Process Design of Natural Gas Treatment using DDR-type Zeolite Membrane

Hiroaki Hasegawa[1], Keiichi Nishida[1], Shuichi Oguro[1], Yasushi Fujimura[1]
Kenji Yajima[2], Makiko Niino[2], Manabu Isomura[2], Toshihiro Tomita[2]
[1]JGC Corporation, Yokohama, Japan
[2]NGK Insulators, Ltd., Nagoya, Japan

Abstract

Natural gas is a widely-used energy source and its demand is increasing. Some of the natural gases, however, contain high levels of CO_2. Membrane separation is highly useful for CO_2 separation from such kind of natural gas. JGC Corporation (JGC) and NGK Insulators, Ltd. (NGK) have been jointly developing a separation process for natural gas treatment using the DDR-type zeolite membrane (DDR Membrane). NGK, a top class manufacturer of ceramic products, has been conducting the synthesis of the DDR Membrane and scaling up the DDR Membrane element. On the other hand, JGC, a world leading engineering company for oil and gas processing, has been conducting process design, membrane housing design for commercial facility and the performance evaluation of the DDR Membrane with high pressure condition which simulates natural gas treatment.

DDR is two-dimensional zeolite with 0.36 x 0.44 nm pores and the DDR Membrane is prepared using hydrothermal synthesis on the surface of porous ceramic substrate. The DDR Membrane has the following features.

(1) Large-Size DDR Membrane

NGK has succeeded in scaling up the DDR Membrane element into a large monolithic structure with a diameter and length of 180 mm and 1,000 mm, respectively (Large-Size DDR Membrane). The membrane area of the single DDR Membrane element is 12 m^2, which is the largest among the inorganic membrane elements in the world to the best of our knowledge(see Fig. 1). The membrane area corresponds to that of 400 tubes of tubular type membrane of 10 mm diameter with the same length. Also pressure resistance of the Large-Size DDR Membrane is 8 MPaG as maximum.

(2) High Separation Performance on CO_2/CH_4

DDR Membrane has high selectivity of CO_2/CH_4 comparing with other zeolite membranes and polymeric membrane[1, 2]. Based on the result of our laboratory testing, the CO_2/CH_4 separation factor of the Large-Size DDR Membrane for equimolar CO_2/CH_4 gas feed is higher than 160 at 303 K and 0.3 MPaG. This separation factor is as same as that of the much smaller size DDR Membrane whose diameter and length are 30 mm and 160 mm, respectively (see Table 1). The performance of the DDR Membrane was not lowered with scale-up.

(3) Applicable to high CO_2 partial pressure condition

The DDR Membrane shows no CO_2-induced plasticization which occurs in the conventional polymeric membrane at high CO_2 partial pressure[3]. Thus the DDR Membrane is applicable to gas fields with high CO_2 partial pressure.

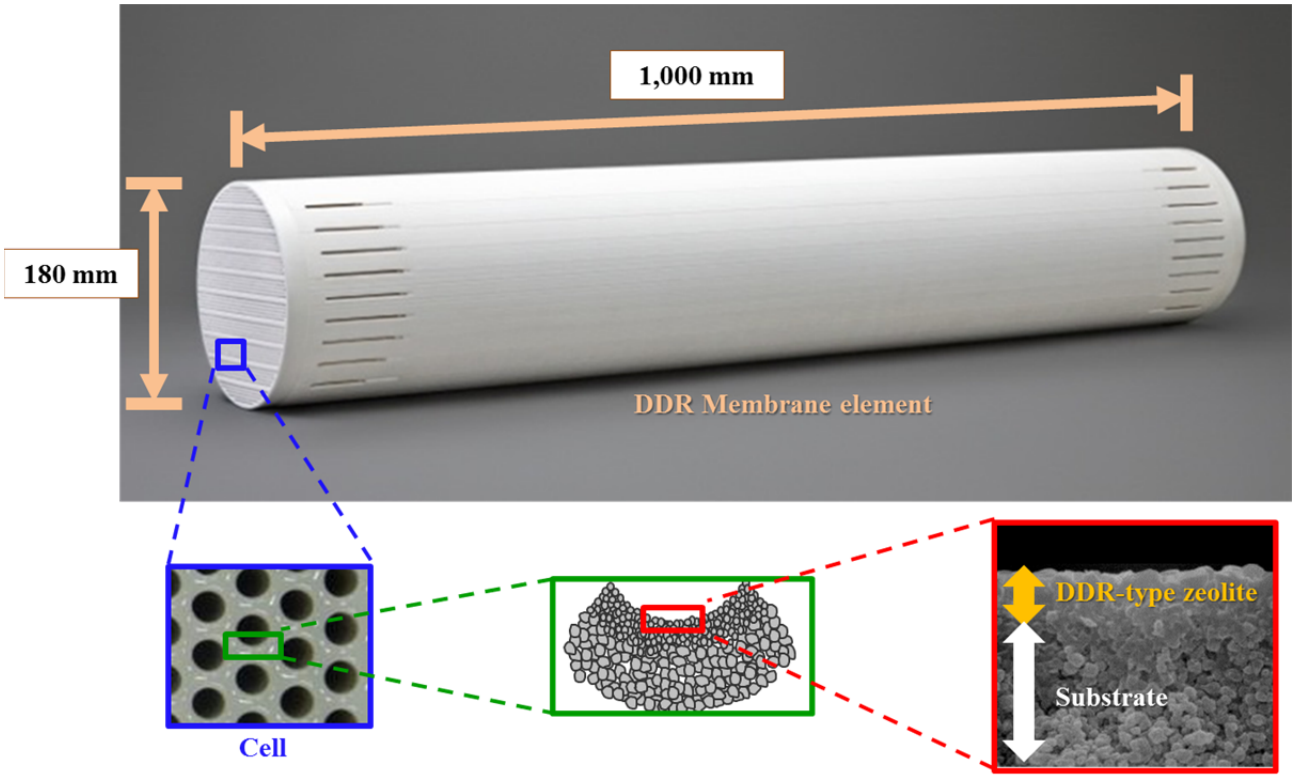


Fig. 1. Overview of DDR Membrane

Table 1. Separation factor of the DDR Membrane

Case	Feed gas composition [mol%]	Feed gas Pressure [MPaG]	Separation factor [-]	Permeate gas composition [%]
CO_2 & CH_4	CO_2 : CH_4 = 50 : 50	0.3	> 160	CO_2 > 99
H_2 & CH_4	H_2 : CH_4 = 60 : 40	0.4	> 100	H_2 > 99
CO_2 & H_2	CO_2 : H_2 = 40 : 60	0.4	12	CO_2 = 89
N_2 & CH_4	N_2 : CH_4 = 50 : 50	0.3	9	N_2 = 90

Membrane size：Diameter 30 mm – Length 160 mm

To evaluate the DDR Membrane for natural gas processing, we simulated the simple material balance based on our laboratory test results of the DDR Membrane. We have utilized the actual conditions of LaBarge gas field in USA as a practical example to evaluate the performance of the DDR Membrane. Gas composition of LaBarge is 65% CO_2, 21% methane, 7% nitrogen, 5% hydrogen sulfide (H_2S), 0.6% helium and others[4]. Separation of CO_2 in LaBarge is basically a solvent absorption and separated CO_2 is used for the enhanced oil recovery (EOR) in LaBarge field. The CO_2 concentration of the gas removed from the solvent absorption is more than 95 mol%. The DDR Membrane can be applied for bulk removal before the chemical absorption. Feed gas containing CH_4 and CO_2 is introduced to the membrane to be separated to the CH_4-rich treated gas by removing CO_2-rich permeate gas (see Fig. 2). The pressures of the feed and permeate gases are assumed as 8.0 MPaG and 0.1 MPaG, respectively. The specified CO_2 concentration of the treated gas is 15 mol% for bulk removal before chemical absorption. As the result of the calculation, the

CH_4 loss of the DDR Membrane is 2.8 % and CO_2 concentration in permeate gas is approximately 99 mol%. This low CH_4 loss improves the yield of CH_4-rich treated gas and high CO_2 concentration in permeate gas is suited for EOR. This means the probability that CO_2 separation technology can be partially replaced from current chemical absorption process to DDR Membrane. Energy requirement can be significantly reduced comparing with chemical absorption process by using the DDR Membrane. As mentioned previously, DDR Membrane can be a solution for natural gas treatment and also EOR application.

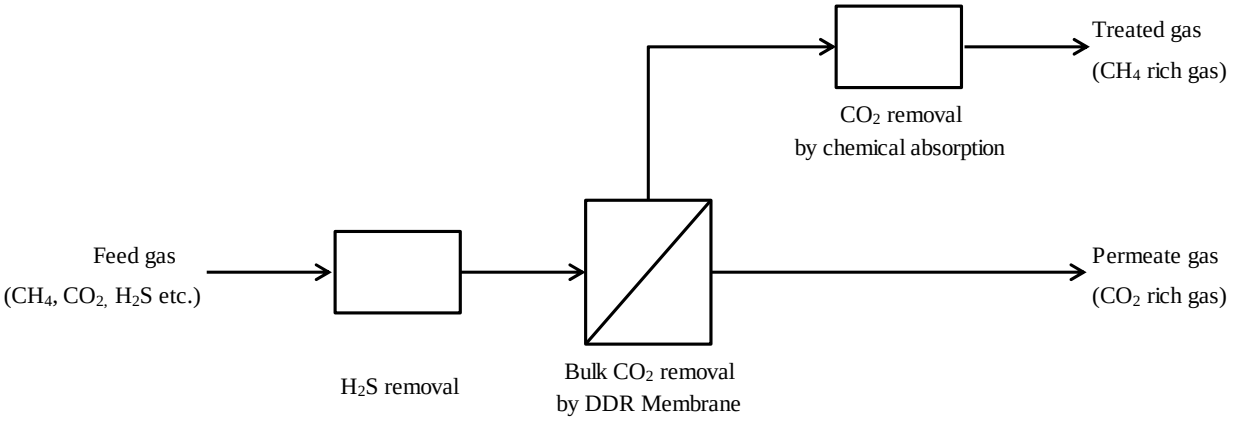


Fig. 2. Process Flow

Reference:

[1]T. Tomita, K. Nakayama, H. Sakai. (2004). Gas separation characteristics of DDR type zeolite membrane. Microporous and Mesoporous Materials. **68**. 71-75.

[2]N. Kosinov, J. Gascon, F. Kapteijn, E. J. M. Hensen. (2016). Recent developments in zeolite membranes for gas separation. Journal of Membrane Science. **499**. 65-79.

[3]A. Bos, I. G. M. Punt, M. Wessling, H. Strathmann. (1999). CO_2-induced plasticization phenomena in glassy polmers. Journal of Membrane Science. **155**. 67-78.

[4]M. E. Parker, S. Northrop, J. A. Valencia, R. E. Foglesong, W. T. Duncan. (2011). CO_2 Management at ExxonMobil's LaBarge Field, Wyoming, USA. Energy Procedia. **4**. 5455-5470.