DEVELOPMENT AND EVALUATION OF PARAFFIN TECHNOLOGY: CURRENT STATUS

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INTRODUCTION

Production problems are plentiful in the oil and gas industry. A common one is production of organic solids where a solid phase forms out of the hydrocarbon liquid or gas. These organic solids take many forms (wax, asphaltenes, diamondoids), and their identification and treatment can be crucial to the exploitation of oil and gas fields. Refs. 1 through 4 discuss some of these problems.

Owing to the challenging nature of solids precipitation, techniques are always under development to identify the deposition of these solids more accurately. This article summarizes some of the more recent technologies and identifies the direction for future means of quantitative determination of solids precipitation.

BACKGROUND

Years ago, problems with solids precipitation were discussed in terms of paraffins or asphaltenes. This dichotomy resists change even today. When organic-solid precipitates are observed in the field, it is not uncommon for the operating engineer to contact the head office and indicate that an asphaltene-precipitation problem exists. When the operating engineer is asked why he or she thinks it is asphaltene, the answer is "because it's dark and it's a solid."

This often is an incorrect means of categorizing solids-precipitation problems. If solids are dark or black and if they cause production problems, they are categorized as asphaltenes. More specific evidence suggests that there is a continuum of organic-solids precipitation. The components that make up most solids precipitates extend from the lighter components, such as paraffins (which can possess molecular weights of less than 400), up to true multicyclic asphaltene molecules with molecular weights in the tens of thousands. Molecular weight, therefore, can be a means of differentiating between these types of solids. Because of the range of asphaltene types and molecular weights, however, molecular weight alone does not suffice for solids characterization.

Additional insight is available by identifying whether the solids are dependent on temperature or pressure changes. Intuitively, engineers recognize that a system where solids precipitation is dominated by temperature reduction probably would be a paraffin problem, whereas those that depend more on pressure change (compositional change) would be classified as asphaltene dominated. This, however, is not without ambiguity because, in many cases, systems that have some degree of temperature dependence may be predominantly asphaltene but the paraffin molecules may act as nucleation sites where the other more extensive and heavier asphaltenic-type molecules can grow and separate from the liquid phase. To identify onset and type of precipitation conclusively, laboratory testing ultimately must be performed. Some techniques for detection are discussed in the following.

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SOLIDS-PRECIPITATION DETECTION

Many improvements have taken place in the measurement of solids precipitation. Originally, the standard technique for determining cloudpoint temperature (the temperature at which solids begin to form) was to place the sample of oil in a temperature-controlled bath with a thermometer immersed in the subject phase. The temperature would then be decreased, and one would watch for a "clouding" to form in the oil, indicating the point of first deposition of microcrystalline suspended solids from solution. The name cloudpoint is derived from this clouding response. The results may vary, however, depending on the visual acuity of the individual watching the experiment. The technique can be enhanced further by conducting the evaluation under a microscope. On the microscopic level, precipitation initiation may be detected more precisely and the cloudpoint temperature identified more accurately. Nevertheless, the subjectivity associated with a visual measurement is still present.

Recently, visible-spectrum and near-infrared (NIR) -laser techniques have been used. **Fig. 1** illustrates an example cloudpoint analysis of an oil with a laser technique. The energy associated with the light transmitted through the sample is on the y axis. The temperature change, as recorded from a thermocouple immersed in the liquid phase, is plotted on the abscissa. Once the cloudpoint is encountered, a precipitous drop occurs in the laser light passing through the sample. The benefit of this laser-based technique is that it is easy to automate and becomes a quantitative measurement of a temperature-dominated solid-phase transition.

A limitation of this technique is that the optical characteristics of the fluid must be such that the light can be transmitted through the fluid; fluid opacity can be a limiting factor for laser systems. NIR laser devices are more effective than visual lasers at transmitting energy through opaque fluids because of their longer wavelength; however, there are still limits to their sensitivity.

Acoustic-resonance techniques also have been developed that respond to a broad range of opacity. The sensitivity of this technique depends on the change in sonic speed with phase transition and is therefore independent of fluid visual characteristics. **Fig. 2** shows the results of an acoustic measurement of cloudpoint with a cloudpoint indicated at 55°C. This same point was confirmed with laser and visual techniques. **Table 1** presents results obtained from NIR, optical laser, and visual techniques and from acoustic resonance. The results are encouraging for the acoustic-resonance approach.

IMPLICATIONS

Because presence of a solid phase does not necessarily mean that production problems will result, the question of why cloudpoint determination is important for paraffin-dominated systems might be asked. Some producing wells do exist that exhibit some solids precipitation but do not plug. However, if sensitive techniques are available for detecting the onset of solids precipitation, avoiding conditions conducive to solids formation constitutes a conservative approach. In our experience, even very small amounts of solids can represent serious production problems. For example, with only 0.5% mass solids detected in the laboratory, more than 600 kg of

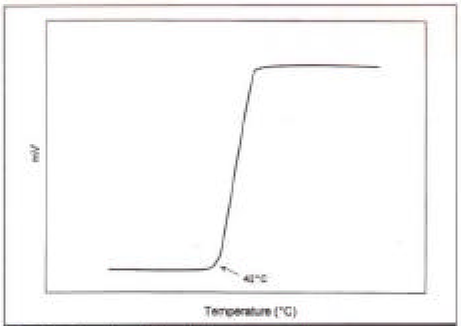

Fig. 1—Laser-based cloudpoint determination.

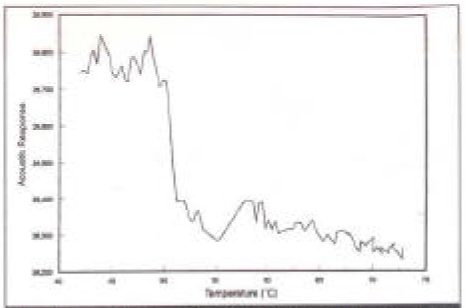

Fig. 2—Acoustic determination of cloudpoint for pure paraffin wax.

TABLE 1—CLOUDPOINT DATA FOR DIFFERENT WAXY OILS

	Technique			
Sample	NIR	Optical Laser	Conventional Visual	Acoustic
Pure American paraffin wax	—	—	55.0	55.4
Sample A	—	42.5	—	41.4
Sample B	34.0	—	—	35.7

Cloudpoint temperatures in °C.

solid phase formed in the field for every 160 m^3 of oil produced. Thus, the ability to determine the onset of solids formation is a requirement for all detection techniques.

On the basis of these types of technologies, a solids-precipitation envelope can be measured (**Fig. 3**). This is done by maintaining temperature while changing the pressure from a high to a low level, which allows detection of the liquid/solid transition. Thus, temperature/pressure conditions conducive to solids formation can be explored fully and reported.

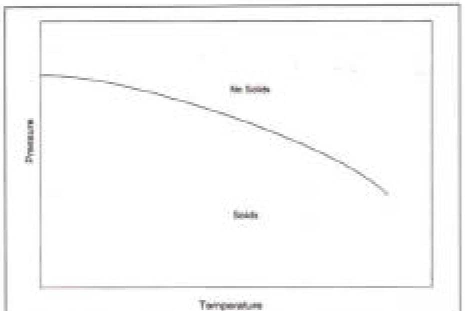

Fig. 3—Solids-precipitation envelope.

There are also a number of reservoirs worldwide that are significantly undersaturated. As a reservoir is depleted, the reservoir fluid comes closer to the solids-precipitation point. Once solids precipitation has occurred and solids begin to separate in situ, production problems (such as in-situ permeability reduction) can be observed. Thus, from an applications perspective, the importance of knowing the onset of precipitation is crucial.

Once precipitation conditions occur, some of the most common techniques to mitigate solids deposition are chemical and temperature manipulation. Results from recently conducted proprietary studies where a number of wax dispersants were tested indicated that the cloudpoint was suppressed by more than 30°C in some cases. By performing a series of tests, such as those identified in Figs. 1 and 2, the efficiency of certain chemicals can be tested rigorously.

Instruments are constantly under development to determine phase-behavior transition accurately for pipeline, wellbore, and production equipment. Some techniques are acoustic based, while others are light-scattering based. The techniques are applicable to many types of phase transition including dewpoints, bubblepoints and solid-phase transition.

CONCLUSIONS

Solids precipitation is an important problem in the upstream petroleum industry. Accurate technologies have been developed to identify solid-phase formation. With these techniques, optimal means of handling solids precipitation can be evaluated and optimized. **JPT**

REFERENCES

1. Katz, D.J. and Beu, K.E.: "Nature of Asphaltic Substances," *Ind. Eng. Chem.* (1945) **37**, 195.
2. Tissot, B., "Connaissance Actuelles sur les Produits Lourds du Petrole," *Rev. Inst. Français du Petrole* (1981) **36**, 429.
3. Won, K.W.: "Continuous Thermodynamics for Solid-Liquid Equilibria: Wax Formation from Heavy Hydrocarbon Mixtures," paper presented at the 1986 AIChE Meeting, 24–28 March, Houston.
4. Thomas, F.B. *et al.*: "Experimental and Theoretical Studies of Solids Precipitation from Reservoir Fluid," *J. Cdn. Pet. Tech.* (January 1992) **31**, No. 1, 22.

SI METRIC CONVERSION FACTORS

bbl × 1.589 873	E−01 = m^3
°F (°F−32)/1.8	= °C
lbm × 4.535 924	E−01 = kg

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