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Gel Permeation Analysis of Asphaltenes from Steam Stimulated Oil Wells*

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Summary

Gel permeation chromatography was used to obtain molecular weight distributions of asphaltenes from 5 wells before and after steam injection. These wells all produce from the same horizon in one Kern River, California, field. A standard Q-mode correlation analysis showed no significant relationship of stimulation response to any of the molecular weight data, i.e., molecular weight distribution before, immediately after, or 200 days after treatment. A standard R-mode analysis showed a significant relationship of the slope of the molecular weight curve before stimulation with the slope just after stimulation, but not with the slope 200 days after stimulation. The wells that returned the least amount of oil per barrel of water injected as steam produced asphaltenes after stimulation very deficient in high molecular weight compounds. It is inferred from this that these materials precipitated within the formation and are restricting flow. At the other extreme, the change in asphaltene molecular weight profile from the most successful stimulation job can best be explained by the introduction of new production sources into the oil flowing towards the well. This is consistent with this well's having received the greatest quantity of steam.

In summary, GPC provides a valuable increase in analytical sensitivity to changes in the fraction of crude most responsible for determining its production flow rate.

INTRODUCTION

The high molecular weight and heterogeneous composition of crude oil heavy ends have presented formidable barriers to fractionation and

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subsequent characterization. Column chromatography, thermal diffusion, molecular distillation, and solvent separation have been the major separation techniques used on petroleum residues in the past. These tools have now been supplemented by gel permeation chromatography (GPC) which may become, if it has not already done so, the most generally satisfactory procedure for obtaining reasonably narrow cuts of crude oil heavy ends for detailed analytical studies. In the present study gel permeation chromatography is applied to asphaltenes from steam stimulated oil wells in the search for a better understanding of the role asphaltenes play in oil production before and after stimulation (*1*).

Steam is commonly injected into a producing oil well to stimulate production. Characteristically, wells which produce low gravity (API) crude from a relatively shallow depth respond most favorably to steam stimulation. The principal beneficial action of steam is the reduction in fluid viscosity brought about by local heating of the formation rock. Several additional processes of lesser importance undoubtedly take place at the same time. One is the clean-up of the well bore and of the production hardware area by the hot steam. Such action increases surface area and exposes additional cation exchange capacity for subsequent interaction with asphaltenes and other basic nitrogen compounds of crude oil. Another action of the steam is the partial degradation of rock and the attendant separation and dispersion of silt and clay. This is shown by increased silica, alumina, boron, iron, and other rock constituents in the produced water after steaming. Also, sanding problems appear or become more severe after steaming. Still another process occurring during steam stimulation is steam distillation of the more volatile crude oil components as steam flows through the volume of partially oil-saturated rock. The oil that remains in place is subjected to higher temperatures for a longer time the closer it lies to the well bore. The effect of this treatment on the composition of heavy ends may be predicted by laboratory studies but several questions remain unanswered. Two of these are the adhesion of the heat-treated residue to the formation rock surface and the effect this coating has on the distribution of the returning crude oil and brine.

The combined chemical and physical effects of steam on the rock, oil, and brine will be reflected in the composition of the fluids produced from the well following the treatment. Careful analysis of these fluids before and after stimulation is the only means available to study these effects. The validity of conclusions from such a study depends on the sensitivity and comprehensiveness of the analytical techniques. Prior to GPC, characterization of the heavy ends of crude oil was a major inadequacy in the analysis of oil field produced fluids. In the present study of steam-stimulated Kern River wells, the samples were a part of a group for which a large amount of analytical data had already been obtained. It was desired to use GPC to obtain fractions so that molecular weight distributions of the asphaltenes could be determined. The molecular weight information, while interesting in its own right, was expected to be a worthwhile complement to the customary data already obtained on the samples. In a sense, a principal objective is to see if the molecular weight distribution adds materially to an understanding of the stimulation process and of the factors that cause success or failure of the treatment.

EXPERIMENTAL SECTION

Crude oil samples were collected at the wellhead and were stored in glass until used. Asphaltenes were separated from the crude by a procedure starting with 20 volumes of pentane added to 1 volume of water-free sample. After overnight standing, the asphaltenes were removed by filtration, washed briefly with pentane, and then exhaustively (12 hr or more) extracted with pentane in a Soxhlet-type apparatus. At the end of this treatment no colored extract was being removed from the asphaltenes. The product was a black free-flowing, finely divided powder.

Gel permeation was carried out by a procedure previously described (*2*) except that a somewhat shorter column (70 vs. 120 cm) was used. Also, the sample was placed on the column in benzene instead of a mixed solvent.

The eluting solvent was 5 volume % reagent grade methanol in reagent grade benzene. The methanol diminishes but does not entirely eliminate absorption of asphaltenes on the styrene–divinylbenzene copolymer gel. The gel was prepared for maximum separation in the 300–30,000 molecular weight range. A manual system of sample collection was used to obtain 18 fractions for molecular weight determination.

Molecular weights were obtained using a Mechrolab vapor pressure osmometer Model 302 operated at 37°C. Chloroform solvent was used and asphaltene concentrations were kept below 10 g/l to minimize association effect (*3*). Other details are given in the previously cited Ref. *2*.

The first fraction, and at times the second, were of lower molecular weight than the subsequent fractions. This anomalous behavior of asphaltene samples has been observed many times in this laboratory. No systematic investigation of this phenomenon has been made or reported in the literature. It has been suggested that this forerun passes through the column in highly associated form because of the 5% methanol added to the eluting solvent. When molecular weights are determined methanol is absent and the aggregates dissociate into lower molecular weight species. This anomalous forerun represents usually less than 5% of the total sample.

Several GPC runs showed some increase in molecular weights in the final few cuts. This probably arises from absorption of part of the sample on the gel surface. Increasing the methanol content of the solvent diminishes this but at the cost of a considerable increase in

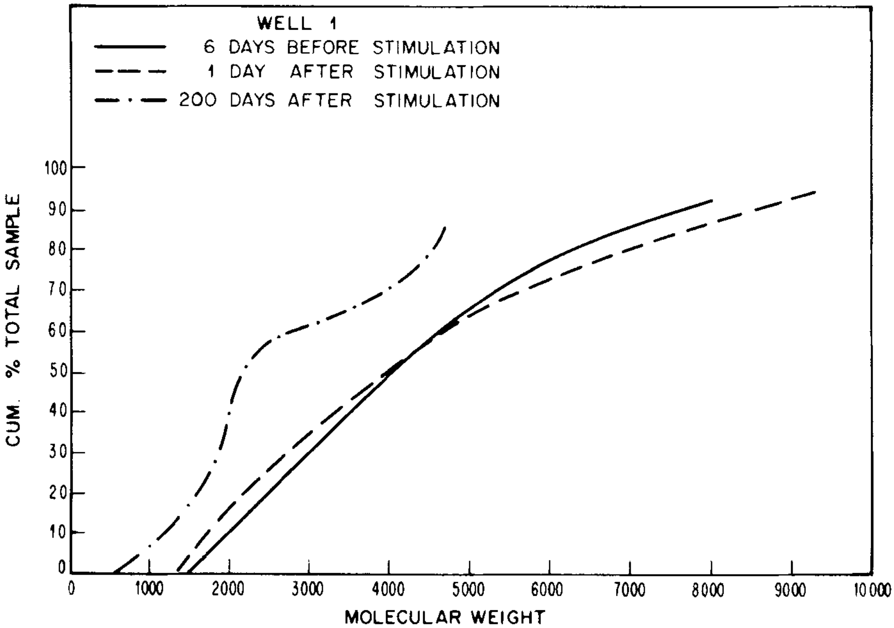

FIG. 1. Molecular weight profile. Cumulative per cent total sample weight vs. molecular weight.

the quantity of low molecular weight forerun. A volume of solvent equal to a complete gel permeation run was passed through the column between samples to minimize cross-contamination due to this tailing effect. Figure 6 shows a typical elution curve with molecular weight plotted against elution volume. Note the low molecular rate forerun in this figure.

RESULTS AND DISCUSSION

The molecular weight distribution of asphaltenes from 5 Kern River wells in this survey are shown in Figs. 1–5. Each Figure shows the profile for the asphaltenes from an oil sample taken before stimulation, 1 day after stimulation, and about 200 days after stimulation. In each Figure the vertical axis is the cumulative weight % of asphaltenes with molecular weight equal to, or less than, a particular value. The horizontal axis is molecular weight. These data will be discussed against a background of production, stimulation, and composition data given in Table 1 (*4*).

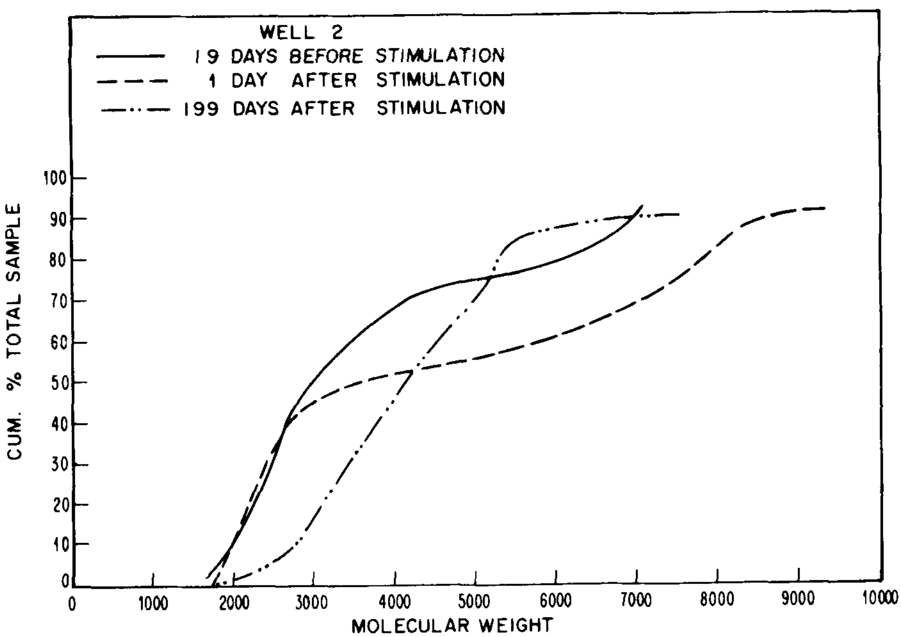

FIG. 2. Molecular weight profile. Cumulative per cent total sample vs. molecular weight.

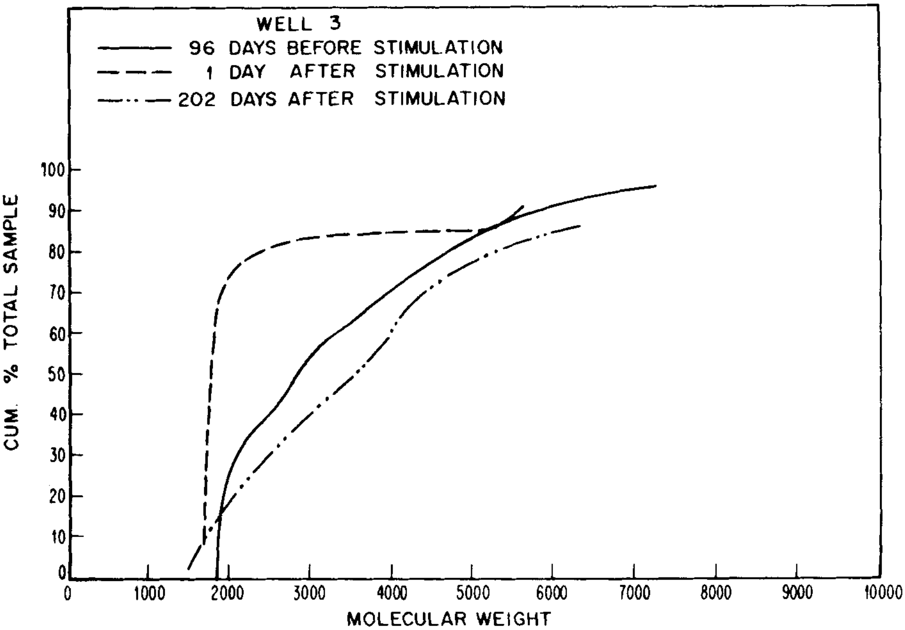

FIG. 3. Molecular weight profile. Cumulative per cent total sample vs. molecular weight.

The mass of data is difficult to assimilate by visual comparison. To help find molecular weight effects that relate to stimulation efficiency, a standard Q-mode correlation analysis was programmed and run by computer. Input information included slopes of the plots of cumulative weight fraction versus molecular weight, taken at 1000 unit intervals. The results of this analysis showed no significant correlation of any of the input variables with the efficiency of stimulation. This does not imply that asphaltenes do not play a role in determining stimulation response, but that molecular weight profiles alone cannot predict successful steam stimulation. An R-mode correlation analysis showed a statistically significant relationship between the slope of the molecular weight profile curve prior to stimulation and immediately after stimulation. No other significant relationships were found.

Note from the molecular weight profile that despite the fact that all 5 wells produced from the same geologic formation, there is a large variation in asphaltene composition in samples taken before stimulation. There is no way to tell whether this is due to differences in crude

TABLE 1

Treatment and Performance Data

Line	Treatment and results	Well 1	Well 2	Well 3	Well 4	Well 5
1	Steam (expressed in bbl of H_2O) injected per vertical foot of oil-bearing sands	26.48	70.08	81.51	77.55	17.31
2	Bbl of oil produced in 200 days per bbl of H_2O injected as steam	0.3304	0.3828	0.6152	0.4770	0.5595
3	Bbl of oil produced in 200 days per vertical foot of oil-bearing sands	8.75	26.83	50.15	36.99	9.69
4	Per cent asphaltenes in oil before stimulation	5.3	4.2	4.7	4.3	4.3
5	Per cent asphaltenes in oil 1 day after stimulation	3.8	4.2	4.7	4.5	4.3
6	Per cent asphaltenes in oil 200 days after stimulation	4.8	5.8	5.0	4.8	5.0
7	Short-term change in asphaltene content (Line 5 minus Line 4)	−1.5	0	0	+0.2	0
8	Long-term change in asphaltene content (Line 6 minus Line 4)	−0.5	+1.6	+0.3	+0.5	+0.7
9	Additional oil gained by stimulation, bbl/200 days	−165	6040	9680	4690	1350

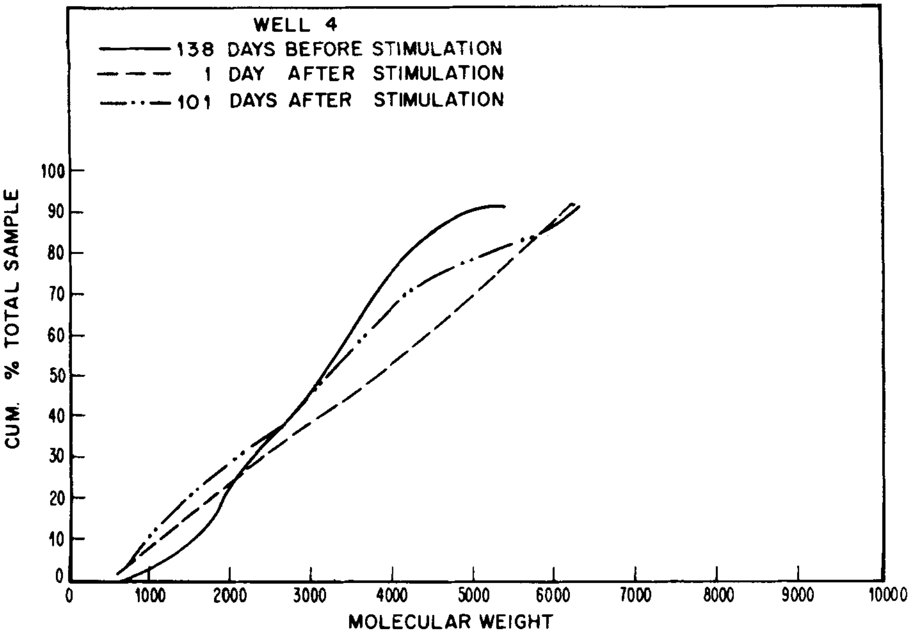

FIG. 4. Molecular weight profile. Cumulative per cent total sample vs. molecular weight.

oil composition as a function of the reservoir region being drained or to natural separation processes, such as absorption and deposition. Since the prestimulation asphaltenes differ widely from well to well, it is necessary to compare changes in composition caused by the stimulation process well by well rather than on an absolute basis. For example, the asphaltene molecular weight profile 199 days after stimulation of Well 2 shows an increased quantity of all components below molecular weight 5200 relative to the prestimulation curve with the same well. Compared with the prestimulation curve for Well 5 however, it would show a much greater increase in quantity of higher molecular weight components across the entire composition range.

Added to the variation in the composition in the prestimulation asphaltene is considerable variation in the stimulation process itself. Line 1 of Table 1 shows that the quantity of steam injected into the wells ranged from 17.31 to 81.51 barrel equivalent of water per vertical foot of oil bearing sand, a factor of 4.7. This variation in quantity of steam injected is included in the steam efficiency calculation, Line 2

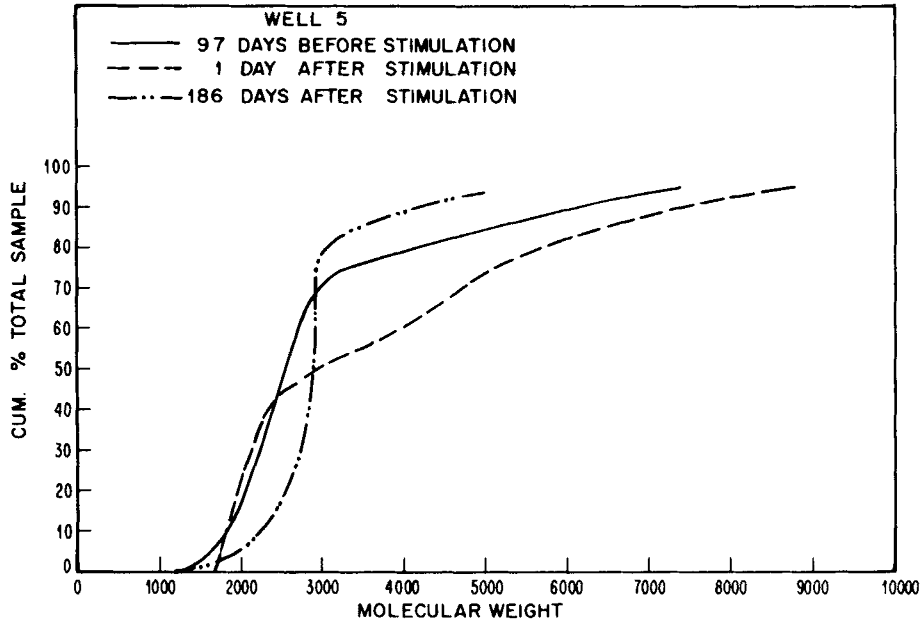

FIG. 5. Molecular weight profile. Cumulative per cent total sample vs. molecular weight.

of Table 1. It is recognized in oil-field technology that the volume of steam injected bears strongly but not rigidly on stimulation response.

Both the molecular weight profile curves and the stimulation efficiency data show clearly that Wells 1 and 3 stand at the extremes of behavior for the 5 wells. In terms of productivity per barrel of injected water, Well 1 is least satisfactory and Well 3 the most. Figure 1 shows that 200 days after stimulation the asphaltenes from this well are unique in the loss of fractions above 4600 molecular weight. This contrasts with the very close correspondence between the curves for prestimulation and 1 day following stimulation asphaltenes. Figure 3 shows the exact opposite behavior for Well 3. The molecular weight profile for asphaltene produced 202 days after stimulation is richer in higher molecular weight species from 1900 up to 6300 molecular weight but is not markedly different from the prestimulation sample. The asphaltenes produced 1 day after stimulation show a unique molecular weight profile, fully 76% of the sample lies at or below molecular weight 2200. In two more fractions amounting to 16% of the

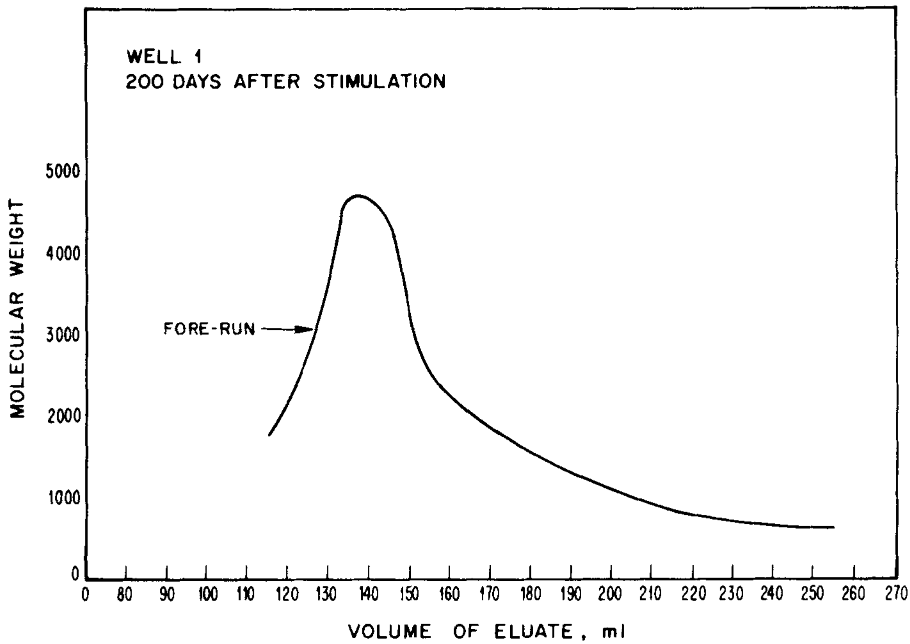

FIG. 6. Typical elution curve. Molecular weight vs. volume of eluate, ml.

sample, the curves rises to 5700, indicating either a selective removal of the intervening molecular weight species from the crude oil before it flowed into the well, the admixture of new production rich in low molecular weight asphaltene, or thermal degradation of heavy components. Wells 2, 4, and 5 represent intermediate cases between Wells 1 and 3 from the standpoint of reproductivity and alteration of asphaltene composition following stimulation.

Well 1, in addition to producing the least oil based on injected steam (Lines 2 and 9 of Table 1), is the only well to show a decrease in asphaltene 200 days after stimulation (Lines 7 and 8, Table 1). From Fig. 1 it will be seen that asphaltene reduction was entirely nonselective 1 day after stimulation but chiefly in the 4700 plus molecular weight range by the end of the 200 day poststimulation period. These results indicate that there is some deposition of asphaltenes from the oil onto the rock surfaces following steam stimulation and that this deposition changes from nonselective to very selective over a 200-day interval. Two important consequences of this process are a reduction of permeability resulting from restriction of flow channels and a change in the distribution in water and oil phases resulting from the development of a new solid phase surface. The quantity of steam injected cannot be the controlling factor in asphaltene composition and content as this variable for Well 1 is bracketed by Wells 5 and 2, neither of which show similar effects (Line 1, Table 1). The mechanism therefore depends on an interaction of steam with locally situated oil, rock, and brine.

For Well 3 the unique shape of the 1 day after stimulation molecular weight profile deserves additional comment. Increased production may be due to the admixture of a second oil stream of different composition. Note that there was no reduction in asphaltenes (Line 7, Table 1). From Fig. 3 it is seen that the 2200–5300 molecular weight range represents 57% of the prestimulation asphaltene sample but only 10% of the sample 1 day after stimulation. Such a reduction in this fraction would be expected to produce a reduction in per cent asphaltene found in the oil. Asphaltene content increased slightly during poststimulation period (Line 8, Table 1). Well 3 received the largest quantity of steam per vertical foot of oil bearing rock; therefore the probability of stimulating a wider distribution of adjacent rock is greatest in this well. A marked change in asphaltene composition soon after stimulation would be a result of the presence of oil from these heretofore unproductive areas, rather than selective precipitation of asphaltenes as suggested for Well 1.

Regarding the possibility of thermal degradation of asphaltenes by the prolonged intensive steam treatment, the results shown do not generally support such a hypothesis. In most cases a slight increase of molecular weights is noted compared with prestimulation values. This is consistent with our concept of asphaltenes stability and structure which favor polymerization rather than degradation. Thermogravimetric studies show that decomposition occurs by cleaving of alkyl groups, generally short ones from an aromatic nucleus, and that this occurs at an appreciable rate only when the temperature approaches 430°C or about twice steam temperature.

CONCLUSIONS

The 15 molecular weight profiles from 5 wells in 1 field show that substantial differences in asphaltene characteristics occur even prior to stimulation. This reinforces the notion of great local heterogeneity of geologic formations, oil brine distribution, and oil composition suggested by almost every detailed study of these topics. Such variation together with a lack of correct information on subsurface processes makes correlation of experiments or analyses very uncertain and limits the elaboration of mechanisms to explain field observations. Nevertheless GPC is of considerable assistance by allowing molecular weight profiles to be constructed for whatever inferences can be drawn within the framework of limitations just described. By confining the discussion to two apparently exceptional examples, a case is made for selective precipitation of asphaltene fractions by steam treating of a crude oil. An equally valid suggestion would be selective absorption of asphaltene by a steam-altered surface. In a second well the most likely explanation of productivity increase in the stimulation of a hitherto unproductive portion of the reservoir. Molecular weight profiles alone cannot predict steam stimulation results, perhaps because in this case the asphaltene content (about 5%) is lower than for many California groups (up to 20%). However, major differences in asphaltene molecular weight profiles during the steam cycle do occur and additional interpretations may become possible when additional subsurface information develops.

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