# AN INVESTIGATION INTO THE REPLACEMENT OF ZIRCON WITH FLUORSPAR. ANDALUSITE AND WOLLASTONITE AS WHITENING AGENT OF THE BODY

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## ABSTRACT

Unglazed porcelain belongs to the group of tiles with low water absorption (less than 0.5 percent). It is extensively and technically used for cladding outdoor walls and indoor floors. The body is usually decorated by different methods employing various kinds of body pigments. One of the important pigments, widely utilized to whiten the body, is Zircon. Zircon is also a useful agent for controlling the shade and shrinkage of the body. However, the price of this strategic imported mineral has increased dramatically in recent years. Therefore, in this study the possibility of replacing Zircon with Fluorspar, Andalusite and Wollastonite was investigated. The shrinkage and water absorption of the new bodies were compared to those of the reference body with a 5 wt.% Zircon content. Then, the samples were characterized by Colorimeter, Dilatometer and X-ray diffraction methods. The results revealed that the Fluorspar cannot be used instead of Zircon because of bloating of the sample caused by volatilization of fluorine. Wollastonite was found to be a good whitening agent, but it would increase the water absorption of the body, which could not be easily modified. However, the sample containing 7 wt.% Andalusite + 3 wt.% Zircon resembles perfectly the properties of the reference sample.

## 1. INTRODUCTION

Porcelain tile are popular for cladding walls, building façades and the floors of busy places. These tiles are superior in comparison with porous and traditional tiles due to features such as whiteness, thermal and abrasion resistance, resistance against freezing, low porosity and natural appearance [1]. They are divided into two groups: glazed and unglazed. Unglazed tiles are the granite tiles, which need to be polished because they are easily seen. This is why the tile body is coloured or whitened; to this end, pigments and Zircon are utilized to colour and whiten the body, respectively [2,3]. Beside, this group of tiles are produced in high amounts worldwide (8 billion $m^2$ in 2011), which encourage the experts to meet the customers' needs beyond their expectations and standard levels using novel approaches [3,4]. Low water absorption (≤ 0.5%), high bending strength (≥ 35 MPa), resistance against abrasion (≤ 175 $mm^3$) and high level of whiteness (L ≥ 75) are among the properties of this group [5].

Zircon ($ZrSiO_4$) is a material that has been used for years for whitening tile bodies and opaque glazes. This material not only whitens the body, but is also effective in controlling dimensional accuracy and making the tile harder; Zircon also modifies the colour performance of pigments and controls the colour shade as well [6,7].

Nowadays, the price of Zircon as an imported product has risen dramatically. which makes its provision difficult. This is why this paper tries to replace Zircon with cheaper and more available materials like Fluorspar. Andalusite and Wollastonite, focusing especially on their role in whitening the body.

## 2. EXPERIMENTAL ACTIVITIES

In this research, experimental tests were performed on granite bodies. referenced "G", having this formula: 50% feldspars, 20% clay and 30% kaolinite and fillers.

Fast mills were loaded with Alumina balls weighing 600g and 400g dried materials; 0.4 percent STPP and 0.6 percent Sodium Silicate were utilized as deflocculants, and the milling time for the optimum residue was 15 minutes. The intended milling time was determined, using the trial and error method to find the optimum residue (residue range is 1% on mesh screen 230).

After obtaining the required residue. the slip was poured on a biscuit and left to dry. To homogenize the granules. the dried material was also loaded in a fast mill. 6% moisture was added to the granules and the material passed mesh screen 18. After 5 hours. the granules were ready for pressing in order to homogenize granule moisture; 450 bar pressure and 10×20 cm were selected for the samples. The samples were put in an oven at 110°C for 5 hr. Then, the samples were sintered in roller kiln with maximum firing temperature around 1189-1194°C for 60 min.

Water absorption. body colour and dimensional changes were measured according to standard ISO-10545. A spectrophotometer (Minolta CR-410) was used for measuring body colour, in which (L) shows the whiteness level, (a) shows the level of red and green (positive number for redness and negative number for greenness) and (b) shows the level of yellow and blue (positive number for yellowness and negative number for blueness. respectively).

The thermal expansion coefficient of the optimum sample was determined in the range 50-500°C using Mechanical Dilatometer (NETZSCH DIL 402 PC). Then. the samples were analysed by X-ray diffraction method (XRD, 40 Philip X'Pert, Co), 10 wt.% Silicon powder was utilized as a standard for quantity measurements. J. Martin-Marquez et al. showed that quantitative mineral analysis. based on the peaks' intensity of each crystal phase, is a suitable way for obtaining the necessary information on the phases present in porcelain tile [8]. Therefore, the intensity of the peaks present was determined using Origin Pro 7.5 SRO software. To minimize systematic error, peak intensity was compared with Silicon peak intensity.

## 3. RESULTS AND DISCUSSION

As mentioned. due to current sanctions and the high price of Zircon in Iran, materials such as Andalusite, Fluorspar, Wollastonite were added to granite tile body in order to cut down the final prices.

The above-mentioned materials were tested in various percentages and were also used in the mixture or not; Zircon was also added to the granite body formula (G) and compared with the reference sample (RG) that contained 5% Zircon.

### 3.1. ANDALUSITE

This material was tested in 5 and 7 percent along with 3 wt.% Zircon compared to the reference sample (5% Zircon), in which the body with 7% Andalusite and 3% Zircon most resembled the reference sample in term of shrinkage. water absorption and colour difference. The results of these samples are briefly reported in Table 1.

### 3.2. FLUORSPAR

This materials was tested in 3 and 5 percent along with 3 wt.% Zircon compared to the reference sample (5% Zircon Silicate), in which no sample was acceptable in terms of dimensional changes. The results of these samples are reported briefly in table 2.

| Properties | | G + 5% Zircon | G + 3% Zircon + 5% Andalusite | G + 3% Zircon + 7% Andalusite |
|---|---|---|---|---|
| Shrinkage (%) | | -9.78 | -9.73 | -9.58 |
| Water absorption (%) | | 0.01 | 0.05 | 0.06 |
| Colour | L | 80.97 | 79.13 | 80.36 |
| | a | 1.79 | 2.02 | 1.73 |
| | b | 8.31 | 7.93 | 8.26 |

*Table 1. The result of adding 5 and 7 wt.% Andalusite to the body containing 3% Zircon.*

| Properties | | G + 5% Zircon | G + 3% Zircon + 3% Fluorspar | G + 3% Zircon + 5% Fluorspar |
|---|---|---|---|---|
| Shrinkage (%) | | -9.61 | -7.24 | Samples Bloated |
| Water absorption (%) | | 0.03 | 0.08 | |
| Colour | L | 81.19 | 80.28 | |
| | a | 1.71 | 1.95 | |
| | b | 7.67 | 8.97 | |

*Table 2. The result of adding 3 and 5 wt.% Fluorspar to the body containing 3% Zircon.*

### 3.3. WOLLASTONITE

This material was tested in 2 and 4 percent along with 3% Zircon compared to the reference sample (5% Zircon Silicate). The sample with 2% Wollastonite and 3% Zircon was lighter by 3 units compared to the reference sample; however. its shrinkage was 1.16 units lower and water absorption rose by 0.5. To make up for shrinkage decrease and water absorption increase in the sample, 2% Potassium Feldspar was added to the mixture. The bodies containing 2% Zircon Silicate, 2% potassium Feldspar, 2 and 4 percent Wollastonite were then studied and compared to the reference composition (5% Zircon). These new compositions could not solve the problem of the dimensional changes. The colour of the 4% Wollastonite sample was quite similar to the reference sample but the difference seen in its dimensional changes prevented us from selecting it as the optimum sample. The results of these samples are briefly provided in tables 3 and 4.

| Properties | | G + 5% Zircon | G + 3% Zircon + 2% Wollastonite | G + 3% Zircon + 4% Wollastonite |
|---|---|---|---|---|
| Shrinkage (%) | | -9.78 | -8.62 | -7.91 |
| Water absorption (%) | | 0.01 | 0.57 | 1.85 |
| Colour | L | 80.97 | 83.97 | 84.57 |
| | a | 1.79 | 1.40 | 1.72 |
| | b | 8.31 | 7.31 | 8.71 |

*Table 3. The result of adding 2 and 4 wt.% Wollastonite to the body containing 3% Zircon.*

| Properties | | G + 5% Zircon | G + 2% Zircon + 2% Wol. + 2% Feldspar | G + 2% Zircon + 4% Wol. + 2% Feldspar |
|---|---|---|---|---|
| Shrinkage (%) | | -9.36 | -9.12 | -8.15 |
| Water absorption (%) | | 0.03 | 0.02 | 0.17 |
| Colour | L | 80.58 | 78.05 | 80.23 |
| | a | 1.81 | 2.13 | 1.89 |
| | b | 7.76 | 4.49 | 8.32 |

*Table 4. The result of adding 2 and 4 wt.% Wollastonite and 2% Feldspar to the body containing 2% Zircon.*

It should be noted that in the double charge Granite bodies, the second charge occupies 20-30 percent of the tile thickness. In this situation, whiteness, dimensional changes, water absorption compatibility make it possible to replace Zircon with another material.

The whiteness factor in 3% Zircon with 7% Andalusite resembles that of the reference body. In this case, the difference between water absorption (0.2) and shrinkage (0.05) parameters can be corrected by adjusting the kiln curve. Price analysis shows that the price of this formula is the same as that of the reference formulas, while, due to the current commercial situation, Andalusite provision is much easier. Note that Andalusite mines can be found in Iran and if this material is processed well, it can be used for this purpose. Using Fluorspar is not recommended due to the gas emissions, Fluorspar vapour and also its effect on shrinkage. If Wollastonite is used, although the whiteness factor is greater than that of the reference body, there will be more water absorption and high dimensional changes. Based on the promising result of the samples containing 3% Zircon and 7% Andalusite, this was selected as the optimum sample and its mineralogical composition and thermal expansion coefficient were compared with those of the reference sample.

## 3.4. XRD RESULT AND THERMAL EXPANSION COEFFICIENT

In Table 4 and Figure 1, the results of the XRD analysis and the thermal expansion coefficient of the reference sample and the optimum sample (3% Zircon + 7% Andalusite) are given briefly.

Quartz, Mullite and Albite phases were recognized in the samples. As shown in Table 5, Andalusite is an Alumina Silicate mixture that leads to an increase in the Mullite and Quartz phase percentage. Besides, the amount of Albite phase in the samples containing Andalusite is negligible. The expansion coefficients of these two samples resemble one another in temperature range (50-500 °C), which confirms the feasibility of using 7% Andalusite along with Zircon.

| Sample | Phase | $\frac{I_{Quartz(101)}}{I_{Si(111)}}$ | $\frac{I_{Mullite(110)}}{I_{Si(111)}}$ | $\frac{I_{Albite(002)}}{I_{Si(111)}}$ | $\frac{I_{BaseLine}}{I_{Si(111)}}$ | Expansion Coefficient (°C$^{-1}$) |
|---|---|---|---|---|---|---|
| G + 3% Zircon + 7% Andalusite | Quartz + Mullite | 2.09 | 0.22 | 0 | 0.46 | $83.24 \times 10^{-7}$ |
| G + 5% Zircon | Quartz + Mullite + Albite | 1.87 | 0.1 | 0.36 | 0.38 | $83.90 \times 10^{-7}$ |

*Table 5. The result of XRD and thermal expansion coefficient of the reference and the optimum sample.*

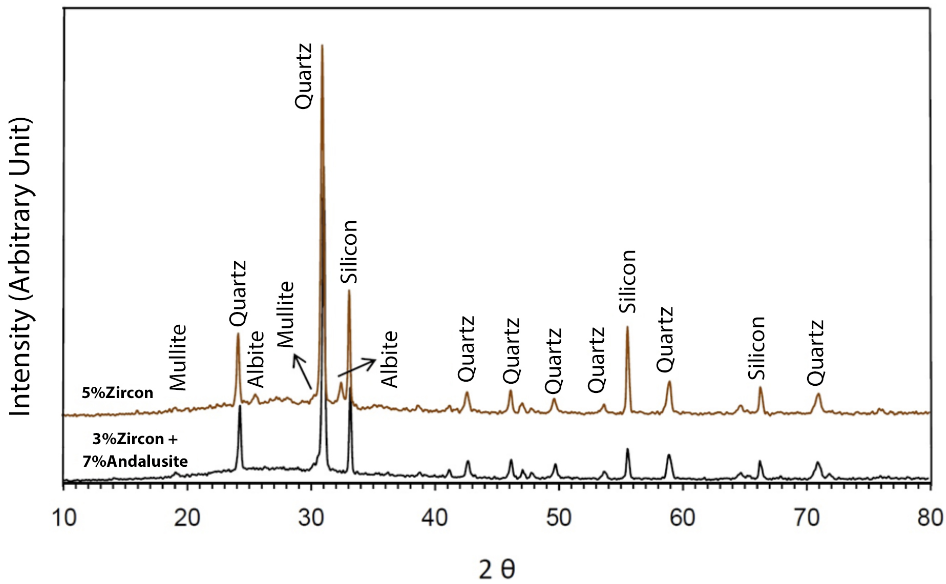


*Fig. 1. The XRD Pattern of the reference sample and the sample containing 3% Zircon + 7% Andalusite.*

## 4. CONCLUSIONS

In this research, the possibility of replacing Zircon with Andalusite, Wollastonite and Fluorspar in the porcelain tile body was studied in order to investigate the whiteness after proper sintering. The sample with Fluorspar was not feasible due to high dimensional changes and bloating. Wollastonite leads to lower shrinkage and adding 2-4% potassium feldspar cannot compensate this problem. On the other hand, bodies containing 4% Wollastonite and 3% Zircon resembled the reference sample (5% Zircon). The properties of the samples with 7% Andalusite and 3% Zircon were quite similar to those of the reference sample, which make it capable of replacing Zircon. Price analysis shows that the price of this sample is the same as that of the reference sample. The price will fall more if local Andalusite is used.

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