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EXPERIMENTAL AND CMG STUDY OF ASPHALTENE PRECIPITATION UNDER NATURAL DEPLETION AND GAS INJECTION CONDITIONS

Reza Hashemi[1], L. K. Kshirsagar[1], Somnath Nandi[2]*, P. B. Jadhav[1], Elias Ghaleh Golab[3]*

[1] *Department of Petroleum Engineering, Maharashtra Institute of Technology, Paud Road, Kothrud, Pune - 411038, India*
[2] *Department of Technology, Savitribai Phule Pune University, Ganeshkhind, Pune - 411007, India*
[3] *Department of Petroleum Engineering, Omidiyeh Branch, Islamic Azad University Omidiyeh , Iran*

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Abstract

Problems associated with asphaltene deposition are key challenges for the upstream industry. In this research work, systematic experimental studies of asphaltene precipitation were conducted for two different Iranian crude reservoirs. Though gas injection in the reservoir enhances the crude productivity, it leads to higher precipitation of asphaltene compared to the natural depletion conditions. State of the art software tool namely CMG was utilized to predict the performance of the reservoirs for natural depletion condition as well as at high gas injection conditions. The CMG based predictions matched well with the experimental observations for both the reservoirs with reasonable accuracy.

Keywords: *Asphaltene precipitation; Gas injection; CMG; Simulation; Enhanced oil recovery.*

1. Introduction

Crude oil trapped in reservoir rock matrix is a complex mixture of hydrocarbons of various molecular weights, though sometimes other organic compounds containing small quantities of hetero atoms like nitrogen, oxygen, and sulfur are also present. The composition of crude varies based on its location as well as its maturity. Main constituents of crude oil are saturated hydrocarbons, aromatics, resins and asphaltenes (SARA). Asphaltenes are heterocyclic unsaturated macromolecules consisting primarily of carbon, hydrogen, and a minor proportion of hetero elements such as oxygen, sulfur, and nitrogen. It is really difficult to measure the molecular weight of asphaltene accurately due to its complex composition and the chemical association behavior [1]. Apart from causing the reservoir formation damage, asphaltene deposits could also result in reversal of the rock wettability to oil-wet, which leads to a lower recovery factor [2].Deposition of asphaltenes in oil wells, pumps, flow lines, pipelines, and production facilities can reduce well productivity, damage pumps, restrict or plug flow line and pipelines and foul production handling facilities [3-4].The precipitation phenomena can change the wetability of the formation of rock from water wet to oil wet which hinders the oil recovery efficiency [5]. Precipitated asphaltenes may also build-up in the near wellbore, reservoir rock and clog the porous matrix of the reservoir during drilling and chemical treatment [6].Injection of miscible or partially miscible gases is a promising enhanced oil recovery technique for many reservoirs. However,earlier studies indicated that the injection of gases namely carbon-dioxide (CO_2), nitrogen (N_2) and hydrocarbons like methane (CH_4), etc. changes the solubility of heavy components in the reservoir oil and causes asphaltene instability [7-9].Knowledge of asphaltene thermodynamic behavior is essential to understand the deposition characteristics. For the effective performance of a producing reservoir and to optimize the production, it is necessary to have accurate predictions of the amount of asphaltene precipitation as a function of the amount of solvent, temperature, and pressure, etc. [10]. The paper deals with a systematic investigation of asphaltene deposition for two reservoirs in Iran. A simulation study based on

Computer Modeling Group (CMG) WinProp module is also conducted in order to predict the asphaltene deposition at various operating conditions.

2. Experimental

Crude samples were taken from two south Iranian oil reservoirs Rag Sefid and Aghajari field, their properties are reported in Table 1. Reservoir fluid compositions and other basic properties were determined by means of the GC-MS (Gas-Chromatography Mass-Spectroscopy) technique and differential liberation tests. The samples were also determined for weight percent's of saturates, aromatics, resins, and asphaltenes. The compositions of the crude samples and the SARA analysis are presented in Tables 2 and 3 respectively.

Table 1. Properties of crude oil samples

Sample	Unit	Aghajari	Rag Sefid
Reservoir temperature	°F	158	212
Saturation pressure	PSIA	2715	2853
Solution GOR	SCF/STB	560	479
API gravity of residual oil	°API	25	22
Reservoir pressure	PSIA	4890	4158

Table 2. Composition of oil samples

Component	Mole percent		Component	Mole percent	
	Aghajari	Rag Sefid		Aghajari	Rag Sefid
H_2S	0.47	2.4	C_6	4.55	5.4
N_2	0.12	0.11	C_7	4.46	3.7
CO_2	2.33	4.94	C_8	3.85	4.28
C_1	38.83	24.01	C_9	2.27	2.87
C_2	6.06	6.89	C_{10}	2.41	2.73
C_3	5.9	5.51	C_{11}	2.56	2.68
i-C_4	1.04	0.9	C_{12+}	19.36	28.18
n-C_4	2.83	2.87	MW of C_{12} fraction	498	432
i-C_5	1.33	1.22	MW of reservoir oil	115	152
n-C_5	1.63	1.31	SG. of C_{12+} fraction @60/60°F	0.961	0.981

Table 3. SARA analysis

Sample	Unit	Aghajari	Rag Sefid
Saturated	wt%	59.58	32.90
Aromatic	wt%	26.12	39.85
Resin	wt%	6.3	12.02
Asphaltene	wt%	8.9	14.4

2.1. High Pressure High Temperature System (HPHT)

Asphaltene weight precipitation change by pressure is detected by High Pressure High Temperature (HPHT) Filtration device and associated IP143 tests [11]. An HPHT filtration system was available to perform natural depletion and with an injection of various gases namely nitrogen (N_2), carbon dioxide (CO_2), and methane (CH_4) injection tests under reservoir temperature. The system can provide reliable result until the pressure range of 10000 psi and temperature up to 482°F. The experimental set up, as represented by Fig.1, comprises of a Pressure-Volume-Temperature (PVT) cell, shaker, hydraulic pump, high pressure metal filter, oven, pressure transducer, high pressure sampler, pressure gauges, and recombination cell system, micron metal filter for the separation of asphaltene particle from original fluid sample in PVT cell.

In these sets of experiments, a conventional pressure depletion process was performed at the reservoir temperature for natural depletion. The experimental procedure in this step is described as follows:

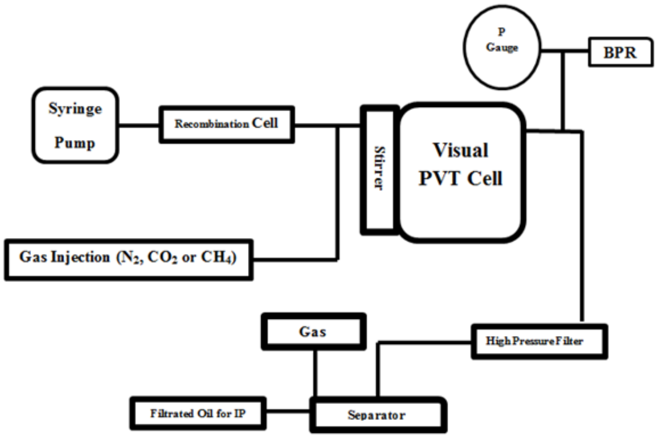

Figure 1. Schematic of the experimental setup

The equilibrium cell was carefully and properly cleaned and set at reservoir temperature. For RagSefid reservoir, the temperature is 212°F, and for the Aghajari reservoir, the temperature is 158°F. The intended oil was first filtered through a proper filter paper to separate any solids present in the oil and then inject into the cell under single phase conditions at reservoir pressure. A magnetic stirrer was used to shake the oil sample for 24 hr and speed up the equilibrium process. The cell pressure was lowered in subsequent predefined steps; at each stage, a high pressure filtration process was performed with a 0.5 filter paper. A limited volume of the sample around 10 ml for each pressure step was allowed to flow into the filter manifold at constant pressure and temperature. In order to avoid alteration of the asphaltene solubility, only a small dropping pressure should be applied around the filter. High pressure helium was applied to sustain a back-pressure on the downstream of the filter so that the fluid sample can flow gently through the filter with only a small pressure drop.

The oil which filtered injected in a separator and the asphaltene amount of the remaining oil is measured by standard IP143 procedure. The difference between the amount of asphaltene of the original sample and the filtered oil at each pressure determines the weight percent of precipitated asphaltene. The weight of precipitated asphaltene is then divided by the weight of the oil sample that is used in the IP143 procedure to give the weight percent of precipitated asphaltene. Since the experimental procedure is set to determine the amount of asphaltene of the filtered fluid, the asphaltene deposition problems in the equilibrium cell and the connection flow lines do not affect the precision of the experiments, and trustworthy data could be collected. Result for natural depletion is represented in Figures 2 and 3 for the crude sample from Rag Sefid and Aghajari oil fields respectively.

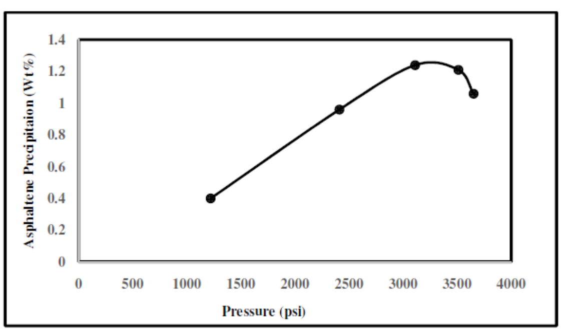

Figure 2. Natural depletion in Rag Sefid sample at its reservoir temperature, 212°F

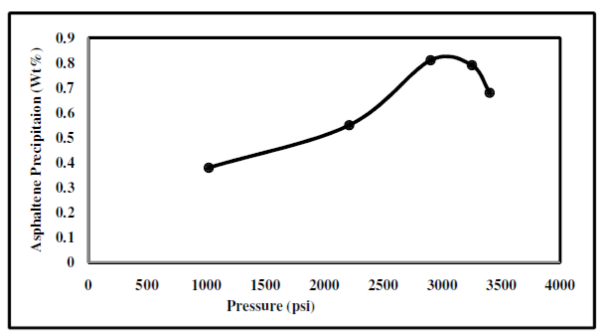

Figure 3. Natural depletion in Aghajari Sample at its reservoir temperature, 158°F

2.2. Gas injection

In this stage, a set of experiments were carried out to study the effect of different agents on the asphaltene precipitation behaviour of oil samples through the gas injection process. In these experiments, N_2, CO_2, and CH_4 gases were used systematically for infusion in miscible conditions. A known volume of new oil was injected into the equilibrium cell at the reservoir temperature while the cell pressure is set above the mixture saturation pressure to avoid phase separation during fluid transfer and recombination of oil and gas samples. In the present investigation, a small amount of gases (N_2, CO_2, or CH_4) was injected separately into the cell under isothermal conditions. The mixture was permissible to equilibrate and settle down for 24 h to ensure full asphaltene precipitation. A high pressure filtration was presented to quantify asphaltene precipitation as a function of pressure. The sampling, filtration, and estimation processes were similar to natural depletion experiments.

3. Results and discussion

To test the effect of nitrogen injection on asphaltene instability, 10 mole percent of N_2 was recombined with Rag Sefid reservoir oil sample at a reservoir temperature of 212ºF. N_2 injection was repeated for the same sample with 15 and 20 mole percent of N_2 at the reservoir temperature of 212ºF. In the similar lines, to understand effects of nature of gas on asphaltene precipitation, other gases namely CO_2 and CH_4 injection were carried out at 10 mol %, 15 mol %, and 20 mol % concentrations. The observations are reported in Figures 4, 5 and 6. It has been observed that with an increase in gas injection, asphaltene precipitation increased. The same procedure was performed with the Aghajari field oil sample with the injection of 10, 15, 20 mole percent at the reservoir temperature of 158ºF. The respective results are reported in Figures 7, 8 and 9 respectively. As evident from these figures, increased gas injection enhances asphaltene precipitation, and it has also been observed that the precipitation is maximum with CO_2 injection and least with methane (CH_4) gas injection (please refer to Figures 4 – 9).

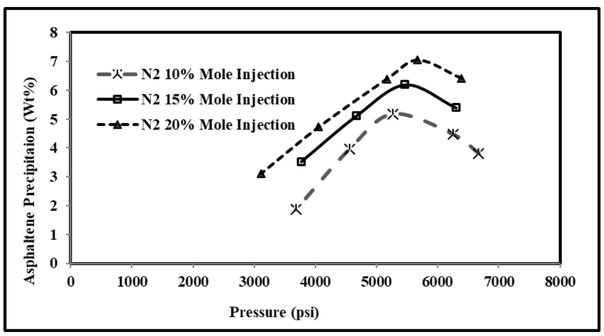

Figure 4. Effect of N_2 injection on asphaltene precipitation for Rag Sefid sample

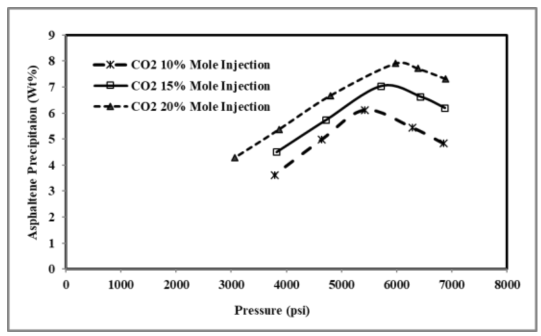

Figure 5. Effect of CO_2 injection on asphaltene precipitation for Rag Sefid sample

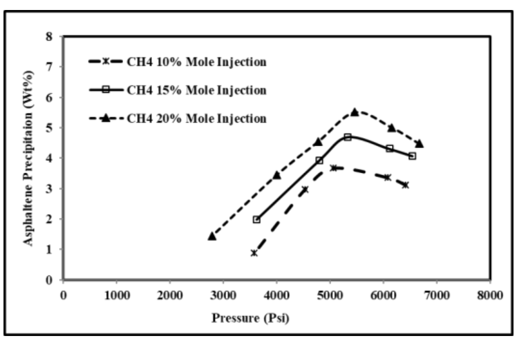

Figure 6. Effect of CH_4 injection on asphaltene precipitation for Rag Sefid sample

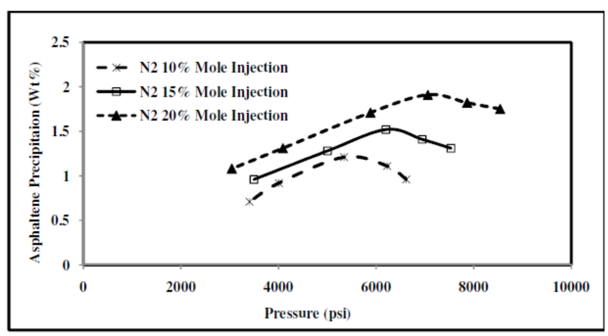

Figure 7. Effect of N_2 injection on asphaltene precipitation for Aghajari sample

Results of Figures 4, 5, 6 indicates that at lower pressures than bubble point pressure, the asphaltene re-dissolution decreases with increasing concentrations of gases and this is due to the formation of complex cluster structures of asphaltene molecules. With increasing pressure, at a pressure below the critical point pressure, the amount of precipitate in the constant concentration of gas increases, and with increasing concentrations of injected gas, this amount of precipitate will be increased. When the injection pressure reaches the point of the bubble point, the maximum amount of asphaltene precipitation will take place, and this precipitation will increase with the increased mole percentage of the gases as evident from Figures 4 for N_2 injection for the Rag Sefid reservoir sample. The identical trend is observed for CO_2 and CH_4

injections as evident from Figures 5 and 6. At higher pressures than that of the bubble point pressure, the amount of deposition is reduced, as the solubility of asphaltene is increased and hence the amount of precipitation will be reduced [5].

But it should be kept in mind that the total precipitate generated will not be disolved again, and this amount of precipitate will be greater than the amount of precipitate produced at the lowest pressure from the bubble pressure. With increasing pressure below the bubble point, the number of precipitate increases, since under these pressures, cluster deposits with complex compounds are created and increase with increasing pressure, preventing the dissolution of precipitates in oil. At the bubble point pressure, the highest precipitate concentration is generated for all the gas concentrations of 10, 15, 20 mole percent injections. It needs to be mentioned that with the increased amount of injected gas to the initial crude sample, the composition will be changed causing an increase in bubble point pressure (P_b). Therefore, with enhanced gas injection, the composition changes leading to the greater amount of asphaltene precipitation. But at higher pressures above the bubble point, the amount of dissolution of the precipitates increased due to the breakdown of the complex cluster structure formed at lower pressures [9].

With the lowering of the reservoir temperature, the mobility of asphaltene molecules in the system will be reduced, and therefore there will be less likelihood of the collision of the asphaltene molecules in the solution. Hence, the rate of clustering of the asphaltene molecules and, consequently, their precipitation will be decreased; it is evident from Figures 2 and 3 as the temperature is reduced, asphaltene precipitation is reduced from 1.3% to 0.8% for normal depletion conditions. The same trend is observed for gas injection conditions also, as evident from comparison of Figures 6 and 9, both with methane (CH_4) injection, while for Rag Sefied field asphaltene precipitation is almost 6% with 20 mol% gas injection vis-à-vis only 1.5% precipitation for Aghajari reservoir which operates at much lower temperature.

4. Simulation study

It will always be beneficial for operational purpose if a mathematical model is available which can predict the asphaltene precipitation with sensible precision. The WinProp module of CMG software was utilized to model and predict the asphaltene precipitation based on experimentally obtained data. CMG group has employed a pure solid model [12], and it can predict the asphaltene precipitation for the natural depletion condition and that for different gas injection conditions. The CMG WinProp package computes fugacity of asphaltene – expressed as pure, dense solid phase represented by Eqn. 1:

$$\ln f_s = \ln f_s^* + \frac{v_s(P - P^*)}{RT} \qquad (1)$$

The prediction is valid for isothermal reservoir conditions of normally depleting reservoirs as well as for the enhanced oil recovery mechanisms via gas injections. As per guidelines [13], the heaviest oil fraction is to be spitted into two components one will be precipitating while the other one is a non-precipitating component. Though they have identical properties but these sub-fractions behave differently with light components, the precipitating fraction has higher interaction coefficient with light hydrocarbons. At the onset pressure for a given temperature as noticed experimentally, fugacity of the precipitated fraction is obtained utilizing equation of state (EOS). This fugacity is considered to be the reference fugacity of precipitation in Eqn. 1. Subsequently, the mole fraction of the precipitating fraction is obtained using Eqn. 2:

$$x_{Asph} = \frac{w_{Asph} \times MW_{Crude}}{MW_{Asph}} \qquad (2)$$

where w_{Asph} denotes weight fraction of asphaltene present in the crude sample having molecular weight MW_{Crude}, the molecular weight of asphaltene is represented by MW_{Asph} and x_{Asph} is the mole fraction of asphaltene precipitated.

For modeling, the used matching parameters are solid molar volume and interaction coefficients between precipitating component and light end components of crude oil. Solid molar volume affects the amount of precipitation at bubble point; higher molar volumes result in higher precipitation values. Interaction coefficients between precipitating and light end hydrocarbons control the precipitation and re-dissolution of asphaltene at pressures below the saturation pressure. Modeling results for natural pressure depletion experiments for both the reservoirs are represented in Figures 10 and 14 respectively. Results of asphaltene precipitation modeling for 20% nitrogen, 20% carbon dioxide, and 20% methane for the Rag Sefid reservoir are provided in Figures 11, 12 and 13. In all these plots, experimental values are provided for effective comparison; it is evident that almost all cased CMG simulation able to pick up the trend well. Similarly, CMG simulations for Aghajari oil samples were performed, and the trend obtained are represented along with the experimental observations in Figures 15, 16 and 17, though there are some deviations, the overall trend is picked up. The significant observation is that the CMG simulation can able to correctly predict the trend of the highest amount of asphaltene precipitation for CO_2 gas injection and the least one for methane injection as observed experimentally (kindly refer to Figures 16 and 17).

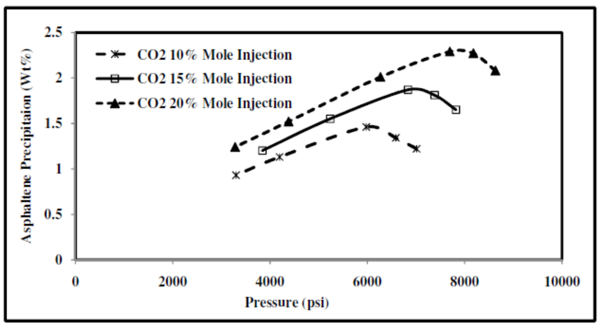

Figure 8. Effect of CO_2 injection on asphaltene precipitation for Aghajari sample

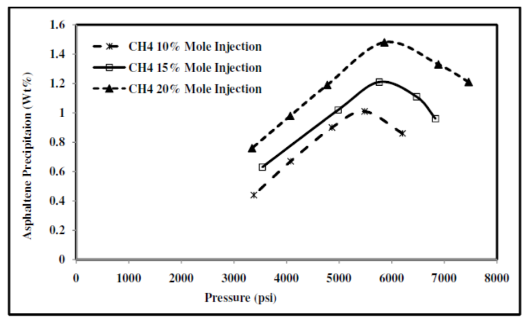

Figure 9. Effect of CH_4 injection on asphaltene precipitation for Aghajari sample

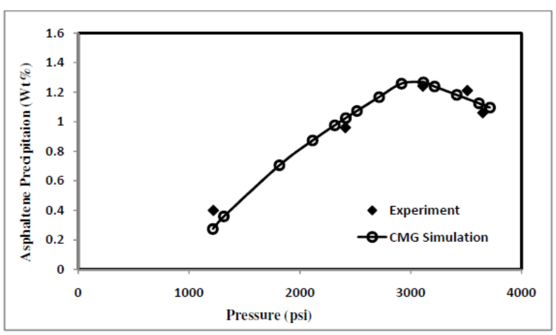

Figure 10. CMG WinProp predictions for natural depletion process in Rag Sefid sample

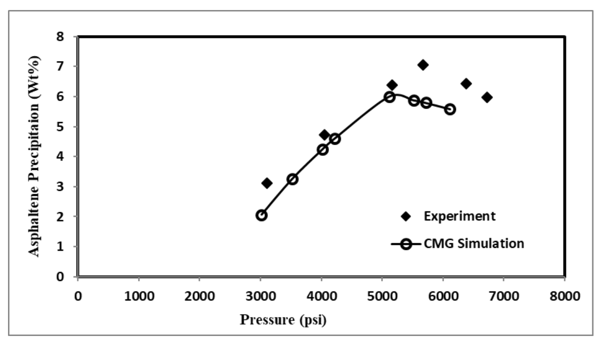

Figure 11. CMG WinProp predictions for 20% N_2 gas injection process in Rag Sefid sample

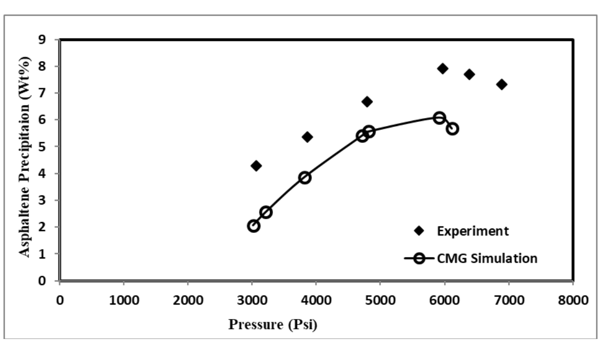

Figure 12. CMG WinProp predictions for 20% CO_2 gas injection in Rag Sefid sample

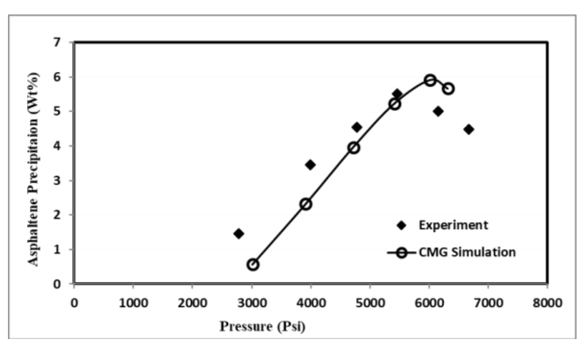

Figure 13. CMG WinProp predictions for 20% CH_4 gas injection in Rag Sefid sample

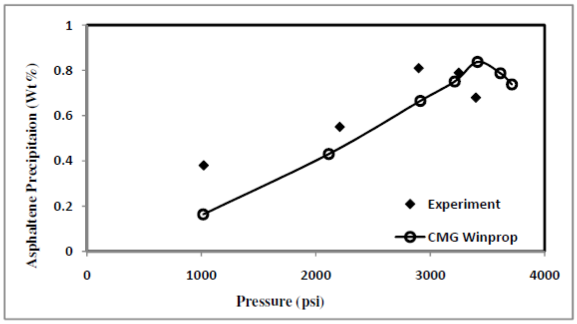

Figure 14. CMG WinProp predictions for natural depletion process in Aghajari sample

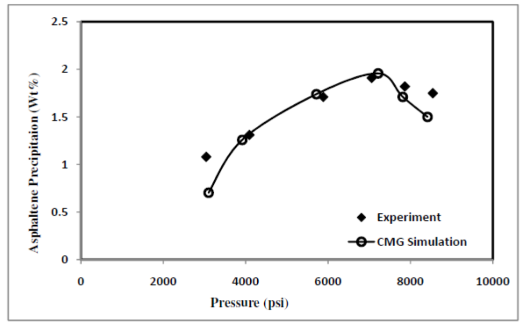

Figure 15. CMG WinProp predictions for 20% N_2 gas injection in Aghajari sample

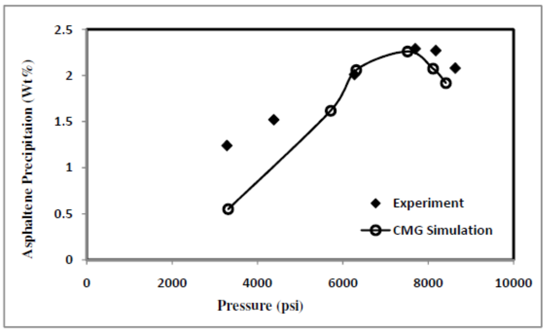

Figure 16. CMG WinProp predictions for 20% CO_2 gas injection in Aghajari sample

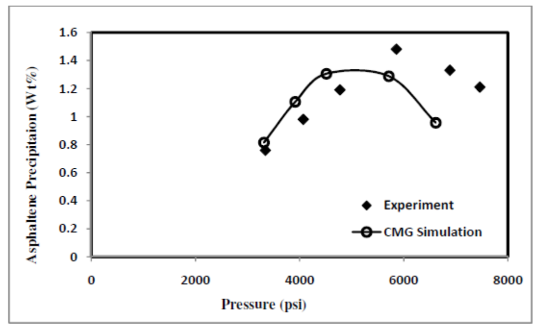

Figure 17. CMG WinProp predictions for 20% CH_4 gas injection in Aghajari sample

5. Conclusion

While the crude reservoirs are injected with CO_2, N_2 and CH_4 gases for enhanced oil recovery, the maximum amount of asphaltene precipitation is reported with CO_2 injection, and minimum amount of asphaltene precipitation is noticed with CH_4 gas injection. Increase in the concentration (mole percent) of gas injection caused an increased amount of asphaltene precipitation for both the crude samples. The experimental observation was well supported by CMG simulations. Below the bubble point pressures, the amount of asphaltene precipitation increased with the increasing pressure. Whereas, above the bubble point pressure the amount of asphaltene precipitation decreases with increasing pressure. A detailed and systematic study of Rag Sefid reservoir and Aghajari reservoir oil samples were conducted in the presence of gas injection. The study will be beneficial in designing the enhanced oil recovery mechanism of the fields using gas injection techniques.

Symbols

API	*Crude specific gravity*	*(°API)*
f_s	*fugacity*	*kPa*
f_s*	*Reference fugacity*	*kPa*
MW	*Molecular weight*	*g/mol*
P	*Pressure*	*psi*
P_b	*Bubble point pressure*	*psi*
R	*Gas constant*	*8.314 J/mol. K*
T	*Absolute temperature*	*K*
v	*Molar volume*	m^3*/mole*
w	*Weight fraction of asphaltene precipitated*	*(-)*
x	*Mole fraction*	*(-)*

Subscripts

Asph Asphaltenes *Crude Crude sample*

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To whom correspondence should be addressed: Dr. Somnath Nandi, Department of Technology, Savitribai Phule Pune University (formerly University of Pune), Ganeshkhind, Pune – 411007, INDIA