# Expanded Applications of LPOP Method to Nonflammable Waste Treatments-11572

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**ABSTRACT**

Fuji Electric Co., Ltd. has developed a Low Pressure Oxygen Process (LPOP) method to stabilize and reduce the volume of nonflammable materials such as ion exchange resins. The LPOP method is a technique capable of reducing the production of soot and tar in the extreme, reducing the volume and weight of radioactive nonflammable materials, and mineralization. We have reported test results of ion exchange resins to date by using FRR (Fuji Resin Reducer) which is the full-scale equipment mounted with LPOP technology. This report describes the results of testing activated charcoal and inflammable/nonflammable liquids as an expanded application of this equipment, and moreover, an application for the collection of noble metals.

## INTRODUCTION

The operation of nuclear power stations produce spent ion exchange resin (hereafter referred to as spent resin), which is radioactive waste generated from the water treatment system of the facility. Spent resin has different radioactive concentrations depending upon the system used to purify it. Spent resin having relatively high radioactive concentration is generally stored first within the site of a nuclear power station and then disposed after attenuation of radioactivity. Storage quantities are increasing steadily year after year. The future plan for low level radioactive waste discharged from nuclear facilities in Japan is for it to be solidified using cement or the like and then to be buried for disposal as a waste package. Burying the spent resin, having relatively high radioactive concentration for disposal, is said to be required on the one hand to reduce disposal quantity from the viewpoint of reduction of burial costs and on the other hand the stabilization treatment for resin from the viewpoint of long term security of waste packages for making the package suitable for burial disposal. In consideration of these requirements, it has become an urgent need to establish a treatment technology to satisfy both volume reduction and stabilization.

Fuji Electric has developed LPOP treatment procedures and equipment, which make available both volume reduction treatment of radioactive spent resin as spent ion exchange resin and stabilization treatment suitable for final disposal. The development of this technology, after demonstrations including hot tests using actual resin by means of prototype equipment [1], and functional test equipment, has achieved performance evaluation using actual scale equipment and investigation tests regarding waste packages[2][3]. This paper reports the overview of LPOP technology, mineralization of ion exchange resin and solidification tests executed for the purpose of evaluating the effect of LPOP treatment targeting burial disposal.

This report is a summary of LPOP technology, its economic utilization method when applied to spent ion-exchange resin and results of application tests when used for activated charcoal and organic solvent.

## 1. OUTLINE OF LPOP TECHNOLOGY

### 2-1 LPOP Technology

LPOP treatment performs controlled combustion of flame retardant materials and their oxidative degradation by means of combination of plasma activity in a low pressure oxygen atmosphere of several kPa not developing to thermal plasma and temperature control by heater heating. The concept of low pressure oxygen plasma treatment using IC plasma is shown in Fig. 1.

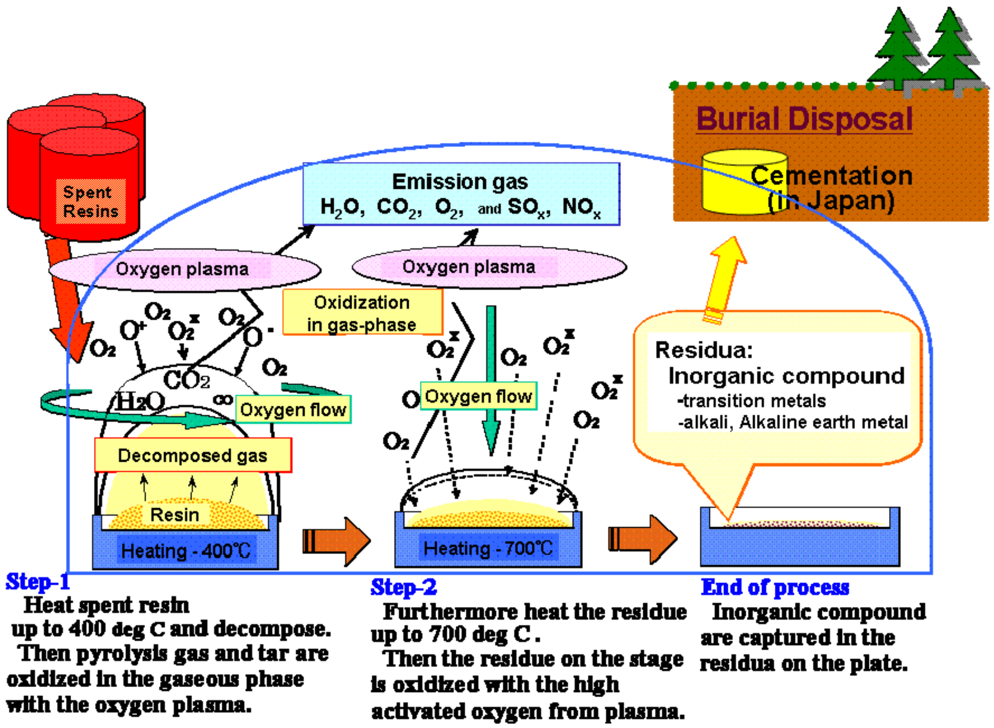


Fig.1 Conceptual diagram of LPOP

Typical ion exchange resin is synthetic resin having a chemical constitution of bridged 3 dimensional polymer base substance introduced with such functional groups as sulfuric acid group ($-SO_3$) and quaternary ammonium group ($-NH_3$). The polymer base substances used in most ion exchange resins are copolymers of styrene and divinylbenzene (DVB) and some of their industrial products are in the form of 14 to 50 mesh (1180 to 300μm) spherical particles or powders[4].

The spent resin used in water treatment systems for nuclear power stations accompanies such metallic ion ingredients as Fe, Ni, Cr and Co and solid ingredients composed of these ingredients.

The process for volume reduction and stabilization treatment of spent resin by means of LPOP is shown as follows. As this process aims at high volume reduction treatment including carbon ingredients in spent resin, it is composed of 2 stages of treatment temperature:

(1) The spent resin is thermally decomposed by heating it to around 400 deg C and the thermally decomposed gas is by oxidation, degraded using oxygen heated and activated by low pressure oxygen plasma. ------- 1st treatment

(2) The carbonized residue is further heated to around 700 deg C using the residue of the 1st treatment and oxygen heated and activated by low pressure oxygen plasma making direct contact with the resin for high volume reduction by promoting oxidative degrading of carbon ingredients ------- 2nd treatment

The 1st treatment generates a large quantity of thermal deposition ingredients and the treated materials have controlled heating temperature by means of an electric heater and by using the circulating gas flow. As this controls the heat flow generated from LPOP plasma flowing into the treated material, “mild treatment” with the controlled progress of combustion even in the oxygen environment is realized. Also, as the circulating flow makes the thermally decomposed gas well mixed with oxygen, the thermally degraded gas generates little soot and combusts well. As the 2nd treatment uses the down flow, which feeds oxygen effectively to the spent resin, the combustion progresses even with the carbonized spent resin. In either treatment of both of these 2 stages, carbon (C), being the major ingredient of spent resin, are oxidized to $CO_2$ and hydrogen (H) to $H_2O$. Functional groups, which exchange the ion, such as $-SO_3$ and $-NH_3$, are oxidized to SOx and NOx and discharged as the exhaust gas. In the above process the spent resin is reduced in volume and at the same time stabilized due to mineralization progress. The transition metals, which had been ion-exchanged, changed to oxides during the treatment process, are left remaining in the residue.

2-2 Actual Scale Test Equipment

The actual scale test equipment is equipped with a low pressure processing chamber about 800 mm in opening diameter and about 1000 mm in height. At the top of the processing chamber, an induction coil connected with a high frequency power supply for generating plasma is installed via a window made of quartz at the ambient pressure side; a vacuum pump for evacuating the processing chamber and an oxygen gas supply system are connected. The processing chamber has a φ650 mm built-in stage for loading and heating the resin and is composed of a hopper and resin supply equipment for supplying resin under low pressure environments, and a resin recovering unit for recovering the incinerated resin after treatment by vacuum under ambient pressure. The exterior view of actual test equipment shown in Fig. 2 [3]

Fig. 2 Exterior View of actual test equipment

2-3 Features

(1)Volume Reduction and Mineralization Performance [5][6][7]

The ion exchange resin contains about 50 % carbon as its ingredient. The treatment including thermal decomposition cannot decompose the resin sufficiently and relatively high carbon ingredients remain even after treatment. This method can oxidize the carbon ingredient effectively to $CO_2$ by using the chemical activity of oxygen plasma. As a result, high volume reduction and weight reduction of the spent resin become possible.

The result of performance evaluation for volume reduction and weight reduction by executing the 2 stages of LPOP treatment as shown in item 2-2 is shown in Fig. 3. As the resin to be treated, an ion exchange resin was produced and used simulating the spent resin by a cold ingredient taking the water quality in nuclear power stations into consideration. The LPOP treatment resulted in a volume reduction rate of more than 90 % (1/10) and weight reduction rate of more than 95 % (1/20).

The volume and weight reduction rates were calculated by the following formula with reference to the water-containing resin after adjunction and adjustment:

Weight reduction rate
= (1 – residue weight / water-containing resin weight) x 100%
Volume reduction rate
= (1 – residue volume / water-containing resin volume) x 100 %
Here the water-containing resin weight
=Dry resin treatment weight x (1 – water content of water-containing resin)

The reduction of C, H, N and S ingredients before and after treatment were evaluated for the purpose of examining the effect of mineralization by means of LPOP treatment focusing on carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) as the ingredients of ion exchange resin. As the result a reduction rate of 99 % for C, H, N and S was achieved. Table 1 shows an example of the results. This result suggests a realization of mineralization of 99 % assuming C, H, N and S ingredients conservatively to represent all of the organic ingredients and considering the reduction of organic ingredients to be mineralization. Calculus equation is as follows:

CHNS Volume reduction
=CHNS each-weight (include in dry-resin) - (include in residue)
/ CHNS each-weight (include in dry-resin)

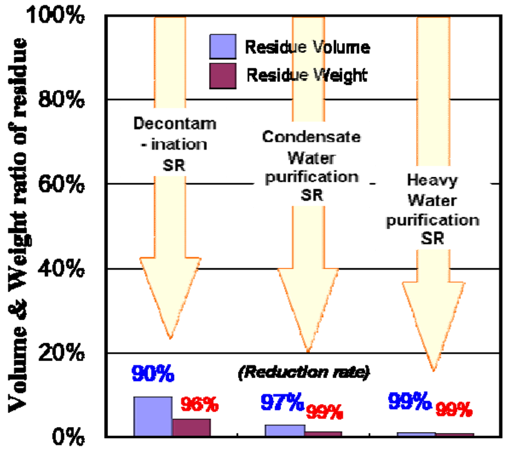


Fig. 3 Results of performance evaluation
for volume reduction and weight reduction

Table.1 Example of LPOP treatment result

| | Spent resin A | Spent resin B |
|---|---|---|
| Relative amount of absorbed | + | +++ |
| Total Weight reduction | 98.2% | 91.8% |
| CHNS Weight reduction | 99.3% | 99.5% |

(3)Plasma Generation

The LPOP of this equipment is generated using a high frequency discharge. The discharge is generated by supplying a high frequency current into an induction coil installed outside the container and has the following features:

a) No risk or concern of deterioration and damage by plasma because the induction coil and insulator can be separated from the plasma.

b) Easy maintenance because no consumable electrode is used.

c) Plasma can be maintained for a wide pressure range and gas ingredients.

(4) Simple structure

No firebrick is required in the treatment container and no furnace waste materials containing radioactive substances are generated. The simple treatment container having a cylindrical construction containing no firebrick is easily maintained, repaired and decontaminated.

(5) Easy operation

All control elements relating to operation are electrically controlled and automatic process control is applicable. Power supply failure migrates to extinction of plasma, shutdown of oxygen supply, stop of heater heating and the reduced volume treatment reaction tends to converge.

**3 Proposal of an economic utilization method**

The LPOP processing can regulate the ratio of volume and/or weight reduction. If this processing is appropriately used according to the initial radioactive concentration of the target spent ion-exchange resin, it can achieve minimization of the processing expense of spent ion-exchange resin.

LPOP processes the resin at two steps of temperature as noted above. The spent ion-exchange resin has advanced its carbonization at the end of the 1st step. This leads to stop progression of volume reduction by finishing stage heating and oxygen supply in midstream of the 2nd step. This operation makes it possible to stop progression of volume and/or weight reduction. Fig. 4 shows an example of progress of weight reduction, predicted from generation of the carbon dioxide and carbon

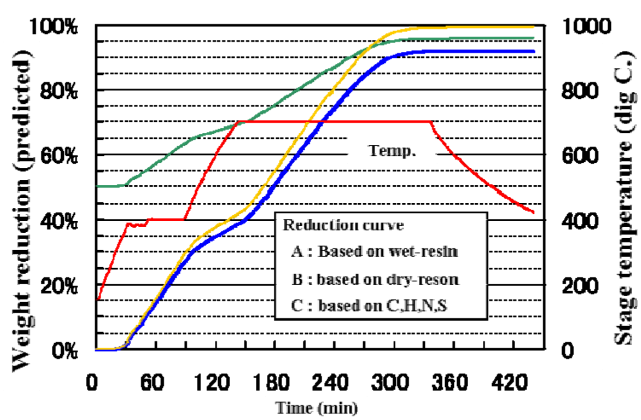


Fig.4 Example of progress of weight reduction

monoxide in LPOP process. In the process shown in this Figure, the residual substance which achieved weight reduction by 80% (reduce to 1/5) can be recovered by stopping stage heating and oxygen supply after about 120 minutes elapsed.

For example, if the class of radioactive waste changes from A to B by reducing the volume from the initial radioactivity density of the spent ion-exchange resin to 1/10, a processing of high economical efficiency which minimizes the amount of wastes can be performed by stopping processing before it reduces the volume to 1/10 using the above-mentioned method.

## 4 Expansion of the application

4-1 Application for the volume reduction of used activated charcoal

Activated charcoal resembles the finished residue in the 1st step in LPOP processing of spent ion-exchange resin and was carbonized. Therefore, the processing for volume reduction of the activated charcoal using LPOP may carry out only step-2 of Fig-1 in the processing for volume reduction of spent ion-exchange resin.

As an example of LPOP treatment of activated charcoal, Table 2 shows the result of having implemented LPOP treatment continuously until the generation of carbon dioxide becomes small. Although the activated charcoal after processing resembles the form before processing, it has a sponge like form composed of only inorganic components. Activated charcoal can also be recovered with desired weight reduction ratio by suspending LPOP processing in a suitable time same as in case of ion-exchange resin. Thus, volume reduction processing of high economical efficiency is achieved.

Table 2 weight and Volume reduction performance for charcoal (granular shape)

| Contents of initial (w/w%) | | | | | | reduction rate (w/w%) | |
|---|---|---|---|---|---|---|---|
| | C | H | N | S | others | weight | Volume |
| Before | 91.2 | 1.1 | 0.8 | 0.2 | 6.8 | 99 | 96 |
| After | 2.8 | 1.5 | 0.1 | 2.9 | 92.7 | | |

4-2 Application for collection of precious metals

Ion exchange resin is one method used to collect precious metals from industrial waste. First, this method dissolves and liquefies the electronic components including precious metals with the chemical treatment. Next, the method collects precious metal ingredients from the liquid using ion exchange resin. Finally, although incineration will recover the metals from ion exchange resin, it is a challenge to minimize the carbon components. Since conventional incineration methods have a large amount of residuals, it needs to employ a long burning time and must repeat numerous cycles of incineration recovery. If LPOP processing is performed, the residue of high quality with little carbon residue (high concentrations) is obtained without evaporating the precious metals. In the end stage process of the precious metals recovery employing chemical treatments, LPOP process is appropriate. An example of the volume reduction result of ion-exchange resin which adsorbed the precious metals is shown in Table 3.

Table 3 the volume reduction result (component of residue)

| Contents of residue (w/w%) | | | | | | reduction rate(w/w%) | |
|---|---|---|---|---|---|---|---|
| Pt | PdO | Au | Ag | SnO | others | weight | Volume |
| 53 | 20.2 | 2.2 | 1.6 | 16.3 | 6.9 | 85 | 83 |

4-3 Application to organic solvent process

Decomposition/detoxification of an organic solvent is also possible by using the LPOP process. Since organic solvents are highly flammable compared to ion exchange resin, the following equipment was used;

It is a system which attaches a plasma generator to processing container sidewalls. In addition, the method of supplying small quantities of solvent continuously into the processing container was employed. The processing conditions are the same as those in the 1st step in the case of processing ion exchange resin.

A result example which processed toluene and chlorobenzene is shown in table 4. When components in flue gas were analyzed, 99.99% was decomposed for both materials.

Table 4. resolve performance for organic solvent

| | toluene | chlorobenzene |
|---|---|---|
| feeding rate (g/min) | 2.33 | 2.67 |
| strength of feed (μg/L) | 33,344 | 38,143 |
| strength of exhaust (μg/L) | < 3 | < 1 |
| resolve ratio | 99.991% | 99.997% |

**5 Summary**

This report describes the outline of LPOP technology, and two research results of testing charcoal (activated charcoal) and inflammable/nonflammable liquids as expanded applications of this equipment, and moreover, an application to the recovery of precious metals.

(1) Treatment test of charcoal

It is possible to reduce the volume and weight of the activated charcoal and mineralize them by the simpler process than the ion exchange resin process. The weight-reduced and mineralized ashes remain with the nature of the activated charcoal.

(2) Recovery of precious metal

In addition to a spent resin treatment, this method allows reduction in volume of the resin component, and efficient recovery of precious metal when ion exchange resins on which precious metals are absorbed are processed. Wet process such as acid melt is a popular process for recovering precious metals such as Platinum, Palladium from electronic circuits like mobile phones. Ion-exchange resins are used in these processes for the purpose of recycling precious metals.

(3) Treatment test of inflammable/nonflammable liquids

It is also possible to perform the incineration treatment of inflammable/nonflammable liquids by adding a mechanism to introduce liquids bit by bit into the equipment.

As mentioned above, the LPOP treatment which utilizes oxygen atmospheres is suitable for the processing of organics. Moreover, since the volume reduction of carbon components is possible by continuing processing, application to precious metals recovery is also achieved. Further development will be continued toward economic applications for radioactive waste of organic nature.

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