

## VOLUME REDUCTION BY OXIDATION

Hiroshi Kuribayashi, Akihiro Yamanaka,  
Yukihiko Koshiba and Akira Hasegawa  
JGC Corporation  
14-1, Bessho 1-chome, Minami-ku, Yokohama, 232 Japan

### ABSTRACT

JGC Corporation has been actively investigating the treatment of various combustible and organic wastes generated at nuclear power stations and reprocessing plants. In particular, JGC has analyzed three new technologies which produce dramatic volume reductions and complete conversion of wastes into inorganic substances for durable storage and disposal. Those technologies are; (1) Incineration, (2) Wet oxidation and (3) Photo-oxidation. Incineration is an excellent volume reducer for combustible wastes, and wet oxidation, using hydrogen peroxide, is also a good way for reducing spent ion-exchange resins without any off-gas problems. Photo-oxidation is a new technology to purify polluted water for recycled use in the stations without the release of contaminated water to the environment. Polluted water may include  $\text{NH}_4^+$ , detergents, chelating agents and other organic decontamination agents. These VR technologies are all based on "Oxidation" from which the title of this paper comes.

### INCINERATION

The first technology examined was an "Incineration" system. JGC's special radioactive waste incinerator is able to incinerate miscellaneous low-level radioactive solid wastes and contaminated oil.

This incinerator's furnace has four chambers, of which the primary and secondary chambers are each equipped with a burner. The primary chamber of the furnace has a combined structure of a slightly declined flat floor and a grate to enable both paper and plastic materials to be well incinerated. The solid wastes charged into the primary chamber are partly pyrolyzed into gases on the floor. While passing through the secondary, tertiary and quaternary chambers, the gases are thoroughly burned. The solids remaining in the primary chamber are completely incinerated and are then removed through the ash outlet.

Flue gas from the furnace is indirectly cooled by air, followed by a dry electrostatic precipitator and a HEPA filter.

The Japan Atomic Energy Research Institute's (JAERI) incineration system, which was designed and constructed by JGC, has successfully maintained operations since 1973, documenting and substantiating the favorable volume reduction ratio of 50 to 100.

#### Typical Basic Design Conditions

##### General

The capacity rate of solids and oils is indicated below:

Miscellaneous solid wastes	50 kg/hr
Waste oils	10 l/hr

##### Objective

Radioactive solid wastes are assumed to comprise, for the most part, of the following flammable materials.

Paper, rags, and wooden pieces	70 wt%
Polyethylene sheets	15 wt%
Polyethylene casings	6 wt%
PVC sheets	4.5 wt%
Neoprene rubber	4.5 wt%

##### Fuels used for Auxiliary Firing

Kerosene or light oil  
Propane or LPG

##### Operation

###### General

The operational procedure described below refers only to an eight-hour-per-day operation in principle. However, continuous operation of the radioactive waste incinerator is more preferable.

###### Classification and Charging of Radioactive Waste for Incineration

After removing the lid on a drum, it is inverted and the contents are discharged into the glove box which is equipped with an air-locked chamber, and classified. In the glove box, the non-combustibles are separated from the combustibles, and the combustibles are packed in cardboard boxes and placed onto a charging unit.

###### Incineration

The incinerator has a combined structure of a flat furnace floor and a grate so that a mixture of paper and plastic materials can be incinerated. This furnace floor is tiled so that ash, when pushed by new boxes charged from the charging inlet, gradually falls down onto the roaster.

To operate the incinerator, the incinerator blower and the exhaust gas blower are first started. Then, propane burners and oil burners are ignited to raise the temperature. At 400°C, charging of radioactive solid wastes can be initiated. The optimal temperature for normal operation is 700°C to 900°C for the primary chamber and 500°C to 800°C for the tertiary chamber. The temperature in the primary chamber is controlled by the flow rate of oil, while the temperature in the tertiary chamber is controlled by propane.

The entire system is operated under negative pressure. The pressure in the glove box is controlled at -5 mmAq, while the pressure inside the incinerator, at -7 mmAq.

#### Off-gas System

Two coolers (No. 1 and 2) are installed to lower the temperature of the off-gas. To provide protection for the electric precipitator and the HEPA filter, the outlet temperature of the No. 1 cooler is controlled at 250°C, while that of the No. 2 cooler is controlled at 100°C.

Most of the ash entrained in the exhaust gas system are collected by the electric precipitator. The collected dust is hammered out by means of an automatic electromagnetic hammer and withdrawn through a lower hopper to the outside.

Upon request, a scrubber can be installed after the HEPA filter to remove acid gas, and the circulating water in the scrubber will be mixed with concentrated aqueous solution of sodium hydroxide to keep its pH slightly alkaline (above pH = 7). The HEPA filter unit comprises of four stages --- a pre-filter, an AEC filter, an activated charcoal filter, and an AEC filter.

#### Ash Removal

The ash produced from incineration is mostly withdrawn from the primary chamber of the incinerator. The ash remaining beneath the roaster is discharged in an ash-receiving tank and withdrawn into a drum.

Incineration of spent ion-exchange resins, however, generates voluminous off-gases containing acid substances, soot and radioactive nuclides which produce pollution problems. Therefore, such resins may be treated by the following alternative method.

### WET OXIDATION

The second technology is an innovative "Wet Oxidation" method. Here, organic wastes, such as spent ion-exchange resins, filter sludges and spent TBP (tributyl phosphate), are completely decomposed in an aqueous solution of hydrogen peroxide under the existence of a catalyst. The reaction occurs at a low temperature of 100°C and at atmospheric pressure. The decomposition process can be executed in batches or continuously, although the batch method is considered to be more suitable because of the simplicity of the system design and the ease of reaction control.

### Typical Basic Design Conditions

#### Treatment Capacity

The Wet Oxidation plant is capable of treating radioactive sludge generated at a 1,100 MW-class BWR plant (except for those from CUW and FPC) per year.

Annual treatment capacity	47 dry-tons/year
Annual operating days	250 days/year
Daily treatment capacity	200 kg-dry/day
Daily operating hours	8 hrs/day

#### Properties of Sludge to be Treated

This plant is intended to treat filter sludge (powdered resin) and spent resin (bead resin). The mixture of cation and anion exchange resin is assumed to be in the ratio 2:1 (on a weight basis). The properties of the sludge and resin are shown in TABLE I. The concentration of the slurry fed to the reactor is expected at 10 wt%.

#### Hydrogen Peroxide

As an oxidizing agent, 35% hydrogen peroxide will be used.

#### Operation

A semi-continuous operation mode will be described below:

#### Feeding

After uniformly mixing 10 wt% sludge slurry in the feed tank, the slurry is fed to the reactor and then mixed with water to prepare a 5 wt% slurry.

#### Heating

A catalyst is added to the reactor so that the concentration of catalyst in the slurry will be several hundreds ppm by weight and then the slurry is heated to 95°C.

#### Reaction

Oxidation reaction procedures under an evaporative condition by continuously feeding 10 wt% slurry, 35 wt% H<sub>2</sub>O<sub>2</sub>, and an antifoaming agent to the reactor while heating the reactor with steam.

#### Residual Liquid Reaction

The feeding of slurry in the above process is then terminated and residual organic matters are decomposed with the continued H<sub>2</sub>O<sub>2</sub> supply.

#### Neutralization

To neutralize the residual liquid, 25 wt% caustic soda solution is added.

#### Evaporative Concentration

The decomposed residual liquid is concentrated by heating it with steam until the concentration of Na<sub>2</sub>SO<sub>4</sub> reaches 25 wt%.

## Discharging

The residual liquid is evacuated from the bottom of the reactor and transferred to the solidification system.

## Features

The special features of this process can be summarized as follows:

### Volume Reduction

Since organic materials in the filter sludge and spent ion-exchange resin can be completely decomposed, the volume reducibility is very high. The volume reduction ratio is observed to be from 5 to 50, depending on the nature of the wastes.

### No Pretreatment

Since the reaction develops in water, the filter sludge and spent resin need not be dewatered before feeding to the reaction vessel.

### No Off-gas Problems

Because the reaction occurs in an aqueous phase, negligible radioactivity is transferred into the vapor phase; that is, almost all of the radioactivity is left in the reaction residue. Therefore, there is no necessity for an off gas scrubber.

### Simplicity

The system is rather simple, consisting principally of the reaction vessel.

### Safety

Maximum safety conditions are expected, since the reaction is conducted at mild conditions of 100°C under the atmospheric pressure.

## PHOTO-OXIDATION

The third technology JGC developed is a "Photo-oxidation" process. This particular method is applicable when decomposing a low concentration of organic compounds dissolved in aqueous wastes. Radioactive liquid streams containing methanol, trimethylamine, hydrazine, ammonia, diethylene glycol, organic acids, EDTA, detergents, and so on, can be upgraded by this process and efficiently recycled for use in power plants.

### Basic Principle

The liquid streams containing organics are fed into a reaction vessel, which is equipped with an UV (ultra-violet) lamp. Depending upon the nature of compounds to be treated, adding ozone or hydrogen peroxide to the solution can accelerate the decomposition rate.

The treatment in this Photo-oxidation process can reduce the concentration of organic compounds to a few ppm in a short period.

### Experimental Results

The Photo-oxidation process has been studied and the oxidation rates for various organic substances in an aqueous phase at low concentrations has been evaluated in the JGC Laboratory.

In the nuclear establishments, we frequently encounter  $\text{NH}_4^+$ , diethylene glycohol, TBP, machine oil, detergents, and decontamination agents. Their oxidation rates with a small photo-oxidizer are summarized in TABLE II. For this fundamental experiment, a 10 W lamp emitting 253.7 m $\mu$  wave was used in a 250 ml volume reactor into which ozone or hydrogen peroxide was injected at room temperature.

The result shows the feasibility of photo-oxidation technology to clean organic contaminants out of foul water for its re-use as reactor coolant without any discharge to the environment.

## Features

The special advantages with this process are:

Organic substances can be completely decomposed in water and carbon dioxide.

No secondary wastes are generated.

This process is applicable to almost all organic compounds especially at their lower concentration.

No oxidizing agents remain in the reaction residue.

These three new technologies have advantages specific to their own design process, but have commonly emphasized maximum safety and efficiency which account for their successfulness.

TABLE I. CHEMICAL COMPOSITION OF RESINS

Chemical Composition (wt%)	Powdered and Bead Resins	
	Cation (H-type)	Anion (OH-type)
Carbon	46.8	67.0
Hydrogen	5.4	8.8
Sulfur	15.0	0.0
Nitrogen	0.0	4.3
Oxygen	32.8	19.9
Total	100	100

TABLE II. PHOTO-OXIDATION

Contaminant	Oxidation Agent	Initial Conc'n*	Initial pH	Hours Elapsed for 90% Conv'n
$\text{NH}_4^+$	$\text{O}_3$	11 - 12	10.3 - 12.0	0.9
	$\text{H}_2\text{O}_2$	11 - 12	10.3 - 12.0	1.4
DEG	$\text{H}_2\text{O}_2$	74 - 94	3.0 - 5.9	0.9
	$\text{O}_3 + \text{H}_2\text{O}_2$	74 - 94	3.0 - 5.9	0.5
Citric Acid	$\text{O}_3$	170	3.0	1.5
Oxalic Acid	$\text{O}_3$	100	2.5	0.5
Formic Acid	$\text{O}_3$	133	2.9	0.9
EDTA-2Na	$\text{O}_3$	212	3.0	2.0
Glycolic Acid	$\text{O}_3$	197	3.0	2.0

\* In wt. ppm