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DEVELOPMENT OF RED WALL TILE COMPOSITION BY DRY GRINDING PROCESS WITH EXPERIMENTAL DESIGN METHOD

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ABSTRACT

In this study, an attempt was made in order to develop a red wall tile body with dry prosess. In order to achieve this, Experiments were designed as $2^4 3^1$ multi-level factorial design, individual effects of main five factors (temperature, clay 1, clay 2, clay 3 and feldspar) and their interactions were determined. 24 formulations are prepared with territorial clays and feldspar (Turkiye). The samples were ground at laboratory hammer mill and unidirectional dry pressed in a die with rectangular cavity (50 mm x 100 mm) .The samples were fired at 1100 ^oC and 1135 ^oC using a fast firing cycle in a laboratory roller kiln. The samples were characterized before and after firing by using XRD, EDX and SEM. The physical properties (linear shrinkage, flexural strength and water absorption) were measured. Results were analyzed by MINITAB 14 statistical software program. The preliminary experimental results showed that it was possible to obtain a dry ground red wall tile body with the properties in accordance with ISO-EN 10545.

Keywords: Dry Grinding, Red Wall Tile, Strength, Experimental Design Method

1. INTRODUCTION

Ceramic tiles are commonly produced from a mixture of raw materials containing clay, flux, and refractory filler. Each raw material within the body formulation contributes differently to the final properties. A broad range of products varying in dimensions, strength, apparent porosity, surface texture, decorative coatings and overall quality are produced by the tiles industry [1].

The wall tiles are characterized by high porosity, low expansion by moisture adsorption, and high dimensional stability. These properties are acquired through the formation of certain crystalline phases during the firing stage, such as calcium silicates and aluminosilicates (gehlenite, anorthite, wollastonite), as a result of the reaction between decomposition products of the clays and calcium oxide, introduced normally as calcite [2].

Most of the energy is consumed in the grinding operations for ceramic industry. Dry milling of ceramic raw materials offers advantages in comparison with the wet milling process. The dry grinding process is an energy saving process. The dry process strongly diminishes the thermal consumption because the spray dryers are not used at this process [3-4]. Regarding energy saving, the dry process strongly diminishes the thermal consumption. Small amount of thermal energy is used in the mills to avoid make dirty the rollers by agglomerations formed by condensation of moisture from the raw materials [5]. And also with dry grinding; no need of processing additives, maintenance and environmental impact reduced [6].

2. EXPERIMENTAL METHODS AND MATERIALS

Red wall tile recipes prepared according to the mixed-level factorial design were presented in Table 1. Clay 1, clay 2 and feldspar were supplied from area around Turgutlu/Manisa/Turkiye and clay 3 from Istanbul/Turkiye. $2^4 3^1$ mixed-level factorial design with three replications was utilized in the experiments. In Table 2 factors (clay1, clay2, clay3, feldspar and firing temperature) and levels are given. Table 3 shows the chemical compositions of the raw materials. According to X-ray spectra of raw materials, clay 1, clay 2 and clay 3 mainly contain quartz, illite, kaolinite and calcite, Na-feldspar contain quartz and albite(Table 4).

The raw materials were first dried at the laboratory oven at 110 ^oC until the moisture were lower than 1% and than separately dry-ground using laboratory hammer mill and were sieved less then 1 mm. Recipe were mixed and granulated with moisture content 6 %. Samples were prepared by uniaxial pressing technique in a 50 mm x 100 mm rectangular die at 300 kg/cm^2, and dried at 110 ^oC. The firing step was carried out in a fast-firing laboratory roller kiln (Nannetti ER-30) at temperatures 1100 ^oC and 1135 ^oC with industrial fast-firing cycle (total 30 min. including cooling). Linear shrinkage and water absorption values were determined in accordance with ISO-EN 10545-3. The flexural strength of the tiles were measured by three-point bending test (model 5581, Instron) at a loading rate of 1 mm/min (ISO-EN 10545-4).

#	Clay 1	Clay 2	Clay 3	Feldspar	#	Clay 1	Clay 2	Clay 3	Feldspar
1	65	10	0	25	13	65	10	5	25
2	65	10	0	20	14	65	10	5	20
3	65	20	0	20	15	65	20	5	20
4	65	20	0	25	16	65	20	5	25
5	70	10	0	25	17	70	10	5	25
6	70	10	0	20	18	70	10	5	20
7	70	20	0	20	19	70	20	5	20
8	70	20	0	25	20	70	20	5	25
9	75	10	0	25	21	75	10	5	25
10	75	10	0	20	22	75	10	5	20
11	75	20	0	20	23	75	20	5	20
12	75	20	0	25	24	75	20	5	25

Table 1. Ratio of the recipes

Factors	Levels		
	Low	Medium	High
Clay 1	65	70	75
Clay 2	10	-	20
Clay 3	0	-	5
Na-feldspar	20	-	25
Firing Temperature (°C)	1100	-	1135

Table 2. Examined factors and their levels

Raw Materials	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI*
Clay 1	62.057	15.166	6.425	0.840	4.470	2.007	0.966	2.643	6.990
Clay 2	72.942	8.977	3.663	0.584	4.717	0.976	1.025	1.454	5.291
Clay 3	62.368	21.246	4.334	1.123	0.504	0.602	0.237	2.240	7.160
Feldspar	73.928	14.161	0.303	0.595	0.893	0.485	8.187	0.359	0.281

*LOI, loss of ignition.

Table 3. Chemical composition (wt.%) of raw materials

Raw materials	Phases
Clay 1	Quartz, illite, kaolinite, calcite, clinochlore
Clay 2	Quartz, illite, kaolinite, calcite, albite
Clay 3	Quartz, illite, kaolinite, calcite, microcline
Na-Feldspar	Quartz, albite

Table 4. Mineralogical analysis of raw materials

Crystalline phases present in the fired tiles was analyzed by X-ray diffraction (Rigaku, Rint 2200, Japan) on randomly oriented powdered samples (1.0 s/step, at scan rate 0.02^o 2θ/s over a range of 10–55^o 2θ). Chemical analysis determined by X-ray fluorescence (XRF-Rigaku ZSX Primus). Microstructural observations were performed on both polished and fracture surfaces of some selected fired samples using a scanning electron microscope (SEM-Zeiss EVO 50) in both secondary (SE) and back-scattered (BE) electron imaging modes after sputtering with a thin layer of gold–palladium alloy in order to prevent charging. Polishing was carried out in accordance with the standard ceramografic procedures. Chemical etching was further employed to reveal the presence of certain crystalline phases by immersing the hydrofluoric acid solution at room temperature for 20 s.

3. RESULTS AND DISCUSSION

144 samples which includes 24 different recipes with two firing temperature and with three replications, linear shrinkage, water absorption, and flexural strength values were measured. The main effects of each parameter (clay 1, clay 2, clay 3, feldspar, firing temperature) and their interactions were given in Table 5. These interactions were analyzed with ANOVA table for each physical properties (linear shrinkage, flexural strength and water absorption). Means of physical properties of three replications of recipes with the firing temperature were given in Table 6.

ANOVA table is used to test the equality of several means. In the ANOVA table, source of variations means factors and their interactions, DF means degrees of freedom, Seq SS means sum of squares and MS means mean square. F distribution is used to inference about differences between factor variance. So, effective and ineffective factors can be determined with F values in ANOVA table. We could use P-value approach for decision making. The error include ineffective factors and their interactions [7].

Main factors	Two factor interactions	Three factor interactions	Four factor interactions
Clay 1	Clay 1*Na-Feld.	Clay 1*Na-Feld.*Clay 2	Clay 1*Na-Feld.*Clay 2*Clay 3
Na-Feld.	Clay 1*Clay 2	Clay 1*Na-Feld.*Clay 3	Clay 1*Na-Feld.*Clay 2* Temp.
Clay 2	Clay 1*Clay 3	Clay 1*Na-Feld.*Temp.	Clay 1*Na-Feld.*Clay 3*Temp.
Clay 3	Clay 1*Temp.	Clay 1*Clay 2*Clay 3	Clay 1*Clay 2*Clay 3*Temp.
Temp.	Na-Feld.*Clay 2	Clay 1*Clay 2*Temp.	Na-Feld.*Clay 2*Clay 3*Temp.
	Na-Feld.*Clay 3	Clay 1*Clay 3*Temp.	
	Na-Feld.*Temp.	Na-Feld.*Clay 2*Clay 3	Five factor interactions
	Clay 2*Clay 3	Na-Feld.*Clay 2*Temp.	Clay 1*Na-Feld.*Clay 2*Clay 3*Temp.
	Clay 2*Temp.	Na-Feld.*Clay 3*Temp.	
	Clay 3*Temp.	Clay 2*Clay 3*Temp.	

Table 5. Main factors and their interactions

#	Temp. ^{0}C	Lineear Shirnkeage %	Flexural Strength N/mm^2	Water absorption %	#	Temp. ^{0}C	Lineear Shirnkeage %	Flexural Strength N/mm^2	Water absorption %
1	1100	-0.513	2.646	21.508	**1**	1135	0.549	5.563	18.179
2	1100	-0.372	6.736	16.137	**2**	1135	0.342	11.100	13.876
3	1100	-0.448	5.803	16.662	**3**	1135	0.372	10.440	14.247
4	1100	-0.422	6.130	15.657	**4**	1135	0.505	11.069	13.924
5	1100	-0.402	6.644	15.777	**5**	1135	0.671	12.303	12.660
6	1100	-0.412	6.525	16.012	**6**	1135	0.628	11.839	13.927
7	1100	-0.435	6.539	16.177	**7**	1135	0.462	12.416	13.303
8	1100	-0.418	5.808	16.406	**8**	1135	0.518	10.505	13.917
9	1100	-0.349	5.618	17.034	**9**	1135	0.859	10.087	14.944
10	1100	-0.395	5.707	16.940	**10**	1135	0.723	9.343	13.984
11	1100	-0.418	5.500	16.651	**11**	1135	0.631	9.310	15.118
12	1100	-0.398	5.901	16.143	**12**	1135	0.697	10.874	14.079
13	1100	-0.312	6.317	15.595	**13**	1135	0.936	11.475	13.695
14	1100	-0.279	5.897	17.504	**14**	1135	0.903	12.369	13.520
15	1100	-0.352	5.968	16.933	**15**	1135	0.814	10.685	14.642
16	1100	-0.325	5.513	16.644	**16**	1135	0.786	10.764	13.875
17	1100	-0.225	6.174	16.186	**17**	1135	1.071	12.218	13.368
18	1100	-0.215	6.557	16.466	**18**	1135	1.174	12.813	13.447
19	1100	-0.249	6.595	16.532	**19**	1135	0.743	8.030	14.483
20	1100	-0.162	6.650	16.121	**20**	1135	1.121	11.314	13.968
21	1100	-0.239	6.211	16.807	**21**	1135	1.171	11.057	13.239
22	1100	-0.126	7.238	15.939	**22**	1135	1.214	11.963	13.137
23	1100	-0.335	5.740	16.953	**23**	1135	0.780	8.485	14.789
24	1100	-0.153	5.498	17.247	**24**	1135	0.833	10.304	13.758

Table 6. Means of three replications experiments of physical properties

ANOVA table which covered meaningful effective main factors and their interactions for linear shrinkage values is shown in Table 7. Examining this table it was determined that besides main factors, interactions factors (clay 2*temperature, clay 3*temperature) were effective with 95 % confidence interval. Main effects are consequently clay 1, clay 2, clay 3 and firing temperature were shown Figure 1. Clay 1, clay 2, clay 3 and their interactions are less effect on linear shrinkage than other effective factors. Firing temperature with 86.1 % is the most significant main factor. In the Figure 2 with increasing the temperature the linear shrinkage also increases. Response is not sensitive for clay 3 and increasing the clay 2, size of the specimen decreases.

Factors	DF	Seq SS	MS	F_o	P
Clay 1	2	0.5345	0.2673	12.76	0.000
Na-Feldspar	1	0.0689	0.0689	3.29	0.072
Clay 2	1	0.3183	0.3183	15.20	0.000
Clay 3	1	27.225	27.225	129.99	0.000
Temperature	1	437.560	437.560	2089.25	0.000
Clay 2* Temperature	1	0.1812	0.1812	8.65	0.004
Clay 3* Temperature	1	0.4158	0.4158	19.85	0.000
Error	135	28.274	0.0209		
Total	143	508.246			

Table 7. ANOVA table for linear shrinkage

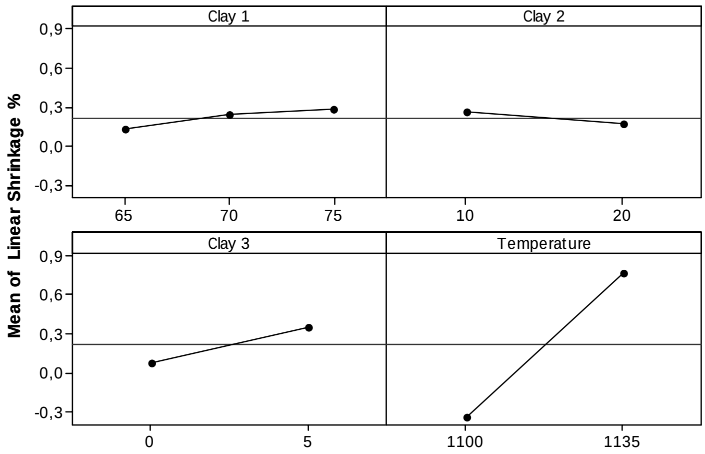

Figure 1. Main effects plots for mean for linear shrinkage value

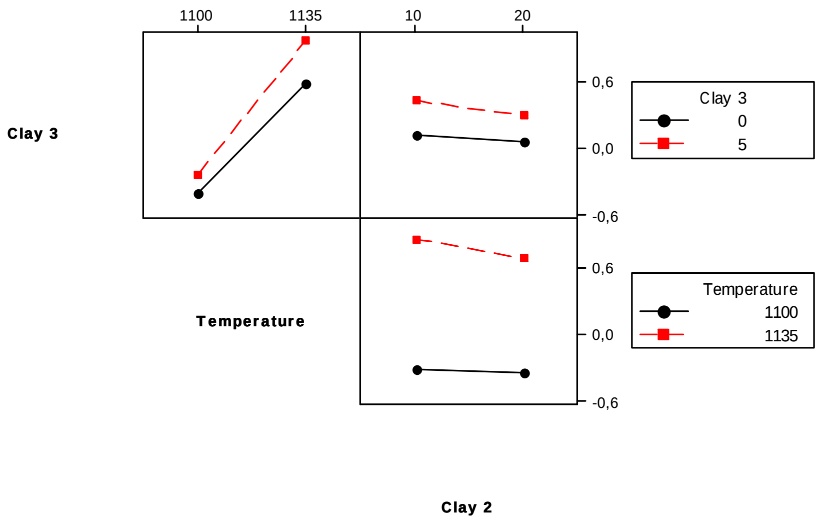

Figure 2. Two factor interaction for mean linear shrinkage value

From the ANOVA table for flexural strength, effective main factors are clay 1, clay 2, and temperature. The effective interactions are clay 1*Na-feldspar, clay 1*clay 2, clay 1*clay 3, Na-feldspar*clay 2, clay 2*clay3 and clay 1*clay 2*clay 3* Na-feldspar. Firing temperature with 66.9 % is the most significant main factor for flexural strength. With the rising of firing temperature, the response increases. In the Figure 4, there is a peak point for clay 1 at medium value; the maximum flexural strength is obtained at this point. One of the effective interaction is clay 2*clay 3. Clay 2 is sensitive for response at clay 3 high level when it decreases the strength increase. Clay 3 is proportional the flexural strength, when clay 3 increases strength improves. At the Na-feldspar*clay 2 interaction; when the clay 2 is at low level and the Na-feldspar is at high level, much higher strength value is obtained. So, Na-feldspar value is determined as high level (Figure 3). For maximum flexural strength; formulation is, clay 1is medium level, clay 2is at low level, clay 3 is at high level and Na-feldspar is at low level. It is known that porosity decreases mechanical strength by effectively reducing the materials cross sectional area. Pores can concentrate stress and reduce the flexural stress necessary to the rupture. The best criterion to indicate the reduction of porosity is bulk density. Generally, the higher the bulk density the higher the modulus of rupture (MOR). MOR is the most widely used method to characterize the mechanical behaviour of traditional ceramic bodies due to its simplicity and is calculated by the three- and four-points methodologies [8-9].

According the ISO-EN 10545, when thickness of the wall tile is lower than 7.5 mm, MOR values must be higher than 15 N/mm^2 and experimental for unglazed tiles results show that the MOR values are lower than 15 N/mm^2. For double firing process when the tile fired with glaze (glost firing) the flexural strength rise about 4-5 N/mm^2. So that, the flexural strength values at 1135 ^{o}C will be appropriate for, ISO-EN 10545.

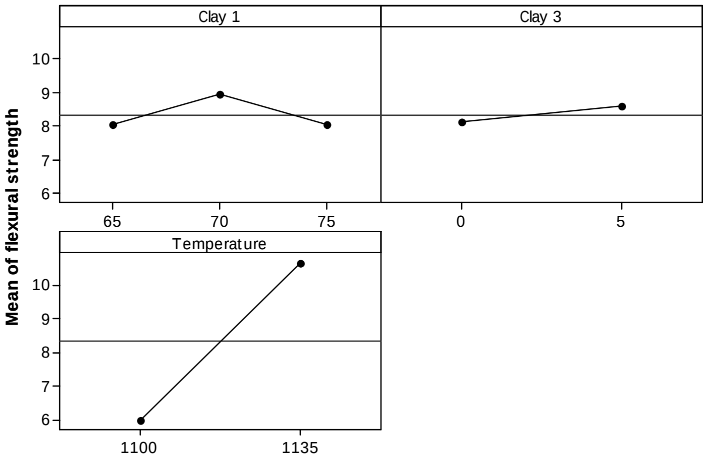

Figure 3. Main effects plots for mean for flexural strength value

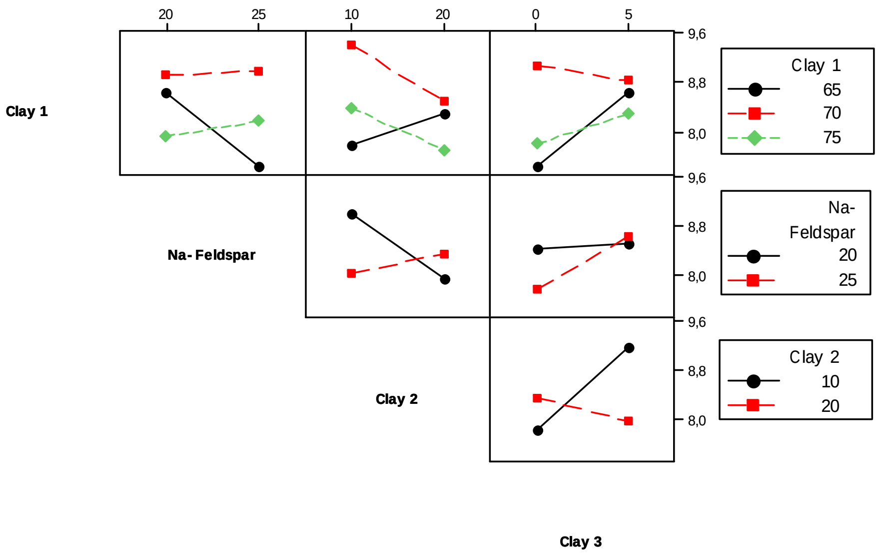

Figure 4. Two factor interaction for mean flexural strength value

Effective main factors are clay 1, clay 3 and temperature for water absorption. Effective two-factor interactions are clay 1*clay 2, clay1*Na-feldspar, clay 1*clay 3 and Na-feldspar*clay 2. Four-factor interaction is effective so that two and three factor interaction can not eliminated from ANOVA table. Firing temperature with 50.9 % is the most significant main factor for water absorption %. In Figure 5 there is a turn point at clay 1 is at medium level like flexural strength. For firing temperature is at high level the minimum water absorption obtained. It can be seen that clay 3's effect is not significant as a main factor. The experimental results showed that it was possible to obtain dry ground red wall tile body with water absorption in accordance with ISO-EN 10545-3. All water absorption values are in the range of 10-20 %. The two-factor interactions were shown Figure 6. At clay 1*clay 2 interaction, when the clay 1 is middle level and the clay 2 is high level, the water absorption is around 15 %.

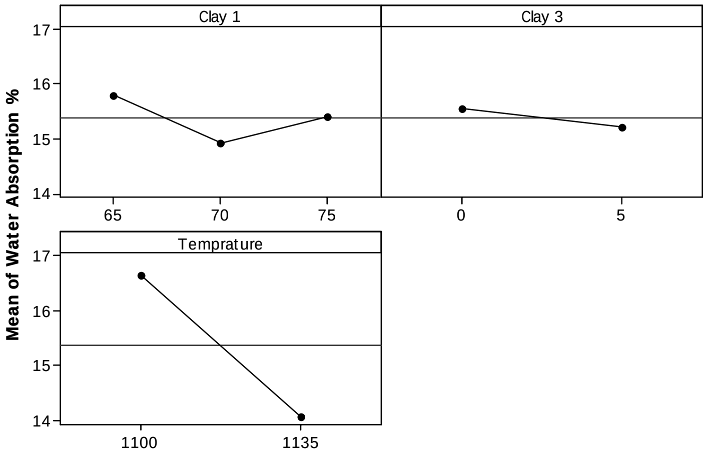

Figure 5. Main effects plots for mean for water absorption

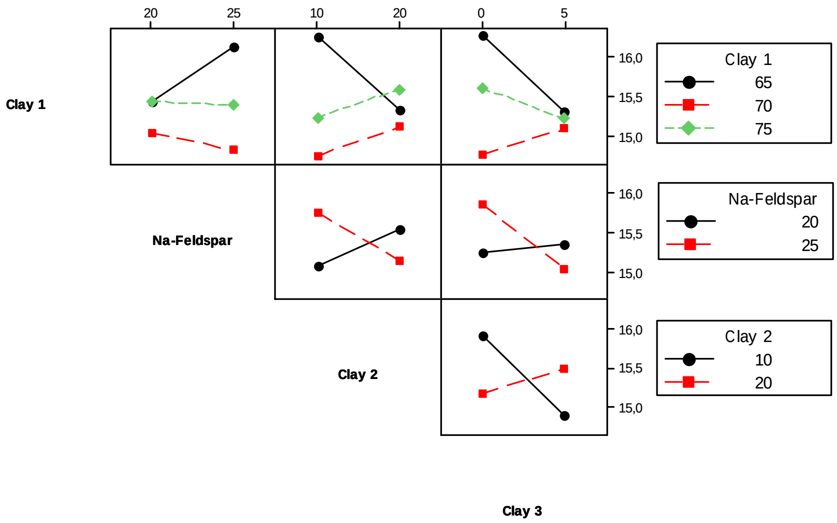

Figure 6. Two factor interaction for mean water absorption

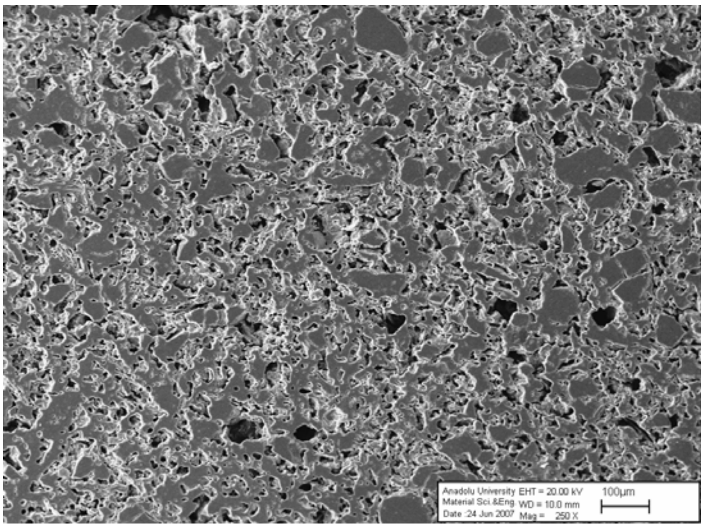

Figure 7. SE image taken from polished surface of recipe 18 fired at 1135 °C.

Maximum flexural strength is obtained at recipe 18. The polished surface of the recipe 18, fired at 1135 ^{o}C exhibits a large amount of irregular shaped porosity with a variety of pore sizes and presence of particles with sharp edges can be taken as characteristics of the initial stages of vitrification (Figure 7). In addition, SE image taken from the etched fractured surface of recipe 18. The crystal structure is spheroidcal in Figure 8. It has been determined calcium, aluminum, silicon and oxygen from the EDX analysis taken from the spheroidcal crystal structure (Figure 9). Those data indicate that spheroidcal crystal structure is anorthite. Ibanez and et.al had been reported that anorthite crystal can be spheroidcal as well as prismatic. [10].

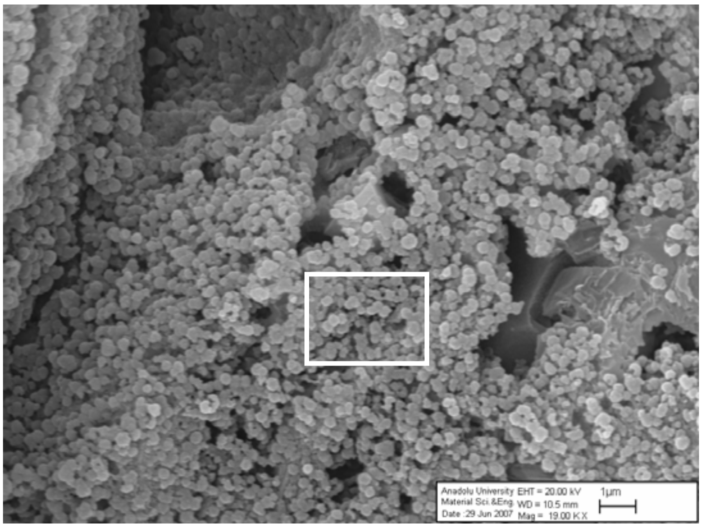

Figure 8. SE image taken from the etched fracture surface of recipe 18 (fired at 1135 ^{o}C)

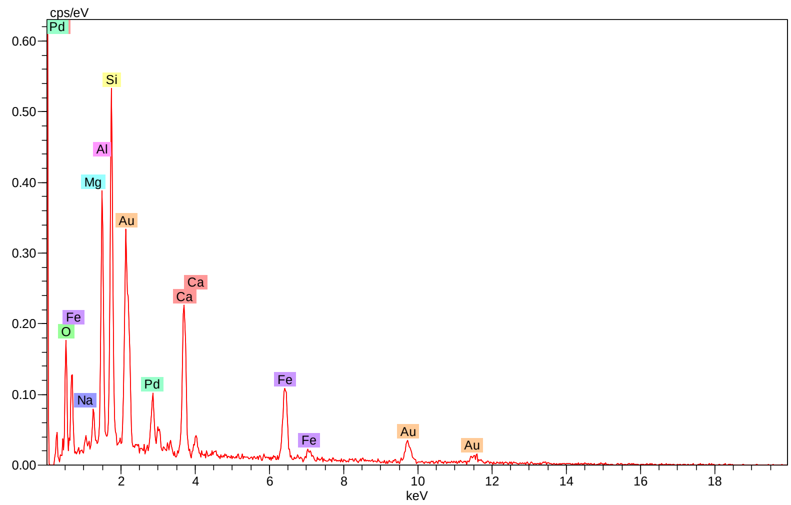

Figure 9. EDX analysis taken from marked area of Figure 8

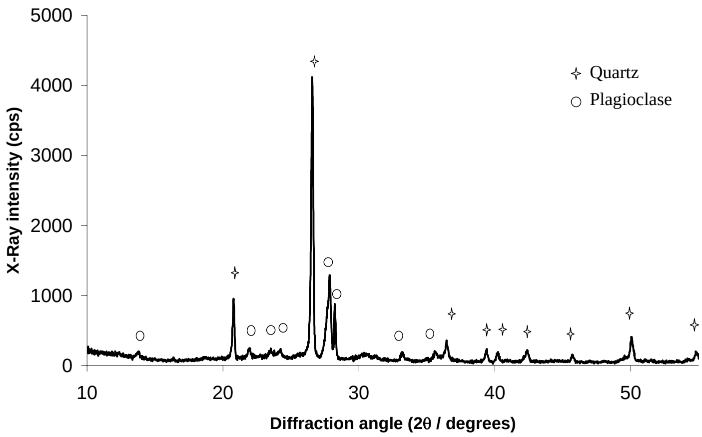

Figure 10. XRD analysis of recipe 18 fired at 1135 °C

The main crystalline phases of the green body disappear during firing and are replaced by new phases development. The presence of quartz and plagioclase are easily detectable in the spectra. Plagioclase consist of solid solutions of albite ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) and anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) [11]. Consequently, formation of a new phase with an intermediate composition between anorthite and albite is expected in the red wall tile body containing considerable amount of CaO. Anorthite which dispersed in alumina-silicate matrix increases mechanical strength of tile body [10-12]. Experimental flexural strength values for recipe 18 verify the role of the crystalline phase of anorthite.

4. CONCLUSIONS

Red wall tiles had been produced from dry ground local clays which contain high amount of illite. The red wall tiles meet ISO-EN 10545 standard requirements. High flexural strength value was obtained at 1135 °C by using clay 1 is medium level, clay 2 is at low level, clay 3 is at high level and Na-feldspar is at low level. Because of the production was realized without using spray dryer, CO_2 emission and energy consumption was decreased.

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