International Journal of Engineering and Technical Research (IJETR)
ISSN: 2321-0869 (O) 2454-4698 (P), Volume-3, Issue-7, July 2015

Scale Inhibitor (SIH 307$^{®}$) Commissioning Using Langelier Saturation and Ryznar Stability Indices in A Crude Oil Production Facility

Ohimor E.O, Oghenejoboh K.M, Odisu T, Iduh D, Onocha O

***Abstract*— The use of Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) as indices for determining the suitability and optimum dosage of a Scale Inhibitor (SIH 307$^{®}$) for an oil production facility through a Bottle Test and Plant Trial was carried out. A sample of the produce water used for the bottle test was collected from the intermediate Pressure (IP) separator outlet. Five prescription bottles were filled to the 100ml mark with the produce water. One of the bottles was kept as a blank while the remaining four were treated with the scale inhibitor (SIH 307$^{®}$) at the rate of 15ppm, 20ppm, 25ppm and 30ppm respectively. Efforts were made to simulate the process temperature and turbulence by immersing the bottles in a water bath at 65^{o}C after proper agitation. The LSI and RSI of the produce water in the treated and untreated prescription bottles were determined using standard methods. The pH, LSI and RSI of the untreated sample were 7.25, 1.10 and 5.06 respectively. The pH, LSI and RSI of the SIH 307$^{®}$ treated samples were 6.68, 0.650 and 5.63 for 25ppm and 6.65, 0.491 and 5.67 for 30ppm respectively. The values of the pH, LSI and RSI of the samples treated with SIH 307$^{®}$ showed a potential to form scale because of the observed reduction of the pH from alkaline to acidic. During the plant test the SIH307$^{®}$ was introduced at the scale inhibitor injection point; a point upstream the inlet of the high pressure (HP) separator. Samples of the produce water were then collected from the outlet of the IP separator at 6 hours interval and analysed for pH, LSI and RSI. The range of results obtained were pH: 7.35 - 7.40; LSI: 0.34 - 0.38 and RSI: 6.59 - 6.73. Though the pH range is in the alkaline region, the result of the LSI and RSI show that the continued use of the scale inhibitor, SIH307* may result in serious fouling.**

***Index Terms*— Scale Inhibitor, Langelier Saturation Index, Ryznar Stability Index.**

I. INTRODUCTION

In the course of oil production, oil, water and gas are co-produced. The water that is co-produced with oil and gas is known as "formation water"; since it form the oil reservoir itself. There can still be another source of water that returns to the surface along with the oil and gas; this water is known as “injection water”; .The later results from intentional water floods carried out to maintain reservoir pressure to increase oil production flow rates [1]. These two primary sources of water which are co-products of oil and gas are of great concern during oil production.

Usually, these waters are at elevated temperatures as a result of their depth below the earth's surface. As the water comes to the surface during oil production activities, the dissolved carbon dioxide comes out of solution as pressure is reduced. This leads to a pH increase and an equilibrium change where the bicarbonate anion decomposes to the carbonate anion and more carbon dioxide [1], [2]. The formation of the carbonate anion and pH increase, gives rise to calcium and magnesium carbonate scaling, which is basically the deposition of mineral solids on the interior surfaces of separation facilities when water containing the carbonates or bicarbonates of calcium and magnesium is heated. Incompatibility of the formation water and the injection water can also result in the precipitation of calcium and magnesium carbonate scales in down-hole equipment [3], [4]. Scale generally, is the carbonate or sulphate compounds of alkaline earth metals such as Calcium, Magnesium and Barium.

Incompatibility of the formation and injection water can also result in the precipitation of calcium and magnesium carbonate scales in down-hole equipment [3], [4]. Scale generally, is the carbonate or sulphate compounds of alkaline earth metals such as Calcium, Magnesium and Barium.

Scale formation is presently a serious problem in the Oil and Gas industry; scale can reduce the internal diameter of pipes and eventually block pipes and pumps used in separation facilities [5]. Scale formation can also greatly affect heat transfer performance. A 1 mm thick scale, for example, can add 7.5% to energy costs, while 1.5 mm adds 15% and 7 mm can increase cost by over 70%. It is more expensive to de-scale than to prevent scale [5]. It is therefore proper to determine the scaling tendency (i.e. scaling potential) of the produce water and injection water in order to apply an appropriate scale inhibitor to prevent or reduce scale formation.

The saturation level (SL) of water in a mineral phase is a good indicator of the potential for scaling due to that specific scalant. SL is a ratio between the ion activity product *(IAP)* and the thermodynamic solubility product (Ksp) of a specific compound in that water (Pierre, 2008). For example, when calcium carbonate ($CaCO_3$) is the scalant, SL is defined as [5]:

$$SL = \frac{a_{Ca^{2+}} - a_{Co_3^{2-}}}{K_{sp}} \qquad (1)$$

Ohimor E.O, Department of Chemical Engineering, Federal University of Petroleum Resources, Ugbomoro, P.M.B 1221, Effurun, Delta State Nigeria Tel: +2348033888418

Oghenejoboh K.M, Department of Chemical Engineering, Delta State University, Oleh Campus, P.M.B. 22, Oleh, Nigeria

Odisu, T, Department of Chemical Engineering, Federal University of Petroleum Resources, Ugbomoro,P.M.B 1221, Effurun, Delta State Nigeria

Iduh D, Department of Chemical Engineering, Federal University of Petroleum Resources, Ugbomoro,P.M.B 1221, Effurun, Delta State Nigeria

Onocha O, Department of Chemical Engineering, Federal University of Petroleum Resources, Ugbomoro,P.M.B 1221, Effurun, Delta State Nigeria

Where $a_{Ca^{2+}} \cdot a_{CO_3^{2-}}$ is the IAP of the two ions involved in the formation of $CaCO_3$, i.e. Ca^{2+} and CO_3^{2-}. K_{sp} is a measure of ionic concentration when dissolved ions and un-dissolved ions are in equilibrium.

When a saturated solution of sparingly or slightly soluble salt is in contact with the undissolved salt, equilibrium is established between the dissolved ions and the undissolved salt. In theory, this equilibrium condition is based upon undisturbed water maintained at constant temperature and allowed to remain undisturbed for an infinite period of time [6]. Water is said to be under-saturated (SL less than 1) if it is able to dissolve calcium carbonate. When water is at equilibrium, SL will be 1.0 by definition. Supersaturated water (SL greater than 1) will precipitate calcium carbonate from water if allowed to rest [6]. As the saturation level increases beyond 1.0, the driving force for the precipitation of calcium carbonate increases [5], [6].

These indices are designed to indicate the tendency of a given water to deposit scales on metal substrates and surely not to predict the absolute corrosivity of specific waters [5]. Generally speaking, scales precipitated onto metal surfaces can provide protection of the substrate from general corrosion [5], [7]. If on the other hand the scales are defective and contain voids and/or cracks, they could lead to localized corrosion. Therefore the assumption that water below saturation level with respect to calcium carbonate is corrosive, while sometimes correct, is not reliable. Hence there is need for other scaling indices. Scaling indices such as Langelier Saturation Index (LSI), Ryznar Stability Index (RSI), Puckorius Scaling Index (PSI), Larson-Skold Index and Oddo-Tomson Index are most times used for accurate analysis of the scaling tendency of most water [5], [8].

The LSI and RSI are probably the most widely used indicators of cooling water scale potential [9], [10]. The LSI indicates the driving force for scale formation and growth in terms of pH as a major variable [11]. In order to calculate the LSI, it is necessary to know the alkalinity (mgL^{-1} as $CaCO_3$ or calcite), the calcium hardness ($mg\ L^{-1}\ Ca^{2+}$ as $CaCO_3$), the total dissolved solids ($mg\ L^{-1}$ TDS), the actual pH, and the temperature of the water (°C) [5],[12]. Water quality or changes in temperature, or evaporation could change the index. The Ryznar stability index (RSI) on the other hand uses a correlation established between an empirical database of scale thickness observed in municipal water systems and associated water chemistry data [5], [11]. Like the LSI, the RSI has its basis on the concept of saturation level [13].

1.1 Process Description and the Problem

One or more of the incoming well fluid is channelled through the test separator (TS) while the others are channelled through the production separator which is also the high pressure separator (HP). Crude from the HP and TS flows into the intermediate pressure separator (IP) for further separation. Crude from the IP flows into the low pressure separator (LP) where final separation of crude, water and gas takes place. The problem associated with the process is the formation of scale in the water outlet line of the IP. Table 1.0 show some of the process parameters of the facility. From the process parameters, the pH and temperature of the IP produce water are relatively high, a condition that favours scale deposition. In order to correct the situation an attempt was made to test the effectiveness of an indigenous scale inhibitor, SIH 307® in control of scale formation.

TTable 1.0 Process Parameters of the facility [14].

Parameters	
Flowrate of IP inlet stream	32000 BLPD
BS&W of IP inlet stream	5%
Gross water production from IP	15000 BWPD
pH of IP produce water	7.57
Temp of IP produce water	66.80 °C
pH of LP produce water	7.29
Temp of LP produce water	64.68 °C
pH of HP produce water	6.50
Temp of HP produce water	73.93 °C
pH of TS produce water	6.64
Temp of TS produce water	74.33 °C
pH of produce water to slop tank	6.12
Temp of produce water to slop tank	60.48 °C

II. MATERIALS AND METHOD

2.1 Materials

The materials used for the experiments were Scale Inhibitor (SIH 307®) a product of Skyward Resources Ltd based in Warri, Delta State of Nigeria; digital pH meter and thermometer, stop watch, micropipette (1- 100µL), 100ml Beakers, 100ml Prescription Bottles, Oakton Multi-parameter tester (capable of reading pH, TDS, Conductivity, Temperature and Salinity), water bath and conductivity calibration standards (1413 µS/cm & 12880 µS/cm). Other materials used were 250ml Conical Flask, 50ml Burette, Retort Stand, Phenolphthalein Indicator, Mixed Indicator (i.e. 0.02g of Methyl Red Indicator and 0.08g of Bromocresol Green Indicator dissolved in 100ml of 95% pure alcohol), 0.02N H_2SO4, 100ml Measuring Cylinder, Potassium Cyanide (10% solution), Standard EDTA titrant (0.004M), Buffer Solution (pH 10), Hydroxylamine Hydrochloride (10%) and Indicator (Erichrome Black T).

2.2. Experimental Procedure

2.2.1 Bottle Test

Produce water sample was collected from the water outlet of the IP (intermediate pressure) separator according to standard sampling procedure [15], [16]. The temperature and pH of the produce water were immediately read and recorded. Five (5) prescription bottles were filled with produce water up to their 100ml mark. One of the prescription bottles was regarded as a blank while the remaining four bottles were treated with the scale inhibitor (SIH 307®) at the rate of 15ppm, 20ppm, 25ppm and 30ppm respectively. The bottles were vigorously hands shaken many times to homogenize the contents. After shaking, the bottles were placed in a water bath operated at the same temperature as that of the IP separator (i.e. 65.5°C). After allowing the contents to settle for 20mins, the pH, conductivity, temperature, total dissolved solids (TDS), Hardness and M-Alkalinity of the water in each of the prescription bottles were determined. The LSI and RSI were then computed for each of the samples in each prescription bottles.

2.2.2 Plant Trial

Based on the result of the bottle test, SIH 307® dosage of 25 – 30 ppm was considered to be effective. However, due to cost considerations, the

lower limit of 25 ppm dosage was chosen for the plant test. Considering the gross water production of 15,000 BWPD (since it is the water phase that is being treated), the 25ppm corresponds to 59.6 L/day of SIH 307®. Thus, the scale inhibitor was commissioned with the chemical injection pump delivering 59.6L/day of SIH 307® at the inlet of the IP. A sample of produce water from IP water outlet was collected just before the commissioning and another sample was collected two hours later, being the transition period; both samples were analysed for pH, LSI and RSI. Thereafter, samples of the produce water from the IP outlet were collected on a 6 hourly basis for analyses.

2.2.3 *Determination of Sample's Physicochemical Parameters*

The pH, conductivity, temperature and total dissolved solids (TDS) of the samples were read with the aid of Oakton® Multi-parameter tester. The Oakton® Multi-parameter tester is fitted with a probe, sensor and LCD screen. The probe is inserted in the water sample and the appropriate mode selected before taking the reading that is displayed in the LCD screen.

The ASTMD 1126 standard titration method was used in determining the total hardness of the samples [15], while the APHA 23208 standard titrimetric method was used for the determination of the M-Alkalinity [16].

2.2.4 L.S.I and R. S. I Calculations

The equations below were used for the calculation of Langelier Saturation Index (ASTM D3739-88) [11]:

$$LSI = pH - pHs$$

$$pHs = (9.3 + A = B) - (C + D)$$

Where:

$$A = \frac{\log_{10}(TDS) - 1}{10}$$

$$B = -13.12\log_{10}\left({}^{o}C + 273\right) + 34.55$$

$$C = \log_{10}\left(Ca^{2+}\ as\ CaCO_3\right) - 0.4$$

Apart from the temperature all other values in brackets have units of mg/L. Also, pH is the measured water pH and pHs is the pH at saturation in calcite or calcium carbonate.

The empirical correlation of the Langelier Saturation Index can be summarized as follows:

- *If LSI value is negative*: No potential to form scale, the water will dissolve CaCO3
- *If LSI value is positive:* Scale can form and CaCO3 precipitation may occur
- *If LSI value is close to zero:* Borderline scale potential

The Ryznar stability index (RSI) uses a correlation established between an empirical database of scale thickness observed in municipal water systems and associated water chemistry data. Like the LSI, the RSI has its basis in the concept of saturation level. The Ryznar index takes the form:

$$RSI = 2(pHs) - pH$$

The empirical correlation of the Ryznar Stability Index can be summarized as follows:

- *If RSI value is 4.0:* Heavy precipitation
- *If RSI value is 5.0:* Light precipitation
- *If RSI value is 6.0:* Limit of precipitation
- *If RSI value is 7.0:* Starting corrosion
- *If RSI value is 8.0:* Heavy corrosion

If RSI value is 9.0: Intolerable corrosion.

III. RESULTS AND DISCUSSION

3.1 Result

The results of the Bottle Test and Plant Trial are presented in Table 3.1 and Table 3.2 respectively.

Table 3.1 LSI and RSI Values from Bottle Test Sample.

Produce water sample	Chemical	Dosage (ppm)	Parameters						LSI	RSI
			pH	Cond. (mS/cm)	Temp. (°C)	TDS (ppt)	Hardness (ppm $CaCO_3$)	M-Alkalinity (ppm $CaCO_3$)		
IP outlet	Blank	0	7.25	27.5	65.50	20.00	125.00	1380/00	.1.10	5.06
IP outlet	SIH 307©	15	7.01	27.20	65.50	19/24	120.23	1392.00	1.54	5.32
IP outlet	SIH 307©	20	6.95	27.70	65.50	19.70	123.13	1428.00	0.80	5.34
IP outlet	SIH 307©	25	6.68	27.60	65.50	19.52	122.00	1418.00	0.654	5.63
IP outlet	SIH 307©	30	6.65	27.60	65.50	19.40	121.50	1406.00	0.491	5.67

Table 3.2 LSI and RSI Values from Plant Test Samples

Produce water sample & sampling Time	Chemical	Dosage (ppm)	Parameters						LSI	RSI
			pH	Cond. (mS/cm)	Temp. (^{o}C)	TDS (ppt)	Hardness (ppm CaCO$_3$)	M-Alkalinity (ppm CaCO$_3$)		
IP outlet Day 1: 0.00 Hr	Transition period	0	7.14	28.08	65.50	19.94	124.63	1442	.1.04	5.06
IP outlet Day 1: 02.00 Hr	Transition period	<15	7.15	29.16	65.50	22.04	137.75	1488	1.07	5.01
IP outlet Day 1: 0.800 hr	SIH 307$^{©}$	25	7.21	28.10	65.50	19.86	124.13	1446	1.07	5.07
IP outlet Day 1: 14.00 hr	SIH 307$^{©}$	25	7.21	27.72	65.50	19.94	124.25	1418	1.06	5.10
IP outlet Day 1: 20.00 hr	SIH 307$^{©}$	25	7.29	28.16	65.50	19.94	124.63	1448	1.15	5.00
IP outlet Day 2: 02.00 hr	SIH 307$^{©}$	25	7.40	6.54	65.50	4.66	29.13	326	0.05	7.30
IP outlet Day 2: 08.00 hr	SIH 307$^{©}$	25	7.36	11.64	65.50	8.20	51.25	434	0.35	6.66
IP outlet Day 2 14.00 hr	SIH 307$^{©}$	25	7.36	7.06	65.50	4.93	30.81	291	-0.02	7.40
IP outlet Day 2: 20.00 hr	SIH 307$^{©}$	25	7.39	8.13	65.50	5.82	36.38	352	0.16	7.07
IP outlet Day 3: 02.00 hr	SIH 307$^{©}$	25	7.41	10.08	65.50	6.99	43.69	434	0.34	6.73
IP outlet Day 3: 08.00 hr	SIH 307$^{©}$	25	7.35	11.20	65.50	7.86	49.13	491	0.38	6.59

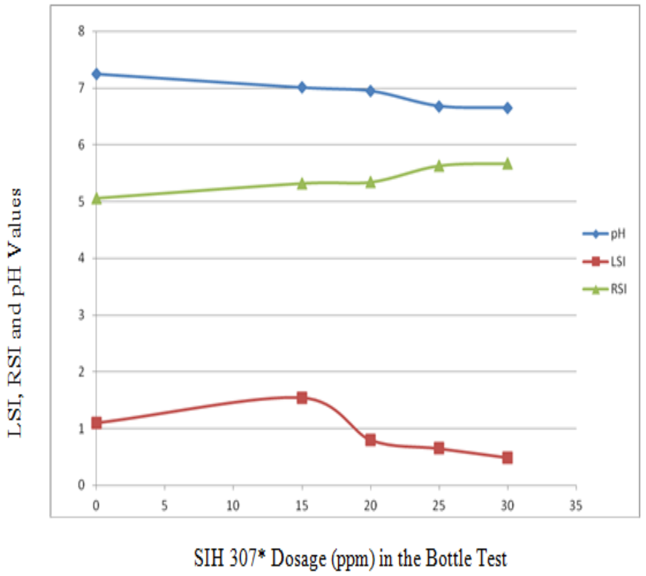

Figure 3.1 LSI, RSI and pH Values Versus SIH 307* Dosage (ppm) in the Bottle Test

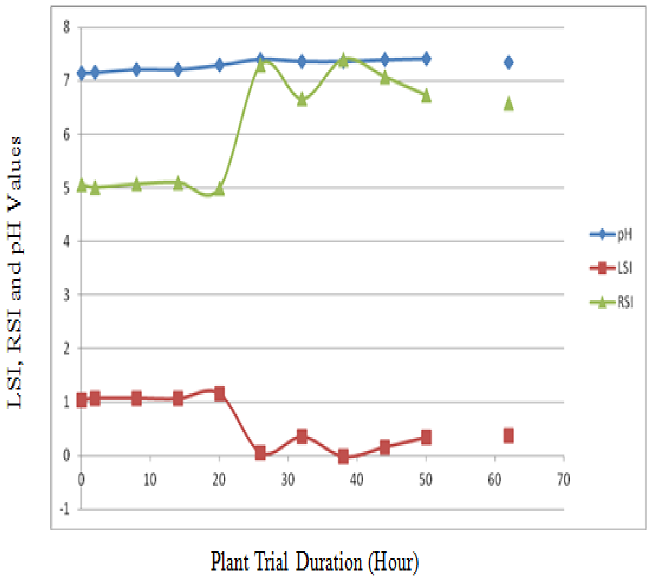

Figure 3.2 LSI, RSI and pH Values Versus Plant Trial Duration (Hour) with 25ppm of SIH 307*

3.2 Discussion of Results

The following observations were made. For the Bottle Test (Table 3.1 and Figure 3.1), the pH, LSI and RSI of the untreated sample were 7.25, 1.10 and 5.06 respectively. The pH, LSI and RSI of the sample treated with 25ppm of SIH 307$^{®}$ were 6.68, 0.650 and 5.63 respectively. While the pH, LSI and RSI of sample treated with 30ppm of SIH 307* were 6.65, 0.491 and 5.67 respectively. The values of the pH, LSI and RSI of the samples treated with SIH 307$^{®}$ showed a relatively slight tendency to form scale when compared with the untreated sample, also a reduction of the pH from alkaline range to acidic was observed, the LSI and RSI values also indicated slight tendencies to form scale or precipitate.

. Based on this observation, the plant trial was conducted on the basis of acidic pH, however, as can be seen from Table 3.2 and Figure 3.2, for the plant trial after the commissioning SIH 307$^{®}$ at 25ppm, the range of values of pH, LSI and RSI were 7.35 - 7.40, 0.34 - 0.38 and 6.59 - 6.73 respectively. The samples of the produce water analysed for the plant test were collected from the outlet of the IP (intermediate pressure) separator at intervals of 6hrs for 60hrs. These ranges of values indicate slight tendencies to form scale despite the fact that the pH value was in the alkaline region.

IV. CONCLUSION

The range of values of pH, LSI and RSI obtained from the experimental plant test run indicate slight tendencies to precipitate and form scale. The pH value ought to be slightly acidic but is in the alkaline region and this will engender precipitation and scale formation. Hence, the tried indigenous scale inhibitor, SIH307$^{®}$ is not effective in reducing scaling tendencies in pipes used in oil field activities. It can also be observed from the results that the Langelier Saturation Index and Ryznar Stability index as well as the pH values are useful indices in the performance evaluation of a scale inhibitor.

REFERENCES

[1] David W.; Kelly H. "http://www.waterworld.com/articles/iww/print/volume-11/issue-1/feature-editorial/steps-for-jar-testing-scale-inhibitors-in-oil-gas-applications.html" Assessed 3rd June, 2015.

[2] S.L.; Paul C.S. "Aquaculture: Farming Aquatic Animals and Plants" John Wiley & Sons. Copyright. 2012.

[3] Merdhah A.B.B. and Yassin A.A.M., 2009. Strontium Sulphate Scale Formation in Oil Reservoir During Water Injection at High-Salinity Formation Water. *Asian Journal of Applied Sciences, 2: 300-317.*

[4] Mike C.; David E.; Phil F.; Matt M.; Ashley J.; George K. "Fighting Scale - Removal and Prevention" Oilfield Review, Texas Autunm 1999.

[5] Pierre R. R., "Corrosion Engineering: Principles and Practice" McGraw-Hill; Publication Date: March 30 2008

[6] Edward G., "Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, John Wiley & Sons. Copyright. 2010.

[7] Kumar S. S.; Suriyanarayanan A.; Panigrahi B. S. "Studies on performance of indices in cooling water system", Indian Journal of Chemical Technology Vol. 19, January 2012, pp. 75-80.

[8] Mohammad F. H, Petrostreamz AS, Michael G and Curtis W (2013): Modeling and Management of Scale Potential in an Oil Field Production, Department of Petroleum Engineering and Applied Geophysics, Norwegian University of Science and Technology.

[8] He, S. L.; Kan, A. T.; Tomson, M. B. "Mathematical Inhibitor Model for Barium Sulfate Scale Control"; Langmuir 1996, 12, 1901-1905.

[9] Pandey, S. R., Jegatheesan, V, Baskaran, K, "Pre-treatment technologies for reverse osmosis during water recovery, in solutions to environmental challenges through innovations in research", Asiatech Publishers Inc., New Delhi, India 2013

[10] Kan, A. T.; Fu, G.; Watson, M. A.; Tomson, M. B. "SPE 74657 Effect of hydrate inhibitors on oilfield scale formation and inhibition"; In SPE Oilfield Scale Symposium;SPE, Richardson,
TX: Aberdeen, UK, 2002.

[11] Pisigan, R.A.; Singley, J.E. "Evaluation of Water Corrosivity Using the Langelier index and relative corrosion rate models," Corrosion/84, Paper No.149, National Association of Corrosion Engineers, New Orleans, LA, 1984

[12] Hudson Jr., H.E. and F.W. Gilcreas, "Heath and Economic Aspects of Water Hardness and Corrosiveness", JAWWA, Vol. 68, 1976, pp. 201-204.

[13] Ferguson, R.J. "Developing Scale Inhibitor Dosage Models," Proceedings of Water Tech '92, Houston, TX. (November 11-13, 1992).

[14] Ohimor, E.O.; Odisu, T. "Report on Scale Inhibitor (SIH 307) Field Test at FPSO-Mystras (December 24 – 30, 2014

[15] Collins, A. G. Geochemistry of Oilfield Waters; Elsevier Scientific: Amsterdam, 1975.

[16] Larson, T.E.; Skold, R.V. "Laboratory Studies Relating Mineral Quality of Water to Corrosion of Steel and Cast Iron," Corrosion-NACE 15, 285t (1958)

Engineer E. O. Ohimor

Engr. OhimorE.O is a PhD student in the Department of Chemical Engineering, NnadiAzikiwe University, Awka. He holds a B.Engand M.Eng. Degrees in Chemical Engineering. He started his career in Chemical Engineering Practice in 1995 and has since worked with many indigenous oilfield services companies as an Application Engineer and later as a Senior Industrial Officer with the Delta State Ministry of Commerce and Industry before moving into academics.

He is currently a lecturer in the Department of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Delta State Nigeria. EngrOhimor E.O., a registered Engineer has over 10 publications in reputable journals.

Dr. K.M. Oghenejoboh

Dr. K.M. Oghenejoboh holds a PhD, M.Eng. and B. Eng. Degrees in Chemical Engineering. He started his teaching career in 2009 at the University of Uyo in Akwa-Ibom State- Nigeria after a stint of about 15 years in the industry. He currently teaches at the Department of Chemical Engineering, Delta State University, Abraka. Dr. Oghenejoboh who had supervised project students in both the undergraduate and post-graduate levels has more 30 journal articles in reputable international journals.

Engineer Odisu T.

Engr. Odisu is a PhD student ofChemical Engineering at the University of Benin-Nigeria after previously bagging a B. Eng. and M. Eng. degrees from the same University. Engr. Odisu who is currently at the final stage of his PhD program has published more than 15 papers in reputable journals

Iduh O. D.

Mr.Iduh, a PhD student in Chemical Engineering of the University of Benin holds a B. Eng. from the University of Beninand an M. Eng. Degree in .Advanced Chemical Engineering with Process Systems Engineering from Imperial College London in 2012

Ms Onocha O.

Ms Ovonomo Onocha holds a B.Eng abd and M.Sc. degrees in Chemical Engineering. She is currently a Lecturer in the Dept. of Chemical Engineering, Federal University of Petroleum Resources, Effurun, Nigeria.