Oil and Gas Industry

Seals and Sealing - Success and Failure

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<u>Introduction</u>

To more completely appreciate the challenges of successful seals and sealing in the oil and gas industry we will briefly review the operating environment. Energy production has moved from the relatively benign "sweet" hydrocarbons to the very complex "sour" environment. The "sweet" environment, even if at higher temperatures, was straight forward in the sense that conventional nitrile and fluoroelastomer (Viton®, Fluorel®) sealing technology was adequate and predictable in service life. The "sour" environment not only occurs naturally but is also developed in low-sulfur sweet wells during secondary recovery by water flooding.

The aggressive "sour" environment is more complex for many reasons:

1. The combinations of CO_2 and H_2S with and without water creates aqueous and non-aqueous electrolytes. An understanding Lewis acid-base interactions is necessary to appreciate the problem potential.

2. Gas concentrations (partial pressures) at temperatures above critical can act as supercritical solvents. Elastomers in this environment are subject to high swells and subsequent extraction of plasticizers, low molecular weight polymers etc.

3. Explosive decompression due to pressure or temperature shifts can cause catastrophic seal rupture.

4. The deliberate introduction of acids (HCL, HF), bases (inhibitors), completion fluids (metal halides, carbonates etc.) and gases (CO_2, N_2) create another set of problems. These interactions are reasonably well understood by only a very few users.

The oilfield environment is unique, there is no other environment with similar problems so there is little technology transfer potential.

<u>Elastomer Considerations:</u> You use what works with some selections defying conventional considerations. Typical elastomers used are:

Nitrile rubber (NBR)
Hydrogenated nitrile rubber (HNBR)
Vinylidene fluoride CO and terpolymers (FKM)   Propylene-tetrafluoroethylene copolymers (FEPM)
Perfluoroelastomers (FFKM)
Ethylene-propylene terpolymers (EPDM) specifically compounded.

Seals Problems Encountered:

      a.   Explosive decompression (XDF) due to high gas pressures
      b.   Seal hardening
      c.   Chemical degradation
      d.   Excessive seal swell.

Service Conditions

The Operating Well Environment

This category has to be broadened in order to better understand the potential gas-liquid-elastomer interactions. For the purpose of this discussion we will break the well fluid category into three separate groups:

Primary: Gaseous and liquid hydrocarbons

Secondary: Carbon dioxide (CO_2), hydrogen sulfide (H_2S), brines

Tertiary: Inhibitors, solvents etc.

Thermodynamics and Elastomers

Elastomers are produced from C_2 and C_4 gases (alkenes, vinyls, dienes). They are supercondensed gases hence subject to all thermodynamic considerations, i.e.; stress (mass), strain (length), time and temperature. Since the polymerization process produces heat (exothermic reaction) the Gibbs free energy of the system is negative. (Ex: rubber burns and the flame is self-supporting). This means life is all down hill once the reaction is initiated (activation energy). Premature seal failures are often very puzzling since they appear as random events. What has actually happened is the activation energy barrier has lowered due to the effect of some random catalytic event. These catalysts can range from acid-base, organometallic, metal ions, enzymes, molecular scale zeolites to inorganic solid surfaces. One must not forget the original "iron age" catalysts were iron oxide and hydrochloric acid. Due to the bulk nature of the seal there is often a substantial time lag before excessive hardening occurs.

The applications of different elastomers in energy production has the potential for a series of interactions that are complex but definable. First, what we might consider as primary production categories:

      a.   Hydrocarbons, liquid-sweet
      b.   Hydrocarbons, liquid-sour
      c.   Hydrocarbons, gas-sweet
      d.   Hydrocarbons, gas-sour
      e.   Hydrocarbons, mixed-sweet
      f.   Hydrocarbons, mixed-sour.

We will now address additional considerations.

Pressure

1.   The effect of pressure on elastomer, gas, and liquid interactions is briefly discussed:

        a.   <u>Hydrocarbons, liquid-sweet</u>, interaction is minimal.

        b.   <u>Hydrocarbons, liquid-sour</u>, interaction can be substantial, as pressure increases, the gas densities (CO_2, H_2S) increase. Basic solubility concepts (commonly referred to as solubility parameter or S.P.) are based on the square root of the cohesive energy-<u>density</u> parameter. As the pressure increases, the gas density increases and the high density gas behaves as a liquid. This is defined by thermodynamics i.e.: partial pressure rules, the gas(es) can reach saturation becoming a liquid if temperature is less than critical temperature-T_c, or achieve super critical state if the gas is above it's T_c. If the gas is both supercritical and having an equivalent liquid density it has a powerful extractive potential. High density supercritical gases have the potential of removing plasticizers, antidegradents and lower molecular weight uncrosslinked elastomer chains creating seal shrinkage due to volume reduction. Either environment can lead to explosive decompression failures (XDF) if the elastomer is not of a sufficiently high engineering modulus. Excessive swelling of the elastomer can result since we are essentially involved with a "mixed solvent" system. CO_2 is a quadrupole molecule and H_2S is a dipole molecule - opposite extremes.

        c.   <u>Hydrocarbons, gas-sweet</u>, Pressure has no effect on methane as the molecule is too bulky to achieve a high density necessary to act as liquid hydrocarbon. It can permeate elastomers however causing explosive decompression. C_2 and higher hydrocarbons readily achieve higher densities under pressure with the gases having a swelling power equivalent to pentane-hexane at their liquid densities. Explosive decompression can also be a problem similar to "b".

        d.   <u>Hydrocarbons, gas-sour</u>, The concurrent production of sour gas i.e.: CH_4, CO_2, & H_2 S is the classic mixed solvent system. The gas molecules are categorized as an octopole, quadrupole and dipole. Simply stated this means CH_4 is a non-polar species, CO_2 is an electron-pair acceptor and H_2S is an electron-pair donor. A subsequent fact is that there is no possibility of a low-swell elastomer in the sour gas environment. What will determine the swell is that particular gas with the strongest physical (acid-base) attraction to some specific monomer creating the polymer. Degree of physical attraction will be density (created by pressure) dependent.

        e.   <u>Hydrocarbons, mixed-sweet</u>, This combination of liquids and gases offer little problems other than possible explosive decompression phenomena.

e.   Hydrocarbons, mixed-sour, This combination of hydrocarbon liquids and gas plus CO_2 and H_2S will cause problems as outlined in "b" and "e".

Temperature

2.   Since all elastomers are essentially "supercondensed gases", temperature will have a dominating effect on interactions.

Service Conditions

Well Fluids: This category has to be refined because of man-made complications such as inhibitor addition, water injection. We will discuss them briefly.

Hydrocarbons, liquid and gas-sweet: Liquid and gaseous hydrocarbons, alone or in combination, offer few unmanageable problems.

Hydrocarbons, liquid and gas-sour: The presence of CO_2 and H_2S and the inevitable presence of water set up a very aggressive corrosion potential. This corrosion problem is inhibited by the injection of film-forming corrosion inhibitors, typically long chain, nitrogen containing compounds, primary, amines. The amines have an abundance of readily available electrons which are donated to the reduction reaction thus preventing the metal from making the transition from M to M^+, leaving it open to reduction-oxidation (REDOX) reactions or corrosion potential. The complications of solubility of inhibitor in the product stream and coating the metal details are achieved by having several typical ingredients in the inhibitor package:

        Amine source (nucleophile)
        Alcohol (forms a protonated alcohol-ROH_2^+)
        Quaternary complexes (phase transfer agent)

Stimulation Fluids: These can range from fracturing fluids, acid treating, dewaxing solvents, water injection and sand control. Looking at each briefly and commenting:

a.   Fracturing Fluids - often incorporating compounds such as potassium carbonate, potassium chloride, etc. The affect of an aqueous solution of potassium chloride is minimal since it has a pH of about 7. An aqueous solution of potassium carbonate is strongly alkaline with a pH of 11.6, on the other hand. This is sufficiently basic to affect all elastomers with the exception of AFLAS® (FEPM).

b.   Acid treating - typically hydrochloric (HCL) and sometimes hydrofluoric (HF) acid solutions. The potential for chemical effect range from; acid-catalysis, promoting reactions on nitrile (NBR) and hydrogenated nitrile (HNBR) elastomers, to excessive swelling of conventionally-cured fluoroelastomers such as Viton® and Fluorel® (FKM). There is no effect on properly compounded AFLAS® (FEPM) fluoroelastomers.

c.   Dewaxing solvents - typically aromatics such as xylene. Fluoroelastomers of the FKM variety are the only low-swell elastomers, NBR, HNBR and FEPM all have high swelling potential but cause no damage to the elastomer after removal from the solvent.

d.   Water injection - typically including nonionic water-soluble surfactants. The stability of sulfates in marine sediments is a function of the REDOX potential and pH. When the REDOX potential approaches zero (7.0 pH) a widely distributed bacteria in the sea water become very active using the sulfate ion as a hydrogen acceptor yielding hydrogen sulfide (H_2S). As a gas, H_2S creates the possibility of explosive decompression in elastomers. H_2S is only marginally soluble in water and a saturated water -H_2S solution has a pH of 4.5. This low pH will create a corrosion potential in metal details necessitating the use of inhibitors. The inhibitors being electron-donors, have a very aggressive attack on Viton®/Fluorel® (FKM) elastomers. There is also a strong possibility of devulcanization of nitrile rubber (NBR) by some aliphatic amines. AFLAS® (FEPM) is relatively unaffected by inhibitors other than some minor swelling.

e.   Sand Control agents - The use of bromine and bromide complexes appears to be too short-term to affect the elastomers in contact with them. AFLAS® (FEPM) would be totally unaffected in long-term service in this environment.

Summary

To survive long-term in the high pressure/high temperature sour hydrocarbon environment the elastomer must have monomers that are non-substituted hydrocarbons or fully substituted hydrocarbons. These elastomers are:

> Perfluorocarbons: (FFKM) - Kalrez®, Chemraz®
> Hydrocarbon - fluorocarbon co,ter and tetrapolymers: AFLAS® (FEPM), VT-R
> 6279 (Dupont)

FEPM (AFLAS®) has been used successfully as packers and seals in 420° F wells since 1982. The formulations all based on 100H, the highest molecular weight available.

Trade Names®		
AFLAS®	Asahi Glass Co.	(FEPM)
CHEMRAZ®	Greene-Tweed Co.	(FFKM)
KALREZ®	Dupont Dow-LLC	(FFKM)
VT-R-6279	" " " "	

Seals Eastern Inc.
Compound Data Sheet

Compound Number: 7182B   Base Elastomer: Aflas 100H

Customer Specifications: Halliburton   ES-R-14-3, ES-R-12
Baker BPS-D202, AP900, C201
Dresser Rand 091-065
REDA MS-10-244

Average Physical Properties: Solar-Caterpillar

ASTM Test Method	Property	Max Value	Min Value
D412	Tensile Strength:	3150 psi	2700
	Ultimate Elongation:	115 %	75
	Stress at Elongation		
	(Modulus) M25:	1120 psi	
	M50:	1660 psi	1300
	M100:	2805 psi	2200
	Strain Energy/Unit Volume at 20% elong:	127 psi	
	Calculated Shear Modulus, G:	2381 psi	
	Calculated Young's Modulus, E:	7144 psi	
	E-secant from the initial slope:	6715 psi	
D624, Die B	Tear Strength:	288 psi	
D2240	Durometer Hardness:	92 Shore A	87
D297, 15.1.2	Specific Gravity:	1.57	
D395, Method B	Compression Set:		
	22 hrs @ 392 °F	23.4%	
	70 hrs @ 392 °F	32.8%	
	366 hrs @ 392 °F	45.7%	

D865	Dry Heat Aged:			
392 °F	Hours:	70	336	1000
	Change in Tensile:	-5.6 %	5.2 %	-1.1
	Change in Elongation:	-2.4 %	39.2 %	42.5
	Change in Durometer:	-3 points	+1 points	-2 points

Explosive Decompression   PASS
(Dresser-Rand 091-065)
(Solar-Caterpillar ES 2028)

D746	Brittle Point:	-40 °F
D1329	Temp. Retraction TR-10:	+36 °F
	Glass Transition:	+37 °F
	Operating Temperature	425 °F
	Shelf Life:	20 years

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