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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

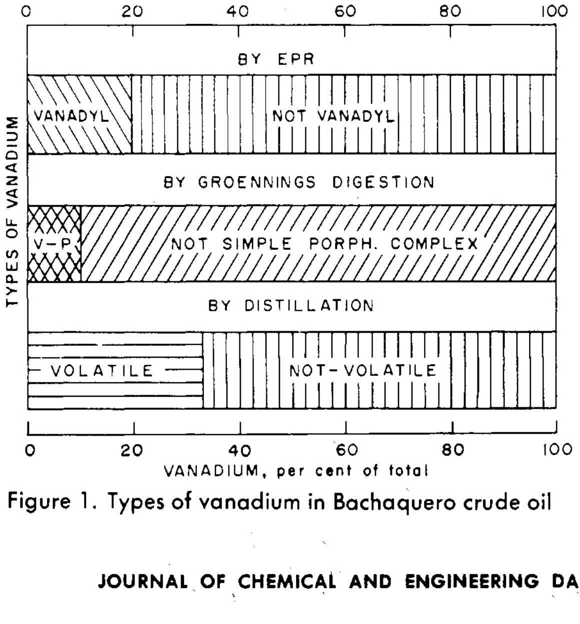

Figure 1. Types of vanadium in Bachaquero crude oil

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Table I. Porphyrins Are Complexed with from 3 to 10% of Vanadium and Nickel in Many Crude Oils

Oil	Location	Residue, %	Porphyrin		Vanadium		Nickel		V + Ni	V/Ni	V + Ni, % Complexed	N_2	
			M/kg.	P.p.m.	M/kg.	P.p.m.	M/kg.	P.p.m.	M/kg.	Mole		M/g.	Wt. %
Bachaquero	Venez.	5.0	790	380	8,430	430	905	53	9,335	9.3	8.5	264	0.37
Boscan	Venez.	4.1	3500	1680	17,600	900	1124	66	18,724	15.7	18.7	436	0.61
Coleville	Canada	10.4	230	110	1,840	94	545	32	2,395	3.4	9.6	200	0.28
Lagunillas	Venez.	4.4	355	170	6,210	317	700	41	6,910	8.9	5.1	207	0.29
N. Belridge	Calif.	6.7	815	390	410	23	1420	83	1,830	0.3	44.6	542	0.76
Rhodes	Kan.	5.9	280	135	2,610	133	565	33	3,175	4.6	8.8	214	0.30
Santa Maria Valley	Calif.	10.1	625	300	5,500	280	2220	130	7,720	2.5	8.1	457	0.64
Tatums	Okla.	7.3	345	165	2,900	148	1220	71	4,120	2.3	8.4	264	0.37
Tia Juana	Venez.	3.3	130	60	3,660	187	410	24	4,070	8.9	3.2	150	0.21
West Texas	Texas	2.2	25	12	450	23	85	5	535	5.3	4.7	57	0.08
Wilmington	Calif.	5.3	415	200	900	46	1020	60	1,920	0.9	21.6	472	0.66

according to the method of Hansen and Hodgkins (*12*). Nitrogen contents were determined by the macro-Kjeldahl method.

Vanadyl contents were determined by electron paramagnetic resonance methods; vanadyl tetraphenyl porphyrin was the calibration standard. Different calibration was required for high and low viscosity samples, because of changes in band shape (*15*). A spectrometer was employed having double modulation, phase-sensitive detection, and second derivative presentation for minimizing interference between the strongest vanadyl band and the near free radical band present in some samples. The vanadyl bands in porphyrins are qualitatively similar to those for solutions of vanadyl salts (*16*). This method determines vanadyl content, which may or may not be complexed with porphyrins.

Volatile vanadium was determined by the distillation method of Bieber and others (*2*) which eliminates entrainment as a source of volatile nonporphyrin vanadium.

The effects of irradiation on vanadium-enriched samples were determined after irradiation in the gamma facility of Phillips Petroleum Co., Idaho Falls, Idaho. The irradiation is supplied by spent fuel elements of the materials testing reactor. Conditions of these irradiations were described previously (*5*).

RESULTS AND DISCUSSION

Although the importance of metals and porphyrins in crude oils has been widely recognized and studied during recent years, no comprehensive study of the interrelationships of these substances has been made. Several facets of the problem of vanadium and nickel in many asphaltic crudes was recognized and examined by Jones. More recently, asphaltic oils were shown to contain considerable amounts of porphyrin complexed vanadium and nickel (*1, 4, 6, 7, 13*).

The results of the vanadium, nickel, porphyrin, and nitrogen determinations (Table I) show that the vanadium-rich oils generally contain about 3 to 10% of their vanadium and nickel as metal-porphyrin complexes. The three marked exceptions are the Wilmington and North Belridge oils from California that contain more nickel than vanadium and the Boscan oil that is unusually rich in porphyrins and vanadium. In general, then, the porphyrins account for only a minor amount of the vanadium present in vanadium-rich oils. However, they may serve as valuable tracers for the compounds that are complexed with vanadium and nickel. Each of the oils contains a considerable amount of nitrogen in excess of that required to complex all the vanadium and nickel present. This generalization is true also for fractions obtained from ultracentrifugation of some of these oils (*9*). Many metal-nitrogen complexes are fairly stable. Therefore, it appears likely that much of the vanadium and nickel of petroleum is present as nitrogen complexes, perhaps as degradation or polymerization products of porphyrins. Some indirect evidence in favor of polymerized porphyrins, which would complex metals but might not be determined as porphyrins, is supplied by observations of synthetic porphyrins. When mesoporphyrin is prepared from hemin, a considerable amount of polymerized porphyrin material often is formed. Unfortunately, little is known of this material and its properties.

Additional light on this problem also is supplied by studies of porphyrin degradation. Porphyrin-metal complexes can be degraded to nonporphyrin complexes thermally (*3*) or by gamma irradiation.

The porphyrins from the several petroleums generally contain a very low percentage of carboxylated types, as shown by recent chromatographic studies (*10*). Pertinent results of these studies are summarized in Table II.

The low maximum amount of carboxylated porphyrins found, 5.4% in North Belridge oil, explains the inefficiency of emulsification fractionation techniques for metal removal (*7*). Although the decarboxylated vanadium-porphyrin complexes are slightly interfacially active, they are low in interfacial activity compared to synthetic carboxylated porphyrin complexes.

The data shown in Table II suggest that appreciable quantities of carboxylated porphyrins are found only in the youngest oils which are richest in porphyrins. However, more information is required to establish the importance of the presence or absence of carboxylated porphyrins as a geochemical tool, with one exception—that the presence of even small amounts of carboxylated porphyrins precludes temperatures over 300° C. during the diagenesis of the oil (*4*).

Until recently, the only metal analyses available were for total metals content. This provides only limited insight of a reaction or process that affects part of the metals. The contents of vanadium in the vanadyl form and as porphyrin complexes are compared in Table III.

The porphyrin contents of the gas oils were determined spectrophotometrically and of the crude oils by the Groennings method. In both cases, from about ½ to ⅓ of the volatile metals are vanadium-porphyrin complexes, which is contrary to previous observations (*1, 2*). Since the errors of the two types of porphyrin analyses are neither compensating nor similar, these results are strongly corroborative. The crude oils (Table IV) contain more vanadyl

Table II. Porphyrin Aggregates from Most Crude Oils Generally Are Decarboxylated

Petroleum	Geologic Age	Porphyrin Content, P.P.M.	Carboxylated, %
N. Belridge	Pleistocene	390	5.4
S. Maria Valley	Piliocene-Miocene	300	1.8
Bachaquero	Cretaceous	380	0.2
Lagunillas	Miocene-Cretaceous	170	0.1
Tatums	Pennsylvanian	165	0.0
Rhodes	Mississippian	135	0.0

than porphyrin vanadium. Since this is not true in carefully prepared distillate fractions (Table III), it must be concluded that crude oils contain some vanadyl-vanadium that is not volatile. This deduction is corroborated by the actual analyses (Table IV) for Tia Juana crude oil which actually contains more vanadyl-vanadium than volatile vanadium. The other three oils do not exhibit this relationship but have various ratios of vanadyl to volatile vanadium.

Experimental identification of the nonvolatile vanadium complexes is badly needed. This difficult problem is not insurmountable. As shown below, some resolution of these materials has been made. Research in this field has been hampered by a lack of knowledge of any properties that may serve as a basis for analytical determination of nonporphyrin fractions.

Studies with porphyrin-rich extracts of petroleum show that all vanadium-porphyrin complexes are of the vanadyl type (Table V).

These vanadium-porphyrin complex concentrates were isolated from the crude oils by chromatography. The methods used were essentially those described for the Tatums extracts by Dunning and Rabon (*8*).

Bachaquero crude oil was chromatographed essentially according to the methods of Moore and Dunning (*14*) to yield a porphyrin-rich concentrate. Comparative work showed that similar concentrates contained vanadium in a vanadyl form. The results of the work are summarized in Table VI.

The hexane and 2-propanol fractions contain an abundance of nonporphyrin, nonvanadyl vanadium and differ widely in polarity. Therefore, this type of chromatographic separation is promising as a precursor to analytical studies of the nonporphyrin metals in crude oil.

The metals concentrate (obtained as the benzene-acetone eluate) was added to an original Bachaquero sample. Porphyrin extraction indicated that the porphyrin content of the oil had been increased from 380 to 490 p.p.m. or 29% by this addition. X-ray analysis for vanadium indicated an increase from 430 to 445 p.p.m. vanadium or 35%. If the deviations of the two methods are considered, this comparison corroborates that most, if not all, of the vanadium added was in the form of the vanadium-porphyrin complex.

Both original and enriched Bachaquero crude oils were distilled in the short-column vacuum still (*2*) until cracking occurred. Excellent agreement in the amount distilled at equal boiling points was obtained between the original and enriched oils. The volatility of the metals in these oils is illustrated in Figure 2.

The metals in the instantaneous overhead (*2*) are very similar for the two oils below an equivalent temperature of 1000° F. However, at higher temperatures, greater amounts of both nickel and vanadium are volatilized in the enriched oil compared to the original stock. Generally, increasing the volatility of the metals displaced the whole curve above the base case. At the 1025° F., equivalent atmospheric cut point (where 58% of both oils have been distilled), the concentration in the still bottoms was 920 p.p.m. vanadium for both oils; the nickel concentrations are 120 and 125 p.p.m., respectively, for the original and enriched oil. There is 110% more vanadium and 40% more nickel in the instantaneous gas oil from the enriched oil than from the original oil. The change in metals volatility apparently indicates that the added porphyrin-metal concentrate comprised a volatile mixture of metal-porphyrin complexes with a narrow boiling range. Therefore, they did not appear in the overhead until an equivalent atmospheric temperature of 1000° F. was reached. Generally (*2*), the metal-porphyrin complexes appear over a range from about 900° to 1250° F. and have an average boiling point of about 1150° F. The concentrate added was a single, small chromatographic fraction which comprised about 3% of the oil and 30% of the metal-porphyrin complex. Therefore, the metal-porphyrin complexes might be expected to be relatively similar types.

Studies of the four forms of vanadium before and after a process or reaction may be expected to furnish considerable light into the mechanisms of the reaction. A South Louisiana gas oil, originally free of vanadium, was enriched with vanadium-porphyrin complex prepared from Bachaquero crude oil by chromatography. Enough of this concentrate was added to give a concentration of 14.0 p.p.m. vanadium in the gas oil. Part of this enriched oil was distilled in a short vacuum column (*2*). The other portion of the enriched gas oil was subjected to 70,000,000 roentgens of gamma irradiation from spent fuel elements of the materials testing reactor. Part of the irradiated sample then was analyzed for porphyrin content and the remainder distilled.

The content of vanadium as the vanadium-porphyrin complex in the irradiated sample was decreased to 4.5 p.p.m. This amounts to a 66% decomposition of the porphyrin complex by irradiation. This figure agrees with earlier observations (*5*) of the stability of such complexes in solvents other than crude oil at equal dosages.

As shown in Figure 3, the bulk volatility of the gas oil was changed very little by the irradiation, although a slight increase in volatility occurred. This also is in agreement with earlier observations (*5*).

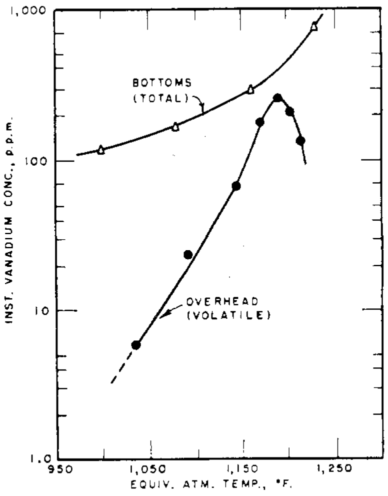

Figure 2. Volatility of metals in original and enriched Bachaquero crude oils

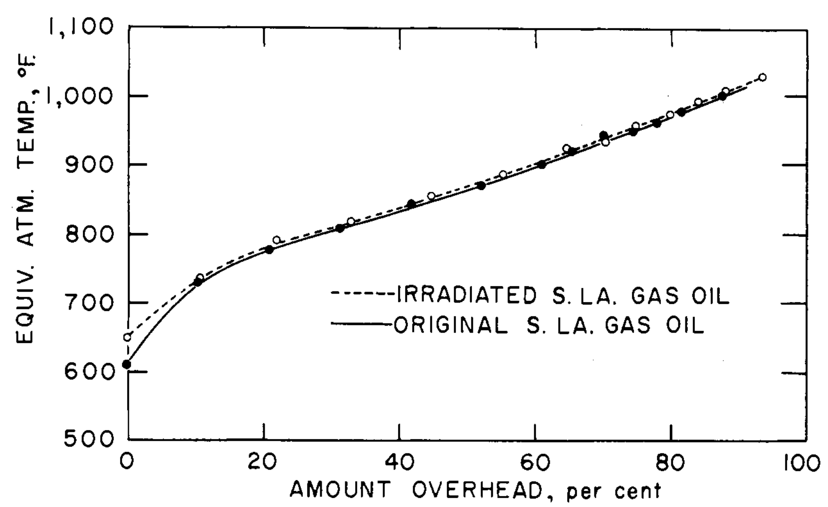

Figure 3. Distillation of irradiated and original vanadium-enriched South Louisiana gas oil

The change in volatilities of the vanadium and nickel contents of the gas oil is illustrated in Figure 4. The volatility of both vanadium and nickel was decreased markedly by irradiation. This is emphasized by consideration of the still bottoms as shown in Table VII.

The volatility decrease resulting from irradiation is made more readily apparent by comparing instantaneous overhead metals concentrations at equal temperatures and bottoms concentrations. This comparison is shown in Table VIII as calculated by the method of Bieber and others (2).

The ratio of vanadyl to total vanadium is nearly constant among the distillate fractions of both the original and irradiated oil (Table VII). This indicates that although two thirds of the metal-porphyrin complexes were decomposed, and the volatility of the vanadium was reduced, the valence state of the vanadium was not changed by irradiation. Acid- and water-washing of the original and irradiated oils did not remove inorganic residues. Therefore, it also can be concluded that the metal-organic complexes were not destroyed by irradiation—rather, they were converted to less volatile forms.

Table III. Vanadyl and Porphyrin-Vanadium Contents of Gas Oils Are in Good Agreement

	Vanadium, P.P.M.		
Gas Oil	Total	Vanadyl	Porphyrin
Bachaquero	20	7.8	9.0
Lagunillas I	0.95	0.38	0.41
Lagunillas II	2.9	1.0	1.3
Lagunillas III	7.6	3.4	4.6

Table IV. All Volatile Vanadium of Crude Oils Is Not Present as a Porphyrin Complex

	Vanadium, % of Total		
Crude Oil	Porphyrin	Volatile	Vanadyl
Bachaquero	10	33	22
Tia Juana	3	11	23
Lagunillas	3	17	13
West Texas	8	27	28

Table V. Vanadium in Vanadium-Porphyrin Complexes from Crude Oils Is Vanadyl Type

	Vanadium, P.P.M.		
Vanadium Complexes	Total	Vanadyl	Porphyrin
Bachaquero	3.0	3.5	2.9
Bachaquero	1.7	2.2	1.7
Rhodes	2.2	2.0	2.5
Rhodes	1.4	1.5	1.6
Tatums	920	670	700
Tatums	380	170	150

Table VI. Vanadyl and Porphyrin Vanadium in Good Agreement for Many Chromatographic Fractions of Bachaquero Crude Oil

	Vanadium, P.P.M.		
Fraction (Eluent)	Total	Vanadyl	Porphyrin
Hexane	290	15	20
Benzene I	430	45	5
Benzene II	600	80	100
Benzene-acetone	1100	420	420
2-Propanol	240	40	65

Table VII. Volatility of Vanadium in Enriched South Louisiana Gas Oil Is Decreased by Irradiation

	Vanadium, P.P.M.					
	Original Oil			Irradiated Oil		
Distillate Fraction	Overhead temp., ° F.	Total V	Vanadyl V	Overhead temp., ° F.	Total V	Vanadyl V
11	970	0.65	0.30	1002	1.06	0.43
12	990	1.60	0.43	1025	2.60	1.05
Bottoms	...	230	95	...	325	161

Table VIII. Calculated Values of Volatile Metals Emphasize Decreased Volatility Resulting from Irradiation

	Metals in Instantaneous Overhead, P.P.M.			
Equivalent Atmospheric, Distn. Temp., ° F.	Original Oil		Irradiated Oil	
	Ni	V	Ni	V
940	...[a]	0.2	...[a]	0.1
970	...[a]	0.7	...[a]	0.3
1000	0.8	3.0	0.09	1.0

[a] Below limits of detection.

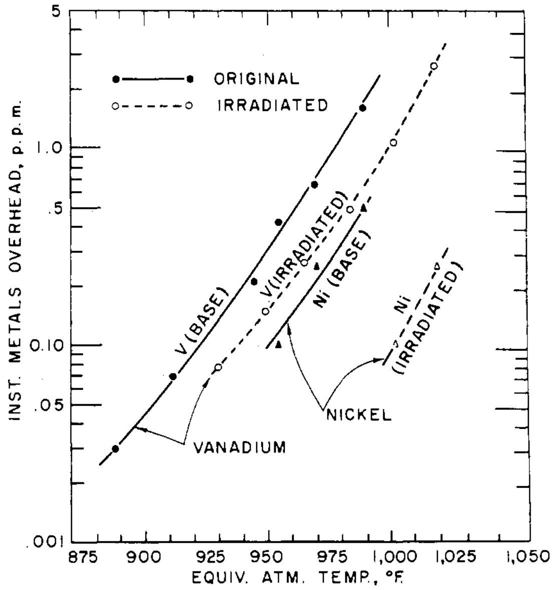

Figure 4. Volatility of metals in irradiated and original enriched South Louisana gas oils

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