



Concentration and Accumulation of Nitrous Oxide in a Cascade Condenser-Reboiler

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1. Introduction

In the main condenser, one of the components of a cryogenic air separation unit (ASU), low volatile impurities (CO₂, N₂O, and hydrocarbons such as CH₄ and C₂H₆) in the air concentrate in liquid oxygen. When concentrated flammable hydrocarbons react with oxygen, they can cause combustion of aluminum, the material of the main condenser, resulting in a sudden increase in pressure inside the ASU. In 1997, a large-scale explosion occurred in an ASU using a down flow reboiler (DFR, Figure 1) ¹⁾. In a DFR, liquid oxygen evaporates as it flows down the heat-transfer surface of the evaporation passages. It is speculated that the explosion occurred because the flow of liquid oxygen in the evaporation passages was obstructed and non-uniform due to N₂O, which is a plugging component, causing the liquid oxygen to totally evaporate in some passages, resulting in an excessive concentration of hydrocarbons contained in those passages. A subsequent N₂O accumulation experiment reported that DFRs can cause local dry-out on the heat-transfer surface and that N₂O tends to accumulate ²⁾. ASUs using DFRs are operated and managed based on these findings, but large-capacity circulation pumps are necessary to prevent heat transfer

surfaces from drying out, and the reduction of energy consumption for these pumps is an issue.

On the other hand, in a cascade condenser-reboiler (Figure 1), liquid oxygen evaporates in the passages as it flows up the core by natural circulation, as in a bath-type (thermo-siphon) condenser-reboiler (Figure 1). This system has been confirmed to be resistant to N₂O accumulation over many years of experience. Therefore, compared with a DFR, sufficient liquid volume is secured and N₂O accumulation is less likely to occur, so a large liquid pump is not required, thus energy reduction can be expected. However, because the distributor used to extract the rising evaporating fluid from the side of the condenser affects the flow, design innovations are required to prevent dryness in the distributor structure, outlet liquid level, etc.

In this paper, N₂O behaviors in the evaporation passages were observed using a pilot-scale cascade condenser-reboiler in order to establish standards for safe design and operation. Dynamic simulations of concentration and accumulation were also performed.

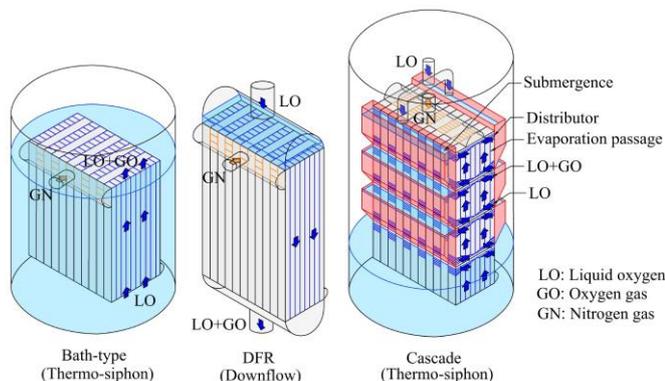


Figure 1 Schematic of the main condenser

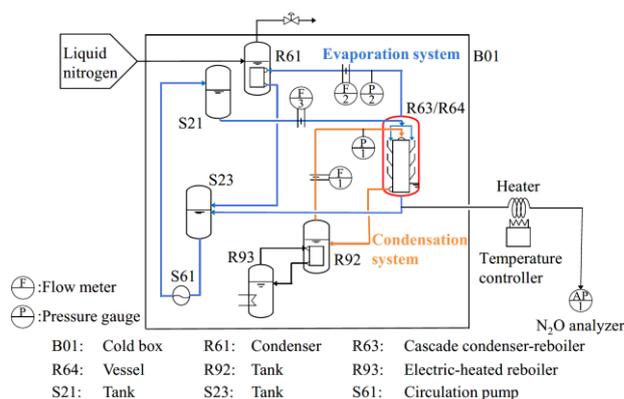


Figure 2 Schematic of pilot scale equipment

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2. N₂O accumulation experiment in pilot scale equipment

Figure 2 shows a schematic of the pilot scale equipment. The equipment consists mainly of a cascade condenser-reboiler R63 (width 250 mm, stack height 426 mm, length 4800 mm) and its outer vessel R64 (diameter 900 mm, length 6690 mm), a condensation system, and an evaporation system. In the condensation system, the liquid nitrogen in reboiler R92 (volume 2.2 m³) is evaporated by the electric-heated reboiler R93, and generated gaseous nitrogen (heating gas) is supplied to the condensation passage of R63. In the evaporation system, liquid nitrogen in tank S23 (volume 0.8 m³) is pumped into tank S21 (volume 1.3 m³) by pump S61 and supplied to R64 (evaporation passage of R63).

The experiment was performed over the condition ranges shown in Table 1. The concentration of N₂O ($x_{out,2}/x_{in,2}$) in the liquid nitrogen at the bottom of R64 was adjusted by changing the evaporation flow rate (F-2), which is controlled by the heating gas flow rate (F-1), and the feed liquid flow rate (F-3). The solubility ratio (ratio of N₂O concentration to solubility³⁾) was adjusted by changing the initial concentration of N₂O and the evaporation pressure (P-2).

At the start of the experiment, N₂O was first dissolved in the evaporation system and liquid circulation operation was performed to keep the N₂O concentration constant, then heating gas was supplied to the condensation passages of R63 to start heat exchange and the N₂O concentration (AP-1) at the bottom outlet of R64 was tracked. The N₂O analysis system consisted of a coil section wound with a sheath heater, a heater temperature controller, and an N₂O analyzer (Nippon Thermo MODEL461). Some liquid nitrogen was continuously extracted from the outlet of R64 and instantly evaporated and fed to an N₂O analyzer.

3. Simulation model

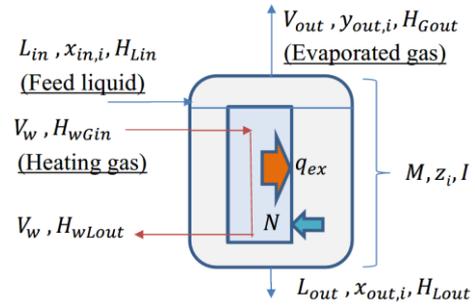
To validate the experimental result, a dynamic simulation of the entire experimental system using the N₂O accumulation model was made for the cascade condenser-reboiler shown in Table 2. The accumulation model mainly consists of the mass and heat balances of R64 and the accumulation rate equation (7), and accumulation is assumed to occur at the mass transfer

Table 1 Experimental conditions

F-1 heating gas flow rate	[Nm ³ /h]	916 to 1711
F-3 feed liquid flow rate	[Nm ³ /h]	1520 to 2397
Solubility ratio ($x_{out,2}/x_s$)	[-]	0.08 to 0.96

Table 2 Fundamental equations of the simulation model

Fundamental equation		
Material balance	$\frac{dM}{dt} = L_{in} - V_{out} - L_{out} - N$	(1)
Component balance	$\frac{dMz_i}{dt} = L_{in}x_{in,i} - V_{out}y_{out,i} - L_{out}x_{out,i} - N$ ($i = 1,2$)	(2)
	$z_i = Ry_{out,i} + (1 - R)x_{out,i}$	(3)
Heat balance	$\frac{dI}{dt} = L_{in}H_{in} - V_{out}H_{Gout} - L_{out}H_{Lout} + q_{ex} + q_{leak}$	(4)
Heat exchange rate	$q_{ex} = V_{out}(H_{Gout} - H_{Lout}) = V_w(H_{wGin} - H_{wLout})$	(5)
Composition of evaporated gas	$y_{out,1} = 1 \quad y_{out,2} = 0$	(6)
Accumulation rate	$N = KACx_s \left(\frac{x_{out,2}}{x_s} - r_{limit} \right)$	(7)



coefficient K with the difference between the solubility ratio ($x_{out,2}/x_s$) and the accumulation limit ratio r_{limit} as the driving force. The simulation was performed using gPROMS ModelBuilder® (Siemens PSE). gPROMS ModelBuilder® is a process simulator that connects modeled devices (MODELS) through PORTs and calculates the entire process. MODELS can be created by the user.

4. Evaluation of N₂O accumulation

4.1 Experimental result

Figures 3 and 4 show the time variation of measured N₂O concentration. The left vertical axis is the N₂O concentration, the right vertical axis is the evaporation flow rate, and the horizontal axis is the measurement time. The blue and orange lines indicate the N₂O concentration and the evaporation flow rate, respectively, with the solid lines representing the measured value and the dashed

lines representing the value calculated by simulation. The green dashed line is the calculated N₂O concentration in the liquid in the inlet to R64.

After confirming that the N₂O concentration has stabilized in the liquid circulation operation, heat exchange is started. Part of the liquid nitrogen evaporates (right vertical axis), and the extremely low volatile N₂O concentrates on the liquid side, resulting in a decrease in inlet N₂O concentration.

In the case shown in Figure 3, the N₂O concentration increased from 90 ppm to 120 ppm after the start of heat exchange and reached a constant value. This indicates that the total amount of N₂O dissolved in the liquid nitrogen in the evaporation system did not change, i.e., no N₂O accumulated in the cascade condenser-reboiler R63, which agrees with the calculated value.

Figure 4 shows the results of the same experiment under lower pressure and lower solubility conditions. When heat exchange was started after the N₂O concentration stabilized at 80 ppm, the N₂O concentration at the outlet increased to 108 ppm and then decreased (the dotted line in the figure represents the calculated value assuming no accumulation). This indicates that the total amount of dissolved N₂O decreased due to the precipitation and accumulation of N₂O in the cascade condenser-reboiler R63.

When the N₂O concentration decreased to 98 ppm, it became stable, which indicated that no further accumulation occurred below this concentration. Based on this result, K and r_{limit} of the accumulation rate equation were obtained, and it was confirmed that this model can reproduce the accumulation behavior of N₂O. It was estimated that 56 g of N₂O accumulated under these conditions (corresponding to a thickness of 0.16 μ m if the N₂O accumulated uniformly on all heat-transfer surfaces). Accumulation at a concentration lower than the solubility (113 ppm) in Figure 4 is considered to be due to the fact that the N₂O concentration at the actual heat transfer surface is higher than that at the outlet of R64.

4.2 Discussion

Comparing Figures 3 and 4, accumulation occurs despite the lower N₂O concentration in Figure 4. This is due to lower N₂O solubility under the lower pressure condition in Figure 4. To investigate the conditions under which accumulation occurs, all data are plotted in Figure

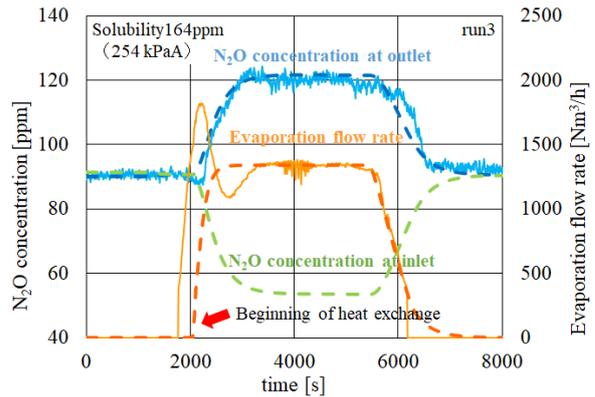


Figure 3 N₂O behavior (no accumulation occurred)

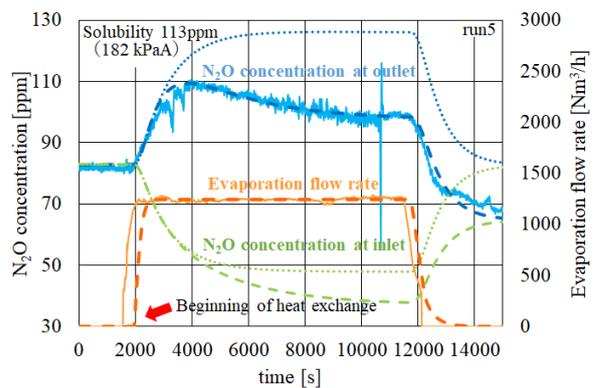


Figure 4 N₂O behavior (accumulation occurred)

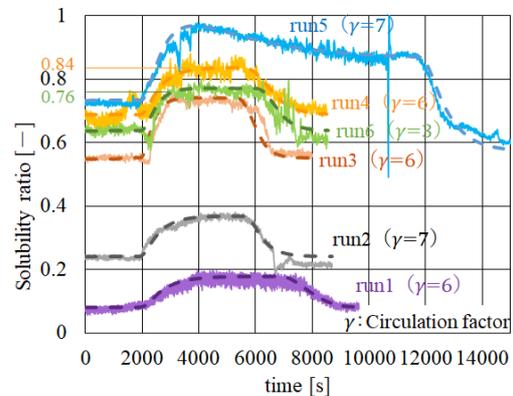


Figure 5 Comparison of N₂O behaviors

5 with the solubility ratio on the vertical axis. The figure also shows the circulation factor, which is the ratio of the liquid flow rate entering the evaporation passage to the evaporation flow rate (the smaller the value, the higher the concentration of N₂O in the evaporation passage⁴⁾).

Figure 5 indicates that accumulation occurred in run5, which has the highest solubility ratio. On the other hand, accumulation did not occur in run4 at a solubility ratio of 0.84, nor in run6 at a slightly lower solubility ratio of 0.76 but with a small circulation factor of 3. In one study of

DFR, it was reported that accumulation occurred at a solubility ratio of 0.001²⁾.

Based on these results, we obtained design standards for the N₂O concentration control value and the circulation factor to prevent N₂O accumulation in air separation units using cascade condenser-reboilers.

5. Conclusion

In order to design and operate ASUs safely, we studied the concentration and accumulation behavior of N₂O in a cascade condenser-reboiler. As a result, it was found that the concentration at which accumulation occurs is higher than that in DFRs, and that operation with the same concentration control value as that of bath-type condensers, of which the maximum allowable N₂O concentration is specified to be about the same as the solubility, is possible. In addition, we obtained important knowledge for establishing standards for the circulation factor in design processes. These results indicate that a large-capacity circulation pump to prevent accumulation is no longer necessary, which can reduce heat input to an ASU. As a result, it is expected that the liquid product yield will be improved, and energy savings will be realized.

By making full use of the condenser design technology for safety and optimization introduced in this paper, we can offer compact, energy-saving, and safe ASUs to meet the diversified needs of the market.

Symbols

A	Effective heat transfer area	[m ²]
C	Molar density	[mol/m ³]
H	Molar enthalpy	[kJ/mol]
I	Total enthalpy	[kJ]
K	Mass transfer coefficient	[m/s]
L	Liquid flow rate	[mol/s]
M	Total mass	[mol]
N	Accumulation rate	[mol/s]
q_{ex}	Exchanged heat	[kW]
q_{leak}	Heat leak	[kW]
R	Ratio of gas	[-]
r_{limit}	Accumulation limit ratio	[-]
t	Time	[s]
V	Vapor flow rate	[mol/s]
x	Molar fraction in liquid phase	[-]
y	Molar fraction in vapor phase	[-]
z	Defined by equation (3)	[-]
γ	Circulation factor	[-]

Subscript

G	Vapor
i	i th component
1	Nitrogen
2	N ₂ O
in	Inlet
L	Liquid
out	Outlet
s	N ₂ O solubility
w	Heating gas side

References

- 1) Van Hardeveld R. M., M. J. Groeneveld, J. -Y. Lehman, D. C. Bull; "Investigation of an air separation unit explosion," *J. Loss prev. Process Lind*, 2001, 14, p167-180.
- 2) Houghton P. A., S. Sunder, A. O. Weist, T. P. Trexler; "Trace Component Accumulation in Downflow Reboilers," *Cryogenic Process Safety and Contaminations*, proceedings of 12th Intersociety Cryogenic Symposium, AIChE 2000 Spring meeting, Atlanta, 2000, p26-33.
- 3) Miller E.J., S.R.Auvil, N.F.Gates, G.M.Gates; "The Solubility of Nitrous Oxide As a Pure Solute and in Mixtures with Carbon Dioxide in Air Separation Liquids," *Cryogenic Process Safety and Contaminations*, proceedings of 12th Intersociety Cryogenic Symposium, AIChE 2000 Spring meeting, Atlanta, 2000, p18-25.
- 4) JIMGA; "Safe Operation of Reboilers/Condensers in Air Separation Units", Revision 2, JIMGA, 2014.