

**Performance of Steam Reforming Technology in a
Long Term Treatment of Waste TBP/Dodecane - 11079**

Akinori NAKAGAWA, Tomoyuki SONE, Toshiki SASAKI,
Osamu NAKAZAWA and Kiyoshi TASHIRO

Japan Atomic Energy Agency
4-33 Muramatsu, Tokai-mura, Naka-gun, Ibaraki 319-1194, Japan

ABSTRACT

A long term pilot scale experiment with steam reforming treatment technology was conducted for volume and weight reduction of uranium contaminated waste tri-n-butyl phosphate/n-dodecane solvent (TBP/dodecane) which was difficult to incinerate. The technology consists of a steam reforming process and a submerged combustion process. In the first process, TBP/dodecane is vaporized and pyrolyzed with superheated steam in a reducing atmosphere. In the second process, the decomposition gases are completely burned in a submerged combustion reactor. A short term treatment test was carried out before the long term test. The test achieved high mass reduction rate of the waste TBP/dodecane at least 99.3% though severe corrosion of the gasification chamber was observed. This problem was solved by sacrificial anode. After the improvement, the system could be operated safely for 960 hours, the averaged mass reduction rate was 99.6% that was slight higher than the short test one.

INTRODUCTION

Radioactive organic wastes are generally treated by incineration that can provide high volume reduction rate. However, some kinds of organic wastes such as phosphate esters are difficult to combust because of generation of corrosive compounds and plugging materials. Phosphate esters are widely used as flame retarders and extraction agents in nuclear facilities. Tri-n-butyl phosphate (TBP) is used to extract uranium and plutonium from aqueous solution of spent fuel in reprocessing plants. When spent TBP is incinerated, it is pyrolyzed into hydrocarbons and phosphoric acid [1, 2] and then, phosphoric acid changes into polyphosphoric acids by thermal condensation [3]. The following formulas show pyrolyzation of TBP (1) and condensation of phosphoric acid (2).



The evaporated polyphosphoric acids stick on the filter and the wall of incinerator and often decrease operating performance.

Several alternative TBP treatment technologies have been developed. Acid digestion [4] is a decomposition process of TBP in the mixed solution of nitric acid and concentrated sulfuric acid at 200-250 °C. Strong acids cause corrosion in a decomposition reactor. Pyrolysis [5] is also decomposition process at 400-650 °C adding neutralizer such as calcium hydroxide for prevention of corrosion. This technology provides good corrosion resistance, however, a large amount of secondary waste is generated.

Japan Atomic Energy Agency (JAEA) has developed a steam reforming treatment technology for volume and weight reduction of radioactive organic wastes that are difficult to incinerate. Steam reforming is a synthesis reaction of combustible gases such as hydrogen and methane from organic materials with

superheated steam [6]. For example, this reaction is used to produce hydrogen for fuel cell [7] and hydrogen generation from biomass [8] or coal [9]. In the JAEA technology, steam reforming reaction is applied for gasification of organic wastes and separation from non-volatile nuclides such as uranium of the wastes.

The JAEA system has two main processes, a steam reforming process and a submerged combustion process. In the first process, wastes that are supplied at a rate of 1-3 kg/h to a gasification chamber are vaporized and pyrolyzed with superheated steam in a reducing atmosphere. Non-volatile residues such as uranium compounds remain in the chamber. A small amount of radionuclide is accompanied with the decomposition gas and is trapped by a filter at the end of the chamber. In the second process, decomposition gases are completely burned in a submerged combustion reactor to prevent soot and dioxins generation.

Short term treatment tests about uranium contaminated waste TBP/dodecane were discussed firstly. In the tests, the averaged gasification rate of the waste and a uranium distribution in the equipments were estimated. Corrosion prevention method of the gasification chamber was investigated. After the investigation, long term treatment tests were performed. In the test, prevention method was confirmed.

EXPERIMENTAL

1. Setup

The demonstration scale steam reforming treatment system (**Figure 1**) has been built at Nuclear Fuel Cycle Engineering Laboratories. The components are a gasification chamber for vaporization of wastes, a metal mesh filter for removal of radioactive nuclides, a submerged combustion reactor for complete decomposition of organic compounds and two stage scrubbers for removal of phosphorous oxides from flue gas.

The gasification chamber is made up a metal cylinder of 120 mm in diameter and 2,200 mm in length with triply separated tubular electric furnaces and a screw feeder for extracting residues. The operation temperature is up to 650 °C.

The metal mesh filter is made of stainless steel with 160 mm in diameter, 500 mm in length and 200 μm mesh.

The submerged combustion reactor is made of castable alumina for corrosion prevention and heat insulation with a cylindrical stainless steel shell. The decomposed organic gas from chamber is completely burned with preheated air. The operation temperature is controlled at about 1,000 to 1,200 °C by changing the air temperature. The burned gas is submerged into the water and is cooled below 80 °C in the quenching tank.

The off-gas is treated through two alkaline scrubbers. A cylindrical mist filter is put after the scrubbers to trap phosphoric fine mist.

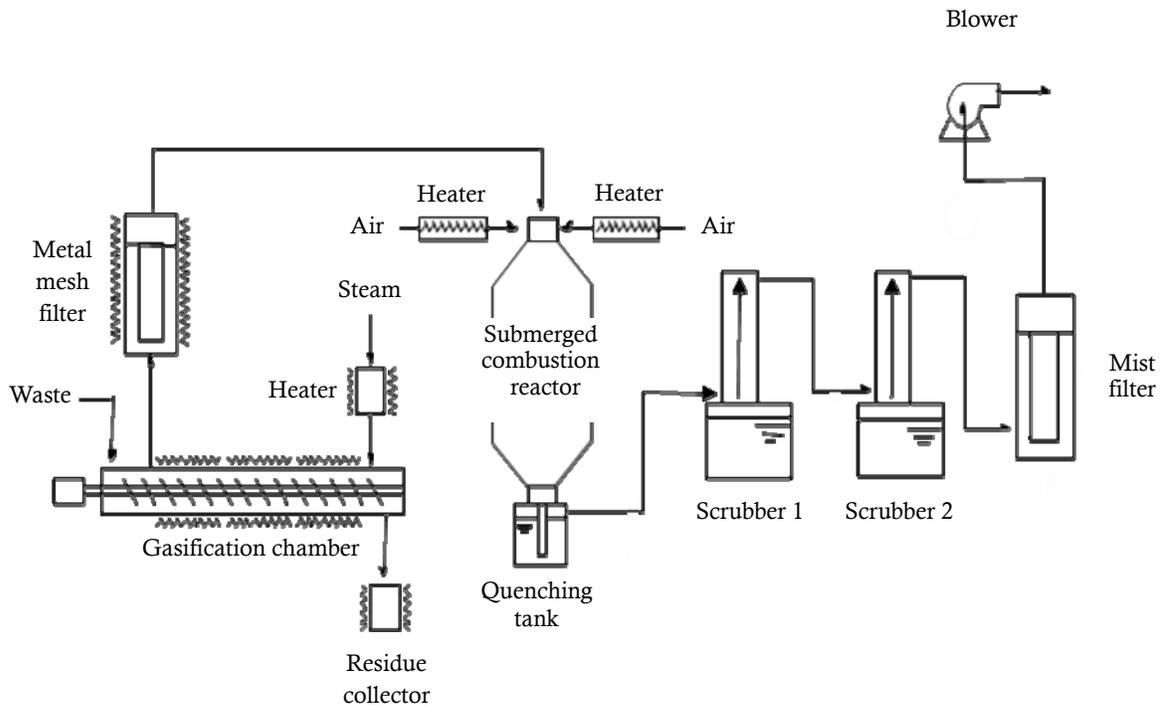


Figure 1. Process flow diagram of the demonstration scale steam reforming treatment system

2. Experimental procedure

Three kinds of test as follows were carried out using uranium contaminated waste TBP/dodecanes. Those chemical compositions are listed in **Table I**.

Table I. Chemical Compositions of waste TBP/dodecanes

	TBP (wt%)	Dodecane (wt%)	U (g/L)	DBP (g/L)	NO ³⁻ (g/L)
Sample 1	30	70	0.01	0.0	0.0
Sample 2	40	60	0.08	0.0	0.0
Sample 3	41	59	0.07	2.6	0.0
Sample 4	48.5	51.5	0.07	0.23	0.76

(1) Short term treatment test

The short term tests for about 10 hours were performed to study the gasification rate, uranium concentration distribution and operational condition. The gasification rate was estimated by residue weight and the uranium concentrations in aqueous solution were measured alpha activity by a ZnS scintillation detector. The waste was fed into the gasification chamber from one side, and

steam heated to 400 °C was fed into it from the counter side. Feed rates of the waste and steam were about 1 kg/h and 4.5 kg/h respectively. The gasification chamber was maintained the temperature of 650 °C. Air heated up to 800 °C was fed into the combustion reactor with the rate of 55m³/h. Temperature of pass from gasification chamber to combustion reactor was maintained 650 °C to prevent deposition of polyphosphoric acids.

(2) Corrosion test

The corrosion test was carried to select the material of the gasification chamber. Four kinds of materials were studied, SUS310S, Sanicro® 28, Hastelloy® C22 and Hastelloy® C276. The size of test pieces was 15×25×3 mm. The pieces were grinded by glass paper and rinsed with acetone. Two material pieces were simultaneously immersed in 100 ml of 95% phosphoric acid. The phosphoric acid was heated up to 250 °C in a Teflon® flask with a condenser to maintain amount of the acid. The immersion time was 5 hours and the phosphoric acid was refreshed each test. The test pieces were washed in water by ultrasonic cleaner and dried in a thermostatic chamber at 40 °C. Corrosion rate was derived from measured weight loss and size of test pieces.

(3) Long term treatment test

The long term treatment tests were carried out to confirm effect of corrosion prevention method that was provided from immersion corrosion test and to estimate operation stability in the test. Operation stability was evaluated by concentrations measurement of CO and NOx in off-gas using a flue gas analyzer (TESTO 350XL). Feed rates of the waste and steam were 3 kg/h and 4.5 kg/h respectively. The gasification chamber was heated to 600 °C. Heated air temperature, feed rate of air and temperature of metal mesh filter and pass from chamber to combustion reactor were controlled the same conditions as the short term treatment test.

RESULTS AND DISCUSSION

1. Short term treatment test

The short term treatment test was performed for totally 135 hours and processed 135 kg (167 L) of the uranium contaminated waste TBP/dodecane. The averaged gasification rate was 99.3%. **Table II** shows uranium concentrations in the aqueous solution. The result showed almost all of uranium was remained in the gasification chamber and the residue collector. Since uranium concentrations in the solution are less than the regulatory level, the solution can be discharged into the environment after a neutralization treatment of phosphoric acid. Exposure possibility of worker during maintenance is relatively low since contamination region is limited. Thus, the steam reforming treatment system can provide not only high mass reduction rate but also good radiological protection.

Table II. Uranium Concentration in Aqueous Solution

	Scrubber 1	Scrubber 2	Mist filter
Uranium Concentration (detection limit)	ND (0.03mg/L)	ND (0.1mg/L)	ND (0.03mg/L)

2. Corrosion test

The corrosion affecting the lifetime of gasification chamber was found in the short test. To solve this problem, corrosion test on some stainless steels and nickel alloys in boiling phosphoric acid was conducted. The results are shown in **Table III**. Hastelloy® C276 had the best corrosion resistance among the materials.

Table III. Corrosion rate in boiling phosphoric acid

	SUS310S	Sanicro® 28	Hastelloy® C22	Hastelloy® C276
Corrosion rate (mm/hour)	0.078	0.019	0.005	0.002

According to the result, a steam reforming test for 50 hours was conducted using Hastelloy® C276. However, pitting corrosion was found at the bottom of chamber. To improve the lifetime, sacrificial anode was tested. Sacrificial anode is used for zinc coating of steel [10]. The mechanism is that the electrons released from corroded anode protects cathode from corrosion. In the immersion test using sacrificial anode of SUS310S, corrosion rate of Sanicro® 28 was one-third of that of Sanicro® 28 without sacrificial anode. This result implies that the sacrificial anode is effective against the pitting corrosion.

3. Long term treatment test

The long term treatment test was demonstrated for 960 hours changing the sample from 1 to 4. The processed TBP/dodecane amounted to 2,633 kg (3,141 L). The averaged gasification rate was 99.6%.

To prevent pitting corrosion, sacrificial anode of SUS310S was used. No pitting corrosion was found on the surface of the gasification chamber made of Hastelloy® C276. By elemental analysis of the residues, 21wt% Fe, 7wt% Cr and 9wt% Ni that were main constituent materials of SUS310S were detected. Residual element was the phosphorus (52wt%). The result implies almost all of the residues comprised corrosion products of SUS310S. The sacrificial anode is an effective method to improve the lifetime of gasification chamber.

Filter plugging was found during the test. The solid samples from the filter were analyzed and the silicon was detected. This result showed that the silicon originated from the impurity of the samples such as silicone oil had caused plugging. In order to remove the clogging material, air was introduced in the gasification chamber for 30minutes. The silicon was oxidized by the air and was removed from the filter.

To keep the environmental regulation, the off-gas was monitored by a gas analyzer during the test period. **Figure 2** shows CO and NO_x concentration in the off-gas of the sample 2. The CO concentration was less than the regulatory level (100 ppm) during the test. The result shows that hydrocarbons were completely decomposed. NO_x concentration was also less than the regulatory level (250 ppm). CO and NO_x concentration were under the regulatory level during all of the long tests.

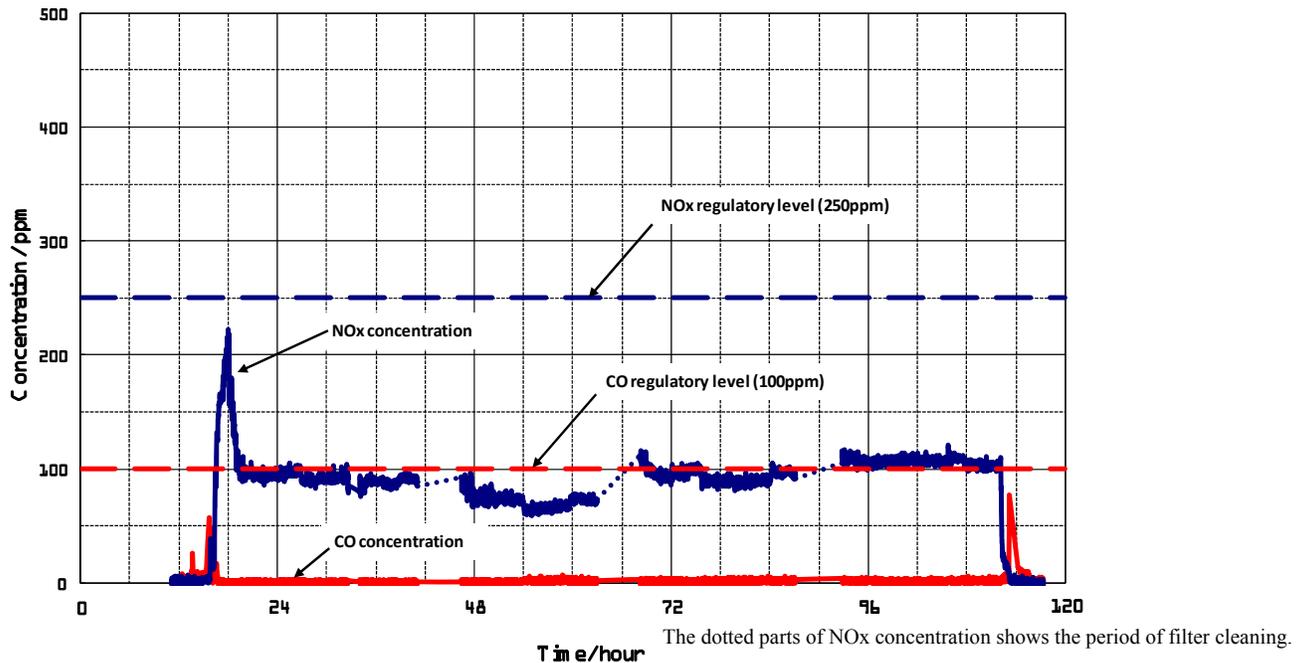


Figure 2. Concentration of CO and NOx in the off-gas

CONCLUSION

The steam reforming technology for volume reduction of the uranium contaminated waste TBP/dodecane was demonstrated. Results of the short term treatment test showed that the steam reforming treatment system in JAEA provided high mass reduction efficiency and separability uranium from waste TBP/dodecane. The averaged mass reduction rate was over 99%. The CO and NOx concentration of the off-gas were less than the regulatory level during all of the long term treatment tests. The liquid waste can be released to the environment. The corrosion of gasification chamber was solved by sacrificial anode. The short and long term pilot scale treatment test was conducted totally over 1,000 hours and processed over 3,000 L of uranium contaminated waste TBP/dodecane successfully.

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