



Solubility and diffusivity of CO₂ in fluoroelastomers and their impact on elastomer sealing in API high-pressure testing

By Xuming Chen, Ray Zonoz,
Hamid Salem, Hoi Ling
Cheng and Jushik Yun

Schlumberger N.V. (SLB)

The CO₂ molecule is a linear molecule with two polar bonds. The two dipoles cancel each other out, making it an overall non-polar molecule due to its linear shape. This unique characteristic likely contributes to the strong compatibility of CO₂ with either polar or non-polar elastomers and plastics, leading to a significantly high solubility and special diffusivity in these materials.

TECHNICAL NOTEBOOK
Edited by John Dick

It is well known that the solubility and diffusivity of CO₂ in elastomers have a strong dependence on pressure and temperature.^{1,2,3} Generally, within a certain pressure and temperature range, the solubility increases with pressure and decreases with temperature, while the diffusivity increases with temperature and its pressure dependence becomes complicated.^{4,5}

Because CO₂ is the most important greenhouse gas, the capture, transportation and sequestration of CO₂ have a great impact on global warming. Investigation into CO₂ solubility and diffusivity in elastomers and plastics at high pressure and various temperatures is crucial for developing non-metal materials for carbon capture and sequestration (CCS) technology.⁶ CCS is one of the major approaches for energy companies to utilize fossil fuels while minimizing environmental impact by reducing CO₂ emissions directly into the atmosphere, and thereby slowing down the global warming.^{7,8}

In the oil and gas industry, according to API Spec 6A, elastomer seals used for certain wellhead and tree equipment shall undergo fixture tests under extremely high pressures and high temperatures using CO₂ as the major pressurization media. At these extreme conditions, the physical properties of elastomers, such as their strength, may undergo changes due to the high CO₂ solubility. This can lead to rapid gas decompression (RGD), decreased extrusion resistance, high gas permeability, and eventually sealing failure.⁹⁻¹³ Therefore, understanding the solubility and diffusivity of CO₂ in elasto-

Executive summary

Solubility and diffusivity of CO₂ in elastomers are important properties for not only oil and gas applications, but also carbon capture and sequestration (CCS). Because CO₂ is the most important greenhouse gas, the capture, transportation and sequestration of CO₂ have a great impact on global warming. Investigation into CO₂ solubility and diffusivity in elastomers and plastics at high pressure and various temperatures is crucial for developing non-metal materials for CCS technology.

In this paper, the solubility and diffusivity of CO₂ in elastomers at extreme high pressure (more than 100 MPa) and elevated temperatures were estimated based on experimental data and theoretical calculations. These results were applied to the fixture test in API-SPEC 6A to calculate the pressure reduction during the pressure holding of an FKM seal under a pressure of more than 100 MPa.

The effects of CO₂ solubility, diffusivity and other test conditions on an elastomer seal were investigated. Understanding the solubility and diffusivity of CO₂ in elastomers under extreme high pressure (more than 100 MPa) and elevated temperatures (more than 100°C) is critical for developing new elastomer seals suitable for high-pressure/high-temperature applications.

mers under extreme high pressure (more than 100 MPa) and elevated temperatures (more than 100°C) is critical for developing new elastomer seals suitable for high-pressure/high-temperature applications.

However, precisely measuring the solubility and diffusivity of CO₂ in elastomers under such high pressures is particularly challenging, and currently, no direct test data is available. Hence, investigating CO₂ solubility and diffusivity at extreme high pressures and elevated temperatures holds great value in the development of new elastomer seals for not only the oil and gas industry but also for CCS applications.

Various approaches have been used to study the gas diffusivity and solubility (or resulting swelling) in many elastomers.^{14,15} The weight approach, also called the gravimetric method, has been used by Chen and many others to investigate CO₂ solubility and diffusivity in different elastomers such as hydrogenated nitrile butadiene rubber (HNBR) and FKM.^{16,17} Although the gravimetric approach is simple, at high temperatures with very high pressures, the fast diffusion of CO₂ and strong RGD effect increase the difficulty of the measurement process, significantly reducing the measurement accuracy. The magnetic suspension balance (MSB) Rubotherm method, also known as the Rubotherm method, has been used to study the mass transport of CO₂ in elastomers such as HNBR and FKM, as well as plastics, with high accuracy.¹⁸⁻²¹ However, the maximum pressure used for current MSB is general-

ly below 15 MPa, making it difficult to measure the solubility and diffusivity of CO₂ at very high pressure.

In this study, the solubility and diffusivity of CO₂ in different FKM elastomers were precisely measured using the gravimetric method and the Rubotherm approach at medium to low pressures under various temperatures. The solubility and diffusivity of CO₂ in elastomers at extreme high pressure (more than 100 MPa) and elevated temperatures were estimated based on experimental data and theoretical calculations. These results were then applied to the fixture tests in API Spec 6A Specification for Wellhead and Tree Equipment, Annex F, to calculate the pressure reduction during the pressure holding of a FKM seal under a pressure greater than 100 MPa. The effects of CO₂ solubility and diffusivity in the elastomer seal and other test conditions on test results were investigated, and the reasonable value of CO₂ solubility and diffusivity at extreme high pressure and elevated temperature were considered. The challenges in the API Spec 6A fixture test using CO₂ as pressurization media at extreme high pressure were reviewed.

Experimental

Materials

Five grades of FKM elastomers (FKM 1, FKM 2, FKM 3, FKM 4, and FKM 5) were investigated in this study. **Table 1** lists their properties and composition information. FKM 1 and FKM 2 are

fabricated from the same FKM base elastomer (type 3 FKM) using the same recipe except that FKM 1 contains 1 percent multi-walled carbon nanotube (MWNT). FKM 3 is a type 3 FKM comprising 33.7 percent carbon black. FKM 4 is a commercial grade FKM (type 3 FKM). FKM 5 is fabricated from a copolymer of vinylidene fluoride and 2,3,3,3-tetrafluoropropylene with 62 wt percent fluorine content, classified as Type 6 FKM based on ASTM D1418.

Measurements and test methods

Differential scanning calorimetry (DSC) measurement

The DSC measurement was carried out using a TA Instrument DSC250 with the modulated DSC technique. All samples were cooled to -90°C and then heated at a rate of 5°C/min up to 120°C, under a nitrogen gas flow. Small sample sizes were used to reduce the thermal lag effect. The T_g (endset point) was analyzed based on TRIOS software from the transition region of the nonreversible heat flow curve. The measured T_g for all FKM samples are listed in **Table 1**.

Solubility and diffusivity from the gravimetric method

The detailed experimental setup and test procedure were described in a previous paper.¹⁶ For a better understanding of the test conditions, the test procedures and sample preparation are provided here. The cured elastomers were cut into disks with a thickness and diameter of 2 and 9.5 mm, respectively.

Fig. 1: A typical desorption of CO₂ from the FKM 1 sample in this study. The data fit well with Equation 1. The diffusivity and solubility could be obtained based on the slope and y-intercept of the regression line.

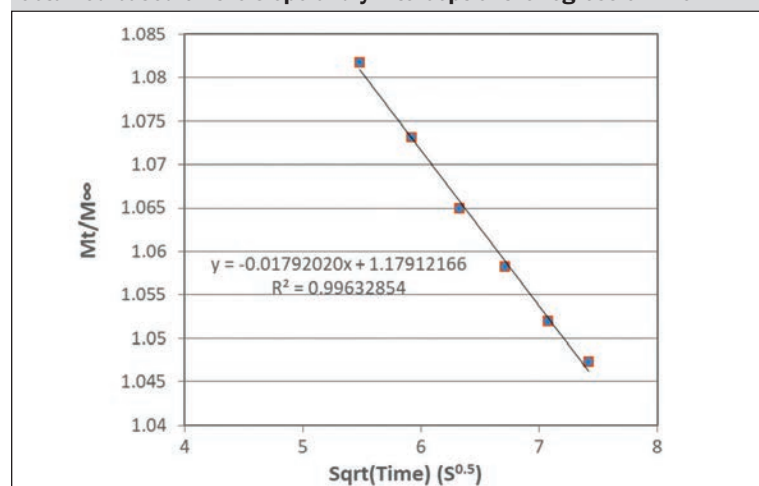
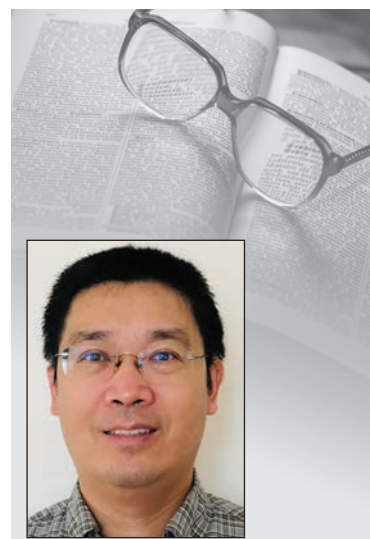


Table 1: Compositions and properties of FKM samples.

Sample	FKM type	T _g , °C (DSC endset point)	Hardness, A	Total carbon black content, wt%	CNT content, wt%
FKM 1	Type 3	-38	89	21.0	1.0%
FKM 2	Type 3	-38	82	21.0	0
FKM 3	Type 3	-43	88	33.7	0
FKM 4	Type 3	-34	88	—	—
FKM 5	Type 6	-11	87	30.0	0



Chen

The author

Xuming Chen is the principal polymer engineer in Schlumberger N.V., which does business as SLB. His primary role encompasses the development of novel elastomers, which involves formulating recipes and optimizing mixing and molding process tailored to BOP packers, wellhead seals and other oil tool applications.

He continuously explores innovative test methodologies to obtain the best elastomers that satisfy diverse mechanical designs and fulfill varied application requirements. He also engages in the qualification of plastic materials and conducts failure analyses on non-metal materials, especially elastomers and plastics for oil and gas applications.

Chen served as the chairman of API 6J2 task group (Testing of Oilfield Elastomers) in 2021 and 2022. He received his Ph.D. in polymer science from Stony Brook University in 2006.

Before joining SLB, he worked for Dow Chemical Co. from 2007-13, where he initiated and led multiple projects on polyolefin, engineering plastics and elastomers for photovoltaic module, food packaging and many other industrial applications.

Each high-pressure vessel was loaded with one sample disk. The sample was soaked in high pressure (10.3 MPa) CO₂ for at least 5 to 6 hours before the measurement. All gravimetric measurements were conducted at room temperature (~22°C).

For the sample with saturated CO₂ under high pressure, first, the pressure was released rapidly, and then the sample was quickly put on a balance to measure the weight at different times. Based on the time dependence of the sample weight, the diffusivity or diffusion efficiency of CO₂ in the polymer was obtained using Fick's diffusion equation for thin film polymers:¹⁶

$$\frac{M_t}{M_\infty} = 4 \left[\frac{Dt}{\pi l^2} \right]^{1/2} \quad \text{Equation 1}$$

where D is the diffusivity, t is the time, l is the film thickness, M_t is the mass at time t, and M_∞ is the mass at an infinite time.

Solubility in this study represents the percentage of CO₂ by
See CO₂, page 16

Continued from page 15

weight that can soak into the initial weight of the polymer. It can be calculated by extrapolating diffusion data to the initial stage when time is equal to 0 from simple diffusion model of Equation 1.

Fig. 1 illustrates a typical desorption of CO₂ from FKM 1 sample in this study. The data fit well with Equation 1. The diffusivity and solubility could be obtained based on the slope and y-intercept of the regression line.

Solubility also could be estimated based on Case-II kinetics. In this situation, the CO₂ diffusion out of the cylinder polymer sample could be described by Equation 2:²²

$$\frac{M_t}{M_{\infty}} = k_1 t^2 + k_2 t + a \quad \text{Equation 2}$$

Here, k_1 , k_2 , and a are parameters determined by the diffusivity and solubility of CO₂ in the rubber. The solubility can be obtained from Equation 2 when time is equal to 0.

Fig. 2 illustrates the CO₂ diffusion out of the cylinder polymer samples based on Case II kinetics using Equation 2 for FKM 1, and the solubility was obtained from the y-intercept of the non-linear fitted line.

Fig. 2: The CO₂ diffusion out of the cylinder polymer samples based on Case II kinetics.

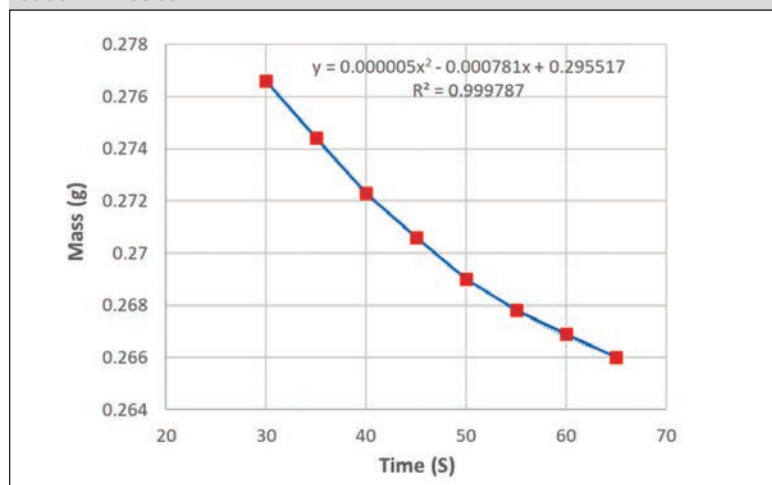


Fig. 3: Test fixture for API Spec 6A fixture test (per API Spec 6A, F.1.13.5.3).

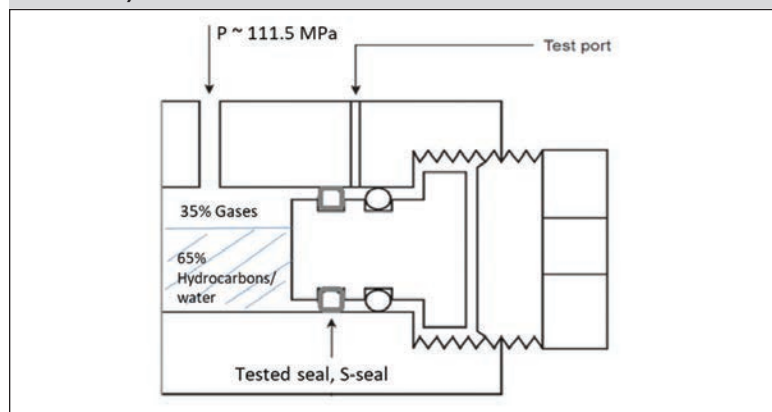


Table 2: Lists the solubility and diffusivity of FKM 1, FKM 2 and FKM 3 measured at 10.3MPa.

Sample	Diffusivity from Fick's equation at 22°C, cm ² /s	Solubility from Fick's equation at 22°C, mg CO ₂ /g FKM	Solubility from Case II release model at 22°C, mg CO ₂ /g FKM	Solubility from MBS at 70°C, mg CO ₂ /g FKM
FKM 1 (1% CNT)	2.29E-6	180	170	150
FKM 2	4.06E-6	300	250	154
FKM 3	—	—	—	166

Solubility and diffusivity from the MBS Rubotherm method

The details of equipment and test procedures for the Rubotherm method were published in previous papers.^{16,18,19} Sample disks of approximately 1-mm thickness and 6-mm diameter were used, and solubility and swelling could be directly measured with the Rubotherm method.

API Spec 6A Annex F fixture test

The fixture test was carried out on an S-seal installed in an SLB high-pressure test fixture. Fig. 3 shows the schematic design of the test fixture. The S-seal was fabricated from FKM 4. The tested procedure followed the API Spec 6A, Annex F, fixture test procedure using a standard FF/HH test medium. In the test fixture, 65 vol percent of the S-seal was immersed in the liquid phase [60 vol percent hydrocarbon (70 vol percent heptane, 20 vol percent cyclohexane, and 10 vol percent toluene) and 5 vol percent water], while 35 vol percent was exposed to gas phase (mixture of 80 vol percent CO₂, 10 vol percent H₂S and 10 vol percent CH₄).

The test was conducted at approximately 111 MPa and 121°C. To avoid pressure fluctuations due to temperature fluctuations and initial diffusion of gases in

liquid phase and elastomers, the system pressure was stabilized for more than 20 hours before the start of 160-hour pressure holding in the fixture test.

Results and discussion

CO₂ solubility, diffusivity and volume swelling in FKM 1, FKM 2 and FKM 3

Table 2 listed the solubility and diffusivity of FKM 1, FKM 2, and FKM 3 measured at 10.3MPa.

FKM 1 and FKM 2 have the same composition, except that FKM 1 has 1 percent MWNT. It seems that with the addition of 1 percent MWNT, the diffusivity and solubility of FKM 1 at 22°C reduced significantly compared to that of FKM 2. Probably, the MWNT reduced the free volume in the elastomer, thus leading to a reduction on solubility and diffusivity.²⁰ The solubility of CO₂ reduced with the increase in temperature, and all three FKM elastomers showed similar solubility at 70°C.

Fig. 4 illustrates the effect of pressure on swelling and CO₂ solubility of FKM 1, FKM 2, and FKM 3 at 70°C. The data were obtained based on the Rubotherm approach. With the increase in pressure, the swelling and the solubility increased simultaneously for all three FKMs. Therefore, high solubility generally leads to high swelling, or high swelling could be considered as high solubility for elastomers in high-pressure gases.

FKM 1 has smaller swelling than FKM 2 due to the addition of 1 percent MWNT, which significantly increases the hardness of elastomer (Table 1) and resists swelling. With the pressure increase, FKM 3 exhibits low swelling at 7.5 MPa, but the swelling increased faster with the increase in pressure.

Probably the types of FKM affect the swelling and the CO₂ solubility.

Effect of temperature and pressure on CO₂ solubility in FKM 4

FKM 4 is a commercial FKM, which was also used in the high-pressure/high-temperature API fixture test in this study. Therefore, more detailed analysis was conducted to estimate the CO₂ solubility and diffusivity at high pressure (up to 100 MPa) and high temperature (121°C). The effect of pressure and temperature on the CO₂ sorption profile of FKM 4 had been investigated in a previous study, and the data is shown in Fig. 5 for our purpose of detailed analysis.¹⁸ The equilibrium gas solubility and diffusivity were estimated based on a simplified Fick diffusion model:¹⁸

$$\frac{S_t}{S_e} = 1 - \frac{8}{\pi^2} e^{-\frac{\pi^2 D t}{l^2}} \quad \text{Equation 3}$$

where D is the diffusion coefficient, l is the thickness of the sample, t is the time, S_t is the solubility at time t , and S_e is the solubility under equilibrium condition.

Fig. 6 shows the effect of temperature (T) on equilibrium solubility (S) when pressure is 3,000 kPa. The data could be fitted into Equation 4, which indicates that the solubility decreases with an increase in temperature. Based on this equation, CO₂ solubility at 121°C under 3,000 kPa could be estimated as 16.25 mg CO₂/g FKM.

$$S = e^{(1714.1/T - 1.5607)} \quad \text{Equation 4}$$

Fig. 7 illustrates the dependence of pressure on CO₂ solubility at 50°C. The inset shows the effect of the pressure on the solubility in the low-pressure region

or in the measurement pressure region. The relationship between the pressure and the solubility can be described as Equation 5:

$$S = 0.0124P + 2.0327 \quad \text{Equation 5}$$

According to Equations 4 and 5, the solubility of FKM 4 at 70°C and 10.3 MPa could be estimated as 97.7 mg CO₂/g FKM. Since the pressure (10.3 MPa) and temperature (70°C) are still within or close to the experimental data range shown in Fig. 5, the estimated result could be considered reasonable.

Since few literature reports could be found on CO₂ solubility in polymers at very high pressure, such as close to 100 MPa, it might be challenging to simply assume that the CO₂ solubility at 100.3 MPa follows the same trend as Equation 5. Briscoe et al found that CO₂ solubility showed a linear increase relationship with pressure up to 40 MPa at 47°C in nitrile rubber, and the linear relationship did not show any divergent trend at 40 MPa; the experiment was stopped at 40 MPa due to the limitation of the experimental setup.²³ However, the swelling effect of CO₂ under very high pressure was reported many years ago.²⁴

The high solubility of gases in elastomers should lead to high swelling. This effect is similar to elastomers exposed to good solvents. Therefore, swelling in high-pressure CO₂ should have a linear dependence with CO₂ solubility, and this was confirmed by our results in Fig. 4. However, the swelling could not be infinity due to the crosslink nature of elastomers, which is different from thermoplastics in good solvents, which could be completely dissolved. So the swelling of elastomers in good solvents or

Fig. 4: The pressure dependence of swelling (A) and solubility (B) of FKM 1, FKM 2 and FKM 3 at 70°C.

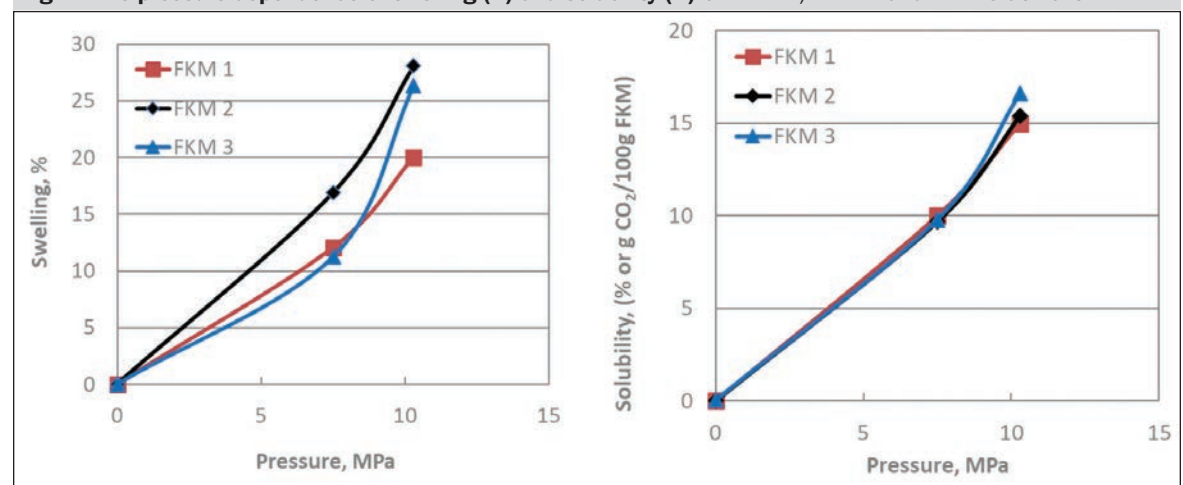
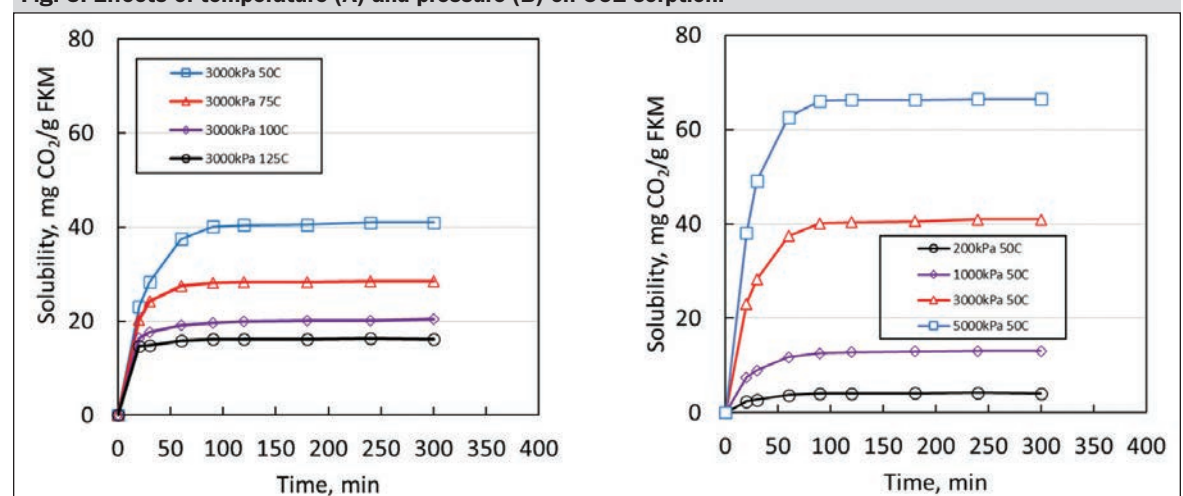


Fig. 5: Effects of temperature (A) and pressure (B) on CO₂ sorption.



Technical

high-solubility gases should have certain limitations. After that, the swelling curve will reach a plateau value.

It has also been found that the swelling of Kalrez 1060 and Aflas (Seals Eastern 7182) linearly increased with CO₂ pressure up to 28 MPa at 100°C. The experiment was stopped at 28 MPa due to equipment limitations. At around 28 MPa, both materials have around 18 percent volume swelling at 100°C. Generally, elastomers could reach more than 50 percent volume swelling in good solvent or 90 percent weight swelling under high-pressure CO₂.²³ So, it is reasonable that the FKM will have an around 40 to 50 vol percent swelling or below 50 percent weight swelling at around 100 MPa and 121°C. Therefore, the estimated solubility based on **Equations 4 and 5** is around 486 mg/g FKM at 100.3 MPa and 121°C.

Effect of FKM type and glass transition temperature on CO₂ solubility

Fig. 8 illustrates the effect of T_g on CO₂ solubility of different FKM at 70°C and 10.3 MPa. The solubility of FKM 5 was estimated based on literature data.¹⁹ FKM 2, FKM 3 and FKM 4 all belong to type 3 FKM. The CO₂ solubility decreased with the increase of glass transition temperatures. It is well known that a larger free volume leads to a lower glass transition temperature of the polymer. This revealing that the CO₂ solubility might be related to the free volume in the elastomers, and a higher free volume could lead to a higher CO₂ solubility.

The types of FKM also affect the CO₂ solubility significantly. For instance, FKM 5, a type 6 FKM, has higher CO₂ solubility than FKM 4, even though it has a much higher T_g. Different types of FKM should have different chemical compatibility with CO₂ molecules, and therefore, our experimental results indicated that the CO₂ solubility is influenced by both the chemical compatibility between elastomer molecular chain and CO₂ molecules and the free volume in elastomers.

Effect of pressure and temperature on CO₂ diffusivity in FKM 4

Fig. 9 illustrates the temperature dependence of diffusivity (D) at 3,000 kPa. The data was obtained from the fitting results of **Fig. 5** using **Equation 3**. The relationship between temperature and diffusivity could be expressed by an Arrhenius equation, as shown in **Equation 6**. This reveals that the diffusivity increases with the increase of temperature. The diffusivity of CO₂ in FKM 4 at 121°C could be estimated as 1.00 × 10⁻⁵ cm²/s at 3,000 kPa.

$$D = e^{(-1574.2/T + 6.3007)} \quad \text{Equation 6}$$

Fig. 10 illustrates the pressure dependence of CO₂ diffusivity over a very broad pressure range. The inset illustrates the relationship between pressure and solubility when pressure is below 5 MPa (**Equation 7**):

$$D = 0.0002P + 3.5625 \quad \text{Equation 7}$$

$$D = D_0 e^{-b(P-P_0)} \quad \text{Equation 8}$$

$$D = D_0 e^{aC(1-\frac{P_0}{P})} e^{\gamma P(1-\frac{P_0}{P})} \quad \text{Equation 9}$$

The pressure dependence of diffusivity in a wide pressure range could be complicated for FKM 4 because the measured CO₂ diffusivity in this study was conducted under 5-MPa pressure; this is far lower than the pressure used in the API fixture test in the next section, which is more than 100 MPa. The pressure dependence of CO₂ diffusivity has been investigated in literature.^{23,25}

The pressure dependence of CO₂ diffusivity in hydrocarbon was found to follow a relationship described in **Equation 8** at pressure up to 69 MPa, where D₀ is the diffusivity at a pressure equal to P₀ (0.1 MPa), and b is a fitted parameter. However, in this case, the solubility of CO₂ was always kept as a constant

value at 0.5 MPa at each measured temperature.²⁵ The estimated b = 0.0062 MPa⁻¹, corresponding to an average relative reduction of 35 percent between pressure of 0.1 to 69 MPa.

This indicated that the pressure only has a minor effect on diffusivity even at a very large pressure range under a constant CO₂ concentration (or solubility). However, the CO₂ solubility should play an important role on its diffusivity. With the solubility increase, the diffusivity should also change. Briscoe et al reported that the effect of CO₂ solubility and pressure on its diffusivity in nitrile rubbers could be expressed as **Equation 9**, where D₀ is the diffusivity estimated by a simple Fick case, and a, β, γ and δ are fitted parameters.

Table 2 lists the estimated parameters for **Equation 9** for the diffusivity of CO₂ in different nitrile rubbers under a pressure below 25 MPa.²³ The positive a value and negative β value reveal

that the CO₂ concentration or solubility positively affects the diffusivity, while the negative γ value and positive δ value reveal that the pressure has a negative effect on diffusivity. A much higher a value than γ value indicates that the increase of CO₂ solubility has a much higher effect on the increase of the diffusivity than the decrease of the diffusivity due to the increase in pressure.

According to the above discussion, the diffusivity of CO₂ in FKM 4 could be estimated in three cases:

Case I: D is only dependent on pressure, which is estimated by **Equation 7**. Based on this, the diffusivity at 121°C and 100.3 MPa could be estimated as 5.49 × 10⁻⁵ cm²/s.

Case II: D keeps a constant value after the measurement pressure (5 MPa) because of the opposite effect of solubility and pressure on diffusivity. The diffusivity could be estimated as 1.15 × 10⁻⁵ cm²/s at 121°C and 5 MPa in this case.

Case III: D follows a relationship similar to **Equation 9**, in which the diffusivity should be fall between Case I and Case II.

CO₂ permeability and the challenge of the API Spec 6A fixture test

In the API Spec 6A fixture test using a standard FF/HH test medium, the test gas is a mixture

of 80 vol percent CO₂, 10 vol percent H₂S, and 10 vol percent CH₄. The gas phase was pressurized to ~111 MPa at 121°C. According to the 20th edition of API Spec 6A Annex F, the pressure reduction during 160-hour holding shall remain within 5 percent of the test pressure or within 3.45 MPa (500 psi), whichever is less, during the hold period. Even in the new version of API Spec 6A (21st edition), such a requirement is also applied during a 1-hour pressure hold.

The pressure reduction could come from seal leakage or simply due to the permeability of the gases through the elastomer seal. Therefore, under such high pressure, the diffusivity and solubility of the test gases in elastomers play a critical and important role for the success of the test. Among three test gases, CH₄ has the lowest solubility and diffusivity in elastomers, and its solubility and diffusivity could be more than 10 times less than CO₂ in polymers.²⁶

The H₂S could have a high solubility in elastomers due to its high swelling to many elastomers.²⁴ However, its permeability in FKM should be much lower than that of CO₂ due to the polarity of the molecule, which could result in a stronger interaction with the FKM molecular chain than that of CO₂. More-

See CO₂, page 18

Fig. 6: Effect of temperature (T) on equilibrium solubility (S) at 3000 kPa.

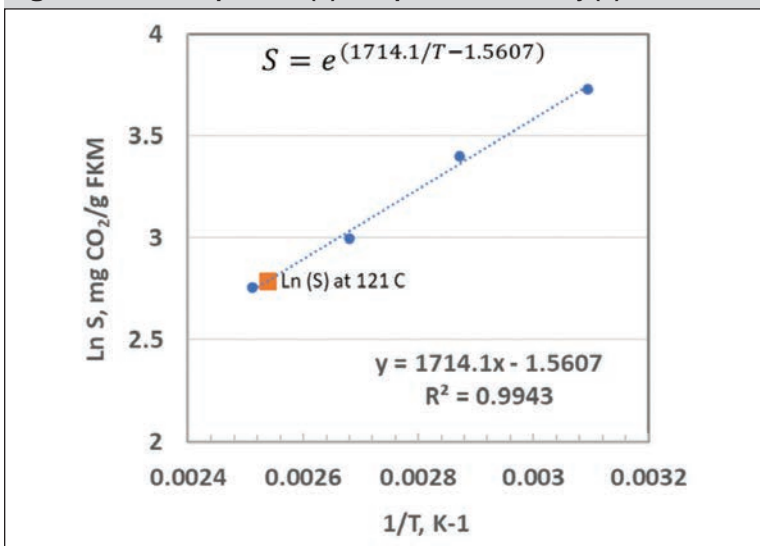


Fig. 7: Effect of pressure (P) on equilibrium solubility (S) at 50°C.

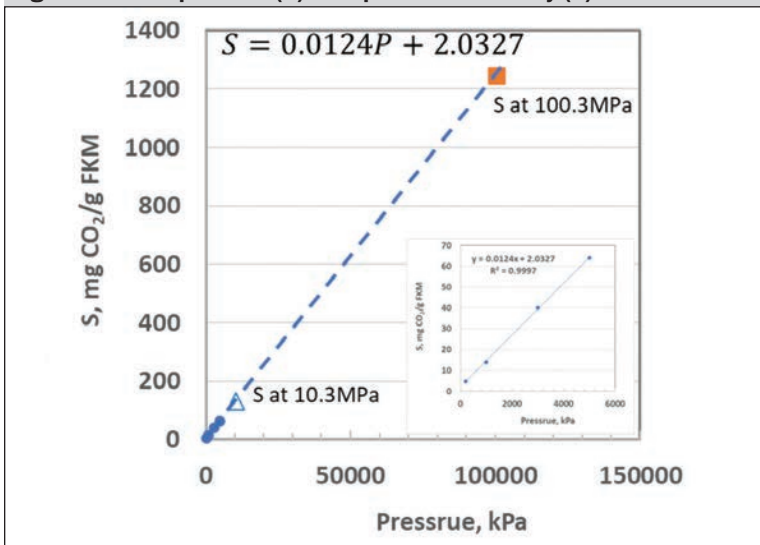


Fig. 8: Influence of Tg of FKM and FKM types on CO₂ solubility.

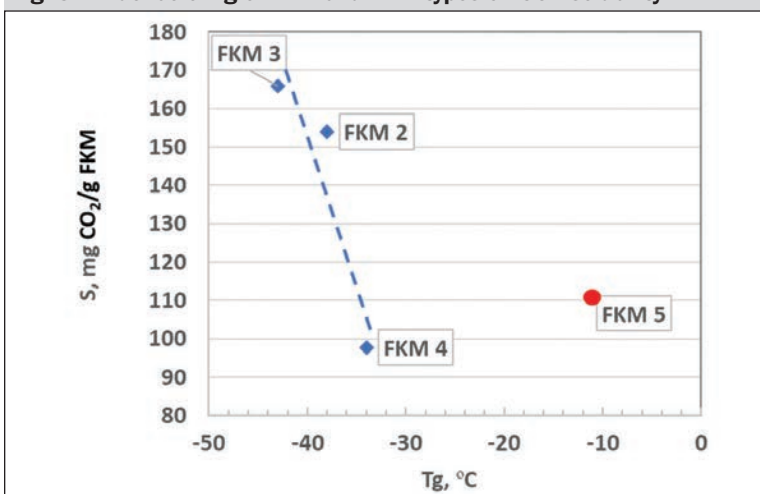


Fig. 9: Effect of temperature (T) on diffusivity (D) at 3000 kPa.

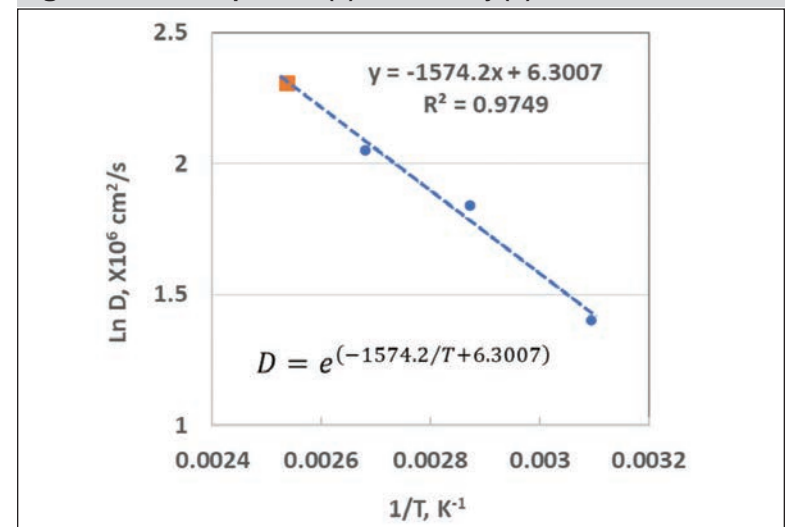
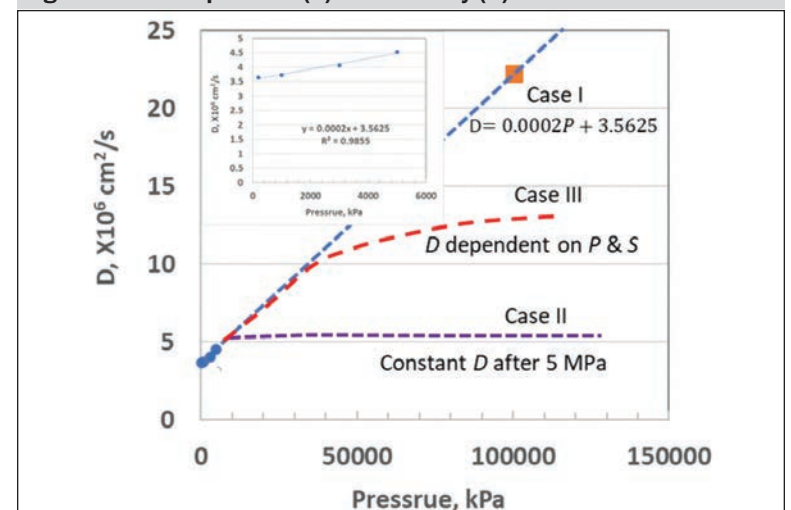


Table 3: Estimated parameters for Equation 9 for diffusivity of CO₂ in different nitrile rubbers.²³

	α	β	Γ	δ
Nitrile A	0.87146	-0.01466	-0.074053	0.009076
Nitrile B	0.28768	-0.005714	-0.133212	0.0023214

Fig. 10: Effect of pressure (P) on diffusivity (D) at 50°C.



CO₂

Continued from page 17

over, the concentrations of H₂S and CH₄ are far less than the CO₂ content in this fixture test. Hence, in this study, we only consider the effect of CO₂ permeability on pressure decrease during the 160-hour pressure holding in the fixture test.

Fig. 11 illustrates the cross section of an S-seal in the gland and the CO₂ gas permeates through the S-seal from the pressurization side to the other side.

Since the system pressure was stabilized at least 10 hours under high pressure and high temperature before the start of the 160-hour pressure holding in the fixture test, the permeability of the gas through the seal could be considered in a steady state. In a steady state, the gas permeating through a seal could be described by Fick's law of diffusion of a gas across a membrane (or an elastomer seal):²⁷

$$Q = PA(P_1 - P_2) / L \quad \text{Equation 10}$$

where, P ($= D \times S$) is permeation coefficient of the seal, which is equal to the gas solubility multiplied by the gas diffusivity in the elastomer seal; A is the surface area available for diffusion; $P_1 - P_2$ is the pressure difference (or partial pressure) of the gas across the seal; and L is the distance over which diffusion must take place, corresponding to the thickness of the S-seal in the axial direction.

$$Q = kPA(P_1 - P_2) / L \quad \text{Equation 11}$$

Fig. 12 illustrates the measured and the estimated pressure during 160-hour holding in the API fixture test.

Through use of **Equation 10**, the estimated pressure decrease could be obtained through two different CO₂ diffusivity scenarios (Case I and Case II). Under the fixture test conditions, the CO₂ was in high-temperature

supercritical state, and the pressure-temperature-volume behavior still satisfies with the ideal gas equation, but with a different gas constant (R). The pressure and temperature dependence of R for CO₂ could also be estimated from the literature.²⁸

At 100 MPa and 121°C, R could be estimated as 11.6 J/(mol.K), which is larger than at standard temperature and pressure (STP) condition (8.31 J/(mol.K)). The calculated results indicated that the estimated pressure decrease for both Case I and Case II is significantly faster than the measured data. This indicates that the pressure decrease estimated from all three cases of CO₂ diffusivity (Case I, Case II and Case III) is significantly faster than the measured data. **Equation 10** should be modified to better match the measured results.

Equation 11 was modified from **Equation 10** with a parameter k . When parameter k equals 0.05, the estimated pressure decrease based on pressure-dependent D (Case I) agrees well with the measured data. These results indicated that the permeability (P) or surface area available for diffusion (A) should be much smaller than the values used in the calculation.

The surface area available for diffusion (A) could be much smaller than expected due to the swelling of the elastomer seal under high pressure and high temperature CO₂, which could lead to a very large volume fill (close to 100 percent volume fill) of the seal in the gland and the diffusion surface area is reduced to the extrusion gap area only. Based on the seal mechanical design, the diffusion surface area could drop around 95 percent. Therefore, probably, the solubility and diffusivity of CO₂ in FKM at around 100 MPa might still hold similar relationships as these obtained below 5 MPa.

During the fixture test, the ratio of fixture volume to seal volume is critically important. A relatively larger fixture volume could hold more test gases and therefore lead to less pressure reduction during pressure holding under the same leakage or permeation conditions. Many oil field test standards, such as ISO 23936-1 and -2 and API RP 6J 2nd edition, have specific requirements for this ratio. Generally, the ratio should be more than 10 or 25 in the aging test of

an elastomer seal. However, API Spec 6A does not have such requirements for this ratio, and this could also bring challenges to pressure holding.

Fig. 13 illustrates the estimated pressure profile during API fixture test with the ratios of 10 and 25 by using **Equation 11** and considering a pressure-dependent D (Case I) and with k equal to 0.05. Compared with the measured pressure, if the ratio of fixture volume to seal volume increased to 10 or 25, the pressure reduction could be significantly lower. So a large ratio of fixture volume to seal volume benefits the pressure holding during API fixture testing, while a small ratio could lead to challenges on this pressure holding.

Conclusions

The solubility and diffusivity of CO₂ in different FKM elastomers were precisely measured using the gravimetric method and the Rubotherm approach at medium to low pressures under various temperatures. The solubility and diffusivity of CO₂ in elastomers at extreme high pressure (more than 100MPa) and elevated temperatures were estimated based on experimental data and theoretical calculations. The types and compositions of FKM significantly affect the CO₂ solubility and diffusivity. For type 3 FKM, the solubility increased with the decrease in glass transition temperature.

The pressure reduction during the pressure holding of an FKM seal under a pressure more than 100 MPa in the API Spec 6A fixture test was calculated based on the above estimated CO₂ solubility and diffusivity. The calculated results indicated that the estimated pressure reduction using all three cases of diffusivity of CO₂ is significantly faster than the measurement. This is because the surface area available for diffusion (A) significantly reduced (more than 90 percent reduction) due to the swelling of the seal under high pressure CO₂. The solubility and diffusivity of CO₂ in FKM at around 100 MPa might still hold similar relationships as these obtained below 5 MPa.

The ratio of fixture volume to seal volume for API fixture test is critically important. A small ratio of fixture volume to seal volume could create challenges for the pressure holding during the API fixture testing.

Acknowledgments

The authors thank J.J. Prejean, Chris Nault, John Tuffs, Taylor Mozisek, Paul Osborne, Amnah Kudia, Steffan Cody, Amit Patil and Anthony Leonardi of SLB, and Buc Slay and Neil Mendes from Alpine Polytech for their help on the API fixture test. Thanks also to the chemical engineering departments of Ohio State University and the University of Houston for their help on CO₂ solubility/diffusivity measurements.

References

- Fogg, P.G. (1992). Solubility Data Series, Volume 50, Carbon dioxide in non-aqueous solvents at pressure less than 200KPa. Pergamon Press, Oxford, Internal Union of Pure and Applied Chemistry. <https://srdata.nist.gov/solubility/IUPAC/SDS-50/SDS-50.pdf>
- Sato, Y.; Fujiwara, K.; Takikawa, T.; Sumarno, Takishima, S.; Masuoka, H. (1999). Solubilities and diffusion coefficients of carbon dioxide and nitrogen in polypropylene, high-density polyethylene, and polystyrene under high pressures and temperatures, Fluid Phase Equilibria 162, 261–276. [https://doi.org/10.1016/S0378-3812\(99\)00217-4](https://doi.org/10.1016/S0378-3812(99)00217-4)
- Fang, Y.; Narayanan Nair, A.K.; Sun, S.; (2021). Sorption and Diffusion of Methane, Carbon Dioxide, and their Mixture in Amorphous Polyethylene at High Pressures and Temperatures, Ind. Eng. Chem. Res. 2021, 60, 20, 7,729–7,738. <https://doi.org/10.1021/acs.iecr.0c06110>
- Briscoe, B.J., Gritsis, D., Liatsis, D. (1992). The concentration and pressure dependent diffusion of carbon dioxide in nitrile rubbers. Phil. Trans. R. Soc. Lond. A. 339, 497–519. <https://www.jstor.org/stable/53995>
- Cadogan, S.P.; Mistry, B.; Wong, Y.; Maitland, G.C.; Martin, J. (2016). Trusler, Diffusion Coefficients of Carbon Dioxide in Eight Hydrocarbon Liquids at Temperatures between (298.15 and 423.15) K at Pressures up to 69 MPa, Journal of Chemical & Engineering Data, 61 (11), 3,922–3,932. DOI: 10.1021/acs.jced.6b00691
- Ansaloni, L.; Alcock, B.; Peters, T.A. (2020). Effects of CO₂ on Polymeric Materials in the CO₂ transportation Chain: A Review. International Journal of Greenhouse Gas Control. 94, 2020 102930; <https://doi.org/10.1016/j.ijggc.2019.102930>.
- Paul, S.; Shepherd, R.; Woollin, P. (2012). Paper presented at Third International Forum on the Transportation of CO₂ by Pipeline, Newcastle, June 2012. TWI, Granta Park, Cambridge CB21 6AL, UK. <https://www.twi-global.com/technical-knowledge/published-papers/selection-of-materials-for-high-pressure-co2-transport>
- Li, J.; Hou, Y.; Wang, P.; Yang, B. (2019). A Review of Carbon Capture and Storage Project Investment and Operational Decision-Making Based on Bibliometrics, Energies, 12(1), 23; <https://doi.org/10.3390/en12010023>
- Vega-Cantu, Y.; Hauge, R.; Norman, L.; Billups, W.E. (2003). ZnBr₂-catalyzed chemical effects in poly (acrylonitrile-co-butadiene). Journal of Applied Polymer Science, 89, 1250–1257. <https://doi.org/10.1002/app.12220>.
- BSc, E.H. (2006). Elastomeric seals for rapid gas decompression applications in high pressure services HSE. RESEARCH

REPORT 485, BHR Group Limited. <https://docplayer.net/20821693-Research-report-485-elastomeric-seals-for-rapid-gas-decompression-applications-in-high-pressure-services-hse.html>.

- Maxwell, A.S.; Roberts, S.J. (2008). Review of Data on Gas Migration through Polymer Encapsulants. Report to NDA —Radioactive Waste Management Directorate. SERCO/TAS/000500/001 —Issue 2. <https://www.scribd.com/document/519915797/Review-of-Data-on-Gas-Migration-Through-Polymer-Encapsulants>
- Briscoe, B.J.; Zakaria, S. (1990). Gas-induced damage in elastomeric composites. Journal of Materials Science, 25, 3017–3023. <https://doi.org/10.1007/BF00584920>
- Embury, P. (2004). High-pressure gas testing of elastomer seals and a practical approach to designing for explosive decompression service. Sealing Technology, 6. DOI: 10.1016/S1350-4789(04)00231-4
- Brandrup, J.; Immergut, E.H.; Grulke, E.A. (2009). Polymer Handbook, Fourth Edition, John Wiley & Sons. http://nguyen.hong.hai.free.fr/EBOOKS/SCIENCE%20AND%20ENGINEERING/MECANIQUE/MATERIAUX/COMPOSITES/Polymer_Handbook/66286_fm.pdf
- Jung, J.K.; Kim, I.G.; Kim, K.T.; Ryu, K.S.; Chung, K.S. (2021). Evaluation techniques of hydrogen permeation in sealing rubber materials. Polymer Testing, 93, 107016. <https://doi.org/10.1016/j.polymer-testing.2020.107016>
- Chen, X.; Salem, H.A.; Zonoz, R., (2017). CO₂ solubility and diffusivity and rapid gas decompression resistance of elastomers containing CNT. Rubber Chem. Technol. 2017, 90 (3), 562–574. <https://doi.org/10.5254/rct.17.83726>
- Chen, X.; Bartos, J.; Salem, H.; Zonoz, R. (2016). In Elastomers for high pressure low temperature HPLT sealing, Offshore Technology Conference, Houston, May 4. <https://doi.org/10.4043/27227-MS>
- Cai, M.; Surve, K.; Zolfaghari, A.; Yun, J.; Bhowmick, A.K.; Krishnamoorti, R. (2021). Sorption of Gases by Fluoroelastomers at Various Pressures and Temperatures, 200th Fall Technical Meeting of the Rubber Division, ACS Paper, Pittsburgh, PA, Oct. 4, 2021. <https://www.proceedings.com/61816.html>
- Cai, M.; Surve, K.; Zolfaghari, A.; Yun, J.; Chen, X.; Bhowmick, A.K.; Krishnamoorti, R. (2022). Effect of Pressure and Temperature on the Sorption of Gases by Fluoroelastomers, Industrial & Engineering Chemistry Research, 61, 16721–16732. <https://doi.org/10.1021/acs.iecr.2c02981>
- Cai, M.; Chen, X.; Bhowmick, A.K.; Krishnamoorti, R. (2023). Pressure Dependence of Glass Transition Temperature in Hydrogenated Nitrile Rubber. Submitted.
- Nelson, M.T., Munj, H.R., Tomasko, D.L. and Lannutti, J.J. (2012). Carbon Dioxide Infusion of Composite Electrospun Fibers for Tissue Engineering. The Journal of Supercritical Fluids, 70, 90–99. <http://dx.doi.org/10.1016/j.supflu.2012.06.007>
- Ritger, P.L.; Peppas, N.A. (1987). A simple equation for description of solute release II. Picking and anomalous release from swellable devices. Journal of Controlled Release, 5, 37–42. [https://doi.org/10.1016/0168-3659\(87\)90035-6](https://doi.org/10.1016/0168-3659(87)90035-6)
- Briscoe, B.J., Gritsis, D., Liatsis, D. (1992). The concentration and pressure dependent diffusion of carbon dioxide in nitrile rubbers. Phil. Trans. R. Soc. Lond. A. 339, 497–519. <https://www.jstor.org/stable/53995>
- Ender, D.H. (1983). Swelling of some oil field elastomers in carbon dioxide, H₂S and CH₄ at pressure to 28MPa, ACS paper 44, Fall 1983. <https://www.proceedings.com/rubber-division-american-chemical-society-acs/>
- Cadogan, S.P.; Mistry, B.; Wong, Y.; Maitland, G.C.; Trusler, J.P.M. (2016). Diffusion Coefficients of Carbon Dioxide in Eight Hydrocarbon Liquids at Temperatures between (298.15 and 423.15) K at Pressures up to 69 MPa, Journal of Chemical & Engineering Data, 61 (11), 3,922–3,932; DOI: 10.1021/acs.jced.6b00691
- Rice, D. L. (1974). DIFFUSION AND SOLUBILITY OF METHANE IN POLYPROPYLENE MELTS, Master's thesis, Georgia Institute of Technology, Aug. <https://repository.gatech.edu/server/api/core/bitstreams/6633d5c5-d30c-41c0-a71f-76604d65749f/content>
- Amerongen, G.J. Van. (1964). Diffusion in Elastomers, Rubber Chem. Technol. 37, 1,065, <https://doi.org/10.5254/1.3540396>
- Engineering ToolBox, (2018). Carbon dioxide—Density and Specific Weight vs. Temperature and Pressure. [online] Available at: https://www.engineeringtoolbox.com/carbon-dioxide-density-specific-weight-temperature-pressure-d_2018.html

Fig. 11: Gas permeates through an S-seal.

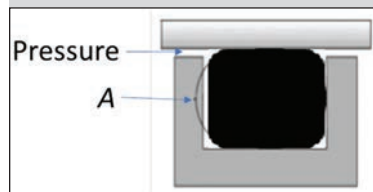


Fig. 12: The measured and estimated pressure during 160-hour holding in API fixture test.

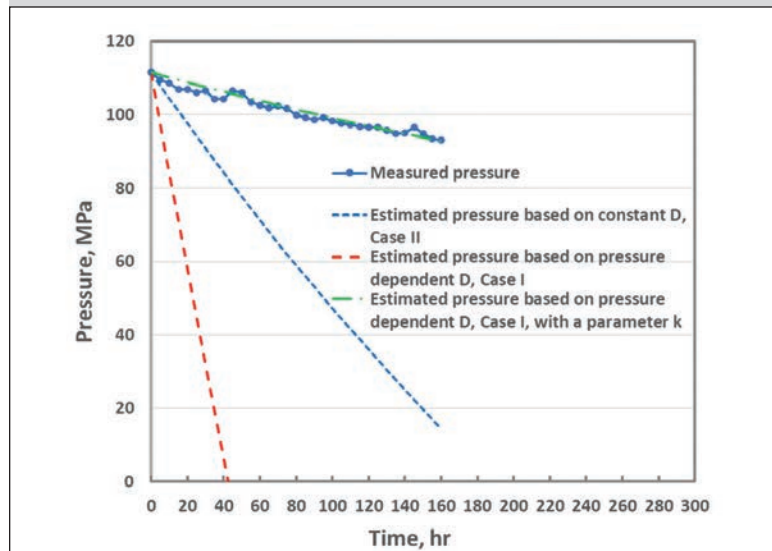


Fig. 13: Estimated pressure profile during the API fixture test with different ratios of fixture volume to seal volume.

