NAG10-153

CAPP

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

NASA/CR-97- 207610

IN-27-CR
078937

HIGH PRESSURE GAS PERMEATION AND LIQUID DIFFUSION STUDIES OF COFLON AND TEFZEL THERMOPLASTICS

Prepared for: CAPP International Consortium

Prepared by: G J Morgan and R P Campion

Document date:
30 November 1994
Revised 5 June 1995
Revised 14 May 1996
Revised 19 February 1997

Document no: CAPP/M.4 Rev C

9063 Bee Caves Road, Austin
Texas 78733-6201, U.S.A.
Tel: 1-512-263-2101

MERL
Tamworth Road, Hertford
SG13 7DG, England
Tel: 44-(0) 1992-500120

CONTENTS

SYNOPSIS

In high pressure gas permeation tests through Coflon and Tefzel, the permeation rate of carbon dioxide was many times faster than that of methane. A 97/3 methane/carbon-dioxide mixture was found to permeate at the same rate as pure methane for both Coflon and Tefzel. With unaged material, both gases permeated slower through Tefzel than Coflon. Arrhenius plots yielded good straight line relationships leading to activation energies for permeation: good extrapolations to other temperatures are possible. Methane permeation was faster at low pressures than at high pressures through Coflon whereas with carbon dioxide the reverse was found, for reasons associated with the high concentration of the CO_2.

Samples cut directly from Coflon pipe gave (a) methane permeation results that agreed well with samples cut from flat extruded bar, and (b) comparable results to those reported by Norsk Hydro using their alternative pipe-section test method. Another feature has been the similarity of all permeation-related coefficients measured at 140C and HP for normal 6mm thick Coflon samples and a thinner version with machined-off surfaces, suggesting a reasonably uniform morphology throughout unaged samples.

Deplasticisation of Coflon in an air oven at elevated temperature resulted in a 17% volume decrease and a subsequent six-fold decrease in methane permeation rate at 140C, thus giving a value close to that reported by Coflexip. High pressure gas permeation can also deplasticise Coflon, by leaching: data from a 60-day test were used to estimate a diffusion coefficient for such deplasticisation. Suggestions are made on how to change the plasticiser to minimise leaching. Replasticisation by permeating gas is unlikely to be a major effect in service.

Ageing Coflon in various gas/liquid mixtures reduced methane permeation compared to unaged samples. Combinations of amine with either hydrogen sulphide or methanol formed a chemically-aged brittle material often with a blackened surface region, again with decreased permeation rates. However, it was not possible to correlate changes in permeation characteristics with degree of chemical ageing due to the underlying decrease in permeation brought about by deplasticisation through leaching by HP gas. Hence permeation at present cannot be used as a single diagnostic tool to assess chemical ageing effects, although diffusion coefficients could give an overview of the closeness of the general chemical structure.

After ageing samples of Tefzel in various of the project test fluids, permeation of methane generally increased (by as much as 50%) compared to unaged samples, although not in a manner which related to the severity of the ageing condition. This has been attributed to the possible loss of low molecular weight polymer components leaving a micro-flawed, more permeable, structure. Coupled with the decreases in permeation that occur for aged Coflon, in service Tefzel could eventually be more permeable than Coflon.

Absorption of a high aromatic oil by Tefzel resulted in swell and increased permeation. Permeation of methane through a methanol-contacting sample of Coflon resulted in a three-fold increase in rate: the Coflon was found to be spongy, and the methanol also permeated through the sample. Using a specially-sealed Tefzel sample, the diffusion coefficient for methanol absorption via large surface faces has been shown to agree with the value obtained separately by a permeation test method, diffusion being much slower than that through sample edges. A similar effect exists, but to a much lower degree, for Coflon: reasons are discussed.

1 INTRODUCTION

The life of fluid-carrying flexible or umbilical pipes during service at elevated temperatures and pressures depends *inter alia* on their resistance to attack by the fluids present and the rate at which these fluids are absorbed by the pipe lining materials. The consequences of fluid ingress into the thermoplastic lining could mean

a) a reduction in its mechanical strength, to increase chances of crack formation and growth and thus a loss of integrity,

b) the occurrence of permeation right through the lining material, with pressure build-up in the outer pipe wall construction (of flexible pipes) or chemical attack (from a hostile permeant) on outer layers of reinforcements.

Therefore it is important within this project to have relevant permeation data for Coflon and Tefzel thermoplastics: the former is plasticised, the latter is not.

A previous report (CAPP/M.2) described experimental equipment and techniques used by MERL when measuring high pressure (up to 5000psi) gas permeation and liquid diffusion through thermoplastic samples cut from extruded bar or pipe, and provided the basic theory involved. Norsk Hydro are also performing gas permeation tests on pipe sections, at up to 100 bars (1450psi) pressure or so, and reporting separately. Some comparisons between data from Norsk Hydro and MERL have been made herein. The tests should be considered as complementary, as the Norsk Hydro test has the obvious benefit of using complete pipe sections, whilst MERL can test at much higher pressures, up to 1000 bar if necessary. The sophisticated analytical measuring equipment of Norsk Hydro can distinguish the individual components of mixed gases and hence the various permeation-linked coefficients whereas MERL, in using pressure increase at constant volume to determine permeation rate, is limited to obtaining single gas data, or apparent (or representative) coefficients for a mixed gas as a whole.

Except for the initial fluid diffusion data for Tefzel described in CAPP/M.2, the present report covers all aspects of fluid permeation and diffusion for Coflon and Tefzel, including all the permeation data accumulated in the project to date. Test gases have mainly been methane (CH_4) and carbon dioxide (CO_2). More high pressure (HP) gas permeation tests have been performed since the last issue of this report, most being concerned with changes in permeation characteristics brought about by ageing in various relevant fluids. This revision supersedes previous issues.

2 THEORY - COMMENTS

The background theory of permeation and diffusion processes is given in detail in reports CAPP/M.2 and CAPP/MT.1, the review document. The equation developed therein for gas permeation through a polymer membrane is

$$q/t = QA(P_1-P_2)/h \tag{1}$$

where q/t is permeation rate, Q is permeation coefficient, P_1 is applied high pressure, P_2 pressure of permeated gas, and A and h are specimen area and thickness respectively. Permeation rate is expressed in terms of volume (conveniently at STP) per time. This equation is used for the MERL high pressure permeation test. In practice, Q has been found to change on occasions as tests progress, so it is MERL policy to calculate Q for a convenient period of time, repeat this calculation for the next period, and so on. In this way, plots of Q versus testing time can be obtained (as will be seen later).

A similar development of theory can be applied to permeation through a pipe lining. The resulting equation is

$$q/t = 2\pi LQ(P_1-P_2)/\ln(r_2/r_1) \tag{2}$$

where L is the length of the pipe, r_1 is its inner radius and r_2 its outer radius. Hence assessments of permeation through real pipe lining situations, *assuming the worst case of unrestricted removal of gas once through*, can be calculated with equation 2 if an appropriate Q has been previously measured. For samples cut from a pipe (curved discs) an equation can be developed from equation 2 by proportionation on an area basis. For the curved disc samples used in the present work

$$q/t = 2.94[\sin^{-1}(0.935/r_1)]Q(P_1-P_2)/\ln(r_2/r_1) \tag{3}$$

CAPP/M.2 and CAPP/MT.1 also show how diffusion coefficient D, solubility coefficient s and concentration c are obtained from the test used to measure Q.

These reports also describe the derivation of the appropriate equation for liquid absorption (or mass uptake experiments), used herein for methanol uptake experiments. The equation is

$$0.5 = (2/h)\,(D_{av}\,t_{av}/\pi)^{1/2} \tag{4}$$

where t_{av} is the time to 50% of the eventual equilibrium mass uptake, 2h is thickness, and D_{av} is average diffusion coefficient.

3 EXPERIMENTAL DETAILS

3.1 HP gas permeation

The general description of the high pressure gas permeation experimental equipment and procedures given in CAPP/M.2 are still relevant to the current work. Permeated gas is measured by pressure build-up, which is converted to equivalent volume build-up using a derivative of the ideal gas law. Gradual optimisation of sample holders and sealing arrangements has led to a standard test geometry for both Coflon and Tefzel. Samples are nominally 6mm thick for Coflon and 3mm thick for Tefzel, values relating well to dimensions when in service. Both types are usually tested as 35mm diameter discs cut from flat extruded sheet but pipe samples can be tested, also. The standard sealing arrangement is that shown in Figure 1. Other figures show the options to use test gas containing water vapour (Figure 2), Coflon samples cut directly from pipe (Figure 3), and methane permeation through samples in contact with a methanol layer on the HP side (Figure 4).

The same equipment was used for a one-off experiment to measure high pressure methanol permeation through Tefzel: to do this, a temperature above the boiling point (65C) of methanol, but below its critical point (240C), was used. With sufficiently high pressures, (according to tables, over 2-300psi for a test temperature of 150C), the HP methanol remained liquid, but any permeating species (at near-ambient pressures) immediately evaporated, and its rate of pressure build-up could be measured as usual. Testing was performed across the pressure range 1200-2500psi (the permeation rate being essentially independent of applied pressure).

3.2 Methanol uptake in pipe sections

Various methanol liquid absorption tests have been performed on Tefzel and Coflon. The effect of absorption along aligned crystalline regions was investigated. This was achieved by using short uniform pipe sections as samples, testing some as such, but modifying others before testing by blanking off the pipe ends (edges) with two steel discs clamped together by an axial nut-and bolt arrangement. In the latter cases, holes were drilled in the discs away from the pipe section sample. In this way, on immersion in methanol, besides having obvious access to the outside surface of the cylinders the liquid also had free access via the drilled holes to the inner surface; however, the methanol could not contact the pipe ends (edges) due to the clamped-on discs. A series of mass uptake measurements at 150C for Tefzel and 100C for Coflon, were performed until equilibrium was achieved and compared to results obtained with the pipe section samples without the ends sealed. Average diffusion coefficients D_{av} were calculated from equation 4.

4 COFLON HP GAS PERMEATION RESULTS AND DISCUSSION

Values obtained after high pressure permeation testing for permeation coefficients Q, diffusion coefficients D, solubility coefficients s and concentrations c are shown in Table 1 for various gases through unaged Coflon (including a previously-deplasticised sample), in Table 2 for methane permeation through Coflon after various ageing exposures in some relevant hostile environments, and in Table 3 for methane permeation through Coflon after a series of Fluid F (wet H_2S + amine) exposures. D, s and c can only be estimated if time lag measurements are made from the initial part of the test plot (with the method used). Hence Q is also quoted from the early part of a test to ensure that like can be compared with like throughout the schedule. The discussion over the next few pages involves data from Tables 1, 2 and 3 and also concerns results from Norsk Hydro[1] and Coflexip[2] work, taken from the Norsk Hydro project reports CAPP/N.1 and /N.2.

TABLE 1 Summary permeation results table for unaged Coflon
Test temperature 140C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
C1	CH_4	5000	0.30	4.1	0.07	23
C10	CH_4	1400	0.40	4.5	0.09	8
		5000	0.25	1.3	0.19	64
C14	CH_4	5000	0.40			
†C2 (3mm thick)	CH_4	5000	0.30	3.9	0.08	27
		10000	0.12	0.6	0.22	150
C7	CO_2	5000	3.0	6.0	0.32	103
C15	CO_2	5000	(2.4)			
C9	97/3 CH_4/CO_2	5000	0.30	"1.4"	"0.20"	"65"
C8	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.20	"1.5"	"0.14"	"48"
C19	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.40			
C20	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.26			
C17 (After deplasticisation in air oven at 140°C for 20 days)	CH_4	5000	0.05	0.9	0.05	17
C22 (long term, 60-days)$^{++}$	CH_4	5000	0.40 - 0.07			
C12 (Elf Atochem supplied pipe)	CH_4	5000	0.29	3.40	0.09	30
**C21 (Norsk Hydro supplied pipe)	CH_4	1040	0.19	2.21	0.09	6

* *Thickness nominally 6mm unless shown otherwise* ** *Tested at 120C*

$^+$ *At STP* $^{++}$ *Eventually significantly deplasticised*

† *3mm thick sample prepared by machining 1.5mm off each face of a 6mm thick sample, to examine for possible skin effects*

Quotation marks indicate apparent values (for gas mixtures)

Test temperature 110C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
C3	CH_4	5000 10000	0.10 0.10	1.9	0.04	14
C14	CH_4	5000	0.11			
C15	CO_2	5000	1.8			
C19	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.1			
C20	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.07	"1.3"	"0.05"	"19"

* *Thickness nominally 6mm*

\+ *At STP*

Quotation marks indicate apparent values (for gas mixtures)

Test temperature 90C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
C14	CH_4	1400 5000	0.08 0.04	1.2	0.05	5
C15	CO_2	5000	0.8	1.7	0.28	98
C19	97/3 CH_4/CO_2 plus H_2O (v)	1400 5000	0.04 0.03	"0.9"	"0.05"	"4"
C43** (Norsk Hydro supplied and tested pipe)	CH_4	1400	0.05	1.3	0.04	4

* *Thickness nominally 6mm*

** *Tested at 95°C*

\+ *At STP*

Quotation marks indicate apparent values (for gas mixtures)

4.1 Deplasticisation and long-term effects

To provide a background for subsequent comparisons, a sample of Coflon (C17) was deliberately deplasticised by heating in an air oven at 140C for 20 days by which time the sample had lost 10.4% by weight (all presumed to be plasticiser which had been present at approximately 12%), accompanied by a 17.7% loss in volume. Permeation testing this sample with CH_4 at 5000 psi and 140C showed a six-fold reduction in Q, from *ca* 0.3×10^{-6} (virgin sample C1) to 0.05×10^{-6} cm^2/s/atm. The equivalent reduction in D was 4-5 times, but little change in s and c occurred. The reduction in permeation rate was taken to be associated with the large decrease in volume.

A further test (C22) was conducted to investigate an alternative deplasticisation process which is a better simulation of flexible pipe service conditions. A permeation test with methane at 5000 psi and at 140C was left to continue for many days (60). The logic was that, at 5000psi, methane is at a liquid-like density and possesses quite a high solubility parameter[3-5] *ca* 9.2 $(\mathrm{cal/cm^3})^{1/2}$, so the plasticiser dibutyl sebacate (9.2 $(\mathrm{cal/cm^3})^{1/2}$) is subjected to a thermodynamic drive to leave the polymer (11.3 $(\mathrm{cal/cm^3})^{1/2}$) and enter the pressurised external gas: the process would involve desorption at the surface, and diffusion of plasticiser from bulk to surface to replace that already desorbed, and so on, on a continuous basis. (The concept of solubility parameter δ for liquids is discussed in CAPP/MT.1: basically, the more similar the δ values for two liquids, or a liquid and a polymer, the more likely they will mix. Gases at high pressures (liquid-like densities) can be treated similarly.) In other words, the pressurised gas leaches the plasticiser out of the PVDF. After the test, drops of plasticiser were observed in the permeation cell. Figure 5(a) is a plot of Q against test time, showing how the permeation coefficient for methane permeation through the Coflon sample decreased with increasing time from 0.4 to 0.07 x 10^{-6} $\mathrm{cm^2/s/atm}$, presumably as plasticiser was removed. Thickness changes with time are also shown in this figure; notice that, although the thickness does not decrease by a similar factor, the thickness reduction shown has apparently caused sufficient loss of internal free volume to cause a significant decrease in permeability; therefore *volume* reduction is the overriding consideration here.

If change in methane permeation coefficient Q values occurs as a direct proportionation of plasticiser loss, it should be possible to use the former to estimate a diffusion coefficient for plasticiser migration during deplasticization under these conditions. Plotting the Q values from Figure 5(a) against root time gives a shape as would be expected for a finite amount of diffusant (see Figure 5(b)). The initial stage is linear but, as the supply of plasticiser in the bulk becomes low, the plot changes to approach a final fully-deplasticised value asymptotically: in Figure 5(b), the oven-deplasticised value of 0.05 x 10^{-6} $\mathrm{cm^2/s/atm}$ has been used here. An appropriate equation for this behaviour is an amended equation 4 (with "0.5" now arising from a 50% reduction in Q rather than a 50% mass uptake), with half-thickness h replaced by thickness H because plasticiser diffusion is one-way (i.e. towards the high pressure) according to the argument above. Taking the effective zero time for deplasticisation to be when the first Q value applies, a diffusion coefficient for subsequent deplasticisation at 140C during methane HP permeation has been estimated as *ca* 5 x 10^{-8} $\mathrm{cm^2/s}$. This value is some 20 times slower than that obtained by TRI for this temperature, using an analytical method, (R.A.Rushing, presentation at December 1995 Steering Committee Meeting, Austin). Reasons why the current value is lower are (a) no deplasticisation occurs out of sample edges, (b) (possibly) some interference between methane and plasticiser diffusing in opposite directions could occur at test pressures as high as 5000psi. Both of these factors are relevant to flexible pipe service.

The long-term decrease in methane permeation rate would obviously be of significance when considering a pipe in service (as plasticiser will inevitably be removed from the liner with time) *if* the continuous presence of produced and permeating fluids in the liner material does not itself have a replasticising effect. Although the methane did not function in this way during this permeation testing, service fluids permeating through liners in the pipe geometry, with the close-fitting zeta layer outside the liners inhibiting permeant escape afterwards, may do so. Medium and short term permeation tests did not reveal this plasticiser loss effect, as discussed in the next section. The time to onset of deplasticisation may vary somewhat for different systems.

A conclusion from the long-term HP methane permeation test is that, all other factors being equal, for stability, the plasticiser type for Coflon should be one with a solubility parameter of 11.3 units or slightly more, so that its molecular attractions to the PVDF would be greater than those to the high pressure service fluids. However, after subsequent discussions it was realised that, for processing reasons , such a step may not be feasible as, from those plasticizers tested, dibutyl sebacate had been found by Elf Atochem during development to be the only suitable one for PVDF.

4.2 General permeation comments - Coflon

Figure 5(c) shows the generally constant nature of Q values from a permeation test (sample C1) with CH_4 at 5000psi and 140C on unaged Coflon over a medium-term test (4 days). Permeation coefficients from another such test first at 90C (Figure 5(d), for sample C14) initially demonstrated a compaction effect as pressure was increased from 1400psi to 5000psi, and then, at the latter pressure, showed how increasing temperature (firstly to 110C and then to 140C) gave larger Q values. Another sample (C10) was measured at 1400psi and 5000psi at 140^C: again, compaction is indicated (Table 1). An average Q from the measurements using these 3 samples at 140C and 5000psi is 0.32×10^{-6} $cm^2/s/atm$.

A general appraisal of Table 1 quickly shows that CO_2 permeation is about 10 times faster than CH_4 permeation through Coflon. Concentrating for a moment now on CO_2 permeation, Figure 5(e) shows the constant nature of Q values from a $5000psi/140C/CO_2$ permeation test on unaged Coflon over a short-term test (1 day). A medium-term test (Figure 5(f)) first involving lower temperatures gave Q values which increased with time for an initial period at each temperature. On this basis, it is likely that Q at 140C had not yet reached equilibrium when the test was stopped. Hence, although both values are included in Table 1, less confidence is placed on the second, and it is quoted in parentheses. As a general comment, values listed in Table 1 are thought to be good representations of basic material permeation characteristics for Coflon, but other factors can reduce these values.

Unless indicated otherwise, subsequent comments relate to measurements after short or medium-term tests. Testing at different temperatures has re-affirmed that Q increases with temperature as does D. Higher pressures tended to decrease Q although usually this is probably influenced more by loss of plasticiser than any decrease in thickness of the sample by hydrostatic pressure ("compaction"). The Q value and other coefficients for methane permeation through the 3mm thick sample (C2, achieved by machining evenly off both sample faces), were the same as for a 6mm sample (C1). This thickness independence indicated that the Coflon did not possess a 'skin' of different crystalline structure sufficient to cause changes in these coefficients. Testing at 140C has confirmed this, since some flow or creep has occurred causing reduction in sample thickness by as much as 10% whilst Q remained essentially unchanged. At the lower temperatures, very little thickness change occurred.

Arrhenius-type plots showing the temperature dependence of the various coefficients for methane and carbon dioxide permeation through Coflon are given in Figures 6-11, including Norsk Hydro test data measured at 75 bar and other literature values. It is worth noting that, whilst MERL used pure gas to obtain these Q values, Norsk Hydro used a $CH_4/CO_2/H_2O$ mixture and measured the amount of individual component permeating[1]. The possibility might exist that the individual constituents of mixed gases permeate at slightly different rates compared to pure single components because of interactive effects. The combined plots generally exhibit good linearity, so that they can be used for extrapolation to other temperatures: it seems that any interactive effects in Norsk Hydro's data are negligible. From Figure 6, for methane permeation, an activation energy E_a for permeation at 75-100 bar was calculated to be 8.0 kcal/mole. Coflexip data[2] (in the same figure) showed much lower permeation rates and a higher E_a (13.9 kcal/mole). This difference is because Coflexip apparently always perform permeation testing on fully deplasticised material (cf last section): such a model agrees with a slower permeation rate and the requirement of more energy (a greater E_a) for the molecules to form large enough holes during kinetic movements to allow diffusion (as part of permeation) to proceed. The air-oven deplasticised result discussed in section 4.1 is also included in Figure 6 for comparison.

Figure 6 shows in addition that methane permeation at 5000psi (345 bar) is slower than at 100 bar, and possesses a higher E_a (12.1 kcal/mole). From Figures 7 and 8, this change is due to decreased gas concentration (solubility coefficient times pressure) rather than diffusion coefficient. It is probably a result of some compaction due to the applied pressure.

For CO_2, permeation plots of Q, D and s (Figures 9-11) have also given straight line relationships when incorporating MERL and Norsk Hydro data, the test permeation rates being considerably different at 345 and 75 bar respectively. However, in this case the faster permeation was associated with the *higher* pressure. The reason is probably associated with the very high gas concentrations at 345 bar, these being enough to plasticise the PVDF (amorphous phase) genuinely, lower its T_g and thus cause increased free volume at test temperature, to enhance diffusion rates. The diffusion and solubility data in Figures 10 and 11 support this model, although the relative importance to the project of CH_4 compared with CO_2 meant that very few results were obtained. The activation energy for CO_2 permeation is calculated as 7.7 kcal/mole from MERL data (345 bar) and 5.7 kcal/mole from the Norsk Hydro data at 75 bar. CO_2 permeated 10-20 times quicker than methane at any test temperature *e.g.* at 345 bar and 140C Q = 3.0×10^{-6} $cm^2/s/atm$ for CO_2 (C7) compared to 0.3×10^{-6} $cm^2/s/atm$ for CH_4), and at 90C 1.8×10^{-6} (CO_2) against 0.04×10^{-6} $cm^2/s/atm$ for CH_4.

Data for mixed gases yield only 'apparent' coefficients due to the test method at MERL (pressure increase of permeating gas). It has been found that the rate of permeation for the wet or dry 97/3 CH_4/CO_2 mixture is in the same range as for pure CH_4

Three samples of pipe have been tested at MERL, one from Elf Atochem (C12) and two from Norsk Hydro (C21) - firstly, part of a pipe originally supplied to them by Coflexip, and secondly, sample C43, which had previously been permeation-tested by Norsk Hydro and then sent to MERL for direct comparison purposes. The first sample was used to compare pipe with flat sheet (also extruded at Elf Atochem) using the equipment at MERL, and the other samples were used to compare results obtained from Norsk Hydro's test method with MERL's pipe sample test method. As can be seen from the value measured for the Elf Atochem pipe sample (C12, $Q=0.29 \times 10^{-6}$) compared with the mean of C1, C10 and C14 ($Q=0.32 \times 10^{-6}$), good agreement occurred. Similarly, to compare the MERL test method with Norsk Hydro's[1], the following results were obtained for CH_4 permeation at 120C and 75 bar with the tested pipe supplied by Norsk Hydro (C21):

MERL	$Q = 0.19 \times 10^{-6}$	and $D = 2.21 \times 10^{-6}$
Norsk Hydro	$Q = 0.22 \times 10^{-6}$	and $D = 1.50 \times 10^{-6}$

and for CH_4 permeation at 95C and 100 bar (C43):

MERL	$Q = 0.05 \times 10^{-6}$
Norsk Hydro	$Q = 0.1 \times 10^{-6}$

The relatively good agreement in coefficients between MERL and Norsk Hydro is encouraging and could, as mentioned before, be due to the different gases used for testing - MERL use single gases and Norsk Hydro a mixture, measuring the individual components as they permeate.

4.3 Permeation after ageing

The results for methane permeation tests all conducted at 140C and 5000psi after Coflon samples had been exposed to some ageing conditions are shown in Table 2 and Figure 12(a). Table 3 and Figure 12(b) show the changes in permeation brought about by ageing in Fluid F only.

The compositions of the project standard reference fluids are:

Fluid	Component mixture
A	Methanol (CH_3OH)
B	97/3 CH_4/CO_2 with H_2O (v)
C	97/3 CH_4/CO_2 dry
D	94/5/1 $CH_4/CO_2/H_2S$ dry
E	94/5/1 $CH_4/CO_2/H_2S$ with H_2O (v)
F	As fluid E plus 1% ethylene diamine
G	As fluid A plus 1% ethylene diamine
H	As fluid B plus 1% ethylene diamine
I	35/35/20/10 Heptane/cyclohexane/toluene/ 1-propanol

The fluids used for ageing were selected from these.

Regarding the samples aged in fluids containing pressurised gas, care was taken when decompressing the samples from 5000 psi prior to permeation testing to minimise any chance of explosive decompression damage; the temperature was allowed to stabilise at ambient before performing a 1-2 hour uniform decompression. No ED damage was observed for any Coflon samples (unlike the case after permeation testing itself when, after testing, the HP gas was often rapidly dumped with the sample still at test temperature, resulting in the formation of many small gas bubbles in the sample).

TABLE 2 Summary permeation results table for aged Coflon (except Fluid F)
Test temperature 140C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
Unaged (average)	CH_4	5000	0.3	4.0	0.08	25
C17 (After deplasticization in air oven at 140C for 20 days)	CH_4	5000	0.05	0.9	0.05	17
C11 (After ageing in gas phase of 97/3 CH_4/CO_2 + H_2O(v) at 5000 psi 140C 14 days) Fluid B(v)	CH_4	5000	0.14	2.1	0.07	22
C27 (After ageing in gas phase of 1/5/94 $H_2S/CO_2/CH_4$ + H_2O(v) at 5000psi 120C 28days) Fluid E(v)	CH_4	5000	0.08	1.1	0.06	20
C25 (After ageing in liquid phase of 1/5/94 $H_2S/CO_2/CH_4$ + H_2O(v) at 5000psi 120C 28days) Fluid E(l)	CH_4	5000	0.10	1.2	0.08	27
C30 (After ageing in gas phase of 97/3 CH_4/CO_2 + H_2O(v) + 1% ethylenediamine at 5000 psi 120C 28 days) Fluid H(v)	CH_4	5000	0.09	1.6	0.06	20
C24 (After ageing in liquid phase of 97/3 CH_4/CO_2 + H_2O(v) + 1% ethylenediamine at 5000 psi 120C 28 days) Fluid H(l)	CH_4	5000	0.21	2.6	0.08	28
C28 "Aged" during test	CH_4 through methanol (Fluid A)	5000	0.94	"5.3"	"0.15"	"43"
C29 (After ageing in methanol + 1% ethylenediamine at 5000 psi 120C 28 days) Fluid G	CH_4	5000	0.05	5.1	0.01	3
C34 (After ageing in 35/35/20/10 Heptane/ cyclohexane/toluene/ 1-propanol at 5000 psi 140C 13 weeks) Fluid I	CH_4	5000	0.08	2.7	0.03	10
C41 (After ageing in 35/35/20/10 Heptane/ cyclohexane/toluene/ 1-propanol at vapour pressure 140C 30 weeks) Fluid I	CH_4	5000	0.14	1.8	0.08	27

* *Thickness nominally 6mm*

$^+$ *At STP*

Quotation marks indicate apparent values

TABLE 3 Permeation results for Coflon aged in Fluid F at 5000 psi
Test temperature 140C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
Unaged (average)	CH_4	5000	0.3	4.0	0.08	25
C17 (After deplasticization in air oven at 140C for 20 days)	CH_4	5000	0.05	0.9	0.05	17
C37 (After ageing in gas phase at 100C for 3 months)	CH_4	5000	0.11	2.1	0.05	18
C39 (After ageing in gas phase at 100C for 6 months)	CH_4	5000	0.04	0.3	0.13	46
C40 (After ageing in gas phase at 120C for 2 weeks)	CH_4	5000	0.08	1.8	0.04	15
C33 (Deplasticized first then aged in gas phase at 120C for 2 weeks)	CH_4	5000	0.04	1.9	0.02	7
C13 (After ageing in gas phase at 120C for 4 weeks)	CH_4	5000	0.12	2.6	0.05	16
C23 (After ageing in liquid phase at 120C for 4 weeks)	CH_4	5000	0.10	1.4	0.07	25
C38 (After ageing in gas phase at 120C for 6 weeks)	CH_4	5000	0.05	2.2	0.02	8
C36 (After ageing in gas phase at 140C for 8 days)	CH_4	5000	0.16	-	-	-
C35 (After ageing in gas phase at 140C for 4 weeks)	CH_4	5000	0.06	2.3	0.03	9

* *Thickness nominally 6mm*

\+ *At STP*

The overall impression from Table 2 is that any ageing procedure except CH_4 through Fluid A (methanol) - see below - decreases permeation rate. The consequence of exposures to Fluids B, E, H and I was to decrease the permeation coefficients to values closer to the deplasticised sample value (C17), as clearly illustrated by histograms in Figures 12(a) and (b). Diffusion coefficients similarly have tended towards the deplasticised value, but both s and c remain fairly consistent with the values for virgin and deplasticised material alike. The reasons for the changes in diffusion rates brought about by deplasticisation have been discussed in section 4.1; the relatively constant nature of the gas concentration before and after deplasticization indicates that solubility of gas in plasticiser, when the latter is performing its plasticising function, is similar to that in PVDF polymer.

In more detail, exposures to Fluid B (97/3 CH_4/CO_2 + H_2O(v) mixture) for 14 days at 140C and 5000 psi (C11) resulted in a decrease in the CH_4 permeation and diffusion coefficients of about 50% whilst the solubility coefficient (and by inference the concentration, as c=sP) had not changed. At the end of this test (of only 2 days duration), Q had decreased a further 50% giving a 'final' value (not shown in Table 2 or Figure 12(a)) close to that observed for the fully deplasticised sample (C17). This result goes further towards indicating that a fully deplasticised sample yields permeation coefficients that are more relevant to the offshore situation than results from virgin material: compared with the long-term CH_4 permeation discussed in section 4.1, Fluid B causes rapid deplasticisation, as would be expected on a solubility parameter argument (with wet CO_2 being present). A more realistic gas than CH_4 in itself apparently does not provide much re-plasticisation (although pipe geometrical effects - the slowing of permeation due to the zeta layer (section 4.1) - could mean that gas plasticisation *is* a factor).

Fluid I, which was introduced to investigate the effect a high aromatic oil has on Coflon and Tefzel, did not cause a drastic change for Coflon, the permeation and diffusion characteristics altering as expected for purely deplasticisation reasons.

A notable exception in one major effect has been the sample (C29 Table 2) aged in the methanol + ethylene diamine mixture (Fluid G). Although Q had decreased significantly, to exactly the same value as the deplasticised sample (0.05×10^{-6} $cm^2/s/atm$), D had greatly *increased*, whilst s and c were very small. This sample had turned black throughout its section and had many surface cracks present (described more fully in CAPP/M.10). These data fit well into a pattern indicated by analytical data from TRI[6]. A bimodal molecular weight distribution was obtained from GPC analysis, with the second peak arising at the high MW end (sample identification T.58) being attributed by TRI as ageing-induced crosslinking. Thus the low s and c values are reasonable. Furthermore X-ray diffraction measurements on the same sample showed a massive reduction in crystallinity, which should certainly result in faster diffusion - hence the high D.

Fluid F ageing (Table 3 and Figure 12(b)), based on H_2S plus ethylene diamine, also produced greater permeation rate losses than those attributable to deplasticisation alone, for instance, the samples for these exposures - 6 weeks/120C, 6 months/100C, and 2 weeks/120C following previous deplasticisation. Samples C13 and C23 (from an early batch) had blackened but this was only a surface effect, and none of the other batches of Coflon suffered a similar amount of darkening. Analytical data (ref 6, also CAPP/M.10) and mechanical property results (CAPP/M.7) indicated that the blackened skin might be less permeable than unaged Coflon, but similar information does not exist at present for the three samples giving the lowest permeation results.

The considerable degradation of Coflon by methanol alone (Fluid A) at 140C has been discussed in detail in CAPP/M.6. How this affects methane permeability has now been investigated (sample C28 Table 2). For this a permeation test was set up with the cell in an inverted position as implied by Figure 4 with a layer of methanol resting on the sample. The cell was heated to 60C (just below the boiling point of the methanol) before applying the HP methane and raising the temperature to 140C as quickly as possible. The resulting rate of permeation of 0.94×10^{-6} $cm^2/s/atm$ was three times faster than occurred in the absence of methanol (Table 1). Upon disassembly of the permeation cell the Coflon was found to be spongy where wetted by the methanol. In addition, it was evident that even in this relatively short test (overnight) the methanol had also penetrated through the Coflon - Viton O-rings sealing the LP region of the cell were swollen and soft, indicative of methanol absorption. This test represented methane permeation *during* methanol ageing. The diffusion coefficient here was as high as in the Fluid G case. Crystallinity was perhaps reduced[6], but less so than for Fluid G. However, the massive deterioration which can occur under these conditions (CAPP/M.6) suggests that other diffusion routes, e.g. between fragmenting regions (at incipient stages), could apply. The high s and c in this case would be expected.

In summary, Figures 12(a) and 12(b) show that, for Coflon, permeation rate after a variety of ageing conditions is lower than the unaged rate, but there is no obvious trend relating ageing to change in permeation, so that permeation cannot at present be used as a diagnostic tool for degree of ageing. The reason probably arises from the dominating overall effect of deplasticisation. However, diffusion coefficients and concentration levels can correlate with certain material structural features, as has been discussed in this section.

From analytical results concerning the degradation of the Coflon, the relative chemical reactivity of the ageing fluids seems to be in the following order:

$$G > F \gg H = E = D = I > C = B$$

At 140C, the physico-chemical attack by A is at least as severe (in a different way) as the G and F attack. Consequences on permeation have generally followed the same sequence.

5 TEFZEL HP GAS PERMEATION RESULTS AND DISCUSSION

The results from the unaged Tefzel HP permeation tests are shown in Table 4.

TABLE 4 Summary results table for unaged Tefzel
Test temperature 150C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
T14	CH_4	5000	0.05	0.55	0.09	33
T15	CH_4	5000	0.08	0.64	0.13	40
T1	CH_4	5000	0.12			
T13	CH_4	5000	0.09			
T16	CH_4	5000	0.10			
T2	CO_2	5000	2.5	4.6	0.5	181
T18	CO_2	5000	(0.6)			
T19	CO_2	5000	(1.2)			
T8	97/3 CH_4/CO_2	5000	0.10	"0.4"	"0.25"	"86"
T9	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.09	"0.34"	"0.27"	"98"
T21	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.20			
T99	methanol	5000	---	0.2	---	0.02

* *Thickness nominally 3mm*
\+ *At STP*
Quotation marks indicate apparent values

Test temperature 120C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^3gas$^+$/cm^3 polymer)
T13	CH_4	5000	0.05	0.21	0.07	24
T16	CH_4	5000	0.03			
T19	CO_2	5000	0.61	3.2	0.19	69
T18	CO_2	5000	0.33			
T21	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.06	"0.98"	"0.07"	"22"
T20	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.10			

* *Thickness nominally 3mm*

\+ *At STP*

Quotation marks indicate apparent values

Test temperature 90C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^3gas$^+$/cm^3 polymer)
T10	CH_4	1400 5000	0.02 0.02	0.21 0.27	0.18 0.08	17 26
T16	CH_4	5000	0.01	0.06	0.11	40
T18	CO_2	5000	0.17	0.39	0.44	136
T20	97/3 CH_4/CO_2 plus H_2O(v)	5000	0.02	"0.35"	"0.07"	"23"

* *Thickness nominally 3mm*

\+ *At STP*

Quotation marks indicate apparent values

5.1 General permeation comments - Tefzel

Five replicate tests for methane permeation at 150C and 5000psi showed a considerable variation in Q values, averaging 0.09 x 10^{-6} cm^2/s/atm. The variability was probably due to errors arising from difficulties in measuring low permeation rate magnitudes.

The permeation coefficient values measured for CO_2 through unaged Tefzel also varied, but the lower values arose from medium term tests which had already completed stages at lower temperatures. Figure 13(a) shows the constant Q at 2.5 to 3 x 10^{-6} cm^2/s/atm obtained during 1 day's testing for sample T2 at 150C/5000psi only. Figure 13(b) shows for T18 increases in Q with time and temperature - but at 150C only reaching (after 2 days) a Q value (0.6 units) well below that obtained for sample T2. Figure 13(c) illustrates how sample T19, tested for 1 day at 120C and then 150C (i.e. with no 90C stage), gave an intermediate result to those above. Hence the sample T2 value is listed in Table 2 for CO_2/5000psi/150C with most confidence. Once again, indications are that, after longer times, other factors can reduce permeation rates from those tabulated. The mechanism might involve a strong association of CO_2 with the Tefzel polymer at low temperatures which is maintained somewhat when temperature is raised.

Arrhenius-type plots for methane, carbon dioxide and mixed-gas permeation through Tefzel are given in Figures 14 to 16 for Q, D and s. (There were no Norsk Hydro data on Tefzel for comparison purposes.) Although only three temperatures have been examined for Tefzel, reasonable straight line relationships have generally been found for the single gases. The activation energy for CH_4 permeation at 345bar was 12.6 kcal/mole (interestingly close when compared to 12.1kcal/mole for Coflon) and 13.6 kcal/mole for CO_2 permeation (8.5kcal/mole for Coflon). Comparing Figures 6, 9 and 14 it can be seen that both CH_4 and CO_2 permeate more slowly through Tefzel than through Coflon at the same temperature (although, for CO_2, at high temperatures above the range measured, the situation should eventually reverse).

Once more CO_2 gave significantly higher permeation rates than CH_4, the difference factor being 10-25 in the range covered here.

The 97/3 CH_4/CO_2 gas mixture (wet or dry) gave the same permeation rates as 100% CH_4 in short term tests but a much faster rate (x2) for longer term tests *e*.g. T20 and T21, although still not as fast as CO_2 permeation. Although Tefzel contains no plasticiser, as a tentative proposal, this observation may also be a plasticiser-like effect - Tefzel contains about 2% of low molecular weight species, which might be removable during exposures. However, from the thickness measurements (not shown herein) any such loss is accompanied by only a small change in volume (*cf.* Coflon $\Delta V = -18\%$) so that perhaps Tefzel retains a slightly 'open' structure, containing 'micro-flaws', after the low molecular weight components have been removed, and permeation is therefore subsequently easier and quicker.

5.2 Permeation after ageing

The results for methane permeation tests all conducted at 150C and 5000psi after exposing Tefzel samples to various ageing conditions are shown in Tables 5 and 6. In complete contrast to Coflon, with just one exception, *increases* in CH_4 permeation rate after the exposure tests have occurred compared to unaged Tefzel (Figures 17(a) and (b)), indicating that any service under these conditions is likely to result in an increase in permeation with time. The data indicate that some correlation may exist between permeation data and degree of ageing for Fluid F, Q appearing to approach 0.2×10^{-6} $cm^2/s/atm$ as ageing progresses. No unusual external features were noted with Tefzel samples after ageing (unlike Coflon, which turned black in some cases), except in Fluid I where swelling had obviously been caused by liquid absorption, resulting in Q values in

TABLE 5 Summary methane permeation results table for aged Tefzel (except Fluid F)

Test temperature 150C

SAMPLE*	GAS	PRESSURE	Q	D	s	c
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
Unaged (average)	CH_4	5000	0.07	0.6	0.11	37
T12 (After ageing in methanol at 5000 psi 150C 14 days) Fluid A	CH_4	5000	0.15	>0.7	<0.2	<68
T11 (After ageing in gas phase of 97/3 $CH_4/CO_2 + H_2O(v)$ at 5000 psi 140C 14 days) Fluid B(v)	CH_4	5000	0.16	1.7	0.1	36
T28 (After ageing in 1/5/94 $H_2S/CO_2/CH_4$ at 5000psi 120C 28days) Fluid D	CH_4	5000	0.18	0.8	0.04	13
T27 (After ageing in gas phase of 1/5/94 $H_2S/CO_2/CH_4 + H_2O(v)$ at 5000psi 120C 28days) Fluid E(v)	CH_4	5000	0.12	0.31	0.36	115
T26 (After ageing in liquid phase of 1/5/94 $H_2S/CO_2/CH_4 + H_2O(v)$ at 5000psi 120C 28days) Fluid E(l)	CH_4	5000	0.12	3.0	0.04	14
T23 (After ageing in gas phase of 97/3 $CH_4/CO_2 + H_2O(v)$ + 1% ethylene - diamine at 5000 psi 120C 28 days) Fluid H(v)	CH_4	5000	0.12	0.62	0.19	67
T24 (After ageing in liquid phase of 97/3 $CH_4/CO_2 + H_2O(v)$ + 1% ethylenediamine at 5000 psi 120C 28 days) Fluid H(l)	CH_4	5000	0.14	1.81	0.07	26
T25 (After ageing in methanol + 1% ethylene - diamine at 5000 psi 120C 28 days) Fluid G	CH_4	5000	0.15	2.81	0.04	12
T33 (After ageing in methanol + 1% ethylene - diamine at 5000 psi 120C 6 weeks) Fluid G	CH_4	5000	0.18	0.8	0.23	78
T35 (After ageing in 35/35/20/10 Heptane/ cyclohexane/toluene/ 1-propanol at 5000 psi 140C 10 weeks) Fluid I	CH_4	5000	0.23	1.0	0.23	79
T31 (After ageing in 35/35/20/10 Heptane/ cyclohexane/toluene/ 1-propanol at vapour pressure 140C 30 weeks) Fluid I	CH_4	5000	0.3	2.8	0.11	37

* *Thickness nominally 3mm*

\+ *At STP*

the relatively-high 0.2-0.3x10^{-6}cm^2/s/atm range. However, Tefzel samples were more susceptible to explosive decompression damage (surface blisters) than Coflon, and care had to be exercised when decompressing aged permeation samples so as not to damage their sealing surfaces or test regions and thus affect subsequent permeation testing. The only relevant analytical data available from TRI for some aged conditions are X-ray diffraction results. Fluids G, I and E (liquid phase) caused the largest increase in diffusion coefficients followed by Fluid H. Although Fluid G caused a great reduction in the crystallinity of Tefzel[6], E and F did not (no data being available for the others) so that D is not a diagnostic tool here. One possible reason is that the diffusion increase in all cases is governed by removal of the 2% low molecular weight polymer, and a retention of a structure with more continuous micro-flaws in it, as discussed in section 5.1.

It is not known why ageing in one case - Fluid F at 120C for 6 weeks - should have reduced permeation rate from the unaged value. More values of crystallinity etc following this exposure would be necessary before opinions could be made.

TABLE 6 Permeation results for Tefzel aged in Fluid F at 5000 psi
Test temperature 150C

SAMPLE*	**GAS**	**PRESSURE**	**Q**	**D**	**s**	**c**
		(psi)	(cm^2/s/atm) x10^{-6}	(cm^2/s) x10^{-6}	(/atm)	(cm^{3}gas$^+$/cm^3 polymer)
Unaged (average)	CH_4	5000	0.09	0.6	0.11	37
T32 (After ageing in gas phase at 100C for 3 months)	CH_4	5000	0.14	1.6	0.09	30
T34 (After ageing in gas phase at 100C for 6 months)	CH_4	5000	0.18	0.6	0.3	104
T36 (After ageing in gas phase at 120C for 2 weeks)	CH_4	5000	0.12	0.4	0.3	104
T17 (After ageing in gas phase at 120C for 4 weeks)	CH_4	5000	0.15	1.5	0.11	40
T22 (After ageing in liquid phase at 120C for 4 weeks)	CH_4	5000	0.12	---	---	---
T37 (After ageing in gas phase at 120C for 6 weeks)	CH_4	5000	0.07	0.6	0.1	35
T30 (After ageing in gas phase at 140C for 8 days)	CH_4	5000	0.15	0.6	0.25	86
T29 (After ageing in gas phase at 140C for 4 weeks)	CH_4	5000	0.18	2.0	0.09	31

* *Thickness nominally 6mm*

\+ *At STP*

6 METHANOL UPTAKE

6.1 Coflon results and discussion

The methanol absorption testing on Coflon pipe samples (and four flat sheet samples) at 100C, conducted as outlined in section 3.2, gave results which were difficult to interpret because of deplasticisation effects. Figure 19(a) shows the plots against root time of all weighings performed, for the various samples. Clearly, after an initial mass gain of 2% over 12-18 hours, significant leaching occurred, which dominated the subsequent weighings. It is fairly common practice for a liquid absorption test to correct for leaching (which causes reductions on mass) by testing with many replicate samples, withdrawing them one at a time at suitable intervals, and drying each at elevated temperature to constant weight: for each sample, comparison with original mass shows the amount leached after its particular exposure time, so that a separate plot of amount leached versus root time can be established, and used to correct the main absorption plot for the test liquid. However, this procedure is more difficult to apply if during the drying period more of the leachable species is lost - this time by evaporation. This is certainly the case for Coflon plasticiser dibutyl sebacate, which normally is deplasticised simply by oven drying at, say, 140C.

Hence only the initial stages of the plots have been examined to obtain approximate data. Figure 19(b) illustrates the positive uptake region. Applying equation 4 gives the data for D_{av} thus obtained for the pipe sample with open ends and the pipe sample with sealed ends (Table 7). It is accepted that these data are approximate as, for each curve, the extensive leaching could have caused the "apparent" equilibrium mass uptake m_∞ to occur at a different time from the real m_∞, and this term is necessary for the calculation so that t_{av} (the time to 0.5 m_∞) can be measured. From the results obtained, the value for diffusion coefficient applying to liquid ingress rather than large faces was larger than that for large sample faces only, but apparently by a factor approaching 2 only - a rather unexpected result for reasons given below.

Returning to Figure 19(a), back-extrapolation of the plots at the first negative-gradient stage following apparent m_∞ ("the leaching rate") leads to a mass uptake reading on the 'y-axis': this zero leaching time value should reasonably be 'real' m_∞. The value obtained (Table 7) was *ca*4-5% methanol uptake (in both cases, as would be expected).

TABLE 7 Methanol mass uptake by Coflon at 100C

	Equilibrium uptake m_∞	**Diffusion coefficient D_{av}***
	(%)	(cm^2/s) x10^{-6}
Pipe sample with open ends	4-5	2.7
Pipe sample with sealed ends	4-5	1.6

** Calculated assuming flat sheet equation - reasonably accurate because pipe diameter not small.*

This work was performed because of the difference of one order of 10 described in CAPP/M.2 in diffusion coefficient measurements for methanol absorption by Tefzel at 150°C when measured by standard liquid mass uptake procedures compared to permeation (discussed again in the next section). The high value in the former case was suggested by Dr J Imbalzano (DuPont) as perhaps arising from methanol ingress into the sample edges, to pass rapidly in-between aligned crystalline regions. The sealed pipe technique should be equivalent to the permeation test, as neither exposes sample edges to methanol. In the present case, the differences in diffusion coefficient between the sealed Coflon pipe value (more representative of service values) and that obtained from an open-ended piece of pipe (and implicitly from simple flat sheet samples) are less significant. This observation apparently indicates less crystal alignment for Coflon than for Tefzel. even though the former is extruded. Possible influencing factors are the higher crystallinity level in Coflon, and the a) plasticiser b) greater thickness c) (possible) existence of thermal gradients across the pipe section when extruding - all of which could lead to some crystal orientation away from the extrusion direction. Errors in the measured D values as a consequence of the influence of deplasticisation during absorption testing must also again be considered.

6.2 Tefzel results and discussion

Figure 18(b) shows the test arrangement and Figure 19(c) gives the 150C methanol uptake results as plots versus root time. From these (assuming m_∞ had been reached), the results in Table 8 were obtained, according to equation 4 in section 2.

TABLE 8 Methanol uptake by Tefzel pipe section at 150C

	Equilibrium uptake m_∞	**Diffusion coefficient D**
	(%)	(cm^2/s) $x10^{-6}$
Flat sheet*	1.9	3.4
By permeation technique*	-	0.2
Pipe with open edges	1.3	3.2
Pipe with sealed edges	1.4	0.3

* *At 1200-2500psi from CAPP/M.2*

As mentioned previously in section 6.1, methanol was found apparently to diffuse faster when measured by standard liquid uptake tests compared to permeation tests. Edge effects were cited as a possible reason, and the present data confirm this view, as the uptake technique when applied to the sealed-edge sample produced a diffusion coefficient very similar to that measured by permeation. This value represents passage through the Tefzel wall. The edge effect was confirmed by the similar overestimates for both flat sheet and pipe samples with edges unsealed. Methanol (or any other liquid of similar solubility parameter) is therefore able to pass rapidly between aligned crystalline regions when the edges as sheet or pipe are exposed. The difference of one order of 10 or more between faces and edges is, however, much greater than the equivalent difference for Coflon, thought to be for the reasons given in section 6.1.

As a final point, as shown in Figure 19(c), the unyielding clamping jig used for the geometry employed for pipe testing (Figure 18(b)) brought about a deformation of the pipe section, due either to the temperature rise or methanol uptake, or both. Fractures were observed in the sample. The point is also discussed under mechanical testing in CAPP/M.3. The sealing concept for methanol uptake was not affected by this phenomenon until final fracturing caused the test to end.

7 CONCLUSIONS

COFLON

- Between 90C and 140C, high pressure carbon dioxide (CO_2) permeation through Coflon is a factor of 10-20 times faster than methane (CH_4) permeation.

- After previous deplasticisation, CH_4 permeation decreased by a factor of six from the level for virgin material to a value similar to that quoted by Coflexip. Deplasticisation is accompanied by a large decrease in volume.

- CH_4 permeation rates at high pressures are lower than at low pressure, due to compaction.

- Series of good Arrhenius plots for each coefficient Q, D and s at various pressures, suitable for extrapolation to other temperatures, have been obtained. The series are necessary because plots at high pressures can differ from those at low, due to compaction, and because of deplasticisation.

- The plots for MERL and Norsk Hydro CH_4 permeation at 75-100bar and different temperatures gave an activation energy (Ea) of 8.0kcal/mole. At 345bar, MERL obtained an Ea for CH_4 permeation of 12.1kcal/mole. For CO_2, an E_a of 7.7kcal/mole was obtained at 345bar.

- A 97/3 mixture of CH_4 and CO_2 permeated through unaged Coflon at a similar rate to the 100% CH_4 value for the range 110C-140C.

- When Coflon was aged in a 97/3 mixture of CH_4 and CO_2 plus water, CH_4 permeation decreased by 50%, probably due to partial deplasticisation. Similarly, long-term (60 day) permeation testing with methane (in itself an ageing process) also gradually brought about a massive decrease in permeation rate, down to the deplasticised level. The high pressure gas leaches the plasticiser out. It was concluded that all data obtained in normal test times would be subject to similar large reductions after long times. However, to make comparisons across different test conditions, data from normal test times should be used.

- From the point of view of resisting deplasticisation by fluid leaching, the current plasticiser in Coflon is not a good choice. One with a high solubility parameter ($\sim 11(\text{cal/cm}^3)^{1/2}$ at least) would theoretically be better, especially if at a higher viscosity.

- The methane permeation coefficients from the 60 day test have been used to provide a diffusion coefficient for plasticiser migration during deplasticisation. The value at 140C was $5\times10^{-8}\text{cm}^2/\text{sec}$, apparently a low value - but applicable to service conditions, because no deplasticisation was via sample edges, and its diffusion direction opposed that of the HP methane permeation.

- It seems unlikely that replasticisation by a permeating gas is a major effect in long-term testing (or service).

- When aged in a 1% hydrogen sulphide (H_2S)/CH_4/CO_2 plus water and amine mixture (Fluid F), CH_4 permeation decreased by over 50% (considerably more so for some conditions). Some discoloration occurred, presumably due to dehydrofluorination; however, the contribution of deplasticisation is not clear.

- Chemical ageing followed by permeation testing was performed on a previously-deplasticised sample to separate the various effects. The role of plasticiser was still the most dominant, but the rate was reduced even further by ageing on Fluid F.

- Complete blackening of the sample occurred when aged in a methanol plus amine mixture. CH_4 permeation decreased to the same value as for deplasticised Coflon. The darkening was again probably due to dehydrofluorination.

- All other ageing exposures also resulted in CH_4 permeation rates decreasing towards that of the deplasticised sample. Although there did not seem to be a connection between the severity of the ageing fluid and the decrease in permeation rate, a limited relationship between diffusion coefficient and crystallinity was suggested.

- CH_4 permeation through unaged Coflon permanently wetted with a layer of methanol was significantly *increased* compared with the rate through virgin material.

- A sample of pipe from Elf Atochem was used to confirm that CH_4 permeation rate through extruded flat bar samples from the same source was the same as that through pipe.

- Samples of pipe from Norsk Hydro (originally obtained from Coflexip) were used to confirm that MERL test techniques gave similar CH_4 permeation results to those obtained by Norsk Hydro.

- The Q value and other coefficients obtained by CH_4 permeation through a thin sample of Coflon (achieved by machining) were the same as for an unmachined thick sample. The coefficients are independent of thickness (as expected), and apparently Coflon does not possess a 'skin' of different crystalline structure sufficient to change permeation characteristics.

- Methanol absorption measured by simple mass uptake tests with flat sheet samples gave results not too different from measurements with sealed pipe samples, the latter preventing methanol ingress via sample edges. The unsealed rate was 66% greater.

TEFZEL

- Between 90C and 150C, high pressure carbon dioxide (CO_2) permeation is a factor of 10-25 times faster than methane (CH_4) permeation.

- All ageing exposures caused permeation rate increases through Tefzel. Loss of low molecular weight species due to ageing might occur, possibly to leave Tefzel with a 'micro-flawed', more permeable, structure. After ageing in a variety of fluids, CH_4 permeation increased by as much as a factor of three. No relationship between crystallinity after ageing with permeation or diffusion coefficient occurred.

- Arrhenius plots of HP CH_4 permeation coefficients gave an activation energy of 12.6 kcal/mole, and for CO_2 an E_a of 13.6 kcal/mole.

- Methanol liquid uptake experiments at 150C with a pipe section of Tefzel having sealed ends, so that absorption was through the large faces only, have proved that a previous permeation-derived measurement of diffusion coefficient at about $0.25 \times 10^{-6} cm^2/s$ was correct. High values previously obtained with simple unsealed liquid uptake samples occurred because methanol entered the sample edges and penetrated rapidly between aligned crystalline regions. This can be valuable to minimise diffusion effects in ageing experiments, but does not relate to service conditions, whereas the low value does.

GENERAL

- For unaged material, CH_4 permeates more than twice as fast through Coflon as through Tefzel at the same temperature.

- For unaged material, CO_2 permeates at a slightly faster rate through Coflon than through Tefzel at the same temperature.

- The HP gas permeation data for both Coflon and Tefzel have generally given sensible and useful trends, and can be rationalised reasonably against some aspects of the morphology of the materials and changes brought about by ageing and deplasticisation (for Coflon).

- Evidence suggests that, after ageing, CH_4 permeation could sometimes become *slower* through Coflon than through Tefzel.

- The greater crystalline orientation effect for Tefzel over Coflon implied by methanol absorption data (unsealed versus sealed-edge samples) probably arises because Coflon samples were thicker, contained plasticiser and for processing thermal history reasons (all of these allowing some orientation across the extrusion flow direction), and perhaps also due to its higher crystallinity level.

REFERENCES

1. J I Skar and C Hansteen, Norsk Hydro report no. 960321RA. Doc.- CAPP/N.2.
2. B Radenac, Coflexip: values quoted in Reference 1 and elsewhere.
3. J C Giddings, M N Myers, L McLaren and R A Keller, 'High pressure gas chromatography of non-volatile species', Science 162, 67-73 (October 1968).
4. J C Giddings, M N Myers and J W King, 'Dense gas chromatography at pressures to 2000 atmospheres', J Chromatographic Sci 7, 276-283 (May 1969).
5. J J Czubryt, M N Myers and J C Giddings, 'Solubility phenomena in dense CO_2 gas in the range 270-1900 atmospheres', J Physical Chemistry 74, (24) 4260-4266 (1970).
6. J W Bulluck and R A Rushing, CAPP/T.4, 12 Dec 95.

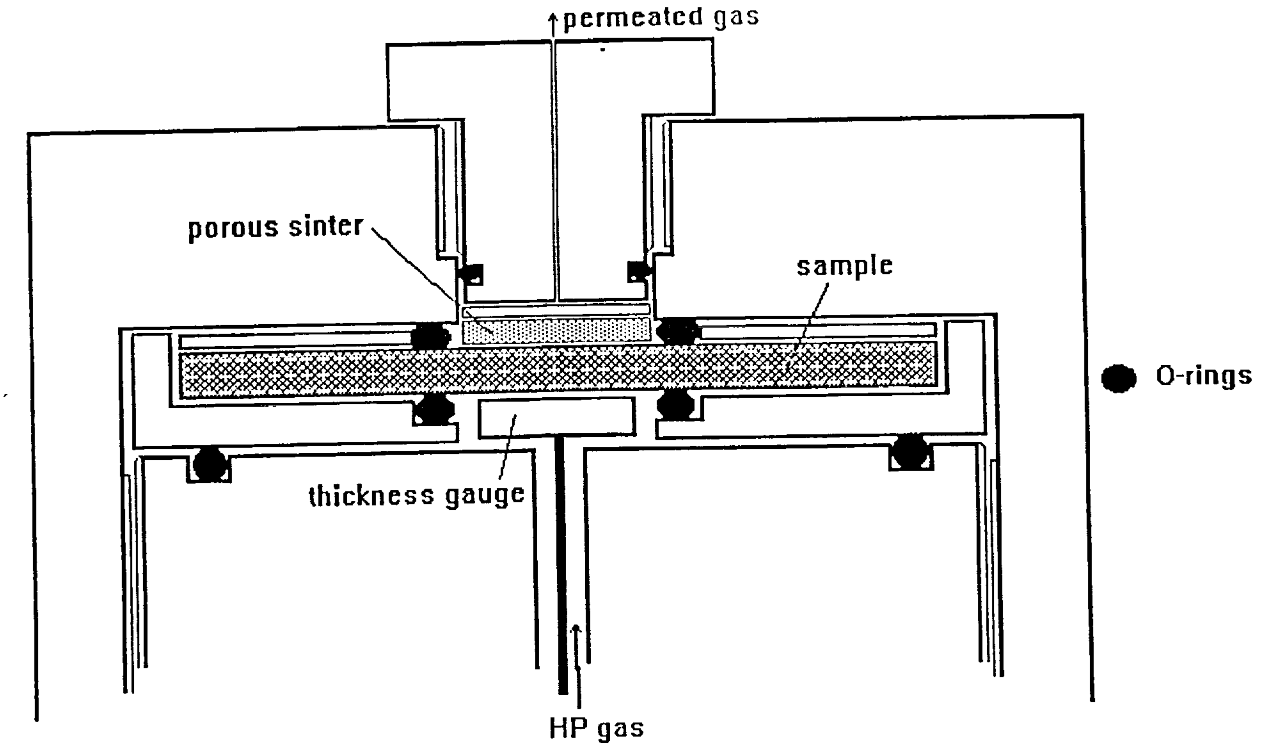

FIGURE 1 HP gas permeation - normal "straight-through" arrangement

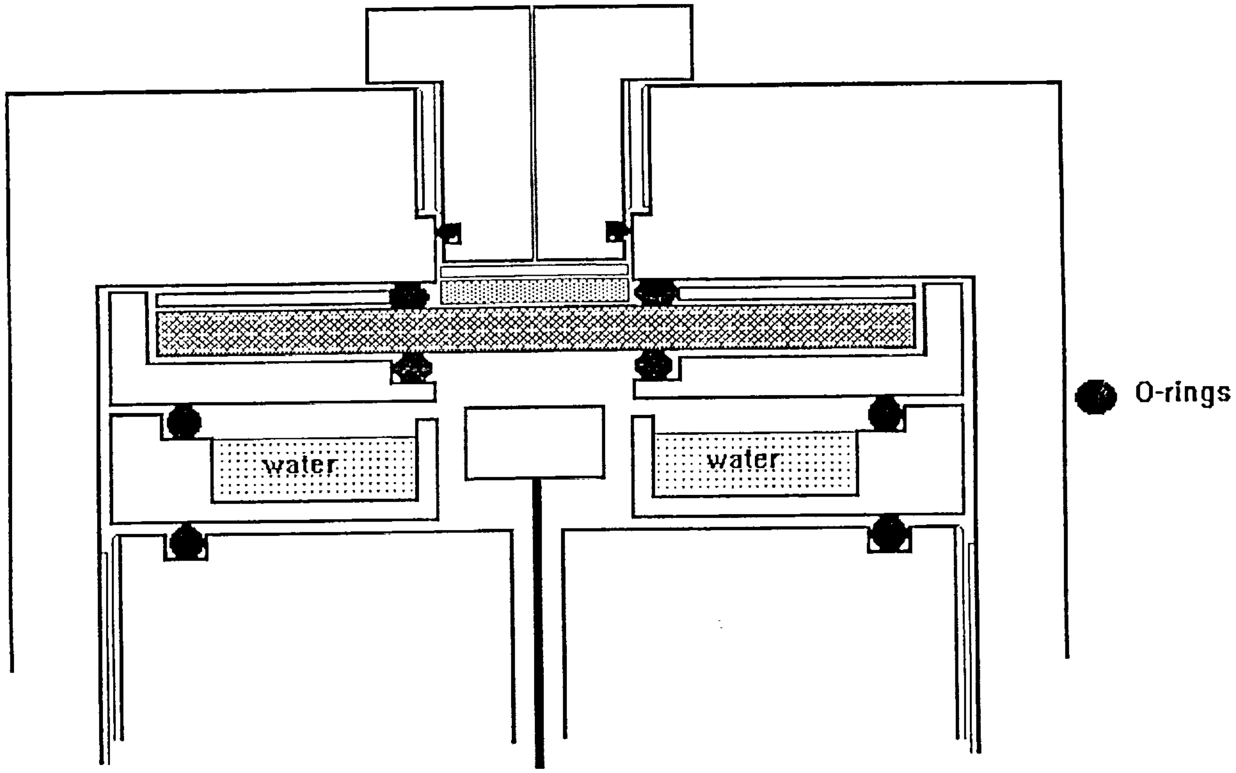

FIGURE 2 HP gas permeation - saturated water vapour arrangement

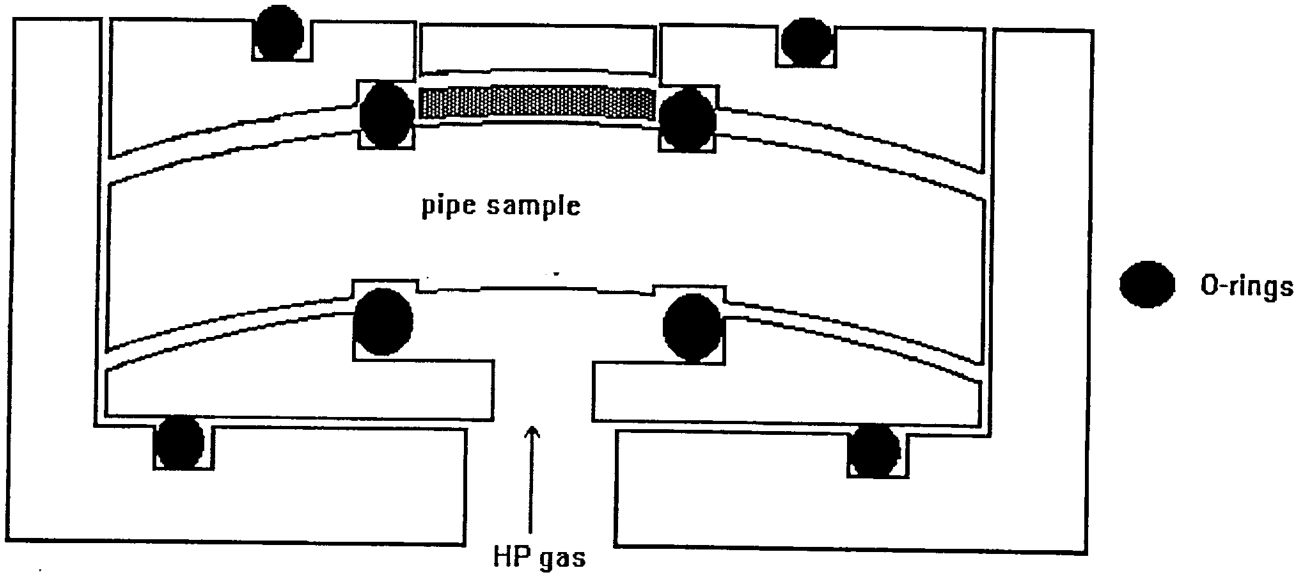

FIGURE 3 HP gas permeation - arrangement for sealing pipe portion sample

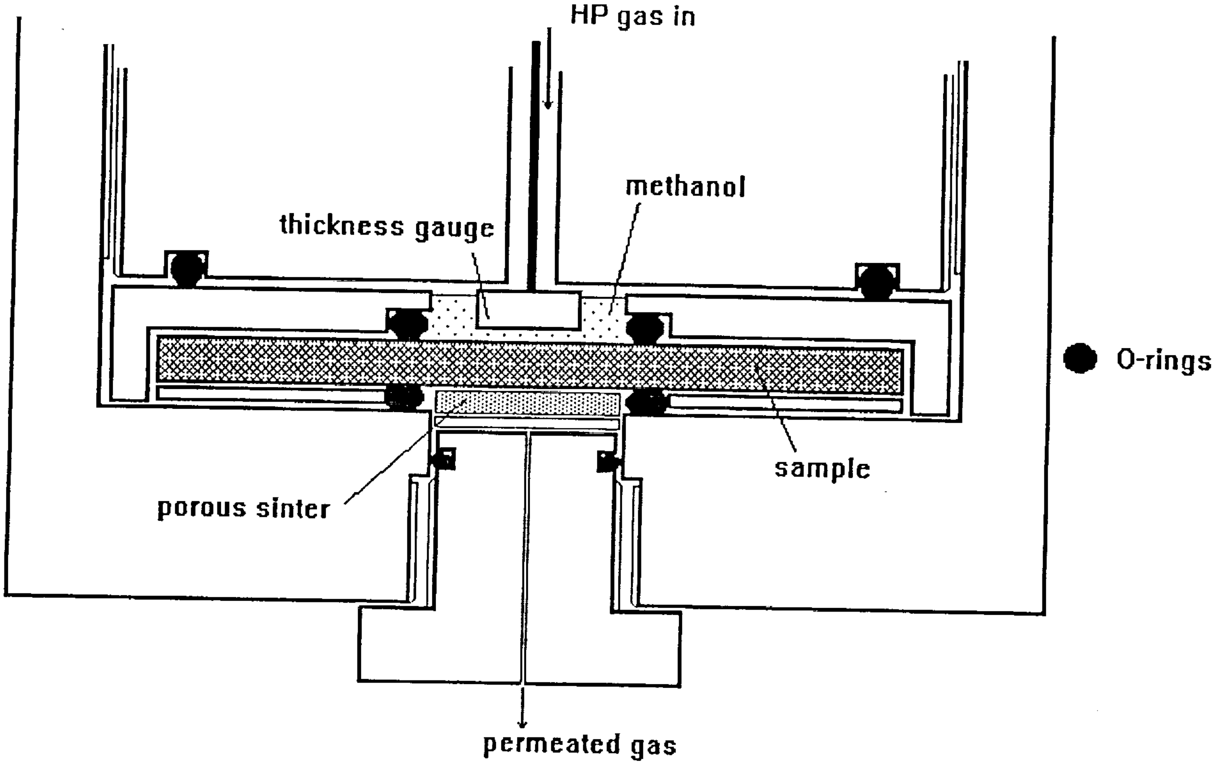

FIGURE 4 Gas permeation through methanol

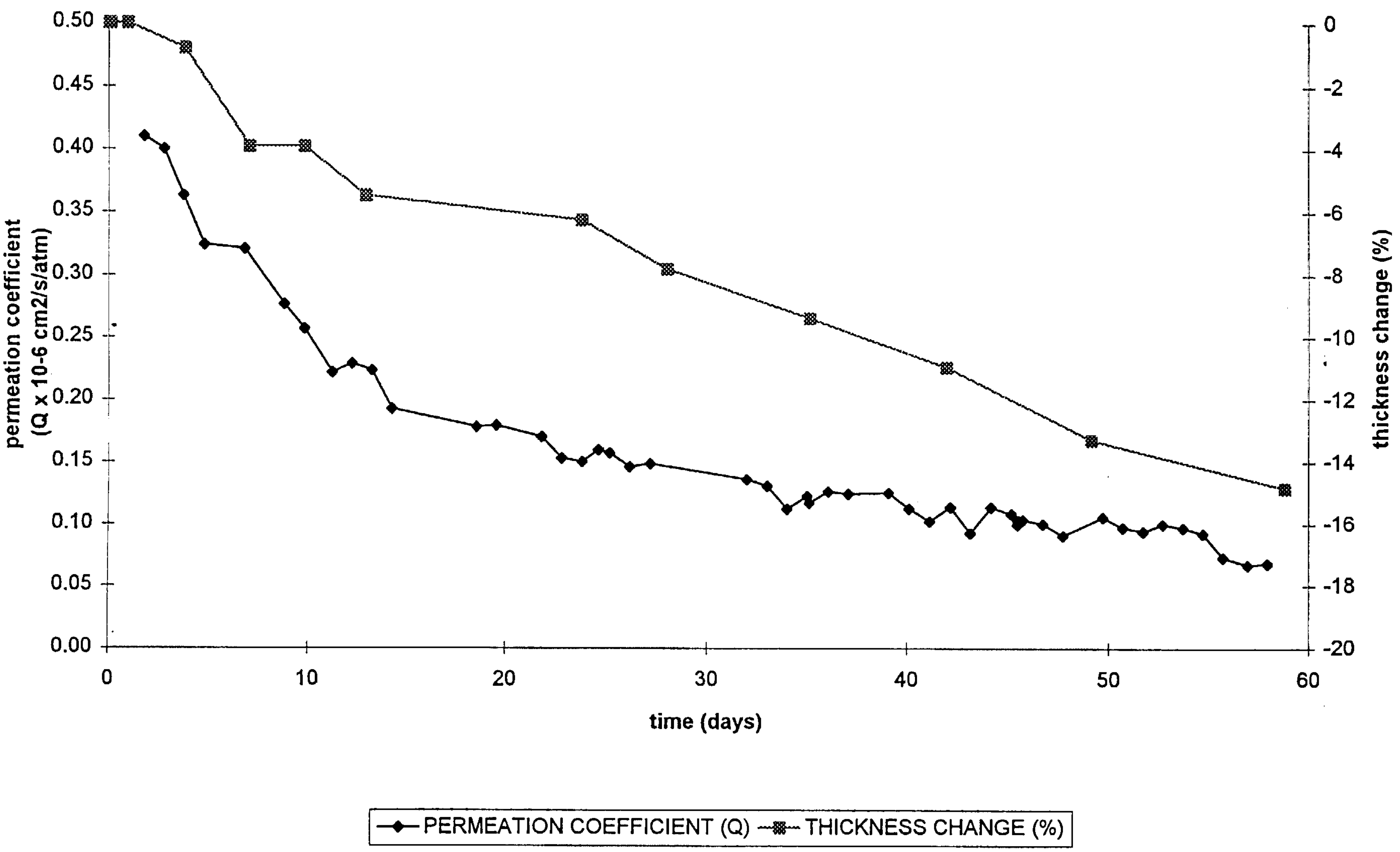

FIGURE 5(a) Effect of plasticiser loss on long term methane permeation at 140 C

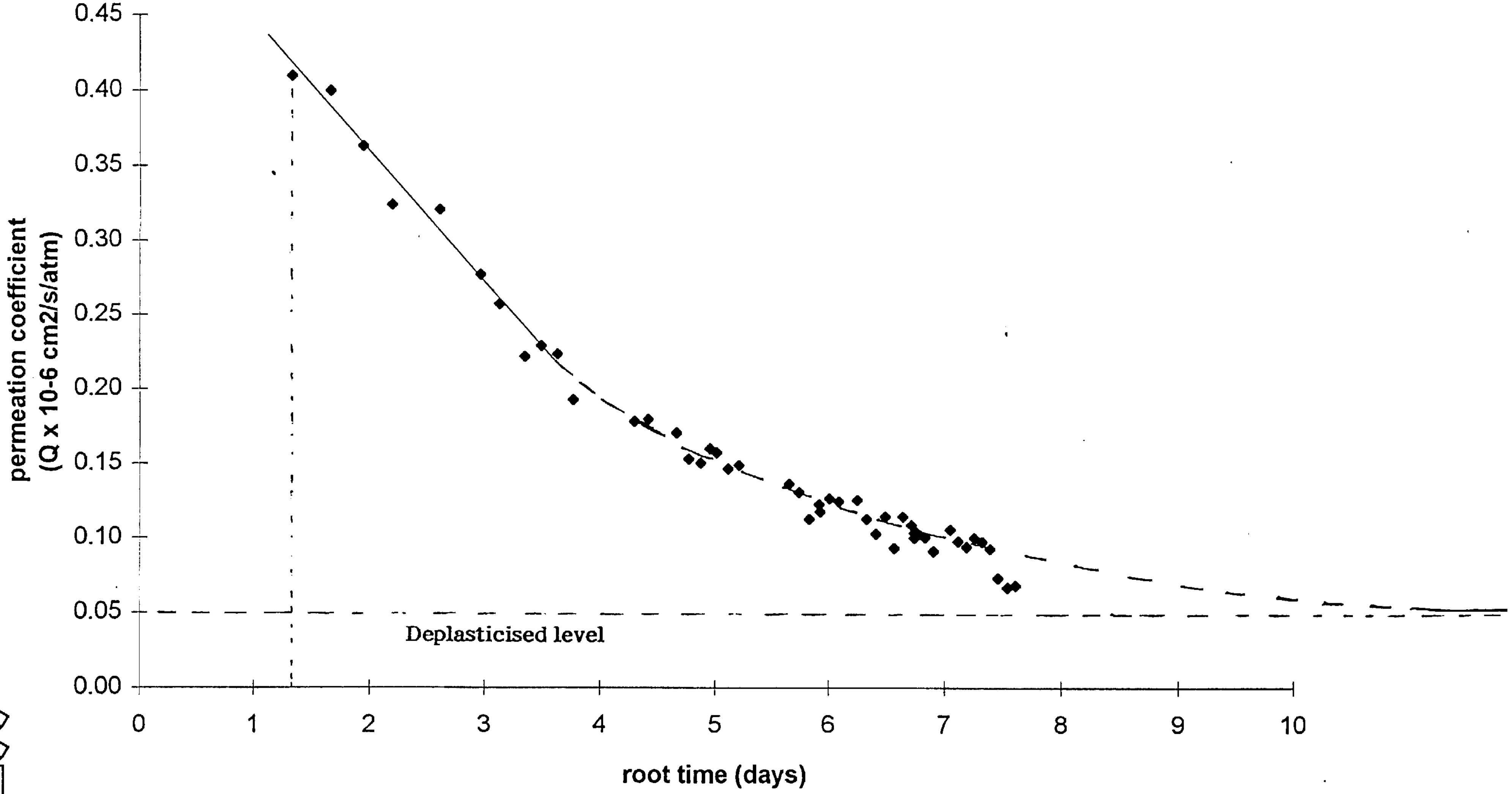

FIGURE 5(b) Diffusion–controlled plasticiser loss: effect on methane permeation coefficients

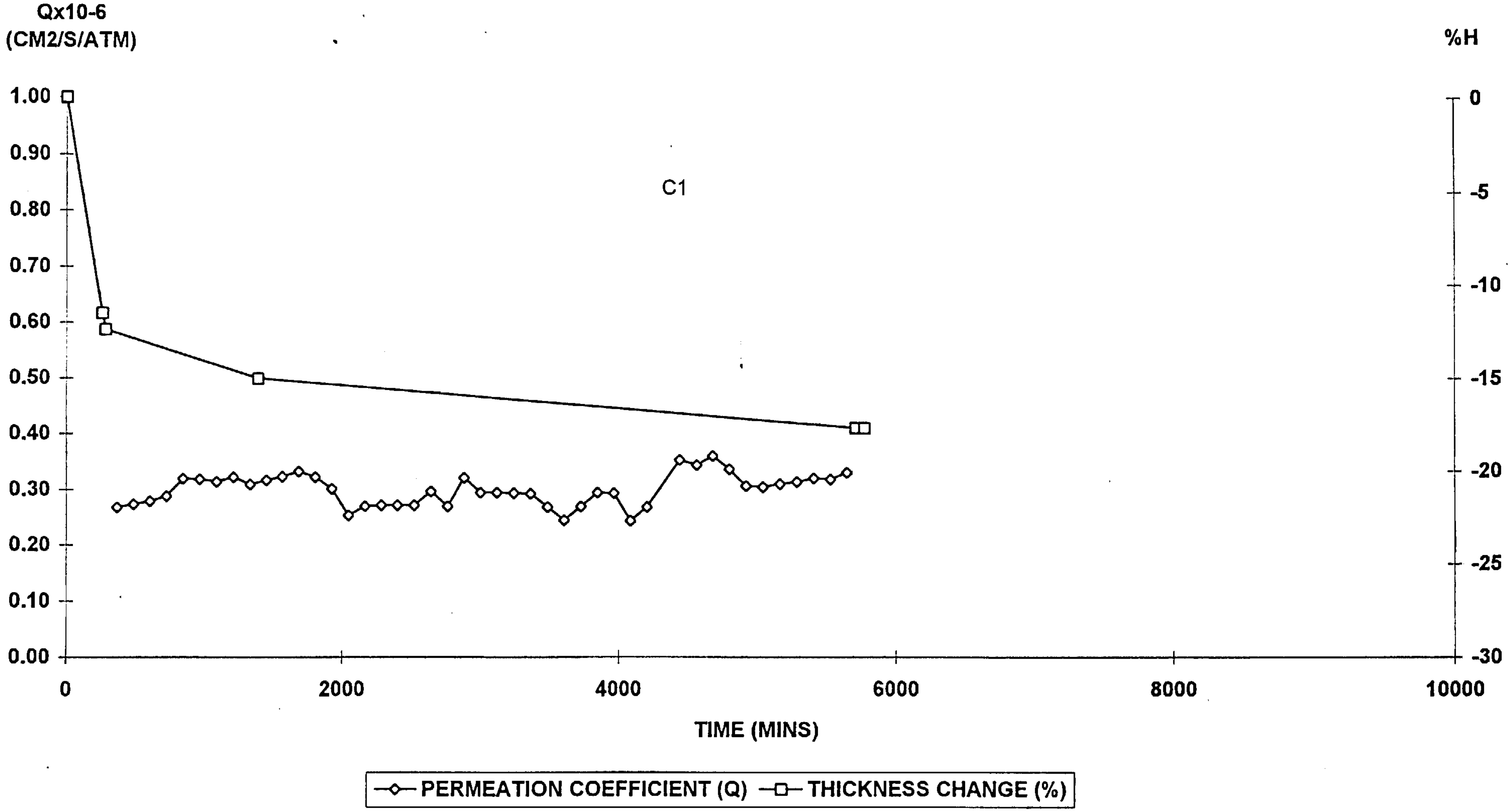

FIGURE 5(c) Graph of Q and thickness change against time for extruded Coflon (6mm) in CH_4 at 5000psi 140 C

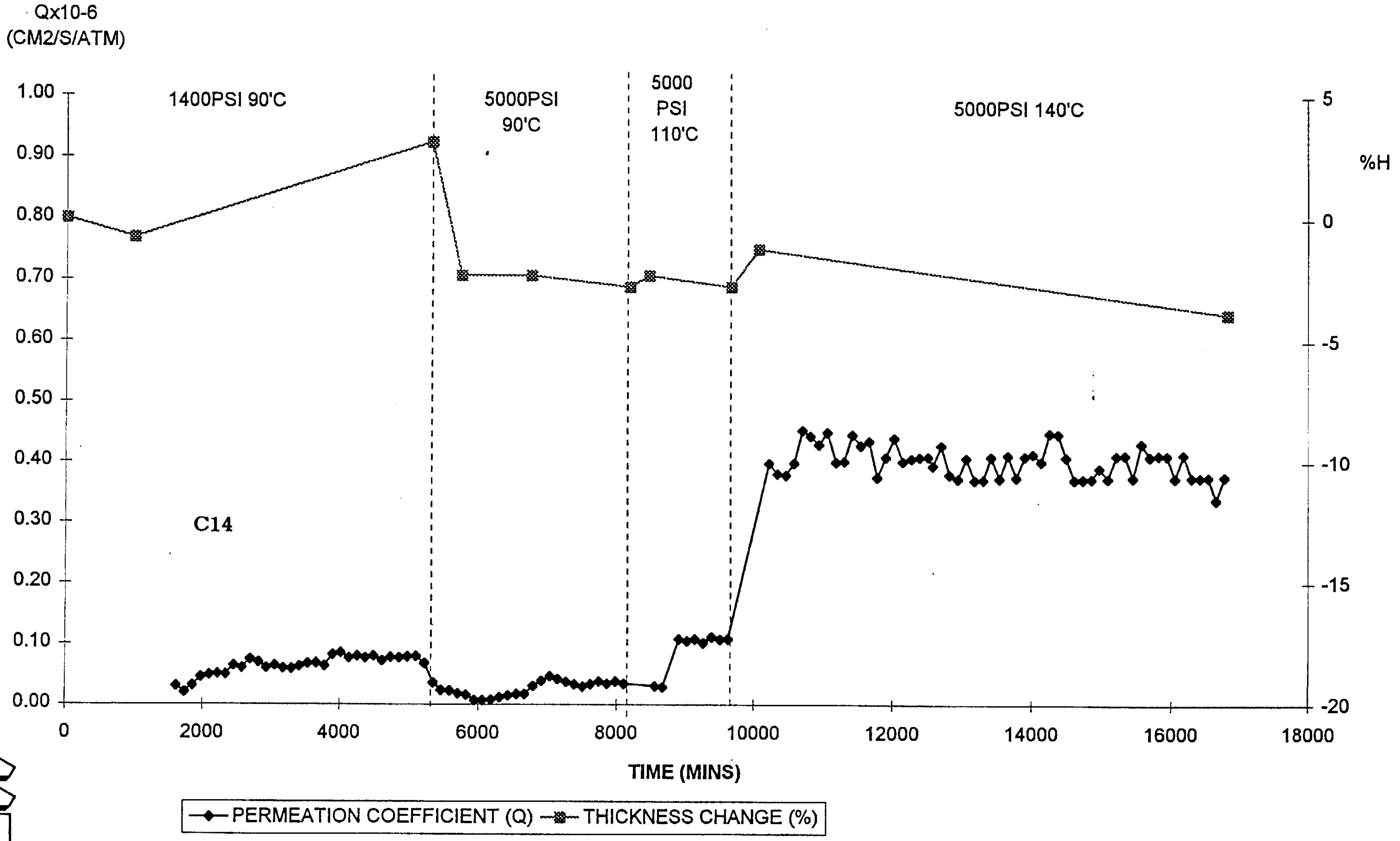

FIGURE 5(d) Graph of Q and thickness change against time result for sample C14, for CH_4 test showing pressure and then temperature increases

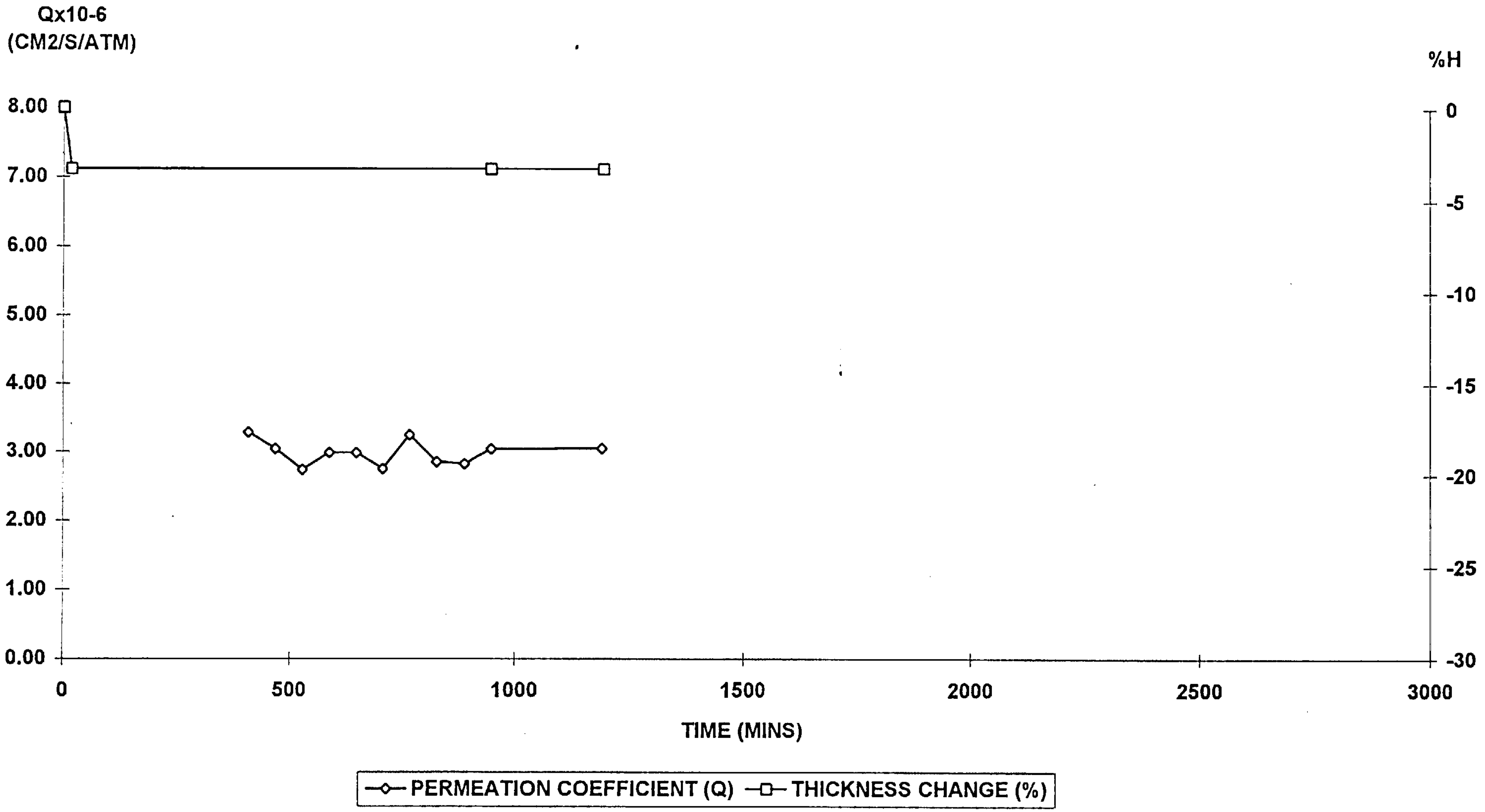

FIGURE 5(e) Graph of Q and thickness change against time for Coflon in CO_2 at 140 C 5000psi

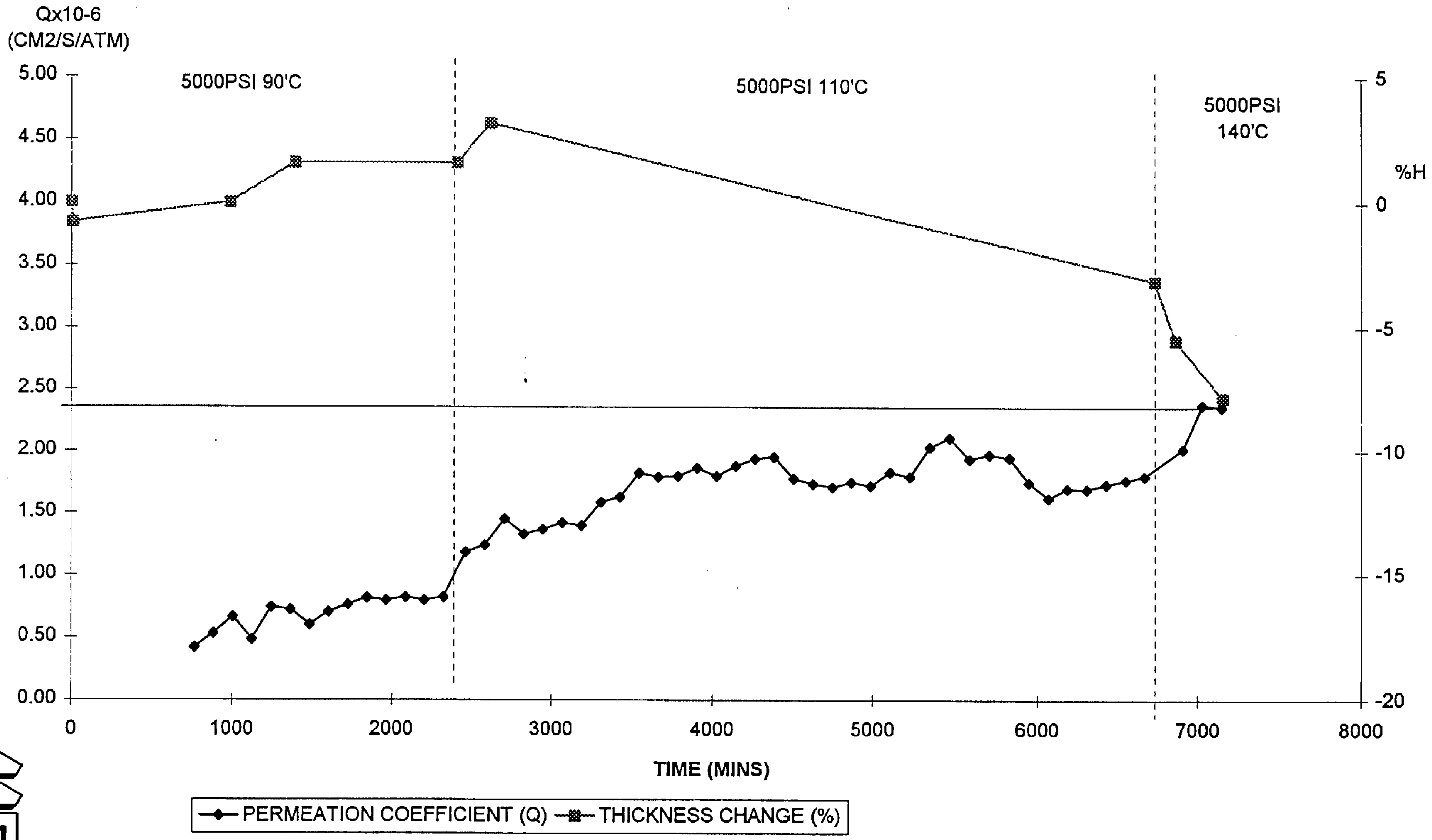

FIGURE 5(f) Graph of Q and thickness change against time - CO_2, 5000psi, various temperatures

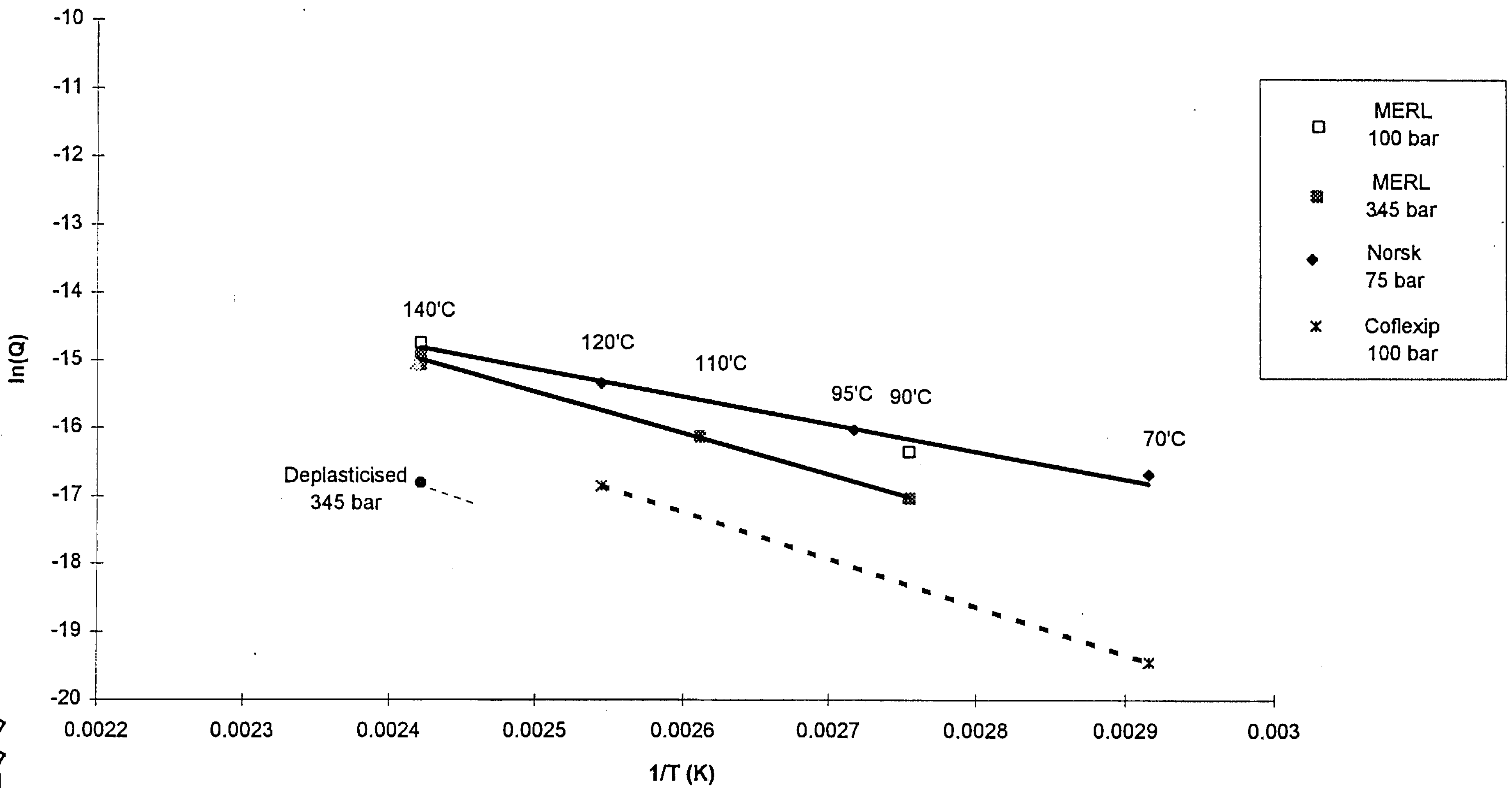

FIGURE 6 Arrhenius plots for methane permeation through Coflon

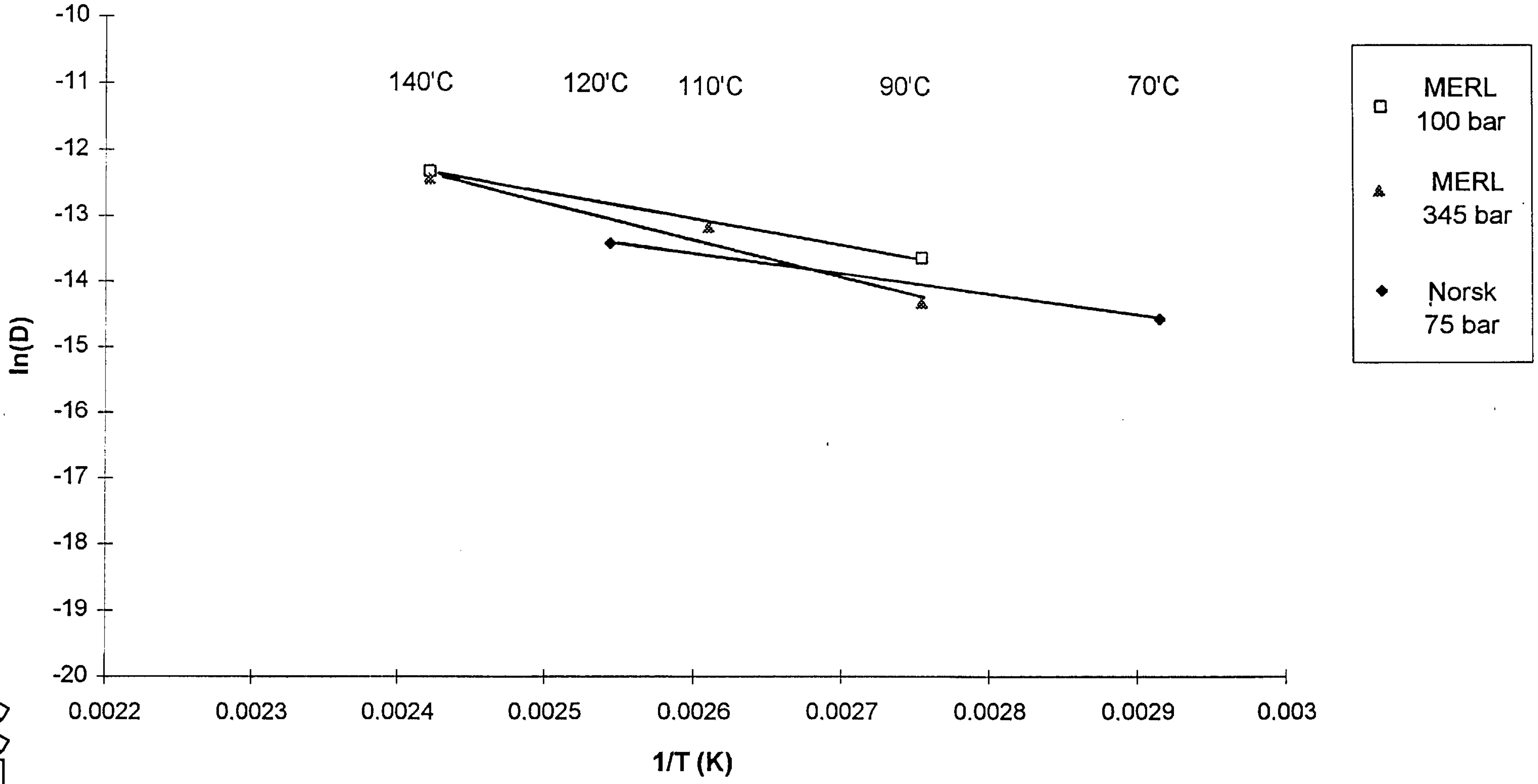

FIGURE 7 Methane diffusion through Coflon at 75-100 and 345 bar

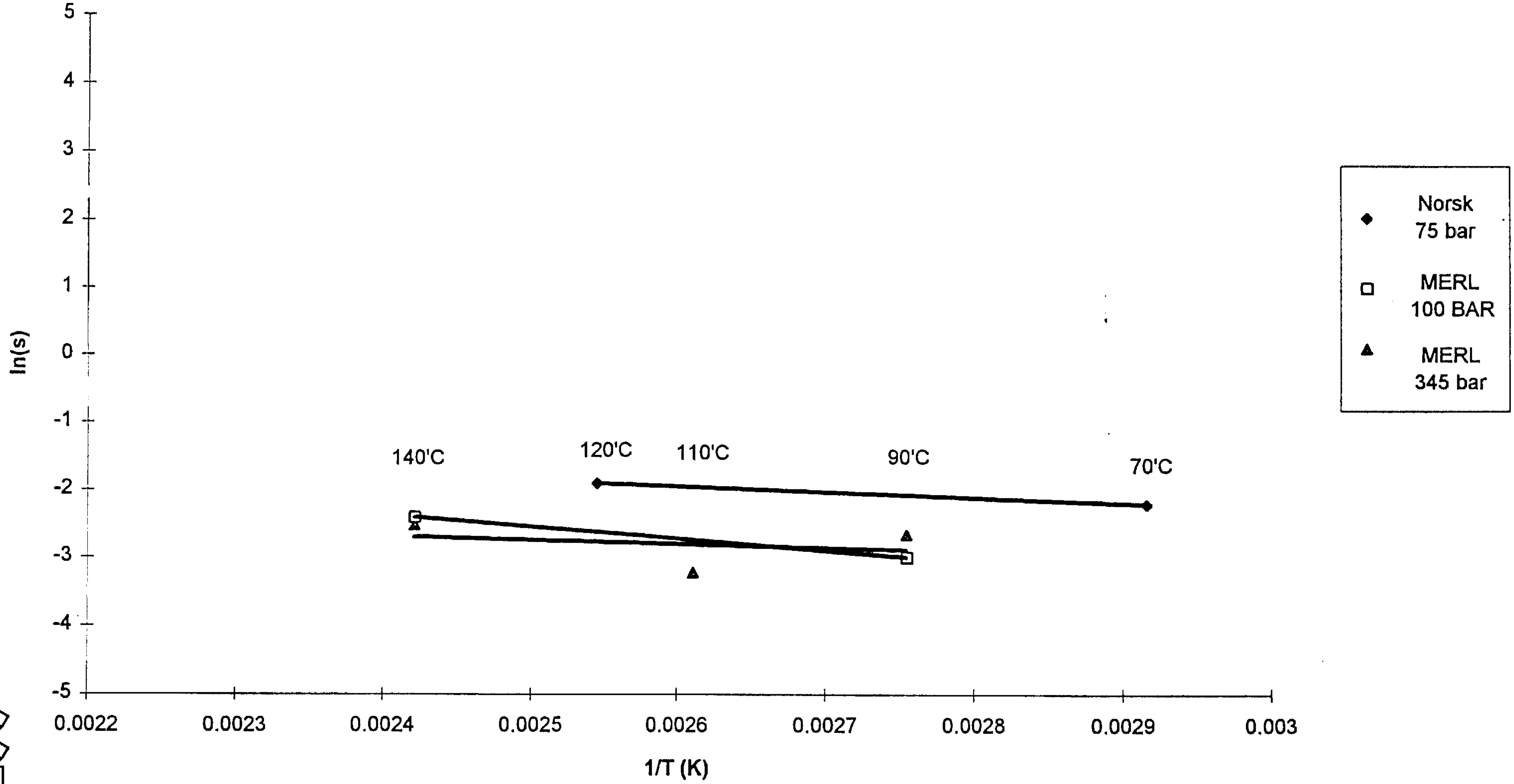

FIGURE 8 Methane solubility in Coflon at 75, 100 and 345 bar

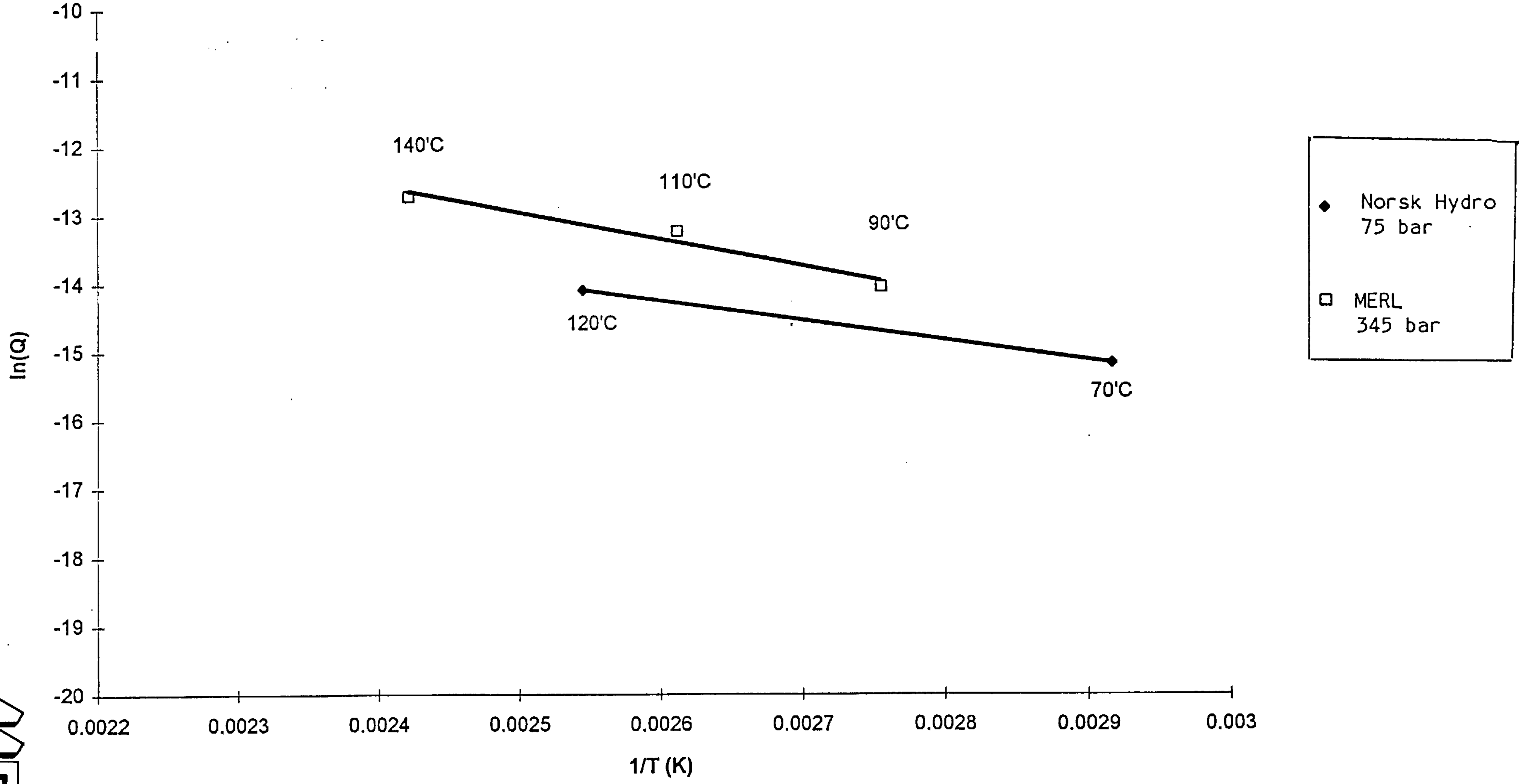

FIGURE 9 Arrhenius plots for carbon dioxide permeation through Coflon at 75 and 345 bar

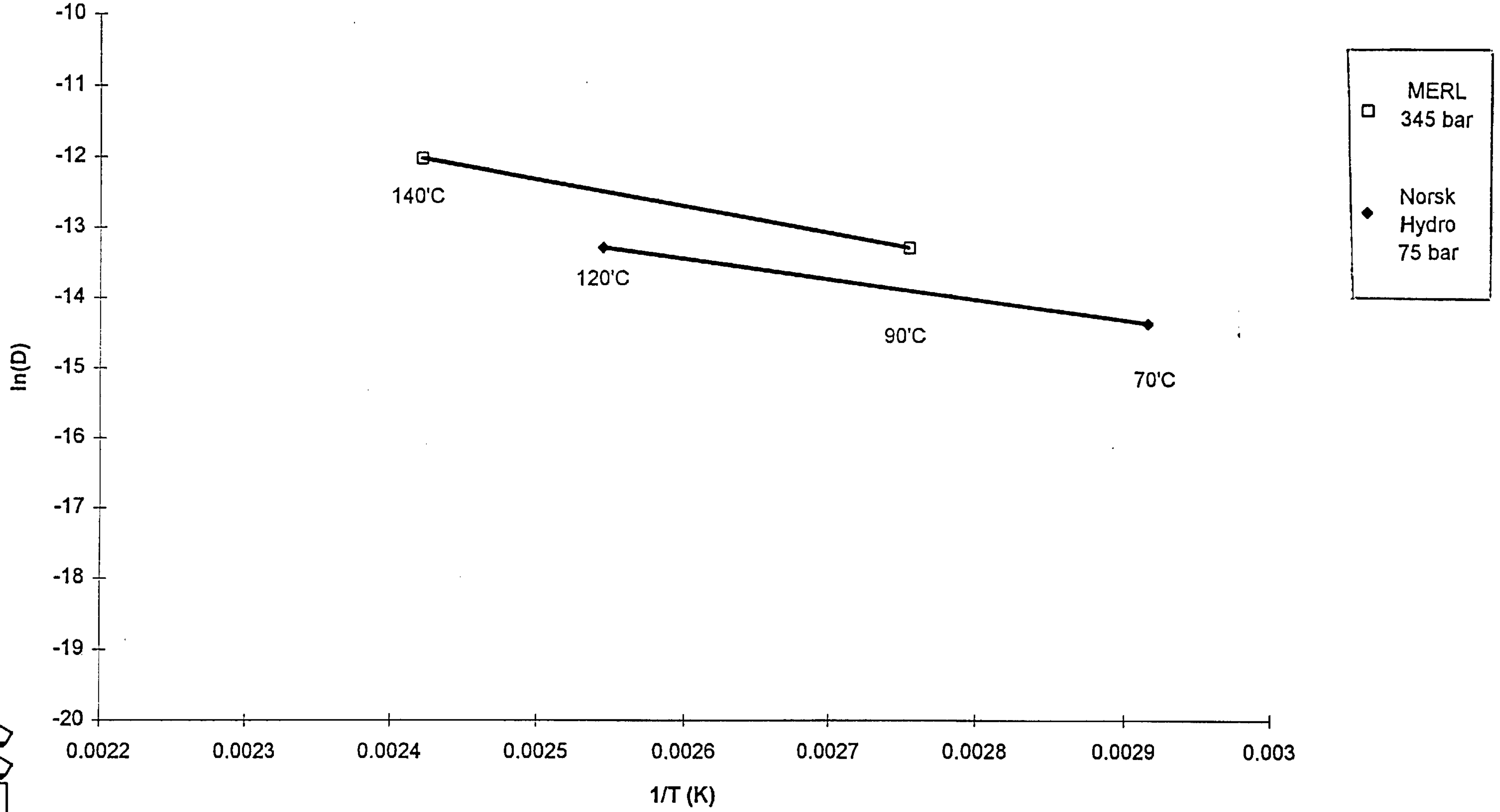

FIGURE 10 Diffusion coefficient Arrhenius plots for carbon dioxide permeation through Coflon at 75 and 345 bar

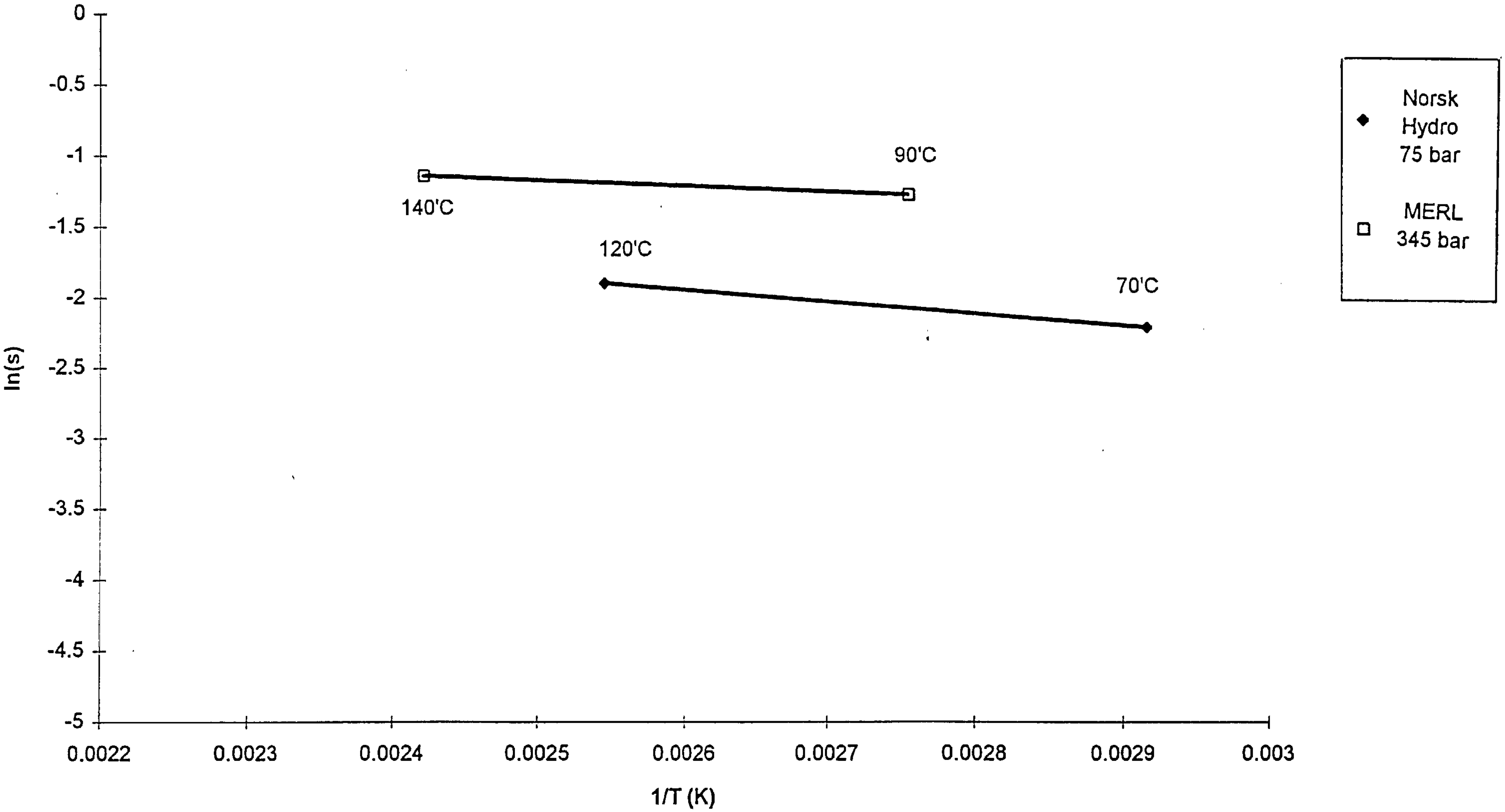

FIGURE 11 Solubility coefficient Arrhenius plots for carbon dioxide permeation through Coflon at 75 and 345 bar

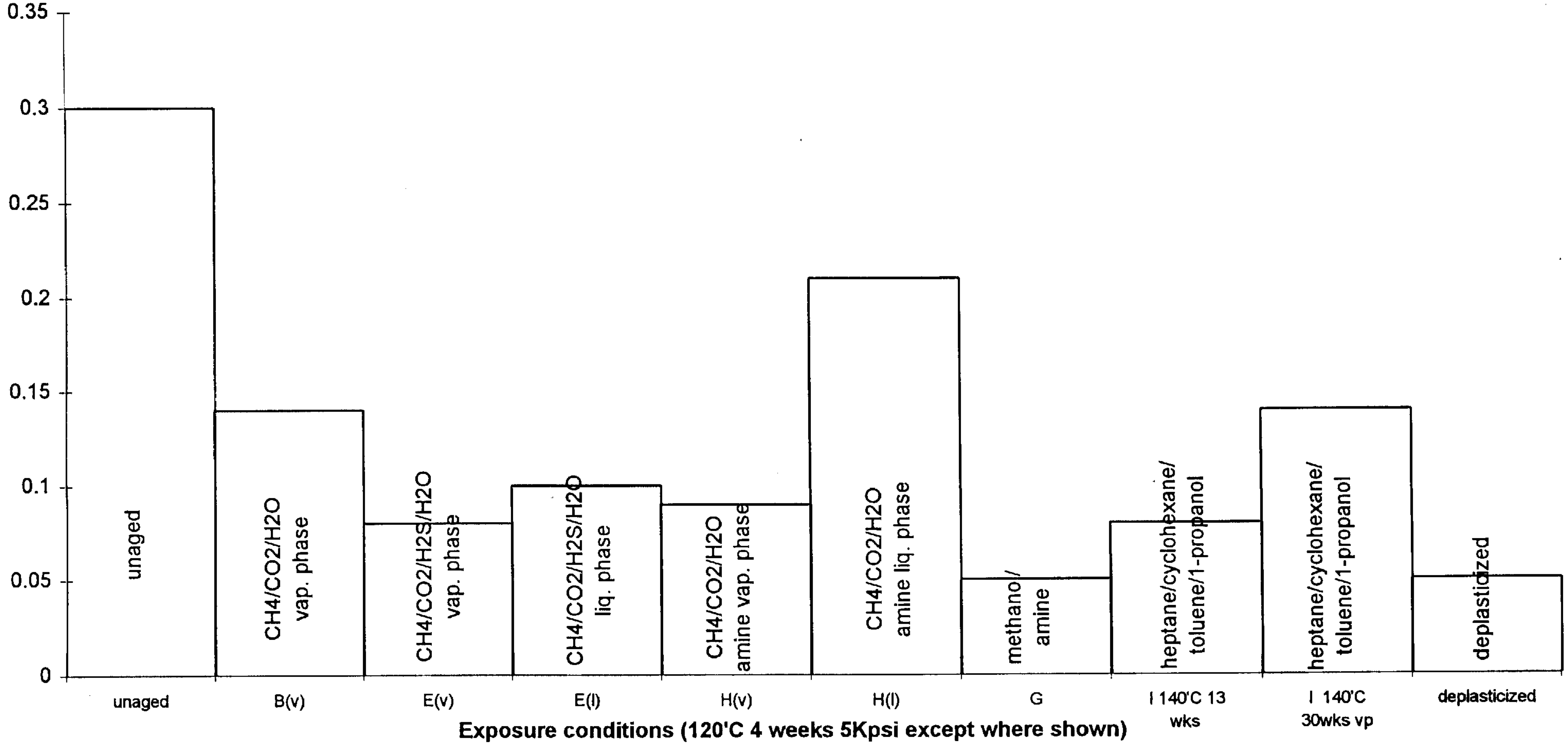

FIGURE 12(a) The effect of ageing (except Fluid F) on the permeation of methane through Coflon

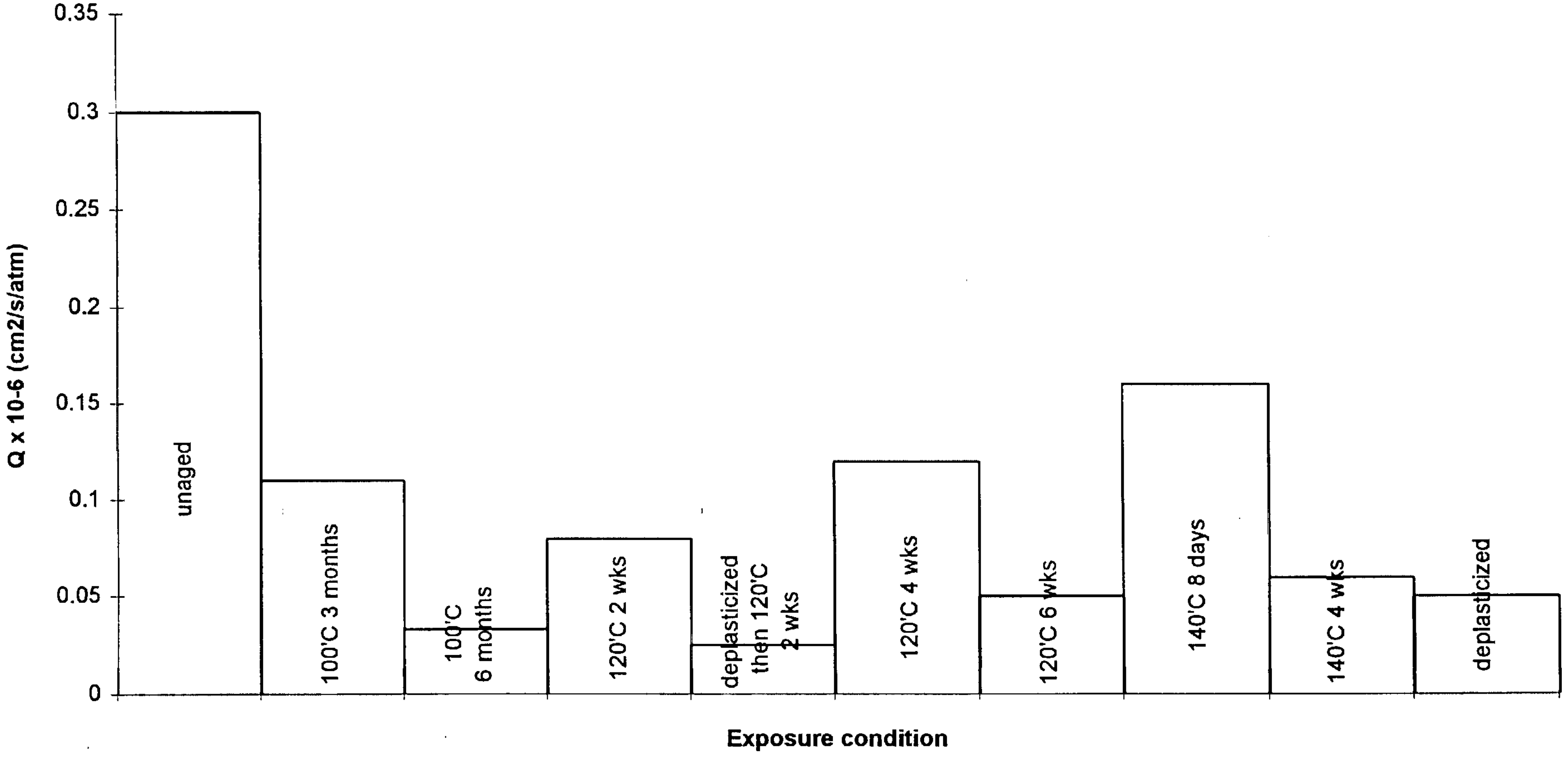

FIGURE 12(b) The effect of ageing in gas phase by Fluid F on the permeation of methane through Coflon

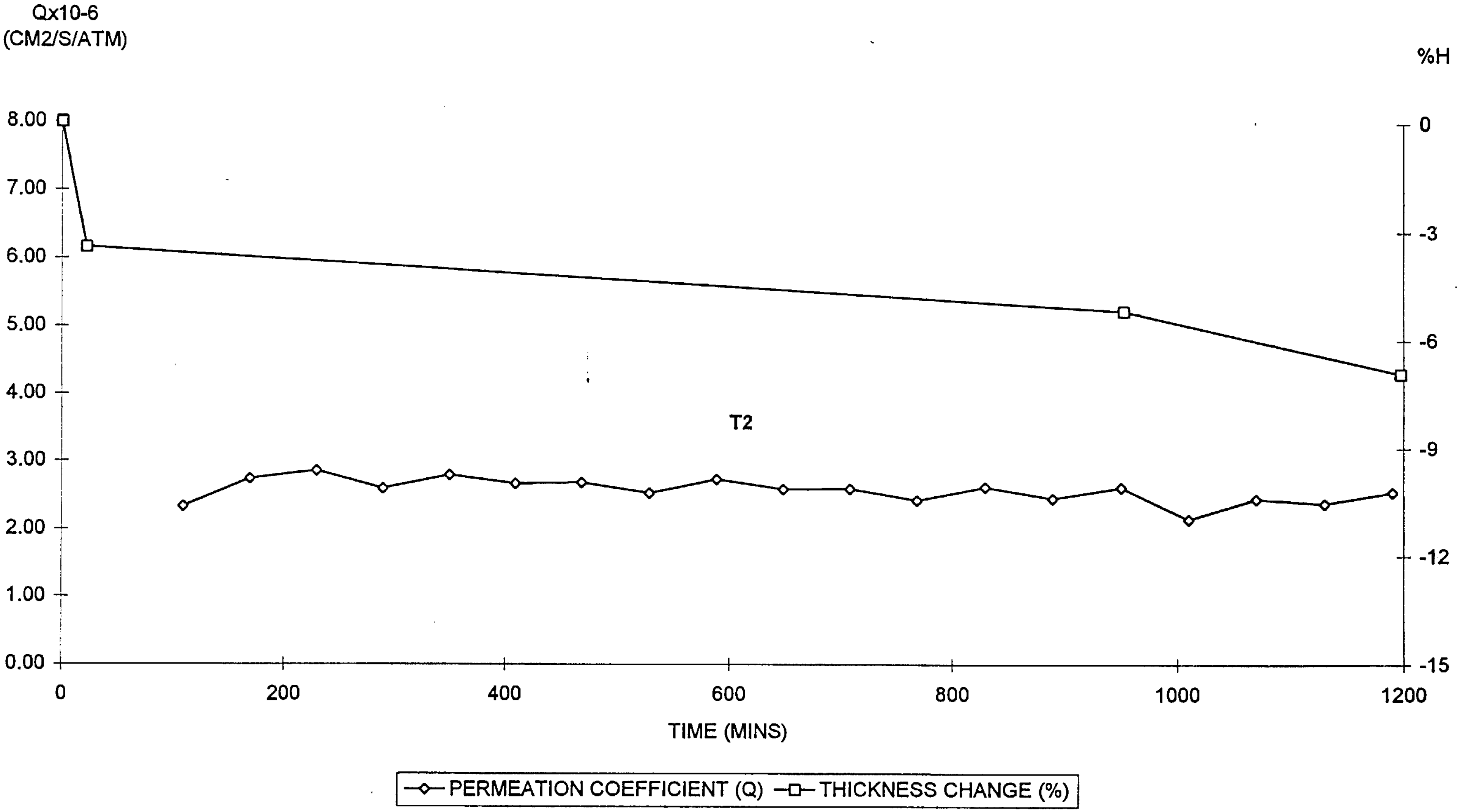

FIGURE 13(a) Graph of Q and thickness change against time for Tefzel in CO_2 at 150 C 5000psi

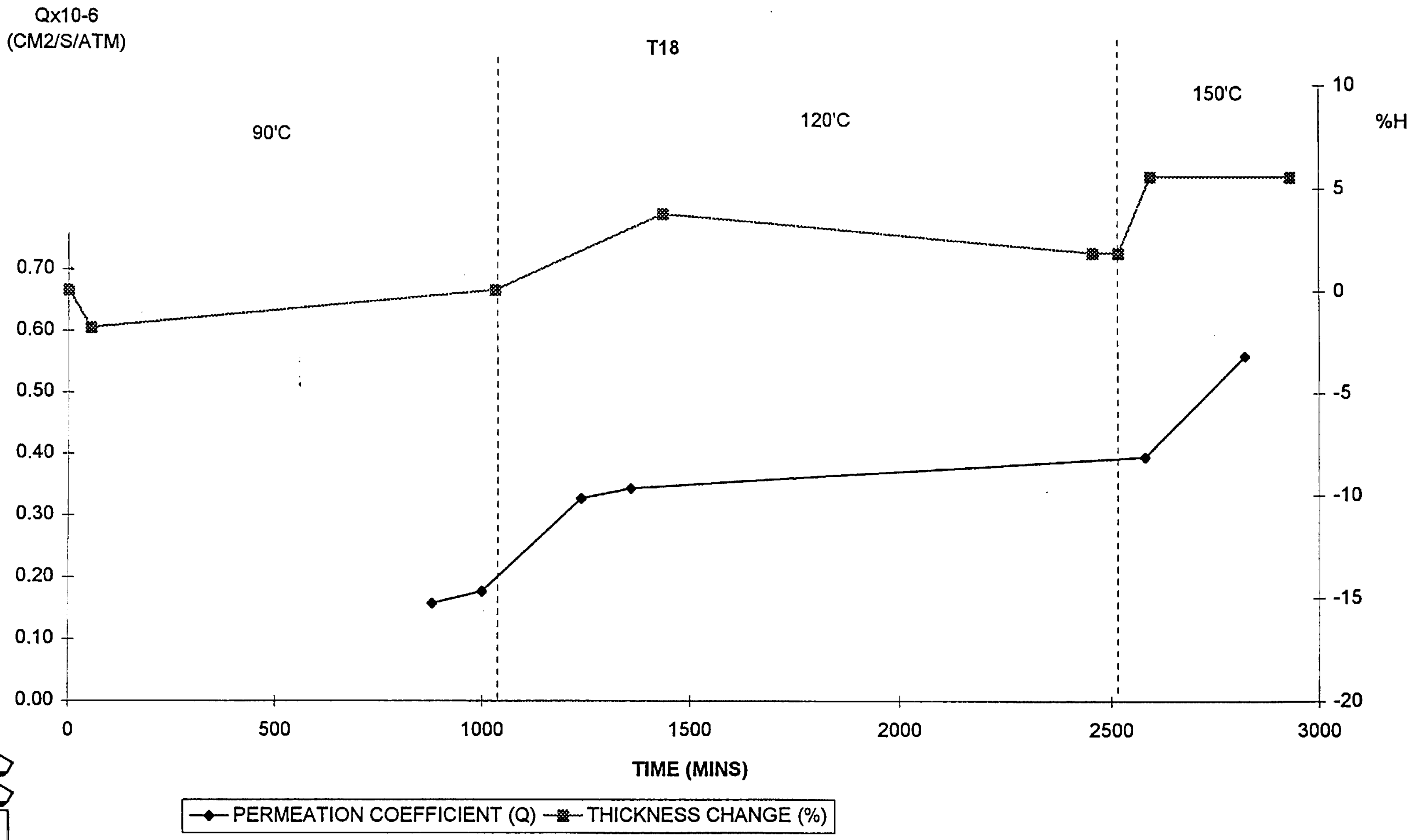

FIGURE 13(b) Graph of Q and thickness change against time – as Figure 13(a), 2nd sample

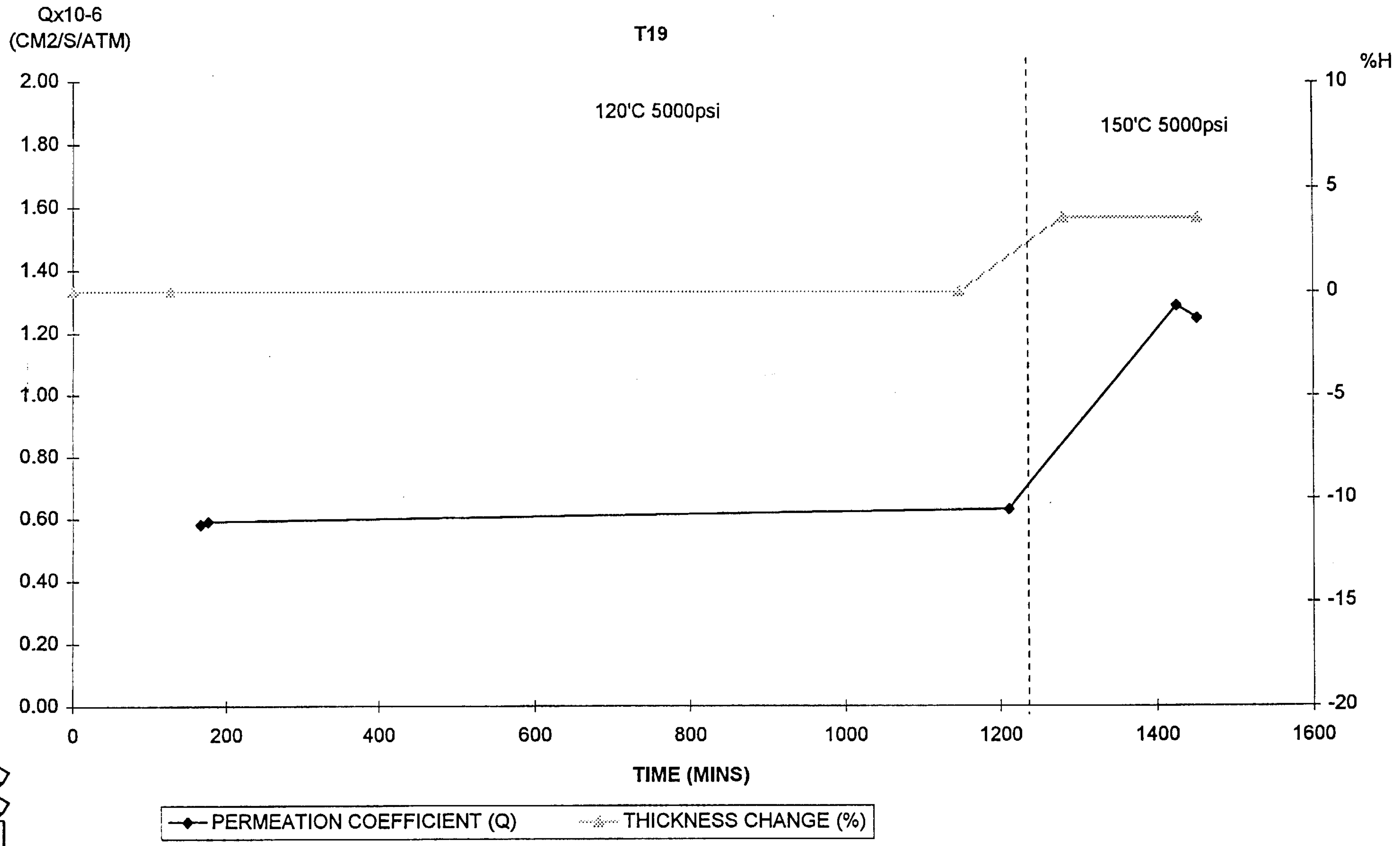

FIGURE 13(c) Graph of Q and thickness change against time – as Figure 13(a) – 3rd sample

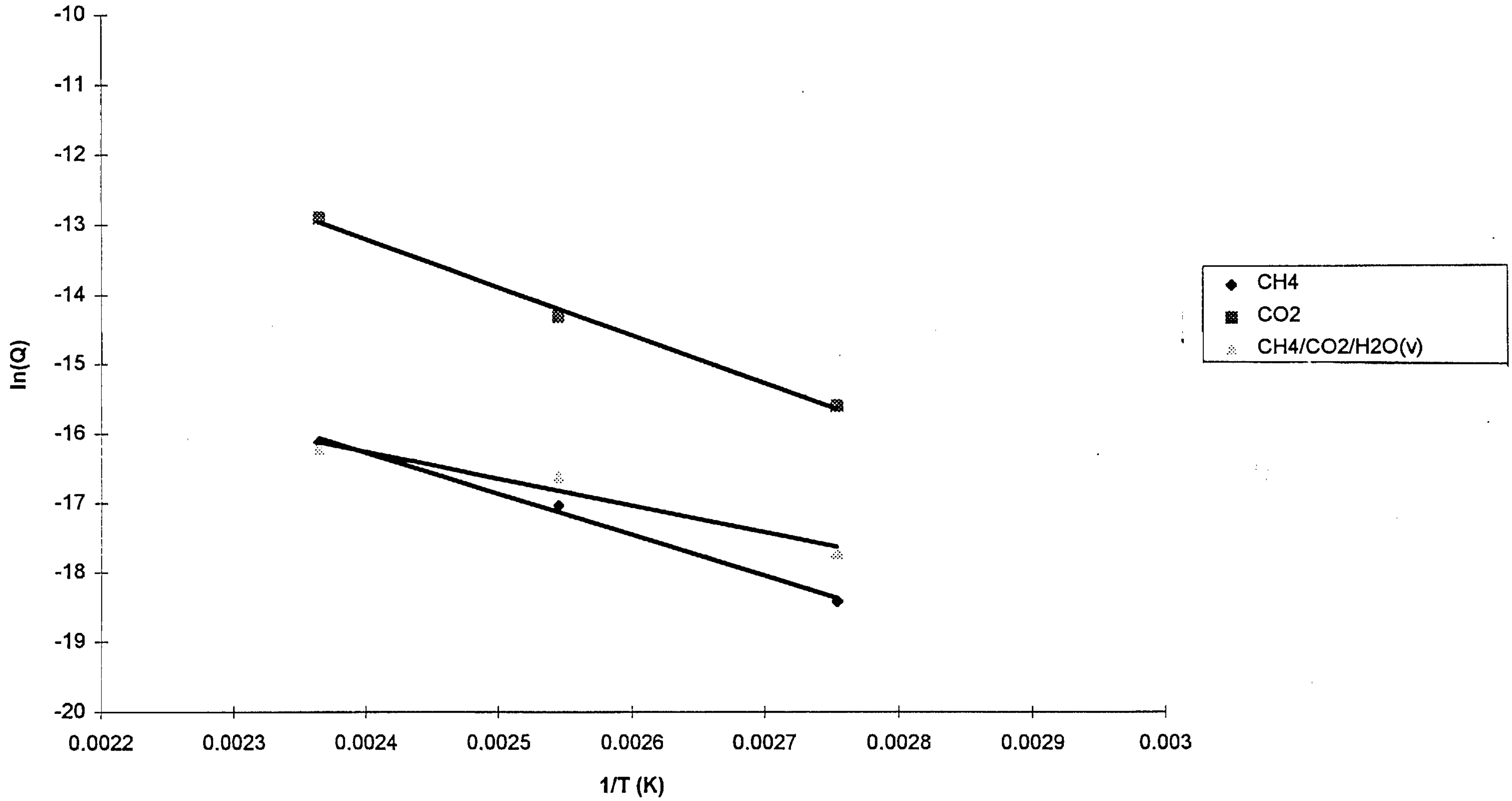

__FIGURE 14__ Arrhenius plots for permeation through Tefzel at 5000psi

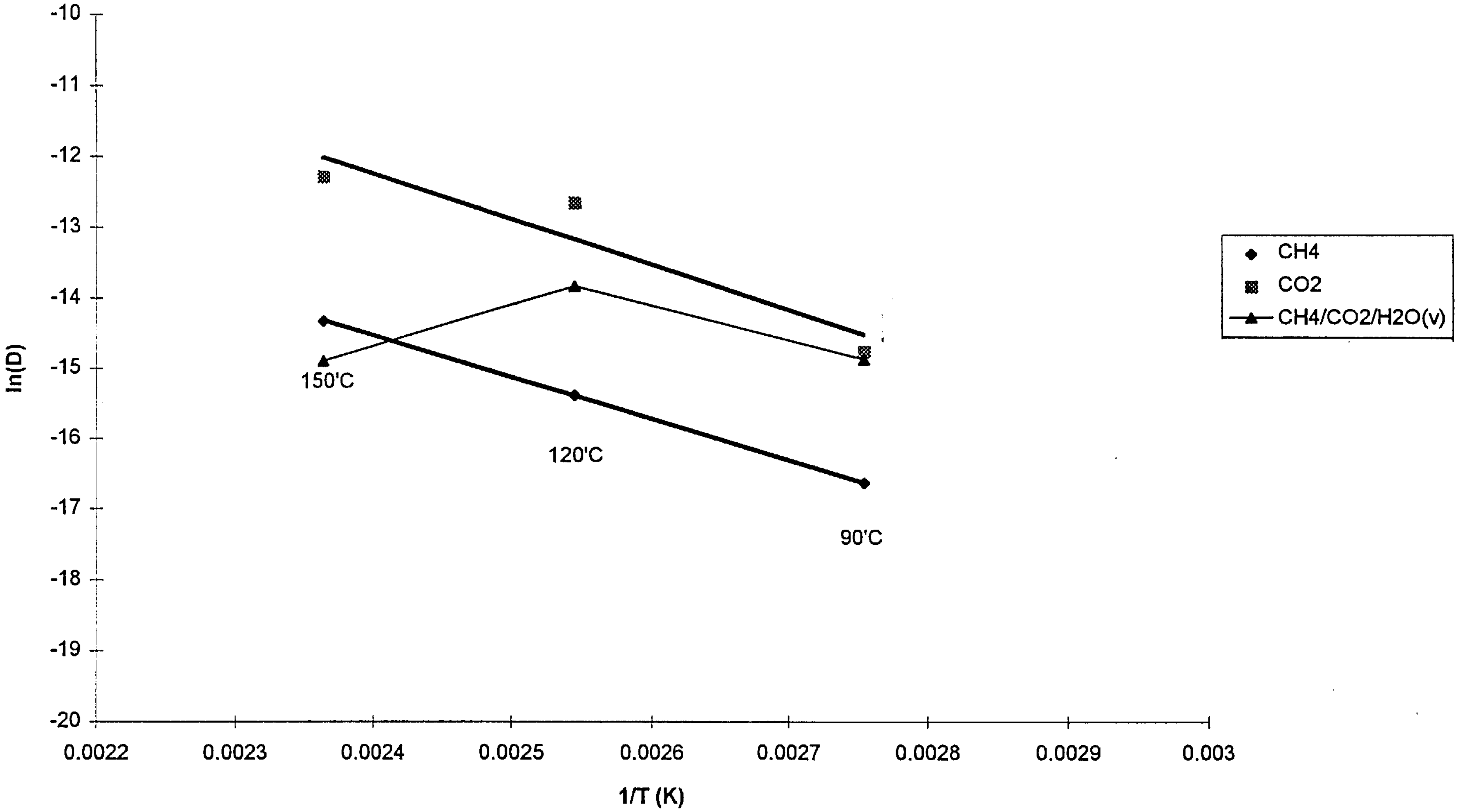

FIGURE 15 Diffusion coefficient Arrhenius plots for permeation through Tefzel at 5000psi

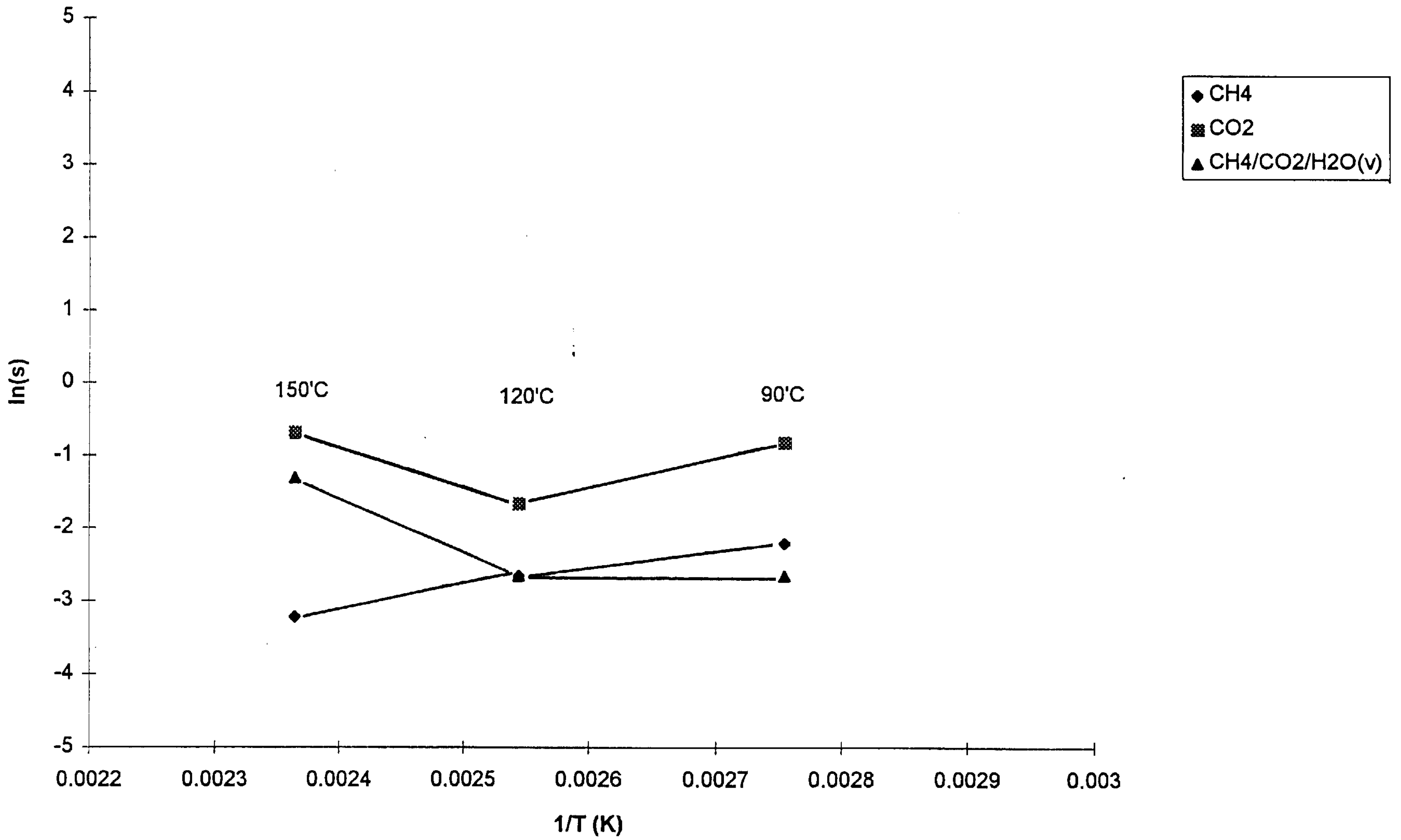

FIGURE 16 Solubility coefficient Arrheniums plots for permeation through Tefzel at 5000psi

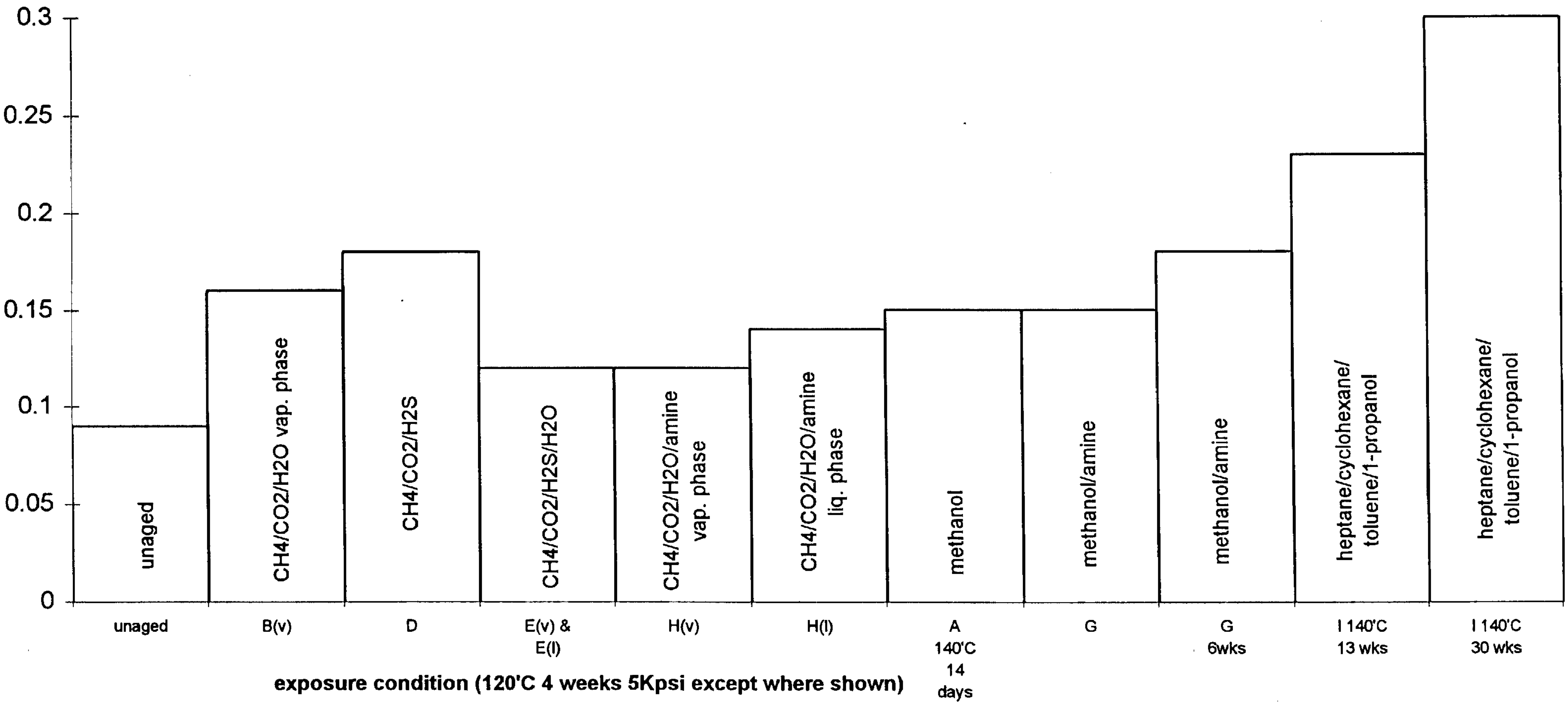

FIGURE 17 (a) The effect of ageing (except Fluid F) on the permeation of methane through Tefzel

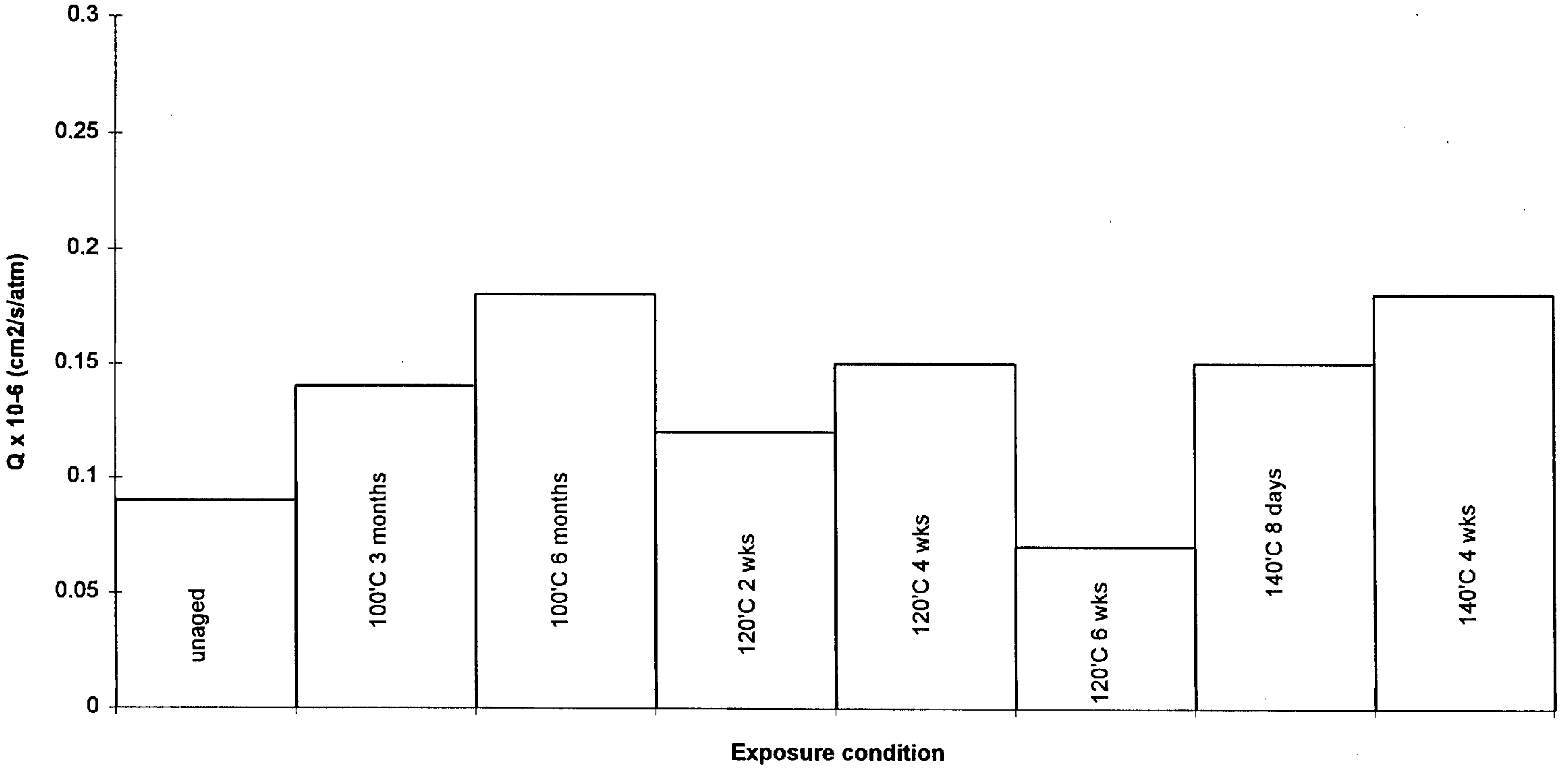

FIGURE 17 (b) The effect of ageing by Fluid F on the permeation of methane through Tefzel

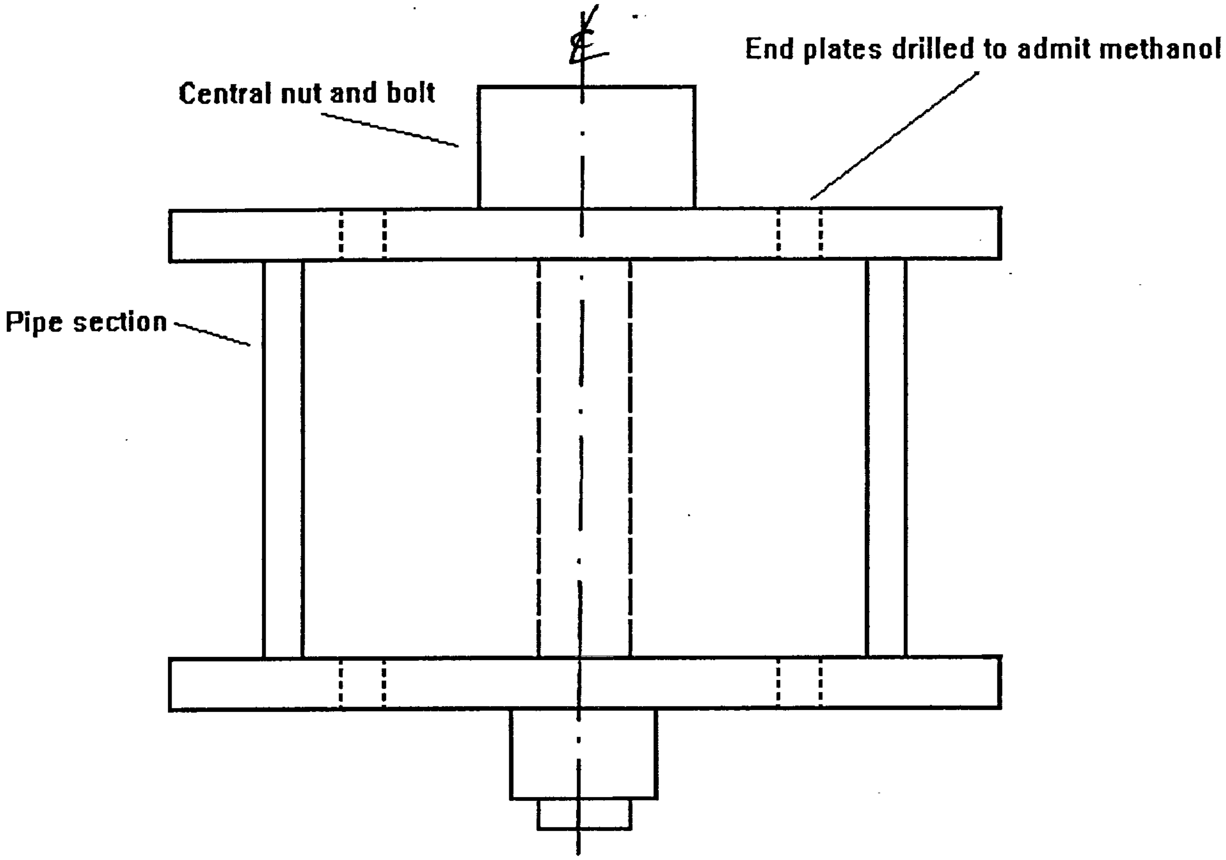

FIGURE 18 (a) Schematic of pipe sealing arrangement

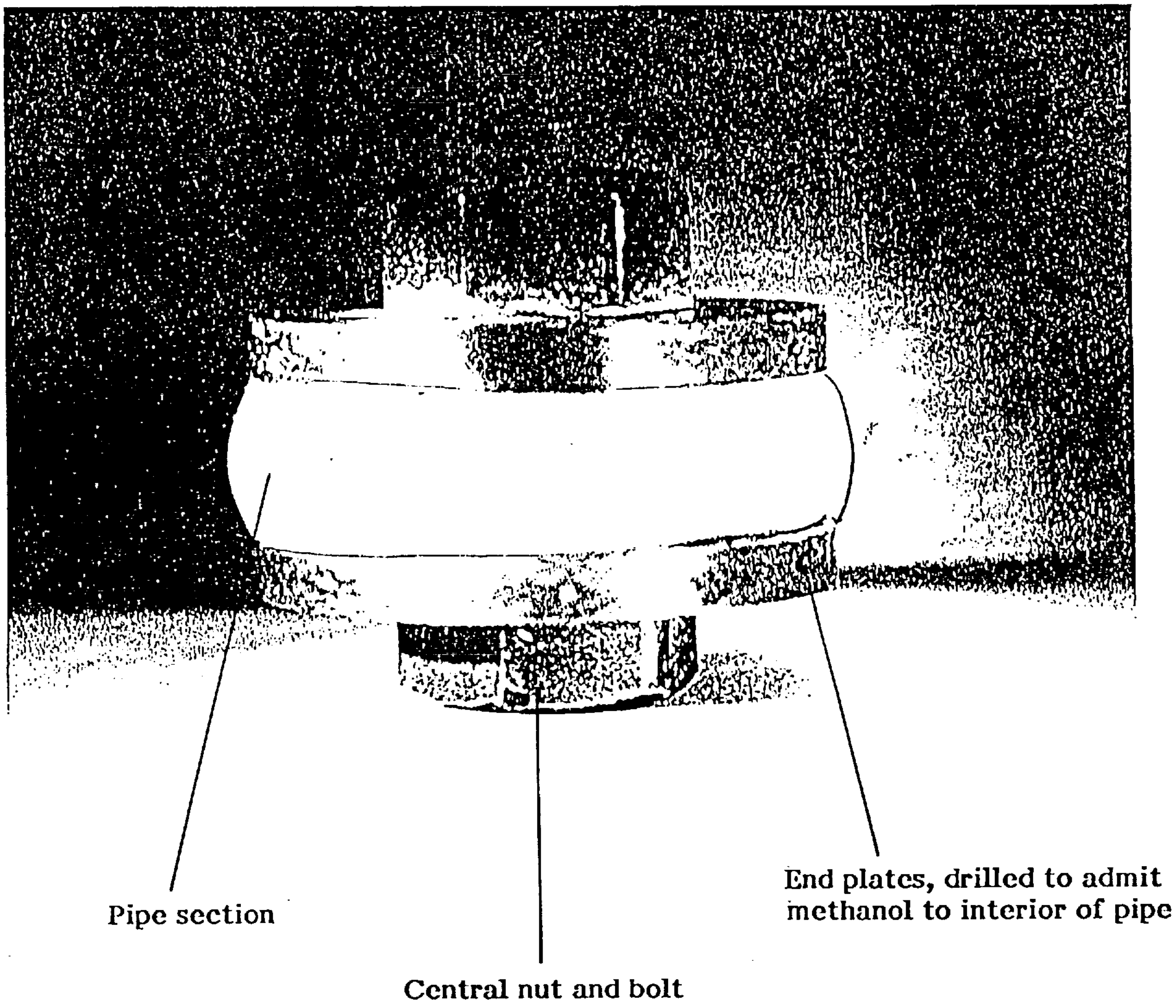

FIGURE 18(b) Arrangement to seal ends of Tefzel pipe for methanol uptake at 150 C

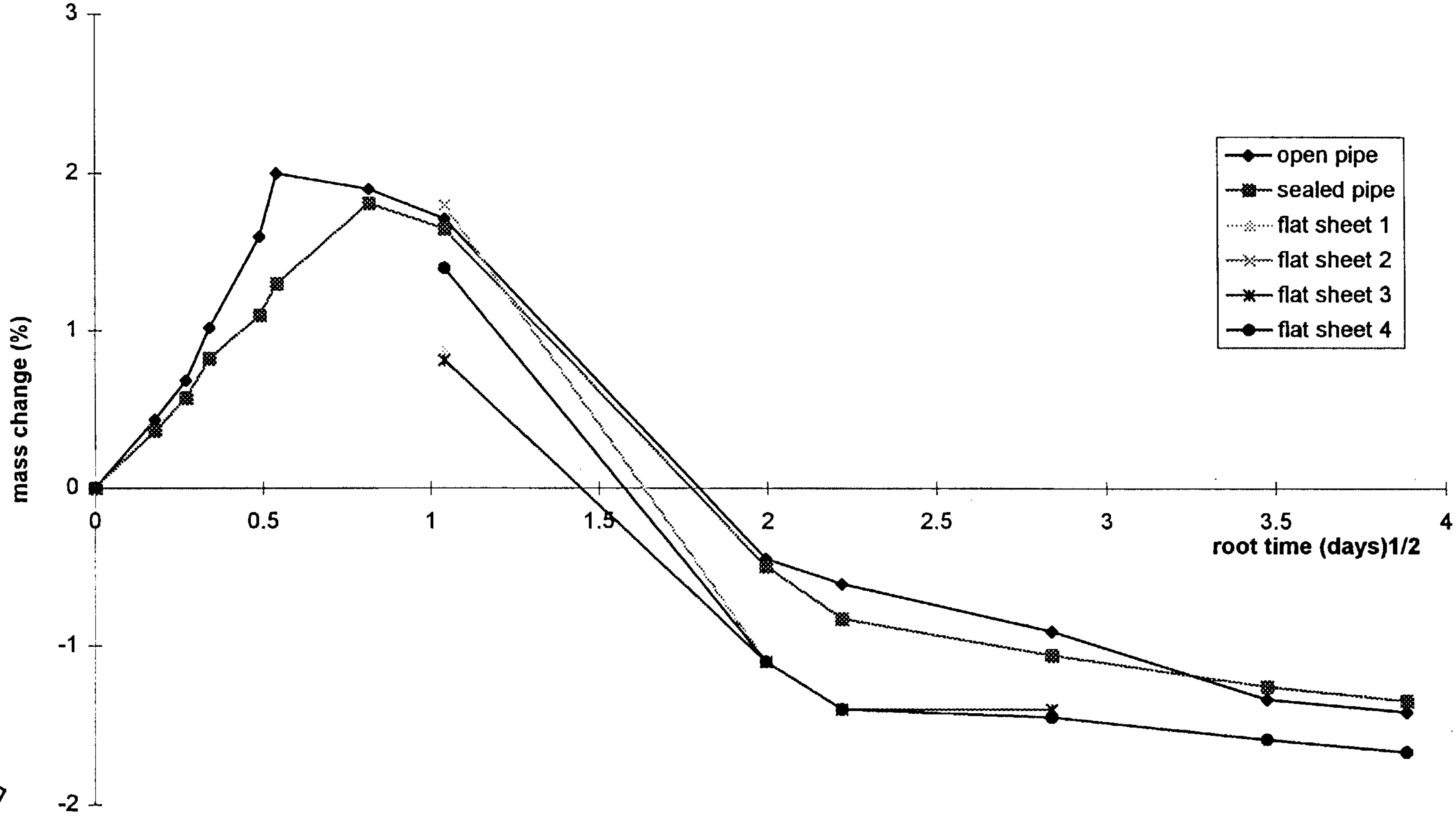

FIGURE 19(a): Absorption of methanol by Coflon at 100 C

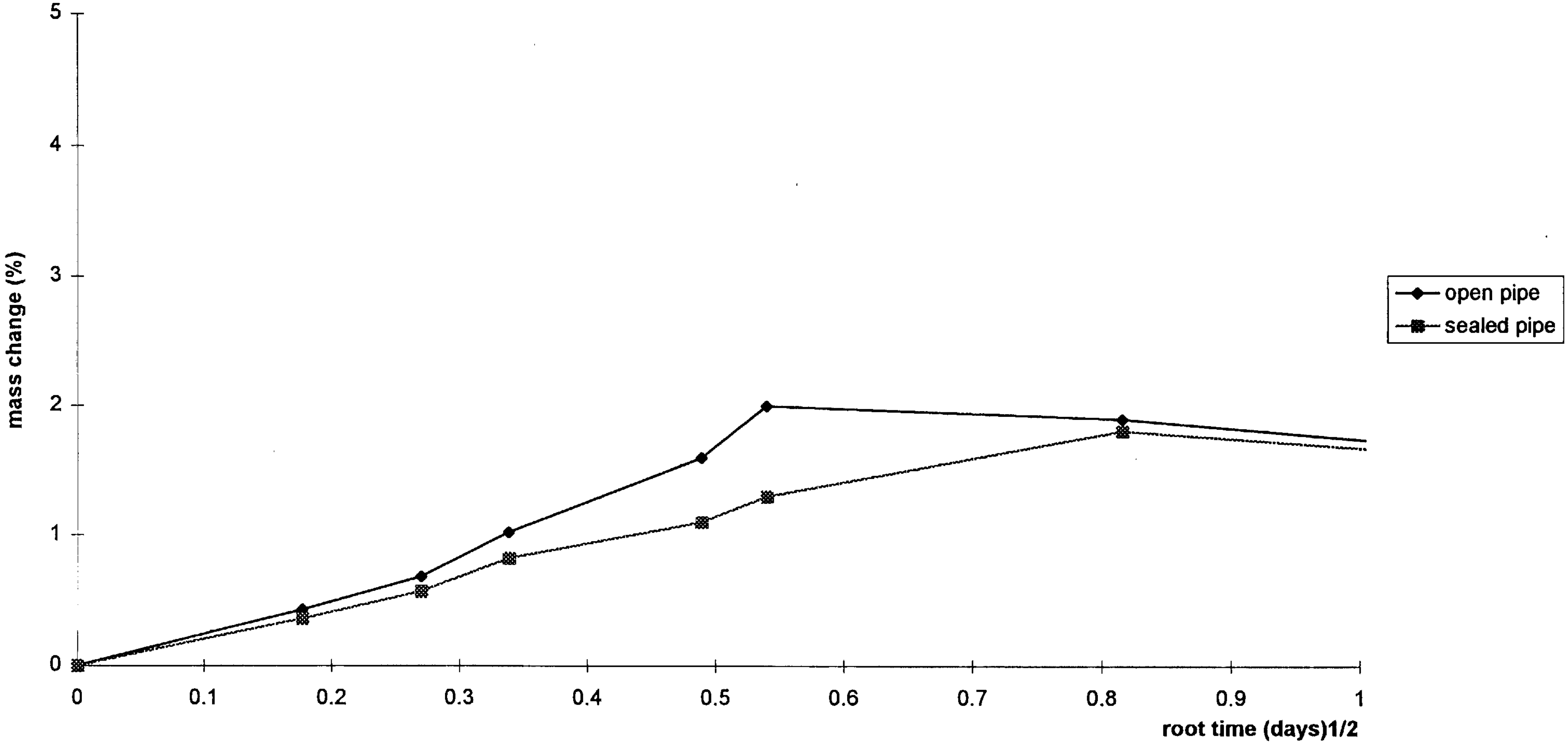

FIGURE 19(b) Absorption of methanol by Coflon at 100 C – positive uptake stage

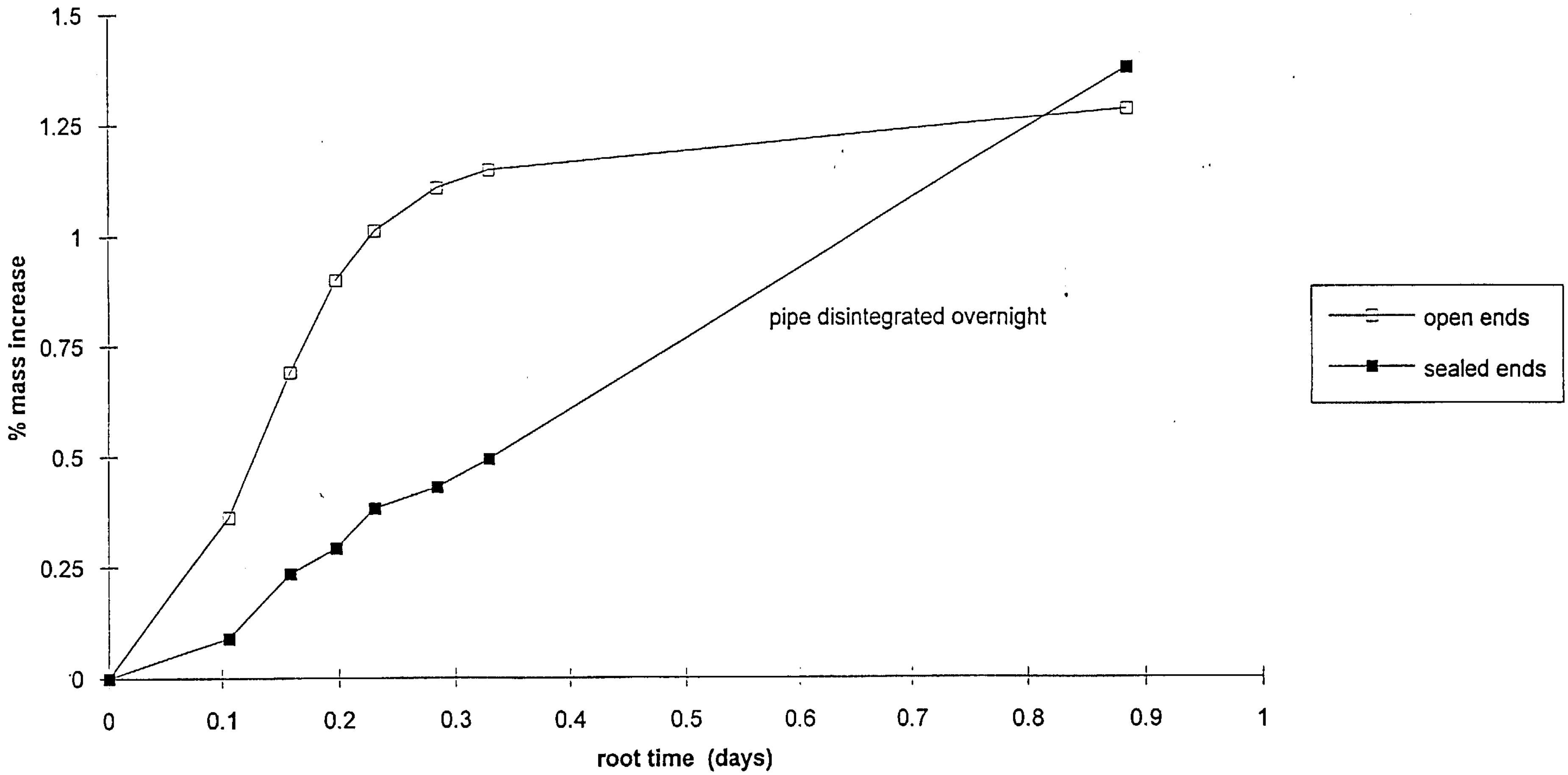

FIGURE 19(c) Uptake of methanol at 150° C by Tefzel pipe with and without ends sealed