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Technological and economical investigation of glaze preparation using dry stirred media mill

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Abstract: Ceramic tiles are the most common building material for floor and wall coverings in many countries. Glazed tiles are produced from mixture of frits and some additional raw materials applied on the surface of green tiles and subjected to a firing process. A new method of processing of glaze that is dry stirred media mill was investigated in a pilot grinding plant. The produced glaze particle size, shape and surface area are measured. The comparison was made with the product of conventional wet discontinue ball mills using the same wall tile glaze recipes. The results indicated that dry stirred media mill can provide product that have finer particle size distribution, more stable product compared to the conventional wet ball milling. The glaze thermal expansion and optical properties such as colour (L, a and b parameters) of the produced glazes were measured and comparison was also made in details. Finally, the microstructural characteristics of the produced glazes were determined using scanning electron microscopy (SEM). The results have shown that dry stirred media mill enhances glaze properties and process economy considerably.

Keywords: ceramic tile, glaze preparation, grinding, stirred media mill

1. Introduction

Ceramic tile glaze and engobes are described as thin, completely glassy coatings on the surface of a ceramic tile product. The main incredients of the glaze and engobe compositions are raw materials such as quartz, frits, fluxes, kaoline and other inorganic additions, which after grinding are suspended in water, and next are implemented by different techniques on the product (Eppler 2000; Shaw, 1971). As is well known, traditional ceramic frits are used in the high or low ratio according to the glaze compositions. Frits are defined by being more in soluble in water than crystallne raw material used to make them, having a lower melting temperature, wider fusion range and by being used as contents in glaze formulations to help produce uniform fired glaze surfaces (Gomes-Tena et al., 2009). In ceramic tile production, glaze and engobe are used to provide colour and surface performance originating from the body. Glazes in significant way influence on most of the final properties of ceramic products, mainly on surface parameters as colour, glossy or roughness. Usually, these properties have been changed by chemical composition and firing parameters (Ghizdavet et al., 2019a). Correlations on composition-processing properties were largely investigated on all scales, from the atomic to macroscopic scales in both academic and industrial environments (Ghizdavet et al., 2019b; Yelda et al., 2006). The possibility of improvement of surface properties by the selective milling and selection of the grain size of group of raw materials were sought by Partyka (2011). It was shown, that in case of the sanitary glazes, an adequate selection of the grain size of quartz, feldspars, zirconium silicate and rest of raw materials, leads to improvement of whiteness and glossy as well as decreasing of roughness of surface (Boudeghdegh et al., 2015). Grinding plays the important role for colorants as optical behaviour is influenced by the fineness of particles and their distribution together with the particles shape. It is well known that a good reflection requires the existence of crystalline particles in the glaze. The colorant will be attributed by narrow particle size distribution of glaze (Partyka et al., 2011). The main drawback of the conventional glaze grinding is the high energy consumption of the grinding process. Wet/dry

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grinding systems are available, each having their advantages and disadvantages (Casasola et al., 2012). It has been observed that different applications in grinding processes in different sectors have a significant effect on grinding efficiency and grain size distribution of the product. There has been some progress in the ceramic body preparations in recent years however the glaze preparation systems remain to use conventional wet discontinue ball mill system.

In ceramic factories frit(s) and raw materials are ground together in wet ball mills even though input materials have different grindabilities. The particle size distributions and the specific surface area of produced glazes are fluctuated batch by batch that result in changes on some important glaze properties such as compatibility with the ceramic body and appearance of glaze. The use of stirred media mill was investigated to produce used wall tile glazes at Kaleseramik Factory in Türkiye. Full technical and economic analysis and the comparison were made with the currently used discontinue wet ball milling system.

2. Materials and methods

2.1. Sample

In this study, KALEFRİT A.Ş. Opaque-bright frit (FRIT A) and transparent frit (FRIT B) produced by glaze quality Grolleg kaolin supplied from Imerys company; Zircon MO from Eggerding and MDS-Al_2O_3 from MARTINSWERK are the other raw materials of the glaze recipe.

The chemical analyses of the raw materials ans frits were carried out with Panalytical Brand Axios Max Model X-ray Spectrophotometer device (XRF, PANalytical, The Netherlands). The mineralogical analyses of the raw materials were carried out with Panalytical Brand X'pert Pro MPD X-ray Diffractometer (XRD, PANalytical, The Netherlands). Chemical and mineralogical analyzes of the materials are given in Table 1.

In traditional glaze preparation methods, the compositions of glaze are ground in discontinuous ball mills in an aqueous medium for the required time to reach the 45 µm sieve residue with the range of 0.5 - 1%. The glaze recipe includes 90% Frit and 10% of other raw materials that is given in Table 1. In the tests, the material composition is kept the same in both grinding tests. The frits are pre-crushed to d_{97} = 250 micron. The kaolin, MDS-6 and Zr MO are the finely ground materials as 99% of these materials passing under the desired ground product glaze size of 40 microns.

Table 1. Chemical analysis of used material in glaze composition (% mass)

Content	Frit A	Frit B	Kaolin	MDS-6	Zr MO
L.O.I	0.05	0,24	11.92	0.25	0.51
SiO_2	56.55	63,83	48.40		32.18
Al_2O_3	2.84	4,1	36.09	99.73	0.78
TiO_2	0.01	0,05	0.18		0.31
Fe_2O_3	0.14	0,13	0.82		0.02
CaO	10.69	12,85	0.07		
MgO	2.63	1,56	0.29		
Na_2O	0.76	2,12	0.07	0.08	
K_2O	1.95	2,73	1.97		
B_2O_3	9.40	5,49			
ZnO	8.46	6,89			
ZrO_2	6.52	0,24			65.70
% quartz	4	6	4,22		
% glass phase	96	88			
% petedunnite		4			
% zircon		2			98,90
% kaolinit			86,63		
% illite			7,15		
% corundum				99,58	
% other			2,00	0,42	

2.2. Conventional glaze preparation system

In glaze grinding, discontinuous ball mills are generally used and wet grinding is done. These ball mills are lined with alumina liner and alumina balls are used as the grinding medium. Grinding in mills lasts until the glaze reaches a certain grain size. Whether the glaze is ground to the desired fineness or not is checked by looking at the percent sieve balance. Grinding the glaze more or less than necessary causes some glaze errors (Arcasoy, 1983). Considering the importance of the relationship between water and grinded raw material, the density of the prepared glaze should be considered. The most commonly used method for controlling and determining the density of the glaze is the liter weight control of the glaze (Arcasoy, 1983). After reaching the appropriate sieve balance, the mill is emptied and the glaze is transferred to the stock tanks for storage. These tanks must be equipped with agitator and closed to prevent collapse. The handles of these mixers should be as close to the bottom and side edges as possible. The arms of the mixers should be operated at appropriate speeds. At high speeds, the glaze may heat up more than necessary or air bubbles may form in it, which may affect the rheological properties of the glaze (Reinosa et al. 2006).

There are a number of mills to produce wall tile glaze production in Kaleseramik Factories where the material was taken and the part of investigation was performed. The glaze recipes feed the mill and operated 10 hours for producing glaze to the desired fineness that is d97 size is 38-40 µm. It is observed that the grain size of the frits in the recipe decreased below 100 -150 µm within the first 2 hours of processing however it takes additional 8 hours to reach the product below 40 µm.

The photo of conventional glaze preparation mils is shown in Figure 1, and the mill technical data is given in Table 2.

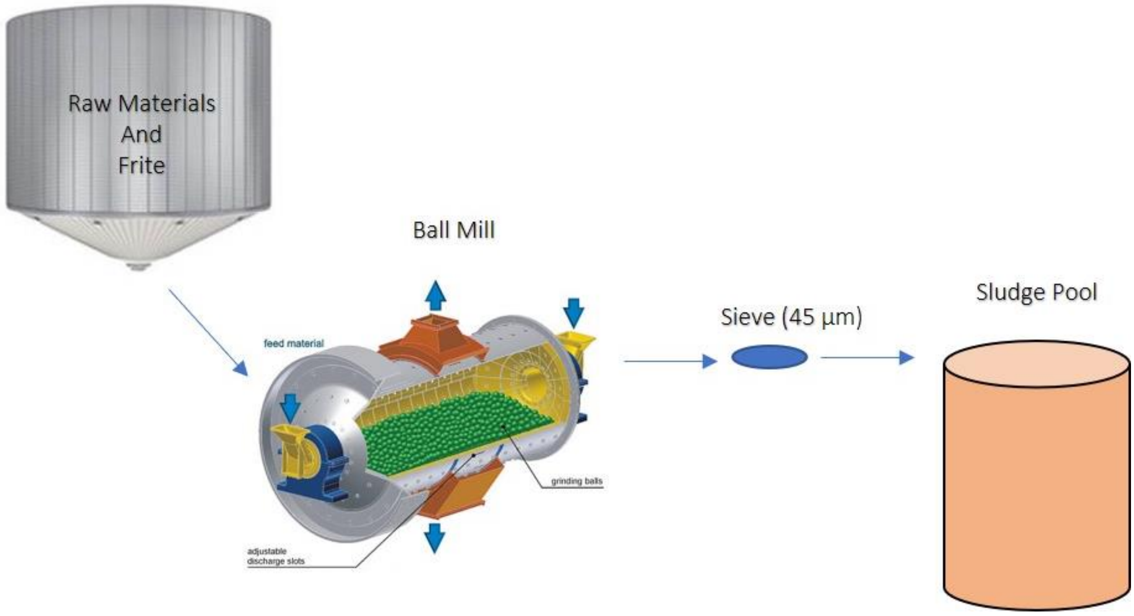

Fig. 1. Conventional glaze preparation (discontinue ball mill)

Table 2. Conventional glaze preparation mill parameters

Design and Operational	Unit	Value
Diameter and length	m	2.5 and 2.5
Al_2O_3 ball media amount	kg	12000
Ball filling degree	%	28
Mill speed	rev/min	16
Material feed	kg	6000
Water amount	dm^3	2100
Grinding additive	kg	26.6
Grinding duration	hours	10

2.3. Dry stirred media mill

Researches have shown that the advantages obtained from attritor type grinders developed in recent years are more than ball grinding mills. Research shows that attritor mills are the most efficient grinders currently available. Attritor mills can be defined as "agitator ball mills" (Schilling and Yang 2000). They are also known as the mill where there are grinding balls in the grinding chamber and the mixer on the shaft moving in the rotary direction. In this research, EIRICH model attritor type ball mill was used.

EIRICH MaxxMill type MM3 was used to produce the wall tile glazes having the similar product fineness of the conventional glaze preparation system. It was also proposed to produce glazes having finer products that would have d_{90} equal to 20 microns and 10 microns. These products could not be produced in conventional preparation system due to technical and cost reasons. The stirred media mill has the grinding chamber that has diameter of 900 mm and the total height of 1700 mm. It is operated in dry mode. A screw conveyor is used for feeding materials. In the grinding chamber, the ceramic grinding balls is filled about 300 kg that are 5-7 mm in diameter. The agitator speed is 451 rev/min and the grinding chamber speed is set to 20 rev/min. Grinding bars are made of tungsten carbide. By means of a bucket elevator, the raw material is taken to a hopper above the mill from where it drops into the mill feeding chute. The ground product is extracted from the mill by a blower and fed to an air classifier. The fine material passes the classifier and is separated in a filter. The coarse material is recycled via the above mentioned bucket elevator back to the inlet into the mill. A weighing unit integrated into the bucket elevator allows measuring the flow of coarse material and facilitates assessing the grinding cycle stability (Figure 2).

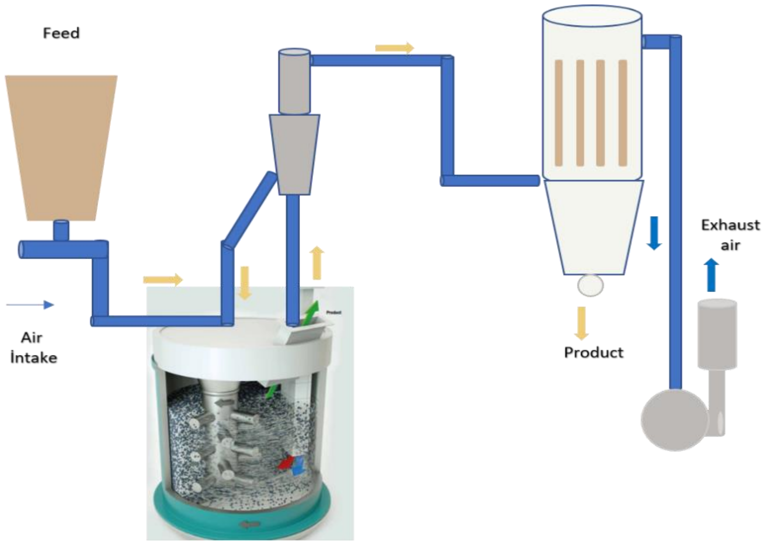

Fig. 2. Stirred media mill system-diagram

Agitated Ball Mill – Separator System: EIRICH Maxx-MILL was selected to monitor the grinding performance of the Agitated Ball Mill. However, since the size of the feed to the system is important, pre-shrinking was carried out at the KALEMADEN facility before the study. The sample size has been reduced to below 250µm.

When the operating parameters affecting the grinding performance of the stirred ball mills are examined; mixing speed, ball density, ball size distribution and charge rate, residence time of the material in the mill, open or closed circuit operation with the separator. Separators have an important function in controlling fine grinding and product size distribution. They are used to select the grains of the desired fineness from the milled product with high efficiency. While the fine grains reaching the desired grain size are separated as the product, the coarse grains are sent to the grinding process again and this cycle continues. Separator rotor speed, air quantity and speed and grain size to be separated can be adjusted. Capacity values will also vary at this rate. All operating parameters of stirred ball mill was shown at Table 3. In particular, the specific energy consumption of frits decreases depending on the classifier speed and through-put. Especially since frits have glassy structures compared to kaolins, their specific energy consumption increases.

Table 3. The Operating parameters of stirred ball mill

Test No:	Through-put kg/h	Classiffier speed rpm	Air (Total air/secondary air classifier) m^3/h	Classifier Return kg/h	Specific Energy Consumption kwh/ton
			Kaolin		
1	250	2880	3500	700	79
2	200	2880	3500	320	96
3	400	1800	3500	450	50
			Frit A		
4	100	2160	3500	560	172
5	250	1080	3500	1000	71
6	300	648	3500	700	61
			Frit B		
7	100	2160	3500	430	170
8	250	1080	3500	1000	69
9	300	576	3500	270	56

3. Results and discussion

Firstly, the particle size distributions and energy performances of glazes ground with dry stirred ball mill and discontinue ball mill were compared. Later, the technical and physical properties of glazes prepared with two different grinding systems were checked against. The glaze recipe is composed of 98% Frit (50% opaque frit A; 38% transparent frit B) - 9% kaolin - 2% Zircon - 1% MDS-6 Al_2O_3. The performances of the STD Glaze prepared with the standard materials available in the discontinuous ball mill and the glaze recipes prepared with the frits and kaolin milled in the Stirred Ball Mill were compared.

3.1. Product fineness and energy consumption - dry stirred media mill

Stirred mills are new systems developed in the last 10 years. It consists of an attritor and a tank. The requirement of such systems is high pump speed. The slip atrium pumped at high speed is taken into the mill and the balls allow the small particles to pass quickly and the large ones to pass through the grids and reduce them to smaller sizes. The grinding medium acts like a sieve, allowing the fines to pass through very quickly, reducing the larger particles to smaller sizes. Uses of Stirred ball mills; It provides fast grinding with narrow size distribution, low maintenance cost and energy consumption. (Da Silva et al. 2001; Santaş 1996; Jones 1960; Robert 2000; Robert, 2005).

When different grinding techniques are used, the product particle size distribution, particle shapes and the surface areas may also change. In the used discontinue ball mill, the grains are amorphous and the surfaces are layered, resulting in an increase in the surface area. The particle size of d_{97}, d_{90}, d_{50} values are given together with the specific surface area of the produced glazes in Table 4. The specific energy consumption values of the products are also included in the same table. First of all, the energy consumptions of conventional systems and stirred ball mills were compared. When these data are examined, it has been determined that the dry stirred media mill is more efficient. The energy consumption for the standard glaze product that is 78.9 kWh/ton in traditional methods that is decreased to 61 kWh/ton in stirred media mill for the same product fineness.

3.2. Linear thermal expansion

The particles were shaped into pellet by applying a uniaxial pressure of 320 kg/cm^2 in a mould (50 mm x 100 mm) and then the pellets were dried at 110°C. Industrial kiln was used for firing dat 1145°C for 46 min. Netzch 402 EP Dilatometer was used to the thermal expansion coefficients. The dilatometer tests results are given in the Table 5.

It can be seen that there is a difference especially between 500-600°C that is mainly caused by the grain size and morphological properties of products. The increase on the thermal expansion values in stirred media mill product is the indication of the glass phase due to the homogeneous particle size distributions. It is obvious that thermal expansion values are affected by particle size distribution.

Table 4. Comparison of discontinue ball mill and stirred media mill

Parameters	Discontinue ball mill (STD.)	Stirred Media Mill		
	Std. Glaze	Glaze $d_{90} \sim 30\mu m$	Glaze $d_{90} \sim 20\mu m$	Glaze $d_{90} \sim 10\mu m$
d_{97}	39.20	36.10	23.86	13.12
d_{90}	30.40	31.80	20.09	9.92
d_{50}	13.30	13.50	9.47	4.96
d_{10}	2.41	3.28	2.83	2.13
SSA (m^2/gr)	0.463	0.410	0.850	1.190
Energy (kWh/ton)	78.9	61	79	172

Table 5. Thermal expansion coefficients of glaze products for grinding systems

Thermal expansion ($x10^{-7}$)	Discontinue ball mill (STD.)	Stirred Media Mill		
	Std. Glaze	Glaze $d_{90} \sim 30\mu m$	Glaze $d_{90} \sim 20\mu m$	Glaze $d_{90} \sim 10\mu m$
α_{300}	57.24	59.73	60.28	60.48
α_{400}	58.47	61.60	61.74	62.02
α_{500}	59.36	63.48	62.58	62.82
α_{600}	60.00	64.23	64.96	65.02

3.3. Evaluation of colour and brightness

The prepared surfaces were evaluated in terms of colour and brightness. The glaze suspensions were applied nonfired engobed tiles, with 0.4 mm glaze coat thickness. The samples were fired at 1145°C for 46 min in a industrial kiln. Finally, the specular reflection index of each sample was measured chromatic coordinates (L* (whiteness), a* (red-green), b*(yellow-blue) color values) with X-rite SP 62 color measuring device. 60° gloss values with Konica Minolto MultiGloss 268Plus model gloss measuring device measured with.

The results of colour and brightness parameter are given in Table.6. It was clearly seen that grinding system and the fineness of products affect these properties. Although it started with samples ground 30µm below the expected colour and whiteness in Stirred media mill studies, it gave better results in samples milled below 20µm. When the surface is examined in terms of structural defects such as cavities and holes, it was seen that grinding below 20 µm was better than others (Kaleseramik Ar-Ge Merkezi, 2020).

Table 6. Colour and brightness values for different glaze products

Colour and brightness	Discontinue ball mill (STD.)	Stirred Media Mill		
	Std. Glaze	Glaze $d_{90} \sim 30\mu m$	Glaze $d_{90} \sim 20\mu m$	Glaze $d_{90} \sim 10\mu m$
L	89.71	89.31	89.31	89.53
a	-0.18	0.02	0.02	0.05
b	3.01	3.82	3.84	3.30
Brightness	92.50	86.4	90.2	92.4

3.4. Hot stage microscopy properties of the products

The effect of the fineness of products on the melting behaviour was measured by using a hot stage microscopy (EXPERT SYSTEM – ODHT heating microscope). The samples were moistened to 5% and formed into 2x2x2 mm cubes with the hand press of the device. It was heated up to 1300 °C with a heating rate of 10 °C / min in order to examine the effect of the fineness on the melting behaviour of the glazes.

A comparison of all dimensions and conventional grinding in the stirred ball mill is given in Table 7. The smaller the d_{90} value, the lower the softening and sintering temperatures.

Table 7. Hot-stage microscopy for different glaze products

	Discontinue ball mill (STD.)	**Stirred Media Mill**		
	Std. Glaze	**Glaze $d_{90} \sim 30\mu m$**	**Glaze $d_{90} \sim 20\mu m$**	**Glaze $d_{90} \sim 10\mu m$**
Softening (°C)	965	950	930	880
Sintering (°C)	1145	1140	1070	1065
Sphere (°C)	1185	1170	1155	1145
Half Sphere (°C)	1215	1200	1195	1180
Melting (°C)	1295	1245	1230	1220

3.5. Evaluation of the microstructure of products

Scanning electron microscopy (SEM) was used to determine the microstructures of the glaze surface. It has been observed that in the stirred media mill, the grains have sharp corners and do not reach as spherically as the grains produced in discontinue ball mills as seen in Figure 3. Figure 3a (std) shows that, in the standard glaze, most of the spherical crystals, particle size is under 3µm. Figure 3b,c and d show that grinded in the stirred media mill, most of the spherical particle size varies between 1 and 2 µm but there are also needle-like crystals grew up 5 µm in the microstructure. Moreover, the microstructure of figure 3d shows that the amount of glassy phase in the glaze is higher than standard and other glazes that grinded stirred media mill. The higher amount of glassy phase can be explained with grinding to the stirred media mill. This type of mills during grinding stage are resulted the narrow particle size and this type distribution of particle size can cause the high amount of glass phase formation.

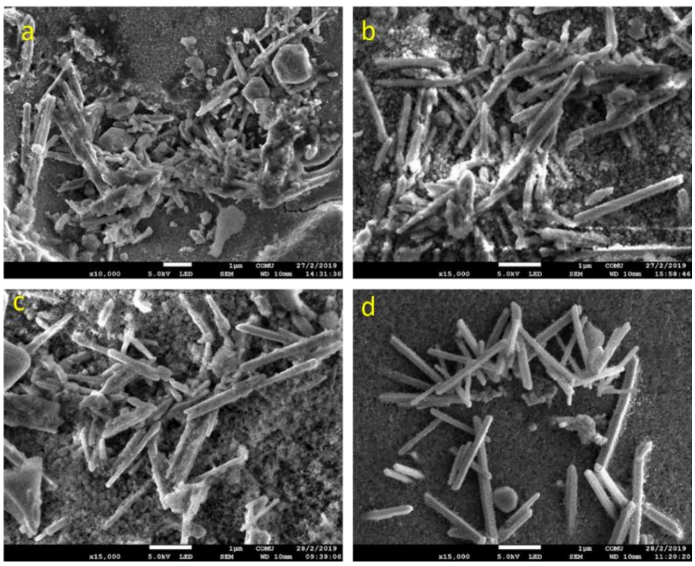

Fig. 3. Microstructures of the glazed products The surfaces images of the glazes taken on SEM and EDX were fully evaluated and documented elsewhere (Kaleseramik Ar-Ge Merkezi, 2020) (a. STD, b. $d_{90} \sim 30\mu m$ c. $d_{90} \sim 20\mu m$, d. $d_{90} \sim 10\mu m$)

4. Conclusions

It has been determined that the grain size distribution affects the quality of the glaze surface. it was observed that the roughness values, the colour and glossy values of wall tile surface can be enhanced by utilizing stirred media mill.

The energy requirement for conventional discontinue ball mill was 78.9 kWh/ton, it was measured as 61 kWh/ton in the stirred media mill for the same wall tile standard glaze product. It was also observed that grinding media consumption and its cost could be reduced due to the utilising more efficient grinding process. Since ceramic production is an energy-intensive process, increasing the energy efficiency in the process and reducing the use of water in grinding also lead to the use of an efficient and effective process in glaze preparation.

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