

Reduction of Sodium Nitrate Liquid Waste in Nuclear Reprocessing Plants

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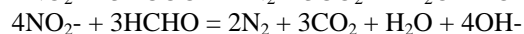
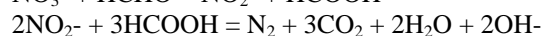
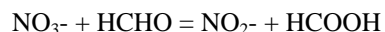
ABSTRACT

Sodium nitrate solution has been generated from nuclear reprocessing plant as a result of neutralization of nitric acid. The sodium nitrate has been immobilized by bitumen, cement or other material in the site and waste packages have been produced. In order to reduce an environmental impact of the waste packages from the reprocessing plant, it is preferable to decompose nitrate ion to harmless gases such as nitrogen. A combination of formic acid and catalyst has been proposed for this purpose. But, the method is inadequate for a full decomposition of the nitrate ion. In addition, a mixture of NO and NO₂ is produced during the reaction.

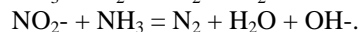
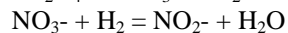
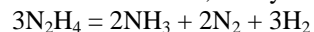
Formaldehyde and hydrazine were selected as reductants and a combined use of Pd-Cu catalyst was tried to decompose the nitrate ion. As a result, the nitrate ion can almost entirely be decomposed without any generation of NO and NO₂.

The test was conducted by 1 L flask. In case of formaldehyde, nitrate ion concentration can be reduced from 0.017 mol/l to 3.9x10⁻⁴ mol/l. In case of hydrazine, nitrate concentration can be decreased from 2.8 mol/l to 9.5x10⁻³ mol/l and ammonium ion is detected. The ammonium ion concentration in the final solution is 0.12 mol/l when 2.8 mol/l nitrate is reduced by hydrazine.

Chemical reactions for formaldehyde on the Pd-Cu catalyst are estimated as combination of:



On the other hand, for hydrazine with the Pd-Cu catalyst:



The fundamental research shows that the combination usage of the Pd-Cu catalyst and formaldehyde or hydrazine is applicable for the reduction of nitrate liquid waste in the nuclear reprocessing plant.

INTRODUCTION

Sodium nitrate solution has been generated from nuclear reprocessing plant of Purex type as a result of neutralization of nitric acid. The sodium nitrate has been stored in tanks or immobilized by bitumen, cement or other material in the site and waste packages have been produced.

In order to reduce an environmental impact of the waste packages from the reprocessing plant, it is preferable to decompose nitrate ion to harmless gases such as nitrogen or carbon dioxide.

In the non-nuclear industries, processes to reduce nitrate ion have been developed by applying bio-degradation, ion exchange, electro dialysis and chemical treatment. However, biodegradation method requires relatively large space and complicated maintenance of activated sludge. Ion exchange and electro dialysis are not intrinsic solution because those methods merely provide countermeasures for separation and concentration of nitrate ion from the effluent. In chemical treatment, nitrate-nitrogen is decomposed by reductant in the presence of catalyst. Therefore, a large space is unnecessary for it.

Hydrogen, organic compounds and inorganic compounds have been reported as reductants of nitrate-nitrogen.[1] It is preferable for reductants not to be accumulated in the nuclear facilities. Therefore, hydrogen and organic compounds are recommended. But, hydrogen requires recirculation system because of the efficient use of the hydrogen gas, which leads to increase of the facility cost.

Formaldehyde and hydrazine are candidate reductants for this purpose. Formaldehyde has been tested with catalyst for the decomposition of nitrate-nitrogen.[2] But, the rate of decomposition is insufficient and the decomposition conditions without evolution of NO and NO₂ have not been sufficiently studied.

Hydrazine has been widely used in the reprocessing plant for reducing Pu ions because of high efficiency.[3, 4]

Formaldehyde and hydrazine were selected as reductants for reasons mentioned above. And reaction of the reductants in the presence of catalyst was investigated in order to decompose nitrate ion without evolution of NO and NO₂.

EXPERIMENTAL

Sodium nitrate solution with wide range of concentration has been produced in the reprocessing plant.[5] The test was carried out for sodium nitrate with different concentrations. A 1 L separable flask was used for the test. In some cases, flow test was conducted by a column of 9.5 cm³ volume.

The pH of the solution was adjusted to ca. 12 before adding reductants. Solutions for the test were kept at ca. 330 K. Pd-Cu catalyst was used in a series of the experiment.

Fig.1 shows the experimental set up. The test conditions are summarized in Table I.

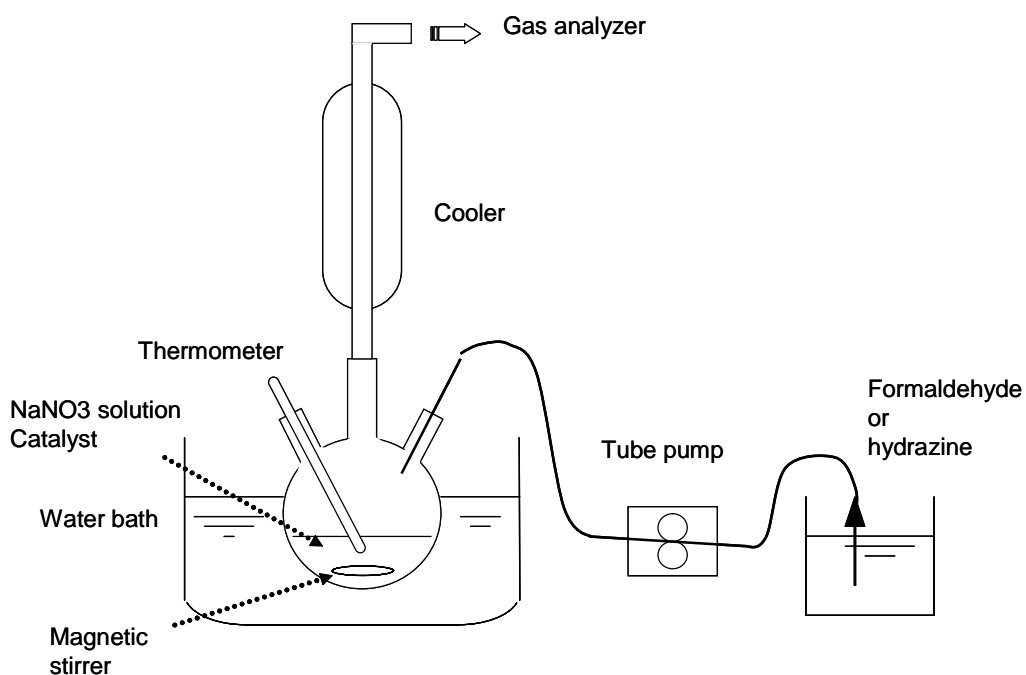


Fig. 1. xperimental apparatus for sodium nitrate decomposition

Table I. Test Conditions for Sodium Nitrate Decomposition

Case No.	1	2	3
Sodium nitrate conc.	0.017 [mol/l]	0.017 [mol/l]	1.3 [mol/l]
pH adjustment	12	12	12
Reductant	37% Formaldehyde	37% Formaldehyde	37% Formaldehyde
How to add the reductant	Lump	Lump	Continuous 15 [ml/h]
Temperature	ca. 330 [K]	ca. 330 [K]	ca. 330 [K]
Batch or flow	Batch	Flow, Flow rate: 5 [h]	Batch
Catalyst	Pd-Cu catalyst	Pd-Cu catalyst	Pd-Cu catalyst

Case No.	4	5	6
Sodium nitrate conc.	1.3 [mol/l]	2.8 [mol/l]	5 [mol/l]
pH	12	12	12
Reductant	Hydrazine hydrate	Hydrazine hydrate	Hydrazine hydrate
How to add the reductant	Continuous 20 [ml/h]	Continuous 20 [ml/h]	Continuous 20 [ml/h]
Temperature	ca. 330 [K]	ca. 330 [K]	ca. 330 [K]
Batch or flow	Batch	Batch	Batch
Catalyst	Pd-Cu catalyst	Pd-Cu catalyst	Pd-Cu catalyst

RESULTS AND DISCUSSION

Experimental results

Fig.2 shows changes in ion concentrations with time, obtained from experiment of the case 1 and the case 3 in Table I. As for the case 1, 98% of nitrate ion is decomposed after three hours of mixing nitrate solution and formaldehyde with catalyst. Nitrite ion is detected at the first stage of reaction. The nitrite ion disappeared after three hours. No ammonia is observed in gas phase. But, 70 ppm ammonium ion is detected in the solution four hours after mixing nitrate and formaldehyde with catalyst.

As for the case 2, pH of the nitrate solution was adjusted to 12. Then, the solution was mixed with formaldehyde. The mixture was fed to the catalyst column under the conditions that space velocity was 5 /h and the column temperature was kept at ca. 330 K. Gas is observed at the outlet of the catalyst column. Nitrate ion concentration at the outlet of the column decreases down to 70 % on average.

As for the case 3, formaldehyde was continuously fed to the flask in order to avoid rapid temperature rise after adjusting pH. The flow rate of formaldehyde was 15 ml/h. Formic acid is observed during reduction of nitrate. Formic acid concentration increases as nitrate ion is reduced. Formaldehyde was stopped feeding at four hours and hydrogen peroxide was added in order to decompose the formic acid. Nitrite and formic acid can be completely decomposed by hydrogen peroxide. Formaldehyde was added again to decompose nitrate ion. As a result, 95% of nitrate ion can be decomposed.

As for the experiment using hydrazine, test was carried out for nitrate solutions of three different concentrations. Fig. 3 shows changes in ion concentrations with time, obtained from experiment of the case 4 and the case 6. As for the case 4, nitrite is detected during the reaction as is the case with the formaldehyde experiment. A rate of decomposition of nitrate ion decreases with decreasing nitrate ion concentration.

In the case 5, nitrite concentration drops from 0.65 mol/l to 2.2×10^{-4} mol/l. Final solution contains 0.12 mol/l ammonium ion. As for the case 6, nitrite concentration reaches 0.5 mol/l and maximum concentration of ammonium ion is 0.3 mol/l. The concentration profiles of the case 5 and the 6 are similar to that of the case 4.

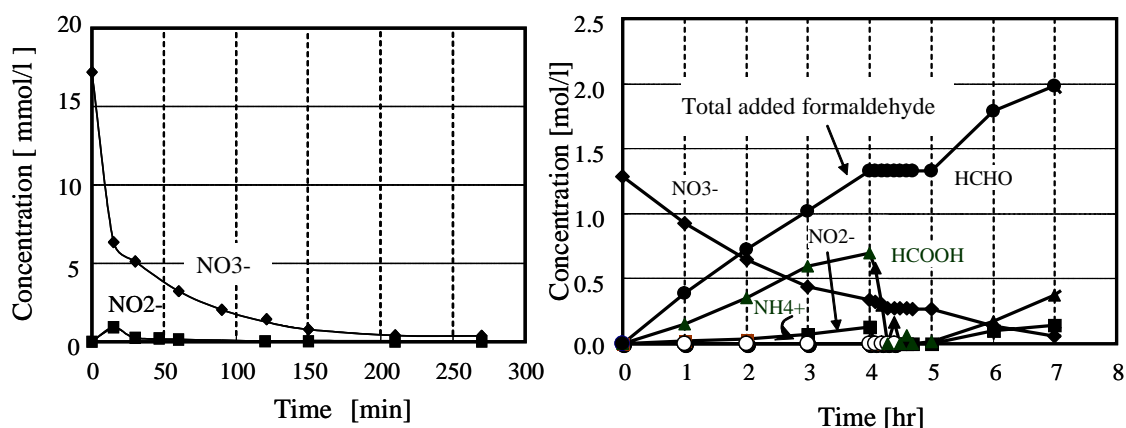


Fig. 2. Changes of ion concentrations in the solution with time. Case 1 to the left. Case 3 to the right

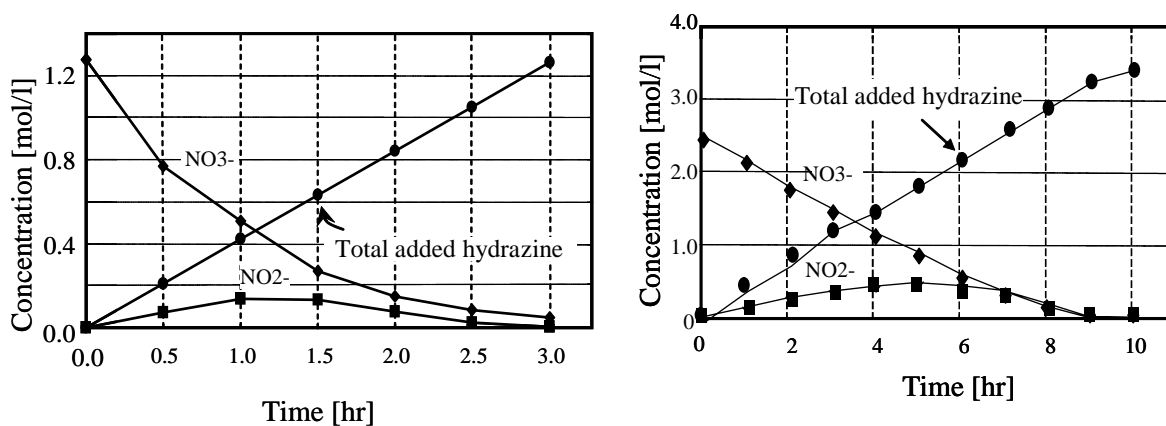


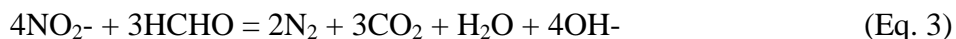
Fig. 3. Changes of ion concentrations in the solution with time. Case 4 to the left. Case 6 to the right

Chemical Reaction

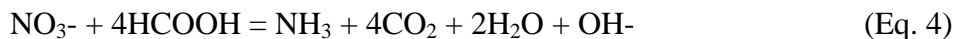
Nitrite ion and formic acid are produced from nitrate by formaldehyde in the presence of catalyst. The formaldehyde subsequently reduces nitrite ion to nitrogen. The reactions are described as:



Formaldehyde reduces nitrite ion in parallel, which can be described as:



Formic acid also reacts with nitrate ion to produce ammonia.



In the reprocessing plant of Purex type, ammonia of high concentration is not preferable in view of avoiding production of ammonium nitrate, which is explosive. Therefore, contact of formic acid and nitrite ion should be increased rather than contact of formic acid and nitrate ion.

In case of chemical reduction by hydrazine, ammonia and hydrogen are produced by decomposition of hydrazine on catalyst.



Hydrogen attacks nitrate ion in the solution to produce nitrite ion, which is subsequently reduced by ammonia under the catalyst.



Ammonia is recommended to react with nitrite ion immediately to avoid accumulation.

Conceptual Design

The fundamental tests clarify the followings:

- Formaldehyde with catalyst reduces diluted nitrate ions without producing formic acid.
- Formic acid can be completely decomposed by hydrogen peroxide.
- Hydrazine with catalyst reduces nitrate having wide range of nitrate solution.
- Ammonium ion is produced when hydrazine is used for reduction of nitrate of high concentration.
- Rate of decomposition of nitrate ion is decreased when a catalyst column is used because of gas generation inside the column.

From the system design point of view, the test results are summarized as:

- Hydrazine as reductant is preferable to decompose nitrate liquid waste because hydrazine can cope with a wide range of nitrate concentration.
- Formaldehyde as reductant is applicable for nitrate liquid waste of low concentration.
- Tank system, in which nitrate liquid waste can be sufficiently in contact with catalyst under agitation, is recommended to achieve a high rate of decomposition.

In order to reduce the waste volume, the treated liquid which has a high Na content should be reused as a reagent of pH adjustment. The system for the treatment was studied and one of examples of conceptual flow is shown in fig. 4.

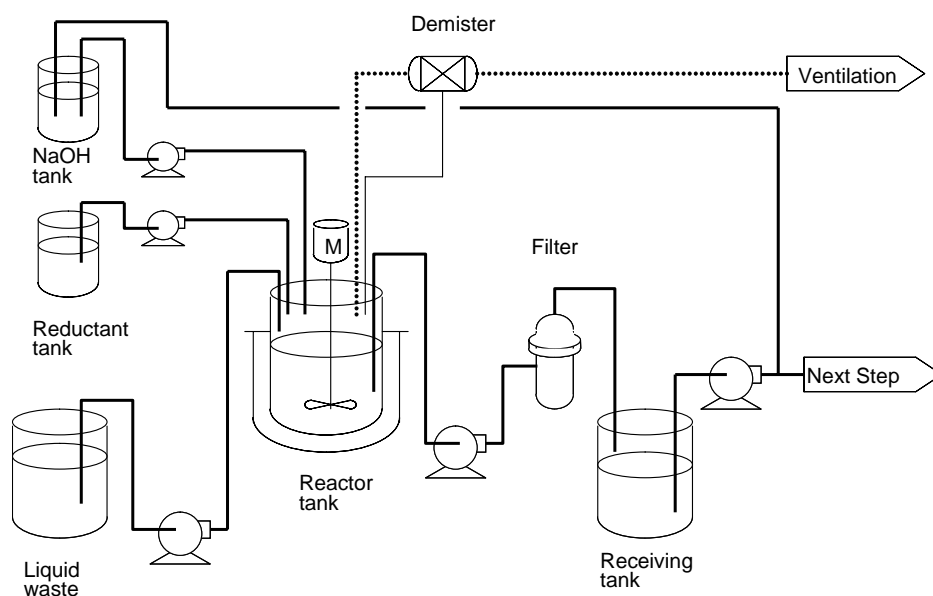


Fig. 4. Conceptual flow of nitrate waste treatment for the reprocessing plant

CHALLENGES

Nitrate containing liquid waste of 0.6 - 4 m³ per MTU (metric ton uranium) has been generated from the reprocessing plant.[6] The liquid waste contains certain amount of chemical compounds such as sodium carbonate, sodium nitrite, tri-butyl phosphate and di-butyl phosphate. Further study mentioned below is planned in order to establish the system for actual application.

- Evaluation of catalyst life
- Effect of other anions and impurities
- Scale up effect
- Ammonium ion removal in case of hydrazine utilization

CONCLUSION

The fundamental research shows that the combination usage of Pd-Cu catalyst and formaldehyde or hydrazine is applicable for the reduction of nitrate solution generated from the reprocessing plant. The conceptual flow, in which sodium is recycled, could be developed based on the fundamental research.

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