Volatility of Metal-Porphyrin Complexes in Petroleum

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TRACE AMOUNTS of nickel and vanadium compounds in petroleum cause problems in both refining and end use of products (*3*). Some of the nickel and vanadium is carried into the gas oils fed to catalytic cracking units. Here it alters catalyst selectivity to favor increased coke and gas productions at the expense of distillate yields. Most of the vanadium concentrates in the residual fuel oil. It combines with various elements, especially oxygen and sodium, and causes corrosion of firebrick and boiler tubes.

Since nickel and vanadium cause debits to the extent of several million dollars a year in catalyst and corrosion losses, much effort has been expended in characterizing the offending compounds.

The occurrence of trace compounds of nickel and vanadium is also of interest to geochemists, since these metals are believed to have important bearings on the origin and recovery of crude oil (*19*).

This work was aimed at pinpointing the types and volatility of nickel and vanadium compounds in crudes.

Seven crudes with a wide range of metal and sulfur contents were studied. Table I lists some pertinent inspections from standard assays of the stocks used. As sweet paraffinic crudes, South Louisiana and San Joaquin (Venezuela) were chosen. Mixed base kerosine-type crudes included Anahuac (U.S.), Sweden (U.S.), and West Texas crudes. Finally, two South American crudes, Bachaquero and Lagunillas, were chosen as representatives of heavy asphaltic fuel crudes.

To measure the volatility and amount of the nickel and vanadium compounds in various oils, several conditions are normally desirable from an experimental viewpoint.

Equipment must be available for carrying out analytical distillations without introducing significant amounts of entrained material into the gas oil distillate.

The oils must not crack under the conditions of distillation.

The ratio of volatile to nonvolatile metals in the distillation feed must be known.

At the beginning of this work, it was not known whether these conditions were being obtained; therefore, a variety of procedures and checks was employed for preparing the oils and for the calculation of results.

The first extensive work on the nature of vanadium and nickel compounds in crude oil was done by Treibs (*19*) some 25 years ago. He was the first to show that some of the metals in various fossil fuels were combined in the form of porphyrin complexes, and he developed valuable techniques for their separation and identification. Recent workers (*5, 6, 11, 15, 16, 18*) have improved these techniques to identify metal porphyrins of different properties in petroleum fractions. It is felt that these porphyrins are biochemical residues from chlorophyll and hemin. One theory holds that the existing stable nickel and vanadium forms were derived from the magnesium and iron porphyrins by a simple exchange with ions in ground waters.

After World War II metal porphyrins became a source of annoyance to refiners. As increased gasoline demands led to higher and higher cut points in gas oil streams fed to catalytic cracking, increasingly severe catalyst contamination via metals deposition occurred. The resulting reduced cracking yields and lowered capacities spurred intensive research by many of the major oil companies (*2-4, 8, 9, 14, 21*). Nickel and vanadium porphyrins were shown to possess sufficient thermal stability to survive refining and enter heavy distillate streams by simple volatilization rather than, as might be supposed, by entrainment.

Woodle and Chandler (*20*) showed that the overhead from a residuum could contain as much vanadium as the distillate produced from the same feed after deasphalting. Since deasphalting removes a large fraction of the vanadium (*10, 18*), this result suggested that several distinct compound types of vanadium were present. Beach and Shewmaker (*3*) support these findings and show that in Bachaquero crude the vanadium compounds are in two distinct classes: a volatile "smear" of metal porphyrin compounds (Class I) and a much larger nonvolatile fraction (Class II) which was primarily associated with the asphalt. The volatile fraction could be separated from the oil by pyridine extraction and had sharp, distinctive spectra characteristic of simple metal porphyrins. In contrast, the nonvolatile vanadium compounds had no distinctive spectrum and were essentially unextracted by pyridine. It was postulated that these materials could be molecules with more than one porphyrin ring or simple porphyrins with asphaltic side chains of very large molecular weight (*1*). To date there is no direct evidence that the Class II compounds are porphyrins.

Further evidence for the two-class theory of metal

Table I. Crude Properties

	Anahuac	Bachaquero	Lagunillas	San Joaquin	South Louisiana	Sweden	West Texas
Boil. range, vol. % on crude							
I.B.P., 375° F.	17.4	6.0	8.5	37.0	25.5	42.0	24.0
375° to 1040° F.	75.5	56.7	56.3	60.3	70.5	57.5	58.0
1040° + bottomsT	7.1	37.2	35.2	0.7	4.0	0.5	18.0
Gravity, °A.P.I.	34.3	15.1	17.4	41.1	37.0	43.8	32.2
Viscosity[a], 100° F.	41	113[b]	1025	35.5	40	31	46
Sulfur, wt. %	0.25	2.55	2.20	0.17	0.13	0.04	1.90
Conradson carbon, wt. %							
1040 + bottoms	9.5	25.0	26.8	18.4	17.1	22.2	7.5
Metals							
p.p.m. Ni	1.1	45	35	0.9	0.9	0.6	3.8
p.p.m. V	0.2	348	265	2.3	0.1	1.8	11.8

[a] Saybolt seconds universal.
[b] Saybolt Furol at 122° F.

distribution was obtained by Ray, Witherspoon, and Grim (*17*). In their study of the colloidal characteristics of petroleum, most of the nickel and vanadium in an Illinois crude could be concentrated in a minor asphaltene fraction by ultracentrifugation.

The volatility determinations of Beach and Shewmaker (*3*) are limited to vanadium in Bachaquero crude. The pyridine extracts were redistilled from a castor oil carrier using a Model CMS-5 centrifugal molecular still (Distillation Products Industries). Successive extracts yielded vanadium compounds of decreasing volatility. Stated another way, the extractable vanadium existed as a group of monomeric volatile porphyrins whose equivalent atmospheric boiling points (*13*) lie largely between 1085° and 1200° F. and whose molecular weights range from roughly 543 to 800. It was felt that all these materials had the same central ring structure and varied in volatility only because of variations in their peripheral groups. Erdman, Ramsey, and Hanson (*8*) extended these findings by the sublimation of various etioporphyrin-I synthetic complexes. This porphyrin was chosen as representative of the alkyl-substituted porphyrins occuring in crude oil. It was quantitatively distilled at 4 microns over the equivalent atmospheric temperature range of 1090° to 1325° F. without appreciable thermal decomposition or dissociation. This study included copper, nickel, vanadium, and iron porphyrins. Most recently, Dunning and coworkers (*7*) performed a microdistillation on a concentrated vanadyl porphyrin extracted from an Oklahoma crude by the Groennings technique (*11*). These results indicated that 55% of the vanadium volatilized between atmospheric equivalent temperatures of 1050° and 1140° F., 25% between 1140° and 1235° F., and 10% between 1235° and 1315° F.

Whereas the volatilities reported by the various investigators were in qualitative agreement, there was wide disagreement as to the amount of volatile metal porphyrins which could be expected to cause trouble in the refining of a particular crude oil. The ratio of volatile and nonvolatile metal for a variety of crudes and the refined estimates of metal porphyrin vapor pressure are reported here.

VAPOR PRESSURE OF PORPHYRINS IN PETROLEUM

Equipment. A short-column vacuum still (Figure 1) was the primary tool used to determine the volatility of the metal fractions in heavy vacuum gas oils. This device usually operates at 40-micron pressure and allows the collection of 13 fractions (without breaking vacuum) via a simple batch Rayleigh distillation. Extensive testing has shown that when properly operated, entrainment of nonvolatiles from the still pot into the overhead distillate is nil. Also, this still is all-glass, so nickel and vanadium from corrosion products are not a problem. If improper operation results in bumping, this can be detected by the presence of more than 1 p.p.m. of iron in the distillate. (The feed oils, having been stored and prepared in steel equipment, are usually high in nonvolatile iron compounds.)

To check thermal decomposition of the carrier oils and the metal compounds in the short-column vacuum still, limited work with molecular stills was carried out. This permitted use of shorter contact times and lower temperatures. These studies verified the results obtained in the short-column vacuum still.

A high vacuum (60 microns) continuous pilot flash vaporization unit was used to prepare metal-rich cuts for analytical distillation in the short-column vacuum still. This unit was capable of achieving equivalent atmospheric cut points in excess of 1300° F., but unfortunately, there was considerable entrainment of pitch into the overhead gas oil stream.

Finally, conventional steel batch stills were employed to top the whole crude, as received, to 900° F. initial boiling point. None of the metals in crude were removed in the overhead streams from this unit.

Procedure. It was impossible to distill the crudes in the short-column vacuum still because the light ends cause mechanical and practical difficulties. Also, many of the bottoms cracked before the still temperature was high enough to volatilize metals. Consequently, all crudes were topped to 900° F. in the steel batch still. The topped residua were next flashed in a high vacuum continuous flash unit at maximum temperature and minimum pressure. This provides as an overhead a nominal 950° to 1250° F. boiling range gas oil which was rich in volatile metals and could be redistilled in a short-column vacuum still without cracking (at temperatures at which the metal compounds are volatile). However, because of entrainment, not all of the metals in these gas oils were volatile. It was possible, however, to remove these from the calculations.

In addition to the above procedures, some of the residua were refractory enough to permit direct use in the short-column vacuum still. Further, some samples of process gas oils, vacuum bottoms, and atmospheric residual feeds were available directly from refinery tests conducted on West Texas and Lagunillas crudes. These served as checks, and the results were integrated with the main body of the data.

The prepared gas oils and residua were distilled in the short-column vacuum still so that a maximum number of cuts in the porphyrin boiling range (above 1000° F.) were obtained. The cracking temperature for any particular stock was detected by inability to maintain vacuum. In most cases, however, the still temperatures could be carried as high as 650° F. without difficulty.

The short-column vacuum still reproducibility was excellent, as shown by the following check runs on a 28% South Louisiana residuum. Distillation characteristics closely check crude assay expectations, and the low scatter in the metals data also inspires confidence in the results.

Run A			Run B		
Distillate, wt. % on feed	Equiv. atmos. temp., ° F.	Ni, p.p.m. in cut	Distillate, wt. % on feed	Equiv. atmos. temp., ° F.	Ni, p.p.m. in cut
10.9	715	. . .	10.9	713	. . .
20.4	777	. . .	20.5	768	. . .
30.2	819	. . .	30.2	811	. . .
39.9	858	. . .	39.9	851	. . .
49.4	890	0.03	49.5	889	0.03
59.0	932	0.06	59.3	940	0.05
68.7	986	0.12	69.0	997	0.14
78.4	1073	0.57	79.0	1083	0.66
87.6	1170	5.4	87.6	1170	5.2

Experience with high boiling reference compounds such as Octoil and Octoil-S has also shown temperature measurements in this still to be within 5° to 15° F. of known values.

Samples from the short-column vacuum still were analyzed for nickel, vanadium, and iron by a wet ash emission spectrophotometric technique (*6, 12, 21*). Limited checks showed an exact correspondence of volatile metal content and porphyrin content in these cuts. This was determined by measuring absorbances in the range 500 to 650 mμ (*3*). Furthermore, similar related work (unpublished) carried out in affiliated laboratories has always shown the volatile metals to be present as simple monomeric porphyrin complexes. It was therefore deemed unnecessary to check each sample for porphyrin content after having already determined the metal analysis on an elemental basis.

Discussion. Figures 2 and 3 show typical distillation data on gas oils rerun in the short-column vacuum still. All

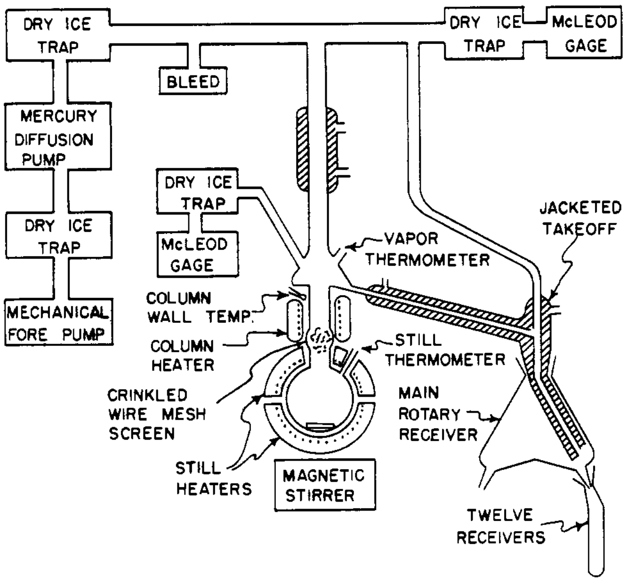

Figure 1. Short-column vacuum still flow plan

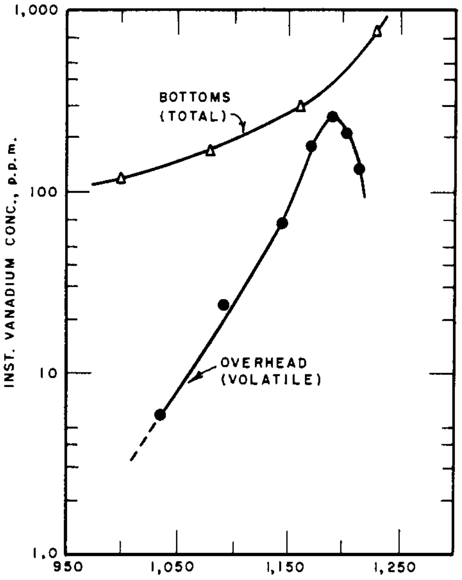

Figure 2. Volatility of vanadium in Tia Juana medium gas oil

distillations showed the characteristic increase in instantaneous overhead metals concentration as distillation temperatures increased. However, in some cases, notably Tia Juana Medium (Figure 2), South Louisiana, and West Texas gas oils, the distillation characteristics were such that, towards the end, the metals concentration in the overhead began to decrease. This was particularly significant, since the instantaneous concentration of metals in the bottoms continued to increase during the distillation, and was actually at its highest level at the end of the distillation. This indicates the depletion of the volatile metals and the presence of "nonvolatile" metals with considerably higher boiling points. Since the analyzed metals concentration in the bottoms, x, includes both volatile and nonvolatile metals, these have to be separated before reliable volatility data can be calculated.

The presence of nonvolatile metals in the feed gas oils is not surprising. Other data on the operation of the continuous vacuum flash pilot unit show that as much as 2 to 5% of the vacuum bottoms may entrain with the gas oil. This pitch can carry with it an appreciable portion of the total gas oil metals content, primarily as the nonvolatile variety (*3*). This limitation of equipment complicated the volatility studies.

In most cases, as represented by Figure 3, cracking took place in the short-column vacuum still before the point of decreasing overhead metals concentration occurred. Stocks differ because the rate of depletion of volatile metals in the bottoms is a function of the initial concentration and volatility of feed metals and of the distillation characteristics of the base oil. In other words, evaporation of oil as well as volatilization of metal affects the instantaneous still pot metals concentration.

By integrating under curves of instantaneous metals concentration *vs.* weight per cent of feed distilled, a measure of the total amount of volatile metals in the gas oil can be obtained. In the many cases where the metals-temperature curve does not show volatile metals depletion (Figure 3), extrapolation must be used to estimate the volatile metals remaining in the still bottoms. A straight line extrapolated to the temperature region, where the distillation curve is likely to begin showing volatile metals depletion, gives a somewhat higher volatile metal content and hence a lower calculated metals volatility than actually exists. Fortunately, based on the shape of these curves and the mathematics involved, a rather large error in the extrapolation has only a slight effect on the calculated volatility. As long as the distillation is carried to about 95% on feed, a tenfold error in the assumption of metals remaining in the still pot will result in only a 15° to 20° F. error in average metals boiling point. However, this error is sufficiently large so that this method cannot be used to calculate an accurate ratio of volatile to nonvolatile metals. It merely gives an idea of the volatility of the metal compounds which do distill.

The calculated vapor pressure of nickel and vanadium compounds in the various gas oils is summarized in Figure 4. These vapor pressures were calculated assuming ideal solutions (Raoult's law) and taking the weight fraction of metals to be equal to the mole fraction. Since the system involves trace components in narrow-cut gas oils, such assumptions are reasonable and greatly simplify the calculations. It is doubtful whether the data justify more elaborate methods. For comparison, the vapor pressures of pure petroleum hydrocarbon boiling at equivalent atmospheric temperatures (*13*) of 1100°, 1150°, and 1200° F. are also shown.

Thus, the metal compounds in the various crudes appear to have comparable volatility regardless of whether they are

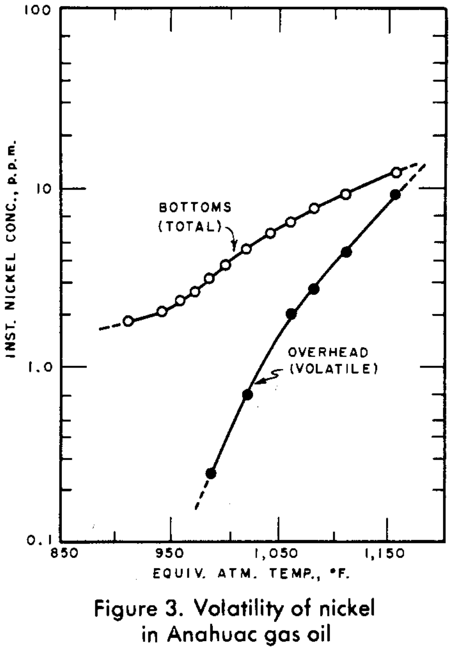

Figure 3. Volatility of nickel in Anahuac gas oil

nickel or vanadium complexes. This is not surprising, since the metallic portion of a porphyrin complex is less than 10 to 15% of the total molecular weight (550 to 650), and there is little reason to believe that the porphyrins chelated with nickel are significantly different from those with vanadium. At high molecular weights, structure has a less important effect on vapor pressure. Furthermore, the volatility of the metals appears to be relatively independent of crude source, even though the amount of volatile metals varies greatly from crude to crude.

Within experimental error, the volatility of the metal complexes in a 900° to 1250° F. gas oil can be bracketed by petroleum hydrocarbons boiling between 1050° and 1200° F., equivalent atmospheric temperature, and having a Universal Oil Products characterization factor, *k*, of 12.0. Although there is some question whether the metal complexes follow the exact volatility pattern of a typical petroleum hydrocarbon, the average trend, particularly at higher temperatures, appear comparable to a petroleum hydrocarbon with an 1150° F. equivalent atmospheric boiling point. Considering the normal distribution of petroleum hydrocarbons, and the differences in volatility pattern over the temperature range, 400° to 620° F. (actual vapor temperature), as shown in Figure 4, it is most probable that the volatile metals are a homologous series of porphyrins rather than a single compound.

The scatter of data within the 1100° to 1200° F. band is due chiefly to the extrapolation errors in determining the amount of volatile metals in a particular gas oil and differences in the amount and type of volatile homologs in each gas oil. To check these extrapolation errors, several entrainment-free oils were prepared for redistillation. To accomplish this, these gas oils were prepared by batch distillations of atmospheric residua in a larger (2.5-liter) short column vacuum still. The entrainment-free gas oils thus produced were then rerun in the small (500-cc.) short-column vacuum still.

Data for redistillation of entrainment-free gas oils from Anahuac, Sweden, and San Joaquin reduced crudes (Figure 5) compared with the previous results on vacuum-flashed gas oils seem to show a slightly greater average volatility. This is because equivalent atmospheric cut points in the larger short-column vacuum still were 100° F. lower than those achieved in the vacuum flash unit. The net result is a gas oil feed with a higher average metals volatility. Thus, agreement with the other results was considered satisfactory.

OCCURRENCE OF VOLATILE AND NONVOLATILE METAL COMPOUNDS

Procedure. The ratio of volatile to nonvolatile metals in atmospheric residua or crudes can be established rather simply by a short-column vacuum still distillation of the atmospheric residuum and determination of the metals-temperature distribution curve for the overhead product. Using the "known" average volatility data presented in Figure 4, the concentration of the volatile metals in the bottoms, x_b, corresponding to the volatile metals in the overhead, y_{oh}, at any point in distillation can be calculated from the relationship

$$x_b = \frac{\pi}{P^0}(y_{oh})$$

where π = total pressure, P^0 = vapor pressure of metal at corresponding still temperature (taken to be similar to a pure hydrocarbon boiling at 1150° F.; middle line of Figure 4), and x, y = liquid and vapor concentration in parts per million (mole fractions of all compounds in narrow cut gas oil are assumed to be same as weight fractions).

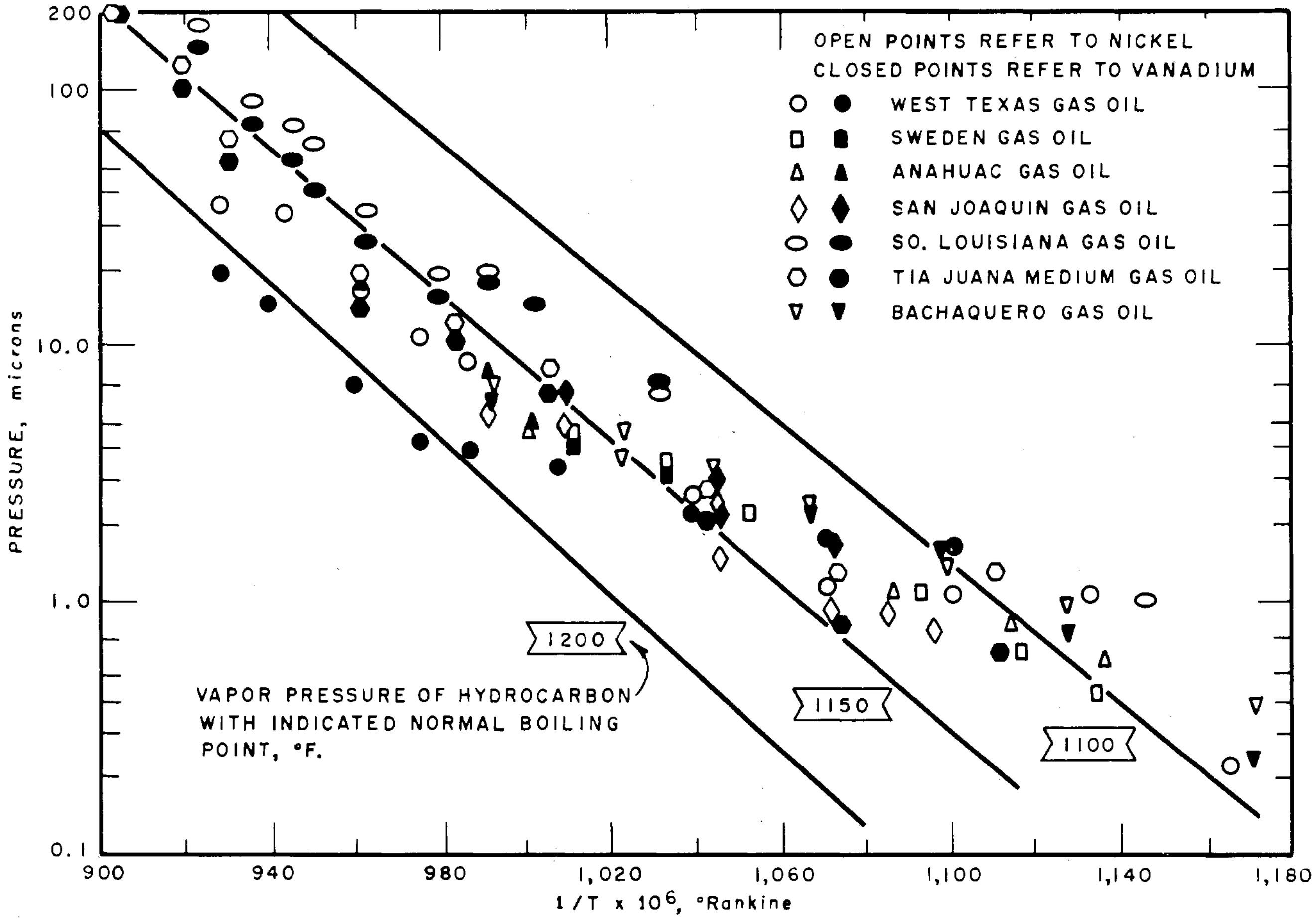

Figure 4. Vapor pressure of metals in vacuum flashed gas oils

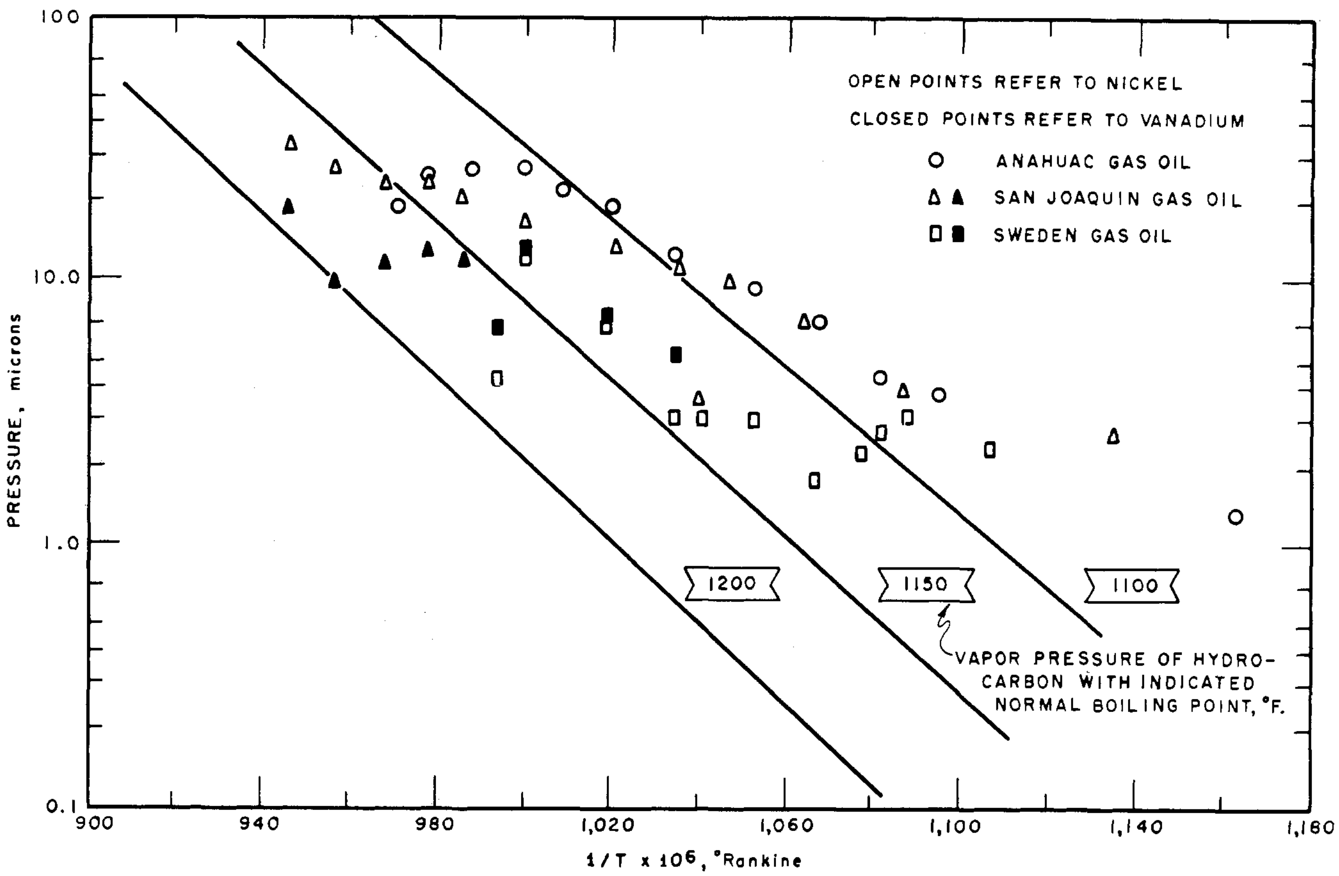

Figure 5. Vapor pressure of metals in entrainment-free gas oils

From a material balance, the concentration of volatile metals in the residuum feed can now be established. Certain residua were capable of distilling in the short-column vacuum still (SCVS) without cracking, and typical calculations for Sweden reduced crude are summarized below.

SCVS Cut No.	Mid-Cut Temp., ° F.	Pressure, Microns	Calcd. % Volatile Metals Ni	Calcd. % Volatile Metals V
9	483	17	21.8	5.6
10	516	15	20.3	4.2
11	574	19	19.0	4.1

The agreement in per cent volatile metals calculated from the various cuts indicates that the assumption of the 1150° F. average was justified. Wrong values for assumed volatility would have resulted in widely diverging answers when the calculations were repeated on other cuts. Bottoms after cut 11 were 14.9% on feed and the amount of volatile metal in the bottoms (as calculated) was of the same order of magnitude as the amount of volatile metals in the total overhead (as measured). It is usually best to repeat the calculation several times during a run and average the results.

Discussion. The total metals content of the crudes studied and the per cent of that total which is volatile are tabulated in Table II. The per cent volatile metals varies among crudes and is different for nickel and vanadium in any one crude. Whether the nickel and vanadium were already present in the living matter from which the oils were derived or whether these metals were introduced later via exchange with ground water minerals is really academic. Either theory would predict differences in the metal compound types in oils of differing age or geographic origin.

The important point is that the volatile metal content rather than the total metal content determines the metal content of gas oil distilled from a given crude.

One hopeful objective of this work was a correlation which would predict the volatile metal content of a crude from the total metal content and other standard crude inspections. Such a correlation would do away with the tedious analytical distillations described here. Unfortunately, no obvious correspondence between the volatile metals and other crude properties has been found.

It had been hoped that the metals extracted by 20% aqueous pyridine from a gas oil or residuum would correlate with the amount of volatile metals obtained as overhead cuts in a deep molecular distillation. Beach and Shewmaker (*3*) studied Bachaquero and suggested that this procedure could be extended to other crudes and therefore offer a simple means of establishing the ratio of volatile to nonvolatile metals. The results of multistage batch aqueous pyridine extractions of Anahuac, San Joaquin, and Sweden gas oils in residua, summarized in Table III, show that the metals removed by extraction do not correlate with the metals volatilized by distillation to 1150° F. or the total volatile metals content estimated from short-column vacuum still distillations by the method discussed in this section. For vanadium especially, the volatile portions are

Table II. Volatile Metal Content of Crudes

Stock	Total Crude Metals, P.P.M. Ni	Total Crude Metals, P.P.M. V	Volatile Metals, % of Total Metals Ni	Volatile Metals, % of Total Metals V
Anahuac	1.1	0.2	52	14
Bachaquero	45	348	31	33
Lagunillas	35	265	23	17
San Joaquin	0.9	2.3	25	5
South Louisiana	0.9	0.1	65	. . .
Sweden	0.6	0.8	20	5
West Texas	3.8	11.8	20	26
West Texas[a]	4.2	8.5	17	27

[a] Volatile metals content determined via centrifugal molecular still; data courtesy of Humble Oil and Refining Co.; all the other data obtained from short-column vacuum still distillations.

Table III. 17% Aqueous Pyridine Extraction of Metals

(5-stage batch extractions)

	Gas Oils[a]				Residua			
Nickel	Bach. (*3*)	Joaquin	Sweden	Anahuac	Bach. (*3*)	Joaquin	Sweden	Anahuac
Feed concentration, p.p.m.	...	2.1	2.4	3.4	...	7.6	5.8	5.9
% extracted	...	54	37	63	...	18	10	18
% volatile to 1150° F. (in SCVS)	...	26	17	41	...	10	4	19
% total volatile (from SCVS)[a]	...	100	90	100	...	...	20	...
Vanadium								
Feed concentration, p.p.m.	79	5.0	5.4	6.1	545	20.7	7.4	1.0
% extracted	91	30	17	56	12	7	Nil	17
% volatile to 1150° F. (in SCVS)	100[b]	1.5	0.8	0.4	20[b]	0.6	0.2	0.2
% total volatile (from SCVS)[c]	...	4.0	4.0	2.0	...	...	4	...

[a] Prepared in laboratory vacuum flash still.

[b] Centrifugal molecular distillation to 1200 + ° F.

[c] Based on extrapolation of short-column vacuum still.

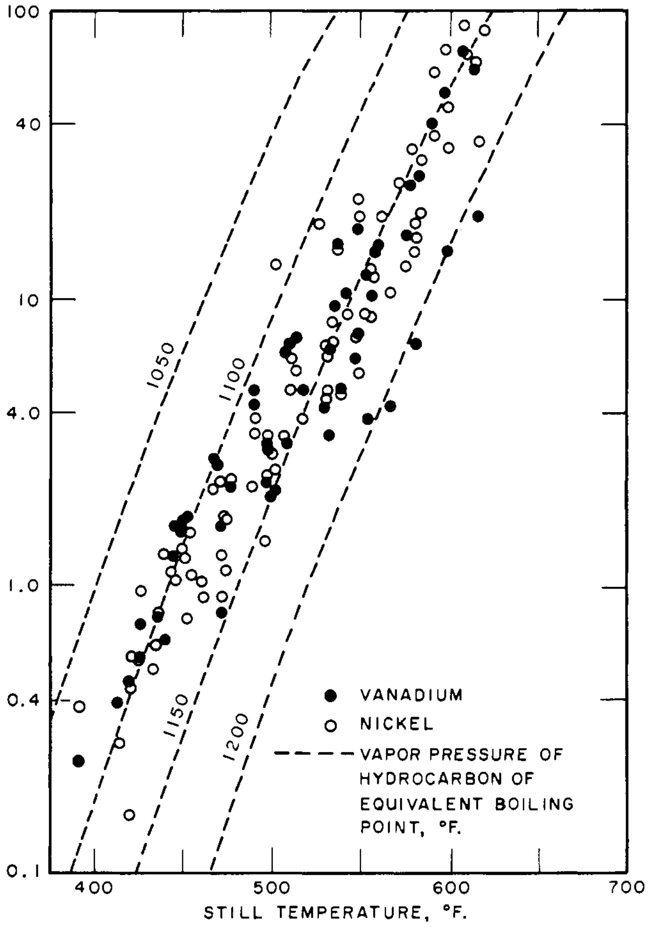

Figure 6. Vapor pressure of organometallic contaminants

considerably lower than the extractable fractions. Volatility, particularly in this higher boiling range, is primarily a function of molecular weight; whereas extractability is a function of both molecular weight and type. There is no obvious reason why the two should correlate. In summary, a short-column vacuum distillation affords the best means for determining the volatile-nonvolatile ratio of metal contaminants in petroleum.

SUMMARY

The vapor pressure data have been assembled in Figure 6. In addition to the data for gas oils (Figures 3 and 4), runs on residua (used to obtain the volatile-nonvolatile split), have been included. Assuming the metal contaminant to be a single pure compound, the vapor pressure of this "pure compound" has been calculated according to the method outlined previously and plotted *vs.* the actual still temperature. No clear differentiation between the volatility of the nickel or vanadium complexes can be made.

Considering the variation in crude types, the correlation of data in Figure 6 is impressive. However, close inspection will show as much as a fivefold variation in vapor pressure at any given temperature. Fortunately, for any one crude the scatter is much less, as shown in Figure 7 (West Texas). This permits some refinements in calculation, and indicates the desirability of obtaining distillations on individual crudes and blends whenever possible. Nevertheless, the assumption of an 1150° F. average boiling point for the metal complexes in a "new" stock is adequate for preliminary engineering approximations.

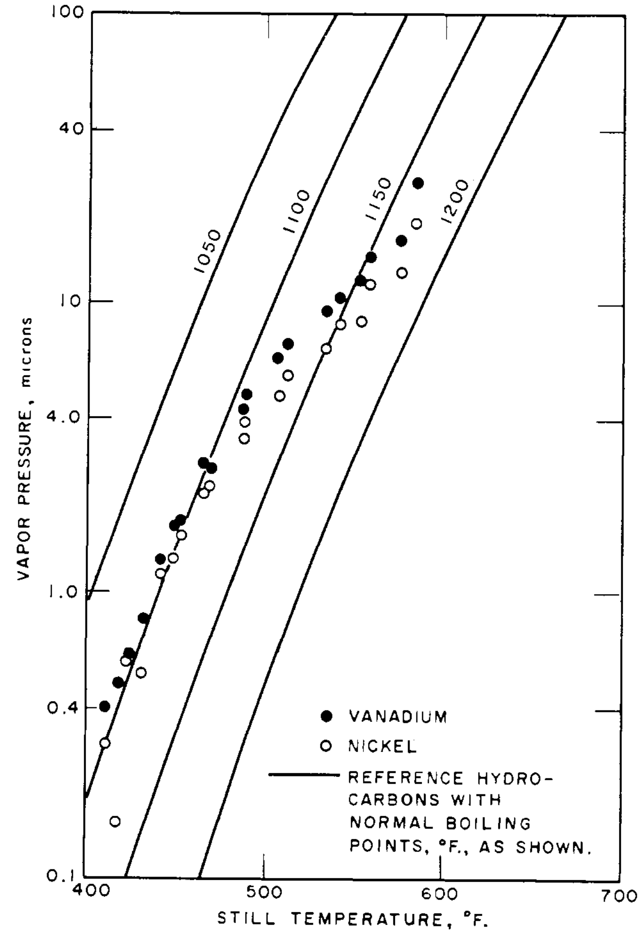

Figure 7. Vapor pressure of metals in West Texas atmospheric residuum

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Porphyrin, Nickel, Vanadium, and Nitrogen in Petroleum

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THE VANADIUM, nickel, and porphyrin contents of a variety of crude oils have been determined. From 3 to 10% of the vanadium in most vanadium-rich oils is present as vanadium-porphyrin complexes. In a few exceptional oils a considerably larger proportion of the vanadium and nickel is present as porphyrin complexes. Some indirect evidence indicates that a large part of the vanadium in many oils is present as nitrogenous complexes.

Studies of total vanadium and vanadium in the vanadyl form and as metal-porphyrin complexes show that from ⅓ to ½ of the volatile vanadium appearing in gas oils is both vanadyl and porphyrin in nature. Additional data show that the vanadium-porphyrin complexes of petroleum are of the vanadyl form. However, all vanadyl vanadium apparently is not in the form of porphyrin complexes.

Bachaquero crude oil was studied most extensively. These results (Figure 1) indicate that there are four types of vanadium in this crude oil: volatile and vanadyl (porphyrin), volatile and nonvanadyl, nonvolatile and vanadyl, and nonvolatile and nonvanadyl.

One sample of Bachaquero crude oil was enriched in vanadium by adding a chromatographic concentrate of metal-porphyrin complex from this oil. Distillation in a short-column vacuum still showed that the metals content in the overhead fractions was not increased until an equivalent atmospheric temperature of about 1000° F. was obtained. Then both vanadium and nickel volatilities increased sharply over a narrow range. This is further proof of the volatility of the metal-porphyrin complexes.

A sample of South Louisiana gas oil also was enriched with metals by adding a similar metal-porphyrin concentrate from Bachaquero crude oil. Part of this enriched gas oil was subjected to a gamma irradiation of 70,000,000 roentgens. Then the enriched and irradiated oils were distilled. Although the metals were still complexed after irradiation, the volatility of both vanadium and nickel was markedly decreased. This corroborates earlier work (*5*) showing that the metal-porphyrin complexes are fairly sensitive to gamma irradiation except in asphaltic media. This indicates the possible utility of irradiation for decreasing the volatility of these metals in refinery stocks.

EXPERIMENTAL METHODS

Porphyrin contents of crude oils were determined by the Groennings digestion method (*11*) with modifications of the colorimetric procedure (*7*). In this method the amount of porphyrin extracted is based on mesoetioporphyrin as a standard. Intensive studies indicate that the method has a precision to about ±5% and comparable accuracy (*14*).

Metals contents of the crude oils were measured by the x-ray fluoresence spectrograph using an external standard. The instrument was standardized each morning and checked by interlaboratory comparison of standards. Very low metal contents were determined by the emission spectrograph

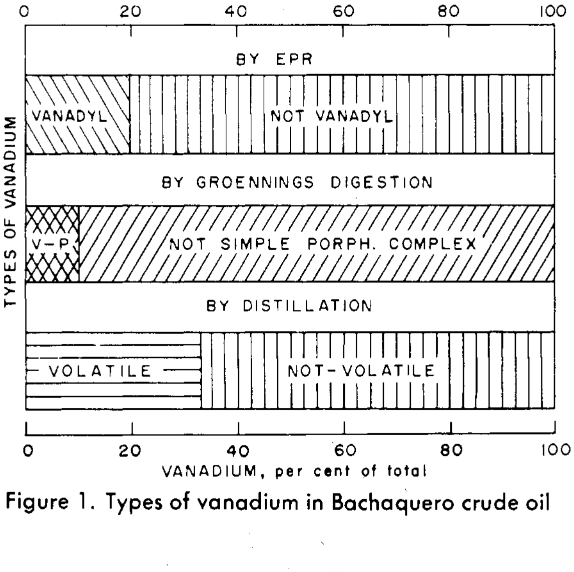

Figure 1. Types of vanadium in Bachaquero crude oil

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