CAPP

International Research Project on the Effects of Chemical Ageing of Polymers on Performance Properties

FLEXIBLE PIPES -
PERMEATION OF METHANE,
CARBON DIOXIDE AND WATER
THROUGH TEFZEL ETFE -
Experiments 1996

Prepared for:	**CAPP Joint Industry Project**
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Flexible pipes.
Permeation of methane, carbon dioxide and water through Tefzel ETFE. Experiments 1996.

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Summary/Conclusion:

The permeation of a mixture of CH_4 and CO_2 (97% CH_4 and 3% CO_2) saturated with water vapour through Tefzel has been studied at 95°C and 25 and 50 bars. Tefzel is the Du Pont trademark of an ETFE (ethylenetetrafluorethylene) which is a copolymer of ethylene and tetrafluorethylene. This material might be used as inner plastic lining of flexible pipes.

The permeability coefficients (***P*** in $cm^2/s \cdot bar$) for CH_4, CO_2 and water at the various temperatures are found to be:

Permeability ($cm^2/s \cdot bar$)		
CH_4	CO_2	H_2O
3.65E-08	2.09E-07	1.62E-06

For methane and carbon dioxide, the permeability of Tefzel is higher than the deplasticized PVDF (Polyvinylidenefluoride), but lower than the plasticized PVDF. For water, the situation seems to be the other way round; Tefzel has a lower permeability than deplasticized PVDF.

Whether the permeability tests on Tefzel at higher temperatures and pressures will be pursued or not, will be considered by the steering committee of the CAPP project in May.

1. Introduction.

This document describes the permeation test of Tefzel ETFE (Ethylene Tetra Fluor Ethylene) performed in 1996.

2. Experimental and testing parameters.

The experiments are performed with a new pressure cell. One advantage of this cell is the possibility of testing on various pipe dimensions, up to 90 mm OD. In principle though, the same experimental set-up as described in the previous report was used in these measurements (/1/,/7/). A drawing of this new cell can be found in App. 4.

The permeation is measured from a pressurised test gas inside a sealed pipe section. The sample pressure is balanced with argon on the outside. The argon gas flushes the outside and brings the permeated gases to a gas chromatograph and a moisture detector for analysis. The saturation of the gas mixtures with water was performed at the actual temperature.

The test series that were planned to be performed on Tefzel are shown in Table 1. Due to system- and component failures, fewer test runs are performed in 1996 than planned. Thus, there are no results ready yet for other pressures and temperatures than described in the table.

The CAPP steering committee will decide (May 1997) whether the tests on Tefzel will be pursued according to plan or not.

Table 1. Overview of the planned testing parameters. One can see that only the 25 and 50 bar at 95°C testing is finished. The gas mixture is fluid B according to the CAPP nomenclature.

Gas mixture (All saturated with water)	Temperature (°C)	Pressure (bar)	Status
97% CH_4/3% CO_2	70	25, 50, 75, 100, 120	Pending
97% CH_4/3% CO_2	95	25, 50	Finished
97% CH_4/3% CO_2	95	75, 100, 120	Pending
97% CH_4/3% CO_2	120	25, 50, 75, 100, 120	Pending

The permeation rates and permeability coefficient were determined as described in the previous reports /1/, /7/. The permeability coefficients were calculated by using equation 1, which applies to a cylinder.

$$P = \frac{q}{t} \cdot \frac{\ln(r_1/r_2)}{2\pi L(p_1 - p_2)} \qquad \text{(Equation 1)}$$

q/t = permeation rate, p_1 and p_2 are the high and low (inside and outside) partial pressures. The dimension of the permeability coefficient is $cm^2/s \cdot bar$.

3. Results.

3.1 Methane and carbon dioxide.

The amount of each gas permeated through the sample and associated permeability coefficients for methane and carbon dioxide at each pressure are given in App. 2. A graphical presentation of permeation rates and concentrations as a function of time can be found in App. 3. Table 2 below shows a summary of permeability data for the gases.

On the 50 bar run, the flow of argon was increased from 20 to 50 ml/min in order to improve the stability of the analysis. The effect of this was that the concentrations increased, and thereby a higher permeability rate was found. However, the increment is insignificant in the scales used for evaluation. Details can be seen on the concentration and permeation charts in App. 3. No explanation could be found yet on this effect.

Table 2. Summary table for methane and carbon dioxide.

Run	Permeability ($cm^2/s \cdot bar$)	
	Methane	CO_2
95°C 25 bar	2.99E-08	1.82E-07
95°C 50 bar I	3.51E-08	1.94E-07
95°C 50 bar II	4.45E-08	2.50E-07
Average	3.65E-08	2.09E-07

For comparative purposes, the average Tefzel permeability is plotted together with the permeabilities of other materials previously tested (Figures 1-2). One can see that for this particular temperature and pressures, the permeability of carbon dioxide and methane through Tefzel ETFE is lower than through Solef and Coflon PVDF.

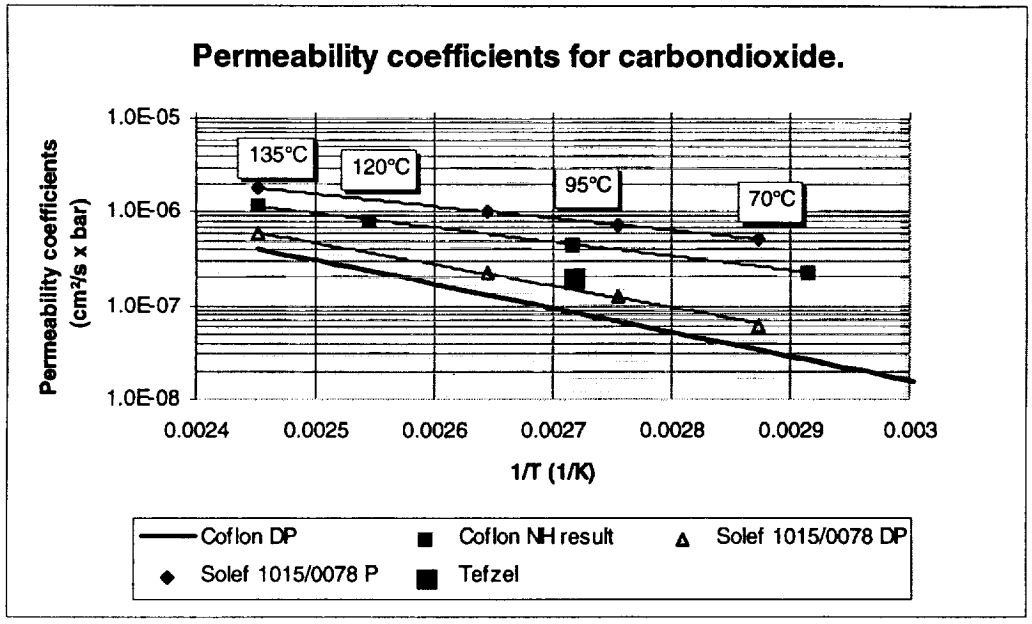


Figure 1. The figure shows the permeability coefficient of CO_2 through Tefzel at 95 °C. Coefficients for plasticized and deplasticized PVDF are also shown. The Coflexip data (Coflon DP) are from /2/ and the Solvay data are from /3/.

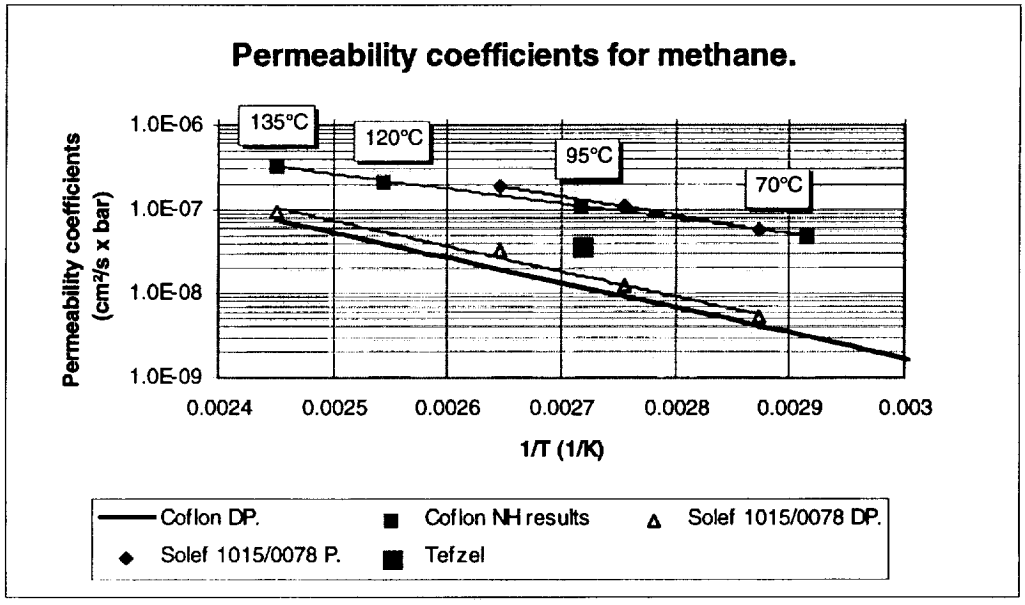


Figure 2. Permeability coefficient of methane through Tefzel at 95 °C. Coefficients for permeation of CH_4 through plasticized and deplasticized PVDF are also shown. The Coflexip data (Coflon DP) are from /2/ and the Solvay data are from /3/.

3.2 Water permeation.

Details regarding the computation of water permeability, and a graphical presentation of permeation rate of water, can be found in App. 1 and 3 respectively. Although there is a relative small change, the water permeability is also in this case increased when the flow rate of argon is increased. Table 3 summarises the permeability coefficient for the various conditions.

Table 3. Summary table for water.

Run	Permeability ($cm^2/s \cdot bar$)
95°C 25 bar	1.48E-06
95°C 50 bar I	1.47E-06
95°C 50 bar II	1.92E-06
Average	1.62E-06

The permeability coefficient is plotted together with previous data on PVDF in Figure 3. From the figure, one can see that the permeability of water trough Tefzel is lower than trough deplasticized PVDF.

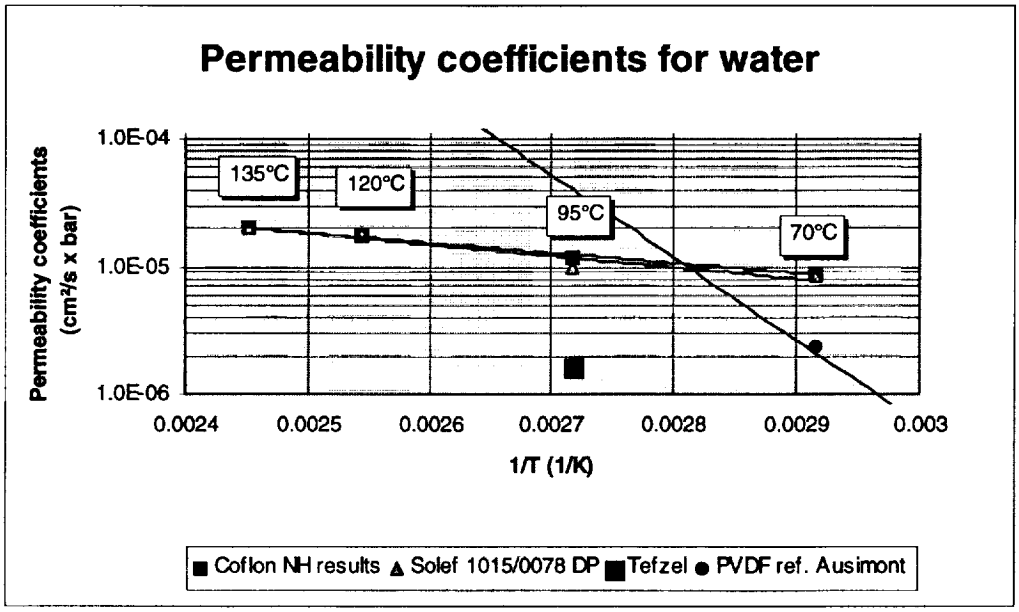


Figure 3. Permeability coefficient of water through Tefzel at 95 C. The coefficients for permeation of water as a function of temperature through deplasticized Coflon is also shown.

Porsgrunn, 1997-04-18

Per Arne Wang

4. References

/1/ J. I. Skar, "Permeabilty of methane and carbon dioxide through plasticized polyamide (PA11) and polyvinylidenefluoride (PVDF). Norsk Hydro Doc. No. 94R_DS6, 1994-09-02. (CAPP/N.1)

/2/ B. Radenac, "COFLON - A material for inner lining of Coflexip flexible pipe". Coflexip report no. 93.05.06, September 1993.

/3/ "Solef PVDF for offshore applications". Presentation in Brussel by Solvay, January 31. 1996.

/4/ Design Guide, "HALAR ECTFE" Ausimont USA. Inc. 1992.

/5/ G. J. Morgan and B. Campion, CAPP/M.4 Rev. B.

/6/ Giddings, Myers, McLaren, Keller, Science 162, 67 - 73 (October 1968).

/7/ Skar, Jan Ivar; Hansteen, Christoffer : "Flexible Pipes. Permeation of methane, carbon dioxide and water trough polyvinylidenfluoride"; Report HRE; 96Q_DC8.DOC; File 972.61.

Appendix 1

Permeation of water.

Water Permeation Measurements

P(vann) er regnet ut fra en regresjon av vanndampens metningstrykk mot temperatur
(Se VANNDAMP.XLS)

kk 25 bar mmentarer	*Tidspunkt Dato og klokkeslett*	*Rel. fukt. %*	*Temp i celle °C*	*P(vann) mbar*	*Barometer*	*Tid fra start timer*	*Flow Ar ml(NTP)/min*	*Vann mmol/min*	*Vann ml(NTP)/min*	*Total tid*
25	27.11.1996 09:12	6.7	21.0	1.664479	1022.0	24.2	20.06	0.00146	0.0327	24.2
26.11.1996 09:00	27.11.1996 11:08	6.6	21.2	1.659925	1022.0	26.1	20.06	0.00146	0.0326	26.1
	27.11.1996 15:16	6.7	20.9	1.654264	1022.0	30.3	20.06	0.00145	0.0325	30.3
	28.11.1996 09:50	6.7	21.2	1.685076	1022.2	48.8	20.06	0.00148	0.0331	48.8
	29.11.1996 08:30	6.8	20.9	1.678955	1005.1	71.5	20.06	0.00150	0.0336	71.5
	29.11.1996 12:48	6.3	21.6	1.623849	1005.1	75.8	20.06	0.00145	0.0325	75.8
								Snitt	*0.0328*	
								Std. dev.	*0.0004*	

kk 50 bar mmentarer	*Tidspunkt Dato og klokkeslett*	*Rel. fukt. %*	*Temp i celle °C*	*P(vann) mbar*	*Barometer*	*Tid fra start timer*	*Flow Ar ml(NTP)/min*	*Vann mmol/min*	*Vann ml(NTP)/min*	*Total tid*
50	29.11.1996 18:40	7.9	21.2	1.98688	998.1	4.7	19.78	0.00176	0.0395	81.7
29.11.1996 14:00	30.11.1996 10:15	7.0	20.6	1.696669	1002.9	20.3	19.78	0.00150	0.0335	97.3
	30.11.1996 18:00	7.0	20.6	1.696669	1009.1	28.0	19.78	0.00149	0.0333	105.0
	01.12.1996 10:15	4.3	20.5	1.035827	1012.1	44.3	19.78	0.00090	0.0203	121.3
	01.12.1996 21:30	7.7	21.1	1.924711	999.1	55.5	19.78	0.00170	0.0382	132.5
	02.12.1996 08:25	6.8	21.0	1.689322	995.1	66.4	19.78	0.00150	0.0336	143.4
	02.12.1996 12:15	6.4	22.0	1.690507	995.9	70.3	19.78	0.00150	0.0336	147.3
								Snitt	*0.0331*	
								Std. dev.	*0.0062*	

kk 50 bar nmentarer	*Tidspunkt Dato og klokkeslett*	*Rel. fukt. %*	*Temp i celle °C*	*P(vann) mbar*	*Barometer*	*Tid fra start timer*	*Flow Ar ml(NTP)/min*	*Vann mmol/min*	*Vann ml(NTP)/min*	*Total tid*
on økt til ~60	02.12.1996 15:57	3.7	22.2	0.989336	996.6	73.9	50.63	0.00224	0.0503	150.9
	02.12.1996 22:05	3.3	21.3	0.835077	997.2	80.1	51.63	0.00193	0.0433	157.1
	03.12.1996 09:05	3.0	22.0	0.792425	998.3	91.1	52.63	0.00187	0.0418	168.1
	03.12.1996 12:50	3.1	22.2	0.828903	999.5	94.8	53.63	0.00199	0.0445	171.8
								Snitt:	*0.0432*	
								Std. dev.:	*0.0014*	

Permeation of water.

Water Permeation

Runs at 95°C

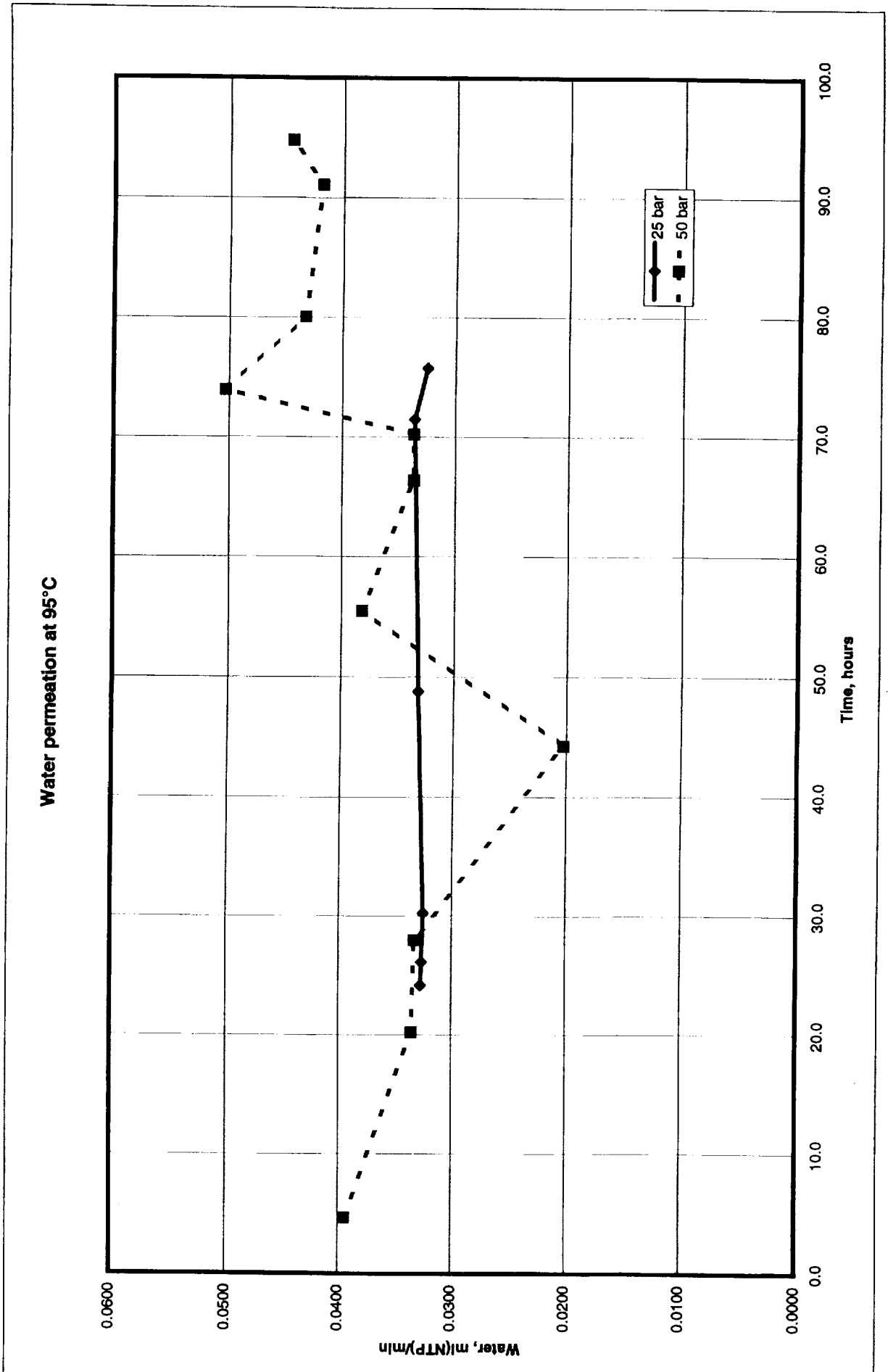
Gas mixture:

Methane, % %m	CO2, % %c
97	3

Test piece no. 3:	L, cm	l, cm	d1, cm	d2, cm	A, cm2
1	0.3386	6.008	7.455	8.083	146.6331315

Run	Temperature T, 95°C	1/T	Water ml(NTP)/min Vm	Pressure total bar p	Water vapour pressure: bar	Permeab. flat Pm	Permeab. cyl. P'm
95°C 25 bar	95	0.002716	0.0328	25	0.8580	1.47E-06	1.48E-06
95°C 50 bar I	95	0.002716	0.0331	50	0.8708	1.46E-06	1.47E-06
95°C 50 bar II	95	0.002716	0.0432	50	0.8708	1.91E-06	1.92E-06
						Average:	1.62E-06

Permeation of water.



Appendix 2

Permeation of gas

Gas permeabilities in Tefzel

Runs at 95°C

Gas mixture:

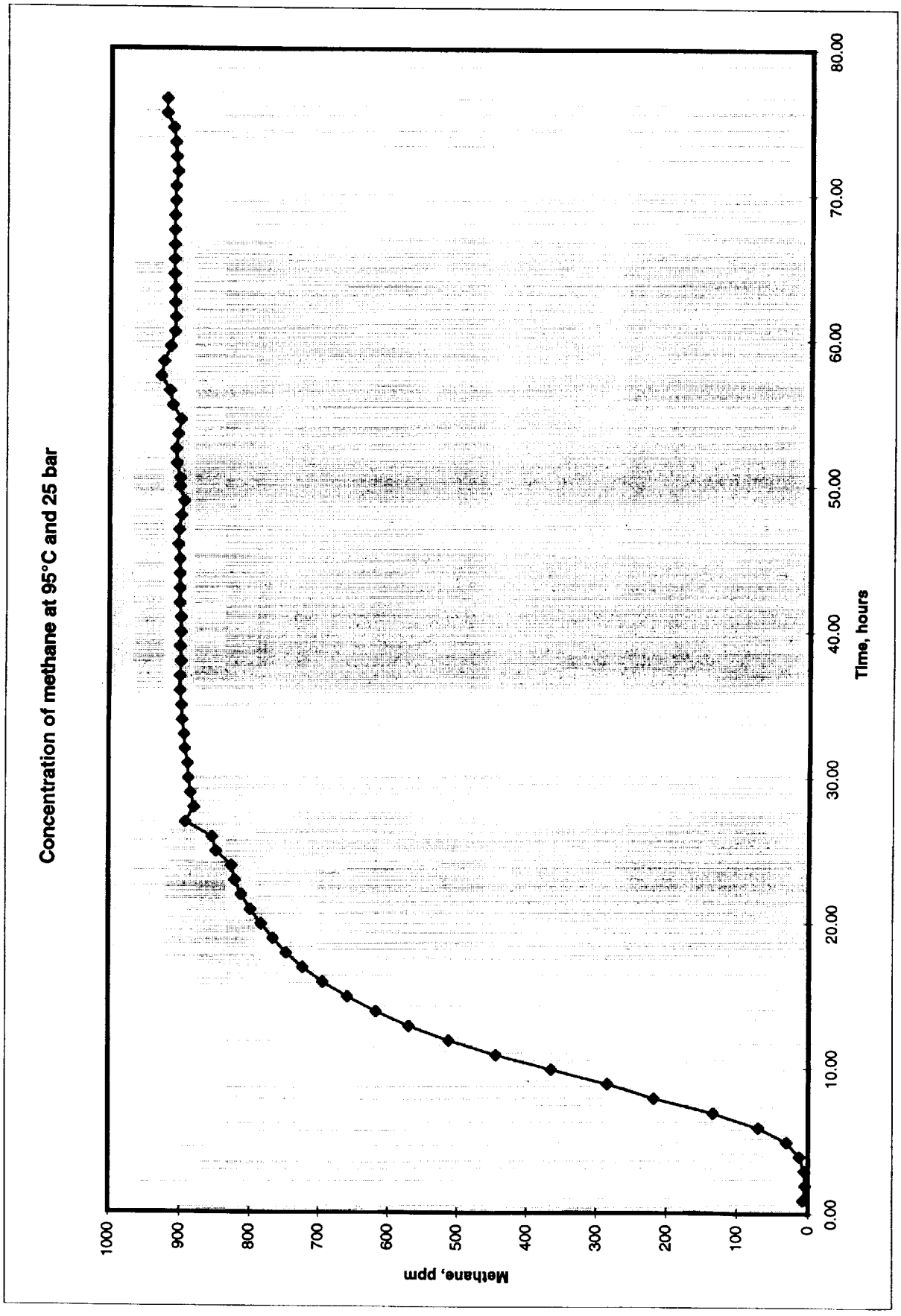
Methane, % %m	CO2, % %c
97	3

Test piece	L, cm	l, cm	d1, cm	d2, cm	A, cm2
1	0.3386	6.008	7.455	8.083	146.63

Run	Temperature T, 95°C	1/T	Methane ml(NTP)/min Vm	Carbon Dioxide ml(NTP)/min Vc	Pressure total bar p	Water vapour pressure: bar p	Permeability, flat		Permeability, cyl	
							Methane Pm	CO2 Pc	Methane P'm	CO3 P'c
95°C 25 bar	95	0.002716	0.01814	0.00341	25	0.858	2.98E-08	1.81E-07	2.99E-08	1.82E-07
95°C 50 bar	95	0.002716	0.04326	0.00742	50	0.871	3.49E-08	1.94E-07	3.51E-08	1.94E-07
95°C 50 bar	95	0.002716	0.05485	0.00953	50	0.871	4.43E-08	2.49E-07	4.45E-08	2.50E-07
								Average	3.65E-08	2.09E-07

Appendix 3

Graphs of gas measurements.



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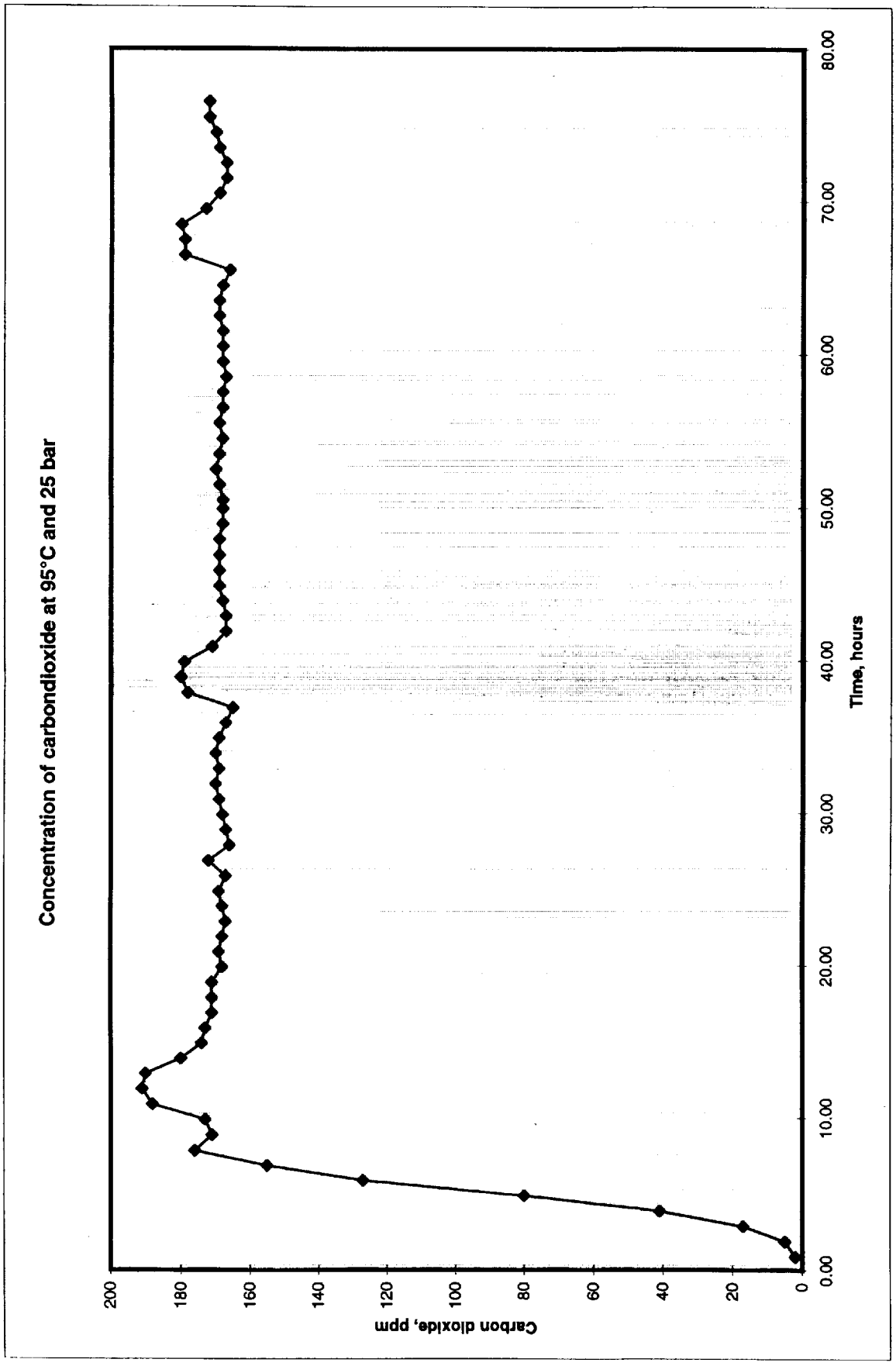

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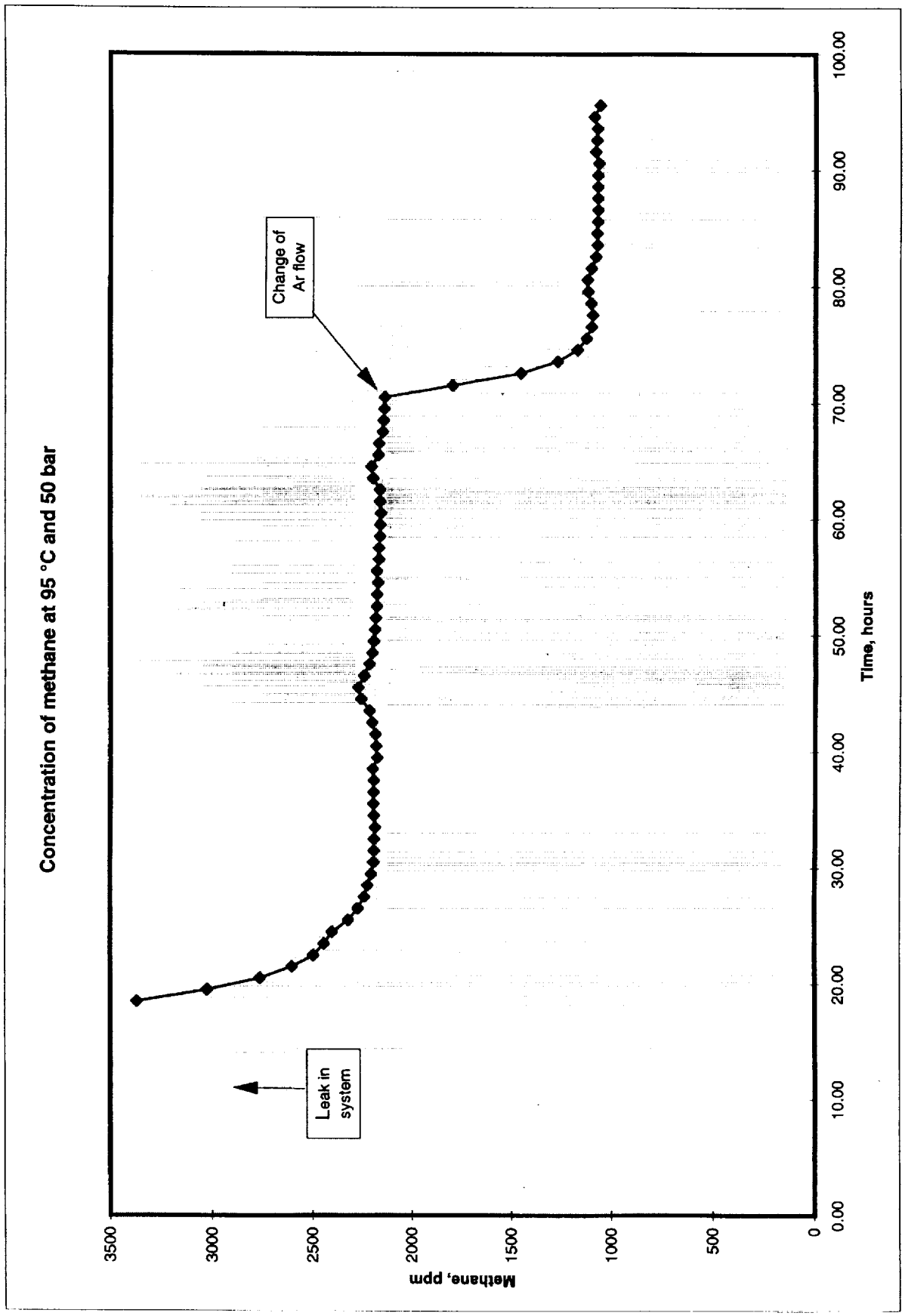
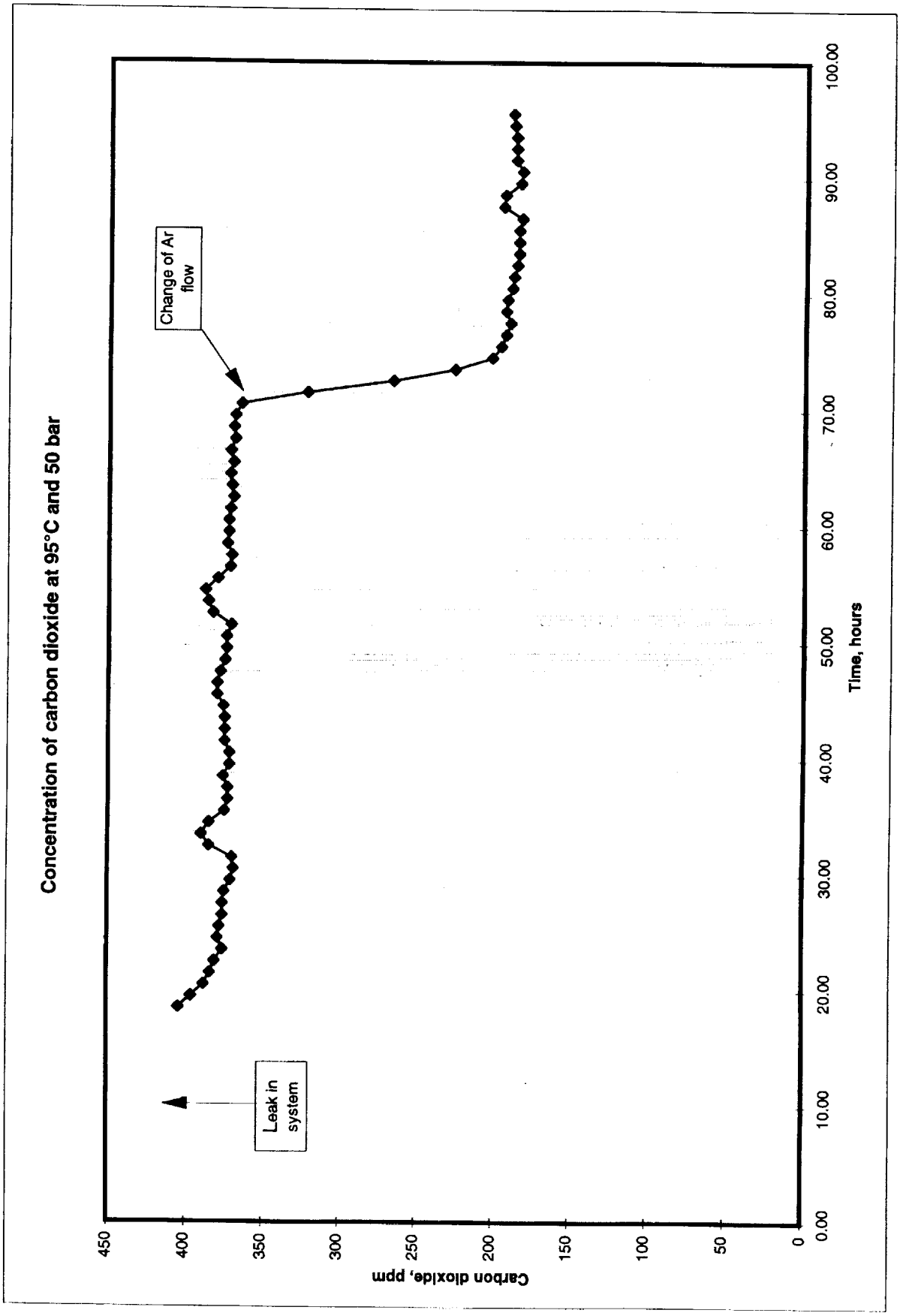
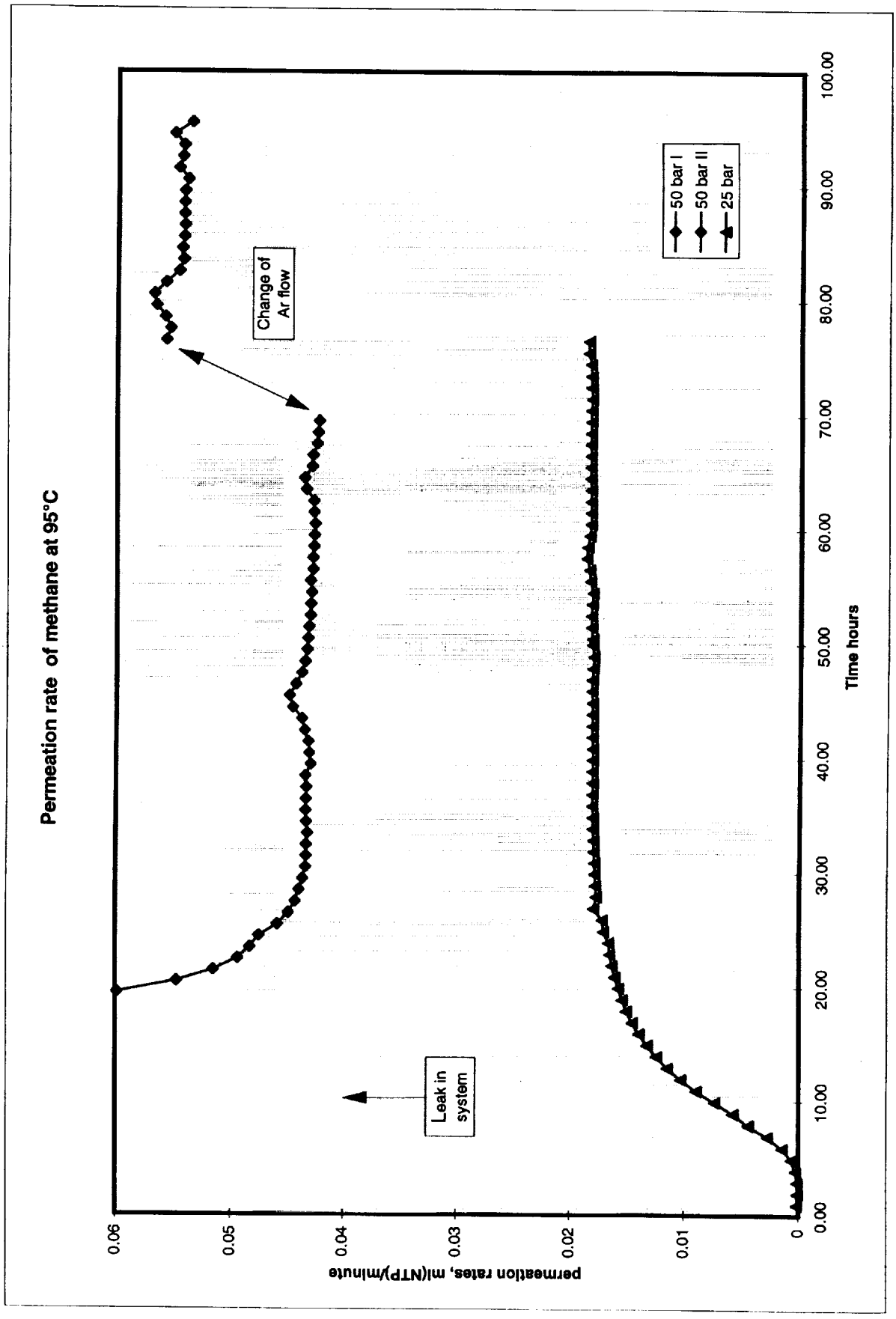


Graphs of gas measurements.



Graphs of gas measurements.



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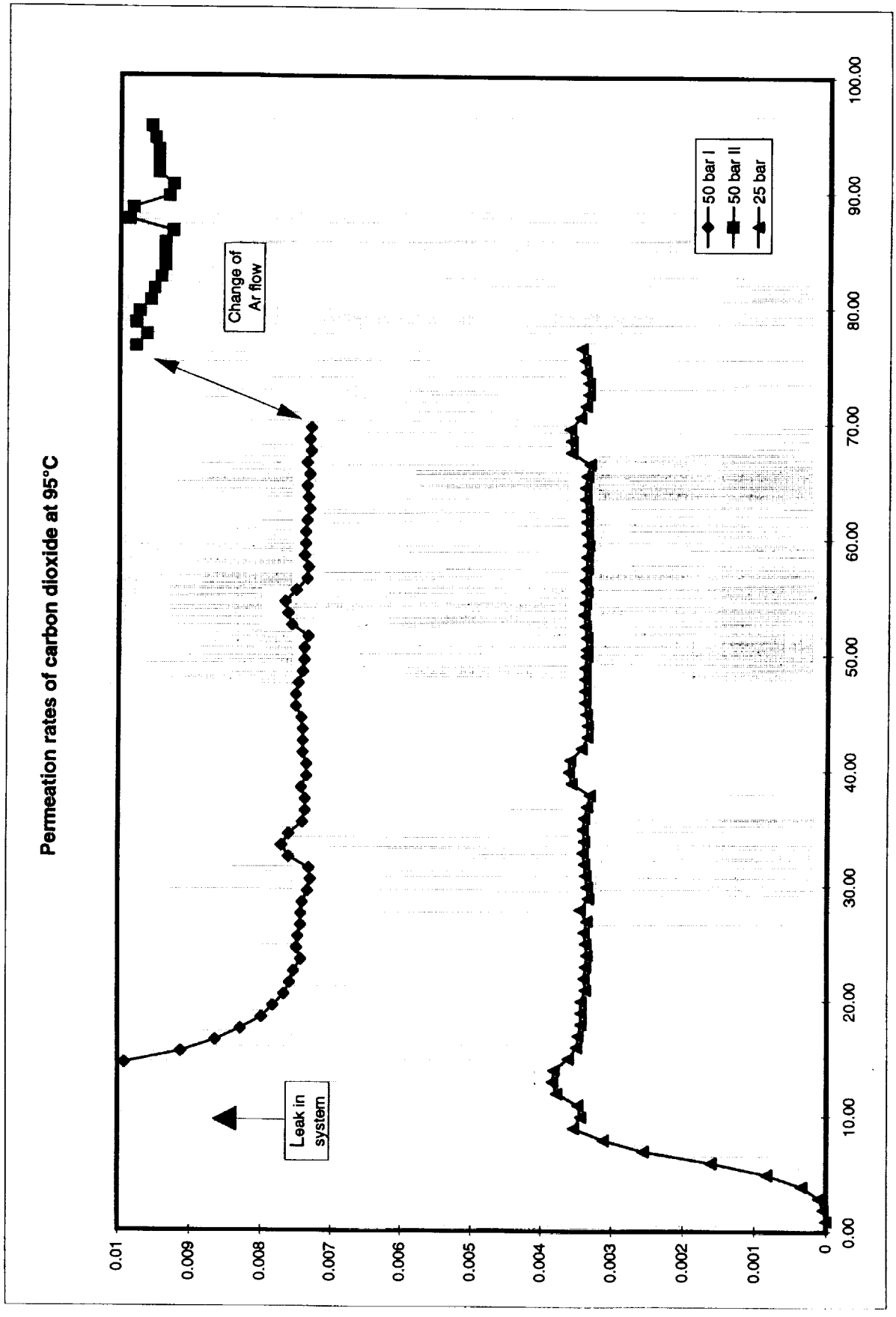
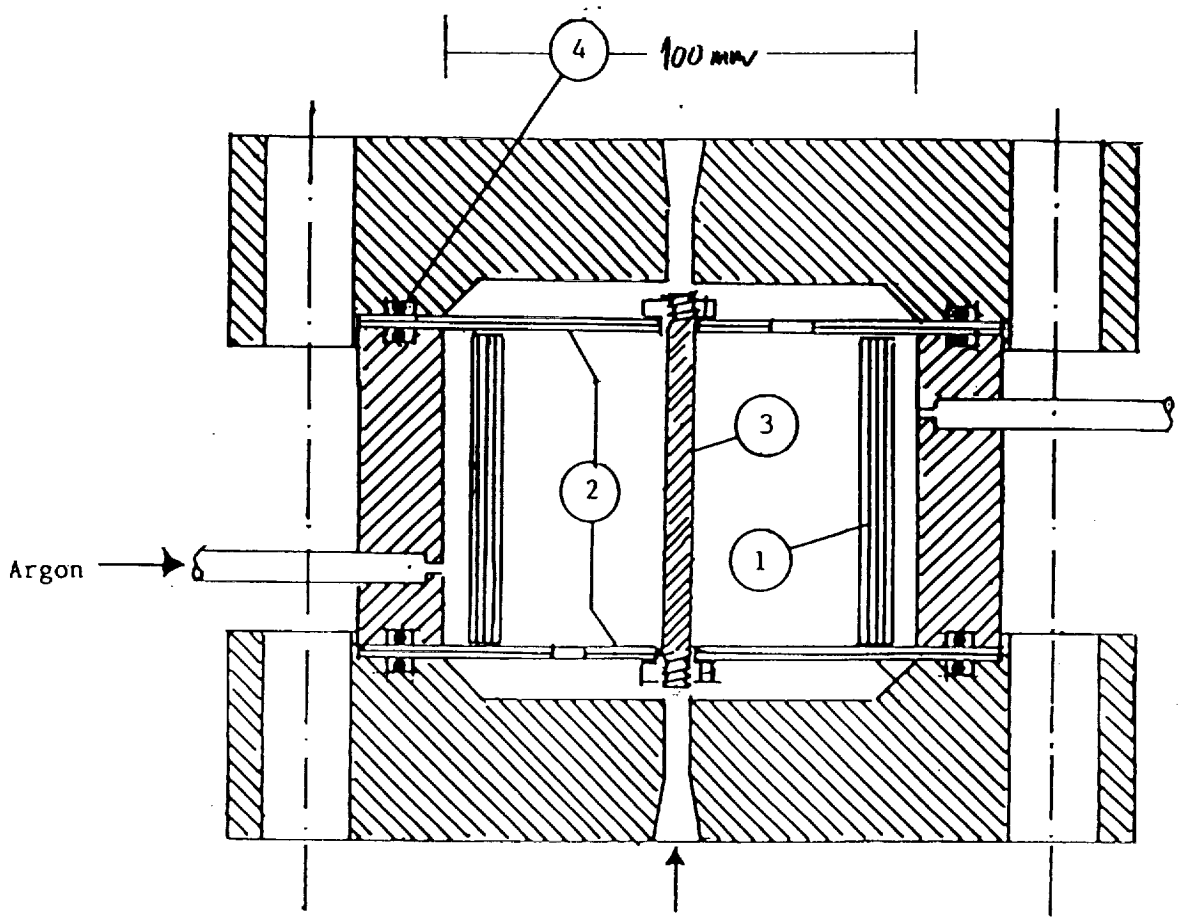


Appendix 4

FORSLAG TIL CELLE SOM KAN BRUKES TIL RØR AV FORSKJELLIG RØRDIAMETER

PERMEATION CELL



1. Prøve av røret
   PIPE SAMPLE
2. Tetningsplater med huller for testgass
   SEALING DISC WITH HOLES FOR TEST FLUID
3. For bolt med muttere
   BOLT WITH NUTS FOR TIGHTENING
4. Tetning med O-ring
   SEALINGS