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Enhancing heavy crude oil recovery: injection of FeNi nanoparticles with steam into porous medium

Mejoramiento de crudos pesados: inyección nanopartículas de Fe/Ni con vapor en el medio poroso

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Abstract
The study focuses on utilizing nanoparticles in heavy crude oil recovery processes, particularly in steam injection operations. Various catalytic reactions, including aquathermolysis, water-gas shift, and cracking, were explored to enhance oil recovery efficiency. Bimetallic nanoparticles (Fe/Ni) of 14 nm size were synthesized for this purpose. The study examined a heavy crude oil of 8°API under steam injection conditions. Additionally, the impact of nanoparticles on recovery factor, water production, SARA fractions, and gaseous products was analyzed. The inclusion of Ni-Fe nanoparticles in the system exhibits promising results in reducing viscosity and enhancing recovery factors. Notably, a decrease in viscosity by 86% and an increase in recovery factor by 72.94% were achieved within the porous medium. Water production was better controlled in the presence of nanoparticles, potentially due to their retention in the sand mediated by Van der Waals forces. The interactions between methane, water, and petroleum molecules in the presence of nickel and iron nanoparticles led to the production of smaller hydrocarbons. Furthermore, catalytic cracking, desulfurization, and hydrogenation reactions were observed to enhance product quality in terms of viscosity and sulfur content. The experimental findings underscore the impact of varying injection cycles on recovery percentages, highlighting the significance of hydrogen in molecular transformations. Overall, the study offers valuable insights into the intricacies of nanoparticle-assisted heavy oil recovery, showcasing potential opportunities for optimizing recovery processes within the oil industry.
Keywords: nanoparticles; recovery factor; steam injection; downhole upgrading; enhanced oil recovery.

Resumen
El estudio se centra en la utilización de nanopartículas en los procesos de recuperación de crudo pesado con operaciones de inyección de vapor. Se exploraron varias reacciones catalíticas: acuatermólisis, desplazamiento de agua-gas y craqueo, para mejorar la eficiencia de la recuperación de petróleo. Se sintetizaron nanopartículas bimetálicas (Fe/Ni) de 14 nm de tamaño. Se examinó un crudo pesado de 8°API a condiciones de inyección de vapor para analizar el impacto de las nanopartículas en el factor de recuperación, la producción de agua, las fracciones SARA y los productos gaseosos. La inclusión de nanopartículas de Fe/Ni en el sistema muestra resultados prometedores con una disminución de la viscosidad del 86% y un aumento del factor de recuperación del 72.94% dentro del medio poroso. La producción de agua se controló mejor en presencia de nanopartículas, posiblemente debido a su retención en la arena mediada por las fuerzas de Van der Waals. Las interacciones entre el metano, el agua y las moléculas de petróleo en presencia de nanopartículas Fe/Ni llevaron a la producción de hidrocarburos más pequeños. Se observó que las reacciones de craqueo catalítico, desulfurización e hidrogenación mejoran la calidad del producto en términos de viscosidad y contenido de azufre.
Palabras clave: nanopartículas, factor de recobro, inyección de vapor, mejoramiento a fonde de pozo, recuperación mejorada de petróleo.

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1 Introduction

There are several methods used to produce heavy crude oil. Some common techniques include: 1. Steam Assisted Gravity Drainage (SAGD), where steam is injected into the reservoir to heat the heavy oil and reduce its viscosity. This allows easier extraction and production (Zhou *et al*. 2023; Kholmurodov *et al*. 2023; Ahmadi *et al*. 2020; Liu *et al*. 2020); 2. Cold Heavy Oil Production with Sand (CHOPS) involves producing heavy oil without thermal stimulation. The oil is extracted by creating channels with high-pressure water or gas, allowing the oil to flow to the wellbore (Nobuo Morita, 2022); 3. Various thermal methods are employed to mobilize heavy crude oil, such as cyclic steam stimulation (CSS) and steam flooding (Zhou *et al*. 2023; Divandar *et al*. 2023; Kholmurodov et al. 2023; Ahmadi *et al*. 2020; Liu *et al*. 2020). These methods involve injecting steam into the reservoir to heat the oil, reduce its viscosity, and enhance its flow toward the production wells; 4. Solvent Injection, solvents like propane, butane, or carbon dioxide can be injected into the reservoir to dissolve and dilute heavy oil, making it easier to flow and produce (Kar *et al*. 2021); and 5. In-situ Combustion, in this method, a portion of the heavy oil is burned in situ to generate heat, which reduces the oil's viscosity and enables its flow toward production wells (Kholmurodov *et al*. 2023; Wu *et al*. 2023; Varfolomeev *et al*. 2021; Ahmadi *et al*. 2020; Liu *et al*. 2020).

These methods for producing heavy crude oil have been effective to a certain extent, but there are still challenges and limitations that are trying to address (Hassan *et al*. 2024). For example, traditional methods like steam-assisted gravity drainage (SAGD) and other thermal techniques can be expensive due to the high energy requirements for steam generation and the surface facilities needed (Kholmurodov *et al*. 2023; Ahmadi *et al*. 2020; Liu *et al*. 2020). These costs can limit the economic viability of heavy oil production, especially in lower oil price environments. On the other hand, heavy oil reservoirs typically have lower recovery rates compared to conventional oil reservoirs. Despite advances in extraction technologies, a significant portion of heavy oil remains trapped in the reservoir. Enhancing recovery techniques is crucial to maximize the production potential of heavy oil reserves.

In this sense, additives and catalysts have been applied in wellbores to increase heavy oil production in combination with other common techniques. For example, surfactants can be combined with thermal methods like SAGD to reduce the interfacial tension between oil and water, allowing for better mobility and displacement of heavy crude oil (Kholmurodov *et al*. 2023; Wu *et al*. 2023; Sircar *et al*. 2022; Negi et al. 2021; Liu *et al*. 2020; Velayati and Nouri, 2020; Cheraghian *et al*. 2020). Polymer flooding can be combined with thermal methods (Hassan et al. 2024; Sircar *et al*. 2022; Lashari *et al*. 2020; Liu *et al*. 2020; Cheraghian *et al*. 2020) or solvent injection (Kar *et al*. 2021; Ahmadi et al. 2020; Liu *et al*. 2020) to improve sweep efficiency and increase oil recovery. Alkaline agents can also be combined with thermal methods or solvent injection to enhance the emulsification and mobilization of heavy crude oil (Kar *et al*. 2021). Finally, catalysts can be used in combination with in-situ combustion or thermal methods to promote reactions that break down heavy oil into lighter fractions, improving its flow properties and increasing production (Kholmurodov *et al*. 2023; Wu *et al*. 2023; Morelos-Santos *et al*. 2022; Suwaid *et al*. 2020; Li et al. 2019). This last point is where this work focuses, the study aims to investigate the potential of using transition metal nanoparticles as catalysts to enhance the recovery of heavy crude oil during steam-based thermal recovery processes.

As it is known, there have been studies exploring the combination of catalysts with thermal recovery techniques for enhanced oil recovery (EOR) (Hassan *et al*. 2024; Birbal *et al*. 2023; Zhou *et al*. 2023; Wu et al. 2023; Panchal *et al*. 2021; Alnarabiji *et al*. 2020; Foroozesh *et al*. 2020; Cheraghian *et al*. 2020). While some promising results have been obtained in laboratory or small-scale pilot studies, the use of catalysts with thermal recovery on an industrial scale is still limited (Zhou *et al*. 2023; Sircar *et al*. 2022; Gaya, 2021; Alarbah *et al*. 2021; Negi *et al*. 2021; Panchal *et al*. 2021; Alnarabiji *et al*. 2020; Foroozesh *et al*. 2020). The main reason for this limited implementation is the complexity and challenges associated with the catalyst application in large-scale thermal recovery operations (Hassan *et al*. 2024; Wu *et al*. 2023; Ko and Huh, 2019).

Nearly all of the challenges comprise: 1. Catalyst compatibility: Selecting the right catalyst that is compatible with the reservoir conditions, including temperature, pressure, and composition, is crucial. Finding a catalyst that can withstand the harsh reservoir conditions and deliver the desired performance can be challenging. 2. Catalyst stability and longevity: Catalysts need to maintain their activity and stability over extended periods of operation, which can be difficult under the high-temperature and high-pressure conditions of thermal recovery. Catalyst deactivation and regeneration are ongoing challenges that need to be addressed for successful implementation on an industrial scale. 3. Scale-up and cost considerations: Scaling up catalyst-assisted thermal recovery processes from laboratory or pilot-scale to industrial scale involves significant engineering and economic considerations. The cost of implementing and maintaining catalysts at a large scale needs to be carefully evaluated (Mukhamatdinov *et al*. 2023). Despite these challenges, ongoing research and development efforts continue to explore the potential benefits of catalysts in combination with thermal recovery techniques (Hassan *et al*. 2024; Wu *et al*. 2023; Panchal *et al*. 2021; Negi *et al*. 2021; Alnarabiji *et al*. 2020; Foroosesh *et al*. 2020).

Nanoparticles could help to overcome the challenges related to the application of downhole catalysts for heavy crude oil recovery (Hassan *et al*. 2024; Wu *et al*. 2023; Sircar *et al*. 2022; Negi *et al*. 2021; Panchal *et al*. 2021; Alnarabiji *et al*. 2020; Foroozesh *et al*. 2020; Medina *et al*. 2019). Nanoparticles have unique properties such as high surface area to volume ratio, tunable surface chemistry, and improved catalytic activity, which make them effective in catalyzing reactions and enhancing oil recovery processes. It is possible to improve the efficiency of heavy crude oil recovery, reduce costs, and minimize environmental impact (Castro *et al*. 2024; Alvarez-Amparan *et al*. 2012; Huirache-Acuña *et al*. 2006), by utilizing nanoparticles as catalysts in downhole applications (Hassan *et al*. 2024; Zhou *et al*. 2023; Wu *et al*. 2023; Ko and Huh, 2019).

Steam recovery and the reactions that occur under downhole conditions are of interest to this work (Birbal *et al*. 2023). These reactions, known as aquathermolysis (Reaction 1), have been studied since 1982 by Hyde (Hyne *et al*. 1982; Clark *et al*. 1983) and later by other researchers. Several catalysts have been studied (Araujo-Ferrer *et al*. 2018) in combination with aquathermolysis, such as transition metals (Fe, Ni, Co, and others) (Varfolomeev *et al*. 2023; Wu *et al*. 2023; Sitnov *et al*. 2022), zeolites (Saeed *et al*. 2022), metal oxides (alumina, silica, and titania) (Varfolomeev *et al*. 2023), supported and unsupported nanoparticles on inert materials (Varfolomeev *et al*. 2023), and mixed metal oxides composed of combinations of various metal oxides (Sitnov *et al*. 2022).

Heavy oil (liquid) + H_2O (steam) $\rightarrow$ light hydrocarbons + gases (CH_4, CO, H_2,) (Reaction 1)

CH_4 (gas) + hydrocarbon (liquid) $\rightarrow$ hydrocarbon(s) (liquid) (Reaction 2)

H_2O (steam)+ CO (gas) $\leftrightarrow$ CO_2 (gas)+H_2 (gas)
ΔG_{423K}=-5.606 kCal, ΔG_{623K}=-4.211 kCal (Reaction 3)

Heavy oil +H_2O $\leftrightarrow$ CO+H_2S + light compounds (Reaction 4)

According to reports, the nanoparticle's integration with aquathermolysis reactions shows promise for the oil industry. Initially, nanoparticles can enhance thermal conductivity, improving heat transfer efficiency in the reservoir during steam injection (Mustafin *et al*. 2020). This can lead to reduced energy consumption and increased oil recovery rates. Additionally, nanoparticles have demonstrated the capability to alter viscosity and surface tension, facilitating the mobility and extraction of oil from the reservoir, thereby enhancing recovery efficiency (Zhou *et al*. 2023; Mukhamatdinov *et al*. 2023; Sircar *et al*. 2022; Negi *et al*. 2021; Lashari *et al*. 2020; Foroozesh *et al*. 2020). Furthermore, observations suggest that nanoparticles can mitigate formation damage caused by steam injection by stabilizing reservoir rock surfaces and preventing pore blockage, thus preserving reservoir permeability (Foroozesh *et al*. 2020). Lastly, the customization of nanoparticle preparation is achievable, providing tailor-made solutions for optimal performance in heavy oil recovery processes (Foroozesh and Kumar, 2020). Also, nanoparticles can be engineered to plug selectively high permeability zones, redirecting steam flow to areas with lower permeability and promoting uniform reservoir heating and oil displacement (Lao *et al*. 2024; Foroozesh *et al*. 2020). Overall, the use of nanoparticles in conjunction with heavy crude oil steam recovery has the potential to enhance the efficiency, effectiveness, and sustainability of the recovery process, making it a promising avenue for improving heavy oil extraction operations.

In this work, to evaluate their impact on the recovery factor, sulfur content, and the quality of the final crude oil, the application of iron and nickel nanoparticles under steam injection conditions is proposed.

2 Theoretical basis

2.1 Heavy and extra-heavy crudes (CP/XP)

Crude oil is a fossil fuel that originates from organic matter collected in sedimentary environments and subjected to heat and pressure over time. It develops from the remnants of light crude oil, with the lighter components lost due to microbial degradation, water flushing, and evaporation. The degree of degradation dictates the heaviness of the resulting crude oil (Zhou *et al*. 2023; Mukhamatdinov *et al*. 2023; Hendraningrat *et al*. 2014). A significant portion of the world's petroleum reserves consists of viscous and heavy hydrocarbons, which pose challenges related to extraction and refinement due to their complexity and cost. Typically, the economic worth of crude oil decreases as its density and weight increase. Conversely, the lighter components obtained through simple distillation are more valuable. Heavy crude oils often contain higher levels of metals and other elements, necessitating more intricate processes for extraction and handling of the byproducts. Given the rising demand and prices for oil, coupled with the decline in production from conventional oil fields, the industry focus in numerous regions is shifting toward heavy oil resource exploitation (Zhou *et al*. 2023; Mukhamatdinov *et al*. 2023; Kholmurodov *et al*. 2023; Farouq, 1973; Speight, 2013).

2.2 *Steam injection*

The technique is employed to inject heat in the form of steam into underground deposits of organic materials through wells to facilitate the production of fuels. The latent heat present in the steam enhances the efficiency of displacement and extraction processes. As the temperature increases, the oil viscosity decreases, enabling it to flow more smoothly and creating a more favorable mobility ratio (Zhou *et al*. 2023; Kholmurodov *et al*. 2023; Speight, 2013).

2.3 *Cyclic steam injection*

The thermal recovery method involving steam injection into a well follows a three-stage process. During the first stage, a steam plug is introduced into the reservoir. In the soaking stage, the well is shut in for several days to ensure uniform heat distribution and oil dilution. Finally, the thinned oil is produced through the same well. This cyclic procedure is repeated as long as oil production remains feasible (Zhou *et al*. 2023; Kholmurodov *et al*. 2023; Guo *et al*. 216; Speight, 2013).

2.4 *Downhole upgrading process*

The downhole upgrading process involves utilizing thermal techniques, with specific additives like hydrogen donors, additives, and catalysts to enhance downhole characteristics. These processes aim to improve the crude oil quality, resulting in a higher proportion of distillable products and ultimately boosting the economic viability of oil recovery. In the same way, the porous medium as a catalytic reactor and the inherent mineral matrix are used. These methods help cut down lifting costs and diminish the requirement for light and medium crudes as diluents to enhance fluidity. This approach also eliminates the necessity for constructing large, costly pressurized tanks, as the well itself, can function as a reactor. Furthermore, these processes can be applied to offshore and onshore wells, including remote or geographically challenging locations. They are versatile enough to handle a wide spectrum of crude oil types, ranging from light to extra heavy, and do not necessitate a specific boiling range as typically required in refineries (Wu *et al*. 2023; Zhou *et al*. 2023; Suwaid *et al*. 2020; Duvudov and Monghanloo, 2017; Weissman, 1996).

2.5 *Aquathermolysis*

Aquathermolysis is a term derived from "aqua" meaning water, "thermo" representing heat, and "lysis" indicating rupture. It refers to a series of chemical reactions that have gained attention in recent years, focusing on the alterations in the physical and chemical attributes of heavy and extra-heavy crude oils (CP/XP) occurring downhole (Hyne *et al*. 1982; Clark *et al*. 1982). Research indicates that the primary mechanism involves a sequence of reactions between water and sulfur in heavy crude oil at temperatures ranging from 473.15 K to 623.15 K. These reactions intensify until they peak just before initiating thermal cracking reactions, resulting in the formation of organosulfur fragments and hydrogen sulfide. Thermal cracking reactions typically commence between 568.15 K and 598.15 K, with water presence facilitating the process. During this phase, amines and phenols present in the oil decompose. The temperature range from 473.15 K to 598.15 K holds significance as these temperatures align with reservoir conditions associated with steam injection techniques. (Zhou *et al*. 2023; Wu *et al*. 2023).

3 Method and procedure

The methodology employed for assessing the recovery factor and behavior of crude oil, water, and bimetallic nanoparticles in the porous medium is depicted in Figure 1. Three experimental runs were conducted: 1) a blank run involving only steam injection, 2) a run using aromatic solvents of monoaromatic and diaromatic types as the matrix supporting the nanoparticles with steam, and 3) a run incorporating the nanoparticles along with steam. The procedure commences with the preparation of the well fluids for injection, followed by conditioning a 30 cm cell packed with sand to replicate reservoir conditions. Subsequent steps involve conducting gas, water, and oil permeability measurements, culminating in displacement tests.

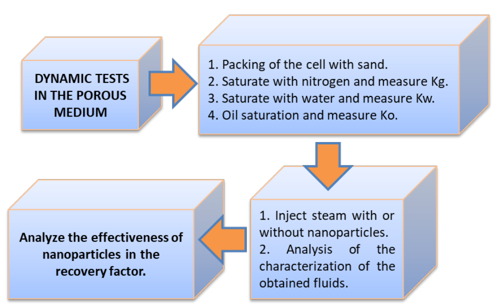


Fig. 1. Experimental setup for dynamic aquathermolysis tests with and without Ni/Fe nanoparticles.

Table 1. Characterization Tests of the used equipment.

Sample	Analytical technique	Analytical principle	Test objective
Heavy oil	Dynamic viscosity of the oil. AE* = 1 %. **MCR-301-Anton Para**	Oil deformation at T = 50 ºC, at a cutting speed of ν = 20 s^{-1}	Determine the initial oil viscosity value at reservoir temperature. (T = 50 ºC)
Heavy oil	Sulfur content of crude oil. AE = 0,2% **Broker S2 Ranger EDXRF**	Wavelength Fluorescence Spectroscopy X-Rays (FRX) ASTM D 4294	Determine the mass percentage of sulfur in the oil.
Heavy oil	Crude oil API Gravity. AE = 0,6 % **Densimeter DMA-4500**	Determination of the corresponding mass of a fixed volume of a fluid. T =15,56 ºC ASTM D 70-03	Classify oil according to API gravity and establish a relationship between its mass and volume
Heavy oil	Saturates, aromatics, resins and asphaltenes (SARA) content in oil AE = 2 % **Water 600 HPLC**	Thin layer chromatography coupled to a flame ionization detector	Determine the distribution of saturates, aromatics, resins and asphaltenes in oil
Heavy oil	Carbon and hydrogen in oil AE=0,001 % **LECO TRUSPEC CHN**	Determination of hydrogen and carbon content by dynamic combustion, by Pregl-Lieb method ASTM D 5291-02	The higher the hydrogen/carbon ratio, the higher the amount of saturates, the better the quality of the oil.
Heavy oil	Nickel and vanadium content in oil. AE= 2 % **Broker S2 Ranger EDXRF**	Wavelength Fluorescence Spectroscopy X-Rays (FRX) ASTM D8252	Determine the nickel and vanadium content associated with the presence of resins and asphaltenes.
Heavy oil	Molecular weight. AE = 2 % **Cryette WR, Systems**	Freezing point of solutions with cryoscopy	Molecular weight determination
Nanoparticles	Morphology and composition of solid samples. AE= 0,5 % **JEM 2100, filamento LaB_6**	Scanning Electron Microscopy (SEM)	Determination of the size and morphology of nanoparticles
Nanoparticles/ Reservoir Sand	Crystalline phases present in a solid. AE = 1 % **PANalytical, XPert PRO, Cu anode**	X-ray diffraction of crystalline powders (XRD)	Identification of crystalline phases of a solid.
Gases	Fuel gas análisis. AE= 0,5 %. **GS/MC 6890 acoplado al espectrómetro de masa 5973**	High resolution gas chromatography	Determine the presence of H_2, O_2, N_2, CO, CO_2, H_2S, alkanes C1-C_5.

**AE: Associated error*

3.1 Characterization techniques

In Table 1 all characterization techniques are shown. As can be see, each component was characterized by a corresponding technique and the equipment used are mentioned.

3.2 Fluid preparation

Table 2 displays the characterization of the Venezuelan heavy crude oil utilized in the studies outlined in this work. The crude oil is notably heavy, possessing an API gravity of 8, high resin and asphaltene content exceeding 35%, and a viscosity surpassing 30,000 Pa*s.

The fluids utilized for the dynamic tests were: i) synthetic reservoir water, ii) synthetic injection water sourced from steam, iii) recombined oil, iv) bimetallic nanoparticles, v) drilling fluid, and vi) completion fluid. The reservoir water comprises sodium bicarbonate, sodium sulfate, sodium chloride, calcium chloride, magnesium chloride in distilled water, sodium carbonate, and potassium chloride. Meanwhile, the steam injection water includes sodium bicarbonate, sodium sulfate, sodium chloride, and sodium carbonate, as detailed in Table 3.

The prepared nanofluid consists of iron and nickel nanoparticles dispersed in a mixed paraffinic and aromatic hydrocarbon, which is a bottom side product from vacuum distillation units, with a density of 0.906 g/ml. The nanoparticles suspension was prepared by reducing two different nickel and iron salts using hydrogen as a reducing

Table 2. Characterization of heavy crude oil.

Property	Heavy crude
Viscosity (Pa*s)	32,450 ± 1
Density (Kg/m^3)	1.0144
°API	8 ± 0.6
Saturated (% p/p)	14.78 ± 0.4
Aromatics (% p/p)	33.19 ± 1
Resins (% p/p)	35.06 ± 1
Asphaltenes (% p/p)	16.97 ± 0.5
Sulfur (% p/p)	3.5 ± 0.04
H/C (%/%)	10.63/85.7± 0.003
Nickel (ppm)	95 ± 5
Iron (ppm)	4.4 ± 2
Vanadium (ppm)	390.2 ± 20

agent. A nonionic surfactant was used for stabilization to prevent particles agglomeration. Nanoparticle synthesis was conducted under initial hydrogen pressures ranging from 2068 to 3447 kPa and temperatures between 150 and 350 °C, with reaction times spanning 8 to 24 hours. The resulting nanofluid is a viscous suspension of nickel and iron nanoparticles with an API gravity of 22°, a boiling range of 350-550°C, and a density of 0.983 g/ml.

3.3 *Porous media properties*

The porous medium under study consists of medium to fine-grained, unconsolidated sandstones. X-ray diffraction (XRD) analysis reveals a composition of 92% kaolinite, with smaller amounts of illite and an illite/smectite mixture. Petrophysical characterization indicates a porosity of 30%, a permeability of 14,000 millidarcies (mD), and initial water saturation (Swi) ranging from 0.16 to 0.30 and an initial oil saturation (Soi) between 0.60 and 0.70.

Regarding pore classification, it was determined that the rock consists of 40% megaporous (>10 μm), 32% macroporous (10 to 4 μm), and 23% mesoporous (4 to 0.35 μm) structures. This indicate that the rock is highly porous and heterogeneous.

The rock-fluid interaction was measured at 12.96 ft/d in terms of interstitial velocity, representing the critical velocity at which fine particles or clays begin to displace from one pore throat to another. Additionally, it was found that the rock is water-wettable.

It should be noted that the experiments conducted in this study utilized the actual rock described in the previous paragraphs.

3.4 *Displacement cell conditioning*

To prepare the cell containing sand from the porous medium, a cylindrical stainless-steel container is utilized to replicate, at a laboratory scale, the conditions of the well under study in the reservoir. The sand is compacted while thermocouples are installed along the entire length of the cell. The process involves three stages to determine the gas permeability (Kg), formation water permeability (Kw), and oil permeability (Ko):

1. Air permeability (Kg) is measured in the cell without fluids.

2. Formation water is injected into the cell at reservoir temperature and pressure until stable conditions are achieved, and the water permeability (Kw) is determined.

3. Recombined crude oil is injected into the displacement cell at a constant flow rate of 0.5 cm3/min until irreducible water saturation is reached. Different flows of heavy crude oil (0.5, 0.4, 0.3, 0.2, 0.1 cm^3/min) are injected, with pressure differentials measured for each flow rate. Subsequently, the injected volumes are quantified, and the equipment is cleaned. The displacement cell is maintained at the temperature, pressure, and saturation conditions of recombined heavy oil, water, and the reservoir sand.

3.5 *Alternate vapor injection testing with nanoparticles*

Alternate vapor injection testing with nanoparticles involves utilizing the equipment as illustrated in Figure 2. The setup comprises five storage units: i) a porous medium cell containing crude oil and water at reservoir conditions, ii) a cell with crude oil mixed with methane, iii) a cell with synthetic injection water for steam, iv) a cell containing bimetallic iron and nickel nanoparticles, and v) a collection cell for the produced effluents. Additionally, there are three pumping units: i) a steam injection pump integrated with the steam generator along with temperature and pressure gauges, ii) a nanoparticle injection pump, and iii) an effluent collection pump. The process entails simulating alternate steam injection at a laboratory scale, mirroring the three typical stages in field operations - steam injection, soaking, and production.

Table 3. Chemical composition of the water used in conducting displacement tests for the three scenarios: 1. with steam only, 2. with steam and solvent, and 3. with steam and Ni/Fe nanoparticles.

Compound	Chemical formula	Reservoir water concentration (g/L)	Injection water concentration (g/L)
Sodium bicarbonate	$NaCO_3$	2.135	0.380
Sodium sulfate	Na_2SO_4	10.960	0.140
Sodium chloride	NaCl	78.910	0.058
Sodium carbonate	Na_2CO_3	0.018	0.148
Calcium chloride	$CaCl_2$*H2O	0.404	-
Magnesium chloride	$MgCl_2$*6H_2O	0.368	-
Potassium chloride	KCl	0.305	-

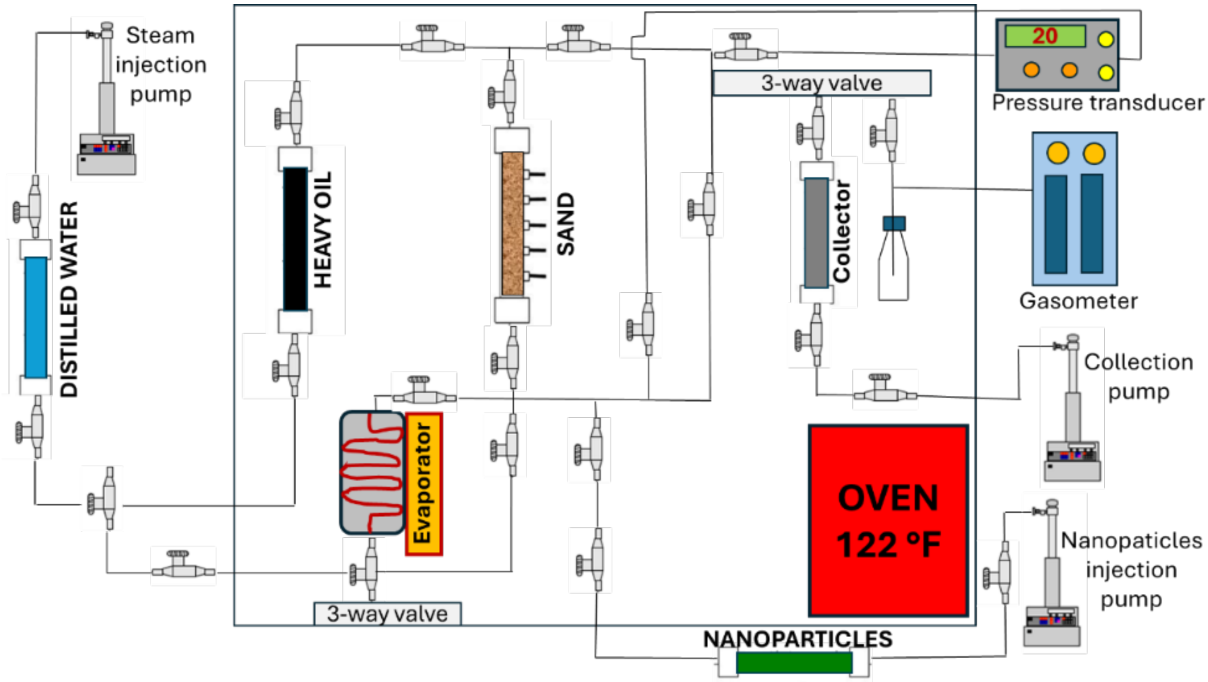


Fig. 2. Experimental setup for conducting displacement tests with and without nanoparticles.

3.6 *Displacement cell conditioning*

The heavy oil recombination involves mixing heavy oil with methane under reservoir conditions of 6619 kPa and 323.15 K, resulting in a gas-oil ratio (GOR) similar to field values (2.41 m3N/bblN). During the steam injection phase into the cell, steam is introduced from an evaporator with 80% quality and a pressure of 7584 kPa, injected for two pore volumes. In the soaking period, the steam inlet to the displacement cell is shut, and the equipment is left to stand for 24 hours at a temperature of 533.15 K. During the production phase of the cell: i) Effluents are generated by the pressure difference within the displacement cell and a production cylinder maintained at reservoir pressure of 6619 kPa. ii) The produced fluids (crude oil, water, and gas) undergo separation via flash distillation at atmospheric pressure. iii) Gas, crude oil, and water are stored in collectors for further characterization, with crude oil and water being separated through decantation at reservoir temperature. This process is referred to as the steam cycle (Figure 2).

In the nanoparticle injection phase, nanoparticles are injected at a mass ratio of 0.2 iron and nickel nanoparticles to heavy crude oil after the steam injection. Subsequently, the cell is sealed, followed by the soaking period and then production, following the outlined methodology. For the production stage, the injector well and producer are the same, allowing the injected fluid to return to its entry point, carrying the displaced fluid in a vertical configuration. Both steam and nanoparticles move from the bottom to the top throughout the control volume during the injection stage. Various factors such as the recovery factor percentage, water produced percentage, nanoparticle recovery percentage, upgrading of the produced crude oil, potential formation damage, and permeability return will be analyzed.

4 Results and discussion

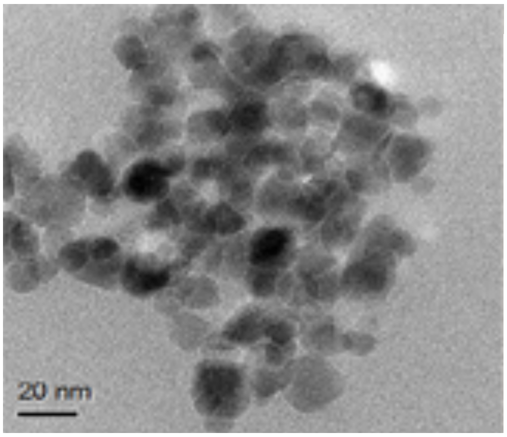
The subsequent results detail the impact of employing Ni/Fe nanoparticles on properties such as viscosity, recovery factor, sulfur content, the quality of the final crude oil determined through SARA analysis, the composition of the produced gases, and water recovery. It is crucial to examine the impact of the solvent mixture as an oil-phase product, as it has the potential to dilute the heavy crude, potentially influencing its viscosity and, consequently, affecting the efficacy of the metallic additive as a catalyst.

4.1 *Synthesis of Fe/Ni metallic nanoparticles*

Elemental analysis conducted by inductively coupled plasma atomic emission spectroscopy revealed an iron concentration of 490 ppm and a nickel concentration of 450 ppm, close to the nominal concentration of 500 ppm for each element. Additionally, Figure 3 depicts the micrograph obtained during electron microscopy analysis, demonstrating a homogeneous system concerning particle size distribution and morphology. The measurement was conducted on 190 particles, indicating a particle size distribution ranging from 8 nm to 18 nm, with a weighted average size of 14 nm.

4.2 *Effect of nickel and iron nanoparticles on recovery factor and the crude oil quality*

According to Table 3, recovery percentages were recorded at 34.29% for steam injection without nanoparticles and 72.94% for steam injection with nanoparticles after three steam injection cycles.



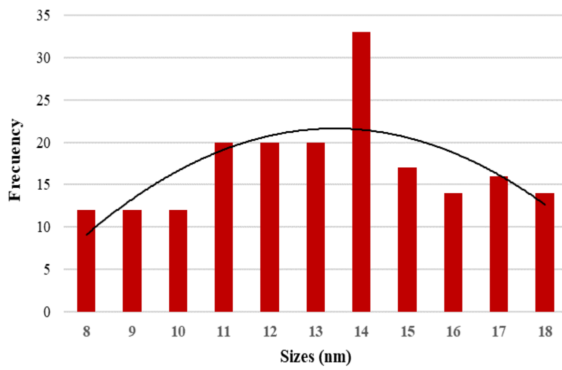


Fig. 3. (a) Micrograph of iron/nickel nanoparticles; (b) Histogram of sizes.

Table 3: Percentage of the final recovery factor in each displacement cycle.

Displacement	% Recovery				
	1st Cycle	2nd Cycle	3rd Cycle	Additional recovery	Total, recovery
Steam injection	29.57	3.64	1.08	-	34.29
Injection of solvent and steam	30.3	11.43	2.88	10.32	44.61
Injection of Fe/Ni nanoparticles and steam	37.81	30.73	4.40	38.65	72.94

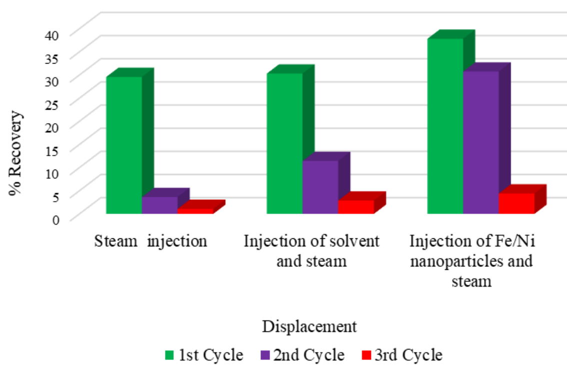


Fig. 4. Percentage of recovery factor for each steam injection cycle.

Scaling these laboratory findings to oil field applications necessitates considerations, such as maintaining an optimal steam injection rate to minimize heat losses in well walls and determining an appropriate soaking time based on field-specific factors and reservoir characteristics. This balance aims to allow heat dissipation without risking steam condensation and potential flooding of the porous medium with water.

Furthermore, the steam displacement tests conducted with an aromatic solvent mixture showcased an increased recovery percentage of 44.61%. This improvement suggests that the oil-based solvent effectively diluted the heavy crude, thereby reducing viscosity and enhancing the flow characteristics of heavy crude oil at the surface.

The observations depicted in Figure 4 indicate that recovery percentages decrease with each subsequent injection cycle across all three displacements. Throughout steam injection and soak periods, the heavy oil's viscosity reduces within the steam zone, leading to the thermal expansion of heavy oil and water. In the initial injection cycle, a significant portion of heavy oil within the porous medium is displaced to the surface. In the second cycle, the remaining heavy oil is extracted, and by the third cycle, there is a minimal production response, possibly due to decreasing pressure and increasing water production.

Upon commencing production, a high-water cut is evident due to condensed steam. Subsequently, crude oil production sharply declines, reaching a point where it is no longer economically viable, prompting a restart of the steam injection cycle.

Also, Figure 4 illustrates the detailed oil recovery factors measured over three cycles of steam injection experiments using various combinations of additives, steam, a nanoparticles matrix (solvent), Ni-Fe nanoparticles, and their combinations under saturated conditions. It is observed that the highest recovery factor was consistently achieved in the first cycle, followed by a general declining trend in subsequent cycles. In a similar experiment, Yi *et al.* 2016 reported that such a decrease in the recovery factor in later cycles can be primarily attributed to the reduced relative permeability of oil in the sand pack near the injection port. With each cycle, as water is injected into the sand pack, water saturation near the injection port increases over time, consequently, reducing the oil's relative permeability.

Furthermore, it is noted that the presence of nanoparticles resulted in a higher recovery factor, particularly showing a substantial increase in the second cycle. It is plausible that Ni-Fe nanoparticles facilitate aquathermolysis, water-gas shift reaction (WGSR), and desulfurization reactions, leading to the cracking of larger hydrocarbon molecules and in-situ hydrogen production. These processes promote the generation of smaller molecules that improve crude oil mobility, thereby influencing the recovery factor. Table 3 demonstrates that the

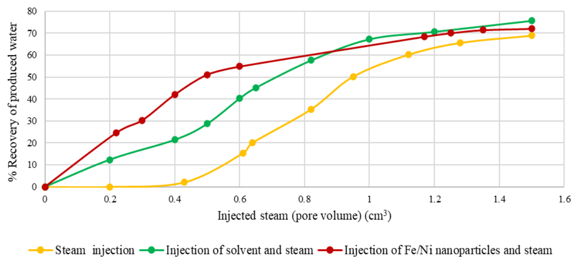


Fig. 5. Water production cut-off based on the injected water volume for the three tests: 1. with steam only, 2. with steam and solvent, and 3. with steam and nanoparticles.

overall recovery factor across the three cycles was elevated when nanoparticles were incorporated into the system. This finding is further supported by water production data, when nanoparticles and steam are introduced, water production is more efficiently regulated, resulting in less significant high-water cut-offs initially. This controlled water production enhances mobility, potentially increasing oil and gas production, as demonstrated in Figure 4. In contrast, when solely utilizing steam, the percentage of recovered injection water tends to be higher. This is likely attributed to rapid steam breakthrough facilitated by permeability channels, leading to elevated water production from the early stages, as shown in Figure 5.

Figure 6 depicts a consistently high methane content in the gaseous effluent observed throughout all dynamic tests, predominantly attributed to initially introduced methane. Interestingly, the methane content decreases notably upon nanoparticles introduction into the system. This suggests that nanoparticles may be promoting alkylation reactions (as per reaction 1) or catalytic cracking reactions or methane can react with water or carbon dioxide to produce a mixture of carbon monoxide (CO) and hydrogen gas (H_2), but in this last case, both reactions are highly endothermic and must be carried out at temperatures at least as high as 900°C (Hawk *et al*. 1986). In the second scenario, a potential explanation for the presence of ethane and propane is the catalytic promotion of cracking reactions involving molecules containing ethyl and propyl radicals.

Methane is known to be highly stable, with a C-H bond energy of 105 kcal/mol, making it relatively inert to chemical reactions at temperatures where thermal dissociation is negligible. Dissociation of methane is typically not measurable in the absence of a catalyst below 525°C (Gold and Gordon, 1986). Methane reactions with saturated hydrocarbons like alkanes and cycloalkanes are not commonly observed. Additionally, aromatics, which are major unsaturated hydrocarbon components of petroleum, do not typically react with methane under ordinary temperatures and pressures. However, alkylation of benzene with methane could potentially occur under specific conditions, such as the presence of nickel catalysts or a strong acid system (Reaction 2).

Nevertheless, to facilitate the production of lower molecular weight molecules responsible for the irreversible viscosity changes, hydrogen could potentially be generated through the water-gas shift reaction (Reaction 3) under the operating conditions of this study. This hydrogen readily reacts with the free radicals generated during the thermal and catalytic cracking of larger hydrocarbon molecules. Notably, the absence of hydrogen in the gaseous products

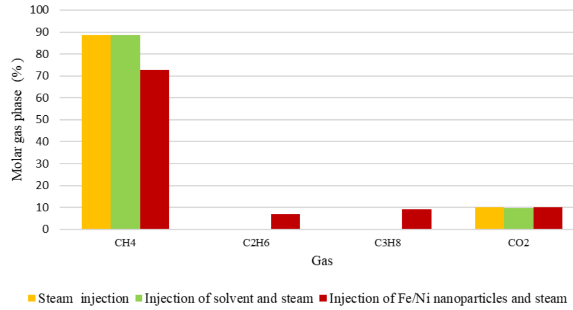


Fig.6. Gases detected in the gaseous products for the three tests: 1. with steam only, 2. with steam and solvent, 3. with steam, and nanoparticles.

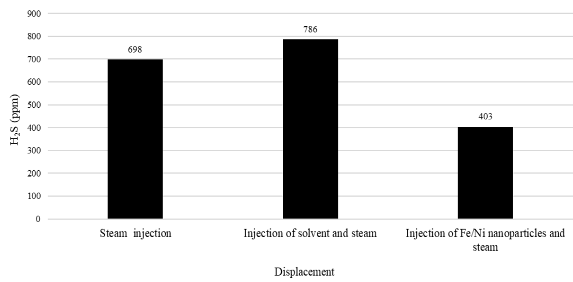


Fig. 7. Hydrogen sulfide generated for the three tests: 1. with steam only, 2. with steam and solvent, and 3. with steam and nanoparticles.

was observed. This consideration is supported by the non-observation of CO in the gaseous products, hinting at its potential consumption in facilitating the water-gas shift reaction.

Figure 7 demonstrates the hydrogen sulfide production in all three displacements, with the lowest concentration observed in the test involving metal nanoparticles. This observation suggests that sulfur may be retained within the structure of the nanoparticle forming metallic sulfides. Previous research posits that iron and nickel metals interact with heteroatoms, particularly sulfur, present in crude oil, potentially forming metal-asphaltene intermediates. This view is supported by studies in the literature (Birbal *et al*. 2023; Vakhin *et al*. 2023; Hamedi and Babadagly, 2013) investigating the interaction of iron and nickel metals with sulfur and nitrogen within heavy crude asphaltenes using quantum mechanics.

According to the research, these metals can disrupt aromatic rings, directly reaching sulfur due to their low binding energy. As a result, Fe-S or Ni-S bonds are created, weakening the strength of C-S bonds, indicative of potential hydrodesulfurization cracking processes. The study also suggests that these complexes might enhance water dissociation and promote hydrogenation reactions, although additional research is necessary to delve deeper into these mechanisms.

In the displacement tests, there was a slight variation in the viscosities of the initial effluents compared to the original crude oil. The initial movement of fluids, during displacement is primarily driven by the steam injection. This suggests a viscosity gradient along the displacement cell arising from the heating effect of steam and the influence of nanoparticles. As illustrated in Figure 8, the injection of nanoparticles resulted in the most significant viscosity

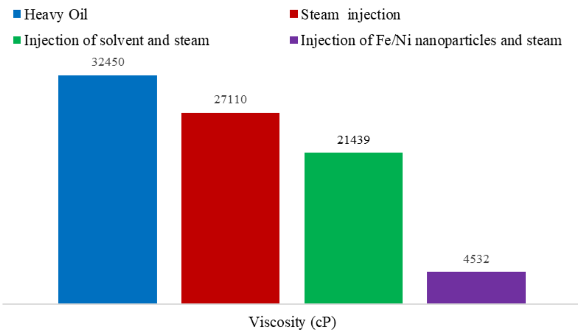


Fig. 8. Viscosity of the crude obtained from the aquatermolytic reaction in the porous medium for the three tests: 1. with steam only, 2. with steam and solvent, and 3. with steam and nanoparticles.

decrease, amounting to 86%. This notable reduction could be possibly attributed to the potential catalytic role of metallic nanoparticles in catalyzing aquathermolytic, cracking, WGS, desulfuration, and hydrogenation reactions (Reaction 4).

Subsequently, in the SARA analysis, obtained via liquid chromatography, there is an uptick in the saturates and aromatics fractions, potentially indicating a trade-off involving the transformation of resins and asphaltenes fractions, as depicted in Figure 9. Among the various displacement methods, the combination of vapor and nanoparticles exhibited the most notable alterations, showcasing a 20% increase in saturates, a 15.15% increase in aromatics, and reductions of 5.71% in resins and 11.764% in asphaltenes. These findings align with results from other research groups (Lam-Maldonado *et al*. 2020), reinforcing the evidence of a physical and chemical enhancement in the heavy crude oil demonstrated by these changes in SARA fractions and viscosity.

Moreover, these findings support the notion that catalytic cracking, desulfuration, WGS, and hydrogenation reactions are indeed occurring, as the product unmistakably comprises smaller molecules. Consequently, the product exhibits improved quality in terms of viscosity, sulfur content, and SARA fractions. It is widely acknowledged that larger molecules exhibit stronger intermolecular forces, including London forces, leading to robust molecular connections. This phenomenon impedes molecular flow, consequently resulting in elevated viscosity levels.

Conclusion

Downhole deployment of Fe/Ni bimetallic nanoparticles under steam injection conditions presents a promising avenue for enhancing heavy crude oils. These nanoparticles facilitate reactions like cracking, hydrogenation, desulfurization, and the water-gas shift process, thereby improving the quality of heavy to medium crude oil.

The production of methane, ethane, propane, hydrogen, and carbon dioxide contributes to viscosity reduction in heavy oil by breaking C-S bonds and hydrogenating resulting free radicals. The absence of carbon monoxide indicates the activation of the water-gas shift reaction by nanoparticles, leading to carbon dioxide formation. The hydrogen produced in this reaction is utilized in the hydrogenation processes of cracked oil.

In displacement tests involving alternate steam injection, recovery rates increased progressively: 34.29% with steam alone, 44.61% with steam and aromatic solvents, and 72.94% with steam and bimetallic nanoparticles. The latter substantial recovery improvement suggests the catalytic role of iron and nickel transition metals in boosting oil production.

Nanoparticle distribution in the reservoir primarily hinges on Van der Waals forces, which can lead to retention within the porous medium while maintaining optimal water cuts during early injection phases, enhancing mobility for increased oil and gas production.

Physicochemical property enhancements of heavy crude oils were observed in the presence of bimetallic nanoparticles, resulting in a significant decrease in viscosity (86%) and sulfur content (12%). SARA analysis exhibited increased saturates and aromatics paired with reduced resins and asphaltenes compared to the original crude composition.

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