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Integrative device and process of oxidization, degassing, acidity adjustment of 1BP from APOR process

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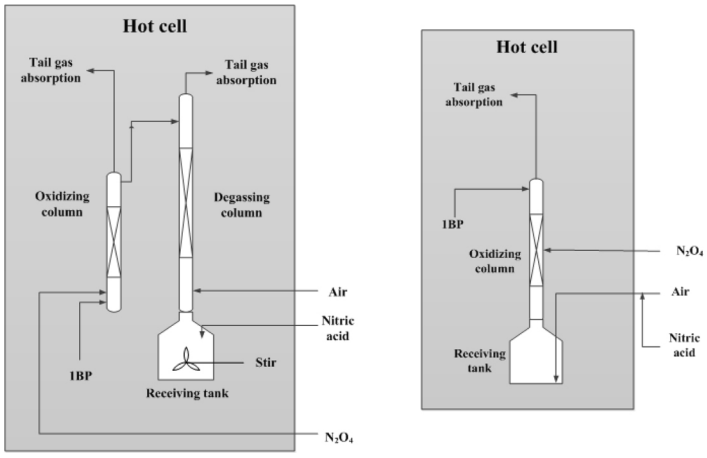
HIGHLIGHTS

- We designed an integrative device and process.
- The utilization efficiency of N_2O_4 is increased significantly.
- Our work results in considerable simplification of the device.
- Process parameters are determined by experiments.

GRAPHICAL ABSTRACT

Previous (left) and present (right) device of oxidation, degassing, acidity adjustment of 1BP.



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ABSTRACT

Device and process of oxidization, degassing, acidity adjustment of 1BP (The Pu production feed from U/Pu separation section) from APOR process (Advanced Purex Process based on Organic Reductants) were improved through rational design and experiments. The device was simplified and the process parameters, such as feed position and flow ratio, were determined by experiments. Based on this new device and process, the reductants *N,N*-dimethylhydroxylamine (DMHAN) and methylhydrazine (MMH) in 1BP solution could be oxidized with much less N_2O_4 consumption.

1. Introduction

In the reprocessing of irradiated nuclear fuels by the Purex process, U/Pu separation is achieved by reducing extractable Pu(IV) to inextractable Pu(III). DMHAN (*N,N*-dimethylhydroxylamine) is used as reductant with MMH (Methylhydrazine) as holding reductant in APOR process(Advanced Purex Process based on Organic Reductants) (Hui, 2001). The Pu production feed from U/Pu separation section, which contains Pu(III), nitric acid, and residual reductants, is called 1BP for short.

Before entering Pu purification section, Pu(III) and reductants in 1BP should be oxidized firstly. Next, residual HNO_2 produced

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in the oxidation reaction should be removed through degassing. Finally, acidity should be adjusted before further Pu purification. Several methods are optional for oxidization of Pu(III) and reductants (Talmont, 1965; Swanson, 1971; Schmieder et al., 1974; Hausberger, in press). Nitrogen oxides is widely used as the oxidant in reprocessing plants, such as UP3 plant in France, ROKKASHO plant in Japan, and THORP plant in UK.

In our previous study (Gaoliang et al., 2011), N_2O_4 (one form of nitrogen oxides) was proven to be an ideal oxidant for DMHAN and MMH, as well as Pu(III). More than 99.9% of Pu(III) in 1BP could be oxidized within 90s by the straight addition of 2 mol of liquid N_2O_4 for every mole of DMHAN and MMH. CH_3OH, HCHO and HCOOH were the main liquid oxidation products, while N_2, C_2H_4 and CH_4 were the main gaseous oxidation products.

Previous studies showed that packing column was a good choice for reaction device between 1BP and N_2O_4. To improve economical performance, the device should be simplified and N_2O_4 consumption should be reduced, which was the objective of this study.

According to previous experimental results, Pu(III) in 1BP could be oxidized immediately once DMHAN and MMH in 1BP were completely oxidized by N_2O_4 (Gaoliang, 2009). Therefore, only DMHAN and MMH oxidization effect was studied in this paper.

2. Experimental

2.1. Reagents and equipment

DMHAN was synthesized and purified as described in Gaoliang et al. (2006). Other reagents used in the experiments were of analytical grade or better and used without further purification. Simulated 1BP (0.1 mol/L DMHAN, 0.15 mol/L MMH and 1.5 mol/L HNO_3) was prepared by mixing DMHAN, MMH and HNO_3.

A Φ50 × 1200 mm glass packing column, and a Φ40 × 600 mm steel packing column were made in China Institute of Atomic Energy.

2.2. Procedure

1BP and N_2O_4 liquid were sent into column by syringe pumps, before entering the column, N_2O_4 liquid was heated to NO_2 gas (N_2O_4 is the dimer of NO_2, boiling point of N_2O_4 was 294.3 K, density of N_2O_4 liquid was 1.45 g/mL, density of NO_2 gas was 3.3 g/L). Air was sent into flask by a gas pump. Air flow rate was measured with a flow meter. After reaction of 1BP and NO_2, the oxidized 1BP in receiving flask was degassed by 2000 mL/min air for about 2 h. The residual MMH and DMHAN in degassed 1BP were determined by Spectrophotometric Method (Chuanbo et al., 2011), and nitric acid concentration was determined by titration.

3. Results and discussion

3.1. Device improvement

The previous and present devices are shown in Fig. 1. In the previous device, both 1BP and N_2O_4 entered from the bottom of the oxidization column where 1BP was oxidized. The oxidized 1BP entered from the top of the degassing column. Residual nitrous acid in oxidized 1BP was washed out with air. The degassed 1BP entered the receiving tank for acidity adjustment. The tail gas from both oxidization and degassing columns was absorbed by alkaline solution.

Low N_2O_4 utilization is one problem of using the previous device. This is caused by low solubility of NO, a gas product of reaction between 1BP and N_2O_4. Unlike NO_2, the released NO is insoluble in 1BP or alkaline solution, thus resulting in low utilization of N_2O_4 and complicated tail gas treatment. Another problem is the high degassing column and overmuch pipelines, which takes too much space and complicate the device. Higher N_2O_4 utilization and device simplification are necessary from the economic perspective.

In present device, in order to increase N_2O_4 utilization, 1BP and NO_2 were changed to react counter currently in the oxidizing column. Air was supplied into the column, so that NO could be oxidized quickly into NO_2 and further reacted with reductants in 1BP. NO_2

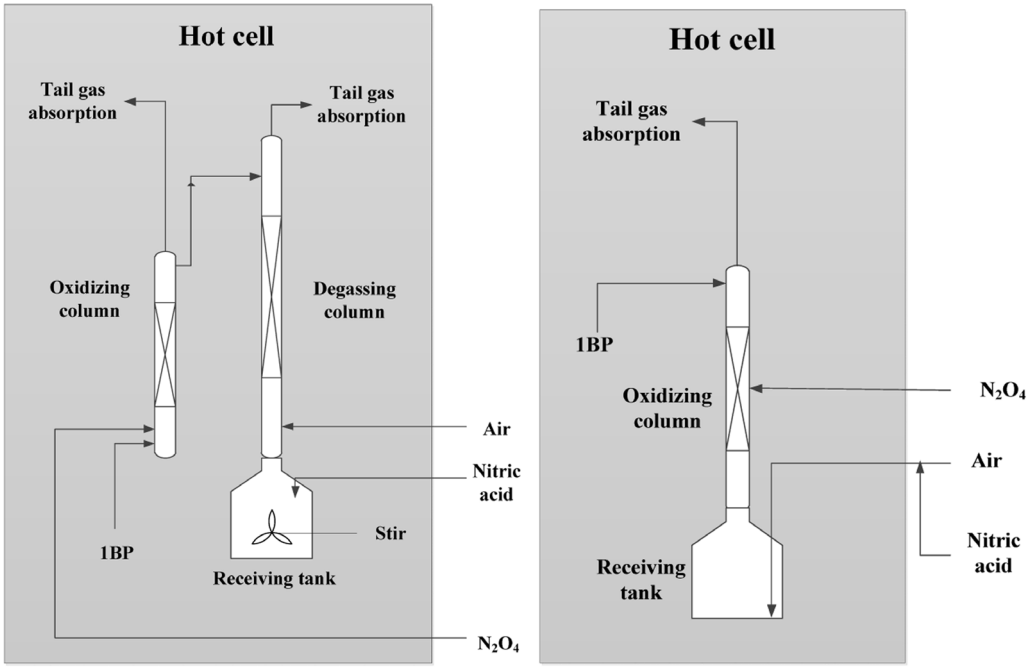

Fig. 1. Previous (left) and present (right) device of oxidation, degassing, acidity adjustment of 1BP.