Memo

To: Marlene Huerta and Arjan Kamp
From: D.D. Joseph
Date: 12/08/98
Re: Discussion points for future research on foamy oil

FOAMY OIL

It is known that some oils called foamy produce an increased oil recovery and/or rate of production in solution gas drive.

- **What is Foamy oil?**

  I have not found any author who gives a useful definition of foamy oil where "useful" means a definition that leads to laboratory tests that can distinguish "foamy" oils from those which are not "foamy".

  In all of my reading I found two and only two characterizations of foamy oil:

  1. Maini (1996) and others say that "the term 'foamy oil' is often used to describe certain heavy oils produced by solution gas drive which display obvious foaminess in wellhead samples."

  2. Huerta et al. (1996), Smith (1998) and others, "Foamy oil may be loosely defined as heavy oil containing dispersed gas bubbles." Here is a definition of foamy oil which we ought to consider:

  •• A foamy oil is heavy oil that gives rise to stable dispersed bubbles under moderate depressurization and to stable foam under severe depressurization.

  Stable dispersed bubbles are protected against coalescence; at least they are resistant to coalescence. *Stable* foam means that foam doesn't collapse for a long time.

  Dispersed bubbles in foaming systems give rise to foam when the bubbles close pack at an interface under gravity (foam heads) or close pack in the bulk (in situ foaming) due to rapid nucleation of bubbles under severe depressurization. The transition from close packed bubbles to foam can be regarded as a topological phase change in which the trapped gas goes from bubbles to polygonal cells defined by thin films and plateau borders (see figure 1).

  The definition •• is operational in that we can carry out these depressurization tests in sand packs and in PVT cells. In PVT cells we can actually *rank order* foamy oils with quantitative measures of *foaminess* (foam height immediately after depressurization) and foam stability (the length of time it takes the foam head to collapse).

  It may be that there are light oils and even polar systems that fit the definition of "foamy". I propose to restrict our considerations to heavy oils found in reservoirs over the world.

Construction of a data base

Let's make a systematic collection of all the reports of good recovery and production under solution gas drive in reservoirs and laboratories world wide to see what are the common properties of these oils. It's surprising that this has not been done and it is an opportunity for us. We could frame our initial effort for this as a paper for the industry in SPE or elsewhere. It is also of great interest to make a database of heavy oils that don't foam and/or don't show improved production and recovery under solution gas drive.

- List of Venezuelan oils

  Zuata
  Cerro Negro
  Tiajuana
  Bachaquero Pesado
  probably there are many others

- List of Canadian oils

  Lloydminster
  || API crude methane   ⎱ Pouladi - Darvish
  Normal Decane methane ⎰   Firoozabadi
  Athabasca crude
  Cold lake bitumen
  Pace river bitumen
  Marguerite Lake
  Wolf Lake

- *Many other oils* from all over the world

What should be in our data base?

The goal here is to predict the oils that will exhibit good recovery and rate of production under solution gas from depressurization tests in a PVT cell. So we need to isolate the data that will distinguish between the oils we call very foamy from the less foamy ones. Here is a guess about what's needed:

  % Bitumen
  % Asphaltene
  % Resin
  % principal dissolved gasses (methane, etc.)
  GOR
  Viscosity as a function of dispersed gas fraction
  Solubility isotherms

The table sent me by Marlene Huerta and Lin Andarcia goes a way toward the presentation I have in mind. It provides a good platform for discussion.

Some physical characteristics of heavy oils

"SARA" Analysis of Venezuelan's heavy oils

Analysis	Hamaca MFB-356	Zuata SDZ-152	Tia Juana ** LSE-4878	Cerro Negro CI-210 (Bottom hole sample)	Cerro Negro CI-210 (Recombined sample)
% Saturated	16.1	16.0	16.4	13.5	12.8
% Aromatics	48.3	46.7	48.0	43.5	41.9
% Resin	22.6	26.1	24.6	30.4	32.4
% Asphaltene	13.0	11.2	11.0	12.6	12.9

** Tia Juana heavy oil doesn't show foamy oil characteristics.

The following data were extracted from the paper SPE-36749 "Understanding Foamy Oil Mechanisms for Heavy Oil Reservoir During Primary Production."

Initial GOR   106 scf/stb   =   18.88 ccgas/cc oil.

Oil volumbe factor "Bo"   1.0881 **RB/STB**.

"Bo" means the relationship between volume of the oil plus associated gas at reservoir conditions and the volume of the same quantity of oil at standards conditions. This factor helps us to know the total volume change of crude due to the partial molar volume of solution gas at every reservoir pressure and constant temperature.

RB means: "reservoir barrel", that is the total volume of crude at reservoir conditions.

STB means: "standards barrel", that is the total volume of the same "RB" quantity but at standards conditions (14.7 psi and 60°F).

The oil volume factor reported above was measured at 60°C (reservoir temperature) and bubble pressure.

For more information about oil volume factor look at "Applied Petroleum Reservoir Engineering", by B.C. Craft and M.F. Howkins, Second Edition, Prentice Hall Englewood Cliffs, NJ-07632, Chapter 1, Sec. 6.2. Pages. 34-37.

We can see that Tia Juana, which is said not to foam, has the smallest percentage of Asphaltene.

- **Some questions.** Do foamy oil solution drive favorable properties increase with % Asphaltene? In looking at the table you could note that Zuata has only a slightly larger % Asphaltene than Tia Juana. The question then is: does Zuata foam just a little more than Tia Juana and a lot less than Hamaca?

- **Solubility.** The fraction of liquified gas (say methane) in the oil at saturation is important. Solubility is a thermodynamic propery, a material property. You can have different, but convertible, measures of colubility; three measures are used.

GOR: volume fraction of the dissolved gas after it vaporizes = vol. released gas/vol oil. This is a large number because the gas volume is large.

Weight fraction (call it γ): Using moles, GOR is convertible to a weight fraction.

Volume fraction (call it ϕ): This is like GOR except that instead of using the volume of released gas, we use the volume of this same mass of gas when it is liquified.

The papers of Svercek and Mehrotra and of Peng, Fu and Bird give solubility both as γ and ϕ in different columns.

In Marlene's fax there is listed one value of GOR and Bo which must be for Hamaca. The values for GOR and Do for Zuata, Tia Juana, and Cerro Negro must be different. Arjan volunteered to write a small program to convert between the three measures of solubility. One of these measures should be given in another row of a canonical comparison table like the one in Marlene's fax.

FOAMINESS & FOAM STABILITY

We have already noted that the height of the head of foam above a crude after depressurization is a measure of foaminess. If we do the same depressurization on different oils we will get different values of foaminess. The "most" foamy oil is the one with the largest foaminess.

The second measure of relevance is foam stability which is measured as the length of time it takes a head of foam to collapse. Champagne gives rise to a big head, but it collapses rapidly. Foam stability may be the critical measure for ranking the performance of foamy oils.

Marlene says and I believe that the time to equilibrium in an unconventional PVT test is a measure of foaminess. This ought to be discussed.

Non-Polar Foams

An excellent paper on this subject is B. Maini and H. Sarma "Role of Nonpolar Foams in Production of Heavy Oils". *Advances in Chemistry Series* 1994, **242** pp. 405-420. They do two things; they give a good discussion of the factors that may stabilize non-polar forms and they do an experiment in a sand pack in which they get in situ foaming under depressurization.

Experiment

"The experimental results show that the in situ formation of nonaqueous foam retards the formation of a continuous gas phase and dramatically increases the apparent trapped-gas saturation. The condition provides a natural pressure maintenance mechanism and leads to recovery of a much higher fraction of the original oil in place under solution gas drive." Though they found increased recovery in their sand pack, they did not see an increased rate of production, so we are not out of the dark. Maini and Sharma do not distinguish between dispersed bubbles and foam yet they find rapid depressurization near the outlet and small pressure declines near the inlet. Maybe the sand pack looks like figure 1.

Conjecture about the stability of non-polar foams

Maini and Sharma discuss four possible mechanisms for the stabilization of non-polar foam: 1) bulk-viscosity of liquid phase, 2) Surfactant layers, 3) insoluble surface films and 4) poor solvents. The fundamentals of foam stability of foaming oil are not understood; the mechanisms mentioned by Maini and Sharma are nothing more than suggestions. I want to say a few words about mechanisms.

Foamy oils are very complicated and I think they are hard to model. The role of asphaltenes, resins, solubility, and surface films can be probed by theory and experiment. I don't know what new experiments can be done but I have some questions that ought to be addressed by experiments that can be formulated after the following discussion of Maini-Sharma mechanisms.
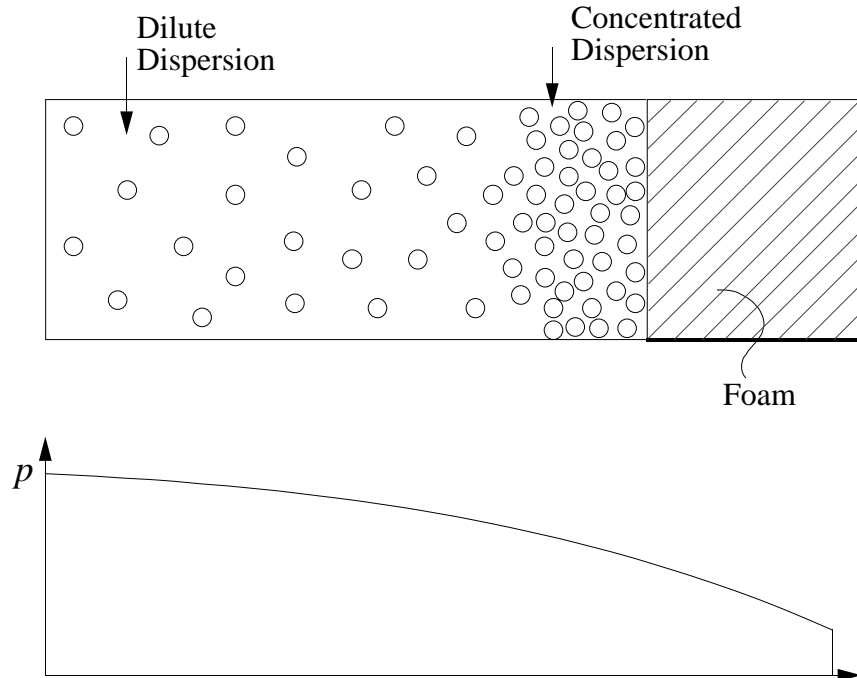
Figure 1: Possible distribution of trapped gas in the experiments of Maini & Sharma.

Mechanisms for stability of non-polar films

1. **Bulk liquid viscosity**. The more viscous the film, the slower the draining. *Bulk viscosity is not enough*, we can find many surpassingly viscous fluids that will not foam. Silicon oils don't foam. To make this point more strongly let's look at the following quotation from the paper, "Solution-Gas drive in Heavey-Oil Reservoirs" by M. Pooladi-Darvish and A. Firoozabadi. Dealy in *Canadian J. Chem Eng.* **57**, 677-683 (1979) studied the rheology of seven Canadian oil sand bitumens; of these the well known foamy Lloydminster crude had the *smallest* viscosity, by an order of magnitude.

   A silocone oil of viscosity of 30,000 cp was caturated with methane with a GOR of 6.5. Using a needle valve, about 42 g of the live oil was expanded into a graduated cylinder at atmospheric pressure. The same experiment was repeated for the heavy oil. In the silicone oil test, gas bubbles formed and coalesced very quickly, creating larger and larger bubbles which floated to the surface and broke away. Withing 30 minutes virtually all of the gas had escaped the silicone oil. The behavior of the heavy oil (50,000 cp, GOR = 6.5) was different. It took about two orders of magnitude longer (50 hours), for the volume of the oleic phase (oil and the dispersed gas phase) to decrease to its final value.

2. **Surface active agents.** This is the usual mechanism which applies to aqueous foams and relies on Maragnoni effects expressed by Gibbs elasticity to oppose drainage. If there are surfactants in crude oil they are not polar and the molecules that are acting amphillic have not been identified in crude oil. Asphaltenes are said to be amphillic in some of the papers I have read, but the meaning of "amphilic" for aslphaltenes in dispersions of methane bubbles in crude oil is not understood by me.

3. **Insoluble surface films.** Maini and Sharma talk about the formation of liquid crystal films studied by Friberg. Clay Radke told me that asphaltenes form films on crude oil; he says all the old workers knew it but there is not a large literature on it. If there really are films, interfacial viscosities exist and may be important.

4. **Incipient phase change.** Ross has done work to suggest that foaminess increases in mixtures near to points of phase separation; they don't say how this may apply to foamy oil. This might suggest that polymers in poor solvents foam more than polymers in good solvents.

Some questions about stability of non polar films

1. Are asphaltenes amphillic in the sense that one part of them likes methane gas and another part bitumen?

2. Do asphaltenes absorb at a methane-bitumen interface? Isn't it true that the existence of an alphaltene film implies such an absorption or concentration?

3. Is there an equivalent of micelles; that is "asphaltene micelles" in the bitumen? Is there anything like a CMC in bitumen with asphaltenes?

4. Are there really asphaltene films at a bitumen methane surface? If there are such, does the asphaltene film facing bitumen like bitumen better than the face facing gas?

5. How is the idea of an asphaltene film reconciled with the idea of an asphaltene network in the bulk?

RHEOLOGY OF FOAMY OIL

Foamy oil is a multiphase material; the presense of different phases complicates the rheology. To simplify the discussion we can start with the

Rheology of dead oil. Dead oil has no dissolved or dispersed gas; we can consider dead oil to be a single phase fluid, though it does have a complicated composition. Rheology is the science which describes the way a given material deforms under the application of stresses. The rheology of multiphase materials is complicated because each distribution of phases in the material leads to a different material and if the distribution of phases changes during deformation the properties of the material will change. For example, oil and water in a pipeline may be transported as oi/water emulsion or a water/oil emulsion, in core-annular flow with water outside and in other nodes. Each of these has a very different resistance to flow. If we try to calculate the viscosity of an oil/water emulsion we will find a number largely different than water/oil emulsion and each will be different than in core-annular flow.

Dead oil

The rheology of dead oil appears not to be very complicated because large viscoelastic effects which are responsible for normal stresses in shear and memory effects in which the present stress depends on the history of the deformation. We have done some tests of even live Zuata and Cerro Negro and found that the viscoelastic effects are small. (Núñez, Ribeiro, Arney, Feng and Joseph, Rod climbing and normal stresses in heavy crude oils at low shears. *J. Rheology, 38 (5), 1251-1270 (1994)*). The aforementioned paper by Núñez gives other references which deal with the rheology of crude oil.

   The main non-Newtonian property of heavy crudes which are not waxy appears to be shear thinning. The waxy crudes exhibit yield stress behavior not seen in heavy oils with small wax content. The oils of the Orinoco belt appear to behave like the Alberta bitumens. J.M. Dealy, Rheological properties of oil sand bitumens, *Canadian J. Chem Eng.*, **57**, 677–683 (1979), measured standard rheological data for different Alberta bitumens and concluded that these oils were only mildly Newtonian at low rates of shear. A rather remarkable decrease in viscosity for intermediate shear rates, of the order of one reciprocal second, led Dealy to some conclusions about the nature of the microstructure. He calls attention to the importance of interactions between maltenes and asphaltene. He says ". . . it seems very likely that the variation in viscosity is a result of the inter-molecular de-aggregation and not changes in molecular conformation as in polymer solutions. (The viscosity graphs will fit (1) below very well, not noted by Dealy.) Dealy also observed a strong temperature dependence of shear viscosity. A very complete collection of references on the rheology of crude oils is given by Dealy. His paper is important for us.
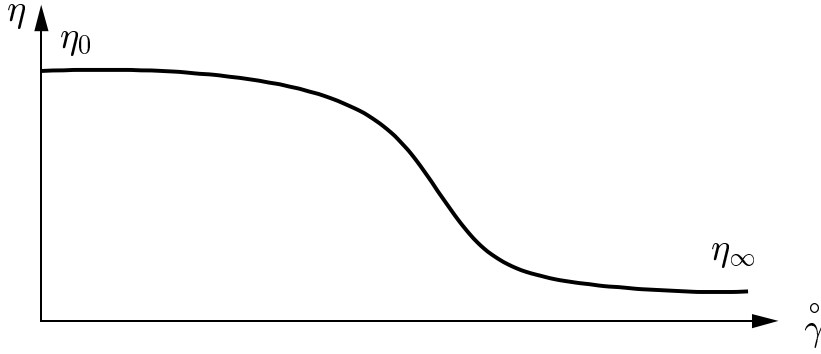
Figure 2: Carreau-Bird graph for shear thinning fluid.

Live oil

Live oil contains dissolved or liquified gases. The liquified gases can be thought to be miscible in the crude and, as we have already noted, the solubility or fraction of the solution that is liquid gas is a thermodynamic property determined by pressure and temperature. When no dispersed gas is present we may think of these liquid gas, bitumen mixtures as a single phase fluid like well mixed glycerin and water. The remarks made about dead oil might apply also to live oil with the caveat that the addition of liquified gases (CO_2, Methane, Nitrogen) reduces the viscosity of the live oil by orders of magnitude. These huge decreases in viscosity which are documented in the work of Svercek & Mehrotra and others is just what you would expect from say, the addition of water to glycerine.

Constitutive models for dead oil and live oil without dispersed gas

The Herschel-Bulkley (HB) model is a very popular description of drilling fluids. It takes into account yield stresses and the shear rate dependence on viscosity. It would be reasonable to fit crude oil data to HB models, but for the non-waxy crudes that are no yield values so that shear thinning alone remains. To describe this I recommend a Carreau-Bird formula for the viscosity η

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + (\lambda_3 \overset{\circ}{\gamma})^2\right]^{\frac{n-1}{2}} \tag{1}$$

where $\overset{\circ}{\gamma}$ is the shear strain rate, η_0 is the zero shear viscosity, n is the power law index and $n \leq 1$ with equality for Newtonian (no shear thinning) fluids and λ_3 is a fitting parameter.

Values of viscosity for dead and live oils should always specify the shear rate $(\overset{\circ}{\gamma})$ and temperature at which the measurement was taken.

Live oil with dispersed gas

The viscosity of a live oil with dispersed gas depends on how the dispersion is placed. We can consider the viscosity of a uniform dispersion, such as arises in *nonconventional* PVT cells. In general, the viscosity would be expected to increase with the volume fraction of dispersed gas. Another case is when the dispersed bubbles foam; the foam does not flow like a dispersion but has a quite different rheology.

We have to be aware that the pressure drops in capillary rheometers could induce outgassing which would effect the viscosity measurement.

At the psuedobubble point at which the coalescence of gas bubbles becomes important we could get fingers of gas. viscosity measurements for very inhomogeneous materials like those which arise from coalescence may not be very useful.