APPLICATION OF INSOLUBLE TANNIN TO RECOVERY OF URANIUM, TRU AND HEAVY METALS ELEMENTS FROM RADIOACTIVE LIQUID WASTE

Kazuhiko Hamaguchi, Wataru Shirato, Yasuo Nakamura, Tatsuro Matsumura*,
Kenji Takeshita**, Yoshio Nakano**
Mitsubishi Nuclear Fuel Co.,Ltd
622- 1 Funaishikawa Tokai- mura Naka- gun Ibaraki- ken 319- 1197 Japan
Tel. 81- 29- 287- 8018 Fax. 81- 29- 282- 7421 E- mail: mnf- mdtc@po1.infosphere.or.jp
* Japan Atomic Energy Research Institute
2- 4 Shirakata- shirane Tokai- mura Naka- gun Ibaraki- ken 319- 1195 Japan
Tel. 81- 29- 282- 6186 Fax. 81- 29- 282- 5937 E- mail: tatsuro@nucef.tokai.jaeri.go.jp
** Tokyo Institute of Technology
4259 Nagatsuta- cho Midori- ku Yokohama 226- 8502 Japan
Tel. 81- 45- 924- 5432 Fax. 81- 45- 924- 5441 E- mail: nakano@chemenv.titech.ac.jp

ABSTRACT

Mitsubishi Nuclear Fuel Co.,Ltd. (MNF) has developed a new adsorbent, TANNIX (tread mark), which is derived from a natural Wattle tannin, for the recovery of uranium, TRU and heavy metal elements in the liquid waste. TANNIX has some advantages that handling is easier than that of standard IX- resin, and that the volume of secondary waste is reduced by burning the used TANNIX.

We have replaced radioactive liquid waste treatment system in MNF from the conventional co- precipitation process to adsorption one by using TANNIX. TANNIX was founded to be more effective for the recovery of Pu, TRU, and hexavalent chromium Cr(VI) as well as Uranium.

INTRODUCTION

MNF has been fabricating PWR fuels. At the fabrication step, ADU(Ammonium Di- Uranate) process has been used for the re- conversion process from UF_6 to UO_2 powder, which generated radioactive liquid waste containing uranium.

In the conventional process, the water glass co- precipitation method had used in order to adopt the regulation of liquid waste release level. That process consisted of multi- handling steps and consumed much acid in order to recover the uranium from co- precipitation and generated secondary solid waste composed of sodium silicate.

In order to eliminate these disadvantages, MNF has developed a new absorbent, TANNIX. TANNIX is able to used easily like as IX- resin in the column, to recover the uranium directly by incineration without leaching process and TANNIX is almost decomposed to CO_2 and H_2O gases.

TANNIN CHARACTERISTICS

Tannin is well known as an astringent of persimmon and tea. It is usually extracted from seeds and leaves containing polyhydroxyphenyl group and is soluble in water to shows acidity. It is utilized as black ink because it produces black color precipitate with Fe^{3+}. Moreover, it is utilized as a material to tan the raw hides because it transforms protein and gelatin into insoluble one in water.

Tannin reacts with uranium and heavy metals in liquid but it has not been utilized for adsorption and separation of uranium and heavy metals in liquid waste, because those reaction products were soluble in water.

Only tannin fixed on fiber or PVA polymer has been used to remove lee in brewing industry in Japan. But the adsorption ability of fixed tannin was law in comparison with original tannin and it is not easy to burn the used tannin.

MNF has researched how to make an insoluble tannin and how to improve its reaction ability to develop the insoluble tannin, TANNIX by crosslinking the tannin with aldehyde. That is, the tannin was dissolved in an alkaline solution and then, formaldehyde was added into the solution, that was heated at 80℃. The massive amount of insoluble tannin was crushed and sieved to small particles.

CHARACTERISTICS AND ADSORPTION ABILITY OF TANNIX

The characteristics of TANNIX are shown in Table I. TANNIX has some excellent characteristics, such as its stability in the wide range of pH and the high adsorption capacity of uranium.

TANNIX adsorption ability for uranium is more than 99%. In the equilibrium tests, it is found that the maximum adsorption amount of uranium is 1.7gU per dry TANNIX. This suggests that more than 2000 times of TANNIX volume can be treated in the case of waste water containing 680 ppb of uranium.

The relationship between uranium adsorption ratio and pH is shown in Fig.1. The column test of uranium is shown in Fig.2.

TANNIX has good adsorption ability not only uranium, but also other elements.

The absorption abilities of TANNIX for TRU elements etc, are shown in Table II. TANNIX has an excellent ability for actinides and heavy metal elements except alkaline elements.

TABLE I Characteristics of TANNIX

Resin Type	Acid Cation
Size Range	0.5- 1.2 mm
Bulk density	0.6 wet- g/cm^3
Moisture Content	70 - 85 %
Max. operation Temperature	80℃
Operation pH Range	2- 11
Max. Absorption Amount of U	1.7gU/g- dry TANNIX

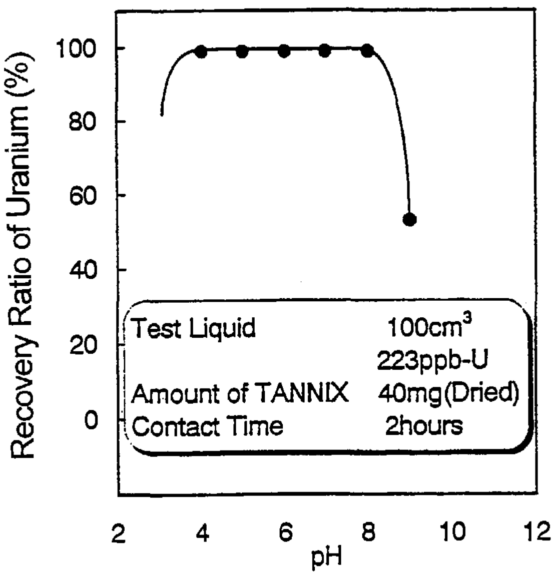

Fig.1 Relationship between Recovery Ratio of Uranium and pH

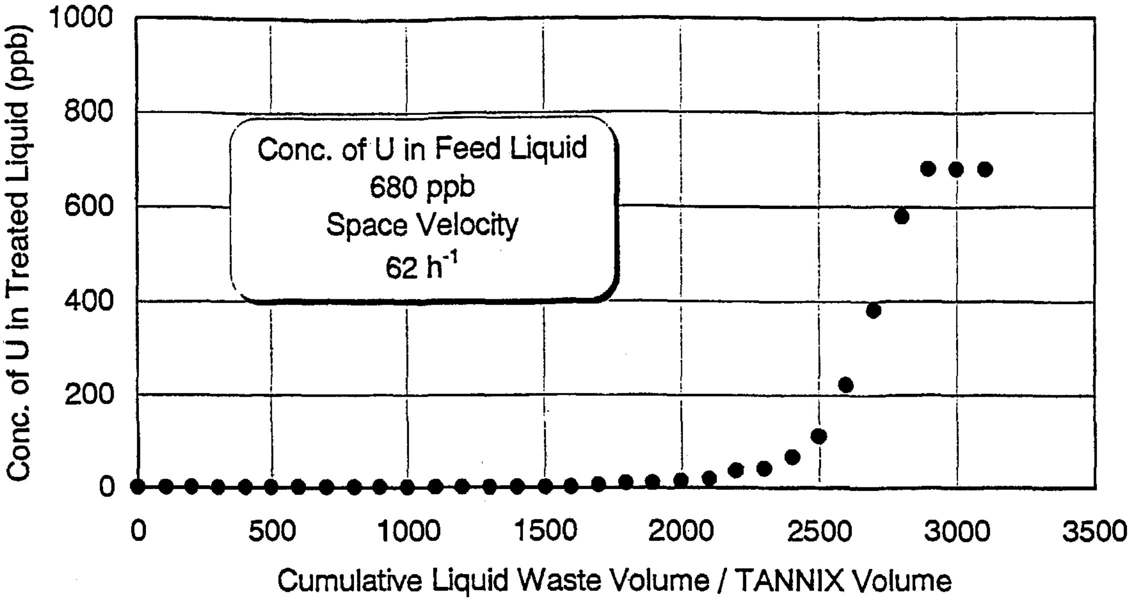

Fig. 2. Break Through Curve of Uranium

TABLE Ⅱ Adsorption Ability of TANNIX for TRU Elements etc

Element	Distribution Coefficient Kd(cm^3/g)	Recovery Ratio 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
Pb	>9500	>95
Cr	4.95×10^4	99.0
Co	5.45×10^4	98.0
Cs	117	31.9

Distribution coefficient (Kd) and Recovery ratio (R) are calculated by following equations

$$R(\%) = (Ci - Ce) / Ci \times 100$$

$$Kd(cm^3/g) = R / (R - 100) \times Va(cm^3) / Wt\ (g)$$

herein, Ci and Ce are the initial and the equilibrium concentration and Va and Wt are the volume of solution and the weight of TANNIX, respectively.

AVANTAGE OF VOLUME REDUCTION

The volume reduction of TANNIX was examined by two methods, air drying and thermal decomposition of TANNIX.

Fig. 3 shows the volume change of TANNIX by hot air drying . When TANNIX was charged in the column and hot air was introduced into the column, the volume of TANNIX was reduced less than 20% of the initial one by drying for 20 hrs, because 70 ~80% of water was removed from TANNIX matrix.

As the granular TANNIX is not agglomerated each other, The discharge of the granular TANNIX from column was easier than that of IX- resin.

Fig. 4 shows the pyrolysis curve obtained by thermal decomposition of TANNIX.

The weight change of TANNIX was measured by a thermobalance. Weight of TANNIX decreased with increasing temperature. The remarkable reduction of weight was observed over 400 ℃, and TANNIX was decomposed completely at 500 ℃.

The thermal decomposition of TANNIX adsorbing uranium was tested in air atmosphere at 750 ℃ for 3 hours. The weight loss of TANNIX reached 98% of the initial one and more than 99.5% of residue was U_3O_8.

The adhesion of remaining carbon in the uranium was less than 5 ppm per U base.

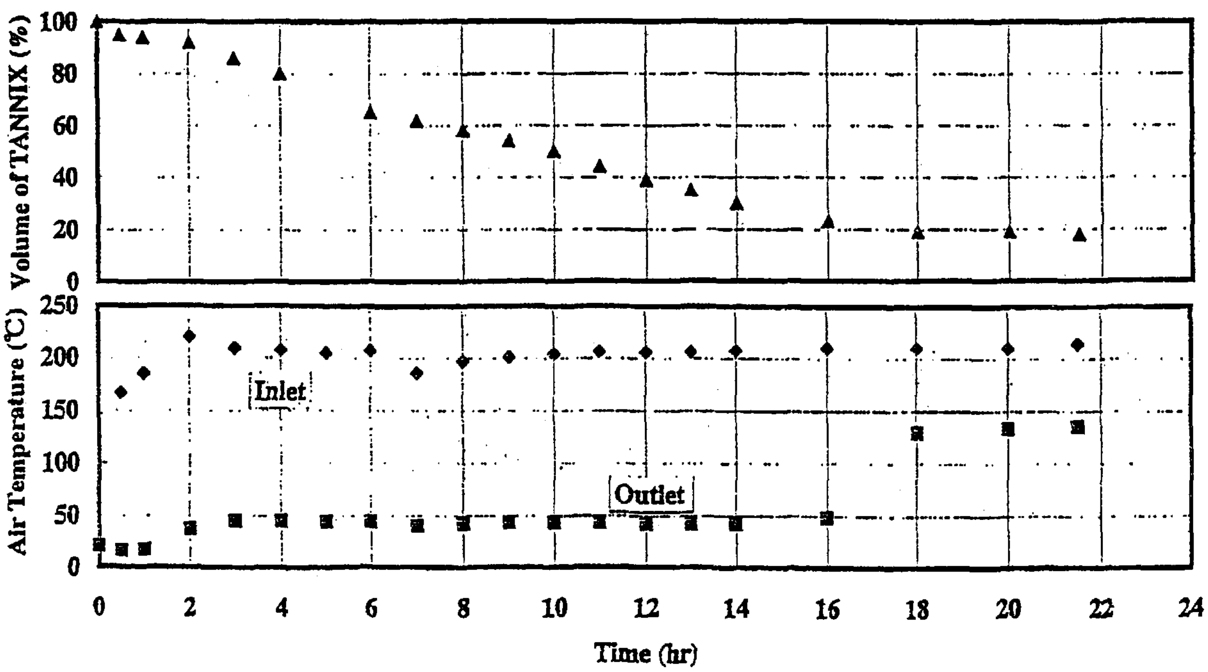

Fig. 3. Volume Reduction of TANNIX with Drying

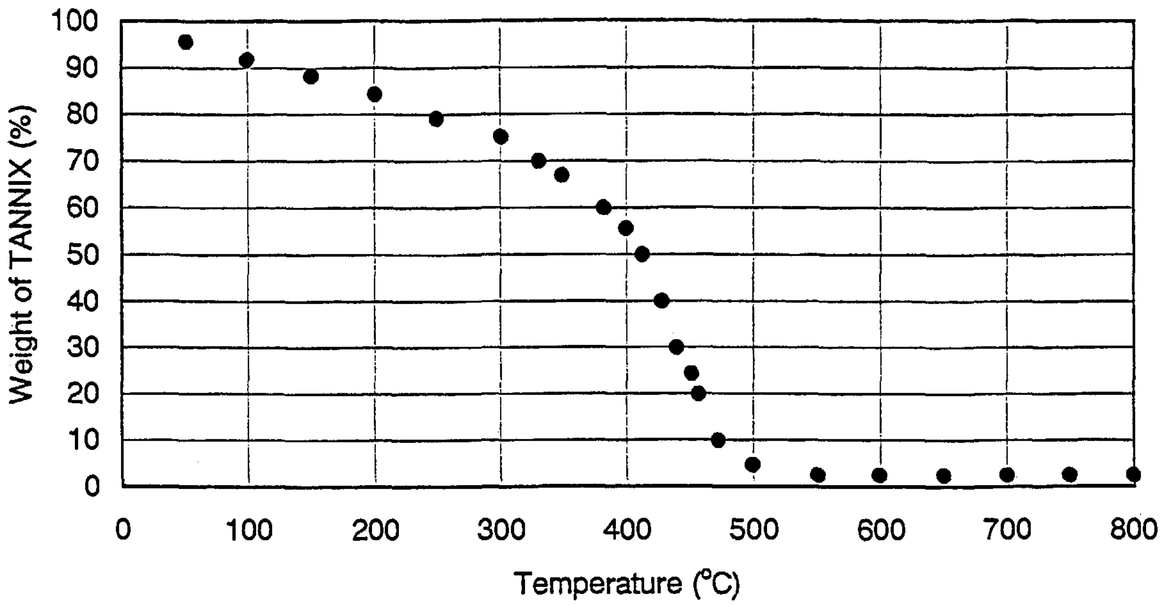

Fig.4 Pyrolysis Curve Measured with Thermobalance in Air

INDUSTRIAL APPLICATION IN MNF

MNF has replaced the radioactive liquid waste treatment system from the conventional water glass co-precipitation process to the column process using TANNIX. The block flow diagrams of both processes is shown in Fig. 5.

In the conventional process, the radioactive liquid generated in the re-conversion unit fed to the precipitation vessel and mixed with water glass. The sludge (cake) is separated by filtration, the activity of remained liquid waste is measured to confirm less than the limiting level and it is discharge to outside of facility. The cake treated in multi- stages in order to recover uranium. This process has some disadvantages that the large amount of chemicals are required for the recovery of uranium and that the large amount of secondary solid waste was formed.

In adsorption process using TANNIX, the radioactive liquid waste fed to TANNIX columns, most of uranium are adsorbed by TANNIX. The activity of liquid waste is confirmed to be less than the limiting level and discharged. The used TANNIX is dried in the column before discharging from column and the dried TANNIX is incinerated in order to recover uranium material. The process is very simple. Any chemicals don t required and the secondary solid wastes are not formed in this process.

The process data are shown in Table Ⅲ.

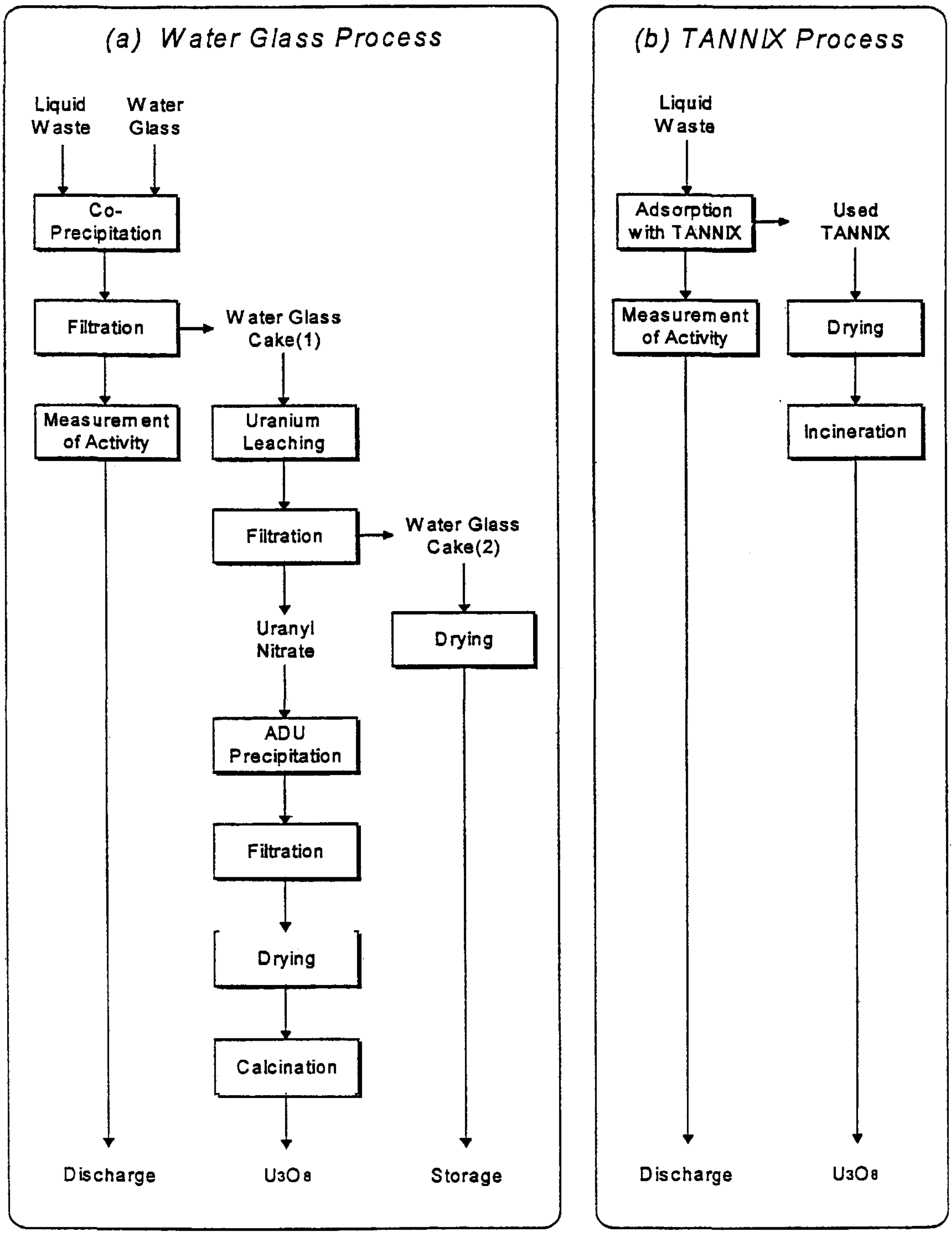

Fig. 5. Comparison of Water Glass Process and TANNIX Process

TABLE Ⅲ Comparison between Water Glass and TANNIX Process Data

	Water Glass Process	TANNIX Process
Chemical Consumption		
Water Glass	7,000 kg- Na_2OSiO_2	Non
TANNIX	Non	6,000kg- TANNIX
HNO_3	3,200kg- HNO_3	Non
NH_4OH	1,300kg- NH_4OH	Non
Secondary Waste	3,400kg (7.0m^3)	Non
Recovered Uranium		
U_3O_8	380kg- U	380kg- U
Amount of Impurities	> 30%	< 0.5%

APPLICATION FOR TRU ELEMENTS

Adsorption to recovery of Pu using TANNIX has been studied by Japan Nuclear Cycle Development Institute (JNC).

The batch and column test were carried out, the recovery of Pu was more than 99% and the decontamination factor of Pu was 10^7 in the liquid waste treatments process of multistage columns.

Adsorption ability of TANNIX for Am has been studied by JAERI, Fig.6 shows the result obtained for Am in a recent investigation, which gives a logarithm plot of Am(Ⅲ) distribution coefficients as a function of nitric acid concentration. Fig.7 shows the temperature dependency of distribution coefficient of Am(Ⅲ) in 0.02M HNO_3 acid.

Temperature and pH dependencies of Am(Ⅲ) are different from that of U, Pu and Np. These results show that Am(Ⅲ) can be separated effectively from other TRU elements by use of TANNIX

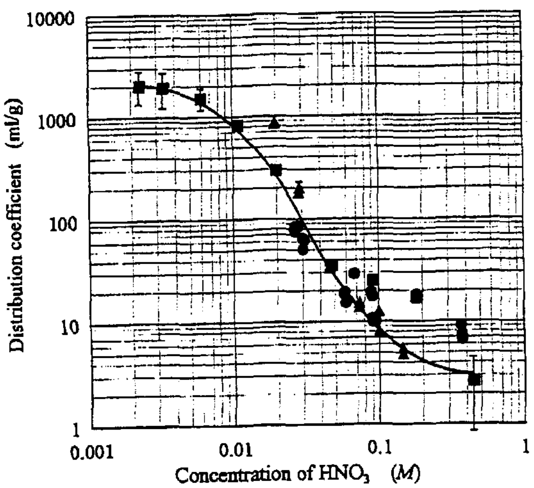

Fig. 6. PH dependency of distribution coefficient of Am(Ⅲ)

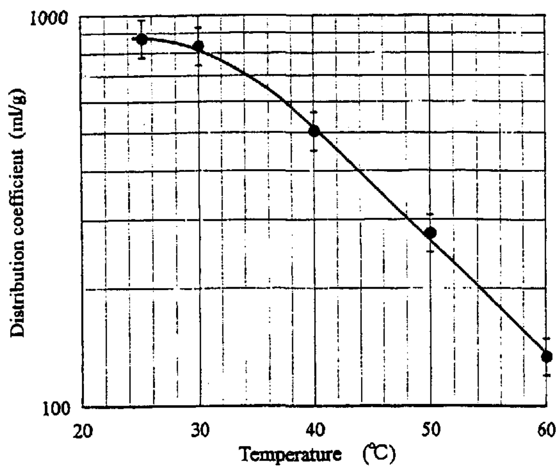

Fig. 7. Temperature dependency of distribution coefficient of Am(Ⅲ)

APPLICATION FOR Cr(VI)

Removal of Cr(VI) has been studied using tannin gel particles at Tokyo Institute of Technology.
TableⅣ shows the relationship between the adsorption capacity of Cr(VI) and the water content of tannin gel particles.

TableⅣ Relationship between the adsorption capacity of Cr(VI) and the water content of tannin gel particles

Water content (%)	60	68	72	78	84
Adsorption capacity (mg- Cr/g- dry tannin)	286	270	244	227	167

The adsorption capacity of Cr(VI) increased with decreasing the water content. These adsorption capacities were much higher than those obtained in conventional ion- exchange resin.

FUTURE

We are trying to improve both adsorption capacity and adsorption rate for heavy metal elements and TRU elements by controlling the micro and macro structure of tannin gel particles.

The modified TANNIX with different microstructure has been developed recently. It is confirmed that the modified TANNIX has high potential in adsorption capacity for rare earth elements as well as Cr(VI).

REERENCES

"A New Method of Using Vegetable Tannin for the Processing of Effluents Containing Plutonium Has Been Developed by PNC". Science & Technology In Japan, 62, p.45, 1997

T.Matsumura, S.Usuda "Application of insoluble tannin to treatment of waste containing americium" Journal of Alloys and Compounds 271- 273 (1998) 244- 247

Nakano, A. Miyazaki, M.Tanaka, M.Konno, 31st Fall Metting of The Society of Chemical Engineers, Japan Vol.3 p137 1998

Y.Nakamura, W.Shirato, H.Yamakawa, N.Fujiwara, Y.Nakamura "Experience on Treatment of LiquidWaste from UF6 to UO2 Conversion Process with Insoluble Tannin" International Conference on Fututre Nuclear System (Global 97). Vol.2, p.1187, 1997

Y,Nakano, K.Takeshita, T.Tsutsumi, Y.Nakamura. "Relation between the Adsorption Capability of Cr(III) and the Particle Structure of Water- Insoluble Tannin" 62nd Annual Meeting of The Society of Chemical Engineers, Japan Vol.3, p.208, 1997

Y.Nakano, K.Takeshita, T.Tsutsumi, Y.Nakamura. "Improvement of Adsorption Capability of Heavy Metal Ion by Controlling the Structure of Condensed-Tannin Gel". 30th Fall Meeting of The Society of Chemical Engineers, Japan, Vol.1, p.207, 1997

Y.Nakano, K.Takeshita, T.Tsutsumi, Y.Nakamura. "Adsorption Cr(VI) onto Polymer Gel Prepared by Crosslinking Condensed- Tannin Molecules". 30th Fall Meeting of the Society of Chemical Engineers, Japan, Vol.2, p.229, 1997

Y.Nakamura, W.Shirato, K.Takeshita, Y.Nakano. "Recovery of Uranium for Fuel Plant Liquid Waste by Water-Insoluble Tannin". 1997 Fall Meeting of the Atomic Energy Society of Japan. Vol.3 p.749, 1997