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실리카젤-물 층을 통과한 누출유의 동특성 변화에 대한 실험식

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Experimental Correlations of Dynamic Characteristics Change in Leaked Oil through Silica Gel and Water

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要　　約

오일이 실리카젤과 물을 通過하여 누출될 때 UOP K 因子는 定溫, 定壓下에서 오일과 물의 流速, 오일이 通過하여온 실리카젤의 量과 오일이 漏出된 以後의 時間의 함수로 나타난다. 또한 오일의 실리카젤에 對한 吸着實驗에서 C_{11} 沸點 범위에 속해 있는 어느 한 成分이 가장 선택적으로 吸着됨을 발견했고 이 成分을 「主」成分이라 칭했다. 이 「主」成分의 濃度 역시 q, W, G 및 t의 函數로 나타내며, 이 「主」成分과 UOP K 因子에 對해서 實驗式을 얻었다. 이 實驗式은 漏出油의 油源 및 源泉油의 特性을 아는데 使用될 수 있다. 이 硏究에서 또한 容積平均炭素數로부터 UOP K 因子와 容積平均沸點을 계산할 수 있는 두 式을 얻었다.

Abstract

During leakage-oil study the dynamic & distributed K factor concept has been suggested and proven. The oil passing out through the silica gel and water, the UOP K factor varies as functions of the oil and water flow rate, the quantity of silica gel the passed through, and the history of the leaked oil under isothermal and isobaric condition. And it was found from adsorption test of oil on silica gel that a component in C_{11} boiling range was the most selectively adsorbed and was taken as a key component. The key component varies also with the q, W, G and t. The empirical equations obtained for these two key variables, K and the key component, could be used for evaluating the original location of the leakage oil source and the original characteristics of the leakage oil.

In this study other two empirical equations was developed; by using these equations the UOP K factor and volume average boiling point can be predicted from volume average carbon number which can easily be calculated from the gas chromatograms of oils.

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1. Introduction

The leakage-oil identification method by which one could evaluate whether a leaked oil is crude or waste, and the method by which one can get the ASTM distillation curves of very small quantities of oil from gas chromatographic analyses via computer, were presented by H.D. YOO.[8] Also, the batch test results were presented, which demonstrated that the oil characteristics would change by selective adsorption on sand or clay by selective solubility in water during the crude oil migration through underground structures.[2,4,5,8].

Fig. 1. shows a model of oil leakage toward the surface of ground from oil pool. In this model oil passes two regions; a selective solubility region in which oil contacts mainly with water, and a selective adsorption region in which oil passes through sand and/or clay.

It has been studied on how the characteristics of leakage oil changes with time, taking the silica gel quantity, oil flow rate and water quantity as parameters, when crude oil leaks out through silica gel and water.

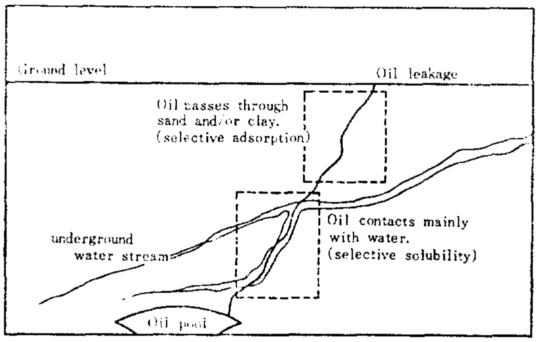

Fig. 1. Model in leakage oil study

The ultimate object of this study is to evaluate the location of the orginal oil pool and the characteristics of the original oil for actual underground systems. The silica gel was used, instead of the sand and clay, to amplify the adsorption phemena because the sand and clay have very small adsorption effects to study in laboratory scales, and this study is on a course to the actual scale.

2. Theory

In leakage oil study it is ultimately aimed to evaluate the oil source. For solving this problem mathematically some equations are needed. The changes of the leakage oil characteristics depend upon the time after leakage t, the quantity of adsorbent the oil passed through G, the quantity of water contacted W, and the leakage flow rate q;

$$\text{oil characteristics} = F(t, G, W, q) \qquad (1)$$

at isothermal and isobaric conditions.

Both of the t and q may be known values, but the values of G and W may be completely unknown, so at least two equations should be established either G or W being assumed. For building the two equations it is necessary to take two key variables which can represent the variation of oil characteristics, which is shown in *Fig.* 2.

Fig. 2-a shows the gas chromatogram of the oil which passed through a silica gel column and *Fig.* 2-b shows that of the original oil. Only the paraffin hydrocarbon peaks are identified and the components between two paraffin peaks are summed up with the latter paraffin boiling range, e. g., components between C_{10}

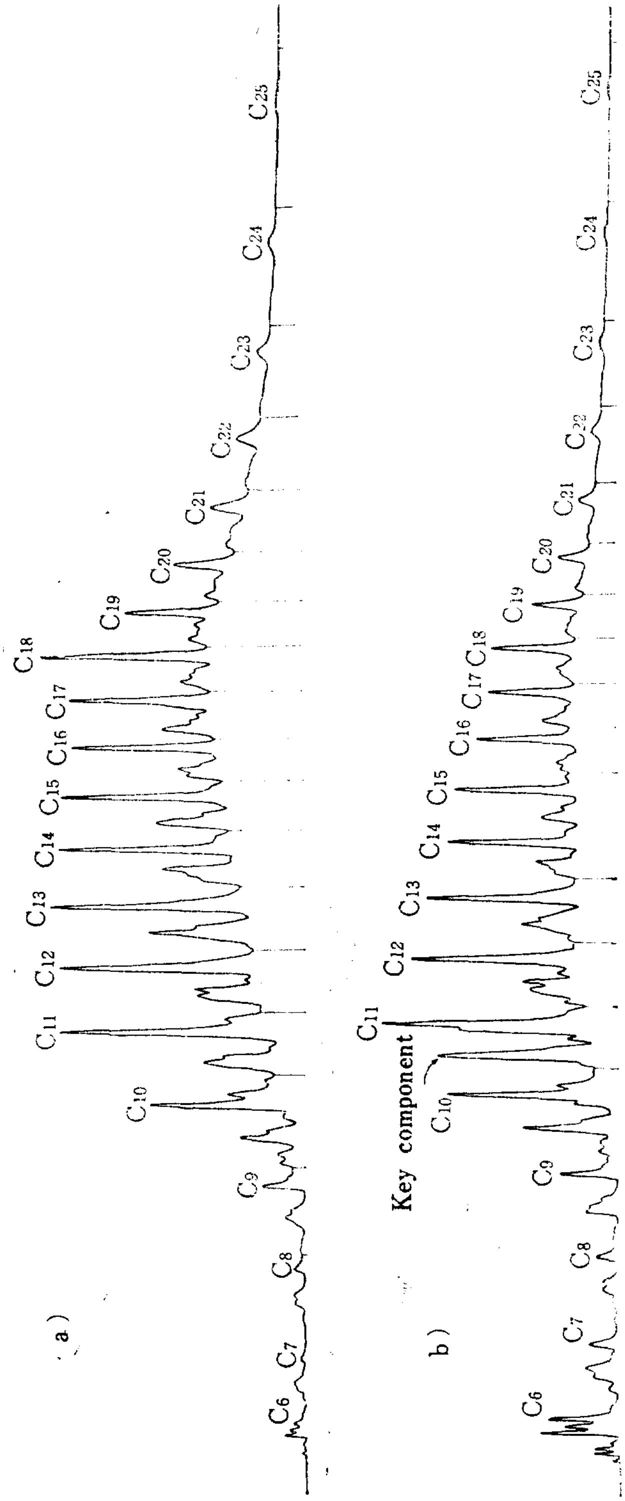

Fig. 2. Gas Chromatograms of Crude Oils

and C_{11} peak are taken as C_{11} boiling range components. This treatment of nonparaffin hydrocarbon fits farely well with experimental data[8]. Since the ratio of each peak area to total area represents almost exactly the volume fraction of each component[1),6)], the volume fraction was used as concentration of each component. It is recognized from *Fig.* 2-a that there is more plenty of heavy components in that oil having passed out the silica gel column than the original, *Fig.* 2-b. This means obviously that the lighter oil components are more selectively adsorbed into silica gel, and also it is known from the two chromatograms that one of the C_{11} boiling range components is most selectively adsorbed, compared with other components. This component is taken as one of the key variables and called key component in the leakage-oil study. As another key variable the well-known UOP K factor, $K=\sqrt[3]{T_b}/s$, may be taken, which is a very useful property in characterizing an oil sample.[3,7)]

When the oil leaks out of the column, the concentration of the key component will vary with time, quantity of silica gel and oil flow rate;

$$f'=f/f_o=f'(t,G,q) \qquad (2)$$

So will do the UOP K factor;

$$K'=K/K_o=K'(t,G,q) \qquad (3)$$

In the leakage oil model, the oil contacts with underground water as well. In the under ground the oil flow rate is so low and the path along which the oil contacts with water is so long that the water may be saturated with oil. Consequently, the changes of oil characteristics depend only on the ratio of oil to water flow rate under isothermal and isobaric conditions;

$$f'=f'(q/W) \qquad (4)$$

$$K'=K'(q/W) \qquad (5)$$

If water solubility of each component be known, the two Eq. (4) and (5) can be developed from simulations.

Both Eq. (2) and (4) indicate the variation of the key component concentration & both Eq. (3) and (5) indicate that of the UOP K factor. Combinations of Eq. (2) with (4) and Eq. (3) with (5) will show the relations of Eq. (1) for each key variable, respectively.

The relations of Eq. (2) to (5) are correlated empirically.

3. Experimentals

As shown in *Fig.* 3-a, the oil flows upward through 2m silica gel column and is sampled at 3 points. These sample quantities should be so small that the system may not be disturbed. The constant temperature water is being cycled to maintain the column isothermal condition. Also from *Fig.* 3-b it is shown that an oil sample is held up in a glass container and given quantity of isothermal water is recycled constantly. The oil is continuously contacted with water until the water is saturated with oil and the oil characteristics in the water do not change any more. It takes about thirty days that the water is saturated with oil. These experiments are all performed at 28°C and 1 atm.

All samples are analysed with the gas chromatograph and from the chromatogram the volume fractions of each boilding range component and key component are obtained. The gas chromatograph used is a Varian 2,800 model with flame ionization detector. A 8 ft×1/8 inch i.d. column packed with 10% O. V. 17 on chromosorb W 80/100 mesh is used. The helium carrier gas flow rate is 30 cc/min and the helium, hydrogen, air flow rate are kept in a 1 : 1 : 10 ratio. The column temperature is programmed from 40°C to 260°C at the rate of 16°C/min.

The ASTM curves of the oil samples used in

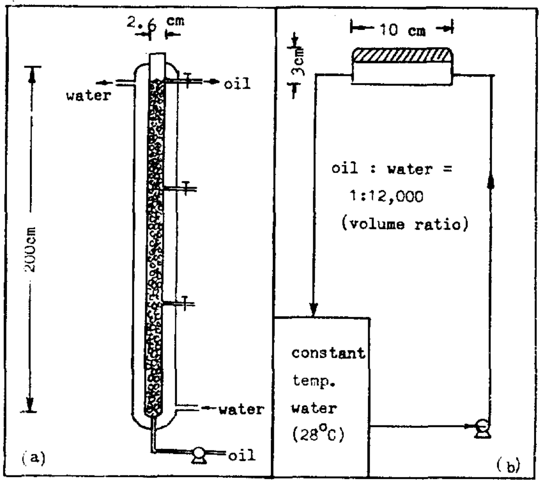

Fig. 3. Equipment used in, (a) adsorption on silica gel & (b) solubility in water of oil.

these experiments are shown in *Fig.* 4. SAMPLE (1), (2) and (3) are rich in light oil, heavy oil & kerosene range component, respectively. SAMPLE (1) was mainly used in this study because the SAMPLE (1) has rich light oil components which are most interesting compositions in this study[8], and SAMPLE (2) and (3) were used for testing the applicability of the emprical equations obtained with SAMPLE (1) for the oil leakage model. *Fig.* 2-b is the gas chromatogram of SAMPLE (1).

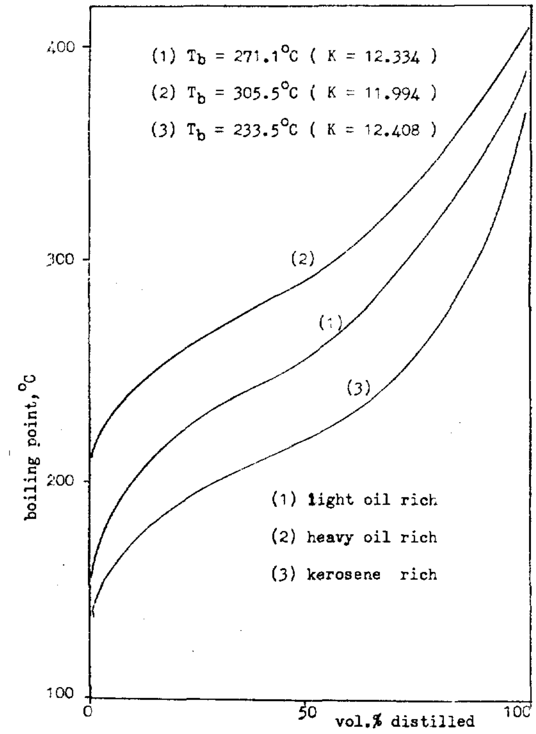

Fig. 4. ASTM curves of samples rich in light oil, heavy oil and kerosene.

The physical properties of the silica gel used in these experiments are shown in *Table* 1.

Table 1. Physical properties of the silica gel used

SiO_2 composition	above 99.5%
surface area	about 700m^2/gram
pore volume	about 0.5cm^3/gram
average pore size	about 30A°
bulk density	average 0.7g/cm^3
moisture content	below 2%

4. Results

4.1 Concentration change of the key component

(1) The effect of silica gel

When fixing the oil flow rate at 2.4cc/min, the concentration change of the key component in the oil passing through the different quantities of the adsorbent is shown in *Fig.* 5, as taking the time zero when the first drop of oil

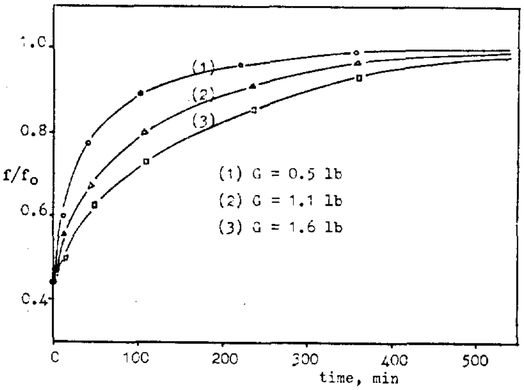

Fig. 5. Variation of the key component after passing through the silica gel column.

is leaked out from the column. It is throught that the curves have a following type equation;

$$f'=f/f_o=1-e^{-(a+bt^n)} \tag{6}$$

Rewriting this equation,

$$ln(1-f')=-a-bt^n$$

By plotting $ln(1-f')$ versus t^n, the coefficents a and b can be obtained. On trials and least square it is found that optimum n value is about 0.6, and that as shown in *Fig.* 6, the a has a value of about 0.6 and b is dependent of the quantity of silica gel G. Plotting b against $G^{-0.11}$, a straight line is obtained as shown in *Fig.* 7 to give

$$b=0.43G^{-0.11}-0.36 \tag{7}$$

Finally, Eq. (2) becomes

$$f'=1-e^{-(0.6+bt^n)} \tag{8}$$

where $b=0.43G^{-0.11}-0.36$

which shows the variation of f′ with respect to t and G.

Also, the relationship of f′ to oil flow rate q is shown in *Fig.* 8. For this figure the adsorbent quantity is fixed by 0.8lb and the oil flow rates are taken as 1.7, 2.4 and 6cc/min. In this case 0.6 is approximately the optimum value of n and the value of a, too, which we can show in *Fig.* 9. And, b has the following values against each flow rate;

$b=0.065(0.756)$, *at* $q=1.7$cc/min

$b=0.086(1.000)$, *at* $q=2.4$cc/min

$b=0.173(2.012)$, *at* $q=6.0$cc/min

Eq. (8) has been obtained at constant flow rate 2.4cc/min, so b′ which is divided by 0.086 is correlated against q. As same method as in *Fig.* 7 we get a straight line by plotting b vs. $q^{0.68}$, as shown *Fig.* 10, which gives

$$b'=0.64q^{0.68}-0.17 \tag{9}$$

Eq. (9) is completed for constant adsorbent

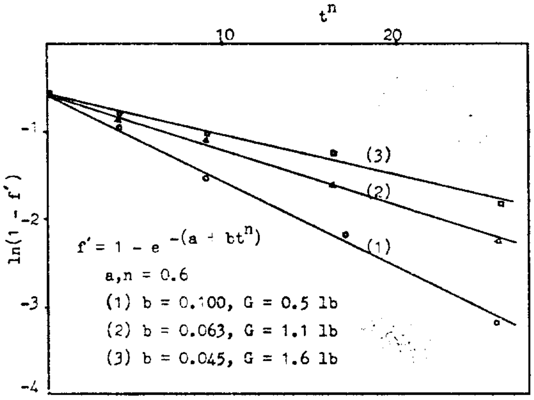

Fig. 6. Relations of in $(1-f')$ to t^n, when $n=0.6$

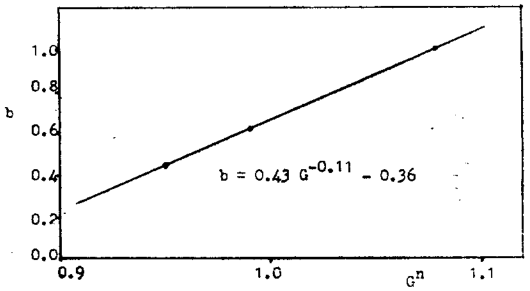

Fig. 7. Relation of b to G^n, when $n=-0.11$

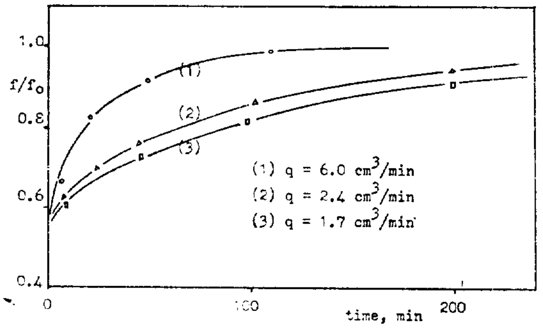

Fig. 8. Variation of the key component after passing out through the silica gel column.

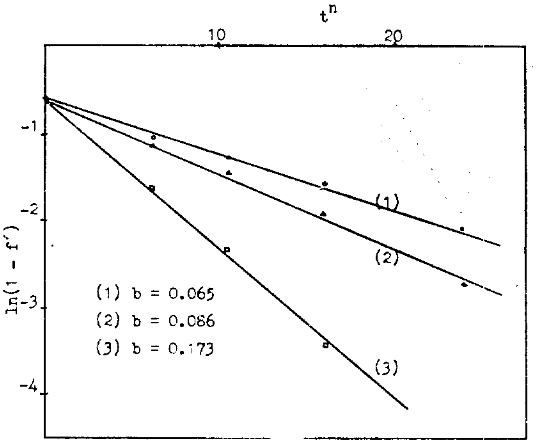

Fig. 9. Relations of ln $(1-f')$ to t^n, when $n=0.6$)

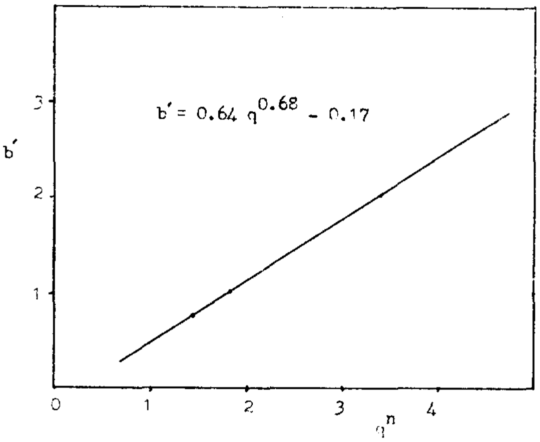

Fig. 10. Relation of b' to q^n, when $n=0.68$

quantity, $G=0.8$lb. Eq. (9) may be applicable to other systems having different silica gel quantities, and Eq. (9) can be combined with Eq. (7) to give the following equation

$$b=(0.43G^{-0.11}-0.36)(0.64q^{0.68}-0.17)$$

Finally, for oil leakage through silica gel columns Eq. 10 is obtained as functions of t, G and q;

$$f'=1-e^{-(0.6+bt^{0.6})} \qquad (10)$$

where $b=(0.43G^{-0.11}-0.36)(0.64q^{0.68}-0.17)$ From this equation the initial concentration of the key component at time zero is independent of G and q. This is due to the effects of competitive adsorption and rapid adsorption rate.

It is necessary to test the applicability of Eq. (10) to other systems. For this purpose different flow rate $q=4$cc/min, silica gel quantity $G=0.8$lb and quite different oil, SIMPLE (2) and (3) are chosen. Inserting the above values of G and q to Eq. (10),

$$f'=1-e^{-(0.6+0.13t^{0.6})} \qquad (11)$$

In *Fig.* 11 the curve represents Eq. (11) and the data points are those of SAMPLE (2) and (3). The SAMPLE (3) rich in kerosene draws a curve across the curve presenting Eq. (11) and the data of SAMPLE (2) rich in heavy oil are scattered around Eq. (11) curve. The standard

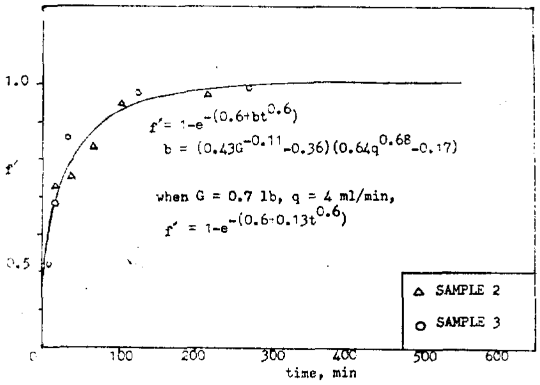

Fig. 11. Applicability of the equation (10)

deviation of the data points for two samples is about 0.045. This deviation is so small that Eq. (10) may be applied to the other systems.

(2) The effect of water.

Using the equipment shown by *Fig.* 3-a and SAMPLE (1) we got the water solubility of each boiling range component as shown in *Fig.* 12. The solubility of C_{11} boiling range components is the largest, next is C_6 boiling range components and C_{26} boiling range components have the smallest solubility. And the key component(the arrow sign in *Fig.* 12) has the solubility of 0.16cc/m^3. With these data we perform the computer simulation to obtaint he concentiation change of the key component against the ratio of oil flow rate q, to water flow rate W. In this simulation it is obtained that the average change of the key component concentration is about 1.3 against the unit change of q/W. Thus

$$f=f_o-(1.3)(W/q)$$

and

$$f'=f/f_o=1-(1.3(W/qf_o)) \qquad (12)$$

Eq. (12) is represented in *Fig.* 13 by the straight line. But the real data taken by the simulation show a curve having the equation of

$$f'=1-(1.6)(W/qf_o)^{1.2} \qquad (13)$$

Up to this point the equations for the key component change have been obtained; Eq. (10)

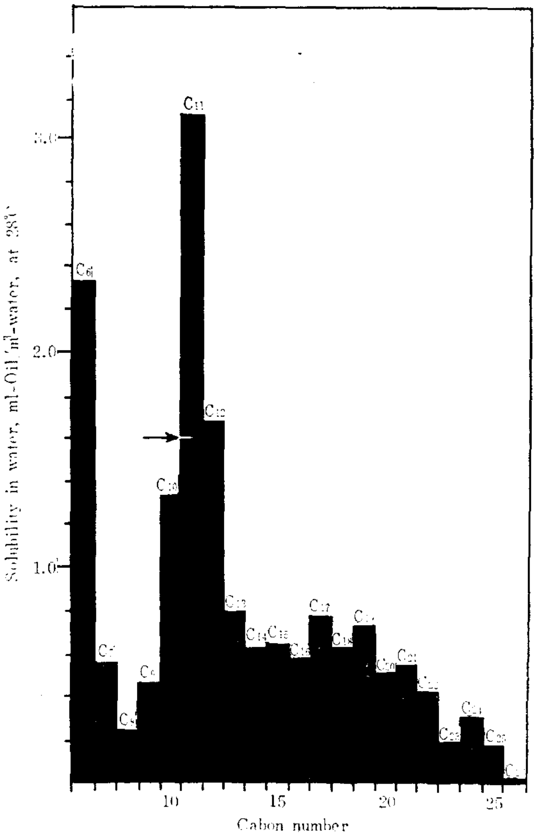

Fig. 12. **Water solubility of each boiling range components.**

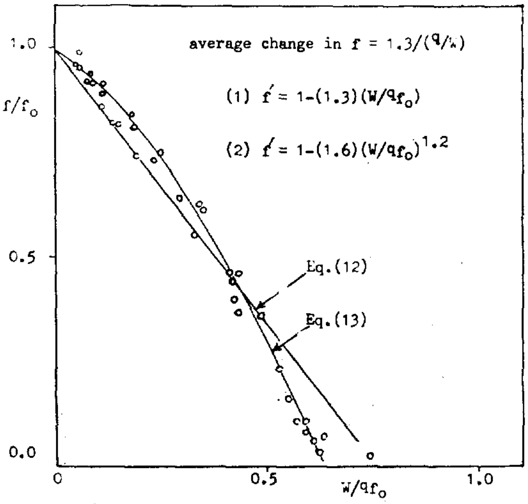

Fig. 13. **Correlation of change in the key component concentration to the quantity of water contacted.**

and (13), in case of the oil leaking out through silica gel and water. Also, it needs to be known that change in the UOP K factor of the oil.

4.2 Change in UOP K factor

(1) The effect of silica gel

The data from the previous experiments give *Fig.* 14, taking silica gel quantity as parameter, and *Fig.* 15, oil flow rate as parameter. In these figures it is shown that the UOP K factor increases at early time and soon decreases. The curves in those figures have the type of equation

$$K' = 1 + t^m e^{-(a+bt^n)} \tag{14}$$

but, in this study, the late time data are more significant than the early time data; the early time effects can be neglected, and Eq. (14) can be written as

$$K' = 1 + e^{-(a+bt^n)} \tag{15}$$

the curve of which is extended by the dotted lines in *Fig.* 14. Introducing the same methods

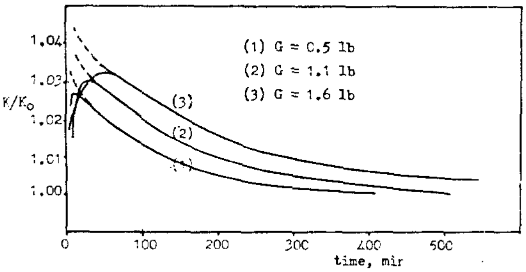

Fig. 14. **Variations of the UOP K factor after passing out the silica gel column.**

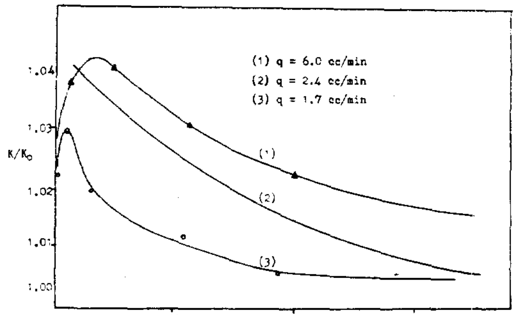

Fig. 15. **Variations of the UOP K factor after passing out the silica gel column.**

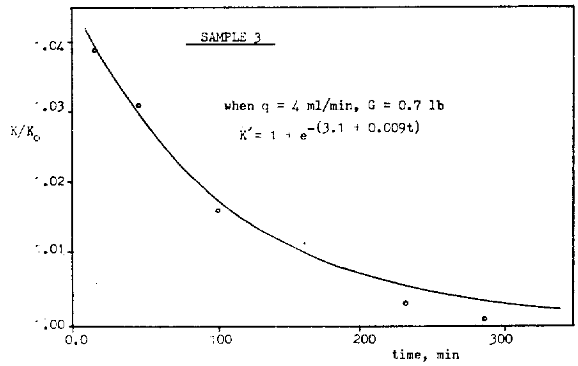

Fig. 16. Applicability of Eq. (16).

as used in getting Eq. (7) and (9), the following results are obtained;

$a=3.1$

$n=1.0$

$b=(1.6G^{1.8}+2.5)(q-063)^{0.8}(10^{-3})$

that is

$$K'=1+e^{-(3.1+bt)} \tag{16}$$

where $b=(1.6G^{1.8}+2.5)(q-0.63)^{0.8}(10^{-3})$

The applicability of Eq. (16) to the other systems is illustrated in *Fig.* 16, in which the standard deviation of the data points for SAMPLE (3) is about 0.05. (The 0.1 difference in UOP K value is significant in oil characteristics.)

(2) The effect of water

The UOP K variation by water solubility is obtained by the following equation;

$$UOP\ K=14.9-0.159C_{av} \tag{17}$$

where C_{av} is volume average carbon number and is definded by

$$C_{av}=\sum_i i f_i \tag{18}$$

in which i is carbon number and f_i is the volume fraction of C_i boiling range components, which can be easily calculated from the gas chromatograms of oils as in *Fig.* 2.

It is shown in *Fig.* 17 that the UOP K's are plotted against C_{av}'s, from which Eq. (17) is obtained. This equation also has the standard deviation of 0.05. Using Eq. (17) and the volume average carbon number obtained by computer simulations, we get the curve in *Fig.* 18 giving the equation

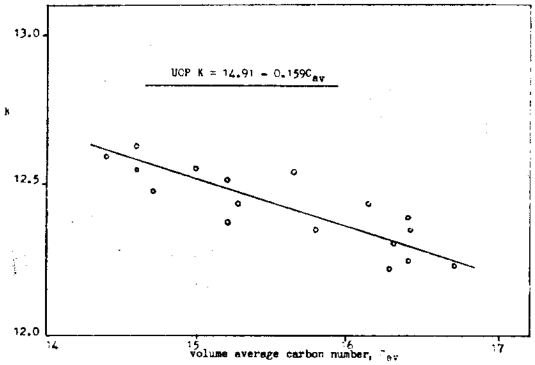

Fig. 17. Relation of UOP K to volume average carbon number

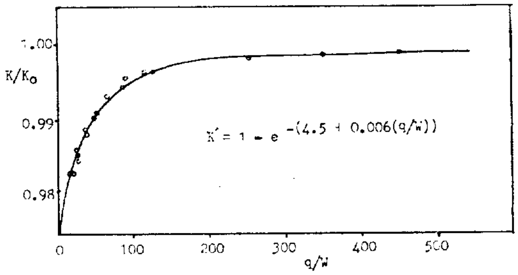

Fig. 18. Dynamic K in water.

$$K'=K/K_o=1-e^{-(4.5+0.006(q/w))} \tag{19}$$

This equation will predict the UOP K factor variation occurring by the effects of selective water solubility of each boiling range component.

4.3 Average boiling point from the average carbon number

The relation of T_b to C_{av} is a fairly good byproduct in this research on the leakage oil. This relation could be generally used with precision in estimating the volume average boiling points from the average carbon numbers of all the oil except the gasoline boiling range oils. Various experimental data give *Fig.* 19 and Eq. (20);

$$T_b=140.4(C_{av}-8.46)^{0.37} \tag{20}$$

which has the standard deviation of 0.7°C.

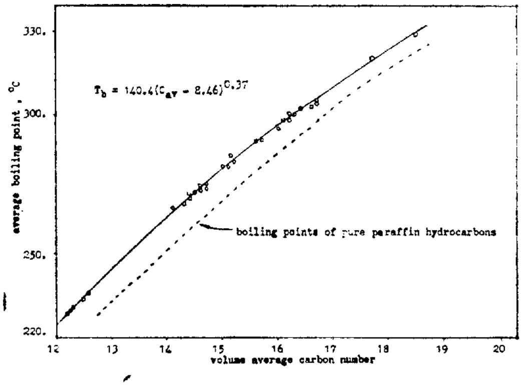

Fig. 19. Volume average boiling point from volume average carbon number.

By using Eq. (20), the digital computation[8] could be avoided, which is used for obtaining the average boiling points from gas chromatographic results, and the ASTM distillation used in getting the average boiling point might be avoided if the gas chromatograph is available.

5. Application

The ultimate object of this research is to predict the location of the oil source and the characteristics of the source oil. It has been obtained that equations for the variations of the key component concentration and of the UOP K factor. Finally these equations can be written as

$$f' = f'(G,\ q,\ t,\ W) \tag{21}$$

$$K' = K'(G,\ q,\ t,\ W) \tag{22}$$

as same type as Eq. (1).

Now, in this leakage oil model study Eq. (21) and (22) can be used; the leakage oil flow rate q and the history of the oil leakage t can be determined, otherwise in determining the t the sample could be taken at two time points, which method may be more precise but needs still more calculations and calculation time, and then assume both values of G and W to satisfy Eq. (21) and (22) simultaneously. Next, compute the f_o or K_o for each leakage (see *Fig.* 20), compare them, and repeat the assumption of G and W before the values of f_o and K_o computed for each leakage are on agreement. Through these procedures the location of the oil source and the characteristics of source oil could be found. *Fig.* 20 shows a model with three leakages. The triangle in *Fig.* 20 presents a plane geometry of each leakage position.

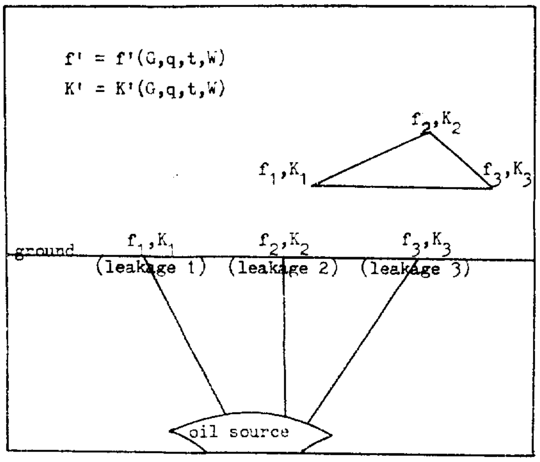

Fig. 20. Model of oil source having three leakages.

6. Conclusions

(1) The dynamic changes of oil characteristics were treated for the oil leaked out through silica gel and water, in which two key variables, the UOP K factor and a C_{11} boiling range component, were chosen to develop the empirical equations for evaluating the leakage oil; Eq. (10), (13), (16) and (19).

(2) The three branch model (*Fig.* 20) which have three paths the oil passes along, was examined to estimate the original location of the leakage oil source and the original characteristics of the leakage oil.

(3) The volume average boiling point can be obtained with high precision, and the UOP

K factor can also be obtained but with low precision, from volume average carbon number; Eq. (17) and (20).

7. Nomenclature

a, b, b', n, m	coefficients in Eq. (5) and (14)
C_{av}	volume average carbon number
f	volume fraction of key component
f_i	volume fraction of C_i boiling range components
f_o	volume fraction of key component of original oil
f'	dimensionless fraction defined by f/f_o
G	quantity of silica gel oil passed through, (lb)
i	carbon number
K	UOP characterization factor, defined by $\sqrt[3]{T_b^R}/s$
K_o	UOP characterization factor of original oil
K'	dimensionless K, defined by K/K_o
q	oil flow rate(cm^3/min)
s	specific gravity of oil at 60°F
t	time(min)
T_b	volume average boiling point(°C)
T_b^R	volume average boiling point(°R)
W	underground water flow rate(m^3/min)

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