, Japan

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ABSTRACT

A new collaborative research project for systematic treatments of radioactive liquid wastes containing various reagents generating in nuclear facilities was started from 2018 initiated by Japan Atomic Energy Agency. The project was named as STRAD (Systematic Treatments of RAdioactive liquid wastes for Decommissioning) project. Tentative targets to be studied under the project are aqueous and organic liquid wastes which have been generated by experiments and analyses in a reprocessing experimental laboratory of JAEA. Currently fundamental studies for treatments of the liquid wastes with complicated compositions are underway. In the STRAD project, process flow for treatment of ammonium ion involved in aqueous waste was designed though the inactive experiments, and decomposition of ammonium ion using catalysis will be carried out soon. Adsorbents for recovery of U and Pu from spent solvent were also developed. Demonstration experiments on genuine spent solvent is under planning.

1. Introduction

Radioactive liquid wastes generated in nuclear facilities such as nuclear power plants, reprocessing facilities, research reactors and laboratories often contain not only radiotoxic isotopes but also hazardous chemicals with high reactivity, low flash or ignition points, potential risks to produce explosive materials combined with other reagents, etc. Characteristics of reagents in the wastes and risks caused by the reagents under decontamination, solidification or disposal procedures should be carefully investigated in advance with practical operation, and then an appropriate treatment process for each item preventing hazardous events has to be designed and adopted. Such the investigations sometimes have not been carried out on waste liquids generated in past experiments or operations, and some of them are still stored in the facilities. In particular, experimental facilities have examined brand-new technologies or chemicals of the day, and liquid wastes lacking

enough safety information or assessment have been possibly accumulated. Dismantling of old nuclear facilities would be a worldwide important task in coming decades, and waste solutions containing radioactivity and the chemicals stored in the facility must be one of the most troubling wastes to be handled in the dismantling procedures. In general, radioactive liquids have to be treated inside the shielded space under specific limitation imposed by the facility due to their radioactivity. Experiences for treating various kinds of the liquid wastes under practical environments are necessary to be gathered for the forthcoming dismantling. Previous studies have already reported various treatment procedures for both radioactive aqueous wastes (IAEA, 1994; IAEA, 1992a; IAEA, 2002; IAEA, 2003; Efremkov, 1989; IAEA, 2013; IAEA, 2004a; Abdel Rahman et al., 2011; Abdel Hahman et al., 2011; Treatment of radioactive, 2006) and organic wastes (IAEA, 1992b; IAEA, 2004b). According to them, treatment methods of radioactive liquid waste can be categorized into removal of radioactive

* Corresponding author.

E-mail address: watanabe.sou@jaea.go.jp (S. Watanabe).

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Fig. 1. Chemical Processing Facility (CPF) of JAEA. (Left) Appearance of the facility, (Right) Hot cells for reprocessing experiments.

elements, removal or destruction of chemicals such as ammonia or organic compounds, separation of phases, concentration, incineration, oxidation, acid digestion and solidification. Treatment procedure for specific liquid waste is expected to be designed by combining the element technologies appropriately. In addition to that, treatment of chemicals have been largely investigated for industrial or environmental applications (Song et al., 2016; Sano et al., 2002; Muralikrishna and Manickam, 2017; Descorme, 2017; Hu et al., 2018; Matis, 1980). Technologies such as chemical decomposition using catalysis and membrane separation are commonly used in the fields, and those can be applied also to the radioactive liquid waste management. It must be possible to establish new technologies suitable for treatments of radioactive liquid waste containing various hazardous chemicals by combining various technologies employed in wide variety of applications.

Japan Atomic Energy Agency (JAEA) has started basic investigation and experimental studies from 2015 to collect experience and intelligence for handling the stored radioactive liquid wastes in practical experimental nuclear facilities. In this investigation, Chemical Processing Facility (CPF, Fig. 1) of JAEA, which is a laboratory for development of fast reactor fuel reprocessing and vitrification and has been working on genuine irradiated MOX fuel for more than 30 years, was selected as a test case facility of the source of various kinds of radioactive liquid wastes. After gathering information about the stored radioactive liquids in CPF, a goal and procedures of the treatment for each target were temporally planned with regarding handling inside the shielded environment and safeties of the treatment procedure and resultant products. Treatments of several kinds of liquids were revealed to be challenging due to their own potential risks and difficulties in handling inside the particular environment. In order to develop appropriate processes for those liquids, several collaborative research programs with several universities and national research organizations were started in 2017. Those different programs were incorporated to be one collaborative research project in order to progress the developments efficiently by activating information exchange and sharing experiences and knowledges. The combined project lead by JAEA was named to be STRAD (Systematic Treatments of Radioactive liquid wastes for Decommissioning) project and started at beginning of 2018. In this paper, overview and operational history of CPF, liquid wastes accumulated in CPF and overview of the STRAD project are summarized.

2. Overview and operation history of CPF

CPF in Nuclear Fuel Engineering Laboratories of Japan Atomic Energy Agency (JAEA) was constructed for researches on reprocessing of spent fast reactor (FR) fuels and on vitrification process of high level radioactive liquid wastes in 1980. The facility contains two lines of hot cells and 4 laboratories for experiments and analyses. Irradiated MOX fuels are possible to be used in hot cells of the facility, and fundamental experiments on small amount of U, Pu and fission products are also able to be carried out inside glove boxes or draft chambers of the

laboratories.

The first experiment on radioactive samples was performed in 1982, then applicability of PUREX process on FR MOX fuels with high burn-up and high Pu content has been examined through 21 times active experiments on 58 irradiated fuel pins of fast reactors (Joyo, Phenix and DFR) from 1982 to 1995. In a series of the aqueous reprocessing experiments i.e. shearing, dissolving and solvent extraction processes, few fuel pins were treated. Fundamental data of vitrification on high level active waste solution generated from Tokai Reprocessing Plant was also collected, and that information contributed to design of Tokai Vitrification Facility (TVF).

Renovation of the facility was carried out in 1996–2002 to start new research projects of advanced aqueous reprocessing and of pyrochemical reprocessing (Aose et al., 2007). The new aqueous reprocessing, which was named NEXT (New Extraction systems for TRU recovery, Fig. 2) process, employs crystallization of U for partial U recovery, U/Pu/Np co-recovery by modified PUREX flow-sheet and trivalent minor actinides (Am and Cm) recovery by solvent extraction or extraction chromatography (Funasaka and Itoh, 2007). More than 10 times experiments for demonstration of the NEXT process in the hot cell have been performed so far, and many achievements have been reported (Ikeuchi et al., 2012; Aihara et al., 2016; Yano et al., 2007; Nakahara et al., 2018; Watanabe et al., 2018a). NEXT process can recover all actinides without isolating Pu and is promising for FR fuel reprocessing. Recovery ratio of all actinides would be more than 99%, and the process is expected to reduce environmental load of nuclear wastes.

For fundamental study of pyrochemical reprocessing, special glove boxes with Ar atmosphere which equip electric furnace were installed in a laboratory under collaboration with Central Research Institute of Electric Power Industry (CRIEPI). Electrorefining of few grams of U and Pu has been successfully accomplished (Kitawaki et al., 2011), and improvement of the process for metallic FR fuel concept is underway. Experimental studies in CPF for new reprocessing technologies are still active.

The accident of Fukushima Daiichi Nuclear Power Stations in 2011 significantly influenced on activities in CPF, and wide variety of analyses on radioactive samples taken in the site are one of the most important present tasks in CPF (Takahatake et al., 2012). Currently, CPF are producing beneficial data for the advanced reprocessing technologies and decommissioning of the damaged reactor. Future operation and maintenance plans of CPF are under discussions in JAEA.

3. Summary of waste liquids accumulated in CPF

About 35 years experimental and analytical activities inside the hot cells and glove boxes have produced plenty amount of radioactive liquid wastes. The facility has waste solution tanks for storage of active solutions. However, CPF does not equip functions of processing the solutions for disposal. On general, nuclear fuel material involved in the waste liquids of CPF are recovered by conventional solvent extraction or by back-extraction operations. The recovered U and Pu are stored as

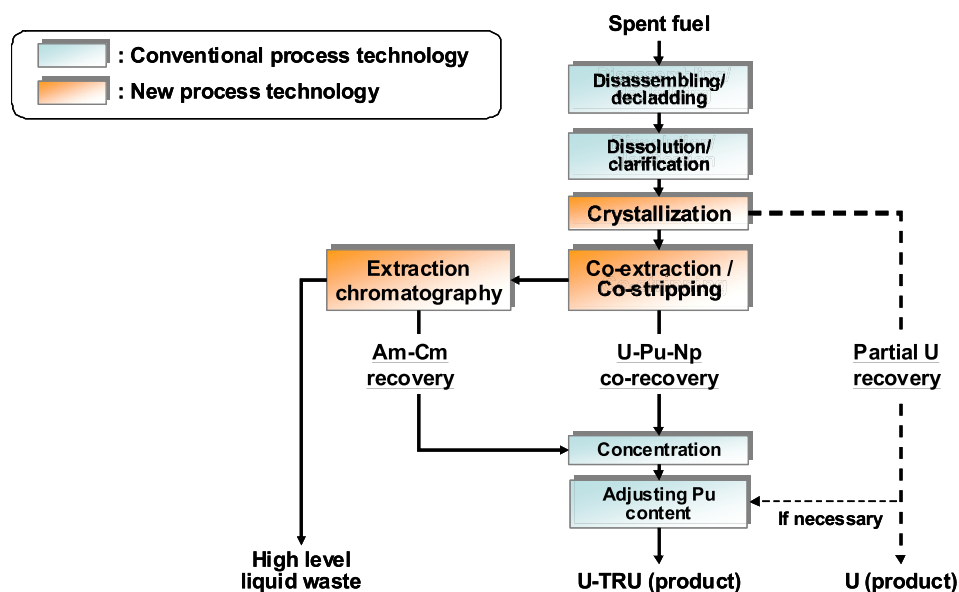


Fig. 2. NEXT process (Funasaka and Itoh, 2007).

oxide form after denitration and conversion operations, and the residual liquids are possible to be transferred to the waste liquid tanks. According to the initial design of CPF, the waste liquid tanks can accept only solutions with relatively simple compositions such as nitric acid with metallic elements which is comparable to high level liquid waste generated in PUREX process or spent PUREX solvent i.e. TBP in normal dodecane and degradation products of them. The solutions containing reactive chemical compounds have not been transferred to the tanks in order to avoid unexpected hazardous chemical reactions caused by contacting with other chemicals, and those have been temporarily stored inside the hot cells or glove boxes separately in individual bottles. Some chemical compounds in the liquids are necessary to be removed or decomposed before mixing with other solutions. Those stored solutions will obviously be one of the most troublesome wastes at the time of decommissioning of this facility. Nevertheless, they would also be interesting and challenging targets to start fundamental studies on their treatment procedures.

As a first step, detail information of the liquids (volume, involved chemicals, use histories, etc.) were investigated through records, experimental reports, interviews and analyses. Fundamental information of the liquids are summarized in Table 1, where only representative chemicals are shown and degradation products of the original compounds are not listed. Nitric acid solutions and spent PUREX solvent (30% tributyl phosphate (TBP) in *n*-dodecane) were not included because they have been sent to the waste solution tanks after recovery of U and Pu. The liquid wastes are categorized by source origins and phases (aqueous or organic) of them.

Aqueous solutions generated in experiments have relatively simple compositions, however they contain reactive chemicals such as hydrazine, lactic acid, phosphoric acid and so on. Those chemicals should not be mixed with other waste solutions in order to prevent precipitation formations or rapid chemical reactions.

Stored organic solvent is so called Transuranic Extraction (TRUEX)

solvent consisting of Octyl (phenyl)-*N,N*-diisobutyl-carbamoylmethylphosphine oxide (CMPO), TBP and *n*-dodecane (Horwitz et al., 1985) which has been used for demonstration of trivalent minor actinides recovery process called SETFICS (Koma et al., 1998). The solvent has been stored with loading U, Pu, Am and Cm for more than 10 years due to failure in lavage of the solvents. Recovery of those elements is necessary for safety reasons, and treatment of CMPO and its degradation products in the solvent might also be worth investigating.

Many kinds of reagents such as ammonium salts, complexing reagents, strong oxidants or reductants and organic solvents were involved in analytical waste liquids. Heating, mixing, concentrating might not be appropriate for some compounds in the liquids due to their reactivity, therefore careful investigation on characteristics of the chemicals and risk assessment on them would be an initial task in advance with considering appropriate treatment procedures.

4. Examples of the treatments

Appropriate treatment procedures of the waste liquids containing various chemicals have to be individually developed after careful risk assessment. Large part of the aqueous experimental wastes and a part of the aqueous analytical wastes have been successfully processed inside the hot cell or glove boxes, and resultant effluents have been transferred into the waste liquid tanks. The treatments have been carried out through following steps; (1) gathering information about the liquids, (2) analyses, (3) devising and reviewing treatment procedure, (4) inactive trial experiments, (5) experiments on small amount of genuine waste solution and (6) treatment on the solution. In considering the treatment procedures, regulations of the facility i.e. restrictions on methods, chemicals and conditions were respected and simplicity of the procedures suitable for remote handling operation by master-slave manipulators was also given importance. In this section, examples of several achievements on the treatments are described. Recovery of

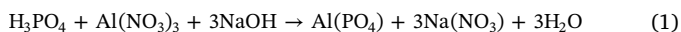
Table 1
Chemicals contained in radioactive waste liquids accumulated in CPF facility.

Source origin	Phase	Representative reagents involved in the liquid wastes
Experiments	Aqueous	Nitric acid, lactic acid, hydrazine, hydroxyl amine nitrate, phosphoric acid Spent TRUEX solvent loading U, Pu and MA: TBP, <i>n</i> -dodecane and CMPO
	Organic	
Analyses	Aqueous	Ammonium salts, chloride salts, ferrocyanide salts, fluoride salts, hydrazine, oxidants, reductants Pyridine, TOPO, Ethyl acetate, xylene, TTA, TBP, DBP, <i>n</i> -dodecane
	Organic	

nuclear fuel material (U and Pu) from the liquid stored inside the hot cells was considered in the respect of the accounting if their concentrations exceeded the detectable limit of UV-vis adsorption analysis (0.2 g/L for Pu and 0.03 g/L for U), otherwise the nuclear fuel material accompanied with the waste from the treatments and were ascribed to be MUF (Material Unaccounted For). U and Pu in the liquids stored in glove boxes were tried to be recovered as much as possible. Decontamination of fission products were not considered in this study.

4.1. Phosphoric acid solution

The solution has been used as an electrolyte of electrolytic decontamination experiments on walls of hot cells. Chemicals contained in the solution were assumed to be only nitric acid and phosphoric acid, and some analyses revealed that it contained 3 mol/L of phosphoric acid, 7×10^5 Bq/mL of ^{137}Cs , 4×10^5 Bq/mL of $^{239}\text{Pu} + ^{240}\text{Pu}$ and 8×10^5 Bq/mL of $^{239}\text{Pu} + ^{241}\text{Am}$. Formation of phosphoric salt precipitation and corrosion of tanks were suspected if this solution was transferred into the waste liquid tank. A goal of treatment for the solution was set to be removal or decomposition of phosphoric ions. Decomposition, ion exchange and solidification were considered as candidate methods, and solidification was employed as a consequence of discussion in simplicity of the operation and in amount of secondary waste. $\text{Al}(\text{PO}_4)$ is known to be a good binder, and fundamental studies or improvement of the binder are still widely performed (Vippola et al., 2004; Mulcahy and Clegg, 2006). AlPO_4 formation by adding $\text{Al}(\text{NO}_3)_3$ and NaOH into the waste liquid was targeted assuming following reaction.



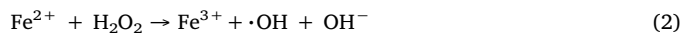
Inactive tests on simulated liquid waste successfully achieved solidification, and formation of amorphous $\text{Al}(\text{PO}_4)$ was confirmed by XRD analysis. A trial experiment on small amount of the waste solution was carried out to check applicability of the procedure. Finally, solidification operations on total 1.6 L of the waste solution have been successfully completed as shown in Fig. 3. In the operation inside the hot cell, 317 mL of 2.16 M $\text{Al}(\text{NO}_3)_3$ solution and 130 mL of 20 M NaOH solution were added into 250 mL of the waste solution through the MS manipulators, and then shaken mechanically for 1 min. Water in the bottle was vaporized after one week of the operation, and content of the bottle seemed to be completely solidified as shown in the photo. Radioactive elements were also solidified with AlPO_4 , where chemical forms of them are considered to be hydroxides because solidification progressed when pH of the solution became larger than 10. Appearance of the solidified waste did not change during 6 month storage, and then they were disposed as solid wastes containing radioactivity. Decontamination of the radioactivity in this procedure and stability of the solidified waste during long time storage have to be investigated further.

4.2. Lactic acid

Lactic acid was used as a complex reagent for back extraction of Pu

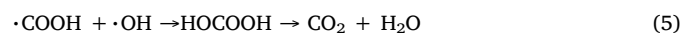
in a modified PUREX process experiment (Kishimoto et al., 1988). According to an internal experimental report, 2 M lactic acid in 4 M nitric acid was used. The report showed that lactic acid form precipitation with Pu few weeks after the experiment. Lactic acid form dimers and polymers under specific condition, and those species possibly contribute to form the precipitation. If the solution is transferred into the liquid waste tank without any treatment, similar precipitations would be formed inside the tank. H_2 gas is also generated when lactic acid is oxidized to be pyruvic acid and the reaction might easily proceed with existence of nitric acid. Those discussions concluded that treatment of lactic acid is necessary for safety storage of the liquid waste.

Analyses on the solution showed that it contained 5×10^{-3} mol/L lactic acid, 4.1 mol/L HNO_3 , 1×10^3 Bq/mL of ^{137}Cs , 2×10^4 Bq/mL of $^{239}\text{Pu} + ^{240}\text{Pu}$ and 1×10^5 Bq/mL of $^{239}\text{Pu} + ^{241}\text{Am}$, where large part of the lactic acid initially prepared might have decomposed or transformed to be pyruvic acid during long time storage. Based on an article (Dutta et al., 2001; Shimamura et al., 2012), adsorption of lactic acid onto activated carbon was examined through batch-wise and column adsorption experiments on simulated liquid waste. However, adsorption efficiency seemed to be insufficient (about 50% recovery by column operation) for our case. As a consequence of several experiments on the lactic acid treatment, oxidative decomposition using Fenton reaction was selected as promising (Dutta et al., 2001; Shimamura et al., 2012), and chemical reactions for the treatment were precisely investigated. In Fenton reaction, hydroxyl radicals are generated by the following equation.



Hydroxyl radical is expected to decompose organic compounds owing to its strong oxidative potency.

Many times inactive tests with various conditions and analyses on the resultant products revealed that lactic acid is decomposed by hydroxyl radicals to produce CO_2 , acetic acid and formic acid without releasing hydrogen gas. Carbon originated from lactic acid was transferred into acetic acid, formic acid and CO_2 with 65.5, 0.3 and 34.2%, respectively. Chemical reactions of the decomposition were estimated to be as follows;



40 L of the solution in the hot cell was processed by the Fenton reaction as shown in Fig. 4, where detail procedure is shown in Fig. 5. Temperature of the solution increased after addition of H_2O_2 solution due to the Fenton reaction. In order to prevent rapid reaction in the respect of safety, reaction temperature was controlled. The temperature was continuously monitored as shown in the photo, and supplying speed of H_2O_2 solution was controlled not to exceed the programmed value. Those operation was not automated but manually performed through the MS manipulators. Bubbles were continuously generated during the decomposition reaction, and the operation was finished and

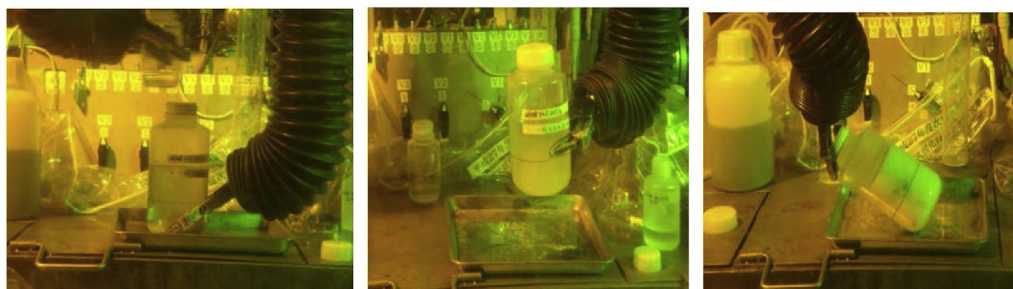


Fig. 3. Solidification operation on the phosphoric acid solution inside the hot cell.



Fig. 4. Oxidation operation on the lactic acid solution inside the hot cell.

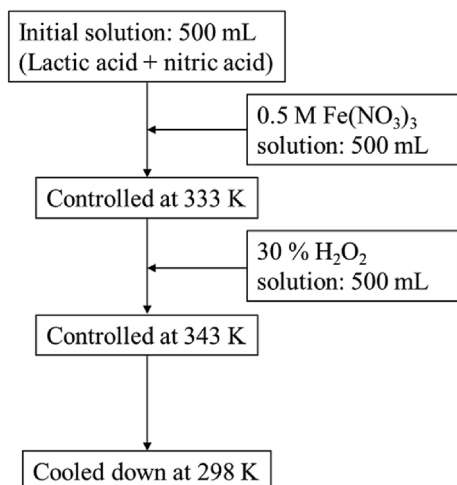


Fig. 5. Flow of lactic acid decomposition operation.

cooled down when the bubble formation was finished. 1–3 batches of the operation have been carried out in one day, and totally 32 days were required to treat all the waste solution. Concentration of total (D-/L-) lactic acid was colorimetrically analyzed after oxidization with nicotinamide adenine dinucleotide. The concentration of lactic acid after the treatment was lower than the detectable limit of the method (0.02 mM), and decomposition performance of lactic acid was estimated to be more than 99%. The effluent involving Fe, acetic acid, formic acid and nitric acid was sent to one of the liquid waste tanks. Those will be treated as high level liquid waste at the stage of decommissioning of CPF. In order to prevent precipitation formation due to Fe contained in the effluent, pH of the liquid waste in the tanks should be controlled to be acidic condition.

As the oxidative decomposition using Fenton reaction is a versatile,

simple and applicable under normal temperature and pressure conditions, the technique is expected to be applied for decomposition of various reactive chemicals inside the hot cell. The Fenton decomposition successfully worked for this system, and the liquid waste was properly treated. Nevertheless, influence of co-existing chemicals on the decomposition performance should be precisely investigated when the technique is applied to other systems.

4.3. Solution containing chloride ions

The solution was generated by series of experiments on pyrochemical process and by analyses on contaminated water containing sea water samples taken at the Fukushima site. So far, chloride ions have not been aggressively treated except in the glove boxes for pyroprocess due to their corrosiveness. In order to transfer the solution into the waste solution tanks, chloride ions had to be removed entirely. The total volume of waste solution of the pyrochemical experiments was 23.1 L, and they contained 10000 ppm of Cl^- , 70 g of U and 12 g of Pu in total. Treatment process of the solution was designed to involve removal of chloride ions and recovery of U and Pu.

In order to achieve above two requirements, removal of Cl^- as precipitation and conventional solvent extraction using TBP for U and Pu recovery were employed. Stoichiometric amount of $\text{Ag}(\text{NO}_3)$ was added into the solution to form AgCl precipitation and to exchange medium from Cl^- to NO_3^- . Inactive experiments showed that concentration of Cl^- ions in the solution was reduced below detectable limit of ion electrode analysis (0.4 ppm). Treatment of the waste solution containing U and Pu was also successfully finished in glove box as shown in Fig. 6, and almost all U and Pu in the solution could be recovered by the solvent extraction (Tada et al., 2017). After supplying $\text{Ag}(\text{NO}_3)$ reagent into the waste liquid bottle, the solution immediately become turbid. The floating AgCl were recovered as white powder by filtering as shown in the photo, and yellow liquids containing U and Pu were obtained. U and Pu did not transferred into the precipitation, and those in the solution were loaded into the PUREX solvent (30% TBP in normal dodecane) through 6 times batch-wise solvent extraction operation. Concentrations of U and Pu in the solution were 14 and 1.8 g/L, respectively. Acidity of the solution was adjusted to be 2 M by adding nitric acid, and 250 mL of the solution was shaken for 15 min after mixing with 400 mL of the solvent. After phase separation, the same solvent extraction operation was repeated. The loaded U and Pu in 2400 mL of the solvent were stripped into 5000 mL of 0.02 M nitric acid solution using centrifugal contactor. Volume of the solvent and back extraction solution were changed depending on the U and Pu concentration of the initial solution. More than 99% of U and Pu were recovered by those operations. Small amount of Pu (0.6 ppb) remained in the solution was tried to be recovered using CMPO impregnated porous silica adsorbent which was developed for trivalent minor actinides recovery in advanced reprocessing (Watanabe et al., 2018b),

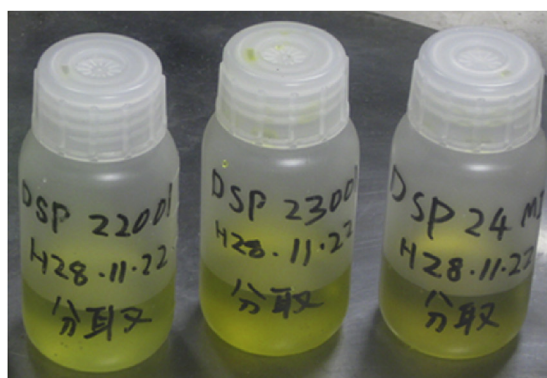


Fig. 6. Waste solution containing chloride ions, U and Pu (left) and the precipitation obtained by the treatment (right).

where U was not detected by α radioactivity measurement. 10 mL of the solution was mixed with 1 g of the adsorbent, and then shaken for 2 h. One time batch-wise adsorption experiments achieved about 84% adsorption of Pu. Stripping of Pu from the adsorbent into H₂O eluent could not be achieved. Therefore an appropriate eluent or treatment procedure for Pu loading adsorbent have to be developed. This operation has been carried out once.

Removal of Cl⁻ has completely finished so far, and U and Pu recovery is still in operation. The AgCl precipitation was currently stored as solid wastes in a stainless steel bottle, and the effluent mainly containing nitric acid was sent to one of the liquid waste tanks. U and Pu were denitrated by microwave irradiation and converted to be oxide form by heating. The product solution obtained by the solvent extraction was heated up to 473 K, and then irradiated by 1500 W microwave for 15 min. The product was heated up to 1023 K for conversion after the microwave irradiation. Nitrate ion were vaporized as HNO₃, and U and Pu in nitric acid solution are considered to become U₃O₈ and PuO₂ forms by these operations (Kato et al., 2005). Chloride ions in the analytical samples of the Fukushima were treated with the same manner with the above solution. Since AgCl is not stable against exposure to light, the final waste is desired to be transformed into more chemically stable form. An appropriate disposal procedure of the AgCl waste is under consideration.

Performance of the above processes and amount of wastes generated in the processes are summarized in Table 2. Volumes of the second wastes were larger than the initial values for any treatments although treatment performance was excellent. Improvement in the processes for reduction in the second waste generation must be one of the most important issues for those processes.

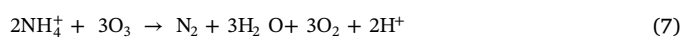
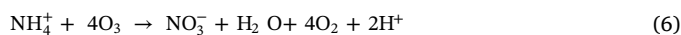
5. New research project: STRAD

As shown in the previous section, several kinds of waste liquids have been successfully treated inside hot cells or glove boxes. However, treatment procedures for large part of solutions generated by the analyses and for organic liquids are still uncertain due to their complicated compositions. Those liquids require specific investigations and examinations to propose well-suited treatment processes. Spent salt generated by pyroprocess experiments are also required to be transformed into chemically stable form since they are hygroscopic and dissolved chloride ions are corrosive. For each target, a special team consisted of JAEA with 2 or 3 organizations were formed, and fundamental studies were started from 2017.

The collaborative studies were combined to be a one project at the beginning of 2018 in order to share experiences and knowledge between collaborators. The purpose of this project is contributions not only to the developments for waste solution treatment in CPF but also to waste management or decommissioning of other nuclear facilities. The project was named as Systematic Treatment of Radioactive waste solution for Decommissioning (STRAD), and targets of study and collaborators are currently increasing to address forthcoming decommissioning of various facilities treating radioactive nuclides. Current representative studies in this project are summarized in Table 3. One of goals of this project is to develop new technologies which can

efficiently progress radioactive liquid waste treatment containing various chemicals of nuclear facilities in all around the world through the fundamental studies for liquid waste treatment of existing facilities like CPF. Enlightening importance of so-called legacy liquid waste management and development of human resources for nuclear engineering though are also objectives of the STRAD. Present activities and role of collaborators in each teams are briefly described below.

Ammonium salts are commonly used in analyses on solution containing Pu for masking Pu, valence adjustment, etc (Hayashiet al., 1986). Formation and accumulation of ammonium nitrate have to be prevented in the respect of safety. In Team 1, purification of ammonium ions in solution with complicated compositions and decomposition of ammonium ions using combination of ozone oxidization with catalyst are developed. Target decomposition reactions which have been assumed for decomposition of ammonium ion by oxidization are followings (Moussavi and Mahdavianpour, 2016);



The purification techniques through ammonia vaporization and adsorption/desorption with zeolites are developed by Tokyo City University and Tokai University, respectively. Ammonium ion in the waste solution is expected to become NH₃ vapor at high pH according to equilibrium constants for NH₃/NH₄ and NH₃ vapor/liquid (Nakazawa et al., 1984). Selective vaporization of NH₃ gas from simulated waste solutions are experimentally investigated in this Team. Some articles reported ammonium ion recovery performance onto zeolites from waste waters (Vassileva and Voikova, 2009; Mazloomi and Jalali, 2016; Guaya et al., 2016; Martins et al., 2017). Our team is developing not only adsorption but also desorption processes as a pretreatment of the decomposition procedure. Those two techniques can be differently adopted depending on compositions of the liquid wastes. Hokkaido University develops the homogeneous catalysts for the decomposition. Treatment of other chemicals and solidification of effluents will also be one of subject of this team. A process flows for decomposition of ammonium ion has already been designed, and demonstration on genuine liquid waste will be carried out soon. Treatment of effluent generated in the decomposition process is currently in investigation.

Organic solvent released from analyses on radioactive sample involve many kinds of organic compounds and radioactive elements. Recovery of the radioactive elements and confinement of reactive organic compounds inside chemically stable material are objectives of Team 2. Hydrophobic ion exchange medium and polymer for the solidification are developed for recovery of cations and the confinement of chemicals, respectively. The hydrophobic ion exchanger based on organic fibers and its efficient disposal methods are developed by Kyushu Institute of Technology. Several ion exchanger were developed and performance of them are in under evaluation. Development phase of this team is still in an early stage. Decomposition technology of reactive organic compounds will also be developed. Solidification of organic liquid inside geopolymer based on (Cantarel et al., 2015) is experimentally examined.

Table 2
Summary of liquid waste treatment.

Target	Processed volume	Treatment	Performance	Solid waste	Liquid waste
Phosphoric acid	1.6 L	Solidified as Al(PO ₄)	100% solidified	4.2 L (Al(PO ₄), hydroxyside salts)	–
Lactic Acid	40 L	Decomposition by Fenton reaction	> 99% decomposed	–	120 L (Acetic acid, formic acid, Fe, nitric acid)
Chloride solution	250 mL	Precipitation as AgCl, U and Pu recovery	> 99% Cl removed > 99% U and Pu removed	1–2 mL (AgCl), 1 g (spent adsorbent)	250 mL (Nitric acid) 2.4 L (spent solvent)

Table 3
Current studies in STRAD project.

Team	Target	Treatment procedure	Collaborators
1	Analytical aqueous wastes	<ul style="list-style-type: none"> > Decomposition of reactive chemicals > Solidification of effluents 	Hokkaido University Tokai University Tokyo City University
2	Analytical organic wastes	<ul style="list-style-type: none"> > Recovery of U and Pu by hydrophobic ion exchanger > Confinement of reactive chemicals inside stable material 	Kyushu Institute of Technology
3	Spent solvents	<ul style="list-style-type: none"> > Recovery of U and Pu by newly developed adsorbent > Decomposition of ligands 	Ibaraki University Shibaura Institute of Technology
4	Spent salts	<ul style="list-style-type: none"> > Removal of U and Pu as precipitations > Cementation of salts 	National Institute for Quantum and Radiological Science and Technology Tokyo City University Tokai University

Spent solvent loading radioactive elements are sometimes stored in facilities. Recovery of the radioactive elements from the degraded solvent is a challenging task because degradation product of the solvent sometimes form complexes with the elements which retard back extraction reaction. In Team 3, new chelating adsorbents are developed to recover the radioactive elements from complexes formed in the degraded solvents. Based on fundamental studies, iminodiacetic acid group was revealed to show affinity to cations loaded in the spent solvents (Nakamura et al., 2018). Currently, adsorption mechanism is investigated by structural analysis on complexes formed in the adsorbent. At the same time, new adsorbent bearing the iminodiacetic acid group are under development. Ibaraki University and National Institute for Quantum and Radiological Science and Technology develop adsorbents using fluorine based molecules and radiation graft polymerization technology, respectively. Those adsorbent are designed to reduce hydrophilicity and enhance phase separation performance. Shibaura Institute of Technology evaluates adoption/desorption performance of the adsorbents. Inactive adsorption experiments showed that some adsorbents can be applicable to the liquid waste treatment, and demonstration on small amount of genuine spent solvent will be performed in near future.

Salts used in pyroprocess experiments involve small amount of U and Pu (few g in 1 kg salt) even after electrorefining procedure due to inappropriate experimental conditions or to drop of recovered product from the cathode. Those are desired to be decontaminated in advance with disposal. Purification technology of spent salts for recycling of the salts have been developed using adsorption onto zeolite (Uozumi et al., 2012). In order to adopt this technique as the treatment, recovery of U and Pu from the zeolite and disposal procedure of the salts have to be developed additionally. Conversion technology of chloride salt into oxide for the disposal of the spent salt has also been developed (Sato et al., 2005). However, the process generates large amount of waste solution containing Cl^- ions and those should be treated as described in 4.3. In this project, simple and efficient process that generates small amount of secondary waste is target technology. A process consists of recovery of the U and Pu from the salts and confinement of corrosive chloride ions inside chemically stable materials is currently studied by Team 4. Tokai University and Tokyo City University develop technologies for removal of U and Pu as precipitation by adding oxygen donor reagent and for distillation of the molten salts, respectively. Development phase of this team is also in an early stage, and experimental set up for high temperature is currently under design. Solidification of the salts is tested by inactive experiments ahead of the front procedures.

Currently above 4 collaborative researches are conducted as a part of STRAD project, and at the same time we are about to start new several programs in this project. One of the programs is to develop new confinement technology of reactive chemicals inside amorphous material. The technology must be versatile and expected to be applied for many kinds of waste solution with complicated composition.

Targets of this project will be reconsidered or supplemented flexibly based on requirements from facilities and organizations who can

collaborate with us. Collaboration with foreign countries is also one of important processes to progress the project efficiently. The STRAD project is expected to produce beneficial waste management database which can be referred worldwide.

6. Summary

Treatment of radioactive liquid waste accumulating in nuclear facilities must be one of the most difficult and challenging tasks in the stages of decommissioning of the facilities. Japan Atomic Energy Agency started a new research project named STRAD (Systematic Treatments of RAdioactive liquid wastes for Decommissioning) to develop new technologies for the treatments with universities, a national institute and a private company. Collaborators and targets of the project are still increasing, and the project is expected to produce valuable technologies which can be used not only for waste management of existing facilities but also for conceptual design of waste management of new facilities. A main goal of this project is to establish liquid waste treatment database which give solutions for legacy liquid waste accumulated in facilities like CPF.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.pnucene.2019.103090>.

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