17th International Mining Congress and Exhibition of Turkey-*MCET2001*, ©2001, ISBN 975-395-4Î7-4 The Application of Colemanite Addition to Floor Tile Glazes

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ABSTRACT: Colemanite ore, a borate mineral, has been used in ceramic glaze recipes due to its low melting point, low solubility and its smoothness on unleaded glazes. In this study, colemanite was added at 2%-10% to a standard glaze recipe and six different recipe samples, including the standard recipe, were preoared. These recipes were applied to industrial-grade ceramic floor tiles. Various physical tests were done on ceramic floor tiles fired at 1180 "C in intensity ovens. The results indicate that the physical properties of the floor tiles did not change considerably and that die surface quality and smoothness of the floor tiles improved with 6%-8% colemanite addition.

1 INTRODUCTION

Ceramic products can be defined as substances produced from inorganic industrial minerals mixed in appropriate proportions, formed into desired shapes and fired in an oven with or without glazes. Ceramic floor tiles, which have a wide variety of applications, consist of a base body overlaid with a hygienic and decorative thin layer of glaze (Arcasoy, 1983). The durability of the surface for its application can be obtained by means of a suitable glaze recipe (Kartal, 1998).

One of the main reasons for the use of glaze recipes in floor tiles Is to make the porous and uneven surface much smoother. In this way, it is much easier to clean die floor tile surfaces. Another reason is to give an aesthetic and decorative appearance to the ceramic floor tiles. In addition, resistance to chemical reactions is provided by increasing the strength and surface hardness of the ceramic floor tiles (Yamik et al. 1999, Özaslan 1993).

The objective of applying the engobe process to ceramic floor tiles is to fill cavities, and obtain a smooth surface and conformity between the ceramic body and its glaze. Engobe is the undercoat material, which covers unwanted stains on the ceramic body, provides conformity between the ceramic body and its glaze by forming a thin layer between them, and improves the appearance of motif applications.

The objective of this study was to investigate the physical properties of floor tiles produced by me addition of colemanite to glaze recipes. The test results are compared with the TS-EN 176 standard for ceramic industrial-grade floor tiles.

Borate mineral affects the melting point of other

oxide minerals such as lead oxide, which has a very low melting point. Both borate (B2O3) and lead oxide (PbO) are contai.ied in glazes which have low melting points. The main advantages of having B2O3 in ceramic glazes are the following (Kartal, 1998):

- It has a very low melting point;
- Gives better flux properties;
- · Decreases thermal expansion;
- Provides resistance to acids;
- Provides better glazing properties by decreasing viscosity;
- Gives more surface brightness.

2 EXPERIMENTAL STUDY

2.1 Samples and procedures

The glaze recipe samples prepared for the tests contained sodium and potassium feldspars, zircon, clay, zinc oxide, talc, corundum, wollastonite and colemanite minerals. The composition of the engobe, which is spread underneath the glaze, included clay minerals, frit, quartz and zircon (Ünaydin, 1993).

For the test, six different glaze recipes were prepared: one standard sample and five samples with colemanite contents of 2%-10%. The chemical compositions of the recipe samples are given in table 1. The seger fonnula parameter of the standard glaze recipe was determined from chemical analysis: $0.082Na_{2}O_{1}$ 0.037K,O, 0.27CaO, 0.417ZnO, 0.614AI,O,, $0.007 Fe_2O_{3}$ 2.493SiO₂, 0.004TiO₂, 0.125ZrO2 mole. The glaze recipes were prepared from this seger formula by the addition of vanous amounts of colemanite. The effects of colemanite addition on glaze quality were investigated.

Table I. Glazerecipe samples with various amounts of colemam'te atIdition.

	Composition (%)									
Industrial mineral	Standard Recipe	N1	N2	N3	N4	N5				
Na-Feldspar	26	25.48	24 96	24.44	23.92	23.40				
K-Feldspar	11	10 78	10 56	10.34	10 12	9.90				
Quartz	12	11.76	11.52	11.28	11.04	10.80				
Zircon	16	15.68	15 36	15.04	14.72	14.40				
Clay	6	5 88	5.76	564	5.52	5.40				
Zinc oxide	2	2.94	2.88	2 82	2 76	2 70				
Talc	4	3 92	3.84	3 76	3.68	3 60				
Corundum	9	8.82	8.64	8.46	8.28	8 10				
Wollastonite	13	12.74	12.48	12 22	11.96	11.70				
Colcmanite		2	4	6	8	10				

All of the glaze recipes from wet grinding were sieved under a size of 45 um. The glaze recipe samples were applied to the ceramic floor tiles by a laboratory pistol (Mercan, 1993). The unbaked floor tiles used in the tests had dimensions of 20x20 cm and were prepared under industrial conditions. The glazing was performed on the ceramic body after the engobe, with a constant density and quantity applied. The glazed floor tiles were fired in a roller-type high-intensity oven. The sample preparation method, firing time, amount of engobe and glaze contents were kept constant. For each test procedure, measurements were performed on eight different samples, and the average of these measurements was taken for all tests. The flow sheet of the experimental study is shown in Figure 1.

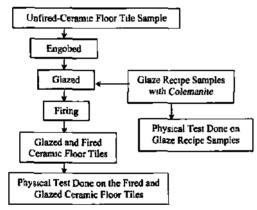


Figure 1. Flow sheet for experimental study.

2.2 Tests applied to glaze samples

Several tests were conducted on the six glaze recipe samples in order to determine the effect of colemanite addition.

2.2.1 Density test on glaze recipe samples

The density test of the glaze recipe samples was carried out using a pycnometer. The results of the density tests are shown in Figure 2 and Table 2. It can be seen from Figure 2 that the density of the samples increased with the addition of colemanite.

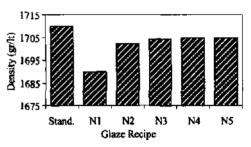


Figure 2 The effect of colemanite amount on the density of glaze recipe samples.

Table 2. Density values of glaze recipe samples with various amounts of colemanite addition

Glaze Samples	Stand	Nl	N2	N3	N4	N5
Density (gr/lt)	1710	1690	1702	1704	1705	1705

2.2.2 Sieve analysis of glaze recipe samples

The glaze recipe samples were sized with a 45-lim sieve. It was observed from the sieve analysis that the oversize proportion did not vary significantly, being in the range of 1.5-1.9%.

2.2.3 Fluxing time of glaze test

The fluxing time of the glaze recipe samples was determined with a ford-cup viscosimeter with a hole diameter of 3mm and volume of 100 ml. The résulta for the fluxing time of the glaze tests are given in Table 3 and Figure 3. It can be seen that the fluxing



time of the glaze increases with increases in colemanite addition.

Table 3. Fluxing time values of glaze recipe samples with various amounts of colemanite addition.

Glaze Samples	Stand.	NI	N2	N3	N4	N5
Fluxing	12.4	15.9	17.2	24.9	32.3	34.5
Time (second)						

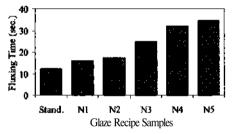


Figure 3. The effect of colemanite addition on fluxing time of glaze recipe samples.

2.3 Physical tests done on glazed ceramic floor tiles

The ceramic floor tiles, in industrial condition, were first engobed, then glazed with various glaze recipes containing various amounts of colemanite, and finally fired in ovens. Various physical tests were performed on these samples.

2.3.1 Water absorption test

The water absorption results for die glazed floor tiles with various amounts of colemanite are shown in Table 4 and Figure 4. It can be seen from Figure 4 that die water absorption values of the glazed floor tiles are very close to each other.

2.3.2 Strength test

The strength values of the glazed and fired floor tile samples with various amounts of colemanite are shown in Table 5 and Figure 5. It was found that the strength of fired floor tile samples is not affected significantly since It is directly related to the composition of the ceramic bodies and the firing temperature.

Table 4. Water absorption values of the glazed floor tile samples with various amounts of colemanite.

Glazed Floor Tile Samples	St.	Nl	N2	N3	N4	N5
Water absorp. (%)	2.9	2.9	2.8	2.9	2.8	2.9

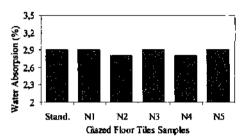


Figure 4. The effect of colemanite content in glazed floor tile samples on water absorption.

Table 5. Strength of fired and glazed floor tile samples with various amounts of colemanite.

Glazed Floor Tile Samples	Stand.	Nl	N2	N3	N4	N5
Strength of fired Tiles (kg/cm ³)	340	337	340	338	338	337

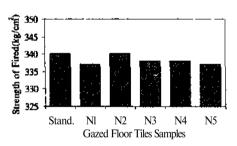


Figure 5. The effect of colemanite content on strengths of glazed and fired floor tile samples.

2.3.3 Harkot and Autoclave tests

The Harkot test was performed on the floor tile samples to determine their strength properties under instantaneous temperature variation. An autoclave tes* was conducted to evaluate the reaction of the floor tile samples under water vapor pressure conditions. The results of the Harkot and autoclave tests for all samples are shown in Table 6. They were found to be satisfactory.

Table 6. Results of Harkot and autoclave tests on glazed floor tile samples with various amounts of colemanite.

Glazed Floor Tile Samples	St.	Nl	N2	N3	N4	N5
Harkot	+	+	+	+	+	+
Autoclave	+	+	+	+		+

2.3.4 Stain test

Glazed ceramic floor tiles are considered to be of first-grade quality when all stains are removed from

them. All the ceramic floor tile samples were found to be first grade after stain tests were performed.

2.3.5 Test for acid-base resistance

The glazed ceramic floor tile samples were subjected to acidic and basic mediums so as to determine their susceptibility to acids and bases. The glazed floor tile samples were subjected to 3% HCl and 30 gr/lt KOH. The results indicate that the floor tile samples are resistant to acidic and basic mediums.

2.3.6 Surface corrosion test

The ceramic floor tiles samples were found to be suitable for use in workplaces and markets after standard surface corrosion tests.

2.3.7 Surface hardness test

A surface hardness test was performed to measure the resistance of the ceramic floor tile samples against scratching. The surface hardness of the floor tile samples was found to be level 6 on the Mohs scale.

2.3.8 Fired color test

Fired color test results for the glazed ceramic tile samples with various amounts of colemanite are given in Table 7. It may be seen that they are very close to each other. In this table, L, a and b correspond to the degree of white, green and yellow, respectively.

Table 7. Fired color test results for the glazed floor tile samples with various amounts of colemanite.

Glazed Floor		Si.	Nl	N2	N3	N4	N5
Tile Sa	mples						
Color	L	86.6	85.62	85.5	86.3	86.74	85.56
	Α	1.1	1.38	1.44	1.45	1.46	1.54
	В	6.8	6.65	6.65	6.00	6.12	6.40

3 RESULTS AND CONCLUSIONS

In this study, the physical properties of ceramic floor tile samples prepared by adding various amounts of colemanite to standard glaze recipes were investigated in relation to its appropriateness for ceramic bodies. The following results were obtained:

1. The density of the glaze recipe samples increased as the amount of colemanite increased.

2. The oversize percentage in the glaze recipe samples was found to be between 1.5% and 1.9%.

3. The fluxing time of the glaze recipe samples increased with increases in the colemanite concentration. The standard glaze recipe samples without colemanite had a fluxing time of 12.3 seconds, while the new glaze recipe samples with colemanite had a fluxing time of 34.5 seconds.

4. The water absorption values of the glazed floor tile samples were found to be in the range of 2.8-2.9%. This is consistent with standard TS-EN 176 for ceramic floor tiles.

5. It was determined that the strength of the fired and glazed floor tile samples was between 337 and 340 kg/cm². This is also consistent with standard TS-EN 176.

6. The results of the Harkot and autoclave tests on the glazed floor tile samples are positive.

7. The stain test and resistance to acid-base test results are consistent with standard TS-EN 176.

8. The corrosion and surface hardness tests on the floor tile samples indicate that they can be classified as rank 4 and level 6 according to standard TS-EN 176 for surface corrosion and the Mohs scale, respectively.

9. The fired color tests showed that the floor tile samples with various amounts of colemanite were similar to the standard floor tiles.

10. The floor tile samples with contents of 6%, 8%, and 10% colemanite had less cavities and much smoother surfaces man the floor tile samples without colemanite, which had dull surfaces. Therefore, the glaze recipes with contents of 6%-8% colemanite should be utilized. This will enable the large potential borate reserves of Turkey to contribute significantly to its economy.

11. Optical and electron microscope measurements of the floor tile samples should be done for future work. This will ensure that fine details and deficiencies caused by engobe, glaze or body are determined more effectively.

REFERENCES

- Arcasoy, A., 1983, Ceramic Technology, Marmara University Faculty of Fine Arts, Publication No: 2, Istanbul, 278 p.
- Kartal. A., 1998, Glaze and Glazing Technique, Ankara, Çizgi Line Printing.
 Mercan, M., 1993, Glazing Techniques, *Turkish Ceramic*
- Mercan, M., 1993, Glazing Techniques, *Turkish Ceramic Association*, Ceramic Glaze Publication No: 7, Istanbul, 141-150.
- Özaslan, B., 1993, Processing Method of Frit and Glaze, *Turkish Ceramic Association*, Ceramic Glaze Publication No: 7, Istanbul, 56-64.
- TS-EN 176, Standards for Ceramic Floor Tiles, Turkey Standards Institute.
- Onaydın, Ö., 1993, The Effect of Properties of Frit Glaze in Floor Tile Glaze, *Turkish Ceramic Association*, Ceramic Glaze Publication No: 7, Istanbul, 79-86.
- Yamik, A., Akbaş, M., Çınar, M. & Karagüzel, C. 1999. The Effect of Calcite and Dolomite Contents on the Physical Properties of Ceramic Floor Tiles Bodies, *Dumlupinar University Journal of Science*: 1, 119-126.

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