

RETENTION OF CRUDE OIL BASES BY CLAY-CONTAINING SANDSTONE

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(Received 28 August, 1967)

Abstract—Retention of basic components of a crude oil by clay-containing reservoir sandstone was studied by flowing crude oil through cores and monitoring the concentration of bases in the effluent. Cores that were H-saturated, H-saturated then aged, and Na-saturated retained 0.82, 0.70, and 0.20 meq base/100 g, respectively. Barium exchange capacity values were 0.86, 0.71, and 0.83 meq/100 g. Subsequent floods with water, toluene, and chloroform-acetone removed oil that had increasing concentrations of base and N, indicating that the basic fraction of crude oil was the most difficult fraction to extract from clay mineral surfaces. Retained bases were nitrogenous and the most tenaciously held bases had base/N ratios approaching unity.

INTRODUCTION

ADSORPTION of ionic and polar organic molecules by clay minerals has received considerable attention in the literature. General surveys on clay-organic interactions have been given by MacEwan (1951) and Grim (1953). Most reports deal with adsorption of organic molecules from the vapor state or aqueous solutions, and there is very little information in the literature about adsorption in non-aqueous or immiscible liquid systems.

This is an interesting area to oil field researchers because an oil reservoir can be considered a large ion exchange bed containing crude oil, water and hydrocarbon gases. Crude oils contain ionic and polar constituents which may be adsorbed on clay surfaces. If adsorption indeed does occur, oil and formation rock properties could be altered significantly as oil flows through a clay bearing formation; especially if the oil and rock are not in equilibrium. As a result of well stimulation and secondary recovery practices, existing oil-rock equilibria are frequently disturbed. Changes in clay surface chemistry such as surface acidity, exchangeable cations and surface cleanliness could have very significant influence on amounts of ionic and polar organic molecules extracted from the crude oil.

The occurrence of organic basic N compounds in crude oil is well documented by Moore, McCutchan, and Young (1951), Deal, Weiss, and White (1953) and recently many others. These basic N molecules probably adsorb on proton saturated or negatively charged sites on clay mineral surfaces. This study was made to determine whether crude oil bases are indeed retained by natural formation surfaces, what effect surface acidity has on their retention, and their extract-

ability by different solvents.

MATERIALS AND METHODS

Formation rock used in the study is an oil bearing sandstone from a California producing zone. The mineral matter is approximately 40 per cent quartz, 40 per cent feldspars, 10 per cent clay minerals and 10 per cent X-ray amorphous material. The clay mineral fraction consists of kaolinite, illite and chlorite. Smectites were not detected by X-ray diffraction. Three 1-in. dia. cores were cut from the formation sample, potted in stainless steel sleeves with epoxy resin and faced to about 2.5 in. length. They were thoroughly cleaned with chloroform-acetone (70:30) solution to remove oil then placed in a fluid flow apparatus for cation exchange capacity measurements, cation saturation and ultimately crude oil flood.

Two cores were H-saturated with 100 ml of 0.1 N HCl, washed chloride free with 70 per cent methanol and finally washed water free with 100 per cent methanol. They were subsequently dried under vacuum at room temperature. One of the H-saturated cores was allowed to stand 8 days exposed to the atmosphere before proceeding whereas the other was subjected to a crude oil flood immediately. The third core was Na-saturated in manner similar to that for H-saturation except in this case 0.1 N NaCl was used. The Na-saturated core was also used immediately after saturation.

A California crude oil with a relatively high concentration of natural bases was used in the study. The oil was cleaned of water and particulate matter by centrifugation and filtered with a 0.45 μ filter. The resulting clean crude oil was passed through the cores at the rate of about 0.5 g/min and the effluent collected in 4-g increments for

subsequent base and nitrogen determinations. A total of about 60 g of crude oil were put through each core then water was flowed until oil was no longer displaced. Similarly, toluene and chloroform-acetone (70:30) solutions followed and each was flowed until little or no additional oil was extracted. Effluent samples containing oil and solvent were collected incrementally during the extractions. Amount of oil in each effluent sample was determined by boiling off the solvent and weighing the residue.

Concentration of natural bases was determined in each sample by titration with perchloric acid in a 40:60 mixture of toluene and acetic acid. Glass and calomel electrodes were used in combination with a Sargent automatic recording titrator. Total nitrogen was determined on several oil samples using a Coleman model 29 nitrogen analyzer.

Barium exchange capacity (Ba-CEC) measurements were made on the cores before and after the sequence of oil and solvent floods. In addition, a K-CEC determination was made after the oil and solvent floods and before the second Ba-CEC measurement. The Ba and K determinations were made with a Perkin-Elmer model 303 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Base retention by sandstone

Concentrations of base in the crude oil effluent samples were plotted against throughput and are

shown in Fig. 1. In the early stages of crude oil injection, the H-saturated core retained more than half of the crude oil bases as indicated by the low concentration of bases in the effluent samples. Later, basicity of the effluent samples approached that for the original crude oil indicating that retention by the sandstone decreased with throughput.

The Na-saturated core removed more bases from the oil during early stages of the flood than later but the quantities removed at any time were considerably lower than for the H-saturated core. Apparently the organic bases did not have as great an affinity for Na-saturated sites as they did for the protonated sites in the H-saturated core. This is also shown in Table 1 which gives total bases retained by each core. The H-saturated core retained 0.73 meq of bases whereas the Na-saturated core retained only 0.15 meq. The values for crude oil bases retained by the cores were determined by material balance.

Behavior of the H-saturated core which was allowed to age for 8 days before flowing crude oil was different than the Na-saturated core or the other H-saturated core which was not aged prior to crude oil flow. In contrast to the other cores, it retained bases at a near constant but slow rate. However, as shown in Table 1, the total amount of bases retained by the core was considerably higher than for the Na-saturated core and nearly as high as for the H-saturated core.

Barium exchange capacity was determined before H- and Na-saturation and again after the sequence

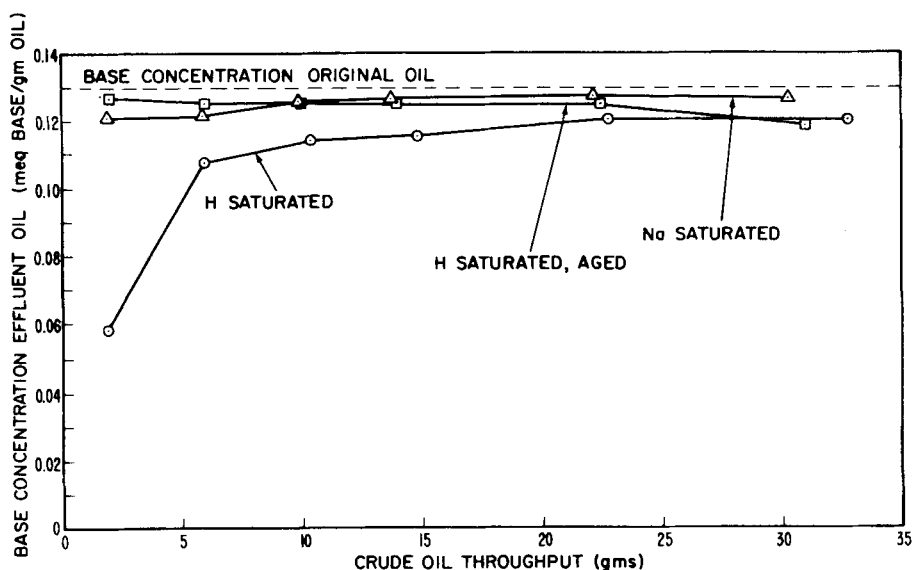


Fig. 1. Concentrations of base in crude oil effluent from H-saturated, aged H-saturated and Na-saturated cores after flowing different amounts of oil.

Table 1. Bases retained and extracted during crude oil and solvent floods

Core	Bases retained (meq)			Bases extracted (meq)				Recovery (%)
	Rock surface	Pore oil	Total	Water	Toluene	Chloroform-Acetone	Total	
H-saturated	0.73	2.14	2.87	0.96	1.45	0.33	2.73	96
H-saturated, aged	0.61	1.84	2.45	0.89	1.32	0.21	2.42	99
Na-saturated	0.15	1.77	1.92	0.79	0.93	0.13	1.85	96

of oil and solvent floods. Both values were similar and mean values are shown under Ba-CEC in Table 2. The amount of crude oil bases retained by the two H-saturated cores is essentially equal to the Ba-CEC of the respective cores. In the case of the aged core, bases retained and Ba-CEC values are 0.07 and 0.71 meq/100 g, respectively, whereas for the unaged core the values are 0.82 and 0.86 meq/100 g. Even though the aged core did not adsorb bases as rapidly as the unaged core, apparently its exchange capacity was completely saturated with organic base during the crude oil flood. It is expected that the most significant change in the core brought about by the 8 day aging is increased Al-saturation and decreased H-saturation. There was no significant change in exchange capacity during the aging process.

The Na-saturated core retained only 0.20 meq bases/100 g yet its exchange capacity is 0.83 meq/100 g. Apparently the natural crude oil bases are not attracted to the Na sites with as much affinity as they are to proton sites. This is contrary to the usual order of exchangeability of most cations on clay surfaces; however, it is in agreement with the order of retention of ammonia on H- and base-saturated clays reported by Mortland (1955) and others. Doehler and Young (1960) reported that quinoline adsorption increased as the acidity of clay was increased. The possible role of basic nitrogen compounds in base retention will be discussed later.

Extractability of adsorbed bases

Immediately after the crude oil flood, water, toluene and chloroform-acetone solutions were

flowed in that order to determine extractability of the adsorbed crude oil bases. As shown in Fig. 2, water displaced only about 30–40 per cent of the oil. Toluene extracted most of the remaining oil and a subsequent chloroform-acetone flood removed only a very small additional amount. Basicity of the water-displaced oil averaged about 40 per cent higher than for the original crude oil as shown in Table 3. Base concentrations in the toluene extracted oil are about the same as for water displaced oil. On the other hand, chloroform-acetone extracts averaged about three times more basic than toluene and water extracts and more than four times more basic than the original crude oil. The extracting solutions removed more bases than were in the interstitial oil; i.e. they also removed basic material that had been retained by the core surfaces.

Table 1 shows the quantity of bases retained by the cores during the oil flood and extracted by solvents. Recoveries were 96, 99 and 96 per cent for the H-saturated, aged H-saturated, and the Na-saturated cores, respectively. The amount of bases extracted by chloroform-acetone (0.33, 0.21 and 0.13 meq) is a sizable fraction of the total bases retained (0.73, 0.61 and 0.15 meq) indicating that chloroform-acetone is a relatively effective extractant for adsorbed crude oil bases. It appears to be much more effective than toluene and this should be considered when cleaning formation rock and cores for water sensitivity and wettability measurements in the laboratory.

After the solvent floods, a K-CEC measurement was made and the data are shown in Table 2. The K-CEC values are about 35–40 per cent of the

Table 2. Crude oil base retention and cation exchange capacity

Core	Crude oil	K-CEC	Ba-CEC
	Bases retained		
	(meq/100 g)	(meq/100 g)	(meq/100 g)
H-saturated	0.82	0.34	0.86
H-saturated, aged	0.70	0.25	0.71
Na-saturated	0.20	0.31	0.83

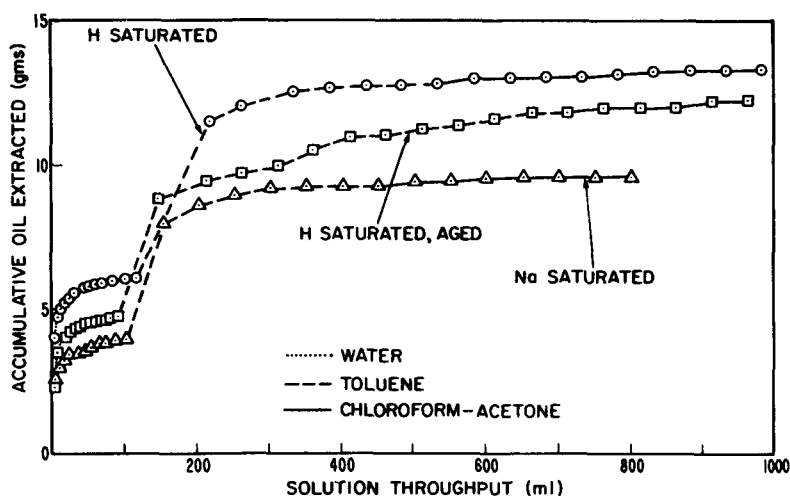


Fig. 2. Accumulative amounts of oil removed from H-saturated, aged H-saturated Na-saturated cores by flowing water, toluene and chloroform-acetone solutions.

Table 3. Concentration of bases in original crude oil and oil extracted from cores with different solvents

Core	Base concentration (meq/g oil)			
	Original crude oil	Oil extracted from cores by		
		Water	Toluene	Chloroform-acetone
H-saturated	0.13	0.16	0.22	0.76
H-saturated, aged	0.13	0.19	0.17	0.46
Na-saturated	0.13	0.20	0.17	0.52

Ba-CEC values indicating that organic bases were replaced by Ba which were not by the previous K-saturation. The difference between Ba-CEC and K-CEC does not necessarily represent the amount of bases remaining on the surfaces after the solvent floods because the KCl treatment could have removed some of the adsorbed bases. On the other hand, the difference between Ba-CEC and K-CEC should not exceed the amount of bases originally retained by the core as it did in the case of the Na-saturated core. The reason for this is not understood. Since Ba-CEC values before and after the series of floods were the same, apparently Ba displaced all of the remaining adsorbed bases.

Basic nitrogen

Although titratable basic nitrogen is a common constituent of crude oil, knowledge of its chemistry and structure is limited. A typical crude oil may contain 0.1–0.6 per cent N of which perhaps 20–30

per cent is basic N. The oil used in this study was chosen for its relatively high concentration of bases; it contains about 0.4 per cent N of which about 40 per cent is basic N. Total N was determined on several of the effluent samples taken during water, toluene and chloroform-acetone extractions. Figure 3 is a plot of equivalents of base/mole of N against total N in the original crude oil and effluent samples taken from the H-saturated core during water and solvent extractions. For practical purposes the ordinate may be considered the basic N/total N ratio.

Water-displaced oil contains more total N and has only slightly higher base/N ratio than the original crude oil. Toluene extracts have essentially the same total N as the water extracts but on the average the base/N ratio is higher than for water extracts. This can be interpreted to mean that water preferentially displaced weaker nitrogen bases which were not titrated by the perchloric

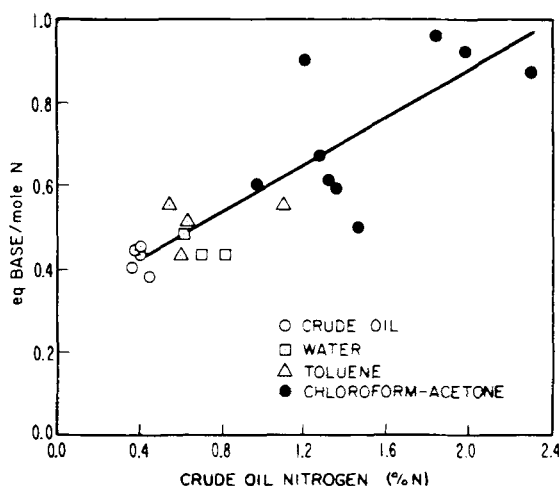


Fig. 3. Total N and base/N ratio of original crude oil and effluent oil removed from H-saturated core by flowing water, toluene and chloroform-acetone.

acid. Chloroform-acetone extracts, on the other hand, have much higher total N values and base/N ratios approach unity in the latter stages of extraction. Apparently, the last increment of organic materials removed from core surfaces by chloroform-acetone is rich in N and each N is a proton acceptor.

A variety of cyclic nitrogen compounds such as quinolones and benzquinolones have been identified in petroleum by Copelin (1964) and others. Nicksic and Jeffries-Harris (1967) propose several basic nitrogen structures whose response in base titrations resembles that of asphaltene. Probably some of them and others attached to larger asphaltene structures are responsible for the observed base retention on clay surfaces.

CONCLUSIONS

Crude oils contain bases which are retained on clay-containing reservoir sandstone. Sandstone cores which were H-saturated, H-saturated then aged, and Na-saturated retained 0.82, 0.70 and 0.20 meq base/100 g, respectively. Their respective

barium exchange capacities were 0.86, 0.71 and 0.83 meq/100 g. On displacing interstitial oil with water, the concentration of base in the oil was about 40 per cent higher than in the original crude oil. Flowing toluene extracted most of the remaining oil which had base concentrations comparable to that displaced by water. A subsequent chloroform-acetone flood removed an additional small amount of oil with base concentrations averaging four times that of the original oil. Basicity of the extracted oil increased with solvent throughput indicating the basic fraction of crude oil is the most difficult fraction to extract from clay mineral surfaces.

Effluent oil basicity and N content are directly related and the base/N ratios approach unity during the latter stages of chloroform-acetone extraction. Apparently the retained bases are nitrogenous and the higher the base/N ratio the more tenaciously the basic nitrogen is held by the clay surface. A variety of cyclic nitrogen compounds have been identified in petroleum and they are probably responsible for the observed base retention on clay-containing sandstone.

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Résumé—La rétention des composants de base d'une huile crue par le grès à teneur d'argile d'un réservoir, a été étudiée en faisant couler de l'huile crue à travers des noyaux et en contrôlant la concentration des bases dans le produit qui s'écoule. Les noyaux, qui étaient saturés de H, saturés de H puis vieillis et saturés de Na, ont retenu respectivement 0,82, 0,70 et 0,20 meq base/100 gm. Les valeurs de capacité d'échange du barium étaient de 0,86, 0,71 et 0,83 meq/100 gm. Les inondations ultérieures avec l'eau, le toluène et l'acétone-chloroforme ont emporté l'huile dont les concentrations de base et de N avaient augmenté, indiquant ainsi que la fraction de base de l'huile crue était la plus difficile de toutes à extraire des surfaces minérales argileuses. Les bases retenues étaient azotées et les bases les plus tenaces avaient des rapports base/N approchant l'unité.

Kurzreferat—Die Zurückhaltung basischer Bestandteile eines Rohöls durch tonhaltige Lager-sandsteine wurde untersucht, indem man Rohöl durch Bohrkerne strömen liess und die Konzentration der Basen im Ablauf überprüfte. Bohrkerne, die H-gesättigt, H-gesättigt und dann gealtert und Na-gesättigt waren, hielten 0,82, bzw. 0,72 bzw. 0,20 meq Base/100 g zurück. Die Austauschkapazitätswerte für Barium waren 0,86, 0,71 und 0,83 meq/100 g. Die nachfolgende Durchflutung mit Wasser, Toluol und Chloroform–Azeton entfernte Öl mit höheren Konzentrationen an Base und N, was darauf hindeutet, dass die basische Fraktion des Rohöls sich am schwersten von Tonmineraloberflächen extrahieren lässt. Die zurückgehaltenen Basen waren stickstoffhaltig und die am hartnäckigsten festgehaltenen Basen hatten Base/N Verhältnisse im Bereich von eins.

Резюме—Удерживание основных составляющих сырой нефти глино содержащим пористым песчаником исследовалось пропуская поток сырой нефти через колонки и контролируя концентрацию оснований в сточных водах. Колонки, которые были насыщены H, насыщены H а затем подвергнуты старению и насыщены Na—сохранили 0,82, 0,70 и 0,20 мг-экв основания/100 г, соответственно. Значения обменной способности бария составили 0,86, 0,71, 0,83 мг-экв/100 г. Последующие орошения водой, толуолом и хлороформ-ацетоном удалили нефть имеющую возрастающую концентрацию основания и N, указывая тем самым, что основная фракция сырой нефти являлась наиболее трудной фракцией для извлечения из поверхности глинистых материалов. Удержанные основания были азотными и сильнее всего удерживаемые базы имели соотношения основание/N доходящие до единицы.