Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Stone, Mark , Orme, Christopher , Peterson, Eric , Benson, Michael , Kaszuba, John , Mroz, Eugene and Haga, Marc(2005) 'Gas Permeation Testing Results from the Mixed Waste Focus Area Improved Hydrogen Getter Program', Separation Science and Technology, 40: 1, 419 — 431

To link to this Article: DOI: 10.1081/SS-200042486

URL: http://dx.doi.org/10.1081/SS-200042486

Separation Science and Technology, 40: 419–431, 2005
ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200042486

Gas Permeation Testing Results from the Mixed Waste Focus Area Improved Hydrogen Getter Program

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Abstract: The gas permeabilities of more than 20 polymers were measured using pure and mixed gas techniques. The motivation was to determine potential materials that could be used to protect hydrogen getter particles from poisons while permitting sufficient hydrogen rates to enable the getters use in TRUPACT types of containers. A rate of five barrers or larger is needed. Of the materials screened in the pure gas tests, more than 15 qualified. Nine materials qualified in the mixed gas tests, but of the nine only three had high CCl_4 rejection rates and four others would greatly reduce the transport of the CCl_4.

BACKGROUND

The Transuranic Package Transporter-II (TRUPACT-II) was developed for the U.S. Department of Energy (DOE) primarily for shipment of contact-handled transuranic (CH-TRU) waste from DOE generator/storage sites to the Waste Isolation Pilot Plant. The NRC imposed a flammable gas (i.e., hydrogen) concentration limit on CH-TRU waste transported using the

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TRUPACT-II to minimize the potential for loss of containment during transport (1). This limit is set at the lower explosive limit of 5 vol % of hydrogen in air. Hydrogen gas generation and accumulation are the result of alpha radiolysis of hydrogenous waste and packaging materials coupled within waste packaging configurations. One method to prevent hydrogen buildup is to employ a hydrogen getter within the containers.

INTRODUCTION

Hydrogen gas getters are materials that irreversibly remove hydrogen from the gas phase. Preferred hydrogen getters are solid materials that scavenge hydrogen (H_2) from the gas phase and chemically and irreversibly bind it in the solid state.

Many potential hydrogen gettering compounds and formulations have been tested (2–4). The best performance has been achieved with 1,4-bis(phenylethynyl) benzene (DEB), a nontoxic, nonmutagenic, crystalline solid.

Because DEB is a dialkyne (containing two triple bonds; see Fig. 1), 1 mole of DEB reacts with 4 moles of hydrogen (2 moles of hydrogen react to form the corresponding dialkene, an additional 2 moles of hydrogen react to form the dialkane). The standard formulation for the "DEB getter" is a mixture of 75% DEB and 25% carbon catalyst (5% Pd on carbon). The uncoated getter granules are shown in Fig. 2.

Previous experiments showed that DEB was unaffected by toluene, hexane, acetone, and methanol. However, as with other noble metal catalyst systems, carbon monoxide (CO) and several chlorinated volatile organic compounds (VOCs) (e.g., carbon tetrachloride, trichloroethylene, trichloroethane, chloroform, and methylene chloride) did inhibit or reduce the reaction of hydrogen with DEB. Some of these materials are present in the waste being shipped. Thus, a program was undertaken to protect the getter from these poisons. One possible solution was to develop semipermeable membrane coatings for the DEB particles that would exclude the poisons while at the same time permit the permeation of the hydrogen through the coating.

Because of the large potential for the catalyst contained in the getter to be poisoned, it was proposed that a polymer coating be applied to the getter to act as a selective gas barrier allowing the transmission of hydrogen and excluding the poisons. The focus of this work has been twofold: (a) find a polymer

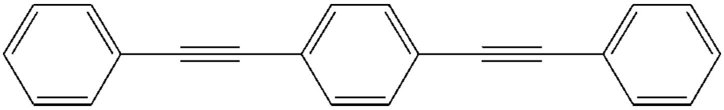

Figure 1. Structure of 1,4-bis(phenylethynyl) benzene.

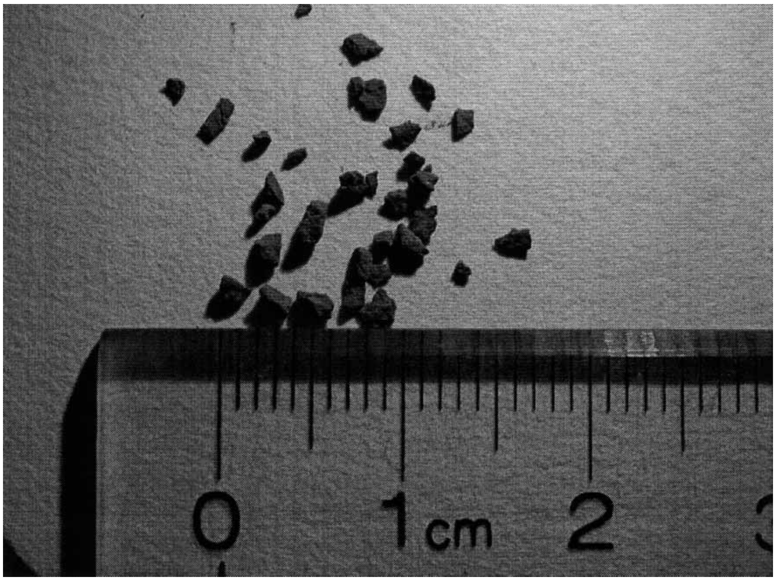

Figure 2. Photograph of the uncoated DEB getter (X20).

membrane that allows the transport of H_2 and acts as a barrier to CO_2 and chlorinated organics and (b) determine if the chosen polymer has the physical and mechanical characteristics needed to allow for the formation of a membrane coating around getter particles. In this work a wide variety of polymers were tested for overall gas permeation properties as well as their permeability to carbon tetrachloride. This paper presents the results of the gas testing that was used to screen and select the materials that potentially would be coated onto the getter particles.

The first phase was the pure gas testing. Pure gas testing was conducted using the time-lag method. The gas permeability measured in the time-lag testing was used to select polymers for the second stage of testing. The second-stage testing included mixed gas testing using a variable volume technique. Mixed gas testing determines the actual separation factor for hydrogen over carbon tetrachloride for each candidate polymer.

EXPERIMENTAL

Polymer Permeability Measurements

Two methods were used to characterize the membranes. One method was a static type of experiment where a pure or single gas is exposed to the membrane. This method is based upon the solution diffusion mechanism. Results from this method give the permeability and diffusivity from which the solubility can be calculated (Permeability = Diffusivity × Solubility). The second method is referred to as the mixed gas technique. This is a dynamic type of test where both the feed gas and permeate gases are continuously swept across the membrane surface. This type of testing allows for gas mixtures that more closely correlate to the end use conditions to be utilized.

Pure Gas Testing

Membranes having thicknesses in the range of 50–200 microns were tested in a pure (single) gas facility at the INEEL. The primary focus of the pure gas test screening has been to determine if the polymers being considered have H_2 permeability high enough to allow H_2 to pass through the polymer at the needed rate. Each polymer was initially tested using six separate gases that might be encountered in a container: He, H_2, N_2, O_2, CH_4, CO_2. All of the pure gas tests were performed at 30°C and 30 psi feed gas pressure. Figure 3 shows the set-up for the tests. The permeation results were obtained using the time-lag method (5–8) in which each material was exposed to the different gases. The observed behavior of the transport of the gases through the membranes was interpreted using the solution-diffusion approach. This process consists of three steps: (a) the gas or vapor dissolves at one surface, (b) diffuses through the film due to the concentration gradient, and (c) desorbs out of the membrane on the low-pressure side. In a typical experiment, both sides of the membrane are evacuated to an equal vacuum. The cell is then isolated and the zero time pressure is noted.

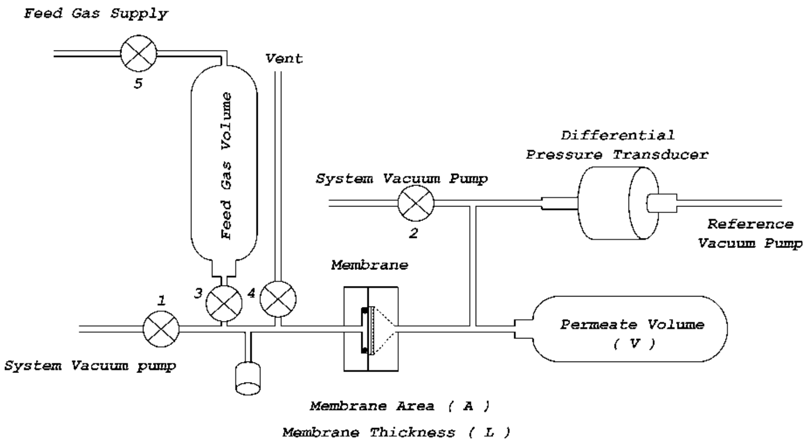

Figure 3. Schematic of the pure gas screening test apparatus.

Next, the feed side is exposed to the test or challenge gas. Finally, the pressure build up on the permeate side is recorded as a function of time. The data are analyzed to yield experimental values for the permeabilities and diffusivities and calculated values for the solubility component of the permeability.

Mixed Gas Testing

The mixed gas screening test differs from the pure gas test in two ways: (a) It is a flowing test where the pure gas is a stagnant test and (b) the feed gas contains mixtures of gases. In the mixed gas experiments a pressurized feed gas flows at a constant rate over the surface of the membrane. Any permeant gases are entrained in a sweep gas that transports them to a set of gas chromatographs (GC) for analysis (9–13). The schematic is shown in Fig. 4. The importance of the mixed gas test was that it allowed the use of a more realistic set of gases, including some of the suspected catalyst poisons.

RESULTS AND DISCUSSION

One of the prime considerations in the development of the coatings was a method for application. After exploring a number of options, spray coating in the Wurster type (14) configuration was selected (Fig. 5). In this process, the particles are levitated upward in the center of a tall cylindrical container. After a certain distance they fall by gravity back down near the walls of the container. A nozzle located at the bottom, center of the container emits an atomized spray of the desired polymer in solution. The spray hits the

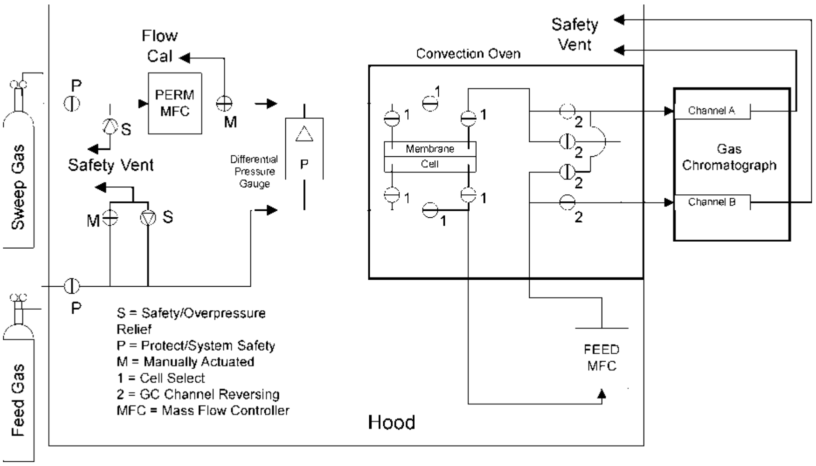

Figure 4. Schematic of the mixed gas test system.

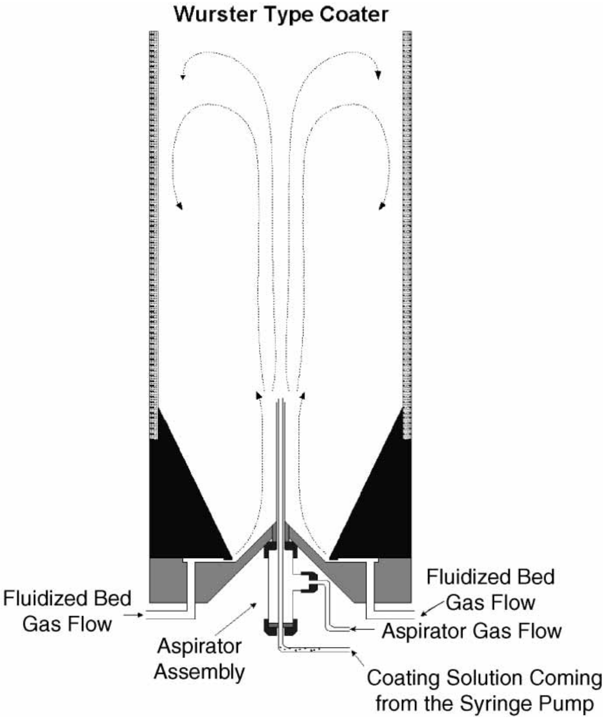

Figure 5. Wurster type coater.

particles and then the solvent evaporates as the particles move upward. By the time they reach the top of their travel most of the solvent is gone and the particles do not stick to one another. The particles then fall back down and the cycle is repeated. This procedure produced a complete coating on the irregular-shaped particles. This process required that the polymers be soluble in a volatile solvent. The solvent that was used primarily was tetrahydrofuran (THF). CMS-3 fluorinated polymer was dissolved in perfluorohexane since it was not soluble in THF.

The films that were used for the gas testing were cast from 3–5% THF solutions onto glass plates or directly onto porous substrates. Film thicknesses were in the 40–100 micron range. One-inch diameter circles were used in all the testing. Table 1 lists the sources for the polymers along with general physical properties.

Pure gas permeability measurements were carried out to validate hydrogen permeabilities, as well as hydrogen perm-selectivity over carbon dioxide. The carbon dioxide selectivity was considered because of carbon dioxides solubility interaction with most polymers. Carbon dioxide typically has a higher permeability than does hydrogen. Carbon dioxide served as an indicator of how

Table 1. Information about the polymers used in this study

No.	Polymer	Manufacturer	Comments
1	Poly(trimethyl silylpropyne) (PTMSP)	Donated sample	
2	Poly(dimethyl siloxane) (PDMS)	Specialty Manufacturing Incorporated	Purchased 125 μm thick film
3	Poly(vinylchloride) (PVC) unplasticized		
4	PVC viscosity = 0.68	Aldrich	MW: 62000
5	PVC viscosity = 1.02	Aldrich	
6	Polyethylene (PE) Bag		
7	Polypropylene	J&M Business Supply	Purchased film
8	Polysulfone	Aldrich	MW: 26,000
9	Polysulfone	Aldrich	MW: 35,000
10	Poly(ethylene terephthalate) (PET)	Soda Pop bottle	
11	Polystyrene	Fisher	Weighing boat
12	Polystyrene	Aldrich	MW: 2,80,000
13	Poly(styrene co-methyl methacrylate)	Polysciences	70 : 30 MW: 2,70,000
14	Poly(styrene co-acrylonitrile)	Aldrich	MW: 1,85,000. 30% acrylonitrile
15	Poly(styrene co-butadiene)		
16	Poly(styrene-co-allylalcohol)	Aldrich	Density – 1.050
17	Poly(methyl methacrylate) (PMMA)		MW: 3,50,000
18	Poly(methyl methacrylate) (PMMA)	Polysciences	MW: 25,000, Sp. Gr. = 1.19
19	Poly(benzyl methacrylate)	Polysciences	
20	Poly(isobutyl methacrylate)	Polysciences	Inherent Viscosity = 0.6
21	Poly(isopropyl methacrylate)	Polysciences	
22	Poly(vinyl butyral)	Polysciences	Sp. Gr. = 1.0
23	Poly(vinyl acetate)		
24	Poly(vinylidene fluoride) (PVDF)	Elf Atochem (KYNAR^{TM})	
25	Poly(vinylidene chloride)	Saran^{TM} Wrap	
26	Poly(ethylene vinyl alcohol) EVAL	Kuraray America	
27	Poly(ethylene terephthalate) PET	Filmquest	
28	Polybutadiene		

(*continued*)

Table 1. Continued

No.	Polymer	Manufacturer	Comments
29	Polyepichlorohydrin	Aldrich	MW: 7,00,000
30	CMS-3 (perfluoro amorphous copolymer)	Compact Membrane Systems, Inc.	
31	Poly bis(trifluoroethoxy) phosphazene (PTFE)	INEEL synthesized	
32	Poly bis(p-fluorophenoxy) phosphazene	INEEL synthesized	
33	Eypel F (fluorinated alkoxy substituted phosphazene)	Ethyl Corporation	

other compressible gases and vapors could interact with the polymers. Pure gas testing showed that polystyrene, poly(vinyl chloride), poly(sulfone), poly (benzyl methacrylate) and poly(vinylidene fluoride) have ideal selectivities that favor hydrogen over the more compressible carbon dioxide, while polymers like poly(ethylene), poly(propylene), and CMS-3 (co-polymer) had neutral selectivity over carbon dioxide. The CMS-3 (co-polymer) has a very high hydrogen permeability of 996 barrers.

Other than the CMS-3 (copolymer), PTMSP and PDMS showed the highest permeabilities to all of the gases tested, as expected, and were included in the testing for comparison purposes with literature values for calibration purposes. The highest hydrogen permeabilities were measured for the CMS-3 resin followed by two other fluorinated polymers, polybis(trifluoroethoxy) phosphazene and Eypel F. All three of these polymers had relatively high values for the other gases too. The next highest set was the styrene-based polymers. The styrene polymers had low permeabilities for helium, nitrogen, and oxygen. However, except for the filled polystyrene weighing boat, the CO_2 permeabilities were less than a factor of 2 lower than that for hydrogen. The results of the pure gas testing are given in Table 2. A wide variety of hydrogen permeabilities were observed. These tests were performed at 30°C.

Table 3 contains the mixed gas permeability results when the feed gas contains 1000 ppm carbon tetrachloride and 5% hydrogen in a balance of nitrogen. Though the permeability results for hydrogen are in agreement with the pure gas results, the carbon tetrachloride permeabilities are very high in many of the polymers that gave the highest hydrogen permeabilities in the pure gas testing. Poly(vinylidene fluoride) has selectivity for carbon tetrachloride over hydrogen of nearly 4, poly(benzyl methacrylate) was 7.3, and polystyrene has shown extreme solubility to carbon tetrachloride with a selectivity of over 1000. The results of the mixed gas tests are given in Table 3.

The polymer that gave the best results using this gas mixture is CMS-3 (copolymer). The CMS-3 (copolymer) has a very high selectivity for

Table 2. Hydrogen-getter polymer pure gas testing summary

	Permeability (barrers, or $\times 10^{-10}$ cm $\times$ cm^3)/(sec $\times$ cm^2 cm Hg)					
Polymer	H_2	He	N_2	O_2	CH_4	CO_2
PTMSP	13,244	5,942	2,899	6,131	6,464	24,492
PDMS	565	316	255	497	761	2,318
PVC/unplasticized	6.4	7.7		1.1	0.3	1.2
PVC viscosity = 0.62	4.59	4.55	0.16	0.37	0.22	0.7
PVC viscosity = 1.02	5.3	1.28	0.52	0.64	0.38	1.08
PE/Bag	17.3	11.1	4.2	6.3	7.7	17.9
Polysulfone MW = 26 K	12	10.5	0.8	1.7	0.4	6
Polysulfone MW = 35 K	11.3	13.3	1.8	2.6	0.1	3.4
Poly(ethylene terephthalate) pop bottle	3.7	6.2	5.1	5	6.7	6.1
Polystyrene (weigh boat)	25.4	19.5	0.5	2.3	0.7	3.2
Polystyrene, MW = 280 K	27.1	0.63	0.47	0.39	1.21	16.4
Polystyrene co-methyl methacrylate	73.10				37.05	51.40
Polystyrene co-acrylonitrile	12.10				3.00	9.25
Polystyrene co-butadiene	8.15				2.30	14.85
Polymethyl methacrylate MW = 350 K	2.4	13		3.3	0.6	0.6
Polyvinyl butyral	10.95				1.15	8.05
Polyvinyl acetate	14.65				0.80	11.95
CMS-3 (perfluoro amorphous copolymer)	996		170	403	113	986
Poly bis (trifluoroethoxy) phosphazene	101.9		43.6	77.9	78.1	282
Poly bis (p-fluorophenoxy) phosphazene	5.84		0.43	1.44	0.91	9.46
Eypel F (fluorinated alkoxy substituted phosphazene)	79.9		32.2	64.9	40.6	375.6

Table 3. Tabulation of the mixed gas test results

	Permeability (Barrers)		Perm selectivity	
Polymer	Hydrogen	Carbon tetrachloride	H_2/CCl_4	CCl_4/H_2
Poly(dimethyl siloxane) PDMS	375–425	10,000–15,000	0.032	31.25
Polyethylene	45	79	0.570	1.756
Poly(propylene)	3.5	1.65	2.121	0.471
Polystyrene	21.4	24,000	0.001	1121.5
Poly(benzyl methacrylate)	2.8	20.5	0.137	7.321
Poly(vinylidene fluoride) Kynar	2.5	9.4	0.266	3.76
Poly(ethylene vinyl alcohol) EVAL	0.11	1.2	0.092	10.909
Poly(ethylene terephthalate) PET	0.13	0.45	0.289	3.462
Poly(butadiene)	68.4	36,44.5	0.019	4.572
CMS-3 perfluoro amorphous copolymer	169.6	9.2	18.435	0.054
CMS-3 cast in house from perfluorohexane	533.4	16.6	32.133	0.031
Poly(p-sec-butyl, p-methoxy, o-allyl) phenoxy phosphazene, Lot# Z-1009-A	8.6	5.98	1.438	0.695
Poly(trifluoroethoxy) phosphazene 1% o-allyl, Lot# TE1-78	77.8	190.7	0.408	2.451
Eypel-F mixed fluoroalkoxy phosphazene	61.9	283	0.219	4.572

hydrogen over carbon tetrachloride of 32. Polypropylene shows limited solubility to carbon tetrachloride with a permeability of 1.65 barrers and a hydrogen selectivity of 2.1.

Table 4 lists the ideal selectivities calculated at the ratios of the measured permeabilities. As expected because of the similar sizes, the H_2/He selectivities are close to one for the most part. Two notable exceptions are the high viscosity PVC and the high molecular weight polystyrene.

The selectivities of N_2, O_2, and CH_4 are mostly all larger than the He and H_2 because of the size differences. Also, for all of the gases except CO_2 the primary factor controlling the permeability is the diffusivity. CO_2 on the other hand is

Table 4. Ideal selectivities of hydrogen relative to the other gases tested

	H_2/He	H_2/N_2	H_2/O_2	H_2/CH_4	H_2/CO_2
PTMSP	2.2	4.6	2.2	2.0	0.5
PDMS	1.8	2.2	1.1	0.7	0.2
PVC/unplasticized	0.8		5.8	21.3	5.3
PVC viscosity = 0.62	1.0	28.7	12.4	20.9	6.6
PVC viscosity = 1.02	4.1	10.2	8.3	13.9	4.9
PE/Bag	1.6	4.1	2.7	2.2	1.0
Polysulfone MW = 26 K	1.1	15.0	7.1	30.0	2.0
Polysulfone MW = 35 K	0.8	6.3	4.3	113.0	3.3
Poly(ethylene terephthalate) pop bottle	0.6	0.7	0.7	0.6	0.6
Polystyrene (weigh boat)	1.3	50.8	11.0	36.3	7.9
Polystyrene, MW = 280 K	43.0	57.7	69.5	22.4	1.7
Polystyrene co-methyl methacrylate				2.0	1.4
Polystyrene co-acrylonitrile				4.0	1.3
Polystyrene co-butadiene				3.5	0.5
Polymethyl methacrylate MW = 350 K	0.2		0.7	4.0	4.0
Polyvinyl butyral				9.5	1.4
Polyvinyl acetate				18.3	1.2
CMS-3 (perfluoro amorphous copolymer)		5.9	2.5	8.8	1.0
Poly bis(trifluoroethoxy) phosphazene		2.3	1.3	1.3	0.4
Poly bis(p-fluorophenoxy)-phosphazene		13.6	4.1	6.4	0.6
Eypel F (fluorinated alkoxy substituted phosphazene)		2.5	1.2	2.0	0.2

notably more soluble, and that factor overcomes the fact that it is larger than hydrogen. This comes from the time-lag analysis of the pure gas data. The permeability of CO_2 is generally larger and so the trend is that the calculated ideal selectivities of hydrogen over CO_2 for the various polymers are close to one in many cases. All three PVC samples, the filled polystyrene, and the PMMA had the highest H_2/CO_2 selectivity values.

CONCLUSIONS

The gas permeabilities of more than 20 polymers were measured using pure and mixed gas techniques. The motivation was to determine potential materials that could be used to protect hydrogen getter particles from poisons while permitting sufficient hydrogen rates to enable the getters use in TRUPACT types of containers. A rate of five barrers or larger is needed, and of the materials screened in the pure gas tests more than 15 qualified. Nine materials qualified in the mixed gas tests, but of the nine only three had high CCl_4 rejection rates and four others would greatly reduce the transport of the CCl_4.

In the pure gas tests, PTMSP and PDMS showed the highest overall permeabilities to the gases in the test matrix. The highest hydrogen permeabilities were measured for the CMS-3 resin followed by two other fluorinated polymers, polybis(trifluoroethoxy) phosphazene, and Eypel F. All three of these polymers had relatively high values for the other gases, too. The next highest set was styrene-based polymers. The styrene polymers had low permeabilities for helium, nitrogen, and oxygen, while the CO_2 permeabilities were less than a factor of two lower than that for hydrogen.

The mixed gas experiment showed that many of the polymers tested are too soluble in CCl_4 for use as a membrane barrier in the presence of CCl_4. The two materials with the best perm-selectivity for H_2 over CCl_4 were polypropylene and the CMS-3 polymer.

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