Instituto Alberto Luiz Coimbra de
Pós-Graduação e Pesquisa de Engenharia
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OPPORTUNITIES AND CHALLENGES OF OIL AND GAS DEVELOPMENT FROM UNCONVENTIONAL RESERVOIRS IN COLOMBIA

Camilo Andrés Guerrero Martin

Tese de Doutorado apresentada ao Programa de Pós-graduação em Planejamento Energético, COPPE, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Doutor em Planejamento Energético.

Orientador: Alexandre Salem Szklo

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OPPORTUNITIES AND CHALLENGES OF OIL AND GAS DEVELOPMENT FROM UNCONVENTIONAL RESERVOIRS IN COLOMBIA, AND POSSIBLE LESSONS FOR ANDEAN COUNTRIES

Camilo Andrés Guerrero Martin

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Orientadores: Prof. Alexandre Salem Szklo

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OPORTUNIDADES E DESAFIOS DO DESENVOLVIMENTO DE PETRÓLEO E GÁS A PARTIR DE RESERVATÓRIOS NÃO CONVENCIONAIS NA COLÔMBIA.

Camilo Andrés Guerrero Martin

Dezembro/2023

Orientadores: Alexandre Salem Szklo

Programa: Planejamento Energético

Esta tese de doutorado se concentra no estudo exaustivo da exploração de reservatórios de petróleo não convencionais na Colômbia, especificamente por meio da técnica de fraturamento hidráulico. A pesquisa está dividida em cinco capítulos que abordam os principais aspectos relacionados a esse tópico. Ela examina as necessidades e as motivações que levam a Colômbia a considerar a exploração de campos de petróleo não convencionais. Analisa os fatores econômicos, energéticos e estratégicos por trás dessa decisão, bem como os desafios e preocupações associados. Também são explorados os aspectos relacionados à viabilidade técnica, aos custos de produção e aos possíveis benefícios econômicos da exploração de campos não convencionais. O fenômeno da precipitação e deposição de asfalteno na produção de petróleo, bem como a aplicação da nanotecnologia para sua inibição e remediação, também são analisados de forma abrangente. Os desenvolvimentos mais recentes nesse campo são discutidos, destacando abordagens inovadoras para prevenir e mitigar problemas relacionados à migração de asfaltenos e finos nos reservatórios. Por fim, uma análise detalhada dos possíveis riscos ambientais associados às operações de fraturamento hidráulico na formação "La Luna", na Colômbia, é dedicada a uma análise detalhada dos possíveis riscos ambientais associados às operações de fraturamento hidráulico na formação "La Luna", na Colômbia. Os possíveis impactos na água, no solo, na biodiversidade e na saúde humana são investigados, fornecendo uma avaliação abrangente dos desafios ambientais e das medidas de mitigação necessárias. Esta tese de doutorado fornece uma visão geral abrangente da exploração e do aproveitamento de reservatórios de petróleo não convencionais na Colômbia, abordando aspectos técnicos e econômicos, bem como considerações ambientais e tecnológicas. Ela fornece uma base sólida para a tomada de decisões informadas no setor de energia e petróleo da Colômbia, levando em conta os desafios e as oportunidades que esse setor apresenta.

Abstract of Thesis presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Doctor of Science (D.Sc.)

OPPORTUNITIES AND CHALLENGES OF OIL AND GAS DEVELOPMENT FROM UNCONVENTIONAL RESERVOIRS IN COLOMBIA.

Camilo Andrés Guerrero Martin

December/2023

Advisors: Alexandre Salem Szklo

Department: Energy Planning

This doctoral thesis focuses on the exhaustive study of the exploitation of unconventional oil reservoirs in Colombia, specifically by means of the hydraulic fracturing technique. The research is divided into five chapters that address the main aspects related to this topic. It examines the needs and motivations that lead Colombia to consider the exploitation of unconventional oil fields. It analyzes the economic, energy and strategic factors behind this decision, as well as the associated challenges and concerns. Aspects related to technical feasibility, production costs and the possible economic benefits of exploiting unconventional fields are also explored. The phenomenon of asphaltene precipitation and deposition in oil production, as well as the application of nanotechnology for its inhibition and remediation, are also comprehensively analyzed. The latest developments in this field are discussed, highlighting innovative approaches to prevent and mitigate problems related to the migration of asphaltenes and fines in reservoirs. Finally, a detailed analysis of the possible environmental risks associated with hydraulic fracturing operations in the "La Luna" formation in Colombia is dedicated to a detailed analysis of the possible environmental risks associated with hydraulic fracturing operations in the "La Luna" formation in Colombia. The possible impacts on water, soil, biodiversity and human health are investigated, providing a comprehensive assessment of the environmental challenges and mitigation measures required. This doctoral thesis provides a comprehensive overview of the exploration and exploitation of unconventional oil reservoirs in Colombia, addressing technical and economic aspects as well as environmental and technological considerations. It provides a solid basis for making informed decisions in Colombia's energy and oil sector, taking into account the challenges and opportunities that this sector presents.

DEDICATORIA

A Dios todo poderoso, Blanca Cecilia y a Laura Estefanía

¡Hasta la victoria, siempre!

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LIST OF ABBREVIATIONS

%	Percentage
ft	Feet
°C	Celsius
°F	Fahrenheit
CO_2	Carbon Dioxide
Md	Milidarcy
Psi	Pound Per Square Inch
Krw	Relative Permeability of Water
Krow	Oil Permeability relative to water
Krg	Relative Permeability of gas
Krog	Gas Permeability Relative to Oil
SiO_2	Silicon Dioxide
AL_2O_3	Aluminium Oxide
MgO	Magnesium Oxide
$MgSO_4$	Magnesium Sulfate or Magnesium Sulphate
Fe_2O_3	Ferric Oxide
SnO_2	Stannic Oxide
CuO	Copper Oxide
$FeCl_2$	Ferrous Chloride
$FeCl_3$	Ferric Chloride
mg/L	Milligram per Liter
FTIR	Fourier-Transform Infrared Spectroscopy
HCL	Hydrochloric Acid
GDP	Gross Domestic Product
AHP	Analytic Hierarchy Process
BMA	Boehmite by Methoxyacetic Acid
CAPEX	Capital Expenditure,
DLS	Dynamic Light Scattering
DLVO	Derjaguin–Landau–Verwey–Overbeek
STB	Stock Tank-Barrel
MMSTB	Million Stock-Tank Barrels
EOR	Enhanced Oil Recovery
EF	Emission Factor
GSCF	Giga Standart Cubic Feet
PTDF	Petroleum Technology Development Fund

PBMA	Pseudo-Boehmite by Methoxyacetic Acid
TCF	Tera Cubic Feet
MBPE	Millions of barrels of oil equivalent
ACPM	Motor Fuel Oil (Aceite Combustible Para Motores)
MSCF	Million Cubic Feet Per Day
GHG	Greenhouse gases
VMM	Valle Magdalena Medio basin
MMV	Middle Magdalena Valley
E&P	Exploration and Production
EIA	Energy Information Administration
R/P	Reserves Production atio
GEE	Gases de Efeito Estufa
IOR	Improved Oil Recovery
PAM	Polyacrylamide
TOC	Total Oil Content
CMG	Computer Modelling Group
LGR	Local Grid Refinement
GOR	Gas Oil Relationship
OPEX	Operational expenditures
TEOS	Tetraethyl Orthosilicate
NPV	Net present value
IRR	Internal Return Rate

LIST OF ACRONYMS

ANH	National Hydrocarbons Agency (*Agencia Nacional de Hidrocarburos*)
API	American Petroleum Institute
CREG	Energy and Gas Regulatory Commission (*Comisión de Regulación de Energía y Gas*)
UPME	Mineral-Energy Planning Unit (Unidad de Planeación Minero Energética)
ECOPETROL	Empresa Colombiana de Petróleos
MINMINAS	Ministry of Mines and Energy

1. INTRODUCTION

1.1. Overview of the Colombian economy and influence of hydrocarbons on GDP.

Dependence on oil income presents a complex challenge for several countries, Colombia being an emblematic example in this scenario. Many nations depend not only on oil production, but also on imports of oil products, resulting in a challenging duality. This situation creates an intricate dilemma for these countries, as they must equate two conflicting challenges: the need to deal with replenishing oil reserves, which is crucial for maintaining revenue, and the growing pressure to carry out an energy transition towards decarbonization, meeting global demands for sustainability.

The complexity is accentuated when potential resources require innovative technologies and are located in sensitive areas. This intensifies the environmental and technical concerns associated with exploiting these resources. In the Andean countries and various global regions, this scenario becomes even more complicated, highlighting the pressing need for strategic approaches and innovative solutions. Colombia, as a representative of this challenge, faces the task of balancing the efficient exploitation of its oil resources with the search for sustainable alternatives to promote a viable energy transition. In this context, international collaboration, research into clean technologies and adaptive strategies become key to tackling this duality and promoting a balanced approach to energy security and environmental sustainability.

Colombia is the 43rd largest world economy in terms of Gross Domestic Product (GDP) (WORLD BANK GROUP, 2023). The Colombian economy has undergone a noteworthy evolution in recent decades, with its performance intricately tied to the hydrocarbon industry, specifically oil and gas production (BANCO DE LA REPÚBLICA DE COLOMBIA, 2023). The nexus between the country's Gross Domestic Product (GDP) and this strategic sector has exerted a substantial influence on Colombia's economic dynamics.

Colombia, over time, has emerged as a major player in oil and gas production in Latin America (STRAMBO & GONZÁLEZ ESPINOSA, 2020). Hydrocarbon resources have played an important role in attracting foreign investment and boosting economic activity. In this way, the energy sector has contributed to GDP, generating significant revenues for the State, and fostering the development of related infrastructure (ESCANDON MILLAN, 2023; MARTÍNEZ & CASTILLO, 2019). Oil and gas production has provided Colombia with a stable source of revenue, enabling investments in other key sectors of the economy (RODRÍGUEZ,2020; MURILLO & RAMOS, 2021). However, this dependence has also exposed the country to the volatility of international oil prices, and highlighted the struggle to replace hydrocarbon reserves. Actually, fluctuations in benchmark oil prices can directly impact government revenues and thus the national budget and development projects.

Figure 1.1. presents the evolution in Colombia's oil revenues (data provided by: COMITÉ AUTÓNOMO DE LA REGLA FISCAL, 2023; MINISTERIO DE HACIENDA Y CRÉDITO PÚBLICO), measured in trillions of Colombian pesos, from 2016 to 2023. The overall trend shows a significant variation, culminating in a substantial increase starting in 2021, where revenues go from 1,400 million dollars to a marked increase of 9,168.57 million dollars in 2023.

In the first years of the analyzed period, from 2016 to 2018, revenues fluctuate, with a low point in 2016 registering 100 million of dollars, possibly indicating a deficit or a decrease in production that affected the country's revenues. From 2017 onwards, a progressive growth is observed, reaching 2,560 Million dollars in 2018.

Figure 1.1. also reveals a significant change in 2019, where revenues experience a considerable increase, reaching US$3,885.71 million. This variation can be attributed to the exploratory activity initiated the immediately preceding year, and to the discovery made in 2018 of the Coyote - 1 well, located in the Middle Magdalena Valley basin, in the municipality of *San Vicente de Churí*, Santander, and Lorito-1 well, located in the

Montecristo hamlet, municipality of *Guamal*, in the department of Meta. In 2020, although revenues decreased with respect to what occurred in 2019, they remained at considerable levels with US$2,314.29 million. However, it is from 2021 onwards that a drastic change is observed, with a decline to US$1,400 million, followed by rapid and sustained growth in 2022 and 2023, reaching a peak of P9,168.57 million. This increase is directly attributed to the exploratory activity initiated in 2019, which has proven successful in terms of production and revenue generation.

This analysis underscores the importance of investment in the exploration and development of petroleum resources for the Colombian economy, as of today. While the increase in revenues is positive, it also highlights the need to diversify the economy and manage these resources strategically to ensure long-term sustainability and mitigate the risks associated with dependence on oil revenues.

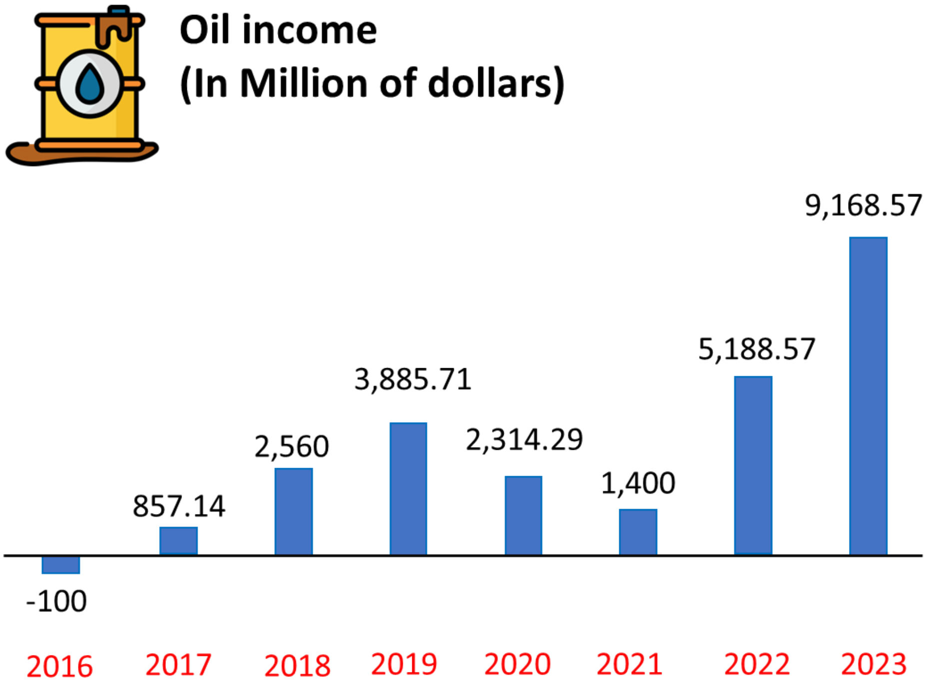

Figure 1.1. Colombian oil revenue in billions of pesos. (data provided by: COMITÉ AUTÓNOMO DE LA REGLA FISCAL, 2023; MINISTERIO DE HACIENDA Y CRÉDITO PÚBLICO, 2023)

Likewise, Figure 1.2 (data provided by: COMITÉ AUTÓNOMO DE LA REGLA FISCAL, 2023; MINISTERIO DE HACIENDA Y CRÉDITO PÚBLICO, 2023) reveals the evolution of the percentage of oil revenues with respect to Colombia's Gross Domestic Product (GDP) during the period from 2016 to 2023. In the base year of 2016, the percentage is zero, indicating an absence of direct contribution of oil revenues to GDP. Starting in 2017, a gradual increase is observed, peaking at 2.2% in 2023. This variation reflects the direct influence of oil prices on the Colombian economy. For instance, the increase in the percentage coincides with years when oil prices are higher, signaling a greater contribution of the oil sector to GDP. For example, in 2019, when the percentage reaches 1.3%, it is likely that this increase is linked to a period of relatively high oil prices. In contrast, the decline in 2021, where the share falls to 0.4%, suggests a vulnerability to oil market volatility and possibly reflects falling prices during the pandemic.

Thus, from Figure 1.2 one can infer the close relationship between oil revenues and Colombia's economic health, highlighting the importance of strategically managing these revenues and diversifying the economy to reduce dependence on a single sector. The variability in the percentage over the years demonstrates the need to address vulnerability to fluctuations in oil prices to ensure long-term economic stability and sustainability.

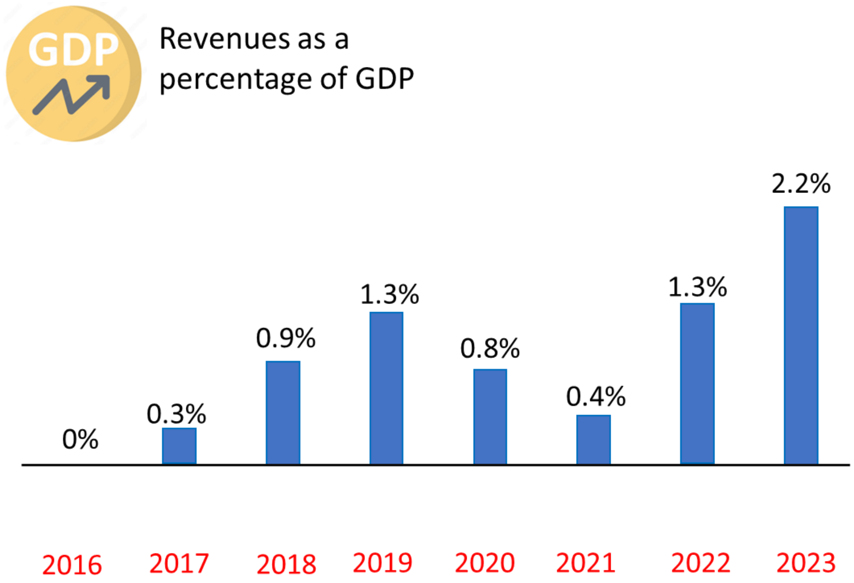

Figure 1.2. Income as a percentage of Gross Domestic Product in Colombia. (data provided by: COMITÉ AUTÓNOMO DE LA REGLA FISCAL, 2023; MINISTERIO DE HACIENDA Y CRÉDITO PÚBLICO, 2023)

On the other hand, Figure 1.3. (Data provided by: MINISTERIO DE COMERCIO, INDUSTRIA Y TURISMO DE LA REPÚBLICA DE COLOMBIA, 2022) provides a detailed view of the percentage of Colombia's main exports, broken down into different economic sectors. In the analysis of exports, the significant participation of crude oil stands out, with 27.8%, followed by coal with 18.5%, coffee with 7.2%, gold with 5.2%, refined oil with 4.6%, and flowers with 3.6%.

The price of oil has an important impact on these exports, especially in the case of crude oil and refined oil, which together account for more than one third of total exports. When oil prices are high, as in periods of robust global demand or geopolitical tensions, crude oil exports tend to generate higher revenues, contributing significantly to the total value of Colombian exports. Conversely, in times of falling oil prices, the value of these exports may decline, negatively affecting the revenues generated by the country.

It can be shown that the price of oil plays a critical role in Colombia's export economy, given its weight in the country's main exports. Colombia's ability to diversify its exports and strategically manage its dependence on natural resources, especially in the energy sector, is, then, crucial to face volatility in international markets and ensure long-term economic stability.

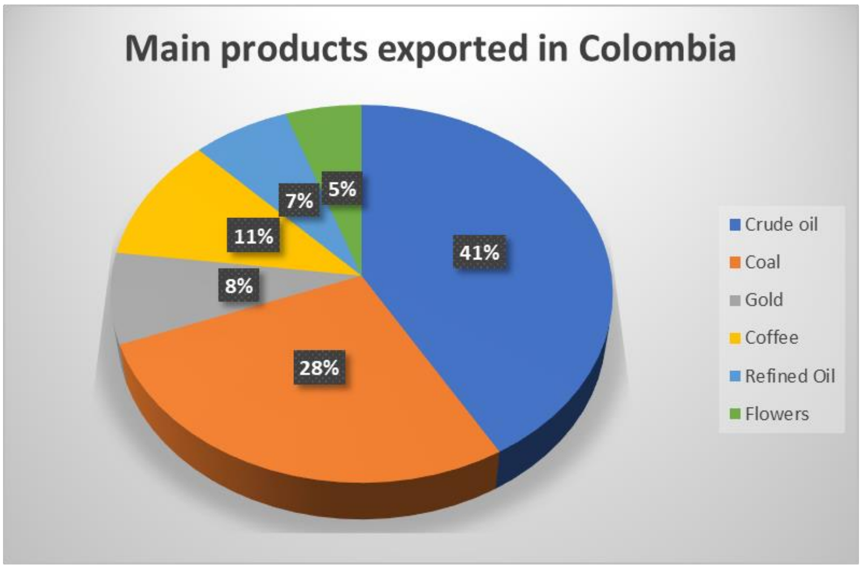

Figure 1.3. Main products exported in Colombia during the year 2022 (Data provided by: MINISTERIO DE COMERCIO, INDUSTRIA Y TURISMO DE LA REPÚBLICA DE COLOMBIA, 2022)

Thus, it can be deduced that oil plays a fundamental role in the Colombian economy, being a key driver for the country's economic growth, Gross Domestic Product (GDP) and exports. As a major source of income, the oil sector contributes to GDP, generating significant revenues for the government and financing infrastructure and development projects. Crude and refined oil exports account for a considerable share of Colombia's foreign trade, providing essential foreign exchange for the country's financial stability. However, this dependence also exposes Colombia to the volatility of international oil prices, underscoring the need to diversify the economy, seek new hydrocarbon reserves, and strategically manage natural resources to ensure long-term economic resilience and then there's the challenge of the energy transition.

The identification and exploitation of new oil and gas reserves in Colombia offer a strategic opportunity to drive the country's energy transition. While diversification of the energy matrix towards cleaner sources is essential, the availability of additional reserves can play a key role during this process. These resources can serve as a transitional source, allowing for continuity of energy supply while simultaneously advancing the development of more sustainable technologies. Investment in advanced extraction practices, as well as carbon capture and storage technologies, can help mitigate environmental impacts and align the Colombian hydrocarbon industry with long-term decarbonization and sustainability goals. Responsible management of these new reserves is essential to ensure an appropriate balance between current energy needs and the transition to a greener future.

1.2. Current Overview of the oil and gas industry in Colombia

Colombia is one of the leading oil-producing countries in Latin America. While it may not be considered a major international crude oil producer, oil production is still significant for the country's Gross Domestic Product (GDP) (GARAVITO et al., 2020), as mentioned before.

Oil production in Colombia started in 1921 and has since then become a relevant contributor to the country's gross domestic product (GDP). This government establishment of a State-owned oil company called ECOPETROL. Authorized by the government, ECOPETROL operates in various regions of the country. In 1985, the presence of 13 sedimentary basins in Colombia was found, categorized into three main groups: continental basins, continental border basins, and oceanic basins (HOOGHIEMSTRA et al., 2022).

Table 1.1 presents the 15 main sedimentary basins in Colombia with significant oil and gas reservoirs and production. The major departments associated with each basin are listed. The table shows the sedimentary basins of the country, the departments that stand out for having the largest amount of reserves and resources are the Department of Santander, which corresponds to the Middle Magdalena Valley basin, and the departments of Meta and Casanare, which belong to the Eastern Llanos Basin production (BARRERO et al., 2007). The numbers in the Table 1.1. refers to the location on the watershed map as shown in Figure 1.4.

Table 1.1. Colombian Sedimentary Basins and reserves (Data provided by: BARRERO et al., 2007)

No.	**Sedimentary Basin**	**Reservoir/Reserves**
02	Caguán-Putumayo	Oilfield discoveries 19 Oil reserves discovered 365 MMSTB Gas reserves recovered 305 GSCF
03	Catatumbo	Wildcat wells 39 Oilfield discoveries 11
04	Cauca-Patía	Wildcat 5 wells
05	Cesar Ranchería	Wildcat wells 14
06	Chocó	Wildcat 5 wells
10	Eastern Cordillera	Discovered fields 10 (8 oil fields - 2 gas fields) Wildcat wells 38

		Oil discovered 1,700 MMSTB
11	Eastern Llanos	Wildcat wells 260 Number of discoveries 68 oilfields, 2 giants, 1 major field.
12	Guajira	Wildcat 18 wells Ballena (1.5 TCF) and Riohacha (86.5 GCF) gas discoveries
13	Guajira offshore	Chuchupa gas field
14	Los Cayos	Discovered oil reserves None Wildcat wells None
15	Lower Magdalena Valley	Wildcat wells 117 Proved oil reserves (Dec/05) 71 MMSTB Field discoveries 17
16	Middle Magdalena Valley	Wildcat wells 296 Field discoveries 41 Discovered oil reserves 1,900 MMSTB Gas reserves discovered 2.5 GSCF
17	Sinú-San Jacinto	Wildcat 44 wells
18	Sinú offshore	Wildcat wells None.
21	Upper Magdalena Valley	Discovered oil reserves 631 MMSTB Discovered gas reserves 123 GSCF Wildcat wells 210 Discovered fields 36

As can be seen in Figure 1.4., the Eastern Plains Basin exhibits a significant presence of oil and gas deposits. This basin, located in the eastern part of the country, encompasses the departments of Meta, Arauca, Casanare, and Vichada. It is evident from the distribution of these basins that the eastern region holds the largest reservoirs of oil and gas.

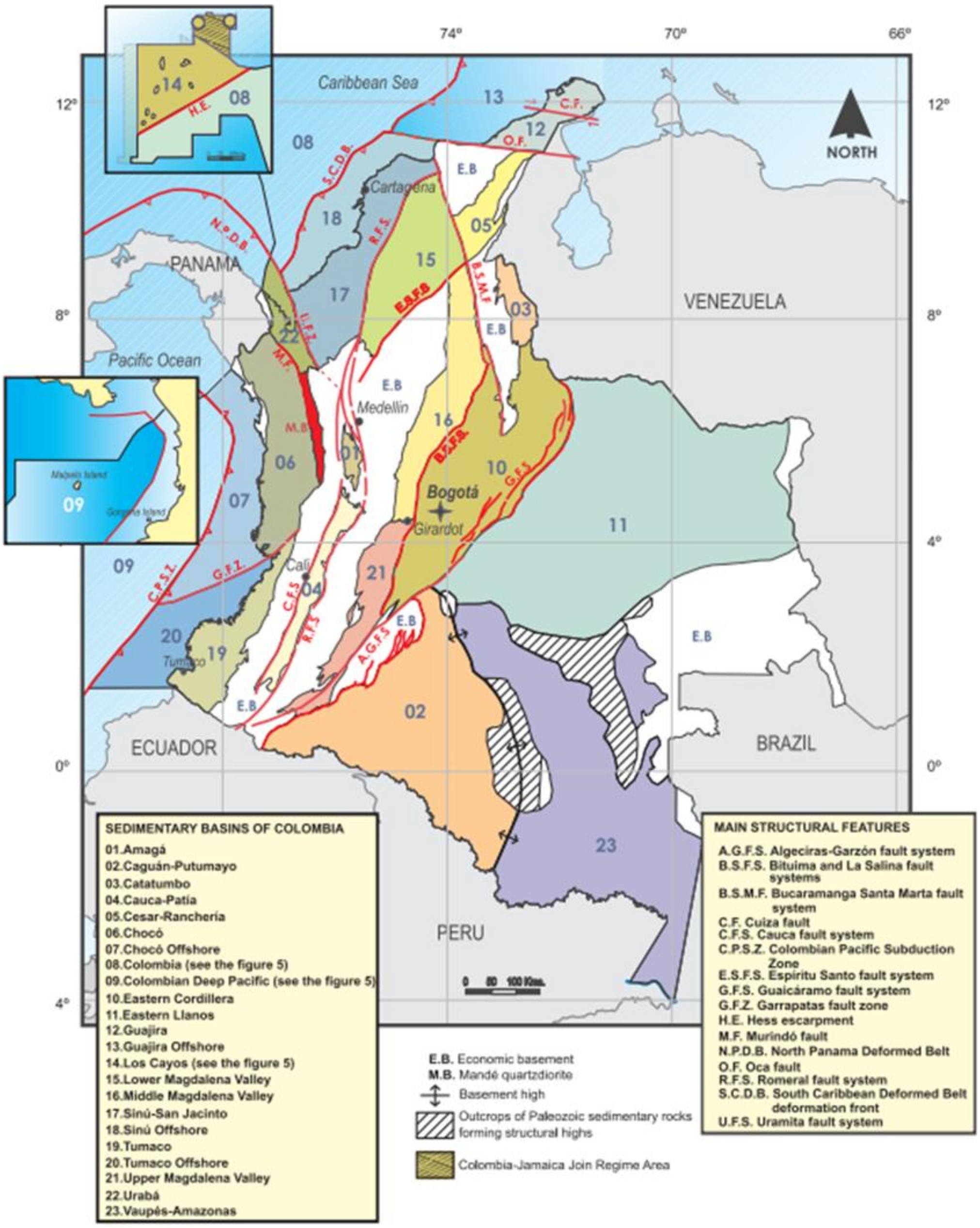

Figure 1.4. Colombian Sedimentary Basins .01, Amagá. 02, Caguán-Putumayo. 03, Catatumbo. 04, Cauca-Patia. 05, Cesar-Ranchería. 06, Chocó. 07, Chocó Offshore. 08, Colombia. 09, Colombian Deep Pacific. 10, Eastern Cordillera. 11, Eastern Llanos. 12, Guajira. 13, Guajira offshore. 14, Los Callos. 15, Lower Magdalena Valley. 16, Middle Magdalena Valley. 17, Sinú-San Jacinto. 18, Sinú offshore. 19, Tumaco. 20, Tumaco Offshore. 21, Upper Magdalena Valley. 22, Urabá. 23, Vaupés Amazonas. (Data provided by: BARRERO et al., 2007)

Regarding oil exploration and production, according to the management report of (*Agencia Nacional de Hidrocarburos, 2021*), exploration was reduced due to the COVID-19 pandemics.

Figure 1.5. (Data provided by: AGENCIA NACIONAL DE HIDROCARBUROS, 2023) shows the number of exploratory wells drilled in Colombia between 2010 and 2022, revealing a fluctuating dynamic in oil exploration activity. In the first years, from 2010 to 2013, a progressive increase is observed, reaching a peak of 131 wells in 2013, suggesting a period of intense search for new oil reserves. However, from 2014 onwards, a marked decrease is evident, reaching only 18 exploratory wells drilled in 2020, this due to impacts from the COVID-19 pandemic.

This variation in the number of exploratory wells has a direct correlation with the number of oil reserves in the country. Years of increased exploratory activity, such as 2013, coincide with a possible discovery and development of new fields, thus contributing to the increase in oil reserves. Conversely, the reduction in well drilling in subsequent years indicates lower investment in exploration, which negatively impacts the incorporation of new reserves to the national inventory.

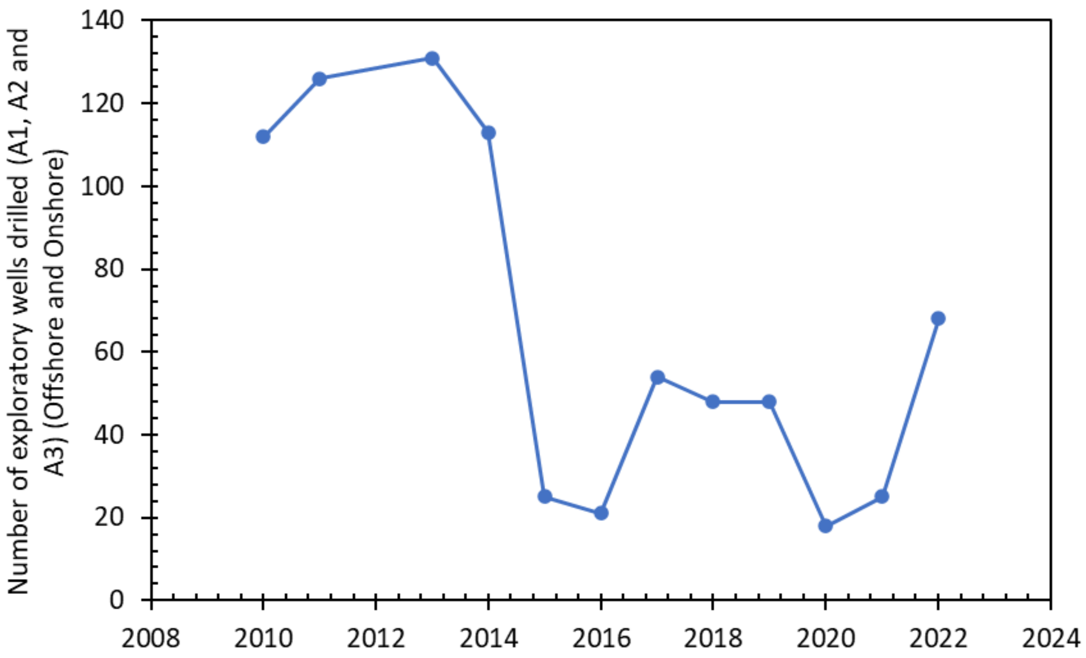

Figure 1.5. Number of exploratory oil wells drilled in Colombia between 2001 and 2022 (Data provided by: AGENCIA NACIONAL DE HIDROCARBUROS, 2023).

On the other hand, Figure 1.6 (Data provided by: AGENCIA NACIONAL DE HIDROCARBUROS, 2023) displays the top 20 oil-producing fields in 2022, with the first four fields located in the eastern plains basin: Campo Rubiales in Puerto Gaitan and Castilla, Castilla Norte, and Chichimene in Cubarral, Meta. The eastern plains basin holds significant potential, leading the State-owned company ECOPETROL to invest in reactivating oil fields in the area. This project aims to achieve a daily production of approximately 200,000 barrels of oil, fulfilling the Colombian oil sector's goal of maintaining a production of 1,000,000 STBD. ECOPETROL's focus is on the fields with the highest production in the country, as depicted in Figure 1.6. Specifically, they plan to implement an extensive drilling and completion plan for 705 wells in 175 clusters, along with 94 pilot wells in the Rubiales field. Additionally, in the Castilla field, they are working on a plant for dehydration, measurement, and dispatch capable of handling 30,000 Bpd, as well as clarifying 600,000 barrels of water per day to meet reinjection quality requirements (LOPEZ, 2019; ECOPETROL, 2022).

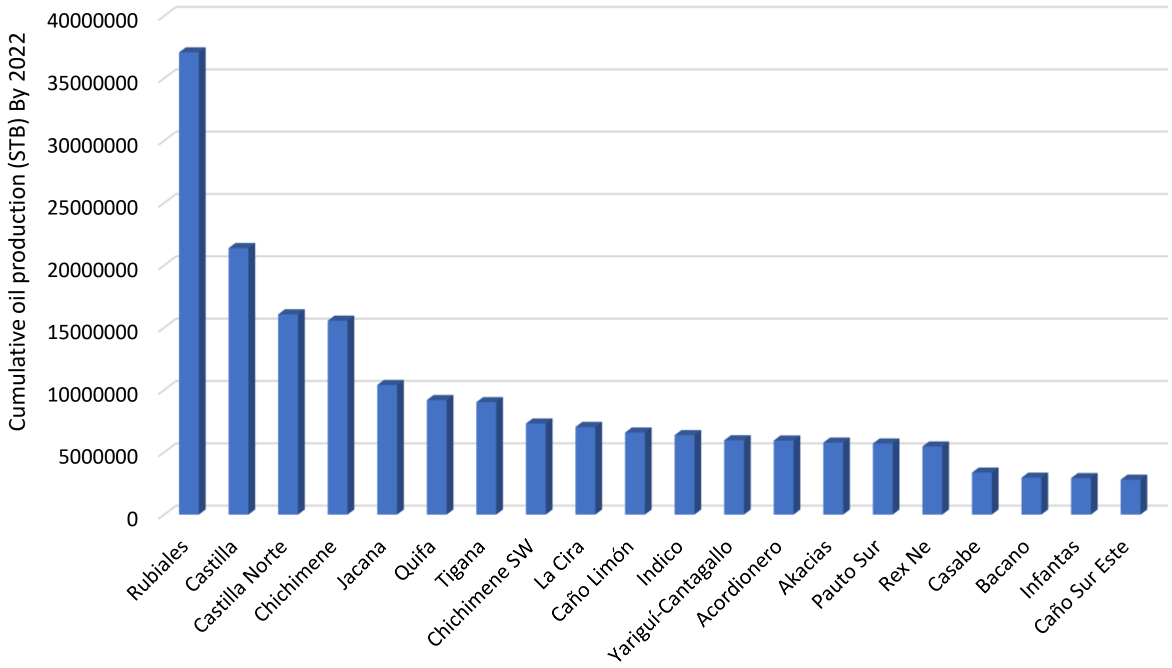

Figure 1.6. Cumulative Oil Production 2022 (STB) (20 major fields) (Data provided by: AGENCIA NACIONAL DE HIDROCARBUROS, 2023).

On the other hand, the estimation of reserves in Colombia follows the methodology established by the U.S. Securities and Exchange Commission (SEC). To ensure accuracy and reliability, 99.8% of the reserves have been certified by three reputable and independent specialized firms: Ryder Scott Company, DeGolyer and MacNaughton, and Gaffney, Cline & Associates (FOX & LEFSRUD, 2021) (VICKNAIR, 2022).

According to ECOPETROL's report for 2022, there was an increase in proven hydrocarbon reserves, which include crude oil, condensates, and natural gas. At the end of 2022, the net proven reserves of the ECOPETROL Group amounted to 2,011 million barrels of oil equivalent (MBPE). Furthermore, the average life of these reserves was estimated to be 8.4 years, indicating the duration for which the current proven reserves can be exploited based on the projected production rates (Table 1.2).

Table 1.2. Proved Reserves Ecopetrol Group 2022 (Millions of barrels of oil equivalent - MBPE) (ECOPETROL, 2023).

Balance of reserves	**2022**	**2021**	**2020**
Initial Reserves	2.002	1.770	1.893

Revisions	63	315	
Enhanced Oil Recovery	81	139	113
Purchases	48	0	30
Extensions and discovery	57	12	43
Sales	0	-3.5	-1
Production	-240	-231	-236

However, when looking at Colombia as a whole, the reserves/production ratio is 7.5 years (Figure 1.7). in this sense, Colombia faces the challenge of maintaining a sustainable balance between oil reserves and current production. This ratio between reserves and production is important to assess the country's ability to maintain a constant supply of oil in the future, and to make national energy planning decisions. The figure of 7.5 years indicates that, under current production conditions, current reserves could be depleted in that period. Therefore, this indicator highlights the need for effective exploration and reserve management strategies to ensure long-term energy security, as well as the importance of diversifying the energy matrix as a precautionary measure in the face of finite oil resources.

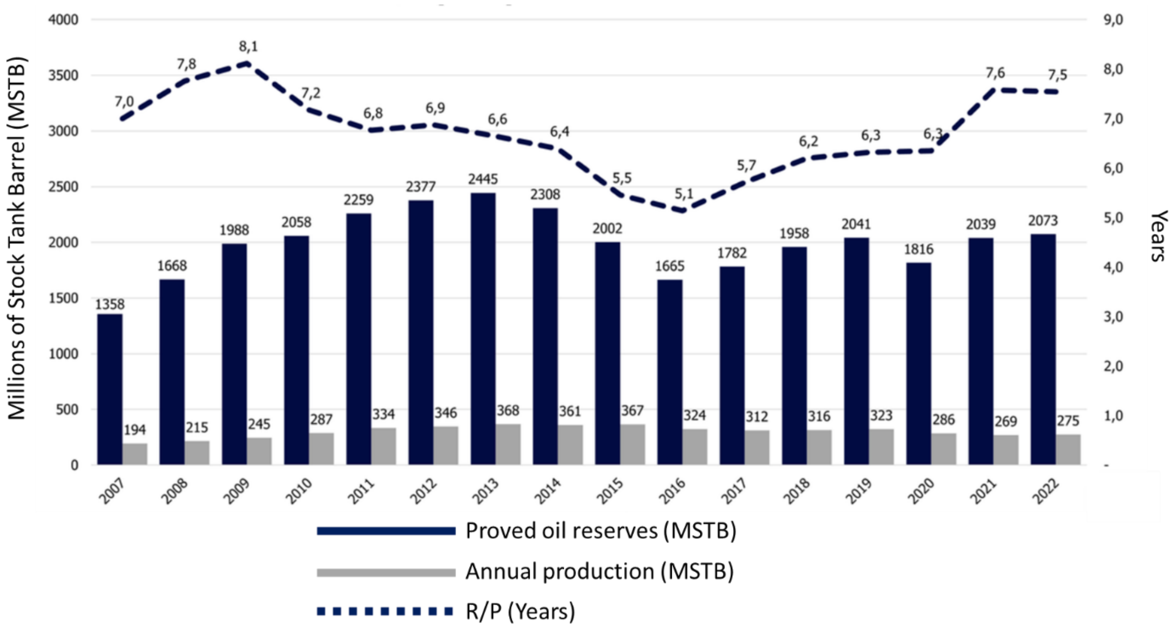

Figure 1.7. Proven oil reserves (MSTB), Annual oil production (MSTB) and R/P (years) (AGENCIA NACIONAL DE HIDROCARBUROS, 2023)

Moreover, the current state of gas in Colombia presents a challenging outlook due to the lack of new reserves. The previous government of President Ivan Duque from (August 7, 2022, to August 7, 2022) aimed to address the issue of gas supply by proposing the Pacific regasification plant, which would transform liquefied natural gas into gas for distribution. However, the current government (which began on August 7, 2022) has taken a more pessimistic stance. The Ministry of Mines has halted the exploration of gas and oil reserves. Nevertheless, existing contracts will remain in effect, according to the minister (HERNANDEZ, 2022).

The main gas-contributing fields in Colombia from 2018 to 2023 are the Cupiagua fields in the eastern plains, Chuchupa in Guajira, and Cusiana Norte in Casanare. Table 3 provides an overview of gas fields located in Colombia, emphasizing the natural gas accumulations in the sedimentary basins of La Guajira, Lower Magdalena Valley, Middle Magdalena Valley, Upper Magdalena Valley, Putumayo, and the Eastern Plains Basin. Table 1.3 shows the fields that contribute the most to the domestic natural gas supply in the country.

Table 1.3. Gas fields in Colombia. Mining and Energy Planning Unit. Ministry of Mines and Energy (UNIDAD DE PLANEACIÓN MINERO ENERGÉTICA, 2023).

Basin	Fields
Catatumbo	Cerrito, Oripaya, Sardinata, Tibú
Cesar Ranchería	La loma
Cordillera Oriental	Gibraltar, Guaduas, Palagua
Guajira	Balle, Chuchupa, Carbón IV-Ven Imps, Petromil, Imp ECP Ballena
Llanos Orientales	Apiay, Calona, Campo Rico, Carmentea, Centauro Sur, Cupiagua, Cusiana, Cusiana Norte, Floreña, Kananaskis, La Estancia, La Punta, Pauto Sur, Ramiriqui, Santo Domingo Centro, Santo Domingo Juape, Santo Domingo Norte.
Valle Inferior del Magdalena	Arianna, Arjona, Bonga, Bullerengue, Clarinete, El Difícil, La Creciente, Mamey, Perdernarlito, Trombón, Planta Regasificación Cartagena.
Valle Medio de Magdalena	Bonanza Incremental, Caramelo, Compae, Corazón, Corazón West, Gala, La Cira Infanta, La Salina, Liebre, Lisama, Lisama Norte, Lisama Profundo, Llanito, Nutria, Opón, Payoa, Payoa

	West, Provincia, Puli, Tesoro, Toposí, Toqui-Toqui, Yarigiua Cantagallo
Valle superior del Magdalena	Cañada N., Dina Terciario, La Hocha, Mana, Rio Opía, Santa Clara.

In terms of gas reserves in Colombia, the UPME (Mineral-Energy Planning Unit) states that proven reserves are primarily located in the Eastern Plains, while probable reserves are found in the Eastern Plains and the Lower Magdalena Medio Valley. The Eastern Plains holds the largest oil and gas reserves in the country, followed by La Guajira in the north.

Despite recent discoveries, the decisions of the national government and the decline in reserves since 2012, as shown in Figure 1.6, pose challenges to Colombia's domestic natural gas supply. Figure 1.7 reveals this scenario, as forecasts suggest that, without exploration and investment in enhanced recovery projects, the current reserves will only las for self-sufficiency in oil until 2028 and natural gas until the end of 2024 (UNIDAD DE PLANEACIÓN MINERO ENERGÉTICA, 2023; AGENCIA NACIONAL DE HIDROCARBUROS, 2023).

The overview of natural gas reserves and production in Colombia (Figure 1.8), with a period equivalent to 7.2 years, highlights the strategic importance of this resource in the country's energy context. Natural gas, having a fundamental role as a transition fuel, emerges as a key component for the transition to more sustainable energy sources. Its versatility and efficiency in electricity generation, as well as its application in industry and transportation, position it as a fundamental alternative in the mitigation of emissions and the diversification of the energy matrix. The need to ensure a constant supply of natural gas thus becomes an essential element to support the transition to a cleaner and more sustainable energy model, highlighting the strategic relevance of the responsible management of reserves and the promotion of technologies and policies that encourage their efficient use.

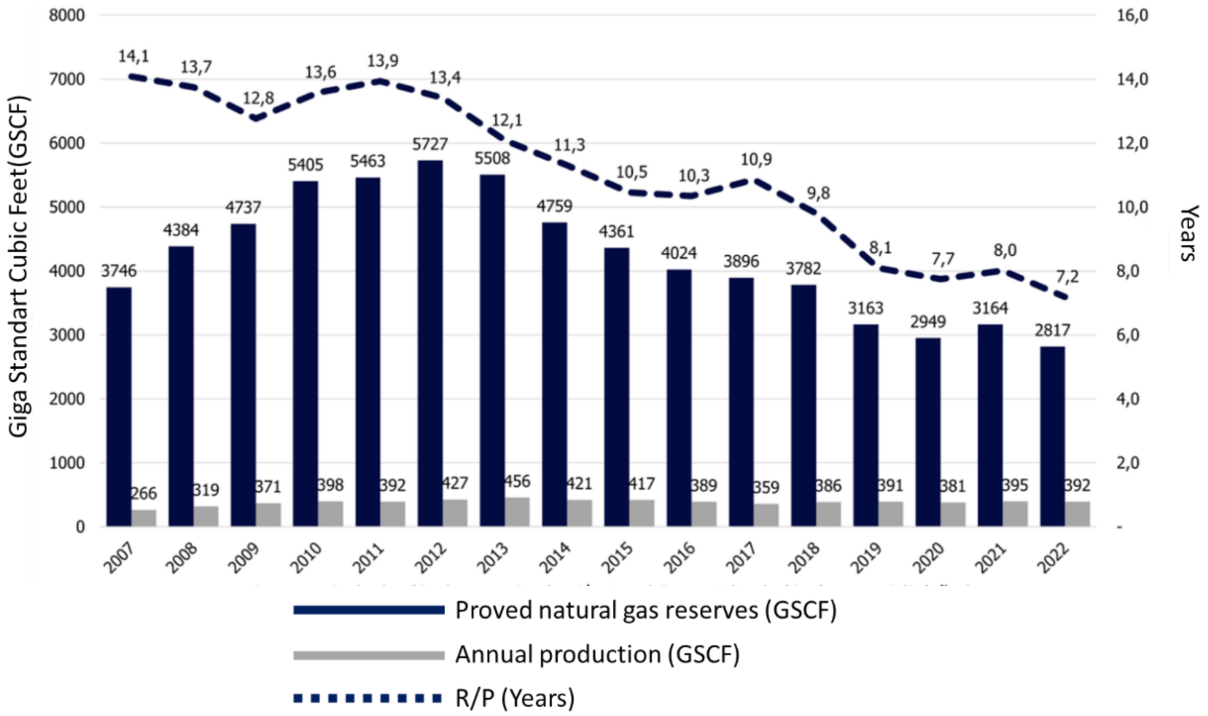

Figure 1.8. Proven Gas Reserves (GSCF), Annual oil production (GSCF) and R/P (years) (AGENCIA NACIONAL DE HIDROCARBUROS, 2023)

Therefore, Colombia faces a critical situation regarding gas supply, with less than two years to find new sources. Failure to do so would require a shift back to using gasoline, ACPM, firewood, or coal as short-term alternatives, which would have environmental implications and hinder Colombia's commitment to reducing greenhouse gas emissions (RÍOS-OCAMPO, ARANGO-ARAMBURO, ARSEN, 2021; LEE, XING, LEE, 2022).

Hence, unconventional reservoirs can offer an important alternative for self-supply and reducing dependence on gas imports. However, the sector faces challenges due to a smear campaign, hindering recognition of the technical advancements made in these alternatives.

Colombia is the third country in South America with the greatest potential of unconventional reservoirs, after Argentina and Brazil, and currently has five types of unconventional reservoirs, including: hydrocarbons associated to shales (Shale Oil or Shale gas); tight oil or gas reservoirs; heavy crudes; according to Sanz (SANZ, 2021), ANH recently found oil sands reservoirs, which are sands impregnated with bitumen, which is a hydrocarbon of very high density and viscosity; and methane gas associated with coal seams.[1]

These unconventional reservoirs are mostly found in the Middle Magdalena Valley basin, more specifically in La Luna formation. The types of unconventional reservoirs in which fracking can be used are shale gas, with the greatest potential to be found in the Magdalena Medio, Cordillera Oriental and Rio Rancheria; shale oil with potential in Colombia in the Upper Magdalena Valley and South Pacific regions, gas associated with coal seams with potential in Guajira, Cesar, Boyacá and Cundinamarca, and gas and oil in tight rocks, with potential in the Middle Magdalena Valley; on the other hand, fracking is not used in oil sands and methane hydrate reservoirs.

Table 1.4 shows the distribution of shale oil resources in Colombia, by each basin, being the Eastern Plains basin the one with the highest value for P50, considering that P50 is best estimate of the value of oil in the reservoir (MCGLADE, 2014; BENTLEY, 2002). The basin with the highest probability of oil in the reservoir is the Eastern Cordillera basin, followed by the Vaupés-Amazonas basin.

Table 1.4. Shale oil distribution in Colombia P10, P50, P90. (UNIDAD DE PLANEACIÓN MINERO ENERGÉTICA, 2023)

Basin	**P10**	**P50**	**P90**
Amagá	14.4	4.2	0.6
Caguán	27,802.8	1,319.4	142.8
Catatumbo	1.918,2	403.2	50.4
Cauca-Patía	195.8	88.2	13.8
César Ranchería	1,108.2	294.6	43.22
Chocó	235.2	71.4	11.4
Cordillera Oriental	7.542,8	2,137.8	327.0

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[1] Natural gas extracted from coal seams. This type of reservoirs due to its high content of organic matter coal retains a large amount of adsorbed gas, and according to the president of the National Hydrocarbons Agency is found in six basins in Colombia, and has the potential to produce 16 billion and 23 billion ([253, 254] Zhang, Z., Mao, J., Yang, X., Zhao, J., & Smith, G. S. (2019). Advances in waterless fracturing technologies for unconventional reservoirs. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *41*(2), 237-251; Kurniadi, S. D., Ryan, A., & Hamidon, Z. R. (2023, September). Strategy for Reducing Environmental Footprint of Hydraulic Fracturing Operations through Engineering Excellence and Operational Efficiency. In *SPE International Hydraulic Fracturing Technology Conference and Exhibition*. OnePetro.)

Guajira	1,373.4	365.4	54.0
Llanos Orientales	68,478.6	10,783.8	1,297.2
Sinú – San Jacinto	4,565.4	1,171.2	169.2
Tumaco	586.8	175.8	27.6
Urabá	943.8	241.8	34.8
Valle Inferior del Magdalena	1,255.2	362.4	55.8
Valle Medio del Magdalena	1,539.0	450.0	69.6
Valle Superior del Magdalena	459.2	139.2	21.6
Vaupés-Amazonas	33,394.2	1,599.0	771.6
Total	151,524.0	19,607.4	3,090.6

Table 1.5 shows the Gas distribution in tight sands for each basin, with the Eastern Plains basin having the highest probability of oil quantity within the basin, followed by the Caguán-Putumayo basin.

Table 1.5. Shale gas distribution in Colombia P10, P50, P90. (UNIDAD DE PLANEACIÓN MINERO ENERGÉTICA, 2023).

Basin	**P10**	**P50**	**P90**
Amagá	0.068	0.010	0.002
Chocó	0.940	0.120	0.030
Caguán-Putumayo	6,720	0.858	0.147
Catatumbo	0.498	0.065	0.009
Cauca Patia	0.310	0.040	0.010
César Ranchería	0.773	0.094	0.019
Cordillera Oriental	15,555	1,977	0.343
Guajira	0.970	0.120	0.020
Llanos Orientales	15,555	1,977	0.343
Sinú San Jacinto	2,504	0.312	0.053
Tumaco	0.538	0.065	0.019
Urabá	0.655	0.078	0.010
Valle Inferior del Magdalena	2,608	0.260	0.045
Valle Medio del Magdalena	2,081	0.260	0.045
Valle Superior del Magdalena	1,463	0.185	0.029
Vaupés Amazonas	2,955	0.384	0.086
Total	43,666	5.540	0.991

Table 1.6 displays contracts for the exploration and exploitation of unconventional hydrocarbons from 2004 to 2017. Based on the Table 1.7, it can be concluded that the

eastern plains and the basins in different sections of the Magdalena Valley are the areas of greatest interest for unconventional reservoirs.

Table 1.6. Unconventional hydrocarbon exploration and exploitation contracts from 2004 to 2017. (AGENCIA NACIONAL DE HIDROCARBUROS, 2023)

Contract/Competitive process	**Contractor (and their percentages in the business)**	**Municipalities (Departments)**
E&E LA LOMA/Direct Contracting E&P 2004	Drummond	Curumaní, Chiriguana, La jagua de Ibirico, El Paso, Becerril, Agustín Codazzi, and La Paz (El Cesar)
E&P CAT 3 /Ronda Colombia 2012	Ecopetrol S.A.	Bochalema, Chináctoca, Cúcuta, Durania, El Zulia, Gramalote, Herrán, Los Patios, Pamplonita, Ragonvalia, Salazar, San Cayetano, Santiago, Sardinata y Villa del Rosario (Santander).
E&P COR 62 /Ronda Colombia 2012	Exxon Mobil Exploration Colombia Limited (50%) Ecopetrol S.A. (50%) (Operator)	Cunday, Villarrica, Purificación, Melgar, Icononzo, Carmen de Apicalá, Dolores y Prado (Tolima).
E&P VMM 16/ Ronda Colombia 2012	Ecopetrol S.A.	Sonsón, Puerto Boyacá, Norcasia, Victoria, La Dorada, Puerto Salgar, Mariquita, Lérida, San Sebastián de Honda, Armero Guayabal y Falan (Antioquia, Boyacá, Caldas, Cundinamarca y Tolima)
E&P VMM 29/ Ronda Colombia 2012	Exxon Mobil Exploration Colombia Limited (50%) Ecopetrol S.A. (50%) (Operator)	Agua de Dios, Anapoima, Anolaima, Apulo, Arbeláez, Beltrán, Cachipay, Fusagasugá, Guataqui, Jerusalén, La Mesa,Nilo, Pulí, Quipile, San Juan deRíoseco, Tibacuy, Coello, Icononzo, Lérida, Melgar, Piedras y Venadillo (Cundinamarca y Tolima).
E&P VMM 5/ Ronda Colombia 2015	Ecopetrol S.A.	Puerto Berrio, Yondó, Barrancabermeja, Cimitarra, y Puerto Parra (Antioquia y Santander).
E&P VMM 9/ Ronda Colombia 2014	Parex Resources Colombia Ldta.	Cimitarra (Santander)
E&P VMM 3- Additional/ Initial contract- Mini Ronda 2008 Additional contract entered into in 2015	Conocophillips Colombia Ventures Limited (80%) (Operator) CNE Oil & Gas S.A. (20%)	Aguachica, San Martín, San Alberto yPuerto Wilches El Cesar y Santander
CR-2 (Conversion)/ Direct contracting 2016	Drummond	San Juan del Cesar y El Molino La Guajira
CR-3 (Conversion)/ Direct contracting 2016	Drummond	Valledupar y San Diego (El Cesar)

However, there are several challenges for implementing fracking in Colombia. These include water contamination, seismic risks, and impact on biodiversity, community conflicts, community displacement, regulatory deficiencies, technical difficulties, and hydrocarbons’ price volatility. Regarding water contamination, there are concerns about the contamination of aquifers and groundwater sources resulting from the release of toxic chemicals during the fracking process. Furthermore, the construction of infrastructure and the exploitation of unconventional reservoirs can have a negative impact on local ecosystems and biodiversity.

The exploitation of this type of reservoirs might be justified by the criteria of dealing with energy security issues in the short term, in addition to allow a smooth transition from the economic dependence on hydrocarbons. Accordingly, it is crucial to remember that Colombia has historically depended on conventional oil and gas extraction to fuel its economic development and secure its energy needs. The introduction of fracking could substantially boost hydrocarbon production, thereby reducing the nation's vulnerability to fluctuations in global oil prices and ensuring a more consistent energy supply in the short term.

Furthermore, fracking has the potential to become an additional source of revenue for the government. These revenues could be allocated for financing social programs, infrastructure, and development projects that would benefit the Colombian populace. This, in turn, could lead to an improved quality of life for citizens and a reduction in economic inequality across the country.

However, it is equally essential to address the technological and environmental challenges and risks associated with fracking. Concerns such as groundwater contamination, the release of toxic chemicals, and seismic hazards must be taken seriously. For fracking to be a viable option in Colombia, stringent regulations and ongoing monitoring are imperative to minimize these risks and ensure the preservation of the environment and the well-being of the population.

Moreover, the concerns of local communities that might be impacted by fracking must be considered. Promoting open dialogue and active community participation in decision-making processes is crucial to address their apprehensions and guarantee that their rights and welfare are upheld.

For the foregoing reasons, Colombia is an emblematic case of hydrocarbon dependence due to the significant contribution of oil and gas to its economy and energy matrix. The exploitation of these resources has historically been an important source of income and a fundamental part of the country's energy generation.

In this context, the exploration and extraction of oil and gas from unconventional reservoirs emerges as a potential option for Colombia's energy security. Diversifying energy sources through the exploitation of unconventional reservoirs could reduce vulnerability to changes in oil prices, while strengthening the country's energy self-sufficiency. Responsible implementation of advanced techniques, such as fracking, could help ensure a stable energy supply in the long term.

However, it is essential to approach this transition with a holistic perspective that considers environmental, technical, and economic impacts. Sustainable management of these resources must go hand in hand with policies that promote energy efficiency, the development of renewable sources and diversification of the economy. A careful approach is also required to mitigate the potential environmental risks associated with the extraction of unconventional reservoirs.

1.3. Objectives and Research Questions.

To tackle the above questions, this thesis is composed of six chapters. In the second chapter: the paper “Technical and economic assessment of the development of a Colombian Tight Oil Reservoir: A simulation case study of *Valle Medio del Magdalena* basin”[2] is presented. This paper was published in the Journal DYNA (Indexed in Scopus and Web of Science; JCR: 0,217)

Colombia has historically been a significant oil and gas producer in Latin America. The decline in conventional oil reserves underscores the imperative to explore and develop new energy sources, ensuring sustained production and continued economic contributions from the energy sector. In this context, Tight Oil exploration and production in Colombia present an opportunity to diversify the country's energy sources, reducing reliance on conventional reserves and enhancing energy security. The energy sector holds a pivotal role in the Colombian economy, contributing significantly to government revenues and employment generation. The economic viability of Tight Oil production has the potential to yield positive impacts on the national economy. Furthermore, in terms of investment and technological development, the evaluation of unconventional reservoir production entails investments in advanced technologies and extraction methods. This can stimulate technological advancement within the country and attract foreign investments into the energy sector. This paper also underscores the critical role of the fiscal regime in project viability.

The third chapter presents the study entitled: *“Asphaltenes precipitation/deposition estimation and inhibition through nanotechnology: a comprehensive review*”[3]. This paper was published in JOURNAL OF PETROLEUM SCIENCE AND ENGINEERING (Indexed in Scopus and Web of Science; JCR: 5.168) Colombia is actively exploring and developing unconventional reservoirs, including shale oil and shale gas, as part of its efforts to diversify its hydrocarbon production portfolio.

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[2] Forero, C. A., Forero, E. J., Guerrero-Martin, L., Szklo, A., Rochedo, P. R., & Guerrero-Martin, C. (2021). Technical and economic assessment of the development of a Colombian Tight Oil reservoir: a simulation case study of Valle Medio del Magdalena basin. Dyna, 88(219), 35-43.

[3] Fuentes, J. F., Montes, D., Lucas, E. F., Montes-Paez, E. G., Szklo, A., & Guerrero-Martin, C. A. (2022). Nanotechnology applied to the inhibition and remediation of formation damage by fines migration and deposition: A comprehensive review. *Journal of Petroleum Science and Engineering*, *216*, 110767.

Asphaltene precipitation presents a common challenge in these reservoirs due to the unique characteristics of unconventional hydrocarbons. The comprehension and effective control of asphaltene precipitation are paramount for optimizing production in such reservoirs. Asphaltene precipitation can significantly reduce production efficiency and lead to escalated operating costs. By formulating strategies aimed at preventing and managing asphaltene precipitation, Colombia stands to enhance the recovery of oil and gas from its unconventional reservoirs, thereby directly benefiting the country's economy. Furthermore, the deposition of asphaltenes within pipelines and oil transportation systems can result in blockages and safety hazards. A firm grasp of asphaltene inhibition and control techniques is imperative to ensure the secure and efficient transport of unconventional hydrocarbons from reservoirs to processing facilities. The utilization of nanoparticles for asphaltene inhibition and removal represents a promising technological avenue. Colombia can reap substantial advantages by adopting these cutting-edge techniques to address the asphaltene-related challenges in its unconventional reservoirs, ultimately bolstering the economic viability of these projects. Comprehensive understanding and proficient management of asphaltene precipitation are pivotal for the prosperous development of unconventional reservoirs in Colombia. This has far-reaching consequences on hydrocarbon production, the nation's economic well-being, and the safety of oil and gas transportation. Moreover, the integration of advanced technologies, such as nanoparticle applications, has the potential to elevate production efficiency and enhance the competitiveness of Colombia's oil industry.

The fourth chapter presents the study entitled: "*Nanotechnology applied to the inhibition and remediation of formation damage by fines migration and deposition: A comprehensive Review*"[4]. This paper was published in Energies (Indexed in Scopus and Web of Science; JCR: 3.2)

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[4] Guerrero-Martin, C. A., Montes-Pinzon, D., Meneses Motta da Silva, M., Montes-Paez, E., Guerrero-Martin, L. E., Salinas-Silva, R., ... & Szklo, A. (2023). Asphaltene Precipitation/Deposition Estimation and Inhibition through Nanotechnology: A Comprehensive Review. Energies, 16(13), 4859.

In the development of unconventional reservoirs, such as shale oil and shale gas, formation plugging caused by the migration of fine particles can significantly hamper production. Effectively managing this issue is imperative for optimizing hydrocarbon recovery in these reservoirs, directly influencing Colombia's production output and revenues. The migration of fine particles can lead to additional costs and operational complexities in the production of unconventional reservoirs. Leveraging nanotechnology to inhibit the migration of these fine particles can mitigate these costs and ensure seamless operations. The deployment of nanoparticles and nanofluids represents an advanced technological approach that can enhance the efficiency and competitiveness of Colombia's oil industry. Embracing these technologies in the development of unconventional reservoirs can position the country at the forefront of the industry. By proficiently controlling the migration of fine particles, the environmental impact associated with unconventional reservoir production can be minimized. This aspect is crucial for adhering to environmental standards and regulations, underscoring Colombia's commitment to environmental compliance.

Chapter 5 is entitled: "*Analysis of potential environmental risks in the hydraulic fracturing operation in the -La Luna- formation in Colombia*". This chapter delves into concepts such as Environmental Risk Management, Environmental Compliance, Sustainability, and the Protection of Unique Ecosystems. The associated paper was published as Major revisions in the Journal Sustainability (Indexed in Scopus and Web of Science; JCR: 3.8).

Evaluating environmental impacts associated with hydraulic fracturing is imperative, aimed at ensuring the responsible management of the industry and averting adverse impacts on Colombian ecosystems. The development of unconventional reservoirs must adhere to environmental regulations and demonstrate sustainability. The study underscores the paramount importance of implementing robust regulatory measures and monitoring systems to guarantee the responsible execution of these activities.

Colombia is endowed with unique and delicate ecosystems. Safeguarding the integrity of these ecosystems during the development of unconventional oil and gas resources is indispensable for preserving ecological equilibrium and safeguarding biodiversity.

The research contributes significantly to the concern surrounding the environmental risks associated with hydraulic fracturing in ecologically sensitive regions. The findings and methodologies presented herein may offer valuable insights for other parts of the world grappling with similar challenges.

The final chapter summarizes the main results of the four studies and provides general conclusions of the thesis, on the challenges and opportunities to develop unconventional resources in Colombia. It also emphasizes the limitations of the study and proposes subjects to further studies.

2. Technical and economic assessment of the development of a Colombian Tight Oil Reservoir: A simulation case study of Valle Medio del Magdalena basin[5]

Abstract

Conventional oil reserves in Colombia are depleted. The country´s reserve-to-production ratio is estimated as 5 years. Therefore, the search for new resources and their conversion into proven reserves are essential. In this case, the production of unconventional reservoirs is an option in Colombia. This work evaluates the technical and economic feasibility of the production of a Tight Oil source rock reservoir, considering parameters such as fracture shape factor, fracture propagation, fracture pressure, international oil price, petrophysical characteristics, fluid properties, drilling cost, completion, and fiscal regime. The methodological development of the work allowed concluding that this reservoir located in the middle Magdalena Valley basin has production potential and that factors such as the type of completion, drilling technique, and cost of lifting the resource have a significant impact on the viability of the project.

Keywords: Unconventional resources; drilling and completion, Middle Magdalena Valley Basin, Tight Oil field,

Palabras clave: Unconventional resources; drilling and completion, Middle Magdalena Valley Basin, Tight Oil field

2.1. Introduction

According to a report released by Mining and Energy Planning Unit (UPME, 2018), MMV Basin is a key tight oil and shale gas region, as shown in Figure 1. This basin is located between the central and eastern mountain ranges of the Colombian territory. It is limited to the North with the Espiritu Santo fault system, to the North East with the Bucaramanga-Santa Marta fault system, to the South-East by the fault system Bituima and La Salina, to the South

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[5] **Published paper**: Forero, C. A., Forero, E. J., Guerrero-Martin, L., Szklo, A., Rochedo, P. R., & Guerrero-Martin, C. (2021). Technical and economic assessment of the development of a Colombian Tight Oil reservoir: a simulation case study of Valle Medio del Magdalena basin. Dyna, 88(219), 35-43.

with the folded Girardot belt and to the West with the Neogene sediments that cover the Serranía de San Lucas and the basement of the Central Cordillera (Figure 2.1).

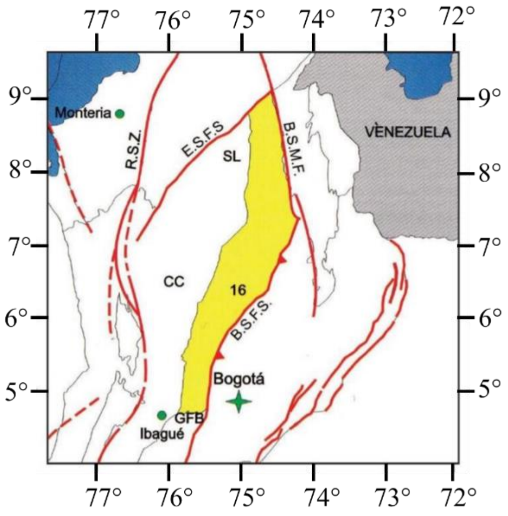

Figure 2.1 Basin under study. (BARRERO et al., 2007)

The La Luna Formation is the principal Cretaceous source rock in the MMV basins. The integration of the lithological characteristics (type of rock, composition, thickness), the petroleum geochemistry parameters and an extensive production database have shown the considered lithological sequence, with excellent percentages of organic matter, higher than 2% TOC and thermally mature, constitutes hydrocarbon generators.

Physical characteristics of the rock type, such as its fractivity, lithological composition, silica content greater than 50%, continuous thicknesses greater than 100 feet, ensure greater operational success in the development of unconventional resources (AGENCIA NACIONAL DE HIDROCARBUROS, 2012) (MARTINEZ & SCHMITT, 2011).

Given this promising data, the main objective of this study is to evaluate the technical and financial feasibility of exploiting this source rock reservoir. The study is original, due to the lack of literature on this type of study in a Colombian reservoir having these characteristics.

2.2. Methodology, materials and methods.

2.2.1. Reservoir simulation

This study used the module of reservoir simulator of CMG to model multiple hydraulic fractures and simulate fluid flow behavior in tight oil reservoirs (CMG). A hydraulic fracture was modeled explicitly using local grid refinement (LGR), which captures the transient flow behavior from shale matrix to fracture (RUBIN, 2010; USECHE-NARVAEZ, MONTEZ-PAEZ, GUERRERO-MARTIN, 2021). Table 2.1 summarized the basic parameters required for the simulation. A basic reservoir model including multistage fractures is shown in Figure 2.2.

Table 2.1 Reservoir Parameters; Well & Fluid Properties.

Parameter	Value	Unit
Depth at top of reservoir	9840	Feet
Net Pay	15	Feet
Initial Reservoir Temperature	250	|°F
Initial Reservoir Pressure @ 0.43 psi/ft	4231	psi
Oil Bubble Point Pressure	2530	psi
Oil Gravity	37	API
Initial Solution GOR	610	scf/stb
Horizontal well length	5000	feet
Swi	0.21	Fraction
Gas gravity	0.8	Fraction
Production time	10957	Days
BHP	2071	psi
Grid Thickness	310	Feet
Porosity	0.048	Fraction
Permeability	0.577	mD

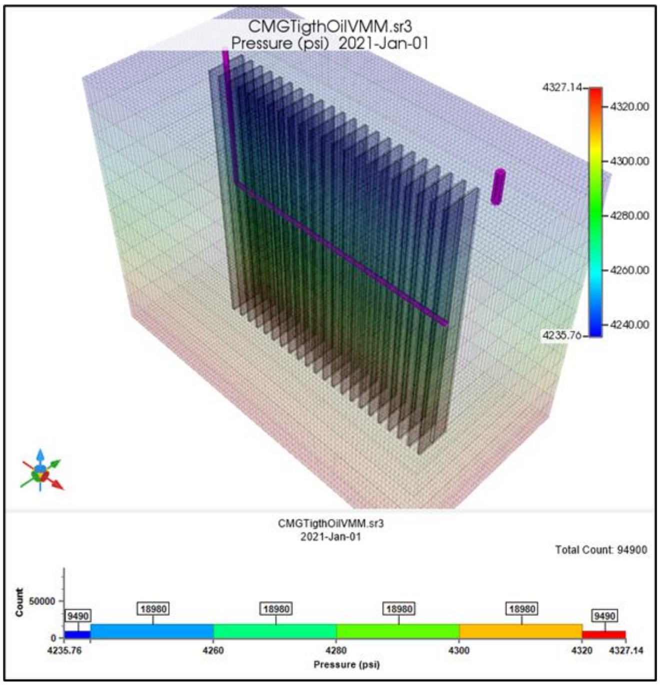

Figure 2.2. A basic reservoir model including 1 horizontal well and 23 hydraulic planar fractures. Source: The author

The assumed relative permeability curves, such a water-oil relative permeability and liquid gas relative permeability, are given in Figure 2.3a and 2.3b, respectively. The base information is supported by the studies made by ANH – Agencia Nacional de Hidrocaros (AGENCIA NACIONAL DE HIDROCARBUROS, 2012), concluding that relative permeability curves in the Colombian shale formation are similar to some major oil-producing unconventional resource plays in North America. Actually, these properties compare favorably to the down dip and up dip trends for the Eagle Ford Formation (CANTISANO et al., 2013).

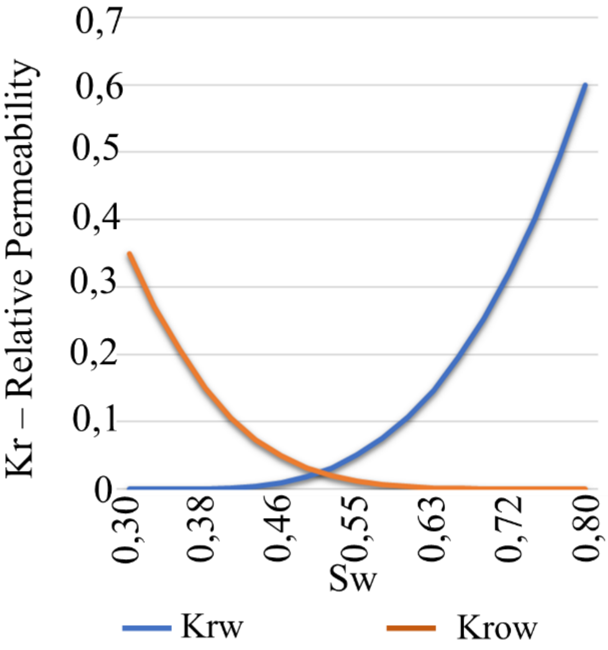

Figure 2.3A. Relative permeability curves Krw & Krow vs Sw. Source: The author

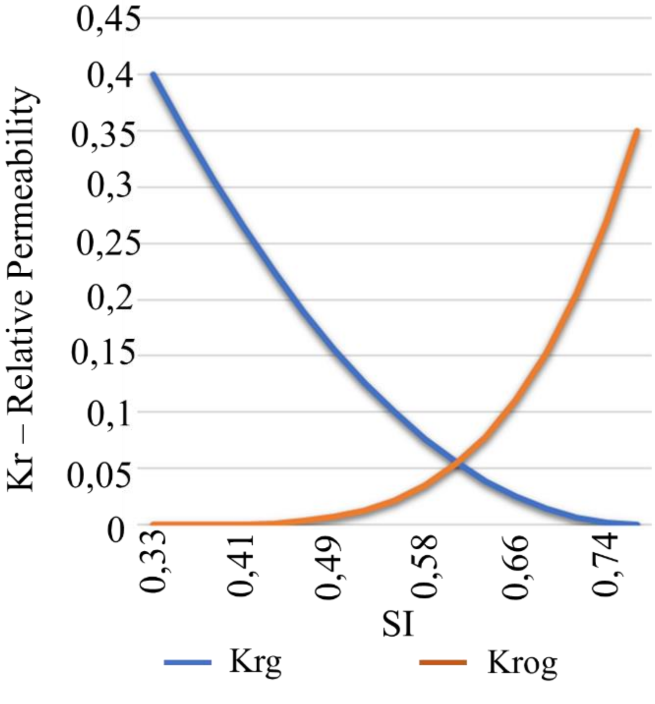

Figure 2.3B. Relative permeability curves Krg & Krog vs Sl.
Source: The author

2.2.1.1 Sensitivity parameters

Seven uncertainty parameters were assessed, including fracture height, fracture half-length, fracture conductivity, hydraulic Fracture Spacing, Rock Compaction, Natural fracture aperture and Natural fracture conductivity. For each one, this study evaluated a reasonable range of values, with the actual maximum and minimum values based on public information of different reports (CANTISANO et al, 2013) (BENAVIDES, 2017)(IBÁÑEZ-RODRÍGUEZ, SÁNCHEZ-DÍAZ, CASTILLO-BASTIDAS, 2016), Table 2.2 includes the most relevant information extracted from the reports.

Table 2.2. Reservoir Parameters; Well & Fluid Properties.

Parameter	Value	Unit	
	Min	Avg	Max
Hydraulic Fracture height (ft)	100	150	300
Hydraulic Fracture half length (ft)	100	350	500
Hydraulic Fracture Conductivity (md*ft)	1	5	50
Hydraulic Fracture Spacing (ft)	200	250	600
Rock Compaction (1/psi)	1.00E-04	1.00E-05	1.00E-06
Natural fracture aperture (ft)	0.000445	0.001	0.001
Natural fracture conductivity (md*ft)	0.01	0.05	0.06

Source: The Author

2.2.1.2. Model Assumption

The following assumptions were established for the evaluation of the model:

- The reservoir is bounded by an upper and a lower impermeable layer.
- The reservoir is isotropic and homogeneous with a constant height, porosity, and permeability.
- The initial reservoir pressure is uniform.
- The reservoir contains a slightly compressible fluid with constant oil density, viscosity, and compressibility.
- Fluid flow takes place only through fractures.
- There is no pressure loss along the wellbore.
- No fracture hydraulic connection.

2.2.1.3. Grid

It was built a reservoir model with a volume of 7400ft X 3800ft X 310ft. The grid representing the reservoir has dimensions of de 94 X 49 X 10, where each cell has one volume de 80ft X 80ft X 31, common size of field blocks to capture a minimum number of frack- frack spacing. The hydraulic fractures are explicit represented by grid cells with a width of 2 ft, to reduce the number of blocks and the runtime, the fracture can be pseudoized to a width with this value. Number of refinement in I, J and K direction is 7 X 7 X 1.

2.2.1.4. Matrix subdivision

This study used a dual-permeability approach with logarithmic local grid refinement near fractures to increase numerical accuracy, while still maintaining computational efficiency. In the dual-permeability model, the porous medium was envisioned as two continuous: one significantly contributes to the pore volume but little to the flow capacity (matrix), while the other significantly contributes to the flow capacity with a negligible contribution to the pore volume (fracture). Yet, in the dual-permeability model, as the matrix continuum has non-zero permeability at the continuum level, the matrix-to-matrix fluid flow is still allowed to take place (WIJAYA & SHENG, 2020). The governing equation for the oil-water dual-permeability model is given by:

$$u = -K\frac{K_r}{\mu} * (\nabla p - \rho g) \qquad (2.1)$$

u represents the phase fluxes, K is the absolute intrinsic permeability, K_r is the relative permeability, μ is the dynamic viscosity, p is the phase pressure, ρ is the phase density and g is the gravity vector (MEDINA-CASAS et al, 2019) (VANEGAS et al., 2019).

2.2.1.5 Shape Factor

The shape factor describes the transmissibility between matrix and fracture. Kazemi and Gilman used the quasi-steady approximation, introduced by Warren and Root, and gave different formulas for the matrix shape factor (KAZEMI et al., 1992), for a rectangle with all sides imbibing, the Equation 2.2. is given by:

$$F_s = 4\left(\frac{1}{{L_x}^2 + {L_y}^2 + {L_Z}^2}\right) * V_m \qquad (2.2)$$

$\boldsymbol{F_s}$ is the shape factor; $\boldsymbol{L_x, L_y, L_Z}$ is the natural fracture spacing in x, y and Z.; and $\boldsymbol{V_m}$ is the volume matrix. Although the location of the fractures is not identified, there representation can be deduced from the shape factor (See Equations 2.3. to 2.7).

2.2.1.6. Natural Fracture Porosity

Fracture porosity is required as input data to build the dual-permeability simulation model. It can be understood as the natural fracture width. Fracture porosity is estimated using the following expression:

$$Fracture\ Porosity = \frac{volume\ of\ i\ fracs + volume\ of\ j\ fracs}{Grid\ block\ bulk\ volume} \qquad (2.3)$$

It is worth highlighting that the fracture porosity is the porosity referenced to the Bulk Volume, not the porosity of the fracture area. The fracture porosity is really small, so no loss is register. In grid block bulk volume,

$$volume\ of\ i\ fracture = no.of\ i\ fracs * volume\ of\ one\ i\ frac \qquad (2.4)$$

Thus,

$$volume\ of\ i\ fractures = \left(\frac{DJ}{DJFRAC}\right) * (DI * natural\ fracture\ apperture * DK) \qquad (2.5)$$

Where $\boldsymbol{DJ}$ is the block width, $\boldsymbol{DJFRAC}$ is the natural of fracture space, $\boldsymbol{DI}$ is the direction and the length of the fracture, and $\boldsymbol{DK}$ is height. Similarly in $\boldsymbol{j}$ direction.

$$volume\ of\ j\ fractures = \left(\frac{DI}{DIFRAC}\right) * (DI * natural\ fracture\ apperture * DK) \qquad (2.6)$$

After replacing the (equation 2.5) and (equation 2.6) into the fracture porosity equation, the following equation is obtained:

$$Fracture\ Porosity = natural\ fracture\ apperture * \left(\frac{1}{DIFRAC} + \frac{1}{DIFRAC}\right) \tag{2.7}$$

When porosity fractures are rather small, some numerical difficulties can arise during the simulation run.

2.2.1.7. Natural permeability

Permeability defines the ability of porous medium to transmit fluids. The presence of open fractures has a great impact on the reservoir flow capacity. Therefore, the fracture permeability is an important factor that determines reservoir quality and productivity. The calculations for obtaining the natural fracture permeability are similar to those for obtaining the porosity**,** in particular the effective permeability.

Equations 2.8 and 2.9 show how the fracture permeability in i direction depends on the conductivity in the same direction and the number of fractures.

$$Fracture\ Perm\ I = \frac{Conductivity\ of\ i\ fracs * no. of\ i\ fracs}{Grid\ block\ width} \tag{2.8}$$

Or

$$Fracture\ Perm\ I = \frac{Conductivity\ of\ i\ fracs * \left(\frac{DJ}{DJFRAC}\right)}{DJ} = \frac{Conductivity\ of\ i\ fracs}{DJFRAC} \tag{2.9}$$

Hence, basically, to obtain the fracture permeability, it is necessary to divide the intrinsic conductivity into the fracture space.

Regarding permeability in j direction, the calculations are the same as those for the i direction. The permeability in the k direction is doubled only if the conductivity in the i direction is assumed to be the same as that of the j direction, as shown in the Equation 2.10

$$Fracture\ Perm\ K = \frac{Cond.of\ i - fracs * no.of\ i - fracs}{Grid\ block\ \ width} + \frac{Cond.of\ j - fracs * no.of\ j - fracs}{Grid\ block\ width} \tag{2.10}$$

2.2.2. Economic evaluation

Integrating the reservoir model and the economic evaluation with a stochastic workflow helps to assess the unconventional opportunities. This study applied a staged approach using Monte Carlo simulation.

The customized tool provides a probabilistic framework for assessing oil projects regardless of their maturity. The focus was on capturing the key project components and their variability according to an intuitive workflow and generating resource and economic metrics (HASKETT & BROWN, 2005). This facilitates a more rigorous comparison of opportunities and better decisions about where to drill the next wells. This also increases portfolio value and helps ensure capital expenditure focuses on projects that are likely to be commercial failures.

The financial analysis is developed through a probabilistic model using the software @Risk. The input and output data of the model cover a wide range via a probabilistic distribution. The economical calculations were adjusted to be performed prior income tax.

2.2.2.1. Inputs used for the financial Sensitivity Study

The incomes from the economic model depend on the outputs from the simulation, specifically the production forecasting.

The operational expenditures (OPEX) from the development stage of the well are mainly related to the production operational expenses, which include lifting costs, such as: flow-back water disposal, well maintenance, minor workover activities like reparations and general & administrative expenses. Transportation costs are also included in OPEX and include the transportation costs from the Valle Medio del Magdalena pipelines. Finally, the price discount of the Colombian blend relative to the dated Brent derived from this blend quality, being equal to 7% ECOPETROL REPORT, 2019. The value of the discount is an average from Valle Medio del Magdalena Basin discounts (WOOD MACKENZIE, 2019)

The average capital expenditures include capital associated with the drilling, completion, stimulation, and facilities. Due to the lack of references for forecasting input data in the economic analysis, since similar projects have never been developed in Colombia, this study used as benchmark the investments and costs in the most important reservoirs in the United States (U.S. ENERGY INFORMATION ADMINISTRATION, 2016), Canada (MISTRÉ, CRÉNES, HAFNER, 2019), and Argentina (RASSENFOSS, 2018). Table 2.3 summarized the inputs for the financial analysis.

Table 2.3. Inputs for the financial analysis

	Parameter	Base Case	Maximum	Minimum	Unit
	Brent >2023	$ 50.00	$ 70.00	$ 30.00	$USD/Bbl
OPEX	Discount Rate	10%			%
	Lifting Costs	$ 20.67	$ 29.06	$ 12.27	$USD/Bbl
	Transportation Costs	$ 1.79			$USD/Bbl
	Discount Sales Contracts	$ 3.33			$USD/Bbl
CAPEX	Drilling	$ 2.56	$ 8.00	$ 0.50	$MUSD/Well
	Completion	$ 4.56	$ 10.60	$ 1.00	$MUSD/ Well
	Facilities	$ 0.46	$ 1.20	$ 0.20	$MUSD/ Well
Gov Take	Royalties	10%			%

2.2.2.2. Economic metrics

Net Present Value and Internal rate of return are the most common metrics to evaluate the economic viability of a project - see Equations 2.11 and 2.12 (BREALEY, Richard A.; MYERS, Stewart C.; ALLEN, 2014)

$$NPV = CF_0 + \frac{CF_1}{(1 + r_1)} + \frac{CF_1}{(1 + r_1)^2} + \cdots + \frac{CF_T}{(1 + r_t)^T} \qquad (2.11)$$

NPV is net present value, CF is the cash flow after-tax, r_1 is the discount rate and T is cash flow time

$$IRR = \frac{CF_1}{(1 + r_1)} + \frac{CF_1}{(1 + r_1)^2} \ldots\ldots + \frac{CF_T}{(1 + r_t)^T} - CF_0 \qquad (2.12)$$

IRR is the Internal rate of return, CF cash flow after-tax, r_1 is the discount rate, T is cash flow time and CF_0 is the total initial investment. To evaluate the project was taken into account these criteria.

- For a single project be successful, its NPV should be positive.
- For independent projects: successful if their IRR are greater than some fixed IRR, the threshold rate/hurdle rate.

Colombia's oil fiscal regime is regressive. The government captures a lower profit share from more valuable fields and a higher profit share from less valuable fields.

Similarly, in Colombia, an average tax of 6% of the lifting cost of the oil produced is generated, which may increase depending on the value of the basin produced. At present there is no legislation in force referring the oil from unconventional reservoirs. Therefore, this work assumes the national average value already in course in the country for conventional reservoirs.

2.3. Results and discussions

2.3.1. Model results

The model was run for the initial parameters of the reservoir; including an Oil & Water contact at 10105 ft and a reference pressure of 8068 psi at 9840 ft. Figure 2.4 shows the changes of the pressure after five years of production. The run time of is 30 years.

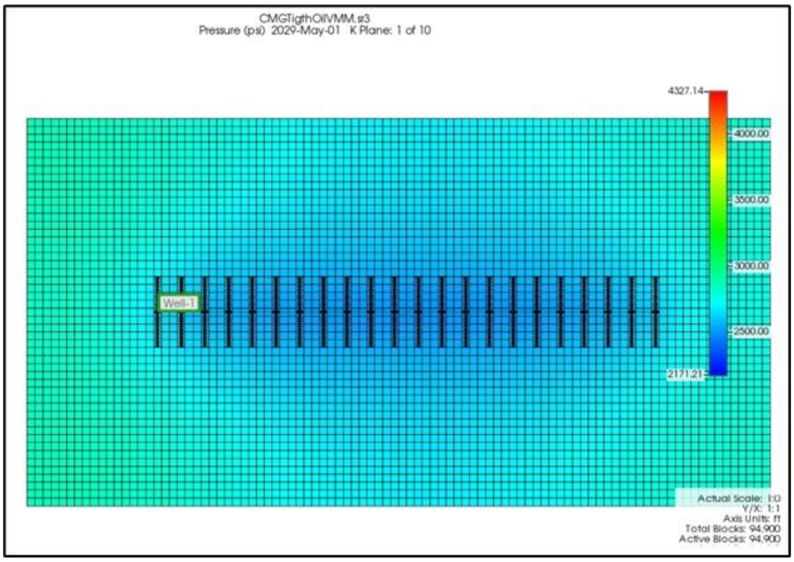

Figure 2.4. A basic reservoir model including 1 horizontal well and 23 hydraulic planar fractures. Source: The author

After performing numerical simulations for the case study, the rate of oil production and cumulative oil production were obtained - see Figure 2.5 and Figure 2.6, respectively. Findings show that there is a wide range of oil rate and cumulative oil production. The ranges for oil rate and cumulative oil production at a 30-year period are obtained as 1.18-1.46 MMBL, which corresponds to a daily production of 35 - 39 bld respectively. The average cumulative oil production and the oil rate were 1.21 MMBL which corresponds to a daily production of 36.9 bld respectively. It is important to note that the oil rate curve in tight oil declines in a short time.

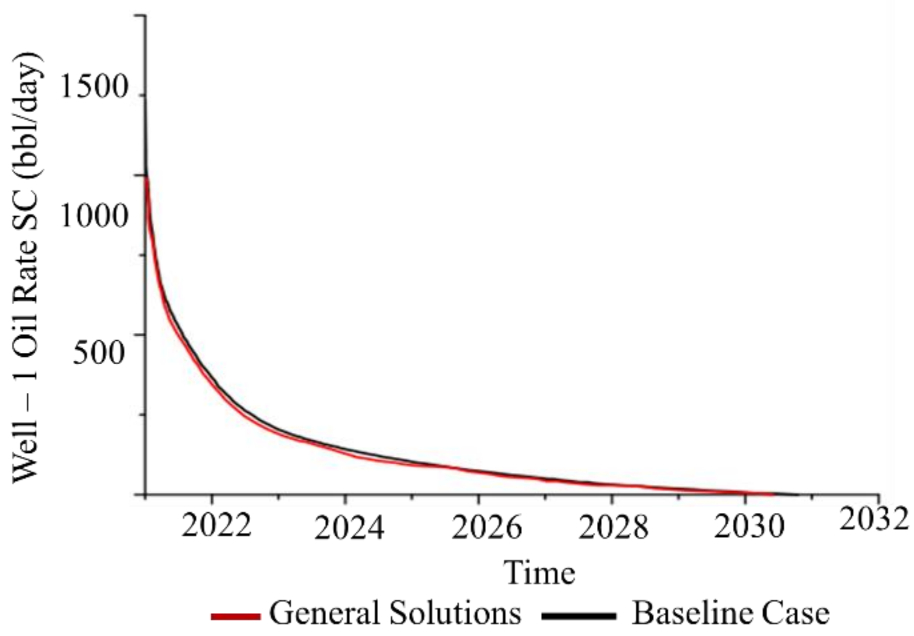

Figure 2.5. Oil production rate. Source: The author.

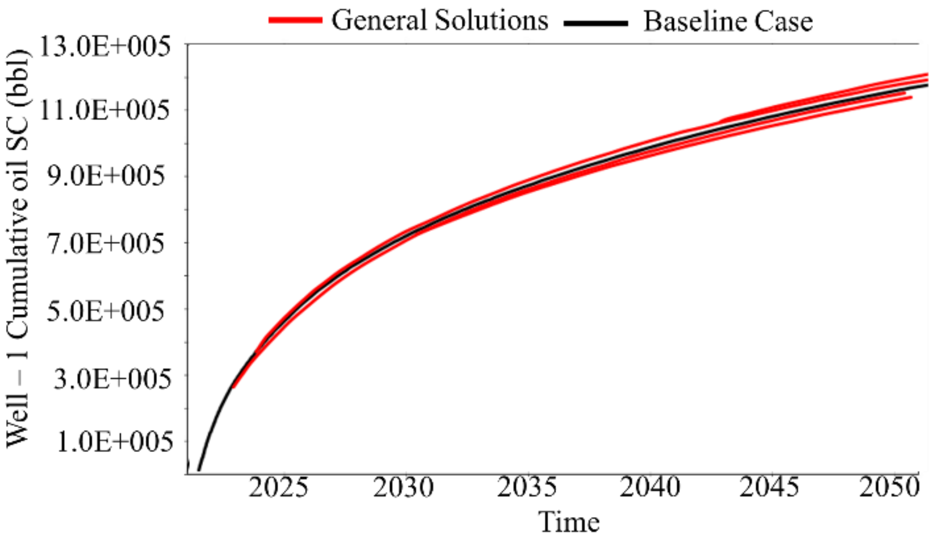

Figure 2.6. Cumulative oil production. Source: The author.

The reservoirs containing light oils have more dissolved gases than reservoir with heavy oils. Therefore, it would be interesting to determine the GOR ranges obtained in the model. The ranges for Solution Gas-Oil Ratio are obtained as 540-573 ft^3/bbl, the average was 555 ft^3/bbl, as show in Figure 2.7.

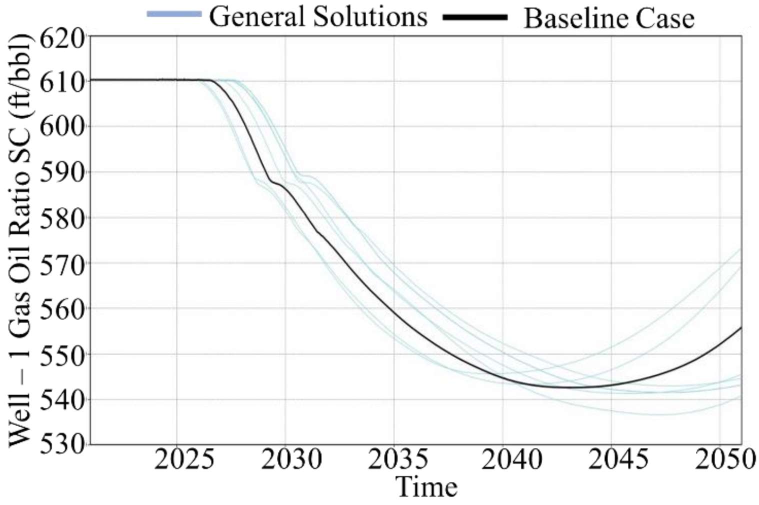

Figure 2.7. Gas oil rate. Source: The author.

The findings are, then, used to build the half-normal plot and the Tornado Diagram to identify the ranking of significant factors affecting cumulative oil production. The half-normal plot at different periods of production for cumulative oil production are presented in Figure 2.8. Any parameter or two-parameters interaction highly deviating from the straight line are recognized as the factors that affect the oil production significantly.

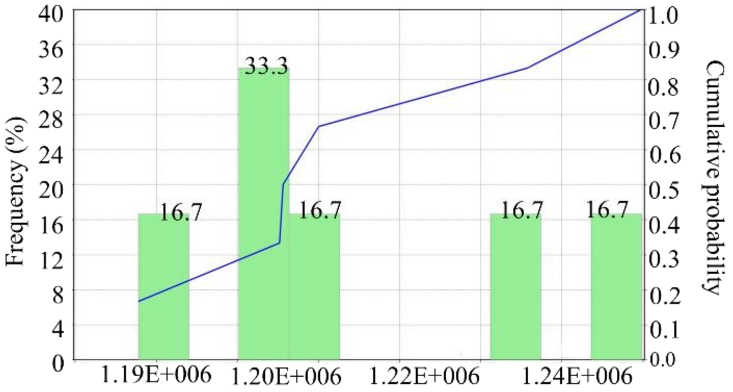

Figure 2.8. The half-normal plot at 30 years of oil production
Source: The author.

The significant and insignificant model parameters are determined by the Tornado Diagram - see Figure 2.9. The rank of important parameters can provide critical insights into performing history matching with field production data in a short-term period. The main influence parameters are the fracture spacing and the fracture half-length.

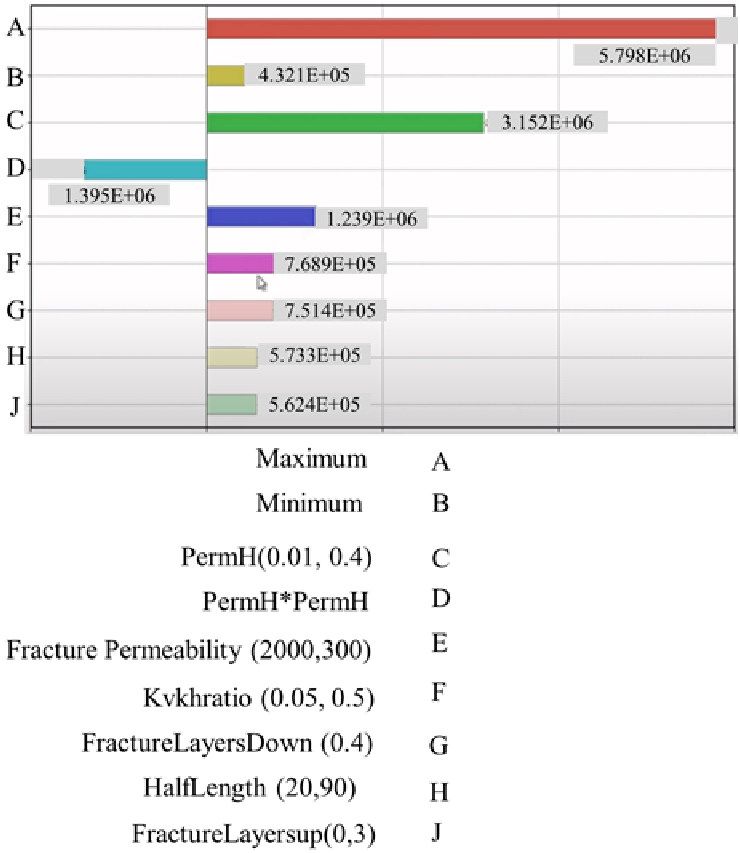

Figure 2.9. Tornado diagram. Source: The authors

2.3.2. Economic results

Based on the production profiles and the assumed expenditures, blend discount-price and fiscal regime, the cash flow model was applied for three scenarios (minimum, mean and maximum) - see Figure 2.10.

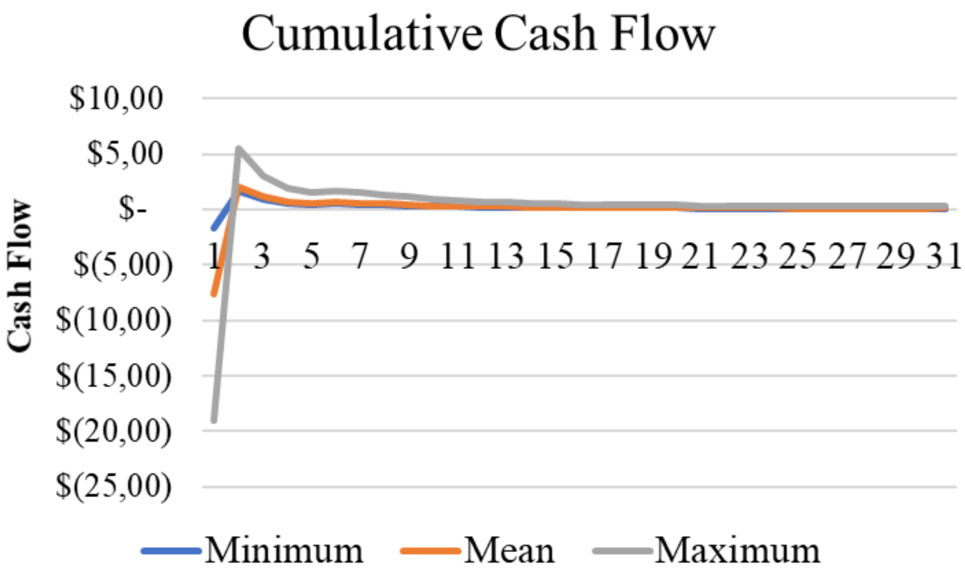

Figure 2.10. Cumulative Cash Flow of the project. Source: The author

Results from the economic evaluation are shown in Figure **Erro! Fonte de referência não encontrada.**2.11 and Figure 2.12. The success probability is 27.5% (NPV≥ 0), and 27.7% (>Discount Rate of 10% p.y), depending on the metric used.

For the Colombian hydrocarbon sector, the valuation of projects usually applies a real discount rate of 10% p.y., as the minimum profitability that the shareholders expect to obtain. For instance, by considering the reports of the main operating companies with contracts with the National Agency of Hydrocarbons to develop activities in Unconventional Reservoirs, and performing an analysis based on the companies´ financial statements, the range of return found hovers between 10%-12% p.y.(CREG,2014). This includes the national territory in exploratory Blocks located in the Magdalena basins -Parex Resources Colombia Ltd. . Conoco Phillips, Canacol Energy Ecopetrol and Exxon Mobil-.

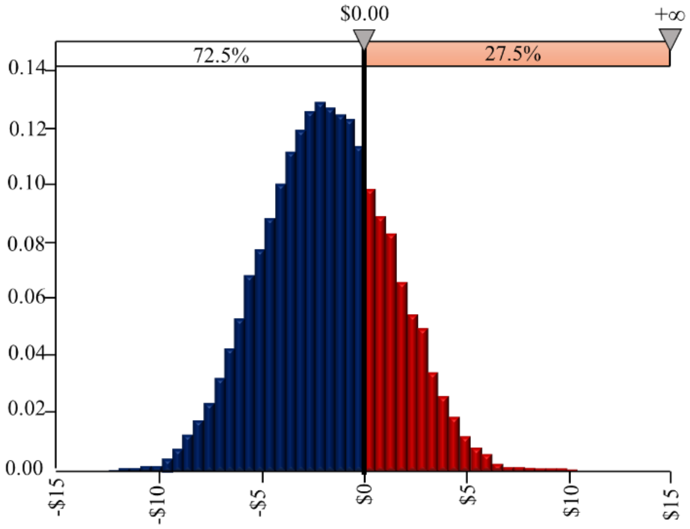

Figure 2.11. Tornado diagram Source: The author

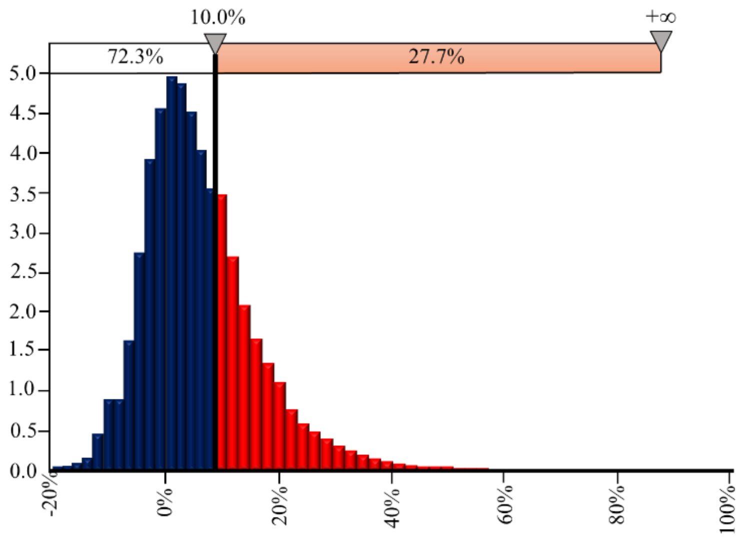

Figure 2.12. Cumulative Cash Flow of the project. Source: The author

The parameters with high uncertainty are identified by analyzing the Tornado Diagram. The Brent Price and production are the most critical parameters for the NPV, with a positively impact on the project. On the other hand, Figure 2.13 shows how completion and lifting cost parameters negatively affects the project.

The IRR tornado diagram is analyzed in the same way. While completion and lifting cost are the pivotal parameters for the IRR, negatively affecting the project, Brent price and production parameter positively affects the project.

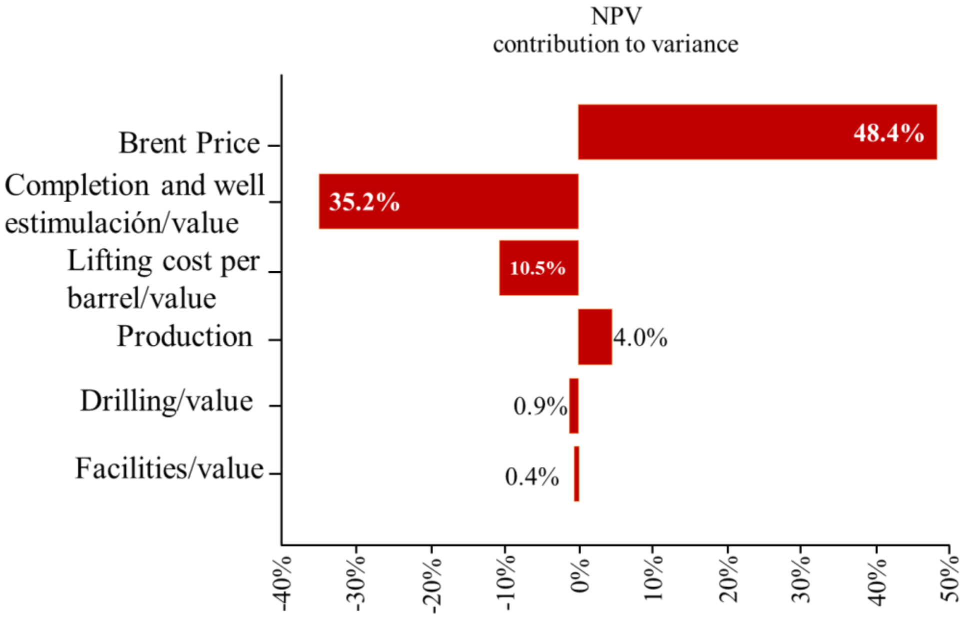

Figure 2.13. Cumulative Cash Flow of the project. Source: The authors

2.4. Conclusions

Through numerical simulations of the rate of oil production and cumulative oil production, there is a wide range of oil rate and cumulative oil production in the assessed basin. The ranges for oil rate and cumulative oil production at 30 years were 1.18-1.46 MMBL, (daily production of 35 - 39 bld respectively), and the average cumulative oil production and the oil rate were 1.21 MMBL (daily production of 36.9 bld respectively). The ranges for Solution Gas-Oil Ratio were 540-573 ft3/bbl, the average was 555 ft3/bbl.

According to financial results, the success probability is 27.5% (NPV≥ 0), and 27.7% (>Discount Rate of 10% annual) is the success probability from an IRR analysis.

The completion and lifting cost are the pivotal parameters for the IRR negatively affecting the project, BRENT price and production parameter positively affect the project.

3. Asphaltenes precipitation/deposition estimation and inhibition through nanotechnology: a comprehensive review[6]

Abstract: Asphaltenes precipitation/deposition is considered a problem of formation damage, which can reduce the oil recovery factor. Besides, asphaltenes can be deposited in pipelines and surface installations, causing serious complications in guaranteeing runoff, decreasing the production of oil wells. The precipitation of asphaltenes can be minimized by reducing the oil production flowrate or by using chemical inhibitors.

Analyzing the stability and precipitation trend of asphaltenes in petroleum is vital for the guarantee of flow. For this purpose, there have been proposed several experimental and numerical methods. Once the risk of precipitation is established, strategies can be formulated for the prevention and diagnosis of deposition problems in production or production training. The tests can be done with dead oil, available in the wellhead, and help in understanding the behavior of the asphaltenes. This review aims to present: (i) the problem related to the precipitation of asphaltenes; (ii) thermodynamic models of asphaltene precipitation; (iii) asphaltene inhibition, control and removal techniques using nanoparticles.

Keywords: Asphaltenes; formation damage; precipitation/deposition

3.1. Introduction

Oil can be subdivided into four fractions, namely: Saturated, Aromatic, Resins and Asphaltenes (SARA). The asphaltenic fraction is the most complex to be characterized, as it consists of the heaviest molecules, of higher polarity and molecular structure containing individual and/or condensed aromatic rings (ARIZA-LEÓN et al.,2012; ARIZA-LEÓN, 2016).

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[6] **Published paper:** Guerrero-Martin, C. A., Montes-Pinzon, D., Meneses Motta da Silva, M., Montes-Paez, E., Guerrero-Martin, L. E., Salinas-Silva, R., ... & Szklo, A. (2023). Asphaltene Precipitation/Deposition Estimation and Inhibition through Nanotechnology: A Comprehensive Review. *Energies*, *16*(13), 4859.

Asphaltenes, due to the variation in oil composition, pressure, and temperature, can precipitate and form solid deposits in the porous media, pipelines, production lines or treatment equipment, bringing several operational problems (ASOMANING, 2003; DEMIRBAS, 2016). Figure 3.1 outlines and identifies the problems related to the precipitation and deposition of asphaltenes in oil fields.

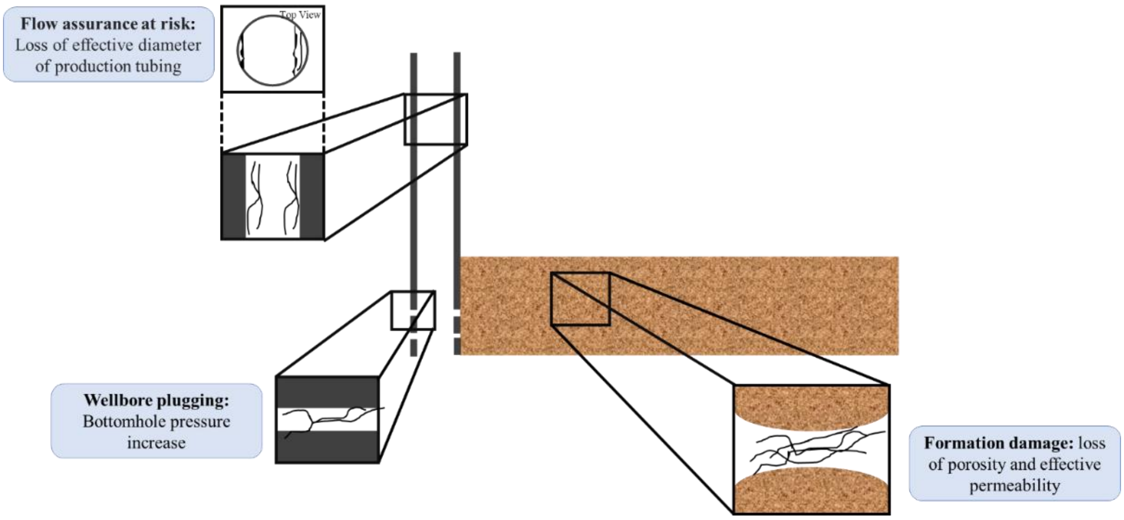

Figure 3.1. Possible operational problems associated with asphaltene precipitation and deposition

These inconveniences generate economic damage, as they can alter petrophysical properties causing severe damage to the reservoir, for example, the presence of asphaltenes in the solid form can lead to the blocking of pores in the production formation, loss of effective porosity, changes in permeability, changes in wettability and increase in oil viscosity (ASOMANING, 2003; LEONTARITIS, K. J.; AMAEFULE, J. O.; CHARLES, 1994; SOULGANI et al., 2011; KHANIFAR et al., 2011).

On the other hand, during the refining process, asphaltenes pose significant challenges and can lead to various issues. One major concern is the formation of coke in equipment, which negatively impacts its operational lifespan and increases maintenance costs. Asphaltenes tend to thermally decompose and form solid carbonaceous deposits, known as coke, on the surfaces of refining equipment. The accumulation of coke restricts the flow of fluids and heat transfer, leading to reduced efficiency and operational problems (LIU et al., 2019; ASOCIACIÓN COLOMBIANA DEL PETRÓLEO, 2014).

The asphaltene agglomeration process can be distinguished in four stages: precipitation, flocculation, aggregation, and deposition (CHAMKALANI, 2012). Among these steps, precipitation is the most difficult process to predict and can be identified when an insoluble phase composed of solids appears in the hydrocarbon (AKBARZADEH, 2007; FIGUERA, 2010; AHMADI & SHADIZADEH, 2012). It is described that, when in equilibrium, asphaltenes are found in petroleum as a colloidal dispersion. When destabilized, insoluble asphalt material is detected (ARIZA-LEÓN, 2012). The pressure at which this occurs, at a given temperature, is named precipitation onset pressure. Knowing this value accurately provides more tools for reservoir and production engineers to make decisions to propose alternatives and solutions to overcome the problem related to the destabilization of asphaltenes (GUERRERO-MARTIN et al., 2018).

Many works involving the determination of asphaltene precipitation at atmospheric pressure are available (MANSUR et al., 2009; LIMA, Aline et al., 2010; GARRETO et al, 2010; GARRETO, MANSUR, LUCAS, 2013; FERREIRA et al., 2015; FERREIRA et al. 2016; PALERMO & LUCAS, 2016; FIGUEIRA. 2017; MAZZEO et al., 2018; BARREIRA et al., 2018; NUNES, 2019). some others investigate the behavior of asphaltenes at reservoir conditions (GUERRERO-MARTIN et al., 2018; BUCKLEY, 2012; WANG, BUCKLEY, CREEK, 2014; BUCKLEY, 1996; BUCKLEY, & WANG, 2002; KURUP et al., 2012; BUCKLEY, 1999; WANG & BUCKLEY, 2003).

3.2. Asphaltenes

Asphaltenes are complex molecules or structures that exist in oils, changing their density and viscosity (AKBARZADEH ET AL., 2007; YANG, Ming-Gang; ESER., 1999). They can be defined, in terms of solubility, as the fraction of petroleum insoluble in n-alkanes (such as n-pentane and n-heptane) and soluble in aromatic solvents (such as toluene) (AKBARZADEH ET AL., 2007; YANG, Ming-Gang; ESER., 1999; HARTMANN et al., 2016). In terms of molecular structure, the most recent and most impacting work was done by Gray et al. 2003. In which the asphaltenes are conceived as associated supramolecules by means of non-covalent bonds.

Over time different classical molecular models of asphaltenes have been developed. In 1940 Nellensteyn (NELLENSTEYN et al., 1924) introduced the possibility that asphaltenes were colloid. This concept lasted for 16 years and was maintained in Pfeiffer and Sall. (1940) (PFEIFFER, SAAL, 1940) work. Later, Dickie and Yen (1967) suggested that asphaltenes have micellar structure. Years later this model was taken as a basis by Wiehe (1994) for the construction of the Pendant-Core and Building Block models, which in 2010 would undergo some substantial modifications proposed by Mullins. Table 3.1 presents the relevance and considerations of each of these models (GARRETO, 2011).

Table 3.1. Summary of publications related to molecular models of asphaltenes (GARRETO, 2011).

Authors	Relevance
Nellensteyn (1924)	Conceptual outline of the colloidal behavior of asphaltenes. Definition of the bases of the main asphaltene separation method by insolubility in heptane and pentane.
Pfeiffer and Saal (1940)	Definition of the micellar structure of asphaltenes in oil.
Dickie and Yen (1967)	Justification for the different values of molecular masses of asphaltenes obtained by different techniques, assigning the highest values to the existence of micelles.
Wiehe (1994)	Introduction of the idea of compositional continuity of oil and its fractions.
Mack (2002)	Relationship between viscosity and concentration of asphaltenes.
Mullins (2010)	Improvement of the Yen model (1961). Effectiveness of critical concentration concepts for asphaltene aggregation.

Several studies involving asphaltenes involve their isolation by solubility difference, the characterization of the isolated fraction, and the evaluation of the phase behavior of model systems. However, different procedures are proposed for the separation of asphaltenes from petroleum. Table 3.2 summarizes the main asphaltene extraction methodologies as well as the considerations necessary to ensure effectiveness in the process (GARRETO, 2011; LEYVA, ANCHEYTA, CENTENO, 2014; MACK, 2002; MOURA, ROSA, 2018; CENTENO et al., 2004).

Table 3.2. Different asphaltene extraction methodologies reported in the scientific literature.

Method	Precipitating Agent	Conditions	Rate Solvent/Sample (mL/g)	Methodology
ASTM D893, 2018	n-C5 commercial	65 ± 5 °C. Filter solids with 150 mL n-C5 at room temperature	10	Centrifuge at 600–700 rpm for 20 min. To decant until only 3 of solution in the tube. Centrifuge again under the same conditions. Dry at ± 105 °C for 30 min.
ASTM D2006, 2006	n-C5 commercial	No heating required	50	Leave to stand for 15 h, filter, and wash three times with 10 mL of n-C5 in each wash.
Bulmer et al., 1979	n-C5 analytical grade and commercial benzene	Heat to dissolve if necessary	40 mL n-C5 and 1 mL benzene	Dissolve in benzene and heat if necessary. Add n-C5 and shake for 5 min. Leave to stand for 2 h. Filter under vacuum. Wash the balloon where the test was performed. Dry at 105 °C.
ASTM D2007, 2019	n-C5 commercial	Requires heating	10	Add n-C5 and shake well. Heat for a few seconds until dissolved. Leave to stand for 30 min. Wash with 10–20 mL of n-C5.
ASTM 6560, 2019	n-C7 and toluene	Requires reflow	100	Add n-C7 and reflux for 1 h. Cool for 1.5 to 2.5 h under light. Filter on Whatman No. 42 paper. Rinse the filter paper with hot n-C7 for 1 h. Keep under reflux with 30–60 mL of toluene in a water bath. Dry at 100–110 °C for 30 min.
ASTM D3279, 2019	n-C7 with purity > 99%	Requires reflow	1000	Add n-C7 and reflux for 15–20 min. Cool for 1 h. Filter under vacuum. Wash three times with 10 mL of n-C7 in each wash. Dry at 107 °C for 15 min.

3.2.1. Asphaltene Precipitation

Several authors agree that the predominant variables that determine the precipitation of asphaltenes are pressure and composition, but temperature can also have an influence on the trend of the asphaltene precipitation of an oil (ESCOBEDO, MANSOORI, 1995; LEONTARITIS, 1996; CARRILLO et al., 2014).

A clear example of the effect of composition on asphaltene precipitation can be observed in processes that require the injection of some type of fluid into the reservoir, such as advanced recovery or well stimulation, where considerable amounts of substances are injected that can destabilize asphaltenes in petroleum. This occurs because such substances generate a change in the oil solubility parameter, and therefore, the precipitation of asphaltenes can occur when the oil is mixed with incompatible substances, with the operations of injection of CO_2, gases, or solvents being critical (CARRILLO et al., 2014; MULLINS, 2008; FOX & LEFSRUD, 2021; VICKNAIR, TANSEY, O'BRIEN, 2022; ECOPETROL, 2022).

This pressure variation causes, at some stage of production, the pressure of the asphaltene precipitation envelope (APE) to be reached, which is the pressure at the start of the asphaltene precipitation. At this point, all dissolute asphalt material in the oil will be precipitated and possibly deposited in the reservoir or in the pipes. Figure 3.2 shows the critical points for precipitation to begin. In general, when the pressure is reduced, the amount of precipitated asphaltenes increases, constituting an inverse relationship (MULLINS, 2008; HIRSCHBERG et al. 1984; HAMMAMI, 2000; RASSAMDANA et al., 1996)

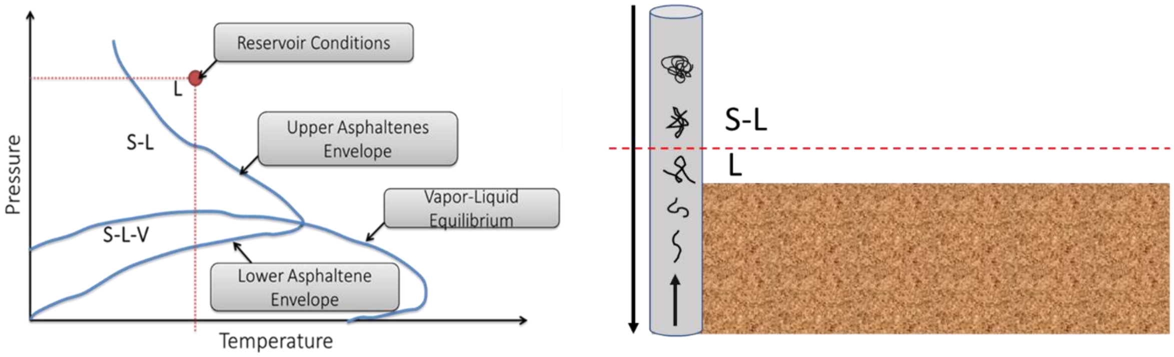

Figure 3.2. Typical phase envelope of asphaltene precipitation.

Additionally, Hartmann (2016), using the UV–visible technique and propane as an asphaltene flocculant solvent, reported a decrease in precipitation onset value with increased pressure. This behavior was attributed to the fact that the propane's solubility parameter changes when subjected to pressure. In Table 3.3, it can be observed that the onset at 5802.51 psi is practically one-fifth of that measured at 362.59 psi (HARTMANN, D, 2016; HIRSCHBERG et al., 1984)

Table 3.3. Effect of pressure on solution precipitation onset for 0.5% by weight of C7 asphaltenes with propane at 56 °C at different pressures: from 362.59 Psi to 5801.51 psi (HARTMANN, D, 2016; HIRSCHBERG et al., 1984).

Pressure	**Translucence (%)**
580,151	110
290,075	123
145,038	143
72,519	161
36,259	190

3.2.2. Thermodynamic Models of Asphaltene Precipitation

To better understand the phenomenon of asphaltene precipitation, it is important to establish the different variables that influence the process. In this way, the identification of thermodynamic conditions brought knowledge about the behavior of asphaltenes [57] (ZENDEHBOUDI et al., 2014).

In 1942, the Flory–Huggins polymeric solution theory was applied to asphaltenes. The asphaltene components were a non-ideal solution, and the amount of precipitated asphaltenes was tested by adding asphaltene mass to a previously prepared polymeric solution (FERREIRA et al., 2015; GABRIENKO et al., 2015). The objective of the work was to demonstrate that the heavy fraction was not soluble in the polymeric solution, thus corroborating that the two substances were not compatible, even having high molar mass. Years later, other researchers included the micellar nature of asphaltene and again tested the theory introduced by Flory and Huggins, obtaining similar results (BURKE, E.; HOBBS, KASHOU, 1990; NOVOSAD, COSTAIN, 1990; KOKAL et al., 1992). On the other hand, Leontaris and Mansoori (1987) proposed a colloidal thermodynamic model, where it was considered that the asphalt molecules were surrounded by resins. Based on the Flory–Huggins polymeric solution model, the researchers determined the potential of an oil to precipitate asphaltenes, considering thermodynamic conditions.

The solid model proposed by Gupta (1986) and Thomas et al. (1992) considered the asphaltic component as a solid and the oily phase as a liquid modeled with cubic state equations, and the precipitation of asphaltenes was represented as a multicomponent solid phase (NGHIEM et al., 1993). Similarly, Chung et al. (1991) (CHUNG, SARATHI, JONES, 1991) modeled two fractions present in heavy petroleum: one of these corresponded to a precipitated fraction, the asphaltene; the other corresponded to a totally soluble and non-precipitable resin. This model aimed to identify the parameters that influenced the stability of asphaltenes and, like the models of Gupta in 1986 and Thomas and collaborators in 1992, also considered this fraction as pure solids.

In 1993, Nghiem et al. developed a state equation (EOS) to predict the precipitation of asphaltenes using thermodynamic considerations. The model consisted of the identification and division of two parts: one would be a material that would tend to precipitate (asphaltene); the other would be a phase that would not precipitate. This EOS was based on the Peng–Robinson equation (PENG, ROBINSON, 1976) and, using diffuse logic and binary interaction coefficients, allowed statistical analysis of asphaltene precipitation in the non-precipitated phase. This work did not consider the micellar nature of asphaltenes. Years later, in 1997 and in 1998, Nghiem and Coombe would complement this equation with calculations of flash vaporization in three phases.

Hirschberg et al., in 1984, presented a work on a liquid thermodynamic model, which describes the behavior of asphalt molecules in the petroleum reservoir, considering variations in pressure, temperature, and the compositional gradient. This model also included the concept of reversibility in asphaltene precipitation described by Fussel in 1979. However, Hirschberg based his model on the Redlich–Kwong state equation (REDLICH & KWONG, 1949).

A constant in the models presented above concerns the asphaltene fraction being represented as a solid or a mass conglomerate, until, in 1996, Victorov and Firoozabadi inserted the thermodynamic micellization model, which presented asphaltenes as micelles contained in oil. This work applied the Peng–Robinson state equation to describe the oily phase that included mixtures of petroleum, with heavy and light components, and employed the Gibbs free energy concept to minimize the size of the micelles, thus ensuring that their molar mass did not exceed the mass value of an oligomer.

After this study, other models were presented as complex equations. In 2004, Chapman et al. modeled a state equation for phase equilibrium prediction based on the statistical association of fluid theory (SAFT). This model gives importance to the impact of the molecular form, the intermolecular association, and the van der Waals interaction forces. Three years later, in 2007, Pedersen and Hasdbjerg expanded the equation using test results from fluid extracted from reservoirs of condensed gas with asphalt content and heavy oil. This model introduces a more realistic behavior of asphaltenes since it allows the modeling of the thermodynamic balance between three phases (liquid, vapor, and solid) (ZENDEHBOUDI et al., 2014).

3.3. Nanotechnology for the Inhibition of Asphaltene Precipitation/Deposition

Crude oils are considered as colloidal dispersions in which the asphaltenes' stability depends on the fluid composition, the pressure and temperature conditions, and the production parameters (ASOMANING, 2003; DEMIRBAS, 2016). Asphaltenes have a self-assembly behavior that is prompted by their particular chemical structure (CHILINGARIAN, YEN, 1994). In this regard, asphaltenes molecules are generally described as island-shaped structures composed of a polyaromatic core with alkyl ramifications and with the presence of heteroatoms such as sulfur, oxygen, and nitrogen (MULLINS, 2011; MULLINS et al., 2011). These heteroatoms enable the asphaltenes' self-assembly by different mechanisms such as acid–base interactions and H-bonding when having H-terminal groups. These aggregation mechanisms are commonly related to the interaction of N-containing (pyrrolic, pyridine, quinoline) and O-containing (carbonyl, carboxyl, hydroxyl) functional groups (NASSAR, HASSAN, PEREIRA-ALMAO, 2011; NASSAR et al., 2012; XIE, KARAN, 2005). The phenomena are governed by the N-containing functional groups that could be found as positively charged species with the ability to interact with the negatively charged oxygen groups due to the difference in electronegativity between the O atoms and other elements such as H (GRAY et al., 2011). Additional aggregation mechanisms associated with π–π stacking due to the stacking of the polyaromatic cores of the asphaltenes and metal coordination complexes derived from the presence of vanadium, iron, and nickel in the asphaltene structures are also observed (CASTILLO, VARGAS, 2016; ROGEL, 2002).

The mentioned aggregation mechanisms were revealed by Gray et al. in 2011 and are schematized in Figure 3.3 Even though these intramolecular forces are weak, the authors stated that the combination of the mechanisms is the factor governing the asphaltene aggregation phenomena (GRAY et al., 2011). Nonetheless, the crude oil composition plays a major role in the aggregation phenomena, as in different studies it was proven that the resins interact with the asphaltene nanoaggregates, limiting their growth and keeping them in their original colloidal form (KOOTS, SPEIGHT, 1975; LEÓN et al., 2002).

The main difference between resins and asphaltenes is their polarity, which is lesser for the resins as these molecules usually have a smaller core with a lower amount of heteroatoms and a higher presence of alkyl substituents (PEREIRA et al., 2007; CARNAHAN et al., 1999). This last characteristic is commonly related to the greater solubility exhibited by the resins, which surround the asphaltene aggregates, keeping them in their colloidal form (PORTE, ZHOU, LAZZERI, 2003). Thus, it is considered that a lack of this fraction enables the asphaltene precipitation/deposition (LEON et al., 2001). Therefore, controlling the asphaltene precipitation/deposition in crude oils with a natural lack of stabilizing agents has been a major concern for the oil and gas industry to avoid productivity losses which are mostly presented in light crude oils (GHLOUM, AL-QAHTANI, AL-RASHID, 2010; YEN, YIN, ASOMANING, 2001; JUNIOR, Luiz FERREIRA, DA SILVA RAMOS, 2006).

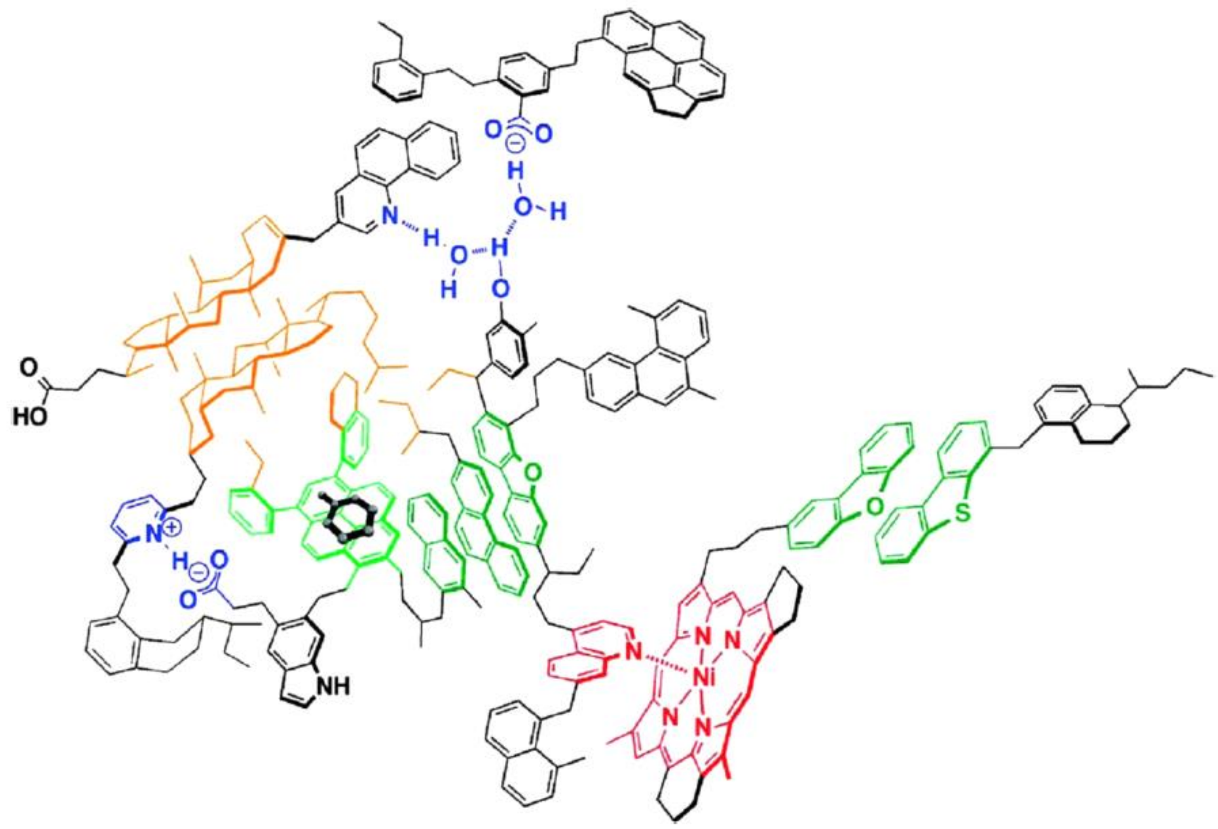

Figure 3.3. Nanoaggregates of asphaltenes exhibiting different interaction mechanisms: acid–base and H-bonding (in blue), π–π stacking (in green), hydrophobic pocket (in orange), and metal coordination (in red). Original figure from (GRAY et al., 2011), reprinted with permission. Copyright (2020) American Chemical Society.

Previously in this manuscript, the thermodynamical models of the asphaltenes were introduced; the next sections will present a discussion of novel nanotechnology-based treatments for the inhibition of the formation damage associated with asphaltene precipitation/deposition. At the nanoscale, it is feasible to develop materials to capture the asphaltenes at reservoir conditions without inducing additional damage due to the small nanoparticle sizes (1–100 nm) (FRANCO, ZABALA, CORTÉS, 2017). The nanoparticles adsorb the asphaltenes in their colloidal state, preventing their aggregation, which provides an efficient technique for avoiding productivity losses and additional interventions for the mitigation of the formation damage process which often are not cost-effective operations (FRANCO et al., 2013).

In this way, many authors have worked on the synthesis and evaluation of different types of nanomaterials with the purpose of determining their adsorptive capacity towards asphaltenes and improving the flow conditions through coreflooding experiments after the asphaltene destabilization is fomented (REZAKAZEMI et al., 2017). A summary of the mentioned studies is presented in Table 3.4.

Table 3.4. Summary of the scientific publications reporting the application of nanoparticles for the inhibition of the formation damage associated with asphaltene precipitation/deposition.

Authors	Year	Nanoparticle	Summary	Methodology	Experimental Ensamble	Source/Synthesis Method	Results
Rezakazemi et al.	2017	γ-Al$_2$O$_3$	Separation of the asphaltene using a ceramic membrane.	Dynamic light scattering (DLS)	Membrane cells	Commercial γ-Al$_2$O$_3$ (size, purity, and the specific surface area are 30 nm, 99.99%, and 90–160 m^2/g)	Raman spectroscopy results revealed a significant rise in the estimated asphaltene molecular sheet diameter from 5.4818 to 13.7866 A.
			The impact of adding alumina nanoparticles on expanding asphaltene's molecular size.				According to DLS data, the addition of nano-alumina increased the molecular size of asphaltenes from 512.75 nm to 2949.55 nm.
Parsaei et al.	2020	Iron oxide	The effect of nanoparticles on asphaltene precipitation was studied by measuring surface tension in the presence of CO$_2$ at different temperatures and pressures.	IFT measurement by using pendant drop method in capillary tubes	Capillary tube	Commercial nanoparticles obtained from US Research Nanomaterials Inc. Houston, TX 77084, USA	The addition of iron oxide nanoparticles to the oil solution reduces the interfacial tension at higher pressures with a steeper slope, showing that nanoparticles can decrease asphaltene precipitation.
							The presence of nanoparticles reduced the amount of asphaltene that precipitated at 50 °C by 16.34% and at 70 °C by 19.65% depending on the temperature.
Ahmadi, Aminshahidy.	2018	CaO and SiO$_2$	The impact of CaO and SiO$_2$ nanoparticle concentration on asphaltene precipitation in the presence of CO$_2$ at different temperatures.	PVT cells to perform natural depletion	PVT cells	SiO$_2$ was bought from Houston Brand company. For the CaO, 10 g CaCO$_3$ was mixed with 5 mL acid solutions of succinic acid, tartaric acid, and citric acid (0.5 g acids dissolved in 5 mL	Temperature increased from 90 C to 100 C during pressure reduction from 2500 Psi to 1500 Psi.
							CaO decreased asphaltene precipitation from (0.32 wt%, 0.62 wt%) to (0.096 wt%, 0.214 wt%); SiO$_2$ decreased asphaltene from

						water) and left to rest for 24 h. This mixture was then dried at 100 °C for 2 h. The samples were heated separately for 2 h at 900 °C.	(0.56 wt%, 1.10 wt.%) to (0.27 wt.%, 0.52 wt.%).
Oliveira et al.	2013	Cobalt ferrite	The use of modified cobalt ferrite nanoparticles as a flocculant agent for asphaltenes.	Nanoparticles are annealed in an effort to modify their structural phase.	UV-Vis spectrophotometer Varian	Through the homogeneous precipitation method, cobalt ferrite nanoparticles were created using deionized water, a 2.0 mol/L solution of $FeCl_3$, and a 1.0 mol/L solution of $CoCl_2$.	The system's asphaltene precipitation is unaffected by the presence of modified nanoparticles, indicating that the particles can help the asphaltene aggregate.
Cortés et al.	2012	SiNi	Analyze the effect of temperature and NiO content on the asphaltene uptake by a hybrid nanomaterial composed of nickel oxide nanoparticles supported on a nanoparticulated matrix of silica gel.	UV-Vis technique to determine the asphaltene adsorption on the nanoparticles.	Nanoparticulated matrix of silica gel	Silica nanoparticles were synthesized by the sol−gel method following an acid route. The gel was prepared from TEOS (tetraethoxysilane), ethanol, water, and HNO_3. The synthesized nanosilica was impregnated with aqueous solutions of nickel nitrate $Ni(NO_3)_2$ in different concentrations (5 and 15 wt%) for 3 h and then dried at 120 °C for 6 h and cured for 6 h at 450 °C.	Asphaltene adsorption increased with increasing nickel oxide concentration in the hybrid nanomaterials at constant temperature. Regardless of asphaltene concentration, the hybrid nanomaterials' ability to absorb asphaltene decreased as the temperature rose.
Kazemzadeh et al.	2014	Fe_3O_4	Examining the effect of Fe_3O_4 nanoparticles on asphaltene precipitation	Bond number measurement and IFT measurement using VIT technique.	The high-pressure chamber was made out of	Commercial nanoparticles. No provider reported.	The intensity of the asphaltene precipitation would be reduced as the the mass fraction of Fe_3O_4 nanoparticles increased.

					a capillary tube at the top.		
Shojaati et al.	2017	γ-Al_2O_3 Fe_3O_4 NiO	The impact of Fe_3O_4, NiO, and -Al_2O_3 metal oxide nanoparticles on synthetic oil was explored in this study in order to reduce the danger of asphaltene deposition and postpone the commencement of asphaltene precipitation.	An indirect technique as opposed to other onset measurement techniques.	Test tubes	Nanoparticles obtained from U.S. Research Nanomaterials, Inc., Houston, TX, USA.	Metal oxide nanoparticles showed a great effect on inhibition of asphaltene precipitation and can be applied as an inhibitor. The instability of asphaltenes and the amount of asphaltene deposits were reduced in the presence of nanoparticles, in the following order of effectiveness: γ-Al_2O_3 > NiO > Fe_3O_4.
Mohammadi et al.	2011	TiO_2 ZrO_2 SiO_2	Study the effect of metal oxide nanoparticles in organic-based nanofluids for stabilizing asphaltene particles in oil.	Oil titration method, making use of the polarized light microscopy technique, to check their potential in stabilizing or destabilizing asphaltene nanoaggregates.	The titration procedure is performed by gradual and step-by-step addition of n-heptane. Then, precipitation of asphaltene was investigated using a polarized light microscope.	TiO_2 Nanoparticles: two different solutions were prepared. Solution prepared by mixing 10 mL of tetraisopropyl orthotitanate with 25 mL of ethanol and 2 mL of ethylenediamine as template under vigorous stirring. 3 mL HCl, 20 mL distilled water, and 10 mL ethanol. Then, it was slowly injected into solution 1 under 40–50 °C and stirred for about 4 h. Zirconium oxychloride ($ZrOCl_2.8H_2O$) was used as the Zr source. The stock solution was prepared by mixing the metal salt solution with a solution of 1.5 g urea	Rutile (TiO_2) fine nanoparticles can effectively enhance the asphaltene stability in acidic conditions and act inversely in basic conditions. It was found that the required amount of n-heptane for destabilizing the colloidal asphaltene is considerably higher in the presence of TiO_2 nanofluids at pH below 4. FTIR spectroscopy shows the changes in n-heptane-insoluble asphaltenes when acidic nanoliquid TiO_2 is used as an inhibitor. According to the results of FTIR spectroscopy, TiO_2 nanoparticles can increase the stability of asphaltene nanoaggregates by forming hydrogen bonds in an acidic medium. At this time, the other materials used in this experiment, as

						and 9 mL LNH3 (25 wt%) at a temperature of 60–80 °C and a pH between 9 and 10. As a surfactant, 2 g ethoxylated nonylphenol (20 mol) was added to form a nanoemulsion.	well as the TiO_2 nanoparticles, are not able to form a hydrogen bond under alkaline conditions; hence, they are not able to prevent the precipitation of asphaltenes.
						20 mL of TEOS was dissolved in a mixture of isopropyl alcohol and ethanol and stirred at 50° C. for about 1 h. To this solution were then added 5 mL of ethylene diamine and 3 g of citric acid. The resulting solution was hydrolyzed to 65% by weight HNO_3 solution for 2 h with vigorous stirring and then refluxed for 24 h.	
Nassar et al.	2011	NiO Co_3O_4 Fe_3O_4	Asphaltenes have been investigated for their oxidation onto different types of nanoparticles, namely NiO, Co_3O_4, and Fe_3O_4.	The asphaltenes containing nanoparticles were separated by centrifugation. The supernatant was decanted and precipitated. Then, the samples were subjected to thermal analysis for estimating the adsorbed amount of asphaltenes and oxidation.	Batch adsorption experiments	Commercial nanoparticles purchased from Sigma Aldrich.	All tested nanoparticles showed high adsorption affinity and catalytic activity for the adsorption and oxidation of asphaltenes in the following order: NiO > Co_3O_4 > Fe_3O_4. The oxidation temperature of asphaltenes decreased by 140, 136, and 100 °C compared to non-catalytic oxidation in the presence of NiO, Co_3O_4, and Fe_3O_4 nanoparticles, respectively.

Tarboush et al.	2012	NiO	Shows that NiO nanoparticles prepared in situ within heavy oil display much higher affinity toward asphaltene adsorption.	Oil characterization, before and after asphaltene adsorption, was conducted using density and viscosity measurements.	Viscosity measurements were determined using a cone–plate Brookfield viscometer model.	Nickel(II) nitrate hexahydrate (99.9985%, Puratronic) was used as the precursor salt. Commercially available nickel oxide (NiO) nanoparticles (dp < 50 nm, 99.8%) were used for comparison.	An asphaltene absorption of 2.8 g asphaltenes/g nanoparticles was reported. Commercial NiO nanoparticles in the same size range exposed to the same experimental conditions adsorbed only 15% of the above value.
Shayan and Mirzayi	2015	γ-Fe_2O_3 α-Fe_2O_3	Synthesized maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3) nanoparticles were used for the adsorption and removal of asphaltenes from the prepared solution.	UV-vis spectrophotometer to determine the maximum peak of adsorption for asphaltene.	Batch adsorption experiments	$FeCl_3$ (ferric chloride), $FeCl_2$ $4H_2O$ (ferric chloride tetrahydrate), HCl (hydrochloric acid, 37%), ammonium hydroxide (NH_4OH, 25% ammonia), methylene blue.	This work showed that the synthesized MNPs and HNPs can be considered as nanoadsorbents of asphaltenes, although MNPs are more efficient.
Zabala et al.	2013	γ-Al_2O_3	Describes the evolution of a fluid containing nanomaterial with high adsorption capacity for asphaltene inhibition.	Upscaling and field trial application	Real in-field conditions	Commercial silica nanoparticles obtained from Petroraza S.A.	Asphaltene content measured in the produced oil increased after the well treatment with the nanofluid containing alumina nanoparticles.
Al-Jabari et al.	2007	Fe_3O_4	Combination of nanoparticle adsorption and magnetic separation for the removal of asphaltenes from heavy oil by adsorption on colloidal magnetite.	Combination of nanoparticle adsorption and magnetic separation	Magnet and UV-Vis spectroscopy	Obtained from Nanostructured & Amorphous Materials, Inc., (130 Benton St, Garland, TX 75042,TX, USA)	Ultra-dispersed magnetite nanoparticles offer several advantages over conventional ones; for example, they provide a large surface of contact, reduce the distance traveled between the adsorbed species and the surface of the solid particles, and are excellent for phase separation with the aid of a magnetic medium.

Hosseinpour et al.	2013	NiO $CaCO_3$ Fe_2O_3 WO_3 MgO ZrO_2	Three different categories of metal oxide nanoparticles with acidic, amphoteric, and basic surfaces were synthesized, and their textural, structural, and acid–base properties were characterized. Asphaltenes are extracted from the dead heavy oil sample, and their structure, elemental composition, and acid–base number are determined. The nanoparticles are then used to adsorb asphaltenes from asphaltene–toluene solutions.	Centrifugation followed by UV−vis spectroscopy of the supernatant liquid	The nanoparticles were mixed in tightly sealed vials	Precipitation method employed for obtaining the different nanostructures	The adsorption capacity of asphalt nanoparticles is between 1.23 and 3.67 mg/m^2 and decreases in the order NiO > Fe_2O_3 > WO_3 > MgO > $CaCO_3$ > ZrO_2, which is accompanied by the synergistic effects of acidity and surface charge.
Li et al.	2018	NiO SiO_2 Fe_3O_4	Investigated effect of nanoparticles on the inhibition of asphaltene particle aggregation in a water-wet micro-sized pore.	Experimental methodology that directly observed asphaltene aggregation at the pore scale.	Water-wet microsized pore	Commercial nanoparticles. SiO_2 nanoparticles (20 nm, ≥99.9%), NiO nanoparticles (40 nm, ≥99.9%), and Fe_3O_4 nanoparticles (20 nm, ≥99.5%)	The nanoparticles can act as inhibitors of asphaltenes, preventing the aggregation of asphaltenes and increasing the stability of asphaltenes in the microcapillaries. Asphaltene particles can easily aggregate with each other in the absence of nanoparticles. On the other hand, the presence of nanoparticles can prevent asphaltene particles from flocculating. This could be mainly

							due to the high surface area to volume ratio, good adsorption capacity, and high degree of suspension of the nanoparticles.
Azizkhani et al.	2019	Fe_3O_4 γ-Al_2O_3	Focused on the asphaltene precipitation by liquid-free asphaltene inhibitors at reservoir conditions.	The vanishing interfacial tension technique was implemented to evaluate the effect of the nanoparticles on minimum miscibility pressure.	PVT cells	Commercial nanoparticles. No provider reported.	Direct inhibitors of asphaltenes (liquid inhibitors) can be considered excellent candidates for field-scale mixed gas injection. Injection of CO_2/nanoparticles reduced the precipitation of asphaltenes compared to injection of pure CO_2 under reservoir conditions. Mixtures containing Fe_3O_4 can perform better than Al_2O_3 solutions as direct inhibitors of asphaltenes.
Varamesh et al.	2019	Fe_3O_4 NiO	Development of a reliable and simple CPA EoS-based approach to model asphaltene precipitation in the presence of Fe3O4 and NiO nanoparticles.	Asphaltene onset in the presence and absence of nanoparticles was measured using dynamic light scattering. Cubic plus association equation of state (CPA EoS) was employed to predict the asphaltene precipitation in the presence and absence of the nanoparticles.	FTIR spectrophotometer	NiO and Fe_3O_4 nanoparticles were synthesized via precipitation from aqueous solutions.	CPA EoS can be used to develop chemical inhibitors of asphaltene precipitation by metal oxide nanoparticles.
Lu et al.	2016	γ-Al_2O_3	Investigated the adsorption of asphaltenes onto Al_2O_3 through 2 methods:	Coreflooding tests	Core	Commercial nanoparticles purchased from Aladdin Reagents Co. Ltd. (Shanghai, China).	The higher the mass fraction of Al_2O_3, the lower the precipitation intensity of asphaltenes.

			(a) by adding a certain mass of nanoparticles in a fixed volume solution with different initial concentrations of asphaltenes				Al_2O_3 nanofluid injection can reduce the amount of oil and reduces permeability because nanoparticles can inhibit asphaltene deposition on the sand surface in a porous medium.
			(b) by exposing a certain amount of asphaltenes in a fixed volume of solution with the addition of different amounts of nanoparticles				
Ezeonyeka et. al.	2018	Fe_2O_3 Fe_3O_4 γ-Al_2O_3	Investigation of the adsorption of n-heptane-precipitated asphaltenes, C7 asphaltenes, from toluene model solutions onto three metal oxide NPs, Fe_2O_3, Fe_3O_4, and Al_2O.	UV−vis spectroscopy at three different wavelengths was compared with thermogravimetric analysis (TGA) results	Sapphire measuring prism	Commercial Fe_2O_3 (dp <50 nm), Fe_3O_4 (20− 30 nm), and Al_2O_3 (<50 nm particle size) were used as adsorbents.	Al2O3 showed the highest adsorption capacity with 385 ± 5 mg/g, followed by Fe_3O_4 and Fe_2O_3. Referring to mg/m^2, however, Fe_2O_3 showed the highest adsorption capacity. TGA analysis showed that NPs promoted the oxidation of adsorbed asphaltenes in the reverse order of their adsorption capacity, qmax (mg/g) ($Al_2O_3 > Fe_2O_3 \approx Fe_3O_4$).
Nassar et al.	2015	SiO_2 γ-Al_2O_3 Fe_3O_4	Commercial nanoparticles of silica, γ-alumina, and magnetite were used as adsorbents to probe the chemical nature of the nanoparticles for asphaltene growth inhibition and to validate the model.	Experimental data on the kinetics of asphaltene aggregation were obtained using dynamic light scattering (DLS) measurements	UV-Vis spectrophotometer through asphaltene model solution in toluene	Commercial nanoparticles purchased from Sigma Aldrich	Under different conditions tested, all nanoparticles reduce the hydrodynamic diameter of large aggregates in solution to different degrees due to adsorption. The influence of the chemical nature of the nanoparticles, the origin of the asphaltenes, the heptol solution, and the temperature was successfully evaluated with DLS measurements.

Tarboush et al.	2014	Fe_2O_3	Presentation of the sol–gel/emulsion method for the in situ production of Fe_2O_3 nanoparticles in heavy oil from their aqueous precursor and comparison of their asphaltene adsorption with commercial Fe_2O_3 nanoparticles.	In situ prepared nanoparticles were recovered by centrifuging the crude oil for 10 min. The recovered samples were analyzed through TGA experiments.	In situ in heavy oil phase starting from their precursor aqueous iron (III) nitrate solution using a sol–gel/emulsion approach.	Iron (III) nitrate nonahydrate (used as the precursor salt), commercial iron (III) oxide (Fe_2O_3) nanoparticles (dp = 20–30 nm, 98%, used for comparison), toluene (99.8%), n-heptane (99%), and/or dichloromethane (DCM) (anhydrous, ≥99.8%, used to wash the nanoparticles recovered from the oil phase for microscopy).	The nanoparticles prepared in situ showed a much higher absorption, 2.6 ± 0.12 g/g, and were much more selective than the asphaltenes. Increasing the concentration of in situ generated particles showed a downward trend in absorption compared to the equilibrium concentration of asphaltenes.
Hashemi et al.	2016	NiO	Possible influence of nickel oxide (NiO) nanoparticles on the destabilization of asphaltene deposits in porous media in the presence of carbon dioxide.	Three experiments were designed to analyze the precipitation process of asphaltenes in the oil stream in porous media and the impact of the presence of nanoparticles in this process. The first experiment consisted of injecting live oil into the heart to analyze the effect of injection pressure and velocity, which also includes the mechanism of elimination of organic matter in the	Carbonate porous matrix	The material used for the synthesis of nickel oxide nanoparticles was nickel acetate ($C_4H_6NiO_4$). First, an appropriate amount of nickel acetate was dissolved in water, and then the solvent, citric acid, was added to the mixture in a stoichiometric ratio to form a homogeneous gel. The droplets of the prepared solution were dispersed in the carrier gas and transported to the reaction medium.	The accumulation of asphaltenes in the heart was reduced from 0.1033 (g) in EXP-2 to 0.0128 (g) in EXP-3 in essentially identical experimental situations.

				natural degradation process.			
				In the second experiment, the asphaltene precipitation inside the core was studied by injecting CO_2 into the core.			
				In a third experiment, nickel oxide nanoparticles were dispersed in CO_2 to study the effect of the presence of nanoparticles on asphaltene precipitation.			
Betancur et al.	2016	SiO_2	Studied the role of the particle size and surface acidity of silica nanoparticles on their interaction and adsorption of asphaltenes	Constructed adsorption isotherms through UV–visible spectrophotometry, as well as estimated the change in the asphaltene aggregation through dynamic light scattering (DLS).	UV–visible spectrophotometer, nanosizer, and core for dynamic tests	Implemented the sol–gel method for the synthesis of silica nanoparticles of different sizes from a tetraethyl orthosilicate (TEOS) precursor. The surface acidity of the nanoparticles was also modified.	It was observed that as the nanoparticle size increased, the adsorption was reduced due to a lesser availability of active sites in the adsorbent surface. Moreover, the acidity had a direct relation to the asphaltene adsorption and disaggregation. In addition, coreflooding tests were carried out with a nanofluid including the best nanoparticles, and the recovery factor had an increment of 11%.
Amin and Nazar	2016	SiO_2 γ-Al_2O_3 TiO_2	The influence of effective factors such as nanoparticle types,	The Taguchi design of experiments (DOE) approach, the	UV–visible spectrophotometer	Commercial nanoparticles purchased from TECNAN.	The nanoparticle type and nanoparticle structure of asphaltenes with an impact of 48.5% and 3.11%,

			asphaltene types, nanoparticle-to-solution ratio of the asphaltene model, and temperature on the adsorption size of asphaltenes on metal oxide nanoparticles was evaluated.	toluene–asphaltene solution model, and a UV–visible spectrophotometer.			respectively, have the highest and lowest proportions of the amount of adsorbed asphaltenes at selected concentrations. Alumina nanoparticles have the highest adsorption, and silica nanoparticles have the lowest adsorption. The temperature has no statistical significance. Asphaltenes with high aromaticity tend to adsorb more onto nanoparticles.
Hosseini-Dastgerdi et al.	2022	SiO_2 Polyacrylamide (PAM)	The study assesses how silica–polyacrylamide nanocomposite might be used for the first time to prevent asphaltene precipitation.	Techniques for polarized microscopy, dynamic light scattering, asphaltene dispersion testing, and viscometry	FTIR polarizing microscope (Olympus), FESEM technique	Using the vapor acid process with sulfuric acid over 1300 C for 48 h, SiO_2 nanoparticles were functionalized. The functionalized nanoparticle solution was then combined in a 1:1 mass ratio with polyacrylamide. By adding a certain quantity of synthesized nanocomposites to distillate water to reach a concentration of 1000 ppm by mass, the silica–PAM nanofluid was created.	The aggregate (asphaltene) size decreases as the dosage of the nanocomposite increases. It is anticipated that the heterogeneities of the nanocomposite surface will produce a number of sites for the adsorption of asphaltene, enhancing adsorption affinity and reducing asphaltene self-association. For the crude oil, the greatest dispersion effectiveness of the nanocomposite was 69% and 79% at doses of 1% and 2.5% nanofluid volume.
López et al.	2020	SiO_2 cardanol	Assess how cardanol/SiO_2 nanocomposites behave in preventing asphaltene damage using a coreflooding test under reservoir circumstances.	Adsorption curves/desorption isotherms of cardanol onto SiO_2 nanoparticles were constructed. Likewise, the	Fourier transform infrared spectroscopy (FTIR), dynamic light	To eliminate any dampness, SiO_2 nanoparticles (SNs) were first dried at 120 °C for 4 h. The beginning wetness technique was used to secure the CDN to the SN surface. The mass of the cardanol	The developed nanocomposites demonstrate significant asphaltene precipitation/deposition inhibition capacity. Additionally, using nanocomposites improves oil recovery by more than 50% when

				relationship between the total surface acidity and the H and K of the SLE model was presented.	scattering (DLS)	sample per gram of SiO_2 nanoparticles was then changed to produce three SiO_2/cardanol nanocomposites (CSNs).	compared to the scenario with asphaltene damage.
Bagherpour et al.	2023	Carboxylate-alumoxane nanoparticles functionalized BMA and PBMA	In this study, the application of two types of carboxylate-alumoxane nanoparticles (functionalized boehmite by methoxyacetic acid (BMA) and functionalized pseudo-boehmite by methoxyacetic acid (PBMA)) for asphaltene adsorption and precipitation was investigated.	BMA and PBMA nanoparticle DLS analysis. Pore size distribution and nitrogen adsorption–desorption isotherm for PBMA were presented.	Ultraviolet−visible (UV−Vis) spectroscopy	Boehmite and pseudo-boehmite were functionalized using the acidic technique to create carboxylate-alumoxane nanoparticles, and are now known as BMA and PBMA, respectively. Aluminum oxide-hydroxide with varying concentrations of H_2O molecules and variable crystal sizes makes up boehmite. Boehmite is frequently used as the main starting material when creating alumina phases.	In comparison to the onset point of the reference synthetic oil, the use of BMA and PBMA delays the commencement of precipitation by 17 and 26%, respectively. The adsorption of asphaltene on the surface of these functionalized nanoparticles is the most important factor for asphaltene removal in the presence of carboxylate-alumoxane nanoparticles. The carboxylate-alumoxane nanoparticles containing asphaltene are eliminated from the system upon centrifugation.
Mahmoudi Alemi et al.	2021	Fe_2O_3 and functionalized SiO_2 nanoparticles F-SiO_2	In a light live oil with a high danger of asphaltene deposition, this study investigates their impacts on asphaltene precipitation and aggregation. High pressure, high temperature (HPHT) reservoir conditions were used for the studies.	TGA mass loss curves of pure asphaltenes and asphaltenes adsorbed onto Fe_2O_3 and F-SiO_2 nanoparticles	OPS technology with a LEUTERT one-phase sampler to have a representative oil sample; HPHT filtration experiments	A straightforward chemical precipitation technique was used to create pure iron oxide Fe_2O_3 nanostructures. In this technique, a quantity of iron(III) chloride hexahydrate ($FeCl_3$, 6H2O) is used.	The results demonstrate that adding 150 ppm of F-SiO2 nanoparticles to live oil before depressurization at 274.9 °F delays the onset of asphaltene by over 600 psi; in contrast, adding the same amount of Fe_2O_3 nanoparticles before depressurization makes the oil more stable and prevents the precipitation of asphaltenes.

Simin Tazikeh	2022	Fe_3O_4	Investigate changes in the surface properties of silica during the precipitation of asphaltenes with magnetite (Fe3O4) nanoparticles.	Images captured by an AFM technique of an A2 asphaltene precipitation on a silica substrate. Changing wettability using the Young–Laplace and modified Wenzel models	Fourier transform infrared spectroscopy (FTIR); atomic force microscopy (AFM)	Polythiophene-coated Fe_3O_4 nanoparticles (Fe_3O_4-PTNP) are synthesized in two steps. First, Fe_3O_4 nanoparticles are synthesized by coprecipitation. Then, they are coated with polydopene using a chemical polymerization technique.	The results show that heteroatoms (e.g., O, N, and S) and aromatic rings as functional groups can affect the process of asphaltene agglomeration and adsorption onto a silica surface. Atomic force microscopy (AFM) is used to obtain adequate topography information.
Gandomkar and Nasrian	2020	Metal oxide nanoparticles (GO, TiO_2, SiO_2, and MgO)	As direct asphaltene inhibitors (DAIs) on asphaltene stability over the period of miscible CO_2 injection, metal oxide nanoparticles (GO, TiO_2, SiO_2, and MgO) have been addressed in this study in the liquid-free mode.	Four metal oxide nanoparticles (GO, TiO_2, SiO_2, MgO) were used as direct inhibitors to stabilize asphaltenes during CO_2 injection into reservoir oil. The nanoparticles have acidic (SiO_2 and TiO_2) and basic (MgO and GO) characteristics.	IFT measurements of chemical properties. Bulk sample and dynamic asphaltene test	Commercial nanoparticles.	The CO_2/GO mixture reduces asphaltene aggregation/deposition and improves oil recovery by 6–25% compared to CO_2 injection alone. Direct asphaltene inhibitors reduce interfacial tension (IFT) and allow miscible gas injection at reservoir pressure and temperature. Metal oxide nanoparticles increase the solubility of asphaltene particles, keeping them in solution.
Azizkhani and Gandomkar	2020	Fe_3O_4 Al_2O_3	This study centered on the inhibition of liquid-free asphaltene precipitation under reservoir conditions. During CO_2 injection, the $F_{e3}O_4$ and Al_2O_3 nanoparticles were utilized as direct asphaltene inhibitors (DAIs).	The interfacial tension technique was used to evaluate the effect of DAIs on the minimum miscibility pressure during CO_2/nanoparticle injection. Asphaltene precipitation in volatile and intermediate oils was	IFT (advanced drop shape analysis) PVT Cell	All the nanoparticles are commercially available, so Fe_3O_4 and Al_2O_3 were used as received. These nanoparticles were used in different concentrations such as 500, 1000, 2000, and 3000 ppm.	The addition of Fe_3O4 and Al_2O_3 to CO_2 reduces MMP in reservoirs. Mixtures with Fe_3O_4 are better asphaltene inhibitors than Al_2O_3 solutions. Solubility is more important than aggregation during CO_2 nanoparticle injection. DAI concentrations above 2000 ppm are not favorable.

	studied by varying the concentration of DAI from 500 to 3000 ppm.	

To improve the understanding of the applicability of nanoparticles and the phenomena surrounding their interactions with asphaltenes, further sections will be introduced. The order for this manuscript section is as follows: (I) synthesis of nanoparticles for the inhibition of the precipitation/deposition of asphaltenes, (II) phenomenological approaches to the asphaltene–nanoparticle interactions, and (III) inhibition of asphaltene precipitation/deposition.

Table 3.5 summarizes the most commonly used systematization techniques, as well as their main advantages and disadvantages. It should be noted that the above advantages and disadvantages are variable depending on the synthesis conditions, materials, and application requirements. It is essential to carefully evaluate each method based on the needs and constraints of the project.

Table 3.5. Advantages and disadvantages of the most commonly used nanoparticle synthesis techniques (FUENTES et al., 2022; IBAÑEZ-GOMEZ et al., 2022; BELLO-ANGULO et al., 2022; HEUER-JUNGEMANN et al., 2019; SHEN & SUN, 2020; RATAN et al., 2020; AHMADI et al., 2021; ALAM et al., 2019; MAHHOUTI et al., 2019; VARANDA et al., 2019; ABDELGHANY et al., 2021; ABAKUMOV et al., 2020; SHAHJUEE et al., 2019; RAMALINGAM et al., 2020; HAMOUDA et al., 2020; REVERBERI et al., 2019; GARCIA et al., 2020; GUERRERO-MARTIN et al; 2023; SALVADOR et al., 2021; ASAB, ZEREFFA, SEGNE, 2020; ASGARI et al., 2019; RODRÍGUEZ-RODRÍGUEZ, et al., 2019; BIBI et al., 2021; REN, 2021; KUMAR, 2020; DÍAZ DE GREÑU et al., 2020; KHERADMANDFARD et al., 2021; AYINDE, GITARI, SAMIE, 2019)

Method	Summary	Advantages	Problems
Chemical synthesis	Nanoparticle synthesis involves controlled chemical reactions using precursors and reducing agents. Common techniques include chemical reduction, chemical precipitation, coprecipitation, and microemulsion.	Chemical synthesis of nanoparticles offers precise control of size and shape, has diverse applications, and is easy to implement in the laboratory.	Chemical synthesis of nanoparticles can require toxic or expensive reagents, be a slow process, and be difficult to scale up for large-scale production.
Thermal decomposition method	Thermal decomposition generates nanoparticles by decomposing precursors at high temperatures in a controlled atmosphere to obtain metallic,	Allows the synthesis of nanoparticles at high temperatures with high purity, especially in the case of metallic and ceramic particles.	Requires special equipment, but there may be problems with stability, aggregation, and generation of unwanted by-products.

	semiconducting, or ceramic particles.		
Wet synthesis	Uses an aqueous solution to generate nanoparticles. Methods such as sol–gel synthesis, hydrolysis, and precipitation in aqueous media are employed. This technique allows precise control of the size and shape of the nanoparticles.	Excellent purity and homogeneity, exact control of nanoparticle size and shape, and suitability for high-volume manufacturing.	It could need additional stages and agents, be sensitive to environmental factors, and demand rigorous supervision.
Microemulsion method	Stable colloidal systems of water, oil, and surfactant are used, achieving high uniformity in particle size and shape.	Guarantees high uniformity in size and shape, greater colloidal stability, and the production of very small particles.	The synthesis of nanoparticles with microemulsions is complex, requires specific temperature and pH conditions, and may involve additional purification and separation steps.
Microwave-assisted synthesis	Can be accelerated using microwave radiation, which allows rapid energy transfer to activate the chemical reaction efficiently.	It accelerates nanoparticle synthesis by providing rapid and uniform heating, reducing reaction time and increasing efficiency. It also allows precise control of reaction conditions.	Requires specialized microwave equipment and adjustments to reaction parameters. Production scale may be limited due to equipment constraints.

3.3.1. Synthesis of Nanoparticles for the Inhibition of the Precipitation/Deposition of Asphaltenes

There are several methodologies for nanoparticle synthesis, which can be divided into two broad classifications: (I) bottom-up and (II) top-down. Bottom-up techniques refer to any experimental methodology which enables the construction or assembly of the nanostructure from smaller structures, molecules, or atoms; top-down techniques are related to the nanostructures obtained from micro- and macroscale materials typically by applying high-energy milling. A schematic of both processes is shown below (Figure 3.5).

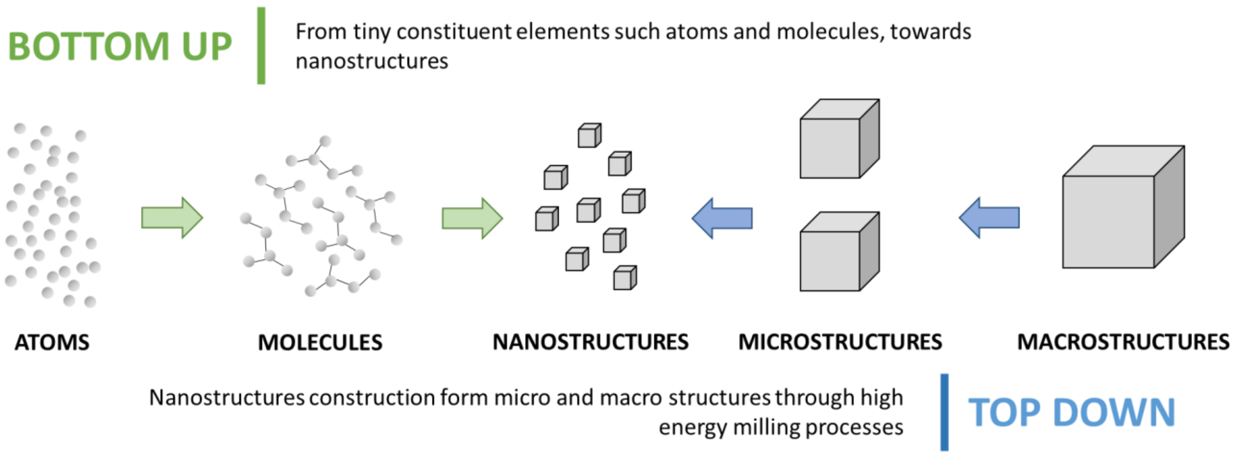

Figure 3.4. Schematic representation of the bottom-up and top-down methodologies for the synthesis of nanoparticles. Figure adapted from (FUNDACIÓN ARGENTINA DE NANOTECNOLOGÍA, 2016).

Nonetheless, the scientific literature shows minor applications of nanoparticles obtained through high-energy milling processes for the inhibition of the formation damage associated with asphaltene precipitation/deposition. Thus, this manuscript describes the nanoparticle synthesis processes related to bottom-up methodologies such as sol–gel, coprecipitation, and functionalization of nanoparticulated supports (FRANCO et al., 2013; CORTÉS et al, 2012; BETANCUR, 2016; MONTES. 2018; MEJIAS-SÁNCHEZ, 2009).

3.3.1.1.Sol–Gel

The sol–gel method has been widely used for the synthesis of different types of materials such as aerogels, ceramics, membranes, and silica nanoparticles (BRINKER, SCHERER, 2013; HENCH, WEST, 1990; JUNG, PARK, 2000). Silica nanoparticles have great applicability in different fields, including the oil and gas industry. In this sense, this type of nanomaterials has been applied for the viscosity reduction of heavy oils (MONTES et al., 2019; MONTES et al., 2019; TABORDA, ALVARADO, CORTÉS, 2017), the optimization of drilling fluids (KURUP, 2012), and the inhibition of the formation damage related to the precipitation/deposition of asphaltenes (CORTÉS et al., 2012; NASSAR, 2015; BETANCUR, 2016; CORTÉS et al., 2016). The process for obtaining the silica nanoparticles through the sol–gel method is particularly simple, and it is summarized below (Figure 3.6). Typically, the process contains three steps: (I) a hydrolysis reaction, (II) the polymerization of the hydrolyzed silica chains via condensation, and (III) the formation of a gel which is characterized as a colloidal suspension (BRINKER & SCHERER, 2013). Moreover, a catalyst favoring the performance of the hydrolysis reaction is usually included, while the gel formation is generally improved by reducing the mixture pH (CORTÉS et al., 2016; SINGH, et al., 2014; TREWYN et al., 2007).

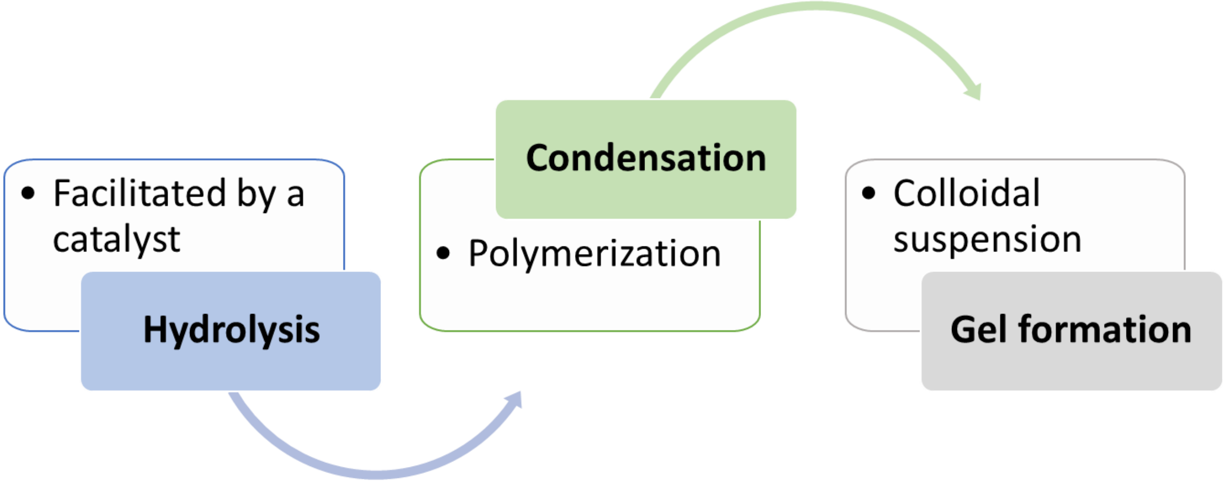

Figure 3.5. Typical sol–gel process for the synthesis of nanoparticles. (The difference in colors shows that each stage of the process is independent of the other.)

Different silicon precursors can be applied for obtaining any type of desired silica nanoparticles. Among the most used are some alkoxides, such as tetraethyl orthosilicate (TEOS), and sodium silicate (BETANCUR et al., 2016; AMIN & SOLAIMANY, 2016; FUNDACIÓN ARGENTINA DE NANOTECNOLOGÍA, 2016; MONTES et al., 2018; MEJIAS-SÁNCHEZ et al., 2009). The synthesis process has a great sensibility in terms of the nanostructure textural properties such as surface area, size, and roughness regarding the precursor/continuous phase ratio, while the catalyst presence plays a minor role in these properties (MEJIAS-SÁNCHEZ et al., 2009).

3.1.1.2. Coprecipitation

The coprecipitation method is mainly used for obtaining magnetite nanoparticles which have a great affinity towards asphaltene adsorption and also have a recoverable advantage compared to other types of nanomaterials due to their magnetic behavior (ARISTIZÁBAL-FONTAL, CORTÉS, FRANCO, 2018).

To obtain magnetite nanoparticles, two salts, namely $FeCl_2$ and $FeCl_3$, are commonly used; the latter is diluted in HCl (2%), and the former is diluted in deionized water. Both solutions are mixed for 15 min, and then a solid suspension is obtained. The magnetic solid is then separated and further dried at 80 °C for at least 12 h.

An analogous methodology is applied to obtain composite materials. Betancur et al. (BETANCUR, FRANCO, CORTÉS, 2016) developed a nanocomposite material based on a core–shell structure, where a magnetite core was used and synthesized using the coprecipitation method, and a silica shell was constructed using the sol–gel method. This composite had the advantage of having a greater affinity towards asphaltene adsorption than the magnetite alone due to the silica inclusion, while its recoverable advantage was maintained.

3.3.1.3. Nanoparticle Functionalization

The nanoparticle functionalization consists of the assembly of some compounds or smaller nanoparticulated systems on a nanometric support. There are several techniques for achieving a functionalized material; however, the incipient wetness technique, which is a rapid and low-cost methodology, has been used for application in the oil and gas industry in most cases (CORTÉS et al., 2012).

The method is shown in Figure 3.7, where it can be observed that from a solution, which is typically formed by hygroscopic salt, the nanoparticulated support is functionalized through continuous and slow dripping. The obtained material is then dried at a temperature of 80–120 °C and further calcined if the functionalizing agent is intended to be a metal oxide (FRANCO et al., 2013).

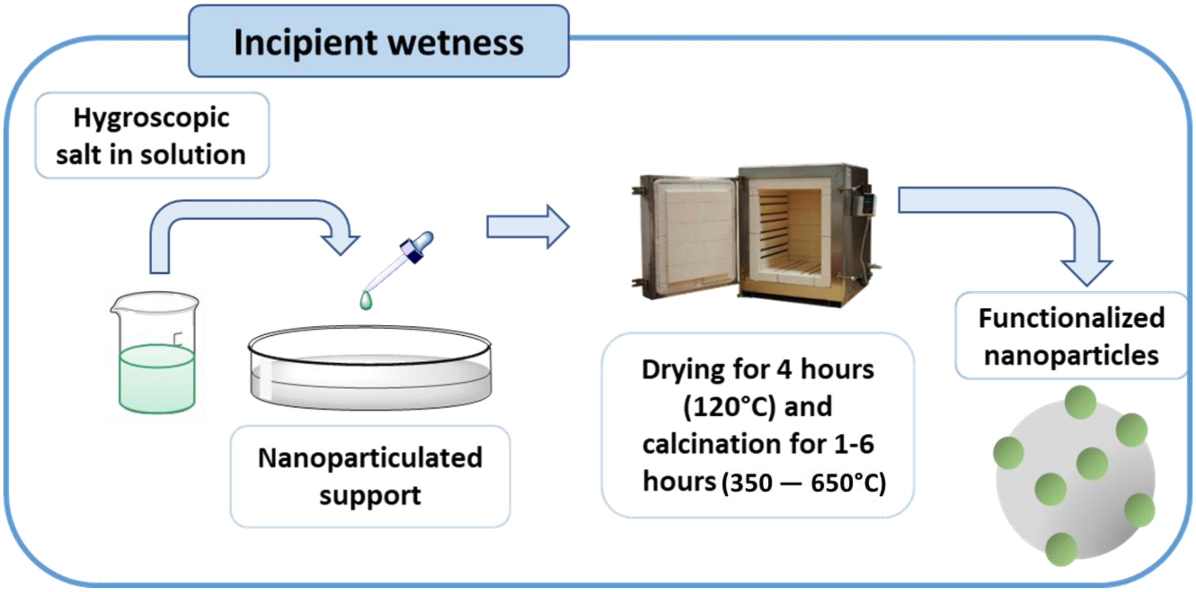

Figure 3.6. Schematization of the methodology for the nanoparticle functionalization through the incipient wetness technique.

3.3.2. Phenomenological Approaches to Asphaltene–Nanoparticle Interactions

3.3.2.1. Behavior of the Crude Oil Fractions in Terms of Their Interaction with Nanoparticles

It should be noticed that asphaltenes are a group of molecules rather than a sole compound even in the same crude oil sample (BENNION, 2002; MULLINS, 2011). In this sense, it has been considered that those differences in the chemical structure of the asphaltenes produce a distinct behavior in terms of solubility for each molecule due to a different polarity (ACEVEDO, 2009). Therefore, several studies have classified the asphaltenes into two groups depending on their solubility and thus their polarity: A1 and A2, with the former being the most polar group. In this regard, it has been identified that A1 has a typical solubility of 90 mg/L in toluene, while A2 has a much higher solubility of up to 5–12% (ACEVEDO, 2010). The difference in the solubility has been attributed to different factors such as higher aromaticity for the A1, i.e., a larger polyaromatic core and/or a higher aromatic rings/alkyl groups ratio, whereas the A2 fraction has a larger amount of alkyl substituents, which facilitates its stabilization in aromatic solvents (ACEVEDO et al., 2009). Consequently, the A2 fraction has a great similarity with resins in terms of chemical structure and role in asphaltene aggregation (ACEVEDO, 2018).

A generic representation of both fractions is presented in Figure 3.8. M1 (A1 fraction) has a larger number of aromatic rings, while M2 (A2 fraction) has an additional alkyl substituent (ACEVEDO, 2018). The higher aromaticity of the A1 fraction hinders its solubility. This lack of solubility facilitates the interaction between A1 species through acid–base and H-bonding mechanisms because of their high polarity. This behavior leads to the formation of nuclei and further small aggregates with which the A2 species start to interact, mainly by π–π stacking positioned on the aggregate borders (ACEVEDO, 2009; ACEVEDO, 2018). Then, the aggregate formation is slowed down until the interaction with resins, which leads to the final formation of the supramolecular assembly and stabilization in the oil matrix (ACEVEDO, GUZMAN, OCANTO, 2010).

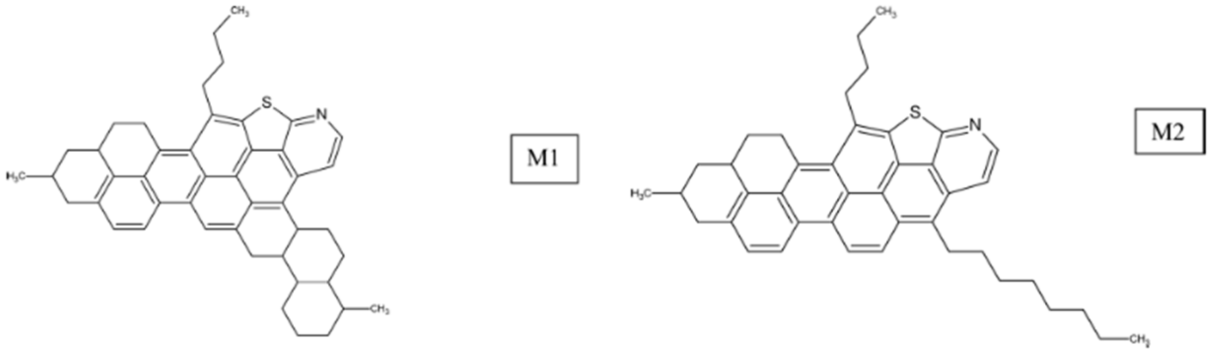

Figure 3.7. Representation of chemical structures for the fractions A1 (M1) and A2 (M2) of asphaltenes. Original figure from (ACEVEDO, 2018), reprinted with permission. Copyright (2020) American Chemical Society.

It is worth mentioning that the shapes of the nanoaggregates are continuously changing (size, molecule arrangement) as the nanoaggregates are susceptible to shearing forces, such as those exerted by the fluids in the porous medium and in the production systems, and to environmental conditions (pressure and temperature) (NASSAR et al., 2015; TORKAMAN, BAHRAMI, DEHGHANI, 2018; RAHMANI, MASLIYAH, DABROS, 2003). However, before the addition of the nanoparticles, the crude oil microstructure is defined as being at equilibrium for at least an interval of time. In this way, the nanoparticles interact with the asphaltenes as their addition disrupts the equilibrium of the crude oil microstructure (NASSAR et al., 2015).

The asphaltene–nanoparticle interactions are guided by the same asphaltene aggregation mechanisms; nonetheless, the asphaltenes' attractive forces towards the surface of the nanoparticles are greater than the asphaltene–asphaltene ones (MONTES et al., 2019). This is explained by two principles: (I) the presence of active sites on the surface of the nanoparticles, where those active sites are generally chemical species with a high dipole moment (MONTES et al., 2019), and (II) the low amount of surface-active groups in the asphaltene structure compared to the surface of the nanoparticulated sorbents (ADAMS, 2014)]. Hence, when the nanoparticles are added to the crude oil, their inclusion leads to a perturbation in the microstructure equilibrium (MONTES et al., 2019; MONTES, 2020). In this regard, several studies have proven that the mentioned disruption is intrinsically fomented by an unconstrained difference in potential (NASSAR, HASSAN, PEREIRA-ALMAO, 2011; NASSAR, HASSAN, PEREIRA-ALMAO, 2011; HASSAN, PEREIRA-

ALMAO, 2011). Thereby, the asphaltene adsorption on the surface of the nanoparticles is spontaneous, and in general, it is exothermic (FRANCO et al., 2013; MEDINA et al., 2019). As with the asphaltene aggregation where nuclei are formed by the most polar species, the asphaltene–nanoparticle interaction is firstly driven by the A1 fraction (ACEVEDO et al., 2018; ACEVEDO et al., 1995). Hence, the A1 fraction interacts with and adsorbs on the adsorbent surface until its active sites are inaccessible either due to being saturated or due to steric effects (ACEVEDO et al., 2018). At this point, it is considered that the adsorbed asphaltenes have formed a monolayer on the nanomaterial's surface (BETANCUR et al., 2016; BETANCUR, FRANCO, CORTÉS, 2016). Moreover, the adsorbed asphaltenes can interact with the free asphaltenes in the crude oil depending on the same steric effects mentioned before; that is, the asphaltenes aggregating on the nanoparticle's surface is the reason why the asphaltene adsorption is ensembled in a multilayer (GUZMÁN et al., 2016). This multilayer is composed mainly of the A2 fraction due to its higher availability compared to the A1. Thus, the interaction between the asphaltenes in the monolayer and the free asphaltenes is driven by π–π stacking (ACEVEDO et al., 2018; ADAMS, 2014). A representation of this phenomenon is shown below (Figure 3.9). It must be clarified that there are different types of active sites that depend on the chemical nature of the nanoparticles, while their availability depends on the synthesis method and on the textural properties of the nanomaterial (roughness, surface area, size) (MONTES et al., 2020; ADAMS, 2014).

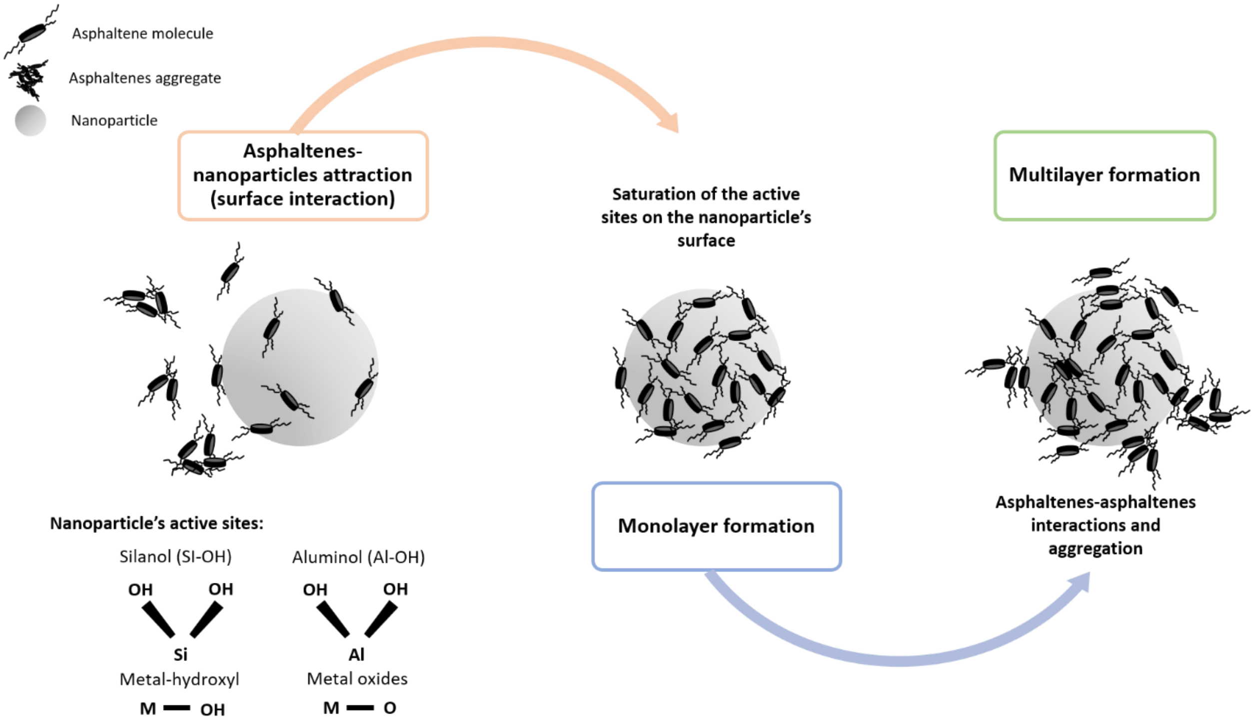

Figure 3.8. Generic representation of the adsorption phenomena of asphaltenes on a nanoparticle's surface.

Even though the resins play a major role in the formation and stabilization of the aggregate by surrounding the A1–A2 assembly, it has been demonstrated that their interaction with the surface of the nanoparticles is almost negligible, and thus, a similar trend is observed for the adsorption (FRANCO et al., 2015), and this is explained by the resins' dipole moment. As for the A2 fraction, the resins have a minor dipole moment compared to the A1 molecules due to their chemical structure which includes a larger amount of alkyl substituents. In this way, the small fraction of resins adsorbed onto nanoparticles could be considered as part of the multilayer assembly alongside the A2 fraction (MEDINA et al., 2019).

3.3.2.2. Adsorption Isotherms: Construction and Modeling

Several methodologies have been proposed to experimentally evaluate the asphaltene adsorption over the nanoparticle surface. Among these techniques are the thermogravimetric decomposition of the adsorbed fraction and colorimetry through UV–visible spectrophotometry (NASSAR et al., 2012; NASSAR et al., 2011; FRANCO et al., 2015; NASSAR, 2010; NASSAR et al., 2013). The most used method is spectrophotometry which includes the development of batch adsorption tests in which model solutions of asphaltenes in toluene are generated from a stock solution (typically of 5000 mg/L). Then, the nanoparticles are added to the different model solutions and further stirred and centrifuged. The adsorbed asphaltenes and the nanoparticulated nanomaterial are deposited, while a supernatant with the free asphaltenes is obtained. It is worth mentioning that the model solutions could be made while varying the asphaltene or adsorbent concentration, and that this differentiated procedure affects the adsorption phenomena. The amount of asphaltenes adsorbed relative to the mass of nanoparticles Q_{ads} (mg/g) is then estimated using the following mass balance (Equation 3.1):

$$Q_{ads} = \frac{(C_i - C_E)}{M} \qquad \text{(Equation 3.1)}$$

Where C_i (mg·L^{-1}) and C_E (mg·L^{-1}) are the initial concentration of asphaltenes in solution and the equilibrium concentration of asphaltenes (i.e., the asphaltene concentration in the obtained supernatant at the time t (min)), respectively, and M (g·L^{-1}) is the mass ratio of the nanoparticles and solution volume.

The adsorption isotherms can exhibit different shapes, with types I and III according to the IUPAC classification being common (THOMMES et al., 2015). These distinct behaviors are mainly related to the availability of active sites on the nanoparticles and also to the amount of A1 asphaltenes that form the monolayer on the nanoparticle surface. In this way, the type I isotherm is observed when the asphaltene concentration is varied in the model solutions, while type III is exhibited when the nanoparticle concentration is varied (GUZMÁN et al., 2016).

To describe an adsorptive process, different models have been developed, involving either (I) a phenomenological approach to the adsorbate–adsorbent interactions or (II) a mere fitting of the experimental data. Different authors have attempted to describe the phenomena related to the asphaltene adsorption on the nanoparticles using the well-known Langmuir and Freundlich models (NASSAR et al., 2012: NASSAR, HASSAN, PEREIRA-ALMAO, 2011). A more specific asphaltene adsorption model was developed by Montoya et al. in 2014 and named the solid–liquid equilibrium (SLE) model; it accounts for the asphaltene–nanoparticle interactions and the assembly of asphaltenes onto the nanoparticle surface in the form of the mentioned monolayer–multilayer phenomena. The model is described by the following equations (Equations 3.2, 3.3, 3.4):

$$C_E = \frac{\psi H}{1 + K\psi} exp\left(\frac{\psi}{q_m \cdot A}\right)$$ (Equation 3.2)

$$\psi = \left(-1 + \sqrt{1 + 4K \cdot \xi}\right)$$ (Equation 3.3)

$$\xi = \left[q_m \cdot q / \left(q_m - q\right)\right] A$$ (Equation 3.4)

where C_E (mg·g^{-1}) is the equilibrium concentration of the adsorbate in the solution; q (mg·m^{-2}) and q_m (mg·m^{-2}) are the adsorbed amount and the maximum adsorption capacity, respectively; A (m^2·mg^{-1}) is the surface area measured through the BET method. K (g·g^{-1}) is a constant related to the self-assembly of the asphaltenes on the surface of the nanoparticle, and H (mg·g^{-1}) is the Henry constant related to the nanoparticle–asphaltene affinity. Thus, the SLE model can predict the adsorption behavior in terms of the asphaltene–nanoparticle interactions.

An example of the above is shown in Figure 3.10. For this case, two different methodologies are used for constructing adsorption isotherms: (I) the use of the experimental data of the adsorption with a fixed mass of asphaltenes (adsorbate), which is represented by the black symbols, and (II) the use of variation in the adsorbent concentration compared to the model solutions, which is represented by the white symbols. Moreover, the M letter for the black symbols represents the nanoparticle dosage that was utilized for obtaining the supernatants. On the other hand, the Ci is the asphaltene concentration in the model solution when varying the nanomaterial.

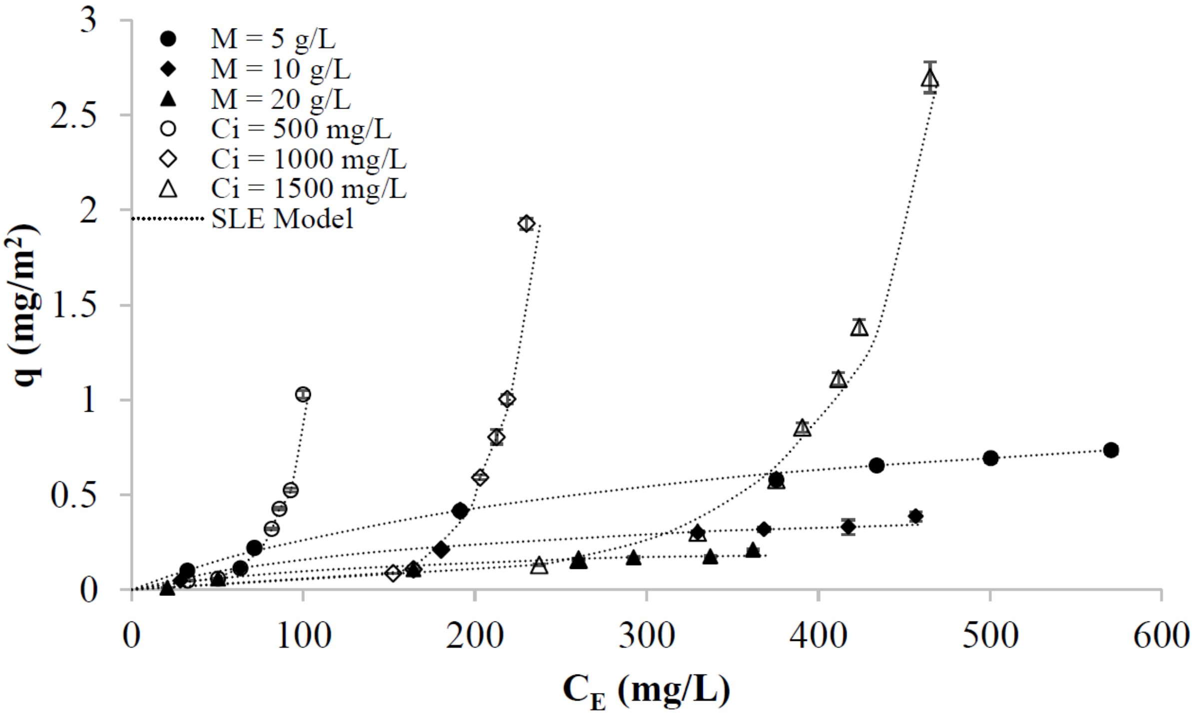

Figure 3.9. Adsorption isotherms for asphaltenes in the presence of silica nanoparticles: Symbols in white correspond to the experimentation with a fixed mass of asphaltenes (adsorbate), while the symbols in black represent the experimentation with a fixed mass of nanoparticles (adsorbent). The continuous lines correspond to the fitting of the SLE model. Original figure from (GUZMÁN et al., 2016), reprinted with permission. Copyright (2020) American Chemical Society.

It would be expected that with an increase in the amount of the nanoparticles, the asphaltene adsorption would be enhanced; however, the contrary was obtained for both isotherm construction methods. For method 1, it was observed that by increasing the number of nanoparticles, both the affinity (slope at low adsorbed amount) and the total amount of adsorbed asphaltenes are reduced. Moreover, even though method 2 exhibits a lower affinity towards asphaltene adsorption, the adsorbed amount of asphaltenes is higher than that in method 1 for several C_E values, and the increase in nanoparticle concentration leads to lower adsorption. Both phenomena are derived from the asphaltene aggregation behavior. However, with a higher adsorbent availability, there would be larger spaces for the interaction of asphaltenes with the A1 fraction of the asphaltenes which forms the monolayer and has a limited amount on the crude oil compared to other compounds (ACEVEDO et al., 2018). Thus, a larger number of nanoparticles would allow the adsorption of individual and separated molecules, rather than the formation of a monolayer which plays a major role in the attraction of the A2 fraction for its assembly in a multilayer ensemble. Moreover, with an increase in the adsorbent concentration, the nanoparticle–nanoparticle interactions are also promoted, and their aggregation would decrease the active site availability for asphaltene adsorption (GUZMÁN et al., 2016; BP, 2022; LYU, LINGJIA, 2023; MOSER, 2001; OCHOA et al., 2016; DHULDHOYA and DUSTERHOFT, 2017; RODRIGUEZ, 2020; KUUSKRAA, STEVENS, MOODHE, 2013; MORENO-ENRIQUEZ, 2022; FORERO, 2021; ISAAC, 2022).

Hence, the asphaltene aggregation behavior plays a major role in the adsorption phenomena over the nanoparticles, as the asphaltene–nanoparticle interactions and affinity plays a major role just in the monolayer formation (KOOTS and SPEIGHT, 1975; REZAKAZEMI et al., 2017; NASSAR et al., 2015; KAZEMZADEH et al., 2015), while further adsorbed molecules depend on the self-assembly of asphaltenes (NASSAR, HASSAN, PEREIRA-ALMAO, 2011; NASSAR et al., 2012; NASSAR, HASSAN, PEREIRA-ALMAO, 2011; NASSAR, 2010). In this sense, planning a stimulation process including nanoparticles for inhibition of asphaltene precipitation/deposition requires rigorous experimentation in order to select the best material in terms of chemical nature and concentrations (GUPTA et al., 2021; ASLANNEZHAD et al., 2021; WANG, CHEN, 2019; LIU et al., 2021).

3.3.3. Inhibition of Asphaltene Precipitation/Deposition: Upscaling through Coreflooding Tests and Field Trial Application

Following the advances in the asphaltene precipitation/deposition inhibition technique using nanoparticles (REZAKAZEMI et al., 2017; AL-JABARI, NASSAR, HUSEIN, 2007; LU et al., 2016; AMIN & SOLAIMANY, 2016; MEDINA et al., 2019), different upscaling processes have been carried out through coreflooding tests, and real field tests have been developed in which superb results have been achieved.

Betancur et al. in 2016 evaluated different silica nanoparticles for the asphaltene adsorption and disaggregation and synthesized a nanofluid with the best nanomaterial to determine the injectivity enhancement through coreflooding tests after inducing asphaltene-associated formation damage. The authors determined that the improved flow conditions for the nanofluid injection would generate an additional recovery factor of 11%. Similar tests were carried out by Franco et al. in 2013 with nanoparticulated alumina functionalized with nickel oxide. The authors obtained a great increase in crude oil mobility as the S_{wr} (residual water saturation) increased by 23% upon nanoparticle injection. The formation damage remotion also caused an increase in the recovery factor of 9%.

It is also well known that several recovery methods such as CO_2 could affect asphaltene stability in crude oil (ZANGANEH et al., 2019). In this regard, Hashemi et al. evaluated the effect of NiO nanoparticles in the removal of asphaltenes from a carbonate porous medium under CO_2 injection (HASHEMI et al., 2016). In this case, the authors observed that the remaining asphaltene concentration in the core was reduced by 88%. Azizkhani et al. also evaluated the effect of nanoparticles as asphaltene inhibitors during CO_2 injection processes (AZIZKHANI & GANDOMKAR, 2020). For the experiments, the authors employed Fe_3O_4 and Al_2O_3 nanoparticles, finding a lower degree of asphaltene aggregation when using the latter. The asphaltene precipitation was reduced by approximately 83% (HASHEMI et al., 2016; YEKEEN et al, 2019).

Accounting for the mentioned advances in the nanoparticle-based treatments for the inhibition of asphaltene precipitation, an approximation towards technique massification was carried out by applying an Al_2O_3-based nanofluid for the inhibition of asphaltene-associated damage in the Cupiagua Sur field (ZABALA et al., 2014). After the nanofluid injection, daily production monitoring was carried out (Figure 3.11), where it was observed that the process not only promoted formation damage removal, but also encouraged reserve incorporation by affecting the production curve declination. The treatment had a perdurability of more than 1 year, and an increment of 150,000 bbl in the cumulative oil production was observed during the first 8 months after the intervention.

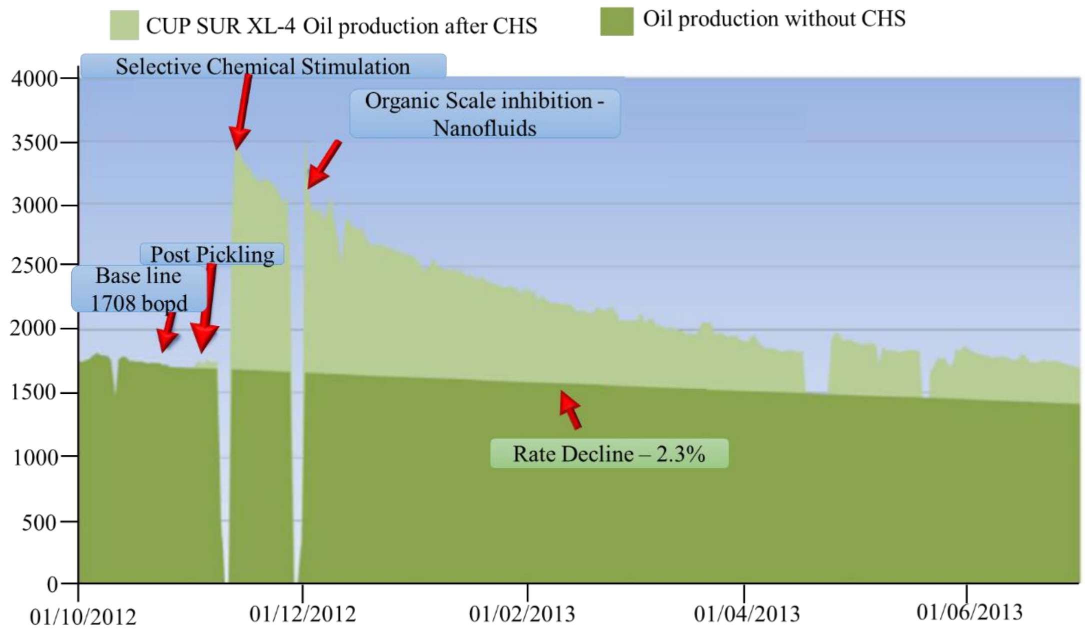

Figure 3.10. Incremental production during the application of alumina-based nanofluids for the inhibition of formation damage related to the precipitation/deposition of asphaltenes. Original figure reported by Zabala et al. in 2014.

3.4. Outlook and New Technologies

As explored extensively in this article, asphaltenes are complex organic compounds found in crude oil that can form insoluble aggregates and cause production problems, such as clogging reservoir pores, reducing reservoir permeability, and decreasing oil flow. The hydrocarbon industry urgently needs to control this class of compounds. Therefore, the four nanotechnology solutions presented are considered new trends for asphaltene control: dispersed nanoparticles, nanosensors, nanostructured coatings, and nanostructured systems for solvent release control (See Figure 3.12). The characteristics of each of these technologies are explained below.

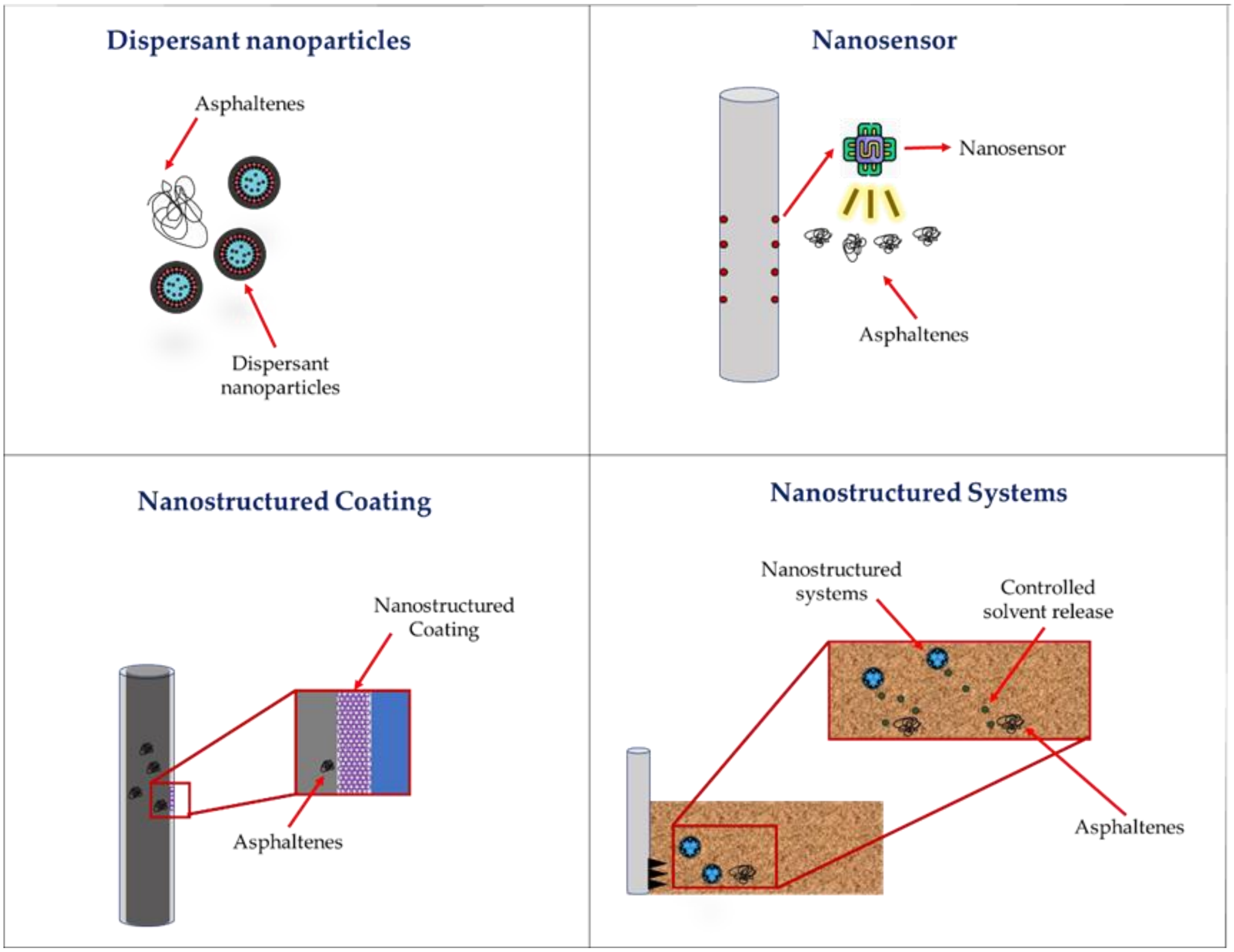

Figure 3.11. New trends for asphaltene control: dispersed nanoparticles, nanosensors, nanostructured coatings, and nanostructured systems for solvent release control.

Dispersant nanoparticles*:* Nanoparticles are being developed to disperse asphaltene aggregates and prevent their precipitation. These nanoparticles can be chemically modified to selectively interact with asphaltenes and prevent their deposition on pipelines and production equipment. These nanoparticles are designed to have nanometer-sized dimensions and are intended to interact with asphaltenes, inhibiting their aggregation and deposition. They can be synthesized using various techniques, and their performance is based on specific surface and chemical properties (ALEMI et al., 2021; ENAYAT et al., 2021).

For the optimal production of these nanoparticles, metal oxides such as silica (SiO_2) and titanium oxide (TiO_2) or metal nanoparticles such as gold (Au) and silver (Ag) are utilized. Subsequently, synthesis techniques such as chemical precipitation, thermal decomposition, chemical reduction, or vapor phase synthesis are employed. Each method has advantages and is selected based on the material and desired nanoparticle characteristics. After the synthesis of the nanoparticles, surface modification can be performed to enhance their affinity and selectivity towards asphaltenes. This involves introducing specific functional groups onto the nanoparticle surface, enabling chemical interactions with the asphaltenes (NGOUANGNA et al., 2022; SAN JUAN-NAVARRO, 2002).

The performance of dispersant nanoparticles is attributed to various active correlations, particularly the electrostatic interaction between the nanoparticles and asphaltenes through different mechanisms. One possibility is through electrostatic interaction, where the charged nanoparticles attract and disperse oppositely charged asphaltene aggregates. Another mechanism is steric interaction, where the nanoparticles adsorb onto the surface of the asphaltenes, preventing their aggregation and deposition. Additionally, the stabilization of dispersant nanoparticles involves controlling the surface charge of the nanoparticles, selecting appropriate functional groups, and optimizing dispersion conditions. These factors contribute to enhancing the dispersing properties and effectiveness of the nanoparticles (KHIDHIR, SIDIQ., 2022; NEGI, SINGH, 2023).

On the other hand, nanosensors offer the potential for real-time monitoring of asphaltene concentration. These devices provide accurate information about the presence and quantity of asphaltenes in crude oil, enabling proactive measures to be taken before production issues arise. Nanosensors are nanostructured devices with dimensions on the nanometer scale (1 nanometer = 10^{-9} m). They can be constructed using various structures such as nanowires, functionalized nanoparticles, carbon nanotubes, or quantum dots. These sensors are designed with selective receptors that exhibit an affinity for asphaltenes. These receptors can be specific molecules or functional groups that interact with asphaltenes, producing a detectable signal for quantification and analysis (SIRCAR et el., 2022; KÜÇÜK, KÜÇÜK, TEMIZEL, 2021).

In line with the above, the interaction with asphaltenes occurs as follows: When nanosensors come into contact with asphaltenes present in crude oil, a specific interaction takes place between the receptors of the nanosensor and the asphaltenes. This interaction can be of a chemical, electrical, or magnetic nature, depending on the design of the nanosensor. Initially, the nanosensor generates a signal. The interaction between the nanosensor and the asphaltenes leads to a change in the physical or chemical properties of the nanosensor, resulting in the generation of a detectable signal. This signal can be electrical, optical, or magnetic and is utilized for quantifying the concentration of asphaltenes (SANDEEP, JAIN, AGRAWAL, 2020; UNAL, SADAK, USLU, 2023).

Subsequently, the signal generated by the nanosensor is detected and analyzed using specific techniques such as atomic force microscopy, fluorescence spectroscopy, magnetic resonance spectroscopy, or electrochemical techniques. These techniques enable the measurement and quantification of the signal generated by the nanosensor, providing information about the presence and concentration of asphaltenes in real time. Finally, nanosensors can be integrated into online monitoring systems, facilitating continuous tracking of asphaltenes during oil production. The data collected by the nanosensors are utilized for making operational decisions and implementing preventive strategies, such as the addition of dispersants or the implementation of cleanup and maintenance measures (DAVOODI et al, 2014; MEHRA et al., 2023).

Among other emerging technologies, nanostructured coatings are applied to the internal surfaces of production equipment to mitigate the adhesion and accumulation of asphaltenes. These coatings possess unique surface properties that impede the adhesion of asphaltenes and facilitate their removal during maintenance operations. Various materials can be utilized for these coatings, including polymers, ceramics, metal oxides, and nanocomposites. These materials are designed to have a nanoscale structure, which can consist of nanometer-thin layers, embedded nanoparticles, or porous structures. These nanostructural features enhance the effectiveness of the coatings in preventing the adhesion and build-up of asphaltenes (SCHULER et al., 2020; HOSSEINI-DASTGERDI, 2019).

It is important to note that nanostructured coatings exhibit unique surface properties, including low surface energy, hydrophobicity or hydrophilicity, and non-stick characteristics. These properties effectively hinder the adhesion of asphaltenes to the coated surfaces and facilitate their subsequent removal. Nanostructured coatings prevent asphaltene adhesion by creating a physical or chemical barrier on the surface. These barriers prevent direct contact between the asphaltenes and the substrate, thereby reducing their ability to adhere and form deposits. Moreover, they aid in the easy removal of asphaltenes during maintenance activities. The special surface properties of these coatings enable easier dislodging or dissolution of the asphaltenes, minimizing the need for extensive mechanical or chemical cleaning procedures. Additionally, these coatings are designed to be durable and stable under the harsh conditions of oil production, withstanding corrosive fluids, high pressures, and elevated temperatures commonly encountered in production systems (SATDIVE et al., 2023; SFAMENI et al., 2022; ABDRABOU et al., 2022; LAHJIRI et al., 2023; TAZIKEH et al., 2022).

Finally, the controlled solvent release is another area of investigation in the field of nanotechnology for asphaltene control. Nanostructured systems are being developed that can release specific solvents at the appropriate time and location to effectively dissolve asphaltenes. This approach aims to prevent the formation of asphaltene deposits and maintain the permeability of reservoirs and production systems (TANG, WANG, 2022; DE S ARAUJO et al., 2022).

These nanostructured systems can take various forms, such as nanoparticles, nanocapsules, or nanostructured matrices. They are designed to contain a specific solvent with the ability to effectively dissolve asphaltenes. The selection of the solvent depends on the chemical composition of the asphaltenes and the solvent's properties of interaction with them (MESHKAT, HOSSEINI-DASTGERDI, PAKNIYA, 2023; LIU, 2023).

These systems can release solvents in different ways. For instance, they may undergo controlled breakdown of the nanostructures, allowing the solvent to be released gradually. Alternatively, they can release solvents through pores in the nanostructured systems or respond to external stimuli, such as changes in pH, temperature, or concentration. The design ensures that solvents are released at the right place and time (GUERRERO-MARTIN, MONTES-PAEZ, LUCAS, 2019; RAZMAN SHAH et al., 2023).

For example, these systems can be employed in oil wells to dissolve asphaltenes present in reservoirs, or in production and refining equipment to prevent the formation of deposits. By delivering solvents directly to the problematic areas, these nanostructured systems offer targeted and efficient asphaltene control (GUERRERO-MARTIN, MONTES-PAEZ, LUCAS, 2019; RAZMAN SHAH et al., 2023; LONG et al., 2022).

3.5. Final Considerations

Asphaltene precipitation is widely studied in the oil industry. Nonetheless, its prediction and control are still challenging. From the experiences acquired observing the fluid in porous media and production lines, it can be concluded that the influence of pressure is the most important factor for precipitation and deposition of the asphalt fraction. However, recent studies show that studying the effect of pressure on asphaltene destabilization by experimental means is challenging, mainly because it requires more time and larger sample amounts. On the other hand, non-pressure tests are relatively simple, although less representative. Whereas several techniques have improved the asphaltene precipitation prediction under pressurized conditions, most of them lack in coupling this sensitivity improvement to other variables.

Although the uncertainty in the prediction of the behavior of asphaltenes hinders their control, several techniques have emerged that provide more technical and economical alternatives for avoiding the problems related to their precipitation/deposition. Nanotechnology is presented in the petroleum industry as one of these novel alternatives for improving existing production mechanisms including the formation damage process associated with asphaltene destabilization. Due to the characteristics of these heavy fractions such as their high dipole moment, nanoparticulated systems can capture them through an adsorption phenomenon. The asphaltene adsorption principle has been widely exploited for inhibiting asphaltene precipitation in processes such as primary and secondary recovery as well as in CO_2 injection and deasphalting scenarios.

Nanoparticles have also been tested in real field conditions in which their application reliability was validated through parameters associated with well productivity enhancement such as skin decrease via formation damage inhibition, recovery increment, and production declination diminishing.

As recommendations for future research, we consider it appropriate to orient future research in nanotechnology for the control of asphaltenes on four fundamental axes: intelligent and responsive nanoparticles, self-assembling nanoparticles, nanoparticles with self-healing capacity, and nanoparticles with detection and monitoring capacity. The first group should be based on the study of multifunctional properties that combine different mechanisms of action for the control of asphaltenes. For example, nanoparticles could be developed that act as dispersants and as solvent-controlled release agents to dissolve asphaltenes.

Similarly, smart and responsive nanoparticles would respond to changes in pH, temperature, or asphaltene concentration. These nanoparticles could be activated under specific conditions to release solvents, dispersants, or other agents that control the formation of asphaltene deposits. In turn, self-assembling nanoparticles whose structures are ordered in the presence of asphaltenes could have specific surface properties to prevent the adhesion of asphaltenes and facilitate their removal.

Finally, nanoparticles with sensing and monitoring capabilities could act as sensors to measure asphaltene concentration and provide valuable information for operational decision making.

4. Nanotechnology applied to the inhibition and remediation of formation damage by fines migration and deposition: A comprehensive Review

Abstract

Formation damage is a problem that occurs in several scenarios where the permeability and productivity of a reservoir can be negatively affected, bringing incalculable economic consequences, innumerable operational problems and, last but not least, irremediable results in the productive life of the well. Fines are mobile particles of the porous medium that are easily detached from the pore cavities causing problems related to permeability reduction in the reservoir generating formation damage. Several mechanisms influence this phenomenon such as the zeta potential of the fines, electrostatic forces, pH, salinity, which are difficult to avoid during production operations. Hence, conventional remediation and inhibition lacks effectiveness to control fines migration/deposition. Nanotechnology has been widely implemented for different applications in the oil and gas industry including fines migration control. Nanoparticles/nanofluids inhibit the fines migration through different mechanisms, being the alteration of the electrostatic charges in the surface of the rock and fines amongst the most important. The present literature review presents an overview on the phenomena underlying the fines migration/deposition and considers the application of nanotechnology for inhibiting this type of formation damage. In this regard, nanoparticles/nanofluids implementation and performance is addressed from a basic phenomenological understanding up to its evaluation at experimental scale accounting for the different processes at which the nanomaterials usage is intended, namely improved oil recovery (IOR), low salinity water (LSW) injection, and hydraulic fracturing.

Keywords

Fines migration/deposition; formation damage; formation damage remediation/inhibition; nanoparticles; nanotechnology; zeta potential.

4.1. Introduction.

Formation Damage as a result of different phases and procedures of oil and gas recovery, brings with it undesirable and incalculable operational and economic problems, among the mechanisms and types of operation are drilling, production, hydraulic fracturing and workover (CIVAN 2015; YUAN, WOOD, 2018). Similarly, the decrease in a well productivity or injectivity due to the natural or induced decline in the permeability of the porous medium is known as, formation damage (BENNION, et al. 1995; BENNION 2002, YUAN and WOOD 2018). It has also been defined as “Any process that negatively compromises the inherent natural productivity of an oil or gas production formation, even leads to a decrease in the injection rate of a water or gas injection well” (BENNION 2002; KANG, XU et al. 2014).

There are several mechanisms associated with damage to the formation that negatively influence and generate problems in different fields and scenarios, for example, asphaltene precipitation and deposition, fines migration, condensate banking, inorganic scale and damage during hydraulic fracturing operations, among others. This is not to mention operational negligence, a very common factor, incalculable problems in economic terms (FRANCO, ZABALA, CORTES, 2017). Particularly, one of the most contributing mechanisms in terms of skin and damage to the formation is migration and subsequent deposition of fines, especially in reservoirs with low permeability and small pore size, where there is a greater chance that this phenomenon occurs (MANSOUR et al., 2020). Figure 4.1 schematizes the main mechanisms leading to formation damage, in which the fines migration is remarked as a mechanical-entrapment phenomenon (BENNION, 2002).

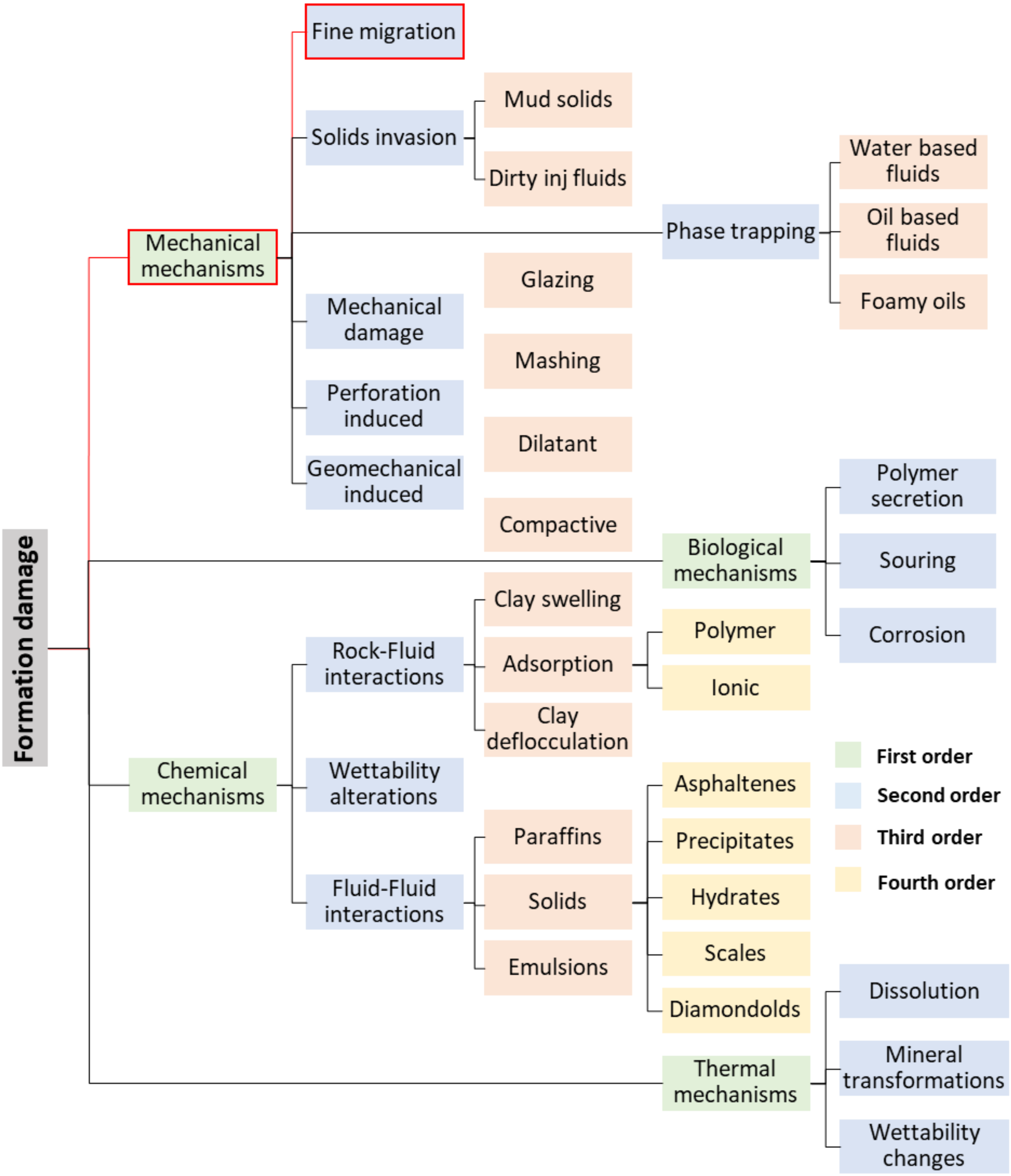

Figure 4.1. Common formation damage mechanisms. The red route indicates the main mechanism of concern for the present review. Adapted with permission of Bennion (2002).

The tiny loose or mobile particles of solid material, which are present in the porous medium of all sandstone deposits, are characterized as migrating fines (EL-MONIER AND NASR-EL-DIN 2011; HAN et al., 2015). These particles previously defined as fines, after a respective geological time, are incorporated into the formation during a deposition process, or are also introduced to the formation during different operations that intervene in a well such as drilling and completion (MUECKE 1979: KHILAR and FOGLER, 1998). One of the main players to formation damage and consequent decrease in the oil productivity is without a doubt, the migration and deposition of particles suspended in the porous medium. This catastrophic process is derived from the phenomenon of trapping and accumulation of migrating particles in some poral throats, which finally ends in the impairment of the permeability in the porous medium (SHARMA & YORTSOS 1986).

When faced with this great challenge, the oil and gas industry has developed different mechanisms to counteract the losses that this generates, therefore some remediation techniques such as matrix acidizing have been suggested to eliminate the fines clogging in the poral cavities of wellbore, the application of clay stabilizers (organic and inorganic) and the optimization of some well completion methods, among them a number of applications have been investigated (FRANCIS 1997; NGUYEN et al. 2005; ROUSSEAU, HADI, NABZAR, 2008, SAMENI et al. 2015). The conventional ways of dealing with the problems related to migration of fines are, for example, the reduction of production rates (this choice is not the preference of any company, until it is strictly necessary to do so); on the other hand, the increase of the flow area through high density perforating, practices such as open hole completions, horizontal wells or fracturing (to reduce interstitial velocity); Among others, also chemical processes such as the addition of stabilizers and thus achieve that the mobile clays adhere to the walls of the poral cavities to reduce their detachment and subsequent deposition (KHILAR, et al. 1990; LAKE, JOHNS et al. 2014). Proper use must be made of chemical stabilizers, which are commonly molecularly heavy polymers, to ensure that they do not cause damage due to physical adsorption problems (Smith and Hendrickson 1965, Fogler, Lund et al. 1976). To fight this problem, minimize formation damage, increase permeability of the zone immediately around the wellbore and improve oil and gas production, another remediation method called sandstone matrix acidizing has also been proposed (WILLIAMS, 1975).

Due to the limitations of the conventional methods for fines migration, nanotechnology emerges as solution for the inhibition of this type of formation damage. Nanofluids have been applied for different purposes in the oil and gas industry (POURAFSHARY, AZIMPOUR et al. 2009; FRIEDHEIM, YOUNG et al. 2012; LI, YUAN et al. 2013; CARPENTER 2016, LAU, YU et al. 2017), including but not limited to drilling (HOELSCHER, DE STEFANO et al. 2012; SHARMA, ZHANG et al. 2012; RAFATI, SMITH et al. 2018), improved oil recovery (IOR) (HUANG, EVANS ET AL. 2010; SRINIVASAN AND SHAH 2014; MONTES, CORTÉS ET AL. 2018; PINZÓN, 2018; MONTES, ET AL. 2019; MONTES et al. 2019; SERGEEV, TANIMOTO et al. 2020), enhanced oil recovery (EOR) (SHAMSIJAZEYI, MILLER et al. 2014, ZHANG, NIKOLOV et al. 2014, SUN, ZHANG et al. 2017, ZHE and YUXIU 2018, LIU, QIU et al. 2020), and in field trials with excellent results (PATEL, SHAH et al. 2018; FRANCO, CANDELA et al. 2020; FRANCO, GIRALDO et al. 2020; MONTES; 2020). Nanofluids are typically made up of particularly small additives, ranging from 1 to 100 nanometers (NETTESHEIM, LIBERATORE et al. 2008; HOBBULOVICH, GUBKIN et al. 2013; MERA, ARIZA et al. 2013; CORTÉS, MONTOYA et al. 2016). Based on the number of nanosized additives in the fluid, these fluids can be classified as simple nanofluid and advanced nanofluid (AMANULLAH AND AL-TAHINI 2009; HOBBULOVICH, GUBKIN et al. 2013; FRANCO-AGUIRRE et al. 2018). After mentioning these dimensional effects, compared to conventional micro and macro scale materials currently applied in a wide variety of processes, materials and operations in the oil and gas industry; Nanomaterials have the particularity and authenticity in mechanical, chemical, thermal and magnetic properties, which leads them to have a superior performance, a higher effectivity and above all a greater acceptance in the industry (FRANCO et al. 2013; FRANCO, CORTÉS et al. 2014; FRANCO, NASSAR et al. 2015, CHERAGHIAN and HENDRANINGRAT 2016; FRANCO, LOZANO et al. 2016).

In different scenarios and special conditions, the performance of nanomaterials is improved with the use of a specific coating film, with this it is achieved that the performance is considerably improved in terms of its adsorption capacity and light emission, its high mechanical resistance, its excellent magnetism, its catalytic properties and its high thermal and electrical conductivity (CHENG, RODAK et al. 2006; DU TOIT, PILLAY et al. 2010, BENNETZEN and MOGENSEN 2014, FRANCO, MONTOYA et al. 2014, CERQUEIRA, PINHEIRO et al. 2017, DASGUPTA, RANJAN et al. 2017, DE MATTEIS, CANNAVALE et al. 2017, DUNCAN and SINGH 2017). This technology also faces challenges such as self-assembly and agglomeration that compromise its stability in a liquid medium and its mobility in the porous medium leading to blockage (MADADIZADEH, SADEGHEIN et al. 2020). However, these difficulties can be mitigated with the addition of viscosifiers, the pH control of the continuous medium and the surface treatment of nanoparticles to guarantee its stability (HE, XU et al. 2016; FAKOYA and SHAH 2017; ALSABA, AL DUSHAISHI et al. 2020). The development of this review accounts for the recent concern of nanoparticles implementation for the formation damage inhibition, particularly, for controlling fines migration/deposition (HUANG, CREWS et al. 2008; MERA, ARIZA et al. 2013; HABIBI, AHMADI et al. 2014; DÍEZ, MEDINA et al. 2020; ELERAKI, NOAH et al. 2020; GIRALDO, DIEZ et al. 2021). It is worth mentioning that the importance and the main objective of this Review is to relate the importance of the application of Nanotechnology as an alternative for optimization of conventional inhibition mechanisms to control formation damage by fines migration and deposition, through a bibliographic analysis, and thus be able to identify the areas of opportunity for improvement, as well as the efficiency of the applied nanoparticles. Thereby, the present review is divided in four sections: I) Mechanisms associated to formation damage by fines migration/deposition, II) conventional treatments for the mitigation of fines migration, III) types of nanomaterials and application for controlling fines migration, and IV) Conclusions and final remarks.

4.2. Mechanisms associated to formation damage by fines migration/deposition

4.2.1. Macroscopic mechanisms leading to formation damage

Any particle that is prone to mobility or is not consolidated or well cemented in the pore space, can be defined as formation fines (HABIBI, AHMADI et al. 2014). These fines are small enough to pass through a four hundred US mesh, and consequently through the poral throats, so they generate damage to the formation after detachment from the walls of the porous medium, which leads to the formation of bridging and plugging between the pores and finally ends in infiltration sedimentation (HUANG, CREWS et al. 2008; ELERAKI, NOAH et al. 2020). Due to their size that does not exceed 37 μm, their migration is facilitated with the flow of fluids in the sandstone reservoirs, causing future plugging of the pores and the imminent decline in permeability (HUANG, CREWS et al. 2008). The classification of these fines is determined by their charge, as clay or non-clay particles, and by their natural deposition or by whether they were introduced to the formation through unnatural processes or operations, such as drilling and completion (CÉSPEDES-CHÁVARRO 2015).

Although the fines are characterized between a range of 0.5 to 40 microns in diameter, they have not been defined chemically or physically, therefore there is no standard where migratory particles can be classified in a porous medium (SARKAR and SHARMA 1990). Sometimes it has been made the mistake of assuming that kaolinite is the only migratory clay or that quartz fines are more common than feldspar-based ones, due to the breadth in the range of mineralogy covered by the Fines, there is not space to generalizing (GRUESBECK and COLLINS 1982). Its chemical richness means that it is enough only with core evaluation to have conclusive results of its true nature. The first solutions for clay fines were the application of clay stabilizers, such as Inorganic Clay Stabilizers (KCl, NH_4Cl, NaCl, KOH, $Ca(OH)_2$), Cationic Inorganic Polymers (ALMUBARAK, ALDAJANI et al. 2015), Organic Clay Stabilizers (Cationic, anionic and nonionic organic Polymers) (DA SILVA, BERTOLINO et al. 2019). Even so, it was evidenced that clay fines are very frequent and do not react to clay stabilizers (ZHOU, GUNTER et al. 1995). Therefore, there must be a balance to stabilize the clay and non-clay fines effectively equal in the control treatments of fines to be an optimal treatment (EL-MONIER and NASR-EL-DIN 2011; EL-MONIER and Nasr-EL-DIN 2011). It is key to a better understanding of this phenomenon, to understand what minerals line are in the pore spaces of a reservoir rock, because generally the migration of fines occurs within the network of pores in sandstone formations (HIBBELER, GARCIA et al. 2003).

Poor acidification procedures and salinity changes in the porous medium can generate an ionic exchange that ends in the destruction of the natural cementation materials of the fines and leads to them detaching from the matrix sandstone and subsequently being mobilized in the medium (KALFAYAN and WATKINS 1990). When the previously detached particles migrate and move until they reach the poral throats, they generate a blockage since the size of this groove is less than the size of the individual particles, or it also happens when several fine particles upon reaching the poral throat are accumulate and compete to pass through the cavity, resulting in the formation of bridges and future sedimentation. Also, an aspect to consider is the wettability, changes in this property can trap the fines in place as they flow in the fluid that moistens them, generally water-wettable. (KALFAYAN and WATKINS 1990). The relationship that exists with plugging potential in the wellbore and completion processes is evident in terms of damage to the formation. The migration of fines can occur by physical or chemical means and is defined by 3 conditions. 1- It is necessary the existence of fines in the poral network of the rock. 2- The influence of a mechanism that causes the detachment of fines to the poral system. 3- There must be a capture mechanism that keeps the fines in the middle, such as bridges, ionic attractions and wettability (MUNGAN, 1965). In addition, another aspect to consider within the reservoir is the critical velocity, which is broadly defined by the maximum velocity of the fluid in the reservoir that can withstand the fines before they are detached from the pore walls (XIAO, WANG et al. 2017). Regarding the relationship between fine particle size and poral throat size, there is a principle called 1/3 to 1/7, which describes the contribution of particle size to bridging / blocking as follows: Particles greater than 1/3 the size of the pores is prone to general blockage of the pores. Particles that remain between 1/7 and 1/3 the size of the pores produce a bridge in the pore throat that generates a greater blockage, and Particulars less than 1/7 the size of the poral throat, can pass through the cavity (FRANCO et al. 2017). Although bridging occurs with particle sizes greater than or equal to 1/3 of the size of the pore throat, bridging is stable if the pore size is less than 2 times the size of the particle. The last relationship is schematized in Figure 4.2.

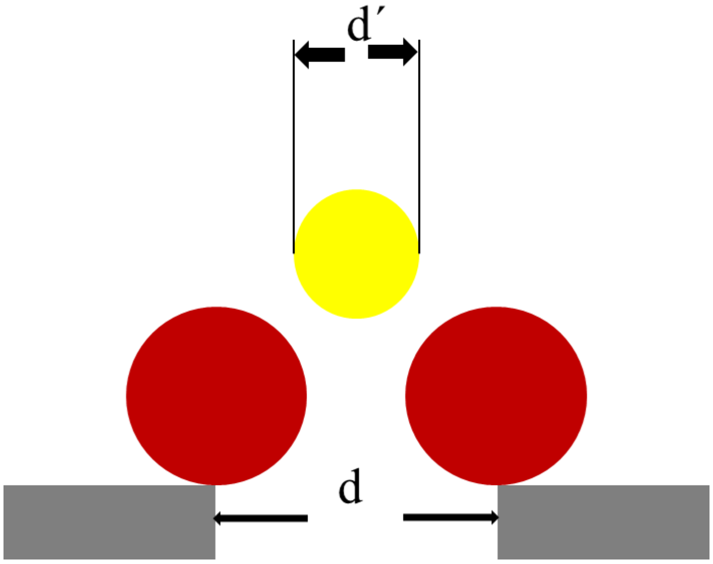

Figure 4.2. Bridging and plugging can be estimated to occur by two empirical relationships. Stable bridging: if pore diameter is < 2 times particle diameter. Bridging: if pore diameter is < 3 times particle diameter. Plugging: if the particle is between 1/3 and 1/7 the size of the pore diameter then it will plug. d is the diameter of the pore throat, d’ is the diameter of the bridging particle. Adapted with permission of Hibbeler, Garcia et al. (2003).

4.2.2. Role of the electrostatic interactions: effect of zeta potential on fines migration

As mentioned before, There are several factors such as changes in pH, wettability, accumulation of fine particles, flow rates, forces of ionic attraction and fractional flow of water and oil, which influence the migration of fines within the reservoir (DÍEZ, MEDINA et al. 2020), nonetheless, one of the most important parameters to account for is the zeta potential. The charge that develops at the interface of the boundary of hydrodynamic shear between solid surfaces as a product of electrostatic repulsion and the attractive forces related to the Van der Waals forces, is defined as Zeta Potential (GRUESBECK and COLLINS 1982), and the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory expresses the total interaction energy between surfaces. The summation of the double layer electrical repulsion (EDLR), the London-van der Waals attraction (LVA), the Born repulsion and the hydrodynamic interaction, defines all the electrostatic forces that interact in the fines migration mechanism (KHILAR, VAIDYA et al. 1990; CHOROM and RENGASAMY 1995; KAKADJIAN, ZAMORA et al. 2007).

Therefore, the zeta potential relates the surface charge of the particle to any absorbed layer at the interface, depending on the nature and composition of the porous medium (KAKADJIAN, ZAMORA et al. 2007). In other words, the previously mentioned factors such as salinity, pH changes and additive concentration, directly affect the Zeta potential. The characteristic values of the Zeta Potential are between -20 and 20mV, within this reading range it is concluded that the effective charge of the particles is so low that the repulsion between them is reduced to the point where flocculation, coagulation and aggregation can occur (VALDYA and FOGLER 1992; DELGADO. 2001). On the other hand, values lower or higher than the mentioned interval are typical of stable suspensions as particles with similar charges tend to have a higher repulsion and dispersibility (DELGADO; 2001). Therefore, a very important parameter to explain the surface charges, the adsorption of ions, how stable the suspended particles are, the electrostatic interactions between fines and the well walls, is the Zeta potential (LEROY, REVIL et al. 2008; TOURNASSAT, CHAPRON et al. 2009).

The DLVO theory was proposed by Derjaguin, Landau, Verwey and Overbeek and shows that the stability of the particles in solution is affected by the total energy of the interactions that influence when two particles are close to each other. The sum of the electrostatic energies that are included are DLR (Double Layer Repulsion), Born Repulsion, base and acid interaction, and hydrodynamic forces. Figure 4.3 schematically shows these forces in a diagram. Note the relationship that exists between the interaction energy of the particles with the repulsion forces involved, such as double-layer repulsion and Van der Waals forces, as a function of the separation distance of the molecules.

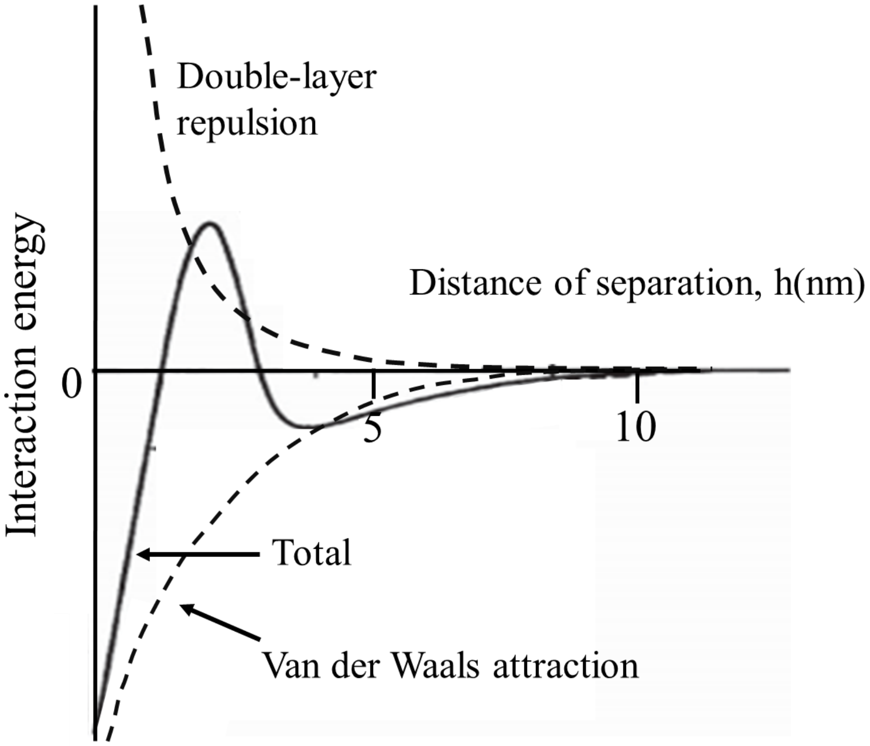

Figure 4.3. Energy of interactions vs. Distance of Separation. Adapted with permission of Ahmadi (KHILAR and FOGLER 1998, AHMADI, HABIBI et al. 2011).

As shown Figure 4 the decrease of the zeta potential when the shear of fines particles decreases. The positive charge of the particles in solution is the main reason why their Zeta potential is decreased. With that been said, the positive charge of the particles in solution reduces the negative surface charge of the fine particles and consequently the Zeta potential becomes more positive, which generates a reduction in the probability of separation of the fine particles from the poral walls thereby reduces their tendency to migrate and settle in the poral throats.

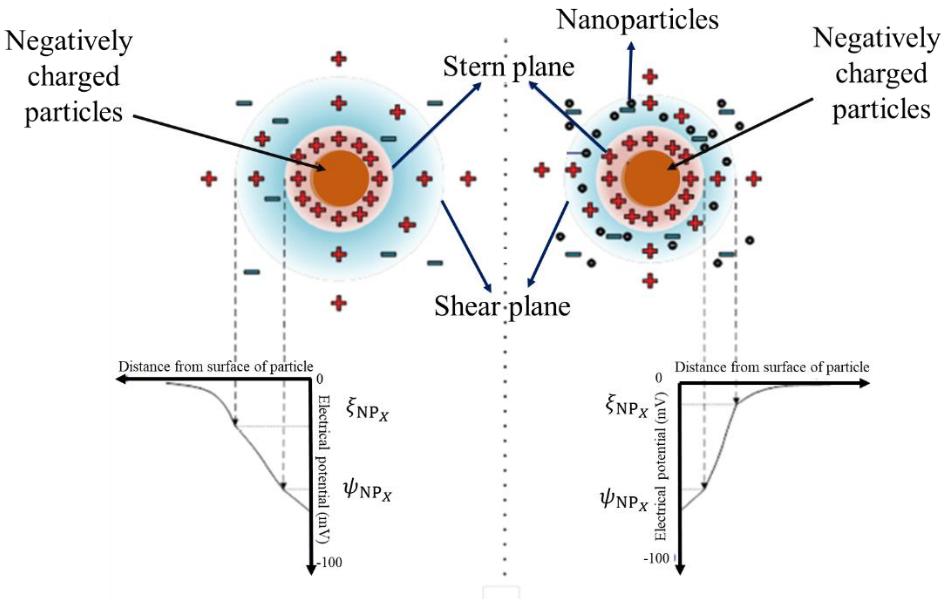

Figure 4.4. Schematic of nanoparticles' effect on the zeta potential and the double layer of fine size particles. Adapted with permission of Madadizadeh, Sadeghein et al. (2020).

The interaction of fines particles and colloidal suspensions depend on attractive forces due to satisfy lowering a potential energy as a result of confined charges and dipoles combined with one or two other forces that serve to push the particles apart, it is basically Van der Waals forces.

The relationship between Electrostatic forces and fines migration arise because of the repulsion originated from the fact that diffuse cloud of counter ions, and as a particles are closer together, the diffusion of the counter ions is limited just because the particles are getting closer together, and that electrostatic repulsion of the counter ions causes them to associate with the surfaces of the particles and the compression of the diffuse double layer causes the reduction in the entropy and therefore a repulsive force.

In General, fines have the same composition as the walls of the porous medium, essentially because they are made of the same material, and because of this, they have the same charges and repel each other, therefore the fines are not retained, and migration is generated after detachment. In relation to the phenomenon of formation damage, this migration and deposition of fines in the pore throats, caused by the repulsion generated by the theory of electrostatic forces that interacts between the fines and the walls of the pore medium, finally ends in the reduction of the effective permeability of the medium, due to the phenomenon previously explained where the size of the fines generates a plugging of the pore throats.

4.2.3 Evaluation of fines migration at experimental scale

4.2.2.1. Steady-state evaluation

By means of a synthetic model with glass beads and sphere shaped, it allows to analyze the behavior of the constants that influence the DLVO Theory mentioned previously, and that react to the purity of the components. That is, if a real rock is used, the composition of the medium should be known, along with all the parameters related to any component. This technique was chosen by several researchers as Wang, Li et al. (2008), Ben-Moshe, Dror et al. (2010), and Li, Sahle-Demessie et al. (2011). The simulation of the porous medium is done through the glass beads in the shape of a sphere, recreating sandstone reservoir rocks and to analyze the retention of fines in a porous medium saturated by water. The fine particles are coated with different types of treatment to study the effect that this coating has on the retention of fines. For each fluid, a specific amount of the particle to be used is mixed in distilled water for hours at 40 °C and then the additive is gradually added to the fluid over an additional hour to avoid agglomeration of particles in the fluid. Next, the fluid is prepared, the particles are immersed in the fluid that has been kept at rest for a day. At this stage, fine particles with high surface energy adhere to the surface energy on glass beads to change the zeta potential as the main retention mechanism. A similar procedure is commonly used in the oil industry for well stimulation and alteration of wettability (SEIEDI et al., 2011; AL-SULAIMANI et al., 2012; JARRAHIAN et al. 2012; RAHBAR et al. 2012, NAZARI MOGHADDAM, BAHRAMIAN et al., 2015). The experimental setup consists of a glass column with a 3 cm diameter and a 15 cm height. A schematic view of the setup is shown in Figure 4.5.

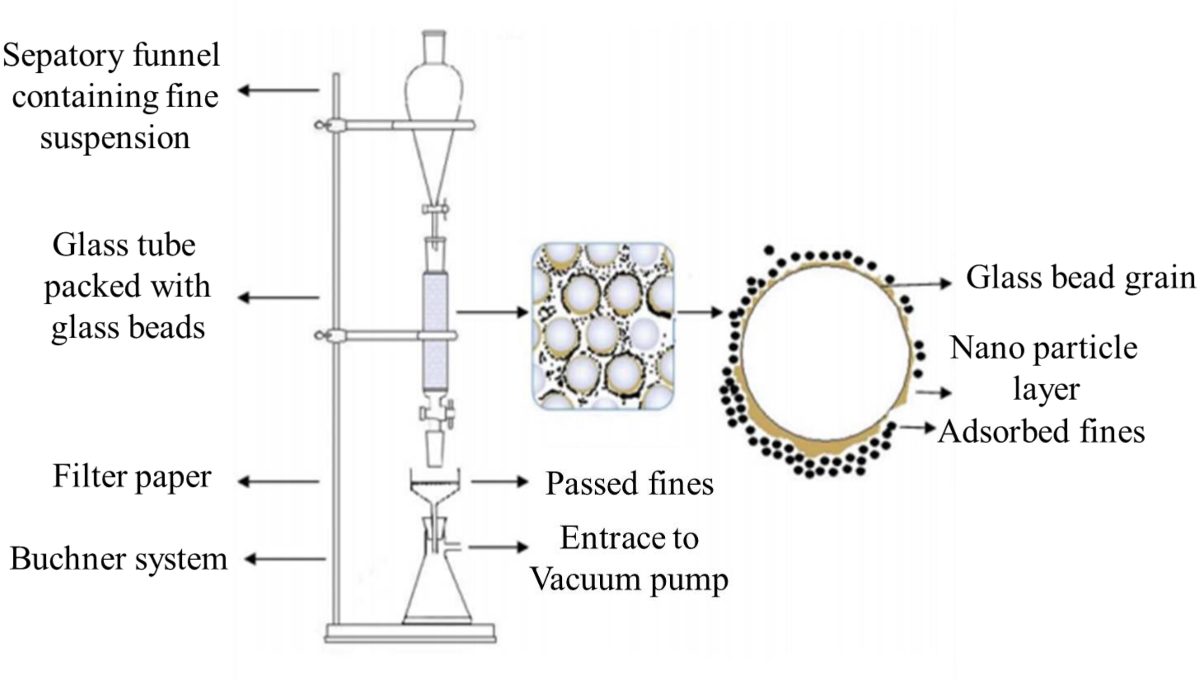

Figure 4.5. Schematic view of set up Adapted with permission of Ahmadi, Habibi et al. (2013).

4.2.3.2. Coreflooding experiments

Several laboratory coreflooding experiments (AHMADI et al., 2011; HABIBI et al. 2013; DÍEZ et al., 2020; GIRALDO et al., 2021) have been performed with increasing velocity to retain fines, which has given a clear idea of how the mobilization and control phenomenon works (OLIVEIRA et al., 2014). The fluid to be injected is positioned in Beaker 1 and pumped at a constant speed. The core support is controlled by the designated valves 14 and 15, two intermediate ports for pressure measurements are located on this support. A hand pump feeds the surge pressure into the core support and the pressure gauge 11 constantly monitors this pressure. Pressure translators 5, 6, and 7 measure the core pressure differential, between the inlet, the ports, and across the first core section, respectively. The pre-calibrated transducers measure pore pressure from 0 to 500 psi. The data receiver 8, delivers a digital report for the measurements of three pressure transducers and transfers it to the PC 9. The fluid is collected in the beaker 4 for additional measurements of electrical resistance, pH, breakdown concentration and distribution. the size of fine particles.

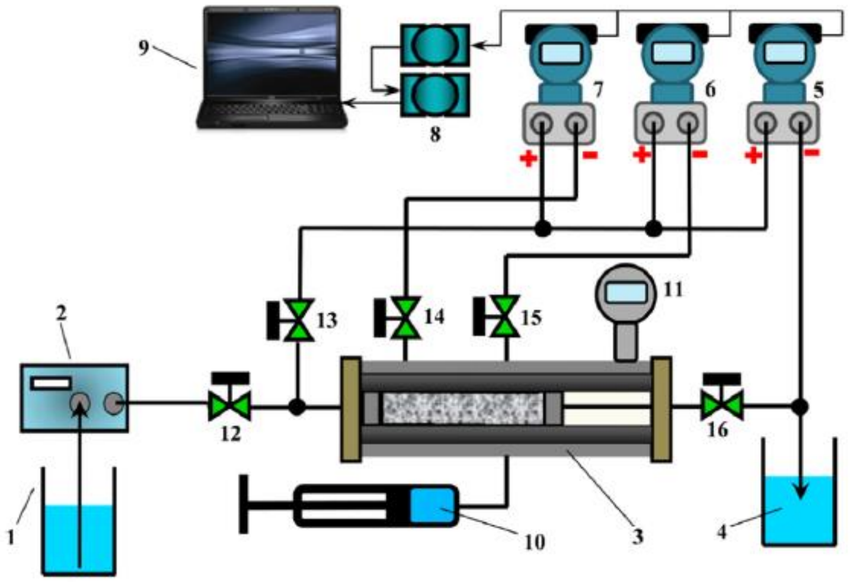

Figure 4.6. Schematic representation of the experimental setup for core flooding: Schematic of laboratory set-up for fines migration in porous media: 1 – injected fluid, 2 – pump, 3 – core-holder with core, 4 – produced fluid, 5,6, 7 – pressure transducers, 8 – data acquisition system, 9 – PC with LabView, 10 – manual pump to maintain overburden pressure, 11 – manometer, 12–16 –control valves. Adapted with permission of Oliveira, Vaz et al. (2014).

To conclude this section, after the bibliographic review, it can be affirmed that formation damage because of migration and deposition of fines is an issue that is affected by multiple parameters and influenced by the following phenomena:

High flows: The critical speed plays a very important role in the migration of fines, which high injection or production flows directly affect this problem.

Wettability Effect: Fines tend to be water-wettable, so wettability is an important consideration in the retention and mitigation of fines in the formation.

Ion exchange: In processes such as salinity and pH change, the surface potential of the fines until flocculation and detachment of the pore walls is generated.

Poorly managed acidifying treatments generate irreversible effects on the matrix.

4.3. Conventional treatments for the mitigation of fines migration

4.3.1. Acidizing

Over time, some techniques have been developed and optimized in the oil industry to mitigate and find solutions to the problem generated by the migration of fines. Among them we find acidification, which is commonly used for the dissolution of fine particles through a process called unblocking, where the main objective is the increase in the size of the poral throat to increase the permeability that was previously affected by the migration of fines (Figure 4.7) (MUECKE, 1979; SHAFIQ et al., 2019). However, the durability of such treatment does not perform satisfactorily, often wells that have undergone this treatment, over time, have disappointing productivity. The high production rates are not maintained and after a while, they have a drastic drop that finally has even more serious consequences after treatment (SHARMA and SHARMA 1994). The presence of inorganic scales is another common problem in these processes, reducing oil production (PORTER, 1989). Additionally, they occur due to the disturbance of the natural state of the fluid, which causes the solubility limit of one or more of its components to be exceeded.

Matrix acidification of sandstone, as an oil and gas production enhancement mechanism, has been used for a long time. It has also played an important role as a remediation and increased permeability process in the area immediately around the well. Some studies effectively show that the application of this treatment becomes effective up to a point, but in most cases its limitations are evident in the compatibility of the training with conventional HCL - HF treatments (THOMAS and CROWE 1981). This is normally the consequence of a rapid flow rate of the fracture, although some wells initially show good stimulation, with the passage of time they experience an exponential deterioration and consequently a rapid decrease in the production rate (Ross, Pierson et al. 1963). This drastic drop in production is observed in two scenarios, both consolidated and unconsolidated sands (WILLIAMS and WHITELEY, 1971). The declines usually are attributed to plugging by migratory clays and other fines. Formation plugging by migratory fines was demonstrated by Krueger (1967).

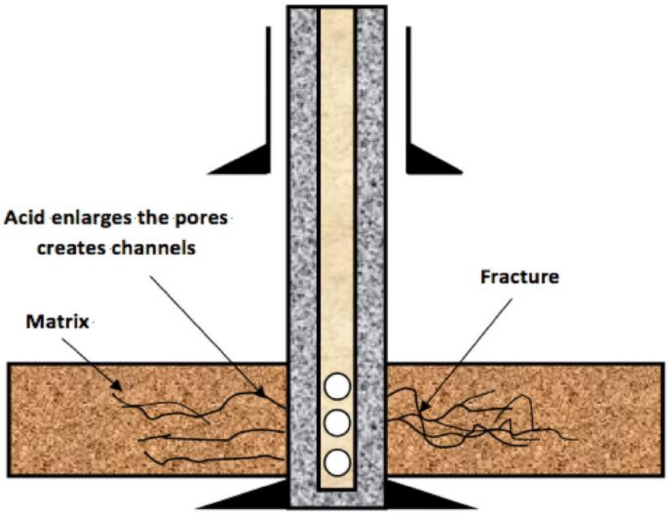

Figure 4.7. Schematic representation of a typical matrix acidizing processes used for removing/diluting the fines blocking the porous medium. Adapted with permission of Shafiq, Mahmud et al. (2019).

4.3.2. Clay Inhibitors

The inclusion of clay stabilizers have been applied as chemical treatments been part of the completion fluids and also in polymers applied in remediation operations (Figure 4.8) (ALAKBARI et al., 2020), resulting in the mitigation and control of fines to improve well productivity (NGUYEN et al., 2005). Normally these treatments require injection of the fluids have a considerable depth and reach within the matrix of the formation, so that there is an interaction between the surfaces of the fines and the pores are in contact with the treatment fluids, therefore abundant volumes of treatment fluids are required to achieve effective results (MCLAUGHLIN et al., 1976). The conventional mechanisms applied in the inhibition of fines consist of the treatment and contact with the fines particles prone to being mobile or that have already been previously detached from the pore walls. An alternative solution to this previously mentioned treatment is to apply temporary clay stabilizers (ZHOU et al., 1995). The main function of these stabilizers is to minimize the tendency to disperse or deflocculate the fines found in the porous medium (MABERRY et al., 1998). da Silva, Bertolino et al. (2019) concluded that after increasing the molar mass of the polyether diamine-based clay swelling inhibitors, a notable inhibition of their swelling is evidenced. The rheological evaluation and the linear swelling results coincide in the results obtained. However, this solution is provisional due to the changes in the salinity of the water after the treatment, resulting in a chemical dispersion and consequently in a susceptibility of the clays to swell again (NGUYEN et al., 2005).

After reviewing and analyzing the limitations of each of the conventional methods for the inhibition and remediation of formation damage by migration and deposition of fines, it will be explored in detail how nanotechnology is proposed to improve the pre-existing problems of these conventional methods.

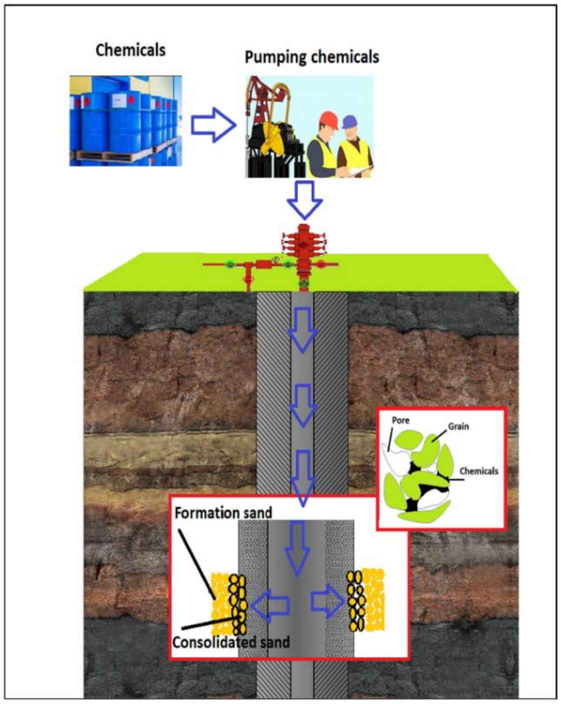

Figure 4.8. Schematic representation of polymers injection for the control of fines migration. Adapted with permission of Alakbari, Mohyaldinn et al. (2020).

4.4. Types of nanomaterials and application to control fines migration

Entering to the field and relating to nanotechnology the focus of review, nanoparticles applied in the control and mitigation of formation damage generated by fines migration and deposition, are specifically designed to generate a monolayer on the surface of the porous medium that contributes to the stabilization of the attractive forces between the fines particle and the rock matrix (RODRIGUEZ-PIN et al., 2009; KONG and OHADI, 2010; MEDINA et al., 2011; KIRTIPRAKASH et al., 2012; FLEMING, 2013). Table 1 describes the different types of nanoparticles applied in the inhibition of fines migration. The main objective of nanotechnology, applied to the inhibition and remediation of formation damage by the migration and deposition of fines, is to change the potential of the surfaces between the fines and the grain surfaces and thus fix them to the walls of the matrix avoiding its detachment at high critical velocity (HUANG et al. 2009; AHMADI et al., 2011; HABIBI et al., 2013; MERA et al., 2013; ARAB, POURAFSHARY et al., 2014; CÉSPEDES-CHÁVARRO 2015; YUAN, GHANBARNEZHAD MOGHANLOO et al., 2015; YUAN et al. 2018, GIRALDO et al., 2021; ZHAO et al., 2021). The reduction in repulsive forces between fines and the matrix walls is also due to the tendency of nanoparticles to stay on the pore surfaces (HUANG, CREWS et al. 2009; ARAB POURAFSHARY et al. 2013; HABIBI et al. 2013; MERA et al., 2013; Yuan, GHANBARNEZHAD MOGHANLOO et al., 2015; ABHISHEK and HAMOUDA 2017; FRANCO et al., 2017; DÍEZ et al., 2020).

4.4.1. Different mechanisms for nanotechnology application for fines migration control

Rodriguez Pin, Roberts et al. (2009) have demonstrated through flow experiments that nanoparticles with proper treatment can be transported through sedimentary rocks, regardless of the rock's low permeability. The transport of colloidal dispersions in porous media has been a very difficult challenge to face, especially when the dispersion concentration is high, for this reason the deviation exposed in this study demonstrates the effectiveness of the application of nanotechnology in these processes. Furthermore, Ahmadi, Habibi et al. (2011) selected and analyzed 3 different types of nanoparticles, magnesium oxide (MgO), silica (SiO_2) and alumina (Al_2O_3), which were chosen based on their specific surface and their ability to trap particles in suspension. The effect for retention of fines of these nanoparticles was evaluated both experimentally and theoretically, resulting in the efficiency of adsorption of fines in grains coated with MgO, has a greater capacity to adhere fines to the surface (Figure 4.9), in comparison with SiO_2 and Al_2O_3 nanoparticles. For Al_2O_3, the repulsion forces are stronger than the attractive forces, leaving the aluminum as the one with the lowest efficiency of the three analyzed particles. These results were validated with theoretical studies also shown and based on Zeta Potential and the total energy of interactions.

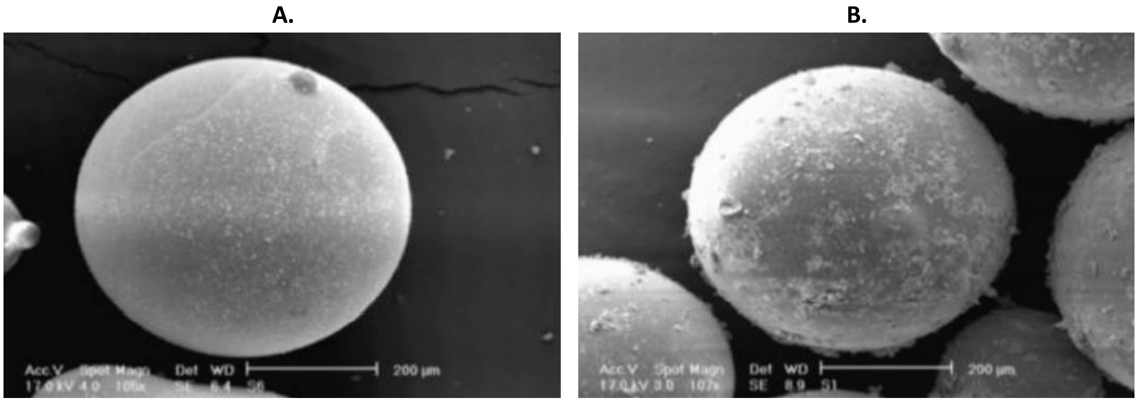

Figure 4.9. Schematic showing glass bead-coated particle with MgO nanoparticles a) before fines retention, and b) after fines retention. The image scale presents a 200 µm reference. Adapted with permission of Ahmadi, Habibi et al. (2011).

Céspedes-Chávarro (2015) have observed that the beds impregnated with nanoparticles showed a greater capacity for stabilizing fines due to their magnetic character, followed by the beds impregnated with SiO_2 and the beds impregnated with Core Shell type nanoparticles, the behavior of the latter related to the low adherence of the nanoparticles to the surface of the sand and glass spheres, decreasing the amount of these in each bed and therefore their effect. At reservoir pressure and temperature conditions, the critical rate before and after the nanotechnology-based treatment was evaluated with results that show a 400% increase in the critical velocity according to the untreated porous medium, which demonstrates the efficacy of this type of treatment. to inhibit detachment, agglomeration, and deposit of fines. Lately in 2018, Franco, Zabala et al. (2017) reported the evaluation of a silica-based nanofluid applied to control and mitigate formation damages generated by a mixture of fine particles of kaolin, quartz and illite composed of 50%, 42% and 7% of its weight respectively. They obtained very satisfactory results regarding the change of the critical rate of migration of fines to scale of laboratory tests. Oil and gas production after nanofluid treatment increased and water production decreased by 40%

Formerly, Habibi, Ahmadi et al. (2013) investigated the fines retention capacity using 9 types of nanoparticles in a dose of 3000 mg/L in sand packs wet with oil and water. They focused on the ability to select nanoparticles to retain only montmorillonite and kaolinite clays at 50:50 wt:wt, concluding that the best nanoparticles to capture fines were aluminum oxide, MgO and zinc oxide nanoparticles, SiO_2 a water base. MgO and Al_2O_3 nanofluids were used to treat porous media and decrease the migration of fines. The results showed that MgO nanofluids, used to treat synthetic porous media, could fix fines more effectively than Al_2O_3 and SiO_2. Subsequently, the effects of MgO nanofluid concentration and fluid flow velocity on the control of fines in synthetic nuclei were experimentally investigated, indicating an optimized concentration for changes in zeta potential and a critical velocity for the release of fines. In addition, Ogolo, Olafuyi et al. (2012) investigated the performance of the nanoparticles in organic and inorganic environments. The essence was to find out the effect of hydrocarbons on the performance of the nanoagents, then in 2013 Ogolo (2013) obtained favorable results for the aluminum Oxide nanoparticles in the laboratory tests carried out, their effectiveness to control and retain migrant fines is much higher than the other nanoparticles. After performing the test, the results regarding the estimated mass of fines captured based on the nanoparticles of Al_2O_3, were 80 cubic centimeters of sand in 0.63g distilled water, 0.52g in brine, 0.8g in ethanol and 0.94 g of Diesel, in the presence of crude oil.

Still in 2013, Mera, Ariza et al. (2013) evaluated in two beds of sand packs moistened in oil and water, the migration and retention of fines with a silica-based nanofluid treated in a dose of 0.02 mass fraction and the suspension of fines simulated by Al_2O_3 microparticles. There is a high affinity between nanoparticles and fines, regardless of the wetting state of the sand, the reaction of fines to treatment with nanoparticles determines a crucial factor in increasing the retention of fines. The best performance treatment under reservoir conditions was evaluated by Díez, Medina et al. (2020), they did core flooding tests at a fixed overload pressure of 34.5 MPa, taking a pore pressure of 6.9 MPa and a System Temperature of 93 ° C, under these conditions the critical rate went from 142.8% to 144.4% for the flow. of water and oil in the presence of the nanofluid, there was a considerable increase thanks to the participation of the nanoparticles of MgO under dynamic conditions, these being the best alternative to apply in mitigating damage to the formation due to migration and deposit of fines. Results are shown on the Figure 4.10.

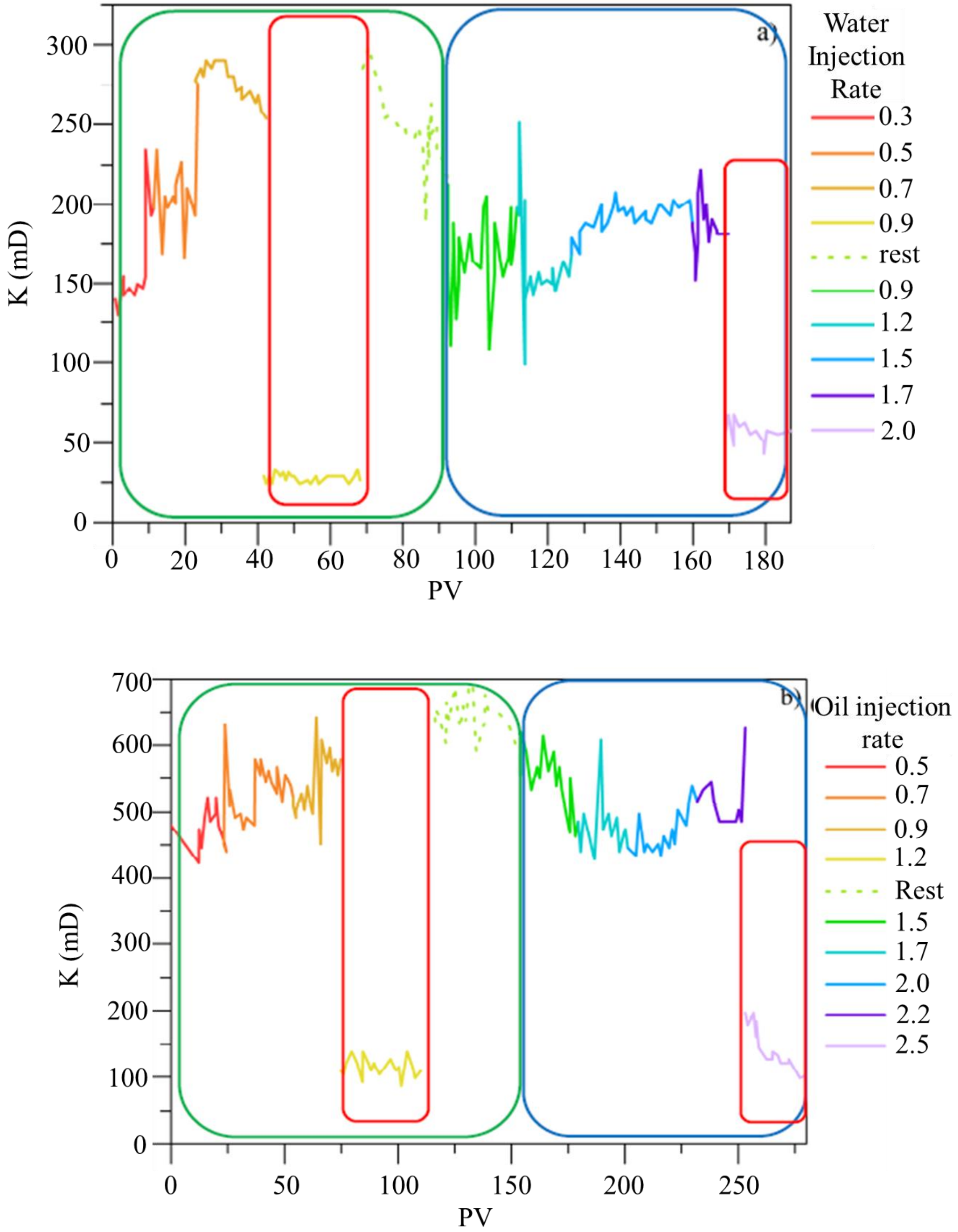

Figure 4.10. Critical rate of (a) water before (green box) and after treatment (blue box) and (b) oil before (green box) and after treatment (blue box) composed of MgO-based nanofluid with 800 mg/L of CTAB adsorbed. Adapted with permission of Díez, Medina et al. (2020).

Later, Giraldo, Diez et al. (2021) found that the capacity to retain and stabilize different types of fines (kaolinite, illite and quartz) using Al_2O_3 nanoparticles at 0.01w%, was increased, having a remarkable increment in the kaolinite retention of more than 50%. The results are observed in Figure 4.11, which presents the breakthrough curves for the sand bed moistened with oil, and the medium with and without treatment.

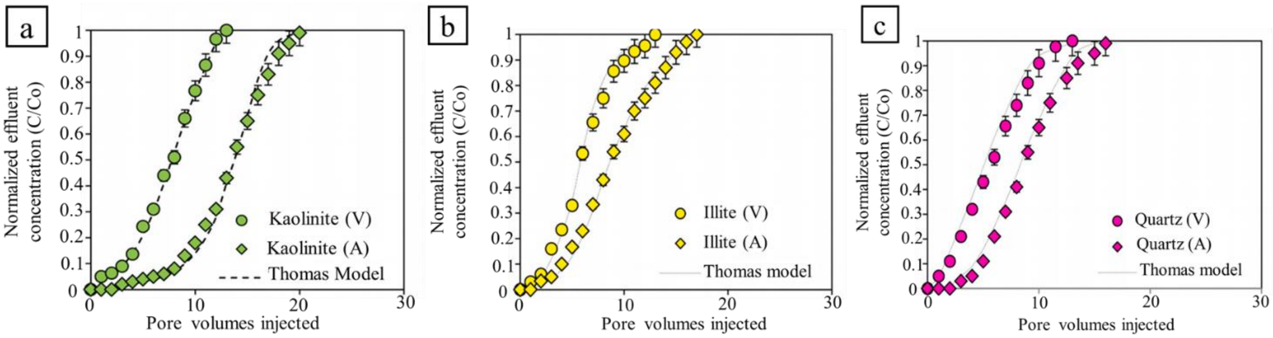

Figure 4.11. Breakthrough curves for oil-wet sand bed with respective adjustment to Thomas Model: a) kaolinite, b) illite, c) quartz. (V) Sand bed virgin without impregnation, (A) sand with impregnation of γ-Alumina. Adapted with permission of Giraldo, Diez et al. (2021)

Earlier, Arab, Pourafshary et al. (2014) found notable results with the application of MgO nanoparticles at a concentration of 0.03 wt%, as at dynamic conditions (coreflooding tests) it was observed that the amount of fines migrating in presence of this nanomaterial was reduced in a 40%. The results were confirmed by employing the DLVO theory for calculating the attractive and repulsive forces of the particles in suspension. The authors observed that the total attractive forces in the medium are increased in the presence of the mentioned nanoparticles, which would benefit the retention of the fines in the rock walls.

The following subsections describe the results obtained in each of the articles related to nanotechnology applied specifically in conventional mechanisms to mitigate formation damage due to fines migration, such as Hydraulic Fracturing and LSW flooding. Referencing in chronological order and analyzing the different results and conclusions of the studies.

4.4.2. Hydraulic fracturing

Nanoparticles have been used in conjunction with hydraulic fracturing to optimize their effectiveness and mitigate their limitations on fines migration control. Basically, Moghadasi, Rostami et al. (2019) described two sets of experiments to investigate the nanosilica effect. The first test set was static and qualitative, which was implemented using glass beads funnel test. The second set of experiments was dynamic, which was executed by the core-flood apparatus. Moreover, DLVO theory was utilized to detect the prevailing mechanism of nanosilica particles in this study. As a result, the nanosilica had a positive impact on reducing the degree of fines migration in both dynamic and static conditions. The calculation of disjoining pressure demonstrated that the negatively charged clay particles are absorbed on the sand proppants because of the positively charged nanosilica particles available in solution. To this end, the nanosilica synthesized in this study is of crucial importance for treating fines migration during the hydraulic fracturing operation. Earlier, Huang, Crews et al. (2008) concluded that nanoparticles have been found to effectively fixate formation fines in fracture proppant pack. The Vioelastic Surfactant (VES) fluid with nanoparticle-strengthening micelle-micelle associations and micelle structures can significantly increase the capacity of proppant suspension in fracturing and frac-packing treatments. Eleraki, Noah et al. (2020), through experimental studies, investigated that MgO Nanoparticles would prevent fines detachment from the pore surfaces and decrease the reduction of permeability at high flow rates more than SiO_2 nanoparticles. The optimum concentration of MgO Nanoparticles was 0.5 g/L as the permeability remediation at this concentration reached 64.83%. Ern, Zamir et al. (2020) based on the results from the assessment shown that bentonite and kaolinite fines are more susceptible to migration in sandstone reservoirs due to their high colloidal stability from their zeta potential measurements and their morphologies. It can also be concluded that SiO_2) is more stable when these nanoparticles are suspended in de-ionized water only, which gives zeta potential values of -26.10 mV. The addition of surfactants (Triton X-100 and Tween 80) has also shown significant results on protected fines migration. Triton X-100 and Tween 80 increased SiO_2-nanofluid zeta potential value at -30.6 mV, which is beneficial for the Nanofluid to travel deeper into the formation to treat problematic areas of fines migration.

4.4.3. Low Salinity Water Flooding

In 2017, Hasannejad, Pourafshary et al. (2017) concluded that, during water injection, SiO_2 nanoparticles have a great capacity to control and mitigate the migration of fines and consequently the highest production or injection rate of the fluid can be obtained. Figure 12 schematically shows the relationship of the average rate of fines effluent versus the interstitial velocity, which indicates the critical velocity of the fluid in that relationship. The injection of nanofluid based on SiO_2 at a concentration of 0.03wt% and 0.01wt% in the porous medium, determined an increase in the critical speed of 0.048 to 0.067 centimeters per second, respectively. The performance in the reduction of migration of fines was 80%, indifferent to the increase in the salinity of the injection fluid.

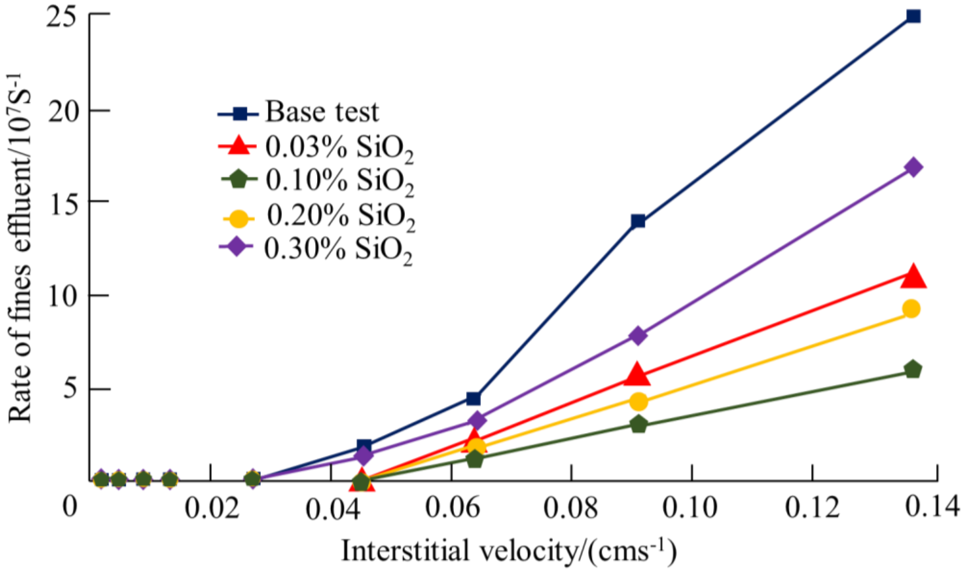

Figure 4.12. Average rate of fines effluent vs. interstitial velocity at 0.3 mol/L injected fluid salinity. Adapted with permission of HASANNEJAD, Pourafshary et al. (2017).

In 2018, Yuan, Moghanloo et al. (2018) came up with an idea to mitigate the migration of fines in the vicinity of the wellbore, a pretreatment of the coating with nanofluids could be implemented prior to injection of low salinity water. Using nanofluids could greatly control the potentially larger pressure drop while continuing the flooding of low salinity water. As side effects, the potential benefit of nanofluid treatment diminishes as more fluids are injected. Assef, Arab et al. (2014) found that the medium treated with MgO nanoparticles has a retention performance of approximately 97% of fines particles under very alkaline conditions. Therefore, pretreatment or prewash, including MgO nanofluid prior to LSW injection, serves to counteract subsequently induced colloid particle migration. The same author, Assef, Pourafshary et al. (2016), indicated that solutions of potassium chloride, sodium chloride, magnesium chloride, and calcium chloride are capable of fixing up to 67, 56, 93, and 91% of fine particles, respectively. These amounts increased greatly by using a very small percentage of MgO nanoparticles. Injection of only 0.01 wt% MgO before the low-salinity brine injection led to an increase in the adsorption capability of monovalent cations salts up to 97%, while for divalent cations salts the increase was up to 100%. In 2019, Moghadasi, Rostami et al. (2019) In addition, several parameters such as temperature, SiO_2 nanoparticles and NaCl concentrations were investigated to determine their relationship with damage to permeability. Obtaining that the temperature has a decreasing effect on the contribution to the damage of the permeability, while when increasing the concentration of nanoparticles of SiO_2 and NaCl, the permeability is more negatively impacted. In the same year, Abhishek and Hamouda (2017) obtained results that helped him to conclude that, with the reduction of direct contact between minerals and water, due to the potential of different SiO_2 nanofluids as modifying agents of the surface of the Berean sandstone, that is, to reduce migration of fines. They directly have a fines retention and control effect. Recently. Arab, Pourafshary et al. (2013) found the Pretreatment with a nanofluid prior to injection of LWS can be a very effective remedy for formation damage. Fines migration is reduced by up to 70% compared to the blank test, after pretreatment with Al_2O_3 nanoparticles. With consistent results as the surface charge of the medium increases to a value of 33.2mV.

4.5. Conclusions

The oil and gas industry will confront greater technique challenges in the coming decades. With the energy resources decreasing rapidly, the difficulty of discovering new oil and gas reservoirs is increasing quickly as well. With the presented critical review of the bibliography related to our topic of interest, we have concluded that the future use of nanotechnology in the oil industry is the key for the development and optimization of some processes currently applied, which lack innovation and suffer many limitations with conventional application mechanisms. Specifically in mitigation and inhibition of formation damage by migration and deposition of fines, after this exhaustive review of the bibliography, a clear opportunity for improvement is evidenced by applying the use of nanotechnology, due to the need to control and manage the underlying phenomena related to this type of formation damage process such as the electrostatic forces that intervene in the detachment of fines from the walls of the porous medium, subsequently migrating until finally covering the pore throats by accumulation and deposition.

Most of the studies addressed using nanoparticles through any conventional mechanism of mitigation and control of fines as mentioned — hydraulic fracturing, LWS (low salinity water) flooding and IOR (Improved Oil Recovery) — report remarkable results on the fines retention, with values between 30% and 60% at standard steady-state conditions while at reservoir simulated conditions with coreflooding setups, the retention can be increased up to 40%. This last greatly impacts the permeability maintenance while increasing the critical velocity more than 100%. For these purposes different types of nanoparticles were implemented, and various studies reveal that the highest performances were obtained when using MgO and Al_2O_3 nanoparticles due to their zeta potential.

Although the results reported in this manuscript demonstrate the nanotechnology suitability for controlling the formation damage associated with fines migration, it is important to emphasize that these types of technologies can be integrated with the conventional pool of techniques for enhancing for enhancing their performance through synergistic effects rather than just replacing them. Finally, nanotechnology can be considered an innovative and unexplored technology, as well as a versatile alternative that can be adjusted to different cases/applications and that can mark a before and after in the oil industry.

Acknowledgements

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Table 4.1. Different types of nanoparticles applied on Fines Migration inhibition by IOR (Improved Oil Recovery), Hydraulic fracturing and LSW (low salt water) flooding

Authors	**Nanoparticle**	**Mechanism**	**Source**
Mansour, Eleraki et al. (2020)	SiO_2 MgO	IOR	Magnesium Oxide (MgO) and Silica (SiO_2) were acquired from Sigma Aldrich
Mera, Ariza et al. (2013)	SiO_2 Al_2O_3 MgO	IOR	SiO_2 and Al_2O_3 were obtained from Sigma-Aldrich (United States)
Díez, Medina et al. (2020)	MgO	IOR	MgO Produced by Sigma-Aldrich (U.S)
Habibi, Ahmadi et al. (2014)	SiO_2 Al_2O_3 MgO	IOR	SiO_2, Al_2O_3, MgO and ZnO purchased from Nano Shell Company
Huang, Crews et al. (2008)	Nanoparticles (proppant packs)	Hydraulic fracturing	No information about producer
Eleraki, Noah et al. (2020)	SiO_2 MgO	Hydraulic fracturing	dioxide (637246 Aldrich) were acquired from Sigma Aldrich, magnesium oxide Nano powder (549649 Aldrich) and it was acquired from Sigma Aldrich
HASANNEJAD, Pourafshary et al. (2017)	SiO_2 Al_2O_3 MgO	IOR	Purchased from the TECNAN company
Abhishek and Hamouda (2017)	SiO_2	IOR	The silicon dioxide NP (637246 Aldrich) acquired from Sigma Aldrich, Drammensveien, Oslo, Norway.

Habibi, Ahmadi et al. (2013)	SiO_2 Al_2O_3 MgO	IOR	The selected nanoparticles are purchased from the Nanoshell Company
Assef, Arab et al. (2014)	MgO	LSW Flooding	Magnesium oxide (MgO) nanoparticle was purchased from U.S. Research Nanomaterials Company
Arab, Pourafshary et al. (2014)	MgO SiO_2	IOR	Nanoparticles were purchased from U.S. Research Nanomaterials Company
Moghadasi, Rostami et al. (2019)	SiO_2	Hydraulic fracturing	The Nanosilica used in this study was synthesized based on the proposed procedure by Choolaei
Ogolo (2013)	$MgSO_4$ Fe_2O_3 SnO_2 Al_2O_3	IOR	Petroleum Technology Development Fund (PTDF)
Arab, Pourafshary et al. (2013)	CuO MgO SiO_2 ZnO γ-Al_2O_3	LSW Flooding	Nanosized gamma alumina (γ-Al_2O_3), copper oxide (CuO), silica (SiO_2), magnesium oxide (MgO), and zinc oxide (ZnO) nanoparticles were purchased from U.S. Research Nanomaterials Company
Huang, Crews et al. (2008)	MgO	IOR	MgO was purchased from U.S. Research Nanomaterials Company
Ogolo, Olafuyi et al. (2012)	MgO Al_2O_3 Fe_2O_3 SiO_2 ZnO	IOR	Petroleum Technology Development Fund (PTDF)
Rodriguez Pin, Roberts et al. (2009)	SiO_2	IOR	SiO_2 nanoparticles from 3M® (St. Paul, MN)
Giraldo, Diez et al. (2021)	MgO SiO_2 γ-Al_2O_3	IOR	Three different nanoparticles of fumed silica (Sigma-Aldrich, St. Louis, MO), γ-alumina (Sigma-Aldrich, St. Louis, MO), and magnetite (Nanostructured & Amorphous Materials, Houston, TX)
Ahmadi, Habibi et al. (2013)	SiO_2 Al_2O_3	IOR	SiO_2, Al_2O_3, MgO and ZnO These nanoparticles are purchased from Nano Shell Company

	MgO		
	ZnO		
Yuan, Moghanloo et al. (2016)	MgO	LSW Flooding	Magnesium oxide (MgO) nanoparticle was purchased from U.S. Research Nanomaterials Company
Zou, Zhang et al. (2014)	SiO_2	Hydraulic fracturing	No information about supplier
Huang, Evans et al. (2010)	(nanocrystals) used to treat the proppant	Hydraulic fracturing	No information about supplier
Ern, Zamir et al. (2020)	SiO_2	Hydraulic fracturing	Magnesium Oxide (MgO) and Silica (SiO_2) were acquired from Sigma Aldrich
	MgO		
Moghadasi, Jamialahmadi et al. (2004)	SiO_2	LSW Flooding	The Nanosilica used in this study was synthesized based on the proposed procedure by Choolaei
Céspedes Chávarro (2015)	SiO_2	IOR	SiO_2 and Fe_3O_4 Produced by Sigma-Aldrich (U.S)
	Fe_2O_3		
Mansouri, Nakhaee et al. (2019)	SiO_2	LSW Flooding	The nanoparticles used in this study were purchased from the TECNAN company.
	Al_2O_3		
	MgO		
Assef, Pourafshary et al. (2016)	MgO	LSW Flooding	Magnesium oxide (MgO) nanoparticle was purchased from U.S. Research Nanomaterials Company

5. Analysis of potential environmental risks in the hydraulic fracturing operation in the “La Luna” formation in Colombia

Abstract

This article presents an in-depth analysis of potential environmental risks associated with hydraulic fracturing operations within the "La Luna" formation in Colombia. Using the Conesa methodology, it assesses the environmental impacts of unconventional reservoir production in Colombia, including water usage, chemical additives, air emissions, and the potential for groundwater contamination. The study incorporates comprehensive data on geological characteristics, operational procedures, and environmental conditions specific to the region. The analysis highlights the need for a proactive approach to managing potential environmental risks associated with hydraulic fracturing in Colombia. The findings underscore the importance of implementing robust regulatory measures, comprehensive monitoring systems, and industry best practices to mitigate and prevent adverse environmental impacts. This research contributes to the ongoing global dialogue on the environmental implications of hydraulic fracturing in regions with sensitive ecological conditions.

The environmental impacts of unconventional reservoirs are widely recognized as a general consensus; however, the absence of applied studies with the rigor of an explicit methodology in Andean countries highlights the need for specific research in this region. This article addresses this gap by proposing a detailed and structured methodology to assess and mitigate environmental impacts in unconventional reservoirs. Emphasizing the importance of knowing the characteristics of reservoir fluids, the research highlights that this critical information is only revealed by drilling exploration wells and PVT (pressure, volume, and temperature) analysis. Obtaining this data is crucial for shaping specific mitigation measures, thus allowing the formulation of a robust environmental management plan tailored to the conditions of the reservoirs in the Andean region. This precise and contextualized approach contributes to close the knowledge gap and promotes more sustainable practices in the exploitation of unconventional reservoirs in this specific geographical context. The methodology used in this study proved its effectiveness by accurately quantifying the risks associated with each of the environmental alterations inherent to the hydraulic fracturing process in the La Luna formation. The results obtained allowed the identification of the critical points most susceptible to environmental impacts, serving as a solid basis for the elaboration of an environmental management plan. This strategic approach not only enabled the delineation of specific mitigation measures, but also facilitated the selection of the most appropriate locations for the implementation of the plan, maximizing the effectiveness of corrective actions. It is noteworthy that the successful application of the Conesa methodology in this unconventional reservoir context evidences the versatility and applicability of this approach, consolidating it as a valuable tool for environmental assessment and effective planning in the hydraulic fracturing industry.

Keywords: Unconventional reservoir, hydraulic fracturing, environmental impact assessment.

5.1.Introduction

Approximately 80% of the global primary energy consumption derives from hydrocarbons, with South America contributing 8.2% and 3.6% of oil and gas production, respectively. Notably, the region possesses 19.5% of the world's proven crude oil reserves and 4.2% of its proven gas reserves (BP, 2022; LYU, FANG, 2023). Consequently, there has been ongoing debates concerning the exploitation of hydrocarbon reserves, which could ensure energy security locally and foster fiscal gains for State development (MOSER, 2001; OCHOA et al., 2016). As part of this discussion, the application of the CONESA methodology has been employed, constituting an unprecedented initiative. Furthermore, the growing reserves and the escalation of production necessitate exploration and extraction from new plays, where the significance of unconventional reservoirs comes into play. South America holds significant potential as a substantial source of unconventional hydrocarbons (DHULDHOYA & DUSTERHOFT, 2017; RODRIGUEZ, HEO, 2020; KUUSKRAA, STEVENS, MOODHE, 2013). Nevertheless, the practicality of oil extraction from unconventional reservoirs hinges on surmounting challenges related to water contamination, environmental degradation, induced seismic activity, and regulatory and institutional complexities.

This research delves into the intricate dynamics of a hydraulic fracturing facility in Colombia, comprehensively detailing its economic benefits, the specific technology utilized, and its associated environmental challenges. A meticulous analysis of the facility's impacts and environmental risks is conducted, followed by a comprehensive outline of the mitigation measures necessary to counteract them. Additionally, this study provides comprehensive guidelines and suggestions for navigating the socioeconomic, institutional, and environmental challenges and opportunities pertinent to the development of similar projects in Colombia and other Andean countries, as well.

To our knowledge, this is the first time that a structured study of the challenges of extracting unconventional hydrocarbons in Colombia and even in Andean countries has been addressed, especially if we consider the different aspects of these challenges. There are studies on the challenge of water consumption in the possible production of shale gas in Brazil (DE CAMARGO et al., 2014). and even several studies on Argentina (EYGUN et al., 2017; SHCHERBA, BUTOLIN, ZIELIŃSKI, 2019; MAUTER et al, 2014). But the literature still does not adequately address Andean countries, particularly countries that have unconventional resources in the Amazon region.

In turn, the Conesa methodology for environmental impact assessment in Colombia stands out as a suitable alternative for several reasons that reflect its effectiveness and adaptability to the particularities of the Colombian context. First, the Conesa methodology has smartly integrated positive aspects of previous methodologies, such as the well-known Leopold methodology and the RAM risk matrix. By incorporating and improving aspects of previous approaches, Conesa is able to take advantage of lessons learned and strengths identified in the field of environmental impact assessment.

Additionally, the widespread adoption and use of Conesa's methodology in Colombia validates its effectiveness and relevance at the local level. The fact that this methodology is widely used in the country suggests that it has proven to be appropriate and reliable for addressing the specific complexities and challenges that characterize Colombia in terms of environmental impacts.

The validation of the CONESA methodology in the present study was carried out through a rigorous analysis of the relevant scientific literature and the detailed review of case studies duly cited in the manuscript. This methodological approach made it possible to support and substantiate the applicability and effectiveness of the CONESA methodology, ensuring its consistency and validity in the research context. Consultation of specialized scientific sources and reference to specific cases provided a solid basis to support the conclusions and ensure the robustness of the methodological approach employed in this study.

At the same time, the results obtained in this study have specific relevance for unconventional reservoirs in the Andean region. These findings constitute a significant contribution that goes beyond the geographical limits of the study, as their applicability extends to Andean countries with geological similarities. Although the uniqueness of each region is recognized, the results serve as a preliminary example and a starting point for future studies in related areas. Adapting the particularities of each region will maximize the usefulness of these results, facilitating knowledge transfer and providing practitioners and industry experts with a solid foundation to address the specific challenges associated with unconventional reservoirs in the Andean context.

Finally, This manuscript addresses this main research question by, first, exploring the complexity of potential impacts from the exploration and production chain of unconventional reservoirs. Then, the research formulates general measures for an environmental management plan to effectively mitigate these adverse effects, focusing on specific and applicable strategies. Finally, the study evaluates the suitability of the CONESA methodology to address the uniqueness of these projects, answering the critical question of whether CONESA proves to be an adequate and efficient approach in the environmental assessment of unconventional reservoirs. How to propose and apply a methodology for assessing the impacts of the production of unconventional hydrocarbons in Colombia, given the different dimensions of these impacts?

5.2.Background

This study applied the analysis to the Middle Magdalena Valley (VMM) basin (Figure 5.1), operated by the Colombian oil company ECOPETROL. This is an unconventional reservoir in Colombia. The La Luna unconventional oil production field, located in the Middle Magdalena Valley (VMM) basin, is the third largest unconventional reservoir in the western hemisphere in terms of volume of reserves and potential for oil and natural gas extraction (FORERO et al., 2021; LIBORIUS PARADA, 2019; BELLO-ANGULO et al., 2022).

Actually, on one side, this study deepens the previous researches on the challenges for expanding oil frontiers in unconventional reservoirs. In fact, the dependence on oil revenues is a complex challenge for several countries. Many countries depend not only on oil production and its exports, but also on imports of oil products. This creates an intricate challenge for these countries, as they must equate two conflicting challenges: the need to deal with replenishing oil reserves, which is crucial for maintaining government revenue, and the growing pressure to carry out the energy transition away from fossil fuels. This complex task is exacerbated when potential oil resources require innovative technologies and are located in sensitive areas. This intensifies the environmental and technical concerns associated with exploiting these resources. In the Andean countries, this scenario becomes even more complicated, highlighting the pressing need for strategic approaches and innovative solutions. An example of this is oil development in the Amazon basin of Ecuador, which has generated a critical intersection between economic progress and the health of local communities (TAHERDANGKOO et al., 2019). Also, in Peru, strategic work on environmental disaster planning for coastal oil spills exposes the need to anticipate and mitigate the risks associated with hydrocarbon (FLORES-MEDINA et al., 2022).

However, more specifically, Colombia is an emblematic country in this case. The Middle Magdalena Valley (VMM) region in Colombia has a complex and layered geology that has led to the development of unconventional reservoirs, particularly in the form of shale gas. Exploration and exploitation of these resources involves a detailed understanding of the geology of the area (SPICKERT, 2014; MORETTI et al., 2010; THOMPSON, 2019).

As well as, the stratigraphic sequence in the Middle Magdalena Valley spans several geologic eras, with a particular focus on the Upper Cretaceous and Tertiary formations (COOPER et al., 1995). Within this stratigraphy, the La Luna Formation emerges as a critical component, hosting hydrocarbon source rocks (RÍOS, C. A., & CASTELLANOS, O. M, 2016).

The source rocks, located mainly in the La Luna Formation, have accumulated organic matter over geologic time (REYES et al., 2021). These rocks are essential for oil and gas generation, and their detailed study provides valuable information on the amount and composition of hydrocarbons present in the region (MASTALERZ, DROBNIAK, STANKIEWICZ, 2018).

As for the tectonic structure, it is related to the Andes Mountains to the west and the Magdalena Basin to the east, resulting in systems such as folds and faults. These structures can significantly influence hydrocarbon migration and reservoir configuration (RANGEL, PARRA, NIÑO, 2000). Now, with respect to the unconventional reservoirs that can be found in the La Luna formation, the presence of shale gas stands out. This type of deposits is trapped in shale layers, sedimentary rocks rich in organic matter (ZUMBERGE, 1984; GOMEZ, 2014). The La Luna Formation is the main generating unit of the basin and has a thickness of approximately 200 feet (ZUMBERGE, 1984; GOMEZ, 2014; TORRES, Emilio J., et al., 2015). TOC ranges from 1.5% to 9.6%, with an average of 3.8%. This formation is currently in the hydrocarbon generation window (AGENCIA NACIONAL DE HIDROCARBUROS, 2023). The predominant oils in the basin have an API gravity exceeding 30º and are of outstanding quality (AGENCIA NACIONAL DE HIDROCARBUROS, 2023; VEIGA, & ZELALIJA, 2014). The correlation between reservoir depth and API gravity is not straightforward. These oils originate from a later expulsion stage, and their elevated thermal transformation accounts for the elevated API gravity (VEIGA, & ZELALIJA, 2014; CABELLO et al., 2018). Efficient extraction of this gas requires the use of advanced techniques, such as hydraulic fracturing (fracking), which allows the gas trapped in the shale layers to be released by injecting fluids at high pressure (MEMON et al., 2022; HE al., 2020). Hydraulic fracturing is presented as the most suitable technique for hydrocarbon extraction in unconventional reservoirs such as shale and tight due to its ability to maximize productivity in low permeability formations (MEMON et al., 2022; HE al., 2020). These types of reservoirs, characterized by a compact source rock, require a solution to release the hydrocarbons trapped in their pores (WILKINS, GEORGE, 2002). Fracking involves injecting high-pressure fluids into the formation, creating fractures that allow for higher permeability and thus more efficient extraction of oil and gas. This technique has proven to be highly effective in the exploitation of shale and tight reservoirs (GANAT, 2020; ZHANG, 2024).

At the time of writing, La Luna Formation, which is the third basin with unconventional oil potential in the Americas, has not been exploited yet. A more rigorous legal framework is awaited to make its exploitation viable; it is currently considered as a contingent resource.

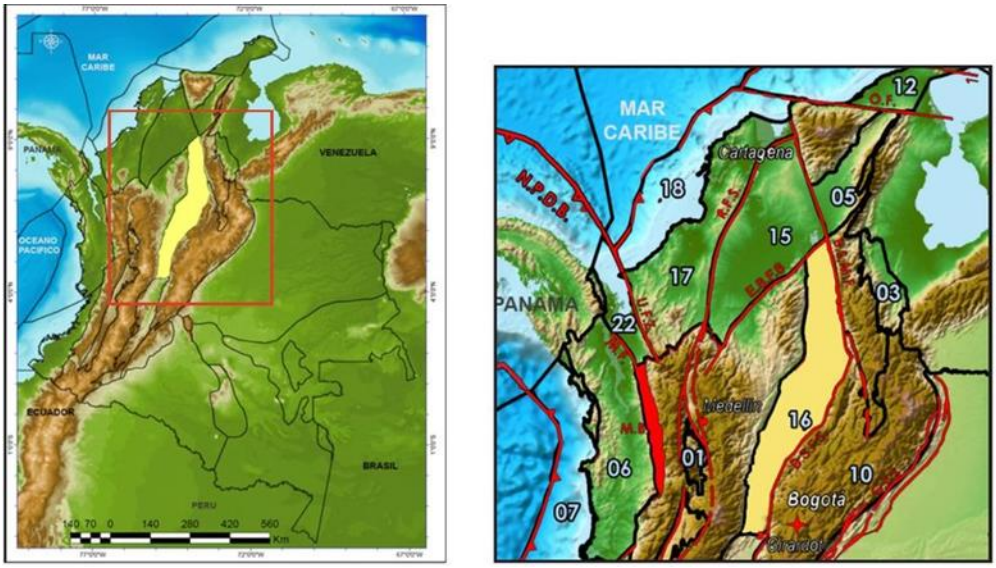
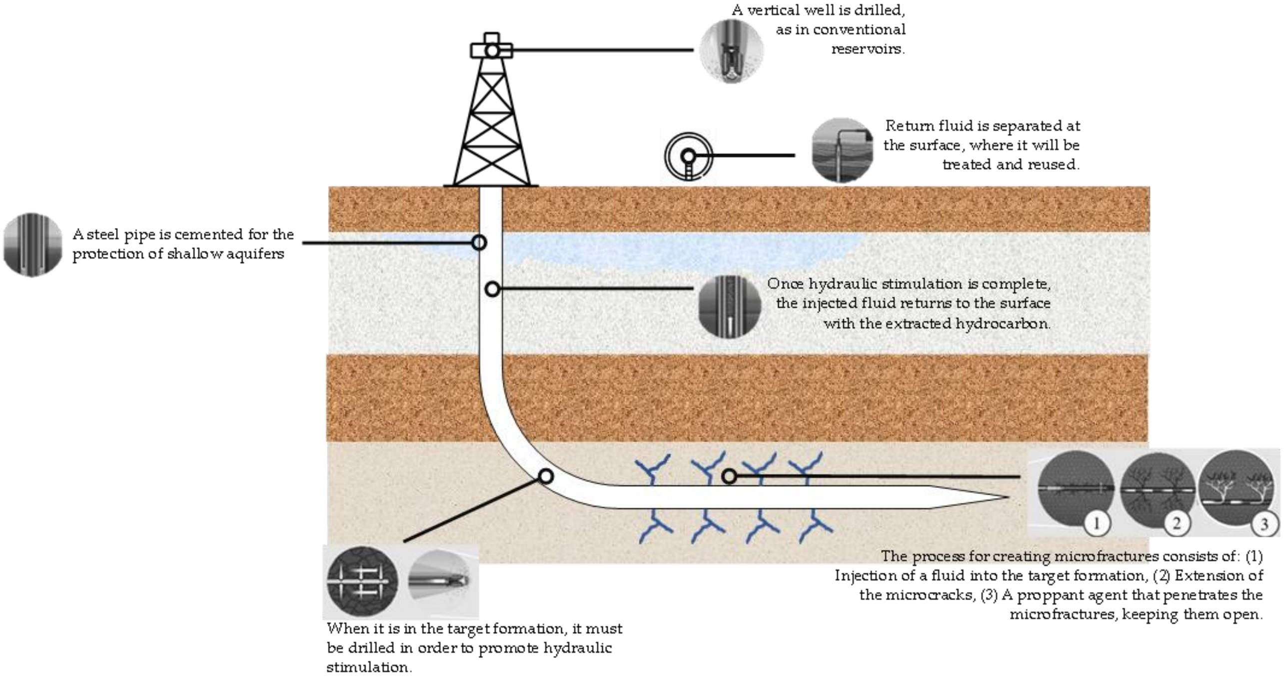


Figure 5.1. Valle Magdalena Medio Basin. (Number 16 in yellow) (MORENO-ENRIQUEZ, 2022; FORERO et al., 2021).

A conventional reservoir is formed through several stages that are governed by a chronological profile: initially, the hydrocarbon originates in a rock called a source rock, characterized by its very fine granulometry and the narrowness of its pores, through the accumulation of marine organic matter in a sedimentary rock in an anaerobic environment. Subsequently, by the effect of the pressure that the oil causes under the rock, the oil is expelled from the source rock, which is called primary migration; then the fluid flows into a formation composed of a sealing rock that prevents it from sliding, where finally the resource lodges in a formation called reservoir rock, which has good permo-porous characteristics; this process is known as secondary migration.

When the deposition of hydrocarbons does not have any of the steps listed before, the concept of unconventional reservoir (UCR) is used (ISAAC et al., 2022; GUPTA, Ishank, et al., 2021; ASLANNEZHAD et al., 2021; WANG & CHEN, 2019; LIU et al., 2021; YEKEEN et al., 2019). These unconventional reservoirs have the uniqueness that two of their basic petrophysical properties, permeability, and porosity, are significantly low. Thus, vertical drilling does not provide eco-nomically viable production rates. For this reason, it is necessary to drill horizontally, applying hydraulic stimulation techniques, which allows optimal drainage areas to be obtained and to generate fractures that allow the hydrocarbons to flow to the canyon beds. Figure 2 shows the most important most important points regarding this technique (GANDOSSI & VON ESTORFF, 2013; VENGOSH et al., 2014; ZHANG & EATON, 2017; ZHANG et al., 2019; SCHULTZ et al., 2018).


A vertical well is drilled, as in conventional reservoirs.

Return fluid is separated at the surface, where it will be treated and reused.

A steel pipe is cemented for the protection of shallow aquifers

Once hydraulic stimulation is complete, the injected fluid returns to the surface with the extracted hydrocarbon.

The process for creating microfractures consists of: (1) Injection of a fluid into the target formation, (2) Extension of the microcracks, (3) A proppant agent that penetrates the microfractures, keeping them open.

When it is in the target formation, it must be drilled in order to promote hydraulic stimulation.

Figure 5.2. Stages of the hydraulic stimulation process (LIU et al., 2019)

Each petroleum reservoir has its specificities regarding mineralogical composition, permeability, porosity, temperature, and pressures. Therefore, different types of fracturing fluids have been developed so that they can be used appropriately for each type of reservoir. Effective hydraulic fracturing stimulation design involves selecting the appropriate fluid and proppant for the operation. The amount of fluid and proppant used, as well as the pressure and injection rate, are closely related to the fracture dimensions and, consequently, to its productivity (SCHULTZ et al., 2018; LIU et al., 2019; ASOCIACIÓN COLOMBIANA DE PETRÓLEO, 2014).

The fracturing fluid must be viscous enough to carry the support agents and to improve the circulation inside the well, avoiding the accommodation of the proppants, generated by the gravitational forces (AHAMED et al., 2019; YAO et al., 2022; BARBOZA, CHEN, LI, 2021).

The viscosity of the fracturing fluid also influences the fracture geometry. If the fluid is too viscous, the vertical length of the fracture may exceed the vertical length of the producing layer, resulting in a lower-than-expected accommodation of the proppants. Figure 5.3

demonstrates the application of the fracking technique being performed with fluids of excessive (left) and moderate (right) viscosity (Figure 5.3) (AHAMED et al., 2019; YAO et al., 2022; BARBOZA, CHEN, LI, 2021; WANNIARACHCHI et al., 2019; Schlumberger, 2020; HUANG et al., 2019).

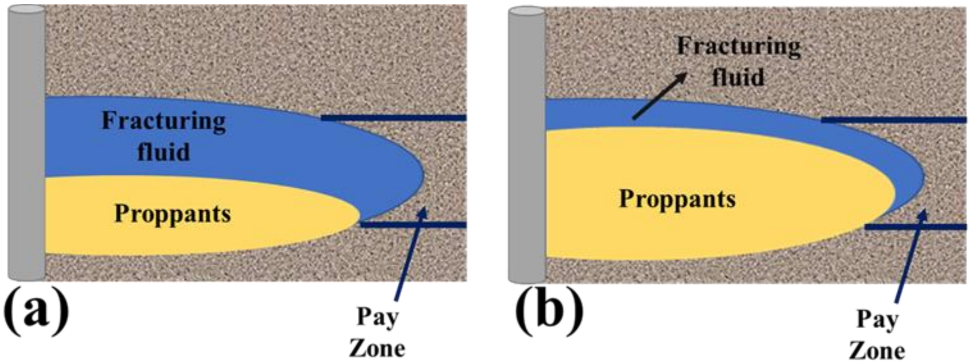


Figure 5.3. Effect of viscosity on fracture geometry and proppant positioning. (a) Entry of the proppant into the fracture created. (b) Expansion of the proppant in the generated permeable channel. Source: Schlumberger Oilfield Glossary (KANG et al., 2020; NYGAARD, 2012).

In parallel, the pumping rate of the fluid is of great importance. This variable is dependent on the density and the friction involved in the flow. In addition, it is important to consider the infiltration of the fluid into the formation, the compatibility with the formation, its displacement in it, among others *(*KANG et al., 2020; NYGAARD, 2012).

A sequence of materials must be added to a fracturing fluid for it to meet the requirements and have a composition that allows the use of the technology possible (Schlumberger, 2020; HUANG et al., 2019; KANG et al., 2020; NYGAARD, 2012; LI & ZHANG, 2019; THOMAS et al., 2019). Table 1 shows the different types of additives and their respective role in hydraulic fracturing.

Table 5.1. Types of additives and their function (NYGAARD, 2012; LI & ZHANG, 2019; THOMAS et al., 2019)

Additives	Function
Gelling agents	They increase viscosity, reduce formation creep and decrease fluid friction

Cross-linkers	Increase the viscosity of the gel formed
Fluid-loss Additives	Optimize the action of the gelling agents by reducing the infiltration of fracturing fluid into the formation
Friction reducers	Decrease fluid friction
Breakers	They are responsible for breaking the gel formed, reducing the viscosity of the fluid, with the objective of helping in the next step of cleaning the fracture
Surfactants	They facilitate the cleaning treatment, reducing the wettability of the rock
Stabilizers	Additives such as sodium thiosulfate and methanol are used to avoid possible unwanted reactions
Fibers	Decrease the settling velocity of the proppants, resulting in a better filling of the fracture interior and, consequently, in a higher conductivity

The infiltration of fracturing fluid into the target layer (leak-off) is an important aspect for planning a hydraulic fracturing project. Therefore, the larger the fracture, the larger the leak-off will be. Cross-linkers are of utmost importance to reduce this leak-off. In the process of modifying the polymeric structure, which constitutes the gelling agents, the cross-linkers help in the formation of the filter cake, a layer of residues deposited on the fracture wall, minimizing the subsequent leak-off of the fracturing fluid. As filter cake formation is a severe process, initially the fracture wall is more exposed to seepage, and an additional amount of fracturing fluid enters the rock, called spurt loss (MCADAMS et al., 2019; WANG et al., 2023).

Oil- or water-based fracturing fluids are most frequently employed in fracking. Since the oil sector uses water-based fluids the most, they are more suitable. Water-based fluids are more widely accessible and less expensive because of this. Due to its relatively high density and minimal risk of combustion and pollution, this type of fluid also benefits from low pumping pressure requirements and favorable gelling agent reactivity. Its relatively high density is a drawback as it makes well cleaning more challenging (MCADAMS et al., 2019; WANG et al., 2023; DAVOODI et al., 2023; ISHAK et al., 2023; SMILOVICH et al., 2023).

On the other hand, oil-based fluids have the advantage of having high viscosity, which helps in the conduction of propellants; having low density, which facilitates the well cleaning[7] process. However, its use involves risks related to combustion and pollution; it demands a higher pumping rate; and has a high cost when compared to water-based fluids (LUO et al., 2023; SHEN et al., 2023; AWEJORI et al., 2023).

On the other hand, the proppant material is the solid particles that enable the propagation of fractures, generating a path of greater permeability and conductivity for the fluid. Its choice must be carefully performed, so that it resists to the closure of the closure of the fracture and ensures the flow of the reservoir (AWEJORI et al., 2023; ZHANG et al., 2023; HE et al., 2023; LIU et al., 2021).

To select the ideal proppant, it is necessary to analyze the density, the crushing resistance, the size, and distribution of grains along the crack, the ease with which the granular material is transported, the roundness and particle sphericity. The support agent must have dimensions and specific mass that allow it to be transported through the fracturing fluid and be minimally degradable over time. This section discuss the properties of the different types of proppants applied (AWEJORI et al., 2023; ZHANG et al., 2023; HE et al., 2023; LIU et al., 2021; TONG et al., 2019; THOMAS et al., 2019; WANG et al., 2020; FU et al., 2019 LI et al., 2019). Table 2 shows the densities and crushing strengths (compressive strength of the particles or grains of the rock formation being fractured.) of the proppants usually used in fracking.

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[7] Well cleaning in unconventional reservoirs refers to the operations performed to maintain the productivity and efficiency of an unconventional hydrocarbon well, such as shale oil or shale gas. These wells often require periodic maintenance and cleanup due to the unique characteristics of unconventional reservoir production. [200-202].

Table 5.2.Propellant properties (LI et al., 2019; LOZANO, MCCUTCHAN, KRZMARZICK, 2019; LIU et al., 2021; KHAN et al., 2021)

Type of propellant	Density (g/cm³)	Crush resistance (psi)
Pure sand	2.65	<6000
Resin coated sand (RCS)	255	<8000
Intermediate-strength proppants (ISP)	2.7 a 3.3	5000 a 10000
High-strength bauxite (HSB)	3.4 ou superior	>10000
Bauxite	2	>7000

Pure sand is widely used, due to its wide availability that reduces the costs for the operation. However, this resource has limited application, since it provides good conductivity and permeability only when subjected to a crushing strength of less than 6000 psi. In this case, the sand can be treated with resin (RCS - resin-coated sand), aiming to provide the sand with a higher crushing strength (LI et al., 2019; LOZANO, MCCUTCHAN, KRZMARZICK, 2019; LIU et al., 2021; KHAN et al., 2021; LIU et al., 2016; REN et al., 2019).

Ceramic proppants have higher crush resistance. They have aluminum in their composition (extracted from bauxite) as their main component, besides having silica and clay at low levels. They are classified into two main types, according to their bauxite content, being called: Ceramic proppants of Intermediate strength ceramic proppants (ISP); High strength bauxite (HSB) (REN et al., 2019 HAQUE, SAINI, SAYED, 2019; CONESA FERNANDEZ-VITORIA, 1997). The intermediate-strength ceramic proppants are derived from bauxite synthesized with a high mullite content. The high-strength ceramic proppants, on the other hand, are derived from synthesized bauxite rich in aluminum oxide. In addition, the IDC is an intermediate density ceramic proppant, known as bauxites (CONESA FERNANDEZ-VITORIA, 1997; RAMESH et al., 2022; GÖK & SODHI, 2021).

5.3.Methods

To assess the impacts of the unconventional hydrocarbon production in the Middle Magdalena Valley (VMM) basin, this study proposes and applies different indicators, which are described in this section. Then, it applies a multicriteria analysis to derive an aggregated impact result. Subsequently, measures are proposed to mitigate these environmental impacts. The main method is based on the Conesa Methodology (CONESA FERNANDEZ-VITORIA, 1997). This methodology was applied by several environmental studies and development projects to assess the potential impacts of human activities on the environment (THIEL, 2018; JOHNSTON et al., 2021). The appropriateness of this methodology depends on several factors, and its use may vary according to the context and the specific objectives of the assessment.

Besides, the Figure 5.4 provides a detailed visual representation of the environmental impact associated with a specific action. In the graphical representation, colors have been assigned to clearly distinguish between beneficial impacts, highlighted in green, and adverse effects, marked in red. What is remarkable about this representation is the inclusion of a timeline that allows observing the evolution of the negative environmental impact from the time of the completion of the action to the defined period of interest. This temporal approach provides a dynamic perspective, facilitating the identification of trends and changes in the magnitude of the negative environmental impact over time. In addition, quantifying the magnitude of adverse impacts provides valuable data for a more accurate and detailed assessment of the long-term effects of the action under consideration on the environment.

It should be noted that, t_{IC} representing time of Interest considered, in turn, t_{CA} represents the time of completion of the action, T_{II} is time of Impact Iniciation, and t_{CM} Corresponding to time of Current Moment.

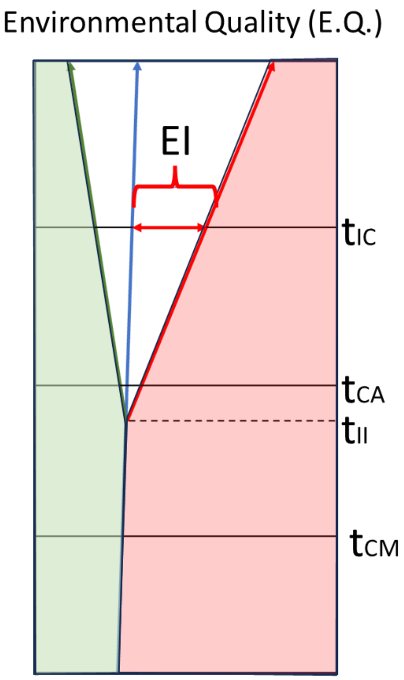

Figure 5.4. Categorization of positive and negative impact

Moreover, the Figure 5.5 shows the negative environmental impact derived from a specific action, using distinctive colors in red. Four lines stand out, representing the degree of incidence of the environmental impact, with the angle formed between these lines and the line representing the evolution of the environment or of a "no action" factor being preponderant. The novelty of this approach lies in the fact that the angle formed provides a visual measure of the severity of the environmental damage, establishing a direct relationship between the extent of the angle and the magnitude of the adverse impact. Thus, the greater the angle, the greater the degree to which the environment is affected, allowing an intuitive interpretation of the severity of the negative environmental impact of the action under consideration. In this way, a direct relationship can be given between the magnitude of the angle and its incidence in terms of impact, thus, for angle 4 will be categorized as total impact, angle 3 and 2 as medium and notable, respectively, and finally, 1 as minimal impact.

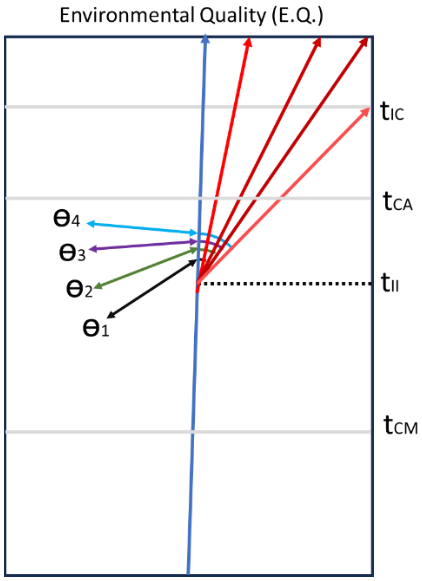

Figure 5.5. Categorization of impact by degree of incidence

On the other hand, Figure 5.6 presented here highlights in an illuminating way the temporality of the impact of an environmental disturbance. In the graphic representation, two key categories can be distinguished, identified as (A) immediate and (B) medium term, clearly indicating the moment at which the harmful effects are manifested in the environment. The ability to categorize the impact as immediate or medium-term based on the harmful disturbance to the environment is crucial for the subsequent assessment and classification of the risk associated with the impact. This temporal approach provides a more detailed understanding of the temporal dynamics of adverse environmental effects, serving as a valuable tool for informed decision making in the management and mitigation of environmental impacts.

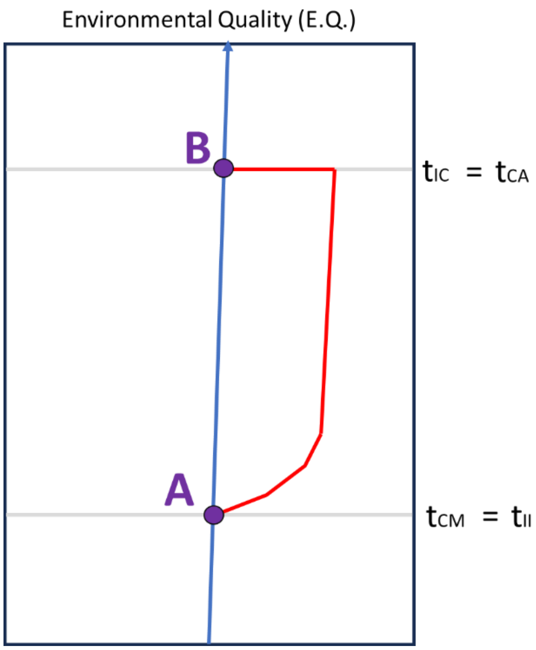

Figure 5.6. Categorization of impact manifestation time

In addition, the Figure 5.7 highlights the duration of an environmental impact and the time required to carry out its quantification and, subsequently, the corresponding remediation. In this graphic representation, the timeline of the impact is clearly observed, indicating the beginning and the end of its manifestation. At the same time, an additional period is identified that covers the time for impact quantification, marking the moment when the detailed evaluation process begins. On the other hand, is very significant about this figure is the explicit connection between the duration of the impact and the time required for its quantification and remediation. This visual approach allows one to appreciate how mitigation and remediation of an environmental impact are intrinsically linked to a precise understanding of its temporal duration. The figure therefore provides a valuable tool for planning effective and timely interventions, facilitating conscious and sustainable environmental management in response to impacts arising from specific actions**.**

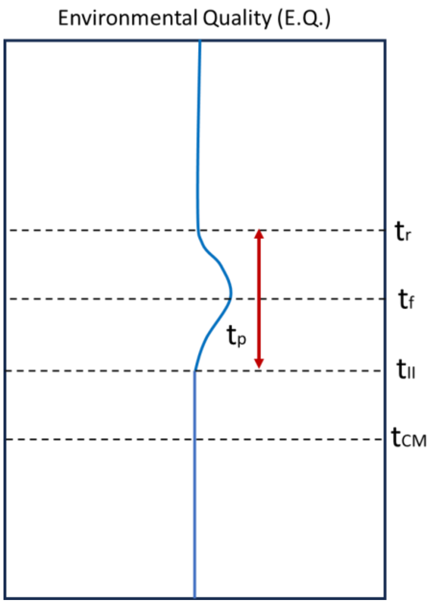

Figure 5.7. Classification of environmental impacts according to their duration.

The assessment of the parameters that make up the environmental impacts is carried out by means of a scale that reflects the importance and seriousness of each qualitative aspect. In this context, the qualitative weight of the intensity of the environmental impact is considerably greater than that of the effect. For example, intensity represents the degree of destruction in a given area, providing a more direct measure of the magnitude of the impact. In contrast, the effect relates to the cause of the impact, whether it is the result of the action being studied or a previous action. Given this qualitative difference, intensity is evaluated on a scale of up to 12 units, considering their midpoints, while effect is quantified in a range of up to 4 units. This hierarchical weighting allows for a more precise and detailed evaluation of environmental impacts, focusing on the dimension of greatest qualitative relevance in the evaluation process.

5.3.1. Intensity (IN)

This indicator assesses the extent to which an activity or action affects a specific factor in a particular area, such as soil, air, or water. The rating scale ranges from 1 to 12, with 12 indicating complete destruction of the factor in the area where the effect occurs, and 1 representing minimal impact. Values falling between these two extremes indicate varying degrees of impact.

The intensity rating scale used in this context ranges from 1 to 12, providing an accurate and detailed tool for assessing the magnitude of the environmental impact. In this scale, the upper end, marked as 12, denotes the total destruction of the factor under study, which translates into an environmental impact of maximum intensity, classified as "Total". In contrast, the minimum value of 1 represents a minimal and insignificant impact, characterized by a low and minimal intensity. Intermediate values on the scale, such as 8, indicate very high or noticeable intensity, 4 reflects high intensity, while 2 is associated with medium intensity. Figure 3 shows the graphic representation of the appearance of impact or manifestation, at the moment any action is performed. This scaling approach provides a precise gradation that facilitates the assessment of the severity of the environmental impact, allowing a detailed classification and a more complete understanding of the magnitude of the effects on the environment.

Table 5.3 displays the ratings for each level of intensity (CONESA FERNANDEZ-VITORIA, 1997; RAMESH et al., 2022).

Table 5.3. Criteria of periodicity, associating rating range and rating value.

Criteria	Rating range	Rating value
Intensity (IN)	Low	1
	Half	2
	High	4
	Very High	8
	Total	12

5.3.2. Extension (EX)

This indicator addresses the area of theoretical influence of the impact in relation to the environment of the project or activity (RAMESH et al., 2022).

- Specific: refers to the impacts generated in the area directly intervened by the project. The physical-biotic component corresponds to the area intervened directly during the construction, operation and dismantling while, for the social element, it correlates to the properties where the said activities will be carried out.

- Limited: refers to those impacts that transcend the areas directly intervened by the project or activity, without reaching the entire study area.

- Extensive: when the impact covers the study area in its entirety and/or can transcend it until it reaches a larger order, municipal affectation, an account, or an ecosystem.

- Total: Refers to the case in which the effect is punctual but occurs in a critical place.

The extent of the environmental impact is evaluated by the percentage of the affected area in relation to the total environment. In the case that the action that originates the impact is highly localized, affecting a minimal area in comparison with the total environment, it is classified as a punctual impact, designated with the value of 1. On the other hand, when the effect cannot be precisely localized within the project environment and has a generalized influence that covers the entire space, it is categorized as a total impact, assigning it the value of 8. Intermediate situations are also considered, which are graded according to the extent of the impact, being considered as partial impact (2) when they affect limited areas and as extensive impact (4) when the influence extends beyond the localized but does not reach the generalization of the total impact. This approach allows a detailed and graded assessment of the extent of the environmental impact, providing a more complete understanding of the spatial distribution of the effects generated by the action in question.

Table 4. shows the criteria and the qualification range of the extension.

Table 5.4. Extension ranking range and rating value.

Criteria	Rating range	Rating value
Extension	Punctual	1
	Partial	2
	Extensive	4
	Total	8
	Criticism	12

5.3.3. Moment (MO)

The "Manifestation or Moment" indicator represents the time gap between the initiation of an action and the commencement of its impact on the environment or the specific medium in question. (GÖK & SODHI 2021, AJIDE et al., 2023). Likewise, the moment can be:

- Long-term: when the effect takes more than 5 years to manifest itself.
- Medium-term: when the time elapsed between the effects caused by an action is between 1 and 5 years.
- Immediate: when the elapsed time is zero and the time is less than one year.

- Critical: results when the effect is immediate and occurs in the vicinity of populations or vulnerable elements.

- The Table 5 shows the criteria and the qualification range of the extension of moment.

The temporal relationship between the action and the manifestation of the impact plays a crucial role in the evaluation. When the time lapse between the occurrence of the action and the onset of the effect is practically nil, reflecting an immediate manifestation, it is assigned a value of (4). On the other hand, if this time lapse is less than one year, it is classified as short-term manifestation, giving it a value of (3). If the period is between 1 and 10 years, it is considered a medium-term manifestation, represented by the value (2). In situations where the effect takes longer than 10 years to manifest itself, a value of (1) is assigned. This temporal approach to valuation allows a detailed differentiation of impacts according to the speed with which they manifest themselves, providing a valuable tool for understanding and managing the temporal effects of environmental actions.

In the process of temporal quantification of environmental impacts, the fundamental concept of Time of Moment (t_m) is introduced. This parameter is defined as the difference between the time of onset of the effect and the time at which the action occurs. In other words, the Time of Moment (t_m) is calculated by subtracting the instant at which the action manifests (T_{CM}) itself from the instant at which the effect starts (t_{ii}) (Equation 5.1). This precise and specific approach makes it possible to accurately measure the time lapse between the impact-generating action and the concrete manifestation of the environmental effect, providing a key tool for detailed temporal evaluation in the analysis of environmental impacts. Providing precise values for the quantification of the parameter.

$$t_m = t_{II} - t_{CM} \qquad \text{(Equation 5.1)}$$

Table 5.5. Value and range of qualification of the extension in the evaluation of environmental impacts

Criteria	Rating range	Rating value
Moment (MO)	Long-Term	1
	Medium-term	2
	Immediate	4
	Critical	8

5.3.4. Persistence (PE)

This indicator refers to the time that the alteration of the variable being assessed will theoretically remain, from its appearance, and from which its recovery process begins, with or without management measures.

Quantifying the permanence of an effect is essential for understanding the duration and magnitude of environmental impacts. In this context, a criterion has been established that assigns values according to the temporal duration of the effect. If the effect is ephemeral or fleeting, as in the case of noise pollution that lasts only for the duration of the sound emission, a value of (1) is assigned. In contrast, if the duration is in the range of 1 to 10 years, it is characterized as temporary or transitory, and a value of (2) is assigned. For effects that persist between 11 and 15 years, they are characterized as persistent or long-lasting, and are assigned a value of (3). When the effect is permanent and irreversible, as in the case of the construction of roads or access roads to a project, the maximum value of (4) is assigned. This approach allows an accurate assessment of the temporal persistence of environmental impacts, providing valuable information for decision making and sustainable project management.

According to this criterion, the impact for its duration can be (Table 6) (CONESA FERNANDEZ-VITORIA, 1997; KOUR et al., 2023; ILAL, IQBAL, BARCELÓ, 2019) [55, 59,60]:

- Fleeting: if the impact persists for less than one (1) year.
- Temporary: if the impact persists for 1 to 10 years.
- Permanent: if the impact persists for an indefinite period or for more than 10 years.

Table 5.6. Value and range of qualification of the Persistence in the evaluation of environmental impacts

Criteria	Rating range	Rating value
Persistence (PE)	Fleeting	1
	Temporary	2
	Permanent	4

5.3.5. Reversibility (RV)

This indicator assigns the capacity of the environment to naturally assimilate a change or impact generated by one or several activities of the project under evaluation, in such a way that it activates self-purification or self-recovery mechanisms, without the implementation of management measures (CONESA FERNANDEZ-VITORIA, VICENTE, 1997; MORERO, RODRIGUEZ, CAMPANELLA, 2015) [55, 61]. The criteria to define the reversibility of the socio-environmental environment are (see Table 5.7):

- Reversible in the Short-term: the natural recovery of the variable to its initial state, without management measures, can occur in less than 1 year.

- Reversible in the Medium-term: the natural recovery of the variable to its initial state, without management measures, can occur between 1 and 10 years.

- Irreversible: the natural recovery of the variable to its initial state, without management measures, is not possible.

Table 5.7. Value and range of qualification of the Reversibility in the evaluation of environmental impacts

Criteria	Rating range	Rating value
Reversibility (RV)	Short-term	1
	Medium-term	2
	Irreversible	4

5.3.6. Synergy (SY)

This indicator considers the amplification of two or more individual effects. The cumu-lative outcome of these effects, triggered by concurrent actions, surpasses what would be anticipated if the actions were to operate independently rather than concurrently. The emergence of new effects on the analyzed factor is integral to the modus operandi of synergism (CONESA FERNANDEZ-VITORIA, 1997; LI et al., 2010; LEMAIRE et al., 2014). The synergism of the effects caused can be (See Table 5.8):

- **Simple:** when an action acting on a component does not present synergy with other actions on the same factor or component.

- **Synergistic:** when an action acting on a component can present synergism with other actions on the same factor or component.
- **Very synergistic:** when it is evident or highly likely that an action acting on a component presents synergy with other actions on the same factor or component

Table 5.8. Value and range of qualification of Synergy in the evaluation of environmental impacts

Criteria	Rating range	Rating value
Synergy (SY)	Without synergism (simple)	1
	Synergist	2
	Very Synergic	4

5.3.7. Accumulation (AC)

This indicator accounts for the progressive increase the manifestation of an alteration on socio-environmental variable(s), considering a continuous and reiterated action. Accordingly, the impact can be single or cumulative (Table 5.9) (CONESA FERNANDEZ-VITORIA, 1997; TALUKDAR et al., 2023).

- Simple: it is the case in which the effect of the activity or impact does not produce cumulative effects.

- Cumulative: it is the case in which, as the action generating an impact is prolonged over time, its severity progressively increases, given the impossibility of the affected variable being able to recover in the same proportion as the action increases spatiotemporally

Table 5.9. The criteria, qualification range and rating value of the accumulation (AC) of moment in Environmental Impact assessment

Criteria	**Rating range**	**Rating value**
Accumulation (AC)	Simple	1
	Cumulative	4

5.3.8. Effect (EF)

This indicator refers to the cause-effect relationship or the manifestation of the effect on a socio-environmental variable because of an activity (See the Table 5.10) (CONESA FERNANDEZ-VITORIA, 1997; WIENS, John A.; PARKER, 1995).

- Indirect: occurs when the impact that is generated on a socio-environmental variable is a consequence of the interaction with another variable, in turn affected by the activity that is being carried out.
- Direct: occurs when the impact being evaluated is a consequence of the activity or action being carried out.

In the evaluation of environmental impacts, the distinction between direct and indirect effects plays an important role in assigning values. When an effect is direct or primary, i.e., it is produced immediately because of the action, it is assigned a value of (4). A clear example of this is the emission of carbon dioxide (CO2), which directly affects air quality in the environment.

On the other hand, indirect or secondary effects, which are more distant or mediate to the action, are assigned a value of (1). An illustrative case of an indirect effect could be the reduction of the index of native species in an area caused by the construction of surface oil installations. Although this impact does not arise immediately, its connection with the initial action is clear, justifying the assignment of a value that reflects its indirect character in relation to the main action. This differentiation in the assignment of values allows for a more precise and detailed evaluation of environmental impacts, considering their direct or indirect nature.

Table 5.10. The criteria, qualification range and rating value of the effect (EF) of moment in Environmental Impact assessment

Criteria	**Rating range**	**Rating value**
Effect (EF)	Indirect	1
	Direct	4

5.3.9. Frequency (FR)

This indicator addresses the regularity of manifestation of the effect, either cyclically or recurrently, unpredictably over time, or constant over time (CONESA FERNANDEZ-VITORIA, 1997; KAN & MILLER, 2022). Accordingly, the impacts, depending on their periodicity, can be:

- **Irregular and discontinuous:** are those whose effect or impact, which due to an action or activity manifests itself through irregular alterations in its permanence (Discontinuous) or those whose effect or impact manifests itself unpredictably over time and whose alterations it is necessary to evaluate them based on the probability of occurrence (See Table 5.11.).
- **Periodic:** it is that effect or impact that, due to an action or activity, manifests itself with an intermittent mode of action and continues over time.
- **Continuous**: is that effect or impact that, due to an action or activity, manifests itself through regular alterations in its permanence.

In assessing the permanence of environmental effects, specific values are assigned to reflect their temporal nature. Continuous effects are given a value of (4), indicating a constant presence over time. Those of a periodic nature, which manifest themselves at regular intervals, are given a value of (2). In the case of irregular effects, such as aperiodic and sporadic effects, an evaluation based on the probability of occurrence is introduced, assigning them a value of (1). However, when the relevance of the impact manifestation so requires, irregular effects may be rated with higher values, such as (2), (3) or even (4). The unpredictability of their occurrence can enhance the degree of manifestation of the effect, and this flexibility in assigning values allows for a more accurate assessment adapted to the temporal complexity of environmental impacts.

Table 5.11. The criteria, qualification range and rating value of the Accumulation of moment in Environmental Impact assessment

Criteria	Rating range	Rating value
Frequency (FR)	Irregular and discontinuos	1
	Periodic	2
	Continuous	4

5.3.10. Recoverability (RE)

This indicator pertains to the potential for complete or partial restoration of the affected factor due to the project, construction, or activity. It specifically addresses the feasibility of returning to the initial conditions before the action, facilitated by the implementation of environmental management measures (CONESA FERNANDEZ-VITORIA, 1997; JACKSON et al, 2015; CHENG, ZHANG, 2020). The criteria for defining recoverability are (See Table 5.12):

- **Immediately recoverable:** if the effects are recoverable through management measures, the affecting action immediately results.
- **Recoverable in the medium term:** if the recovery can occur through management measures after the event occurred, and in a period of no less than 1 year.
- **Mitigable:** if the corrective actions used mitigate the effects produced.
- **Irrecoverable:** if the consequences produced by the activities cannot be recovered through environmental management measures.

Table 5.12. The criteria, qualification range and rating value of the Recoverability (RE) of moment in Environmental Impact assessment

Criteria	**Rating range**	**Rating value**
Recoverability (RE)	Immediately recoverable	1
	Recoverable in the medium term	2
	Mitigable	4
	Irrecoverable	8

5.3.11. Aggregated Importance (I)

The Conesa methodology, designed to evaluate environmental impacts, is based on the weighting and rating of specific variables in the evaluation equation. The weighting values and rating ranges associated with each variable are derived directly from the rating and percentage weighting assigned to that variable in the methodology framework. It is important to note that this methodology is based on adjustments of values from other widely used methodologies.

Then, in terms of the aggregated importance (I) and the rating system, this study aims at combining the rating criteria described before. Hence, this aggregated importance depends on the extent of the impact, its intensity, its persistence, the effect, etc. In our study, we propose that importance should be defined as the sum of all the indicators, except the intensity that should be multiplied by three (3) and the extension that should be multiplied by two (2). This is because these two criteria are relevant in determining the significance of an impact. As the aim of this study is to stress environmental impacts, it highly weights those indicators more related to them, considering that the first challenge is the intensity of an impact, then its extension CONESA FERNANDEZ-VITORIA, 1997).

In particular, the extent variable is characterized by having a multiplier factor of 2, since the severity weighting of this parameter represents up to 24% in the equation. On the other hand, the intensity variable has a multiplier factor of 3, as it triples the weighting percentages assigned to the rest of the variables studied. This strategic approach reflects the relative importance of each variable in the overall assessment of environmental impacts, thus allowing for a more accurate and realistic weighting of the environmental effects of a specific action (Table 5.13 shows the parameter weighting).

The numerical values assigned to the parameters (1-12), (1-8), (1-4) in this case represent the units of importance within the evaluation system. These values provide a quantitative scale that allows weighting and ranking the relevance of each parameter in relation to others. The assignment of these numbers facilitates a more objective and structured evaluation, allowing a clear comparison of the relative importance of different factors within the analysis framework.

Table 5.13. Weighting value of qualitative criteria in the Conesa methodology

Variables		Rating range	Weighting percentage
IN	INTENSITY	1 – 12	23.1% - 36%
EX	EXTENSION	1 - 12	15.4% - 24%
MO	MOMENT	1-8	7.7% - 10%
PE	PERSISTENCE	1 - 4	7.7% - 10%
RV	REVERSIBILITY	1 - 4	7.7% - 10%

SY	SYNERGY	1 - 4	7.7% - 10%
AC	ACCUMULATION	1 -4	7.7% - 10%
EF	EFFECT	1 - 4	7.7% - 10%
FR	FREQUENCY	1 - 4	7.7% - 10%
RE	RECOVERABILITY	1 - 8	7.7% - 10%

The Conesa methodology equation for environmental impact assessment is based on key theoretical foundations of environmental impact assessment (EIA). First, it is based on the process of impact identification, where the possible adverse effects associated with a specific action are analyzed and recognized. Subsequently, it relies on the assessment and categorization of these impacts, evaluating their magnitude, importance, and nature.

The weighting of impacts constitutes another essential pillar of the methodology, assigning weighted values to each impact according to its relative relevance. The sum or aggregation of impacts is an integral process, where a weighted combination of the identified impacts is made to obtain an overall assessment of the environmental impact.

The definition of ranges and categories provides a qualitative framework for classifying impacts, facilitating the interpretation of the results. In addition, Conesa's methodology establishes correlations with other widely used methodologies, adapting and adjusting values based on previous experiences and accumulated knowledge in the field of environmental impact assessment.

The importance of the impact makes it possible to prioritize the impacts and thus determine the required environmental management actions. The formula used to determine the importance of the impacts is presented below (Equation 5.2):

$$\mathrm{IMPORTANCE\ (I)} = (3\mathrm{IN} + 2\mathrm{EX} + \mathrm{MO} + \mathrm{PE} + \mathrm{RV} + \mathrm{SY} + \mathrm{AC} + \mathrm{EF} + \mathrm{FR} + \mathrm{RP})$$ (Equation 5.2)

Table 5.13 summarizes the indicators for the evaluation of the impacts. Within each qualification criterion, there is an assessment that oscillates between 1 and 12, where the values are assigned according to the quantitative characteristics determined for each of the impacts.

Table 5.13. Weighting of criteria for assigning environmental impact risks in energy projects.

Criteria		Rating Value
INTENSITY (IN)	Low	1
	Half	2
	High	4
	Very High	8
	Total	12
EXTENSION (EX)	Punctual	1
	Partial	2
	Extensive	4
	Total	8
	Criticism	12
MOMENT (MO)	Long-Term	1
	Medium-Term	2
	Immediate	4
	Critical	8
PERSISTENCE (PE)	Fleeting	1
	Temporary	2
	Permanent	4
REVERSIBILITY (RV)	Short-Term	1
	Medium-Term	2
	Irreversible	4
SYNERGY (SY)	Without Synergism (Simple)	1
	Synergic	2
	Very Synergic	4
ACCUMULATION (AC)	Simple	1
	Cumulative	4
EFFECT (EF)	Indirect	1
	Direct	4
FREQUENCY (FR)	Irregular and discontinuous	1
	Periodic	2
	Continuous	4
RECOVERABILITY (RE)	Immediately recoverable	1
	Recoverable in the medium term	2
	Mitigable	4
	Irrecoverable	8
IMPORTANCE	Low	<25
	Moderate	25 to <50
	Severe	50 to 75

	Critical	>-75

In order quantify the indicators, initially, different sources of information were gathered, including scientific papers, field reports, and resolutions of State entities. To identify the most relevant literature contributions, a bibliometric analysis was performed using the VOSviewer tool of Scopus. VOSviewer is an analysis and visualization tool that is based on specialized network analysis and visualization techniques, providing the ability to graphically represent patterns and relationships within bibliometric and scientific datasets. The 100 most relevant references published from 2017 to 2023 were originally taken. The keywords used for this task were: environmental impact AND hydraulic fracturing AND unconventional reservoir, AND petroleum industry. The preliminary bibliographic study yielded the networks of the most prominent authors (Figure 5.10), also in the Figure 8 and in the Figure 9 the most common keyword interactions are observed. Once this information was filtered, 43 bibliographic references were studied to assign values to each parameter described in Table 5,15 (JACKSON et al., 2015; CHENG & ZHANG, 2020; GARAVITO et al., 2020; HOOGHIEMSTRA et al., 2022; BARRERO, 2007; BARRERO, 2007; AGENCIA NACIONAL DE HIDROCARBUROS, 2021; LOPEZ, 2019; AGENCIA NACIONAL DE HIDROCARBUROS, 2022; AGENCIA NACIONAL DE HIDROCARBUROS, 2023; FOX & LEFSRUD, 2021; VICKNAIR, TANSEY, & O'BRIEN, 2022; ECOPETROL, 2022; HERNÁNDEZ, 2022; UNIDAD DE PLANEACIOÓN MINERO-ENERGÉTICA, 2023; AGENCIA NACIONAL DE HIDROCARBUROS, 2023; RÍOS-OCAMPO, 2021; HENAO, and DYNER, 2020; LEE, XING, & LEE 2022; ECOPETROL-ANH, 2022; SANZ, 2021; TATOMIR et al., 2018; ZOBACK & KOHLI, 2019; ELLAFI, 2020; BELYADI, FATHI, BELYADI, 2019; ALI, 2020; ZHANG, 2019; KURNIADI, RYAN, HAMIDON, 2023; WANG, 2022; ESSIEN, WHITE, MOHAMMADI, 2022; CALDWELL, 2022; ZHOU, 2023; TAO, 2022; BADJADI, 2023; VENGOSH, 2014; SOEDER, 2018; HITICK & SREBOTNJAK, 2017; YAZDAN, 2020; ELLIOTT, 2017; HWANG, 2023; WANG, 2023; JIN, 2022; SHI, 2023). In turn, field reports and documents from governmental entities were evaluated to help in the numerical estimation.

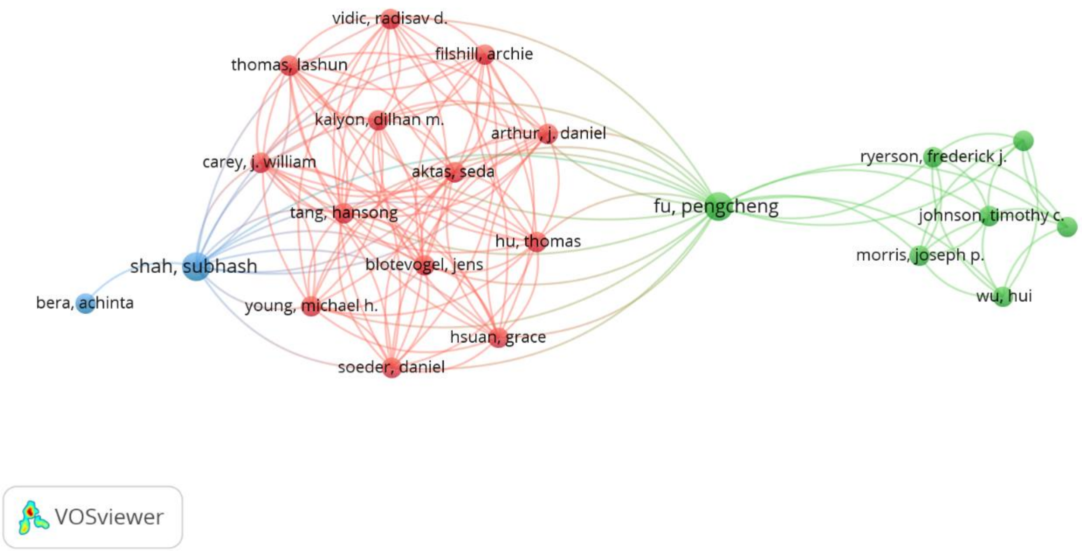

Figure 5.8. VOSviewer tool Scopus basic view.

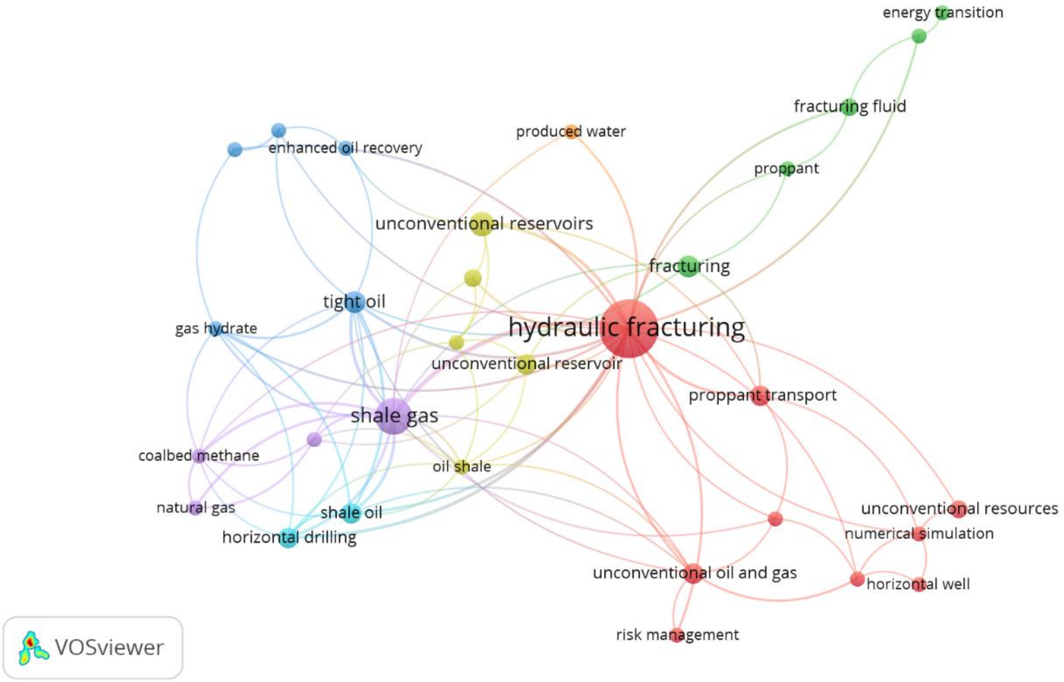

Figure 5.9. Keywords searched concerning environmental impacts and environmental complexity of the exploration and production chain of unconventional reservoirs.

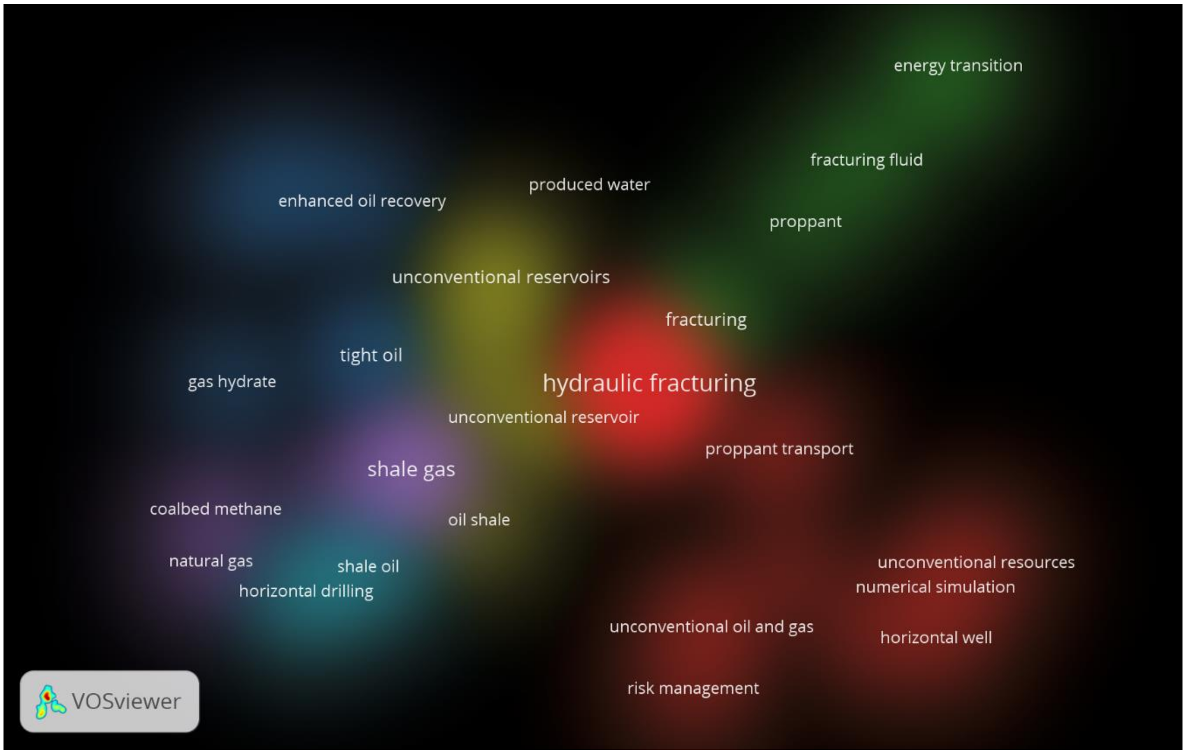

Figure 5.10. Heat map: keywords searched concerning environmental impacts and environmental complexity of the exploration and production chain of unconventional reservoirs.

Subsequently, a score is given for each of the parameters that were discretized. Finally, a simple sum is applied to determine the importance of the occurrence. Similarly, a spider diagram (Figure 5.8) is prepared to visually identify the criticality of an impact. The spider graphs of the environmental impacts can be found in **Appendix A.**

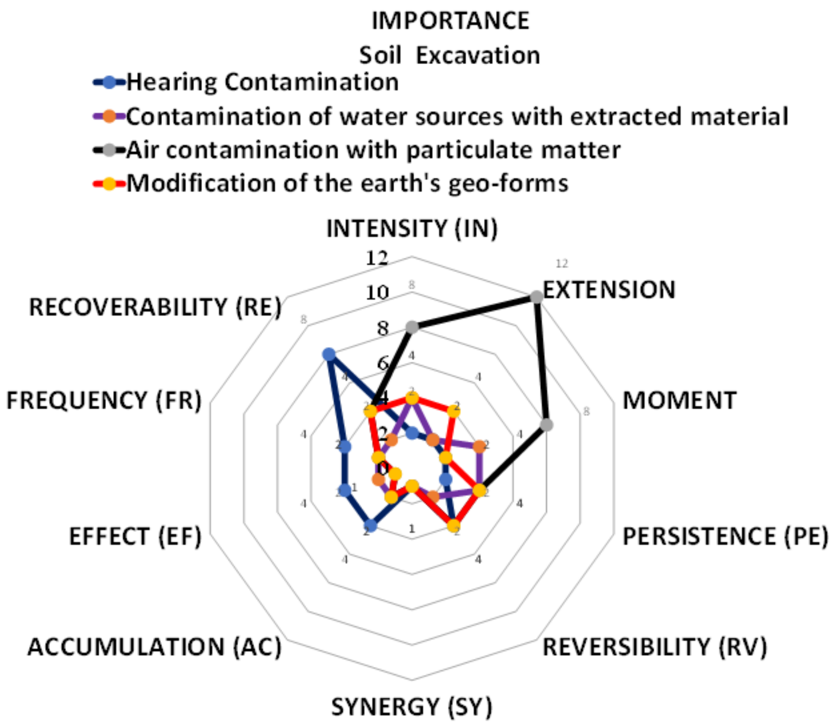

Figure 5.4. Spider graph of environmental impacts (Soil excavation), resulting from the Conesa methodology.

5.4. Results and discussions

Table 5.15 contains the environmental impact matrix for a possible unconventional petroleum production facility in the *La Luna* formation of Colombia.

Table 5.15. Matrix of environmental impacts on hydraulic fracturing in the Middle Magdalena Valley basin in Colombia (JACKSON et al., 2015; CHENG & ZHANG, 2020; GARAVITO et al., 2020; HOOGHIEMSTRA et al., 2022; BARRERO, 2007; BARRERO, 2007; AGENCIA NACIONAL DE HIDROCARBUROS, 2021; LOPEZ, 2019; AGENCIA NACIONAL DE HIDROCARBUROS, 2022; AGENCIA NACIONAL DE HIDROCARBUROS, 2023; FOX & LEFSRUD, 2021; VICKNAIR, TANSEY, & O'BRIEN, 2022; ECOPETROL, 2022; HERNÁNDEZ, 2022; UNIDAD DE PLANEACIOÓN MINERO-ENERGÉTICA, 2023; AGENCIA NACIONAL DE HIDROCARBUROS, 2023; RÍOS-OCAMPO, 2021; HENAO, and DYNER, 2020; LEE, XING, & LEE 2022; ECOPETROL-ANH, 2022; SANZ, 2021; TATOMIR et al., 2018; ZOBACK & KOHLI, 2019; ELLAFI, 2020; BELYADI, FATHI, BELYADI, 2019; ALI, 2020; ZHANG, 2019; KURNIADI, RYAN, HAMIDON, 2023; WANG, 2022; ESSIEN, WHITE, MOHAMMADI, 2022; CALDWELL, 2022; ZHOU, 2023; TAO, 2022; BADJADI, 2023; VENGOSH, 2014; SOEDER, 2018; HITICK & SREBOTNJAK, 2017; YAZDAN, 2020; ELLIOTT, 2017; HWANG, 2023; WANG, 2023; JIN, 2022; SHI, 2023).

Area	Activities	Description of the activity	Potential Impacts	Occurrence	Control measures
Building the primary phase of the project	Construction of access roads	Removal of natural plant cover	Deforestation	🟨	Reforestation with local plants
			Biodiversity loss	🟩	Sound contention wall
			Fauna displacement	🟩	Re-faunalization of the area, creation of animal preservation areas
			Changing soil properties	🟩	Organic matter filling, addition of carbonates and bentonites
		Soil Excavation	Hearing Contamination	🟩	Temporary retaining walls
			Contamination of water sources with extracted material	🟩	Gutter construction
			Air contamination with particulate matter	🟥	Periodic air quality measurements, installation of air purifiers in the region
			Modification of the earth's geo-forms	🟨	Backfilling of sedimentary material in situ
		Embankment construction	Terrain stability	🟥	Compensated and compacted fillings
			Restitution of removed soil	🟥	
	Construction of surface facilities	Removal of vegetation cover	Forest involvement	🟥	Forest restoration
			Fauna displacement	🟨	Revegetation with native plants
			Habitat alteration	🟨	Reforesting the area
		Soil Excavation	Destruction of the habitat of microorganisms	🟥	Install the extracted soil in a green area to avoid damage
			Air contamination by particulate material	🟨	Periodic measurement and air purification
			Soil instability	🟨	Soil fills with material like the soil in the region
	Mobilizing and assembling equipment on site	Transportation of machinery, equipment, and supplies.	Hearing Contamination	🟥	Sound walls
			Contamination of surface waters adjacent to the area due to chemical spillages.	🟨	Hydrological studies that indicate the effects on water dynamics and measures to correct the effects on them
			Particulate matter survey	🟥	Periodic air quality measurements, installation of air purifiers in the region
		Assembling the derrick, containers, waste pools, and fluid storage tanks.	Hearing contamination	🟩	Sound walls
			Wildlife displacement	🟥	Revegetation with native plants
			Solid waste generation	🟥	Transport of materials preferably to inert recovery and recycling facilities

Area	Activity	Description of the activity	Potential Impacts	Occurrence	Control measures
Drilling & Completion	Well drilling	Sand removal	Subsoil instability	🟨	Containment Structures
			Hearing contamination	🟩	Insulated walls
			Wildlife displacement	🟨	Revegetation
		Water consumption	Pressure on water resources, increasing scarcity rates	🟥	Reuse of urban wastewater with prior treatment
		Drilling Mud injection	Pollution of water sources and soil	🟨	Gutter construction. Pool of tailings and drill cuttings, for subsequent treatment and use as input for allowance. .
	Supply of wastewater boreholes and cuts	Solid particle generation	Soil pollution	🟨	Monitoring the volume of fluid contained in swimming pools. Acting on a mitigation plan.
		Generating wastewater with chemical content	Resource pollution	🟨	Implementation of more environmentally friendly chemicals
	Lining and cementing the well walls	Gas Leak	Air pollution	🟥	Records to confirm cement adhesion
			Groundwater pollution	🟥	High-quality cement between the walls of the well and the pipe
Hydraulic fraturating	Injection of water mixed with chemicals	Water consumption	Pressure on water resources, increase in the scarcity index	🟥	Reuse of urban wastewater with prior treatment
		Presence of chemical substances	Pollution of Water Resources	🟥	Treatment plants
	Fracture fluid return	Generation of heavy metals and radioactive materials of natural origin	Pollution of groundwater resources	🟨	Pipe integrity tests, cement and cement adhesion to the formation
		Filtering the fluid with chemical substances	Air and water pollution	🟨	Records to confirm cement adhesion
	Waste disposal in pools and tanks	Generation of wastewater contaminated with chemical substances	Pollution of Water Resources	🟥	Location of treatment stations, periodic measurement of water pollutant values and safety valve system to prevent flow of polluted fluid.
		Excess residual fluid	Pollution of soil and water sources adjacent to the area	🟨	Monitoring the volume of fluid contained in pools. Methodology for the

					constant disposal of waste ponds.
		Evaporation of minor constituents present in the fluid	Air pollution		Gas emission control network; strategies for reducing natural gas emissions; Systems for converting natural gas into energy (GTW Gas-To-Wire technology).
			Surface water pollution		Construction of gutters; water treatment for waste disposal, water treatment for livestock consumption and crops.

The application of the CONESA methodology in the evaluation of unconventional reservoirs has proven to be an effective approach to measure and evaluate the associated environmental impacts. Through this method, it was possible to break down the incidence of each effect into 10 specific variables, allowing a detailed understanding of the critical aspects. This decomposition facilitated the identification and proposal of more appropriate mitigation plans to address the challenges of unconventional reservoirs. However, it is important to note that the CONESA methodology requires a significant volume of data to make informed decisions. In the case of unconventional reservoirs, the limitation in the availability of specific data may affect the ability of the methodology to provide accurate details on mitigation measures. While this may present some limitations in the development of specific measures, the preliminary study using the CONESA methodology is still valuable in providing an overview of the process, paving the way for environmental licensing, and highlighting key areas that require attention in future research and data collection.

Results show that the most serious environmental concerns and areas of significant attention are water contamination, greenhouse gas emissions, air quality impacts, and landscape and land use changes. One of the primary points of concern is groundwater contamination. During the fracking process, substantial quantities of water, sand, and chemicals are injected at high pressure into the ground to fracture the rocks and release the hydrocarbons. There is a risk that some of these chemicals and fracking fluids could migrate into underground aquifers, potentially contaminating drinking water supplies. Studies indicate concerns on water contamination associated with fracking, including the presence of toxic chemicals and heavy metals in groundwater (VENGOSH, 2014; SOEDER, 2018; HITICK & SREBOTNJAK, 2017; YAZDAN, 2020; ELLIOTT, 2017). Nevertheless, the magnitude and frequency of these occurrences vary depending on location and fracking practices. Mitigation measures for such impacts include return flow fluid management, which involves the proper handling of return flow fluids containing potentially contaminating chemicals and materials. Research suggests that reusing and treating these fluids can reduce the risk of water contamination (HWANG, 2023; WANG, 2023; JIN, 2022; SHI, 2023; WU, 2023; JIANG, 2022). Additionally, well monitoring, which entails the rigorous monitoring of wells before, during, and after the fracking operation, can help identify and prevent potential leaks and contamination (GHOLAMI, RAZA, IGLAUER, 2021; GUO et al 2022; SIDDIQUA, HAHLADAKIS, AL-ATTIYA, 2022; PRESLO, 2021; VAVERKOVÁ, 2022).

Similarly, the hydraulic fracturing process and unconventional oil and gas production release greenhouse gases into the atmosphere, including carbon dioxide (CO_2) and methane (CH_4). Methane is significantly more potent than CO_2 in the short term, making it a significant concern for climate change. The technical literature has shown that methane emissions associated with fracking can be considerably high if proper management practices are not implemented (WILSON, 2023; BRAUERS, 2022; SOEDER, 2021; ZHANG, RUPP, GRAHAM, 2021; MENG; 2022). These emissions can result from leaks in wells, equipment, and pipelines, as well as intentional releases during well purging. Accurate quantification of these emissions is an evolving area of study. In terms of impact mitigation strategies, controlling leakage through the application of technologies and practices to reduce methane leakage from wells, equipment, and pipelines is fundamental. Early detection and repair of leaks can minimize emissions. Additionally, implementing emissions regulations, which involves adopting stricter regulations and standards to limit methane emissions, is essential. The technical documents provided for the construction of the matrix support the effectiveness of these actions in reducing greenhouse gases (KUEPPERS, 2004; HOLZ-RAU & SCHEINER, 2019; GILLINGHAM, KENNETH, JAMES, 2018; THIEL, WOODS, BILEC, 2018; MOHSIN, 2021).

Fracking can also bring negative impacts on local air quality. The operation of heavy equipment, natural gas combustion, and fugitive emissions contribute to the release of air pollutants, such as nitrogen oxides (NOx) and volatile organic compounds (VOCs), which can have adverse effects on human health and the environment. The presence of air pollutants has been identified in areas near fracking operations, leading to concerns about the exposure of local communities to health risks (ALLSHOUSE et al., 2019; JOHNSTON & CUSHING, 2020; BOLDEN et al., 2018; WOLLIN et at., 2020). In this case, impact mitigation strategies are divided into two categories. The first involves emission control technologies, such as low-emission burners and capture devices – for example, selective catalytic reduction options for NOx (LIBORIUS PARADA, 2019; BELLO-ÂNGULO et al., 2022). The second is minimum distances. Establishing minimum distances between fracking operations and populated areas can help reduce the exposure of local communities to air pollutants (TRAN et al., 2021; JOHNSTON et al., 2021; BANAN & GERNAND, 2021).

Regarding changes in landscape and land use, the development of infrastructure for unconventional oil and gas extraction, such as drilling platforms and roads, can have a significant impact on the landscape and land use. This can result in the fragmentation of natural habitats and the degradation of wilderness areas. To mitigate these environmental impacts, proper planning of fracking operations and infrastructure consolidation can minimize the fragmentation of natural habitats and reduce the impact on the landscape. Similarly, post-fracking restoration suggests that effective restoration of areas affected by fracking can help mitigate long-term impacts (HOLLOWAY, 2018; SELENT, 2023; XU, 2018).

Flowback water management in hydraulic fracturing is an important element in environmental risk assessment and in the formulation of mitigation plans. This process involves the return to the surface of the water used during fracturing, bringing with it a complex mixture of chemical components, some of which are deliberately added during operation. The complexity of this fluid makes its treatment a challenging and costly task, especially considering that an in-situ treatment plant is required. This significant investment highlights the importance that the industry must assign to the responsible management of flowback water, not only from an economic perspective but also from an environmental sustainability approach.

Also, one of the most critical and sensitive aspects of hydraulic fracturing is the possibility of contaminating aquifers. Aquifers, vital sources of drinking water, are resources that must be protected as a priority. Hydraulic fracturing involves the injection of pressurized fluids into the subsurface, raising concerns about the possible migration of chemicals into the water table. This risk is accentuated by geological variability, aquifer heterogeneity and the complexity of subsurface flow. The prevention of aquifer contamination therefore becomes an imperative task that requires rigorous control and monitoring measures to ensure the protection of these vital resources.

It is important to highlight that the CONESA methodology, when applied in the evaluation of unconventional reservoirs, plays a central role in the identification and quantification of environmental risks associated with hydraulic fracturing. The creation of a matrix that encompasses the entire exploration and production chain facilitates a detailed understanding of the potential impacts at various stages of the process. In this context, flowback water management and prevention of aquifer contamination stand out as key elements assessed by the CONESA methodology. The results obtained from this matrix become fundamental inputs for environmental impact studies, providing detailed and specific information that will guide decision making in policy formulation and environmental licensing processes.

The application of CONESA not only contributes to a deeper understanding of the risks associated with unconventional reservoirs, but also establishes a basis for the adoption of more sustainable and responsible practices. The methodology not only addresses environmental challenges in isolation, but integrates a holistic perspective that considers economic and social aspects. In the specific case of flowback water management, the CONESA matrix offers a framework for the identification of specific mitigation measures, thus providing practical guidance for the implementation of responsible flowback water treatment and management strategies.

In terms of environmental care, however, responsible water management stands out. The use of large quantities of water in the hydraulic fracturing process highlights the importance of its sustainable management, focusing on the reduction of consumption, reuse and adequate treatment of flowback water.

In addition, the adoption of advanced technologies and the implementation of emission reduction practices are crucial to minimize these effects and preserve air quality in the surrounding areas.

Also, proper waste management is also an essential point. The generation of solid and liquid wastes during drilling and hydraulic fracturing operations requires rigorous measures for their management and disposal. The application of recycling practices, safe treatment and responsible disposal are fundamental aspects to avoid negative impacts on the environment.

5.5. Final Remarks.

The environmental impact matrix applied by this study allowed the preliminary evaluation of the impacts associated with hydraulic fracturing projects in unconventional reservoirs. The information contained in the matrix can be used for other projects in Latin America and worldwide.

The main results of this study applied to La Luna in Colombia indicates that the most challenging impacts include water contamination, deforestation and the emission of greenhouse gases. First, water contamination has emerged as one of the most worrisome issues related to oil development in the La Luna region. Unconventional oil extraction operations often involve the intensive use of chemicals and the generation of large volumes of contaminated wastewater, which can compromise groundwater and surface water quality, negatively affecting local flora and fauna, as well as nearby human communities.

In addition, deforestation and natural habitat degradation represent another critical environmental challenge. The expansion of infrastructure related to oil development, such as road construction and the installation of drilling rigs, has led to the loss of sensitive habitats and biodiversity in the La Luna watershed. This alteration of the natural environment can have lasting impacts on the local ecology and delicately balanced ecosystems.

Another challenging impact is the emission of greenhouse gases and their contribution to climate change. Oil extraction in the unconventional La Luna basin involves the release of greenhouse gases during extraction and processing operations, which can exacerbate global warming and its associated consequences, such as rising temperatures, changes in weather patterns and extreme weather events.

The application of the CONESA methodology proves to be a comprehensive and effective tool to address the guiding questions of this work, providing a matrix of environmental impacts that highlights the negative risks associated with hydraulic fracturing in unconventional reservoirs. This matrix, resulting from the detailed analysis contemplated by CONESA, provides a holistic view of potential impacts along the exploration and production chain. In line with the questions posed, environmental risks are identified and quantified, with special attention to critical aspects such as flowback water management, possible contamination of aquifers and other adverse effects.

The highlight of the CONESA methodology is its ability to go beyond the simple identification of risks by proposing general mitigation measures within the same environmental impact matrix. This proactive approach allows not only to recognize environmental challenges, but also to address them with specific strategies designed to minimize negative effects. The inclusion of these measures in the matrix consolidates the methodology as a comprehensive tool that not only assesses, but also guides towards practical and applicable solutions.

Despite the lack of some important data, such as the quality of crude oil produced, CONESA demonstrates its usefulness in responding to the need to categorize the impacts of hydraulic fracturing. The ability of the methodology to adapt to scenarios where information may be limited highlights its versatility and its ability to provide meaningful results even under conditions of uncertainty. This translates into a valuable preliminary tool for environmental assessment, highlighting critical areas and allowing informed decision making even in situations where complete information may not be available.

In summary, it is important to recognize and address these challenging environmental impacts of oil development in the unconventional La Luna basin in Colombia. If the country´s energy plan prioritizes developing unconventional resources, careful planning and the implementation of sustainable practices are required to mitigate these negative effects and promote an appropriate balance between resource exploitation and environmental conservation for present and future generations.

However, it is worth stressing that the Conesa methodology has limitations related to its simplified methodological structure. In our case, the quantification of indicators was based on the literature, while on a more technical and bottom-up approach it could have been based on specific studies for the La Luna formation. In addition, the aggregation of impacts could have been based on a more structured multicriteria analysis, for example an AHP method. Therefore, this study should be viewed as a preliminary assessment that needs to be followed by in-field studies.

6. Conclusion of the Thesis

Firstly, the main findings of each chapter will be summarized. Then, main conclusions will be highlighted to address the research questions compiled in the introduction of the thesis.

CHAPTER 2

The study confirms that conventional oil reserves in Colombia are depleted, and the country faces a reserve to production ratio estimated in five years. This situation highlights the pressure to seek new sources of energy resources and convert them into proven reserves to ensure the sustainability of the oil industry in Colombia.

The work focuses on the evaluation of the technical and economic feasibility of producing a source rock Tight Oil reservoir, which implies the exploration of unconventional resources. This option represents an important opportunity for Colombia in its quest to guarantee oil supply.

The feasibility assessment relies on critical parameters, including technical factors like fracture shape factor, fracture propagation, and fracture pressure. Economic factors, such as international oil prices, petrophysical characteristics, fluid properties, drilling costs, completion, and fiscal regime, are also considered.

The study identifies the production potential in the Tight Oil reservoir located in the Middle Magdalena Basin, indicating the feasibility of oil extraction from this geological formation. It is emphasized that project feasibility is strongly influenced by key decisions related to well completion, drilling techniques, and the costs associated with resource extraction. These decisions must be carefully considered in both the planning and execution phases of the project.

CHAPTER 3

Assessing the stability and precipitation tendency of asphaltenes in oil is essential to ensure a steady flow. For this purpose, various experimental and numerical methods have been proposed to predict the risk of precipitation**.**

Assessing asphaltenes' stability and precipitation tendencies for maintaining a consistent flow of oil. Additionally, it clearly states that various experimental and numerical methods have been suggested to predict these risks.

Once the risk of asphaltene precipitation is established, strategies can be developed to prevent and diagnose deposition problems during production or well training. These strategies are critical to ensure continuous flow and efficient production.

This paper highlights the importance of addressing the problem of asphaltene precipitation in the oil industry and provides an overview of approaches ranging from understanding asphaltene stability to the application of nanoparticle chemical techniques to mitigate this problem. Effective asphaltene management is crucial to ensure the efficiency and continuity of oil production.

CHAPTER 4

Through a detailed analysis of the current literature, it has become evident that the application of nanomaterials in this area represents an innovative and effective strategy to overcome the challenges associated with fines migration and deposition in the hydrocarbon industry.

Nanotechnology offers various tools and approaches, from nanofluids to functionally modified nanoparticles, which have proven to be highly efficient in inhibiting and remediating damage caused by fines migration. These advances not only improve the efficiency of oil and gas production in unconventional reservoirs, but also contribute significantly to environmental sustainability by reducing the need for more invasive traditional practices.

In addition, the importance of understanding the nano-level interactions between nanotechnological agents and reservoir fines has been highlighted. The ability to selectively control the mobility of fines through surface engineering and manipulation of physical properties at the nanoscale underscores the transformative potential of nanotechnology in this specific application.

CHAPTER 5

The objective of the research is to provide valuable information to policy makers, regulators, and industry stakeholders in Colombia. This allows them to make informed decisions on the development of unconventional oil and gas resources, balancing the need for energy resources with the preservation of the environment.

The study also contributes to the global dialogue on the environmental implications of hydraulic fracturing in regions with sensitive ecological conditions. This suggests that lessons learned in Colombia may be relevant to other areas of the world facing similar challenges.

This research emphasizes the importance of responsible management of environmental risks associated with hydraulic fracturing in Colombia. It provides critical information to make balanced decisions to take advantage of unconventional resources while protecting the country's natural environment. In addition, the study contributes to the global conversation about the sustainability of the oil and gas industry in ecologically sensitive contexts.

During this doctoral research, three main research questions were proposed (see Introduction), aiming at evaluating the exploitation of unconventional reservoirs in Colombia. These questions with some adjustments could also be elaborated to other countries facing the challenge of decreasing conventional petroleum production and fiscal and energy increasing dependence.

Therefore, these questions were formulated for exploring the main aspects related to challenges and opportunities of the unconventional petroleum exploitation, focusing on disruptive technologies, environmental impacts, as well as technical and economic strategies in the development of unconventional reservoir fields.

The first question, "*What are the challenges and technologies involved in the development of unconventional reservoirs?"* was comprehensively addressed. This research revealed a profound understanding of the technical challenges inherent for the exploitation of unconventional reservoirs in Colombia, as well as the emerging technologies that have evolved to face these challenges. This has resulted in the consolidation of valuable knowledge for the industry.

In fact, chapters 3 and 4 provided answers to this question by highlighting that the development of unconventional reservoirs faces distinctive challenges requiring advanced technological solutions. In this case, nanotechnology emerges as an innovative response to address specific issues in the production of these reservoirs. Notably, the application of nanoparticles has demonstrated potential in mitigating sand production, a prevalent challenge in such reservoirs. The manipulation of nanoparticle properties and control of z-potential enable their effective use in stabilizing formations and preventing sand migration into the wellbore.

Furthermore, nanotechnology offers solutions for asphaltene precipitation in porous media by facilitating their solubilization in crude oil. This capacity to dissolve asphaltenes contributes to optimizing production by appropriately reducing the flowing bottomhole pressure (Pwf), thereby enhancing extraction efficiency in unconventional reservoirs. Consequently, the strategic application of nanotechnology to these specific challenges can play a pivotal role in improving the productivity and efficiency of unconventional reservoirs.

In a global scenario increasingly focused on innovation and sustainability, it is imperative that emerging countries like Colombia adopt a proactive approach to developing Research and Development (R&D) in strategic sectors, especially in the exploitation of unconventional reservoirs. Exclusive dependence on technology imports can undermine energy autonomy and the ability to adapt to specific challenges.

On the other hand, the traditional geological analogy may not be sufficient to fully comprehend the complexity of unconventional reservoirs, necessitating a more refined and innovation-oriented approach. Investment in internal R&D would enable Colombia to cultivate local technical and scientific expertise, allowing it to address the unique challenges presented by these reservoirs.

Instead of merely being a passive importer of technology, Colombia should adopt an energy planning strategy centered on actively promoting research and innovation. This involves strategic partnerships between the government, academic institutions, and industry to drive R&D programs. These collaborations could result in the creation of centers of excellence dedicated to the study of unconventional reservoirs, providing specialized knowledge and solutions adapted to the Colombian context.

An effective strategy must also address issues related to regulation, tax incentives and energy policies that favor investment in R&D. By creating a favorable environment for innovation, Colombia can attract local and international talent, promoting the transfer of knowledge and technology.

When assessing the maturity of the industry and academia in Colombia regarding nanotechnology applied to asphaltenes, sand prevention, and hydraulic fracturing, an encouraging scenario unfolds. The adoption of nanoscale technologies presents opportunities to optimize processes and address specific challenges in the exploitation of unconventional reservoirs. The intersection between industry and academia in Colombia demonstrates significant progress, with researchers and professionals collaboratively working to implement innovative solutions.

The application of nanotechnology to address challenges related to asphaltenes, sand prevention, and hydraulic fracturing not only showcases the adaptability of the Colombian industry but also underscores academia's commitment to the continuous exploration of more efficient and sustainable approaches. This collaborative effort serves as evidence of the country's potential to spearhead advancements in technologies applied to the hydrocarbon sector, emphasizing a critical synergy between academic research and the practical needs of the industry.

Concerning the second question, *"What are the potential environmental impacts of the exploitation of unconventional reservoirs and what are the possible solutions to mitigate these impacts?"*, significant findings have been presented by this thesis. Actually, Chapter 5 not only identified the potential environmental impacts deriving from the unconventional petroleum activities in Colombia, but also proposed specific solutions and strategies to mitigate these adverse effects, thereby contributing to the sustainable development of the industry.

The exploitation of unconventional reservoirs involves various environmental impacts that require careful evaluation and effective mitigation. The Conesa methodology has proven to be suitable for assessing environmental impacts in this context, providing an understanding of the impacts of petroleum activities on biodiversity, air, soil, and water quality, among other aspects.

Regarding aquifer contamination, a primary risk associated with the exploitation of unconventional reservoirs, it is crucial to implement preventive and corrective measures. Identifying and consistently monitoring potential sources of contamination, along with the application of geological and chemical barriers, are key practices to mitigate this risk. The adoption of advanced technologies, such as well casing and early detection systems, can significantly contribute to preventing the infiltration of contaminants into underground aquifers.

For the treatment of flowback water, a viable and sustainable solution involves the implementation of advanced water treatment systems. Technologies like reverse osmosis, thermal evaporation, and biological methods enable the recovery and treatment of flowback water, thereby reducing the risk of surface water body contamination and ensuring its reuse in future operations. Continuous improvement in treatment technologies can enhance the efficiency and cost-effectiveness of these practices.

Additionally, the restoration and rehabilitation of affected areas form an integral part of potential solutions. Implementing reforestation and ecological restoration programs in impacted areas can help mitigate the long-term effects on biodiversity and natural habitat.

It is essential that Colombia adopts a balanced approach, integrating a solid regulatory framework, incentives for technological development and robust environmental standards.

In terms of regulation, it is necessary to establish a clear regulatory environment to encourage investment in the exploitation of unconventional reservoirs. Transparent licensing guidelines, operational safety regulations and clear parameters for environmental responsibility are essential steps. Specific tax incentives for companies that invest in R&D can stimulate local innovation.

In technological development, Colombia must invest in research and collaborations between government, industry and academic institutions. Fostering technologies adapted to the Colombian reality will optimize the exploitation of unconventional reservoirs, ensuring efficiency and sustainability. In addition, promoting the transfer of technology and the training of specialized professionals will contribute to a solid technical base.

With regard to environmental standards, Colombia must adopt a proactive stance in defining and enforcing strict rules. Establishing clear criteria for monitoring and mitigating environmental impacts is crucial to ensuring responsible exploitation. However, inflexibly imposing technologies can limit innovation, so creating an adaptable regulatory environment and robust standards is more effective.

Similarly, concerning the third question *"What is the optimal production strategy for unconventional reservoirs?"*, Chapter 2 tried to help answering it, by showing that the optimal production strategy for unconventional reservoirs involves the implementation of advanced techniques that maximize hydrocarbon recovery in an efficient and sustainable manner. In this context, planar fracture hydraulic fracturing has been identified as playing a crucial role in maximizing production from an emblematic unconventional reservoir in Colombia.

Significantly, this study has shown that in order to maintain stable production over time fracture and re-fracture become an effective strategy. As the original fractures close over time, periodic application of additional fracturing becomes crucial to maintain a steady flow of hydrocarbons to production wells. This approach not only prolongs reservoir life but also ensures continuous, optimized production.

Another essential component of the strategy is the creation of a "well factory." This involves drilling multiple wells in a specific formation, each connected to a fracturing system. Interconnecting these wells allows a more efficient reservoir management and helps maximizing the project's Internal Rate of Return (IRR) and Net Present Value (NPV).

The potential to extract resources from unconventional reservoirs represents a significant opportunity for Colombia's energy planning. This development can diversify the country's energy matrix, reducing dependence on traditional sources and strengthening energy security. The exploration of unconventional reservoirs offers the possibility of increasing self-sufficiency, generating employment and fostering economic development, while contributing to fiscal revenues through taxes and royalties. However, it is essential to address the associated environmental and social challenges, implementing effective mitigation measures and meeting sustainable standards. A balanced approach that considers both the benefits and negative impacts will ensure that unconventional resource extraction contributes effectively to energy resilience and meeting long-term environmental goals.

Therefore, this doctoral thesis constitutes a significant contribution to the energy planning landscape in Colombia, particularly in the context of developing unconventional reservoirs. The insights derived from this research not only enhance our comprehension of the technical and environmental complexities associated with these reservoirs but also offer valuable guidance for the Colombian government's energy planning decisions.

During a period where the diversification of energy sources is imperative for the country's sustainability and energy security, the detailed and well-supported information presented in this thesis establishes a robust foundation for evaluating the potential and challenges of unconventional reservoirs in the Colombian context. These findings can serve as a roadmap for the formulation of policies and strategies aimed at maximizing economic and energy benefits while minimizing the environmental impacts associated with these operations.

When assessing the maturity of the industry and academia in Colombia regarding nanotechnology applied to asphaltenes, sand prevention, and hydraulic fracturing, an encouraging scenario unfolds. The adoption of nanoscale technologies presents opportunities to optimize processes and address specific challenges in the exploitation of unconventional reservoirs. The intersection between industry and academia in Colombia demonstrates significant progress, with researchers and professionals collaboratively working to implement innovative solutions.

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In conclusion, this doctoral thesis not only adds valuable knowledge to energy planning in Colombia but also exemplifies the dynamism and collaboration between academia and industry in the adoption of advanced technologies. The information presented equips the Colombian government to make informed decisions that foster the sustainable development of energy resources, taking into careful consideration the technical, economic, and environmental aspects associated with unconventional reservoirs.

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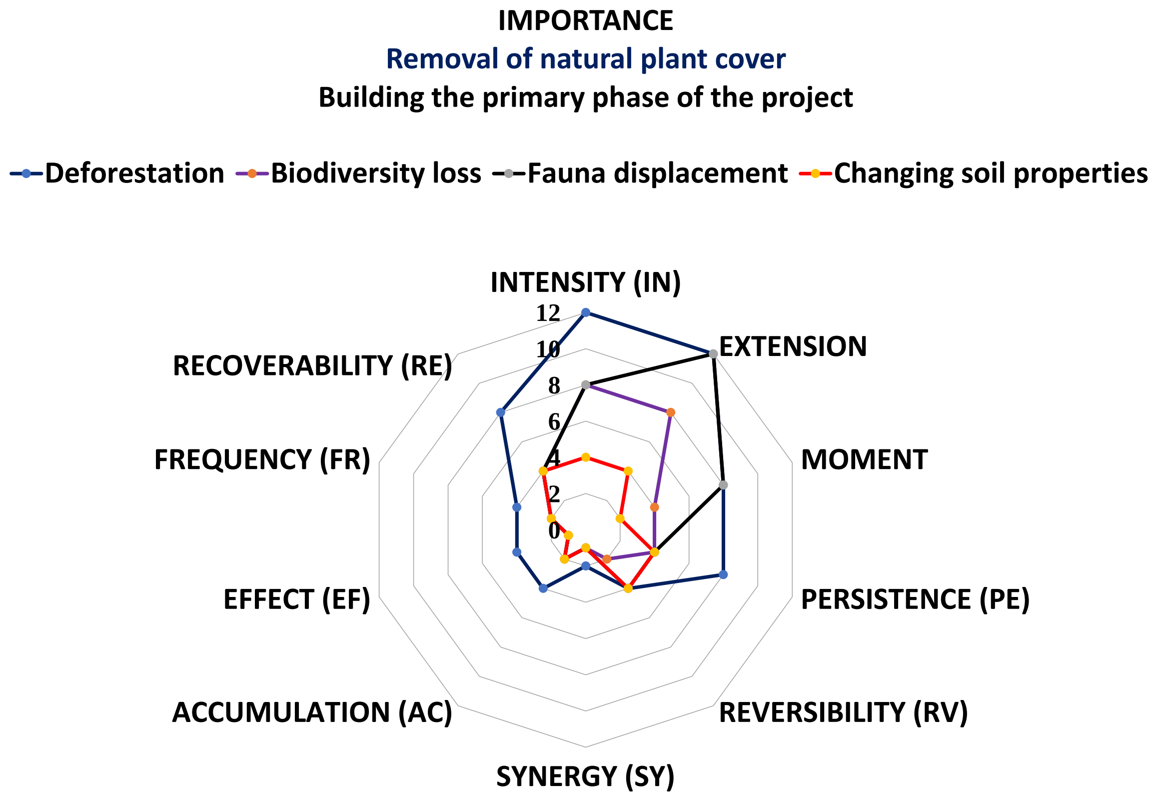
APPENDIX A


IMPORTANCE
Removal of natural plant cover
Building the primary phase of the project
Deforestation
Biodiversity loss
Fauna displacement
Changing soil properties
INTENSITY (IN)
EXTENSION
MOMENT
PERSISTENCE (PE)
REVERSIBILITY (RV)
SYNERGY (SY)
ACCUMULATION (AC)
EFFECT (EF)
FREQUENCY (FR)
RECOVERABILITY (RE)
12
10
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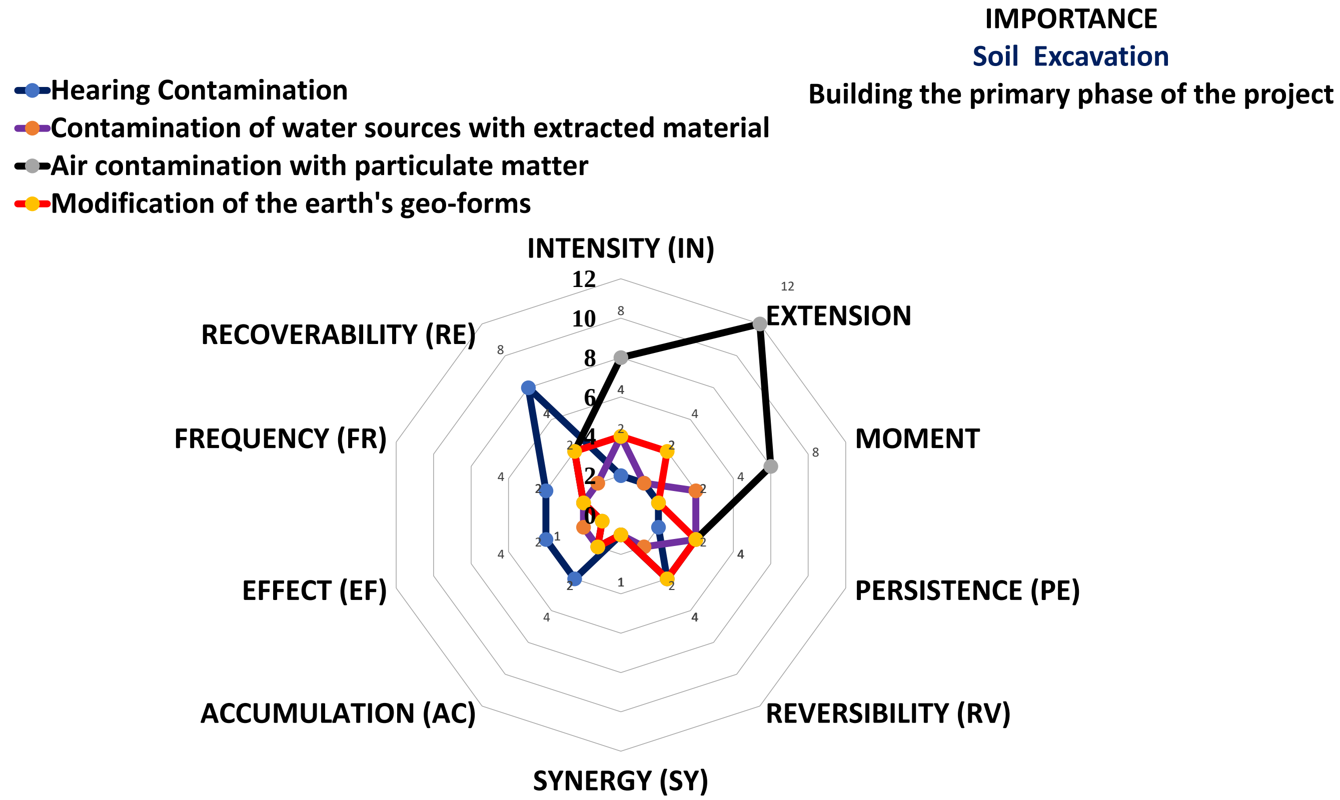
IMPORTANCE
Soil Excavation
Building the primary phase of the project
Hearing Contamination
Contamination of water sources with extracted material
Air contamination with particulate matter
Modification of the earth's geo-forms
INTENSITY (IN)
EXTENSION
MOMENT
PERSISTENCE (PE)
REVERSIBILITY (RV)
SYNERGY (SY)
ACCUMULATION (AC)
EFFECT (EF)
FREQUENCY (FR)
RECOVERABILITY (RE)
12
10
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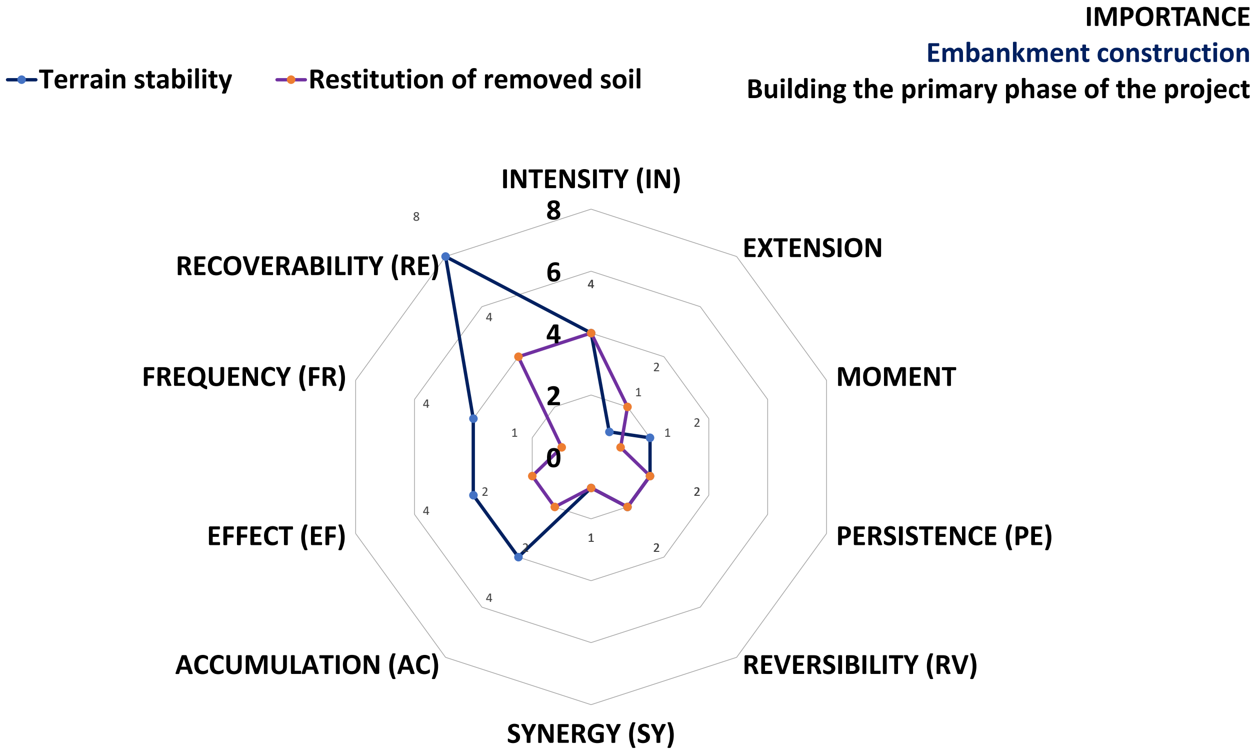
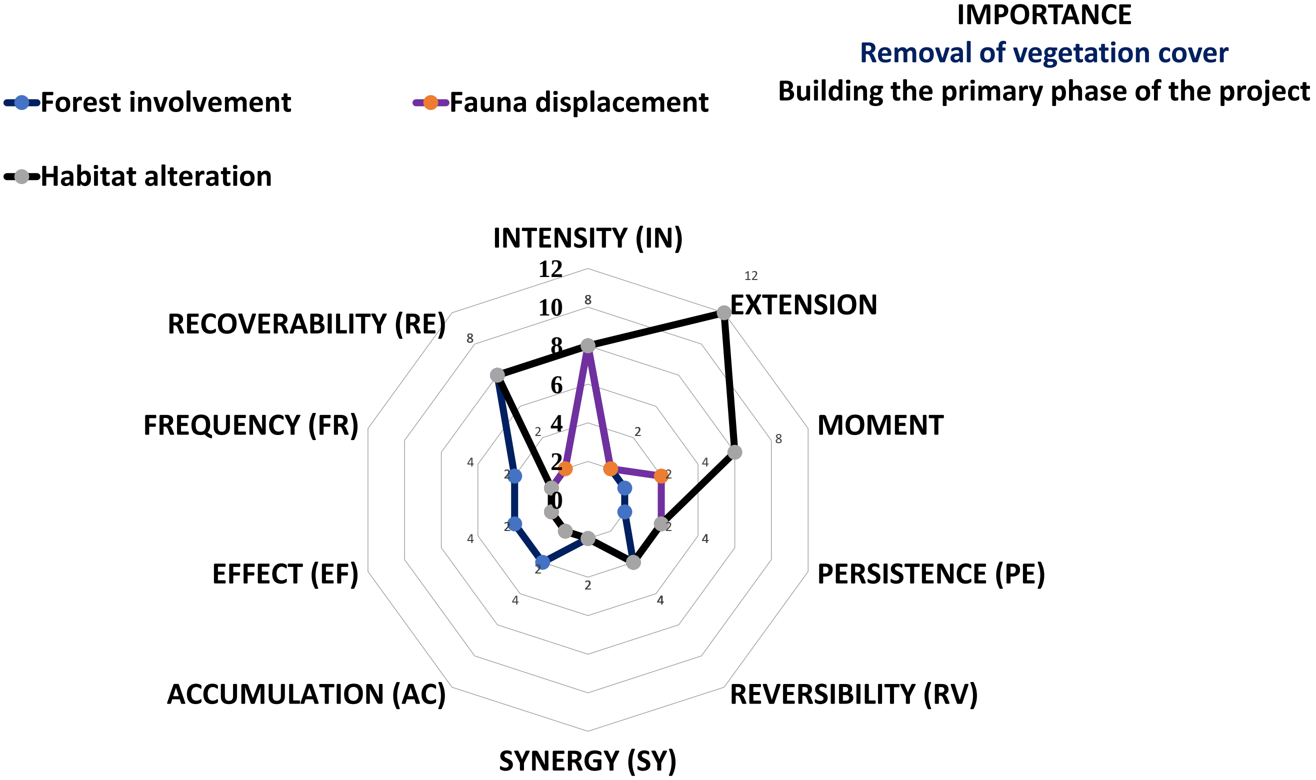
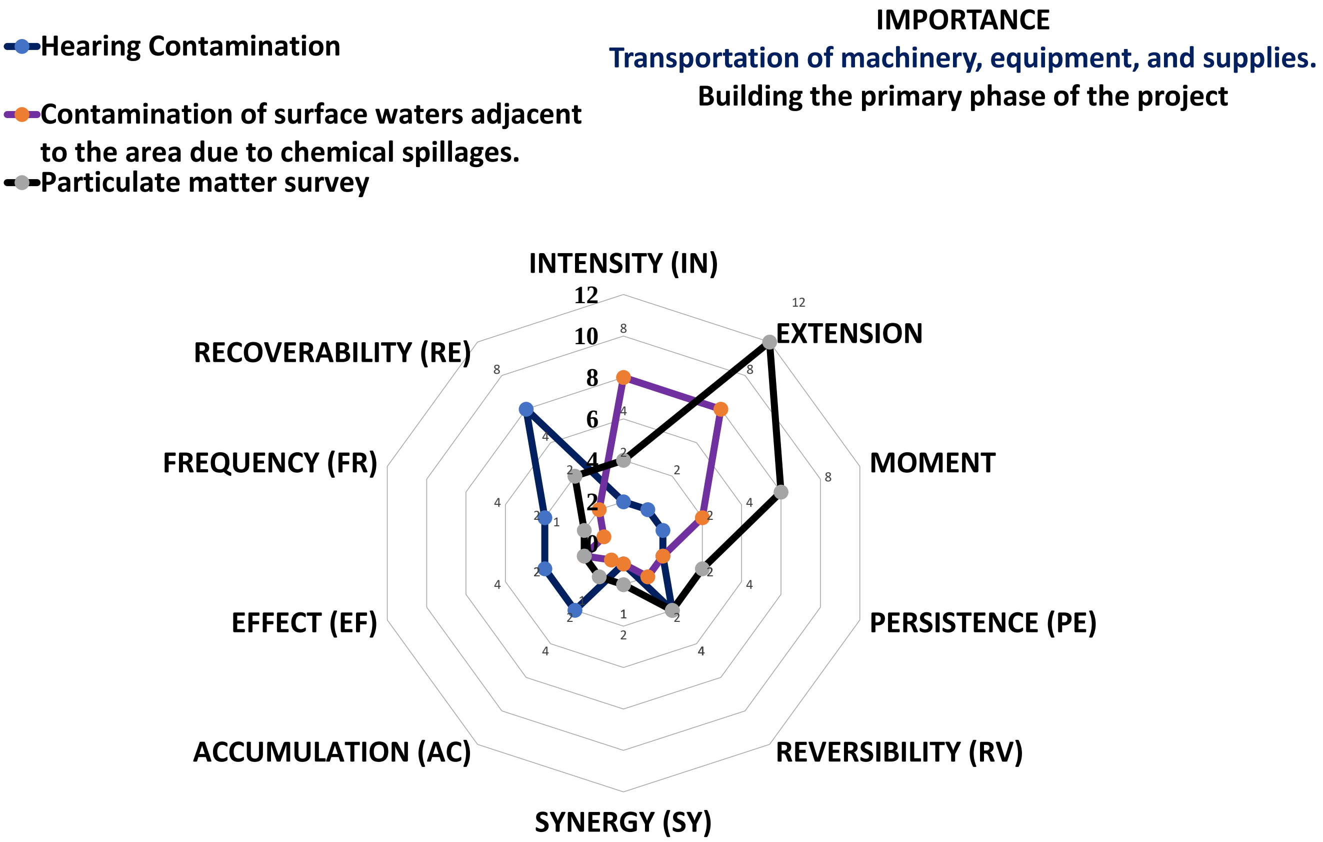


IMPORTANCE
Embankment construction
Building the primary phase of the project



IMPORTANCE
Removal of vegetation cover
Building the primary phase of the project



IMPORTANCE

Transportation of machinery, equipment, and supplies.

Building the primary phase of the project