Investigation of the Effect of the Efficiency of Catalysts on Early Destruction of Direct Reduction Reformer Tubes

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Abstract

The catalysts of the direct reduction unit play a significant role in producing reducing gases and the lifetime of the reformer tubes. In this paper, reducing the efficiency of catalysts on the early destruction of direct reduction reformer tubes will be investigated. Cold compressive strength test, XRF, and BET analysis were performed on intact and used catalysts. Also, the microstructure of the destroyed tube was examined by a scanning electron microscope, and the sulfur amount was measured. The results show that in used catalysts compared to intact catalysts, the specific surface area is reduced, and the access amount to areas containing nickel is reduced. Access to nickel-rich areas will be drastically decreased, and reforming reactions will not be performed well. This lessens the efficiency of the catalysts and breaks them down; hence several reformer tubes are exposed to higher temperatures, and their service life will be considerably reduced. Due to precipitations, the sulfur amount available in the destructed tube is equal to 0.1%, ten times the allowable sulfur content in the reformer tube alloy.

Keywords: Catalyst, Special Surface, Reformer Tube, Hot Corrosion, Microstructure.

1. Introduction

Today, steel is one of the main materials of the industrial world. Moreover, its production is identified by high energy consumption relative to carbon dioxide emission. 6% of human-made greenhouse gases (CO_2) result from the universal production of steel. Using consistent methods in producing steels, including direct reduction, followed by steelmaking in an electrical arc furnace, decreases CO_2 emission compared to the other methods [1)]. Direct reduction is one of the transformation procedures of pellet to sponge iron. In this method, a natural gas, as the initial substance to produce a reducing gaseous mixture, mainly consists of hydrogen and carbon monoxide and produces in the reformer container in the vicinity of catalysts. For several years, nickel-based catalysts have been employed to reduce gas in the direct reduction units [2-4)]. Three different types of neutral, active, and semi-active catalysts are used in the direct reduction unit. Catalysts are placed into the tubes, and the input gas is broken down in the reformer container at the box reformer temperature of ~1100°C and produces a reducing gas, including CO and H_2, in its outlet. Consequently, this gas is injected into the furnace and is responsible for reducing oxide pellet. The service life of the catalyzers is about five years. Deactivation of catalysts occurs thanks to sulfur, halogens, and carbon compounds. This results in creating serious problems in the direct reduction units. Reformer tubes' life decrease, and their perforation are examples of these problems [5)]. Usually, reformer tubes

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will have a service life of about 8 to 10 years. However, some cases will be perforated from the top in less time (about five years) and lose their efficiency, which will eventually lead to a decrease in the efficiency of the reformer and lessen production. Moreover, this research will investigate reducing the efficiency of catalysts on the early destruction of the direct reduction reformer tubes and their preventing methods.

2. Materials and Experimental Procedure

Intact and used special surface catalysts were utilized to examine the catalysts; also, three tests of BET, XRF, and cold compressive strength were carried out on them. Moreover, according to the reference standards of ASTM E3 [6)], ASTM E407 [7)], and ASTM E883 [8)], a metallography test was carried out on the destructed tube shown in Fig. 1. Glyceria solution used for etching the samples, scanning electron microscopy (model: JEOL), and EDS analysis were employed to study the microstructure and determine the type of destruction. The percentage of sulfur near the crack after chipping was measured using the ELTRA carbon and sulfur measuring device.

3. Result and Discussion

3.1. Review of Results on Catalysts

According to Table 1 related to the active catalyst, the percentage of nickel for both intact and used catalysts shows a low decrease; this is also true for semi-neutral catalysts. Nickel is responsible for playing the role of catalyst in the reforming reactions, and therefore, there is no case in terms of the active elements to accomplish the reforming reactions. However, the special surface in both active and semi-active catalysts shows severe reduction so that the accessibility to nickel-rich areas decreases, and the reforming reactions will not work well. Since these reactions are endothermic, the temperature of the tube wall will be increased when they do not progress. Fig. 2 indicates a picture of the discharged catalyst. Low flow will pass through the desired catalyst because they are several crushed. Also, because the tube wall temperature will be more than the other tubes attributable to the heat exchange with the reformer, the tube can be seen brighter than the others from the cleanout of the reformer.

Fig. 1. Image of the destroyed tube.

Table 1. Catalysts Analysis.

Sample	**Active**	**Active**	**Semi- Active**	**Semi –Active**
Parameter	Fresh	Used	Fresh	**Used**
Surface Area (m²/gr)	2.9	0.5	5.2	**0.108**
Ni %	13.38	10.79	8.25	**7.60**
CCS kg/f	235	233	212	**209**

Fig. 2. Crushed catalysts discharged from the destroyed tube.

3.2. Study of diagrams related to the temperature difference of various points of reformer

The ceiling and floor temperatures of the reformer container are monitored in different places using 16 thermocouples. In recent months, it is observed that the temperature difference between two sides of the reformer's roof is about 50°C to 60°C; there is a similar difference, but lower compared to the ceiling, at the floor, and the reformer temperature is higher in the last beys (towards the stack) than the other parts. This difference is present in Fig. 3. Fig. 3(a) related to the two reformer thermocouples and their 3-day history. As can be seen, the temperature difference at the beginning of the diagram reaches about 50°C. Figure 3(b) shows all the thermocouples installed at the ceiling of the reformer weekly. As can be seen, the difference between the temperatures is significant; the same diagram is offered for three months in Fig. 3(c). The difference in the temperatures does not seem high at first, but then it increases. Therefore, the temperature on one side of the reformer (stack side) is generally 50°C higher than the other part. Accordingly, the second half of the reformer tubes (stack side) are at higher temperatures since all pipes have a relatively equal flow gas. It is well understood by observing the cleanout of the reformer so that the number of the hot tube from bey No. 7 to No. 14 is higher than the other parts. It should mention that there are some dark wall tubes in bey No. 1 to No. 7, which indicating they are cold.

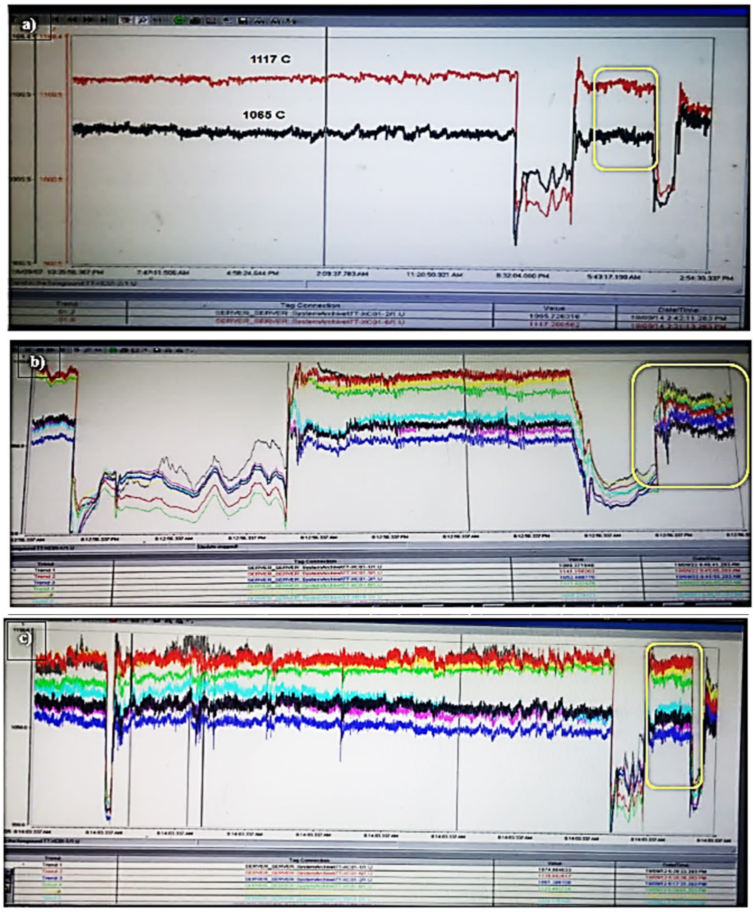

Fig. 3. Graphs related to reformer ceiling temperatures: a) 3 days, b) weekly, and c) 3 months.

Hence, when the reformer temperature is kept constant, some reformer tubes are at higher temperatures, and their life is reduced. It is confirmed by the perforation of 3 of the reformer tubes in Bey No. 14 and the hot tubes observed in the second half of the reformer.

Thus, based on the importance of temperature difference and the need for the temperature balance of the reformer box, several studies were conducted, leading to recommending two solutions:

1) The number of main torches of the reformer is 196, and their orifice size is equal to 65.4 mm. Subsequently, it was decided to add some orifices with two sizes of 38 mm and 33 mm in monthly repairs so that the smaller and bigger ones applied at higher and lower temperature parts, respectively. Therefore, the temperature of the different parts is adjusted by decreasing or increasing the amount of passing gas flow.

2) Since the return and its gas distribution are done from the furnace side, the gas used for fueling the burners is supplied from the return gas plus natural gas (if needed). Also, the return gas after passing through the upper scrubber carries some moisture and soft sponge particles with it. Therefore, the gas nozzles of the main burners may be clogged in the first bays. It was necessary to open and inspect the nozzles during the first monthly repairs. Figure 4 shows the open nozzles of the Bey No. 1 reformer. According to Fig. 4, sediment is formed in the reformer nozzles. This causes the nozzle to clog, the necessary flow for the burners to pass, and sediment deposition on the catalysts. By moving from Bey 1 to Bey 14, the clogging is reduced. Fig. 5 shows one of the selected nozzles in the reformer as an example.

Fig. 4. Reformer main burner nozzles.

Fig. 5. The main burner nozzle in Bey No. 6.

It is also extensively confirmed by the temperature changes of the reformer from Bey No. 1 to 14. Therefore, the reformer nozzles were cleaned entirely, and 38 mm orifices were utilized in rows 2, 3, 4, and 7 in the main torch one by one; on the other hand, in the parallel rows on the side of the stack, 33 mm orifices were employed. After starting the unit and normalizing it, the temperature difference between the two sides of the reformer decreased by 10 to 15 °C. It is shown well at the end of the diagrams (marked) presented in Fig 3. (a) to (c).

3.3 Microstructure Study

Based on the SEM results, several oxides were observed around the crack. Moreover, alkaline and alkaline earth elements were observed in the sample. For further investigations, the reasons for the destruction, the percentage of sulfur in the area close to the crack was measured using ELTRA carbon and sulfur measuring device after chipping; its value is equal to 0.1%, which is ten times the sulfur available in the alloy. Furthermore, the EDS results from the fracture surface confirm alkaline elements like sodium, resulting in hot corrosion in this area presented in Figs. 6 and 7. According to the working temperature of the segment, which is higher than 900°C, EDS results, and sulfur percentage, the destruction of the segment occurred under the influence of corrosion type I [9, 10].

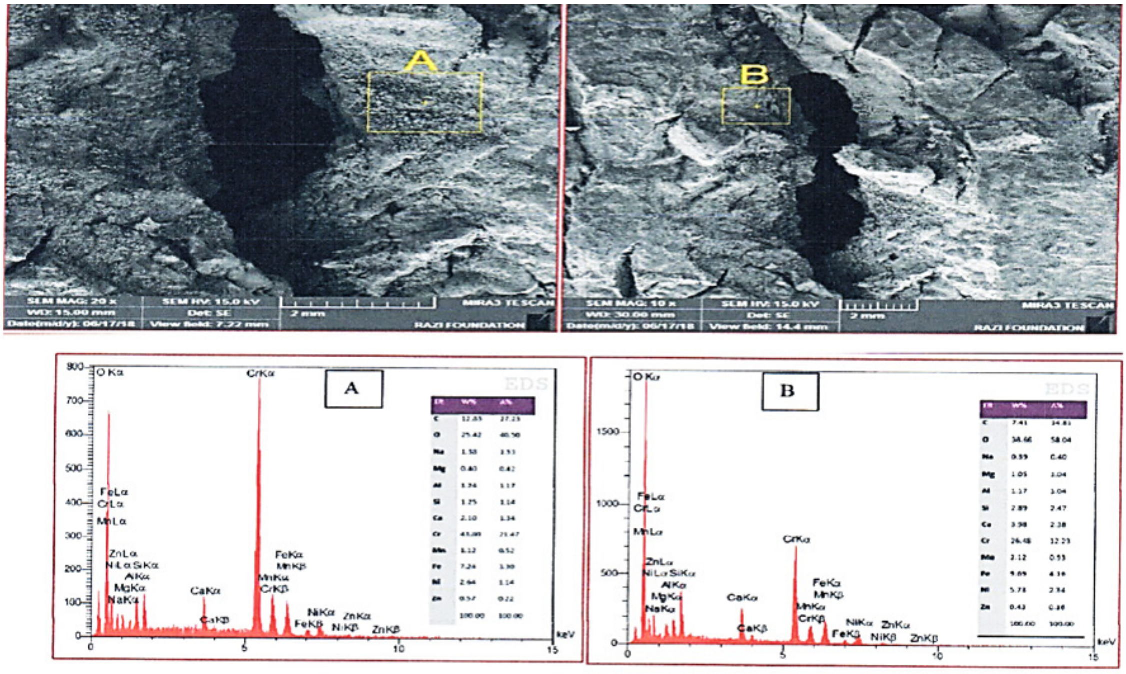

Fig. 6. Destroyed surface images with EDS analysis.

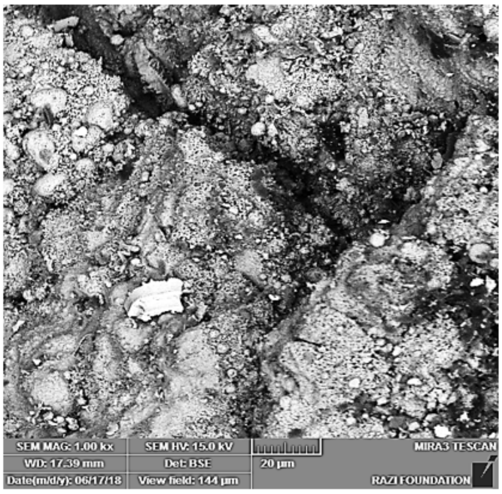

Fig. 7. Image of the failure area at higher magnification.

4. Conclusion:

Regarding the investigations conducted in this research, the destruction factors of the reformer rube are as follows:

- Catalysts crushing under the influence of high temperature and thermal shock.
- Reducing the efficiency of the catalysts under the influence, reducing their surface special.
- The operation of numerous tubes at higher temperatures, the catalysts crushing, and the clogging of their nozzles by sediments.

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