PARTITIONING OF HIGH LEVEL LIQUID WASTE IN CHINA

C. XU
Institute of Nuclear and New Energy Technology, Tsinghua University
Beijing, China
Email: xuchao@tsinghua.edu.cn

J. CHEN
Institute of Nuclear and New Energy Technology, Tsinghua University
Beijing, China
Email: jingxia@tsinghua.edu.cn

G. YE
Institute of Nuclear and New Energy Technology, Tsinghua University
Beijing, China

X. LIU
Institute of Nuclear and New Energy Technology, Tsinghua University
Beijing, China

Abstract

The main development of high level liquid waste (HLLW) partitioning in China was briefly reviewed. Chinese high level liquid waste has been stored for several decades. How to manage the historic HLLW is a serious problem. A total partitioning process has been developed at Tsinghua University. The process consists of the following three extraction cycles: actinides removal by TRPO extraction, Sr-90 removal by dicyclohexyl-18-crown-6-ether extraction and Cs-137 removal by calix [4] arene extraction. Based on the partitioning process, the hot test facility including 72-stage miniature centrifugal contactors was set up in the hot cell. About 300Ci HLLW was continuously partitioned within 160 hours through this facility. After 120-hour operation, 30%TRPO-kerosene was recycled without any treatment. The average values of decontamination factor were determined to be more than 3×10^3 for α activity and more than 10^4 for Sr-90/Cs-137, respectively. These results demonstrate that Chinese historic HLLW can be transferred into non-α and intermediate/low level waste by the total partitioning process.

On the other hand, developing nuclear energy has been chosen as one of important direction for energy resources in China. The development of nuclear energy cannot be separated from the support of the nuclear fuel cycle. How to effectively manage the nuclear fuel cycle, especially high level waste from the commercial reprocessing plant, to support the sustainable development of nuclear energy is an intractable problem in China. Partitioning of HLLW provides an option to reduce the high level waste which needs be disposed in the geological repository. The research work on partitioning of commercial HLLW is under process in China.

1. PARTITIONING OF HLLW

1.1. Management of high level waste

High level liquid waste (HLLW) comes from the reprocessing of spent nuclear fuel, i.e. Purex raffinate. The safe treatment and disposal of HLLW is very important in the management of nuclear waste and crucial to the sustainable development of nuclear energy. The partitioning and transmutation (P&T) of long-lived radionuclides such as minor actinides from HLLW is an attractive method to reduce the long-term risk of high level waste.

However, there is a very long way to go in the field of long-lived nuclides transmutation. The near-term objective of HLLW management is to reduce the long-term risk in disposal and the treatment cost. A supposed program in Fig. 1 is to separate HLLW into α waste, high radioactive waste and non-α intermediate level waste (ILW). So, the main purpose of partitioning is to realize the highly efficient removal of actinides and Sr-90/Cs-137 from HLLW.

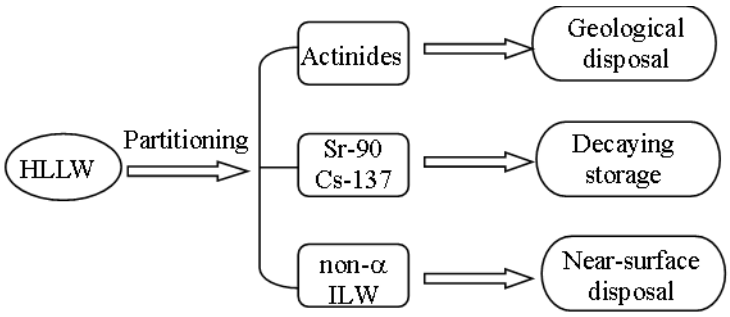

FIG. 1. Program of HLLW partitioning.

1.2. Partitioning technology

Partitioning of HLLW, especially for actinides separation, has been studied for several decades. Some partitioning processes, such as TRUEX process [1], DIMAEX process [2] and TRPO process [3], were developed and have continuous improvement.

Recently, new trends appeared in the field of HLLW partitioning. Some new ligands were developed for the aqueous process. For example, the ARTIST (Amide-based Radio-resources Treatment with Interim Storage of Transuranics) process was developed by the Japan Atomic Energy Agency (JAEA) [4], in which TODGA (Tetraoctyl-diglycol-amide) and DHOA (di-n-hexyl-octanamide) were used as the organic ligands. DOTGA process is worth of attention because European scientists also show very strong interest [5]. Pyro-process was paid a lot of attention recently. Most research focused on the electrorefining technology [6].

Some new alternative methods to conventional solvent extraction methods were presented such as supported liquid membranes, ion exchange resins and extraction chromatography [7]. The extraction chromatographic procedure employs solid extractant which is prepared by impregnating ligands with inert support materials such as poly(4-vinylpyridine), silica gel, and so on.

Another trend is to combine the partitioning with modified Purex process to integrate the reprocessing. UREX+ process [8], one of the key attributes in US-DOE's AFCI plan should be the typical representative.

The removal of Sr-90 and Cs-137 is also important to reduce the heat release of high level waste. The popular technology for Sr-90 and Cs-137 removal is crown-based solvent extraction, for example dicyclohexyl-18-crown-6 as extractant for Sr-90 and calixarene as extractant for Cs-137 [9].

2. PARTITIONING RESEARCH IN CHINA

2.1. Partitioning process

In 1980s, actinides partitioning process from commercial HLLW was developed based on trialkyl(C_6-C_8) phosphine oxide (TRPO) extraction [10]. Figure 2 shows TRPO process. Actinides are extracted by 30% TRPO-kerosene. Am(Cm), Np+Pu and U are stripped by nitric acid, oxalic acid and Na_2CO_3, respectively. TRPO process was tested using German WAK HLLW with good partitioning efficiency in 1992 [11].

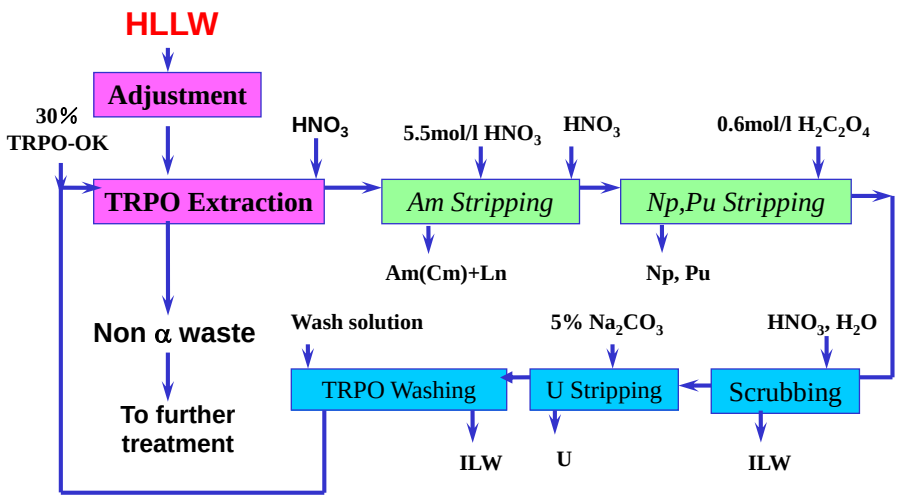

FIG. 2. Flowsheet of TRPO process.

From 1990, TRPO process was applied to separate Chinese highly saline HLLW. Meanwhile, the Sr and Cs separation technology from highly saline HLLW was studied. The crown ether was selected as the extractant for Sr separation and potassium titanium hexacyanoferrate (II) as inorganic ion exchanger for Cs removal. Around 2000, a total (actinides, Sr and Cs) partitioning process was presented [12]. In 2005, a pilot facility was built to test processes for actinides, Sr and Cs partitioning with Nd and Zr simulating Am and Pu, respectively. In 72-hour pilot test, the experimental decontamination factors (defined as the content ratio of metal in HLLW to in raffinate) are >3000 for U, >500 for Nd, >1000 for Zr, ~160 for Sr, ~100 for Cs, respectively [13], which demonstrated the feasibility and reliability of the total partitioning process and the used separation equipments.

After pilot test, the disadvantage of ion exchange operation for Cs removal appeared because of more complicated controlling under radioactive condition compared with solvent extraction operation. Calixarene was introduced to extract Cs from HLLW instead of ion exchanger. Finally, the improved total partitioning process consists of three extraction cycles (see Fig. 3): actinides separation by TRPO extraction, Sr separation by crown ether extraction and Cs separation by calixarene extraction.

2.2. Hot test

A 5h hot test for TRPO process, Sr removal by crown ether extraction and Cs removal by ion exchange was finished in 1996. In order to test the modified process with three extraction cycles, a 160h hot test for the total partitioning process based on solvent extraction was carried out in 2009. 72-stage miniature centrifugal contactors were employed in a hot cell. About 300 Ci Chinese highly saline HLLW was partitioned. Figure 4 shows the partitioning result. The average decontamination factors are more than 3,000 for α activity, and more than 10,000 for Sr-90 and Cs-137, respectively [14]. These results completely meet the requirement to change high level waste into non-α and intermediate level waste.

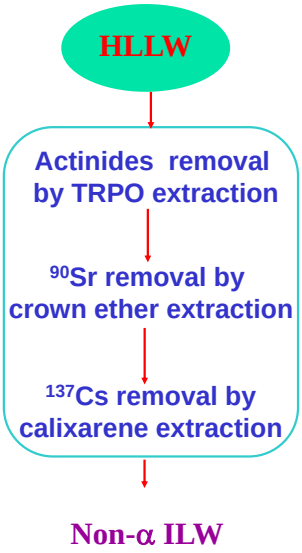

FIG. 3. Total partitioning process of three extraction cycles.

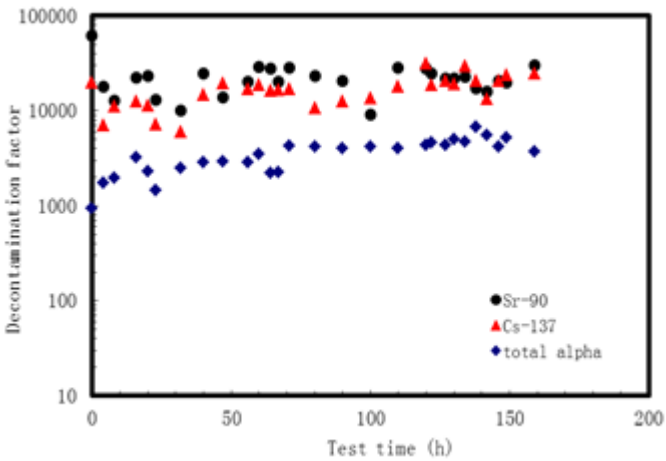

FIG. 4. Decontamination factors of α activity, Sr-90 and Cs-137 in the hot test.

3. PROSPECT

In the future, we have two tasks in HLLW partitioning. On the one hand, a pilot hot test facility should be built to demonstrate our total partitioning technology for highly saline HLLW partitioning.

On the other hand, the growing electricity demand is stimulating the nuclear power expansion in China. With the discharge of spent fuel, the commercial reprocessing plant rose to an agenda. The treatment of commercial HLLW is concerning subsequently. Chinese scientists agree that P&T-based advanced nuclear fuel cycle is the best option to solve the problem of high level waste. So, the further study on the partitioning of commercial HLLW and integrate the Purex process and partitioning process are in progress. Because of the difference between the highly saline HLLW and the commercial HLLW, we must adjust the management objective of HLLW to simplify the process and reduce the cost. Figure 5 shows the simplified concept of HLLW management. Actinides and fission products are just separated from each other. Actinides separation from HLLW is the preferred alternative considering the transmutation of TRUs in the future. However, high separation factor of actinides must be achieved to ensure change the raffinate fission products into non-α waste. This is the main challenge for TRPO process in the future.

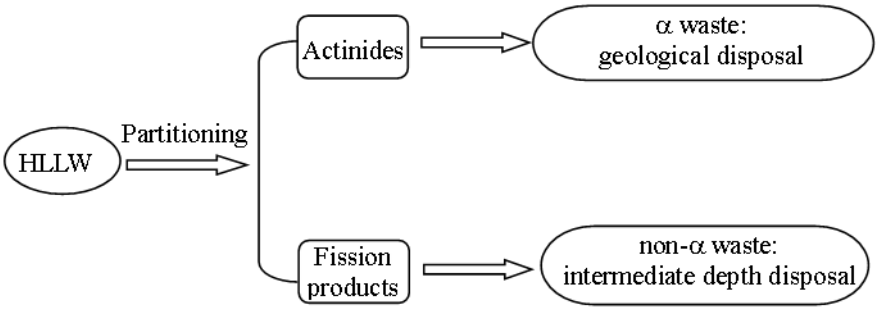

FIG. 5. The simplified concept of HLLW management.

REFERENCES

[1] HORWITZ, E.P., SCHULZ, W.W., The TRUEX process: a vital tool for disposal of U.S. Defense nuclear waste. Edited by Cecille L, Casarci M and Pietrelli L. New Separation Chemistry Techniques for Radioactive Waste and Other Specific Application, London UK: Elsevier. p21 (1991).

[2] CUILLERDIER, C., MUSIKAS, C., HOEL, P., et al. Malonamides as new extractants for nuclear waste solutions, Sep Sci Technol. **26** (1991) 1229-1244.

[3] ZHU, Y.J., SONG, C.L., Recovery of neptunium, plutonium and americium from highly active waste by tralkyl phosphine oxide extraction. Edited by Morss LR and Fuger J. Transuranium Element Symposium 1990. Washington D.C: American Chemical Society. p318 (1992).

[4] TACHIMORI, S., SUZUKI, S., SASAKI. Y., A process of spent nuclear fuel treatment with the interim storage of TRU by use of amidic extractants. Journal of the Atomic Energy Society of Japan. **43** (2001) 1235-1241.

[5] MAGNUSSONA, D., CHRISTIANSENA, B., GLATZA, J.-P., et al., Partitioning of minor actinides from Purex raffinate by the TODGA process. Proceedings of Global 2007. Boise, USA, Sep. 9-13, (2007) 713-718.

[6] UOZUMI, K., IIZUKA, M., GLATZ, J.-P., et al., Demonstration of pyropartitioning process to recover TRUs from genuine high-level liquid waste Proceedings of Global 2009, Paris, France, September 6-11, (2009) 1225-1232.

[7] WEI, Y.Z., ZHANG, A.Y., KUMAGAI, M., et al., Development of the MAREC process for HLLW partitioning using a novel silica-based CMPO extraction resin. J. Nucl. Sci. Technol. **41** (2004) 315–322.

[8] PEREIRA, C., UREX+ process overview. Topical Seminar Series on Nuclear Fuel Separation Processes, March 25-26, 2008. www.nuclear.gov/pdfFiles/DOENRCUREXSeminar.pdf

[9] DELMAU, L.H., BONNESEN, P.V., ENGLE, N.L., et al. Combined extraction of cesium and strontium from alkaline nitrate solutions. Solv. Extr. Ion Exch. **24** (2006)197-217.

[10] ZHU, Y.J., An extractant (TRPO) for the removal and recovery of actinides from high level radioactive liquid waste. ISEC'83, p9, Denver, Colorado, USA, 1983.

[11] GLATZ, J.-P., SONG, C.L, KOCH, L.B. H, HE, X.M., Hot Tests of the TRPO process for the removal of TRU elements from HLLW, Proceedings of the Global 1995 Conference, Versailles, France, Sept. 10-14. **1** (1995) 548-555.

[12] SONG, C.L., WANG, J.C., LIANG, J.F., Treatment of highly saline HLLW by total partitioning process. Proceedings of Global 1997, Yokohama, Japan, October 5-10. **1** (1997) 475-480.

[13] CHEN, J., WANG, J.C., JING. S., A pilot test of partitioning for the simulated highly saline high level waste. Proceedings of Global 2007. Boise, USA, Sep. 9-13, (2007) 1831-1835.

[14] CHEN, J., WANG, J.C., DUAN, W.H,. FENG, X.G,. Partitioning of High level liquid waste. Proceedings of GLOBAL2011, Makuhari, Japan, Dec.11-16, 2011. Paper No. 449417.