漏出油類分析과 動的因子 K의 概念을 利用한 源泉油質의 評價

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Leakage Oil Analysis and Evaluation of Source Oil by the Dynamic K Factor Concept

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要 約

漏出油類 分析研究를 普遍的인 方途로 施行하고, 보다 優秀한 評價를 爲하여 動的因子 UOP K의 概念을 紹介하였다. 油類 見本 分析의 一例로 x, y, z, 및 θ가 固定될 時 K因子를 決定 하는데 必要로 하는 ASTM 蒸溜法으로 沸點및 比重曲線을 求하였으며, 原油로 假定하여 水素含量을 推算하고, 實驗値와 比較하였다. 不純物 分析도 하였고, 國內 油類製品의 混合實驗및 工業廢油와도 檢討하였다. 見本 沸點 曲線은 隣接國의 原油의 것들과 比較하여 봤으며, 少量見本을 使用할수 있는 GC分析을 하였고, ASTM分析間의 關係를 確立 하였다. 流出 油類가 地下에서 流動할 時는 油類의 性質이 變할수 있다. 즉 $K=F(x, y, z, \theta)$. 이러한 動特性은 源泉 油質의 判斷에 큰 難點을 준다. 이 動的因子 K의 糾明을 爲한 基礎 研究를 敢行하여 油類의 水中溶解 特性과 固體에의 吸着 特性 等이 作用함을 證明 하였고, 3軸과 時間에 따라 油類性質을 變化시킨다고 본다. 이러한 研究의 窮極 目的은 地上漏出油類 見本을 數地點에서 鑑定하여, 漏出油類의 源泉을 찾고 또 源泉油質을 判明 하는데 있다.

Abstract

Leakage oil analysis study was made following the routine procedures, and dynamic UOP K factor concept has been introduced hoping to evaluate the sample better. Oil analysis example is presented by way of ASTM distillation for boiling and specific gravity curves to determine K factor while x, y, z, and θ are fixed. The sample was taken as crude oil and predicted hydrogen content which later was checked experimentally. Impurity analysis was conducted to make some judgements on possible source. Known local petroleum product mixing tests were made along with the locally available waste industrial oils to compare with the sample. The boiling point curve of this sample

was also compared with those of the crude oil analyses of the neighboring nations. In order to lessen the sample quantity requirements, GC analysis was made, and a bridge is established between ASTM analysis. When oil leaks through an underground structure, the oil characteristics may not remain constant. "K"=F (x, y, z, θ). This dynamic and distributed effects present serious difficulties in identifying the true characteristics of the source oil. Some general basic studies were undertaken on the dynamic K, and it is considered that the factors such as selective oil solubility in water, selective adsorption on solids, would be significant which might contribute toward the oil characteristic change as a function of 3-D location and time. The ultimate objective of such studies would be to predict and locate the oil source and its characteristics from the ground level steady state leakage oil at different localities.

Introduction

Often one is faced with an oil analysis & evaluation problem, the oil sample being a leakage oil or other unidentified hydrocarbon mixture. In USA, these problems are frequently dealt by evironmentalists to prevent oil pollution. Regardless of the sample source and the final objective, it would be desirable to identify the oil sample characteristics and to know of its past including the source location and source quantity if at all possible.

When oil leaks, most likely it flows through porous media of heterogeneous nature, during which the oil characteristics could change (*Fig. 1*). Thus, an above ground oil sample is only identified at a time and a location. In order to
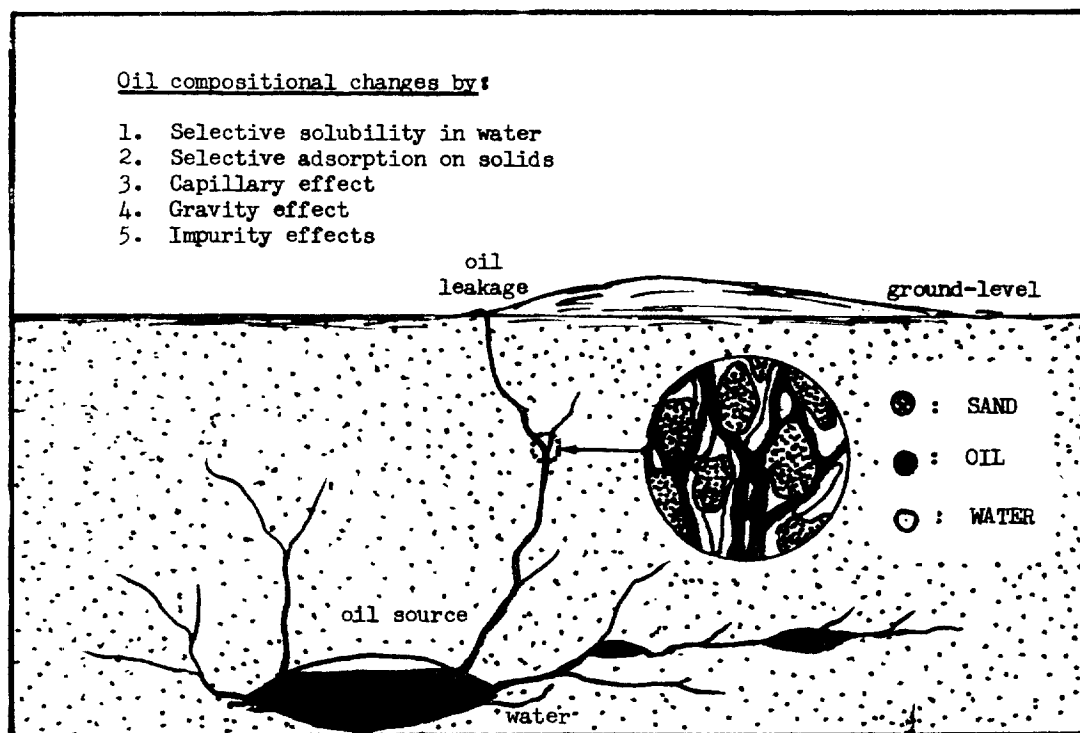

Fig. 1. Oil leakage phenomena.

evaluate a sample confidently, one has to know how the oil flow past history might have influenced on the characteristics. This makes the prediction of Korean Crude Oil characteristics from leakage oil, if and when exists, becomes rather difficult.

In this paper, efforts have been made to test an oil sample and investigate extensively to reason out all possible scientific angles, as to what might have happened to the samples during the past flow history. The engineering correlation of the phenomenological studies to make predictions of the past is considered somewhat outside the scope of this work. However, from the present study, proper judgements can be made on the merit of the correlation and prediction study which may lead to the source location and estimation of the source quantity, from the more accepted routine oil analysis techniques, such as ASTM distillation curves, and UOP "K" factors. In this respect, the current work can be considered as a preliminary oil leakage model study to an extent which offers qualitative explanations.

Theory and Method

The elementary concept of the oil characterization by Universal Oil Products' K factor is an old subject and is well accepted.

$$K= \frac{\sqrt[3]{T_b}}{SpGr} \qquad (1)$$

(Where T_b= average boiling point, $°R$; SpGr at $60°F$; K= UOP characterization factor) As yet, this equation has received very little theoretical interpretations, as it is based on empirical correlations[16]. Nevertheless, this K factor does represent an important characteristic of an oil sample through which a whole series of other petroleum properties can be predicted on 3-variable correlation charts with which engineers

are very familar[7], e. g. wt% hydrogen as a function of K and average boiling points as a parameter, or better known as Hougen and Watson's CPP charts. Then, according to the petroleum product specifications on boiling point and specific gravity ranges, % fractional product formations are obtainable, such as 26% straight run gasoline.

Alternatively, chemical analysts tempt to utilize gas chromatography to analyze an oil sample, while engineers tend to boil it. GC method requires much less sample quantity while ASTM distillation needs 100cc sample. Serious attempts have been made to establish a bridge between ASTM and GC analyses. The % composition from the GC results, have been used to predict a distillation curve, by making multicomponent batch distillation calculations with the known vapor pressure and equilibrium data[3] (*Fig.* 2).
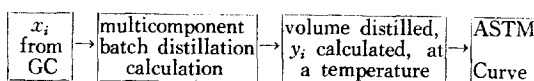
Fig. 2. GC results to ASTM Curve.

For quick routine conversion and for other correlation studies to relate GC to K value, a digital computer program is developed.

Thus far, the analysis method is restricted to identify a sample obtained without any regard to location and time. Therefore, the K value commonly used is only a steady state point function. This concept must be corrected and extended to general case to evaluate an oil sample more successfully and accomplish ultimate oil leakage analysis objectives.

$$K=F\ (x, y, z, \theta) \qquad (2)$$

Though the K is distributed and dynamic in the sense of mathematical description, the physical phenomena which contribute for the K value change need to be defined and proved experimentally. The attributing factors that
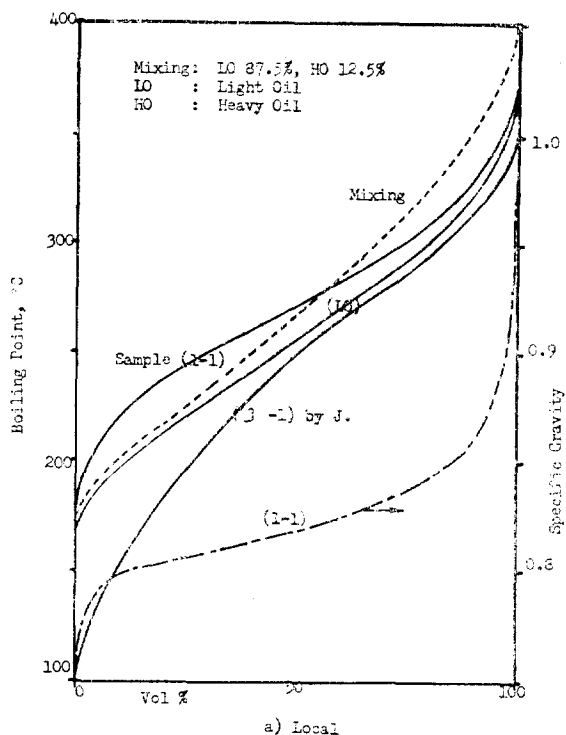
distribute K values and make unsteady are considered to be:

1. Selective solubility of oil in water[3,4].
2. Selective adsorption of oil in porous structure in underground[8~10,13~15,17].
3. Capillary effect[6,15].
4. Gravity effect[6].
5. Impurity effects[15].

The last 3 effects have not yet been isolated and proved experimentally. The relative significances must be known based on a sophisticated engineering model study, which incorporates the above effects in *Eqn.* (2). The entire simultaneous effects should result in a momentary or equilibriated K value at a location with which one is already familiar.

Oil Analysis

An oil sample referred to sample 1-1 was analyzed, by more or less routine techniques available in an analytical laboratory. The analyses conducted were: wt% Hydrogen, % Sulfur, ppm Fe, ppm Sb, ppm Na, ASTM distillation and specific gravity, and GC analysis. The results are summarized in *Table* 1. The ASTM distillation and specific gravity curves are shown in *Fig.* 3a, designated by curve 1-1, along with other significant data to compare. The distillation procedure was adopted from the ASTM micro distillation procedure[1,11], though the natural gas heating was substituted by the electrical heating.

It was found that the sample 1-1 has a fair amount of S about that of distillate from 3 % S crude oil, low gasoline, low heavy oil hydrocarbon mixture, dominantly light oil with a $K=12.0-12.1$. It also contained somewhat high ppm Fe, beyond the handling errors, and detectable amount of bearing metal, and low
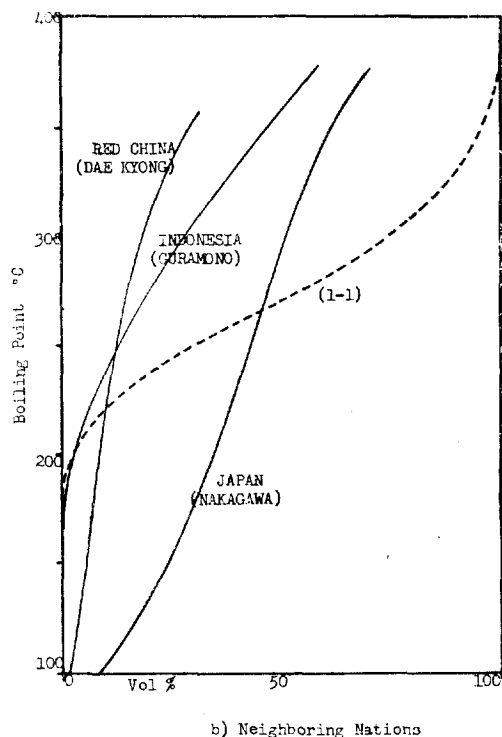

a) Local

b) Neighboring Nations

Fig. 3. Comparison of ASTM Curves.

salt content. These are rather inconclusive data so far as impurities are concerned. The GC analysis indicated a good bell-shaped distribution of hydrocarbon components. When the sample was assumed as a crude oil with a $K=12.10$, the CPP chart prediction resulted in 13.8% wt hydrogen in comparison to 13.6% by actual analysis, which is a good check.

Table 1. Results of oil sample analyses

Sample #1-1

H_2 % wt : 13.6% (actual)

                13.8% (predicted via K factor)[7]

    Fe : less than 30 ppm & 10 ppm

    Sb : less than 0.1 ppm

    Na : 5.3 ppm

S% wt : 1.14%

    K : 12.0-12.1 $\left(K = \dfrac{\sqrt[3]{T_b}}{s} \right)$

  ASTM : Curve 1-1, *Fig.* 3a
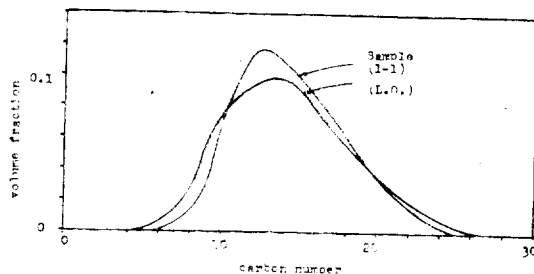
    GC : *Fig.* 5 and 6

Fig. 5. GC results of sample (1-1) and light oil.

Tests were carried out with locally available waste industrial oils, but none came close to sample 1-1 (*Fig.* 3a and 4). Also mixing tests were conducted with different proportions of locally available petroleum products (*Fig.* 3a), but here again nothing came as close as the light oil. However, when the analysis of sample 1-1 was compared with those of the crude oils of the neighboring nations[5], there were significant differences and were dissimilar (*Fig.* 3b).

The GC analysis results are shown in *Fig.* 5 and 6 and upon making the multicomponent batch distillation calculations, a predicted distillation curve was obtained. The comparison of the predicted and actual distillation curves is presented in *Fig.* 7, which shows a good agreement between the two methods. The small deviations are resulted from the two different experimental errors, and the assumptions made during the prediction calculations. This shows the reliability of both analyses. Other oil samples 2-1 and 3-1J were analyzed, and the results are presented in *Fig.* 8 and 9.

The net result is that the analyses are accurate, but the interpretation for the sample evaluation is not really possible without the extended "K" concept.
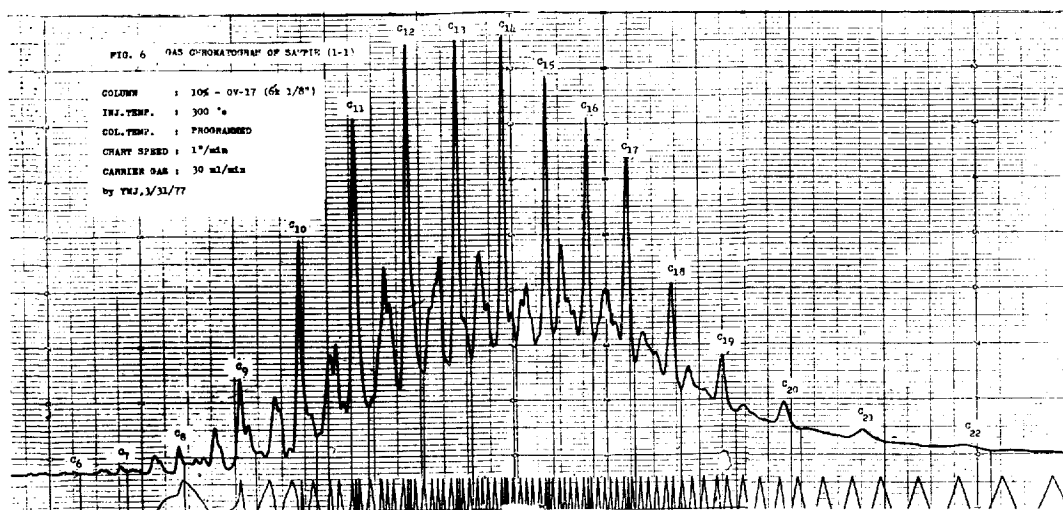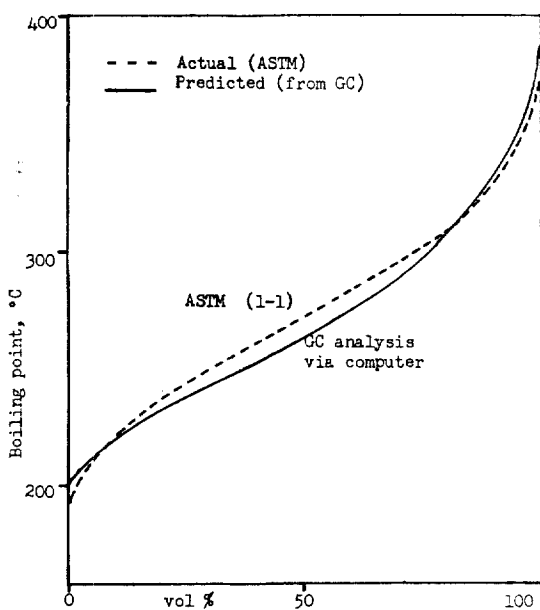

Fig. 4. The ASTM Curves of Waste oil, Heavy oil and Kerosene.

Fig. 6.   Gas chromatogram of sample (1-1).

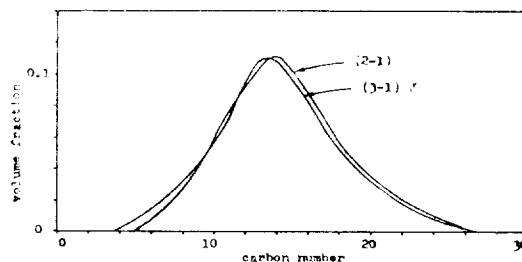Fig. 7.   Comparison of GC results with ASTM.

Fig. 8.   GC Results of sample (2-1) and (3-1)J.

1-1 is a point function at a given time (but unknown from the time zero when it departed from the oil source) and at a given x, y, z (but unknown point of origin), in reference to Eqn. (2). Our prime intention would be to find the characteristics of the oil source, and it probably would be a big mistake to assume that these two would be same, if and when K is distributed in 3 dimensions and dynamic with respect to time.

There were strong convictions that oil would selectively[3,4] dissolve in water during leakage flow, as shown in *Fig.* 10, and the hydrocarbons would adsorb selectively, depending on

Dynamic K Factor Concept and Application

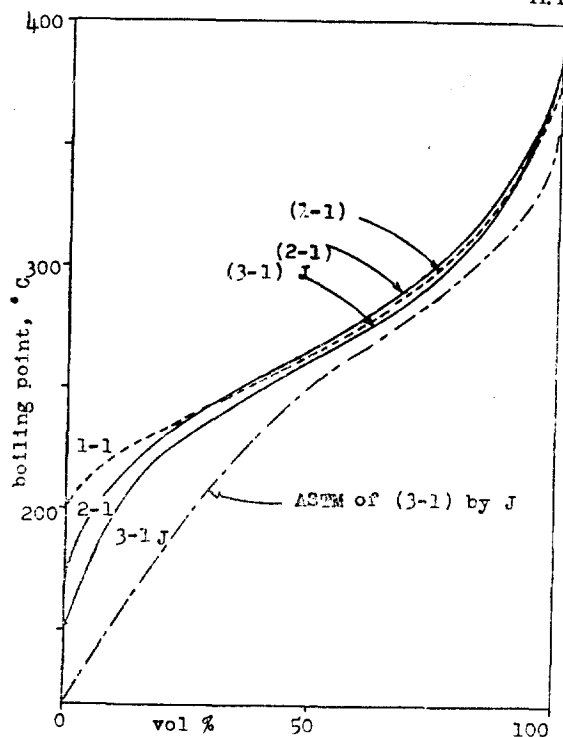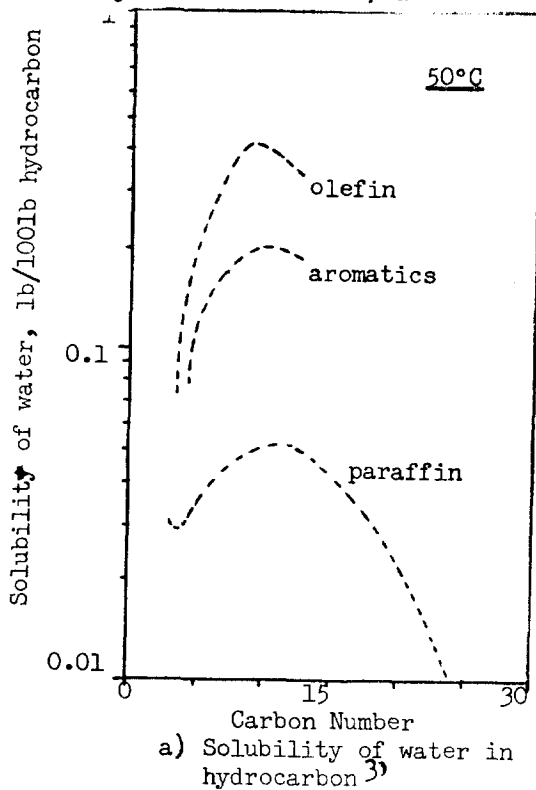The K=12-12.1 value obtained for sample

Fig. 9. Results of GC analyses.

molecular size and structure, and the adsorbing surface[13, 17].

Experiments were performed to isolate the solubility effect of oil in water, and the selective adsorption effect of oil on solids for the purpose of demonstration of the phenomenological causes. For the laboratory study, continuous water washing of oil sample was done for solubility study, while silica gel and activated carbon were used for adsorption study to obtain exaggerated results. *Fig.* 11 shows the equipment used for these studies, while the results of the dynamic K demonstrations are presented in *Fig.* 12. The summary of the results is given in *Table* 2. Since the distance the leakage oil might travel may extend upto 2 miles, these small effects can result in significant overall oil characteristic changes in boiling point, specific gravity, and K value; and these changes can not be overlooked for oil evaluation. It indeed
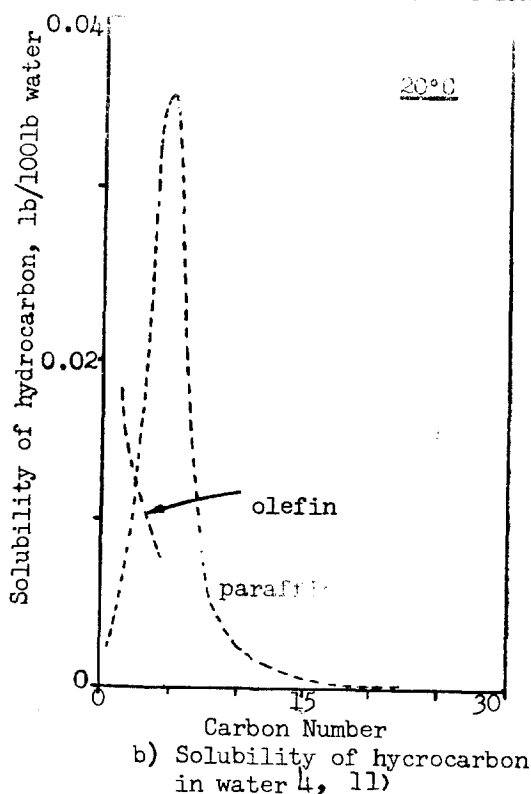

a) Solubility of water in hydrocarbon [3]

b) Solubility of hycrocarbon in water [4, 11]

Fig. 10. Correlation of solubility data.

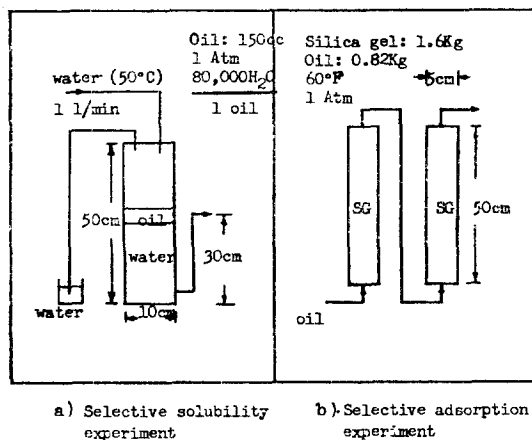a) Selective solubility experiment

b) Selective adsorption experiment

Fig. 11. Laboratory equipment.

Table. 2.   Distribution and dynamicity of K factor

a) Selective Solubility of Oil in Water:

$50°C$, 1 Atm, $\left(\dfrac{1}{80,000} \dfrac{Oil}{H_2O} \right)$ wt. ratio

$(SpGr)_1 = 0.8138$

$(SpGr)_2 = 0.8325$

bp Difference $= 487 - 538 = 51°F$ (average)

GC & ASTM-*Fig.* 12

b) Selective Adsorption of Oil on Silica Gel:

$17°C$, 1 Atm, $\left(\dfrac{1}{2} \dfrac{Oil}{S.G.} \right)$ wt. ratio

$(SpGr)_1 = 0.8165$

$(SpGr)_2 = 0.8046$

bp Difference $= 482 - 509 = 27°F$ (average)

GC & ASTM-*Fig.* 12

$K_1 = 12.067$ $(s_1 = 0.8139)$
$K_2 = 12.003$ $(s_2 = 0.8325)$

final (2)

initial (1)

wt. ratio of oil to water
$(50°C) = 1:30,000$

a) Selective solubility of crude oil

$K_1 = 12.004$ $(s_1 = 0.8165)$
$K_2 = 12.298$ $(s_2 = 0.8046)$

final (2)

initial (1)

wt. ratio of oil to silica-
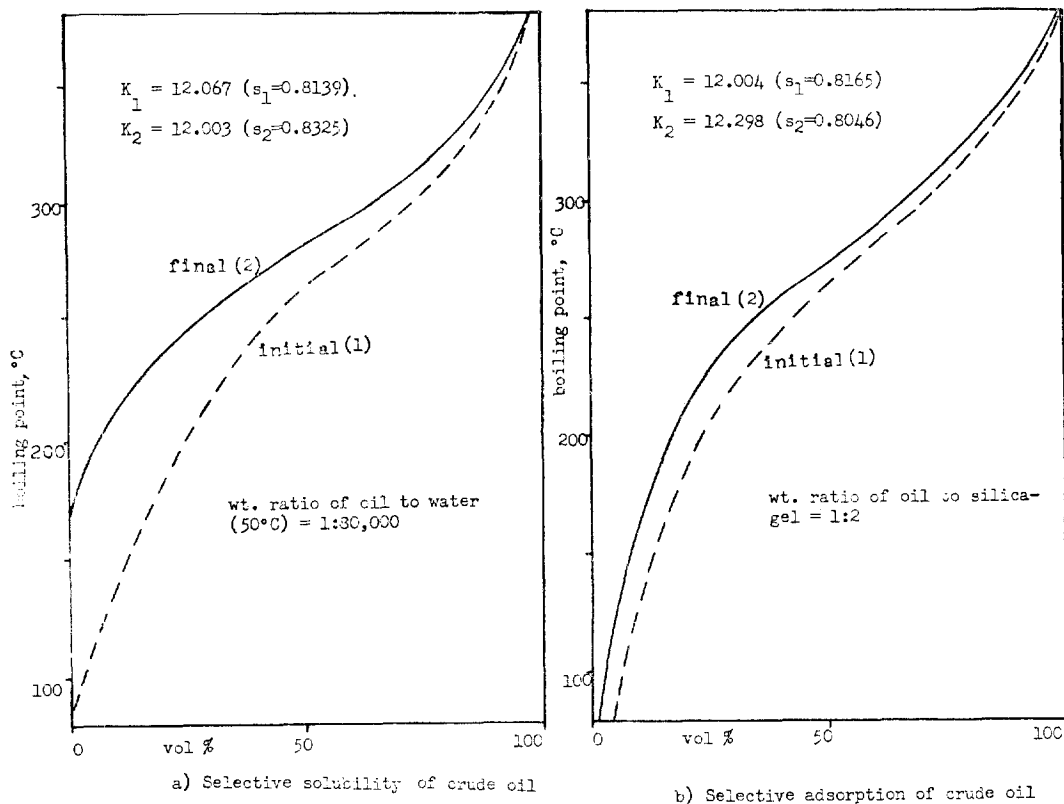gel = 1:2

b) Selective adsorption of crude oil

Fig. 12.   Dynamic K data.

would be shortsighted to draw up any conclusions based on an analysis which is only a point function, without the extended K considerations. The experimental studies on the effects of gra-vity, capillary force, and impurities have not yet been conducted. Since the oil leakage phenom-enon occurs at extremely low Reynolds number[2] ranges, these effects too could not be ignored.

When the oil flow rate is very high, the leakage is very aged, and the flow distance is very short, then the dynamic K factor concept is not necessary for oil evaluation as these effects would be negligible, $K_1 (\theta) = K_{source} (\theta)$.

Since the *Eqn.* (2) is proven to be true, in essence, one must exercise imaginations as to what might have happened to the sample 1-1 starting from the origin since the time of departure from the oil source. Application of this concept is shown in *Fig.* 13 how the samples 1-2, 1-3, would be different in characteristics compared to the sample 1-1, even if the source is common. These samples are to be distinguished from samples 2-1, and 3-1 in that these may or may not have a common oil source as this has not yet been proven.

A successful model study can lead to the location of the source or can confirm whether the sources are actually common or not. More elaborate study with field tracer injection study (oil soluble, and inert to solid) at point 1 might lead to the estimation of the original oil source quantity, though may be slow, tedious and inaccurate, based on the transient tracer concentration changes at point 1 toward the terminal steady state concentration. Insufficient geological data and physical constants on the selective oil composition changes, must be supplemented to develop a good physical system dynamic model[12]. For each hydrocarbon component, the unsteady simple material balance partial differential equation would include diffusion, bulk flow, solubility, adsorption and accumulation terms. And the simultaneous solution for multicomponent system could lead to an overall K in *Eqn.* (2) theoretically. A simple correlation model is currently being developed based on experimental data.

Reliable oil evaluation requires dynamic model

study along with point oil leakage sample analyses, at as many points as possible, to locate oil source, to identify source oil, and even the source quantity estimation. A hasty one point oil leakage sample analysis can lead to very little useful information for oil evaluation and could be misleading.
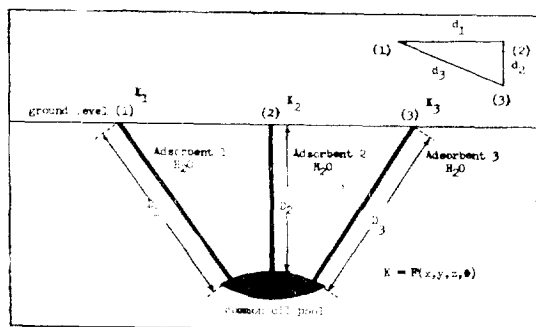

Fig. 13.   Application of dynamic K factor concept.

Conclusion

An oil leakage (sample 1-1) is analyzed, with which as yet no locally known waste industrial oil nor locally obtainable petroleum product mix can match the properties. The light oil was the closest, but still different; the steady state oil leakage analysis at a time and at a location does not disclose sufficient information for proper evaluation. A reliable bridge is established between GC and ASTM analyses. The distributed and dynamic K concept is introduced and proven, which can explain qualitatively about the sample's past and area distribution. Selective oil solubility in water and selective oil adsorption have significant effects toward "K" value changes of the oil. Further theoretical and experimental quantitative model study could lead to source location, and identify the source oil characteristics, and possibly be able to estimate the oil source

quantity, from the leakage oil analyses at various points at ground level.

Acknowledgement

Nomenclature

D_i, d_i: distance i

    K: UOP characterization factor

    K_1: K at point 1

    s: specific gravity

    T_b: molal average boiling point, °R

x, y, z: coordinates

    x_i: mole fraction of i component in liquid phase

    y_i: mole fraction of i component in vapor phase

    θ: time

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