Determination of corrosion products for steam and flue gas injection environments using thermodynamic simulation

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Abstract. Thermal recovery processes using steam injection with combustion gases (flue gas) have shown positive results in the recovery of heavy crude oil over the conventional process, by integrating different recovery mechanisms. However, under the operating conditions, the injection of these fluids generates highly corrosive environments that have an impact on the deterioration of the materials, resulting in risks and operational costs. Therefore, it is necessary to determine the theoretical corrosion products that can be generated in these processes. This research focused on the study of API N-80 carbon steel exposed to a steam and flue gas atmosphere, at pressure and temperature conditions in the ranges of 800 psia - 1100 psia (55 bar - 75 bar) and 520 °F - 560 °F (270 °C - 290 °C) respectively. Based on this environment, to determine the theoretical corrosion products, a thermodynamic simulation stage was developed using HSC Chemistry software, which was used to generate Pourbaix, Ellingham and thermodynamic equilibrium diagrams. It was found that the main theoretical corrosion products corresponded to oxides, carbonates, and hydroxides, among which the significant presence of iron (III) oxide (Fe₂O₃), iron (II, III) oxide (Fe₃O₄) and iron carbonate (II) (FeCO₃) was corroborated.

1. Introduction

Heavy and extra-heavy crude oil reservoirs have become more important in recent years because of the decrease in the availability of resources such as light crudes and the increase in energy consumption [1]. Therefore, there is a need to find new methods to increase the recovery factor because oil production by conventional techniques has been limited [2]. Thermal recovery methods contribute to the exploitation of this type of reservoirs, where viscosity reduction acts as the main recovery mechanism [3,4].

Cyclic Steam Stimulation (CSS) is the most used thermal recovery method worldwide, according to Villaquirán, et al. [5], 40% of the enhanced oil recovery projects correspond to steam injection. Pérez et al. [6], point out that hybrid technologies have been developed with the objective of improving the performance of thermal recovery; one example is the injection of steam and combustion gases (flue gas). The flue gases used in this process (mostly composed of carbon dioxide (CO₂) and nitrogen (N₂)), are generally the product of the combustion of the steam generation process.

Although this method can increase the recovery factor and reduce CO₂ emissions [7-9] there are different associated problems; one of the main ones lies in the corrosive effects that produce the deterioration of the materials commonly used in the injection process. There are several variables
involved in corrosive processes; researchers such as Pradilla, et al. [10] and Wang, et al. [11] point out that among the main ones are pressure, temperature, pH of the medium, fluid velocity and oxygen content.

In steam and flue gas injection processes, high temperature (>500 °F) and pressure (800 psia - 1200 psia) values are found, so it is necessary to study the corrosion behavior of carbon steels such as API N-80 under the variation of these parameters. Other researchers found that the increase in temperature generates an increase in the corrosion rate until the protective films were formed, which caused a decrease in the corrosion rate [12]. On the other hand, for the case of pressure, in investigations of carbon dioxide atmospheres it was shown that there is a linear relationship between the partial pressure of this compound with the corrosion rate [13-15].

Corrosion studies such as that of Orozco, et al. [16] and Orozco, et al. [17], have employed simulation as a phase prior to experimentation to obtain the behavior of the system in thermodynamic equilibrium and thus observe the theoretical corrosion products formed.

The present research work focused on the study of the formation of theoretical corrosion products in steam and flue gas environments injection on API N-80 steel using the simulation tool HSC Chemistry.

2. Methodology

2.1. Description of the study atmosphere

The present research work focused on determining the theoretical corrosion products in steam-flue gas injection environments on API N-80 carbon steel. To determine the compounds formed in the corrosion process in the system, it was necessary to know the mass composition of the API N-80 steel and the molar composition of the steam-flue gas mixture in the same stream.

2.1.1. Chemical composition of steel used in the study. Table 1 reports the mass composition of API N-80 steel used by Li, et al. [18] in their study; this information was the starting point for carrying out the simulations in this research work. It should be noted that, the main components of the alloy were used for the construction of the Pourbaix diagrams, which are Iron (Fe), Manganese (Mn) and Carbon (C), evaluated at the established conditions and considering the mass percent of the elements.

| Table 1. Chemical composition of the API N-80 grade steel used in the study. |
|-------------------------------------------------------------|
| Steel | C (%) | Si (%) | Mn (%) | P (%) | Cr (%) | V (%) | Fe (%) |
|-------|-------|-------|--------|-------|--------|-------|--------|
| API N-80 | 0.35  | 0.30  | 1.45   | 0.02  | 0.12   | 0.11  | 97.64  |

2.1.2. Injection stream composition. Table 2 presents the molar composition for the flue gas stream after the dehydration and extraction of the oxygen process were performed and Table 3 report mass compositions of the flue gas and injection (steam-flue gas) streams, respectively, according to previous work by Pérez, et al. [19], for a Colombian oil field in the Middle Magdalena Valley.

| Table 2. Molar composition of CO₂ and N₂ in the flue gas stream. |
|-------------------------------------------------------------|
| Molar percentage | %   |
| N₂              | 89  |
| CO₂             | 11  |

| Table 3. Mass composition of the steam-flue gas injection stream. |
|-------------------------------------------------------------|
| Mass percent | %   |
| Flue gas     | 52.3|
| Vapor        | 47.7|

Based on the composition of the flue gas stream proposed in the work done by [19], the molar percentages for the injection flow were determined in Table 4.
2.1.3. Determination of operating conditions. Considering that the process would take place in a field of the Colombian Middle Magdalena Valley and according to the working conditions established for that location, it was determined that for steam-flue gas injection techniques the pressure and temperature variables are in the ranges of 800 psia - 1100 psia (55 bar - 75 bar) and 360 °F - 570 °F (180 °C - 300 °C) respectively. The present research work considered studying three representative values of the pressure range described above. The selected values were: 800 psia, 950 psia, and 1100 psia (55 bar, 65 bar, and 75 bar), for which the corresponding temperatures were determined using the Antoine equation, which describes the relationship between temperature and vapor saturation pressure of pure substances, thus obtaining the following values: 520 °F, 540 °F, and 560 °F (270 °C, 280 °C, and 290 °C). Table 5 summarizes the conditions that were studied, first an analysis of the temperature and pressure variables was performed, where for each pressure the described temperature range was evaluated, and, in an analogous manner, the procedure was performed for each temperature.

2.2. Simulation stage/thermodynamic study
The theoretical corrosion products were determined from a thermodynamic simulation stage with the purpose of obtaining the pressure and temperature variables behavior, from the construction of different diagrams (Pourbaix, Ellingham and thermodynamic equilibrium). In this research work the simulation tool used was the HSC Chemistry software. It should be noted that the simulation stage considered the mass percent of the three main elements in the alloy.

2.2.1. Construction of the Pourbaix diagram. The present research emphasized the study of the corrosive effects of a saturated steam; however, when considering the energy losses inside the pipeline in the injection process, condensation can occur, which leads to an atmosphere with wet steam. Based on this consideration, the use of Pourbaix diagrams was feasible, whose objective was to obtain an initial approximation of the theoretical corrosion products in the steam-flue gas injection process.

2.2.2. Construction of the Ellingham diagram. The main objective of this diagram was to review the spontaneity of the reactions and the products formed in the system.

2.2.3. Construction of the equilibrium diagram. The HSC equilibrium module allows the equilibrium compositions of multiple components in heterogeneous systems to be calculated. The chemical reaction system, with its phases and species, and the compositions of the elements were specified. The quantities of products at equilibrium under isothermal and isobaric conditions were calculated. It was also necessary to specify the potentially stable substances and phases, as well as the quantities and temperatures of the components; this procedure must be carried out properly to avoid giving rise to possible errors. The steel/gas molar ratio used for this simulation was 1/1000. This ratio was selected considering the criteria followed in the research of Alviz, et al. [20].
3. Results

3.1. Determination of theoretical corrosion products

For this stage, Pourbaix, Ellingham and thermodynamic equilibrium diagrams were used as main tools, carrying out an analysis of the theoretical corrosion products in the study atmosphere for API N-80 steel.

3.1.1. Diagram of Pourbaix. Once the simulations were carried out, it was observed that the behaviors evaluated for each main element of API N-80 steel at the conditions of Table 5 were similar despite the variation of pressure and temperature conditions. The theoretical corrosion products determined for the conditions of the research work at variable pH can be seen in Figure 1, Figure 2, and Figure 3. Table 6 compiles all the products that could occur, of which oxides, carbonates and hydroxides are the main ones.

| Conditions | Diagram | Products |
|------------|---------|----------|
| Atmosphere CO2 N2 H2O T = 520 °F - 560 °F (200 °C - 300 °C) P = 800 psia - 1100 psia (55 bar - 75 bar) | Fe Mn C | Fe₂O₃, Fe (OH)₃(-a), FeCO₃, Fe₂MnO₄, Fe (+2a), Fe₂O₃, Fe, HFeO₂(-a) |
| | Mn C Fe | MnO₂(-a), MnO₃, MnO₂(-2a), MnCO₃, MnO*OH, Fe₂MnO₄, Mn₂O₃, MnO₂(-2a), MnC₃, Mn |
| | C Fe Mn | HCO₃(-a), CO₃(-2a), CO₃, MnCO₃, MnC₂, C₂H₄O |
3.1.2. Ellingham diagram. Figure 4 corresponds to the Ellingham diagram constructed for the steam-flue gas injection system, from which it was concluded that among the products with a higher Gibbs free energy delta were compounds such as: Mn₃O₄, MnO*OH and MnCO₃, which, being in the lower part of the diagram, have a higher spontaneity of formation.

3.1.3. Equilibrium diagram. Figure 5 shows the equilibrium diagram for the system under study at a pressure of 800 psia (55 bar) and a temperature range of 520 °F - 580 °F (270 °C - 300 °C); similarly, Figure 6 shows the equilibrium diagram for a working temperature of 520 °F (270 °C) and a pressure range of 800 psia - 1100 psia (55 bar - 75 bar).

Figures 5 and Figure 6 were constructed from Table 6 showing the products that could be present, determined from the Pourbaix diagrams constructed. It should be noted that the ones that occur in greater proportion are the iron compounds: Fe₂O₃, Fe₃O₄ and FeCO₃; compared to the Ellingham Diagram, where the manganese components were the ones that presented greater spontaneity of formation, the iron products are present due to the proportion that iron occupies within the alloy (API N-80 steel).
Figure 5. Equilibrium diagram for temperature of 520 ºF and a pressure range of 800 psia - 1100 psia.

Figure 6. Equilibrium diagram for pressure of 800 psia and a temperature of 520 ºF - 560 ºF.

4. Conclusions
The theoretical corrosion products for API N-80 steel were obtained through thermodynamic simulation using HSC Chemistry software considering the implementation of a thermal recovery process with a steam-flue gas atmosphere. The components were formed at the established conditions with temperature and pressure ranges from 520 ºF to 560 ºF and 800 psia to 1100 psia, respectively.

Using HSC Chemistry software, the Pourbaix, Ellingham and thermodynamic equilibrium diagrams were constructed, determining that the compounds present in greater quantities in equilibrium for the system studied were: Fe₂O₃, Fe₃O₄ and FeCO₃, which were corroborated with experimental results of similar studies reported in the literature for carbon steels.

From the construction of the Ellingham diagrams, it was possible to observe that the theoretical corrosion products that present a greater spontaneity of formation are: Mn₃O₄, MnO*OH, MnCO₃. However, the equilibrium diagrams showed that iron compounds predominate in the corrosion process due to the high proportion of this element in the chemical composition of steel.

Since the products determined through the simulation were found in significant proportions, a more detailed experimental study is required to understand and quantify the corrosive process. Additionally, the implementation of inspection, monitoring and mitigation techniques is recommended for the development of a pilot project at field scale.
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