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Hydraulics Research Division
Canada Centre for Inland Waters

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ABSTRACT

Laboratory experiments were carried out to investigate the aging of crude oil on ice. The experimental temperatures varied from -5°C to -40°C and the mean air velocity above the ice surface ranged from 0 to 0.65 cm/sec. Two types of crude oil, Norman Wells and Pembina, were studied. The crudes were poured on flat ice surfaces and oil samples were withdrawn at selected intervals. Viscosity, density and surface tension were determined as a function of the elapsed time. All of these physical parameters were found to increase as the oil ages; the higher the temperature or the higher the air flow rate, the greater the increase. Gas chromatography was used to monitor the changes in the n-alkane concentrations as a result of aging.

CARACTERISTIQUES DE VIEILLISSEMENT DU PETROLE BRUT SUR LA GLACE

E.C. Chen et B.F. Scott

Centre canadien des eaux interieures, Environnement Canada

Burlington (Ontario) Canada

RESUME

On a effectué des expériences en laboratoire pour étudier le vieillissement du pétrole brut sur la glace. Les températures expérimentales ont varié de -5°C à -40°C et la vitesse de l'air au-dessus de la surface glacée s'est maintenue entre 0 et 0.65 cm/sec. Les essais ont porté sur deux genres de pétrole brut, soit les pétroles Norman Wells et Pembina. On les a versés sur des surfaces de glace planes et on en a prélevé des échantillons à des intervalles définis. On a déterminé la viscosité, la densité et la tension superficielle en fonction du temps écoulé. On a constaté que chacun de ces paramètres physiques augmentait avec le vieillissement de l'huile; plus la température ou le taux d'écoulement de l'air était élevé, plus grande était l'augmentation. On a eu recours à la chromatographie en phase gazeuse pour contrôler les changements dans les concentrations en n-alcanes, résultant du vieillissement.

INTRODUCTION

Due to the activity of the oil and gas industry in arctic and sub-arctic areas, there is reason for concern about crude oil spillages on ice. In order to assess the effect of such spills, the aging characteristics of crude oil on ice should be understood.

A number of papers (1-3) have been published on the aging of crude oil on water, while field tests on the aging of crude oil on ice also have been conducted by several investigators (4-6). However, the aging of oil on water may differ from that of oil on ice since it involves dissolution and emulsification, and field data, which were obtained without experimental control, have revealed little quantitative information. Laboratory studies on the evaporation of crude oil to simulate its aging in a cold environment have been reported (7, 8), but the tests were not carried out on an actual ice surface. This paper reports the results of a laboratory investigation on the aging of crude oil on ice under controlled experimental conditions.

In this paper, only gross physical changes of the oil were measured. Measurements of these parameters at the submacroscopic level would provide information pertinent to the aging of oil and how the gross physical parameters change. However, the result would be applicable only to the oil investigated and similar studies would have to be initiated for each type of oil.

EXPERIMENTAL PROCEDURES

Experiments were carried out in an environmental chamber (Revco Low Temperature Freezer, 127 x 60 x 46 cm, $\pm$ 0.1^{o}C). Flat ice surfaces were prepared by freezing water in a rectangular aluminum tray (28 x 48 x 8 cm). An air compressor was used to simulate a flow of air over the ice surfaces. The mean velocity of air flow was varied from 0 to 0.65 cm/sec, and the air temperatures ranged from -5^{o}C to -40^{o}C. Norman Wells and Pembina crude oils were used in this investigation. Their physical properties are given in Table I.

For a typical run, the experimental temperature and the air flow were regulated to the desired level; one litre of crude oil, sealed in a glass container, was first allowed to cool to the experimental temperature and then poured on the ice. The oil covered the entire ice surface, i.e. 28 x 48 cm, to a thickness of 0.75 cm. Oil samples were withdrawn at selected intervals and the changes in viscosity, density and surface tension were determined as a function of the elapsed time. For each sampling, a total of 30 ml of oil was collected from different locations in the tray to ensure that a uniform sample was obtained. Only two samples were taken from the same tray so that no significant difference in the oil thickness would be caused by the sampling. More tests were made to allow further aging of the oil samples. The tests continued for two weeks.

The viscosity, density and surface tension of the oil were measured, respectively, by a viscosimeter (Haake Rotovisko), a pycnometer and a Fisher Autotensiomat. All the measurements were made at 20^{o}C.

A gas chromatograph (GC) was used to monitor the changes in n-alkane content of the oil. The GC was a Perkin-Elmer model 900 equipped with a flame ionization detector and an OV-225 SCOT column. Only n-alkanes with vapour pressures lower than n-octane were analyzed because of incomplete peak resolution of higher vapour pressure compounds. The chromatograph was operated using temperature programming ($35^{o}C$ to $210^{o}C$, at $4^{o}C/min$) after a six-minute initial delay.

During the analysis of the chromatogram, the peaks corresponding to the resolved components of the oil were separated from the unresolved continuum under these peaks (9). The relative concentrations of n-alkanes were then obtained by dividing the areas under these peaks, respectively, by the area under the n-hexadecane peak.

Accordingly,

$$C_i = A_i / A_{16} \quad \text{(1)}$$

where C_i is the relative concentration of the n-alkane; A_i and A_{16} are, respectively, the peak areas related to the n-alkane and the n-hexadecane. The areas were determined using the regular triangulation method (0.5 height x width at half height). Hexadecane was chosen as the standard because the evaporative losses of this compound in an oil matrix under the experimental conditions would be minimal (9, 10) and it was well resolved in the chromatogram.

RESULTS AND DISCUSSION

The aging data obtained are presented in Figures 1, 2, 3 and 4. The changes in viscosity and density as a function of temperature (-5°C, -20°C, and -40°C) and air velocity (0, 0.37 and 0.65 cm/sec) are shown in Figure 1. It is seen that both visosity and density of the oil increase with elapsed time. This confirms the findings of the field tests (4, 5 and 8); a comparison of the data is given in the Appendix (Figures A-1 and A-2). The results are all characterized by a linear pattern after an initial rapid increase during the first day. Higher temperatures or air flow rates give a greater increase in both viscosity and density. This is not unexpected, as the aging process, under the experimental conditions, mainly involves evaporation of the more volatile components of the oil; a higher temperature or a higher air flow rate will increase the rate of evaporation.

An empirical correlation for the linear increase of viscosity as a result of aging (see Figure 1) may be derived as follows. As the slope, m, and the intercept, k, of the μ vs. t lines increase in value with the air temperature, T, and the air velocity, V, one may assume that

$$m = a + bT + cV + d(TV) \quad \text{(2)}$$

$$k = a' + b'T + c'V + d'(TV) \quad \text{(3)}$$

The constants in the above equations may be determined from data of the six lines shown in Figure 1. It results that

$$\mu = (0.684 + 0.012\,T + 0.489\,V + 0.046\,TV)\,t + (7.856 + 0.057\,T\ 8.784\,V + 0.236\,TV) \quad \text{(4)}$$

Similarly, an empirical equation may be obtained for the density:

$$\rho = (1.4 \times 10^{-3} + 1.7 \times 10^{-5}\ T + 1.3 \times 10^{-3}\text{-}V)\ t$$
$$+ (0.852 + 2.3 \times 10^{-4}\ T + 2.8 \times 10^{-2}V + 6.8 \times 10^{-4}TV) \ldots (5)$$

where

μ = viscosity of the oil, cP

ρ = density of the oil, g/ml

T = air temperature, ^{o}C

V = air velocity, cm/sec

t = elapsed time, days

Equations (4) and (5) apply only to crude oils having properties and composition similar to that of Norman Wells crude (with an absolute % deviation of less than 10%) and may not be applicable under a different environmental condition.

The total change in surface tension, as a result of aging for the crude oil studied in these experiments, is small (from 1 to 6 x 10^3 N/m) as illustrated in Figure 2. These results are consistent with those of the viscosity and density, namely a rapid increase in the beginning, then a slower linear increase with elapsed time, and the higher the temperature, or air flow rate, the greater the increase. These results are compared with those reported by Glaeser and Vance (4) in the Appendix (Figure A-3).

The maximum increase in viscosity, density and surface tension shown in Figures 1 and 2 are, respectively 600%, 6% and 21%. The measurement of viscosity is, therefore, preferable to those of density and surface tension as an indication of oil aging. The degree of aging for each oil depends very much on the temperature and the air flow above the ice surface, as is seen from Figure 1. If the movement of the air above the ice is relatively small and the temperature is low, very little evaporation will occur, and hence, small changes in the physical properties will be observed.

In Figure 3, the changes in viscosity and density of Norman Wells crude oil with those of Pembina crude oil are compared. The trend of experimental results for both crudes are similar; the only difference being the slopes of the lines, which is mainly caused by different contents of the volatile components in the crude.

The results of the GC analysis for Norman Wells and Pembina crude are shown in Figure 4 where the relative concentrations of n-alkanes (from C_9 to C_{15}) for samples of different age (0, 5 and 10 days) are compared. It can be seen that the concentrations of nonane, decane, undecane and dodecane decrease as the oil ages. This confirms the loss by evaporation of these compounds as a result of aging. However, no decrease in concentration is observed for tridecane, tetradecane and pentadecane. This indicates that the evaporative loss for n-alkanes having a molecular weight greater than that of dodecane is insignficant. As the sample size is constant, the losses in the lower boiling components will have a concentrating effect on the higher boiling compounds. The evaporative losses for nonane, decane, undecane and dodecane are much greater than the concentrating effects. For tridecane, tetradecane and pentadecane, however, the concentrating effect exceeds the evaporation losses; the relative concentrations of these compounds, therefore, show a slight increase with the age of the oil.

The crude oil contains a substantial amount of n-alkanes lighter than nonane as is seen from the sample chromatogram (Figure 5). An appreciable loss of these light n-alkanes, together with other highly volatile hydrocarbons is undoubtedly responsible for the rapid increase in the viscosity, density and surface tension during the first day of aging.

CONCLUSIONS

Based on the results obtained, the following conclusions may be drawn:

(1) The changes in physical properties as a result of aging are mainly caused by the evaporation of the more volatile components in the oil. Evaporative losses of n-alkanes with vapour pressure higher than dodecane are insignificant.

(2) The viscosity, density and surface tension of a crude oil aging on an ice surface exhibit a rapid initial increase followed by a more gradual linear increase with elapsed time.

(3) The degree of aging, by evaporation, depends very much on the temperature and the air movement above the ice surface; the higher the temperature or the air flow, the greater the change in the physical property of the oil.

(4) The viscosity of the oil was found to undergo the greatest changes and could be considered as a useful guide for measuring the degree of aging.

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TABLE 1. PROPERTIES OF CRUDE OILS

	Norman Wells Crude	Pembina Crude
Pour Point °C	-50	-10
Sp. gr. at 20°C	0.830	0.846
Viscosity at 20°C, cP	6.1	9.5
Surface Tension at 20°C, N/m	28.1×10^{-3}	27.8×10^{-3}

Partial Analysis of Oil

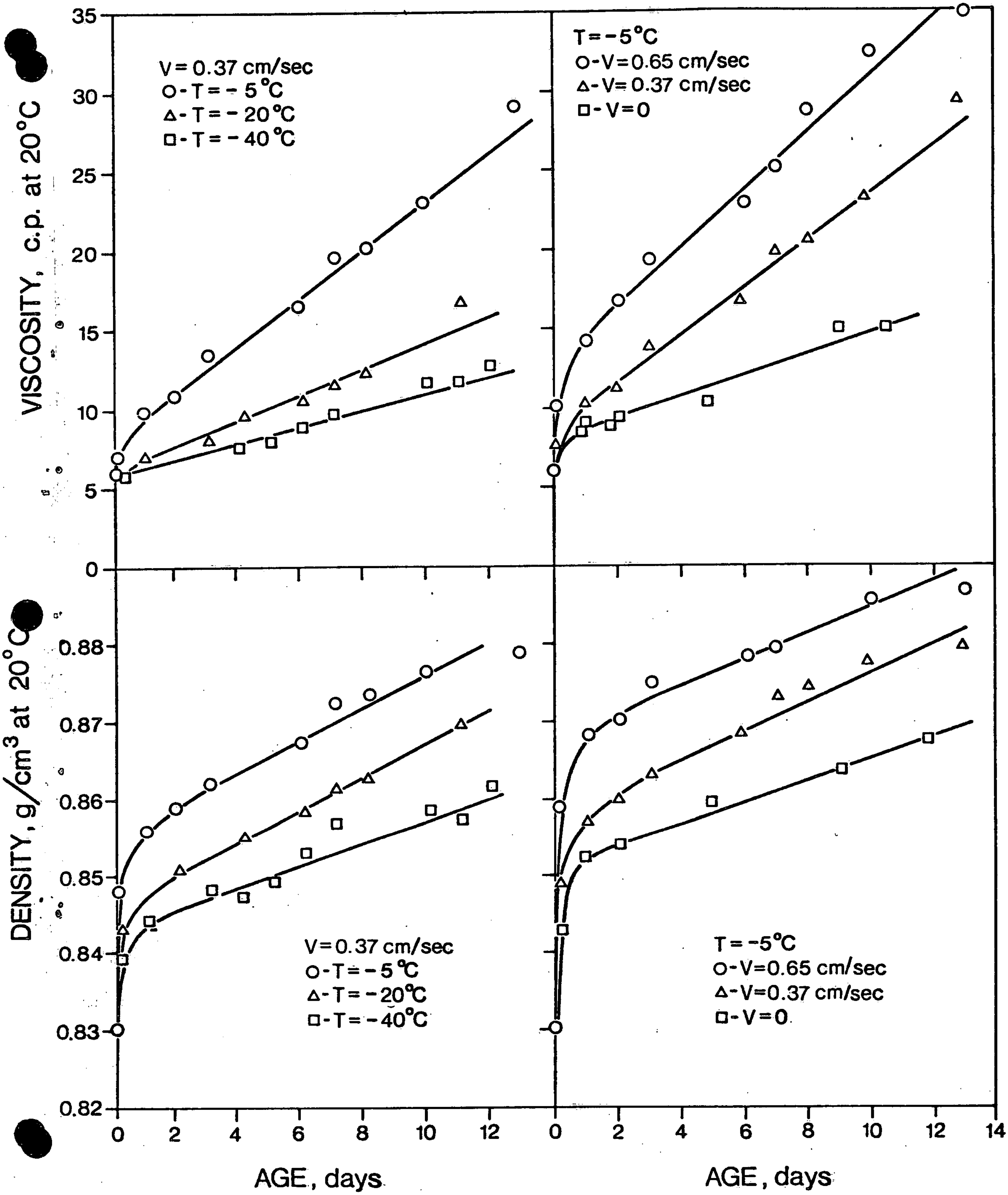
Distillation, U.S. Bureau of Mines Method [1]

Distillation Cut (T°C)	Norman Wells Crude cumulative wt % of oil distilled at temperature T	Pembina Crude cumulative wt % of oil distilled at temperature T
50	2.1	1.7
75	4.4	3.7
100	9.4	7.7
125	16.7	13.2
150	22.1	18.1

[1] U.S. Bureau of Mines Bulletin 490, 1951

FIGURE 1

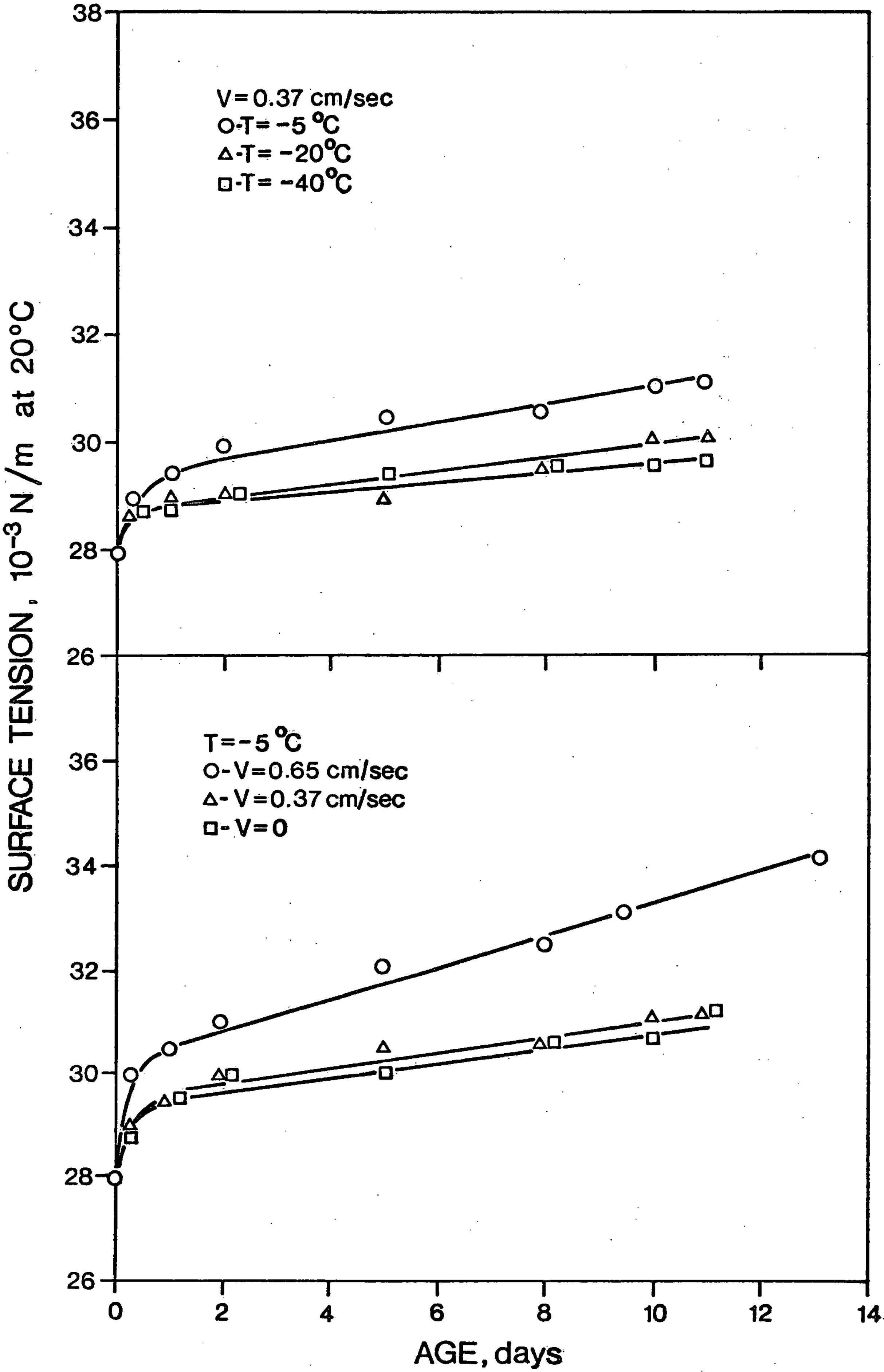
Changes in viscosity and density of Norman Wells crude oil as a function of air temperature and velocity.



VISCOSITY, c.p. at 20°C
DENSITY, g/cm³ at 20°C
V = 0.37 cm/sec
O - T = - 5°C
Δ - T = - 20°C
□ - T = - 40°C
T = -5°C
O - V = 0.65 cm/sec
Δ - V = 0.37 cm/sec
□ - V = 0
V = 0.37 cm/sec
O - T = - 5°C
Δ - T = -20°C
□ - T = -40°C
T = -5°C
O - V = 0.65 cm/sec
Δ - V = 0.37 cm/sec
□ - V = 0
AGE, days
AGE, days

FIGURE 2

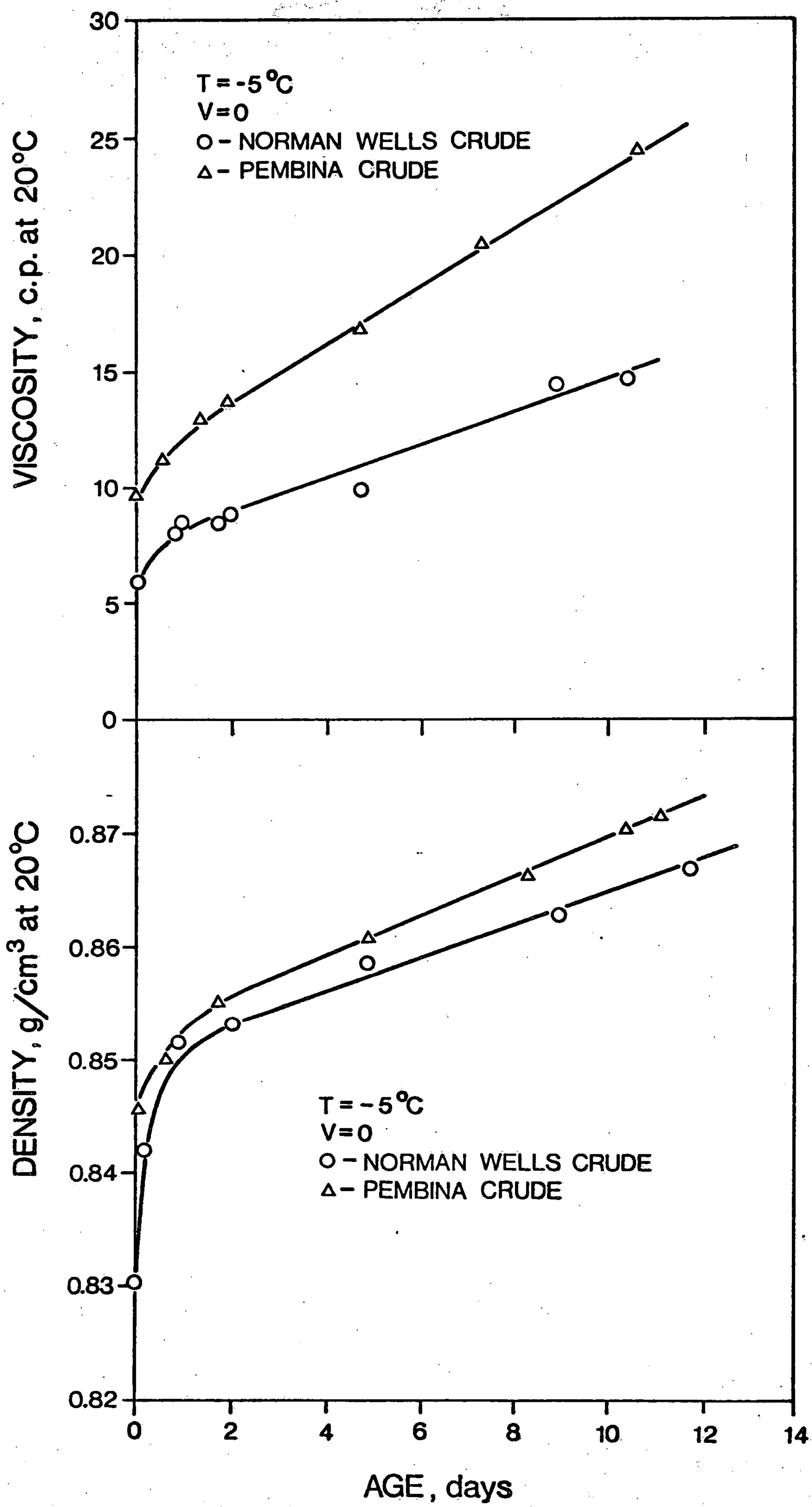
Changes in surface tension of Norman Wells crude oil as a function of air temperature and velocity.



V=0.37 cm/sec
O-T= −5 °C
Δ-T= −20°C
□-T= −40°C
T= −5 °C
O- V=0.65 cm/sec
Δ- V=0.37 cm/sec
□- V=0
SURFACE TENSION, 10^{-3} N/m at 20°C
AGE, days

FIGURE 3

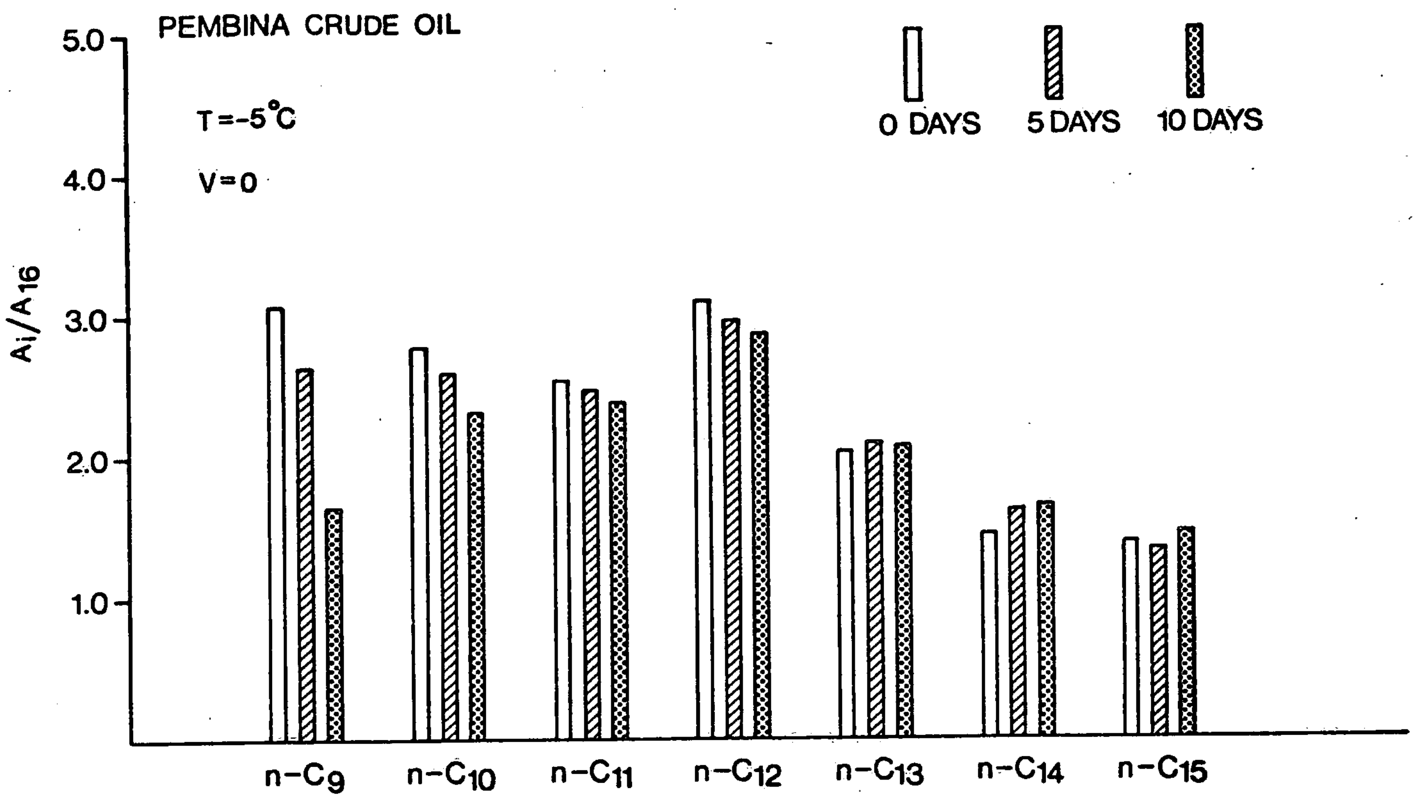
Changes in viscosity and density vs. time for two different crude oils.



T = -5 °C
V = 0
O - NORMAN WELLS CRUDE
Δ - PEMBINA CRUDE
VISCOSITY, c.p. at 20°C
0
5
10
15
20
25
30
DENSITY, g/cm3 at 20°C
0.82
0.83
0.84
0.85
0.86
0.87
T = -5 °C
V = 0
O - NORMAN WELLS CRUDE
Δ - PEMBINA CRUDE
0
2
4
6
8
10
12
14
AGE, days

FIGURE 4

Plots of relative concentration of n-alkanes
as a function of elapsed time.


PEMBINA CRUDE OIL
T=-5°C
V=0
0 DAYS
5 DAYS
10 DAYS
A_i/A_{16}
5.0
4.0
3.0
2.0
1.0
n-C9
n-C10
n-C11
n-C12
n-C13
n-C14
n-C15

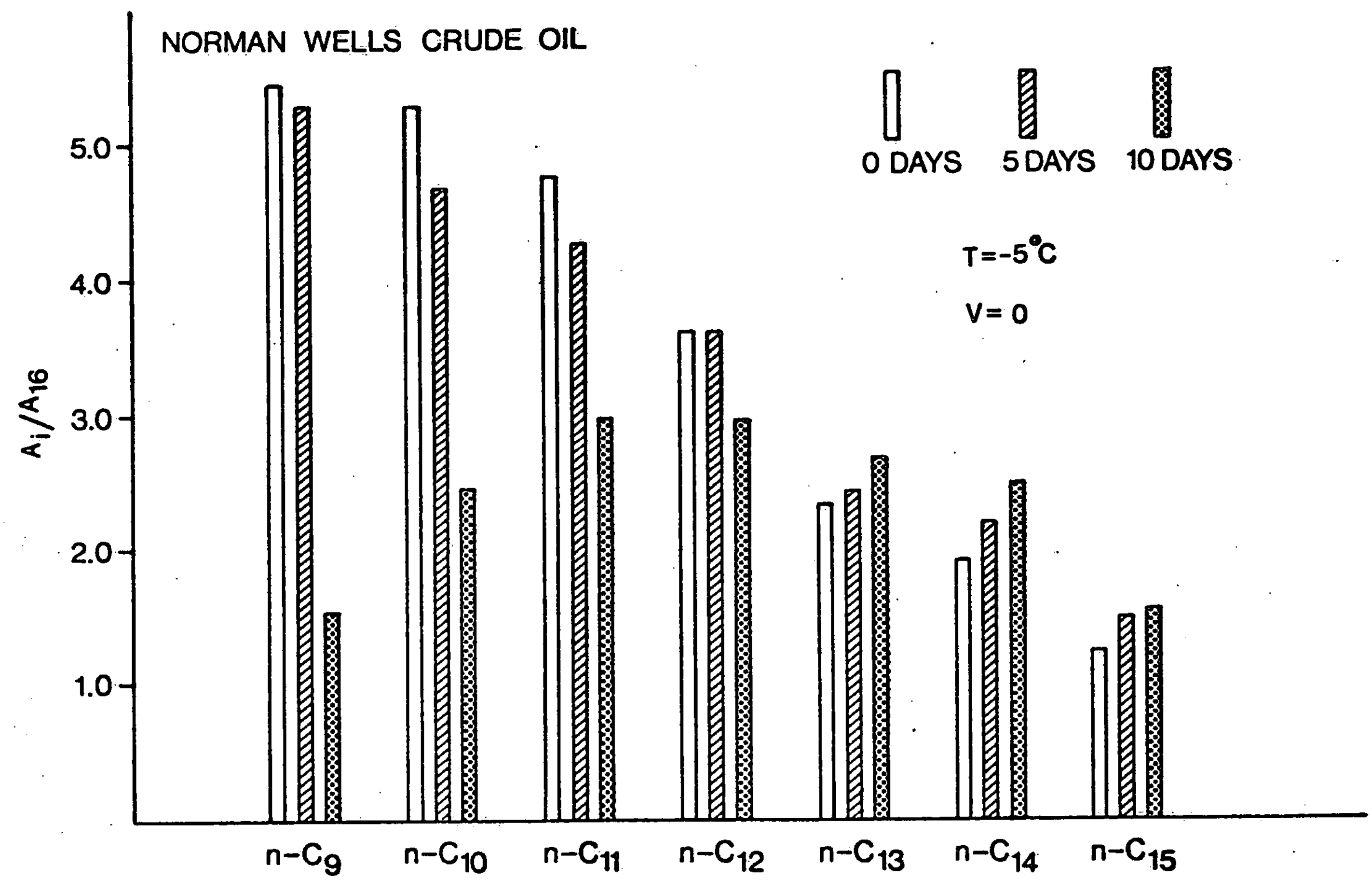
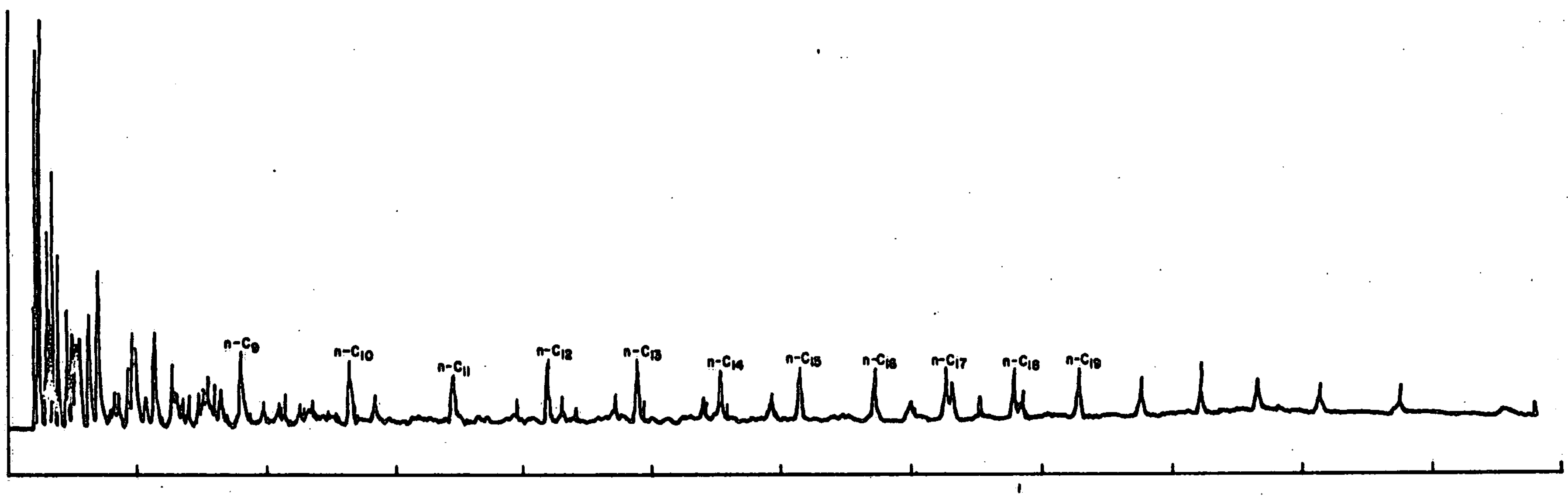

NORMAN WELLS CRUDE OIL
0 DAYS
5 DAYS
10 DAYS
T=-5°C
V= 0
A_i/A_{16}
5.0
4.0
3.0
2.0
1.0
n-C9
n-C10
n-C11
n-C12
n-C13
n-C14
n-C15

FIGURE 5

Sample chromatographic trace for fresh
Pembina crude oil.


n-C9
n-C10
n-C11
n-C12
n-C13
n-C14
n-C15
n-C16
n-C17
n-C18
n-C19

APPENDIX

Comparison of the present data with those reported in the literature.

Figure A-1

Comparison of viscosity data with those from the field tests

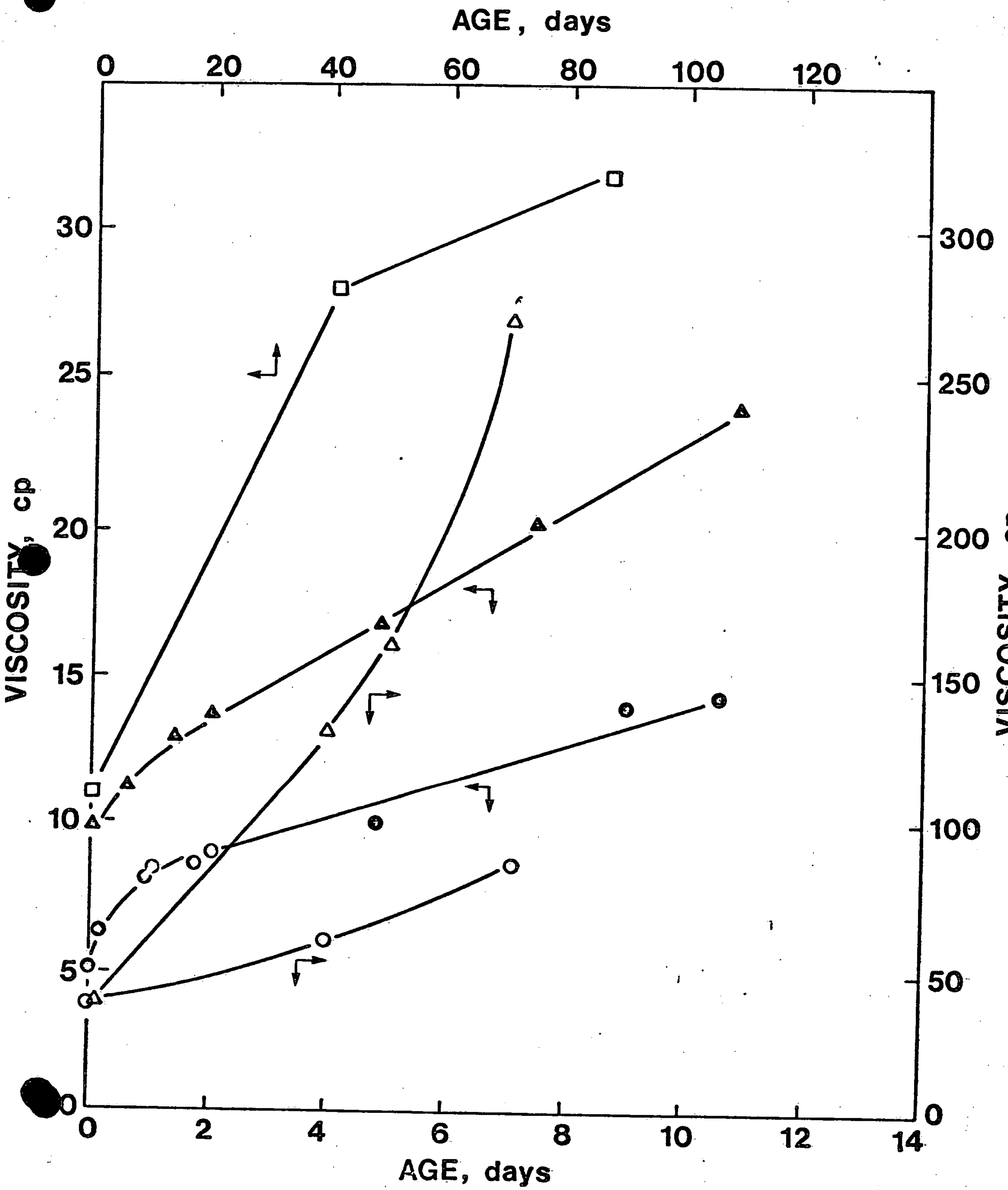
● - present work, Norman Wells crude aged at -5°C with a mean air velocity of 0.37 cm/sec; measured at 20°C.

▲ - Present work, Pembina crude aged at -5°C with a mean air velocity of 0.37 cm/sec; measured at 20°C.

△ - Glaeser and Vance, Prudhoe Bay crude, field test with temperature from 0.5° to 11°C and an average wind speed of 10 knots; measured at 20°C.

○ - McMinn, Prudhoe Bay crude, field test with temperature from -30° to -14°C and wind speed from 12 to 50 knots; measured at 20°C.

□ - NORCOR, Norman Wells crude, field test with an average monthly temperature of -32°C and wind speed of 12 MPH; measured at 0°C.



AGE, days
0
20
40
60
80
100
120
VISCOSITY, cp
30
25
20
15
10
5
0
300
250
200
150
100
50
0
2
4
6
8
10
12
14
AGE, days

Figure A-2

Comparison of density data with those from the field tests

● - present work, Norman Wells crude aged at -5°C with a mean air velocity of 0.37 cm/sec; measured at 20°C.

▲ - present work, Pembina crude aged at -5°C with a mean air velocity of 0.37 cm/sec; measured at 20°C.

△ - Glaeser and Vance, Prudhoe Bay crude, field test with temperature from 0.5° to 11°C and an average wind speed of 10 knots; measured at 20°C.

○ - McMinn, Prudhow Bay crude, field test with temperature from -30° to -14°C and wind speed from 12 to 50 knots; measured at 20°C.

□ - NORCOR, Norman Wells crude, field test with an average monthly temperature of -32°C and wind speed of 12 MPH; measured at 0°C.

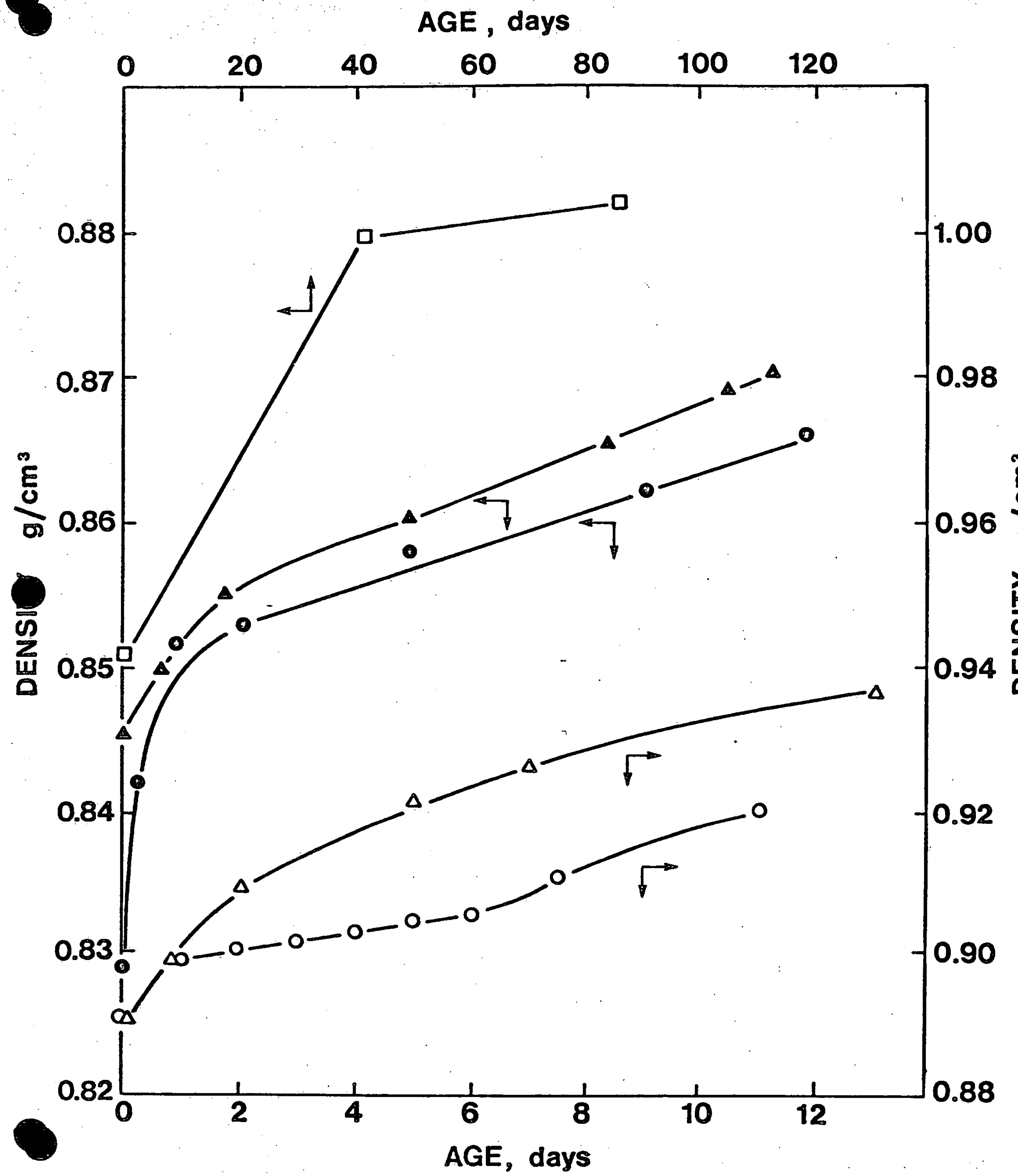

AGE , days
0
20
40
60
80
100
120
0.88
0.87
0.86
0.85
0.84
0.83
0.82
DENSITY g/cm³
1.00
0.98
0.96
0.94
0.92
0.90
0.88
DENSITY g/cm³
0
2
4
6
8
10
12
AGE, days

Figure A-3

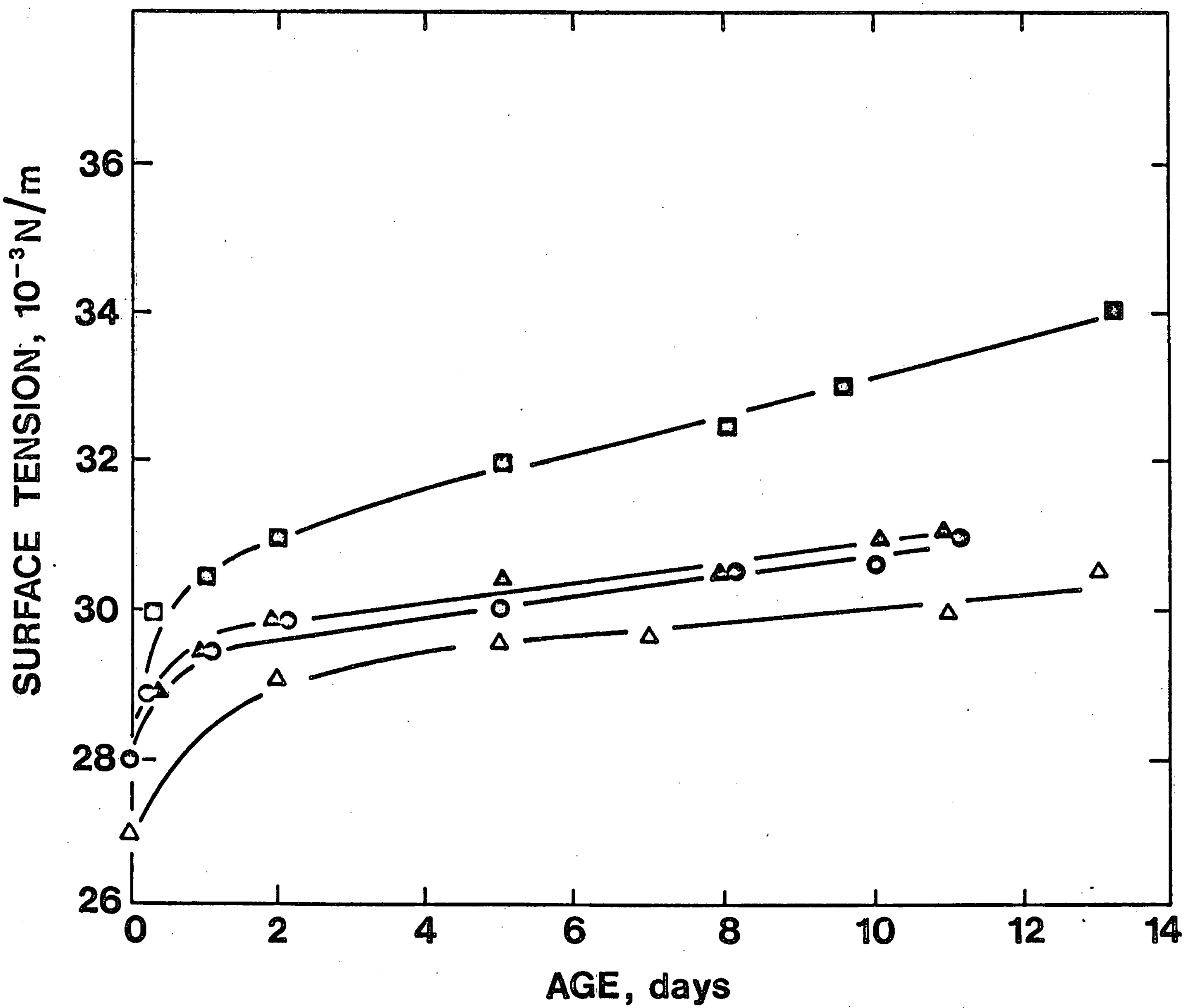
Comparison of surface tension data with those from the field test

■ - present work, Norman Wells crude aged at -5°C with a mean air velocity of 0.65 cm/sec; measured at 20°C.

▲ - present work, Norman Wells crude aged at -5°C with a mean air velocity of 0.37 cm/sec; measured at 20°C.

● - present work, Norman Wells crude aged ar -5°C with stagnant air flow; measured at 20°C.

△ - Glaeser and Vance, Prudhoe Bay Crude, field test temperature from 0.5 to 11°C and an average wind speed of 10 knots; measured at 20°C.



SURFACE TENSION, 10^{-3}N/m
36
34
32
30
28
26
0
2
4
6
8
10
12
14
AGE, days