JAERI-M
91-199

DEVELOPMENT OF VOLOXIDATION PROCESS FOR

TRITIUM CONTROL IN REPROCESSING

November 1991

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Development of Voloxidation Process for Tritium Control in Reprocessing

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A study on the voloxidation process has been conducted in order to contribute to the development of tritium control process in the head-end of reprocessing. The oxidation and reduction behavior of a slightly irradiated UO_2 fuel and the tritium release behavior from the fuel were obtained in experiments by using a ball mill type reactor (capacity: 2 kg-UO_2/batch).

The results are summarized as follows:

1) The oxidation reaction of the fuel in cladding was described with "a constant flux model".

2) The reduction reaction of the pulverized powder was described with "a core diminishing model".

3) About 60% of the tritium was released with the oxidation of the fuel and additional treatment of sweeping with nitrogen gas for 2 hrs was needed to release more than 99.9% of the tritium. It was found that the reduction step for tritium release was not required after the oxidation.

4) Several technical data were obtained on the stability of rotary seal of voloxidizer and on the confinement of powder fuel by a

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nickel fiber filter.

The results of preliminary system analysis using the experimental data show that the voloxidation process without reduction step is effective to confine tritium into a small part of reprocessing plants.

再処理施設におけるトリチウム管理技術である
ボロキシデーション法の開発

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　再処理前処理工程におけるトリチウム管理技術であるボロキシデーション法に関するプロセス開発を行なった。実験には工学規模のボールミル型反応器（処理量：2kg/バッチ実験）を用い，微照射燃料の酸化及び還元反応速度に及ぼすプロセスパラメーター（酸素濃度，水素濃度，温度，反応器回転数など）の影響及びトリチウムの放出挙動を調べた。その結果以下のことが知られた。
　1)　被覆管付きUO_2ペレット燃料の酸化反応はコンスタントフラックスモデルで表現できる。
　2)　U_3O_8粉末燃料の還元反応は球減少モデルで表現できる。
　3)　燃料中のトリチウムの約60％は燃料の酸化時間で放出されるが，99.9％以上の放出率を得るにはさらに約2時間の窒素ガスによる追い出し操作が必要である。
　4)　また，ボロキシデーション反応器の回転シール部の安定性及びニッケル繊維フィルターによる粉体燃料の閉じ込め性に関する技術データを得た。
　これらの結果をもとに行ったシステム予備評価の結果は，酸化工程のみからなるボロキシデーション法が再処理施設におけるトリチウムの管理技術として有効であることを示している。

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1. INTRODUCTION

Tritium(T) is mainly formed via ternary fission. The thermal fission yield is about 0.012 % and 0.025 % for ^{235}U and ^{239}Pu[1], respectively. Tritium content of spent fuel increases with increasing burnup and with Pu content in LWR fuel. 50 to 60 % of the tritium present in the fuel remains with zircaloy cladding after dissolution of the chopped fuel[2-3]. The residual 40 to 50 % is oxidized and dissolved in dissolver solution in water form (HTO). Only a very minor fraction of hydrogen gas form(HT or T_2) and HTO escapes during the chopping. The distribution of tritium between fuel and cladding seems to be dependent on temperature distribution in a fuel rod which is influenced by linear heating rate of fuel, but to be much less dependent on the average burnup. The zircaloy cladding contains the tritium mainly as hydride(ZrT_x)[3].

The radiotoxic influence of tritium is relatively small to the environment[3]. However, some interests for the collection are shown according to the ALARA principle[4]. Tritium control in reprocessing facility will be more important to reduce radiation exposure of personnel. Several processes for the collection or the confinement have been studied. They are categorized into non-aqueous and aqueous process. Voloxidation[5-6] is one of the former processes and the isotopic separation of tritium combined with tritiated water recycle process[7-8] is one of the latter processes.

A study has been conducted in JAERI to evaluate the process feasibility on both voloxidation and tritiated water recycle processes[9-10]. As for the voloxidation, a two-step process which consists of oxidation and reduction
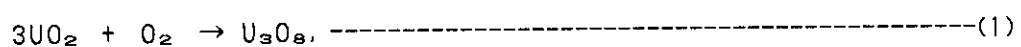
steps of spent fuel was studied to make more complete release of tritium from fuel. Oxidation and reduction behavior of a slightly irradiated UO_2 fuel and tritium release behavior from the fuel were obtained in experiments using a bench scale ball-mill type reactor. Some technical data on process equipments were also gained. Experimental results are outlined in this paper.

2. VOLOXIDATION PROCESS

The outline of the LWR fuel head-end process employing the voloxidation is illustrated in Fig.1. In the voloxidation step, the chopped fuel is oxidized before dissolution to pulverize the fuel and to make release of tritium with other volatile fission products such as iodine, ruthenium, and krypton. Released fission products can be trapped in the off-gas treatment system applied suitable trapping methods[1] and be treated as a small volume of waste. Preliminary studies, however, showed that volatilization of iodine and krypton was insufficient, while tritium was almost quantitatively released during oxidation of the fuel[5]. At present the major purpose of the voloxidation process is to remove tritium from spent fuel before it is dissolved.

Oxidation of spent fuel is carried out at a temperature of 400 - 600 °C in a stream of air or oxygen. The oxidation reaction of UO_2 is represented as the following equation:

$$3UO_2 + O_2 \rightarrow U_3O_8, \text{---(1)}$$

$$\Delta H_{298} = -320.3 \text{ kJ/mol-}U_3O_8 [12].$$

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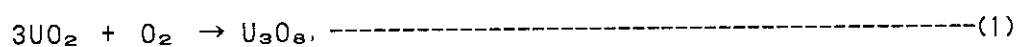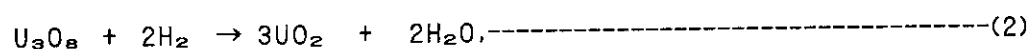
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When UO₂ pellet fuel with cladding is oxidized to U₃O₈, the fuel is transformed to powder form because of change of crystal structure of UO₂. So the oxidation product is mechanically separated from cladding. In the pulverization, tritium dissolved in UO₂ or contained in the lattice crack or pore of the fuel will be released from the fuel.

Reduction of the U₃O₈ formed in the oxidation will additionally promote fuel pulverization and enhance tritium release. The reduction reaction is represented as the following equation:

$$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O, \text{---(2)}$$

$$\Delta H_{298} = -251.7 \text{ kJ/mol-}U_3O_8{}^{12}.$$

In the voloxidation process tritium will be removed from spent fuel before dissolution and effectively collected in the off-gas treatment system in a small volume of a concentrated tritium waste. Additionally, the powder fuel will be separated from cladding before dissolution and be more easily dissolved in a nitric acid solution. These effects will simplify the dissolution operation.

3. EXPERIMENTAL

3.1 Materials

UO₂ pellet containing 750 ppm Li₂O was supplied from Mitsubishi Metal Industries Inc. and used as a simulated spent fuel. This fuel was slightly irradiated in JAERI research reactor: JRR-4, for about 200 seconds in neutron flux of 8×10^{13} n/(cm²·s). The isotopic content of ⁶Li which contributes to

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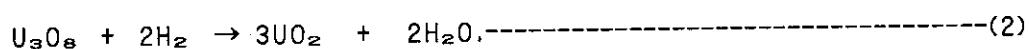
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tritium generation by the reaction: $^6Li(n, \alpha)T$ was 200 ppm. Properties of the fuel are listed in Table 1. The UO_2 pellet is 9.2 mm in diameter and 15.5 mm long. In order to simulate a chopped spent fuel in cladding, two pieces of pellet fuel were inserted in a 50 mm zircaloy-4 tube with pins at the both ends to prevent fall of the fuels.

3.2 Voloxidation Process Equipment

The flow sheet of the experimental equipment called "VULCAN" is shown in Fig.2 and a view of the equipment in hood is shown in Fig.3[13]. The equipment consists of three sections: gas supply system, ball-mill type reactor(voloxidizer), and off-gas treatment system. A view of the voloxidizer is shown in Fig.4. The voloxidizer of which capacity is 2 kg-UO_2 per batch is 200 mm in diameter and 600 mm long. 20 balls of incoloy alloy 800H with diameter of 30 mm ϕ were used to enhance the pulverization effect. A semi-contact gland packing seal system supported by nitrogen gas purge was adopted for the rotary part. A nickel fiber filter(holder size: 69 mm $\phi \times 19$ mmt, fiber thickness: 50μ m ϕ) was installed in the outlet of the voloxidizer in order to prevent the dispersion of powder from the voloxidizer. The off-gas treatment system was composed of several chemical traps: silver impregnated adsorbents for iodine, copper oxides for conversion of tritiated hydrogen gas to tritiated water, and molecular sieves for tritiated water collection. Pipings of the off-gas treatment system were heated at about 60 ·C using a ribbon type electric heater to prevent deposition of tritiated water.

3.3 Analysis

The oxidation behavior of the simulated spent fuel was monitored by measuring oxygen concentrations in both the feed gas and the off-gas. The reduction behavior of the simulated spent fuel oxidized to U_3O_8 in the oxidation step was monitored by measuring the concentration of water vapor in the off-gas. The release behavior of tritium from the fuel was monitored using a gas flow counter. Tritium content in the fuel was measured after dissolving the fuel in a nitric acid solution. After distillation treatment of the nitric acid solution, tritium concentration in the distilled water was measured by a liquid scintillation method.

3.4 Experimental Procedure

(1) Oxidation Step

The simulated fuel of 500 - 2,000 g was charged to the reactor. The reactor was rotated at a rate of 2 - 24 r.p.m. and heated up to a temperature of 350 - 550 °C in a stream of nitrogen gas. After the reactor temperature was reached, a mixture of oxygen and nitrogen gases was supplied as a feed gas to start oxidation reaction of the fuel. The oxygen gas concentration in the feed gas ranged from 10 to 40 % and the flow rate ranged from 0.5 to 2.5 ℓ /min. As a tritium carrier, water vapor with nitrogen gas was supplied from inlet or outlet of the reactor during the experiment. Partial pressure of water vapor in the off-gas was about 2.2×10^4 ppm. After the end of oxidation of the fuel, oxygen gas supply was stopped and only nitrogen gas was supplied. When tritium concentration in the off-gas dropped to a detection limit of the gas flow counter, the heater of reactor was turned off.

(2) Reduction Step

After an oxidation experiment, a reduction experiment was conducted. 500 g of the fuel which was previously oxidized was charged to the reactor. The reactor was rotated in the range of 6 - 12 r.p.m. and heated up to a temperature of 510 - 720 °C in nitrogen gas feed. After the reactor temperature was reached, a mixture of hydrogen and nitrogen gases was supplied as a feed gas to start reduction reaction of the fuel. The hydrogen gas concentration in the feed gas ranged from 1.5 to 17 % and the flow rate ranged from 1.5 to 2.0 ℓ/min

4. RESULTS AND DISCUSSION

4.1 Oxidation Behavior of UO_2 Pellet Fuel

Effects of process parameters such as oxygen concentration in the feed gas, flow rate of the feed gas, reactor temperature, rotation rate, and crushing ball were studied on the oxidation rate of the simulated spent fuel(UO_2 pellet fuel). Changes of oxygen concentrations in both the feed gas and the off-gas, and of fraction of the oxidized fuel with reaction time are shown in Fig.5. This figure shows that oxygen concentration in the off-gas is nearly constant during oxidation reaction indicating that the oxidation rate of the fuel is constant through the oxidation reaction. A view of the oxidation products with cladding is shown in Fig.6. The fuel was pulverized and decladded completely. O/U ratio of the product: 2.62 measured by gravimetric method showed that the UO_2 fuel was almost completely oxidized to U_3O_8.

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Thus the oxidation behavior of the fuel is represented by "a

constant-flux model" as reported by Goode[5]. This model assumes the followings:

(1)Oxidation of the fuel progresses on the both ends in cladding.

(2)Oxidation product of U_3O_8 is pulverized and continuously separated from the unoxidized fuel with rotation of the reactor.

The oxidation reaction of the fuel is represented by the following equations:

$$\omega = - \frac{1}{A} \cdot \frac{W}{t} , \text{------------------------------------(3)}$$

$$t_o = 0 \ ; \quad W = W_o,$$

$$W = W_o - \omega \cdot A \cdot t, \text{------------------------------------(4)}$$

where

$W_o=$ weight of initially charged simulated spent fuel[g]

$W =$ weight of the fuel at time t[g]

$\omega =$ oxidation rate of the fuel[g/(cm$^2 \cdot$hr)]

$A =$ cross-section of the fuel[cm^2]

$t =$ reaction time[hr].

Dividing both sides of Eq.(3) by W_o, the following equation is obtained:

$$1 - \frac{W}{W_o} = \frac{\omega}{W_o} \cdot A \cdot t. \text{------------------------------------(5)}$$

The left term in Eq.(5) is fraction of the oxidized fuel. The oxidation rate: ω is calculated from the slope of the curve in Fig.5. The effects of several reaction parameters on the oxidation rate of the fuel are described using the oxidation rate: ω in the following sections.

(1) Effect of Reactor Temperature

The oxidation behavior of the fuel was studied mainly in the temperature range of 350 - 550 °C. The relation between the oxidation rate and reactor temperature is shown in Fig.7. The curve has a gentle peak at about 450 °C. The oxidation rate increases with reactor temperature up to 450 °C. However, above 450 °C the oxidation rate decreases gradually. From these results, it is found that the optimum reactor temperature is about 450 °C.

It was considered that at a temperature above 450 °C the generated reaction heat exceeded the heat removal transfer rate of the voloxidizer with local sintering of the fuel as a consequence.

(2) Effect of Oxygen Concentration in Feed Gas

It is expected by Eq.(1) that the oxidation rate of the fuel depends on the oxygen concentration: C_o in the feed gas. The oxidation rate is actually proportional to the oxygen concentration in the feed gas in the range of 0 - 40 % as shown in Fig.8. The relationship between the oxidation rate of the fuel and the oxygen concentration is represented as follows:

$$\omega = k_1 \cdot C_o^{1.2}, \text{\textemdash\textemdash\textemdash\textemdash\textemdash\textemdash}(6)$$

where k_1 = rate constant[$g/(cm^2 \cdot hr \cdot \%^{1 \cdot 2})$].

At the flow rates of the feed gas of 0.5 and 1.5 ℓ/min, k_1 are 0.15 and 0.088 [$g/(cm^2 \cdot hr \cdot \%^{1 \cdot 2})$], respectively. The higher oxygen concentration in the feed gas, the higher oxidation rate is obtained. However, it was concluded that air was more convenient for the process simplicity.

(3) Effect of Flow Rate

The effect of flow rate of the feed gas on the oxidation rate of the fuel is shown in Fig.9. The oxidation rate of the fuel was increased linearly with the flow rate of air from 0.5 to 1.5 ℓ/min. However, at larger flow rate than 1.5 ℓ/min the oxidation rate was not increased due to the occurrence of sintering. We concluded that the flow rate of 1.5 ℓ/min is appropriate for the oxidation at 480 °C and 2 r.p.m.. At the flow rate, the oxidation rate was about 3.0 $g/(cm^2 \cdot hr)$.

(4) Effect of Rotation Rate of Reactor

The rotation rate of reactor is of the factors influence on both oxygen gas diffusion and heat transfer in the reactor. The effect of rotation rate of reactor on the oxidation rate of the fuel is shown in Fig.10. The oxidation rate is almost constant in the range of 2 to 24 r.p.m.. These data indicate that at an even low rotation rate such as 2 r.p.m. the fuel is sufficiently agitated so that the fuel was oxidized to U_3O_8.

(5) Effect of Crushing Balls

The effect of crushing balls on the oxidation rate of the fuel was

studied. The oxidation rate of the fuel was 3.1 g/(cm²·hr) without crushing balls but increased to 4.0 g/(cm²·hr) with 20 crushing balls of 30 mm in diameter. The effect of the crushing ball was not so large. The fuel was effectively crushed by cladding and the oxidation product was separated. And significant deformation of cladding by crushing balls was observed depending on the amount of balls. The oxidation should be conducted without balls.

(6) Effect of Amount of Charged Fuel

The upper limit of the charged fuel in the reactor is one of the important parameter to design the reactor with regards to a capacity, heat transfer and gas mixing. Effect of the amount of charged fuel in the reactor on the oxidation rate was studied using 2.0 kg in stead of 500 g under the same conditions. The experimental result showed that the oxidation rate was increased by 45 % at the condition of more than twice of a stoichiometric flow rate of oxygen gas. It is considered that increase of amount of the fuel bring the same effect as crushing balls in an adequate agitation.

(7) Effect of Fuel Density

The effect of fuel density on the oxidation rate was shown in Fig.11 in the range of fuel density from 74 to 95.5 % of theoretical UO_2 density. In each oxygen concentration of 10, 15, and 20 % in the feed gas, the oxidation rate of the fuel was remarkably decreased with increase of the fuel density. The density of spent fuel generally decreases with burnup because of the swelling. The oxidation rate of major parts of high burnup fuel will be much

higher than that of a slightly irradiated UO_2 fuel. The oxidation rate of

irradiated UO_2 fuel(28,000 MWD/t-U) in Point Beach Reactor was reported to be

5.9 $g/(cm^2 \cdot hr)$[14].

On the basis of these experimental results, optimum conditions which

provide maximum oxidation rate are summarized in Table 2. The density of

spent fuel which has reached a burnup of 45,000 MWD/t-U is estimated to be

about 85 % on the basis of the data reported by Berman[15]. From the Fig.11,

the oxidation rate of the spent fuel is estimated to be about 7 $g/(cm^2 \cdot hr)$ at

the conditions.

4.2 Reduction Behavior of U_3O_8 Powder Fuel

Figure *12* shows that production rate of water vapor in the off-gas and

hydrogen gas pressure in both the feed gas and the off-gas in the reduction

of previously oxidized fuel. The fraction of reduced fuel: $1 - F^{1/3}$ as a

function of time ratio: t/t_0 is shown in Fig. *13*. The fraction increases roughly

in proportion to the time ratio with a slope of 0.95. This means that the

reduction of the fuel is generally expressed by a core diminishing model

controlled by a chemical reaction defined as following equations:

$$\frac{W}{W_0} = (1 - \frac{Z \cdot t}{\rho \cdot r_0})^3, \text{---(7)}$$

$$t_0 = \frac{\rho \cdot r_0}{Z}, \text{---(8)}$$

$$F = \frac{W}{W_0}, \text{---(9)}$$

$$\frac{t}{t_o} = 1 - F^{1/3}, \text{--(10)}$$

where   Z = reduction rate of U_3O_8 powder fuel[g/(cm²·hr)]

   t_o = time for complete reduction of the fuel[hr]

   ρ = density of the fuel[g/cm²]

   r_o = radius of the fuel[cm].

The reduction rate: Z is known to be in proportion to the concentration

of hydrogen gas and to be described as a following equation[16]:

$$Z = k_2 \cdot C_{H2}^N \cdot exp(- \frac{E}{R \cdot Tm}), \text{-------------------------------(11)}$$

where k_2 = rate constant[hr⁻¹·%⁻ᴺ]

   C_{H2} = concentration of hydrogen gas[%]

   N = concentration dependence exponent[−]

   E = activation energy[kJ/mol]

   R = gas constant[kJ/(K·mol)]

   Tm = temperature[°K].

The effect of hydrogen gas concentration on the reduction rate:Z is

shown in Fig. 14 at temperatures of 510, 560 and 720 °C. At each temperature,

an approximately linear relationship existed between the concentration of

hydrogen gas and the reduction rate of the fuel on log-log plot. The slope

of the each line was about 0.9. The experimental data gave the activation

energy of the reduction of the fuel of 4.5 kJ/mol. On the basis of the

experimental data, the following reduction rate equation was obtained:

$$Z = 1.2 \times 10^2 \cdot C_H{}^{0.9} \cdot \exp \left(- \frac{9.500}{T_m} \right) \text{ ------------(12)}$$

4.3 Tritium Release Behavior

Tritium release behavior was studied in both the oxidation and reduction steps. Tritium in the simulated spent fuel was almost completely released in the oxidation step; therefore only the oxidation step is described.

By heating the voloxidizer in nitrogen gas atmosphere tritium release from the fuel started at about 150°C. The amount of tritium released during this pretreatment, however, was very small, less than 0.1 % of the total amount of tritium initially produced in the fuel.

Changes of tritium concentration in the off-gas and of the oxidation rate of the fuel with reaction time in run No.T-A are shown in Fig. 15. In this run water vapor as a tritium carrier was added from the inlet of the voloxidizer to prevent the deposition of released tritium on the process line or the adsorption on the voloxidizer wall. The water vapor pressure was about 2.2×10^4 ppm in the off-gas.

At the beginning of the oxidation, the oxidation rate of the fuel rapidly increased to 2.8 g/(cm²·hr), while the tritium concentration in the off-gas gradually increased to about 2 Bq/cm³. About 60 % of the tritium was released in the oxidation of the fuel which was continued for about 6 hrs. After the termination of oxygen consumption, the feed gas was switched to nitrogen. In nitrogen gas atmosphere, however, tritium release still continued. The sweeping time of about 2 hrs was needed to make complete release of the tritium deposited on the process line and/or adsorbed on the voloxidizer

wall. More than 99.9 % of tritium was released by this treatment.

In order to investigate the effect of water vapor on the tritium release behavior, water vapor was added from outlet of the reactor in run No. T-B. Water vapor pressure was controlled to be about 2.2×10^4 ppm in the off-gas in the run. Fractions of the released tritium and the oxidized fuel in both the run No. T-A and the run No. T-B are shown in Fig.16 and Fig.17, respectively. The concentrations of oxygen gas in the feed gas were 20 % in run No.T-A and 35 % in run No. T-B, respectively. The oxidation rate of the fuel in the run No.T-B is much higher than that in the run No. T-A. In run No. T-B, most of the tritium was released with oxidation of the fuel as that in the run No. T-A. But there is significant difference between two runs as to tritium release rate at both the beginning and the ending. In run No. T-A, in which the oxidation rate is much lower than that in run No. T-B, the tritium release began at a higher rate at the beginning and ended within a shorter time after the end of the oxidation. In run No. T-A, more than 99.9 % of the tritium was released in 2 hrs after the end of the oxidation of the fuel. While, in run No. T-B, about 4 hrs after the end of the oxidation was needed to release more than 99.9 % of the tritium. In both runs, high enough tritium release ratios of more than 99.9 % were obtained in the oxidation step of about 10 hrs.

Considering the difference in tritium release behavior between two runs, it is found that some parts of tritium released from the fuel might deposit on the process line and/or the adsorption on the voloxidizer wall. The deposition of tritium may be responsible for the time lag of the tritium release to the oxidation of the fuel.

The tritium sweeping time of about 2 hrs was needed to make complete release of the tritium. By this additional treatment more than 99.9 % of tritium was released.

The tritium release fraction in the reduction step was found to be very small. As shown in the above oxidation experiment, effective tritium release was obtained. Therefore, we conclude that the voloxidation process consisting of only oxidation step will provide effective tritium release and simplify the process system.

4.4 Equipment Design Considerations

The handling of radioactive powders under a high radiation condition is one of the technical problems to be solved in the voloxidation process development. A broad technical expertise related to the equipment design was built up during the experimental work[13]. The feasibility tests of a nickel fiber filter to confine fuel powders and of the rotary seal system of the voloxidizer were mainly investigated in the present study.

The nickel fiber filter was installed in the outlet of the voloxidizer. The particle size distribution of the oxidation and reduction products in the voloxidizer are shown in Fig.18. The average particle diameter of the oxidation product(U_3O_8 powder) in the voloxidizer was 4.83 μm, and that of the reduction product(UO_2 powder) was 3.85 μm. After the oxidation and reduction experiments, about 95 – 99 wt% of the total amount of the initially charged fuel remained in the voloxidizer and 1 – 5 wt% of the fuel was trapped in the filter. Only 0.1 wt% was transferred to the down stream. These data show that the nickel fiber filter effectively confined the powders

within the voloxidizer furnace.

As to the rotary seal system, figure 19 shows a semi-contact gland packing equipped with a nitrogen gas purge system. Requirements of rotary seal system are to prevent the outer leakage of the process gas containing radioactive powders and to make the inner leak rate of purge gas as low as possible. It was confirmed that the inner leak rate of purge gas was represented by the following equation presented by Tsukizoe[17], as shown in Fig.20.

$$q = f \cdot \frac{\pi \cdot d_m \cdot \varepsilon^3}{24 \cdot \eta \cdot P_o \cdot L} \cdot (P_H^2 - P_L^2), \text{------------------------(13)}$$

q = inner leak rate of purge gas[ℓ/min]

f = correction factor: 9×10^5[-]

d_m = diameter of the cylindrical clearance[m]

ε = clearance at the gland packing[m]

η = coefficient of viscosity of purge gas[kg·sec/m²]

P_o = atmospheric pressure[kg/cm²]

L = length of the cylindrical clearance[m]

P_H = outer pressure(purge gas pressure)[kg/cm²]

P_L = inner pressure[kg/cm²]

In this equation, inner leak rate of purge gas is proportional to a function of a differential pressure:$P_H^2 - P_L^2$ kg²/cm⁴. At P_H=1.2 kg/cm² and P_L=1.1 kg/cm², the inner leak rate of purge gas at the inlet of the voloxidizer was about 0.1 ℓ/min, which was less than 10 % of the flow rate of the feed gas. It was found that the leak rate could be controlled by

adjusting both the purge gas and the feed gas pressures through the experiment. The rotary seal system kept its favorable gas seal function for more than 600 hrs of the total operation time.

Release fractions of volatile and semi-volatile fission products such as iodine, ruthenium, and cesium were measured under voloxidation conditions. At a temperature of 500 to 700 °C in a small scale experiment, 18 to 38 % of iodine was released in an oxygen stream but scarcely released in a nitrogen and/or hydrogen gas stream[18]. Less than 11 % of ruthenium and less than 4.3 % of cesium were released in an oxygen stream. The released fission products were deposited on the cooler surfaces of the off-gas line. Some means to control the deposition are needed.

Further technical development should be conducted to establish the voloxidation technology. Major step in this development are:

1)Proving the process with actual spent fuel.

2)Scale up of voloxidizer.

3)Process development of the off-gas treatment system.

4)Development of remote maintenance and radioactive powder handling.

4.5 Preliminary System Analysis

On the basis of the experimental results, preliminary system analysis was conducted of the head-end voloxidation process. The capacity of the plant assumed is 5 tons of spent fuel per day.

(1)Flowsheet concept with major material flow

Figure 21 shows the conceptual flowsheet and the material flow including

tritium balance. The process consists essentially of oxidation of chopped fuel(UO_2) to U_3O_8 in a stream of air before dissolution. Daily input of tritium in the plant of 5 tons of spent fuel per day is 7.4×10^{13} Bq. 50 % of the tritium is assumed to be present in the fuel and the rest exists in the cladding. In the voloxidation step, 99 % of tritium in the fuel is assumed to be released to the off-gas system in HTO or HT form and is trapped by chemical traps. The rest of the tritium in the fuel is dissolved in the fuel solution and in the hulls.

(2)Voloxidizer sizing

Two continuous voloxidizer are considered to treat the amount of fuel in the plant. They are operated in parallel. The diameter of voloxidizer is chosen by criticality safety considerations. Assumed diameter is 0.25 m based on the minimum critical diameter for 4 % enriched ^{235}U fresh fuel[19]. Length of voloxidizer is determined, based on the following conditions.

1)Residence time of the fuel in the reactor for oxidation reaction and tritium sweeping is 4 hrs,

2)Dimension of chopped fuel is 9.2 mm in diameter and 30 mm long,

3)Fuel inventory in the voloxidizer is 25 %,

4)Balls to crush fuel are not added.

The required length of each voloxidizer is calculated to be 10 m.

(3)Off-gas treatment system

The key item to be considered is the order of trapping of related semivolatile and volatile fission products. Semi-volatile fission products

e.g. ruthenium, are collected immediately after the voloxidizer. Volatile fission products e.g. iodine, are collected before tritium converter in order to prevent the dispersion of their fission products. Tritium in hydrogen gas form is converted to water vapor by copper oxides. Tritiated water vapor in off-gas is adsorbed by molecular sieves. This water can be recovered.

(4)Effect on dissolution step

Rapid fuel dissolution and simple dissolver operation due to absence of hulls will facilitate the introduction of a continuous dissolver concept more easily. In some cases voloxidation treatment may make it difficult to dissolve the Pu rich fuel. Stone, et al. reported that the weight of insoluble residues was increased in the dissolution of voloxidized fuel[20]. An additional step of hull leaching will be required to make effective fuel recovery and improve the waste management.

(5)Tritium waste generation

Amount of tritium collected in the off-gas treatment system is about 3.7×10^{13} Bq/day and that of tritium in hull is about 3.7×10^{13} Bq/day. Small volume and high concentration of tritium waste recovered from the off-gas treatment system will facilitate adaptation of various advanced fixation compounds such as metal hydrides and inorganic hydrates.

5. CONCLUSION

A study on the voloxidation process has been conducted in order to

e.g. ruthenium, are collected immediately after the voloxidizer. Volatile fission products e.g. iodine, are collected before tritium converter in order to prevent the dispersion of their fission products. Tritium in hydrogen gas form is converted to water vapor by copper oxides. Tritiated water vapor in off-gas is adsorbed by molecular sieves. This water can be recovered.

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5. CONCLUSION

A study on the voloxidation process has been conducted in order to

contribute to the development of tritium control process in the head-end of reprocessing. Experiments using a ball mill type voloxidizer(capacity: 2 kg-UO_2/batch) were conducted in order to obtain process data on oxidation and reduction behavior of a slightly irradiated UO_2 fuel and on tritium release behavior from the fuel. The results are summarized as follows:

1)The UO_2 pellet fuel was oxidized and pulverized to U_3O_8 powder without sintering of the fuel in the mixture of oxygen and nitrogen gases at about 450 °C. The oxidation reaction of the UO_2 fuel with a zircaloy cladding was described with "a constant flux model".

2)The U_3O_8 powder fuel which was produced by oxidation of the UO_2 fuel was reduced to UO_2 powder within 2 hrs in the mixture of hydrogen and nitrogen gases at 720 °C. The reduction rate of the fuel was described with "a core diminishing model".

3)Experimental data showed that about 60 % of the tritium was released with the oxidation of the fuel and that more than 99.9 % was released by additional treatment of sweeping for 2 hrs. It was found that the reduction step for tritium release was not required after the oxidation step.

4)Several technical data were obtained on the stability of rotary seal(gland packing system) of voloxidizer and on the confinement of powder fuel by a nickel fiber filter. Major technical problems to be solved are emphasized.

The results of preliminary system analysis using the experimental data show that the voloxidation process without reduction step will open the possibility of effective tritium confinement and immobilization. However, several technical problems such as a scale up of large voloxidizer must be

solved before the realization.

ACKNOWLEDGMENTS

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Table 1 Properties of simulated spent fuel.

FUEL TYPE	PWR FUEL
DIMENSION	9.2 mmϕ $\times$ 15.5 mmL WITH ZIRCALOY-4 CLADDING
FUEL DENSITY	74 - 95.5 % OF THEORETICAL UO_2 DENSITY
Li_2O CONTENT	750 ppm (^{6}Li:200 ppm)
IRRADIATION	8×10^3 n/(cm^2·s)$\times$200 s
TRITIUM CONTENT	1.5 $\times$ 10^6 Bq/g-UO_2

Table 2 Optimum oxidation conditions.

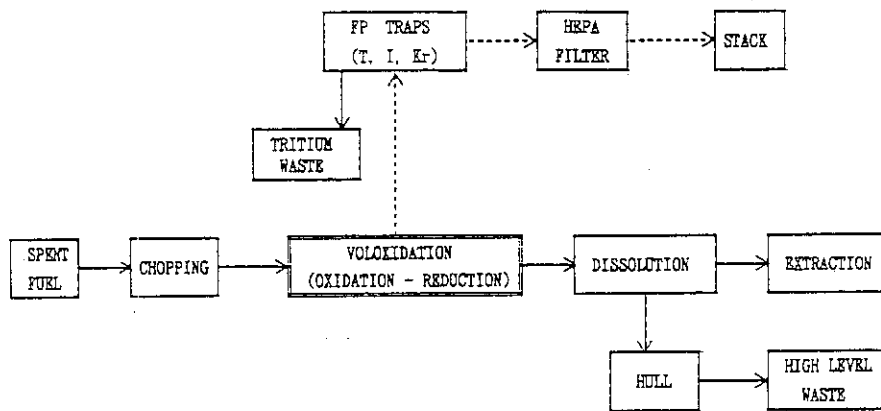| PARAMETERS	CONDITIONS
FEED GAS	AIR
FEED RATE OF OXYGEN GAS IN AIR	TWICE AMOUNT REQUIRED STOICHIOMETRICALLY
REACTOR TEMPERATURE	450 °C
ROTATION RATE	2 r.p.m
EXPECTED OXIDATION RATE: ω OF SPENT FUEL	7 g/(cm^2·hr)

```
┌──────────────┐       ┌────────┐         ┌───────┐
│  FP  TRAPS   │┄┄┄┄➤  │ HEPA   │┄┄┄┄┄┄➤ │ STACK │
│  (T, I, Kr)  │       │ FILTER │         │       │
└──────────────┘       └────────┘         └───────┘
      ▲         ▲
      │         ┊
┌──────────┐    ┊
│ TRITION  │    ┊
│  WASTE   │    ┊
└──────────┘    ┊
                ┊
┌────────┐   ┌──────────┐   ┌─────────────────────┐   ┌─────────────┐   ┌────────────┐
│ SPENT  │➤  │ CHOPPING │➤  │    VOLOXIDATION     │➤  │ DISSOLUTION │➤  │ EXTRACTION │
│ FUEL   │   │          │   │(OXIDATION - REDUCTION)│  │             │   │            │
└────────┘   └──────────┘   └─────────────────────┘   └─────────────┘   └────────────┘
                                                            │
                                                            ▼
                                                       ┌───────┐        ┌────────────┐
                                                       │ HULL  │➤       │ HIGH LEVEL │
                                                       │       │        │   WASTE    │
                                                       └───────┘        └────────────┘
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Fig. 1 Outline of the process employing voloxidation in LWR
fuel head-end.
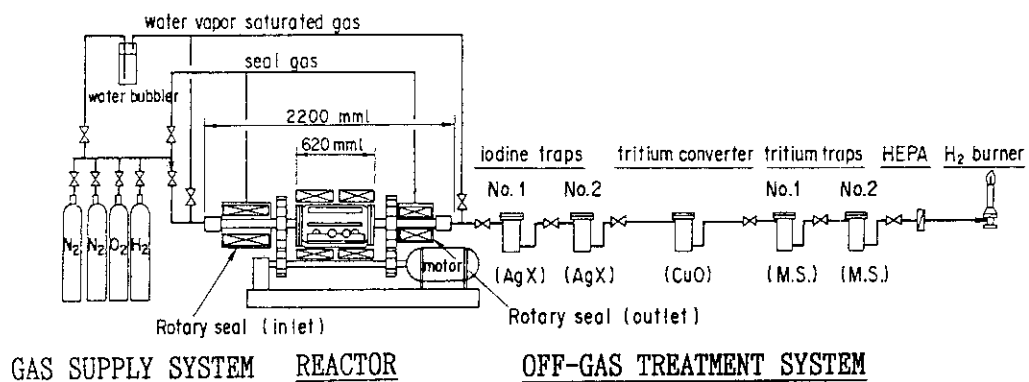
Fig. 2 Flowsheet of the voloxidation process equipment (VULCAN).
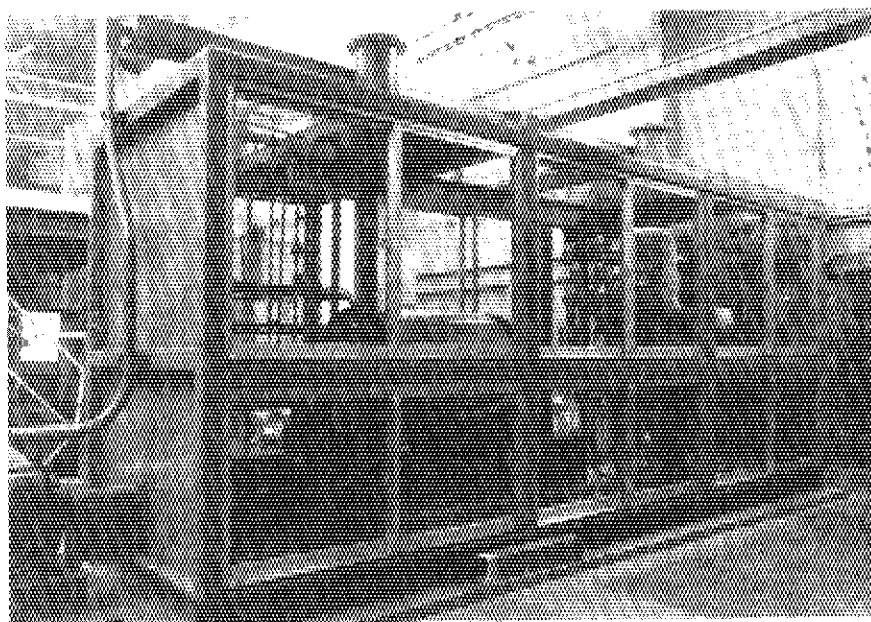
Fig. 3 View of the voloxidation process equipment in hood.
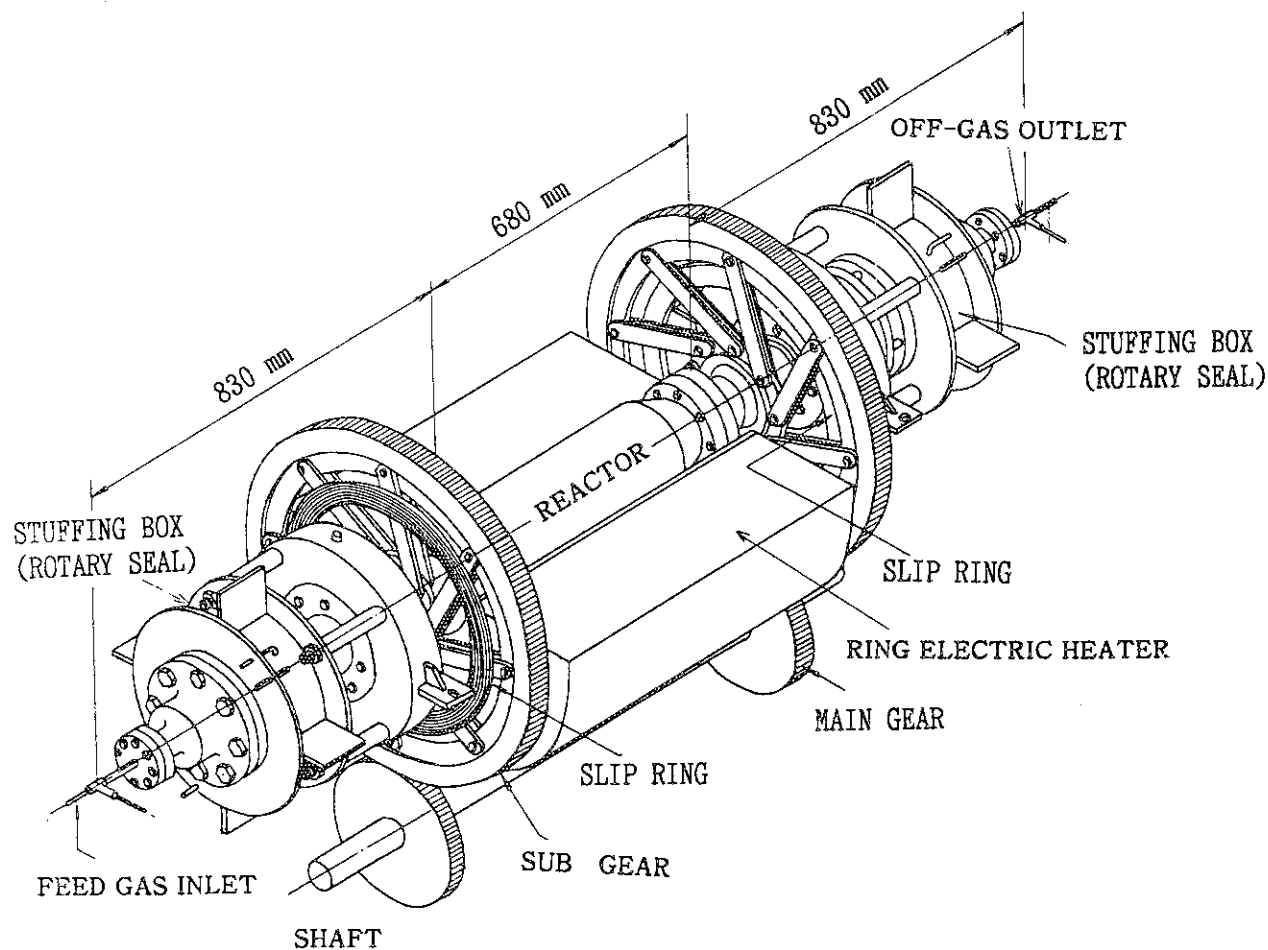
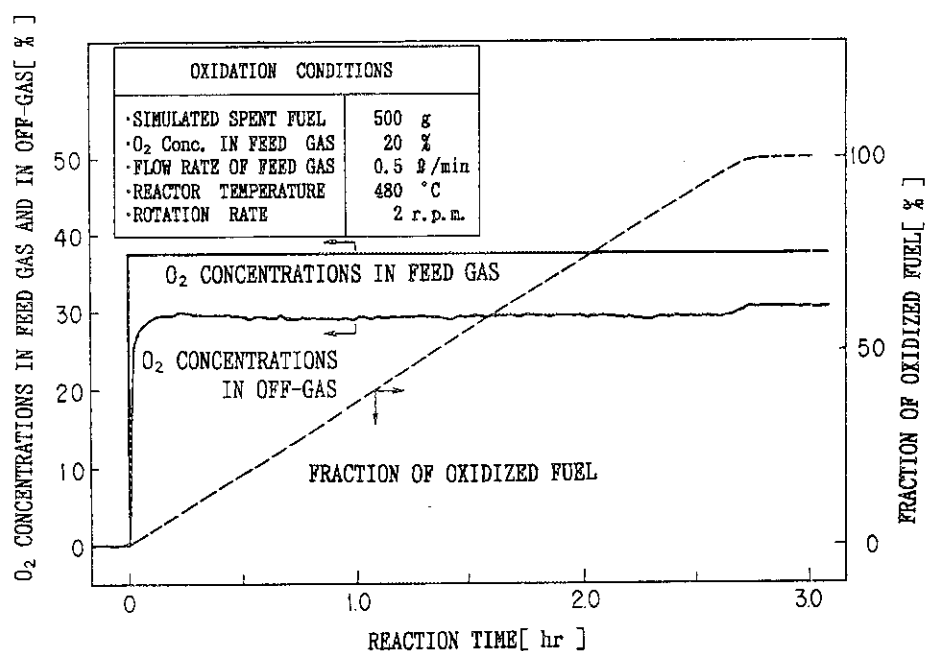
Fig. 4 View of the voloxidizer (VULCAN).

OXIDATION CONDITIONS

·SIMULATED SPENT FUEL	500	g
·O_2 Conc. IN FEED GAS	20	%
·FLOW RATE OF FEED GAS	0.5	ℓ/min
·REACTOR TEMPERATURE	480	°C
·ROTATION RATE	2	r.p.m.

O_2 CONCENTRATIONS IN FEED GAS

O_2 CONCENTRATIONS IN OFF-GAS

FRACTION OF OXIDIZED FUEL

O_2 CONCENTRATIONS IN FEED GAS AND IN OFF-GAS [%]

FRACTION OF OXIDIZED FUEL [%]

REACTION TIME [hr]

Fig. 5 Changes of oxygen concentrations in both feed gas and off-gas
and of fraction of oxidized fuel with reaction time.
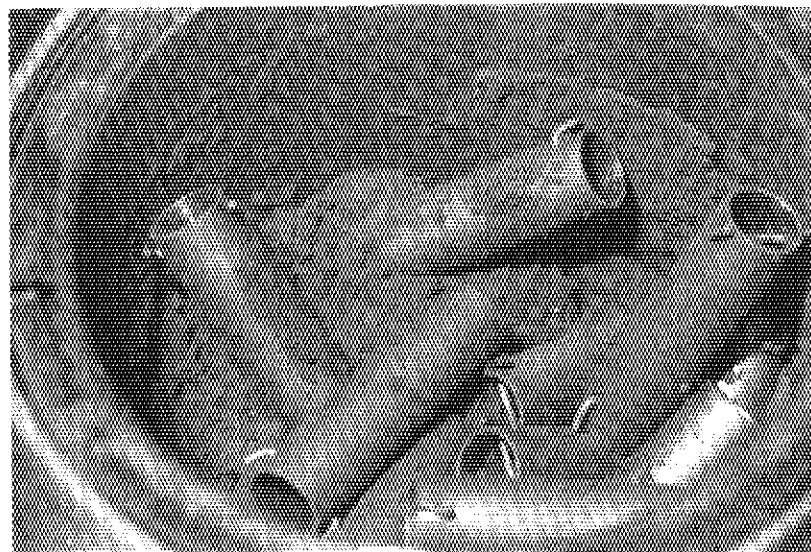
Fig. 6 Oxidation product (U_3O_8 powder) and cladding.
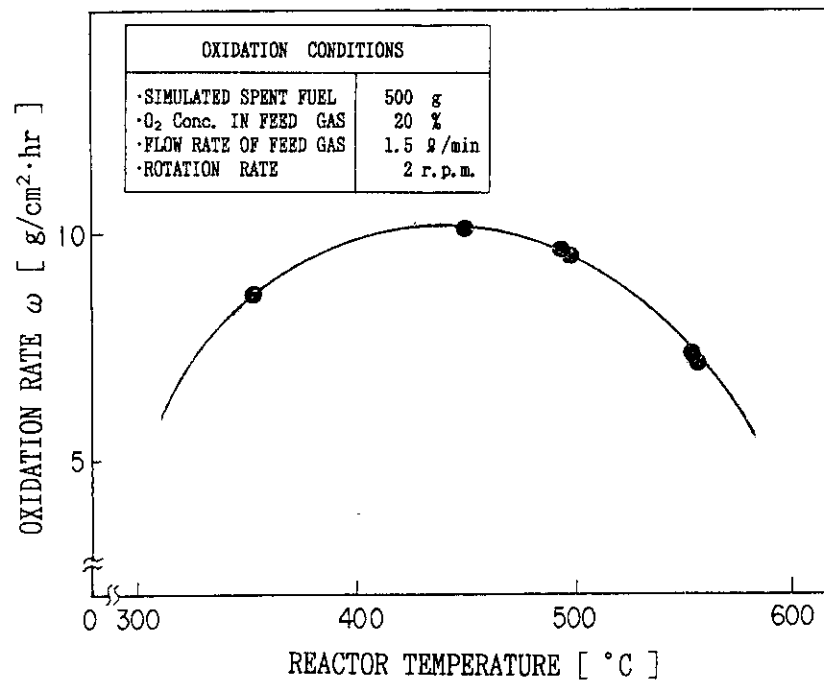
Fig. 7 Effect of reactor temperature on the oxidation rate of the fuel.
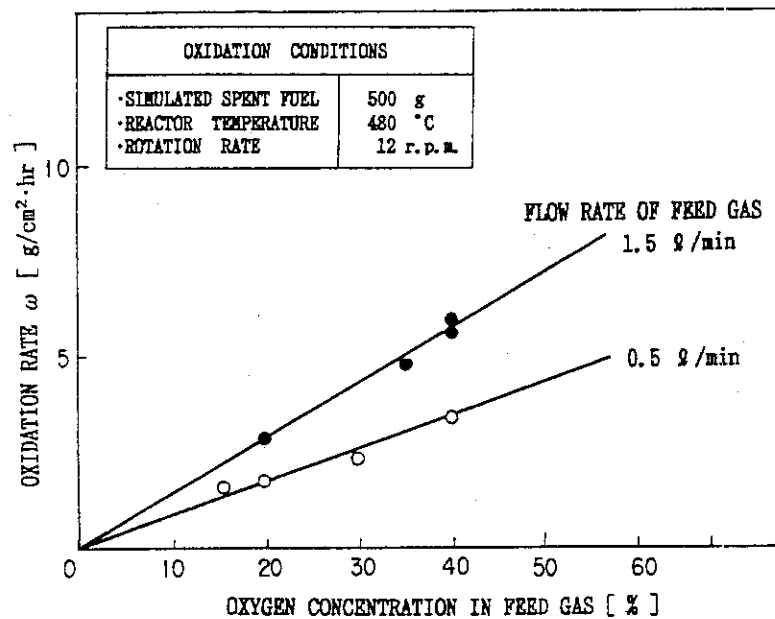
Fig. 8 Effect of oxygen concentration in feed gas on the oxidation rate
of simulated spent fuel.

OXIDATION CONDITIONS	
·SIMULATED SPENT FUEL	500 g
·O$_2$ Conc. IN FEED GAS	20 %
·REACTOR TEMPERATURE	480 °C
·ROTATION RATE	12 r.p.m.

OXIDATION RATE ω [g/cm^2·hr]

FLOW RATE OF FEED GAS [ℓ/min]
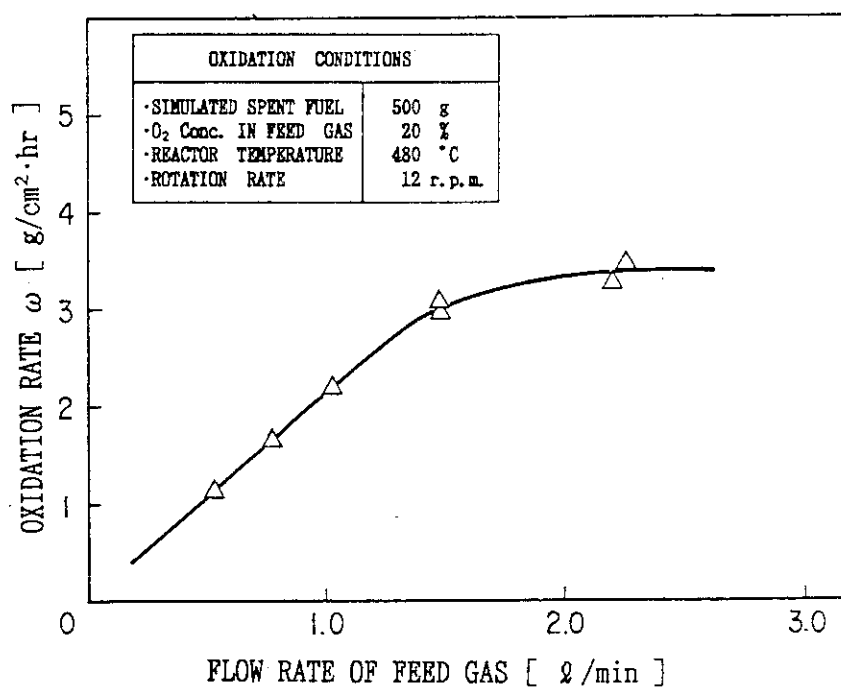
Fig. 9 Effect of flow rate of feed gas on the oxidation rate
of simulated spent fuel.

OXIDATION CONDITIONS	
·SIMULATED SPENT FUEL	500 g
·O$_2$ Conc. IN FEED GAS	20 %
·FLOW RATE OF FEED GAS	1.5 ℓ/min
·REACTOR TEMPERATURE	480 °C

OXIDATION RATE ω [g/cm^2·hr]

ROTATION RATE OF THE REACTOR [r.p.m.]
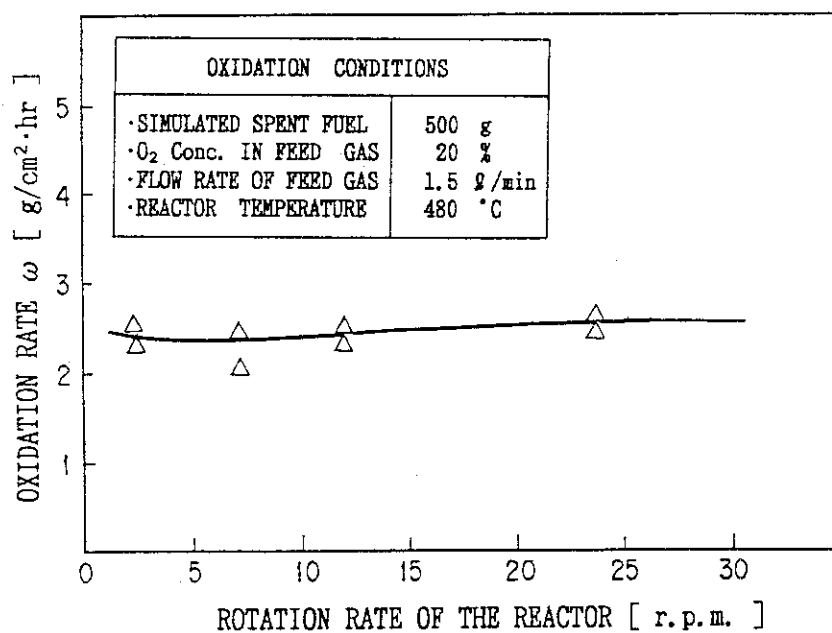
Fig. 10 Effect of rotation rate of the reactor on the oxidation rate
of simulated spent fuel.
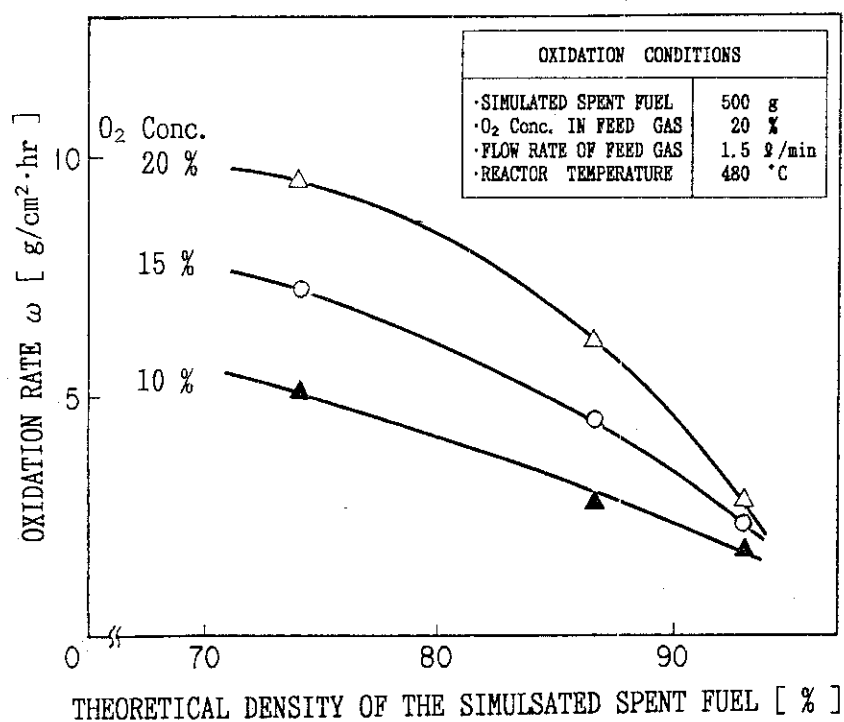
Fig. 11   Effect of theoretical density of simulated spent fuel
          on the oxidation rate of the fuel.
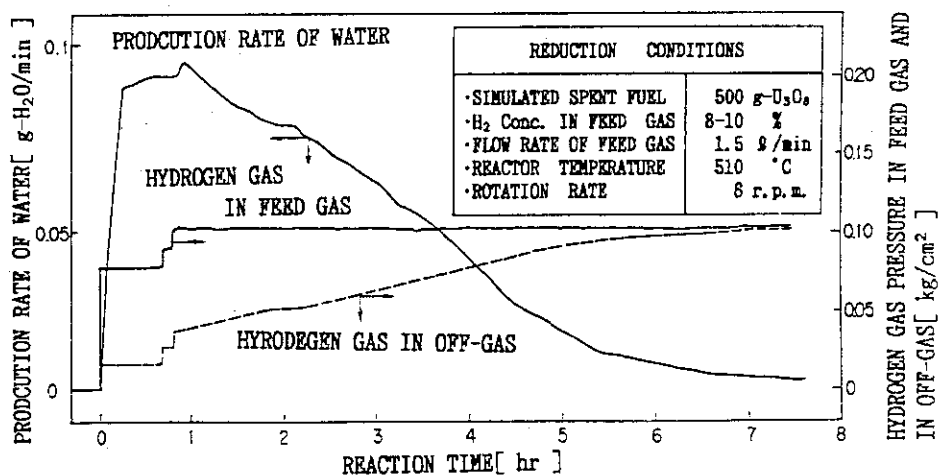
Fig. 12   Production rate of water by reduction of U_3O_8 fuel and
          changes of hydrogen gas pressure in both feed gas and
          off-gas with reaction time.

Fig. 14 Effect of concentration of hydrogen gas
in feed gas on the reduction rate of
U_3O_8 fuel.

Fig. 13 Fraction change of reduced U_3O_8
fuel:$1-F^{1/3}$ with time ratio:t/t_0.
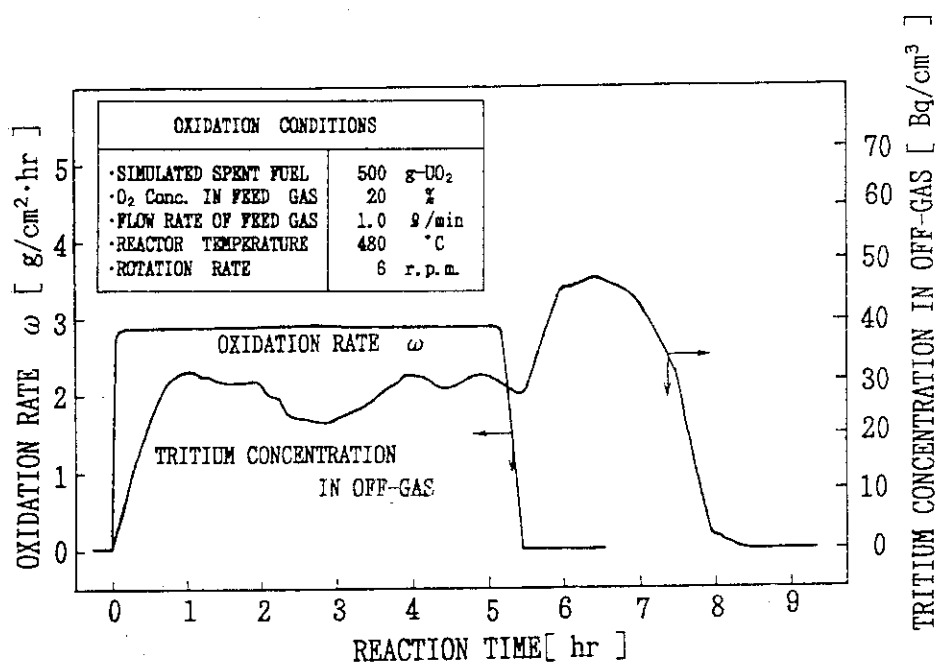
Fig. 15 Oxidation rate of UO$_2$ fuel and tritium concentration in off-gas with reaction time.
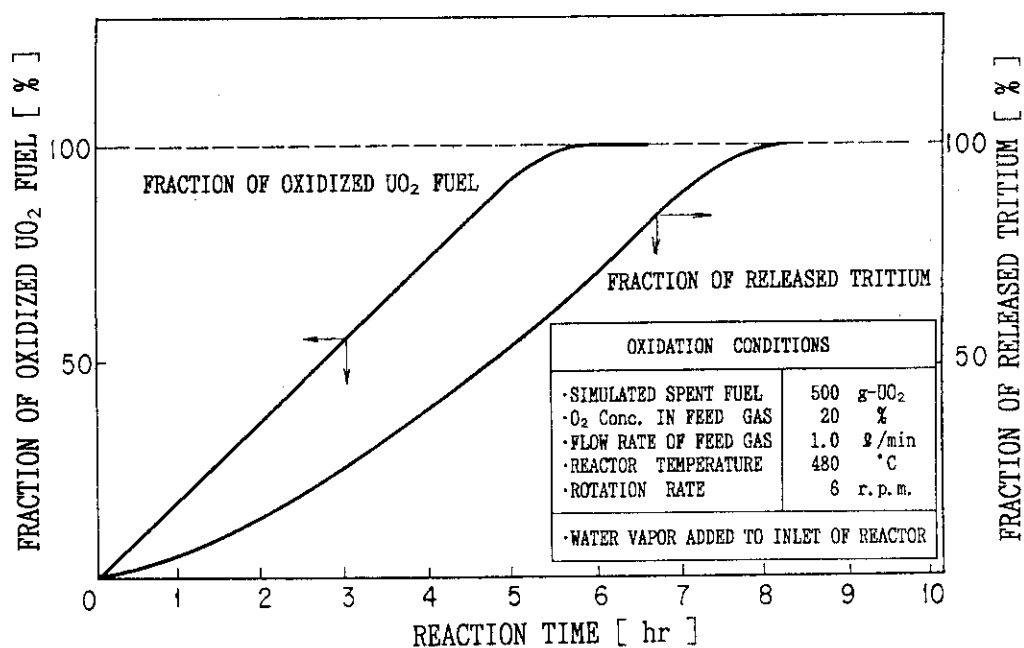
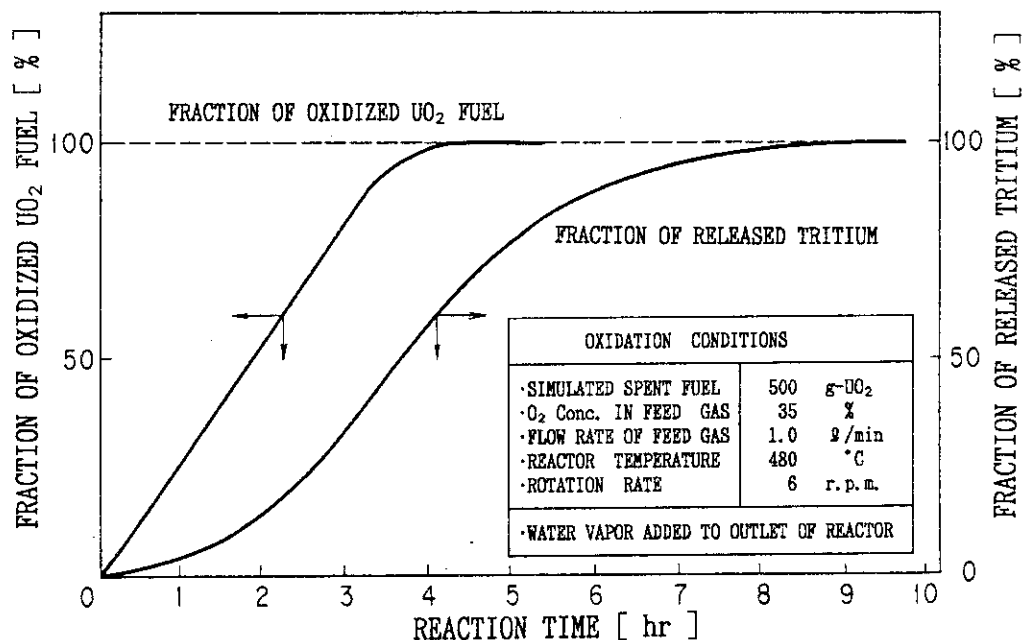Fig. 16 Fraction changes of oxidized UO$_2$ fuel and released tritium with reaction time in run No. T-A.

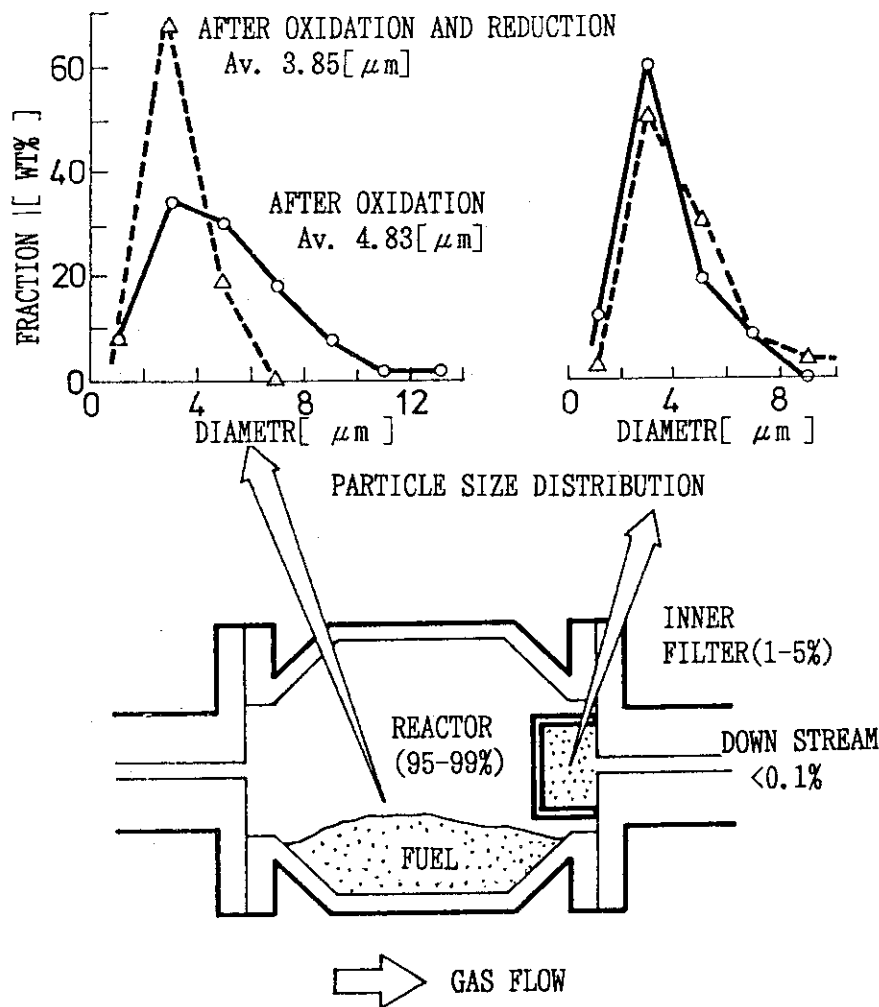**Fig. 17** Fraction changes of oxidized UO$_2$ fuel and released tritium with reaction time in run No. T-B.

Fig. 18 Particle size distribution of oxidation and reduction products and powder distribution in the equipment.
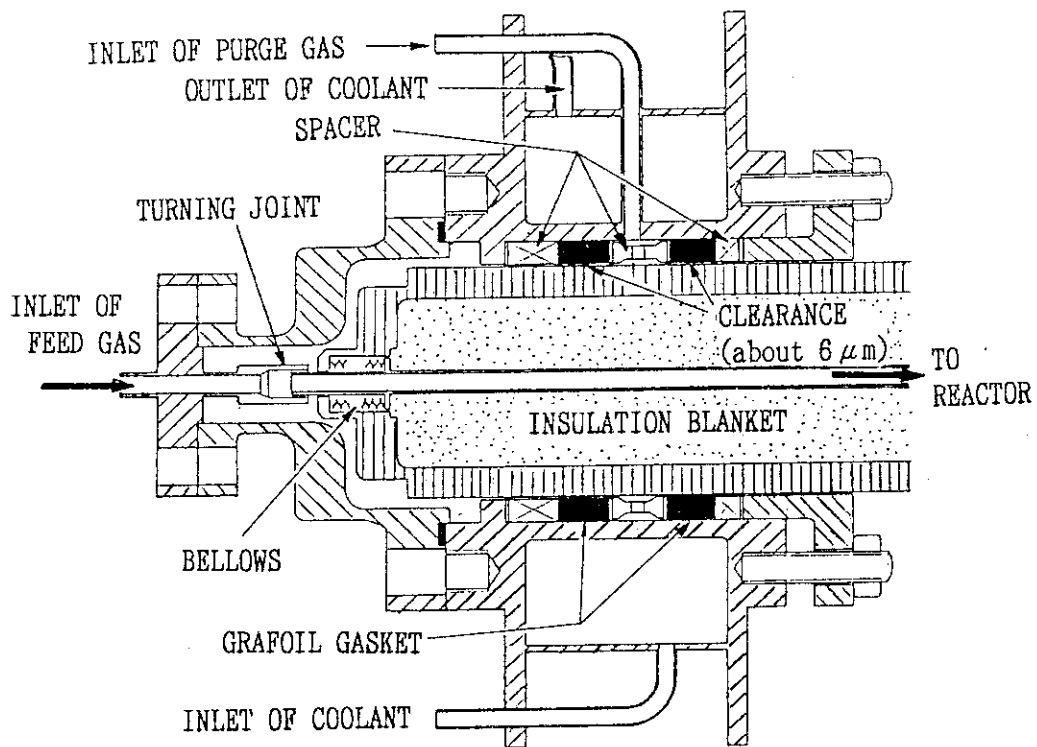
Fig. 19 Rotary seal system.

$$q = f \; \frac{\pi \cdot d_m \cdot \varepsilon^3}{24 \cdot \eta \cdot P_0 \cdot L} \; (P_H{}^2 - P_L{}^2)$$

$$f = 9 \times 10^5$$

INNER LEAK RATE OF PURGE GAS   q [ℓ/min]

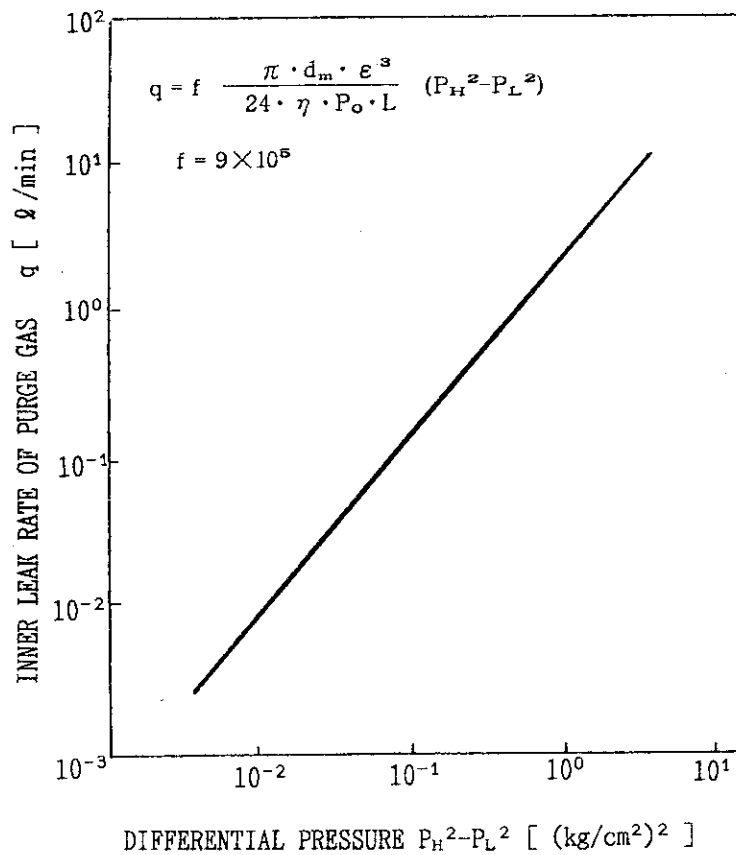DIFFERENTIAL PRESSURE $P_H{}^2 - P_L{}^2$ [(kg/cm²)²]

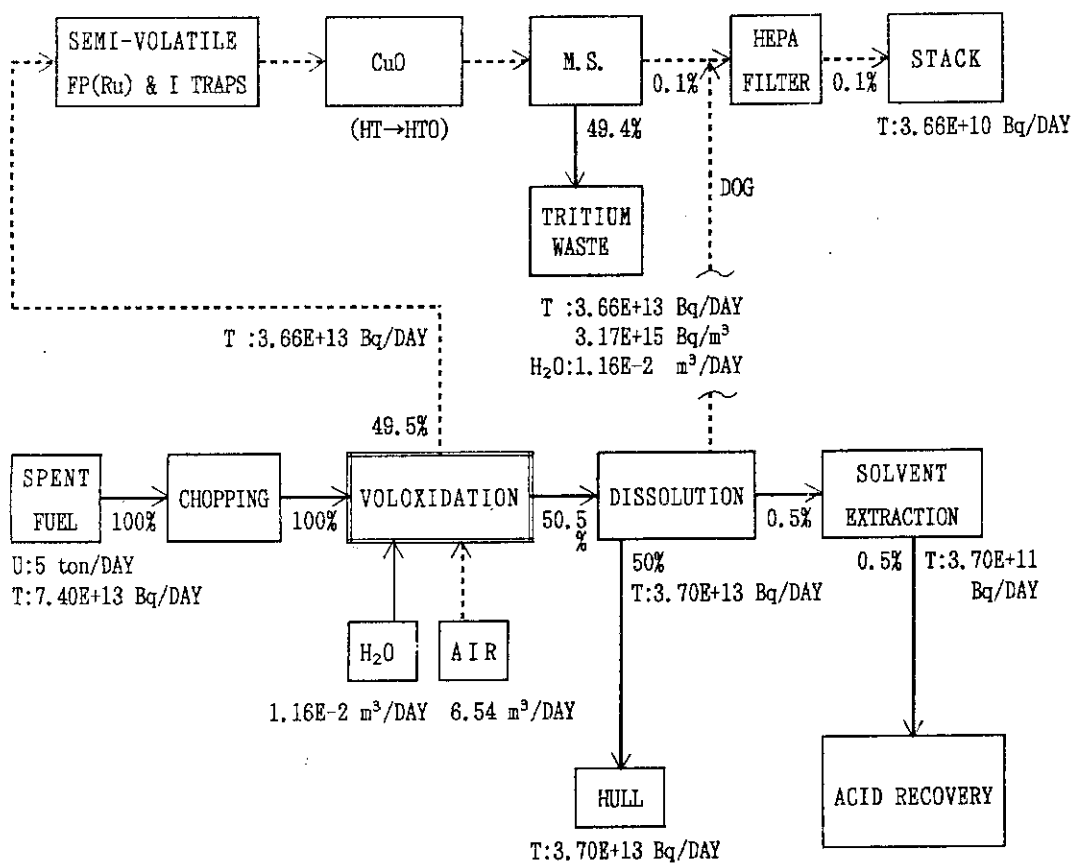Fig. 20 Inner leak rate of purge gas as a function of differential pressure.

Fig. 21 Conceptual flowsheet and tritium distribution in reprocessing plant.