QFL5931/MPT6009 – Química Verde

Fluidos Supercríticos – Aula 2

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Fluidos Supercríticos

- Equipamentos para alta pressão
- Segurança em alta pressão

Equipamentos para experimentos com CO_2 supercrítico

Fonte de Gás Pressurizado: CO_2

- Cilindro com tubo pescador (“eductor”) para coletar a fase líquida no fundo do cilindro;
- Purgar até fase líquida chegar na bomba;
- Pressão ao redor de 55 bar;
- Cuidado com pureza!

Fonte de Gás Pressurizado: Bombas

- Bomba Seringa;
- Bomba pistão (contínua);
- Pressure Boosters

Reatores e Outros Componentes: Materiais

- Aço Inox 316 (cuidado com corrosão por stress);
- Hastelloy (para ácidos na presença de cloreto);
- Alumínio não tem resistência mecânica;
- Cuidado com temperatura! Resistência cai rapidamente com seu aumento.

Reatores e Outros Componentes: Materiais

Table 2.2 Overview of selected metal materials which are accredited for high-pressure reactors.

Material number (AISI) Symbol *New designation*	Density ($g\,ml^{-1}$)	Maximum application temperature (°C)	Surface polishing	Machinability	Tensile strength, R_m ($N\,mm^{-2}$) Yield point, $Rp_{0.2}$ ($N\,mm^{-2}$)	
1.4306 (304 L)	7.90	200	++	+	460–680 (640)	
X 12 Cr 13	**Resistant against:** nitric acid (up to high temperatures and concentrations) and many				20 °C	170
X10Cr13	organic acids, intergranular attack				100 °C	147
	Unstable against: chloride-containing media, sulfuric acid				200 °C	118
1.4429 (316 LN)	7.98	400	+	0	580–800 (680)	
X 2 CrNiMoN 17 13 3	**Resistant against:** intercrystalline corrosion (increased chemical stability)				20 °C	275
X2CrNiMoN17-13-3	**Unstable against:** seawater				200 °C	175
					300 °C	140
1.4571 (316 Ti)	7.98	400	–	+	500–700 (600)	
X 6 CrNiMoTi 17 12 2 (V4A)	**Resistant against:** most organic acids, phosphoric acid, dilute sulfuric acid, sodium				20 °C	215
X6CrNiMoTi17-12-2	hydroxide solution, ammonia, steam				100 °C	185
	Unstable against: halogen-containing media, hot alkali metal hydroxides, concentrated				200 °C	167
	nitric acid, concentrated sulfuric acid, hot hydrogen sulfide, 30% hydrogen peroxide				300 °C	145
					500 °C	120
2.4617 [7]	9.22	500	–	–	745–1000	
NiMo28 (Hastelloy B-2)	Very good resistance in reducing media, e.g. hydrochloric, sulfuric, hydrofluoric and				20 °C	407
	phosphoric acid. Well resistant against chloride-induced stress corrosion cracking				204 °C	361
	Unstable against: oxidizing compounds, ferric or cupric salts				316 °C	336
					427 °C	319

Reatores e Outros Componentes: Materiais

2.4600 [8]	9.22	700	–	–	885	
NiMo29Cr (Hastelloy B-3)	Same excellent resistance to hydrochloric acid and other strongly reducing chemicals as B-2 alloy, but with significantly better thermal stability at higher temperature, fabricability and stress corrosion cracking resistance				20 °C 204 °C 427 °C 649 °C	400 330 285 290
2.4610 [9]	8.64	550	–	–	700–900	
NiMo16Cr16Ti (Hastelloy C-4)	**High resistance to corrosion**. Virtually the same corrosion resistance as alloy C-276. Good resistance against highly oxidizing salts, pitting, stress corrosion cracking and intercrystalline corrosion. For pressure vessels with high requirements concerning durability in the range between –196 and 400 °C **Unstable against:** concentrated hydrochloric acid				20 °C 93 °C 204 °C 316 °C 427 °C 538 °C	335 301 264 247 236 205
2.4602 [10]	8,69	700	–	–	800	
NiCr21Mo14W (Hastelloy C-22)	**High resistance to corrosion**. Better overall corrosion resistance in oxidizing corrosives than C-4, C-276 and 625 alloys. Outstanding resistance to localized corrosion and excellent resistance to stress corrosion cracking				20 °C 204 °C 427 °C 760 °C	372 283 241 214
2.4819 [11]	8.89	550	–	–	700–1000	
NiMo16Cr15W (Hastelloy C-276)	**High resistance to corrosion**. Versatile, corrosion-resistant alloy. Very good resistance to reducing and mildly oxidizing corrosives. Excellent stress corrosion cracking resistance with very good resistance to localized attack **Unstable against:** alkali metal hydroxides at higher temperatures				20 °C 204 °C 316 °C 427 °C 538 °C	365 263 235 235 226
2.4675 [12]	8.50	650	–	–	740	
NiCr23Mo16Cu (Hastelloy C-2000)	**High resistance to corrosion**. Most versatile, corrosion-resistant alloy with excellent resistance to uniform corrosion in oxidizing or reducing environments. Excellent resistance to stress corrosion cracking and superior resistance to localized corrosion compared with C-276 alloy				20 °C 204 °C 427 °C 538 °C 649 °C	350 283 216 214 209

Reatores e Outros Componentes: Materiais

Material number (AISI) Symbol *New designation*	Density (g ml^{-1})	Maximum application temperature (°C)	Surface polishing	Machinability	Tensile strength, R_m (N mm^{-2})	
					Yield point, $Rp_{0.2}$ (N mm^{-2})	
2.4643 [13]	8.22	550	–	–	700	
NiCr33Mo8 (Hastelloy G-35)	**High resistance to corrosion.** Excellent resistance to corrosion in highly oxidizing media and acidic chloride environments. Outstanding corrosion resistance to oxidizing acids, alkalis, and chloride-containing media. Especially suited for oxidations in scH_2O with chloride-containing systems				20 °C 93 °C 204 °C 427 °C 649 °C	330 313 248 215 184
2.4816 [14, 15]	8.43	550	+	–	500–750	
NiCr15Fe (Inconel 600)	Very good resistance in many oxidizing and reducing media even at high temperatures **Unstable against:** strong oxidizing solutions such as hot, concentrated nitric acid, less hydroxide resistant than Inconel 625				20 °C 200 °C 427 °C 649 °C	240 230 203 183
2.4856 [11]	8.44	850	–	–	690–900	
NiCr22Mo9Nb (Inconel 625)	**Resistant against:** chloride ions, stress corrosion cracking, pitting, crevice and high-temperature corrosion, and also carburization. Durable in oxidizing media. Outstanding strength and toughness in the temperature range from cryogenic to 800 °C **Unstable against:** alkali metal hydroxides at higher temperatures				20 °C 204 °C 760 °C 871 °C 982 °C	496 429 381 241 75
3.7065 [15]	4.51	400	+	++	370–550	
Titanium (grade 4)	**Resistant against:** chloride-containing or oxidizing media. Stable against wet chlorine gas, chlorine dioxide, nitric and other acids **Unstable against:** sulfuric acid, sodium hydroxide, and (most notably) hydrofluoric acid				20 °C 205 °C 315 °C 425 °C	550 250 165 145

Materiais de Vedação

- Teflon é muito usado, mas há outros materiais com maior resistência mecânica.

Materiais de Vedação

Table 2.3 Overview of sealing materials used for high-pressure purposes [16].

Sealing material	Price[a]	Low temperature	High temperature	Compression set[b]	Wear/ abrasion[b]	
Perbunane (nitrile–butadiene rubber, NBR) Copolymer of butadiene and acrylonitrile	A	−35 °C	120 °C	2	2	
	Description: excellent resistance to petroleum-based oils and fuels, water and alcohols. Nitrile also has good resistance to acids and bases, except those with a strong oxidizing effect **Limitations:** avoid highly polar solvents (acetone, methyl ethyl ketone, etc.) and direct exposure to ozone and sunlight				scCO_2 scH_2O scNH_3 scMeOH scC_3H_8	2 5 5 5 2
Viton (fluorinated rubber, FKM or FPM) Copolymer of vinylidene fluoride and hexafluoropropylene	D	−25 °C	205 °C	1	2	
	Description: excellent resistance to petroleum products and solvents. Very good high-temperature performance **Limitations:** avoid polar solvents, amines, anhydrous ammonia, hydrazine, and hot acids				scCO_2 scH_2O scNH_3 scMeOH scC_3H_8	5 5 5 5 1
Teflon (polytetrafluoroethylene, PTFE)	D	−155 °C	230 °C	5	2	
	Description: probably the most frequently used sealing material. The gas permeability is low. Has the tendency to flow at higher temperatures (>100 °C). A variety of composite material exists which fulfill the demands for different applications. Due to the low elasticity, processes with cooling intervals are critical **Resistant against:** nearly all organic and inorganic chemicals **Unstable against:** elementary fluorine under pressure or at high temperatures, fluorohalogen compounds and alkali metal melts				scCO_2 scH_2O scNH_3 scMeOH scC_3H_8	2 5 1 4 1

(Continued)

Materiais de Vedação

Sealing material	Price[a]	Low temperature	High temperature	Compression set[b]	Wear/ abrasion[b]	
PEEK (polyether-ether-ketone)	D	−200 °C	250 °C	5	2	
	Description: not as inert as Teflon but much lower tendency to flow at higher temperatures (hardly any softening). Due to the low elasticity, processes with cooling intervals are critical **Resistant against:** most chemicals **Unstable against:** concentrated sulfuric and nitric acid, some halocarbons (e.g. dichloromethane)				$scCO_2$ scH_2O $scNH_3$ scMeOH scC_3H_8	1 5 1 2 1
Kalrez, Simriz, Chemraz, Parafluor (perfluorinated rubber) Copolymer of tetrafluoroethylene and perfluorovinyl ether.	H	Up to −20 °C	Up to 325 °C	2	2	
	Description: excellent resistance to almost all chemicals. Excellent outgassing performance in vacuum environments. Probably the best, but also the most expensive elastomer. A variety of composite materials for special applications exists **Limitations:** avoid low molecular weight, fully halogenated fluids and molten alkali metals. Especially strong oxidizing acids may cause some swelling. Helium permeability is slightly higher than that of fluoroelastomer compounds. Specific Simriz compounds provide better low-temperature performance and amine resistance				$scCO_2$ scH_2O $scNH_3$ scMeOH scC_3H_8	1 5 1 1 1
Self-energizing metal O-rings [17–19]	J	−250 °C	1100 °C	1	2	
	Description: the application of metal seals is expedient if a combination of high temperatures, high pressures, and/or swelling solvents such as ethers, halocarbons, aldehydes, and ketones are used. Their possible catalytic activity is detrimental **Design:** the seal is a spring-actuated, pressure-assisted sealing device consisting of an adapted metal (or polymer) jacket partially encapsulating a corrosion-resistant metal spring energizer. The spring forces the jacket lips against the gland walls, a process that is assisted by the system pressure				$scCO_2$ scH_2O $scNH_3$ scMeOH scC_3H_8	1 1 1 1 1

[a] A = low; J = high.
[b] 1 = Recommended; 2 = satisfactory; 3 = poor; 4 = marginal; 5 = not recommended.

Materais de Vedação

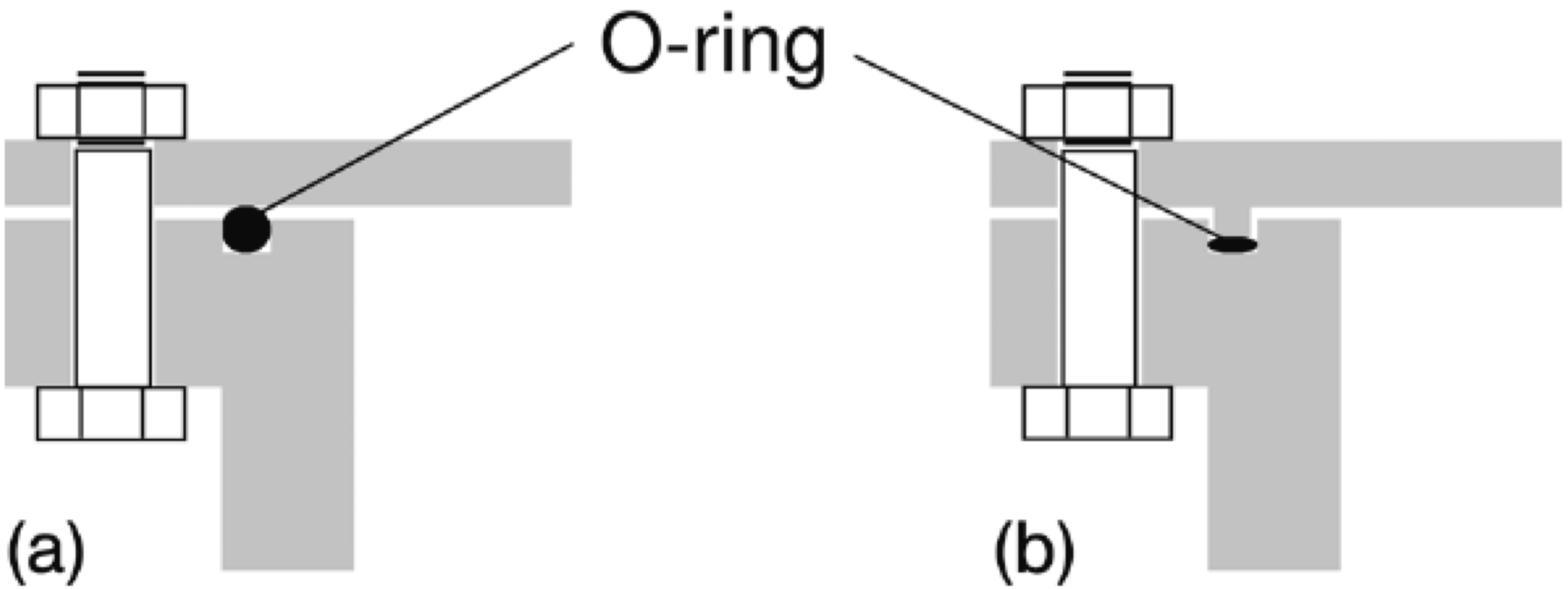
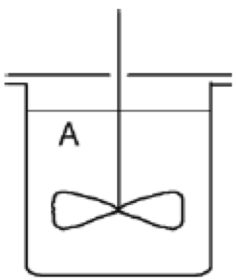


Figure 2.1 Schematic diagrams of different O-ring seal design.

Tipos de Reatores

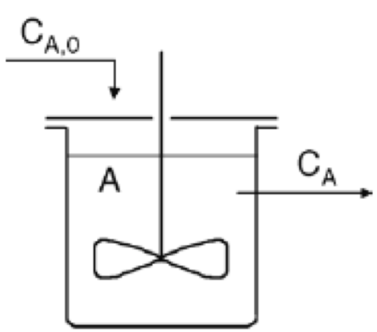
- STR = "stirred tank reactor" – batelada ou contínuo

STR



- Single- and multi-phase reactions [46]
- Useful for preliminary screening
- Easy use of *in situ* spectroscopy [28, 47, 48] and calorimetric measurements [49]

CSTR



- Homogeneous reactions
- Multiphase catalysis with a stationary, non-volatile liquid [50, 51]

Tipos de Reatores

- "Variable or fixed volume view cells" – batelada ou contínuo

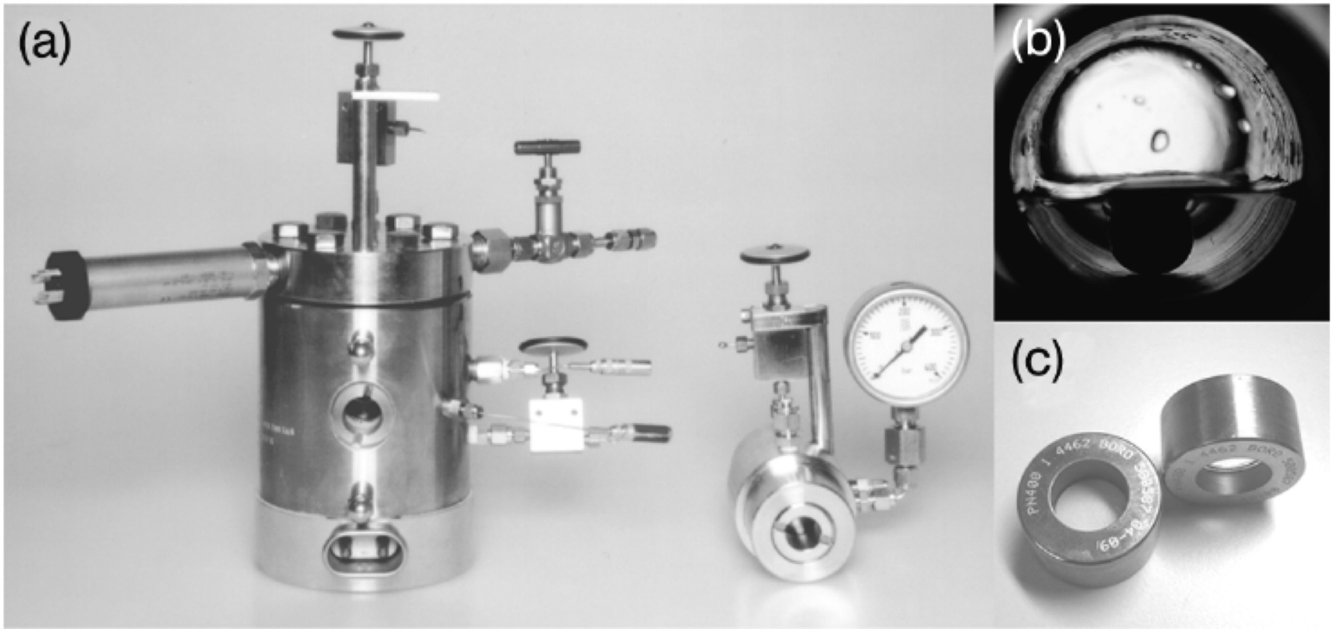


Figure 2.5 Window-equipped autoclaves (a), view through the windows of the autoclave (b), and metal fused high-pressure windows (c).

- PFR - “Plug flow reactors”

PFR

- Homogeneous reactions
- Fixed-bed technology with a homogeneous SCF-phase [38, 52, 53]

- RMN

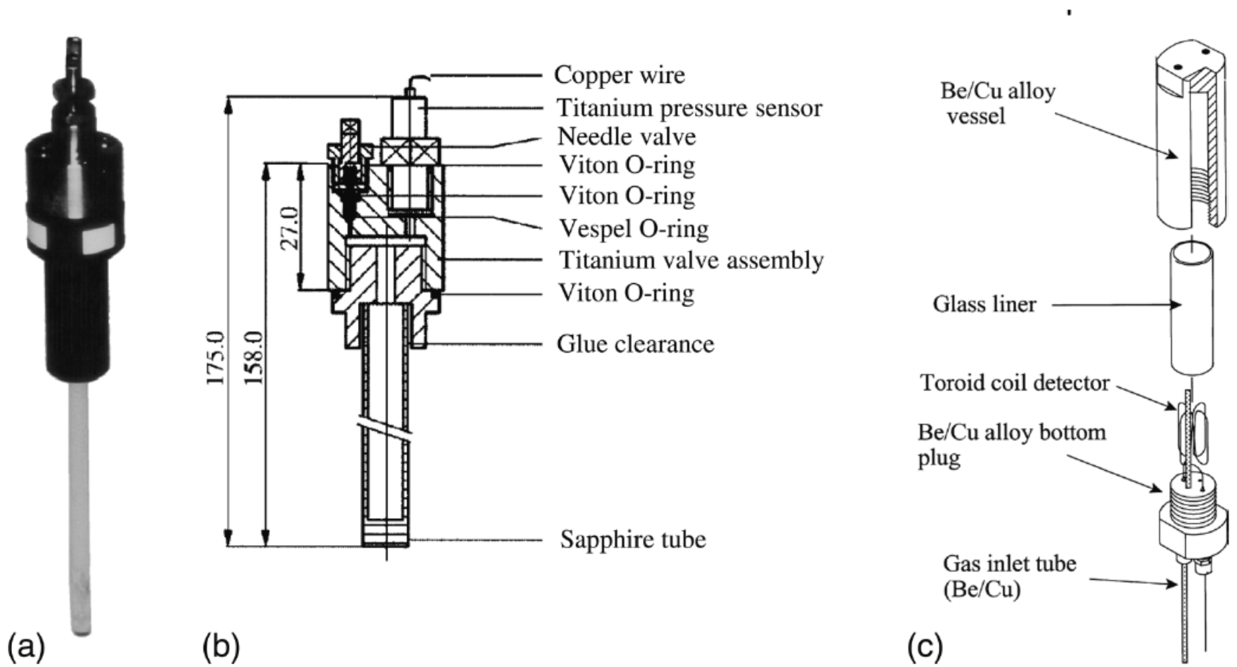


Figure 2.2 (a) Photograph and schematic diagram of an NMR high-pressure cell and (b) a diagram of an NMR high-pressure probe. (a) Reproduced with permission from [32], copyright John Wiley & Sons, Ltd. (b) Reproduced with permission from [29], copyright Elsevier.

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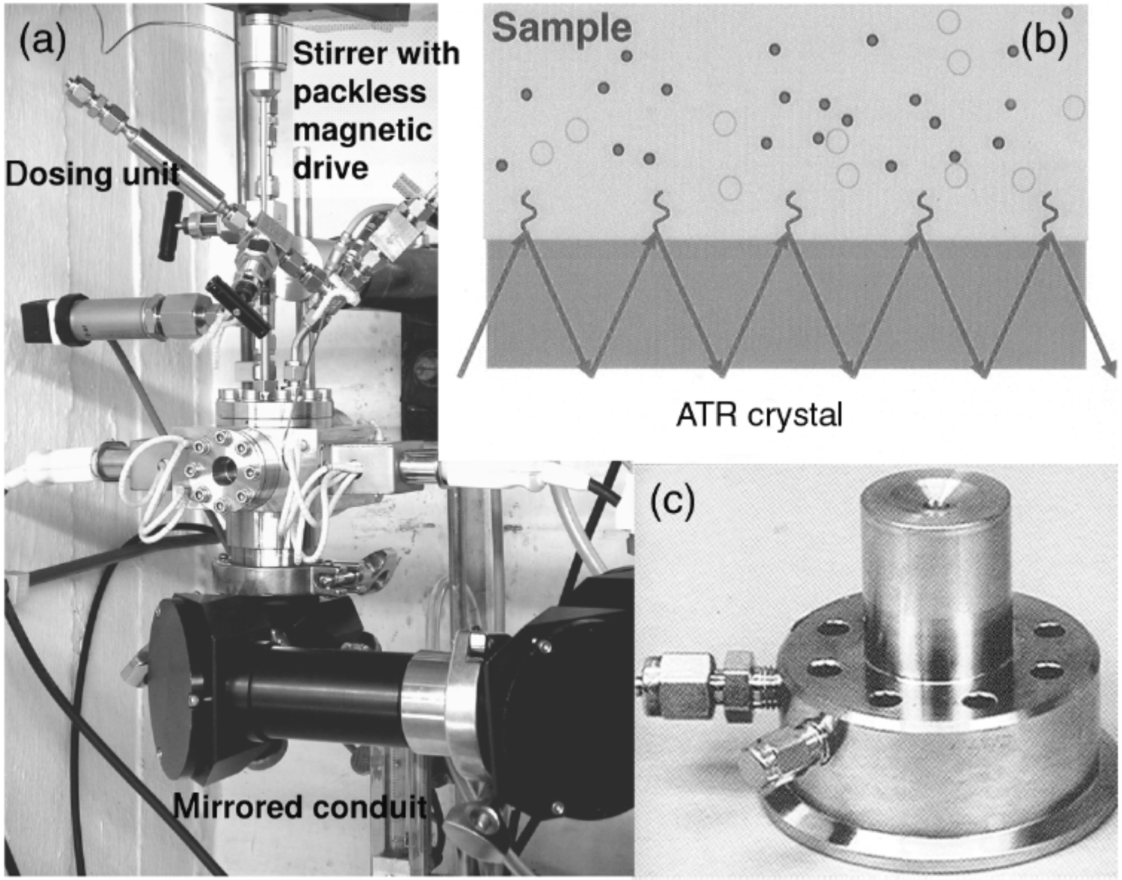


Figure 2.7 (a) Setup for high-pressure ATR–FTIR inline measurements with the ATR probe at the bottom of the reactor (a rotation of the reactor allows a measurement from the top); (b) IR beam reflection in the ATR crystal; (c) high-pressure ATR probe. Copyright Mettler-Toledo Autochem.

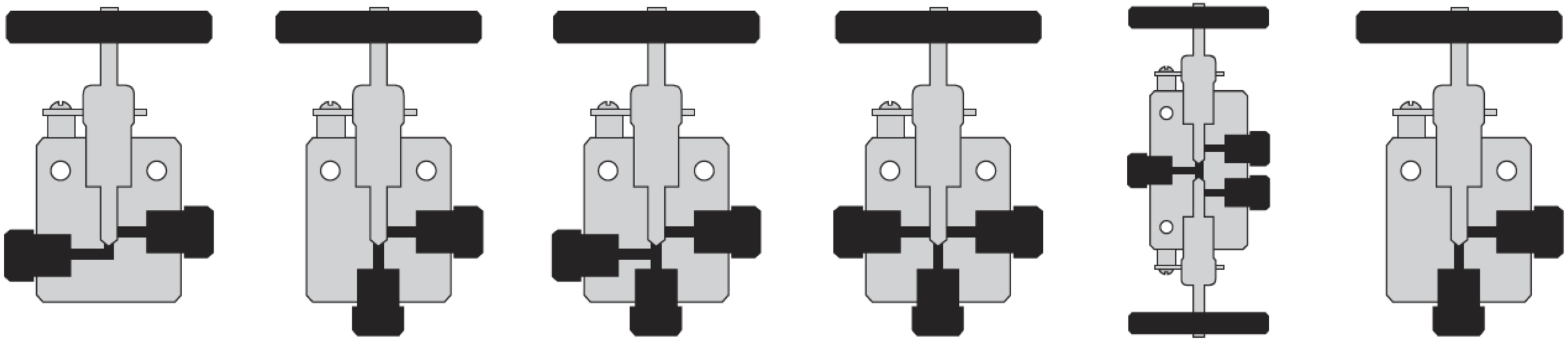
Válvulas

Table 2.5 Overview of common valves for SCF handling.

Valve type	Characteristics	Available pressure rating (MPa)
Ball valve	"On/off"	10–60
Plug valve	"On/off", simple design	5–20
Metering valve	"Flow rate adjustment"	5–15
Needle valve	"On/off"- or "flow rate adjustment" (depending on the stem tip design)	10–60; special designs: up to 1500
Pressure relief valve	Protect the vessel and its components from overpressure ("proportional" or "on/off")	1–200 (desired value is exactly adjusted by the manufacturer)
Check valve	Ensures flow in one direction only	0.1–1000
Diaphragm valve	"On/off"- or "flow rate adjustment" (depending on the design), all-metal containment, packless	5–30

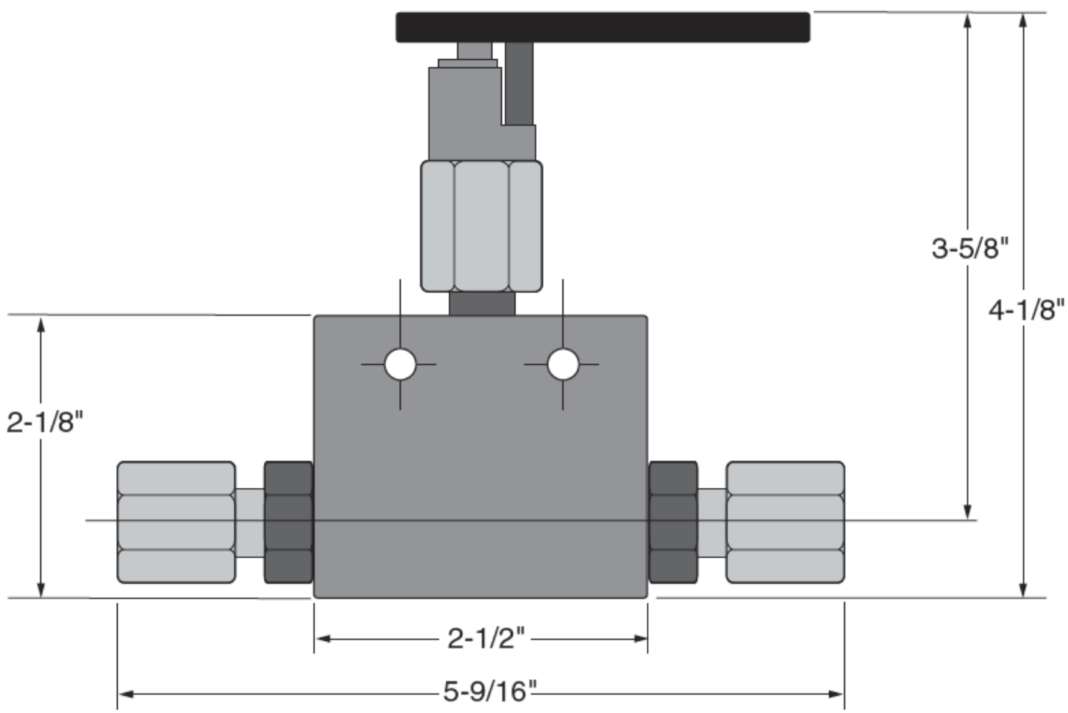
Válvulas

- Diversos tipos (1 via, duas vias, etc)



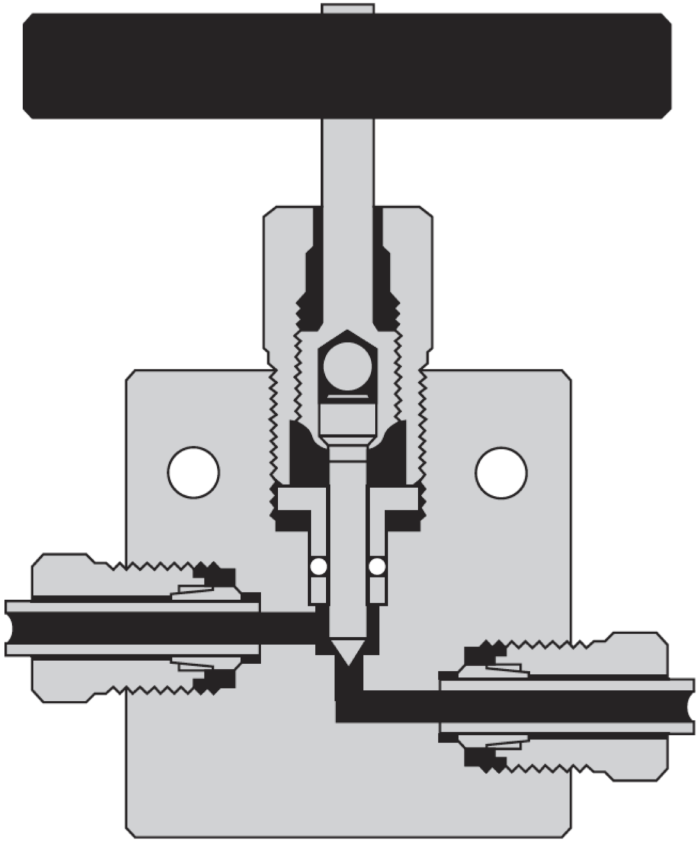
Válvulas

- Ball (bola) – “on/off” sem regulagem fluxo



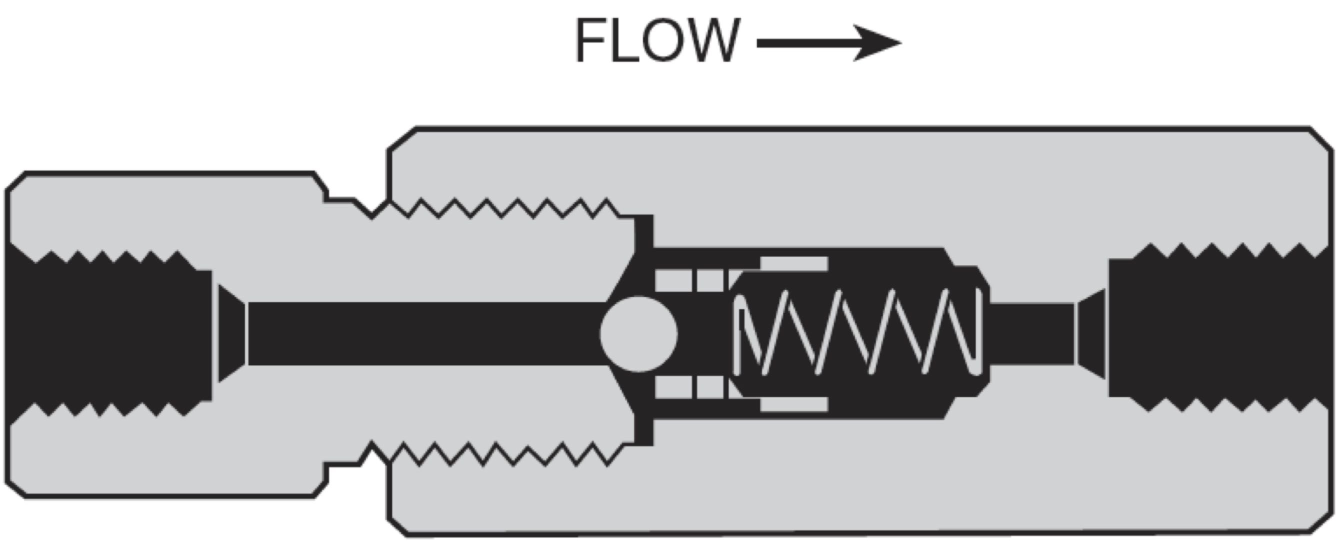
Válvulas

- Agulha (fluxo regulável)



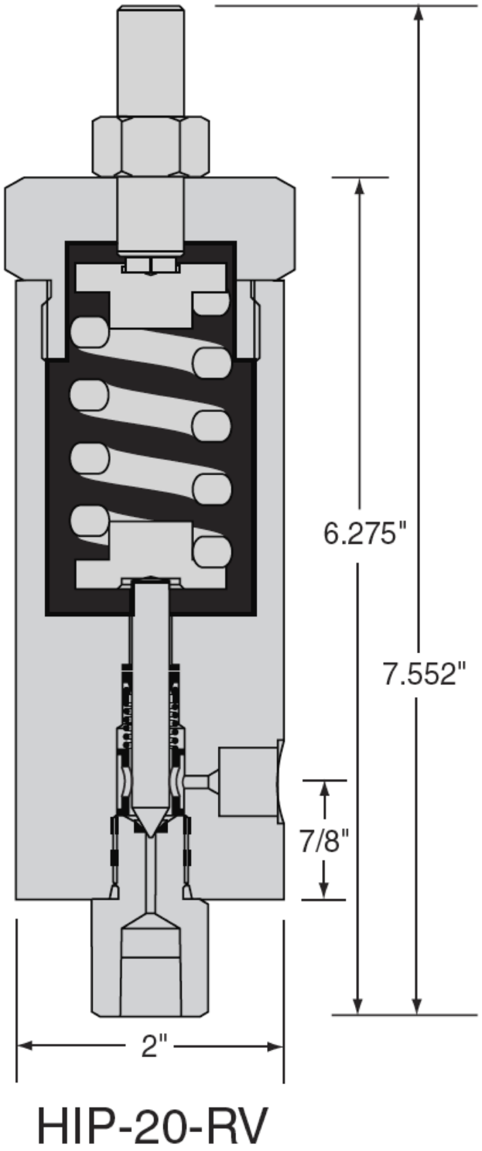
Válvulas

- "Ball Check" – fluxo num só sentido

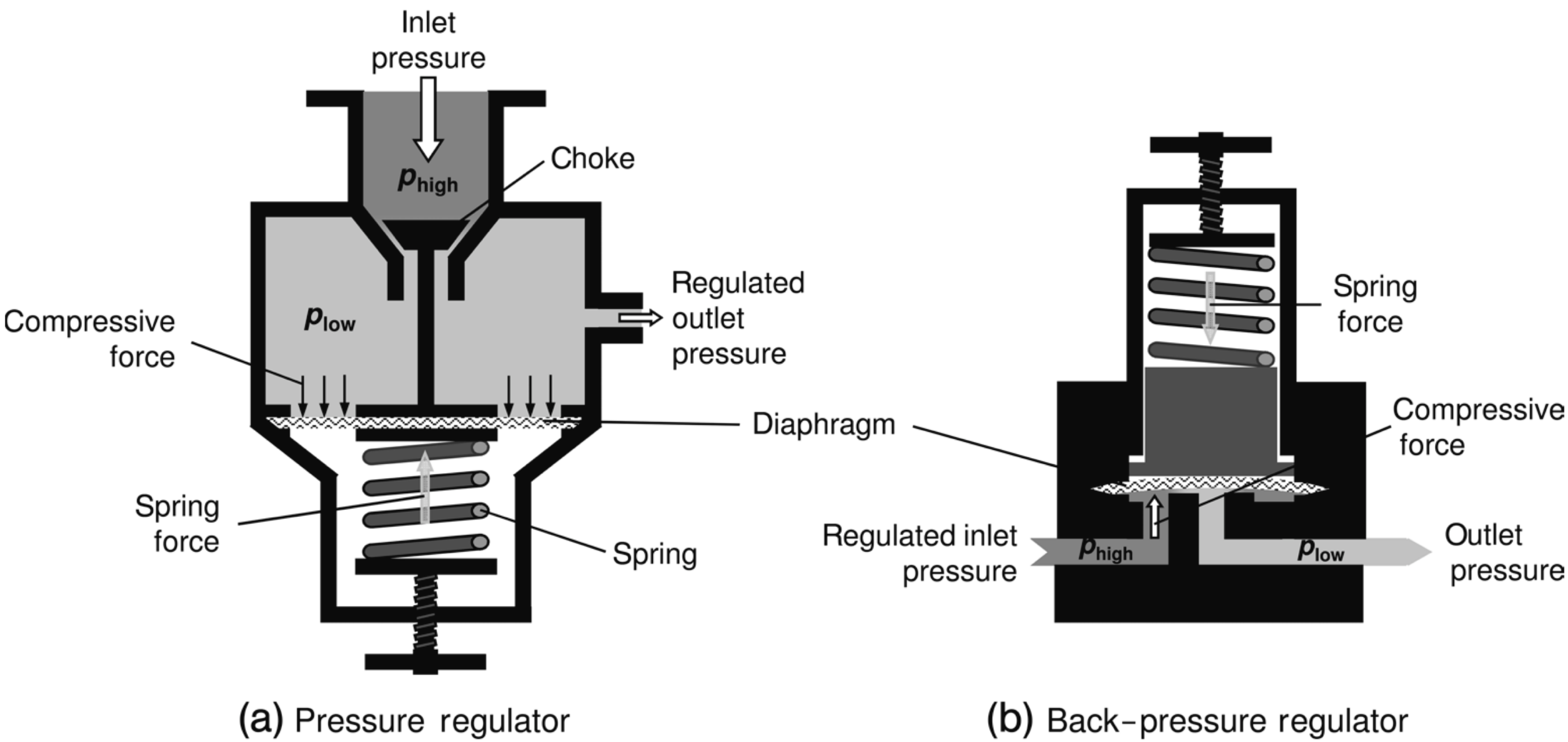


Válvulas

- “Relief” – válvula de alívio



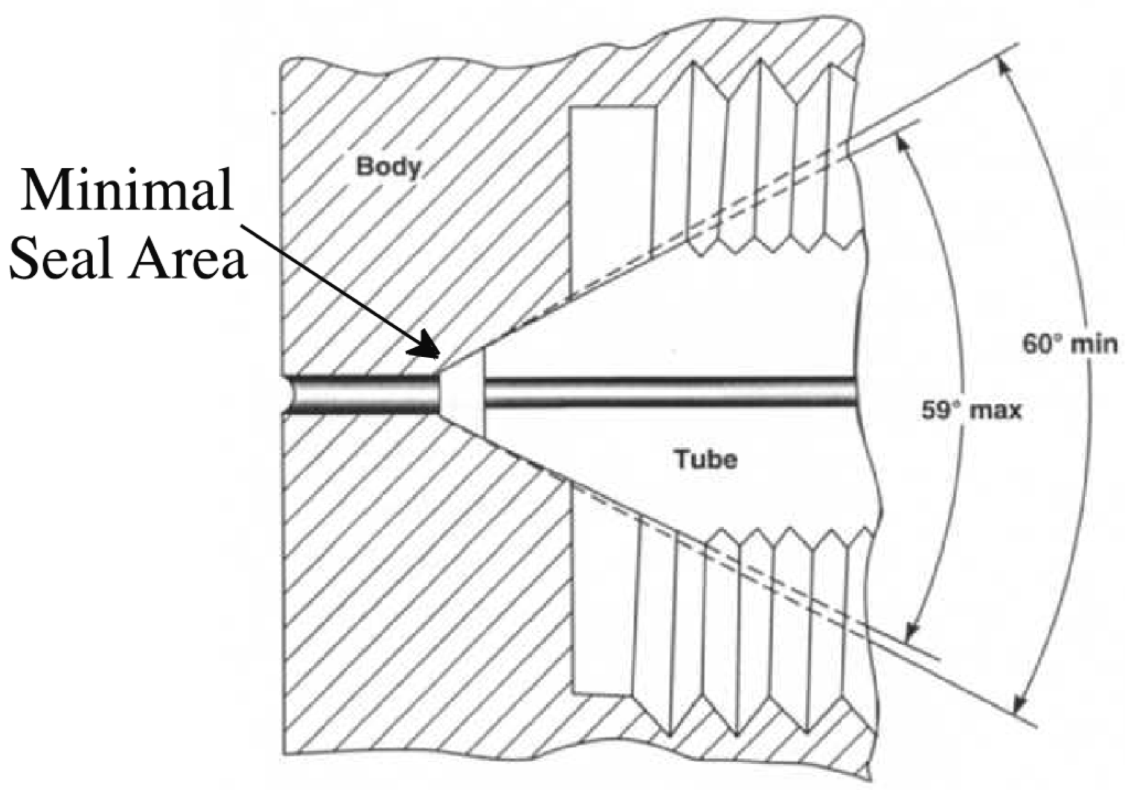
Reguladores "Back-Pressure"

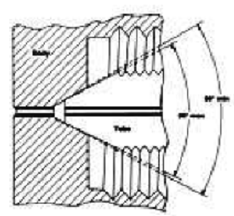


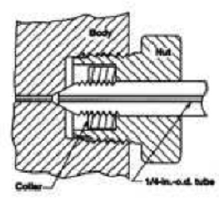
Química Verde: Solventes Alternativos

Conexões

- Aço inox – Diâmetro de 1/16"ou 1/8", normalmente

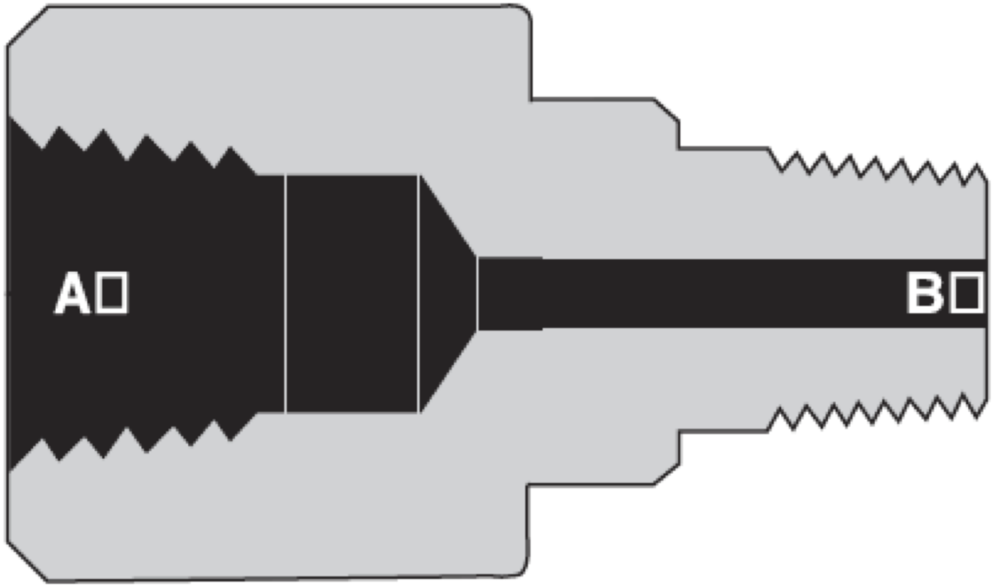






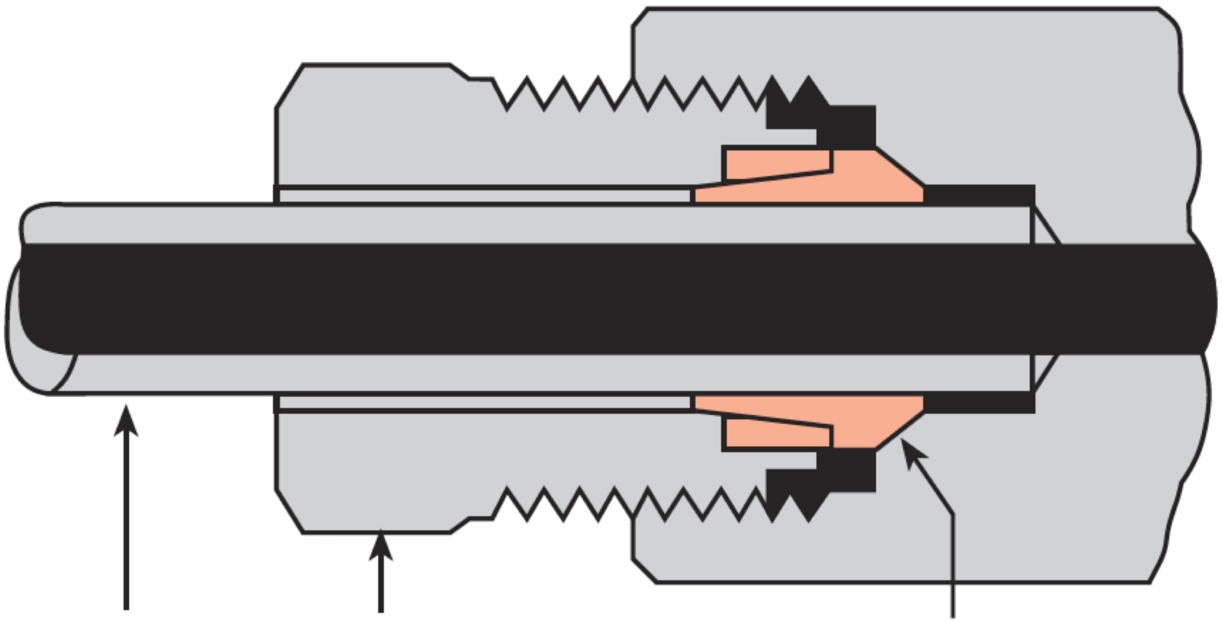
Conexões

- “NPT” – Pressões Baixas



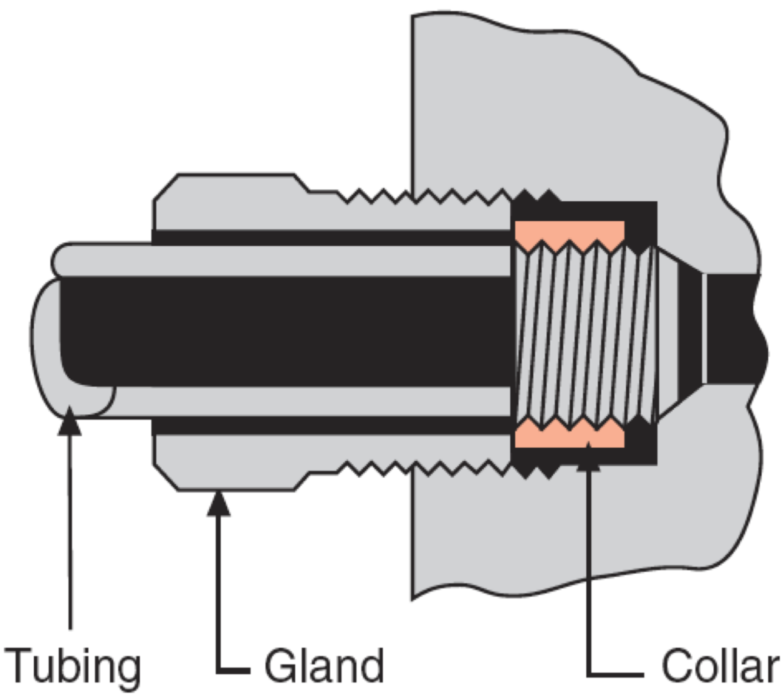
Conexões

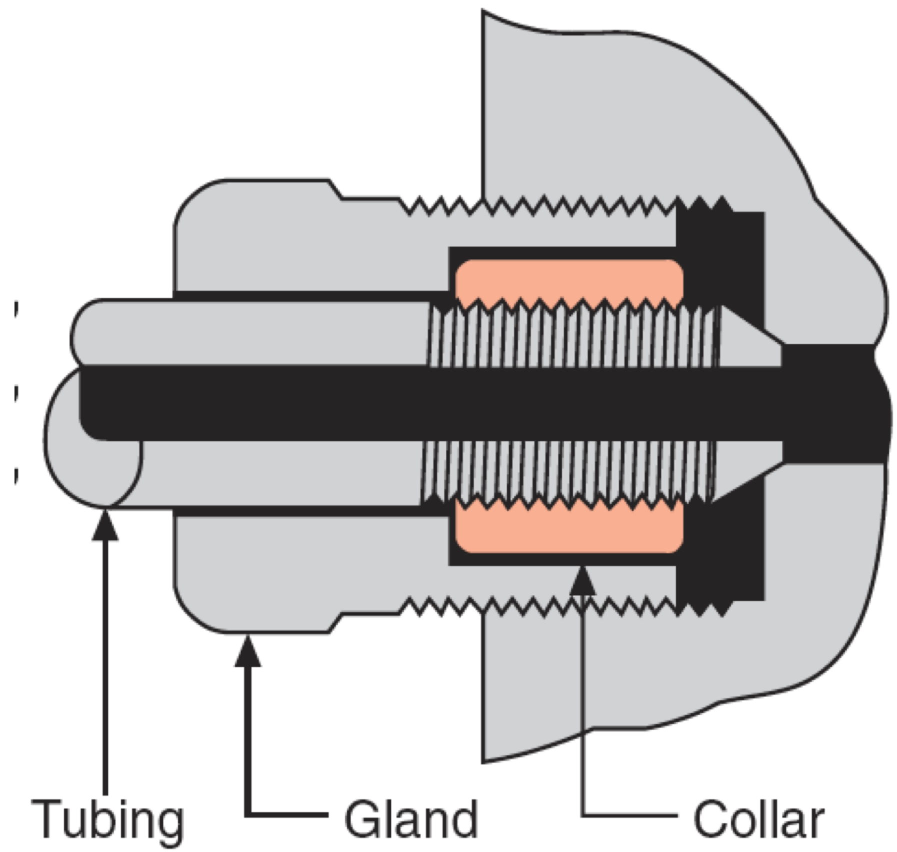
- “Taper Seal” – Pressões Médias



Conexões

- “Cone & Thread” – Pressões A



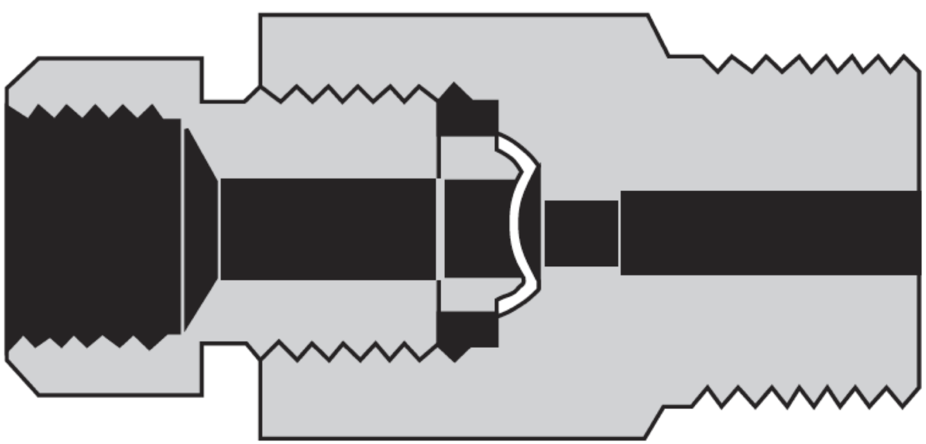


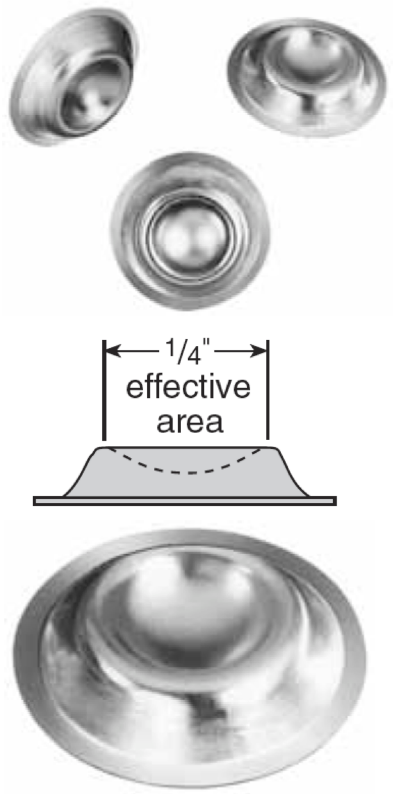
Tubulação

- Aço inox – Diâmetro de 1/16” (flexível e permite corte com cortador de tubo) ou 1/8”, normalmente;
- Sem costura

Discos de Ruptura

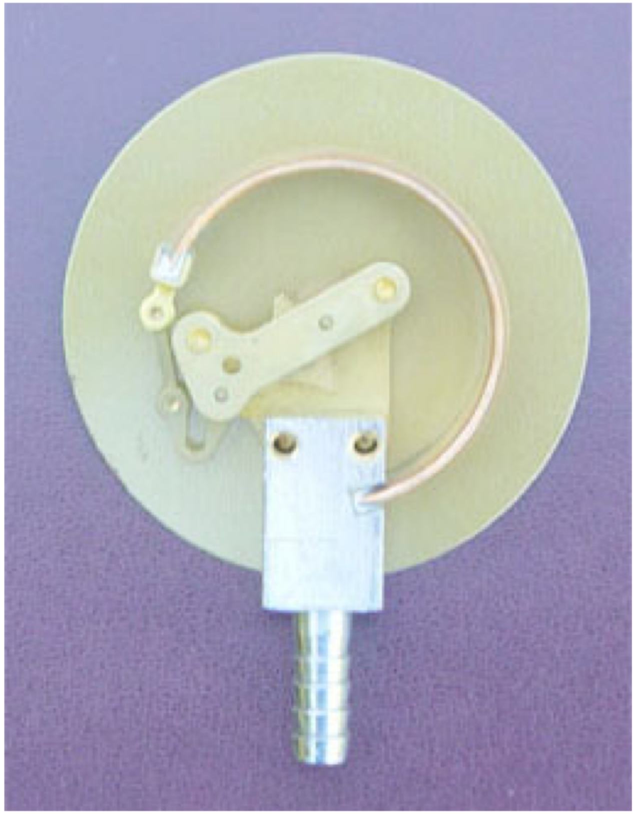
- Rompimento em pressão igual (ou menor) que a MAWP a uma dada T;
- Pressão de ruptura cai com aumento de T.





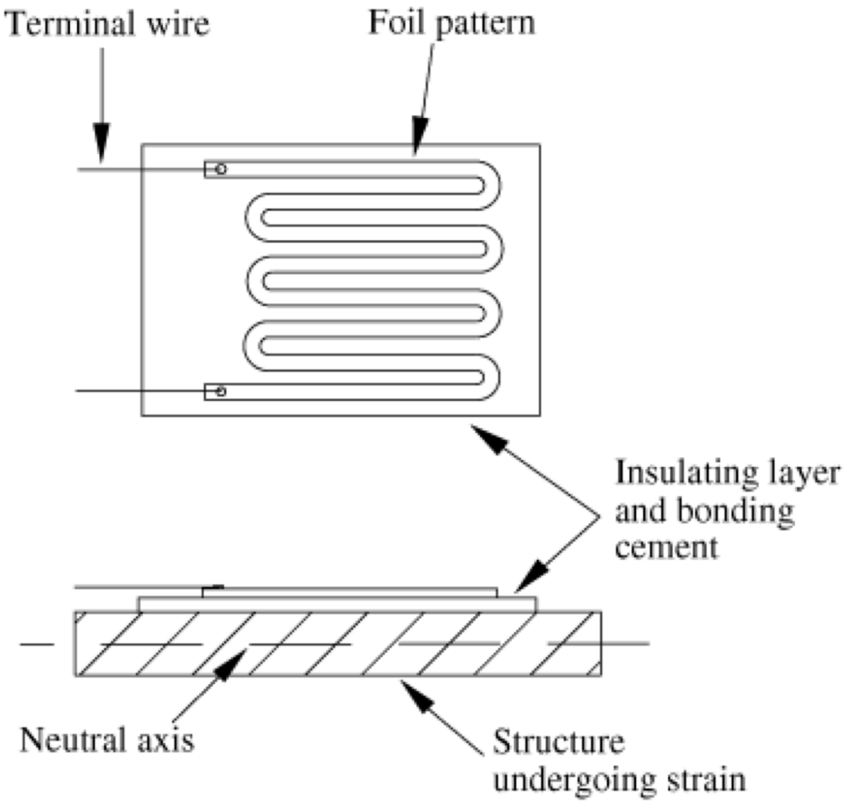
Manômetro

- Para medir a pressão – Tubo de Bourdon.



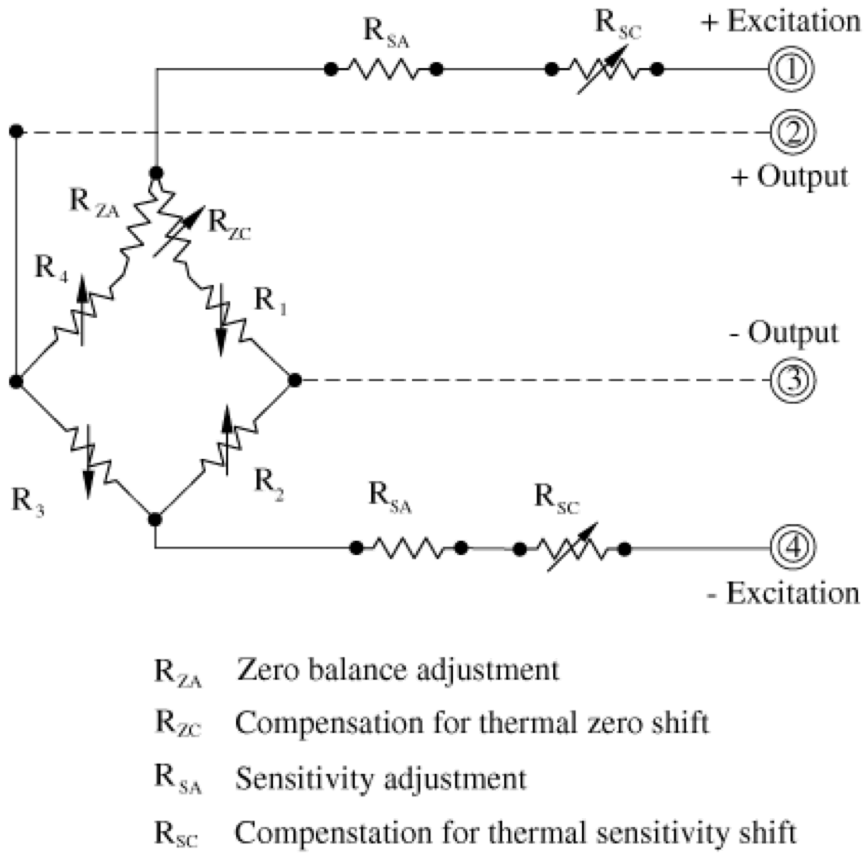
Manômetro

- Para medir a pressão – Transdutor de Pressão – Strain-Gage.



Manômetro

- Para medir a pressão – Transdutor de Pressão.



Aquecimento e Controle de Temperatura

- Termopares e controladores PID.

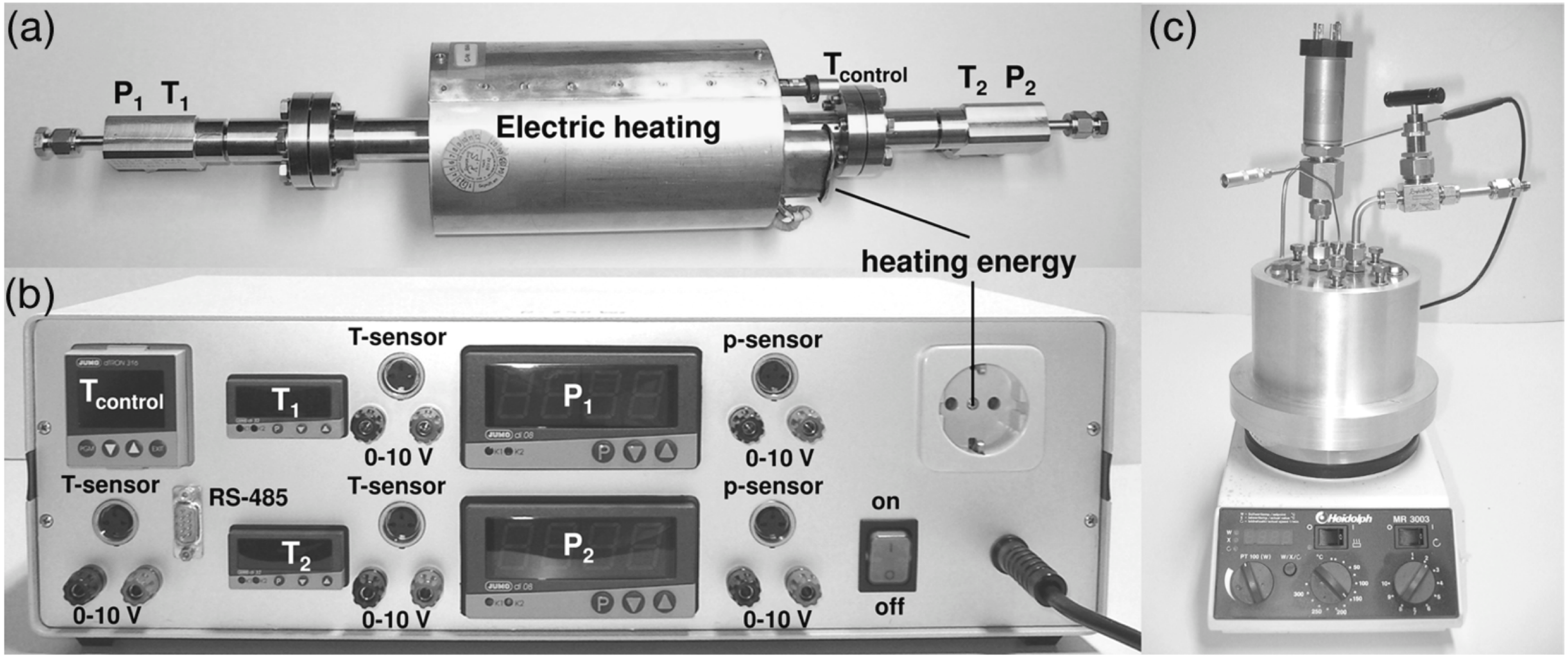
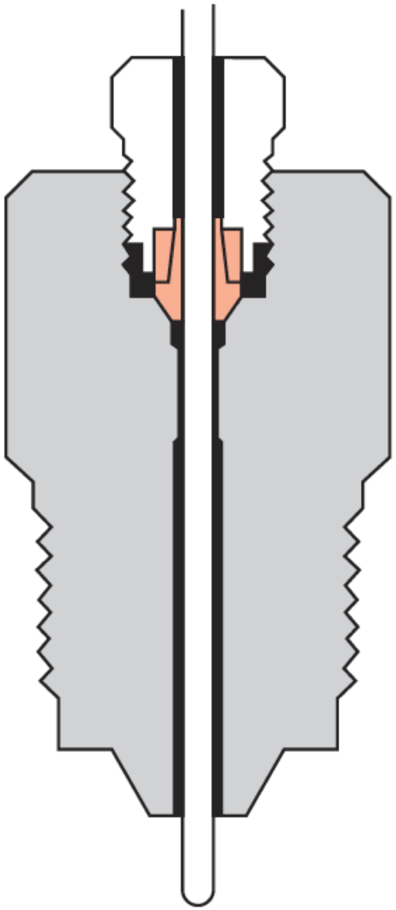


Figure 2.3 Plug flow reactor (PFR) with an outer electric heating unit (a), temperature and pressure control unit for the PFR (b), and stirred-tank reactor setup which is heated in a metallic top frame of a magnetic stirrer (c).

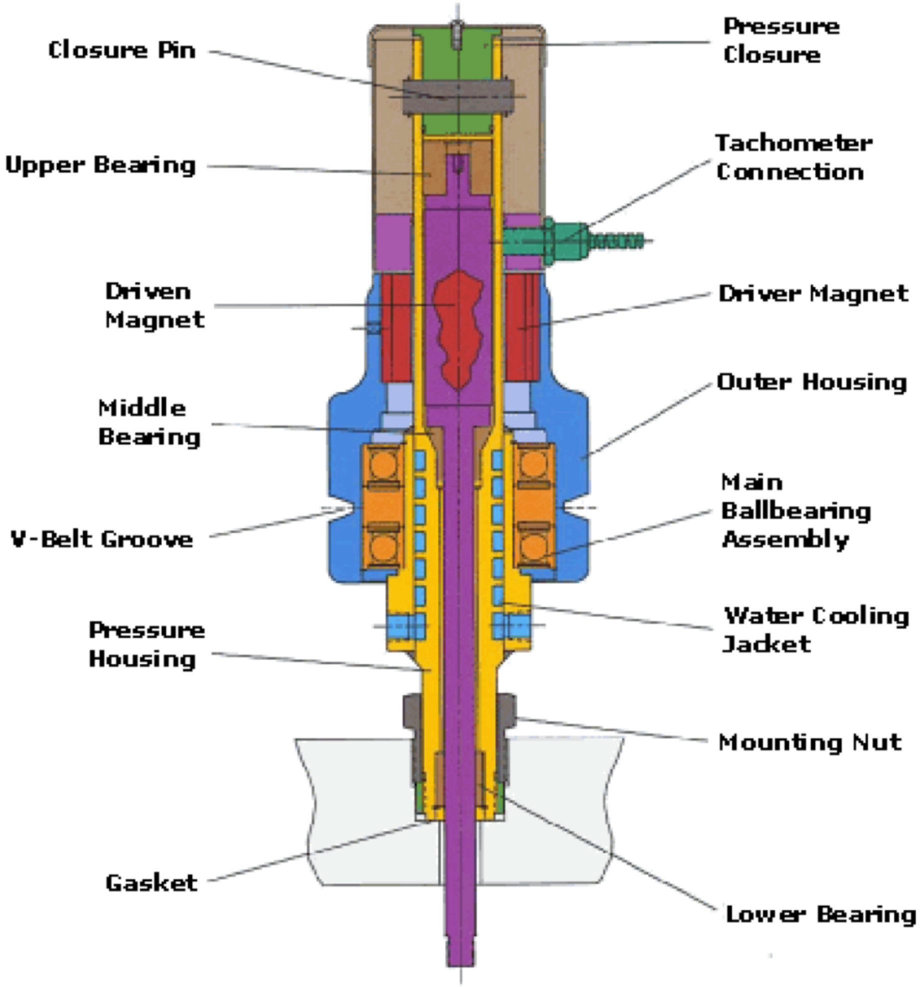
Aquecimento e Controle de Temperatura

- Termopares e controladores PID.



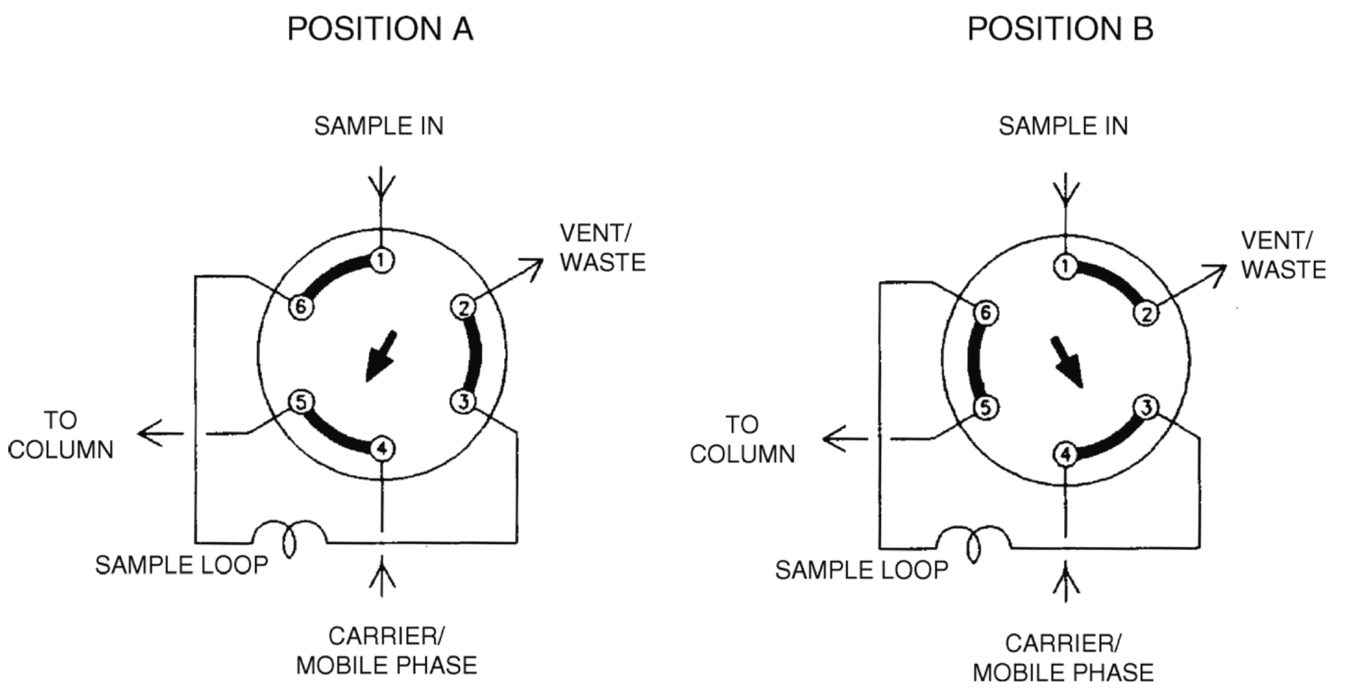
Agitadores

- Acoplamento magnético



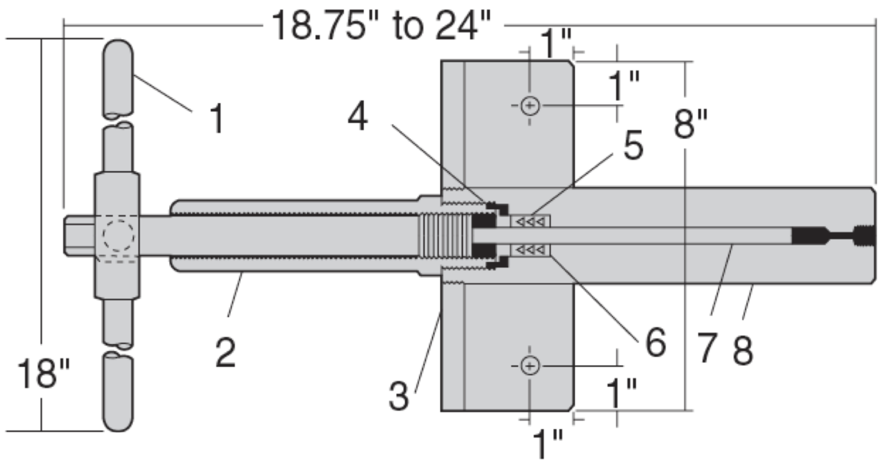
Amostragem

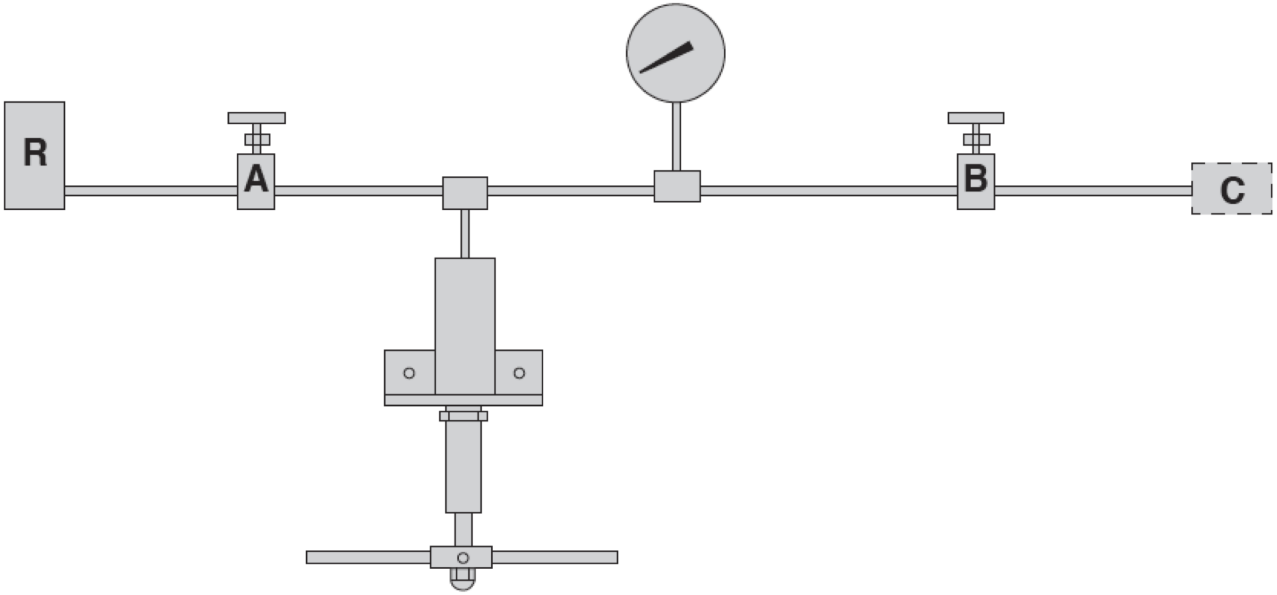
- Válvulas de amostragem (com “loops”)



Amostragem

- Bombas manuais





Segurança em Alta Pressão

Lei dos Gases

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Lei dos Gases

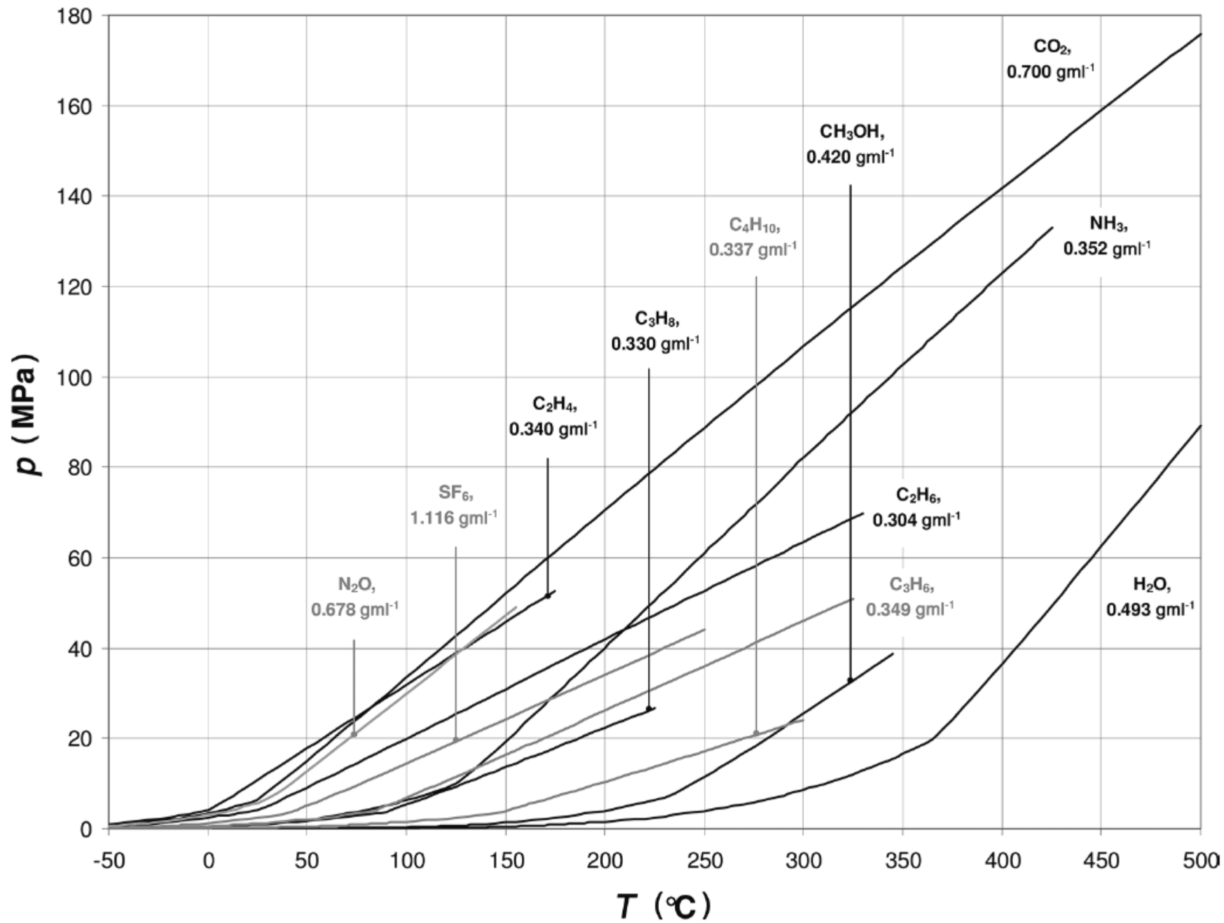


Figure 2.8 Calculated pressure–temperature curves for frequently used SCFs (density = $1.5\rho_{crit.}$) [68].

Energia “estocada” em um fluido comprimido: trabalho em uma descompressão

Gás (Equação de Baker)

$$W = \frac{P_i V_i}{\gamma - 1}\left[1 - \left(\frac{P_f}{P_i}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

Líquido

$$E = \frac{P_i^2 V_i}{2\kappa}$$

Onde:

- P_i e P_f são as pressões inicial e final, respectivamente;
- V_i é o volume do vaso;
- γ é a razão C_P/C_V, ou expoente adiabático (≈1,3 para CO_2)
- κ é o módulo “bulk”(≈2,2 GPa para água a 31°C)

Energia “estocada” em um fluido comprimido: trabalho em uma descompressão

CO2

$$W = \frac{P_i V_i}{0,3}\left[1-\left(\frac{P_f}{P_i}\right)^{\frac{0,3}{1,3}}\right]$$

H2O

$$E = \frac{P_i^2 V_i}{4,4x10^9}$$

- Perigo real a partir de 1.000 lbf-ft (1.358 J ou 0,3g de TNT) – critério do Pacific Northwest National Laboratory (PNNL)

Energia "estocada" em um fluido comprimido: trabalho em uma descompressão

Pressão (bar)	Volume (mL)	W CO2 (J)	W CO2 (g TNT)	W H2O (J)	W H2O (g TNT)
10	100	$1,4 \times 10^{2}$	0,03	0,02	5×10^{-6}
100	100	$2,2 \times 10^{3}$	0,5	2,3	5×10^{-4}
350	100	$8,7 \times 10^{3}$	1,9	27,9	6×10^{-3}
100	1.000	$2,2 \times 10^{4}$	4,7	22,7	5×10^{-3}
500	1.000	$1,3 \times 10^{3}$	27	568	0,12

- Gás (ou fluido compressível) armazena muito mais energia que um líquido incompressível

Onda de choque de uma explosão: 1000 lbf-ft (0,3g TNT)

The blast wave for an over-pressure event in a system with 1000 lbf-ft is calculated using a 4 inch sphere as an example pressure vessel:

$r := 2 \cdot in$	Radius of Sphere
$V_1 := \frac{4 \cdot \pi \cdot r^3}{3} = 33.51\ in^3$	Volume
$P_0 := 15 \cdot psi$	Atmospheric Pressure
$P_1 := 260 \cdot psi$	Vessel Pressure (245 psig)
$k := 1.4$	Ratio of Specific Heats for Air
$E_{Ba} := \frac{P_1 \cdot V_1}{k - 1} \left[1 - \left(\frac{P_0}{P_1} \right)^{\frac{(k-1)}{k}} \right]$	Equation 4.2 (Baker)

Onda de choque de uma explosão: 1000 lbf-ft (0,3g TNT)

$E_{Ba} = 1372\,J$ converts to $E_{Ba} = 1012 \cdot lbf \cdot ft$	Energy
$E_{TNT} := 4850 \cdot \frac{J}{gm}$	TNT equivalent Energy of Explosion (Lee's Section 17.4, page 17/22)
$z_1 := 200 \cdot ft$	Worst Case - scaled distance for "Minimum overpressure for debris and missile damage" with overpressure of .2 psi - .4 psi. (See FPH, Table 2.8.1.)
$z_2 := 15 \cdot ft$	Worst Case - scaled distance for "eardrum rupture" with overpressure of 5.1 psi - 14.5 psi. (See FPH, Table 2.8.1.)
$z_3 := 6.7 \cdot ft$	Worst Case - scaled distance for "lung damage" with overpressure of 29.0 psi - 72.5 psi. (See FPH, Table 2.8.1.)

Onda de choque de uma explosão: 1000 lbf-ft (0,3g TNT)

$$D = z \cdot \sqrt[3]{W_{TNT}}$$

Distance from blast point for related consequence. (See FPH, example calculation pages 2-95 and 2-96.)

$$W_{tnt} := \frac{E_{Ba}}{E_{TNT}} = 2.828 \times 10^{-4} kg$$

Energy Equivalent in TNT, kg

$$W_{TNT} := \frac{W_{tnt}}{kg} = 2.828 \times 10^{-4}$$

Energy Equivalent in TNT, Unitless Conversion

$$D_1 := z_1 \cdot \sqrt[3]{W_{TNT}} = 13 \cdot ft$$

Maximum distance for debris and missile damage.

$$D_2 := z_2 \cdot \sqrt[3]{W_{TNT}} = 12 \cdot in$$

Maximum distance for eardrum rupture.

$$D_3 := z_3 \cdot \sqrt[3]{W_{TNT}} = 5 \cdot in$$

Maximum distance for lung damage.

Onda de choque de uma explosão: 1000 lbf-ft (0,3g TNT)

	Volume 1	Volume, in^3 at	Distance (inch)							
Diameter	cu-in	1	2	3	4	5	6	8	10	12
0.0625	1.28E-04	5	35	117	274	533	919	2170	4228	7295
0.125	1.02E-03	5	37	120	281	543	933	2195	4268	7352
0.25	8.18E-03	6	40	128	294	564	963	2247	4348	7467
0.5	6.54E-02	8	48	144	322	606	1023	2352	4511	7700
1	0.52	14	65	180	382	697	1150	2572	4849	8181
1.5	1.77	22	87	221	449	796	1288	2806	5204	8682
2	4.19	34	113	268	524	905	1437	3054	5575	9203
3	14.14	65	180	382	697	1150	1767	3591	6371	10306
4	33.51	113	268	524	905	1437	2145	4189	7238	11494
5	65.45	180	382	697	1150	1767	2572	4849	8181	12770
6	113.10	268	524	905	1437	2145	3054	5575	9203	14137

	Absolute Pressure for 1000 lbf-ft	Pressure Resultant (psi)								
0.0625	40000000	1113	146	44	19	10	5.56	2.36	1.21	0.70
0.125	4900000	997	136	42	18	9	5.37	2.28	1.17	0.68
0.25	620000	850	126	40	17	9	5.27	2.26	1.17	0.68
0.5	80000	640	110	36	16	9	5.12	2.23	1.16	0.68
1	11000	407	88	32	15	8	5.01	2.24	1.19	0.70
1.5	3450	272	70	28	14	8	4.73	2.17	1.17	0.70
2	1560	195	58	24	12	7	4.55	2.14	1.17	0.71
3	535	116	42	20	11	7	4.28	2.11	1.19	0.73
4	258	76	32	17	10	6	4.03	2.06	1.19	0.75
5	152	55	26	14	9	6	3.87	2.05	1.22	0.78
6	101	43	22	13	8	5	3.74	2.05	1.24	0.81

Segurança em Sistemas Pressurizados

- Orientação de segurança antes de usar o equipamento;
- Perguntar ao pesquisador responsável antes de fazer experimentos com equipamento alterado;
- Não fazer experimentos se tiver dúvidas de segurança;
- Relatar qualquer problema não usual (rompimento de disco de ruptura, vazamento de janelas, etc);
- Não abandonar vasos pressurizados aquecidos;
- Não exceder a Pressão Máxima de Trabalho (MAWP) do sistema

Segurança em Sistemas Pressurizados

- Orientar janelas de safira para os lados (nunca na sua direção);
- Usar escudo de policarbonato sempre que trabalhar com janelas de safira;
- Nunca olhar diretamente para uma janela de safira;
- Usar proteção adequada para os olhos;
- Nunca trabalhar em sistema sem disco de ruptura;
- Ter cuidado ao abrir válvulas e reatores.

Segurança em Sistemas Pressurizados

- A pressão máxima de trabalho (MAWP) de um sistema pressurizado é sempre a do componente de menor MAWP;
- O disco de ruptura no sistema deve ter valor de ruptura menor que a MAWP;
- Jamais isolar disco de ruptura com válvulas.