Utilization of Hard Rock Dust in Ceramic Glaze Formulation

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Abstract. The research focuses on the utilization of hard rock dust for formulating ceramic glazes. The rock dust was collected from Maddhapara Granite Mining area, Dinajpur, Bangladesh. Chemical compositions of raw materials were analyzed by XRF. Rock dust is characterized by high SiO₂, K₂O, and Na₂O with low content of ferromagnesian element. For Rock dust minor amounts of components may be present, which will mostly affect the color of the fired product (Fe₂O₃,MnO,TiO₂,Cr₂O₃). Others (MgO,K₂O,Na₂O) will act as fluxes and may have a strong effect during sintering. Ceramic glazes containing up to 30 wt% rock dust were prepared. The glaze slurries were applied onto ceramic tiles, which were sintered at 1050 to 1100°C with slow and rapid heating rate. Different glaze mixtures containing rock dust were prepared and analyzed for micro hardness and glossiness. Microstructures of the ceramic glaze were observed by FESEM (Field emission scanning electron microscopy). The results indicated that the properties of ceramic glaze were better sintering with slow heating rate and confirmed that dust can be used in glaze formulation. Therefore utilization of hard rock dust in glaze formulation may be new possibility for recycling and conserving natural resources.

1. Introduction

At present, the growth rate of the global production of glazed tiles increased more than other ceramic products with improved aesthetic appearance, gave it a prominent role in the tile market. According to several researches [1-3], uses of natural product have become an important aspect in the ceramic industry, in order to optimize and reduce the consumption of natural resources.

Ceramics industries having a wide variety of process routes. The development of new glass ceramic glazes is limited by some constraints, mainly derived from the heating conditions such as final firing temperature and heating rate. Now most research focus to the development of new glaze products with smoother surfaces and desirable mechanical and chemical properties under similar sintering conditions [4].

There are several reuse and recycling solutions for granite and marble wastes, both at an experimental phase and in practical applications [5-7]. Granite is an igneous rock, with feldspar, quartz and mica as major components and marble is a crystalline metamorphic, shows non-plastic behaviour. Their major constituents are silica (SiO₂) and alumina (Al₂O₃) with minor quantities of lime (CaO) and alkaline oxides (Na₂O, K₂O) which acts as fluxing agent. Iron oxide content is also significant, due to the sawing process, and will promote a dark colour of the ceramic products, [8-10]. In many studies using granite and marble wastes as raw material in the production of glaze ceramic tiles have been performed [1,6,7].

The hard rock obtained from Maddhapara Granite Mining Company, Bangladesh contains tonalite and granodiorite associated with granodioritic gneiss, granite and adamellite [11]. This mining project...
produces huge amount of rock dust which is a waste and causing environmental pollution. During the blasting and crushing process, the fine particles can cause more pollution than other forms of dust unless stored properly and further utilized. The aim of the present work is to utilization of maximum quantities of hard rock dust as raw material in the glaze formulation to develop glazed ceramic tiles.

‘2. Experimental’

‘2.1 Materials’
In this study, Rock dust, feldspar, sand, lime stone (CaCO₃) and Li₂O₇B₇ were used as raw materials glaze composition. Rock dust and feldspar was collected from Maddhapara Granite Mining Company Limited, situated in the district of Dinajpur, Bangladesh. River Sand also used for glaze formulation, which was processed in IMM (Institute of Mining, Mineralogy and Metallurgy, Bangladesh Council of Scientific and Industrial Research, (BCSIR), Joypurhat laboratory.

| Raw Materials  | Wt%      |
|----------------|----------|
| Rock dust      | 20-30    |
| Feldspar       | 20-25    |
| Sand           | 10-15    |
| CaCO₃          | 10-15    |
| Li₂O₇B₇        | 10-15    |

‘2.2 Preparation of the Glaze’
Chemical composition of raw materials analysis of the samples was performed by XRF (X-ray fluorescence). The raw materials were crushed, pulverized and ball milling to powder in form. Prepare a slip with a composition of raw materials (table 1) and adequate water to apply the materials. Pouring the slip on to natural ceramic body and dry the sample about 10 to 15 minutes. Then the specimens were fired to get the final glaze product by heat treatment of 1000-1150 °C temperature in an electric furnace for 30 minutes under heating rate of 5°C/min and 10°C/min (table 2). Then various properties were analyzed.

| Sample | Temperature(°C) and rate |
|--------|--------------------------|
| S1     | 1050, 5°C/min            |
| S2     | 1050, 10°C/min           |
| S3     | 1100, 5°C/min            |
| S4     | 1100, 10°C/min           |
2.3 Characterization of the Glaze

Glossiness of the prepared glazes was determined by NOVO-GLOSS LITE™ statistical gloss meter. Micro hardness was measured by Vickers indentation using Micro-hardness Tester (HMV-2T, Shimadzu Corporation, Japan). Microstructures of surface of glazes were studied by FESEM-JEOL JSM-7600F.

3. Results and discussion

3.1 Characterization of Raw Materials

The chemical compositions of main raw materials analyzed by XRF are shown in Table 3. From ‘Table 3’ it is evident that rock dust predominantly contains SiO₂ with considerable amount of Al₂O₃ and minor amounts of components present, which will mostly affect the color of the fired product (Fe₂O₃, TiO₂). Fluxing agents (Na₂O and K₂O) are present in both rock dust and feldspar. Feldspar contains 15.2% K₂O, which is excellent for glaze formulation rather than market available feldspar. Sand contains 97.7% SiO₂, which have a great influence for crystallization of glaze formulation.

‘Figure 1’ shows the particle size distribution of raw powder where, grinding a set of natural raw materials into a powder and found the particle size of the powder was less than 70 microns.

Table 3. Chemical compositions of the main raw materials.

| Compound | Rock dust | Feldspar | Sand |
|----------|-----------|----------|------|
| SiO₂     | 53.57     | 63.1     | 97.7 |
| Al₂O₃    | 16.51     | 17.2     | 0.21 |
| Fe₂O₃    | 9.07      | 0.95     | 1.15 |
| K₂O      | 3.15      | 15.2     | 0.13 |
| CaO      | 0.76      | 0.95     | 0.16 |
| Na₂O     | 3.01      | 1.67     | -    |
| MgO      | 4.48      | 0.07     | -    |
| TiO₂     | 0.76      | 0.02     | -    |
3.2 Characterization of the Prepared Glaze

The color of glaze of the ceramic tile can be changed with the help of various pigments, waste products, or natural raw materials containing a lot of colorific oxides. ‘Figure 2’ show that variety of colors can be obtained by varying the proportion of waste in the composition. S2 samples were found with some bubbles, whereas, S1 found no bubbles which was formulated with slow heating rate at 1050°C.

The prepared glaze coatings obtained were with a smooth surface and had a mat or semi-glossy appearance. Table 4 shows the glossiness and micro hardness of the prepared glaze. The glossiness of S1, S2 and S3 samples were better (46.23, 47.06 and 48.66) than S4 samples. Therefore, slow heating rate might be better for glaze development.

Vickers hardness depends on the type and amount of crystalline phases, composition of residual glassy phases and porosity of the glaze surface. It has been seen that S3 and S4 samples achieved highest micro hardness, however, Vickers hardness of S1 and S2 were better for glazed ceramic tiles.
The glaze coatings that had been obtained on heating temperature 1100°C, 5°C/min (S3) was considerably better than other samples in response to glossiness and hardness.

Table 4. Glossiness and Micro hardness of the prepared glaze.

| Sample | Glossiness | Micro hardness (HV) |
|--------|------------|---------------------|
| S1     | 46.23      | 649                 |
| S2     | 47.06      | 621                 |
| S3     | 48.66      | 865                 |
| S4     | 44.80      | 981                 |

Figure 3. Microstructure of the surface of the glaze for (a) S1, (b) S2, (c) S3 and (d) S4

‘Figure 3’ show the surface micro structure of the glaze tiles of the prepared samples. The morphology of S1 sample was almost smooth but crack was found and S2, which was formulated at 1050 °C shows smooth surface with very fine crystals. S3 and S4 samples, which developed at 1100 °C temperature show glossy and smooth surface because of the high content of fluxing.

4. Conclusion

- In this research low firing temperature glazes were formulated using hard rock dust, and feldspar that collected from Maddhapara Granite Mining area, Bangladesh.
The temperature for development of glaze can be reduced to 1050°C which is low for ceramics.

This low firing temperature glazes were prepared using high percentages (70%) of waste and natural materials.

The development of glaze with hard rock dust, which is dumping as a waste material will be a new route in ceramic industries as well as production cost of glazed ceramic tiles will be lower and better for environment.

5. References

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