NEW LIQUID WASTE CONTROL WITH TANNIN ADSORBENT

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ABSTRACT

Since 1971, the Mitsubishi Nuclear Fuel Co., Ltd. (MNF) has been fabricating PWR fuels and developing related technology and processes. In the UF_6 reconversion lines of MNF, the ammonium diuranate (ADU) process has been operating and the newly developed process of liquid waste treatment was installed last year. The characteristic of this process is to use insoluble tannin adsorbent which has been developed by MNF. The tannin adsorbent is not only an effective means to adsorb heavy metals such as uranium and plutonium but is also easy to incinerate at low temperature. Control of radioactive liquid waste from nuclear facilities is generally implemented by co-precipitation. However, it produces secondary wastes suchas noncombustible materials which include radionuclides and it is anticipated that the storage and disposal of those wastes will be at high cost. Those are the reasons why tannin adsorbent has an advantage, and why MNF develops it.

INTRODUCTION

At present, UO_2 is mainly used as the fuel for nuclear power plants. The process which transforms UF_6 into UO_2 is called the reconversion process and there are both wet and dry processes. In the wet reconversion process, UF_6 is hydrolyzed to a UO_2F_2 solution, then an ammonium solution is added and ammonium diuranate (ADU) is precipitated. After filtration and drying, ADU is calcined and UO_2 powder is produced. When ADU slurry is filtered, a large amount of radioactive liquid waste containing uranium is generated and is discharged after reducing the radioactive concentration below the release limit criteria. Radioactive liquid waste containing uranium is generated in not only the fuel fabrication plant but also in uranium refineries, enrichment plants and other nuclear facilities.

These radioactive liquid wastes have been treated by co-precipitation using $FeCl_3$ and adsorption with charcoal and/or ion exchange resin. But, after liquid waste treatment, precipitates and used adsorbents have turned into secondary radioactive waste and have been packed into drums for storage. Disposal management of this waste is costly and will become a problem in the near future.

MNF has developed new adsorbent called 'TANNIX' (trade mark) which is produced from tannin. TANNIX is a natural material and does not generate any secondary radioactive waste.

INSOLUBLE TANNIN (TANNIX)

It has been well known that there are many kinds of plant which can adsorb uranium and heavy metals. Tannin is well known as an astringent from the persimmon and tea and it is a complex compound of polyoxyphenol contained in seeds and leaves. Tannin is soluble in water.

Tannin shows acidity in solution and produces a black colored precipitate with Fe_3^+, which is utilized as black ink. Moreover, tannin transforms protein and gelatin to be insoluble in water, which is utilized to tan raw hide.

Though tannin reacts with heavy metals (including uranium) in liquid, it has never been utilized for separation of heavy metals in liquid because those reaction products are soluble in water. Therefore we have transformed tannin into an insoluble form by polymerizing 'wattle tannin' (condensed tannin) with aldehyde. That is, wattle tannin is dissolved in an alkaline solution, formaldehyde is added then it is heated. This produces massive insoluble tannin.

After then it is crushed into pieces and sieved for easy use.

Specifications for TANNIX

Specifications for TANNIX are shown in Table 1. TANNIX has excellent characteristics, that is, the gases generated during incineration are harmless to the environment because its elements consist of only carbon, hydrogen and oxygen. In addition its volume is dramatically reduced by incineration and of course it has an excellent ability as an adsorbent for actinides, such as uranium, neptunium, americium, curium and plutonium, and heavy metals, such as chromium, cadmium and lead, in liquid.

Moreover, as TANNIX can recover uranium selectively from liquid containing sodium, magnesium and so on, TANNIX can recover uranium from sea water.

Table 1   Specification for TANNIX

Resin Type	Acid Cation
Size Range	0.5 - 1.2 mm
Bulk Density	0.65 wet-g/cm^3
Moisture Content	70 - 80 %
Max. Operating Temperature	80C
Operating pH Range	2 - 11
Max. Adsorption Amount of U	1.7g-U/g-dry TANNIX

Adsorption ability of TANNIX for Actinides

The adsorption ability of TANNIX for uranium is shown in Fig. 1. TANNIX adsorbed more than 99% of the uranium in a liquid ranging between a pH of 4 and 8 . From the results of an adsorption equilibrium test, it is found that the maximum adsorption weight of uranium per TANNIX weight (dry) is 1.7. And the adsorption ability by a column test with TANNIX is shown in Fig. 2. It was found that TANNIX could treat liquid waste containing 680 ppb of uranium about more than 2000 times the volume of TANNIX.

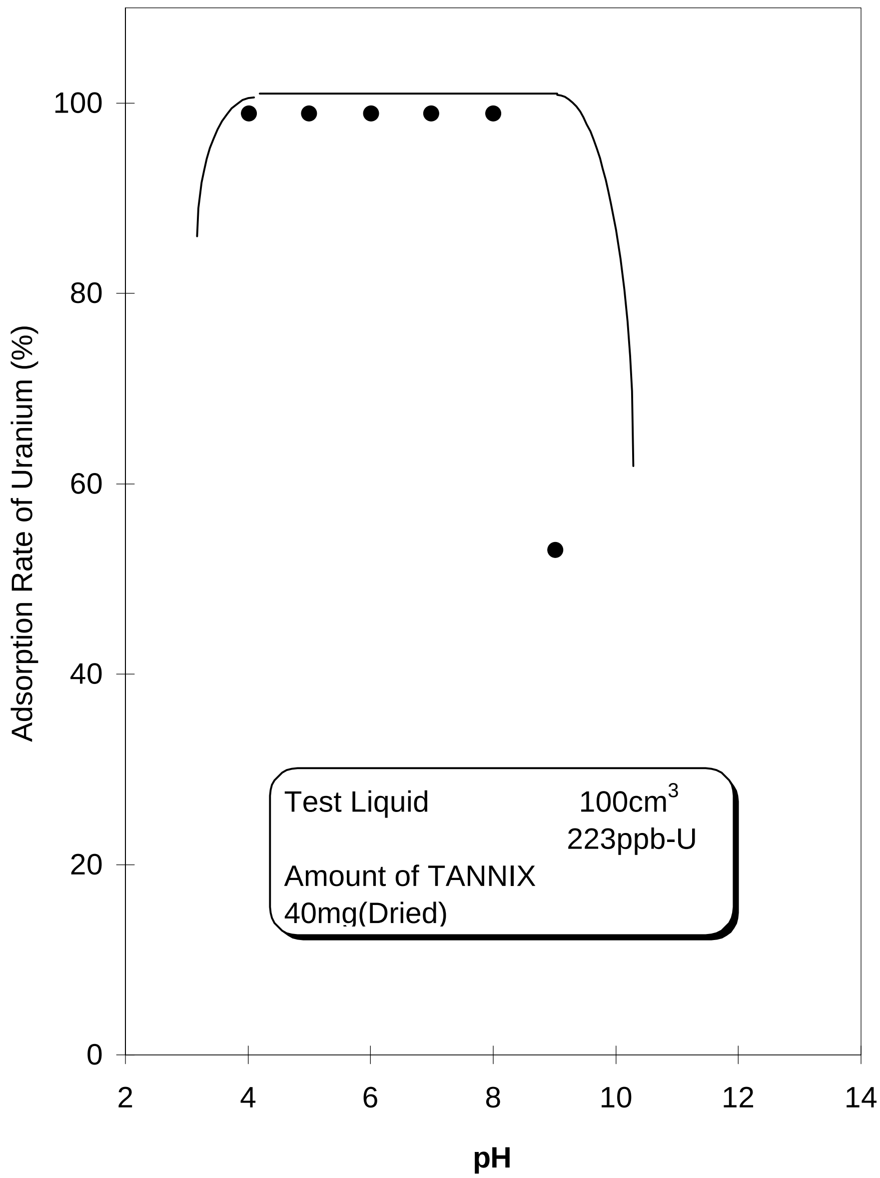

Fig. 1 Relation of Adsorption Rate and pH

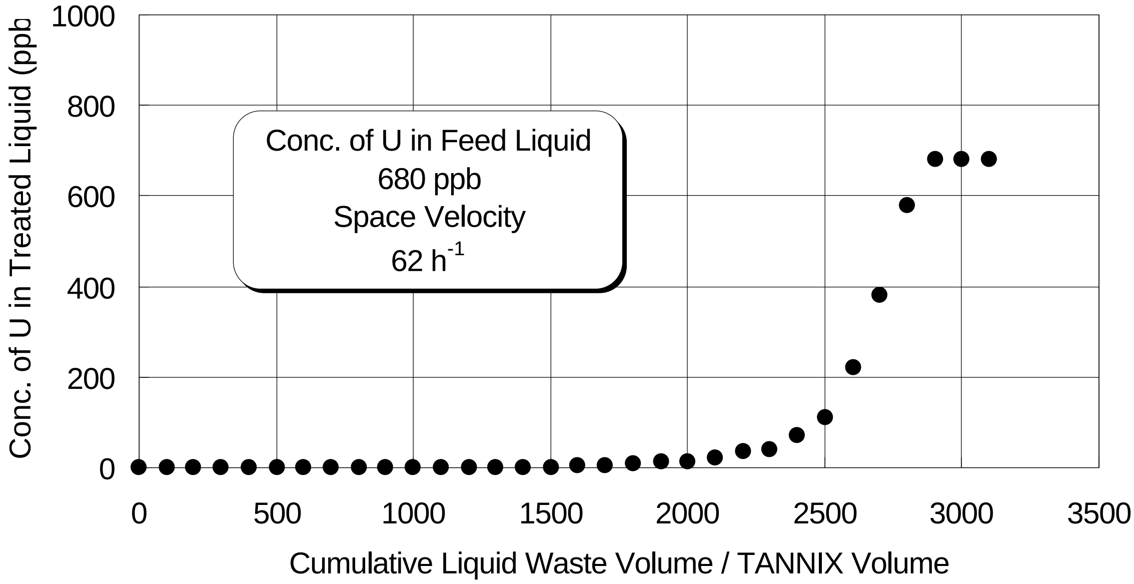

Fig. 2 Change of Adsorption Ability of Column

The adsorption abilities for actinide elements are shown in Table 2. TANNIX has high distribution coefficients for actinides.

Table 2 Adsorption Ability of TANNIX for Actinide elements

Element	Distribution Coefficient Kd (cm^3/g)	Adsorption Rate R (%)
U	9.38×10^5	99.5
Np	4.05×10^4	97.6
Am	5.77×10^4	96.7
Cm	4.97×10^4	96.1
Pu	5.40×10^4	> 99

Distribution coefficient (Kd) and adsorption rate (R) are calculated by the following equations.

$$R\ (\%) = (C_o - C_e) / C_o \times 100$$

$$Kd\ (cm^3/g) = R / (R - 100) \times V_{liquid}(cm^3) / W_{TANNIX}(g)$$

where C_o and C_e are the initial and the equilibrium concentration and V_{liquid} and W_{TANNIX} are the volume of liquid treated and the weight of TANNIX, respectively.

Adsorption abilities of TANNIX for plutonium and americium have been studied and reported by the Power Reactor and Nuclear Fuel Development Corporation (PNC) and the Japan Atomic Energy Research Institute (JAERI), respectively.

Incineration of TANNIX

The change in weight of TANNIX during its thermal decomposition was measured with thermobalance. The result is shown in Fig. 3. The weight decreased with the elevating temperature, and it was remarkable over 400 ^oC, and then weight loss saturated at over 500 ^oC. This shows that thermal decomposition of TANNIX finishes at 500 ^oC.

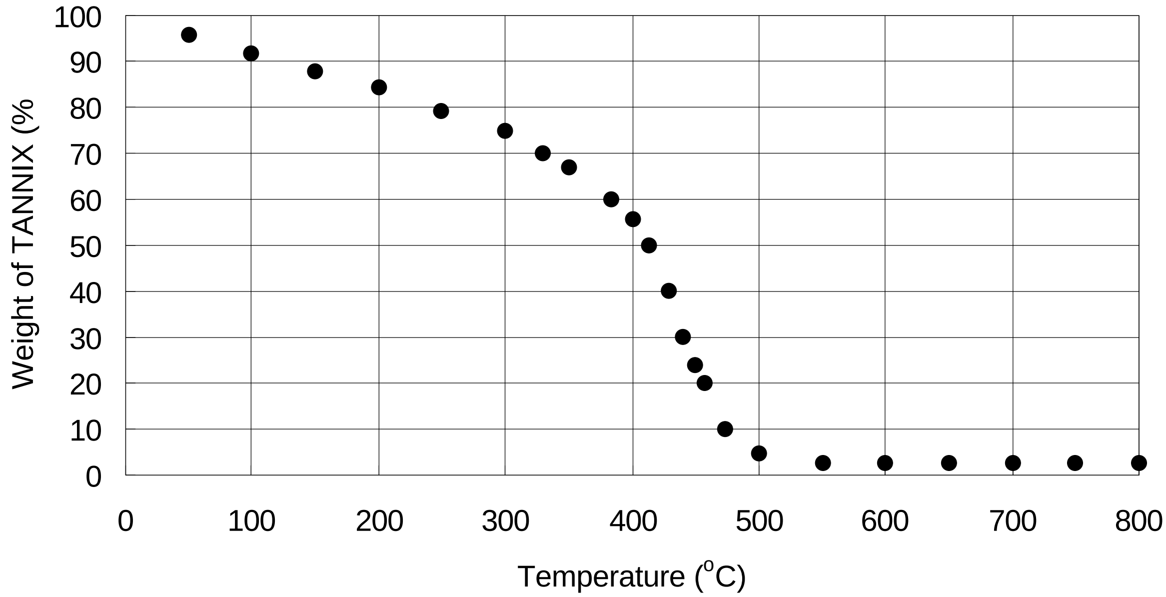

Fig. 3 Pyrolysis Curve of Dried TANNIX in Air

Volume reduction of TANNIX

After adsorption of uranium, TANNIX was heated to be decomposed in air with an electric furnace at 750 ^oC for 3 hours. After cooling, the volume of residue was measured and also it was analyzed. The volume reduction rate Vr was calculated as following equation.

$$Vr = (V_1 - V_2) / V_1 \times 100 \quad (\%)$$

where V_1, V_2 are the initial and the residual volume, respectively.

The results of calculations are shown in Table 3. The reduction rate is over 98%. The results of an element analysis of the residue are shown in Table 4. These data conclude that uranium exists as stable U_3O_8 and TANNIX is burned up completely.

From these data, when TANNIX is used as an adsorbent, it is understood that uranium in the liquid waste is adsorbed more than 99% and that uranium is recovered with high purity by only incineration, and secondary radioactive waste is not generated at all.

Table 3 Volume Reduction Rate

Initial Volume ($\times 10^3$ cm^3)	**Residual Volume ($\times 10^3$ cm^3)**	**Volume Reduction Rate (%)**
16	0.2	98.8
73	0.8	98.9
145	2.0	98.6

750 ^oC x 3 hours in air

Table 4 Results of Analysis of Residue

U_3O_8	> 99.5 %
C	< 5 ppm
Other metal elements	< 0.5 %

Adsorption Ability of TANNIX for Heavy Metals

Moreover, heavy metal elements are well-adsorbed with TANNIX. It is known that TANNIX adsorbs more than 95% of lead, chromium and cobalt and more than 90% of mercury. These results are shown in Fig. 4. In particular, it is noted that TANNIX has an excellent adsorption ability for 6 valence chromium. From these results, TANNIX has been studied as an adsorbent for harmful heavy metals and useful metals.

UTILIZATION OF TANNIX

A waste liquid treatment system with TANNIX has already been applied in many places.

In MNF, the waste treatment system was introduced last year. The annual amount of liquid waste containing uranium from reconversion process is about 7,000 m^3. Though 35 drums per year were generated as secondary radioactive solid waste with the conventional system, using the co-precipitation method, the number of drums per year decreased to only one with the present system using TANNIX.

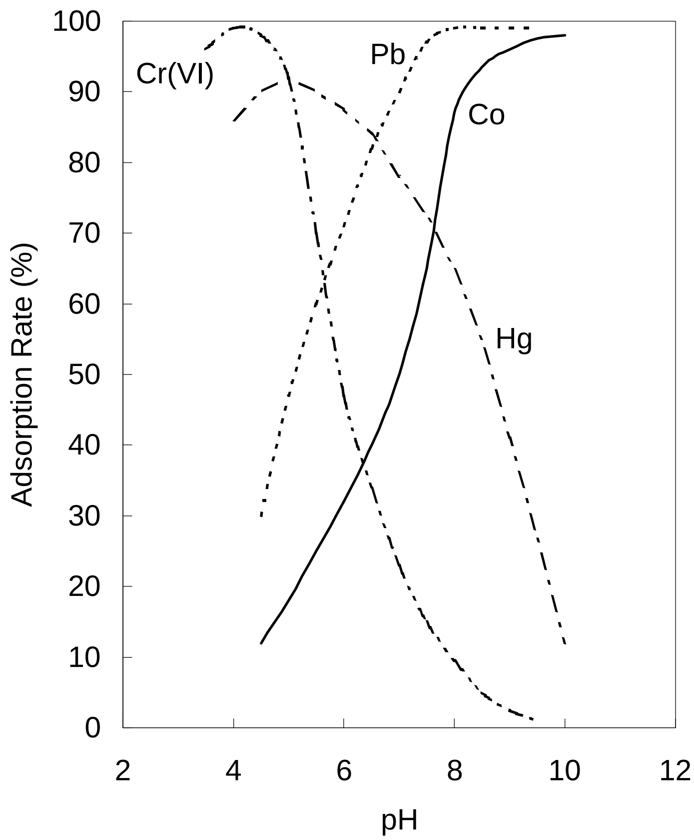

Fig. 4   Relation of Adsorption Rate and pH

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KEY WORDS

Tannin, insoluble, TANNIX, adsorbent, secondary waste, uranium, actinide, heavy metals.