ELSEVIER

Ceramics International 26 (2000) 485–493

CERAMICS
INTERNATIONAL

Utilization of bauxite waste in ceramic glazes

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Received 15 June 1999; received in revised form 26 June 1999; accepted 1 September 1999

Abstract

Red mud (bauxite waste) emerge as by-product from the caustic leaching of bauxites to produce alumina and it causes serious problems such as storing and environmental pollution. In this study, red mud, which is the industrial waste of Seydişehir Aluminium Plant (Turkey), was investigated for use in the making of ceramic glazes in the ceramic industry. The chemical and the mineralogical investigations indicated that major constituents of the red mud were hematite (α-Fe_2O_3) and sodium aluminium silicate hydrate (1.01 $Na_2O.Al_2O_3.1.68\ SiO_2.1.73\ H_2O$). The production of the porcelain, vitreous (sanitary ware glazes), tile and electroporcelain glazes was done using the red mud. The glazes, which contain different compositions and properties, were examined. Their surface properties, the chemical strength of glazes in 3% HCI and 3% NaOH and abrasion resistance were investigated experimentally. It was found that the addition of up to 37 wt% of the red mud waste was possible in the production of the glazes.

Keywords: A. Firing; B. X-ray methods; D. Traditional ceramics

1. Introduction

Aluminium can be extracted from bauxite, which is a compound of aluminium hydroxide, iron dioxide, silicon dioxide, kaolin and titanium. The first stage is to extract alumina (Al_2O_3) from the ore through the Bayer process, which is used with one or two exceptions, throughout the world. In this process, ground bauxite is reacted with sodium hydroxide under heat and pressure forming sodium aluminate [$NaAl(OH)_4$], residue which is then purified and decomposed. As a result of decomposition, the aluminium hydrate is calcined at 950–1200°C, thus yielding alumina. The second stage is the electrolysis process. In the electrolysis cells, with the aid of a direct current, liquid aluminium is obtained from alumina. The liquid aluminium, being alloyed when required is then cast into the desired molds [1,2].

Red mud emerges as by-product from the caustic leaching of bauxites to produce alumina, and its major constituents are Fe_2O_3, Al_2O_3, SiO_2, Na_2O and CaO, with little amounts of Zr, Y, Th, U and rare earth elements as trace constituents. Approximately 35–40% of the processed bauxite goes into waste as red mud. Red mud is the biggest problem in producing alumina. This waste present serious problems of storing and environmental pollution. Although studies in this area have been done since 1950, improved processes have mostly not been put into practice because of economic reasons [3–6]. There were nearly 3 million tons of red mud waste accumulated at the Seydişehir Aluminium Plant (Turkey) between 1973 and 1996. There is not yet an economic way or an application of plant scale to utilize this red mud.

Much has been said about the possibility of using the red mud as a cheap source of raw material for the manufacture of low-cost ceramic products [4,6]. However, there are very few studies on using the red mud for producing ceramic glazes. Hence, very little useful data are available to aid in an assessment of the potential of red mud ceramic glazes.

From earlier researches it was seen that red mud consists of several oxides which can form a glassy phase after sintering. SiO_2, CaO and Na_2O may be responsible for the glassy phase. Because of this, red mud is a potential raw material for the production of ceramic glazes.

Most commercial glazes have a large number of constituents. It is therefore desirable to have a system of representing composition that permits easy comparisons. The method of the presenting molecular formulas

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PII: S0272-8842(99)00083-8

of glazes in general use is that originated by Seger, but somewhat modified. The oxides are listed in three or more columns, the first containing those of monovalent and divalent elements, the second those of trivalent and the third those of tetravalent elements. The sum of the first column is brought to one [10]. This classification is rigidly required by the structure of the empirical formula, which is consistently expressed in the following form:

RO	R_2O_3	RO_2
mols of bases = 1.00	mols of neutral (amphoteric) oxides	mols of acid oxides

R is the general symbol for the metallic atoms and O for oxygen [8]. It is found that all the network modifiers fall in the first column and the network formers in the second, third and fourth columns [10]. In this study, Seger formulas of the glazes were calculated by using the red mud and other raw materials.

Red mud consists of SiO_2, Na_2O, CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, TiO_2. These oxides are very important constituents of several types of glazes. Na_2O, K_2O, CaO, MgO are the network modifiers. SiO_2, Al_2O_3, Fe_2O_3, TiO_2 are the network formers. The red mud contains 30–60 wt% Fe_2O_3 [6]. The effect of iron compounds in glazes is also a matter of colour. Various colours are imparted to glazes by iron. Ferric oxide (ferric ions, Fe^{3+}) as a network former with a four-fold coordination produces a brownish colour. When the same ferric ions are in six-fold coordination and are a network modifier, a weak yellow–pink appears. Ferric iron in glass produces reddish colours. A wide variety of colours is possible from minor amounts of iron present. Ferric oxide is not so strong a flux and its solubility in the glaze is moderate to low [8]. In the present work, red mud was used as a raw material for the preparation of the glazes. The amounts of the included oxides of the red mud were determined. In the glaze compositions that were chosen, insufficient amounts of the oxides after using the red mud were completed from the other raw material. Red mud was used as a main raw material in these glazes. As the glaze types, tile, porcelain, vitreous and electroporcelain glazes were chosen. From the literature, the composition of these glazes was fixed and their Seger formulas and physical properties calculated. The production of these glazes was done using the red mud and other raw materials. Thermal shock test, chemical resistance test and resistance to abrasion test were applied to the glazed samples. Because of the insufficient literature data, it seemed necessary to undertake an experimental study directed especially at the red mud ceramic glazes to determine their potential of the ceramic glazes.

In this study, from earlier researches it was seen that Turkish red mud consist of several oxides which can form a glassy phase after sintering. From this point of view, the objective of the present work is the use of the red mud for producing ceramic glazes.

2. Experimental procedure

2.1. Materials and methods of characterization

The red mud sample was supplied by Seydişehir Aluminium Plant (Konya, Turkey, producing 200 000 tons of alumina per year) [2]. At the raw glazes, the red mud was used after calcined at 500°C for 4 h using a heating rate of 3°C/min. Kaolin, K-feldspar and bentonite were obtained from Mihaliccik, Cine and Kütahya regions of Turkey, respectively. Other raw materials were SiO_2, $ZrSiO_4$, MnO_2, Cr_2O_3, ZnO, MgO, H_3BO_3, $Na_2B_4O_7$ (calcined at 350°C), PbO, $CaCO_3$, KNO_3, Na_2CO_3. These were used at analytical purity.

The chemical analysis of the samples were done using an atomic absorption spectrophotometer (Rank Hilger, Atom Spek H-1580), a digital photometer (Dr. Lange LP 2 W) and wet chemical methods. The loss on ignition of the red mud was measured gravimetrically in a muffle furnace (Heraeus) at 1100°C. Thermal analysis measurements (TG and DTG), using a simultaneous thermal analysis instrument (Netzsch-429) were performed. Sample weight was 100 mg and the heating rate was 10°C/min under air atmosphere with Al_2O_3 powder as reference material. The temperature limits were 20 and 1200°C. X-ray diffraction (XRD) studies on the samples were undertaken using a Philips X-ray diffraction unit (Model PM 9901/00). The particle size of the materials was measured by using a sedigraph (5000 D Micromeritics). Baume degrees of the glazes were measured with an areometer.

2.2. Formulation and processing of the glazes

The ceramic bodies were chosen as tile, porcelain, sanitary ware (vitreous) and electrical porcelain (electroporcelain). The clay body for tile was assured from Bozüyük Ceramic Works of Turkey. Other clay bodies were obtained from Yarımca Porcelain Works of Turkey.

The clay body muds were moulded into square bars with dimensions 1×10×10 cm at the factories. From these bars, biscuits with dimensions 1×5×5 cm were prepared.

As the glaze types tile, porcelain, vitreous chine sanitary and electroporcelain (high-voltage insulators) glazes were chosen. From literature the composition of these glazes were fixed and calculated their Seger formulas (empirical ceramic formula). Afterwards, percent and batch compositions of these glazes from empirical formulas were calculated by using the red mud and other raw materials [7–11]. From every type of glazes, 18 pieces which contain different compositions and properties were prepared (total of 72 pieces). Their physical properties were also determined.

On the basis of the dependence of the properties of glasses upon composition, it is possible to compute physical properties, e.g. density, coefficient of thermal expansion, tensile strength, compressive strength, hardness factor, coefficient of surface tension and heat (thermal) conductivity, according to the general formula:

$$P = c_1x_1 + c_2x_2 + c_3x_3 + \ldots + c_nx_n \qquad (1)$$

in which P is the property, c is the percentage weight of an oxide component, and x_1, x_2, x_3 and x_n are their appropriate factors [8].

The ratio of the acid to the base is shown like that

$$\text{Acid/base ratio} = \frac{\text{Sum of the mol of the acid oxides}}{\text{Sum of the mol of the base oxides}}$$

Fe, Co, Ni, Mn, and Cu oxides as the basic oxides, and Sn, Ti, As, Si and B oxides as the acid oxides are used at the calculations [7].

The coefficient of melting computes from that relations [13]:

$$F = \frac{100x}{x+y} \qquad (2)$$

$$x = \left[\frac{20}{17}(Al_2O_3 + ZrO_2) + SiO_2\right]0.38 \qquad (3)$$

$$y = RO + B_2O_3 + Sb_2O_3 \qquad (4)$$

where F = the coefficient of melting, RO = mol of the basic oxides.

The formula used for the oxygen ratio is:

$$\text{Oxygen ratio} = \frac{2S + 3B}{3Al + 1} \qquad (5)$$

where S, B, Al are mol of SiO_2, Bi_2O_3 and Al_2O_3, respectively [7]. Also, the mol ratio Al_2O_3/SiO_2 was calculated for the each glaze formula. Factors and formulas for computing some properties of glazes from composition and the limit values of the physical properties have been taken from the literature [7,8,10,12,13].

2.3. Glaze application and firing

The glaze materials were weighed, the mixture was ground in a ball mill and screened through a 75 μm (200 mesh) screen. Enough water was added to reach a pouring consistency (50 °Be) and was mixed with the magnetic stirring for preparation of a homogeneous mixture of the glaze constituents and water, free from coarse particles and lumps. The characteristics concerning the mud at 50 °Be are given as follows:

Specific gravity	(g/cm^3)	1.529
Solid quantity	(g/l)	856.557
Water quantity	(g/l)	672.443

A dipping method was used for the glaze application. For tile, porcelain and vitreous glazes, the clay bodies were fired at 900°C for 3 h in a muffle furnace (Heraeus model) and the biscuits were cooled naturally in the furnace. Then the biscuits were washed with a brush for removing powders and were dried at 105°C in the oven. Glazed biscuits were fired as follows. Porcelain (1050–1400°C), vitreous (1050–1280°C) and electroporcelain (1050–1380°C) glazed biscuits were fired in the oxidative tunnel kiln at Yarımca Porcelain Works of Turkey. Tile glazed biscuits were fired at 1000–1250°C for 3 h in the electrical furnace in our laboratory.

2.4. Experiments for the fitting of the glaze to the body

2.4.1. Determination of the crazing

Crazing is recognized as due to differences in thermal expansion between body and glaze. Stresses in the glaze layer will always result when the reversible thermal expansions of the glaze and body are not identical. If the coefficient of expansion of the glaze is greater than that of the body (below the softening temperature of the glaze) then, during initial cooling, the glaze layer will develop tensile stress. Because glazes are characteristically weak in tension, glaze layers subjected to tensile stress will rupture (craze) [8]. This may cause it to break in fine irregular cracks known as crazing. This tension was commented according to type, number and size of the crazes.

2.4.2. Harkort test (thermal shock test)

In this test method, the glazed sample was heated to 100°C and plunged into water at room temperature (17.6°C), then examined for craze lines. When none was found, the temperature was raised another notch and the sample requenched. The procedure was repeated until a temperature was found where the glaze crazes. The resistance to crazing was then reported as the maximum temperature from which the quench could be made without creating crazing [8]. The relation between the temperature and the resistance time against crazing is given in Table 1.

2.4.3. Chemical resistance test (resistance to acids and bases test)

The glazed surfaces of the samples were washed with methyl alcohol. Then they were treated in 3% HCl

Table 1
The relation between the temperature and resistance time against crazing for the glazed samples [14]

Temperature (°C)	Resistance time against crazing
120	First 8 days
150	3–4 months
160	15 months
180	2–3 years
200	Continuously

solution for 7 days at 20°C and were treated in 3% NaOH solution for 7 days at 20°C. Afterwards, the glazed surfaces were inspected visually and with a hand lens for colour, gloss, crazing, bubbles, orange peeling, etc. [15].

2.4.4. Resistance to abrasion test (sand blast test)

In this test method, the glazed sample in the form of a plate was mounted at an angle of 22.5° and subjected to a blast of 80 mesh silica sand. Fixed quantities of 30 kg per blast were employed at 15 min. Sands were poured to samples from an interval 47 mm length and 185 mm height. The samples were weighed before and after the experiments to discover the weight loss [10,14]. A measure of the abrasion resistance was taken as the amount of glaze removed by the blast.

3. Results and discussion

The chemical analyses of the mud and the calcined red mud are given in Table 2.

The particle size analysis of the red mud and the calcined red mud revealed a size distribution between 5 and 35 μm in all samples. 88% of the particles are finer than 10 μm in the red mud and 80% of the particles are finer than 10 μm in the calcined red mud [16]. From the thermal gravimetric analysis curves (TG and DTG) for the samples, weight losses are measured and are given in Table 3. Also, Fig. 1 shows the thermal gravimetric analysis diagrams for the samples.

The red mud dehydrates free water absorbed on the surface of the particles between 240 and 350°C, and bound water between 460 and 590°C. Weight losses were observed between 700 and 780°C and between 850 and 940°C for SO_3 and CO_2, respectively. The DTG peak temperatures 290, 530, 750 and 900°C represent the temperatures at which the rate of mass-change is at a maximum and are clearly not the temperatures at which the sample begins to lose mass or the final temperature, which is the temperature at which the sample completes reaction. The organic matter in red mud also burns at 370°C [17]. The free water, the bound water and the organic matter in the red mud were removed by being calcined at 500°C.

Table 2
Chemical analysis of red mud and calcined red mud

Compounds	Composition (wt%)	
	Red mud	Calcined red mud
Fe_2O_3	35.73	37.07
Al_2O_3	23.29	25.61
SiO_2	12.08	13.83
TiO_2	4.08	6.50
Na_2O	7.40	7.62
K_2O	0.28	0.34
CaO	2.81	3.16
MgO	0.76	1.77
CO_2	2.40	2.80
SO_3	1.34	1.03
Loss on ignition (1100°C)	8.66	–

Table 3
The weight losses of the red mud and the calcined red mud

Temperature (°C)	Weight losses (%)	
	Red mud	Calcined red mud
110	0.97	0.24
290	2.72	1.38
530	4.77	2.26
750	6.10	3.14
900	7.07	4.16

An X-ray diffraction diagrams of red mud and calcined red mud are given in Fig. 2. X-ray diffraction results of red mud and calcined red mud showed that the phases were found as hematite (α-Fe_2O_3), sodium aluminium silicate hydrate (1.01 Na_2O. Al_2O_3. 1.68 SiO_2. 1.73 H_2O), sodalite [$Na_4Al_3Si_3O_{12}(OH)$], sodium silicate (Na_2SiO_3), sodium aluminium oxide ($NaAlO_2$), iron titanium oxide (Fe_2TiO_5), calcium silicate ($CaSiO_3$), sodium titanium oxide ($Na_2Ti_3O_7$), sodium carbonate (Na_2CO_3) and sodium iron oxide ($NaFeO_2$) except for red mud [16]. Table 4 shows the results obtained from the XRD analysis of the red mud and calcined red mud. The X-ray diffraction and chemical analysis studies of the red mud showed that the red mud was mainly consisted of SiO_2, Na_2O, CaO, Al_2O_3, Fe_2O_3, MgO, K_2O and TiO_2. These oxides are very important constituents of several types of glazes. Because of this property, red mud may be used as a glaze raw material.

3.1. Utilization in the ceramic glazes of red mud

Computed Seger formulas and physical properties of the red mud and the calcined red mud samples are given in Tables 5–7.

From Table 7 it can be seen that the physical properties of the red mud and the calcined red mud were not suitable for using as the glaze raw material alone. Their values were not within the limit values of the physical properties given in the literature [13,16] for the successful glaze types. Therefore, these properties must be corrected with other raw material additives.

This result was verified experimentally. A glaze was prepared using the red mud alone and applied to the tile body. The tile glazed body was fired at 1100°C for 3 h in the electrical furnace. The glaze surface was matt and had large crazes. It has not shown glaze properties. This structure is given in Fig. 3.

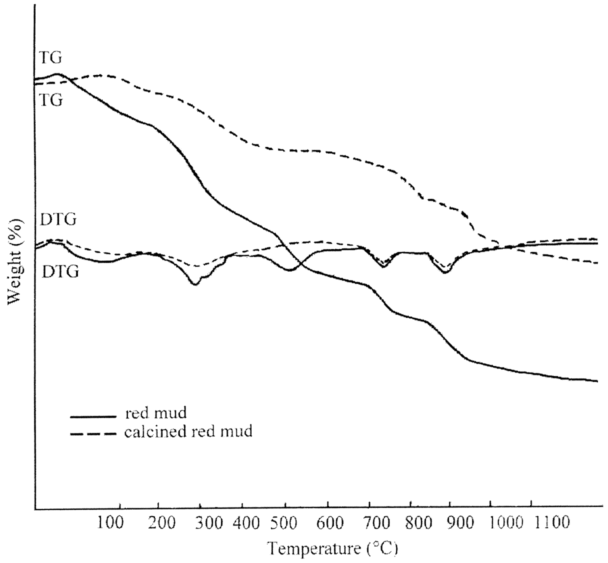

Fig. 1. TG and DTG analysis curves of red mud and calcined red mud.

3.2. *The appearance properties of the finished glaze*

3.2.1. *Porcelain glazes*

The glazes which were prepared with the calcined red mud and named as the raw porcelain glaze, with notation P_1–P_{10}, were successful except for P_8. These glazes have different equivalent values of the oxides at the Seger formulas. The equivalent values of the oxides were at these intervals: Na_2O (0.01–0.20), K_2O (0.14–0.30), MgO (0.05–0.10), CaO (0.45–0.63), ZnO (0.00–0.25), Al_2O_3 (0.30–0.50), Fe_2O_3 (0.00–0.30), B_2O_3 (0.00–0.35), SiO_2 (2.37–6.00), TiO_2 (0.00–0.05) and ZrO_2 (0.00–0.20). All of them have a glossy surface known as bright glazes. Colours of these glazes were observed as yellow, mustard, brick red, dark brown. P_{11}–P_{15} glazes which prepared with addition calcined red mud at the amounts increase gradually to a glaze composition that chosen were successful outside P_{15}. The calcined red mud wt% using at these glazes were 0.00, 11.81, 21.58, 29.57, 36.95, respectively. The amount of the ferric oxide varied from 0.00 equivalent to 0.40 equivalent at these glazes (0.00, 0.10, 0.20, 0.30, 0.40); other oxide equivalents were the same. Increasing the amount of calcined red mud in the formula, the glazes were matt, dark colour, burn and with pore. P_{16}, P_{17} and P_{18} fritted glazes have a glossy surface and obtained a range of colours from mustard to brown. In these fritted glazes a part of the materials and the remaining raw materials were added on. These frit and raw mixture glazes were successful. The amounts of the ferric oxide were 0.10, 0.15 and 0.20 equivalents at the fritted glazes, respectively.

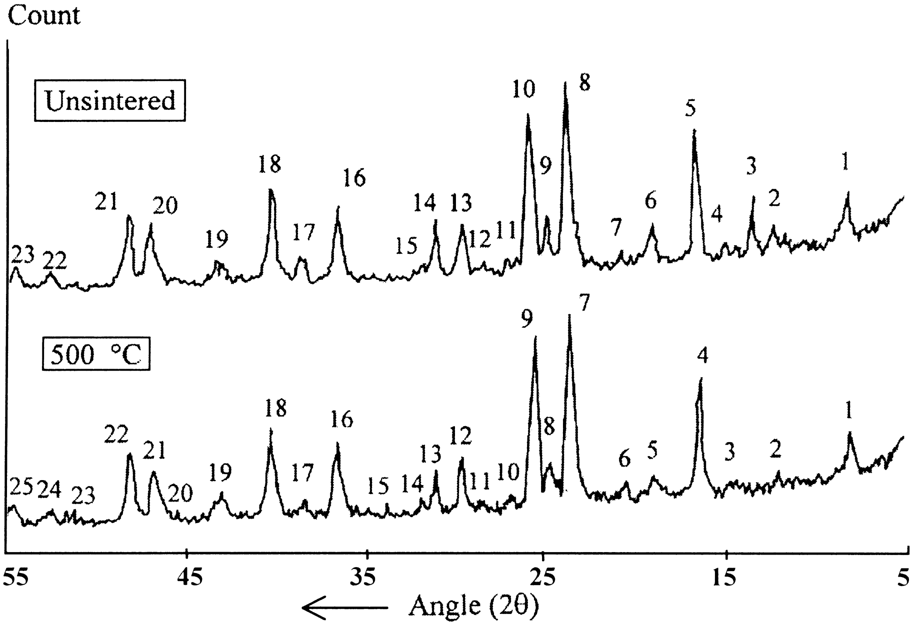

Fig. 2. XRD diagrams of red mud and calcined red mud.

Table 4
XRD analysis of samples

Mineral names	Formulas	Peak no.	
		Red mud	Calcined red mud
Hematite	α-Fe_2O_3	8, 10, 13, 14, 18, 19, 20, 21, 23	7, 9, 11, 12, 16, 18, 19, 21, 22, 25
Sodium aluminium silicate hydrate	1.01 $Na_2O.Al_2O_3$.1.68 SiO_2.1.73H_2O	2, 3, 4, 5, 6, 9, 14, 17	2, 4, 5, 8, 13, 17
Sodalite	$Na_4Al_3SiO_3O_{12}$ (OH)	1, 5, 9	1, 4, 8
Sodium silicate	Na_2SiO_3	7, 9, 11	6, 8, 10, 17
Sodium aluminium oxide	$NaAlO_2$	8, 9, 19, 20, 21	7, 8, 19, 21, 22
Iron titanium oxide	Fe_2TiO_5	13, 16, 17, 22	12, 23, 24
Calcium silicate	$CaSiO_3$	12, 13, 16	12, 13, 16
Sodium titanium oxide	$Na_2Ti_3O_7$	7, 11, 15	6, 14
Sodium carbonate	Na_2CO_3	7, 9, 11	6, 8, 10
Sodium iron oxide	$NaFeO_2$	–	12, 20

Table 5
Computed Seger formula of the red mud

0.623 Na_2O		1.051 SiO_2
0.016 K_2O	1.192 Al_2O_3	0.313 TiO_2
0.262 CaO	1.166 Fe_2O_3	0.285 CO_2
0.099 MgO		0.088 SO_3

Table 6
Computed Seger formula of the calcined red mud

0.541 Na_2O		1.015 SiO_2
0.016 K_2O	1.105 Al_2O_3	0.358 TiO_2
0.195 CaO	1.020 Fe_2O_3	0.279 CO_2
0.248 MgO		0.057 SO_3

Table 7
Computed physical properties of the red mud and the calcined red mud

Physical properties	Red mud	Calcined red mud
Coefficient of thermal expansion 10^{-5} (mm^3 °C^{-1})	3.79	4.09
Coefficient of surface tension (dyn cm^{-1})	390.287	425.43
Thermal conductivity (kcal m^{-2} °C^{-1} s^{-1})	0.9859	1.091
Density (g cm^{-3})	2.85	2.47
Tensile strength (kg mm^{-2})	2.972	3.331
Compressive strength (kg mm^{-2})	43.368	49.179
Hardness factor	239.114	265.802
Acid/base ratio	0.212	0.231
Coefficient of melting	61.99	47.956
Al_2O_3/SiO_2 ratio	1.134	1.089
Oxygen ratio	0.46	0.47
Molecular weight (g mol)	518.70	439.02

3.2.2. Vitreous glazes

Raw vitreous glazes prepared using calcined red mud and named as V_1–V_{10} glazes were successful except V_7, V_9 and V_{10}. These glazes have different equivalent values of the oxides at the Seger formulas. The equivalent values of the oxides were at these intervals: Na_2O (0.01–0.10), K_2O (0.08–0.15), MgO (0.00–0.09), CaO (0.01–0.55), ZnO (0.15–0.27), Al_2O_3 (0.22–0.37), Fe_2O_3 (0.00–0.30), B_2O_3 (0.00–0.35), SiO_2 (2.60–4.50), TiO_2 (0.00–0.05) and ZrO_2 (0.00–0.18). V_7 does not have a smooth surface. V_9 showed crawling and V_{10} showed pin holes. The high viscosity of glaze causes pin holes. It is corrected with 0.1 mol SrO added to the Seger formula. V_{11}–V_{15} glazes which prepared with addition calcined red mud at the proportions increase gradually to a glaze composition that chosen were successful. The calcined red mud wt% using at these glazes were 0.00, 5.92, 10.86, 20.38 and 28.14, respectively. The amounts of the ferric oxide were 0.00, 0.05, 0.10, 0.20 and 0.30 equivalent at these glazes. These glazes have a glossy surface and their colours were observed as white, beige brown and black. V_{16}–V_{18} fritted glazes were matt and at cream, brown colours with designed. The amounts of the ferric oxide were 0.05, 0.15 and 0.10 equivalents at the fritted glazes, respectively.

3.2.3. Tile glazes

The glazes which prepared with the calcined red mud and named as the raw tile glazes, with notation A_1–A_{10} were successful except for A_1. These glazes have different equivalent values of the oxides at the Seger formulas. The equivalent values of the oxides were at these intervals: Na_2O (0.02–0.40), K_2O (0.04–0.22), MgO (0.00–0.19), CaO (0.14–0.70), ZnO (0.00–0.20), PbO (0.00–0.45), Al_2O_3 (0.26–0.38), Fe_2O_3 (0.00–0.30), B_2O_3 (0.08–0.80), SiO_2 (2.56–3.80), TiO_2 (0.00–0.05). A_1 has the tensile crazing. Here, the expansion coefficient of the glaze was higher than that of the body and the glaze showed fine irregular cracks known as crazing. To decrease its expansion coefficient, the amount of silica is increased and the amounts of fluxing agents are decreased. Alterations of glaze composition must of course be made within limits [10]:

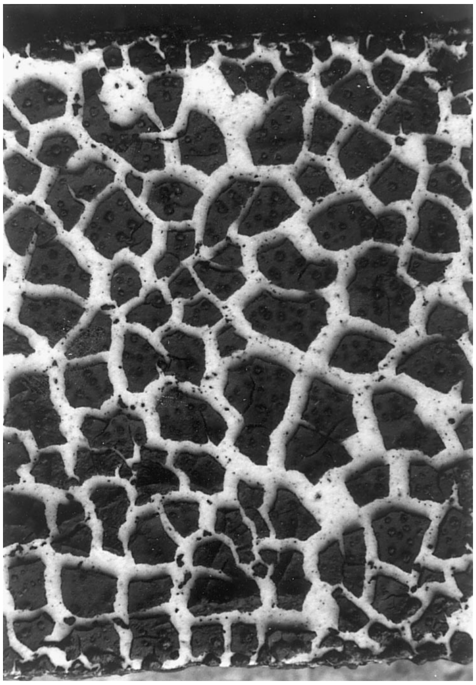

Fig. 3. Tensile crazing of the red mud glaze.

ratio silica:	flux between 2:1 and 3:1
ratio alumina:	silica between 1:4.2 and 1:5.5

The colours of these glazes were observed as cream–yellow, mustard, green, brown and black. A_{11}–A_{15} glazes were semi-matt and the range of colour from white to brown. These glazes were prepared with addition of calcined red mud with the amounts increased gradually to a chosen glaze composition. The calcined red mud weight percents of these glazes were 0.00, 6.07, 11.73, 21.30, 29.65. The amounts of the ferric oxide were 0.00, 0.05, 0.10, 0.20, 0.30 equivalents at these glazes. All of them were successful. The fritted glazes known as A_{16}–A_{18} were unsuccessful except for A_{16}. A_{17} has the peeling and A_{18} did not mature. The amounts of the ferric oxide were 0.15, 0.25, 0.10 equivalents at the fritted glazes, respectively.

3.2.4. Electroporcelain glazes

Raw electroporcelain glazes were prepared with addition calcined red mud and named as E_1–E_{10}. These glazes were successful except E_4, E_5, E_9 and E_{10}. These glazes have different equivalent values of the oxides at the Seger formulas. The equivalent values of the oxides were at these intervals: Na_2O (0.05–0.13), K_2O (0.11–0.32), MgO (0.00–0.35), CaO (0.20–0.70), ZnO (0.00–0.35), Al_2O_3 (0.39–0.71), Fe_2O_3 (0.06–0.45), B_2O_3 (0.00–0.10), Cr_2O_3 (0.00–0.15), SiO_2 (2.00–6.28), TiO_2 (0.01–0.08), ZrO_2 (0.00–0.10), MnO_2 (0.00–0.40). Unsuccessful glazes were matt and had a burnt-like appearance. All of the glazes were observed as brown and black colours. E_{11}–E_{15} glazes which were prepared with addition of calcimined red mud with the amounts increased gradually to a chosen glaze composition had a matt, burnt-like appearance except for E_{11} and E_{12}. The calcined red mud wt% used for these glazes were 0.00, 7.61, 14.69, 18.41 and 27.14. The amounts of the ferric oxide were 0.00, 0.10, 0.20, 0.30 and 0.40 equivalent at these glazes. The wt% of the calcined red mud are used to define the glazes that show also gradual increase at the ferric oxide amounts of the chosen compositions. Other oxide equivalents at the Seger formulas are the same. The increase gradually at the ferric oxide amounts was used as the main criteria for these types of the glazes. The fritted glazes with notation E_{16}–E_{18} were unsuccessful as expected. The amounts of the ferric oxide were 0.25, 0.20 and 0.10 equivalents at the fritted glazes, respectively. These glazes were unmatured and showed a structure with poles. Many larger electrical porcelain pieces cannot be refired for maturing the glaze because of the high risk of dunting. The glaze must, therefore, be applied to the raw piece and must not mature too rapidly in the single firing.

3.3. The results of experiments for the fitting of the glaze to the body

All of the glaze types did not show the tensile crazing apart from V_7, V_9, V_{10}, A_1, A_{17} and A_{18} glazes. This showed that the expansion coefficients of the glazes and bodies fitted to each other.

All of the glazed samples (except for A_1) resisted the thermal shock test (Harkort test) which made at 100, 120, 150, 160, 180 and 200°C. None of them showed the tensile crazing. In this state, the prepared glazes will resist a long period of time against crazing.

The resistance to 3% HCI solution of the glazed samples are positive except V_3, A_9, A_{14} and A_{15}. These glazes have a surface with knobs. Other glazes protected their colours and glosses. All glazes are resistant to a test made with 3% NaOH solution. No change was observed in their colours and glosses. The results of resistance to abrasion test measured using the system developed by Scott are illustrated in Table 8.

From Table 8, it was seen that P_8, P_{14}, P_{15}, P_{17} and P_{18}, namely porcelain glazes, showed larger abrasion values. These glazes have more red mud content from others. When the Fe_2O_3 content of the glazes was too high (larger than 0.30 equivalent) the appearance began to spoil.

V_9 and V_{18}, namely vitreous glazes, showed larger abrasion values. These glazes have too high PbO values. PbO values are 0.90 equivalent at V_9 and 0.30 equivalent at V_{18}. It has been said that the abrasion resistance of the glaze is decreased importantly as the content of lead rises. Also, high B_2O_3 and alkali values decrease the abrasion resistance of the glaze. Al_2O_3, SiO_2 and

Table 8
The results of resistance to abrasion test of the glazes

Porcelain glazes	Abrasion (mg)	Vitreous glazes	Abrasion (mg)	Tile glazes	Abrasion (mg)	Electro porcelain glazes	Abrasion (mg)
P_1	0.40	V_1	6.20	A_1	10.62	E_1	2.48
P_2	1.84	V_2	1.22	A_2	13.48	E_2	1.34
P_3	6.96	V_3	9.92	A_3	1.22	E_3	4.66
P^4	2.14	V_4	4.80	A_4	6.82	E_4	17.9
P_5	2.82	V_5	0.86	A_5	0.36	E_5	4.96
P_6	5.96	V_6	5.32	A_6	4.44	E_6	25.48
P_7	3.12	V_7	5.34	A_7	8.14	E_7	3.98
P_8	23.44	V_8	2.76	A_8	0.32	E_8	6.60
P_9	4.08	V_9	65.41	A_9	3.98	E_9	29.52
P_{10}	1.96	V_{10}	9.94	A_{10}	9.18	E_{10}	57.62
P_{11}	2.78	V_{11}	0.52	A_{11}	5.32	E_{11}	2.24
P_{12}	1.86	V_{12}	0.50	A_{12}	6.26	E_{12}	1.34
P_{13}	2.64	V_{13}	0.58	A_{13}	5.18	E_{13}	1.68
P_{14}	12.70	V_{14}	0.32	A_{14}	3.96	E_{14}	4.14
P_{15}	10.22	V_{15}	0.38	A_{15}	2.56	E_{15}	5.40
P_{16}	3.04	V_{16}	6.04	A_{16}	4.48	E_{16}	–
P_{17}	23.74	V_{17}	3.98	A_{17}	–	E_{17}	–
P_{18}	25.02	V_{18}	24.82	A_{18}	–	E_{18}	2.82

ZrO_2 increase the abrasion resistance of the glaze [8]. A_1 and A_2 tile glazes have a little higher abrasion values than others. A_1 has the tensile crazing anyway and A_2 has high PbO value. E_4, E_6, E_9 and E_{10} electroporcelain glazes showed larger abrasion values. Fe_2O_3 values of these glazes are 0.20, 0.35, 0.40 and 0.45 equivalent, respectively.

These values found for unsuccessful glazes are smaller than the values quoted in Turkish Standards TS 3451 for the abrasion of tile glazes [18]. According to these standards, the average abrasion value is 80 mg. In the examinations, for all of the glaze types the average abrasion value was accepted as 10 mg. Some changes occurred in the glazes which showed values more than 10 mg, for example, becoming dull with impaired gloss on the abraded surfaces. From the total of 72 glazes, only 13 pieces exceeded 10 mg value. This shows that the prepared glazes are resistant to abrasion. According to the results of experiments for the fitting of the glaze to the body, the number of the unsuccessful glazes is only 29.

The calcined red mud wt%, which were used at the successful porcelain glazes, ranged between 7 and 23. On the fritted glaze, the founded red mud increased more than 17 wt% the abrasion values. The limit equivalent values at the Seger formulas of the oxides which founded at the successful porcelain glazes are as follows:

Na_2O	0.01–0.20		
K_2O	0.14–0.24	Fe_2O_3	0.00–0.30
MgO	0.05–0.10	B_2O_3	0.00–0.35
CaO	0.45–0.63	SiO_2	2.37–4.60
ZnO	0.00–0.25	TiO_2	0.00–0.04
Al_2O_3	0.30–0.45	ZrO_2	0.00–0.20

The calcined red mud wt% used at the successful vitreous glazes ranged between 6 and 29. At the fritted glazes these values were at the interval 9–24 wt%. The limit equivalent values at the Seger formulas of the oxides which founded at the successful vitreous glazes are as follows:

Na_2O	0.01–0.10		
K_2O	0.08–0.15	Fe_2O_3	0.00–0.30
MgO	0.00–0.09	B_2O_3	0.00–0.35
CaO	0.44–0.55	SiO_2	2.60–4.00
ZnO	0.15–0.27	TiO_2	0.00–0.05
Al_2O_3	0.22–0.35	ZrO_2	0.00–0.18

The calcined red mud wt% used at the successful tile glazes ranged between 5 and 30. It was found that the addition of up to 23 wt% of the red mud waste was possible in the production of the fritted tile glazes. The limit equivalent values at the Seger formulas of the oxides which founded at the successful tile glazes are the following:

Na_2O	0.04–0.29	Fe_2O_3	0.00–0.30
K_2O	0.04–0.18	B_2O_3	0.08–0.80
MgO	0.00–0.19	SiO_2	2.56–3.60
CaO	0.20–0.70	TiO_2	0.00–0.05
ZnO	0.00–0.20		
PbO	0.00–0.45		
Al_2O_3	0.26–0.38		

The calcined red mud wt% used at the successful electroporcelain glazes ranged between 5 and 37. The fritted electroporcelain glazes were unsuccessful. These glazes were containing to the red mud at interval 17–32 wt%. The limit equivalent values at the Seger formulas

Table 9
The limit values of the physical properties for the successful glazes

Properties	Types of glazes			
	Porcelain	Vitreous	Tile	Electroporcelain
Coefficient of thermal expansion 10^{-5} (mm^3 °C^{-1})	2.20–2.52	2.13–2.35	1.99–2.60	1.93–3.06
Coefficient of surface tension (dyn cm^{-1})	352–378	348–384	287–373	369–385
Thermal conductivity (kcal m^{-2} °C^{-1} s^{-1}	1.84–2.01	1.85–2.06	1.61–2.12	1.54–1.96
Density (g cm^{-3})	2.33–2.73	2.34–2.78	2.41–4.73	2.14–2.35
Tensile strength (kg mm^{-2})	2.75–8.63	7.89–9.06	6.42–9.18	6.50–7.86
Compressive strength (kg mm^{-2})	87–96	86–98	80–102	69–103
Hardness factor	265–340	253–301	255–313	260–350
Acid/base ratio	0.86–1.29	1.05–1.39	0.92–1.36	0.62–1.67
Coefficient of melting	30.96–50.26	32.07–48.04	39.46–57.26	19.32–50.28
Al_2O_3/SiO_2 ratio	0.09–0.13	0.08–0.15	0.09–0.10	0.11–0.19
Oxygen ratio	2.65–4.18	3.20–4.13	3.01–4.67	2.65–4.13
Molecular weight (g mol)	286–428	273–400	331–411	315–563

of the oxides which founded at the successful electroporcelain glazes are as follows:

Na_2O	0.05–0.10	Fe_2O_3	0.00–0.30
K_2O	0.12–0.26	B_2O_3	0.00–0.10
MgO	0.03–0.35	Cr_2O_3	0.05–0.15
CaO	0.30–0.48	SiO_2	2.00–6.28
ZnO	0.05–0.27	TiO_2	0.00–0.05
Al_2O_3	0.39–0.71	ZrO_2	0.00–0.05
		MnO_2	0.00–0.35

For the unsuccessful glazes, some values of oxides remained out of these limit equivalent values. The limit values of the physical properties for the successful glazes are given in Table 9.

4. Conclusion

The X-ray diffraction results of red mud and calcined red mud showed that they consisted of the phases such as hematite, sodium aluminium silicate hydrate, sodalite, sodium silicate, sodium aluminium oxide iron titanium oxide, calcium silicate, sodium titanium oxide, sodium carbonate and sodium iron oxide. The red mud includes the oxides SiO_2, Al_2O_3, Fe_2O_3, Na_2O, K_2O, CaO, MgO, TiO_2, which were determined from the chemical analysis studies.

The wt% of the most red mud, which were used at the successful porcelain glazes, are 23, at the vitreous glazes are 24, at the tile glazes are 30 and at the electroporcelain glazes are 37. The colours interval of the glazes was observed as cream, beige, yellow, mustard, green, red, brown and black. These glazes generally have a glossy surface. The practical results of this research demonstrated the possible use of the red mud as a pigment and glazes raw material.

References

[1] T. Gozmen, H. Yuzer, E. Kalafatoglu, T. Balkas, The utilization of the red mud, Publication no. 114, Tubitak Marmara Research Centre, Chemistry Research Department, Gebze, 1983 (in Turkish).
[2] Etibank, Seydişehir, Aluminium Plants Introducing Catalogue, Seydişehir, Turkey, 1984.
[3] R.S. Thakur, B.R. Sant, Utilization of red mud, Journal of Science and Industrial Research 33 (1974) 408–418.
[4] F. Puskas, Process for the utilazition in the ceramic industry of red mud from alumina plants, US patent 4 368 273, 1983.
[5] S. Lal, Rehabilitation of bauxite afforestation, part II, Indian Forester 119 (9) (1993) 708–713.
[6] M. Kara, F.O. Emrullahoglu, The utilization of Seydişehir red mud as the construction material, 2nd Int. Ceram. Congress Proc., Vol. 1, Istanbul, Turkey, 1994, pp. 181–189 (in Turkish).
[7] F. Isman, Ceramic Technology, The Academy of Fine Arts in Istanbul, Technical Publications Series, Istanbul, 1969 (in Turkish).
[8] C.W. Parmelee, Ceramic glazes, Cahners Books Division of Cahners Publishing Company, New York, 1987.
[9] F.H. Norton, Fine ceramics technology and applications, R.E. Krieger Publishing Company, New York, 1978.
[10] F. Singer, S.S. Singer, Industrial ceramics, Chapman and Hall, London, 1979.
[11] J.W. Conrad, Contemporary ceramic formulas, McMillan Publishing Co. Inc., New York, 1980.
[12] W.G. Lawrence, Ceramic science for the potter, Chilton Book Company, USA, 1972.
[13] I.A. Sengil, A.O. Aydin, K. Yildiz, The utilization in the ceramic industry of the colemanite consentrator wastes, Project for the Tubitak, INTAG-602 (YAG-21), Gebze, 1993 (in Turkish).
[14] A. Arcasoy, Ceramic Technology, Gençlik Bookstore, Istanbul, 1983 (in Turkish).
[15] Z. Mete, H. Tanisan, Ceramic Technology and Applications, Vol. I, Izmir, 1986 (in Turkish).
[16] N. Yalcin, Utilization in the ceramic industry of red mud, Ph.D. thesis, Sakarya University, Turkey, 1996.
[17] W. Wendlant, Thermal methods of analysis, Interscience Publishing, USA, 1964.
[18] E. Özmen, Hardness at the glazed surface, 2nd Int. Ceram. Congress Proc., Vol. 1, Istanbul, Turkey, 1994, pp. 190–195 (in Turkish).