Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21864

108 (2018) 106–111
March

Calcium carbonate scale in steam generator in enhanced oil recovery

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Received 4 August 2017; Accepted 30 December 2017

ABSTRACT

This article presents a case of scale on steam generator pipe of high pressure resulting from a failure in the ion exchanger unit of the water system power supply. This generator was injecting steam into oil wells for enhanced oil recovery at a temperature and pressure of about 350°C and 17.0 Mpa, respectively. For safety and operational performance, routine inspections on the steam generator are carried out. The steam injection was interrupted by a thick layer of incrustation in a vapour injection pipe. Analysis showed a scale of calcium carbonate ($CaCO_3$), magnesium and iron silicate [$(Mg,Fe)_3Si_2O_5(OH)_4$], magnesium hydroxide [$Mg(OH)_2$], and calcium and magnesium carbonate ($CaCO_3.MgCO_3$) with a thickness of 1.8 to 2.3 mm adherent to a film of magnetite (Fe_3O_4), which protects the carbon steel pipe from generated steam. To put the steam generator in safe operating condition again, the scale of calcium carbonate was removed with hydrochloric acid solution and a corrosion inhibitor. Chemical analyses and X-ray diffractometry analysis were performed in order to identify the scale formation on the inner walls of the pipe. Laboratory testing showed that acid removal with a mixture of hydrochloric acid and hydrofluoric acid with propargyl alcohol (corrosion inhibitor) achieved efficiency exceeding 90%.

Keywords: Scale; Calcium carbonate; Steam generator; Operational failure; Corrosion

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1. Introduction

An oil field, during its productive life, goes through several stages from discovery until its discontinuation. The extraction of oil from the reservoir rock is termed primary recovery when oil is driven to the surface by natural mechanisms. Secondary recovery involves the injection of natural gas or (fresh or salt) water for the purpose of maintaining pressure in the reservoir at a desired level. Tertiary recovery or enhanced oil recovery (EOR) methods are gaining importance as worldwide resources of crude oil become increasingly limited. EOR can involve various methods including the injection of gases (N_2, CO_2 and hydrocarbon), chemical products (polymers, surfactants and alkalis), steam, etc., which aim to remove the oil in the reservoir rock that has not yet been removed by primary and secondary recovery [1–3].

Surface steam injection is the most common EOR process used in heavy oil production onshore. Nevertheless, there are limitations due to heat loss in deep reservoirs and offshore fields. Fig. 1 is a representative schema showing steam injection and oil recovery from a reservoir rock at an onshore well.

The introduction of heat to the reservoir rock causes a temperature rise in both the rock and fluids, reduces the viscosity of the oil present and facilitates removal of the residual oil that is still in the rock aggregate. This is normally accomplished through the injection of hot fluid, in processes known as cyclic injection or continuous steam injection.

The greatest limitation on thermal injection methods is the heat lost on steam generation, in distribution lines, in the well and in the reservoir, as well as in adjacent rock layers and in the aquifer.

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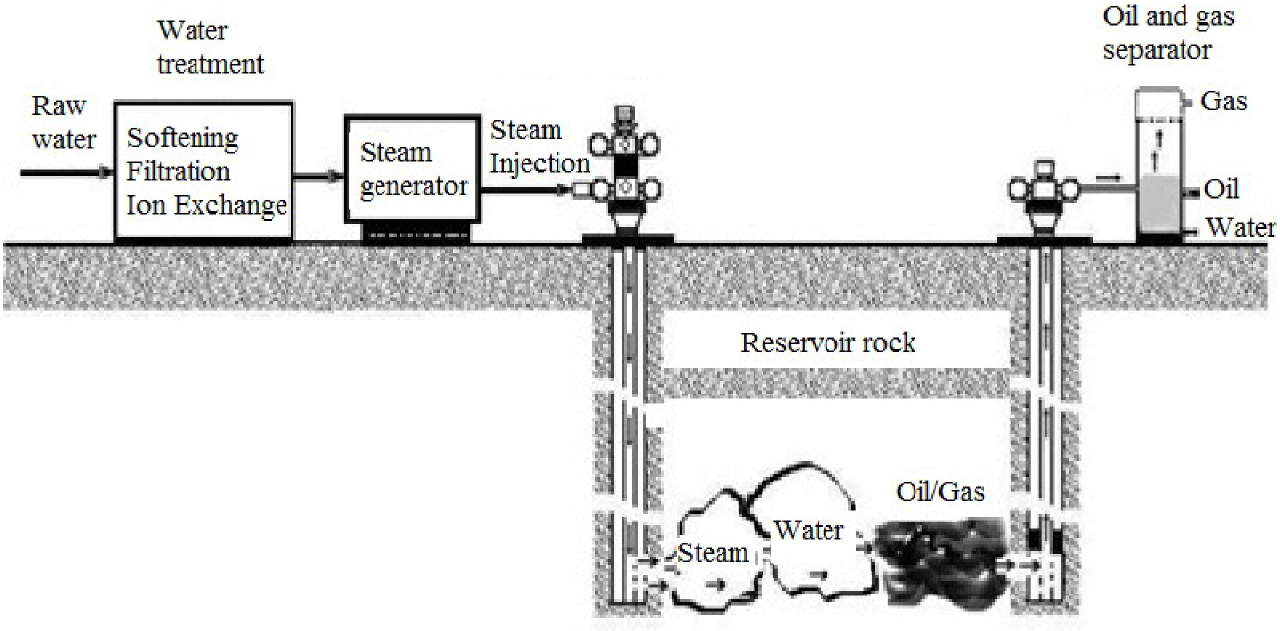

Fig. 1. Scheme showing steam injection and oil recovery.

The steam used for injection into oil wells is produced by steam generators of special type, usually mounted on skids to facilitate transport. These generators are composed of two heating stages (convection and radiation) and are designed to work with high pressure. They employ a forced circulation technique in such a way that the water and steam only passes once through the boiler tubes, termed once-through boiler (OTB). There is no accumulation of water in the pipes and, depending on heating conditions, about 75%–85% of the mass of water is transformed into steam. Positive displacement pumps the steam and the net mass is injected into wells with a pressure of 17 Mpa and temperature of 350°C [4]. Steam injection is a relevant option for exploiting petroleum in heavy oils recovery and mature oil fields [5,6].

Corrosion and formation of deposits (scale) inside tubes are two factors causing operational problems and compromising the integrity of steam generation equipment. Thus it is vital that the water supply meets the standards of quality for use in boilers. However, operations in inhospitable regions make it difficult to control the quality of the water supply required and necessary for a steam generator.

Internal corrosion of carbon steel pipes of a steam generator is mitigated by a protective film of magnetite (Fe_3O_4) adherent, uniform on the metallic surface. This film is formed by direct reaction of carbon steel with water (steam), in the absence of dissolved oxygen (O_2) and temperatures in the range of 200°C–300°C, as shown in the following reaction:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \tag{1}$$

Oxygen is damaging primarily because it initiates pitting corrosion, possibly through action of differential aeration cells. To eliminate or inhibit the corrosive action of the dissolved oxygen, corrosion inhibitors (oxygen scavengers), usually with base of sodium sulphite (Na_2SO_3) or hydrazine (N_2H_4), are added [7–9].

The formation of inorganic deposits (scale) in internal pipes is due the contamination of the water that feeds the steam generator. Usually, these contaminations occur because of operational failure of the water treatment unit. These occur in the form of calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and silicate (SiO_3^{2-}) ions. The high temperature and the steam generated transform these salts into adherent scales, creating a thermal insulation [8,10].

It is important to note that scale that occurs inside the tubes of the steam generator can reduce the thermal efficiency of steam generation, because the incrustation behaves as a thermal insulator, and compromises the flow of steam injected into the injector well. Here we carry out an evaluation of the scale, aiming to identify the process of deposition that occurred inside the steam generating tubes and which can compromise the integrity of the steam generator and consequently affect, mechanically and economically, oil recovery wells.

2. Materials and methods

The steam generator that is being evaluated has operated continuously for 6 months and, during preventive maintenance, the occurrence of scale with a thickness of 1.8–2.3 mm and a reduction in the rate of steam generation has been verified. 10 cm lengths of the tube were sectioned (Fig. 2) in order to determine the nature of the scale and the procedures for chemical cleaning of the tubes with a mixture of hydrochloric acid, hydrofluoric acid and corrosion inhibitor.

2.1. Crystalline phase analyses

Four samples of scale were removed from the inside of the tube; samples 1 and 2 have been removed from a region of carbon steel-magnetite while samples 3 and 4 are superficial. Chemical analyses for identification of the chemical species

Fig. 2. Samples of scales removed for analysis.

of the scale were carried out using X-ray diffractometry. The crystalline phases were determined by X-ray diffraction with a D8-Bruker diffractometer, Cu Kα X-ray tube, Ni-filter, 0.02 step, 0.2 s and a position sensitive detector (LynxEye). Note that this method of analysis only identifies crystalline chemical species. Chemical analysis (wet method) of carbonate (CO_3^{2-}) and silicate (SiO_3^{2-}) was carried out to assist in the determination of the scale constituents.

2.2. Dissolution of samples of scale

In order to evaluate the removal and the consequent dissolution of the scale of these steel carbon tubes, acid dissolution tests were conducted. Six samples were used with three for each laboratory condition. The assay consisted of placing 0.5 g sample (scale) in a polytetrafluoroethene (PTFE) tube containing 40 mL of hydrochloric acid (HCl) solution at 5% and 1% hydrofluoric acid (HF) (by mass) and additions of 1% of corrosion inhibitor (propargyl alcohol). The exposure time was 1 h and temperatures were set at 25°C and 50°C. The corrosive solutions were agitated with a magnetic bar.

Process efficiency of removal was calculated using the expression:

$$\text{Removal efficiency (\%RE)} = [(W_1 - W_2)/W_1] \times 100 \qquad (2)$$

where W_1 is the initial mass and W_2 is the final mass. The final mass was calculated after the end of the process. This consisted in filtering the resulting solution. The filter paper was washed with distilled water, acetone and ethyl alcohol. It was then placed in an oven for 1 h at 120°C. Finally, after cooling to room temperature, the final mass (W_2) was determined, discounting the weight of the filter paper.

2.3. Gravimetric test (mass loss)

To evaluate the action of the mixture consisting of HCl and HF on the steam generator's tubes, mass loss tests were prepared with carbon steel coupons to represent the tubes.

This evaluation employed a plate (coupon) of carbon steel with the following composition: 0.12% carbon, 0.24% Mn, 0.035% Si, 0.011% S and 0.009 P%. From this, steel plate coupons were made with the following dimensions: 45 mm × 15 mm × 10 mm. The metal surface was prepared with 100 and 250 grade sandpaper. They were washed with water and alcohol and dried with hot air, then weighed to the nearest 0.0001 g.

Three coupons of carbon steel were placed in PTFE bottles of 500 and 300 mL of the solution of hydrochloric acid solution at 5% (by mass) and 1% hydrofluoric acid (HF) (by mass) and corrosion inhibitor (propargyl alcohol), at concentrations of 0.5, 1.0 or 1.5 mL/L, were added. Tests were run for 1 and 3 h, and temperatures of 25°C and 50°C, resulting in 12 unique combinations of concentration, exposure, and temperature (Tables 2 and 3). The corrosive solution was agitated with a magnetic bar.

The corrosion rate (CR) and the efficiency of corrosion inhibitor ($\%E_i$) was defined by the following expressions:

$$\text{Corrosion rate} = \text{CR} = [(w_1 - w_2)/S \cdot t \text{ (mg/cm}^2\text{ h)}; \qquad (3)$$

$$\text{Efficiency } (\%E_i) = [(w_1 - w_2)/w_1] \times 100; \qquad (4)$$

where w_1 and w_2 are the weight loss (mg) of carbon steel coupons in the absence and presence of corrosion inhibitor, S = area (cm^2) and t = exposure time (h).

3. Results and discussion

The raw water that fed the steam generator was from an artesian well and was subjected to a simplified treatment of hardness removal (softening), filtration and finally put through an ion exchanger unit with cationic sodium ion exchanger resin as shown in Fig. 3.

In the softening process, hydrated lime and soda ash are added to react with bicarbonates (HCO_3^-), carbonates (CO_3^{2-}), dissolved CO_2, calcium (Ca^{2+}) and magnesium (Mg^{2+}) salts that commonly cause the hardness of water. The sludge formed mainly of calcium carbonate and magnesium hydroxide is represented by the following reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 + 2\ H_2O \qquad (5)$$

$$Mg(HCO_3)_2 + 2\ Ca(OH)_2 \rightarrow 2\ CaCO_3 + Mg(OH)_2 + 2\ H_2O \qquad (6)$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2\ NaOH \qquad (7)$$

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \qquad (8)$$

The filtration aims at removing suspended matter that can penetrate the steam generation equipment. The calcium and magnesium ions that were not removed by the softening process will be removed by the cationic sodium ion exchanger resin (Na_2R). Typical exchangers are in the form of macroporous beads and cause the following reactions:

$$Na_2R + Ca^{2+} \rightarrow CaR_2 + 2\ Na^+ \qquad (9)$$

$$Na_2R + Mg^{2+} \rightarrow MgR_2 + 2\ Na^+ \qquad (10)$$

When the resins are saturated with calcium and magnesium ions they are regenerated by sodium solution (NaCl).

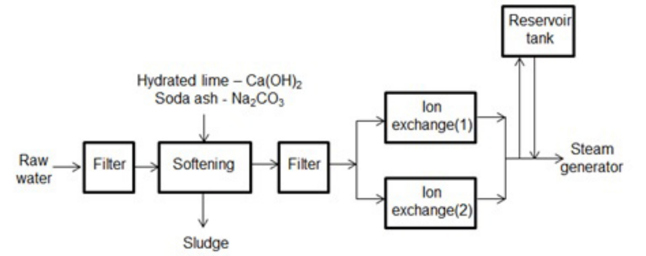

Fig. 3. Simplified treatment for water that fed the steam generator.

It is essential that the treatment uses two units: one in operation and the other in regeneration. A reservoir tank is meant to prevent any processing error by holding a volume of treated water, ready to be injected into the steam generator. Table 1 compares the average results of raw water coming from an artesian well and water after treatment.

Fig. 4 shows the results of X-ray diffraction with semi-quantitative analysis of the crystalline phases found in the samples. On average, the results of samples (1, 2 and 3) show the following chemical composition: 61% of $CaCO_3$, 21% of (Mg, Fe)$_3$Si$_2$O$_5$(OH)$_4$, 13% of $Mg(OH)_2$ and 7% of $CaMg(CO_3)_2$. Considering the absence of $Mg(OH)_2$, sample 4 has the following chemical composition: 68.5% of $CaCO_3$, 23.6% of (Mg,Fe)$_3$Si$_2$O$_5$(OH)$_4$ and 7.9% of $CaMg(CO_3)_2$. As can be seen, the major phase is calcite ($CaCO_3$) and all of others phases are compounds are also based on hydroxides or carbonate. However, sample 4 does not present the $Mg(OH)_2$ as brucite, which cannot be explained with the given water analysis.

The water chemical analyses presented in Table 1 (for a week of continuous operation) showed no significant change based on established standards. However, additional information indicated that the ion exchange unit was out of normal operation four times, for approximately 2 h each, over a period of 6 months.

Chemical analysis (average) of treated water that feeds the generator indicates that alkalizing agents were added during softening, with a pH in the range of 10–11. Due to occasional variations in composition, common to many raw water supplies, it is often difficult to control the chemical balance of water with hydrated lime and soda ash in the softening unit. This could facilitate contamination of the steam generator with calcium and magnesium ions.

Table 1 also shows that the cationic resin unit reduced Ca^{2+} and Mg^{2+} ions present in the water supply. However, the operational failures in this unit may have caused migration of Ca^{2+} and Mg^{2+} ions to the steam generator.

Considering this fact, it can be assumed that the Ca^{2+} and Mg^{2+} ions made contact with bicarbonate and carbonate, generating calcium/magnesium carbonate and magnesium hydroxide. This is supported by the analyses of the scale by X-ray diffraction, as shown in the following reactions:

$$Ca^{2+} + 2\ HCO_3^- \rightarrow Ca(HCO_3)_2 \qquad (11)$$

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O \qquad (12)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (13)$$

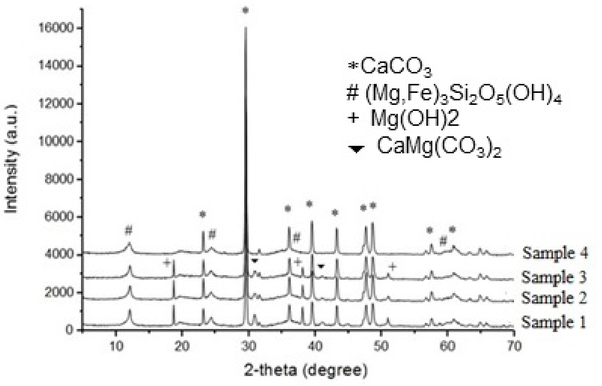

Fig. 4. X-ray diffraction of samples 1–4 of a steam generator pipe tube.

Table 1
Results of the chemical analysis performed on the water supply to the steam generator for a week

Determinations	Artesian well	Treated water
Calcium, Ca^{2+}, mg/L	21.2–25.4	0.0–1.0
Magnesium, Mg^{2+}, mg/L	12.3–13.2	0.0
Iron, Fe^{3+}, mg/L	0.3–0.5	0.3–0.5
Bicarbonate, HCO_3^-, mg/L	210.0–245.5	0.0–1.5
Carbonate, CO_3^{2-}, mg/L	0.1	24.0–120.0
Sulfate, SO_4^{2-}, mg/L	0.2–0.3	0.3–0.5
Chloride, Cl^-, mg/L	1.0–1.3	1.0–1.1
Hydroxyl, OH^-, mg/L	0.0	45.0–97.3
Silicate, SiO_3^{2-}, mg/L	12.0–14.3	13.0–18.3
pH	6.8–7.2	10–11

$$Ca^{2+} + Mg^{2+} + 2\ CO_3^{2-} \rightarrow CaMg(CO_3)_2 \qquad (14)$$

$$Mg^{2+} + 2\ OH^- \rightarrow Mg(OH)_2 \qquad (15)$$

$$x\ Mg(OH)_2 + 3\text{-}x\ Fe(OH)_2 + 2\ SiO_2 + w\ H_2O \rightarrow (Mg,\ Fe)_3Si_2O_5(OH)_4 \qquad (16)$$

The masses (W_1) found in dissolution testing of samples of scale with the mixture of HCl and HF were negligible: it is acceptable to consider it as practically 100% efficient. It was also observed that the increase in temperature and acid concentration favoured the rapid dissolution of scale.

Fig. 5 presents a diagram of the acid removal of scale with an acid mixture (HCl + HF), in order to illustrate the process of chemical cleaning. HCl prefers to attack carbonates and hydroxides while the hydrofluoric acid is a specific reagent for SiO_2 and inorganic silicates. Therefore, the removal of these scales with mixtures of HCl and HF is very efficient [11–13].

The reactions of acid dissolution are presented below:

$$2\ HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O \qquad (17)$$

$$4\ HCl + MgCO_3.CaCO_3 \rightarrow CaCl_2 + MgCl_2 + 2\ CO_2 + 2\ H_2O \qquad (18)$$

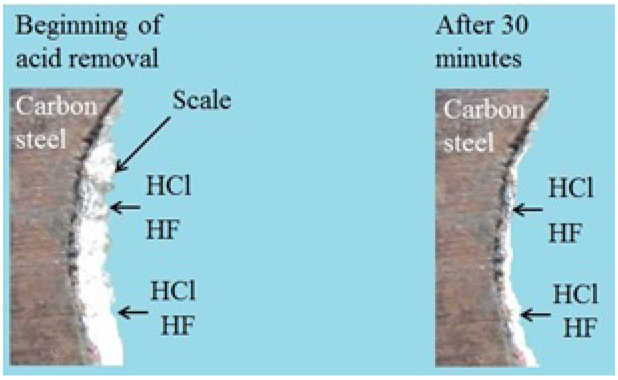

Fig. 5. Diagram of the acid removal of scale.

$$2HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2\,H_2O \quad (19)$$

$$4\,HF + SiO_2 \rightarrow SiF_4 + 2\,H_2O \quad (20)$$

$$6\,HF + SiO_2 \rightarrow H_2SiF_6 + 2\,H_2O \quad (21)$$

The gravimetric test results of the addition of propargyl alcohol (corrosion inhibitor) presented in Tables 2 and 3 refer to the average of three steel carbon coupons.

The results of mass loss assays showed that the addition of propargyl alcohol (2-propyn-1-ol) in a mixture of HCl and HF provided excellent protection to the carbon steel with an efficiency of 97%.

The literature [11,14–16] has shown that the corrosion inhibitors based on propargyl alcohol have presented excellent performance in protection of carbon steel in hydrochloric acid solutions in all concentration and temperature combinations. The good adsorption capacity of propargyl alcohol molecules by carbon steel is linked to its π-electrons, which interact with metallic surfaces and consequently form triple bonds, HC≡C–CH–OH [17].

Finally, two points of caution should be made regarding this work. First, considering the toxicity of propargyl alcohol, laboratory tests must be performed in a fume hood. Second, acid removal was only carried out in the laboratory in samples taken from the steam generator, not on site.

4. Conclusions

The evaluation of scale on a steam generator, the chemical removal of that scale and anti-corrosion protection using corrosion inhibitors was studied on the basis of laboratory tests and references. The following conclusions may be drawn:

- The occurrence of the scale inside the steam generator tubes was due to operational failure in the treatment of water;
- The scale's main chemical composition was: 61% of $CaCO_3$, 21% of $(Mg, Fe)_3Si_2O_5(OH)_4$, 13% of $Mg(OH)_2$ and 7% of $CaMg(CO_3)_2$;
- Mixtures consisting of hydrochloric acid and hydrofluoric acid were excellent at removing scale adhered to carbon steel;
- Mixtures of HCl and HF are particularly corrosive to carbon steel and a corrosion inhibitor should be included;
- Propargyl alcohol (2-propyn-1-ol) is an effective corrosion inhibitor for reducing the corrosion rate of carbon steel in mixtures of hydrochloric acid and hydrofluoric acid solutions with efficiency up to 97%.

Table 2
Results of tests of mass loss of carbon steel coupons in a solution of 5% hydrochloric acid (HCl) solution (by mass) and 1% hydrofluoric acid (HF) (by mass) and additions of a corrosion inhibitor (propargyl alcohol)

Corrosion inhibitor concentration mL/L	Mass loss (mg/cm^2)			
	25°C		50°C	
	1 h	3 h	1 h	3 h
0	4.32	7.88	15.33	23.54
0.5	0.34	0.66	0.64	0.82
1.0	0.25	0.57	0.44	0.73
1.5	0.22	0.32	0.35	0.65

Table 3
Results of tests of efficiency (%E_i) of carbon steel coupons in solution of 5% hydrochloric acid (HCl) (by mass) and 1% hydrofluoric acid (HF) (by mass) and additions of corrosion inhibitor (propargyl alcohol)

Corrosion inhibitor concentration mL/L	Efficiency (%)			
	25°C		50°C	
	1 h	3 h	1 h	3 h
0.5	92.12	91.62	95.82	96.51
1.0	94.21	92.76	97.12	97.32
1.5	94.90	95.93	97.71	97.23

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