THE COLOR CHANGES WITH THE FINNISH EARTHENWARE CLAY AND CALCIUM OXIDE IN STONEWARE GLAZES

Hortling, Airi and Siren, Kirsi-Marja
Department of Ceramic and Glass Design
University of Industrial Arts Helsinki, 1992

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Abstract

The Finnish Earthenware clay is a low fired composition. It has high iron content and gives red coloring effect after firing. The Analyze of The Finnish Earthenware is very like the famous Albany Slip from Canada. As low fired clay it is useful for the ceramist artist as a plastic clay material, but it is also available to mix in powder form with the different raw materials and to fire as stoneware slip glaze. The Calcium oxide gives with iron oxide different red brown or yellow colors. For this case calcium raw materials, such as whiting, dolomite, and wollastonite have been chosen. The amount of the Earthenware is used between 50-90% of the glaze. For the testing and the comparing the glazes have fired in oxidation and reduction atmosphere. The iron oxide turns easily color from the yellow brown to green depending on the kiln atmosphere and the amount of the oxide. Calcium oxide helps the color changes to turn from yellow to green tones in stoneware temperature. The color tone changes also during the practically glazing method. The thickness of the glaze surface gives different color tone. Thin surface is darker and the thick is lighter. The changes in the glazes have been analyzed with comparing oxides in the different empiric formulas.

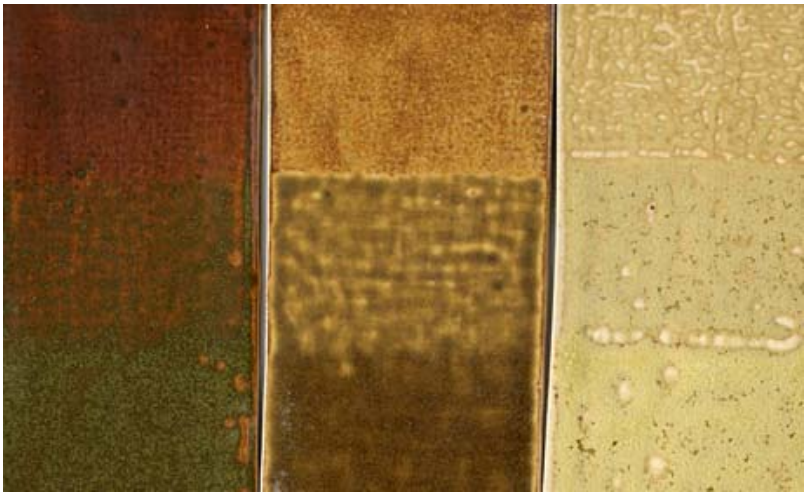

Fig: Glazes LPL2 (cone 8), LPL3 ((cone 10) and LPD5 (cone 10)

1 Introduction

The Finnish Earthenware clay has a composition firing at low temperature. It has high iron content and gives a red color after firing. The analyze of the Finnish Earthenware clay is close to that of the famous Albany Slip clay, which is mined in New York State, in U.S.A.

As a low-firing clay the Finnish earthenware clay is useful for the ceramic artist as a plastic material. In powder form it can also be mixed with other raw materials and fired as stoneware slip glazes like Temmoku and Celadon (Koreana 1991).

Calcium oxide mixed with iron oxide gives different red brown or yellow colors. In this case raw materials including calcite, such as whiting, dolomite, and wollastonite are chosen. The amount of the Earthenware clay is between 50-90% of the glaze.

In order to test and compare the glazes, they have been fired in oxidation and reduction atmospheres. The iron oxide changes easily color from brown to green depending on the kiln atmosphere and the amount of the oxide. The addition of calcium oxide changes the color tone into the yellow direction. The brown color caused by iron turns from orange to greenish yellow at higher stoneware temperatures.

The changes in different color tones are also dependent on the thickness of the glaze during the glazing. The thick layer is lighter than the thin one.

The changes in the glazes have been analyzed by comparing the content of the oxides in their empiric formulas.

2 Experimental

2.1 Raw materials

In the present work dolomite, wollastonite and whiting, which contain calcium carbonate, are used with low-firing red clay. These minerals are all mined in Finland, but because of their too big particle sizes they are not generally used in the ceramic, but only in the building industry.

2.1.1 Finn slip and Albany slip

Finnish clay which turns red under firing is called Finn slip in the present work and the corresponding American clay is called Albany slip. Because of their similar compositions they also have very similar properties.

The Finn slip contains 5-6 % iron oxide. At the department of the Ceramic and Glass Design applied research concerning low firing clays has been performed and suitability as stoneware glazes has been tested (Salmenhaara, 1968)

In the present work a low firing clay from Somero, which contains 9,0 % iron oxide and starts to melt to a glaze at 1220 ^{O}C it has been investigated. The clay forms a nice glaze surface at 1260 - 1300 ^{O}C (Oc. 9-12).

At the department of the Ceramic and Glass Design in Helsinki applied research concerning different types of low firing clays from Finland and their suitability as stoneware glazes has been tested by the great teacher Kyllikki Salmenhaara (1968).

The Finnish low firing earthenware, clay which turns red during the firing process, is called Finn slip in the present work and is used for brick making in Somero. It contains 9 % percentage iron oxide and starts to melt to a glaze at 1220 ^{O}C. The clay forms a nice glaze surface at temperatures between 1260 - 1300 ^{O}C (Oc. 9-12).

The Finnish low firing clay, Finn slip, is close to that of the famous Albany slip clay. The Albany slip origins from a clay mine in New York State, USA, which is closed today. Albany slip- name is nowadays used to describe the common type of low firing red clay, which melts to a glaze at stoneware temperature. A synthetic Albany slip has been suggested by Rowan (1988). Also other suitable clays have been presented instead of Albany slip clay like American Cedar Heights Redart Clay (table 1).

Table 1: Analysis of Finn slip and Albany slip

Chemical analysis:					
Oxide	Finn slip[1)]	Albany s.[2)]	Albany s[3)]	Albany s.[4)]	Redart clay[5)]
SiO_2	50,0	59,48	57,6	59,48	64,27
Al_2O_3	17,1	11,54	14,6	10,60	16,41
Fe_2O_3	9,0	4,13	5,2	4,13	7,04
CaO	1,5	6,28	5,8	6,28	0,23
MgO	3,3	3,35	2,7	3,35	1,55
K_2O	4,2	2,75	3,2	2,75	4,07
Na_2O	2,0	0,40	0,8	0,40	0,40
TiO_2	-	0,90	0,4	0,90	1,06
MnO	-		-	0,08	-
C	3,7		-	-	-

1) Finn slip, Somero red clay, Brick factory of Kultela, Finland
2) Abany slip, Salmenhaara 1964, Tichane 1978: 204 ja Zakin 1981:89
3) Albany slip, Nelson 1966: 286 ja Smyser 1988:49
4) Albany slip, Cooper et al.1984: 49
5) Cedar Heights Redart Clay, Smyser 1988:49

In the present work an old Albany slip delivered by, The POTTERY SUPPLY HOUSE Ltd to Finland, is used as a reference for the Finn slip (table 1, Salmenhaara 1964).The melting region of this Albany slip is between 1170-1190 ^{o}C.

2.1.2. Additives to Finn slip and Albany slip

Calcium oxide mixed with iron oxide gives different red brown or yellow colors. In this case three raw materials including calcium carbonate have been chosen. Dolomite, wollastonite and whiting are used with low-fired Finn slip clay. These minerals are all mined in Finland, but because of their too big particle sizes, they are not generally used in the ceramic, but only in the building industry.

2.1.2.1 Whiting

The calcium carbonate, which is used in the tests is impure and from Maalarimestarit Ltd. Its exact analyze is not known. Decomposition reaction: $CaCO_3$ -> (900 ^{o}C) CaO + CO_2

2.1.2.2 Dolomite

The dolomite, which consists of calcium- and magnesium carbonate comes from Norway.

Dolomite, Elkim Ltd, Norway	
Chemical analysis:	
Al_2O_3	0,10
Fe_2O_3	0,06
CaO	30,27
MgO	21,6
L.O.I. CO_2	47,37

2.1.2.3 Wollastonite FW, $CaSiO_3$

Wollastonite is a rather rare calcium silicate mineral. The wollastonite found in Finland contains a small amount of iron oxide and melts at 1390 - 1410 ^{o}C.

Wollastonite, Partek Ltd, Lappeenranta Chemical analysis (1991):			
SiO_2	52,00	+	1,0 %
CaO	43,20	+	0,7 %
Al_2O_3	1,00 %		
MgO	1,00 %		
Na_2O	max.0,20 %		
K_2O	max.0,20 %		
Fe_2O_3	max 0,25 %		
S	0,02 %		
P	0,02 %		
L.O.I.	max 1,20 %		

2.2 The glaze formulas

The planning of glazes with these materials aim at obtaining yellow slip glazes, which have covering properties. The effects of raw materials on the color and melting point with Finn slip clay in glaze mixtures will be investigated.

Table 2: Glazes, LPD, LPW and LPL

Glazes,	**LPD, LPW and LPL**				
Raw-material	**1**	**2**	**3**	**4**	**5**
Finn slip clay (LP)[1)]	90	80	70	60	50
Dolomite (D)[2)]	10	20	30	40	50
Wollastonite (W)[3)]					
Whiting (L)[4)]					

1) Finn slip, Somero red clay, Brick factory of Kultela, Finland
2) Dolomite, Elkem Ltd, Norway
3) Wollastonite FW, Partek Ltd, Lappeenranta, Finland
4) Whiting, Maalarimestarit Ltd, Helsinki, Finland

The percentages of Finn slip in the glazes are 90, 80, 70, 60 and 50%. The corresponding percentages of dolomite, wollastonite and whiting are 10, 20, 30, 40 and 50%

The glazes have been prepared at three different thicknesses because it is very typical for this type of the slip glaze to be influenced by the thickness. The thickness affects the formation of the crystallized surface and the color. From a thin to a thick glaze surface the color changes from dark brown to yellow.

2.3 Firing

Each mixture has been fired as a test piece at three different temperatures. One of these firing methods has been wood firing. The temperatures varied between, 1240 - 1260 ^{o}C (Oc 8-9). The temperatures in the electric kiln have been 1250 and1300 ^{o}C (Oc. 8 and 11).The rates of temperature rising have been 60 and 100 ^{o}C per hour and the soaking at the final temperature lasted 10 minutes.

The changes in the glazes have been analyzed by comparing the varying content of the oxides in the different empiric formulas.

3. Results and discussion

Typical for the slip glaze is their viscosity and their mat surface. The glazes, which are mat have covering properties and form tight yellow crystal-nets. The formation of the crystals depends on the degree of melting of the viscose glazes. A high content of crystals gives a light color. Glazes, which melt, are transparent. The darkness of the glaze depends on the amount of iron oxide used. Calcium oxide and magnesium oxide, affect the viscosity of the glaze. The color change caused by iron oxide depends on the change of the ratio of calcium oxide and aluminum oxide. The ratio of iron oxide, calcium oxide and aluminum oxide affects the color changes caused by iron oxide. Therefore, the ratios of iron oxide, calcium oxide and aluminum oxide from the analyses of the test glazes. In the results iron oxide is compared to the other variable compounds, and it is observed that the ratio of aluminum oxide is constant and the ratio of calcium oxide changes.

The glaze series LPW1-LPW5 of Finn slip and wollastonite all melt and form even surfaces, which changes from pale (LPW1) to transparent and shining (LPW5). Mixtures changes from transparent and glossy to dark temmoku.

Table 3a: The calcium- and aluminum oxide rations of glazes LPW1 -5

LPW[1)]	Fe_2O_3	CaO	Al_2O_3
1	1	0,72	1,19
2	1	0,42	1,19
3[2)]	1	2,33	1,19
4	1	3,5	1,19
5	1	5,21	1,19

1) See Table 2, glaze mixtures

2) The underlined figure values correspond to yellow glazes

In the glazes LPD1 - LPD5 of Finn slip and dolomite, there are too much aluminum oxide compare to the amount of silica. A high content of magnesium oxide forms yellow crystals, which occur as a crystal cover on the surface of the glaze.

Table 3b: The calcium- and aluminum oxide rations of glazes LPD1 -5

LPD[1)]	Fe_2O_3	CaO	Al_2O_3
1	1	0,51	1,19
2	1	0,96	1,19
3	1	1,52	1,19
4[2)]	1	2,28	1,19
5	1	3,35	1,19

1) See Table 2, glaze mixtures

2) The underlined figure values correspond to yellow glazes

The glaze series LPL1- LPL5 of Finn slip and the whiting contain 0,82 equivalents of CaO from the RO-group of the empiric formula. The glazes LPL4 and LPL5 do not form continue surfaces, but are so called structure glazes. The ratio of aluminum oxide and silica to calcium oxide in the empirical formula is too high to able to smooth the surface of the glaze.

Table 3c: The calcium- and aluminum oxide rations of glazes LPL1 -5

LPL[1)]	Fe_2O_3	CaO	Al_2O_3
1	1	0,80	1,19
2	1	1,62	1,19
3[2)]	1	2,67	1,19
4	1	4,06	1,19
5	1	5,60	1,19

1) See Table 2, glaze mixtures

2) The underlined figure values correspond to yellow glazes

3.1 Color

The color caused by iron oxide depends on the changes in the ratio of calcium oxide to aluminum oxide. From the analyses of the test glazes we have calculated the ratio between iron oxide, calcium oxide and alumina oxide. In the results the effect of iron oxide has been compared with the effect of the other components. It can be concluded that the content of alumina stays constant and the ratio number of calcium oxide changes.

The color caused by iron oxide depends on the changes in the ratio of calcium oxide to aluminum oxide. From the analyses of the test glazes the ratio between iron oxide, calcium oxide and aluminum oxide has been calculated.

In the results iron oxide has been compared with the other components. From this can be concluded that the content of aluminum oxide stays constant and the ratio number of calcium oxide changes. When the ratio number of calcium oxide is higher than 2 the effect

of the iron oxide with calcium oxide causes yellow color changes. When the ratio of iron oxide and calcium oxide is below 2 the colors of the glazes are brown or brown- yellow.

3.2 Observing by stereomicroscope

By stereomicroscope different crystallization patterns of the test glazes has been observed. Least crystallization is observed in the glaze mixtures containing Finn slip and wollastonite, which melt best. By microscope you can find out a weak crystal formation at the interfaces, where the clay body and the glaze have their contact surface.

In the glazes containing Finn slip and dolomite**,** the crystallization occurs at the surface. At the interface between the clay body and the glaze there is a different glass phase. The crystals are yellow and lighten in the dark color of the glaze surface.

In the glaze series, containing Finn slip and whiting, a lot of yellow crystals are formed, when calcium oxide reacts with silica.

4 Conclusions

The analyses of the glaze series containing Finn slip and whiting, and Finn slip and wollastonite have been compared to the analysis of the Albany slip clay.

Differences are seen in the concentrations of aluminum oxide and silica and in the amounts of calcium and iron oxide, which influence the melting of the surface.

When Finn slip is applied as a glaze wollastonite should be used as one raw-material, because it contains silica and calcium oxide.

Silica influences the darkness of the glaze color. Wollastonite alone cannot be used as a silica source and pure silica has to be added. The composition of a Finn slip corresponding to Albany slip should be 80 % Finn slip clay, 10 % wollastonite and 10 % silica.

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