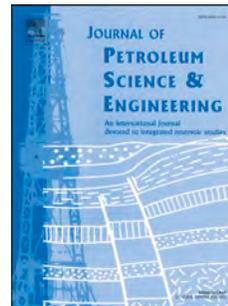


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Harshkumar Patel, Subhash Shah, Ramadan Ahmed



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## Effects of Nanoparticles and Temperature on Heavy Oil Viscosity

Harshkumar Patel, Subhash Shah, and Ramadan Ahmed, The University of Oklahoma; Ucan Sezai, YPF

### Abstract

1 The objective of this research is to investigate the efficacy of nanoparticles in reducing the viscosity of  
2 heavy oil. In this study, three types of metal oxide nanoparticles (CuO, Fe<sub>2</sub>O<sub>3</sub>, and NiO) are employed, and  
3 their effect on heavy oil viscosity is examined at three different concentrations (0.05, 0.1, and 0.5 wt.% of  
4 oil). For all test fluids, rheological measurements were obtained at four different temperatures ranging  
5 from 27 to 71°C. The experimental work is conducted with two extremely viscous heavy oil samples having  
6 viscosity of approximately 77 and 350 Pas at ambient temperature. This study is unprecedented in terms of  
7 viscosity of heavy oil samples investigated. The heavy oil samples used in this study are 9 to 40 times more  
8 viscous than those used in previous similar studies.

9 The addition of nanoparticles resulted in a notable reduction in viscosity of both heavy oil samples.  
10 For each type of nanoparticles, 50 to 70% viscosity reduction was observed. The level of viscosity  
11 reduction is sensitive to the types of nanoparticles, their concentration, and fluid temperature. Moreover,  
12 the results indicate existence of an optimum concentration of nanoparticles at which maximum viscosity  
13 reduction occurs. This optimum concentration is a function of the metal type and fluid temperature.

14 To explain observed viscosity alteration behavior, the paper provides a theoretical overview of  
15 various molecular-level physical and chemical interactions between nanoparticles and heavy oil.  
16 Additionally, the study presents a new heavy oil viscosity data and delineates some of the challenges  
17 associated with viscosity measurement of heavy oil.

18 This research provides valuable information for future rheological and core-flooding studies  
19 involving nanoparticle stabilized solvent-based emulsions. Besides, remarkable viscosity reduction  
20 obtained in this work reinforces the industry's interest in developing an economically feasible  
21 nanoparticle-based technique and helps to solve real problems in the field.

22 **Keywords:** Heavy oil, nanoparticles, rheology, viscosity reduction, oil recovery, optimum concentration  
23  
24

## 1 **1. Introduction**

2 Heavy oil, extra heavy oil, and bitumen constitute about 70% of worlds' total oil reserves (Schlumberger,  
3 2006); yet, most of it has remained untapped. The primary reason is high viscosity reduces their mobility  
4 and results in commercially unfavorable low-productivity wells. Thermal recovery techniques often used  
5 to recoup these reserves involve introducing heat into reservoirs to reduce oil viscosity. However, the  
6 methods have limited commercial application because of high costs, low efficiency, technical complexity,  
7 and operational challenges. Non-thermal means such as pump assisted production, cold production with  
8 sand, horizontal and multilateral wells, or water flooding have primarily been neglected due to low  
9 recovery.

10 With emerging of nanotechnology, many research efforts are being directed toward employing  
11 nanoparticles in improving heavy oil recovery. The use of nanoparticles with heavy oil is not new. The  
12 earlier applications of nanoparticles were primarily as catalysts to improve the efficiency of ex-situ  
13 upgrading of heavy oil and bitumen. The first comprehensive efforts to employ nanoparticles for  
14 enhancing heavy oil recovery were made by Clark et al. (1990). They used metallic nanoparticles to  
15 improve production in steam stimulation process. To date, several researchers (Farooqui et al. 2015;  
16 Hascakir et al., 2008, 2010; Li et al. 2007; Shokrlu and Babadagli, 2010, 2011, 2014) have confirmed the  
17 benefits of using metallic nanoparticles to improve thermally assisted heavy oil recovery techniques. At  
18 high temperatures (typically >100-150°C), metallic (Ni, Cu and Fe) nanoparticles, initiate aquathermolysis  
19 process, which transfers hydrogen from steam to oil via water gas shift reactions (WGSR). The process  
20 results in hydrolysis of C-S bonds and eventually reduction of oil viscosity (Fan et al., 2004, 2002; Muraza  
21 and Galadima, 2015). In addition to upgrading heavy oil by cleavage and removal of Oxygen, Sulfur, and  
22 Nitrogen derivatives, nanoparticles have also been identified to increase thermal conductivity.

23 Almost all the research work so far has been focused on the high-temperature (>120°C) effects of  
24 nanoparticles in which catalytic properties of nanoparticles play the more dominant role than their  
25 viscosity reducing the behavior. Surprisingly, very limited research has been undertaken to examine the  
26 application of nanoparticles in non-thermal recovery. Few recent studies have indicated that nanoparticle  
27 can alter heavy oil viscosity even at ambient temperature (Hascakir et al., 2010; Shokrlu and Babadagli,  
28 2014; Srinivasan and Shah, 2014).

29

Hascakir et al. (2010) examined the effects of three types of iron powders (Fe, Fe<sub>2</sub>O<sub>3</sub>, FeCl<sub>3</sub>) on heavy oil viscosity and observed notable viscosity alteration even without heating the oil. For example, the addition of 0.5 wt.% Fe<sub>2</sub>O<sub>3</sub> resulted in 37 % viscosity reduction in the first sample and interestingly increased the viscosity of the second sample by 15%. Shokrlu and Babadagli (2014) studied the effects of Cu, Fe, and Ni particles for thermal application in absence and presence of aqueous medium such as steam. They also observed viscosity reduction by nanoparticles at ambient temperature. They reported a maximum viscosity reduction of 10% with Canadian heavy oil sample having a viscosity of 8.5 Pas at ambient temperature. Their observations indicated viscosity alteration to be dependent on nanoparticles size, type, concentration, and temperature. Recently, Srinivasan and Shah (2014) also observed 20-30% viscosity reduction with CuO nanoparticles with heavy oil from Oklahoma (0.6 Pas at 21°C)

These compelling observations on low-temperature viscosity reduction by nanoparticles open the doors for nanoparticles in non-thermal applications.

## 2. Objectives

The experimental work presented in this document is aimed at investigating low-temperature viscosity reduction by nanoparticles. This study would help examine the possibilities of employing nanoparticles for improving non-thermal heavy oil recovery techniques.

In this study, three different metal oxides - copper (II) oxide, iron (III) oxide and nickel (II) oxide were selected, and their effects on heavy oil viscosity were examined at three different concentrations. Two different highly viscous heavy oil samples (70 and 350 Pas at ambient temperature) were employed. All viscosity measurements were performed at temperatures of 27, 38, 49, 60, and 71°C. The heavy oil samples used in the present work are 9 to 40 times more viscous than those used in previous studies (Hascakir et al., 2010; Shokrlu and Babadagli, 2014; Srinivasan and Shah, 2014).

## 3. Theory

### 3.1 Heavy Oil Rheology

Heavy oils are complex fluid consisting of a liquid phase and a structured phase (mainly asphaltenes). As a result, they may exhibit weak non-Newtonian behavior. According to Dion, (2011), heavy oil rheology is determined by mainly three parameters - deformation rate (shear rate), composition, and temperature. Typically, heavy oils exhibit Newtonian behavior. However, the presence of yield stress and the shear-thinning tendency is not rare. When the heavy oil is sheared, microstructures of asphaltenes are stretched and break down and results in decreased apparent viscosity with shearing time. This process is not instantaneous, and therefore, heavy oil often exhibits time-dependent rheological behavior, i.e., thixotropy.

1 Heavy oil viscosity is directly correlated to asphaltene content. With the increase in asphaltene  
2 concentration, these molecules aggregate and increase the viscosity. Argillier et al. (2002) observed the  
3 presence of a critical concentration beyond which the viscosity dramatically increased up to 20 times. As  
4 examined by Pierre et al. (2004), the presence of resin can also affect heavy oil viscosity.

5 Heavy oil rheology is highly sensitive to temperature changes. As per (Pierre et al., 2004), its  
6 behavior typically varies from almost an elastic solid at low temperatures to shear thinning fluid at  
7 moderate temperatures, and more Newtonian behavior at higher temperatures with a steady reduction in  
8 viscosity. Temperature values separating these zones depend on oil composition. At extremely high  
9 temperature (typically >150°C), thermal cracking of heavier components initiates.

### 10 **3.2 Reliability of Heavy Oil Viscosity Data**

11 Majority of heavy oil studies often fail to consider and discuss the aspect of reliability of viscosity data.  
12 Very few researchers (Alkandari et al., 2012; Miller, 2003; Miller and Erno, 1995) have attempted to  
13 identify and address the issue of accuracy, reproducibility, and reliability of heavy oil viscosity data.

14 A reproducibility error of up to 10% is common even after repeated runs under a controlled  
15 laboratory environment (Miller and Erno, 1995). Several factors contribute toward the poor reliability –  
16 the majority of which are associated with heavy oil sample acquisition, transportation, storage, and  
17 viscosity measurement technique. These factors have been discussed in detail by Miller (2003).

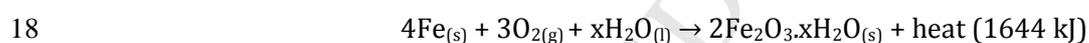
18 As defined by Miller and Erno (1995), ideal heavy oil viscosity is obtained from uncontaminated  
19 sample preserved at or correctly restored to reservoir conditions, and using a perfect viscometer having no  
20 inherent limitations. Heavy oil viscosity is practically measured cost-effectively. i.e., using an affordable  
21 apparatus and dead oil samples acquired and prepared without involving expensive operations. It is  
22 almost impossible to obtain the real heavy oil viscosity; however, in the present work, care has been taken  
23 to minimize the error in measurement and provide accurate viscosity data.

### 24 **3.3 Viscosity Alteration by Nanoparticles**

25 As discussed earlier, nanoparticles have been observed to alter heavy oil viscosity at ambient temperature.  
26 At elevated temperature, the catalytic properties of nanoparticles are responsible for viscosity reduction.  
27 However, at low-temperature, molecular-level physical interaction or chemical reaction between  
28 nanoparticles and heavy oil is believed to be dominant. This section summarizes the primary mechanisms  
29 (Ostwald Ripening Process, Exothermic Chemical Reactions, Particle Aggregation and Formation of  
30 Coordination Complexes) responsible for the low-temperature viscosity alteration by nanoparticles. Based  
31 on literature review, it appears that some of these processes reduce viscosity while the others lead to  
32 viscosity increase instead.

1 **Ostwald Ripening Process:** This is a prominent process driven by thermodynamics and describes the  
2 tendency of smaller particles or crystals to coalesce and form increasingly larger and more stable  
3 structures. Asphaltene molecules that are primarily responsible for high heavy oil viscosity typically  
4 remain positively charged in the presence of an external field (i.e., surface charge). Depending on their zeta  
5 potential, nanoparticles are either electrically attracted or repulsed by the asphaltene molecules. For  
6 example, Cu and NiO nanoparticles are negatively charged and have zeta potentials of -77 mV and -35 mV  
7 respectively at pH=7 (El-Kemary et al., 2013; Shokrlu and Babadagli, 2014) and naturally attracted by  
8 asphaltene molecules to their surface. Agglomeration of these structures makes bulk oil less viscous.  
9 Shokrlu and Babadagli (2014) confirmed this phenomenon by observing clustering of asphaltenes and  
10 nickel particles under a microscope.

11 **Exothermic Chemical Reactions:** Unlike copper and nickel, iron (III) oxide has a zeta potential of +20 mV  
12 at pH=7 (Shokrlu et al., 2014) and would disperse asphaltene molecules and increase the bulk viscosity.  
13 However, Hascakir et al. (2010) observed viscosity reduction with the addition of iron oxide. This  
14 observation can be attributed to Exothermic Chemical Reactions initiated by nanoparticles (Hascakir,  
15 2008). These reactions occur at a molecular level and hence, do not increase the temperature of the bulk  
16 fluid. Nonetheless, it can be hypothesized that the heat generated locally can weaken some chemical bonds,  
17 break them with little external energy, and decrease viscosity. One such reaction is rusting of iron,



19 The dissociation energy of C-S, C-N, and C-O bonds that make up complex structures of asphaltene  
20 molecules are 713, 750, and 1076 KJ/mole respectively (Luo, 2007). The heat generated by exothermic  
21 reaction would break these bonds and result in simpler compounds and hence, less viscosity. Similar to  
22 rusting, homogenous mixing of iron (III) oxide can lead to the formation of magnetite ( $\text{Fe}_3\text{O}_4$ ) which is also  
23 an exothermic process (Hascakir, 2008). Larger surface area of nanoparticles, and presence of saline water,  
24 acid compounds or oxidants in heavy oil can accelerate the reaction between iron and oxygen (Shokrlu and  
25 Babadagli, 2014).

26 Heavy oil is a complex compound, and hence, a detailed investigation at a molecular level is necessary  
27 to fully understand all the physical and chemical processes that may contribute to viscosity alteration.

28 **Particle Aggregation:** At high concentration, nanoparticles can aggregate, and the process may dominate  
29 over inter-molecular processes. In other words, heavy oil may behave as a Nano-suspension, and its  
30 viscosity would increase with nanoparticle concentration (Rudyak, 2013). The increment is believed to be

1 dependent on particle size, metal type, the degree of aggregation, size of clustered particles and presence of  
2 asphaltene molecules.

3 **Formation of coordination complexes:** Additionally, at high concentration, transition metal  
4 nanoparticles can form coordination complexes with asphaltene molecules and increase its viscosity  
5 (Shokrlu and Babadagli, 2014). At high concentrations, nanoparticles can accelerate the oxidation of liquid  
6 hydrocarbons to form hydroperoxides, which further react and polymerize with each other and increase  
7 the molecular size and complexity of structure (Jia et al., 2016). In addition to high concentration, increase  
8 in temperature would also increase the rate of these reactions, resulting in the adverse effect of viscosity  
9 increment.

#### 10 4. Experimental Setup and Methodology

11 A rotational viscometer was used for all rheological measurement at ambient and elevated temperatures. A  
12 viscometer compatible heater cup was used for heating fluid samples.

13 To investigate the effect of nano-sized particles, three different metal oxides – copper (II) oxide,  
14 iron (III) oxide and nickel (II) oxide were employed. For each type of particle, three different  
15 concentrations (0.05, 0.1, and 0.5 wt.%) were examined. Two heavy oil samples (referred hereafter as  
16 Sample A and Sample B) were used. The Saturates, Asphaltenes, Resins and Aromatics (SARA) composition  
17 and basic physical properties of typical heavy oil from the same field is present in Table 1. The  
18 characteristics (particle size, molecular weight, and color) of the nanoparticles are listed in Table 2.

19 **Table 1:** Heavy oil composition and basic physical properties (Ucan et al., 2014)

SARA Composition Analysis	
<b>Asphaltenes</b>	10.95 mol%
<b>Resins</b>	26.09 mol%
<b>Aromatics</b>	36.59 mol%
<b>Saturates</b>	24.29 mol%
<b>Density</b>	0.978 kg/cm <sup>3</sup> (13°API)
<b>Thermal conductivity</b>	1.33 x 10 <sup>-7</sup> W/m/K

20  
21  
22

1 **Table 2:** Nanoparticles specifications

Property	Copper (II) oxide	iron (III) oxide	Nickel (II) oxide
Chemical Formula	CuO	Fe <sub>2</sub> O <sub>3</sub>	NiO
Molecular Weight	79.55 g/mol	159.69 g/mol	74.69 g/mol
Appearance (Color)	Black	Red-brown to brown	Dark green to very dark green/black/green-black
Appearance (Form)	Powder	Powder	Powder
Average particle size	≤ 50 nm	≤ 50 nm	≤ 50 nm
Surface are (m <sup>2</sup> /g)	25-40	40-60 (for 20-40 nm size)	50-100 (for 10-20 nm size range)

2  
3 The fluid samples were prepared by pouring oil into the viscometer cup and simultaneously  
4 sprinkling the desired amount of nanopowder to ensure proper mixing. A blender was not employed  
5 because of two reasons: (i) to avoid shear degradation of oil, and (ii) to prevent inconsistency in  
6 nanoparticle concentration because of oil remained stuck to the blender walls and blades while  
7 transferring it to the viscometer cup.

8 As per the manufacturer safety guidelines, nanoparticles used in the study can cause a health  
9 hazard. Specifically, oral, dermal, and respiratory irritation or toxicity. Following manufacturer safety  
10 guidelines, eye shields, hand gloves, particle respirator, personal protective equipment were used while  
11 handling the nanomaterials, preparing the fluid samples, and running the tests.

#### 12 **4.1 Challenges in Viscosity Measurement**

13 Monitoring of heavy oil sample acquisition, its storage, and transportation were beyond the control of the  
14 authors. However, the experimental procedure was carefully planned to eliminate or minimize sources of  
15 errors, maintain consistency, and improve the reliability of the data. Both oil samples used were extremely  
16 viscous with viscosity of 72 and 358 Pas at 24°C. Primary challenges were controlling temperature and  
17 minimizing the effects of shear degradation and viscous heating. The temperature in the viscometer was  
18 controlled manually using thermostat knob on the heater cup. Temperature variation during the test was  
19 ±3%. Further details are provided in Patel (2016).

20

1

## 2 4.2 Reproducibility of Measurements

3 To determine the reproducibility of the data, three independent viscosity measurements were performed  
 4 using three different batches of samples from both heavy oils. Summary of reproducibility error calculated  
 5 for the samples is presented in Table 3. Error values ranging from 2 to 10% are common even for labs  
 6 specialized in heavy oil and bitumen analysis (Miller and Erno, 1995).

7

**Table 3:** Reproducibility of viscosity measurements

Temp., °C	Deviation from averaged measurement	
	Heavy oil Sample A	Heavy oil Sample B
38	4.2%	13.9%
49	4.6%	6.8%
60	14.2%	4.7%
71	10.4%	9.8

8

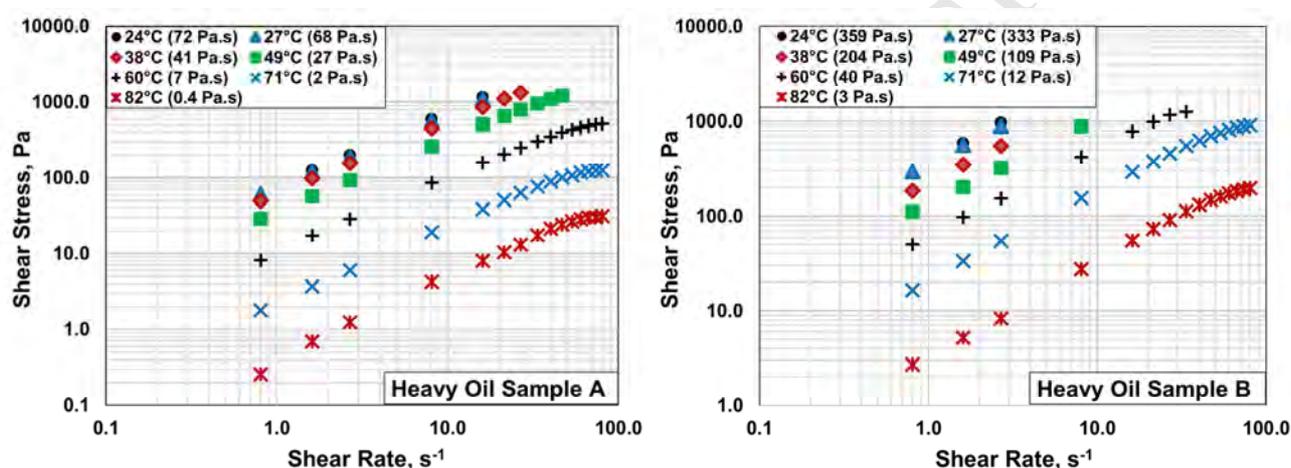
## 9 5. Results and Discussion

### 10 5.1 Rheology of Heavy Oil Samples

11 Rheograms for oil Samples A and B are provided in Fig. 1. The fluids exhibit Newtonian behavior at low  
 12 shear rates and shear thinning at higher shear rates. The lower apparent viscosity values at high shear  
 13 rates can be either due to stretching of asphaltene microstructures or because of slight viscous heating. The  
 14 rheological behavior of oil samples can be described using the power law model  $\tau = K_v \gamma^n$ , where  $\tau$  and  $\gamma$  is  
 15 shear stress and shear rate respectively. Model parameters - fluid behavior index (n) and consistency index  
 16 ( $K_v$ ) can be determined from slope and intercept of a logarithmic plot of shear stress and shear rate. The n  
 17 and  $K_v$  values calculated for both samples at various temperatures, are presented in Table 2.

18

1 Fluid behavior indices of greater than 0.9 confirm strong Newtonian behavior. It should be noted  
 2 that the increase in temperature strengthens the Newtonian behavior as indicated by 'n' values  
 3 approaching 1.0. This is expected, as the increase in temperature tends to dissociate asphaltene molecules  
 4 into small fragments, reducing the effect of shear stretching. Shear thinning observed in this study was not  
 5 significant, and hence, the average Newtonian viscosity is employed in the discussion to simplify the  
 6 comparison. The Newtonian viscosity was obtained by fitting a straight line with zero intercept on shear  
 7 stress versus shear rate data. These representative viscosity values are presented in Table 4.



9  
 10 **Figure 1:** Rheograms for heavy oil Sample A (left) and B (right) at various temperatures

11 The viscosity of both samples is graphically presented in Fig. 2. It can be seen that their viscosity is  
 12 highly sensitive to temperature and follows a similar trend. As discussed earlier, dissociation of asphaltene  
 13 molecules and thermal upgrading of heavier compounds could be the key reasons for viscosity reduction  
 14 with temperature.

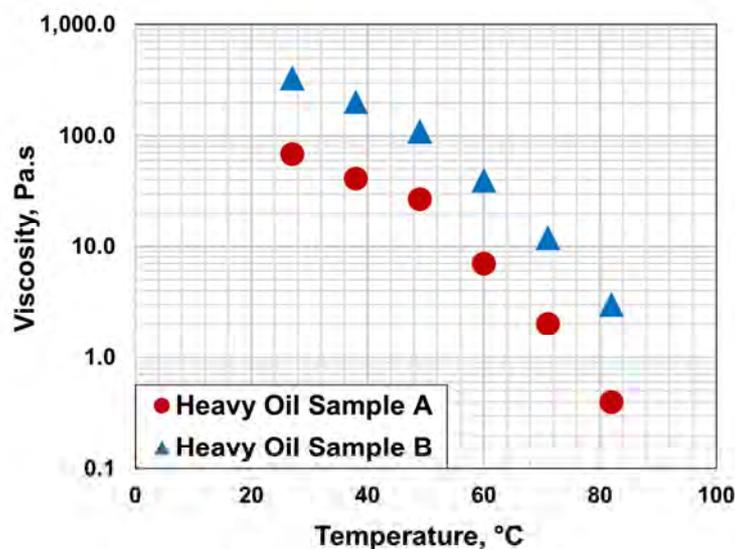
Figure 3 represents viscosity of an already tested heavy oil sample that had been heated up to 82°C and then kept at ambient condition for 24 hours. The data indicates that the oil sample practically regained the original viscosity. This confirms that the amount of lighter fractions vaporizing from the oil while increasing temperature up to 82°C was insignificant.

**Table 4:** Power law parameters of heavy oil samples at various temperatures

T, °C	Heavy Oil Sample A				Heavy Oil Sample B			
	n	$K_v$	$\gamma, s^{-1}$	$\mu_N, Pas$	n	$K_v$	$\gamma, s^{-1}$	$\mu_N, Pas$
27	0.963	75.1	0.8 - 16.1*	67.7	0.921	362.3	0.8 - 2.7*	333.4
38	0.942	61.8	0.8 - 26.8*	41.4	0.910	224.4	0.8 - 2.7*	204.1
49	0.926	36.9	0.8 - 46.9*	26.6	0.906	133	0.8 - 8.0*	108.8
60	0.910	11.5	0.8 - 80.5	6.9	0.885	63.4	0.8 - 33.5*	39.9
71	0.949	2.5	0.8 - 80.5	1.7	0.881	22.8	0.8 - 80.5	12.0
82	1.041	0.4	0.8 - 80.5	0.4	0.962	3.5	0.8 - 80.5	2.6

n is fluid behavior index (dimensionless),  $K_v$  is consistency index ( $Pas^n$ ),  $\gamma$  is the shear rate range ( $s^{-1}$ ), and  $\mu_N$  is the representative Newtonian viscosity (Pas)

\* At low temperatures, because of high viscosity, the current spring-bob configuration did not permit shear stress measurements over the desired shear rate range of 0.8 to 80.46  $s^{-1}$



**Figure 2:** Viscosity of heavy oil samples as a function of temperature

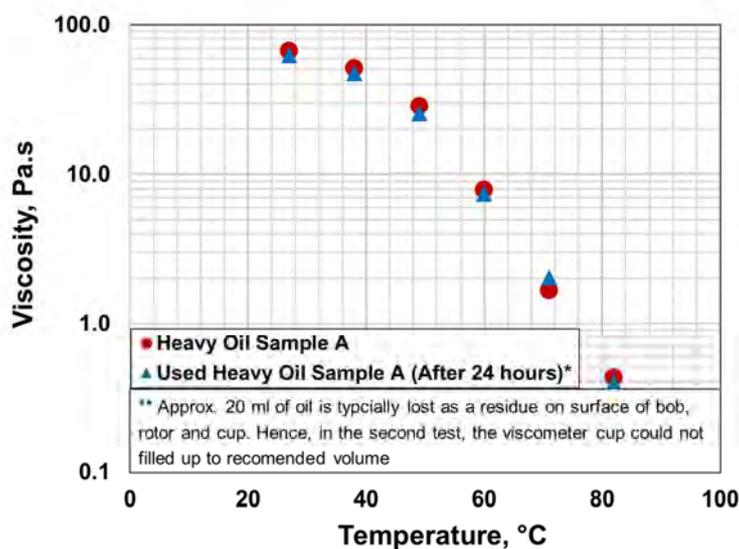


Figure 3: Viscosity of used heavy oil samples as a function of temperature

## 5.2 Effect of Nanoparticles

For high temperature ( $>120^{\circ}\text{C}$ ) thermal recovery applications, nanoparticles have been identified to improve the overall quality of heavy oil by reducing viscosity, increasing API gravity, enhancing H/C ratio, minimizing carbon residue (MCR), and removing sulfur and nitrogen content (Hashemi et al., 2014). It is possible that nanoparticles lead to similar changes for low-temperature application as well. Considering the fact that the viscosity is the primary factor affecting production, only rheological alteration of heavy oil samples by nanoparticles have been examined and reported in following sections. Other possible physical and chemical alterations were beyond the scope of the present work and were not measured.

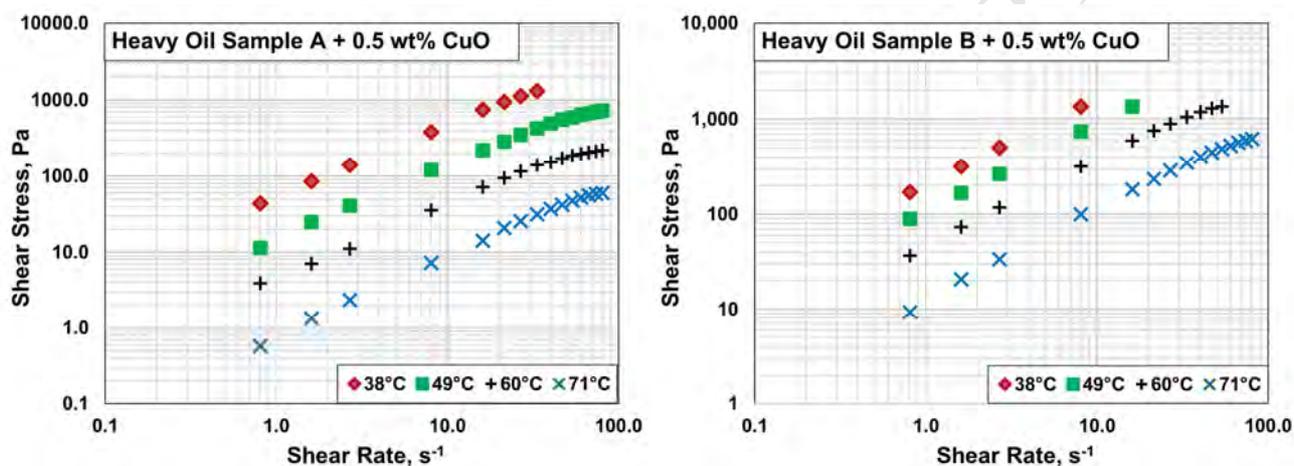
### 5.2.1 Copper Oxide (CuO)

The rheological behavior of the oil samples did not change with the addition of CuO nanoparticles. As shown in Fig. 4, the rheograms of oil samples containing high (0.5 wt%) concentration of CuO are similar to that of base oil samples (Fig. 1). Low concentration nanoparticles also exhibited similar rheograms.

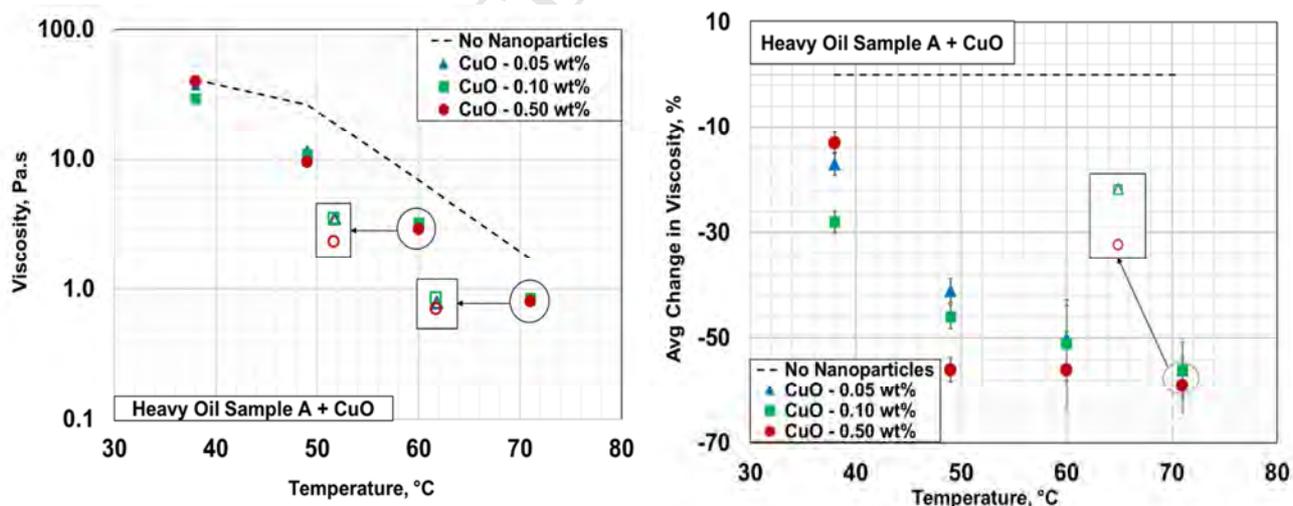
The addition of CuO resulted in a notable viscosity reduction in both heavy oil samples. The reduction varied not only with particle concentration but also with temperature. The average percentage reduction in viscosity achieved by the addition of these nanoparticles is graphically presented in Figs. 5 and 6. It should be noted that the average viscosity reduction was calculated by the averaging percentage reduction in apparent viscosity measured at each shear rate. For Sample A, the viscosity reduction ranged from 13-17% at  $38^{\circ}\text{C}$  to as high as 56-59% at  $71^{\circ}\text{C}$ . In case of Sample B, comparatively less reduction in viscosity was observed, i.e., 8 to 19% at  $38^{\circ}\text{C}$  and 25 to 36% at  $71^{\circ}\text{C}$ .

1 The viscosity reduction by CuO can be attributed to the Ostwald ripening process discussed earlier.  
 2 CuO particles (zeta potential = -77 mV at pH=7) create an electrical field that attracts positively charged  
 3 asphaltene molecules to their surface. Agglomeration of these structures makes bulk oil less viscous.

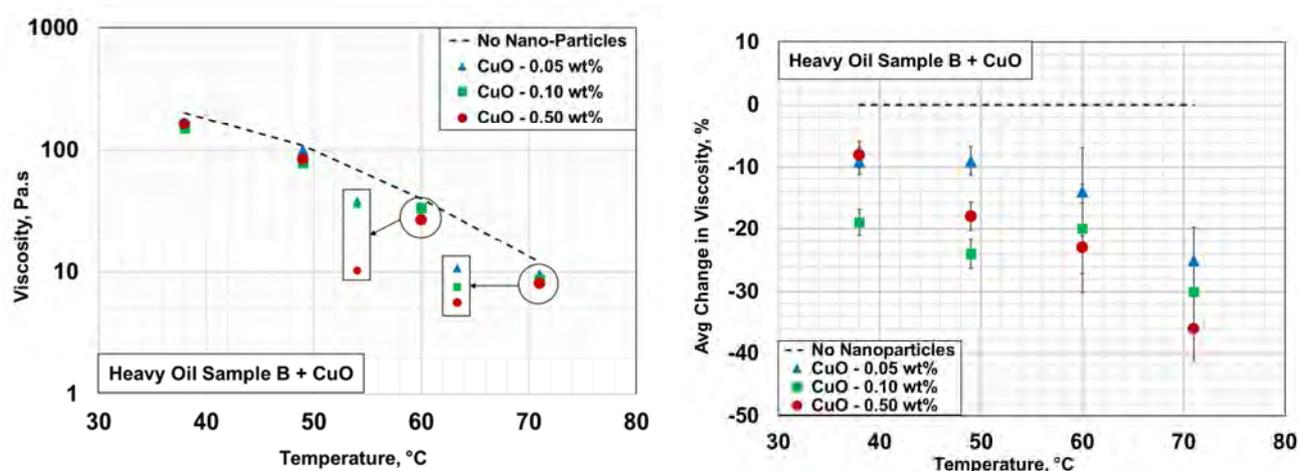
4 Interestingly, the viscosity reduction improved with temperature. The improvement can be  
 5 attributed to the weakening of the hydrogen bond within heavier compounds of the oils (Kershaw et al.,  
 6 1980). The viscosity reduction along with improved thermal conductivity increase efficiency of thermal  
 7 upgrading of heavy oil, resulting in further decline in viscosity.



8  
 9 **Figure 4:** Rheogram of heavy oil Sample A (left) and B (right) containing 0.5 wt% copper oxide  
 10 nanoparticles at various temperatures



11  
 12 **Figure 5:** Change in viscosity of heavy oil Sample A caused by copper oxide nanoparticles at various  
 13 temperatures



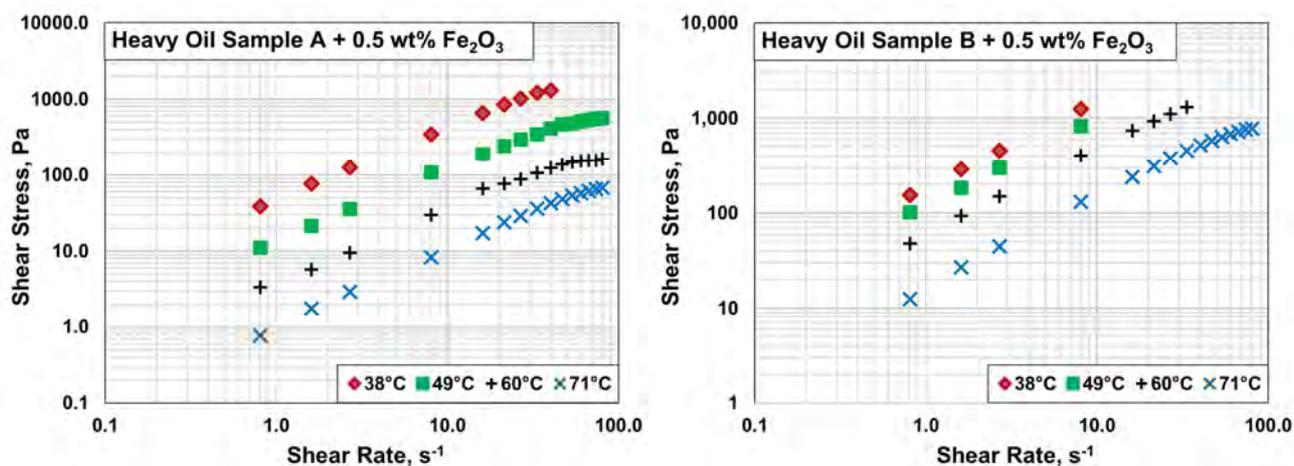
**Figure 6:** Change in viscosity of heavy oil Sample B caused by copper oxide nanoparticles at various temperatures

The amount of viscosity reduction achieved in this study is unprecedented and significant in comparison to previous studies (Shokrlu and Babadagli, 2014; Srinivasan and Shah, 2014). Observed differences were 10% with micron-sized CuO and 10-27% with nano CuO copper oxide particles. However, these studies used heavy oils with significantly lower viscosity than the ones employed in this study.

Results also indicate that viscosity reduction depends on nanoparticles concentration. The effect of particle concentration and determination of optimum level is discussed later.

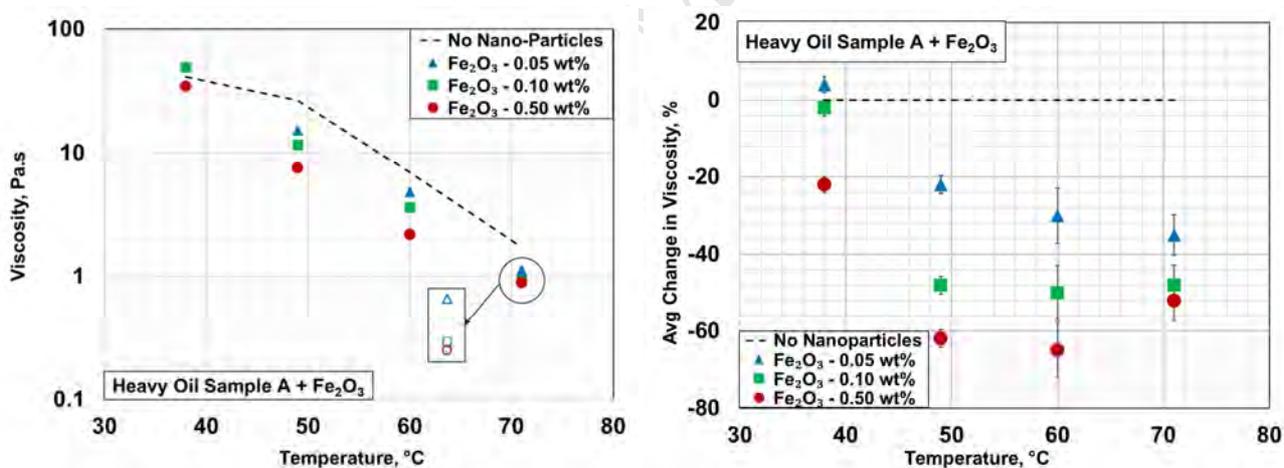
### 5.2.2 Iron Oxide ( $\text{Fe}_2\text{O}_3$ )

Similar to CuO, the rheological behavior of oil samples did not exhibit notable alteration with the addition of  $\text{Fe}_2\text{O}_3$  nanoparticles. As shown in Fig. 7, the rheograms of oil samples containing high (0.5 wt%) concentration of  $\text{Fe}_2\text{O}_3$  are similar to that of base oil samples (Fig. 1). Fluids with low concentrations of  $\text{Fe}_2\text{O}_3$  nanoparticles also exhibited similar rheograms.

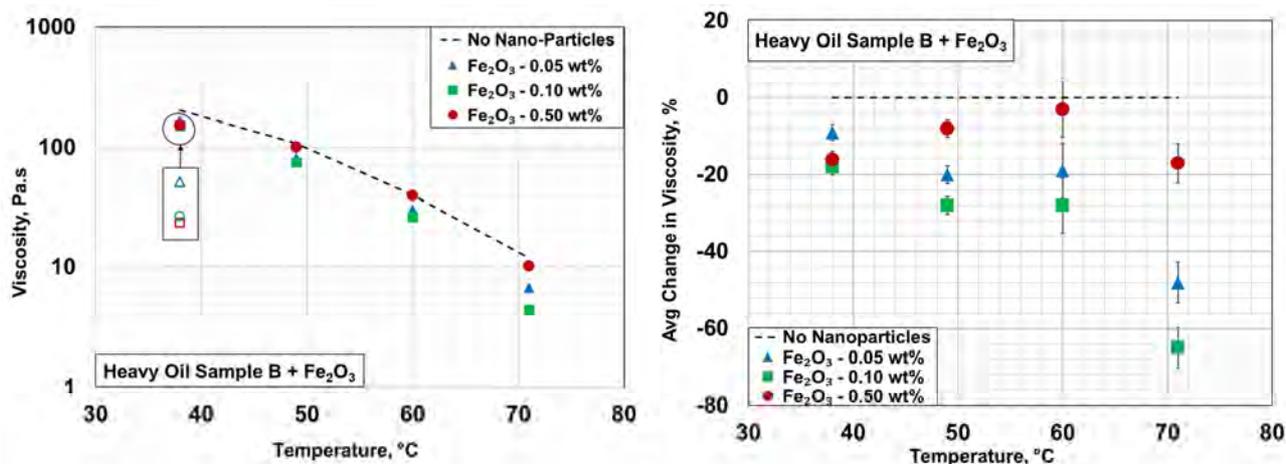


1  
2 **Figure 7:** Rheogram of heavy oil Sample A (left) and B (right) containing 0.5 wt% iron oxide nanoparticles  
3 at various temperatures

4 The addition of Fe<sub>2</sub>O<sub>3</sub> nanoparticles also resulted in a notable reduction in viscosity of heavy oil  
5 samples. Fluid behavior indices of greater than 0.9 were observed in all samples confirming the Newtonian  
6 behavior. The average percentage reduction in viscosity caused by Fe<sub>2</sub>O<sub>3</sub> is presented in Figs. 8 and 9.



7  
8 **Figure 8:** Change in viscosity of heavy oil Sample A caused by iron oxide nanoparticles at various  
9 temperatures



**Figure 9:** Change in viscosity of heavy oil Sample B caused by iron oxide nanoparticles at various temperatures

For Sample A, the viscosity reduction ranged from 2 to 22% at 38°C to as high as 35 to 52% at 71°C. In case of Sample B, comparatively less viscosity reduction was observed that is 9 to 16% at 38°C and 17 to 48% at 71°C. Since viscosity reduction also depends on oil composition, dissimilar viscosity reduction at the same particle concentration is expected. Previously, Hascakir et al. (2008) tested micron size Fe and Fe<sub>2</sub>O<sub>3</sub> particles with two moderately viscous oil samples (0.6 and 0.7 Pas at 24°C) and achieved viscosity reductions of 34 and 88%, respectively. Shokrlu et al. (2014) observed a decrease of only 8-10% using the micro- and nano-sized Fe particles.

Unlike CuO, Fe<sub>2</sub>O<sub>3</sub> exhibits positive zeta potential, and hence, they would disperse asphaltene molecules. Therefore, instead of Ostwald ripening effect, some other mechanisms, possibly exothermic chemical reactions (see Section 3.3) are expected to induce viscosity reduction.

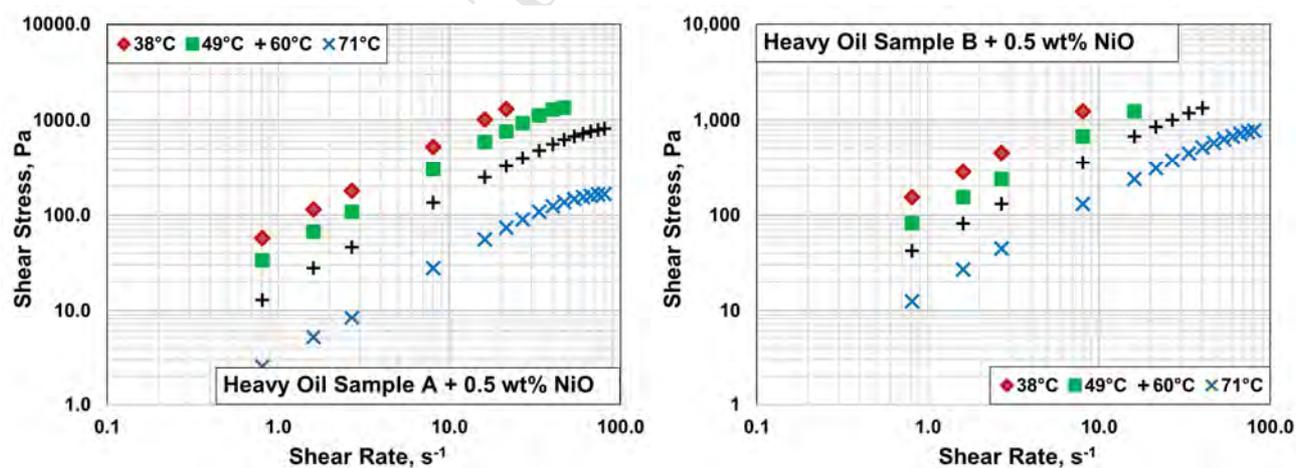
Fe<sub>2</sub>O<sub>3</sub> also exhibited improvement in viscosity reduction with temperature. The weakening of hydrogen bond, improved thermal conductivity, and accelerated chemical reactions are the possible causes for this behavior. Interestingly, the effect of Fe<sub>2</sub>O<sub>3</sub> nanoparticles on viscosity reduction was more distinct than that observed with the addition of CuO nanoparticles.

### 5.2.3 Nickel Oxide (NiO)

Similar to CuO and Fe<sub>2</sub>O<sub>3</sub>, NiO also did not alter the rheological behavior of oil samples. As shown in Fig. 10, the rheograms of oil samples containing high (0.5 wt%) concentration of Fe<sub>2</sub>O<sub>3</sub> are similar to that of base oil samples (Fig. 1). Also, oil samples with low concentrations of NiO displayed similar rheograms.

Among the three types of nanoparticles used in the present work, NiO exhibited slightly more viscosity reduction than CuO and Fe<sub>2</sub>O<sub>3</sub>. Moreover, the variation in viscosity alteration with concentration was significant. As expected, after the addition of nanoparticles, oil sample retained their original rheological behavior. The average percentage change in viscosity achieved with NiO is presented in Figs. 11 and 12. For Sample A, the viscosity reduction ranged from 7 to 70% depending on the concentration and temperature. In case of Sample B, the reduction varied from 13 to 64%.

Like CuO, the Ostwald ripening process is believed to be the dominant mechanism leading to the viscosity reduction in Nickel oxide. The Zeta potential of NiO is -32 mV at pH of 7. Nickel oxide also exhibited an improvement in viscosity reduction with temperature. This trend can be attributed to the weakening of the hydrogen bond. Shokrlu and Babadagli (2014) have examined the effect of Ni nanoparticles and noted a maximum of 8% reduction as opposed to 70% observed with NiO in the present study. There are few possible reasons for this noticeable difference in performance. Viscosity of oil samples tested in this study are 8 and 40 times higher than viscosity of oils used in the previous work. Hence, oil samples in the present study have more asphaltene content. Besides, they employed Ni particle while in the current investigation NiO particles were used. These differences suggest that intermolecular physicochemical interactions may have also been different in both cases.



**Figure 10:** Rheogram of heavy oil Sample A (left) and B (right) containing 0.5 wt% nickel oxide nanoparticles at various temperatures

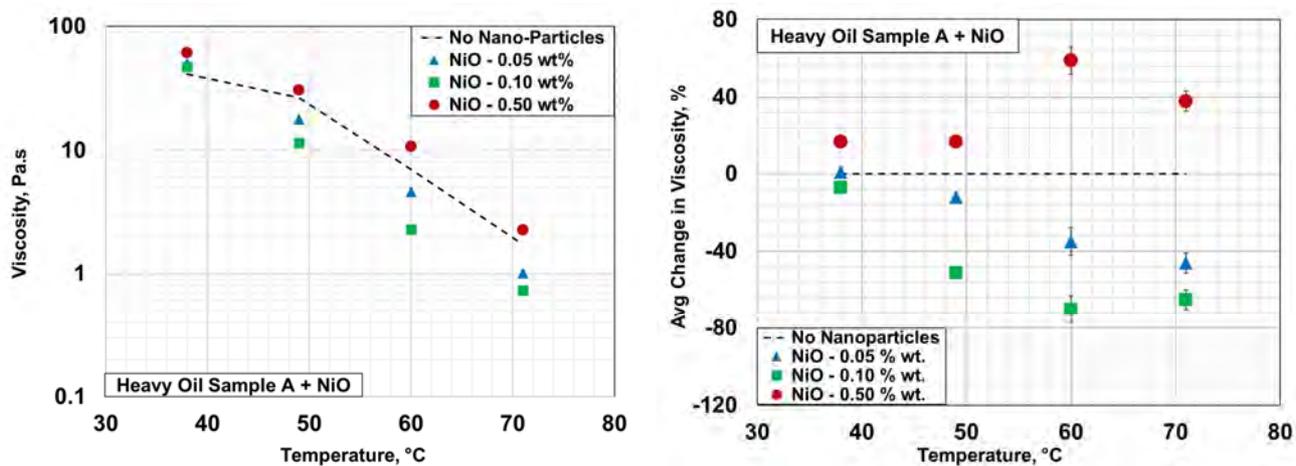


Figure 11: Change in apparent viscosity of heavy oil Sample A caused by nickel oxide nanoparticles at various temperatures

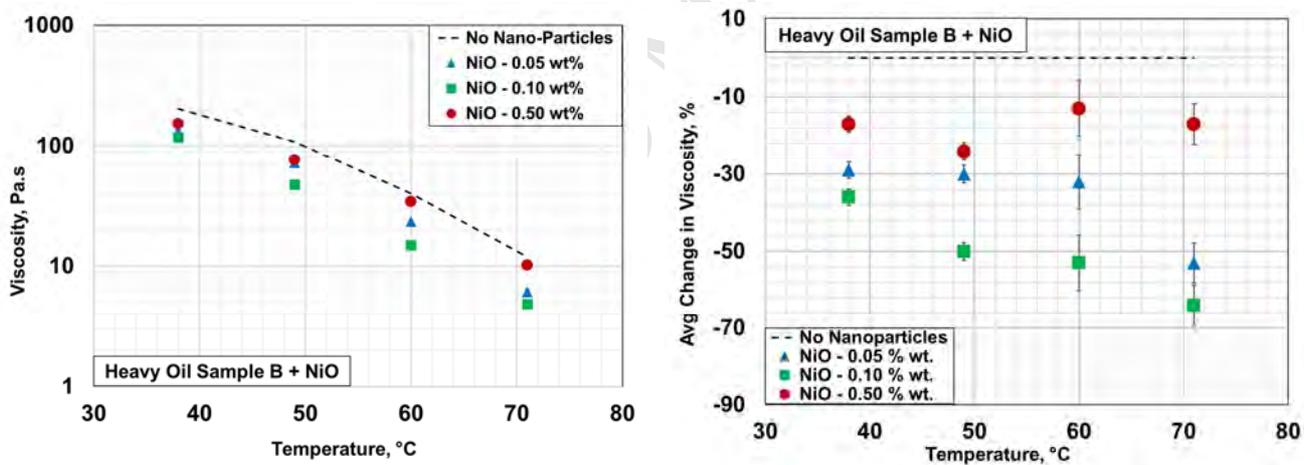
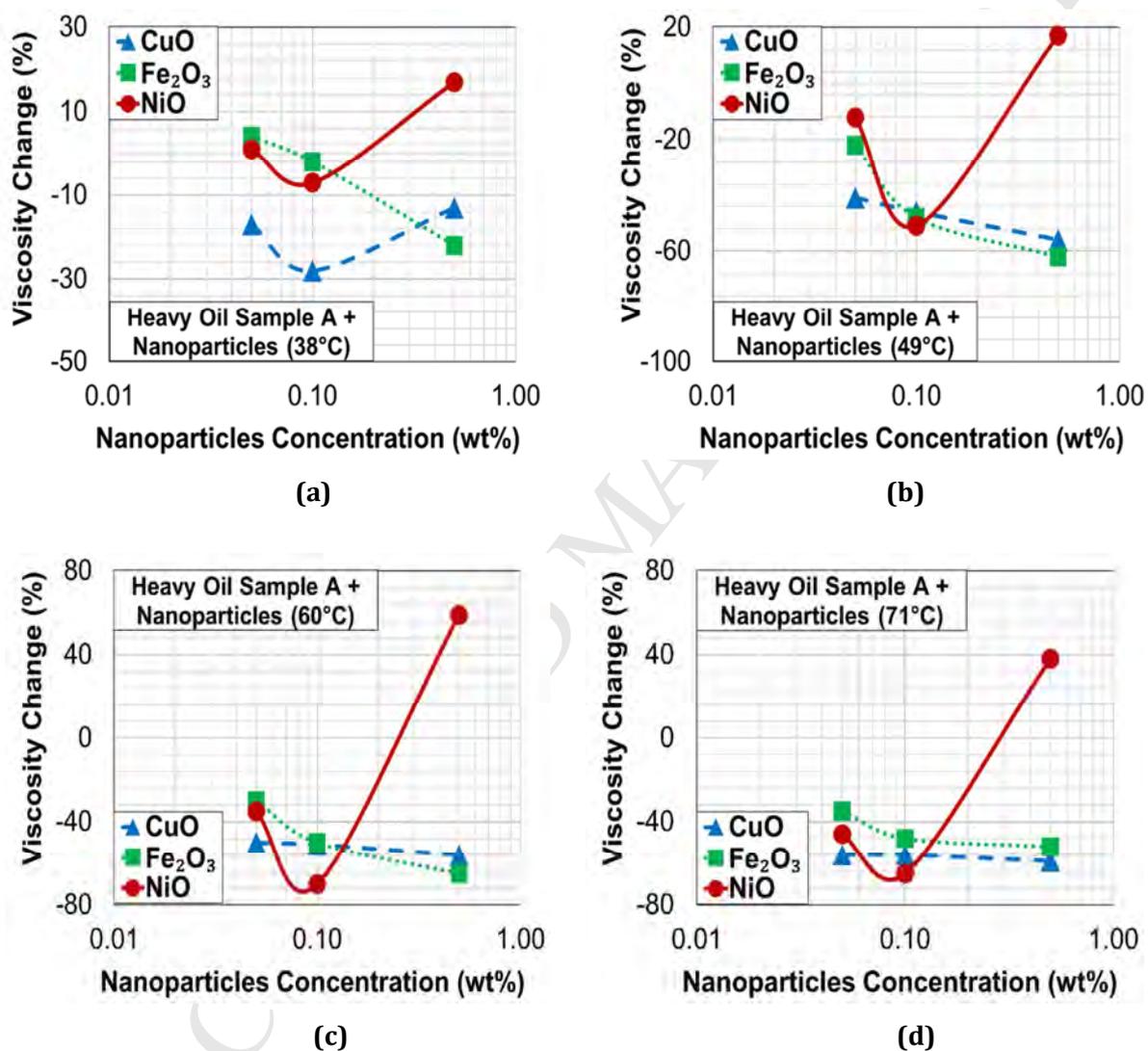


Figure 12: Change in apparent viscosity of heavy oil Sample B caused by nickel oxide nanoparticles at various temperatures

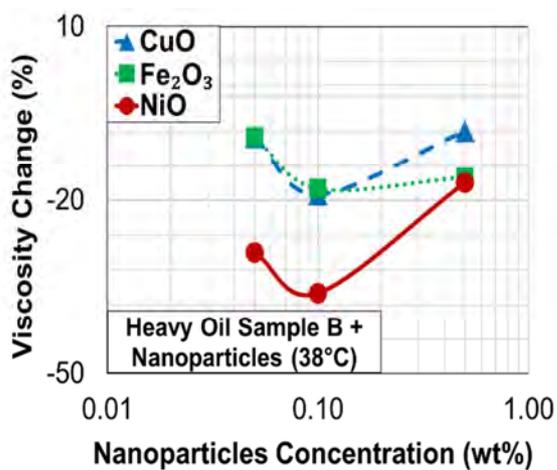
### 1 5.2.4 Optimum Concentration

2 Observed viscosity alteration with CuO, Fe<sub>2</sub>O<sub>3</sub>, and NiO indicated a presence of optimum concentration.  
 3 This optimum point depends on particle concentration, metal type, temperature, and oil composition. The  
 4 optimum concentration was determined by plotting an average percentage change in viscosity as a function  
 5 of particle concentration (see Figs. 11 and 12). Summary of optimum concentration is listed in Table 5.

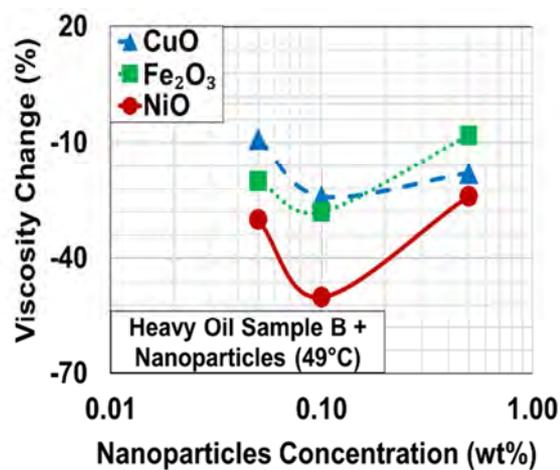


8  
9  
10 **Figure 11:** Percentage change in viscosity of Sample A as a function of nanoparticle concentration at (a)  
 11 38°C, (b) 49°C, (c) 60°C, and (d) 71°C

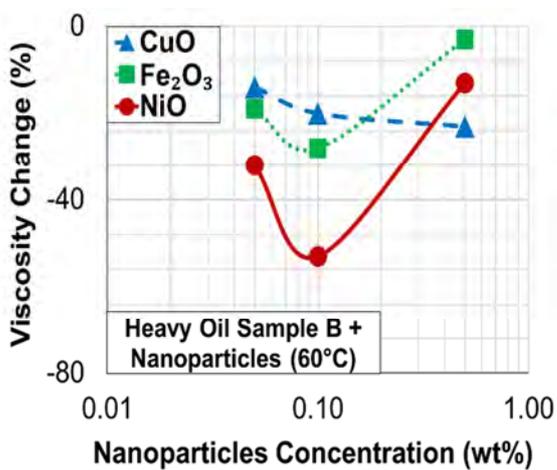
12  
13



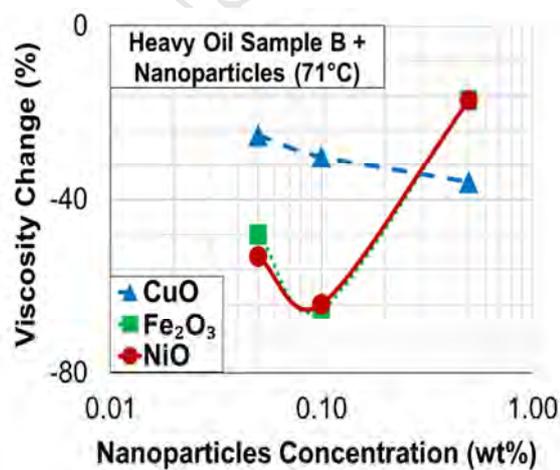
(a)



(b)



(c)



(d)

**Figure 12:** Percentage change in viscosity of Sample B as a function of nanoparticle concentration at (a) 38°C, (b) 49°C, (c) 60°C, and (d) 71°C

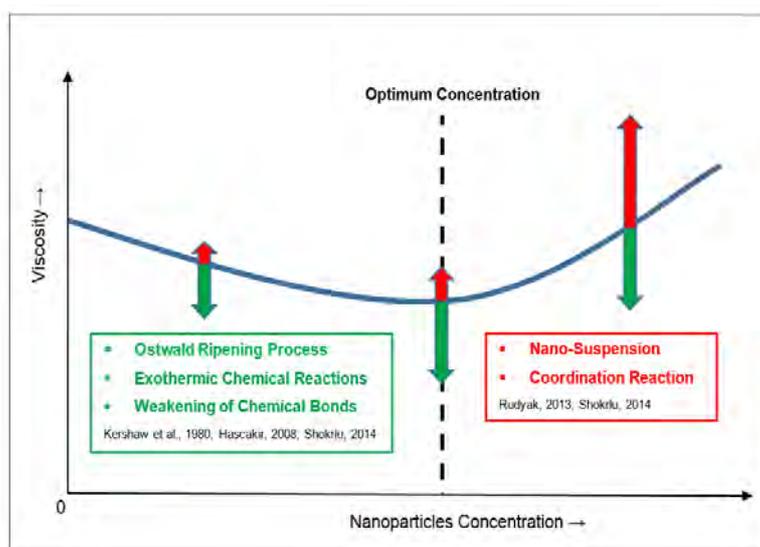
1 Based on the results, it can be hypothesized that at low nanoparticle concentration, viscosity-  
 2 reducing mechanisms such as Ostwald ripening and exothermic chemical reaction dominate. With the  
 3 increase in concentration, the effects of “nano-suspension” and coordination complex become prominent  
 4 and increase the viscosity. It is likely that viscosity alteration is also caused by other physicochemical  
 5 processes that have not been explored by researchers yet. The mechanisms responsible for low-  
 6 temperature viscosity alteration are graphically summarized in Fig. 13. The optimum concentration  
 7 increases with temperature. The increase can be attributed to a progressively dominant thermal upgrading  
 8 of heavier compounds and enhancement of the rate of exothermic chemical reaction with temperature. At  
 9 very high temperature (>100°C), aquathermolysis would become dominant, and the effect of particle  
 10 concentration would be diminished.

11 **Table 5:** Optimum concentration (%wt.) of nanoparticles at different temperatures

Heavy Oil Sample	Nanoparticles Type	38°C	49°C	60°C	71°C
<b>A</b>	CuO	0.1	≥ 0.5	*	*
	Fe <sub>2</sub> O <sub>3</sub>	≥ 0.5	≥ 0.5	≥ 0.5	*
	NiO	0.1	0.1	0.1	0.1
<b>B</b>	CuO	*	0.1	≥ 0.5	≥ 0.5
	Fe <sub>2</sub> O <sub>3</sub>	0.1	0.1	0.1	0.1
	NiO	0.1	0.1	0.1	0.1

\* Undetermined because variation in viscosity due to concentration was less than the measurement error.

12



**Figure 13:** Low-temperature viscosity alteration by nanoparticles (Not to scale). Mechanisms highlighted in green and red are responsible for viscosity reduction and increment respectively.

Interestingly, NiO nanoparticles exhibited a marked difference in their performance with a change in concentration. For example, in case of Sample A, at 49°C, increasing the concentration from 0.05 to 0.1 wt.% improved viscosity reduction from 12 to 51%. However, a further increase in concentration to 0.5 wt.% resulted in adverse effect and increased the viscosity by 17%. The increase indicates the presence of some unknown molecular level reactions other than those discussed so far. Further research at the molecular level from the chemistry point of view is essential to understand the mechanisms responsible for this behavior.

As can be observed from Table 5, concentration of 0.1 wt.% is the most common optimum point. This matches with those observed by Shokrlu and Babadagli (2014). In some cases, the optimum point cannot be identified conclusively because of high reproducibility error. In few cases, the optimum point appears to be even higher than 0.5 wt.%.

## 6. Summary of Results

The viscosity of heavy oil Sample A reduced from 67.7 to 0.4 Pas when heated from 27 to 71°C. Sample B was approximately five times more viscous than Sample A with viscosity of 333.4 Pas at 27°C and 2.6 Pas at 71°C. When fitted to the power law rheology model, both samples displayed fluid behavior index values of greater than 0.9, indicating Newtonian behavior.

1 Addition of nanoparticles provided notable viscosity reduction. At the optimum nanoparticle  
2 concentration, depending on the metal type, viscosity reductions of 59 to 70% for Sample A and 36 to 65%  
3 for Sample B were achieved.

4 The degree of viscosity reduction was observed to be a function of the type of nanoparticles, their  
5 concentration, oil composition, and temperature of the fluid. In most of the cases, the optimum  
6 concentration was observed to occur near 0.1 wt.% and shifted towards 0.5 wt.% (or, greater) with  
7 temperature.

## 8 **7. Conclusions**

9 The experimental work presented in this paper is unique; especially, in terms of viscosity of heavy oil  
10 samples tested. As expected, the viscosity data generated has reasonable reproducibility. The results  
11 helped validate the efficacy of metal oxide nanoparticles in reducing heavy oil viscosity at low  
12 temperatures. Additionally, the trends of viscosity variation with change in nanoparticles concentration  
13 and temperature have also been established.

14 Nanoparticles alone may not be an economically viable option for enhancing heavy oil recovery.  
15 Nonetheless, it is imperative to examine the interaction of nanoparticles with heavy oil and their effect on  
16 rheology. This study provides essential information, which can support future research in the area of  
17 nanoparticle stabilized solvent-based emulsion flooding.

## 18 **Acknowledgment**

19 The authors would like to extend their sincere gratitude to the University of Oklahoma for providing  
20 necessary resources and granting the permission to publish this work.

## 21 **Nomenclature**

22  $\gamma$ : Shear Rate,  $s^{-1}$

23  $\mu_N$ : Representative Newtonian viscosity, Pas

24  $n$ : Fluid behavior index, dimensionless

25  $K_v$ : Viscometer consistency index,  $Pas^n$

26

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**Highlights**

- Small amount nanoparticles can alter the viscosity of heavy oil.
- Oils used in this study were more viscous than those used in previous studies
- Heavy oil viscosity is examined at three nanoparticle concentrations.
- Experiments were conducted with two extremely viscous heavy oils.
- Results indicate an existence of optimum concentration of nanoparticles.
- Optimum concentration is a function of the metal type and fluid temperature.