Nano Silicate Ceramic Coating Material Applied to Increase the Emissivity and Efficiency of Primary Reformer Radiant

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Abstract

Nano silicate ceramic material prepared in this research for coating the walls of the primary reformer unit in the state company of fertilizers. It is applied to increase the emissivity and thermal efficiency to improve the properties of insulation materials. Moreover, it is increasing the working operation time for catalyst tubes and reducing the carbon dioxide emissions. Nano coating materials were prepared by using different refractory materials that include silica, filed spar, alumina, manganese dioxide and magnesium oxide. The preparation method was done by calcination and firing these materials then crashing to get extremely fine powder. The results show that coating materials consist mainly from quartz crystalline and glassy phase structure with a grain size of 158 nm and penetration between 10 to 20 mm when using different concentration 0.5 to 1.0 % for total mix. The emissivity of primary reformer insulation materials was increased with 30 % comparing with insulation materials without coating.

Keywords: High emissivity coated, glassy phase, insulation, reformer, refractory.

1. Introduction

The main problems that facing reformers are include energy liberated transferred by radiation and increase in the fuel consumption. which cost the company more money and time to replace and repair the damage area of reformers. Therefore, many scientist and researchers have been focusing on this problem by using different types of refractory materials and make it as a particles to get the best specification and insulation surface[1]. Emissivity of any surface is a function of wavelength, direction, temperature and surface conditions which is defined as the radiation of materials. The effectiveness of the energy as thermal radiation includes visible radiation and infrared radiation. Also, it is defined as a measuring of the efficiency of surface radiation in which the surface emits thermal energy. Recently, researchers have been focused on the development of high emissivity coated by using ceramic fibers and refractory bricks for furnaces and reformer sections in the refining, petrochemical and iron steel plants \([2]\). I. Benko studied a new method which increased the radiation heat transfer of furnace refractory lining through applied a high emissivity coating material to emissivity of ceramic fiber insulations by 45% and Shamotte with 20 % \([3]\). Baskara Aji Nugraha was increased the production of Ammonia plant by using ceramic coating in the primary and secondary reformers. The ceramic coating was decreased the fuel consumption and the fouling effect that causes scales on catalyst tubes red-colored material \([4]\). P. B. Jensen et. al applied ceramic coating in furnace walls which lead to increase the emissivity in the furnace box and improve the efficiency with the mechanical properties of bricks \([5]\). In this research, new types of Nano refractory materials were prepared to applied in the primary reformer for the state company for fertilizing company in the south region of Iraq. The ceramic coating material that prepared was examined and testing by using different device such as XRD, EDX, SEM, XRF and FTIR with Master Sizer 2000 Laser to find the grain size.
2. Experimental Work

2.1 Materials

The main materials that used in this research are include silica oxide SiO$_2$, Alumina oxide Al$_2$O$_3$, Magnesium Oxide MgO, Calcium oxide CaO, Manganese oxide MnO and Calcium Florid CaF$_2$ with sodium silicate and potassium silicate as binding materials as shown in Table 1.

| Table 1. Specification of liquid binder |
|----------------------------------------|
| Binder               | % Na$_2$O : K$_2$O | SiO$_2$:Na$_2$O | SiO$_2$:K$_2$O |
| Sodium Silicate       | 12                | 3.5:1           | ------         |
| Potassium Silicate    | 15                | ------          | 4:1            |

2.2 Preparation Procedure

Different percentages of fine materials that include SiO$_2$, MgO, MnO, CaO, CaF$_2$ and Al$_2$O$_3$ were mixed by using potassium silicate and sodium silicate with percentage of 85 % w/v solution. They were mixed for 10 minutes and calcinated in the furnace with temperatures between 700 – 800 °C for 10-15 minutes as shown in Fig.1 and Fig. 2.

Intensive experimental work has been made to change the oxides percentage of the composition of the ceramic coating by selecting the class of basic or acidic oxides with different temperatures at 800, 1000, 1100 and 1200 °C.

3. Results and discussion

3.1 Chemical Composition

The chemical composition of ceramic coating materials that prepared in this research shown in Table 2.

| Table 2. Chemical composition of silicate ceramic |
|-----------------------------------------------|
| SiO$_2$ – Al$_2$O$_3$ % | MgO % | CaO % | MnO % | CaF$_2$ % |
| 65                  | 15    | 20    | 20    | 10      |
3.2 Morphology
The samples that were gold-coated were examined in a INSPECT S 50 that is supplied by FEI scanning electron micro-scope coupled to an energy dispersive spectrometer EDS of sintering sample at 1100 °C has been taken in different magnification at 5000 X to 250 000 X. The scanning electron microscopic picture shows that there is a multi-lamellar quartz grains as present in figures 3 and 4. These resulted enhanced the capacity of coating by increasing the emissivity and prevented permeability acid or base gases to walls. Therefore increasing the durability of the bricks and decreased the corrosion rate. Moreover, thermal efficiency of the furnaces box, uniform temperature distribution and life time of the catalyst tubes were promoted.

![Figure 3. SEM images of sample silicate ceramic showing a multi-lamellar](image1)

![Figure 4. SEM images of sample silicate ceramic showing crystalline structure](image2)
The atomic percentage of the elements was found by using EDXS analysis device and the results show in Table 3 and Figure 5.

![Figure 5](image1.png)

**Figure 5.** EDXS analysis of sintering phases showing high amount of silicon and other oxides.

| Element | O | Si | Mn | Al | Na | Ca | Mg |
|---------|---|----|----|----|----|----|----|
| Percentage % | 65 | 12 | 4  | 2  | 4  | 4  | 3  |

Table 3 indicates that the elements found in the highest quantities were oxygen and silicon in addition to manganese, calcium, aluminum and sodium. This was expected, since silica SiO$_2$ alumina and Al$_2$O$_3$ are common constituents in most ceramic materials.

### 3.3 Effect Nano Silicate Penetration on Coating Behavior.

In this study the effect of Nano particles size by measuring penetration inside the refractory bricks was carried out by addition 0.5 to 1% at 1100°C of Nano particles in total mix after inspection the grain size in Master Sizer AD 2000 from MALVERN INSTRUMENTS LIMITED made in U.K. The results shown in Fig. 6 the particle size distribution between 158 nm to 549 nm and the cross section between 10 to 20 mm show in Fig 7.

![Figure 6](image2.png)

**Figure 6.** Distribution of grain size of glassy sample.
3.4 XRD and XRF analysis

The measurements were taken at room temperature in a Panalytical (Xpert-pro) pw, 3050/60 diffractometer equipped with a copper tube, with a 40 kV x 20 mA power supply, which is available at university of Basra. The results are shown in Table 4 and Figure 8 shown high intensity with a very high quality of quartz crystallinity in (2Ø) 26.50 of sintering degree of sintering and glassy phase. Moreover, the results in XRF were taken at room temperature in a Panalytical (Epsilon 3-XL) Dy 1540 are shown in Table 5 and in Fig. 9 show the 70 % silica as in glassy phase.

| Pos. 2Ø | Height | d-spacing  °A |
|---------|--------|---------------|
| 26.641  | 170.46 | 3.34600       |
| 42.835  | 0.5904 | 2.11122       |

**Table 4.** XRD analysis for preparing ceramic coating materials

**Figure 8.** XRD Pattern of glassy phase sample showing high intensities of quartz.

| Element | Si | Mn | Al | Na | Ca | Mg |
|---------|----|----|----|----|----|----|
| Percentage % | 55 | 4.2 | 7  | 3  | 5  | 11 |
3.5 FTIR spectroscopy analyzed.

The measuring was identified from 400 to 4000 cm\(^{-1}\) using a FTIR model 8400 S Fourier transform infrared spectrophotometer of transmittance spectra of samples sintering in 1000 °C and glassy phase in 1100 °C as shown in Fig. 10 and the assignment of the bands are shown in Table 6. The characteristic bands almost at 1043, 877 and 504 cm\(^{-1}\) are corresponding to the stretching bending and out of plane of Si–O bonds, respectively. The position and the shape of the main Si–O vibrational band at 1043 cm\(^{-1}\) show a stoichiometry silicon dioxide structure. Moreover, some impurity vibrational bands are seen in the FTIR spectra which were shown in Table 6.

| Functional groups       | Sintering sample cm\(^{-1}\) | Glassy sample cm\(^{-1}\) |
|-------------------------|-----------------------------|---------------------------|
| Si–O deformation        | 458                         | 473                       |
| Si–O bending            | 877                         | 870                       |
| Si–OH stretching        | 940                         | 935                       |
| Si–O–Si stretching      | 1042                        | 1050                      |
| C–O bending             | 1622                        | 1623                      |

Figure 9. XRF analysis of sintering and glassy phase.

Figure 10. FTIR spectra of both sintering and glassy phase.
4. Application:
The preparation ceramic coating materials that prepared in this research was applied in the primary Reformer of the State company of Fertilizer in the south region of Iraq. It is used to coat Shamotte bricks that lined in the laboratory furnace with temperature of 1100 °C and the results shown in Fig. 11 and 12 as the glassy phase. Therefore, the ceramic coating material was applied to coat the gates bricks of reformer. Heating of walls and coated position was measured by using Infrared IR device and the result shows in Table 7. The results show that temperature in the walls and gates was decreased with 27°C.

![Shamotte brick, coated and glassy ceramic coated](image_url)

**Figure 11.** Shamotte brick, coated and glassy ceramic coated

![Heating of wall and coated position](image_url)

(A) (B)
Figure 12. Heating measured by IR for walls and gates (A) without coated and (B) with coated.

Table 7. Results analysis by infrared IR device for gates reformer positions and walls

| Number Position | Temperature Walls °C | Temperature without coated °C | Temperature coated °C |
|-----------------|-----------------------|-------------------------------|-----------------------|
| C 15            | 89.3                  | 80                            | 61.5                  |
| C 122           | 82.4                  | 85                            | 54.4                  |
| C 111           | 74.0                  | 78                            | 47.1                  |
| C 113           | 74.3                  | 82                            | 48.3                  |
5. Conclusion:

1. The emissivity of primary reformer insulation materials was increased by 30% compared with insulation without coating.
2. Ceramic coating material that applied lead to produce quartz phase.
3. High amount of silicate and multi-lamellar were obtained after sintering with glassy phase.
4. Ceramic coating material was penetrated with thickness of 10–20 mm in the refractory bricks at sintering temperature of 1100°C.

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