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The effect of phlogopite mica on the sintering point and colour of a clay body

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In Finland the apatite mineral (calcium phosphate) is mined by Kemira Chemicals. Apatite occurs in small amounts in various rock types, but economical reserves in Europe are rare ones. In the Siilinjärvi apatite mine, situated in the Eastern part of Finland, the mined ore contains 10 % apatite, 65 % phlogopite, 20 % calcite and dolomite together and 5 % other minerals. The apatite concentrate is used the production of phosphoric acid. Phlogopite is a by-product and it is sold as a trade name "Kemira Mica" for the different types of fillers (1). Apatite has been used in dental ceramics and as a raw material in manufacturing of glass.

In the work being presented here, the application of phlogopite is investigated with clay bodies and glazes, fired at different temperatures. As a casting slip, phlogopite has been mixed with lowfired earthenware clay with high iron content (9%). The clay is common in Scandinavia and is fired in the temperature area, 1000 - 1050^{o}C. The addition of phlogopite mica gives a higher temperature resistance and higher sintering area, 1100 - 1150^{o}C. The casting properties of clay body including the phlogopite are excellent. Fired at a temperature of 1100^{o}C the water absorption is 8 %. The final softening and sintering point is 1150^{o}C. The fired colour turns from orange to red.

At a high fired temperature, phlogopite was tested in white clay body with feldspar and china clay. It was noticed that phlogopite mica increases melting process in stoneware body and lowers the sintering temperature 100^{o}C. The absorption of water is 0,6% when fired at 1100^{o}C. The iron content of phlogopite causes a beige colour in the fired clay body. The use of phlogopite lowers the firing expenses and saves energy.

1. Introduction

There is in Finland a lot of potential minerals for the various applications of the ceramics. Phlogopite is one. Phlogopite is produced as a by-product (6.000 tpa) in Kemira Chemicals Siilinjärvi apatite mine Apatite production is about 700.000 tpa apatite concentrate for the phosphoric acid production.

In apatite ore phlogopite is the main mineral (65%). Macroscopically phlogopite is reddish brown, dark brown or black. The grain size varies from fine grained to coarse (2). The feed to the plant is the form of tailing from the apatite concentration. In the mica plant phlogopite mica is wet grinded, classified to certain fractions, dried and packed. The fractions are sold to the world markets as a trade name "Kemira Mica".

Fig. Apatite mineral (green colour) has 60% phologopite mica (black colour). Test tile is fired 1260^{o}C with 15 min soking time and colour of phlogopite mica turns brown red.

The aim of the present research is to explain the suitability of phlogopite-mica as a raw material for clay bodies. The reactivity of mica was investigated by mixing it together with low fired Finnish earthenware clay and as a substitute for talc in stoneware clay body. The magnesium oxide in phlogopite rises the sintering temperature in a low fired earthenware and lowers the sintering temperature in a high fire earthenware when used in small amounts. The mica also affects the colours and shrinkage of clays at different temperatures. In a corresponding way soapstone has been investigated as a substitute for talc (3). There is the stove manufacturing of soapstone in the Eastern part of Finland, and soapstone as sawing-residue is used as a by-product in different clay bodies. Soapstone has been used in thermal shock resisting saggars in Arabia porcelain factory in the past.

2. Raw materials

In these tests phlogopite mica has been ground to a particle size of 200 mesh as is the case with other raw materials, which were used in this investigation. Besides phlogopite mica and Finnish earthenware clay, the other raw materials such as Quartz FFQ, Feldspar FFF have come from

Finland. China-clay Grolleg is from ECC International. Phlogopite (magnesium mica) is used to replace the Talc (magnesium silicate), included in the stoneware clay body K84 (4). There are given the analysis of the Finnish raw materials in table 1.

Table 1: Chemical analysis of the Finnish raw materials.

Oxide	Phlogopite[1] w-%	Earthenware[2] w-%	Stoneware body K84 w-%	Quartz[3] w-%	Feldspar[3] w-%
SiO_2	40.5	50.0	68.35	98.50	67.20
Al_2O_3	9.8	17.1	22.34	0.80	18.30
Fe_2O_3	4.7	9.0	0.33	0.02	0.13
FeO	5.5	1.5	-	-	-
TiO_2	0.4	-	-	-	-
CaO	0.1	1.5	0.25	0.04	0.50
MgO	24.5	3.3	3.34	0.01	<0.03
K_2O	10.4	4.2	3.62	0.15	7.70
Na_2O	0.1	2.0	1.75	0.20	5.00
P_2O_3	0.1	-	-	-	0.14
F	1.1	-	-	-	-
H_2O	3.3	-	-	-	-
L.O.I.	-	3.7	-	0.14	0.39

1) Kemira Chemicals.1996 Siilinjärvi (4)
2) Kultela Brick factory, Somero.1992
3) Partek Minerals, Kemiö.1996

3. The experimental part

Phlogopite was heated alone up to 1300^{o}C. The mica stayed granular during the burning and was coloured orange brown. "Kemira Mica" was tested as a thin layer mixed with water as 90 - 60 weight% together with Feldspar 10 - 40 weight-% and fired at maximum temperature 1250^{o}C. Feldspar and mica melted together forming glaze surface. Mica replaced 10 weight% Talc in the clay K84. The other compounds in the clay were china clay Grolleg ECCI 40 weight%, Feldspar FFF 35 weight-% and Quartz FFQ 15 weight-%. The chemical analysis of phlogopite clay bodies are presented in table 2.

Test cups were cast and easily unfastened from the plaster mould. The tiles used in testing were cast with the stoneware clay F2 and fired in a gradient kiln to the maximum temperature of 1220^{o}C (Sc.7). The cast test cups of the stoneware clay F2 were fired in the gradient kiln to the temperature 1180^{o}C (Sc.1). The lower temperatures used were more suitable than higher, because the earlier test pieces had partly distorted and slightly expanded at the first chosen temperature 1220^{o}C. The low fired clay body PF1 was tested with mica of 10 weight%. The other raw materials were Finnish Earthenware clay 45% and Quartz FFQ 45%. The analysis of the clay bodies are given in table 2.

Table 2: Chemical analysis of the Stoneware clay body F2 and the Earthenware clay body PF1

Oxide	F2 clay body (Sc.7) w-%	PF1 clay body (Sc.1) w-%
SiO_2	**65.69**	**75.70**
Al_2O_3	**23.34**	**9.47**
Fe_2O_3	1.39	5.5
CaO	0.25	0.73
MgO	**2.81**	**4.87**
K_2O	**4.78**	**3.25**
Na_2O	1.74	0.97

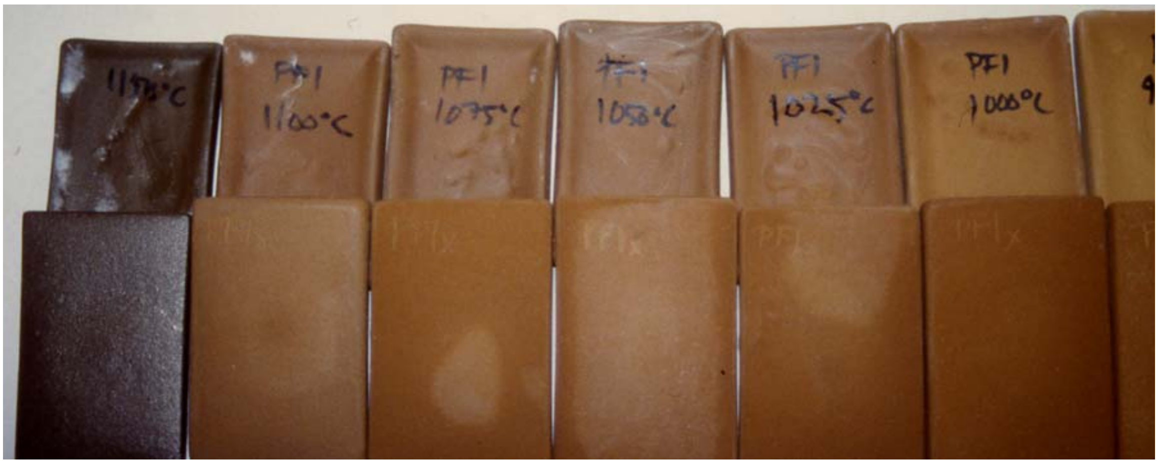

Fig. Test tiles PF1, 1150 - 950 ^{o}C, gradient of earthenware clay body

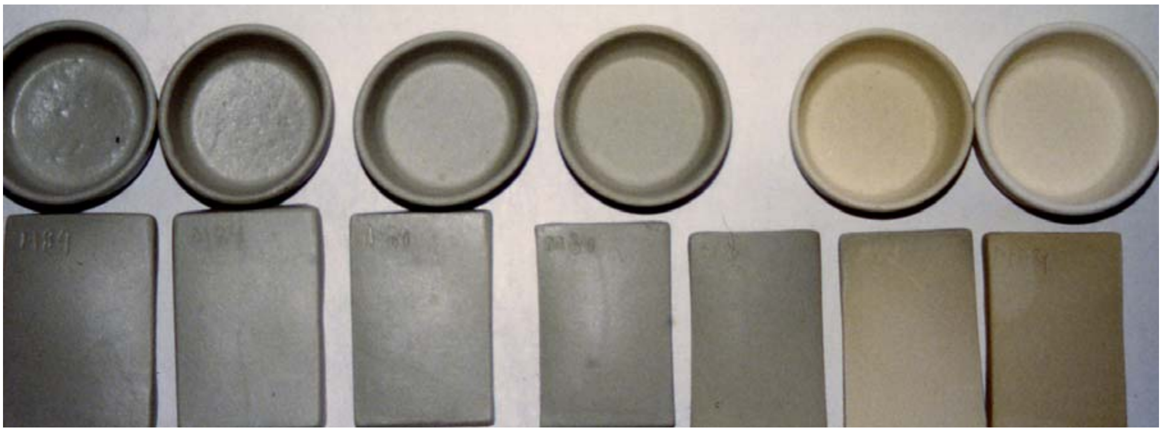

Fig. Test tiles F2, 1220 - 1075 ^{o}C, gradient of stoneware body

If the casting slip is containing mica, it stays homogenous, even if it is not used within a few days. The weakness of the clay bodies are high thixotropy. In small test cups the walls are thin and smooth after casting. When test cups were casted, a wall thickness of roughly 4 mm was formed within 7 minutes. The wall of the test cups loosen easily from the plaster mould. The dry wall of the test cup is very hard and durable even if it is thin. Special care does not need to be taken in the handling of the test tiles or cups. The particles of the clay bodies are positioned closely and tightly together.

4. Results and discussion

In the file in American Ceramic Society, Ceramic Abstracts from years 1976 - 1996 the general use of Apatite and Phlogopite was clarified in Ceramics. With the keyword Apatite 641 references were detected and with the phlogopite word 32 references were detected. According to the search apatite mineral is used in bio ceramics and phlogopite in glass-manufacturing.

Table 3. Results for gradient firing of the clay bodies F2 and PF1.

Clay body F2, Gradient firing 1220°C				Clay body PF1, Gradient firing 1100°C			
Temperature °C	Colour	Shrinkage-1) %	Absorption2) %	Temperature °C	Colour	Shrinkage1) %	Absorption2) %
1220	grey	8	0	**1100**	**brown red**	**8**	**9**
1200	grey	8	0	**1075**	**red**	**7**	**14**
1175	grey	12	0	1050	red	7	14
1150	beige	13	0.1	1025	red	7	15
1125	**beige**	**15**	**0.1**	1000	ochre	6	18
1100	**beige**	**17**	**0.1**	975	orange	5	21
1075	cream	13	4	950	orange	5	22
1050	light cream	7	18	925	yell. ochre	4	23

1) ASTM C326-82(1992)
2) ASTM C373-88(1994)

The gradient indicates that the earthenware F2 is best suited for the temperature region 1100 - 1150°C. The shrinkage is largest within this temperature region. The test tile is self polishing when it is sintering, which is a benefit of the earthenware mixture as a product. The sintered plate has a beige colour. Within the short temperature interval 1075 - 1100°C the earthenware F2 is shrinking and sintering, and also changing colour.

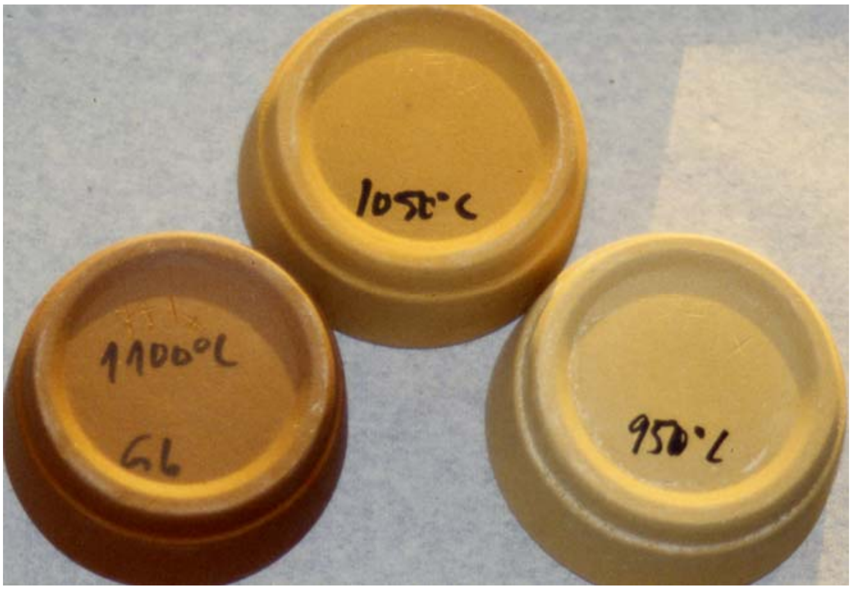

Fig. Earthenware test cups without glazing.

Observations of the colour: When fired the colour of the Earthenware PF1 changes from orange-yellow to brown-red. Throughout it is seen that the phlogopite increases the orange-glow of the earthenware compared to, for example the corresponding fired gradient using Finnish red fired earthenware to which quartz has been added. The colour of PF1 stays stable at the maximum temperature between 1050 - 1100^{o}C. The changes in the total shrinkage and the decrease in absorption indicate that sintering starts after 1075^{o}C. The tests also indicate that when the earthenware is fired above 1100^{o}C and additionally sintered, it becomes very dark and continues to shrink. In the cast cups we aimed at and succeeded in saving the bright red, typical terracotta colour.

Fig. Eathenware test cups are glazed with lead free borax frit glaze, which turns the colour bluish and grayish brown.

4. Conclusions

The present results can be used in the tile- and brick industry both because of the colour and porosity. The Ecological ideas aim at making products using Finnish minerals which give an esthetic feature. These ideas may be transferred to other cultures (3). The discovering of co-operation between industries is an important part of research on earthenware and glaze application.

Phlogopite increases in the low temperature range, temperature stability and widens the firing-interval. Because it is possible to use 1100^{o}C as maximum temperature it is easier to develop glazes. Instead of using low-soluble lead glazes, it is possible to use several lead free glazes as alternatives. Iron containing earthenware is an orange-red when used in such clay.

When used in stoneware clay bodies phlogopite mica lowers the sintering point from temperature range 1200^{o}C to 1100^{o}C. Thus significant savings in electrical energy is obtained. The tiles are self polishing on the surface, and you do not need to use any glazes. The sintering area of the earthenware clay is wide. Mica is suitable to use for wall tiles, which are once fired. The colour of the Earthenware is warm, orange beige or grayish brown.

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