SE LING HIGH PRESSURES UNDER SOUR CONDITIONS

ABSTRACT

Sealing high pressure gases with elastomers is a problem as elastomers are
essentially a supercondensed gas. The primary interactions (type of gas,
heat, pressure) and secondary interactions (water, inhibitors, etc.) that
lead to seal failures are reviewed and discussed.

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NOMENCLATURE

C   concentration (Henry's law)

D   diffusion, diffusivity

E_v energy of vaporization

     EPDM,   ratio 2E/lP (Table II)

     FKM-1,   ratio 1TFE/1P (AFLAS®)

     FKM-2,   ratio 3.5 VF_2/1HFP(FLUOREL®, VITON®)

     FKM-3,   ratio 1.8 VF_2/1.2HFP/lTFE(FLUOREL®, VITON®

     FKM-4,   ratio 1.4 VF_2/1.3HFP/1TFE(FLUOREL®, VITON®

     FFKM,   ratio 2TFE/1PMVE (KALREZ®)

H_v heat of vaporization

P   permeability or permeation coefficient

P_c critical pressure

S   solubility of solubility coefficient

T   temperature - kelvin

T_c critical temperature

V   molar volume

V_c critical volume

δ solubility parameter

μ dipole moment value

ρ density

SUBSCRIPTS

C   critical value (thermodynamic)

d   dispersion component of solubility parameter

h   polar component of solubility parameter

p   dipole component of solubility parameter

r   reduced value (actual value : critical point value)

INTRODUCTION

Primary Environment

     Deep drilling in Mississippi basin and western Canadian
fields is uncovering hot, high-pressure natural gas fields
containing high percentages of both hydrogen sulfide (H_2S) and
carbon dioxide (CO_2). The sour gas production conditions (1),
100 MPa pressure ($\cong$15,000 psi) at temperatures as high as 238°C
(460°F), create a difficult environment for elastomeric seals.
The high temperatures indicate that the gases are in their
supercritical state (Table 1).

TABLE 1

Physical Properties - Gases

	CH_4	CO_2	H_2S
Critical temperature-T_c (^oK)	190.1	304.2	373.6
Critical pressure-P_c (MPa)	4.64	7.38	9.01
Critical volume-V_c (dm^3/kg)	6.153	2.137	2.867
Critical density-P_o (kg/dm^3)	0.163	0.468	0.349

The high pressure raises the gas density, and this causes the gases to have extraordinary solvent power (2,3,4,5). The totally dissimilar chemical and molecular aspects of the three gases create a "mixed solvent system" which is very difficult to seal.

Secondary Environment

The inevitable presence of water makes the CO_2 and H_2S very acidic and therefore necessitates large scale use of inhibitors to prevent corrosion. Oil soluble (film forming) amines create a persistent liquid hydrocarbon environment that can cause pronounced permanent swelling of various elastomers. Low molecular weight alcohols may also be injected to prevent freezing (clathrates). Equilibrium shifts of pressure or temperature can subject the seals to potential explosive decompression.

These primary or secondary environments or their combination can lead to seal failure through physical change or time-dependent chemical modification.

The various potential failure mechanisms are briefly reviewed below, on the basis of relatively limited knowledge.

DISCUSSION

Critical Phenomena

The critical temperature T_c of a gas is the temperature above which the gas cannot be liquefied no matter how high the pressure.

The critical pressure P_c is the lowest pressure at which a gas liquefies at its critical temperature.

The critical molar volume V_c is the volume of one mole at the critical pressure.

The critical pressure, critical molar volume, and critical temperature are the values of pressure, molar volume, and thermodynamic temperature at which the densities of coexisting liquid and gaseous phases just became identical. Figure 1 is a schematic pressure-temperature (P-T) diagram illustrating the location of the supercritical fluid region.
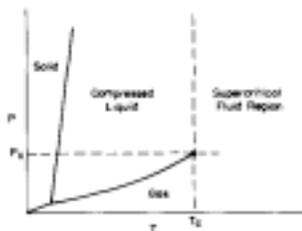
Fig.1 Gas Pressure-Temperature Phase Diagram

Gas Thermodynamic Properties

The key thermodynamic properties for methane, carbon dioxide, and hydrogen sulfide are detailed in Table 1. Methane, a simple hydrocarbon, has the least solubility in the elastomers under discussion. This is verified by its solubility parameter. The minimum interaction is due to both the molecular

symmetry, which offers no opportunity for either a permanent dipole moment or hydrogen bonding attractions, and the minimum density it reaches under high pressure. Carbon dioxide has both a small permanent dipole and an uneven electric charge distribution, creating the potential for multiple types of associations, including strong hydrogen bonding. Hydrogen sulfide is an unsymmetrical molecule and therefore has a permanent dipole as well as active hydrogens available for hydrogen bonding. For more detailed molecular descriptions of the gases, see references (6,7).

Elastomer Considerations

Three elastomers are under current consideration for use as sealing components. The rationale for their usage is briefly outlined:

Ethylene-propylene terpolymer (EPDM). DOE sponsored investigations (8) with associated publicity have created considerable interest. Although these polymers are not oil resistant, they undergo little interaction with methane, even at high pressures, because methane's maximum gas density values are relatively low.

Tetrafluoroethylene-propylene copolymers (FKM). AFLAS® , a half fluorinated elastomer, has greater heat resistance than EPDM. Oil resistance is imparted by the polar tetrafluoroethylene component. Although the hydrogen-fluorine ratio is about 1/1, these polymers have a minimal tendency for dehydrofluorination due to heat or a basic (high pH) environment.

Tetrafluorethylene-perfluorovinyl methyl ether (FFKM). KALREZ® , a totally fluorinated elastomer, has had good acceptance in sour crude service. It has the best overall heat and fluid resistance of any elastomer currently available. The difficulty in molding large sections coupled with high cost has limited sealing designs to those utilizing O-rings and V-rings.

Other Elastomers

Hydrofluorocarbon elastomers containing vinylidene fluoride (VF_2) monomers (FLUOREL® , VITON®) have an inherent tendency to dehydrofluorinate, yielding hydrogen fluoride. The reaction is initiated by heat and basic environments. VF_2 or 1,1-difluoroethylene is technically a geminal difluoride, and the fluorine is readily eliminated by a base. This is essentially the mechanism utilized to create the original cure site to crosslink such fluoroelastomers.

Hydrogenated nitrile rubber. HNBR is essentially an ethylene-acrylonitrile copolymer. Reacting the basic nitrile (NBR) elastomer in solution with hydrogen eliminates most of the highly reactive double bonds in the butadiene backbone segments, converting them into ethylene units. Preliminary data on hydrogen sulfide gas mixtures appear promising but should be verified. The possibility of hydrogen sulfide reacting through the acrylonitrile-cyano groups, as proposed by Pfisterer et al. (9), should be considered.

Table 2 and Figure 2 provide simplified reviews of fluorine-containing elastomers and applications for which they should be considered serviceable. Table 2 shows that all elastomers under consideration are polymerized from gaseous monomers. Thus, elastomers can be simplistically considered as being essentially

supercondensed gases or liquids.

TABLE 2

Elastomer Monomers

Monomer Description

Substituted[1]	Alkene
(non)	ethylene-E
	propylene-P
(partial)	vinylidene fluoride-VF$_2$
(fully)	tetrafluoroethylene-TFE
	hexafluoropropylene-HFP
	perfluoromethyl vinyl ether-PMVE

(1)   Monomers are substituted if one or more hydrogen
   are replaced with another element.
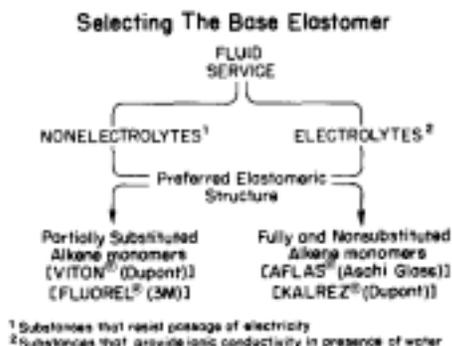
Fig. 2 Elastomer Selection

Gas-Elastomer Interactions

    Reid et al. (10) note that gas-liquid equilibrium
calculations at high pressures are more difficult
than those at low and moderate pressures
because of
    1. Lack of information on actual molar volume.
    2. Complexity of the equations needed to calculate
       the vapor-phase fugacity coefficient.
    3. Supercritical components.
    4. Little understood supercritical phenomena
       such as retrograde condensation.
    Fortuitously, however, the supercritical gases have
been incorporated into high pressure gas chromatography.
The use of high pressure gas (200 MPa) as a solvent in
macromolecular separations has developed an additional
modest information base for gas-elastomer interactions
(2,3,4,5), which has been drawn on for this paper.
Solubility Parameters
    The solubility parameter concept as summarized by
Hansen and Beerbower (11) is basic to any discussion of
elastomer-gas interactions. Hildebrand and Scott (12)
designated the energy of vaporization per cubic
centimeter as the cohesive energy density (ced) and its
square root as the solubility parameter δ, thus:

$$\delta = \left(\frac{\Delta H_u - RT}{V}\right)^{1/2} = \left(\frac{\Delta E_v}{V}\right)^{1/2} = (ced)^{1/2} \qquad (1)$$

where ΔH_v and ΔE_v are the heat and energy of
vaporization respectively, and V is the molar volume.
    Hildebrand wrote a book titled "Solubility of
Non-Electrolytes" (12). He recognized that there are
specific interactions between electrolytes (polar
liquids) that are not as easily rationalized as those

between non-electrolytes (non-polar liquids). Later work
by Burrell (11) and refinements by Hansen (11) led to
commonly accepted solubility parameter concept whereby
$\Delta E = \Delta E_d + \Delta E_p + \Delta E_h$. Thus, the true energy of
vaporization of a liquid ΔE, is the sum of the
dispersion forces (common to all matter), ΔE_d , permanent
dipole forces, ΔE_p, and miscellaneous, including
hydrogen bonding, forces, AE_h. Molar volume, V, is a key
number in the solubility parameter equation. Liquids are
approximately 1000 times as dense as gases at standard
temperature-pressure conditions (25°C, 0.1 MPa).
Compression of a gas to 100 MPa (1000 bars) creates a
high density fluid-like gas that has properties like
those of a liquid but is highly mobile, like gas.
Hirschfelder and Roseveare (13) developed an equation
applicable to gases at high pressures based on the
observation that, at high temperatures, the internal
energy (ΔE_v) of a gas at a constant temperature is a
linear function of its density, and that at sufficiently
high temperatures the molecules behave like rigid,
non-attractive spheres, which is not an illogical
assumption on the basis of the Lennard-Jones molecular
attraction-repulsion potential curves (Fig. 3).
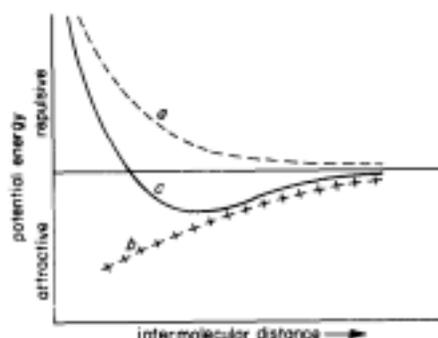
Fig.3 Lennard-Jones Potential
     (van der Waals picture)
     (a) repulsion curve
     (b) attractive curve
     (c) net resultant curve

    Czubryt et al. (5) comment that high pressure gas
solubility parameters are functions of only this
density, ρ, and are approximated by the linear
relationship

$$\delta_{gas} = \delta_{liquid}[\rho/\rho_{liquid}] . \qquad (2)$$

    Earlier work by Giddings et al. (3,4) suggests
that by using reduced properties for density (ρ_r)
(ratio of apparent density to critical density) the
following equation roughly approximates solubility
parameters of compressed gases at higher pressures:

$$\delta = 1.25 \, P_c^{1/2}[\rho_r/\rho_r \text{ liquid}] \qquad (3)$$

Summary: Gas-Elastomer Solubility Parameters
    The poor correlation between swelling effect and
theoretical calculated solubility parameters of gases
(Table 3) and elastomers (Table 4) indicates the need for
a better data base.

TABLE 3
Gas Solubility Parameters [(1)]
(kJ/mol)

	CH_4	CO_2	H_2S
dispersion-δ_d	9.2	11.1	19.4
dipole-δ_p	0	7.2	8.2
H-bonding-δ_h	0	7.2	8.2
Solubility parameter(δ)	9.2	15.1	22.6

(1) Ref. 20

TABLE 4
Elastomer [(1)] Solubility Parameters [(2)]
(kJ/mol)

	EPDM	FKM-1	FKM-2	FKM-3	FKM-4	FFKM
δ_d	16.4	15.5	15.3	14.3	13.5	12.0
δ_p	2.0	7.1	6.6	5.1	4.7	2.9
δ_h	0.6	10.0	9.2	7.	6.5	3.5
δ	16.6	19.8	19.2	16.7	15.7	12.9

(1) Refer to Appendix for description
(2) Ref. 20

Ender (1) has recently published extensive original data that should be thoroughly reviewed by competent thermodynamicists. His paper reports volume changes of AFLAS®, KALREZ® and EPDM in H_2S, 20 MPa(2900 psi), 125°C of 67%, 25%, and 61% respectively. Similar data for CO_2, 20 MPa, 100°C is 42%, 37%, and 13% respectively. His data indicate that the solubility parameter corrections for Hydrogen bonding δ_h and dipole forces δ_p are probably inappropriate. This is logical when considering physical properties of liquids and elastomers at elevated temperatures:
at 100°C, water is a gas, and elastomer lose 60% of their tensile strength. This would also provide additional verification of Hirschfelder's statement (13) that molecules behave as rigid, non-attractive spheres at high temperatures. Reid et al (10) are recommended for more intensive background.

Elastomer Compounding Variables

Non-elastomer components in the compounded elastomer, such as fillers, curatives, and processing aids, can also produce pronounced swelling effects. Fedors (14) has pointed out the substantial effects of fillers on water absorption. The unusually high swelling of AFLAS® compared with EPDM and KALREZ® in hydrogen sulfide and carbon dioxide noted by Ender (1) is probably due to the triazine curative with its strong hydrogen bonding carbonyl oxygens. This effect would be similar to the reaction between acetone and acetylene so successfully utilized in acetylene storage tanks.

Supercritical Gas Effects

The technique of using high pressure supercritical gases to solvate molecules of high molecular weight (400,000 and higher) has potentially serious complications with elastomers. Giddings (3) noted the disappearance of fluorocarbon 0-rings "except a small residue" in supercritical ammonia at 20 MPa. These were probably made of an early type of amine cured elastomer whose crosslinks hydrolyzed in the basic environment. The polymer, of well below 400,000 mw, was apparently solvated by the system.

The residue noted by Giddings consisted of the normal carbon black fillers and metal oxides typically used for compounding.

Explosive Decompression

Elastomers in contact with any gas at sufficient pressure ultimately become supersaturated. The period of time and the pressure involved are of little consequence because the failure, which is due to fracture or blistering, occurs at relatively low pressures. In a supersaturated state, the gas coexists in the elastomer as a liquid. An equilibrium shift of pressure, temperature, or concentration causes bubble formation at a flaw site in the elastomer, neatly described by Gent (15). The ability of the elastomer to perform as a pressure vessel strong enough to contain the expanding liquid depends on the simple relationship 5G/2, where G is the shear modulus of the elastomer. Figure 4, from Gent (16), shows that a 95 durometer elastomer has a shear modulus of 10 MPa.
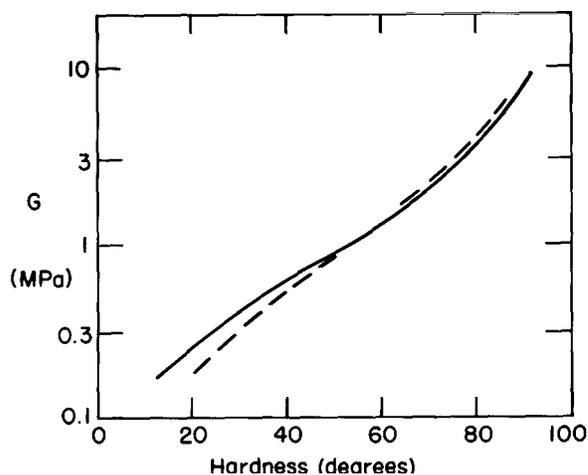
Fig.4   Shear Modulus (G) vs. Hardness
(———) Shore A scale
(---) IRHD scale
(Gent, Ref. 16)

Thus, the safe operating range of a 95 durometer seal in a high pressure gas environment is 25 MPa. Developing a multiphase network in the elastomer, as described by Hirasuna et al. (8), can more than double this value, but the formulations are relatively intractable and still have a shear modulus below the desired value of 40 MPa. A 40 MPa shear modulus in polymers is achieved only by crosslinking an elastomer to an "ebonite" stage of using plastic with 50% or more microcrystallinity, such as PTFE. In Ender's paper (1), various degrees of elastomer damage due to the explosive decompression phenomenon are noted in relation to the discussion on permeation of elastomers. Low solubility gases such as methane would tend literally to "explode" within the seal on decompression. Gases with higher solubility might first tend to undergo retrograde condensation, then migrate as a liquid through the elastomer phase, and literally "boil off" the surface as a gas, causing littledamage. Retrograde condensation, a not too well-known thermodynamic phenomenon, was a problem commonly encountered by people doing high pressure gas chromatography (2,3,4,5) until they modified their equipment.

Permeation of Elastomers

The passage of a gas through an elastomer has been reviewed by several researchers, Van Amerongen

(18) being the most quoted. The basic interactions, diffusion, permeability, and sorbtion (solubility), are categorized as transport phenomena. These have been adequately defined and quantified by Van Krevelin 19), whom we quote:

1. Diffusivity or coefficient of diffusion: D
    D is the amount of matter (m) passing per second through a unit area, under the influence of a unit gradient of concentration (the "driving force"), as expressed in the equation

    $$\frac{dm}{dt} = DA\left(\frac{dc}{dx}\right). \qquad (4)$$

    The dimension of D is m^2/s.

2. Permeability or permeation coefficient: P
    P is the amount of substance passing through a polymer film of unit thickness, per second, per unit area, and at a unit pressure difference. It is normally expressed in the following dimensions:

    $$10^{-9}m^3(STP)/m \cdot s \cdot Pa$$

    where m^3(STP) is the amount of gas in m^3 at standard temperature and vessure (273 K, 1 bar). [1 bar = 10^5 N/m = 10^5 Pa(pascal) = 0.1 MPa.]

3. Solubility or solubility coefficient: S
    S is the amount of substance (gas) per unit volume of solvent (polymer) in equilibrium with a unit partial pressure (0.1 MPa), as expressed in the equation

    $$C = Sp \text{ (Henry's law).} \qquad (5)$$

    For simple gases S is usually given in $10^{-5}m^3$ (STP per m^3 polymer per bar, its dimension therefore being

    $$10^{-5}m^3(STP)/m^3 \cdot Pa.$$

    The three quantities mentioned are interrelated by the equation

    $$P = D \cdot S. \qquad (6)$$

Elastomer-Gas Response

The gases discussed are in their supercritical state, above their critical temperature (T_C), and are therefore no longer capable of being liquefied by increased pressure. When dissolved in the elastomer, they form a true solution, i.e.; a liquid, albeit one having a high vapor pressure. The degree of solubility depends on the type of elastomer, nature of the gas, pressure, and temperature.

Since permeability (P) is considered to be the product of diffusivity (D) and solubility (S),

$$P = D \cdot S. \qquad (7)$$

D and S will be central to the discussion.

Diffusivity (D)

Gas nucleation in elastomers was addressed by Gent (15) using gases of varying solubilities (argon, nitrogen, CO_2) in nonpolar elastomers (natural rubber and SBR). Diffusion values for the three gases were quite similar for comparable elastomers, the rate of diffusion increasing with temperature. Solubility values were relatively independent of temperature. Van Krevelin (19) comments that, for the simpler

gases, the interactions are weak, with the gas molecules acting as "probes of variable size." Diffusion rates of equivalent gases in different elastomers vary widely, as reported by Van Amerongen (18).

Summary - Diffusion

a. Highly dissimilar gases (A, N_2, and CO_2 have similar diffusion rates in non polar elastomers)(Gent).

b. Identical gases have a wide range of diffusion rates in different elastomers (Van Amerongen).

c. Temperature universally increases diffusion rates.

Solubility (S)

Since all elastomers are subject to some degree of diffusion, the solubility (S) component of the equation $P = D \cdot S$ is reviewed. Beerbower (20) recently covered gas-elastomer solubilities in detail using Ostwald and Bunsen coefficients but without specifically detailing Henry's law, which has great relevance to potential gas-elastomer interactions.

Henry's Law

This law essentially states that, at any given temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas above the liquid at equilibrium. The law as formulated,

$$C = Sp$$

where c is concentration,
    S is solubility, and p is pressure,

is considered accurate at lower pressures and temperatures. Ender (1) verifies the law as applied to gas-elastomer interactions. The law indicates that doubling the gas pressure doubles the solubility. The law is also valid for gas mixtures with the partial pressure used for each gas. This indicates the absolute certainty of a strong gas-elastomer interaction with the nonpolar-polar sour gas combinations. Maron and Prutton (21), among others, have pointed out that the strict applicability of Henry's law is limited to lower pressures. At higher pressures the law becomes less exact, and the proportionality constants exhibit considerable variation. The nonlinearity is of little significance, as Ender's work points out the extensive gas-elastomer (swelling) interaction at relatively low temperatures (100 to 125°C) and pressures (30 MPa).

SUMMARY

Elastomers utilized for sealing high pressure sour gas will be subject to a predictable series of events, some more manageable than others. Chemical and thermal stability can be achieved by materials selection. Elastomer swelling, a thermodynamic response, is a function of gas pressure, elastomer type, and compounding ingredients. Explosive decompression is a strength of materials phenomenon. Elastomeric seals should be used with caution in high pressure sour gas service.