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SYNTHESIS OF SYNTHETIC BRINE TO ESTIMATE CARBONATE SCALE INDEX IN OIL INDUSTRY

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ABSTRACT

The decreased oil production due to scaling in production equipment results in costs. In oil wells, ions such as calcium, barium, carbonate, sulfate, magnesium, sodium, and chloride are commonly present in formation water. Excessive solubility of ions can trigger precipitation or what is often called scale. This study focuses on creating synthetic brine with a composition resembling field formation water as an alternative solution for rapid laboratory-scale measurement of the scale index. In this study focus on carbonate and bicarbonate scale. The stages of the research involves synthetic brine preparation, physical and chemical testing of the brine, comparison with formation water, and calculation of the Stability Index (SI) using Stiff & Davis method. The results indicate that synthetic brine can be prepared based on laboratory analysis of field samples by estimating the materials and masses present in formation water, thus allowing replication using natural or chemical materials in the laboratory while considering parameters such as pressure, temperature, and pH during the manufacturing process. The pH significantly impacts the risk of scale formation, where a slightly basic pH, around pH 8, supports higher concentrations of carbonate ions (CO_3^{2-}) and bicarbonate ions (HCO_3^-), thereby increasing the risk of scale formation.

Keywords: bicarbonate scale, carbonate scale, formation water, scale, synthetic brine

I. INTRODUCTION

The problem of reduced oil production often arises due to the scaling in production equipment, this scaling causing the narrowing of the oil production pathway diameter. During the production process, formation water becomes associated with hydrocarbons to the surface, along with dissolved components therein. This leads to the produced fluid having a diverse composition and substances (Olajir, 2015). Throughout production, fluids experience pressure and temperature changes, causing certain dissolved components to stabilize as solids and precipitate (Time., 2011).

Water plays a significant role in scale deposition or scaling problems in oil and natural gas fields. Dissolution of different mineral components enriches formation water with ions. Formations water may contain ions including Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Strontium (Sr^{2+}), and Barium (Ba^{2+}), with total dissolved solids approaching 400,000 mg/L (Kamal, 2018). Scale comprises organic, inorganic, and crystalline water compositions (Jinling, Silicon containing scale forming characteristics and how scaling impacts sucker rod pump in ASP flooding, 2009). Scale can form from a single-phase mineral, but typically arises from the saturation of multiple elements in solution, pH and temperature changes, or the combination of two chemicals (Olajir, 2015). Scale deposits commonly consist of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), strontium sulfate ($SrSO_4$), carbonate (CO_3^{2-}), iron, and other insoluble solids (B. Senthilmurugan, 2011), (Jinling, Silicon containing scale forming characteristics and how scaling impacts sucker rod pump in ASP flooding, 2009), (Dickinson).

Scale becomes problematic when formed in large quantities, depositing on pathways traversed by produced water such as perforation holes, tubing, flowline and separators. Solid-scale deposits can rapidly reduce production rates within hours, requiring substantial treatment costs (Al Salami, 2010, November). Scale can also cause formation damage in reservoirs, loss of flow or blockages in flowlines, energy decline, corrosion, and other unforeseen issues impacting safety and profitability in the oil industry (El-Said, 2009)

As one solution to mitigate scale-related issues, this study aims to create synthetic brine using chemical and natural materials to replicate the initial water formation composition, so that it can save the use of natural formation water. This research serves as an alternative for testing scale indices focus on carbonate scale in laboratories.

Formation water is a complex mixture of various ions, minerals, and organic materials. The chemical composition of formation water varies significantly depending on geographical location and reservoir geology conditions. Formation water associated with oil and gas (during production) contain a variety of compounds in the form of ions, including cations (positively charged ions) and anions (negatively charged ions) (Liestyana, 2018, October). According to Collins (1975), the major ions commonly found in formation water include calcium (Ca^{2+}), magnesium (Mg^{2+}), barium (Ba^{2+}), strontium (Sr^{2+}), iron ($Fe^{2+}/^{3+}$), chloride (Cl^-), and sulfate (SO_4^{2+}).

Scale is a mineral deposit formed due to changes in physicochemical conditions such as temperature, pressure, and water composition. Excessive concentrations of mineral ions beyond equilibrium conditions can lead to the deposition of scale, which obstructs flow in wells, production equipment, and pipelines (Musnal, 2013). These deposits typically consist of calcium carbonate ($CaCO_3$), barium sulfate ($BaSO_4$), and calcium sulfate ($CaSO_4$) (Table 1). According to Mackay and Jordan (2003) (Mackay, 2003), scale formation can lead to well productivity decline, equipment damage, and increased operational costs. Therefore, testing and predicting scaling are crucial steps in formation water management in the oil and gas industries.

Stability index (SI) is a value used to assess the potential tendency for mineral deposition in a solution. This index measures how close a solution is to saturation concerning specific compounds. A positive scale index indicates that the solution is saturated and likely to form deposits. Conversely, a negative scale deposition index indicates that the solution is less saturated and tends to dissolve deposits.

Table 1. Type of Scale
(Source: (Liestyana, 2018, October))

Type Of Scale	Chemical Formula	Important Factors
Calcium Carbonate (Calcite)	$CaCO_3$	Pressure, Temperature, Total dissolved salt
Calcium Sulfate:		
Gypsum	$CaSO_4.2H_2O$,	Pressure, Temperature, Total dissolved salt
Hemihydrate	$CaSO_4.1/2H_2O$	
Anhydrite	$CaSO_4$	
Barium Sulfate (Barite)	$BaSO_4$	Pressure, Temperature, Total dissolved salt
Stronsium Sulfat (Calestite)	$SrSO_4$	
Iron compounds:		
Ferro Carbonate	$FeCO_3$,	Corrosion result, dissolved gas, and pH
Ferro Sulfide	FeS,	
Ferro hydroxide	$Fe(OH)_2$,	
Ferro oxide	Fe_2O_3	

In oil fields, carbonate and bicarbonate scales can significantly impact production efficiency and equipment integrity. These scales form when dissolved carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions in water exceed their solubility limits, leading to the precipitation of minerals like calcium carbonate ($CaCO_3$). The formation of these scales is influenced by factors such as temperature, pressure, chemical composition, and pH levels.

II. METHODS

In the process of preparing synthetic brine, laboratory materials such as calcium, barium, carbonate, sulfate, magnesium, sodium, and chloride can be utilized by dissolving them in deionized water or through mixing processes. Subsequently, experiments are conducted to observe the mass changes of one or several minerals in the formation water formula with various mineral ions to determine the minimum threshold for scale formation on production equipment. Brine testing is performed using complexometric methods for the chemical and physical analysis of formation water, similar to field formation water testing. Complexometric methods are analytical techniques used to determine the concentration of metal ions in a solution by forming a stable complex through volumetric titration. In this method, metal ions in the solution react with a titrating agent to form a measurable complex or precipitate. One example of using complexometric methods is titration with $AgNO_3$ as the titrant. This process involves the formation of AgCl precipitate, which is used to determine the concentration of Cl^- ions in the solution.The next step involves testing the scale index content and analyzing experimental and research results by comparing synthetic brine preparation outcomes with chemical and physical tests of formation water.

In the testing of synthetic brine and formation water, complexometric methods are employed on samples containing formation water mineral ions. The addition of this method aims to form bonds with mineral ions and produce measurable complex compounds to determine the chemical content of scale-forming minerals in formation water. An example of a commonly used complexing agent solution for Ca ions is Ethylenediaminetetraacetic Acid (EDTA) (Kamal, 2018). Determining ion content in synthetic brine is useful for understanding the required material composition in testing, thereby achieving compositions that induce scale formation from formation water using the Stiff & Davis Stability Index method.

Synthetic brine made from carbonate rock is formulated based on the analysis results obtained from testing samples of oilfield formation water in Indonesia (BinMerdhah & Yassin, 2010). In each experiment, this synthetic brine solution is prepared by dissolving salts from carbonate rocks in deionized water followed by filtration. According to research conducted by Zhang et al. (2015) (Zhang, 2015), synthetic brine can accurately replicate the chemical conditions of formation water and is suitable for systematic laboratory studies. The results of these tests can be used to develop accurate prediction models and design effective scale control programs Possible materials include NaCl, KCl, $CaCO_3$, $MgCO_3$, $MgCl_2$, $BaCl_2$, Na_2CO_3, and Na_2SO_4. The produced water samples from the field were tested in the laboratory using API RP 45 water analysis for water formation, and the results will be used as a reference for synthetic brine production. The chemical composition test results of the formation water samples from LDK Formation can be seen in Table 2.

Table 2. Chemical Composition of Formation Water from LDK Formation

Parameters	Value
Salinity	12900 ppm
pH	8.38
TDS	10750 mg/L
Na^+	4312 mg/L
K^+	37 mg/L
Ca^{2+}	25.1 mg/L
Mg^{2+}	44.8 mg/L
Ba^{2+}	0.023 mg/L
Fe^{2+}	0.305 mg/L
Cl^-	6973 mg/L
CO_3^{2-}	73.5 mg/L
SO_4^{2-}	12.1 mg/L

The results indicate a high potential for calcium carbonate ($CaCO_3$) scaling due to high concentrations of calcium ion and carbonate, supported by a pH of 8.38. The concentrations are Ca^{2+} 25.1 mg/L, CO_3^{2-} 73.5 mg/L, however, the solubility in water for calcium carbonate is 0.013 g/L, so, in this natural formation water calcium carbonate scale not yet formed.

III. RESULTS AND DISCUSSION

The estimated mass can be calculated using the following formula:

$$\text{Mass material} = \frac{\textit{laboratorium result x 1 mol}}{\textit{Mass molar ion}} \text{ x Mass Molar material} \quad (1)$$

The synthetic brine is produced by determining the chemical compounds present in the formation water. Laboratory test results are used to select materials for the study. Estimated masses required for each substance are calculated and the results are shown in Table 3.

Table 3. Chemical Composition of Formation Water from LDK Formation

Material	Mass (g/L)
NaCl	11
KCl	0.07
$CaCl_2$	0.025
$MgCl_2$	0.18
$BaCl_2$	0.004
Na_2SO_4	0.04
Na_2CO_3 = $MgCO_3$ = $CaCO_3$	0.35

The calculated mass results are used in the production of synthetic brine. Several subsequent experiments are conducted to determine the brine formula that mimics the characteristics of formation water in the field, considering the values of CO_3^{2-} ion, Mg^{2+}, Cl^-, and pH.

Based on the calculations and simulations of Cl^- addition and pH adjustments, the results for chemical concentration, anion and cation levels, and stability index are presented in Table 4, Table 5, and Table 6.

Table 4. Experiment 10 synthetic brine measurement results with $CaCO_3$ Chemical Concentration

Parameters	Value
Salinity	N/A
pH	8
Na^+	4302 mg/L
Ca^{2+}	25.1 mg/L

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Parameters	Value
Mg^{2+}	150 mg/L
Cl^-	6800 mg/L
CO_3^{2-}	72 mg/L
SO_4^{2-}	300 mg/L
HCO_3^-	42.7 mg/L
OH	0 mg/L
Fe	0 mg/L

Table 5. Experiment 10 synthetic brine measurement results with CaCO3 Anion - Cation

Anion	BM	mg/L	Me/L	Cation	BM	mg/L	Me/L
Cl^-	35.5	6800	191.55	Fe^{2+}	56	0	0
SO_4^{2-}	96	300	6.25	Ca^{2+}	40	25.1	1.255
CO_3^{2-}	60	72	2.4	Mg^{2+}	24	150	12.5
HCO_3^-	61	42.7	1.4	Na^+	23	4320.4	187.84
OH^-	17	0	0				
Total			201.5	Total			13.755

Table 6. Calculation of Synthetic Brine CaCO3 Stability Index

Ion	Concentration		Correction Factor	Ionic Strength
	BM	Me/L	Me/L	
Cl^-	35.5	191.549	0.00005	0.009577465
SO_4^{2-}	96	6.25	0.00001	0.0000625
CO_3^{2-}	60	2.4	0.0015	0.0036
HCO_3^-	61	1.4	0.00005	0.00007
Ca^{2+}	40	1.255	0.00005	0.00006275
Mg^{2+}	24	12.5	0.001	0.0125
Fe^{2+}	1000	0	0.0015	0
Ba^{2+}	Negative	Negative	-	-
Na^+	23	188	0.001	0.187844296
	Total Ionic Strength			0.213717011

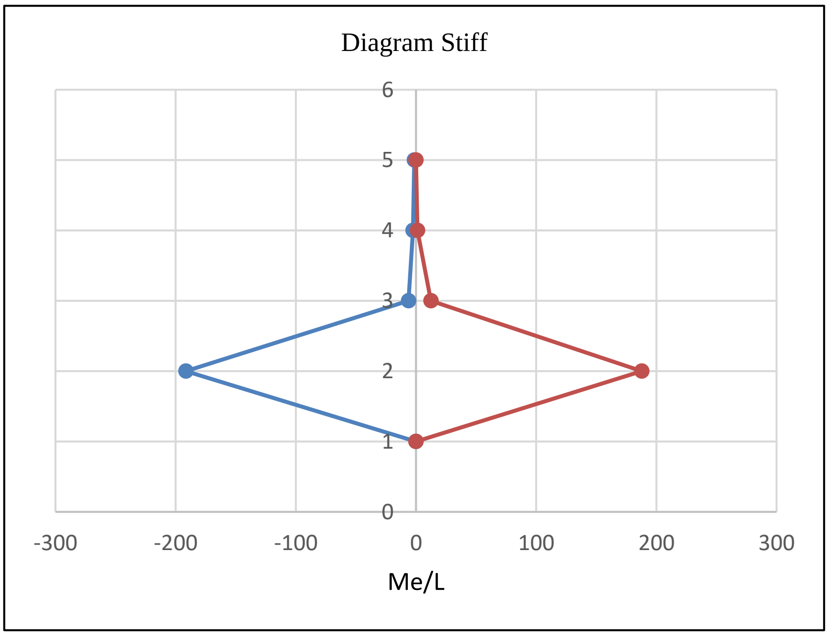

Figure 1. Stiff Diagram Graphic with $CaCO_3$ Material

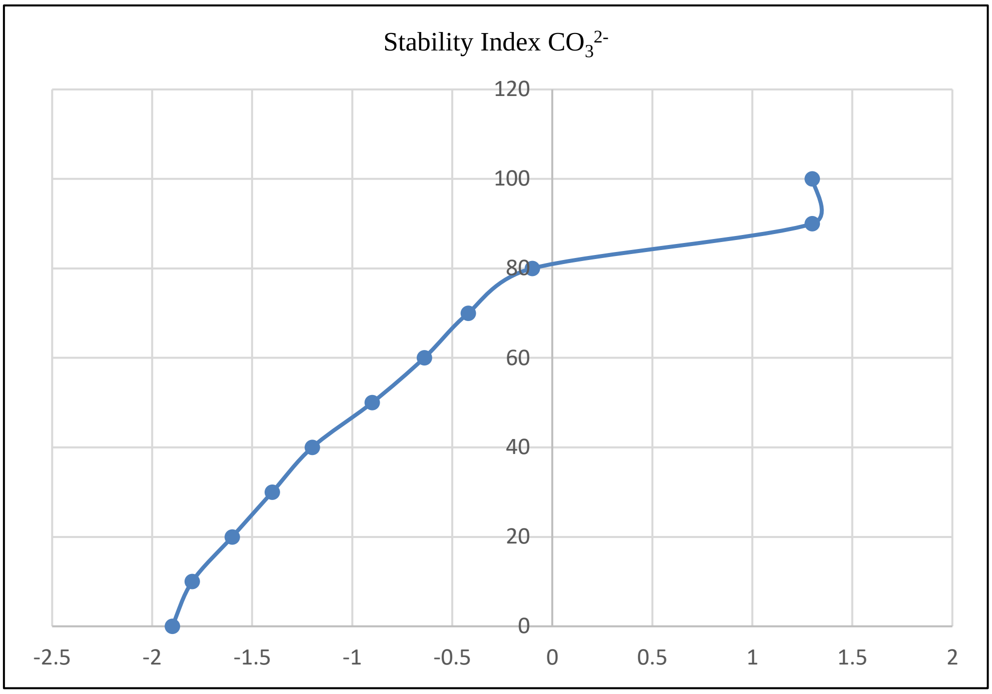

Figure 2. Stability Index (SI) graph at various material sample temperatures $CaCO_3$

Based on the results of the graph in the pH 8 simulation with Cl– adjusted to field conditions, the following observations can be made, the concentrations of Ca^{2+} and CO_3^{2-} ions were quite high. Based on this possibility, it can indicate a high potential for the formation of scale calcium carbonate supported by the presence of pH conditions.

According factors contributing to solution behavior include solutions tend to cause scaling when specific ion concentrations reach saturation and begin to precipitate as solids. Carbonate ion concentration at 72 mg/L and Ca^{2+} at 25.1 mg/L at pH 8, there is a high potential for calcium carbonate scale formation. Carbonate ions (CO_3^{2-}) are more available to react with calcium at basic pH, forming $CaCO_3$ precipitates. Aside from scaling, the solution can become corrosive due to chloride ions interacting with metals.

This analysis highlights the complex chemical interactions influencing scaling and corrosion in the studied solution.

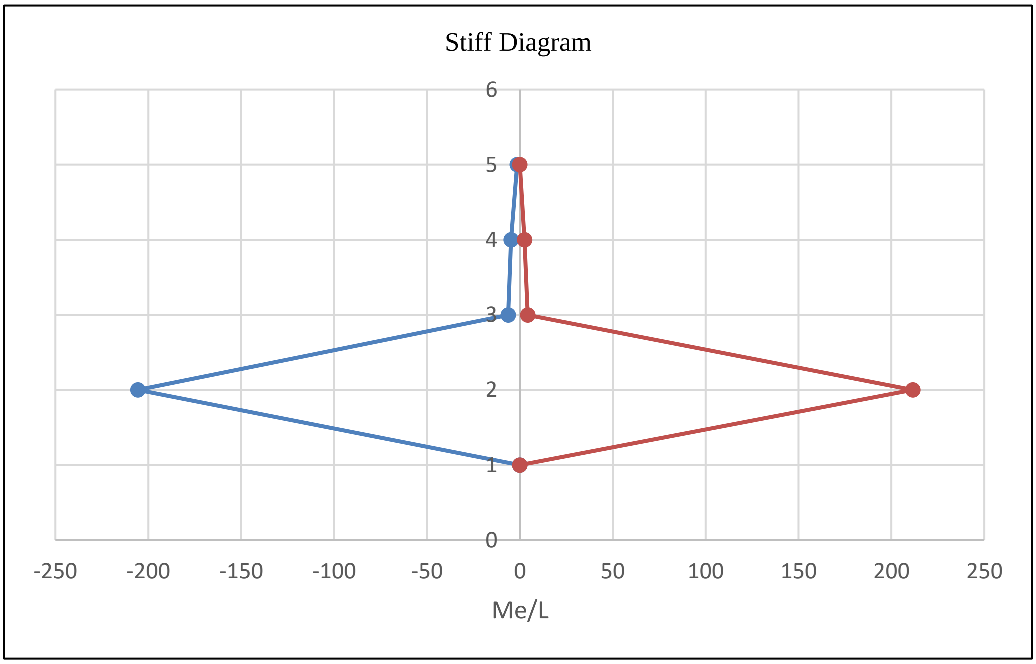

Figure 3. Stiff Diagram Graphic with CaCO3 Material and simulation add Mass $CaCO_3$ with NaCl

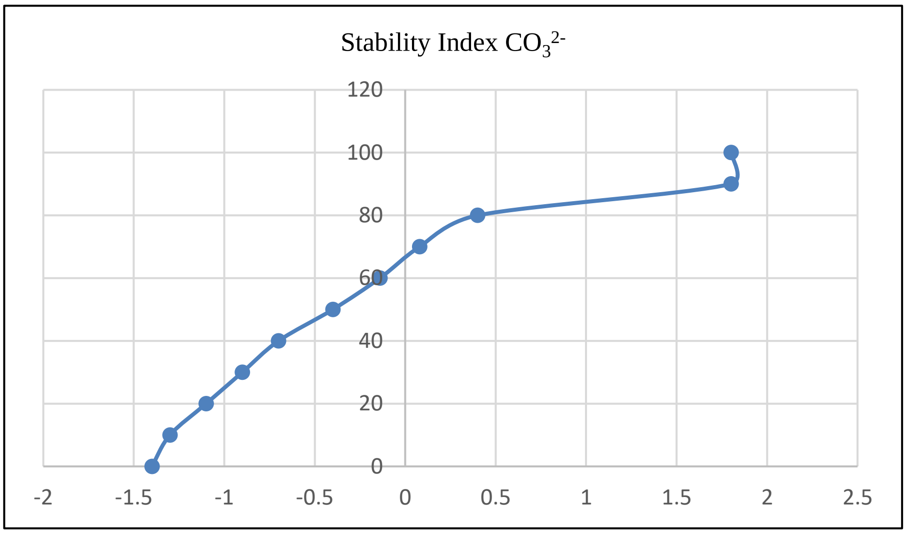

Figure 4. Stability Index (SI) graph at various material sample temperatures CaCO with pH 8.5

Based on existing data and simulations, the addition of mass of $CaCO_3$ material has an effect on the addition of anions - cations in NaCl compounds, Ca, CO_3 and Mg ions. The addition of $CaCO_3$ mass is used as the main ingredient which gives a greater possibility of calcium carbonate scale starting to form. Scale formation is influenced by the pH condition of the sample. The amount of sample pH is influenced by the amount of anion-cation NaCl material that reacts with the sample. Then with the amount of Mg ions will be low, the results obtained that the scale began to form at a temperature of 65^0C with a pH of 8.5 which is not much different from the sample from the conditions in the field.

IV. CONCLUSION

The conclusions that can be drawn from the above tests are:

1. Synthetic brine can be made by paying attention to the results of laboratory tests of field samples with parameters that affect temperature and pH.
2. The method of this test uses the titration method of complexionometry for measuring the concentration of Alkalinity, Cl- levels, and measurements using the Magnesium and Sulfate Instant Test Kit based on the color difference formed for measuring Mg2+ and SO42+ levels.
3. The pH parameter also has an influence on the speed of scale formation at various temperatures, at a simulated pH of 8.5 it illustrates that scale will begin to form at temperatures of 700C - 800C while at a measured pH of 6 corrosion will tend to form.
4. Provides an overview of the dominance of the tendency of scale formation or corrosion that will be flowed in production equipment used in consideration of the selection of industrial equipment construction materials (Jiecheng, 2011)
5. Synthetic brine are the samples that have the most similar characteristics to the formation water in the field.
6. The addition of CaCO3 and NaCl masses has an effect on the magnitude of the associated anions and cations and the pH formed so that at a pH of 8.5 scale calcium carbonate begins to form.

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