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Application of ideal temperature gradient technology to optimize the chemical exchange and distillation process of boron isotopes separation by $(CH_3)_2O$-BF_3 complex

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ABSTRACT

To exert the optimum effect, the chemical exchange process to boron isotope separation was investigated. In this enrichment method the distillation of dimethyl ether-boron trifluoride complex, which was one of the most efficient industrial methods for purification of isotope boron-10, was optimized. In chemical exchange process of boron isotopes separation two chemical reactions occur. The first one is the decomposition reaction that is an endothermic reaction. The second one is the exchange reaction that is a pyrogenic reaction. With increasing temperature, the decomposition reaction is speeded while the exchange reaction is slowed down. Affecting on both decomposition and exchange reactions, the temperature gradient of column is very important. The separation column is covered by 18 tubular electrical heaters with 350 W power. Each electrical heater is controlled by a separated monitor controller. The monitor controlling system can apply accurate, continuous and various vertical temperature gradients of distillation column. The highest separation factor for each theoretical stage was determined 1.026 at T_{bp} = 92 °C and $\partial T/\partial Z$ = 7.56 °C/m. T_{bp} of complex in industrial plant of boron enrichment is 97 °C and the maximum separation factor for a theoretical stage was recorded 1.016 in uncontrolled temperature gradient of distillation column.

1. Introduction

Natural boron includes two stable isotopes: 19.8% ^{10}B and 80.2% ^{11}B mole percent [1]. ^{10}B isotope is a top absorbent of thermal neutrons with 3837 barns of thermal neutron absorption cross section that is five times more than the natural boron and 7.67×10^5 times more than ^{11}B isotope [2]. The excellent property of ^{10}B isotope made it possible to be widely used in most industries. For example in nuclear industry, ^{10}B is a main element in making the control rods of reactor power [3]. Some other and even more important applications of ^{10}B are in disclosing neutrons in order to measure neutron reactors fluxes. Furthermore, ^{10}B is used in nuclear physics laboratories and medical radiation. Also ^{10}B isotope is mainly applied to the neutron shielding materials, or with lithium, chromium and other elements [4]. So the separation of ^{10}B from natural boron has received considerable attention at present [5–10]. There are a variety of methods on the boron isotopes separation, such as chemical exchange reaction and distillation in boron trifluoride method [11], ion exchange in boric acid solution method, counter current recycle membrane cascades in boron trifluoride method [12], low-temperature distillation of boron fluoride-methyl fluoride complex method [13], infrared laser method [14], etc. Among them chemical exchange reaction and distillation for the separation of the boron isotopes have been credited with authentic industrialized production. Extensive research has been done to separate isotopes of boron since May 1943. In addition, a research program was initiated to study various methods of reducing boron compounds. Among them the chemical exchange method was highly regarded by the experts. In this method, the complex of donor-boron trifluoride and the gas of boron trifluoride exchange according to the following reversible reaction (1):

$$\text{Donor}^{\bullet}\ {}^{11}BF_3\ (l) + {}^{10}BF_3(g) \leftrightarrow \text{Donor}^{\bullet}\ {}^{10}BF_3\ (l) + {}^{11}BF_3\ (g) \quad (1)$$

In this chemical reversible reaction the stability of complex is the most important factor for the selection of the donor. Several donors were studied that the most important ones include diethyl ether $[(C_2H_5)_2O]$, dimethyl ether $[(CH_3)_2O]$ and anisole $[C_6H_5OCH_3]$ [15]. The pilot plant was produced for all three types of the complex and the results were compared.

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Nomenclature

N	number of theoretical stages
N_0	number of initial theoretical stages
N_{eff}	number of effective theoretical stages
N_{min}	the minimum number of theoretical stages
ΔN	number of ineffective theoretical stages
n	number of theoretical stages of column
x_D	mole fraction of ^{10}B at top of column
x_w	mole fraction of ^{10}B at bottom of column
ΔZ	height difference between the top and bottom of column
T_{Top}	temperature at the top of column
T_{Bottom}	temperature at the bottom of column
T_{bp}	bubble point temperature of complex
$T_{opt,bp}$	optimum bubble point temperature of complex
$\partial T/\partial Z$	temperature gradient of column
$(\partial T/\partial Z)_{opt}$	the optimum temperature gradient of column
$(\partial T/\partial Z)_{cr}$	the critical temperature gradient of column
α_i	fractionation factor of each theoretical stage
$\alpha_{overall,calc}$	calculated overall fractionation factor of column
α_{ave}	average fractionation factor of each theoretical
$\alpha_{overall,meas}$	measured overall fractionation factor of column
J	the sum of the squares of the errors

Table 1
The results of Hooker Electro Chemical Company.

18 days trial period	Initial amount of water (%)	Corrosion (mm/year)
Hast–alloy–C	1	0.02
Copper	1	2.75
Monel	1	0.51
Stainless steel 316	1	12.42
Red brass	1	1.6

The fractionation factors of each equilibrium stage in optimal conditions for these systems were: 1.016 for $(C_2H_5)_2O$-BF_3, 1.016 for $(CH_3)_2O$-BF_3 and 1.029 for $C_6H_5OCH_3$-BF_3 [16–20]. The chemical exchange systems were compared with $(C_2H_5)_2O$-BF_3. It was found that the decomposition rate of complex $(CH_3)_2O$-BF_3 was about 20 times less and whose unit production capacity was 100 times more than $(C_2H_5)_2O$-BF_3 [21]. The donor of dimethyl ether was recognized to be better than that of diethyl ether. The anisole-boron trifluoride which have larger fractionation factor than dimethyl ether-boron trifluoride complex because of its economic disadvantages were not regarded as feasible. Its disadvantages are as follows: I – high corrosion complex of anisole-boron trifluoride; Hooker Electro Chemical Company in a research on the problems of anisole process, performed corrosion test on hast–alloy–C, copper, monel, stainless steel 316 and red brass. Testing conditions similar to these in the pilot process were considered. A corrosion test was carried out by Hooker Electro Chemical Company as listed in Table 1 [22].

According to the above results it is inferred that in the presence of a little water (1%) the corrosion rate of anisole-boron trifluoride system (especially for stainless steel 316) is rocketing. II – High decomposition of anisole-boron trifluoride complex; a grave problem of decomposition in both laboratory and bench scale Anisole Analysis in the Research of ORGDP was investigated [23]. The results showed that the water content in the solvent, the metal surface in contact with the solution, the type of metal and the metal surface quality were effective on the decomposition rate of complex. The decomposed complex is a catalyst to continue the decomposition reaction. Due to these reasons, using of complex anisole-boron trifluoride is not economical. The only advantage of anisole-boron trifluoride complex compared with dimethyl ether-boron trifluoride is its significant separation factor although its disadvantages are considerable. Finally, dimethyl ether-boron trifluoride complex was selected as the best and the most economical complex. A pilot plant was set up at the Columbia laboratories and the development work was carried out by the American Cyanamid Company, which began work in February 1944. Production of separated ^{10}B as the dimethyl ether- boron trifluoride complex began in January 1945 and the original order was completed in May 1945. The American Cyanamid Plant completed the production of the required amount of crystalline product of specified purity in June 1945 [24]. The experimental samples of ^{11}B were prepared in the pilot plant in Columbia. The current paper is going to show that with changing the distillation column temperature conditions and performance of the condenser, chemical exchange with dimethyl ether-boron trifluoride complex is optimized and the fractionation factor of this system is equal to 1.026. With these results chemical exchange and distillation by dimethyl ether-boron trifluoride complex is regarded as the best industrial method of chemical exchange in the world.

2. Experimental

2.1. Materials and instruments

In the present paper, basic materials used include boron trifluoride and dimethyl ether (industrial grade of China). The instrument of inductively coupled plasma atomic emission spectrometry (ICP, Varian Turbo 150AX) was used for determination of the concentration of boron. Also in order to determine the molar ratio of boron isotopes the instrument ICP-Mass Spectrometer was used.

2.2. Synthesis of dimethyl ether-boron trifluoride complex

The liquid complex of dimethyl ether-boron trifluoride was quickly formed by the contact of two gases of boron trifluoride and dimethyl ether. This reaction was reversible and pyrogenic for this reason the reaction was carried out in a double glazing reactor with a refrigerant in the outer wall.

2.3. Construction and set up

Separation system block diagram is given in Fig. 1. The system consists of eight parts: *a* – Separation column, it is comprised of two separately packed columns with Raschig ring packings in size of 7 mm and specific surface area of 130 m^2/m^3. The height of each separate column is 90 cm and its bore is 5 cm. The separation column is covered by 18 tubular electrical heaters with 350 W power. The height of each electrical heater is 10 cm. The heaters are firmly placed around the column. Each electrical heater is controlled by a monitor controller and also has a thermal sensor that reports the temperature of the heater to the monitor controller. The offset temperature for each controller is 0.1 °C also the outer surface of column is properly insulated with fiberglass. b – Monitor controlling system, it contains 20 separated controllers 18 of which control 18 tubular electrical heaters of separation column and 2 of which separately control the electrical heaters of condenser and dry packed column. c – Condenser which is a packed column 50 cm in height and 10 cm in diameter is packed by Raschig ring packing (size 7 mm). In this system, the vapor is condensed by increasing contact surface, decreasing of flow rate and decreasing of temperature around 40–50 °C. The condenser is covered by five electrical heaters similar to electrical heaters of separation column (10 cm in height and 10 cm in diameter). Also each electrical heater is separately controlled by the monitor controlling system. The condenser is located in a case equipped with a fan. The fan is controlled by a