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Identification of Formation Scale and Modeling of Treatment Fluid

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Abstract

The formation of mineral scales is one of the most common problems in oil wells around the world and despite great technological developments by engineers, this problem remains without an effective solution. Scale may form anywhere from the reservoir formation to the well bore; affecting tubing, choke valve and production equipment. This work was undertaken to experimentally identify the composition of mineral scales that occur in a typical Niger Delta oilfield well location. Three methods were used in the analysis; The quantitative, atomic absorption spectrometer (AAS) and X-ray fluorescence (XRF) spectrometric testing equipment. Scale samples from production valves were collected from two fields in Niger Delta. Test results indicated that the main constituents of the scale were iron oxide, calcium carbonate and iron carbonate, typical of sandstone and carbonate reservoirs found in the Niger Delta. Though 15% HCl was faster than 10% HCL in dissolving the scales, 10% HCl with corrosion inhibitor is recommended for field application to avoid intense corrosion of pipes, valves and tubing used in the production lines. Results validated from the model equation indicated a high level of accuracy with less than 2% accuracy, hence, could be used to predict the optimum time and concentration of HCL without going through rigorous laboratory testing protocols, thereby, serving operation time and cost.

Keywords: Scale formation, oilfield systems, Niger Delta, acid treatment, corrosion inhibitors, modeling.

Introduction

Experience in the oil industry has indicated that many oil wells have suffered flow restriction because of scale deposition within the oil producing formation matrix and the downhole equipment, generally in primary, secondary and tertiary oil recovery operations as well as scale deposits in the surface production equipment[1] Scale formation in surface and subsurface has been recognized to be a major operational problem. It has also been recognized as a major cause of formation damage either in injection or producing wells. Scale in oil field systems is a relative common occurrence involving the deposition of dissolved minerals salt on processing equipment occurring as a result of super saturation of mineral ions in the process fluids. This supersaturating of ions is caused by several factors. An important contributor is the production of high salt content formation water from the well. This increases the ionic concentrations, possibly leading to deposition of scales[2]. As production of a well increase over time, there exists a decrease in the production rate of the particular well owing to plugging materials, fluid invasion, organic and inorganic solid deposition due to change of some physical property like temperature, pressure, solubility etc[3].

The deposition of the materials in the pore throat of the formation could prevent the normal natural flow of hydrocarbon towards the well bore. As production continues, the deposit increases[3]. Apart from loss of production and damage to equipment, in some cases it can also result in an HSE problem[4]. One of HSE concerns of scaling tendencies is the danger associated with NORM. In the reservoir, it reduces near wellbore permeability; resulting in high skin and lower inflow. In wells it causes flow restriction resulting in higher pressure losses or lower throughput. In flow-lines and surface facilities, among others, it causes Loss of equipment functionality (especially pumps and pressure relief valves) and corrosion.

Corrosion is the destruction of metals and alloys by chemical and electrochemical reactions with its environment. It is a natural phenomenon which cannot be avoided, but it can be controlled and prevented using appropriate preventive techniques like metallic coating, anodic protection, cathodic protection and using inhibitors, etc. The organic inhibitors containing hetero atoms like oxygen, nitrogen, sulphur and phosphorus, etc show better corrosion inhibition by forming protective film on the metal surface[5].

The plugging materials can damage production system, process materials etc, to which removal is necessary and important. Carbonate scales are the most common scales encountered in oilfield operations. Calcium is most often the cation, but also barium and strontium carbonates are possible. There is need to identify the causes of scale formation in oilfield systems and proffer prudent preventative management and designing suitable treatment fluid[6].

The objective of this work therefore was to investigate experimentally the metallic compositions of scale samples, design and model suitable treatment fluid for optimum removal of scale deposits in oilfield production lines.

Material and Methods

Scale samples were collected from a flow station in Niger Delta field. Three experimental methods namely; the AAS, XRF-S, and the quantitative were used to identify the minerals and the composition of the scales: Test procedures were as per specifications in equipment test manuals. The treatment or dissolution of the scale was modeled as applicable. For the AAS method, the samples were analyzed by aspirating through the nebulizer using the atomic absorption spectrophotometer (BULK SCIENTIFIC, 205) and for the XRF-spectropometer, test was done using model NO XEPOS 03 STD GAS.

Results and Discussion

The results of the metal composition analyses by AAS method is presented in table- 1. The result for the X-ray Fluorescence Spectrometry method is presented in table-2 and 3. The quantitative method is represented in table- 4.

Table-1
Metal Identification of Different Scales using AAS Method

Parameters	Results of Analysis Scale from Production
Calcium (mg/kg)	19.625
Total Iron (mg/kg)	1.150
Lead (mg/kg)	<0.001
Zinc (mg/kg)	0.61
Magnesium (mg/kg)	2.250

Modeling of the Treatment Fluid: To establish optimum treatment time and concentration of the HCL solution, the time it took 2g of the sample to dissolve was plotted against various concentration of the HCl. Figure-1 as indicated gave a logarithmic graph with the best regression value and hence most suitable treatment fluid dissolution pattern. With equation of type: $Y = m \ln(x) + c$.

The Model equation therefore becomes:

$$Y = -11.0\ln(x) + 30.89 \quad (1)$$

Where y = time it takes to dissolve 2g of scale, x = the conc. in % for HCl

Therefore, equation 1 is the model equation that can be use to obtain the time requires to dissolve 2g of scale of different concentration.

Table-1 presents metal composition of scale sample analyzed using the ASS method. Total Iron value was 11.50mg/kg, calcium was 196.25mg/kg and zinc 0.61mg/kg.

The metal and its oxide analysis were carried out using the X-ray fluorescence spectrometer. Results are presented in table-2 and 3. Test results indicated high concentrations of calcium (3799 mg/kg), manganese (1040mg/kg), iron (1050mg/kg) magnesium (728mg/kg) and other metals of various compositions.

One major advantage of using the XFR method is its ability to determine the oxides of metals. Table 3 presents the oxides of the metals as identified from the sample and their concentrations in percentage.

Table-4 indicated result with the quantitative method. Different percentage concentrations of HCl solutions were added to the scale sample, and reactions showed various degree of effervescence and dissolution. For 1%, 2%, 5%, 10% and 15% HCL concentrations respectively, complete dissolution of scale was achieved after 30hrs, 20hrs, 14hrs, 5hrs and 30mins respectively. From quantitative result inference, the scale is probably calcium carbonate, for those that bubbled vigorously without turning the acid yellow or probably iron oxide for those that bubbled slowly and turned the acid solution yellow[7]. With the various results obtained using the three methods, the main constituents were iron oxide, calcium carbonate and iron carbonate and the scales was acid soluble. This validated previous work on this that matrix acidizing can be very effective to enhance productivity and maximize recovery in oil and gas wells in both sandstone and carbonate reservoirs[8].The most suitable solvent for the treatment is therefore HCL, however, the choice of an optimum concentration is critical because of the corrosive tendency on the production tubings and valves. Corrosion of mild steel and its alloys in different acid media have been extensively studied[9]. It has been reported that addition of certain organic compounds bearing hetero atoms, retards the corrosion of mild steel in acidic environments [10-11].

Though 15% HCl was faster than 10% HCL in dissolving the scales, 10% HCl with corrosion inhibitor is recommended for field application to avoid intense corrosion of pipes, valves and tubing used in the production lines. This observation on the acid strength is probably the only reliable statement that can be made in predicting whether a carboxylate will be an inhibitor and even this prediction may relate only mild steel[12]. Metal and their alloys are exposed to aggressive environment under atmospheric condition during the manufacture, processing, storage or transportation and can accelerate the degradation of the metal, alloys and their products. The effective use of surfactants for corrosion inhibition depends upon the application environment and properties of metals as well as nature of surfactants[13-14]

Results validated from the model equation indicated a high level of accuracy with less than 2% accuracy, hence, could be used to predict the optimum time and concentration of HCL without going through various laboratory testing protocols, thereby, serving operation time and cost.

Table-2
Scale minerals as identified by using X-ray Spectrometry Method

Symbol	Element	Concentration (mg/kg)	Abs. Error (mg/kg)
Mg	Magnesium	728	61
Al	Aluminum	< 20	(0.0)
Si	Silicon	< 5.1	(0.0)
P	Phosphorus	447.6	1.8
S	Sulfur	106.5	0.6
Cl	Chlorine	33.1	0.2
K	Potassium	< 10	(0.0)
Ca	Calcium	3799	200
Ti	Titanium	< 3.3	(3.3)
V	Vanadium	< 1.0	0.0
Cr	Chromium	10.8	0.6
Mn	Manganese	1040	4
Fe	Iron	1050	20
Co	Cobalt	< 35	(0.0)
Ni	Nickel	9.5	1.7
Cu	Copper	18.1	0.9
Zn	Zinc	48.5	0.7
Ga	Gallium	1.9	0.5
Ge	Germanium	< 0.2	(0.1)
As	Arsenic	< 0.5	(0.1)
Se	Selenium	< 0.2	(0.1)
Br	Bromine	0.3	0.1
Rb	Rubidium	1.4	0.2
Sr	Strontium	1731	2
Y	Yttrium	2.5	0.2
Zr	Zirconium	0.1	0.1
Nb	Niobium	0.1	0.1
Mo	Molybdenum	0.1	0.1
Ag	Silver	1.8	0.8
Cd	Cadmium	< 2.9	(0.0)
Sn	Tin	0.1	0.1
Sb	Antimony	0.1	0.1
Te	Tellurium	0.1	0.1
I	Iodine	0.1	0.1
Cs	Cesium	0.1	0.1
Ba	Barium	1351	20
La	Lanthanum	0.1	0.1
Ce	Cerium	0.1	0.1
Pr	Praseodymium	29.2	4.2
Nd	Neodymium	33.9	4.6
Hf	Hafnium	< 2.5	0.0
Ta	Tantalum	50.1	1.5
W	Tungsten	5.3	2.5
Hg	Mercury	1.8	1.0
Ti	Thallium	0.6	0.2
Pb	Lead	10.7	0.4
Bi	Bismuth	< 0.8	0.0
Th	Thorium	1.5	0.4
U	Uranium	7.6	0.4

Table-3
Scale minerals oxides as identified by using X-ray Spectrometry Method

Symbol	Element	Concentration %	Abs. Error %
MgO	Magnesium	1.208	0.010
Al_2O_3	Aluminum	< 0.0038	(0.0)
SiO_2	Silicon	< 0.0011	(0.0)
P_2O_5	Phosphorus	0.1026	0.0004
SO_3	Sulfur	0.02660	0.00015
Cl	Chlorine	0.00331	0.00002
K_2O	Potassium	< 0.0012	(0.0)
CaO	Calcium	53.15	0.03
TiO_2	Titanium	< 0.00055	(0.00054)
V_2O_5	Vanadium	< 0.00018	(0.0)
Cr_2O_3	Chromium	0.00158	0.00008
MnO	Manganese	0.1343	0.0005
Fe_2O_3	Iron	1.501	0.003
CoO	Cobalt	< 0.0044	(0.0)
NiO	Nickel	0.00121	0.00021
CuO	Copper	0.00227	0.00011
ZnO	Zinc	0.00604	0.00009
Ga	Gallium	0.00019	0.00005
Ge	Germanium	< 0.00002	(0.00001)
As_2O_3	Arsenic	< 0.00006	(0.00001)
Se	Selenium	< 0.00002	(0.00001)
Br	Bromine	0.00003	0.00001
Rb_2O	Rubidium	0.00015	0.00002
SrO	Strontium	0.2047	0.0002
Y	Yttrium	0.00025	0.00002
ZrO_2	Zirconium	0.00001	0.00001
Nb_2O_5	Niobium	0.00001	0.00001
Mo	Molybdenum	0.00001	0.00001
Ag	Silver	0.00018	0.00008
Cd	Cadmium	< 0.00029	(0.0)
SnO_2	Tin	0.00001	0.00001
Sb_2O_5	Antimony	0.00001	0.00001
Te	Tellurium	0.00001	0.00001
I	Iodine	0.00001	0.00001
Cs	Cesium	0.00001	0.00001
Ba	Barium	0.1351	0.002
La	Lanthanum	0.00001	0.00001
Ce	Cerium	0.00001	0.00001
Pr	Praseodymium	0.00292	0.00042
Nd	Neodymium	0.00339	0.00046
Hf	Hafnium	< 0.00025	(0.0)
Ta_2O_5	Tantalum	0.00612	0.00018
WO_3	Tungsten	0.00066	0.00032
Hg	Mercury	0.00018	0.00010
Ti	Thallium	0.00006	0.00002
PbO	Lead	0.00115	0.00005
Bi	Bismuth	< 0.00008	(0.0)
Th	Thorium	0.00015	0.00004
U	Uranium	0.00076	0.00004

Table-4
Scale Identification of Sample from Production Manifold Valves using Quantitative Method

Test data	Observation
Sample + 50ml H_2O	Not soluble in water. Form lumps
Sample + 50ml Chloroform	Dissolved partially. Endothermic reaction. No bubbles were observed and no dissolution after 24hrs
Sample + 50ml of 1% HCl solution	Bubbled slowly, dissolved slowly with effervescence. Completely dissolved after 30hrs.
Sample + 50ml 2% HCl solution	Bubbled and dissolved at faster rate. Completely dissolved after 20hrs.
Sample + 50ml 5% HCl solution	Bubbled vigorously and dissolved at a much faster rate. Complete dissolution after 14hrs.
Sample + 50ml 10% HCl solution	Bubbled vigorously and dissolved faster. Complete dissolution after 5hrs.
Sample + 50ml 15% HCl solution	Dissolved and bubbled vigorously. Complete dissolution after 30mins.

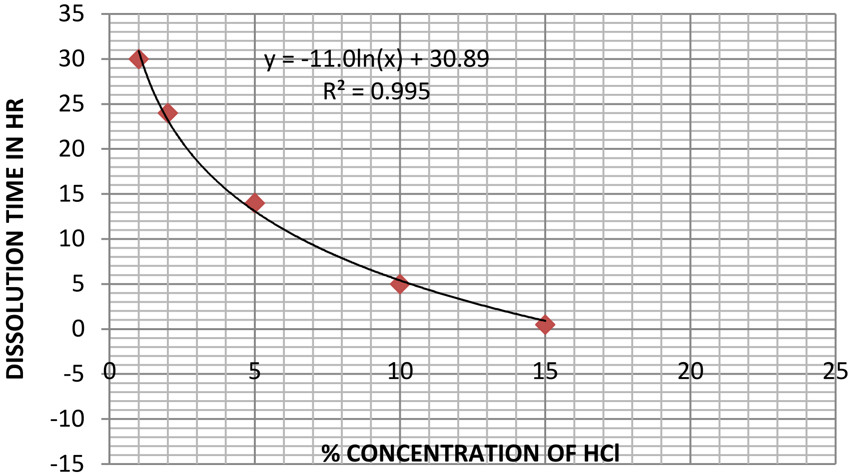

Figure-1
Time require for various conc. of acid to dissolve 2g of scale for production scale

Table-6
Testing the validity of the model

Concentration in % of HCl	Exp. time of dissolution hr	Validated time of dissolution Hr
1	30	30.89
2	20	23.26
5	14	13.19
10	5	5.56
15	0.5	1.1

Conclusion

Test results indicated that the main constituents of the scale were iron oxide, calcium carbonate and iron carbonate, typical of sandstone and carbonate reservoirs found in the Niger Delta

The XRF method has the capability to detect the oxides and a wider range of other metals that the AAS could not. Most importantly is the detection of radioactive materials like Thorium and Uranium.

Quantitative method can be used to show the chemical reactions of the scale sample in terms of the rate of dissolution after the metals and its oxides have been determined.

The model equation can be used to predict the optimum time and concentration of the acid without going through various laboratory testing protocols thereby serving operation time and cost.

Though 15% HCl was faster than 10% HCL in dissolving the scales, 10% HCl or less with corrosion inhibitors is recommended to be used for field application to avoid intense corrosion of pipes.

1t is recommended also that the XRF method should be used if it is critical to determine scale metal compositions and its oxides as well as other trace elements.

One of HSE concerns of scaling tendencies is the danger associated with NORM, therefore prudent and strict safety measures should be adhered to when handling scale analysis and job execution in the field.

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