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Escuela de Ciencias Químicas e Ingeniería

Título: Material selection for oil production processes based on actual Ecuadorian oil reserves characteristics

> Trabajo de integración curricular presentado como requisito para la obtención detítulo de Petroquímico(a)

Autor: BASTIDAS GONZALEZ, RICHARD NELSON

**Tutor:** PhD. VILORIA VERA DARIO ALFREDO **Co-Tutor:** PhD. MARVIN JOSE RICAURTE

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DARIO Dr. VILORIA VERA, DARIO ALFREDO, Ph.D. ALFREDO VILORIA VERA 19:39:47 -05'00' Tutor

Hacienda San José s/n y Proyecto Yachay, Urcuguí | Tlf: +593 6 2 999 500 | info@yachaytech.edu.ec





Dr. PALMA CANDO, ALEX URIEL , Ph.D. Miembro No Tutor CARLA SOFIA YASELGA NARANJO

YASELGA NARANJO, CARLA Secretario Ad-hoc

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# Dedication

This work is dedicated to my family, specially to my parents!

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I would like to say thanks to my parents because they are my support for every achievement that I have achieve. They are my motivation and my inspiration.

I would like to say thanks to all of my family, because they always believe in me.

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### Resumen

En la actualidad, los yacimientos de crudo en Ecuador contienen crudo más pesado que los que se procesaban cuando se construyeron las facilidades de producción, tales como campos para la exploración del petróleo, oleoductos, refinerías, etc. La declinación natural de yacimientos conllevo a un aumento de la producción de agua, lo que impacto considerablemente a la confiabilidad y continuidad operacional; por lo tanto, los problemas de corrosión en todo el proceso involucrado desde el campo petrolífero hasta el producto final han aumentado. Una adecuada selección de materiales, así como el uso de tratamientos químicos deben ser considerados desde las etapas de diseño; considerando como principal campo petrolero el campo Sacha, las características de su crudo y las condiciones de operación a las que será sometido el material. Para este estudio fue necesario analizar los posibles problemas de corrosión que se pueden presentar. Para la determinación de la formación de escamas se utilizó el modelo Langelier y el modelo Stiff-Davis, considerando las condiciones de boca de pozo, en cuyo caso se descartaron con base en los valores obtenidos de -0,04 y 0,11 respectivamente. Para la determinación de la corrosión por CO<sub>2</sub> se utilizaron los modelos De waar-Milliams y De waard-Lotz, en cuyo caso se desarrolló y utilizó un perfil de presión y temperatura para obtener los valores estimados para cada punto del pozo de producción. Según De waar-Milliams, las velocidades de corrosión varían de 1,25 mm / año a 39,73 mm / año y según De waard-Lotz pueden variar de 4,40 mm / año a 58,62 mm / año; en ambos casos los valores obtenidos representan un problema operacional inminente, por lo que es necesario considerar el uso de una tubería de acero de altas prestaciones. Según la Tabla de Selección de Materiales propuesta por Vera de DNV.GL con una presión parcial de CO2 del orden de 10<sup>2</sup> y una presión parcial de H<sub>2</sub>S insignificante, el material que se recomienda utilizar es el 13-Cromo.

*Palabras claves:* CRA's, cloruros, H2S, datos PVT, métodos de producción, integración subsuelo-superficie, carga frontal.

## Abstract

Nowadays, Ecuador's crude oil reservoirs contain heavier crude oil than those processed when production and processing facilities, such as oil fields exploration, pipelines, and refineries. The natural decline of reservoirs increases the water production, which significantly impacted reliability and operational continuity; therefore, the corrosion problems in all of the oilfield processes to the final product have increased. An adequate material selection and the chemical treatment usage have to be considered from the design steps, considering Sacha oilfield as the principal oilfield in Ecuador and its crude oil characteristics and its operational conditions to which the material will be subjected. For this study was necessary to analyze the possible corrosion problems that could present. Langelier model and Stiff-Davis model were used for scale formation determine, considering wellhead conditions, in which case were discarded based on the values obtained of -0.04 and 0,11 respectively. De waar-Milliams and De waard-Lotz models were used for CO<sub>2</sub> corrosion determine, in which case a pressure and temperature profile were developed and used in order to obtain the estimated values for each point of the production well. According to De waar-Milliams the corrosion rates varies from 1,25 mm/yr to 39,73 mm/yr and to De waard-Lotz it can varies from 4,40 mm/yr to 58,62 mm/yr; in both cases the values obtained represent an inminent operational problem, for this reason the use of a high-performance steel pipe is necessary to be considered. According to Material Selection Table propoused by Vera from DNV.GL with a  $CO_2$  partial pressure in the order of  $10^2$  and a negligible H<sub>2</sub>S partial pressure the material that is recommended to be used is 13-Chrome.

*Keywords:* CRA's, chlorides, H<sub>2</sub>S, CO<sub>2</sub>, PVT data, production methods, subsurface-surface integration, front end loading.

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# **ABBREVIATIONS**

GE	Specific Gravity
BSW	Basic Sediments and Water
Т	Temperature
GOR	Gas to Oil Ratio
Boi	Volumetric Factor of the Oilfield
TDS	Total Disolved Solids
pHs	Saturation pH
pCa	Negative Logarithm of Calcium Concentration
pHCO₃	Negative Logarithm of Bicarbonate Concentration
p <i>Ksp</i>	Negative Logarithm of Solubility Product Constant
pK <sub>2</sub>	Negative Logarithm of the Bicarbonate Ionization Constant
K	Constant of Salinity
LSI	Langelier Saturation Index
ISSD	Stiff-Davis Saturation Index
pAlk	Negative Logarithm of Alcalinity
Si	Ionic Strength
Zi	Ion Valence
Ci	Ion Concentration
$f_g^{co_2}$	Fugacity of CO <sub>2</sub>
$y_g^{CO2}$	The CO <sub>2</sub> Molar Fraction in the Gas Phase
$y_t^{CO2}$	The CO <sub>2</sub> Molar Fraction in the Surface
$C_{aq}^{CO2}$	The CO <sub>2</sub> Concentration in Aqueous Phase

CRt	Corrosion Rate (De waard-Milliams Model)
Vcr	Corrosion Rate (De waard-Lotz Model)
Vr	Independent Flow Contribution
Vm	Dependent Flow Contribution
U	Liquid Flow Rate
Dh	Hydraulic Diameter
PCO <sub>2</sub>	Partial Pressure of CO <sub>2</sub>
MMscf	Million Standard Cubir Feets
BWPD	Barrels of Water per Day
BOPD	Barrels of Oil per Day
BFPD	Barrels of Fluid per Day

## **CHAPTER 1: INTRODUCTION**

#### **1.1 PROBLEM STATEMENT**

The Ecuadorian recovery factor has changed over time because the principal methods of production have to be changed based on the production decline. Initially, the production method was by hydraulic push. Nowadays, recovery methods such as water reinjection have to be used specially in the principal oilfields such as Sacha located at Ecuadorian east in the Orellana province in order to maintain its production. The change of the recovery factor and an inadequate material selection can increase the corrosion problems presented in the different pipelines, process equipment or deposits, producing the deterioration of the facilities and even catastrophic events. Nowadays, Sacha oilfield represents the country's highest income in terms of oilfields, and according to its reserves, it will continue representing. Its actual reserve has changed across time as everywhere. Therefore, for this reason, an analysis of its current conditions is necessary to determine the correct material selection for future projects.

#### **1.2 OBJECTIVES**

#### **1.2.1** GENERAL OBJECTIVE

Study and identify the impact of the recovery factor on the corrosion behavior in Sacha oilfield facilities in order to determine the suitable material selection.

#### **1.2.2** Specific Objectives

- Study the hydrocarbon industry's present situation, oil reserves globally, and Ecuadorian oilfields' current and future situation.
- Study the Sacha oilfield impact on the country's economy, its chemical composition of crude oil and the operational conditions.

- Study and analyze the possible corrosion problems presented in Sacha oilfield, by using the principal corrosion identification models.
- Analyze and interpret the results obtained to propose the correct material to be used in future Sacha's wells based on the results obtained.

## **CHAPTER 2: BACKGROUND**

#### 2.1 CORROSION IN THE HYDROCARBON INDUSTRY

Corrosion is one of the principal problems in the hydrocarbon industry from the beginning, representing one of the major losses of money and generating possible catastrophic disasters.

According to NACE's basic manual, "Corrosion is the deterioration of a material, especially metals resulting from its contact with the environment" (NACE, 2014).

The fight with the corrosion problems in the oil industry can present in different sceneries and by different factors that can be external or internal. The external factor is the environment, which begins in the oilfield and finishes in the refinery location. The internal factors depend on the crude oil's chemical characteristics, especially in chlorides content,  $CO_2$  or  $H_2S$  content.

According to the Chemical review "Corrosion – The longest war", the corrosion maintenance for BP represents from 25 to 30% of their operational cost. This is an important data to consider because engineers need to have present that it can increase depends on the environmental conditions, such as it is the Ecuadorian case.

According to the actual Petroecuador EP annual budget in 2015, the money earmarked for operation and maintenance service is 577.285,738 USD as it is shown in the Annex A.

Corrosion is extremely important for the hydrocarbon industry, especially if the economic and financial aspects are considered because it represents inspections and maintenance costs or even if the environmental impact is considered. There are two types of associated costs, one that is directly related to corrosion and the other indirect related to it. There are costs such as maintenance, loss of production, product contamination, cost of overdesign or environmental penalties for the first type. The indirect ones are security, the collapse of nearby structures, leaks or indirect product contamination. Corrosion cannot be avoided, but it can be controlled, and its impact can be reduced. There are different ways, but the principles are using good chemical protection and the correct material selection based on the environmental conditions, the operational conditions and the crude oil characteristics to control the main corrosion problems presented.

#### 2.1.1 PRINCIPAL CORROSION PROBLEMS IN HYDROCARBON INDUSTRY

#### 2.1.1.1 CO<sub>2</sub> CORROSION

 $CO_2$  corrosion is one of the most common corrosion problems in the hydrocarbon industry, and it could be known as sweet corrosion. It can be produced by different possible sources such as formation fluids, aeration, make-up water, or bacterial activity. In most cases, it is caused when the  $CO_2$  has contact with the production or transportation water, and the principal affected areas are the internal well section or the transport lines.



FIG. 1. CO<sub>2</sub> CORROSION MECHANISM (VILORIA, 2014)

The reaction between  $CO_2$  and water gives carbonic acid, which is a weak acid. Then, the dissociation reaction occurs rapidly, especially at high temperatures, and finally, the reaction with iron occurs to produce ferrous carbonate. The formation of a ferrous carbonate scale on the surface generates iron passivation, which gives way to corrosion.

According to the NACE standards, the partial pressure of  $CO_2$  is an essential parameter to determine if corrosion by  $CO_2$  will be present, as shown in Table. 1.

TABLE. 1. PROBABILITY OF CORROSION BASED ON CO<sub>2</sub> PARTIAL PRESSURE (CASTELLAN, 1987)

Partial pressure of CO <sub>2</sub> (bar)	Probability of corrosion	
< 0,5	Less probable	
$0,5 < Pco_2 < 2$	Possible	
>2	Assured	

This kind of corrosion can be controlled with the use of inhibitors or corrosion-resistant alloys, commonly known as CRA's.

#### 2.1.1.2 H<sub>2</sub>S CORROSION

 $H_2S$  corrosion is one of the most common corrosion problems in the hydrocarbon industry, and it could be known as acid corrosion. It can be produced by different possible sources such as formation fluids, the degradation of drilling muds, or bacterial activity.



FIG. 2. H<sub>2</sub>S CORROSION SCHEME (HIMIPEX OIL LTD, 2015)

The hydrogen sulfide can affect any part of the production system at the moment of contact with water, and it is necessary to have a concentration of 5 ppm in the formation water to consider the production fluid as acid.

When the hydrogen sulfide reacts with different iron oxides to form iron sulfides, those iron sulfides increase the corrosion velocity. When iron sulfides precipitate, micro galvanic cells can form, which generates localized corrosion such as pitting or cracks. This corrosion problem can be controlled by using specific materials, which can form an organic film to sequester  $H_2S$ . Other options can be metals resistant to sulfur stress corrosion, nitrate treatments or biocides.

#### 2.2 CRA'S

"CRA is an alloy intended to be resistant to general and localized corrosion or environmental cracking in environments that are corrosive to carbon and low-alloy steels" (ISO 13680). Corrosion-resistant alloys' principal objective is to control corrosion in the well, and they are chosen because chemical inhibition is not practical. The normative requirements are the API5CRA and NACE MR0175. The principal CRA's that are available for the hydrocarbon industry are Martensitic Stainless Steels, Duplex Stainless Steel and Nickel Alloys. In order to determine if it is necessary to use a corrosion-resistant alloy is important to analyze the following factors: H<sub>2</sub>S partial pressure, CO<sub>2</sub> partial pressure, chloride content, produced water rate, bicarbonate content, free sulfur content and the operational parameters because all of these components determine the corrosion impact.

One of the principal materials used in the hydrocarbon industry is the high-performance steels to supply the necessity and the high demands concerning productivity, reliability and security. High-performance steels increase the structure's lifetime and increase production time, which is essential in the hydrocarbon industry and reduces maintenance costs.

## CHAPTER 3: SACHA'S OILFIELD

#### **3.1 SACHA'S OILFIELD**

The Sacha Oilfield known as the block 60, which is located in the Orellana province at the northeast of the Ecuadorian Amazonia. It is delimited by Eno-Ron oilfield at the north, Culebre-Yulebra oilfield in the south, Shushufindi at the east and Paraiso at the west as it is shown in the Fig. 3.



#### FIG. 3. SACHA'S OILFIELD LOCATION

(ANNUAL REPORT OF THE HYDROCARBON POTENTIAL OF ECUADOR 2018) Directly cited from: <u>https://www.recursosyenergia.gob.ec/wp-content/uploads/2019/11/Informe-</u>

Anual-del-Potencial-Hidrocarburi%CC%81fero-del-Ecuador-2018.pdf

This oilfield has been operated by Petroecuador EP since 2021. However, Sacha oilfield was discovered by the Texaco-Gulf consortium in 1969 and immediately passed to be one of the most important oilfields in Ecuador. Sacha currently produces 71,400 barrels per day. This is why it is considered one of the "jewels of the corona" of the Ecuadorian oil sector. Sacha is referenced as one of the most productive oilfields in the Ecuadorian Hydrocarbon industry.

According to the Annual Report of The Hydrocarbon Potential of Ecuador 2018, the total oil reserve in Ecuador is 2,695 million barrels divided into 1,632 million barrels of proved reserves, 314 million barrels of probable reserves and 749 million barrels of possible reserves. The 88.33% of the total oil reserve in Ecuador is managed by the public company Petroamazonas EP. This percentage comprises 1,390 million barrels of proved reserves, 259 million barrels of probable reserves and 731 million barrels of possible reserves. Based on the data shown in Fig. 4 and Fig. 5 Sacha's Oilfield play an important role in the Ecuadorian hydrocarbon industry.



#### ECUADORIAN TOTAL PROVED RESERVES

FIG. 4. TOTAL PROVED RESERVES PER ASSET (ANNUAL REPORT OF THE HYDROCARBON POTENTIAL OF ECUADOR, 2018)





According to Fig. 4 and Fig. 5 Sacha has the biggest proved reserve in Ecuador with 291,9 million barrels with a production of 66.473 barrels per day and an annual income of 1370 million dollars in 2018. These numbers make Sacha the oilfield with the highest income in Ecuador even it does not have the highest daily production. This highest income can be credited to its crude oil characteristics, which are better than in the other oilfields.

Based on the data given by the annual report of the hydrocarbon potential of Ecuador, Sacha has 419,06 million barrels between proved, probable and possible reserve, which represent the 15.55% of the total oil reserve in Ecuador. Therefore, the study of Sacha oilfield is necessary to know its current condition and the best way to optimize and take advantage of the field resources and preserving its facilities.



FIG. 6. ACTUAL CONDITION OF SACHA FIELD RESERVES (ANNUAL REPORT OF THE HYDROCARBON POTENTIAL OF ECUADOR, 2018)

According to Fig. 6 Sacha field has 125.72 million barrels approximately to explode, which with a constant production represents more than 5 years of life time.

Nowadays, water reinjection method is used in the different wells in Sacha field in order to increase the oil recovery. This increase at the same time the probability of corrosion based on the formation water characteristics and the environment; because open system used for reinjection water generate corrosion by microorganism, corrosion by CO<sub>2</sub> or by the chlorides present in the formation water. These corrosion problems lead to the abandonment of a well such as SAC-100 (Landazuri, 2015).

The Sacha oilfield conditions, the projection for the future and corrosion problems presented motivate the engineers to analyze the chemical control used and the metallurgy selection, because the downhole conditions, the crude oil characteristics and the environmental conditions are affecting and increasing the corrosion problems presentes in the processes involved in the hydrocarbon industry from the downhole to the final consumer.

#### **3.2 GEOLOGICAL STRUCTURE OF SACHA'S OILFIELD**

Sacha oilfield is formed by an asymmetric low relief anticline failed to the west; the field is cut by fault that originates in the basament and which probably controled the sediments deposition. The oilfields in Ecuador in the eastern basin are related to the mesozoic era between the lower, medium and upper cretaceous that correspond to the Hollin, Napo and Basal Tna formation as it is shown in he stratigraphic column in the Fig. 7 (Romero and Gomez, 2010).





<sup>(</sup>BABY ET. AL, 2013)

The four main strata of the stratigraphic column are Hollin, Napo T, Napo U and Tena; their importance is based on their content of crude oil and gas.

The Basal Tena lithology is composed by sandstone with a porosity of 19 percent, no average permeability, recovery factor from 20-30 percent, and no gas-oil relation. Napo is divided into two sections Napo U, and Napo T. Napo U is composed basically of sandstone and shale with a porosity of 17 percent, an average permeability of 210 MD, a recovery factor of 39 percent and a gas and oil relation of 220, which means that is suitable for gas production. Napo T is composed of sandstone, shale and limestone with a porosity of 14 percent, an average permeability of 325, a recovery factor of 33 percent and a gas-oil relation of 325. Finally, the most important is Hollin, which is composed of sandstone. It has an average porosity of 16 percent, an average permeability of 690, a recovery factor of 33 percent and a gas-oil relation of 14; this means that the principal strata of interest is Hollin, because it is where the crude oil comes from for production (Romero and Gomez, 2010).

The percentage of water and the average salinity percentage are important aspects of the oilfield when a production project is running. The Basal Tena has an average salinity from 24000 to 36000 ppm Cl<sup>-</sup> and a 31 percent of water saturation. The Napo U has an average salinity from 25000 to 45000 ppm Cl<sup>-</sup> and 25 percent of water saturation. Napo T has an average salinity from 20000 to 25000 ppm Cl<sup>-</sup> and 14.8 percent of water saturation. Finally, Hollin has an average salinity from 500 to 3500 ppm Cl<sup>-</sup> and 35 percent of water saturation (Romero and Gomez, 2010).

#### **3.3 SACHA'S OIL CHARACTERISTICS**

The crude oil characteristics are absolutely important to determine how to treat the crude oil and the production method that will be used. The principal characteristics are the API gravity, the specific gravity, the viscosity and the water&sediments percentage, as shown in the Table. 2. In Sacha Oilfield's case, it is divided in two principal zones are South Sacha and North Sacha.

Characteristics	South Sacha	North Sacha	
API°	26,9	25,2	
GE	0,895	0,903	
Viscosity (cp at 80°F)	50,6	58,74	
Viscosity (cp at 120°F)	13,54	21,63	
BSW (%)	35,38	56,61	

TABLE. 2. SACHA'S CRUDE OIL CHARACTERISTICS (FERNANDEZ AND GAIBOR, 2009)

#### 3.4 PVT DATA

The pressure, volume and temperature are important parameters to be considered when oilfields are producing because they are the initial operation condition considered when the production method will be selected. In Sacha oilfield, the PVT data is divided based on the different formations shown in Table. 3.

	Reservoir				
Parameter	BT	U	Т	Hs	Hi
Temperature (°F)	181	219	221	225	225
Initial pressure (psi)	3587	4054	4146	4450	4450
Bubble pressure (psi)	870	1170	1310	550	80
GOR (SCF/B)	150	284	389	93	93
API°	24,1	22,8	30,3	27,3	29,7
Boi (BY/BN)	1.117	1.2302	1.3726	1.1334	1.1625

TABLE. 3. PVT DATA SACHA OILFIELD (ROMERO AND GOMEZ, 2010)

#### **3.5 FORMATION WATER COMPOSITION**

The formation water is the one that is coming from the reservoir, from lateral formations such as aquifers or the reinjection process known as secondary recovery. It is a big percentage of the production fluid, especially in the actual crude oil characteristics. The composition of the formation water can be different in each producing well based on the different kinds of geological formations, the treatment of the crude oil, the production method and the chemicals used. In general, this water has many minerals in the saturation limit, and when they go beyond, they can generate scale.

	com obilion (	<i>cindele</i> , <b>2</b> , <b>1</b> , <i>i</i> ,
Property	Unids	Value
Total Hardness	ppm	2200
Calcium Hardness	ppm	1800
Magnesium Hardness	ppm	400
Alkalinity	ppm	350
Na <sup>+</sup>	ppm	5759
Calcium ion	ppm	720
Magnesium ion	ppm	96
HCO <sub>3</sub>	ppm	434
Iron ion	ppm	4,5
Sulfate ion	ppm	3
Cl <sup>-</sup>	ppm	10200
pH		6,33
TDS	ppm	17223
Temperature	°F	127
CO3 in brine	ppm	330
H3S in brine	ppm	1,5
Disolved oxygen	ppb	10
Haze	NTU	23,4
SST	ppm	29
Oil in brine	ppm	22,3
Residual Fosfate	ppm	27

TABLE. 4. FORMATION WATER COMPOSITION (CARRILLO, 2017)

## **CHAPTER 4: METHODOLOGY**

To make the correct material selection for a production well in an specific oilfield in this case Sacha's Oilfield was necessary to follow the steps described in Fig. 8. First, it was necessary to study and determine three important factors, which are the actual industry situation, the principal corrosion problems presented in the hydrocarbon industry and determine the oilfield to be studied (case study). Second, it was necessary to find all the available information about the operational conditions and oilfield characteristics in order to analyze them and identify the possible corrosion problems that could present. Third, based on the possible corrosion problems and on the available oilfield data and characteristics, the principal correlation models used to determine corrosion in oil production were considered and selected. In the case of scale formation prediction Langelier saturation index was used and the Stiff-Davis saturation index was used to reconfirm and compare with the LSI obtained. In the case of CO<sub>2</sub> corrosion prediction De waard-Milliams and De waard-Lotz models were used in order to obtain the corrosion rate and know the CO<sub>2</sub> impact in the pipeline used. Finally, with both results the material selection diagram shown in Fig. 10 was used to determine the adequate material for Sacha's Oilfield conditions and stream, and contrasted with the actual material used in Sacha's oilfields which is based on API 5L GRB.



FIG. 8. METHODOLOGY DIAGRAM

#### **4.1 SCALE FORMATION PREDICTION**

Different models can predict the scale formation to determine the fouling potential in the different oil fields. The principal methodology used for Scale formation prediction is based on the saturation conditions evaluated by a saturation index or saturation grade. The saturation index allows engineers to calculate and determine the scale formation capacity based on the formation water's physical-chemical characteristics. Nowadays, the saturation index can be determined by different mathematical models that evaluate the effects caused by the variation of pH, temperature, pressure in the formation water to generate solid deposits. The principal methods used are the Langelier Saturation index, Stiff-Davis index and Oddo-Tomson index.

#### 4.1.1 LANGELIER SATURATION INDEX (LSI)

The Langelier saturation index gives the grade of Saturation of the formation water concerning calcium carbon formation. The formation water is part of the production fluid, which is why it is absolutely important to consider it to discard this incrustation in all production lines. Langelier can be interpreted as the change in pH required to reach the water equilibrium. In other words, is the difference between the current pH and the saturation pH necessary to avoid changes in the composition.

This saturation index model's main restriction is that the Langelier Saturation model is valid with constant temperature for moderate salinity and systems with pH<9. This model takes the K<sub>2</sub> (second dissociation) and the Ksp (constant of the product solubility) as values that only depend on the ion concentration, which means that they do not depend on the temperature, pressure or the ionic force. Another important point to consider is that the pH values used are taken at the wellhead not at the downhole, which in the oil production case is the most critical point considering that it has a different and higher temperature. Finally, it does not consider the presence of other ions such as  $Mg^{2+}$ ,  $Ba^{2+}$  or the presence of  $CO_2$ ; for this is necessary to consider the concentrations of each ion present in the solution (Villafañe, 2010).

The (Eq. 1) represents the Langelier equation used for the calculus of the saturation pH. This equation involves the negative logarithm of the calcium concentration (pCa), the concentration of bicarbonate (pHCO<sub>3</sub>) and the equilibrium constant (pK).

$$pH_s = pCa + pHCO_3 - pK \qquad (Eq. 1)$$

This equation can be expressed in terms of the negative logarithm of the bicarbonate ionization constant  $(pK_2)$  and the negative logarithm of the solubility product constant (pKsp), which is the (Eq. 2).

$$pH_s = (pK^2 - pKsp) + pCa + pAlcalinity$$
 (Eq. 2)

Therefore, the saturation index is the determinate by (Eq. 3).

$$IS = pH - pH_s \tag{Eq. 3}$$

This model will be used to determine in a quality way if there will be bicarbonate scale formation based on the value obtained of the LSI. According to the Langelier model, when the index value obtained is negative, there is no forming incrustation because the CaCO<sub>3</sub> is going to be dissolved by the water. When the index value obtained is positive the formation of the incrustation is going to happen, which means that the CaCO<sub>3</sub> is going to precipitate. Finally, when the value obtained is equal to zero this means that the system is in equilibrium.

#### 4.1.2 STIFF-DAVIS SATURATION INDEX (ISSD)

The Stiff-Davis saturation index is an extension of the Langelier index to determine the formation of incrustations of CaCO<sub>3</sub> produced by the formation water of the oilfields. This model allows engineers to predict the tendency to deposit CaCO<sub>3</sub> in order to overcome limitations produced by the water with high solid content and its impact on the scale formation. Stiff Davis index is based on the saturation level concept, but the solubility product is modified empirically. This index calculation is recommended, especially for oilfields.

This model used three equations that are an extension of the Langelier model to obtain the saturation index.

$$ISSD = pH - pH_s$$
 (Eq. 4)

This equation is the last used to determine the Stiff-Davis index (ISSD), which is the difference between the saturation pH calculated and the formation water's real pH. The saturation pH is calculated by the (Eq. 5), including the K constant of salinity which can be determined by using the correlation between the molar ionic strength and the temperature shown in Fig. 9, which is in the literature available for Stiff-Davis saturation index calculation, the composition and the temperature of formation water (Villafañe, 2010).



FIG. 9. CORRELATION FOR K VALUES DETERMINE (PATTON, 1995)

$$pH_s = K + pCa + pAlk \quad (Eq. 5)$$

Therefore, the Stiff-Davis equation can be expressed and used as the (Eq. 6).

$$ISSD = pH - K - pCa - pAlk \qquad (Eq. 6)$$

The K value is determined by using the correlation (Fig. 9) between the ionic force and the temperature of formation water. For the calculus of the ionic force (Si) the (Eq. 7) is used in which the Ci is the concentration of ions in mole per liter and the Zi is the ion valence.

$$Si = \frac{1}{2} \left( C_{1} Z^{2} + C_{2} Z^{2} + \dots + C_{n} Z^{2} \right) \quad (Eq. 7)$$

The Stiff-Davis saturation index interpretation is the same as the Langelier saturation index, which will allow engineers to predict CaCO<sub>3</sub> incrustations.

#### 4.1.3 ODDO-TOMSON SATURATION INDEX

The Oddo-Tomson index model is widely used in the Hydrocarbon Industry for scale formation determine, but in this study is not used because the program for this calculations which is the ScaleCorr 6.0 could not be used, because lack of license. It is described in the based on it importance in the Hydrocarbon Industry. This model includes corrections for the fugacity effects and the changes in CO<sub>2</sub> solubility, considered a function of the temperature, pressure and percentage of water with an additional improvement which is that the pH is not necessary. The restrictions that this model has been three. The first one is that de ionic force has to be between 0 to 4; the temperature has to be between 0 to 200°C, and finally, the pressure has to be between 0 to 20000 psig. The Oddo-Tomson index calculus is based on four equations for biphasic fluid and three equations for monophasic (Villafañe, 2010). In the case of biphasic systems, the next four equations (Eq. 8), (Eq. 9), (Eq. 10) and (Eq. 11) are used to determine the formation of incrustations produced by CaCO<sub>3</sub>. These equations involved new terms such as the fugacity of CO<sub>2</sub> ( $f_g^{CO2}$ ), the CO<sub>2</sub> molar fraction in the gas phase ( $y_g^{CO2}$ ), the CO<sub>2</sub> molar fraction in the surface ( $y_t^{CO2}$ ), the ionic force (Si), the million standard cubic feet produced in standard conditions (MMscf), the barrels of water daily produced (BWPD) and the barrels of crude oil daily produced (BOPD).

In the case of monophasic systems two equations (Eq. 12) and (Eq. 13) are used for determine the saturation index and one new value is added, which is the CO<sub>2</sub> concentration in aqueous phase ( $C_{aq}^{CO2}$ ). And when the pH is measured, engineers can use the (Eq. 14) directly.

This model differs from the Langelier and Stiff-Davis models because they consider thermodynamic ideality, but Oddo-Tomson considers the deviations of the activity coefficient depending on temperature, pressure or ionic force changes. The error range of the other models produced by the measure of pH taken in the surface is eliminated because it is not necessary.

$$l_s = \log\left[\frac{(Ca^{+2})(HCO_3^{-})^2}{py_g^{CO_2}f_g^{CO_2}}\right] + 5,85 + 15,19x10^{-3}T - 1,64x10^{-6}T^2 - 5,27x10^{-5}p - 3,334(Si)^{0.5} + 1,431(Si)$$
(Eq. 8)

$$pH = \log\left[\frac{f}{py_g^{CO_2}}\right] + 8,60 + 5,31x10^{-3}T - 2,253x10^{-6}T^2 - 2,237x10^{-5}p - 0,990(Si)^{0.5} + 0,658(Si)$$
(Eq. 9)

$$f_{g}^{CO_{2}} = \exp\left[p_{(2,84x10-4 - \frac{0.255}{T+460})}\right]$$
(Eq. 10)

$$y_g^{CO_2} = \frac{y_t^{CO_2}}{1 + p \, \frac{f_g^{CO_2}(5 \, BWPD + 10 \, BOPD)x10^{-5}}{MMscf \, (T + 460)}}$$
(Eq. 11)

$$l_s = \log\left[\frac{(Ca^{+2})(HCO_3^{-})^2}{C_{aq}^{CO_2}}\right] + 3,63 + 8,68x10^{-3}T + 3,55x10^{-6}T^2 - 6,56x10^{-5}p - 3,42(Si)^{0.5} + 1,37(Si)$$
(Eq. 12)

$$pH = \log\left[\frac{(HQ)}{C_{aq}^{CO_2}}\right] + 6,39 - 1,198x10^{-3}T + 7,94x10^{-6}T^2 - 3,53x10^{-5}p - 1,067(Si)^{0,5} + 0,559(Si)\right]$$
(Eq. 13)

$$l_{s} = \log[(Ca^{+2})(HCO_{\overline{3}})^{2}] + pH - 2,76 + 9,88x10^{-3}T + 0,61x10^{-6}T^{2} - 3,03x10^{-5}p - 2,348(Si)^{0,5} + 0,77(Si)$$
(Eq. 14)

#### **4.2 CO<sub>2</sub> CORROSION PREDICTION**

CO<sub>2</sub> corrosion prediction is absolutely important in order determine the impact of CO<sub>2</sub> present in the fluid flow of production in the facilities of production. The principal methods used are De waard-Milliams and De waard-Lotz, in which cases the operational parameters are considered (temperature and pressure) and allows engineers to know the corrosion rate. This means the wear of the production pipe per year due to corrosion.

#### 4.2.1 DE WAARD-MILLIAMS METHOD

The De Waard and Milliams method is a predicting model for  $CO_2$  corrosion based on the correlation between temperature and partial pressure of  $CO_2$  in order to obtain the corrosion rate in millimeters per year, as it is shown in (Eq. 15).

$$Log(CR_{t}) = 7.96 - \frac{2320}{T + 273} - 5.55x10^{-3}T + 0.67\log(PCO_{2})$$
(Eq. 15)

This equation has changed after comparing it with the experimental results obtained, specifically the constants of the formula shown in (Eq. 16).

$$Log(CR_t) = 5.8 - \frac{1710}{T + 273} + 0.67 \log(PCO_2)$$
(Eq. 16)

#### 4.2.2 DE WAARD-LOTZ MODEL

To validate the De waard-Milliams model, De waard -Lotz generates a model of corrosion rate based on the velocity in the absence of surface scale with a parallel resistance model. This was plasm in the next equation, in which Vcr is the corrosion rate to determine, Vr is the independent flow contribution denoting the reaction rate, and Vm is the flow-dependent contribution denoting the mass transfer rate (Ossai, 2012).

$$\frac{1}{Vcr} = \frac{1}{Vr} + \frac{1}{Vm}$$
(Eq. 17)

To determine the value of Vr and Vm two more equations were modeled, the (Eq. 18) to determine Vr value and the (Eq. 19) to determine Vm, where U is the liquid flow rate and Dh is the hydraulic diameter of the pipe.

$$Log(Vr) = 4.93 - \frac{1119}{T + 273} + 0.58 \log(Pco_2) \qquad (Eq. 18)$$
$$Vm = 2.45 \frac{U^{0.8}}{Dh^{0.8}} Pco_2 \qquad (Eq. 19)$$

According to the equations determined, this model considers the influence of the fluid in the possible corrosion process presented and, in the pipeline, directly. This model validates and gives a clearer vision of the corrosion's behavior and the effect on the pipeline.

#### 4.3 MATERIAL SELECTION DIAGRAM

According to Jose Vera from DNV the material selection of a production pipeline can be determined by the partial pressure of CO<sub>2</sub> and partial pressure of H<sub>2</sub>S, considering that according to the calculus the scale formation can be discarded (Vera, 2016).

This material selection is based on the effect of CO<sub>2</sub> and H<sub>2</sub>S present in the fluid flow on the structure of the pipeline. This diagram is valid for high-performance steels subsoilstructures such as the casing tube and the production pipe. In the Fig. 10 different stainless steels are shown such as J55 which is casing tube material, 13-Cr which is a material of pipe production. As it is shown in the diagram the different CRA's (13-Cr MSS, several duplex steels and Ni-based) are specified with their respective boundaries of stress. In the left side are 13-Cr MSS and the duplex steels for low H<sub>2</sub>S content and high CO<sub>2</sub> content, where the corrosion impact will be done by CO<sub>2</sub> as Sacha's case. In the right side are the Ni-based alloys for more corrosive environments beginning in high H<sub>2</sub>S content and low CO<sub>2</sub> content environments to high H<sub>2</sub>S content and high CO<sub>2</sub> content environments.



FIG. 10. MATERIAL SELECTION DIAGRAM (VERA, 2016)

## **CHAPTER 5: RESULTS AND DISCUSSION**

#### **5.1 HYDROCARBON INDUSTRY IN THE WORLD**

Nowadays, most of the reserves are of heavy crude oil, so the technology and operational conditions have to change day by day. One of the principal ways to illustrate and confirm it is by studying the relation oil reserve-production. This rate gives a clear idea of each country's oil industry current situation and the comparison with its previous years lets engineers know if something happens. BP Company every year makes a statistical review of the world reserves, production and consumption of the different energy sources called "Statistical Review of World Energy". A simple graphic of the rate reserves-production such as Fig. 11 can help to analyze the actual hydrocarbon industry's situation.



FIG. 11. RELATION RESERVE-PRODUCTION OF OIL COUNTRIES (STATISTICAL REVIEW OF WORLD ENERGY BP, 2020)

According to the values showed in the Statistical review maked by BP, there are three kinds of oil country based on their rate reserves-production. The first ones and the most important are those with big reserves and high production (green), such as Saudi Arabia, country with one of the highest oil production and one of the biggest proved oil reserve. Its current proved reserve is 297.6 thousand million barrels with a production of 11.83 million of barrels per day, and if this is compared to previous years, both factors have increased. Therefore, Saudi Arabia is an oil country with a good future projection of 68.9 years to take advantage of its reserve and which guarantees it that it can supply its necessities and remain in the market competitively.

The second ones are those countries with big reserves but with low production (yellow), such as Iran, Iraq or Venezuela. In these cases of Iran, Iraq and Venezuela, their rates reserves-production are too high, which means that they are not making the most of their resources because something affect their industries, in which cases are their geopolitics situations. This kind of example let engineers have a broader point of view and understand that they have to consider all of the possible factors that can affect the hydrocarbon industry.

The third ones are those with small reserves and low production (red), such as China , Ecuador or Colombia. China represents a particular case which can be found in the small reserves and low production section with the particularity, that even when its reserves are small, it has a rate of reserves-production of is 18.7 years; this happens because its production is too low. By comparing Chinese oil production with its consumption, an important fact can be determined: its consumption is almost four times its production. Based on this previous information and checking the data of the last years, it can be inferred that China is one of the principal importers of crude oil globally and according to the historical; there is an increase of 9.5% to the previous years. According to the reserves' actual situation, production, and consumption of oil countries, the world's reserves continue decreasing, and day-by-day new technologies are necessary to increase the reserves founded and increase the production. Thus, it is necessary to have controlled all of the factors that can affect the hydrocarbon industry, such as political situation, environmental conditions, types of reserves, methods for recovery, or even international conflicts.

#### **5.2 AMERICA'S OIL INDUSTRY SITUATION**

The Americas situation is particular because there are countries for each section. Here engineers have particular cases to study to understand how different factors in a country can influence in its industries but especially in hydrocarbon industry, which is the principal source of energy for most countries. For this is necessary to locate in America's situation by the information supplied by important companies such as BP Company in its annual review "Statistical Review of World Energy". Information that is showed in Table. 5 and Table. 6. *TABLE. 5. RESERVE, ANNUAL PRODUCTION AND RATE OF PRINCIPAL OIL COUNTRIES IN AMERICA (STATISTICAL REVIEW OF WORLD ENERGY BP, 2020)* 

Country	Reserve (Thousand million Barrels)	Anual Production (Thousand million barrels per year)	Rate (years)
Argentina	2,4	0,23	10,61
Brazil	12,7	1,05	12,09
Colombia	2	0,32	6,18
Ecuador	1,6	0,19	8,26
Peru	0,9	0,05	17,36
Trinidad&Tobago	0,2	0,03	6,68
Venezuela	303,8	0,34	906,68
Otros	0,5	0,04	11,61
Total	324,1	2,25	144,04

Country	Consumption	Production	Percentage of
Country	(MBPD)	(MBPD)	consumption
US	19400	17045	113,82
Canada	2403	5651	42,52
Brazil	2398	2877	83,35
Mexico	1733	1918	90,35
Venezuela	356	918	38,78
Colombia	347	886	39,16
Argentina	599	620	96,61
Ecuador	249	531	46,89
Peru	262	142	184,51
Trinidad&Tobago	39	82	47,56
Others	1294	118	1096,61

TABLE. 6. OIL CONSUMPTION OF PRINCIPAL OIL COUNTRIES IN AMERICA

(STATISTICAL REVIEW OF WORLD ENERGY BP, 2020)

United States is one of those particular cases. US is a country with moderate reserves and has the highest production globally as it is shown in Table. 5 and Table. 6, which is attributed to its technology of production, which is fracking. This technology consists of a high-pressure injection of water, sand, and chemicals to break the rock and release the hydrocarbon. However, its production is not enough because its consumption is bigger than its production as it is shown in Table. 6 with a percentage of consumption around 114%. US even has a strategic oil reserve of 645 million barrels, but its rate reserve-production is only 11 years, which does not guarantee their future oil market.

Venezuela's case is important to analyze because it has the biggest reserve in the world with 303,08 thousand million barrels and has the right technology to take advantage of its resources and lead the market, but its political situation does not allow it to be like that. Every year its production decrease and its economic situation have been affected and the

stability of its population. If the government does not take any action, Venezuela's hydrocarbon industry situation will go from bad to worse.

As we can see in the Table. 5 the America situation is absolutely alarming, specially for those countries in which cases their economy depends on the hydrocarbon industry such as Ecuador. In those cases is necessary to find an alternative energy source in the next 5 to 8 years because, according to their rate reserve-production, those are the years that their reserves have left if they do not find more proved reserves.

#### **5.3 ECUADORIAN HYDROCARBON INDUSTRY**

#### **5.3.1 PRINCIPAL PROCESSES FOR PRODUCTION IN ECUADOR**

#### **5.3.1.1 SEISMIC SURVEY**

A seismic survey is the first step for determining where an oilfield is, its capacity and potential. A seismic survey is necessary to begin oil exploitation; it consists of generating seismic waves and measuring the time it takes for the wave to reflect and be detected by the geophone (Villamarin and Carrera, 2010).

#### 5.3.1.2 DRILLING

In Ecuador, the cluster drilling method is used to reduce the number of platforms and deforestation (Villamarin and Carrera, 2010).

#### **5.3.1.3 HYDROCARBON EXTRACTION**

The fluid is obtained by the lateral or lower aquifers' hydraulic thrust or by the different artificial methods such as electro submersible pumping, mechanic pumping, gas lift or by water reinjection method currently used.

Once at the surface level, the fluid from the different wells is integrated through a manifold system. Therefore, the fluid is directed to the process plants to separate the oil, gas and the formation water (Villamarin&Carrera, 2010).

#### 5.3.2 ACTUAL SITUATION OF ECUADORIAN OILFIELDS

According to the information acquired from the Statistical Review of World Energy 2020 and to the Ecuadorian Hydrocarbon Minister, Ecuador's oil production is around 531 thousand barrels per day, and a total volume of 1.6 thousand million barrels of crude oil proved reserve. This means that Ecuador has a reserve-production rate of 8.4 years if the production is constant and they do not find new reserves.

The scheme for the exploitation and production of crude oil in Ecuador is doing by the public industry called Petroecuador EP and the private industries such as Repsol, Petroriental, Andes Petroleum and other private companies. The public company Petroecuador EP manages approximately 1.39 thousand million barrels of the total proved reserve of Ecuador, and the private companies manage the other 242 million barrels of the proved reserve (Chiluisa and Merino, 2018). According to the Ecuadorian hydrocarbon secretariat, Ecuador has 71 production blocks between Petroamazonas EP and the private companies (hydrocarbon secretariat, 2016).



FIG. 12. ECUADORIAN OILFIELDS (HYDROCARBON SECRETARIAT, 2016)

In the annual report of Ecuador's hydrocarbon potential, the detail of the percentage of accumulate production, proved reserves, probable reserves, and possible reserves of each oilfield are described. Most of the oilfields in Ecuador are mature oilfields, in which cases there are no future projects to recover the probable and possible reserves, but oilfields such as Sacha or Auca represent the future oil sources. This happens because according to The Minister of Non-Renewable Energy Sacha, Shushufindi and Auca have the 21%, 19% and 18% respectively of the proved reserves of Ecuador, representing 806.2 million barrels (Chiluisa and Merino, 2018).

TABLE.7. PROBABLE AND POSSIBLE RESERVES PRINCIPAL OILFIELDS(ANNUAL REPORT OF THE HYDROCARBON POTENTIAL OF ECUADOR, 2018)

Oilfields	Probable reserves	Percentage represented	Possible reserves	Percentage represented
Sacha	56 <i>,</i> 98	22	70,18	9,6
Auca	41,44	16	92,84	12,7
ITT	54,39	21	496,35	67,9

The three main oilfields that lead the proved reserves in Ecuador are Sacha, Shushufindi and Auca; the ones for the total probable reserves are Sacha, ITT and Auca with 22%, 21% and 16% respectively; and the ones for the total possible reserves are ITT, Auca and Sacha with 67.9%, 12.7% and 9.6% respectively as it is shown in Table. 7. This is why these four oilfields are important for the hydrocarbon industry and the country's economy's stability; they represent the present and the future of the industry.

#### **5.4 SCALE FORMATION RESULTS**

#### **5.4.1 LANGELIER RESULTS**

According to the results obtained in the Langelier index calculus for the range of temperature used (120°F-160°F), there will not be any carbonate formation. The ideal range of the Langelier index is between -0.3 and 0.3. This allows engineers to discard a possible formation of carbonate scale.

Temperature (°F)	pHs	LSI
127	6,37	-0,04
135	6,29	0,04
140	6,24	0,09
145	6,2	0,13
150	6,15	0,18
160	6,06	0,27
165	6,01	0,32
170	5,97	0,36
176	5,91	0,42

TABLE. 8. LANGELIER METHOD RESULTS FOR SACHA'S FORMATION WATER

For this calculation was necessary to take the pH of 6,3 of the wellhead as a constant and the TDS, calcium concentration and carbonate concentration as constant with the wellhead values shown in the Table. 8, those values taken from the Table. 4 were applied in the in the Lenntech Calculator for each temperature for Langelier Saturation Index calculation.



FIG. 13. GRAPHIC TEMPERATURE VS LSI

In the Table. 8 and Fig. 13 is shown the behavior of the salts dissolved in the formation water, especially the total solid dissolved, the ion calcium and the bicarbonate based on the temperature changes and by taking the pH of the sample of formation water as a constant. This method is not exact because it does not cover the total temperature from the downhole to the wellhead of the oilfield; but it clarifies what can happen. The results obtained show the difference between the real pH and the saturation pH, the Langelier saturation index that varies from -0.11 to 0.27. These values indicate that there will not be scale formation, but it is necessary to consider that the real pH can vary with the temperature changes, representing a possibility of scale problems. In this case, an inhibitor can be used to prevent and cover that possibility.

#### 5.4.2 STIFF-DAVIS RESULTS

For the Stiff-Davis index calculation was necessary to convert the ions' concentrations taken from the Table. 4 to molar concentration (Table. 9) in order to calculate the molar ionic strength (Table. 10) with the values obtained and by applying them in the Eq. 7.

Ions	Concentration (mg/L)	Concentration (mol/L)
Na <sup>+</sup>	5759	0,2504
Ca <sup>2+</sup>	720	0,018
$Mg^{2+}$	96	0,004
HCO3 <sup>-</sup>	434	0,0071
$Fe^{2+}$	4,5	0,00008
SO4-	3	0,00003
C1-	10200	0,2877

TABLE. 9. RESULTS OF IONS' MOLAR CONCENTRATIONS OF THE FORMATION WATER

TABLE. 10. RESULT OF MOLAR IONIC STRENGTH

Si (ionic force)	
0,316775	

By using the Fig. 9, the K value can be determined. First we have to put in the X axis in the value of the molar ionic strength obtained and go up to the temperature of the point of the studied conditions, which in this case is the wellhead temperature and at this point the value of the Y axis is the value of K factor.

TABLE. 11. K VALUE OBTAINED BY THE CORRELATION DIAGRAM

K	K Factor
	2,32

Temperature	pН	K factor	pCa	pALK	ISSD
127	6,33	2,32	1,75	2,15	0,11

TABLE. 12. STIFF-DAVIS SATURATION INDEX OBTAINED

Finally the ISSD value is obtained by the application of the Eq. 6 in which the pCa and pALK are the negative logarithm of calcium concentration and alkalinity respectively and the K value obtained before shown Table 11. The ISSD value obtained is in the ideal range, and there is not a big difference from the Langelier value obtained for the Wellhead conditions. This indicates that there will not be a scale formation problem. For a larger study of the oilfield is necessary to know the characteristics and conditions not only from the wellhead but also downhole. This is important to understand the behavior in all of the production pipeline to determine if it is necessary to reduce the possibility of incrustations formation.

According to the values obtained with the two methods of scale formation and based on the history of corrosion problems in Sacha, the incrustation problems can be discarded. This allows us to analyze the possibility of corrosion by CO<sub>2</sub>, which will be analyzed by De waard-Milliams and De waard-Lotz methods.

#### 5.5 CO<sub>2</sub> CORROSION PREDICTION RESULTS

#### 5.5.1 DE WAARD-MILLIAMS RESULTS

For De waard-Milliams model is necessary to determine the partial pressure of  $CO_2$ for each section of the production pipeline with the respect temperature of each point. For this, it was necessary to determine a pressure profile (Table. 13) and temperature profile which is the second column in Table. 14 by using the wellhead conditions (Table. 4) and the downhole conditions (Table. 3) and divide them by a referential depth of Hollin formation which according to Romero & Gomez is 10160 fts or 3100 meters. This Value obtained is going to be the pressure or temperature gradient, which is going to be multiplied with the meters of the point that we want to determine and added to the head pressure taken from Minda Theses in this case or head temperature taken from Table. 4. Then, the partial pressure was obtained by the product between the concentration which according to Leiva is 9% and the operational pressure as it is shown in the Table. 13.

				Partial
Depth (m)	Pressure	Concentration	Partial Pressure	Pressure
	(Psia)	CO <sub>2</sub> (%)	CO <sub>2</sub> (Psia)	CO <sub>2</sub> (mpa)
0	340	9	31	0,21
300	738	9	66	0,46
600	1136	9	102	0,71
900	1534	9	138	0,95
1200	1933	9	174	1,20
1500	2331	9	210	1,45
1800	2729	9	246	1,69
2100	3127	9	281	1,94
2400	3525	9	317	2,19
2700	3923	9	353	2,43
3000	4322	9	389	2,68
3100	4454	9	401	2,76

TABLE. 13. PARTIAL PRESSURE OF CO<sub>2</sub>

By using the De waard-Milliams equations (Eq. 15 and Eq. 16) the corrosion rate is determined. It is important to consider the two equations in order to obtain a bigger range of corrosion rate. This allows making a better material selection because it shows the

possible sceneries and the impact that  $CO_2$  will have on the production pipeline. The corrosion's behavior presented in the different sections is shown in the Table. 14 and the corrosion rate profile obtained for each equation is shown in the Fig. 14 and Fig. 15.

Partial	Temperature	Log(crt)	CRT (Eq. 15)	Log (crt)	CRT (Eq. 16)
Pressure	(°C)	(Eq. 15)	(mm/yr)	(Eq. 16)	(mm/yr)
CO <sub>2</sub> (mpa)					
0,21	52,77	0,33	2,15	0,10	1,25
0,46	58,04	0,67	4,64	0,41	2,55
0,71	63,32	0,90	7,89	0,61	4,11
0,95	68,59	1,09	12,18	0,78	6,02
1,20	73,87	1,25	17,81	0,92	8,38
1,45	79,14	1,40	25,12	1,05	11,26
1,69	84,42	1,54	34,50	1,17	14,76
1,94	89,69	1,67	46,41	1,28	18,97
2,19	94,97	1,79	61,36	1,38	24,02
2,43	100,24	1,90	79,96	1,48	30,02
2,68	105,52	2,01	102,89	1,57	37,10
2,76	107,28	2,05	111,62	1,60	39,73

TABLE. 14. DE WAARD-MILLIAM RESULTS OF CORROSION RATE PROFILE

These values shown in Table. 14 were obtained by using the partial pressure profile and temperature profile in the Eq. 15 and Eq. 16 described for De waard-Milliams model, all those calculations were made in Excel. This gave us estimated corrosion rates for each point in the production well the operacional conditions and the CO<sub>2</sub> content.



FIG. 14. CORROSION RATE PROFILE OBTAINED BY (EQ. 15)

According to the Fig. 14, the corrosion rate increased directly proportional to the pressure and temperature. This equation indicates a corrosion rate range from 2,15 mm/yr to 111,33 mm/yr. These values are alarming because by using a carbon steel pipe with the typical dimensions used in Sacha's oilfield which has a thickness of 0,237 inches (6,02 millimeters); this represents that it will be necessary to change the pipeline in the best case once every three years or in the worst case eighteen times every year or less by considering the use of coating.



FIG. 15. CORROSION RATE PROFILE OBTAINED BY (EQ. 16)

According to the Fig. 15 the corrosion rate increased directly proportional to the pressure and temperature, this equation indicates a corrosion rate range from 1,25 mm/yr to 39,64 mm/yr. These values obtained are reasonable, even if we consider using a carbon steel pipe with coating by reducing the changes produced to once every six years and in the worst-case six times or less every year. In the (Eq. 16), the temperature and partial pressure are not the only parameters considered for determining the corrosion rate, liquid flow rate is considered. This parameter is necessary to be considered because it affects and increase the corrosion problems presented in production pipeline.

Based on the values obtained with both equations (Eq. 15) and (Eq. 16), the CO<sub>2</sub> corrosion is a significant problem to be considered.

#### 5.5.2 DE WAARD-LOTZ RESULTS

For the correct application of this model, it was necessary to take the characteristics of the actual production pipeline used in Sacha's oilfield. The diameter used was 4,5 inches, which in meters is 0,1143 meters. Another factor considered is the liquid flow rate obtained by the continuity equation and the value is 2,83 meters per second. This model covers more aspects of the corrosion by CO<sub>2</sub> considering a significant fluid dynamic aspect.

TABLE. 15. LIQUID FLOW RATE AND DIAMETER FOR A TYPICAL SACHA'S OILFIELD

Liquid flow	Conversion factor	Diameter			Liquid flow
(BFPD)	(m³/s)	(m)	Dh (m)	Area (m <sup>2</sup> )	rate (m/s)
15728,94	1,84x10 <sup>-6</sup>	0,1143	0,1143	0,01026	2,83

In order to perform the De waard-Lotz model it was necessary to use the temperature and partial pressure profiles calculated for the De waard-Milliams method, the liquid flow rate in meters per second and the hydraulic diameter of the pipeline, as it is shown in the Table. 15. For the corrosion rate calculation is necessary to calculate the flow independent contribution by applying the Eq. 18 denoting the reaction rate and the flow-dependent contribution by applying the Eq. 19 denoting the mass transfer rate. Finally with both values the Eq. 17 was applied in order to determine the corrosion rate.

Depth (m)	Partial Pressure CO <sub>2</sub> (mpa)	Temperature (°C)	log (Vr)	Vr (mm/yr)	Vm (mm/yr)	Vcr (mm/yr)
0	0,21	52,77	1,10	12,68	6,74	4,40
300	0,46	58,04	1,35	22,55	14,62	8,87
600	0,71	63,32	1,51	32,72	22,51	13,34
900	0,95	68,59	1,64	43,84	30,40	17,95
1200	1,20	73,87	1,75	56,20	38,29	22,77
1500	1,45	79,14	1,85	70,03	46,18	27,83
1800	1,69	84,42	1,93	85,49	54,06	33,12
2100	1,94	89,69	2,01	102,74	61,95	38,65
2400	2,19	94,97	2,09	121,94	69,84	44,41
2700	2,43	100,24	2,16	143,25	77,73	50,39
3000	2,68	105,52	2,22	166,81	85,62	56,58
3100	2,76	107,22	2,24	174,91	88,16	58,62

TABLE. 16. CORROSION RATE OBTAINED BY DE WAARD-LOTZ MODEL

According to the values obtained in the Table. 16 the CO<sub>2</sub> corrosion effect is significant and matches with the values obtained by the De waard-Milliams model shown in the Table. 14.



FIG. 16. CORROSION RATE PROFILE OBTAINED BY DE WAARD-LOTZ MODEL

As shown in the Fig. 16, the tendency indicates that the corrosion rate increases with all of the parameters involved in the model's equations.

#### **5.6 DISCUSSION**

As we see, Sacha is one of the main oilfields in Ecuador with a lifetime longer than the other ones based on the probable and possible reserves, which generates the necessity of a long lifetime facility. The use of new methods of recovery such as water reinjection increases the corrosion problems presented in oilfields. This recovery method is used in Sacha oilfield. This represented an important point to be analyzed to discard all of the possible corrosion problems and determine if it is necessary to use high-performance steel in the subsurface-surface section.

The data obtained by Langelier and Stiff-Davis models indicate that there will not be scale formation based on the Sacha's formation water characteristics. According to the Langelier model's values for the profile temperature from the wellhead or cero meters to 1800 meters, the index saturation is in the ideal range from -0,3 to 0,3. This value of index saturation gives the certainty that there will not exist scale formation and it was verified with an alternative method, the Stiff-Davis model.

The Stiff-Davis model considers the ions' concentrations; therefore, this model only applies to a specific point where the formation water was analyzed. The Stiff-Davis saturation index calculation for the wellhead gives us a value of 0,11 which means that there will not exist incrustation formation. By comparing the values obtained by the Langelier and Stiff-Davis method, we can see that they are similar, and both are in the ideal range of saturation index to eliminate the possibility of scale formation.

For the CO<sub>2</sub> corrosion problems, the De waard-Milliams and De waard-lotz methods are the principal used. According to De waar-Milliams results obtained, the CO<sub>2</sub> corrosion is significant, it increases with the temperature and pressure, making the corrosion rate increase to 111,33 millimeters per year according to the (Eq. 15) and to 39, 64 millimeters per year according to the (Eq. 16). Both graphics obtained from the results have a similar tendency, are described by a second-degree equation and give a clear idea of the impact generated in the pipeline especially in the downhole section.

In the case of De waard-Lotz model other parameters are considered especially the influence of the flow of fluid related to the specifications of the pipe used. In this case, the maximum flow rate was considered and the specifications of a typical pipe used in Sacha's oilfields; By using these values and the pressure and temperature profile, the range of corrosion rate obtained goes from 4,399 millimeter per year in the wellhead to 58,61 millimeter per year in the downhole. By comparing these values obtained with the De waard-Milliams results of the corrected equation (Eq. 16) it is clear that the flow of the fluid has an influence in the corrosion produced by CO<sub>2</sub>.

These results obtained by the two models allow engineers to know that they can not use steel carbon pipe, because, with these corrosion rates, it will be necessary to change the structure constantly. Some engineers could think that it can be controlled by using a correct chemical treatment, but with these high rates of corrosion, it could not be.



According to the Material Selection Diagram (Fig. 10), using the partial pressure of  $CO_2$  which is in the order of  $10^2$  and the partial pressure of H<sub>2</sub>S which is in the order of  $10^{-1}$ , and by considering the operational variables (temperature and pressure) and the actual Sacha's reserves conditions, the correct material to be used in Sacha's oilfields is 13-Chrome to reduce the maintenance cost and to avoid possible operational problems, which can represent a future disaster. This high-performance steel compared with the API 5L GRB material (surface material recommended) used in Sacha's wells will increase the relation benefit-cost, especially based on thinking Sacha as an actual and future project for economy sustainable.

## CONCLUSION AND RECOMMENDATIONS

The natural decline of reservoirs increases the water production, which significantly impacted reliability and operational continuity; therefore, the corrosion problems in all of the oilfield processes to the final product have increased. This is why oil industries have had to resort to new recovery methods such as water injection. This affect the operational conditions and change the fluid of production characteristics such as chloride content, corrosive agents, water and sediments. For this reason is necessary to do a correct analysis of the possibility of scale formation and the CO<sub>2</sub> or H<sub>2</sub>S corrosion in order to take the correct material selection and the correct preventive method. Sacha is one of the most important reserves of crude oil of Ecuador for this moment and for the future based on its proved, probable and possible reserves and the country's profits. By the analysis of its actual characteristics, the principal operational problem that Sacha can presents is CO<sub>2</sub> corrosion, and according to the values obtained, even if inhibitors are used, this will represent money for future changes; Therefore, in this case, a correct material selection can help to avoid or reduce the future problems and expenses. This is why a correct material selection in the hydrocarbon industry represents one of the most important processes. It is necessary to consider and study all of the variables when we are going to determine and select the corrosion processes to be studied. For future projects is absolutely important to repeat the study with the other hydrocarbon industry processes such as transport or refining processes in order to determine the adequate material based on the actual conditions and optimize running costs.

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## ANNEX

#### Annex A: Ecuadorian Hydrocarbon Industry Annual Budget (2019)



#### PETROAMAZONAS EP EJECUCION INVERSIONES - REPORTES - INFORMACION CONSOLIDADA EJECUCION DEL PRESUPUESTO Expresadas en Dolares Programa + 27

Actividad - Grupo Gasto - Item - FTE -DEL 1RO DE ENERO AL 31 DE DICIEMBRE DE 2019

EJERCICIO 2019 SALDO POR DESCRIPCION ASIGNADO DEVENGADO % EJEC DEVENGAR BLOQUE CENTRO 12300 Inversiones en Consorcios y Subsidiarias 164,947,874 101, 192, 121 63,755,753 61% 18200 Sismica y geofísica ú û 05 0 13300 Ó 0 0 0% Exploración 13400 Perforación - Desarrollo 1,061,885 104,059 557,818 47% Facilidades de producción 11,904,015 100.073.090 -4,769,681 12500 TIME 2,429,779 Asset Fijo (quenta solo en Orade) 2,899,665 459,857 34% 14000 TOTAL BLOQUE CENTRO 202,813,442 142,799,667 60,013,774 70% BLOQUE OESTE 12300 Inversiones en Consorcios y Subsidiarias 674,192,260 666,663,565 7,529,495 99% 0% 13200 Signically geoficial 0 0 0 13300 Exploración ō. 0 0 10% 12400 2,569,602 Reforación - Decarrollo -787,673 3,357,275 -11% 13500 Facilidades de producción 2,614,615 2,152,091 1,462,524 60% 14000 Asset Filo (questa solo en Oracie) 152,107 121,209 30,999 60% 680,529,585 668,149,192 TOTAL BLOQUE DESTE 12,380,393 98% BLOOUE ESTE 0 12200 Signica y geofísica 6 0 10% 13300 Exploración 0 0 0 0% 12400 Perforación - Decarrollo 177,740,890 155,125,046 22,618,845 87% 12500 Facilitades de producción 92,165,197 87,063,449 5,081,748 94% 14000 Accet Fijo (cuenta solo en Oracle) 420,503 5,049 412,454 2% TOTAL BLOQUE ESTE 270,329,590 242,216,543 28,113,047 90% BLOQUE NORTE 12:300 Inversiones en Consorcios y Subsidiariai 459,964,305 447,893,314 11,970,991 97% 13200 Signica y geoficica 0 0 0 0% 18900 Exploración û -1,044 1,044 10% 13400 30,870,124 Perforación - Decarrolio 17,091,182 6,221,058 63% 12500 Facilidades de producción 13, 126, 970 12,567,657 98% 761,213 14000 Asset Rijo (cuenta solo en Oracle) 1,436,855 1,119,008 317,348 70% TOTAL BLOQUE NORTE 531,721,213 512,447,059 19,274,154 96% OGE SECTORIAL 13200 0 Siunica y geofisica ō 0 0% 133300 ú 0 û 0% Exploración 18400 Perforación - Determolio Ó 0 ù ch. 13500 36,333,610 24,056,187 2,277,423 Recilidades de producción 91% -302,400 102,400 One 14000 Asset Fijo (cuenta solo en Oracle) 0 TOTAL OGE SECTORIAL 26,333,610 23,753,787 2,579,823 90% **EXPLORACION** 18200 Signica y geofísica 165,494,153 -1,676,945 167,161,097 -1% 18900 Replanden 0 0 0% 0 165,484,153 TOTAL EXPLORACION -1,676,945 167,161,097 -1% TOTAL EJECUCION INVERSIONES PETROAMAZONAS 1,877,211,593 1,587,689,304 289,522,288 85% 0 1,587,689,304 0



PETROAMAZONAS EP

EJECUCION DE COSTOS Y GASTOS E INVERSIONES - REPORTES - INFORMACION CONSOLIDADA EJECUCION DEL PRESUPUESTO

Expresados en Dolares Programa = 27

Actividad - Grupo Gasto - Itert - FTE -DEL 180 DE ENERO AL 31 DE DICIEMBRE DE 2019

EJERCICIO 2019

	DESCRIPCION	ASIGNADO	DEVENGADO	SALDO POR DEVENGAR	% EJEC
	GASTOS DE PERSONAL				
10	Remunerationet Identuales	144,940,711	147,468,093	-2,526,383	1025
12	Aportes y Cargas Sociales	45,132,478	45,150,197	12,281	1005
14	Indemolationet	16,857,411	14,096,771	2,760,659	945
TOTAL GASTOS DE PERSONAL		206,982,619	206,716,062	266,557	100%
	SERVICIOS GENERALES				
20	Váticos y Gastos de Viaje	417,072	206,024	209,049	505
H	Servicios Addicos	640,830	413,038	230,791	Gette
24	Seguras	8,147,373	8,886,614	300,759	979
25	Publikidad y Propaganda	176,000	120,918	55,182	695
26	Arrendamientos	170,035,925	155,925,053	1,909,673	905
27	Capacitación	100,000	57,640	42,360	505
TOTAL SERVICIOS GENERALES		181,360,200	176,612,187	4,748,013	97%
	SERVICIOS OPERACIÓN U MANTENIMIENTO				
28	Fletes y Transporte	15,492,553	15,102,154	390, 399	975
28	Servicios de Operación	417,366,922	404,132,739	13,234,103	975
29	Servicios de Mantenimiento	69,269,392	58,469,158	900,233	995
TOTAL SERVICIOS OPERACIÓN Y MANTENIMIENTO		502,128,867	487,704,051	14,424,815	97%
	MATERIALES Y SUMINISTROS				
40	Materiales de Operación	98,937,925	85.794,583	13.140.342	875
41	Materiales de Mantenimiento	19,230,099	18,889,258	341,442	9.09
0	Combustibiles y Lubricantes	154,775,358	158,238,460	536,899	1005
TOTAL MATERIALES Y SUMINETROS		276,943,983	262,922,300	14.021.682	95%
	IMPUESTOS Y TIANSFERENCIAS				
60	impuettos y Costribudores	23,913,477	23,371,785	541,092	9.8%
TOTAL IMPUES	STOR Y TRANSFERENCIAS	23.913.477	23.371.785	541,692	98%
	GASTOS FINANCIEROS				
20	filantos Filmanderos	29,151,379	29,123,150	28,229	100%
TOTAL GASTOS FINANCIEROS		29,151,379	29,123,150	28,229	100%
	TOTAL COSTOS & GASTOS SIN DD&A	1,220,480,525	1,186,449,535	34,030,989	97%
	DEPRECIACIÓN y AMORTIZACIÓN				
50	Santo de Depreciación y amontización.	0	2,090,149,055	-2,030,149,055	0%
TOTAL DEPRECIACION Y AMORTIZACION		0	2,030,149,055	-2,030,149,055	
TOTAL EXECUTION DETROAMATONAC		3 603 603 113	3 994 436 636	555 EE5 536	
TOTAL EJECUCION PETROAMAZONAS		3,097,692,117	2,774,138,839	323,353,278	90%